

Engineered Sn doped TiO₂ bifunctional catalyst for improved hetero-photocatalytic oxidation of arsenite in water

By

Hany Fathy Abdelmageed Ramadan Heiba

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Department of Earth Science and Engineering

Department of Chemistry

Centre for Doctoral Training - Advanced Characterisation of Materials
(CDT-ACM)

London Centre for Nanotechnology

Imperial College London

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Abstract

Millions of people worldwide are exposed to arsenic contaminated water. TiO_2 photocatalytic oxidation (PCO) of As(III) to the less toxic As(V) which can be easily removed is a challenging process due to several reasons particularly the bandgap limitation and the poor quantum efficiency.

Here, a procedure was developed to accurately determine the oxidation rates of As(III) which is challenging. The calculated photon and energy absorption by TiO_2 were 36.7 and 44.9 %, respectively. Finally, the quantum efficiency (QE) as a potential measure of the PCO was determined.

$\text{SnO}_2@\text{Sn-TiO}_2$ and $\text{Sn-TiO}_2@\text{SnO}_2$ photocatalysts were synthesised and characterised using XRD, Raman, XPS, DRS, LEIS, EDX, HR-TEM, SEM, S-TEM and FTIR. These analyses revealed that at low doping ratios, SnO_2 formed the shell of the catalyst ($\text{SnO}_2@\text{Sn-TiO}_2$), whereas higher Sn doping ratio developed a Sn-TiO_2 shell alongside a core of SnO_2 ($\text{Sn-TiO}_2@\text{SnO}_2$). Increasing Sn-doping resulted in a shift in the conduction and valence band edge energies accompanied with a reduction in the bandgap. The smallest bandgap in $1\text{Sn}:1\text{TiO}_2$ (2.87 eV) is linked to the improved electron-hole separation. $\text{Sn-TiO}_2@\text{SnO}_2$ and $\text{SnO}_2@\text{Sn-TiO}_2$ improved the PCO of TiO_2 by ~94 % to 145 %. For the first time, the PCO rate was accurately determined by mounting both adsorbed As(V) (using XPS) and aqueous As(V) (spectrophotometry).

TAS experiments showed a long-lived charge carriers in $1\text{Sn}:1\text{TiO}_2$. The initial transient absorption signal was ~2 times higher than anatase TiO_2 , suggesting early timescale (pre- μs) suppression in the electron-hole recombination in $1\text{Sn}:1\text{TiO}_2$. The scavenger studies show that the hydroxyl radical ($\text{OH}\cdot$) is the main oxidant. Lastly, the controls of experimental parameters on the PCO of As(III) over $1\text{Sn}:1\text{TiO}_2$ were studied. These controls include the distance between the light source and the solution surface which shows a high effect on the photon flux reaching the solution, the QE and PCO rate.

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1 Introduction

Water is a very basic source for existence of life on the earth and the availability of clean water for human use is a critical issue across the world. The increase of population, industrial activities and modernization has negatively affected the water resources. It has been reported that 1.2 billion people do not have access to clean drinking water. Every day, about 2 million tons of agriculture and industrial wastes are being discharged into the water bodies which pollute them thus causing the death of around 14,000 people per day [1].

Many water pollutants such as heavy metals, crude oil, dyes, pharmaceuticals, surfactants and pesticides being discharged from domestic and industrial resources. These pollutants are extremely hazardous to aquatic life, human beings, plants and animals [2]. Therefore, water pollution has become a major global issue. The compounds of arsenic, a highly toxic element, present in water have a bad impact on the health of the world population and become a matter of global concern [4,5]. The main sources of arsenic are classified as anthropogenic and geogenic. The major arsenic anthropogenic sources involve mining industries, herbicides, pesticides, fungicides, fossil fuels, wood preservatives, crop dedication, tanneries and semiconductors [3–5]. Geogenic sources include weathering of rocks and minerals in addition to volcanic eruptions. Every year the dissolution of arsenic-rich minerals and rocks mobilise 2380×10^5 kg and 612×10^5 kg arsenic respectively [3,6]

Currently, arsenic-contaminated water has been reported worldwide particularly in Bangladesh, Argentina, Cambodia,, China, Mongolia, North Mexico, Nepal, India, Vietnam, Myanmar, Poland, Korea, Japan, New Zealand, USA, Iran, and Pakistan. [1].

Water polluted with arsenic is well-known to cause several types of cancer in addition to black foot disease. In 1993, the World Health Organization (WHO) introduced a new guideline for the permissible arsenic in drinking water of 10 µg/L. Afterwards, the US Environment Protection Agency (USEPA) and the European Union and China replaced the old standard of 50 µg/L and adopted the new arsenic levels in drinking water at 10 µg/L [7].

In natural waters, arsenic exists mainly in the inorganic species (arsenite As(III)) and arsenate (As(V)) . In oxic conditions where water contains free molecular oxygen, As(V) species exist mostly as oxyanions H_2AsO_4^- (pH 3–6) and HAsO_4^{2-} (pH 8–10), but the As(III) exists primarily in the

neutral form (H_3AsO_3) under anoxic water conditions (e.g. groundwater $\leq$ pH 9.2). The neutral As(III) species is more toxic and mobile than As(V) anionic species, and is it is harder to be eliminated by traditional water treatment methods [8].

It is a necessity to develop an efficient arsenic removal technology to deliver safe drinking water to the affected areas [7]. Therefore, conventional methods have been developed to remediate hazardous pollutants from polluted water however most of them have practical limitations [9]. Photocatalytic oxidation coupled with adsorption has been considered as an effective and inexpensive technology in water treatment for arsenic removal.

The process of arsenic removal requires an initial oxidation step for converting As(III) to As(V) followed by post-treatment such as coagulation or adsorption of As(V) [8].

This oxidation step can be accomplished by using oxidants such as oxygen (O_2) and/or ozone (O_3), chlorine, manganese dioxide (MnO_2), hydrogen peroxide (H_2O_2), Fenton's reagent ($\text{Fe(II)}/\text{H}_2\text{O}_2$), ferrate (VI), UV photolysis, and UV catalysed titanium dioxide (UV/ TiO_2) [8]. The UV/ TiO_2 photocatalysis has been commonly deemed as the best effective method for peroxidation of As(III) [8]. However, there are still two intrinsic drawbacks which limit the practical applications of UV/ TiO_2 photocatalysis. The first is its quite wide bandgap (3.2 eV) of TiO_2 which limits the range of its light absorption to the UV range. The second is the rapid recombination of photogenerated electron/hole (e^-/h^+) pairs which significantly lowers the quantum efficiency [10].

Recent studies [11–13] showed that mixing semiconductor photocatalysts (TiO_2 and SnO_2) often show superior photocatalytic activity due to heterojunction effects that reduce electron hole recombination rates through separation of the energy levels which in turn enhance the quantum efficiency.

In this study, the effect of TiO_2 doping with different molar ratios of tin on the bandgap is investigated, energy level separation and the final photocatalyst structure control (e.g. $\text{Sn-TiO}_2@/\text{SnO}_2$ and $\text{SnO}_2@/\text{Sn-TiO}_2$). The significant changes when TiO_2 is doped with Sn is mechanistically investigated using a wide range of state of art techniques including (XRD, XPS, LEIS, HE-TEM, SEM, S-TEM, FT-IR). The oxidation kinetics, mechanism and main oxidant during

the photocatalytic oxidation of As(III) over Sn-TiO₂@SnO₂ composite are determined. The primary structure and objectives of this thesis as follows:

Chapter 2: provides a background about As(III) contamination, possible remediation technologies, previous studies and possible improvement of the TiO₂ photocatalysis properties.

Chapter 3: describes the experiments, characterisation techniques and methods.

Chapter 4: shows the development of low-cost analytical methods, the determination of oxidation rates and quantum efficiencies during the photocatalytic oxidation of As(III) over TiO₂.

Chapter 5: Synthesis and characterisation of the Sn-TiO₂@SnO₂ and SnO₂@Sn-TiO₂ heterophotocatalysts and their application in the photocatalytic oxidation of arsenite, As(III), using surface sensitive techniques.

Chapter 6: provides the photochemical studies such as Transient Absorption Spectroscopy (TAS) and the photon flux in addition to solution parameters (e.g. pH, photon flux, salinity, scavengers, loading of the catalyst and As(III) concentration) which influences the photocatalytic oxidation of As(III) over 1Sn:1TiO₂ (Sn-TiO₂@SnO₂).

Chapter 7: draws together the findings of the previous chapters, summarises recommendations for further research on this topic and describes the future steps required to bring the TiO₂-based photocatalysis treatment to the practical in the real world.

Chapter 8: concludes the new understandings provided by this thesis into the effect of the ratio of Sn doping on the final structure of the synthesised Sn-doped heterophotocatalyst and a conclusion of the photocatalytic oxidation-adsorption approach towards the removal of As(III) using Sn doped TiO₂.

List of publications

The peer reviewed publications are as follows

1. **Heiba HF**, Bullen JC, Kafizas A, Petit C, Skinner SJ, Weiss DJ. (2022). The determination of oxidation rates and quantum yields during the photocatalytic oxidation of As (III) over TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry*, 424 (113628), <https://doi.org/10.1016/j.jphotochem.2021.113628>. Based upon chapter 4.
2. Bullen JC, **Heiba HF**, Kafizas A, Weiss DJ. (2022). Parasitic light absorption, rate laws and heterojunctions in the photocatalytic oxidation of arsenic (III) using composite TiO₂/Fe₂O₃. *Chemistry—A European Journal*, 28(16), <https://doi.org/10.1002/chem.202104181>. Based upon chapter 6.
3. Corby S, Tecedor MG, Tengeler S, Steinert C, Moss B, Mesa CA, **Heiba HF**, Wilson AA, Kaiser B, Jaegermann W, Francas L. (2020). Separating bulk and surface processes in NiOx electrocatalysts for water oxidation. *Sustainable Energy & Fuels*. 4(10):5024-30. <https://doi.org/10.1039/D0SE00977F>.
4. Kirby ME, Bullen JC, Hanif MD, **Heiba HF**, Liu F, Northover GHR, Resongles E, Weiss DJ, (2020). Determining the Effect of pH on Iron Oxidation Kinetics in Aquatic Environments: Exploring a Fundamental Chemical Reaction to Grasp the Significant Ecosystem Implications of Iron Bioavailability. *Journal of Chemical Education*. 97 (1) 215–220. <https://doi.org/10.1021/acs.jchemed.8b01036>
5. **Heiba HF**, Kafizas A, Petit C, Weiss DJ. (2019). Narrowing the bandgap of TiO₂ by Sn doping and its application in the photocatalytic oxidation of As(III) and crude oil. A presentation talk in CDT-EPSRC retreat conference, Girona, Spain.

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1. **Heiba HF**, Bullen JC, Kafizas A, Petit C, Fearn S, Skinner SJ, Weiss DJ. Synthesis and characterisation of the Sn-TiO₂@SnO₂ and SnO₂@Sn-TiO₂ heterophotocatalysts and their application in the photocatalytic oxidation of arsenite, As(III), using surface sensitive techniques. Submitted and under peer review. Based on Chapter 5.

2. **Heiba HF**, Bullen JC, Kafizas A, Petit C, Weiss DJ Heterojunction, photochemical processes and experimental controls during the photocatalytic oxidation of As(III) using 1Sn:1TiO₂. Based on chapter 6.

Non-peer reviewed publication as follows

1. Weiss D, Bullen J, **Heiba H**, Kafizas A, Cass A, Vilar R, Childs P, Skinner S, Salaun P, Mondal P, Majumdar S, (2019). Arsenic contaminated groundwater - A problem in India and the UK. *Royal Society of Chemistry - Environmental Chemistry Group Bulletin*.

2 Review of Literature

2.1 Arsenic (As) in the environment

Arsenic (As) is the 20th most abundant element naturally existing in the earth's crust, cycling through water, land, air, and living systems. Arsenic levels in the environment increase because of some anthropogenic activities and natural processes. Arsenic is one of the most toxic contaminants found in the environment [14]. Inorganic arsenic exists in various oxidation states (-3, -1, 0, +3 and +5). However, the predominant arsenic species are oxyanions of trivalent arsenite and pentavalent arsenate. The extent of arsenic toxicity is dependent on its oxidation state as arsenite, i.e. As(III) is more harmful [15] and more mobile [16] than arsenate, i.e. As(V). The redox potential (E_h) has a major control on arsenic speciation in the natural environment (Figure 2.1) and As(V) is the thermodynamically stable form in aerobic oxidizing water, while As^(III) is dominant in reduced conditions (Figure 2.2). Arsenic can be found in the ecosystem in different chemical forms such as monomethylarsonic acid [MMA; $\text{CH}_3\text{AsO}(\text{OH})_2$], dimethylarsinic acid [DMA; $(\text{CH}_3)_2\text{AsOOH}$], trimethylarsineoxide [TMAO; $(\text{CH}_3)_3\text{AsO}$], arsenobetaine [AsB; $(\text{CH}_3)_3\text{AspCH}_2\text{COOH}$], arseno-choline [AsC], arsenosugars [AsS], arsenolipids etc [17].

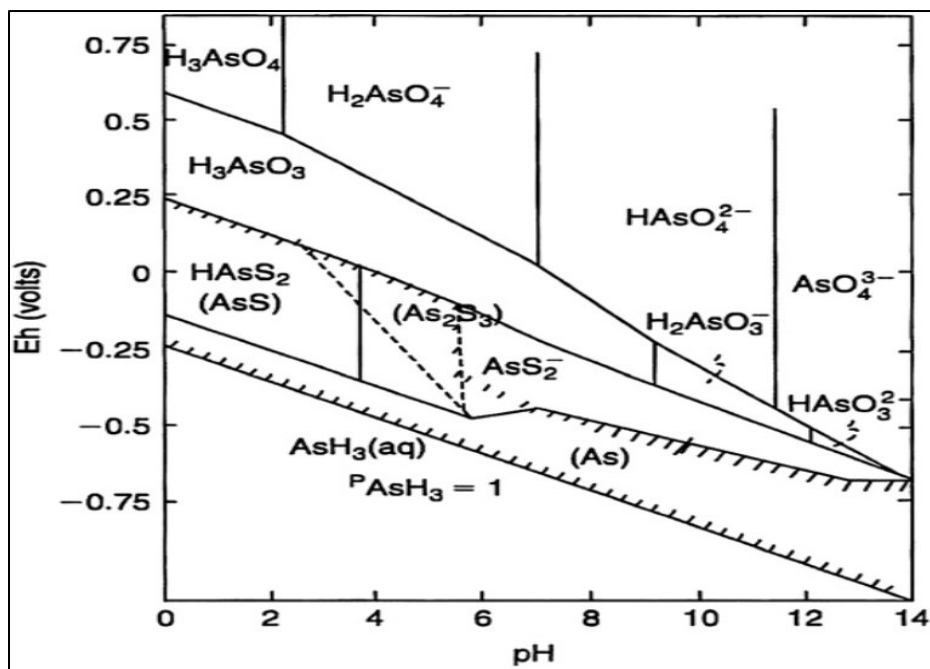


Figure 2. 1. The EH-pH diagram for arsenic speciation at 25 °C and 1 atmosphere [18].

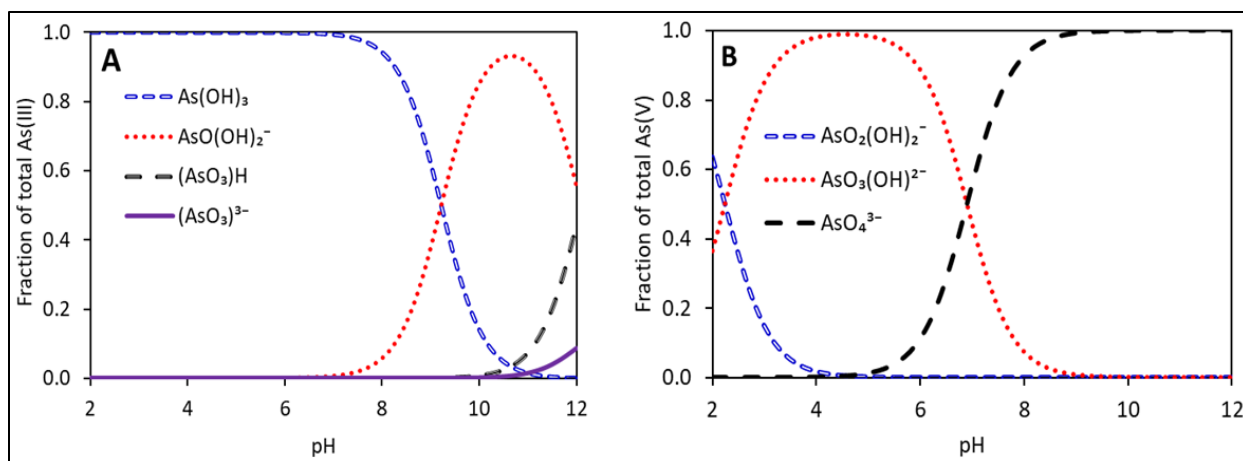


Figure 2. Distribution of As(III), As(V), species as a function of pH at 25°C [18].

Water pollution with arsenic has been reported in different countries across the world such as the Americas (Argentina, Chile, Mexico, Peru, USA), Europe (Hungary, Romania, Finland) and Asia (Bangladesh, , India, Nepal, Hanoi, Vietnam, China, Mongolia, Thailand, Japan) [18].

Rock weathering, geochemical reactions, volcanic emissions and anthropogenic activities (e.g. burning of fossil fuels and arsenical pesticides) lead to leaching of arsenic in the form of arsenite As(III) and arsenate As(V) to ground water [19].

In the natural reducing environment of groundwater, arsenic exists primarily in an oxyanion form of trivalent arsenite As(III) which is neutral in charge, H_3AsO_3 . However, in the oxidizing environment of surface waters, it occurs as pentavalent arsenate As(V), that is negatively charged. According to the World Health Organization (WHO), the permissible limit of arsenic in drinking water is 10 $\mu\text{g/L}$. Human are exposed to arsenic via different sources such as drinking water, agricultural products irrigated with polluted water and food cooked using contaminated water [9].

Arsenic naturally exists in freshwater systems (e.g. rivers and lakes) in the concentration range of 0.15–0.45 $\mu\text{g/L}$ according to the catchments' origin, availability, and geochemistry [17]. In contaminated rivers, arsenic concentrations usually vary between 0.1 to 2.1 $\mu\text{g/L}$ with an average of 0.8 $\mu\text{g/L}$. The principal source of contamination is input from ground water, evaporation process due to geothermal process and the bedrock lithology. Lao River of Northern Chile is an example of a freshwater body with extremely elevated concentrations of arsenic (up to 21,000 $\mu\text{g/L}$) [20]. Mining activities also cause a high As concentrations in river waters. For

example, water of Mole River, New South Wales, Australia contains As concentrations in the range (from 110–600 µg/L to 13,900 µg/L) due to the mining and processing activities of arsenopyrite ores [21]. Arsenic levels in lake waters are similar to or less than that recorded for river waters. The geothermal sources and mining process increase arsenic pollution in lake waters. Compared to rivers, in mine affected lake waters, arsenic concentrations are in general lower due its adsorption onto Fe-oxides under neutral pH, and its natural accumulation in lake sediments [17].

Arsenic concentrations in lake water are subjected to the thermal stratification where the dissolved arsenic concentration surface water is highest during summer and lowest in winter. The phenomena of thermal stratification in lake water causes the release of As into the water column from bottom sediments as a result of the decrease of O₂ levels in the bottom water because of high biological activities and redistributed throughout the lake waters [17,22]. Worldwide, the most As polluted areas are the large deltas and along main rivers from the Himalayas with the Bengal delta (45 million are exposed), the Red River Delta and the Mekong Delta in South and South-East Asia (>10 million exposed) [17,23].

Arsenic is the 14th most abundant element in seawater with concentrations usually less than 2 µg/L [24]. It exists as organic compounds including trivalent methylarsonite (MAs(III)) and dimethylarsinite (DMAs(III)); and pentavalent methylarsonate (MAs(V)), dimethylarsinate (DMAs(V)) and trimethylarsine oxide (TMAs(V)O). These organic forms are formed naturally by marine flora, industrial and agricultural pollution [25] and in both trivalent and pentavalent inorganic forms. Arsenic concentrations in seawater differs from that in estuarine waters which is influenced by industrial, agricultural and mining effluents. The As concentrations is markedly affected by the physical mixing of the fresh and seawater masses where the salinity increases the solubility of As and eventually increases the As concentration [17]. The continuous increase in sea level due to climate change has a great impact on mobility and migration of pollutants by modifying several natural phenomena in the geochemistry and hydrology of the subsurface environment [26]. This will increase the release and migration of arsenic from the sediments and the groundwater through desorption and degradation to the water masses. Arsenic tends to

complex with the counter ions, which normally increase with salinity, such as Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , and Cl^- which result in an increase in its solubility [27].

2.2 Arsenic toxicity

Arsenic is toxic to plants and animals and inorganic arsenicals are carcinogens in humans. Arsenic causes a wide range of toxicity to human such as peripheral system disorders, kidney dysfunction, skin lesions, injury to the cardiovascular and nervous system while long term exposure can develop cancers to brain, liver, kidney, and stomach. A wide range of arsenic toxicity has been determined that depends on arsenic speciation. Inorganic arsenic species are more harmful than organic species to living organisms, including humans and other animals [18,19]. Due to these severe toxicity the World Health Organization (WHO) has made a strict regulation and decreased the permitted arsenic level in drinking water from 50 to 10 $\mu\text{g/L}$ [28].

2.3 Analytical speciation of arsenic

Various analytical methods have been developed to analyse arsenic; however many of these techniques fail to differentiate between different arsenic species and are often unsuitable for on-site analysis due to the complexity of the method [29]. Inductively coupled plasma mass spectrometry (ICP-MS) is the one of the most used techniques for arsenic analysis but can only determine the total arsenic concentration, with the cost of analysis being relatively high. Other sensitive techniques are graphite furnace atomic absorption (GFAAS) and hydride generator atomic absorption spectrophotometry (HG-AAS) which has detection limits (MDL) ranging from 0.5 to 50 mg/L , but both remain expensive and suitable for determination of total arsenic [30]. Over the last few, coupled analytical techniques have been developed to differentiate between arsenic species, such as hydride generatively inductively coupled plasma atomic emission spectrometry (HGICP- AES), capillary electrophoresis inductively coupled plasma mass spectrometry (CE-ICP-MS), high performance liquid chromatography inductively coupled plasma mass spectrometry (ICP-MS), electro-thermal atomic absorption spectrometry (ETAAS), hydride generation atomic fluorescence spectrometry, anodic and cathodic stripping. However, these techniques are again quite expensive and require skilled operators to carry out the measurement. Another drawback of that these heavy-weighted complex instruments is that they cannot be used

on-site [30,31]. Therefore, developing sensitive, accurate and inexpensive methods for measuring arsenic levels and species are much needed.

2.4 Current remediation technologies

Considerable efforts have been put in place to primarily reduce human exposure to arsenic from drinking water. Several treatment technologies were developed to treat arsenic contaminated water such as oxidation, co-precipitation, adsorption, ion-exchange, membrane technologies, and subsurface arsenic removal (SAR) (Table 2.1, adjusted from [9]). Among all, adsorption is the most promising adopted method as it does not produce undesirable toxic by-products and the used adsorbents can be regenerated for reuse up to reasonably good number of cycles [32]. In addition to adsorption, a modified biosand filter (BSF) called the Kanchan Arsenic Filter (KAF) has successfully developed and employed as a low-cost household-scale treatment filter. KAF has effectively removed arsenic (> 80%) from arsenic contaminated water however the filter run slowly and clog more quickly at higher turbidity [33,34].

Table 2. 1: Common arsenics remediation technologies; advantages and disadvantages.

Technique	Advantages	Disadvantages
Ex-Situ		
Oxidation (air, UV, ozone, ox. agents)	- Simple and cost effective. - Fast and simple.	- Highly contaminated As sludge. - High dose of oxidizing agents: Extra costs and chemical waste.
+ Filtration	- kills microbes and oxidizes other impurities.	- Some oxidants release toxic by-products.
+ Precipitation (Alum / iron coagulants)	- Efficient As removal and reduction of corrosion.	- competing ions reduces the efficiency.
Adsorption (active carbon, activated alumina, ferric hydroxides)	- Well established, cheap and commercially available - High removal efficiency - Improves taste and odor - Simple and suitable for domestic use.	- Produces toxic solid waste - Regeneration/reuse of the adsorbent - Optimum pH conditions required - Suspended particles and other salts influence the adsorption efficiency.
Ion exchange (synthetic resins, zeolites) Membrane filtration (NF, RO)	- High efficiency and versatile process - Ion-exchange resin: well-defined medium and high capacity. - Well established process useful at households' level. - Removes contaminants such as dissolved salts, turbidity. - No sludge is produced. - Highly effective towards As, also with high TDS.	- Poor efficiency for As ^(III) removal - Very expensive - Toxic waste and disposal problem - Replacement and regeneration of resins - Very expensive due to resins costs, operation and maintained costs - Produces highly contaminated waste water - Membranes are prone to scaling and fouling - Water recovery rates is very low (10-20%)

Table 2. 1: continued

In-Situ

SAR (Subsurface Arsenic Removal):	- Negligible solid or liquid waste production	- High dependency on hydrogeological and geochemical conditions (e.g. pH, redox)
Oxidation (air) + Sorption/Co- precipitation	- Low cost and low maintenance	- Competing ions can reduce As adsorption
	- Protects well and pumps from clogging	- Addition of iron sometimes needed
	- Adsorption (Fe, Mn) and oxidation of other substances (organic matter)	- As immobilization in long-term uncertain
	- If ox. with air: no use of chemicals	- Air oxidation slow process especially for manganese
Permeable Reactive Barrier (ZVI, iron slag, Fe/Al-oxides, multifunctional barriers)	- No waste production in the surface	- High initial costs and involves complicated drilling
	- Low operational and maintenance costs	- High permeable and reactive/adsorbent materials needed
	- No large installations or equipment on the surface	- Dependency on physical and geochemical conditions
		- Long-term effectiveness uncertain
Bioremediation	- Cost effective.	- High dependence on soil chemistry, climate, hydrogeo-dynamics, environ. conditions etc.
(Biosorption/-transformation;	- Plants/microbes decrease pollutant leaching into soil and groundwater.	- Disposal of As bearing waste
Phytoextraction/-stabilization;	- Combination for bioenergy production from biowaste possible. p Microorganisms growth have positive effects on soil and groundwater	- Use of soil amendments (iron, organic matter, phosphorous) sometimes needed.
Hyperaccumulation, etc.)		- As mobility increased by some soil nutrients /competing ions

2.5 Oxidation of arsenite

As(III) is about 60 times more toxic than As(V) and more difficult to remove from contaminated water using adsorption and other remediation techniques [35]. Therefore, As(III) is typically removed by two consecutive processes; first is the oxidation of As(III) to As(V) and in second step the less toxic As(V) is immobilized by another technology such as adsorption, precipitation, or ion exchange processes. Photocatalysis is one of the most effective methods for the purification of wastewater containing arsenic, in particular As(III). Photocatalytic oxidation using TiO₂ based photocatalysts is an effective technology for oxidation of As(III)/organic arsenic to less toxic As(V) which can be easily immobilized [36].

2.5.1 Homogenous oxidation

Homogenous oxidation is a rapid technique that is usually operated using dissolved oxidants which can undergo thermodynamically spontaneous oxidation with O₃, Cl₂, ClO₂, and KMnO₄. Homogenous oxidation is a promising technique for the rapid oxidation of As(III). However, in practical applications, homogenous oxidation faces some issues, such as the operational cost and the difficulty in chemical production, storage and transportation [37,38].

Table 2. 2: Main reactions involved in the thermodynamically spontaneous As(III) oxidation [37].

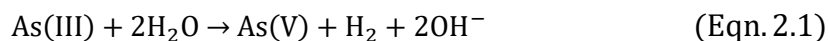
Oxidants	Hydrogen Standard Potential (V, 25 °C)	Oxidation reactions	Ref.
Oxygen [O ₂]	1.23	$2\text{H}_3\text{AsO}_3 + \text{O}_2 = 2\text{H}_2\text{AsO}_4^- + 2\text{H}^+$	[39]
Ozone [O ₃]	2.07	$3\text{H}_3\text{AsO}_3 + \text{O}_3 = 3\text{H}_2\text{AsO}_4^- + 3\text{H}^+$ $1.231\text{H}_3\text{AsO}_3 + 1.077\text{O}_3 = 1.231\text{H}_2\text{AsO}_4^- + 1.231\text{H}^+ + \text{O}_2$	[40]
Hypochlorite [ClO ⁻]	1.7	$\text{H}_3\text{AsO}_3 + \text{ClO}^- = \text{H}_2\text{AsO}_4^- + \text{H}^+ + \text{Cl}^-$	[41]
Chlorine dioxide [ClO ₂]	1.27	$5\text{H}_3\text{AsO}_3 + 2\text{ClO}_2 + \text{H}_2\text{O} = 5\text{H}_2\text{AsO}_4^-$ $+ 7\text{H}^+ + 2\text{Cl}^-$	[41]
Permanganate [MnO ₄ ⁻]	1.68	$3\text{H}_3\text{AsO}_3 + 2\text{MnO}_4^- = 3\text{H}_2\text{AsO}_4^- + \text{H}^+ + \text{H}_2\text{O} + 2\text{MnO}_2$	[42]
H ₂ O ₂ / HO• (Fenton)	1.78 (H ₂ O ₂) /2.80(HO•)	$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O}_2 = \text{H}_2\text{AsO}_4^- + \text{H}^+ + \text{H}_2\text{O}$	[43]

Although other weak oxidants such as hydrogen peroxide (H₂O₂), dissolved oxygen (O₂), persulfate, and ultraviolet (UV) have the advantage of being low cost, they have slow oxidation rates and so are frequently not used for As(III) oxidation. However, these oxidants are being explored to improve As(III) oxidation via heterogeneous catalysis [37].

2.5.2 Heterogeneous photocatalysis

Heterogeneous photocatalysis is a light-induced phenomenon which can be defined as an acceleration of the photoreaction in presence of a catalyst [44]. The catalyst absorbs light and develop electron-hole pairs; the electron is promoted to the conduction band (CB) and is responsible for reduction reactions while the hole is generated in the valence band (VB) and is responsible for oxidation reactions [45]. However, the appropriate thermodynamic properties (e.g. bandgaps and CB/VB levels) do not assure the progress of a photochemical reaction; this is also controlled by the intrinsic lifetime of the charge carriers and the kinetics of the photochemical processes that occur on heterogeneous photocatalysts. [46,47]. The overall oxidation efficiency of a photocatalyst is controlled by various factors such as the incident light wavelength and absorption coefficient of the catalyst, the reaction media, the catalyst structure at micro- and nano-levels, catalyst surface area and surface composition, catalyst crystallinity and the optical properties of the catalyst [48].

Recently, photocatalytic oxidation has been increasingly applied in environmental applications such as solar fuels [49] water splitting [50] and CO₂ reduction [51], water effluent [52], dye oxidation [53], air remediation [54]. Photocatalytic oxidation is an emerging, low-cost method for oxidizing As(III) to As(V) while water is reduced (eqn. 2.1 represents the overall reaction) and thus facilitates arsenic adsorption and removal processes, and it is therefore considered in the current work. Photocatalysis can rapidly oxidize As(III) to As(V) if the redox potential of the As(V)/As(III) couple is less than the valence band potential (i.e. the photo-generated holes have enough thermodynamic potential to oxidize As(III) to As(V)). Once As(III) is converted to As(V), it can be removed by an effective method such as adsorption or coagulation [55].



Photocatalysis has many advantages: i) it is considered an environmentally safe method when non-toxic catalysts are used, , ii) no harmful chemical wastes are produced, iv) less energy-intensive than conventional treatment methods and iii) can be combined with other physical and chemical technologies (e.g. adsorption and membrane separations) [55].

Studies have considered the use of various photocatalysts such as copper oxide (CuO) and zinc oxide (ZnO) [56,57] and g-C₃N₄ [58] for the oxidation of As(III); however titanium dioxide (TiO₂) is the most popularly studied material due to its chemical stability, resistance to corrosion, non-toxicity, optical properties, high effectiveness and low toxicity [54]. Table 2.3 summarises the efficiency of TiO₂ photocatalysts for the photooxidation of arsenite.

Table 2. 3: TiO₂-photocatalyzed oxidation of As(III) under air equilibrium condition [28].

Catalyst	[As(III)] (mg/L)	Catalyst Concentration (g/L)	pH	Light source	Light irradiance	Time (min)	Oxidation	Ref.
TiO ₂ (Degussa P25)	39.375	2	9	400 W medium pressure Hg arc lamp	1.83×10^{-5} (Einstein.min ⁻¹)	30	~100%	[38]
TiO ₂ (Degussa P25)	0.1	0.01	5 – 9	1000 W Xe short-arc lamp, $\lambda < 320$ nm	3×10^{-5} (Einstein m ⁻² s ⁻¹)	3.3	>98%	[59]
TiO ₂	3.75	1.5	3, 9	300 W Xe arc lamp (Oriol), $\lambda > 300$ nm	<i>ns</i>	120	~100%	[60]
TiO ₂ (Degussa P25)	100	0.25	7	250 W medium pressure Hg arc discharge lamp, $\lambda > 300$ nm	<i>ns</i>	60–90	0.8	[61]
TiO ₂ (Degussa P25)	37.5	0.5	3	300 W Xe arc lamp (Oriol), $\lambda > 300$ nm	<i>ns</i>	180	>90%	[62]
TiO ₂ (Degussa P25)	37.5	0.5	9	300 W Xe arc lamp (Oriol), $\lambda > 300$ nm	<i>ns</i>	180	~77%	[62]
Pt-TiO ₂	37.5	0.5	3, 9	300 W Xe arc lamp (Oriol), $\lambda > 300$ nm	<i>ns</i>	180	~100%	[62]
TiO ₂ (Degussa P25)	1	1	<i>ns</i>	16 phosphor-coated low-pressure Hg lamp, $\lambda = 350$ nm	$(1.5-5) \times 10^{16}$ (photon.s ⁻¹ .cm ⁻²)	7	~100%	[63]
TiO ₂ (Degussa P25)	7.5	0.01	3	4 W UV lamp ($\lambda_{\text{max}} = 352$ nm)	1.56×10^{-6} (Einstein.L ⁻¹ .s ⁻¹)	30	~40%	[64]
TiO ₂ (Degussa P25)	3	0.1	9	125 W high-pressure mercury vapor lamp, max = 365 nm	12.5 (mW.cm ⁻²)	~12.5	~100%	[65]
TiO ₂ (Degussa P25)	0.062	0.05	6.3	8 W lamp (UVP model UVL-28), $\lambda = 365$ nm	7.8×10^{16} (photons.s ⁻¹)	10	~100%	[66]
TiO ₂ (Degussa P25)	0.188	0.05	6.3	8 W lamp (UVP model UVL-28), $\lambda = 365$ nm	7.8×10^{16} (photons.s ⁻¹)	15	~100%	[66]
TiO ₂ (Degussa P25)	0.622	0.05	6.3	8 W lamp (UVP model UVL-28), $\lambda = 365$ nm	7.8×10^{16} (photons.s ⁻¹)	60	~100%	[66]
TiO ₂ (Degussa P25)	5.63	0.1	3	4 W UVA lamp ($300 < \lambda < 400$ nm)	<i>ns</i>	40	~80%	[67]
TiO ₂ (Degussa P25)	3	0.05	6.4	9 W lamp (Radium Ralutec, 9 W/78), $350 < \lambda < 400$ nm	4.69×10^{-6} (Einstein.min ⁻¹)	10	~100%	[68]
TiO ₂ (Degussa P25)	5	0.05	6.4	9 W lamp (Radium Ralutec, 9 W/78), $350 < \lambda < 400$ nm	4.69×10^{-6} (Einstein.min ⁻¹)	10	~100%	[68]
TiO ₂ (Degussa P25)	10	0.05	6.4	9 W lamp (Radium Ralutec, 9 W/78), $350 < \lambda < 400$ nm	4.69×10^{-6} (Einstein.min ⁻¹)	30	~100%	[68]
TiO ₂ (Degussa P25)	20	0.05	6.4	9 W lamp (Radium Ralutec, 9 W/78), $350 < \lambda < 400$ nm	4.69×10^{-6} (Einstein.min ⁻¹)	30	~100%	[68]
TiO ₂ (Degussa P25)	15	0.5	3	300-W Xe arc lamp (Oriol), $\lambda > 300$ nm	3.46×10^{-3} (Einstein.L ⁻¹ .min ⁻¹)	180	~100%	[68]

ns = not stated

2.6 Mechanism of photocatalysis

The heterogeneous photocatalysis mechanism can be summarised in four successive steps as presented in Figure 2.3: (i) harvesting of the incident light; (ii) charge separation via through photogeneration of the charge carriers (electron/hole); (iii) charge migration, transport, and recombination; and (iv) utilisation of the charge carriers (photocatalytic reduction and oxidation reactions). Consequently, the overall photocatalytic potential is greatly dependent on the cumulative effects of these four consecutive steps [47].

Upon UV irradiation, an electron (e^-) from valence band is excited into the conduction band of the photocatalyst leaving behind a positive hole (h^+) in the valence band. The reactions of e^- and h^+ with O_2 and H_2O in the reaction medium produces free radicals such as O_2^- , $HOO^\bullet$, and $HO^\bullet$ (Fig. 2.4) which eventually drive the photocatalytic oxidation/degradation reactions [51].

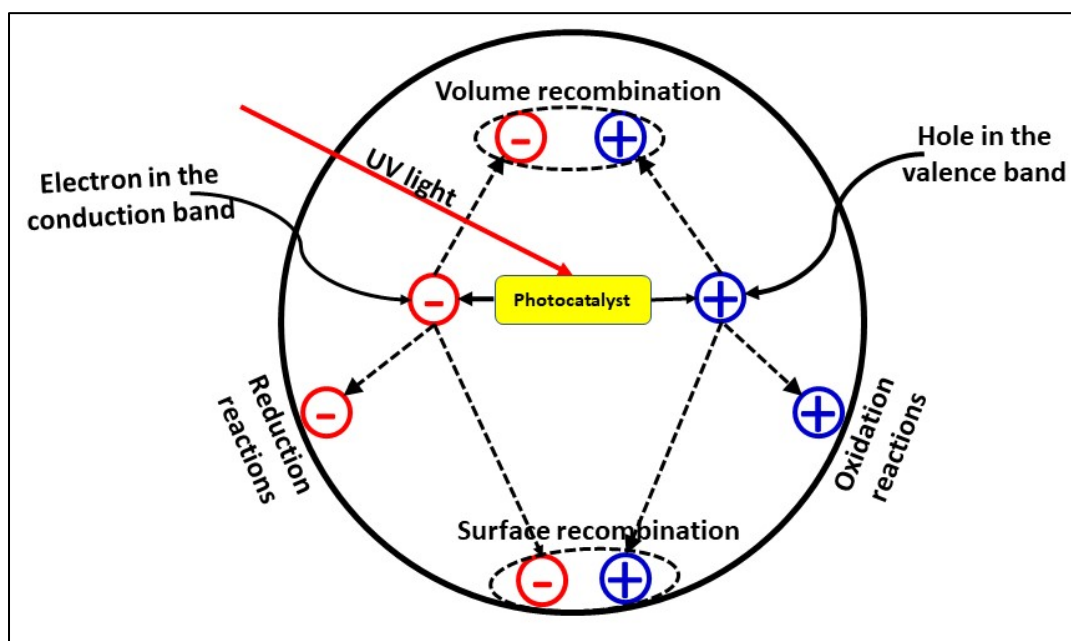


Figure 2. 3. Schematic diagram summarizing the processes that occur in a photocatalyst upon irradiation with ultra-bandgap light.

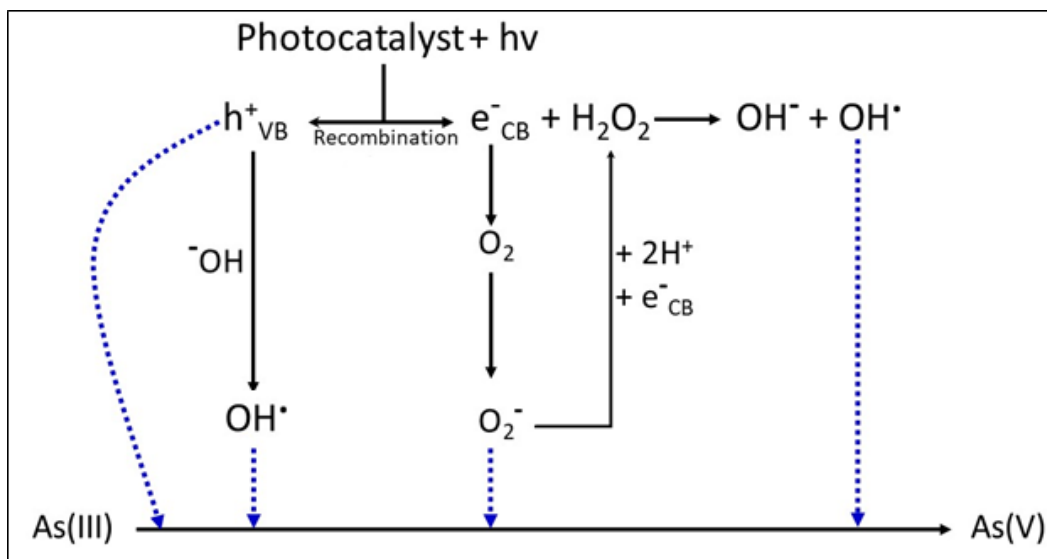


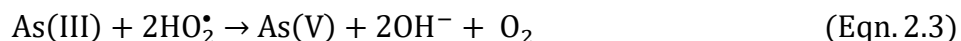
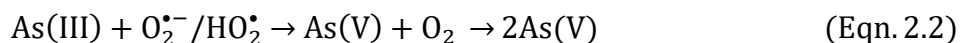
Figure 2. 4. Schematic pathways for free radical generation during photocatalytic oxidation (modified from [69,70]).

2.7 Rate determining step during photocatalysis

The mechanism of the photocatalysis is well described however, the rate limiting step remains as a controversial issue since no agreement has been reached over the exact identity of the major oxidant species among the oxygen radical species or the direct valence band hole oxidation of As(III) [71]. Generally, there are some existing assumptions as follows.

2.7.1 Superoxide ($O_2^{\bullet-}$) as the major oxidant

Lee and Choi [60] argued that superoxide is the main oxidant when they found that the presence of excess dissolved oxygen enhanced the photooxidation due to generation of superoxide ($^{\bullet}O_2$) eqn. 2.2 & eqn. 2.3 while the addition of $^{\bullet}OH$ radical scavenger. e.g. excess tert-butyl alcohol, did not decrease the rate of As(III) oxidation, they concluded that $O_2^{\bullet-}$ leads the main oxidation not the $^{\bullet}OH$ radical. The study concludes the feasibility of $O_2^{\bullet-}$ formation but that is not thermodynamically feasible because the redox potential of $O_2/O_2^{\bullet-}$ is - 0.16 at pH 7 [72].



Another study by Ferguson et al., [66] found that the photocatalysis of As(III) was completely inhibited in N_2 -purged samples and addition of CCl_4 , indicating that holes and $^{\bullet}OH$ radicals do not

play the essential role during the photocatalytic oxidation of As(III). In addition, the reaction of As(III) with an $\cdot\text{OH}$ radical (or hole) was followed by an instance reaction for electron transfer resulting in a null cycle eqn. 2.4. and 2.5.



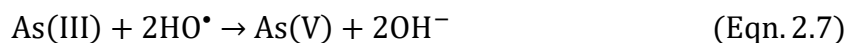
2.7.2 Direct hole (h_{VB}^+) as the major oxidant

Guan et al., [28] found that excess methanol, a scavenger of adsorbed $\text{OH}\cdot$ did not inhibit the oxidation of As(III), so $\text{OH}\cdot$ seemed not to be the main oxidant. However when excess formic acid, a VB hole scavenger was added, the As(III) oxidation was greatly reduced which showed that superoxide played a small role in the oxidation of As(III). Therefore, the best rationale regarding the photocatalytic oxidation of As(III) seemed to be the direct electron transfer between As(III) and positive holes eqn. 2.6.



2.7.3 Hydroxyl radical ($\cdot\text{OH}$) as the major oxidant

During the photooxidation of methylated arsenic species, Xu et al., [73] found that the addition of $\cdot\text{OH}$ radical scavengers, i.e. superoxide dismutase, sodium bicarbonate, tert-butanol, and sodium azide decreases the photocatalytic oxidation rates so they argued that hydroxyl radicals ($\cdot\text{OH}$) are the main reactive oxygen species (eqn. 2.7). For example, Xu et al., [73] found that the addition of tert-butyl alcohol ($\cdot\text{OH}$ radical scavengers) dramatically inhibited the degradation rate of the methylated arsenic species over TiO_2 , suggesting that $\cdot\text{OH}$ is the main oxidant.



2.8 Practical limitations of TiO_2 and possible enhancements

The practical applications of TiO_2 in the photocatalytic oxidation of arsenite are significantly hindered by some limitations as follows.

1- The TiO_2 photocatalyst is only active when irradiated by UV light, due to its wide energy bandgap (3.2 eV), which seriously restricts its applicability under sunlight, since the solar

spectrum contains only a small UV proportion (~4%) that reaches the Earth from the Sun. Overcoming this wide bandgap limitation, can be achieved by several ways such as (i) Doping of metals (e.g. Cu, Sn, Co, Ni, Cr, Mn and Fe) which can result in the formation of a solid solution and the development of new energy levels due to the mixing of cationic d orbitals that primarily form the conduction band. This can reduce the bandgap and retard electron-hole recombination (Fig. 2.5 A); but more often it reduces the potential energy of charge carriers due to the formation of deeper level trap states (i.e. defects in the material). Overall, the outcome is better light absorption but a less active material per photon absorbed [74]; (ii) Doping of non-metals (e.g. C, N, S, B, P, F and I); non-metals do not act as charge carriers and their role as recombination centers might be diminished, which again can result in the formation of a solid solution and the development of new energy levels due to the mixing with anionic p orbitals that primarily form the valence band. This can also reduce the bandgap or retard electron-hole recombination (Fig. 2.5B); (iii) coupling TiO_2 with other semiconductors to form a composite that widens light absorption to higher wavelengths and can increase charge carrier separation and lifetime through charge transfer processes [75].

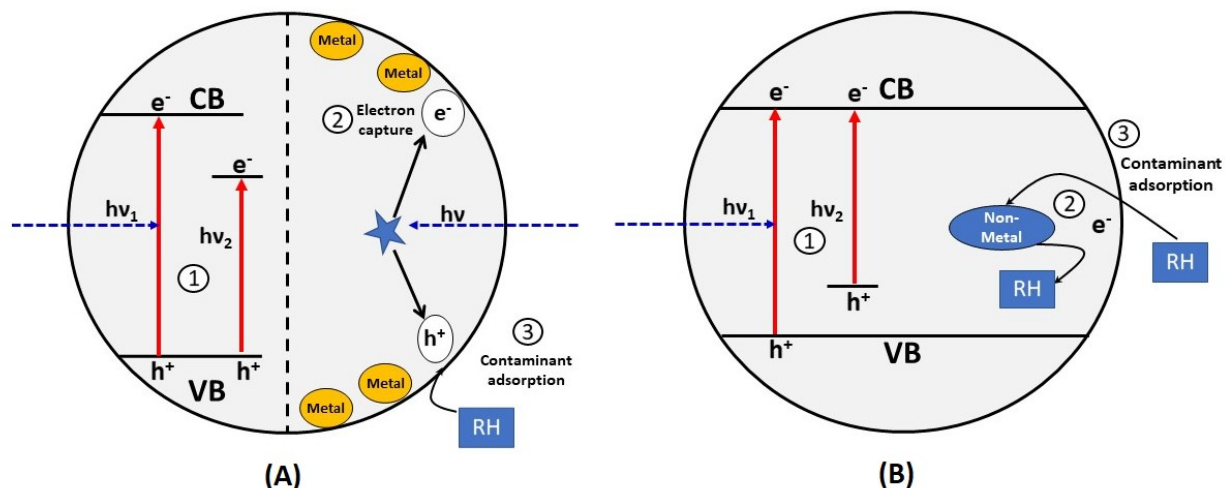


Figure 2. 5. A- (Effect of metal-doping in TiO_2 photocatalysis: 1- bandgap reduction ($h\nu_1$: TiO_2 ; $h\nu_2$: metal-doped TiO_2); 2- restriction of electron/hole recombination; & 3- increase the adsorption of contaminants (RH)). B- (Effect of non-metal doping on the photocatalysis potential of TiO_2 : 1- bandgap reduction ($h\nu_1$: TiO_2 ; $h\nu_2$: non-metal doped TiO_2); 2- enhancement of electron transfer from the bulk of the TiO_2 structure to the surface region (reaction sites); & 3- increases the adsorption of contaminants (RH)) [75].

2- The photocatalytic reaction of TiO_2 is limited by the fast recombination rate of electron-hole pair compared to the chemical reaction rate thereby limiting the overall efficiency of the photocatalytic process. The charge carrier transfer time is longer compared with the electron-hole recombination time. Therefore, most of the photogenerated charge carriers undergo recombination instead of being captured [51,76].

To suppress this negative electron-hole recombination process and improve the efficiency, several methods have been applied such as, (i) anchoring of certain electron withdrawing groups (EWGs) such as phosphates, borates, sulphates, etc., on the surface of TiO_2 have been examined [76]. (ii) coupling with metal oxides (e.g. Fe_2O_3) to form bicomposite material which enables it to act as an electron-transfer channel and acceptor, thereby suppressing the photogenerated carrier recombination and enhancing the photocatalytic activity (iii) surface organic modification by visible light-induced dye-sensitized; dyes have a lower redox potential than the corresponding ground state and so when the redox potential is lower than the conduction band (CB) of TiO_2 , an electron may be injected from the excited state of the dye into the CB of TiO_2 (so improve electron-hole separation) (iii) the crystal structure of TiO_2 used, where anatase has been found to be more effective than rutile despite the bandgap of anatase being marginally higher (3.2 eV for anatase and 3.0 eV for rutile) [75].

3- Although a lot of work has been done on the photocatalysis, there is a gap between the laboratory and industrial application [77]. TiO_2 -based photocatalytic oxidation of arsenic remains uncommercialised due to the treatment cost which includes the preparation of the catalyst [28], the pre-oxidation process and post-treatment of photocatalyst and by-products of the oxidation [28,78]. For example, micro- or nano-scale photocatalysts are difficult to be separated after the photocatalytic reaction by classic separation methods, requiring prolonged operations, and complex equipment, leading to high operational costs [28]. In order to solve the issue of difficult separation and recovery of powdered photocatalysts, some researchers have immobilized catalysts on different supports such as activated carbon, glass, clays and zeolite [79].

4- TiO_2 possesses low reduction but high oxidative power. The idea of coupling of two semiconductors to overcome the disadvantages of their pure phases appears to be promising since it can improve the light absorption and charge carriers' separation efficiency [80].

Therefore, it is highly desirable to develop a visible-light driven TiO_2 photocatalyst with a lower electron-hole pair recombination rate and high intrinsic activity towards the photocatalytic oxidation of arsenite to arsenate. When it comes to the modification of TiO_2 catalyst, a lot of studies has been carried out and nicely presented in these reviews [81–85]. In this study, TiO_2 was doped using different molar ratios of tin (Sn) for the PCO of As(III). Sn doped TiO_2 has been used previously in batteries [86–92], gas sensors [93–95], solar cells [96–100], photocatalysis [12,101–103] of organic compounds. These studies show a promising effect of doping TiO_2 with Sn higher through the suppression in the electron-hole recombination and a marginally lower bandgap.

2.9 Time-resolved analysis of the photocatalytic process

The kinetics of the fast photocatalytic processes induced by the photon absorption and are not often studied. Investigation of this processes is, however, very important to understand the photocatalyst performance and therefore design a better photocatalytic system [104]. The recombination processes during the photoinduced reactions being on the (ps to ns) timescale and continue into the ms timescale where full recombination occurs. An overview of these possible photoinduced reactions inside the photocatalyst and in the solution presented in Figure 2.6. This can be suppressed through modifying the photocatalyst, or reactions of these charge carriers with surface species. To understand the factors that control photocatalytic efficiency, one should probe the charge carrier dynamics and determine the timescales of charge carrier trapping, intrinsic electron-hole recombination and reactions with surface species [104,105].

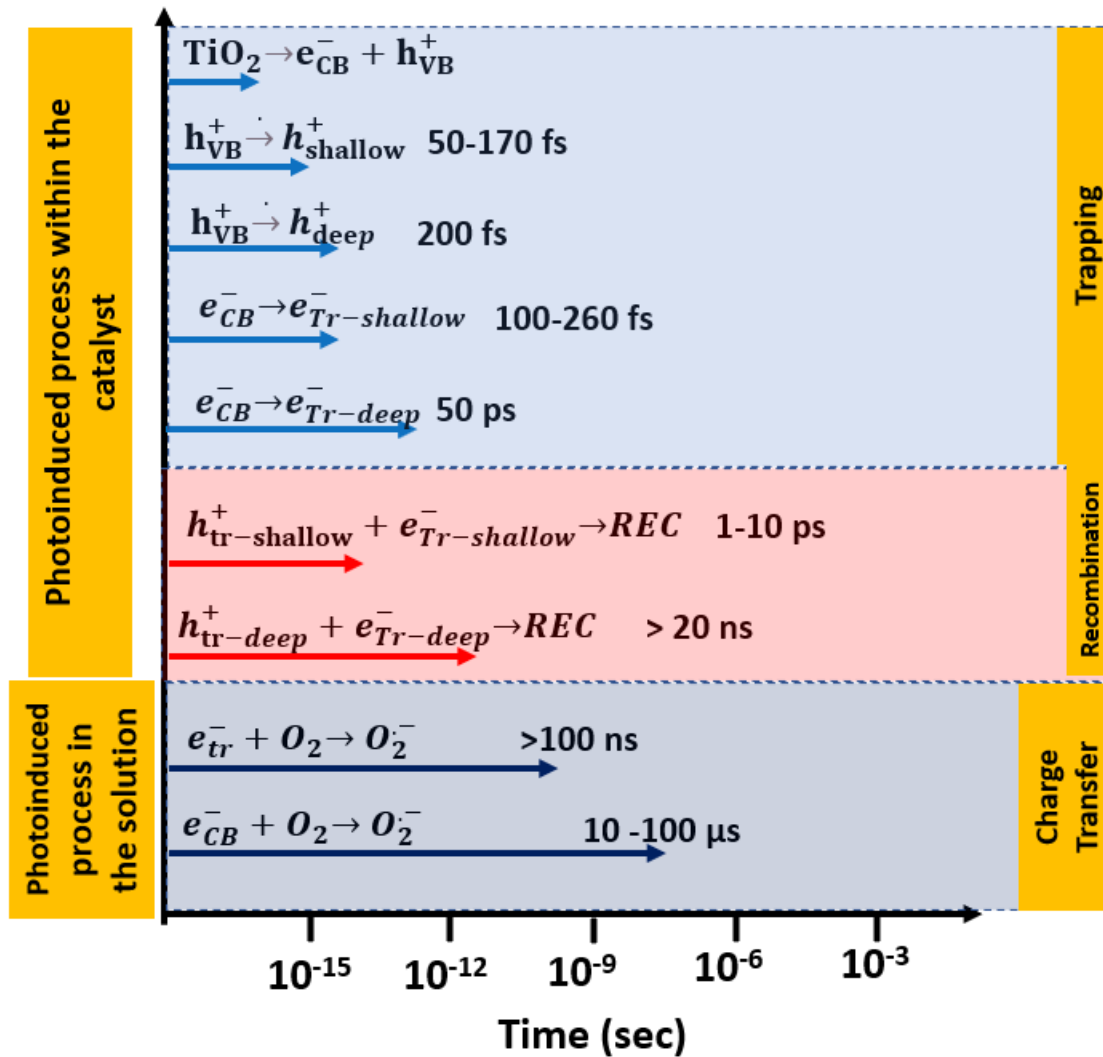


Figure 2. 6. Photoinduced processes and reactions that occur in TiO_2 photocatalysts, and the typical corresponding time scales in which these processes can occur, (REC= Recombination, ps = picosecond, ns=nanosecond).

To understand these processes, time-resolved absorption spectroscopy (TAS) is widely employed because its high resolutions (~ 100 fs) and its ability to identify the nature of the transient species through the use of chemical scavengers or computational modelling [105,106].

In TAS, samples are excited using laser pulse being detected by time-resolved optical spectroscopy from the UV to the IR region employing white light for analysis. Thanks to improvement of the measuring techniques, it is now possible to make measurements on the femtosecond time scale [104].

In TAS of TiO_2 , trapped holes absorb light most strongly at around 500 nm and electrons absorb light most strongly at around 800 nm [107]. There are some limitations to study the reactions

dynamics of holes and electrons in colloidal solutions in TAS experiments such as i) the colloidal stability is limited only to specific solvents, pH and optical absorption and the solvent can limit the spectroscopic measurement in the near-IR and IR wavelength ranges [105]. TAS measurements can be performed in the presence of electron or hole scavenger to elucidate absorption signals, however, in some cases TiO_2 does not disperse well colloidal solution. The TAS limitations in colloidal solutions can be overcome by preparing powder films or by fixing colloidal TiO_2 on a substrate and ultimately TAS measurements can be performed in the near-IR and IR ranges [104,105].

For the usual light irradiation in photocatalysis, it is crucial to measure the transient absorption under the weak-excitation condition to get the actual reaction dynamics. The excitation pulse must be adequately low to that extent that prevents the enhanced migration of the charge carriers to the adjacent particle and therefore undergo the second-order electron–hole recombination. This effect is called trap filling [108–111].

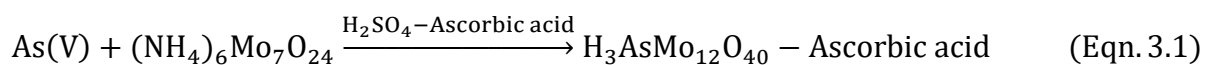
Trap filling does not happen in photocatalytic reactions under sunlight or simulated sunlight conditions, consequently, it is a necessity to perform TAS measurements in weak-excitation condition to conduct a real correlation with the experimental conditions [112]. It worth to note that TAS studies of electrons and holes reaction dynamics in TiO_2 can be easily conducted at nano to microsecond scale but measurements at femto to picosecond scales are not yet fully understood [105]. One of the early studies on the charge transfer dynamics was done by Rothenberger et al. [113] who used colloidal TiO_2 nanoparticles in their study. Rothenberger et al. found that the respective time for the electron transfer to the surface traps was 30 ps, while the hole trapping time was slower on average of 250 ns [113]. Another study was done by Yang and Tamai [114] who studied the charge carrier dynamics using colloidal TiO_2 particles by means of femtosecond laser flash photolysis spectroscopy. The study found that the trapping time of the electrons (260 fs) was longer compared to that of holes (< 50 fs) [114].

3 Materials and Methods

3.1 Arsenic analysis techniques

3.1.1 Validation of spectrochemical UV-Vis molybdenum blue method

The speciation of aqueous As(V) and As(III) was determined using a modified colorimetric molybdenum method [115,116]. The analytical solution was prepared by subsequent dissolving the following reagents in 100 mL ultrapure water: 0.5 g ammonium molybdate, 0.04 g potassium antimony tartrate, 4 mL H₂SO₄ (95-99%), 0.5 g ascorbic acid. As(V) also forms arseno-molybdate complex with molybdate. However, the exact chemical reaction is unclear (Nagul et al., 2015), it is expected to be as shown in eqn. 3.1 [116]



Determination of the maximum absorption peak of arseno-molybdate was performed by adding 80 µL of the previously prepared analytical solution to 1 mL of 5 mg/L As(III) and 5 mg/L As(V), then samples were shaken and left for 1 h. Only As(V) sample developed a blue colour. Finally, the samples were placed individually in 1 cm cuvette pathlength and the absorbance was scanned in the wavelength range (350 - 1000 nm) using Jenway 7315 spectrophotometer. The maximum absorption peak of the blue arseno-molybdate complex was found at 882 nm, as presented in Figure 3.1 while As(III) solutions remained colourless, showing that the molybdate method is selective towards As(V) and not As(III).

Total arsenic As(T) concentration in the solution was measured through the initial pre-oxidation of the sample's species [As(III)] to As(V) by adding 120 µL of 0.32 mmol/L potassium permanganate (KMnO₄) to 1 mL of each aliquot while shaking. The sample was left for 1 h to allow complete oxidation, then the amount of As(V) [representing total As] was determined using the aforementioned molybdenum blue method.

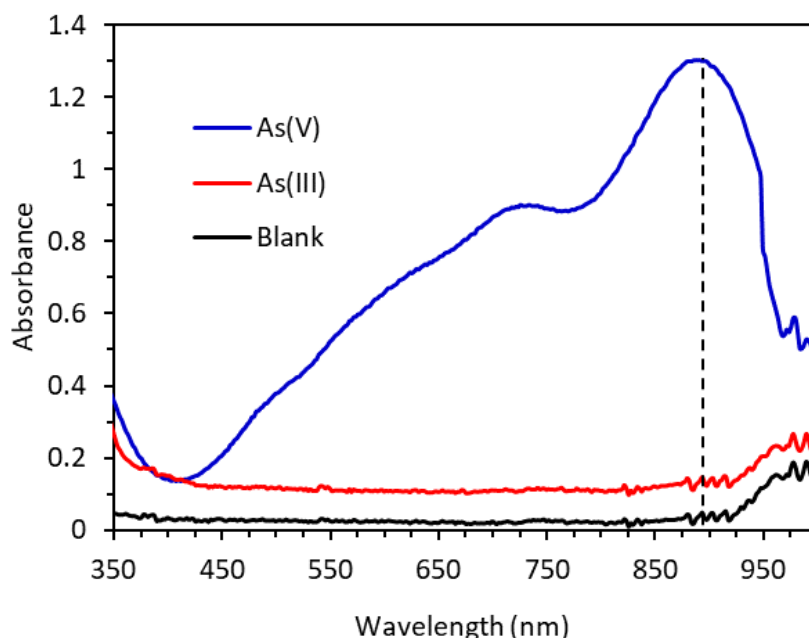


Figure 3. 1. UV-VIS scan for blank, 5 mg/L As(V) and 5 mg/L As(III), 80 μ L of 100 mL analytical solution (0.5 g ammonium molybdate, 0.04 g potassium antimony tartrate, 4 mL H_2SO_4 and 0.5 g ascorbic acid) was added to 1 mL of 5 mg/L As(V) and 5 mg/L As(III), then samples were shaken and left for 1 h.

To validate the method, a range of standard solutions (100 to 10,000 μ g/L total arsenic) varying in arsenic fractions (100% As(III), 50% As(III) +50% As(V), 100% As(V)) were measured using the molybdenum blue method [115,116]. As(V) was measured through the direct addition of molybdenum reagent. The results presented in Figure 3.2A, for 100% As(III) solutions, show that the As(III) and total arsenic levels were approximately equal for the range of concentrations measured, with no As(V) being detected. This is because the dye preferentially complexes with As(V) ions to generate a blue colour. Figure 3.2B, for 50% As(III) +50% As(V) solutions, shows the concentration of total arsenic is approximately double the As(III) and As(V) concentrations. Figure 3.2C, for 100% As(V) solutions, shows that the concentration of As(V) is approximately equal to the concentration of total arsenic, with no As(III) being detected. Therefore, it is reasonable to conclude that the molybdenum blue method can successfully differentiate between As(III) and As(V), where molybdate can selectively interact with As(V) and develop the blue colour of arsenomolybdate complex.

ICP-MS (Agilent 7900 quadrupole ICP-MS with a helium collision cell) was used to assess the accuracy of the spectrochemical molybdenum blue method in its determination of As

concentrations. As presented in Figure 3.3, the molybdenum blue method showed both high accuracy and precision compared with ICP-MS.

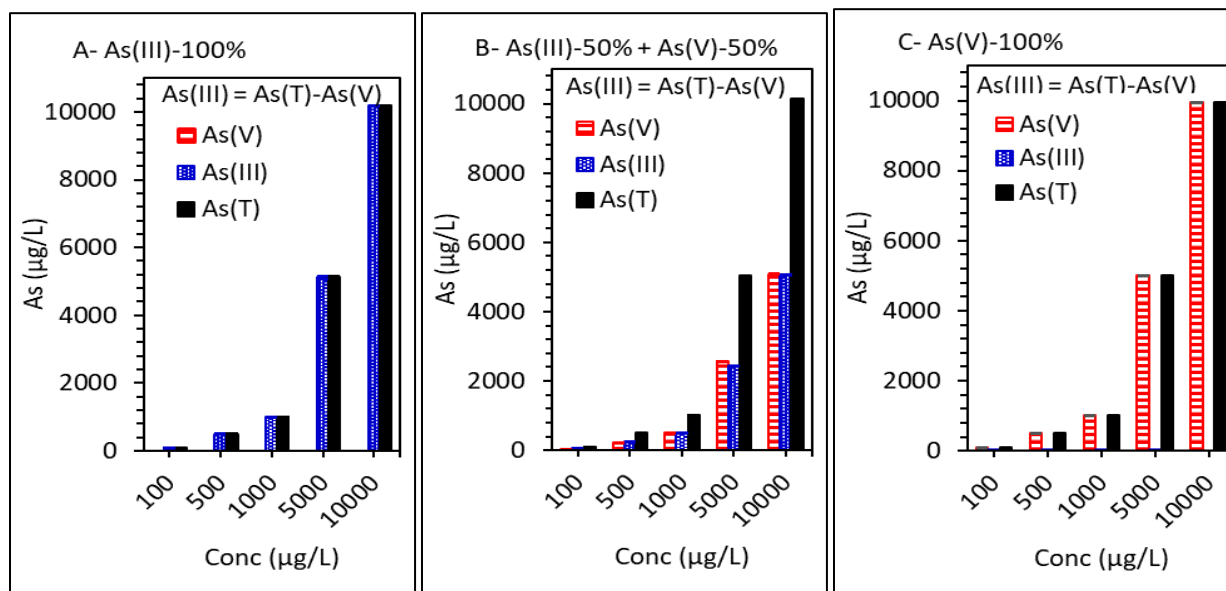


Figure 3. 2. Analysis of arsenic species using the spectrochemical molybdenum blue method [A- stock solution were prepared as 100% As(III), B- Stock solutions were prepared as 50% As(III) + 50% As(V) and C- stock solutions were prepared as 100% As(V)]. [As(III)] is determined by, (i) measuring [As(III)] using Mo method, (ii) oxidising the reaction solution with $KMnO_4$ and measuring [As] total using Mo method and finally (iii) taking $[As(III)] = [As]_{total} - [As(III)]$.

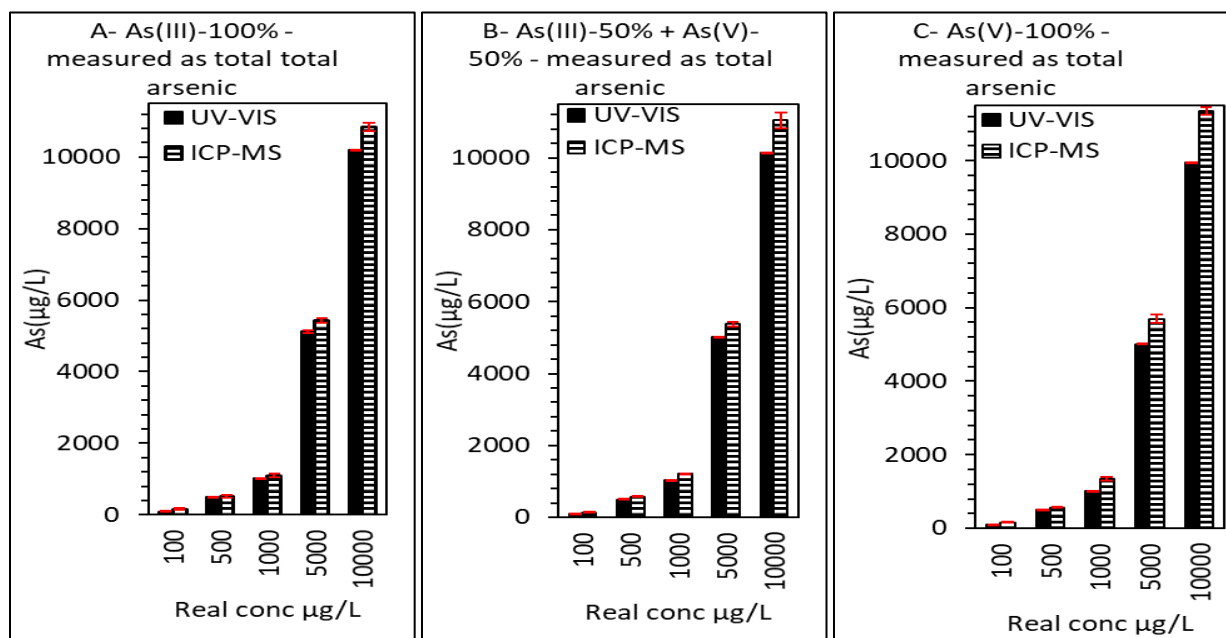


Figure 3. 3. Total arsenic concentration measured by UV-Vis and ICP-MS [A- stock solution were prepared as 100% As(III), B- Stock solutions were prepared as 50% As(III) + 50% As(V) and C- stock solutions were prepared as 100% As(V)].

3.1.2 Square wave anodic stripping voltammetry

Concentrations of As(III) were determined electrochemically, using square wave anodic stripping voltammetry (SWASV) and a previously described method [117,118], using the Metrohm 663 VA Stand, the IME663 interface and the General Purpose Electrochemical System (GPES) software. Detection was made using a 25 μm diameter gold microwire working electrode, iridium wire auxiliary electrode, and a silver-silver chloride reference electrode ($\text{Ag}/\text{AgCl}/\text{NaNO}_3(1\text{M})$). The working electrode was conditioned each day by performing a cyclic voltammetry (CV) scan in 0.5 M H_2SO_4 . The electrode was conditioned at -2.5 V (30 s), followed by 5 repeat scans between -0.2 and +1.5 V (scan rate 1 V s^{-1}). For arsenic analysis, samples were acidified to pH 2 with 0.01 M HCl in the presence of 40 μM hydrazine to prevent oxidation of arsenic. Afterwards, the solution was purged of oxygen by bubbling nitrogen for several minutes prior to analysis. To detect arsenic, the working electrode was first conditioned at +0.7 V (5 s) then arsenic was deposited at -0.7 V (20 s). Arsenic was then stripped using a sweep between -0.5 and +0.7 V. The square wave profile had an amplitude of 50 mV, frequency of 50 Hz, and 8 mV step size. The background scan was recorded under the same operating conditions but the deposition time was reduced to 1 s only to decrease arsenic deposition, and then the background subtracted from the analytical scan. The peak derivative (representing the current) was used for quantification, giving a better precision than peak height and peak area. Uncertainties were calculated from the standard error between 2 or 3 measurements of the same example. Inductively coupled plasma mass spectroscopy

Concentrations of total arsenic were validated using inductively coupled plasma mass spectroscopy (ICP-MS), using the Agilent 7900 quadrupole ICP-MS with a helium collision cell. Samples were acidified by addition of 2% (v/v) HNO_3 . An external calibration curve was recorded using a certified single-element standard (Fluka, $1000 \pm 4 \text{ mg/L}$, trace CERT), and the data was normalized to internal standards (yttrium).

3.2 Synthesis of TiO₂, Sn-doped TiO₂ and SnO₂

3.2.1 Sol-gel (SG) Synthesis

Unmodified TiO₂ and Sn-doped TiO₂ were synthesised using a sol-gel method. A series of different molarities (0.1, 0.25, 0.5 and 1 M) of tin tetrachloride (SnCl₄) were dissolved in ethanol as presented in Table 3.1 (pure TiO₂ was prepared by substituting SnCl₄ for 5 mL deionised H₂O). The SnCl₄ suspension was added dropwise at room temperature to 1 M solution of titanium(IV) tert-butoxide (Ti[OC(CH₃)₃]₄) (*i.e.* 5.12 mL of Ti[OC(CH₃)₃]₄ dissolved in 15 mL ethanol). After stirring continuously for 2 h, a sol was produced, which was left for 24 h at room temperature. The obtained xerogel was subsequently calcined at 450 °C for 4 h, and the catalyst was ground to obtain a fine powder [119].

A pure SnO₂ reference sample was synthesised in accordance with literature methods [120,121]. A transparent sol solution was prepared by dissolving 5 g SnCl₄ in 100 mL of absolute ethanol under vigorous magnetic stirring for 30 min. At a controlled rate, ammonia solution was then added dropwise while stirring until reaching of pH of ~8–9. Afterwards, the hydrolysis and condensation reactions were initiated by adding 10 mL of distilled H₂O dropwise under continuous stirring for 2 h. The resulting gel was then dried at 70 °C for 1 h to remove traces of ethanol impurities. Then, the powder was calcinated at 400 °C for 2 h. Finally, the material was cooled down to room temperature. The resulting material is referred to as SnO₂.

Table 3. 1: Calculation of Sn:Ti molar ratios used in Sn-TiO₂ sol-gel synthesis.

	SnCl ₄ *	H ₂ O	Ti[OC(CH ₃) ₃] ₄ **
TiO ₂	-----	5ml distilled H ₂ O and 10ml C ₂ H ₅ OH	5.12 ml Ti[OC(CH ₃) ₃] ₄ dissolved in 9.88 ml C ₂ H ₅ OH
0.1Sn:1TiO ₂	0.17 ml of SnCl ₄ dissolved in 14.82 ml C ₂ H ₅ OH	-----	5.12 ml Ti[OC(CH ₃) ₃] ₄ dissolved in 9.88 ml C ₂ H ₅ OH
0.25Sn:1TiO ₂	0.44 ml of SnCl ₄ dissolved in 14.56 ml C ₂ H ₅ OH	-----	5.12 ml Ti[OC(CH ₃) ₃] ₄ dissolved in 9.88 ml C ₂ H ₅ OH
0.5Sn:1TiO ₂	0.88 ml of SnCl ₄ dissolved in 14.12 ml C ₂ H ₅ OH	-----	5.12 ml Ti[OC(CH ₃) ₃] ₄ dissolved in 9.88 ml C ₂ H ₅ OH
1Sn:1TiO ₂	1.76 ml of SnCl ₄ dissolved in 13.24 ml C ₂ H ₅ OH	-----	5.12 ml Ti[OC(CH ₃) ₃] ₄ dissolved in 9.88 ml C ₂ H ₅ OH

*SnCl₄, Mwt = 260.5 g/L, density 2.23 (each mole of SnCl₄ contains one mole of Sn).

**Ti[OC(CH₃)₃]₄ Mwt = 340.32 g/L, density 0.998 (each mole of Ti[OC(CH₃)₃]₄ contains one mole of TiO₂).

3.2.2 Thermal diffusion (TD) synthesis

Different molar ratios (from 0.1 to 1) of SnCl_4 were mixed with one molar TiO_2 -anatase in an agate mortar pestle for 1 h. The mixture was then placed in a crucible and annealed in a muffle furnace at 973 K for 8 h. Afterwards, the mixture was allowed to cool down to room temperature and grinded in the mortar pestle and again calcinated at 1,173 K for 8 h. Finally, the samples was cooled down to the room temperature and the catalyst powder obtained [122].

3.3 Materials characterisation

The crystal phases of the catalysts were investigated using a Bruker D2 Phaser X-ray diffractometer (XRD) equipped with a Lynxeye detector. The instrument uses a Cu source for X-ray generation ($V = 40$ kV, $I = 30$ mA) with Cu $K_{\alpha 1}$ ($\lambda = 1.54056$ Å) and Cu $K_{\alpha 2}$ radiation ($\lambda = 1.54439$ Å) emitted with an intensity ratio of 2:1. Patterns were recorded over the 2θ range from 5 to 90° . Models were fit to the data using GSAS and EXPGUI software [123].

Raman spectra were recorded using a Horiba LabRam Infinity equipped with a helium-neon laser (633 nm, 25 mW). The system was calibrated to a silicon reference (520 cm^{-1}) and samples were analysed over the 200 to 1200 cm^{-1} range. Standard patterns were acquired from the RRUFF project database.

Surface chemical analysis was performed using X-ray photoelectron spectroscopy (XPS) with a ThermoScientific K-Alpha⁺ X-ray photoelectron spectrometer equipped with a MXR3 Al K_{α} monochromatic X-ray source ($h\nu = 1486.6$ eV). Samples were dried at 100°C for 24 hours to remove the physically adsorbed water prior to analysis. Survey spectra and the binding energy regions of the O1s, C1s, Ti2p, Sn3d, As2p regions (20 scans) were recorded. Models were fit to the XPS data using CASAXPS software [124].

The outermost surface atomic layers were analysed using low energy ion scattering (LEIS) with the IONTOF Qtac 100 instrument. Before analysis, samples were pumped down to vacuum overnight to remove adsorbed water. LEIS survey spectra were obtained using a 3 keV He^+ primary ion beam with a current of $\sim 5\text{ nA}$ and a raster field of view 1 mm^2 . The current density was measured using a Faraday cup before and after each depth profile run. To remove surface impurities, depth profiling was carried out using successive cycles of He^+ ion with overall ion dose

reaching $\sim 5.3 \times 10^{15}$ ions/cm². The ion dose is the number of ions per acquisition time is calculated by eqn. 3.2 and the ion dose density is the dose per acquisition area.

$$\text{Dose} = I \frac{t}{e} \quad (\text{Eqn. 3.2})$$

where I is the supplied current in amperes (A), t is the rastering time (time per acquisition in seconds where each acquisition corresponds to one data point), and e is the electron charge (1.6×10^{-19} coulomb).

The bulk elemental analysis was measured using SEM-EDX (JEOL 6010LA).

The surface micrographs were obtained using a high-resolution LEO Gemini scanning electron microscope (SEM) operating at 5 kW in secondary electron mode (InLens detector), JEOL 2100F TEM/STEM operating at an accelerating voltage of 200kV.

Surface functional groups were identified using a ThermoScientific NICOLET is5-iD7 ATR attenuated total reflection infrared (ATR-IR) spectrometer. Samples were scanned over the 4000 - 400 cm⁻¹ range without preliminary grinding.

3.4 Determination of the bandgap using DRS

The Tauc method for determining the bandgap energy presumes that the energy-dependent absorption coefficient (α) can be expressed by eqn. 3.3 [125].

$$(\alpha h\nu)^{\frac{1}{\gamma}} = (h\nu - E_g)B \quad (\text{Eqn. 3.3})$$

where h is the Planck constant, ν is the photon's frequency, E_g is the bandgap energy, and B is a constant. γ is a transition-dependent factor which equals to 2 or 1/2 for an indirect and a direct transition bandgap, respectively. The energy-dependent absorption coefficient (α) is replaced by $F(R)$, the relative absorption coefficient that is measured from diffuse reflectance spectra (DRS) using of dry powder held between glass slides using Shimadzu UV-2700 spectrophotometer, equipped with an integrating sphere, in the 190-1400 nm wavelength range. Then the Kubelka–Munk function was applied (eqn. 3.4).

$$F(R) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (\text{Eqn. 3.4})$$

where R is the reflectance, while K is the absorption coefficient and S is the scattering coefficients. Replacing α by $F(R)$ yields eqn. 3.5.

$$(F(R)hv)^{\frac{1}{\gamma}} = (hv - E_g)B \quad (\text{Eqn. 3.5})$$

By using Tauc equation and plotting the absorption coefficient against the photon energy, the bandgap can be calculated [125]. To calculate the TiO₂ bandgap, eqn. 3.5 was justified by $\gamma = 2$ (presuming an indirect bandgap) while the standard SnO₂ bandgap was calculated using $\gamma = \frac{1}{2}$ considering the indirect SnO₂ bandgap [126].

3.5 Photocatalytic oxidation (PCO) and adsorption of As(III)

A stock solution of 1000 mg/L As(III) was prepared by dissolving 0.66 g of As₂O₃ in a beaker containing 5 mL of 1 M NaOH, followed by 30 min shaking, then transfer to a 500 mL volumetric flask and complete to the mark with deionized water (Milli-Q). Working solutions were prepared by sequential dilution of the stock solutions.

Parallel photocatalytic oxidation (PCO) experiments were conducted using a suspension of 100 ml of a specified concentration of As(III) and a specified weight of TiO₂, Sn-TiO₂ or SnO₂ photocatalyst (As stated in each figure caption). The pH was adjusted to 7.41 (Unless otherwise stated in the figure caption) using 1 M HCl and 1 M NaOH. The suspension was irradiated with UV while keeping magnetic stirring using a purpose-made photoreactor (Figure 3.4). The distance between the UV lamp (18 W UVA lamp – 370 nm; Sylvania) and the sample surface was 1.8 cm (unless it changed in the effect of distance between light source and the solution surface). At that distance the light irradiation was 5.59 mW/cm² and thus total irradiance received by the PCO reactor surface was 114.03 mW where the reactor surface area was 20.4 cm² (the lamp power measurement and calculation is described in section 3.7). The lamp was centrally placed over the lamp to allow a uniform light irradiance exposure to the sample. The UV lamp was allowed to warm up for 15 min before the start of each experiment and its power was periodically monitored every week to avoid the irradiation instability over the course of the experiments. The UV lamp was turned on during in the oxidation step while it was off in the other experiment used to evaluate the adsorption fraction.

Sequential experiments were carried out by stirring suspensions in the dark for 2 hr, and time t=0 corresponds to when the ultraviolet lamp was switched on. Parallel experiments, TiO₂ was added to the solution of As(III) at time t=0, with or without ultraviolet irradiation. Aliquots (2 mL) were

collected at predetermined time intervals (1, 3, 5, 10, 20, 40, 60 and 120 mins) and centrifuged to separate TiO₂ from the aqueous phase. Finally, the supernatant was analysed for arsenic species as explained in (section 3.2.1). The PCO yield was calculated with a correction for the directly adsorbed As(III) (*i.e.* the decrease in As(III) concentration which is not due to oxidation). This correction was applied at each time interval using eqn. 3.6.

$$[\text{As(III)}]_{\text{oxidised}} = [\text{As(III)}]_{\text{dark}} - [\text{As(III)}]_{\text{under UV}} \quad (\text{Eqn. 3.6})$$

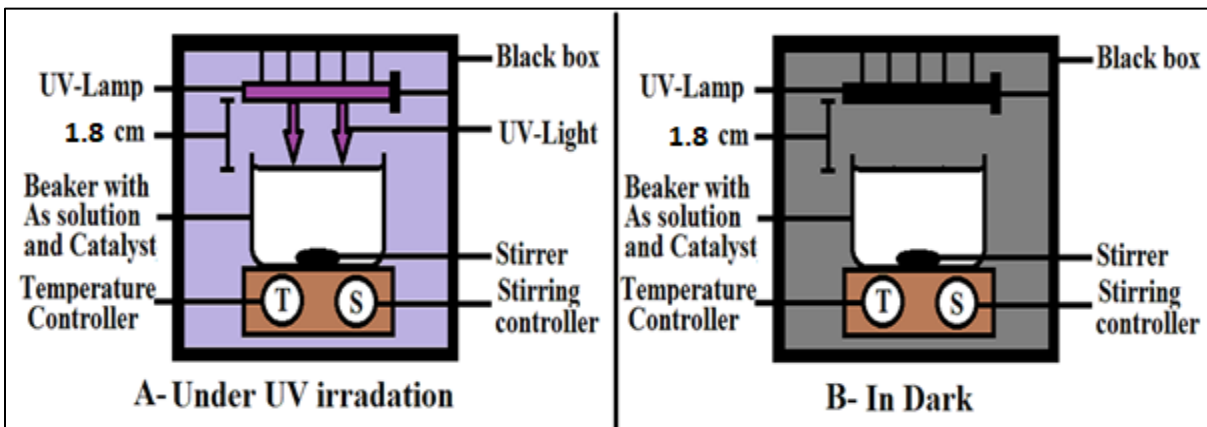


Figure 3. 4. Schematic representation of the photoreactor (A- Samples under UV irradiation for PCO and B- Samples in dark while UV is off for adsorption correction).

3.6 Analysis of aqueous and surface adsorbed As(V) and As(III)

The speciation of aqueous As(V), As(III) and As(T) was analysed using the colorimetric molybdenum method [115,116] as previously described in section 3.1.1.

XPS was used to analyse the surface adsorbed As(III) and As(V). Along the PCO experiment, 2 mL of the sample was collected at each time interval and centrifuged for 1 h. Afterwards, the catalyst was separated and dried overnight in the oven at 70 °C and finally analysed for As(III) and As(V) using XPS.

3.7 Measuring the lamp power

The lamp power was measured using an optical power meter (PM 100, Thorlabs) connected to a power sensor (S120UV, Thorlabs). To accurately measure the lamp power, the visible light reaching the power meter should be excluded. Therefore, its lamp power in mW/cm² is the difference between the lamp power without applying light filter and the lamp power while applying a long pass (LP) Filter < 400 nm [that allows all light with λ > 400 nm to pass through].

Then the calculated lamp power was divided by the detector area and finally the output was multiplied by the photocatalysis reactor area. The calculations steps are summarized in eqn 3.7.

$$\text{Lamp power (mW)} = \frac{[P_{\text{(without filter)}}(\text{mW}) - P_{\text{(400 nm LP filter)}}(\text{mW})]}{A_{\text{power meter detector}}(\text{cm}^2)} * A_{\text{PCO reactor surface}}(\text{cm}^2) \quad (\text{Eqn. 3.7})$$

Where $P_{\text{(without filter)}}$ is the lamp power without using light filter, $P_{\text{(400 nm LP filter)}}$ is lamp power while applying 400 nm LP light filter, $A_{\text{(power meter detector)}}$ is the power meter detector area and $A_{\text{(PCO reactor surface)}}$ is the surface area of the PCO reactor being exposed to the light.

For example, at 1.8 cm distance between the lamp and the solution surface, $P_{\text{(without applying light filter)}} = 6.201 \text{ mW}$, $P_{\text{(LP Filter 400 nm)}} = 1.811 \text{ mW}$, $A_{\text{(power meter detector area)}} = (0.79 \text{ cm}^2)$ and the $A_{\text{PCO reactor surface area}} = 20.4 \text{ cm}^2$. Therefore, the light irradiation = 5.59 mW/cm^2 and the total irradiance received by the PCO reactor surface = 114.03 mW .

3.8 Determination of the quantum efficiency (QE)

The spectral output of the UV lamp (18 W UVA lamp, $\lambda=370 \text{ nm}$, Sylvania) used in our PCO experiments was measured using an Ocean Optics detector (USB4000-VIS-NIR) equipped with a fiber optic cable (QP600-2-UV/BX) and processed using Spectra Suite software, scanning its emission from 350 nm to 1000 nm. The light irradiance was measured as described in section 3.7. To determine the photon flux, various short pass filters were used to prevent visible light from the lamp reaching the power meter ($\lambda < 400 \text{ nm}$, $\lambda < 475 \text{ nm}$ and $\lambda < 610 \text{ nm}$). Emission spectra were adjusted to achieve the corresponding measured photon energy output (J) using eqn. 3.8:

$$J = \frac{h\nu}{c} \quad (\text{Eqn. 3.8})$$

where h represents the Planks constant, ν the frequency in (Hz) and c the light speed in cm.s^{-1} . Lamp power was then converted to photon flux ($\text{cm}^{-2}.\text{s}^{-1}$) using eqn. 3.9:

$$\text{photon flux } (\Phi, \text{cm}^{-2}.\text{s}^{-1}) = \frac{\text{lamp power } (\text{W/cm}^2)}{\text{photon energy (J)}} \quad (\text{Eqn. 3.9})$$

The optical transmittance of powder suspensions of the photocatalyst (0.01 g/ 100 mL) was measured using a Shimadzu UV-2700 equipped with an integrating sphere. The transmittance was converted to molar absorptivity (ϵ , $\text{M}^{-1}.\text{cm}^{-1}$) at different pathlengths (l) using the Beer-Lambert law (Eqn. 3.10):

$$\varepsilon = \frac{A}{(C \cdot l)} \quad (\text{Eqn. 3.10})$$

where A is the absorbance, C is the molar concentration and l is the pathlength in cm.

The extent of the photon flux ($\text{cm}^{-2} \cdot \text{s}^{-1}$) at a given depth was determined using eqn. 3.11:

$$I_{\text{abs},\lambda,l} = I_{0,\lambda} (1 - 10^{(-\varepsilon_{\lambda} \cdot c \cdot l)}) \quad (\text{Eqn. 3.11})$$

where $I_{\text{abs},\lambda}$ represents the photon fraction absorbed at the wavelength (λ) and pathlength (l), $I_{0,\lambda}$ is the overall emitted photon flux at λ , ε_{λ} ($\text{M}^{-1} \text{cm}^{-1}$) is the molar absorption coefficient, c (M) is the concentration of TiO_2 in water and l (cm) is the pathlength of the light solution.

The quantum efficiency (QE) expresses the ratio between the number of converted species and the number of photons absorbed by the photocatalyst (Eqn. 3.12):

$$\phi = \frac{\text{reaction rate}}{\text{rate of photon absorption}} \quad (\text{Eqn. 3.12})$$

The reaction rate and the photon absorption rate are given by eqn. 3.13 and 3.14 respectively:

$$\text{Reaction rate (moles} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) = \frac{\text{reacted species (moles)}}{\text{time(s)} \cdot \text{surface area (cm}^2\text{)}} \quad (\text{Eqn. 3.13})$$

$$\text{Photon absorption rate (moles} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) = \frac{\text{absorbed photons (moles)}}{\text{time(s)} \cdot \text{surface area (cm}^2\text{)}} \quad (\text{Eqn. 3.14})$$

3.9 Calculations of adsorption and PCO kinetic rates

To calculate the adsorption kinetics, the adsorption capacity of TiO_2 at time t (Q_t) and at equilibrium (Q_e) which were calculated using eqn. 3.15 and eqn. 3.16 respectively.

$$Q_t = \frac{(C_o - C_t)V}{m} \quad (\text{Eqn. 3.15})$$

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (\text{Eqn. 3.16})$$

where C_o , C_e and C_t represent arsenic concentrations ($\mu\text{g/L}$) at the time (0) and at time (t) respectively, V is the sample volume in liter (L) and m is the TiO_2 mass in grams (g).

The first order kinetic rate, k_1 (min^{-1}) is calculated using eqn. 3.17.

$$\frac{\ln C_t}{C_i} = -kt \quad (\text{Eqn. 3.17})$$

Pseudo-second-order (PSO) kinetics is calculated using eqn. 3.18.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (\text{Eqn. 3.18})$$

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the second order rate coefficient.

The standard deviation values were calculated based on the linear fitness of the points.

3.10 Transient Absorption Spectroscopy (TAS) investigations

The experimental set-up were used as reported by Jiamprasertboon et al. [127], using a 355 nm laser, however some alterations were made; (1) an increase in the frequency of the laser pulse to ~ 1 Hz. (2) The measurements of the diffuse reflectance were between 600 and 1000 nm using 100 nm increments. (3) 100 laser pulses were used to calculate each kinetic trace, except for experiments in As(III) suspensions.

Here, in order to reduce the error of progress of As(III) photooxidation due to the laser pulse, an average of 10 pulses was collected at each wavelength (in a random order), with triplicate measurements (a total of 30 pulses at each wavelength). (4) Samples were measured as (a) a dry film in air, (b) in water (c) in 2mM AgNO_3 (d) in methanol (d) 1 mg/L As(III) in Molybdate.

The optical density change (ΔOD) at time (t), and wavelength (λ), is related to the change in the intensity of light (transmitted or reflected) through the eqn. 3.19:

$$\Delta\text{OD}(t, \lambda) = -\log \left(1 + \frac{\Delta I(t, \lambda)}{I_0(\lambda)} \right) \quad (\text{Eqn. 3.19})$$

Where I_0 is the intensity of light (transmitted or reflected) before the laser pulse [128].

A component additive prediction (treating SnO_2 , TiO_2 and 1Sn:1TiO₂ phases within the composite photocatalyst as non-interacting components) was calculated to assess the opportunity of charge transfer across the 1Sn:1TiO₂ heterojunction. First, to determine the half-lives of the transient absorption, then to model transient absorption decay curves using a power-law decay (eqn. 3.20).

$$[h^+]_t = A t^{-\alpha} \quad (\text{Eqn. 3.20})$$

where $[h^+]_t$ is the holes concentration at time t (defined by the change in optical density, ΔOD), t is time (seconds), and A & α are the fitting parameters [129]. Parameters A & α were optimized to improve the (R^2) fit between experimental and modelled data. During fitting, data before 0.1

and after 100 ms were excluded due to interference from the laser pulse and loss of material suspension respectively. TAS spectra were standardized to unity at $t=100\ \mu\text{s}$, with the normalized value of A calculated via eqn. 3.21:

$$A_{\text{normalised}} = \frac{1}{0.0001^{-\alpha}} \quad (\text{Eqn. 3.21})$$

The half-lives ($t_{1/2}$) of TAS spectra were finally determined by reordering of eqn. 3.20 to eqn. 3.22.

$$t_{1/2} = \left(\frac{1}{2} \cdot \frac{1}{A_{\text{normalised}}} \right)^{-\frac{1}{\alpha}} \quad (\text{Eqn. 3.22})$$

3.11 Chemicals and reagents

The list of chemical and suppliers are listed in Table 3.2.

Table 3. 2: List of chemicals used in this study.

Chemical	Supplier company
Tin tetrachloride (SnCl_4)	Sigma Aldrich
Titanium(IV) tert-butoxide ($\text{Ti}[\text{OC}(\text{CH}_3)_3]_4$)	Sigma Aldrich
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	VWR
Arsenic trioxide (As_2O_3)	Sigma Aldrich
Sodium Hydroxide (NaOH)	VWR
Hydrochloric acid (HCl)	AnalaR
Nitric acid (HNO_3)	AnalaR
Ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$)	Sigma Aldrich
Potassium antimony tartrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2$)	AnalaR
Sulphuric acid H_2SO_4 (95-99) %	VWR
Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$)	Sigma Aldrich
Potassium permanganate (KMnO_4)	Sigma Aldrich
Silver nitrate (AgNO_3)	Sigma Aldrich
Isopropanol ($\text{C}_3\text{H}_8\text{O}$)	VWR
Methanol (CH_3OH)	VWR
Rebamipide Anhydrous	Sigma Aldrich
Dimethyl Sulfoxide (DMSO)	VWR
Superoxide Dismutase (SOD)	Sigma Aldrich
P-benzoquinone	Sigma Aldrich
Magnesium Chloride (MgCl_2)	Sigma Aldrich
Sodium Sulfate (Na_2SO_4)	Sigma Aldrich
Calcium Chloride (CaCl_2)	Sigma Aldrich
Potassium Chloride (KCl)	Sigma Aldrich
Potassium Bromide (KBr)	Sigma Aldrich
Sodium Bicarbonate (NaHCO_3)	Sigma Aldrich
Boric Acid (H_3BO_3)	Sigma Aldrich
Strontium Chloride (SrCl_2)	Sigma Aldrich
Sodium Fluoride (NaF)	Sigma Aldrich

4 Determination of oxidation rates and quantum efficiencies during the photocatalytic oxidation of As(III) over TiO_2

4.1 Introduction

Arsenic is a potent carcinogen, with tens of millions of people exposed to dangerous levels worldwide [130]. Due to severe toxicity, in 2009 the World Health Organization (WHO) imposed strict regulations lowering the permitted level of arsenic in drinking water from 50 to 10 $\mu\text{g/L}$ [18,19,28]. The toxicity of arsenic is determined by its speciation: inorganic arsenic is more harmful than organic arsenic [18,19]. Inorganic As(III) is 60 times more toxic than inorganic As(V) [131] because inorganic As(III) can easily bind with certain proteins and transported into the cell. In contrast, As(V) cannot enter the cell by such mechanism. Thus As(III) is more soluble and difficult to excrete [132].

The removal of As(III) from contaminated water is more challenging [133] since it predominantly forms non-ionic species at neutral and acidic pH (H_3AsO_3), whereas As(V) exists as anionic species (H_2AsO_4^- and HAsO_4^{2-}) [134]. Therefore, effective water treatment necessitates the oxidation of As(III) to As(V) prior to its removal using strategies such as adsorption, precipitation, or ion exchange [135].

Photocatalytic oxidation (PCO) of As(III) to As(V) using TiO_2 is a promising solution [36] due to the high chemical stability, corrosion resistance, non-toxicity and photocatalytic activity of the material [54]. The accurate determination of oxidation rates is crucial to successfully implement photocatalysts into arsenic treatment plants [136], however, this is challenged by various process that occur during the experimental determination, such as co-occurring adsorption (Figure 4.1).

Table 4. 1: Experimental conditions used in literature in the PCO of As(III) using TiO₂

Light source (nm)	Light irradiance	TiO ₂ (g/L)	[As (III)] (mg/L)	pH	Scavengers	Dark absorption (hr)	Analysis method	reference
Xe short-arc lamp ($\lambda < 320$ nm)	<i>ns</i>	0.001- 0.05	0.1	5,7,9	<i>ns</i>	<i>ns</i>	[As(III)] HPLC-ICP-MS	[59]
Hg lamp (High pressure)	12.5 (mW/cm ²)	0.01, 0.1	3-20	4, 9	Benzoic acid, salicylic acid, 17 μ M Fe(III)	2	[As(V)] UV- Vis/molybdenum blue	[65]
UVC lamp (254 nm)	8.9 (mW/cm ²)	0.01-1	0.1-1	6.7	<i>ns</i>	2	[As(III)] Anion exchange/HGAAS	[137]
Xe arc lamp (>300 nm)	$5.77 \cdot 10^{-5}$ (Einstein L ⁻¹ s ⁻¹)	0.5	15	3	Formic acid, methanol, or t- butanol	0.5	[As(V)] Ion chromatography	[138]
UVA lamp (8 W, 365 nm)	<i>ns</i>	0.05	42	6.4	NaNO ₃	<i>ns</i>	[As(III)] LC-ICPMS	[66]
Hg lamp (125 W, $\lambda_{\max} = 366$ nm)	$127 \cdot 10^{-6}$ (Einstein s ⁻¹ L ⁻¹)	1	39	3	0.4 M MeOH	<i>ns</i>	[As(V)] UV-Vis molybdenum blue	[139]
Xe arc lamp (300 W, < 300 nm)	<i>ns</i>	1.5	37	3, 9	t-BuOH	<i>ns</i>	IC-ICPMS	[60]
Hg lamp (125 W, $\lambda_{\max} = 366$ nm)	<i>ns</i>	1	25	7	<i>ns</i>	0.5	[As(V)] UV- Vis/molybdenum blue	[140]
UV lamp (320 -700 nm)	4.25 (mW/cm ²)	0.25	1-100	4, 7, 9	<i>ns</i>	1	[As(V)] UV- Vis/molybdenum blue	[141]

ns = not stated

Like most mineral oxides, TiO_2 adsorbs As(V) with the formation of covalently-bonded inner-sphere surface complexes [142]. This can form a significant proportion of the total arsenic added to a TiO_2 suspension when the total arsenic concentration is low. Most studies measure the PCO of As(III) on TiO_2 using the sequential method, where first the experiment is run in the dark until As(III) adsorption reaches an equilibrium and then the kinetics of PCO are measured starting from the point at which the UV light source is turned on [56,143,144]. However, if one measures the kinetics of PCO using aqueous As(III) alone, the desorption of As(III) from TiO_2 , following the competitive adsorption of As(V) , will possibly lead to an underestimation of the PCO yield. In contrast, if one measures the PCO of As(III) using the parallel method, where two identical solutions are measured in parallel, with one being in the dark and the other in the light, without accounting for equilibrium adsorption the adsorption of As(III) to TiO_2 should lead one to overestimate the PCO kinetics (unless one corrects for the fraction of adsorbed As(III)).

The primary techniques used to determine arsenic speciation are (i) solid phase extraction using ion exchange resins to analyse both As(III) and As(V) [145], (ii) determination of $[\text{As(V)}]$ using UV-Vis spectroscopy molybdenum blue method [115,116], and (iii) determination of $[\text{As(III)}]$ using anodic stripping voltammetry [118].

Many PCO studies monitor the PCO kinetics using $[\text{As(V)}]_{\text{(aq)}}$ alone (Table 4.1). In these studies, the adsorption of As(V) in both sequential and parallel experiments will lead to underestimation of the true PCO yield. The competitive adsorption between As(III) and As(V) is a complex process, whilst As(V) shows a stronger affinity for the inner sphere complexation to mineral oxide surfaces, adsorption capacities are often greater for As(III) at neutral pH, due to the formation of multilayer surface precipitates [146]. Consequently, when a significant fraction of total arsenic is adsorbed, the speciation of the adsorbed phase must be accounted for. Additionally, there are other important processes that can affect the determination of PCO rate of As(III) by TiO_2 and are often overlooked in the literature and poorly quantified to date. These include the UV induced photolysis of As(III) (i.e. light-mediated and not catalyst-mediated oxidation to As(V)). Aqueous phase UV photolysis of As(III) is significant under certain conditions, and the PCO quantum efficiency is greater than unity have been reported using short-wave UV irradiation [147]. In addition, the ionic strength of the electrolyte ions and the presence of ions such as chloride (Cl^-)

and bicarbonate (HCO_3^-) are known to promote other photocatalytic reactions through the formation of reactive oxygen species (ROS) intermediates [148,149].

Equally important is the determination of the quantum efficiency (QE) of the PCO of As(III) by TiO_2 , which is often not reported [147]. The quantum efficiency offers a more universally comparable measure of the photocatalytic activity due to the vastly different experimental set-ups and light sources used to date in the PCO of As(III) to As(V) [150].

4.2 Aims and objectives

The aim of this study was to characterise and to better understand the processes that control the determination of As(III) PCO rates, and to develop guidelines for best practice. To this end, the possible differences in the calculated PCO efficiency was assessed when, (i) determining $[\text{As(V)}(\text{aq})]$ using the spectrochemical UV-Vis molybdenum blue method, (ii) determining $[\text{As(III)}(\text{aq})]$ using anodic stripping voltammetry (ASV) and (iii) using calculated As(III) concentration from measured As(V) and total As using ICP-MS. Second, the widely used sequential method was compared with an alternative strategy, where two experiments are run in parallel, one under UV light to drive the PCO reaction, and the other in the dark as an absorption control. The parallel method is superior to the sequential method, as it provides a point of reference of As(III) adsorption to TiO_2 for each time interval where As(III) is determined (analytically or calculated) during the PCO reaction (where the sequential method relies on a single measure of absorption at equilibrium). Third, the quantification of other processes on PCO rates, such as the direct photolysis (due to UV irradiation) and the reaction medium (e.g. HEPES buffer and ionic strength). Forth, the quantum efficiency of the PCO reaction is determined to show how this measure can provide insight on how the setup can be improved. And finally, recommendations on the experimental set up that should be used when measuring the PCO of As(III).

4.3 Results and Discussions

4.3.1 Physical characterisation of anatase TiO_2

Characterisation of the material structure is crucial in PCO studies therefore, XRD analysis was used to determine the crystal phases present in commercial TiO_2 . The results presented in (Appendix 9.1, Figure 9.1A) indicate a TiO_2 composition of 85.5 wt% anatase and 14.5 wt% rutile,

with an average crystallite size of 25 nm in both phases; in line with previous studies [151]. SEM analysis showed a homogenous distribution of spherical-like structures with dimensions less than 50 nm in diameter (Appendix 9.1, Figure 9.1B). Characterisation of surface functional groups is important in studying the adsorption phenomena. IR characterisation of the TiO₂ sample (Appendix 9.1, Figure 9.1C) reveals bands at 660 cm⁻¹ for Ti-O-Ti lattice vibrations [152] and 400–650 cm⁻¹ for Ti–O stretching modes [153]. XPS analysis was used to confirm the purity of the TiO₂ surface (Appendix 9.1, Figure 9.1D & Table 9.1) and determine the valence band energy (Appendix 9.1, Figure 9.1E). Titanium (as Ti⁴⁺) and oxygen were present with 17 % and 51.9 % abundance by mass respectively (Appendix 9.1, Table 9.1). Valence band analysis suggested a valence band energy relative to the Fermi level of 2.85 eV [154] which covers the oxidation potential of water.

4.3.2 Spectrochemical analysis of arsenic species and cross-calibration using electrochemical and mass spectrometry

Spectrochemical analysis using the UV-vis molybdenum blue method was used to determine As(III) and As(V) concentrations in solution during the PCO of As(III) using TiO₂. The method is described and validated in detail in chapter 3 (section 3.1). To further validate the spectrochemical the UV-vis molybdenum blue method, PCO experiments were also performed and the As(III) and As(V) concentrations measured using electrochemical SWASV and mass spectrometry ICP-MS methods. Figure 4.2 compares the As(III) oxidation kinetics calculated by monitoring [As(III)_(aq)] and [As(V)_(aq)]. In the first case, ASV is used to directly monitor the decrease in [As(III)_(aq)]. In the second case, [As(III)_(aq)] is calculated by subtracting [As(V)_(aq)] from [As_(Total)] where the spectrochemical method is used to determine [As(V)_(aq)] and ICP-MS to determine total [As_(aq)]. PCO experiments were carried out using a commercially available photocatalyst (Degussa P25 TiO₂). The measured concentrations for the same samples using both ASV and spectrochemical analyses are in very close agreement (Figure 4.2A). First order kinetics were observed using both analytical methods (Figure 4.2B). The respective reaction rates were 0.086 ± 0.004 min⁻¹ (R²=0.995) and 0.106 ± 0.005 (R²=0.993) for the ASV and spectrochemical UV-Vis molybdenum blue method, respectively. The T-test was 0.022 which means that there is a significant difference between the results if the two analytical techniques which should be

considered. In our subsequent PCO measurements, changes in arsenic concentrations were measured exclusively using the spectrochemical UV-Vis molybdenum blue method.

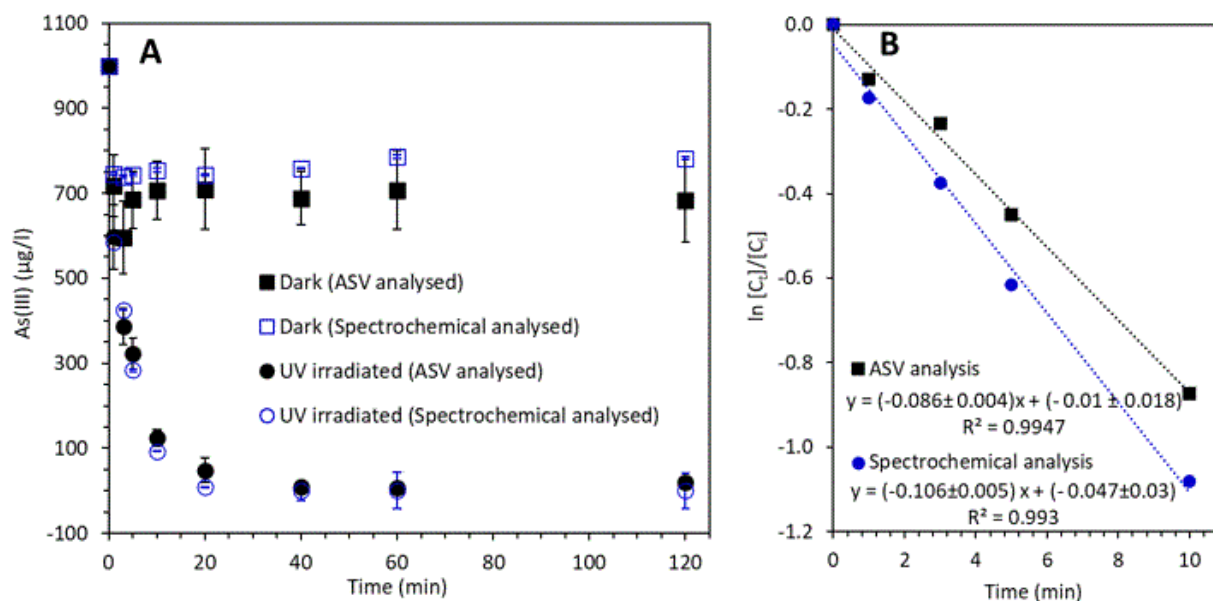


Figure 4. 2. PCO of As(III) on P25 TiO_2 analysed using ASV and UV-Vis molybdenum blue method (UV/Vis) [100 ml solution of As(III) = 1,000 $\mu\text{g/L}$, P25 TiO_2 = 0.01 g, pH = 7.4]. A- Decreases in [As(III) (aq)] with time. As(III) was measured directly using ASV or calculated using As(T)-As(V) with As(V) directly measured using UV-Vis. B- Linearised first order kinetic plots using the As(III) concentrations from Figure 4.2A. The error bars represent the standard error based on triplicate measurements.

4.3.3 Correction of directly adsorbed As(III), parallel versus sequential methods

Figure 4.3 shows the results of two photo oxidation experiments, one carried out using the sequential method (dark adsorption followed by UV irradiation) and one using the parallel method (one dark adsorption and one UV irradiation experiment run in parallel). Both As(III) and As(V) form inner-sphere covalently bonded surface complexes with TiO_2 (as shown in XPS results in section 3.5), resulting in a significant proportion of arsenic being adsorption during the determination of PCO kinetics (i.e. 30% as shown in Figure 4.3A). To calculate the reaction kinetics in case of sequential method, the amount of arsenic adsorbed (before turning the UV lamp on) is subtracted from the total decrease in arsenic at each point. In case of parallel method, at each time interval, the amount of arsenic absorbed in the dark is subtracted from the decrease in arsenic seen under UV light as presented in Appendix 9.2 (Figure 9.2).

The data were fit to first order kinetics and the statistical parameters. For the sequential and parallel methods (without adsorption correction), parallel methods (after adsorption correction) the PCO rate constants were $0.13 \pm 0.001 \text{ min}^{-1}$ and $0.083 \pm 0.006 \text{ min}^{-1}$ and $0.040 \pm 0.004 \text{ min}^{-1}$ respectively.

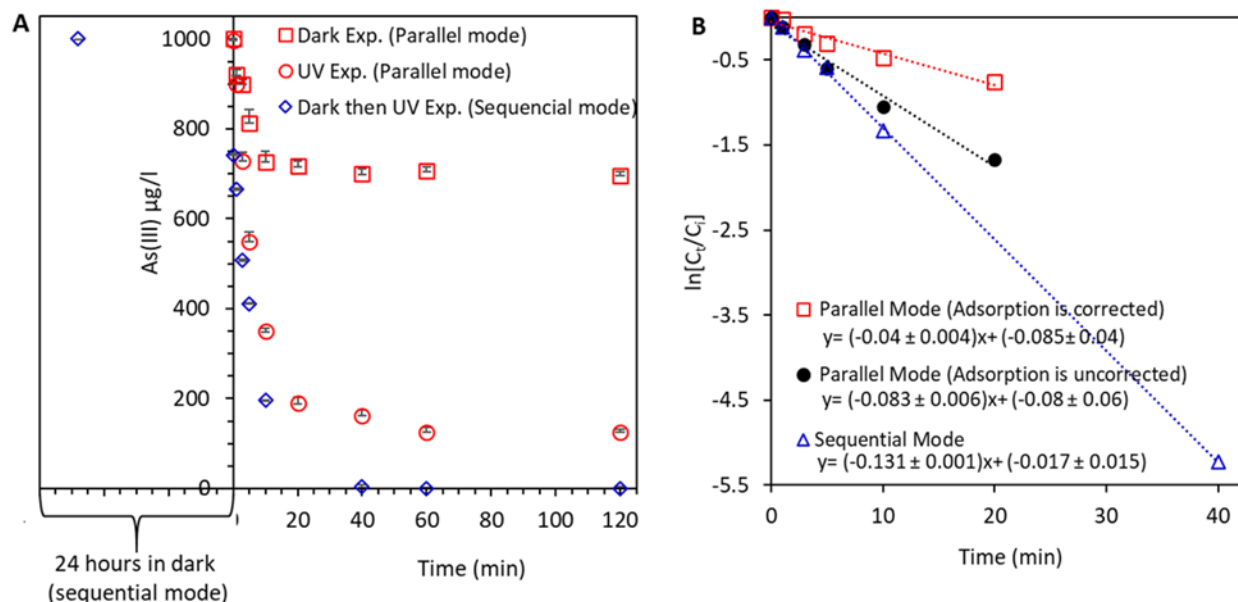


Figure 4. 3. A- PCO of As(III) on TiO_2 for sequential (dark adsorption followed by UV irradiation) and in parallel methods (one reaction carried out in the dark and one reaction carried out in UV light, in parallel). B- First order kinetics for sequential mode, parallel mode without As(III) adsorption correction and parallel mode after As(III) adsorption correction [100 ml solution of As(III) = 1,000 $\mu\text{g/L}$, TiO_2 = 0.01 g, pH = 7.4].

In the parallel mode, the PCO rate constant without correction of the directly adsorbed As(III) is twice the PCO rate constant after correction of the directly adsorption As(III). This is because the decrease in As(III) due to direct adsorption was counted as being oxidized, where in fact it is not. The rate constant (k_1) is lower (38%) for the in-parallel method than the sequential method. In the sequential method, the adsorption of As(III) to the surface of TiO_2 is initially allowed, and then the subsequent decrease at each time interval is related to one initial reference point which is the concentration after adsorption in dark (742.2 $\mu\text{g/L}$), and is significantly less than the starting concentration (1000 $\mu\text{g/L}$). The difference between these two values causes a significant increase in the calculated PCO rate for the sequential method.

4.3.4 Evaluation of PCO rates based on [As(III)] and [As(V)]

In order to describe the PCO of As(III) more precisely, the PCO rate constants were calculated and compared in two ways: (i) based on the depletion of aqueous As(III) applying eqn. 4.1 (option 1), and (ii) based on the generation of aqueous As(V) applying eqn. 4.2 (option 2). The results presented in Figure 4.4 show that the PCO yields are underestimated by 7.1% at equilibrium (after 2 hrs) when the kinetics are derived from changes in As(V) concentrations. This difference can be explained by considering the speciation of TiO₂-adsorbed arsenic. As(V) has a higher affinity to be absorbed on TiO₂ than As(III) [155], and the adsorbed As(V) fraction is masked from the solution and not captured by the spectrochemical method employed herein, as illustrated in Figure 4.5 (this argument is further supported by the latter XPS study). Therefore, the decrease in As(III) concentration is recommended for a more precise calculation of the PCO rate.

$$As_{\text{(oxidised at time X)}} = [As(III)]_{\text{(in dark at time X)}} - [As(III)]_{\text{(under UV at time X)}} \quad (\text{Eqn. 4.1})$$

$$As_{\text{(oxidised at time X)}} = [As(V)]_{\text{(under UV at time X)}} - [As(V)]_{\text{(in dark at time X)}} \quad (\text{Eqn. 4.2})$$

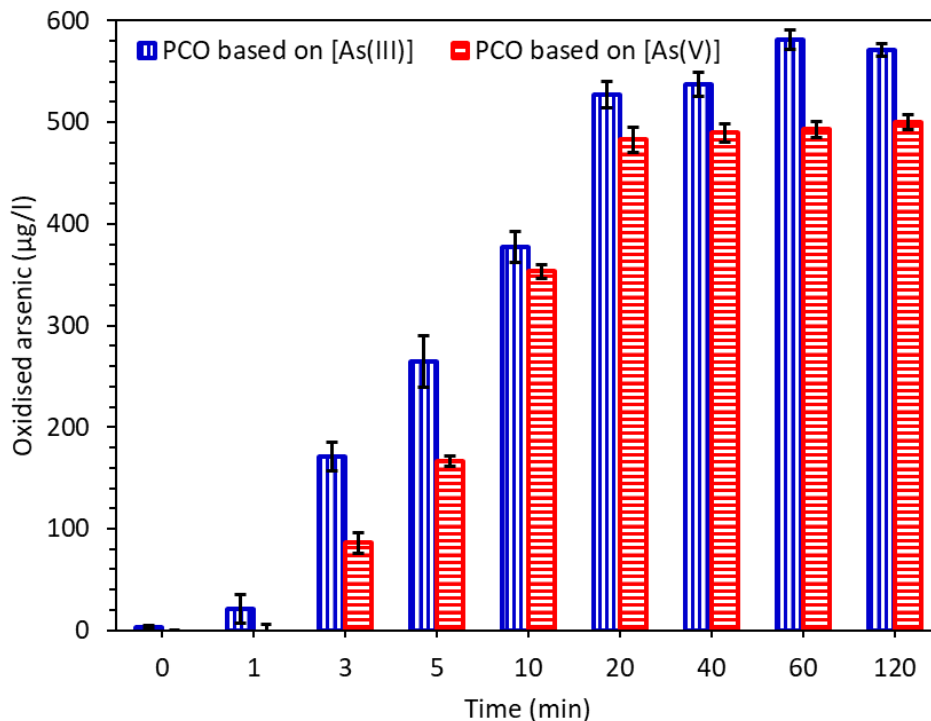


Figure 4. 4. The oxidized fraction of arsenic based on changes in the As(III) and As(V) concentration [100 ml of As(III) = 1,000 µg/L, TiO₂ = 0.01 g, pH 7.4], error bars represent the standard deviation.

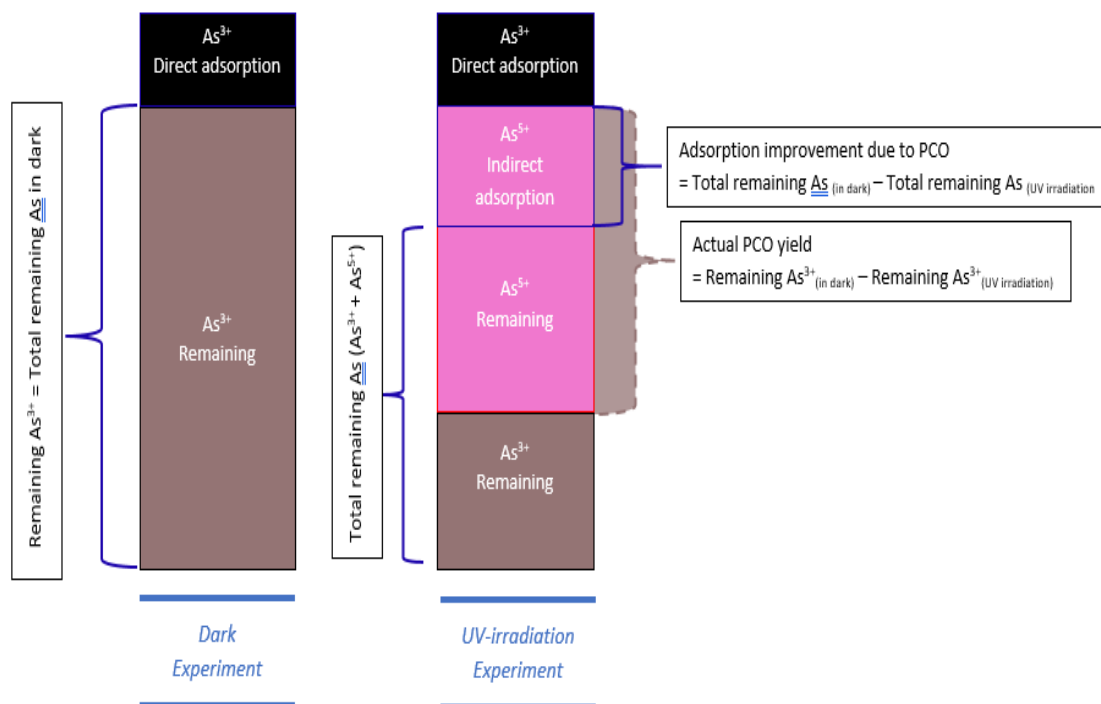


Figure 4. 5. Correction of the directly adsorbed fraction of As(III) during parallel experiments “where the direct adsorption represent the amount of As(III) adsorbed without oxidation and the indirect adsorption represents the amount of As(V) adsorbed after oxidation”.

To measure the surface adsorbed fraction of As(V), XPS was used to investigate the arsenic species adsorbed to the surface of TiO₂ after the PCO of As(III). A series of experiments were performed where the concentrations of As(V) and As(III) were monitored under UV irradiation and As(III) in the dark. After 2 hr, samples were centrifuged and TiO₂ was collected, dried, and analysed using XPS. The XPS survey scan for TiO₂ before and after photocatalysis is shown in Figure 4.6. The results before PCO exhibit the binding energies (BEs) of C 1s, Ti 2p, O 1s, Ti2s at ~ 285, 459, 530.1, and 563 eV, respectively [156]. After the PCO experiment, a new XPS peak is observed at ~1327 eV, which is attributed to As 2p, in addition to changes in the O1s peak position and intensity (Figure 4.7), which are indicative of arsenic species binding to the surface of TiO₂. The XPS peak deconvolution for As (2p) presented in Figure 4.8 reveals the presence of arsenic (~1324-1331 eV) bound to the surface of TiO₂ after As(V) and As(III) adsorption under UV irradiation, and As(III) adsorption in the dark. The findings show that after adsorption and PCO of As(III), only As(V) is detected on the surface of TiO₂ at ~1327.6 eV. Whereas, with As(III) adsorption in the dark, only As(III) is detected on the surface of TiO₂ at ~1326.5 eV [157,158].

Previous findings show that the adsorbed As fraction after UV irradiation is mainly As(V), which supports our argument that As(V) adsorbs preferably on TiO₂ compared to As(III) [157]. Therefore, using aqueous As(V) as a measure for the oxidation process underestimates the PCO rates by failing to account for the significant amount of As(V) adsorbed to the surface of TiO₂. Since As(III) is a minor adsorbed species, determination of PCO kinetics using aqueous As(III) will likely provide a more accurate and precise PCO rate (as the error associated with adsorbed As(III) is smaller).

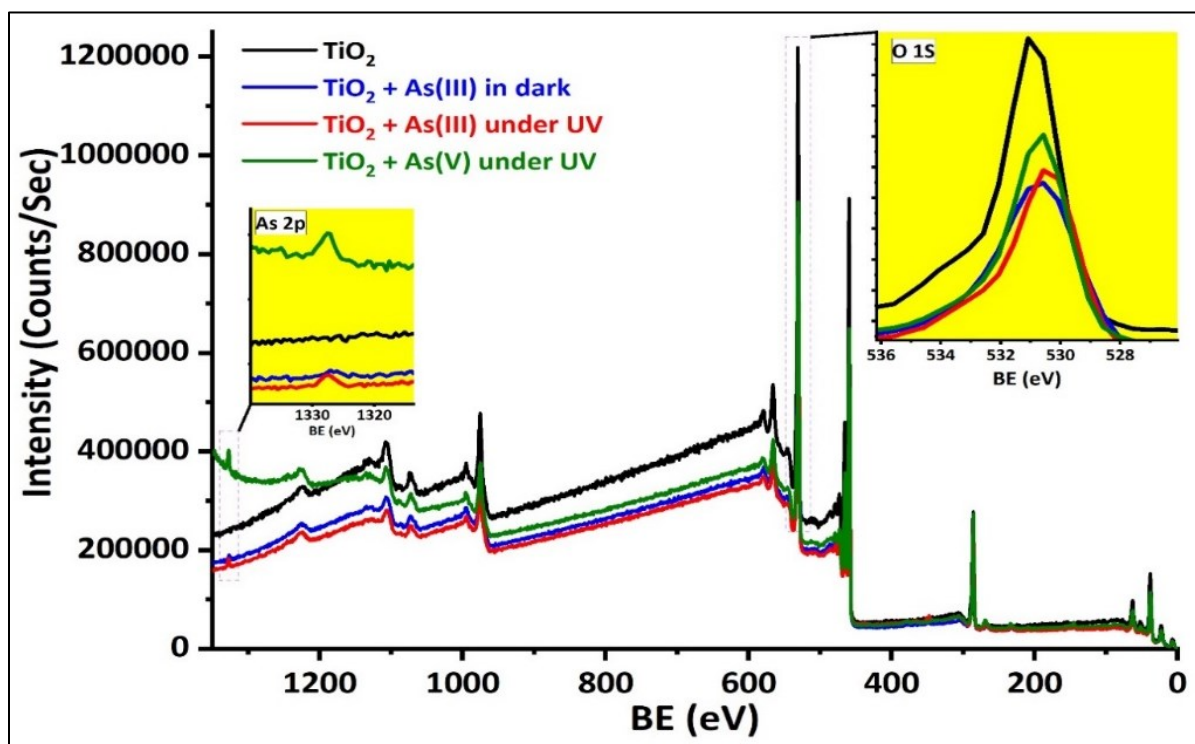


Figure 4. 6. XPS survey scan for TiO₂ before and after adsorption of: (i) As(III) in the dark, (ii) PCO of As(III) under UV light, and (iii) adsorption of As(V) under UV light [100 ml of As(III)/ As(V) = 100 µg/L, TiO₂ = 0.01 g, pH 7.4, 2 hrs].

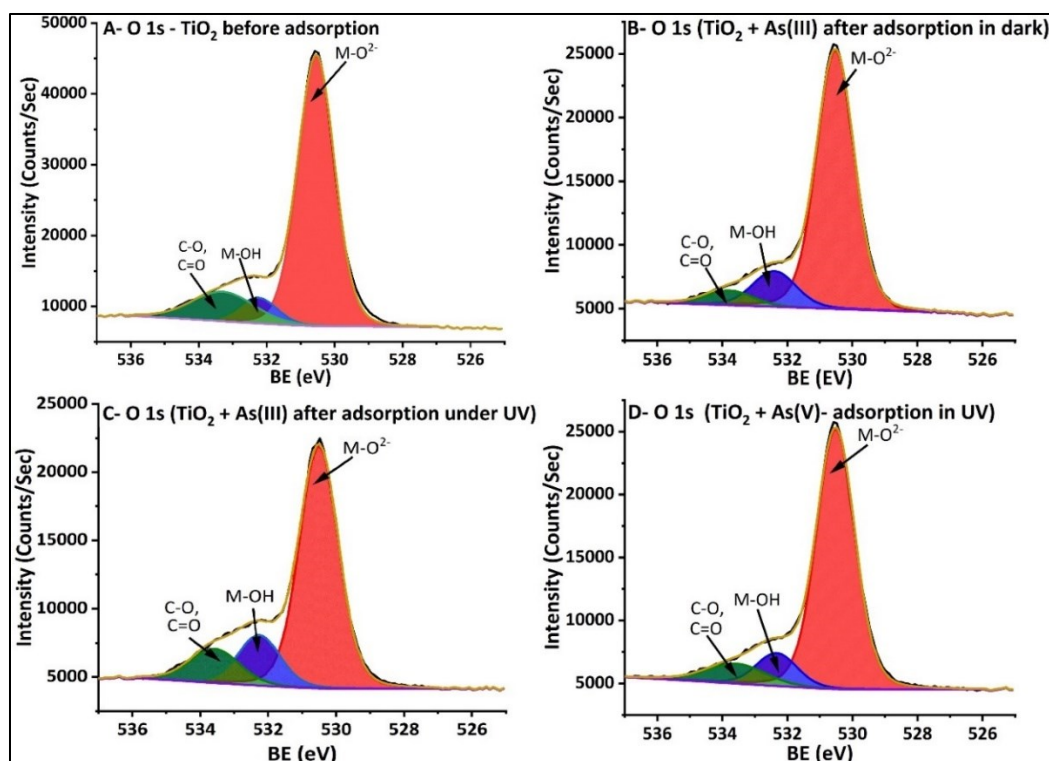


Figure 4. 7. Core level scans of the O1s environment: A- TiO_2 before adsorption, B- $\text{TiO}_2 + \text{As(III)}$ in the dark, C- $\text{TiO}_2 + \text{As(III)}$ after UV irradiation and D- $\text{TiO}_2 + \text{As(V)}$ after UV irradiation [100 ml of $\text{As(III)}/\text{As(V)} = 100 \mu\text{g/L}$, $\text{TiO}_2 = 0.01 \text{ g}$, pH 7.4, 2 hrs].

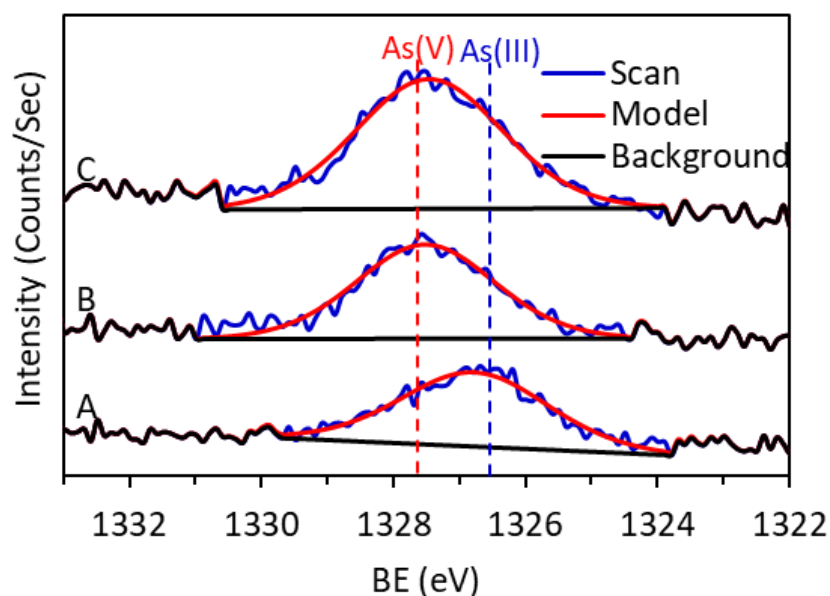


Figure 4. 8. XPS core scan for the As 2p binding energy region in A- TiO_2 anatase after adsorption of As(III) in the dark, B- TiO_2 anatase after adsorption of As(III) under UV PCO where the remaining concentration of As(III) in solution was $126 \mu\text{g/L}$, and C- TiO_2 after adsorption of As(V) under UV [100 ml of $\text{As(III)}/\text{As(V)} = 100 \mu\text{g/L}$, $\text{TiO}_2 = 0.01 \text{ g}$, pH 7.4, 2 hrs].

4.3.5 Effect of PCO on the adsorption rates and capacity

One advantage of the parallel method is the capacity to distinguish between the adsorbed and oxidised fraction of arsenic at any time. Therefore, it is possible to calculate the PCO kinetics based on the remaining As(III) concentration in addition to the adsorption kinetics based on the remaining total arsenic concentration. The adsorption kinetics in the dark and under UV during the parallel experiment was calculated based on the remaining total arsenic concentration in the dark and under UV irradiation, where the kinetics was best fit with pseudo-second order adsorption (PSO) kinetics (eqn. 3.17), as shown in Figure 4.9. The calculated parameters, presented in Table 4.2, show that the adsorption capacity is close to experimental values, where the experimental and calculated adsorption capacities under UV irradiation were 3.093 ± 0.01 and 3.184 ± 0.01 mg/g and in the dark were 2.4 ± 0.03 and 2.6 ± 0.03 mg/g respectively. The PCO resulted in a ~23% increase in adsorption (where adsorption capacity increased from 2.38 mg/g in the dark to 3.09 mg/g under UV irradiation after 120 mins). This increase in the adsorption is thanks to the PCO of As(III) to As(V), which has a greater tendency to be adsorbed by TiO_2 .

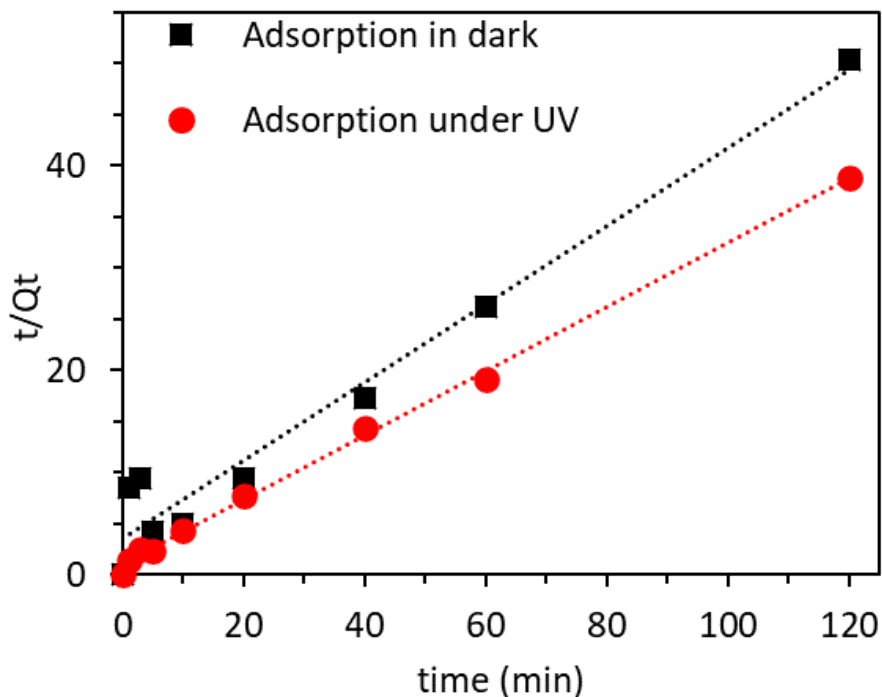


Figure 4. 9. PSO adsorption kinetics of As(total) on TiO_2 in dark and under UV irradiation.

Table 4. 2: Adsorption kinetic parameters of As(III) over TiO₂ in dark and under UV.

PSO Kinetic parameters		
Parameter	adsorption in Dark	Adsorption in UV
q _e exp.	2.383	3.093
q _e calculated	2.616	3.184
k ₂	0.137	0.092
Slope SE	0.028	0.006
Intercept SE	1.335	0.268
RSS	70.715	2.854
Pearson's r	0.981	0.999
R ²	0.963	0.998
MSE	10.102	0.408
F-value	183.489	3068.625
Prob>F	0.000	0.000

4.3.6 Contribution of UV and visible light to direct photolysis of As(III)

Light oxidises As(III) through both PCO and photolysis [147]. The contribution of photolysis using UV and visible light was investigated in non-buffered media (100 ml of As(III) = 1,000 µg/L, pH = 7.4) without the addition of photocatalyst. Results showed that UV and visible light respectively contributed to 3.1% and 1.1% of the total As(III) oxidation after 2 hours (Figure 4.10). UV light is more energetic than visible light and has a greater capacity to generate reactive oxygen species, and therefore contributes to a greater photolysis yield. Although UV photolysis contributed to the oxidation of As(III) (3.1%; 18 W UVA lamp, λ_{max} = 370 nm, 2 hrs of irradiance), it was minimal in comparison to the contribution of PCO, which oxidised more than 80% of As(III) to As(V) under the same conditions, as also seen in Figure 4.3.

Previous studies in literature show an agreement with our findings. Tian et al., 2012 [159] reported that there is no significant change in As(III) concentration under visible light photolysis (using As (III) = 2 µg/L, 1 hr of irradiance). Whereas under UV irradiation, Wang et al., 2016 [8] reported a 4.1% oxidation (using As (III) = 200 µg/L, 30 W UVC lamp, λ_{max} =254 nm, 20 mins of irradiance).

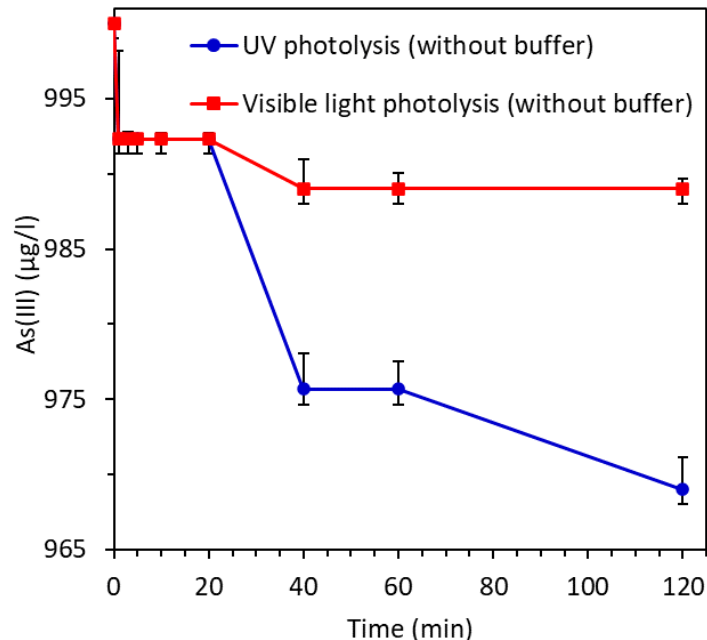


Figure 4. 10. Effect of photolysis on the PCO yield of As(III) [100 ml of As(III) = 1,000 µg/L, pH 7.4, error bars represent the SD based on 2 repeats].

4.3.7 Effect of solution composition on the PCO rates

4.3.7.1 Effect of HEPES buffer on PCO rates

HEPES buffer is used to maintain reaction pH during the PCO of As(III) to As(V) [160,161], however, no previous work has investigated its contribution to the oxidation process. This is despite the fact that HEPES buffer is known to promote the generation of intermediate oxidants; otherwise known as reactive oxygen species (ROS) [162]. In this work, the effect of HEPES on the PCO of As(III) to As(V) was studied by comparing activity in the HEPES-buffered system against an unbuffered solution. Figure 4.11 shows that HEPES buffer enhanced the PCO yield, compared to unbuffered experiments, in both UV light and dark, by 12.6% and 32.8%, respectively. This rise in the oxidation yield in HEPES is likely due to the HEPES buffer stimulating free radical generation (e.g. $\dot{\text{O}}\text{H}$ radicals) that mediate the oxidation of As(III) to As(V) [162]. Our finding is further supported by Masson et al., 2008 and Lepe-Zuniga et al., 1987 [163,164] who reported that HEPES buffer generates hydrogen peroxide, which boosts the oxidation rate. The contribution of HEPES buffer towards As(III) oxidation is therefore significant and should be considered during the PCO rate calculations.

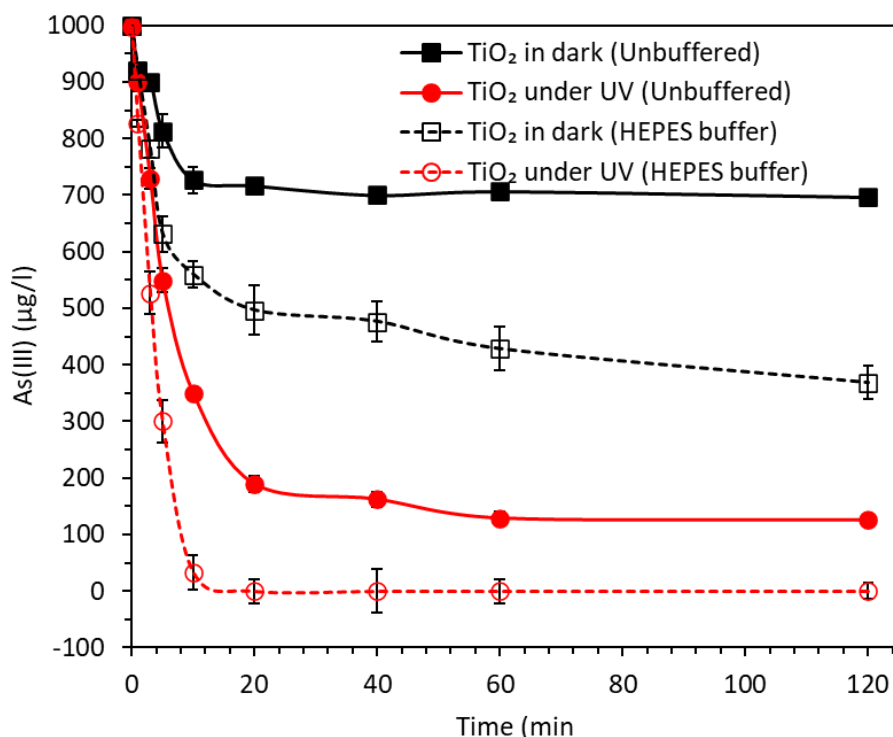


Figure 4. 11. Effect of HEPES buffer on the PCO of As(III) [100 ml of As(III) = 1,000 µg/L, TiO₂ = 0.01 g]. pH was adjusted to pH 7.4 using 10 mM HEPES for the buffered experiment and using NaOH/HNO₃ for the unbuffered experiment, error bars represent the SD.

4.3.7.2 Effect of ionic strength on PCO rates

The effect of ionic strength on the PCO yield was studied, since previous studies have shown enhanced photocatalytic degradation of other contaminants in the presence of Cl⁻ due to the formation of ROS intermediates [148,165]. This experiment was conducted using synthetic seawater with different ionic strengths. The detailed results are presented in Figure 4.12, and the summarised results Figure 4.13. The results demonstrate that the higher ionic strength of seawater increases the PCO activity of TiO₂. This is attributed to the increasing presence of Cl⁻ ions that can assist the PCO of As(II) through the formation of reactive oxygen species eqn. 4.3 to eqn. 4.6 [166–169]. First, Cl⁻ is oxidised by the photogenerated hole and forms chlorine (Cl₂) eqn. 4.3, and in turn hypochlorous acid (HClO) eqn. 4.4. The formation of Cl₂ and HClO depend on the pH, and in neutral conditions HClO is a major component [166,167]. HClO is a strong oxidant which can either oxidise As(III) to As(V) (eqn. 4.5), enhancing PCO rates, or decompose to O₂ and Cl⁻ (eqn. 4.6) [170].

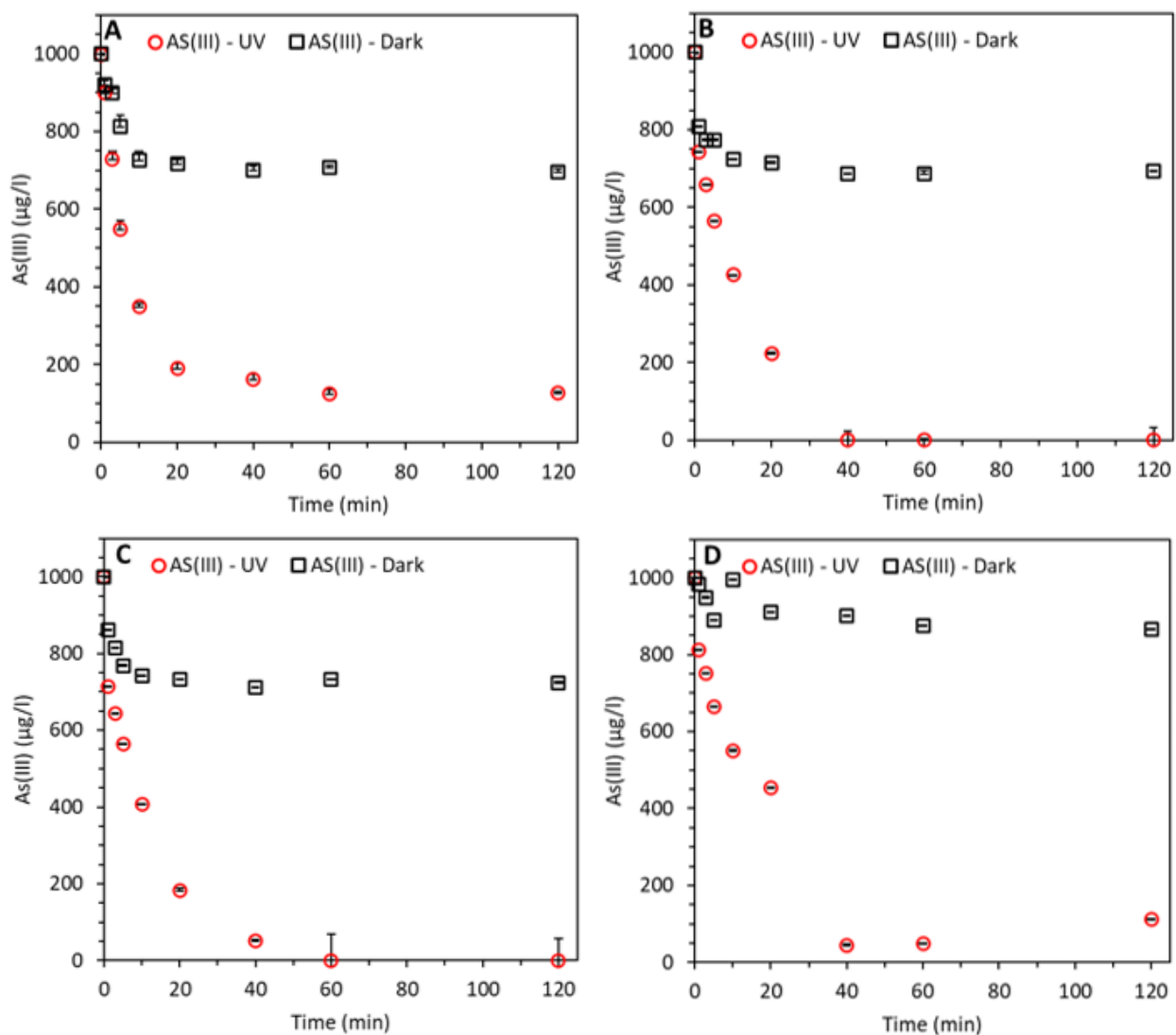
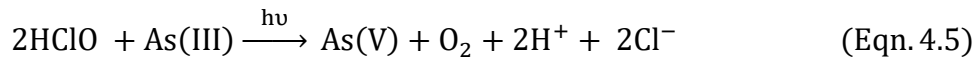
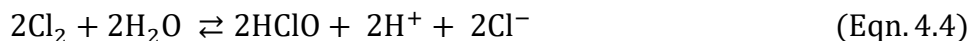


Figure 4. 12. Effect of seawater ionic strength on the PCO of As(III), A- Distilled water, B- Seawater (25%), IS=0.175, C- Seawater (50%), IS=0.35, D- Seawater (100%), IS=0.7 using (0.01g TiO_2 , 100 ml of 1000 $\mu\text{g/l}$ As(III), seawater was prepared according to ASTM D1141-98 method..

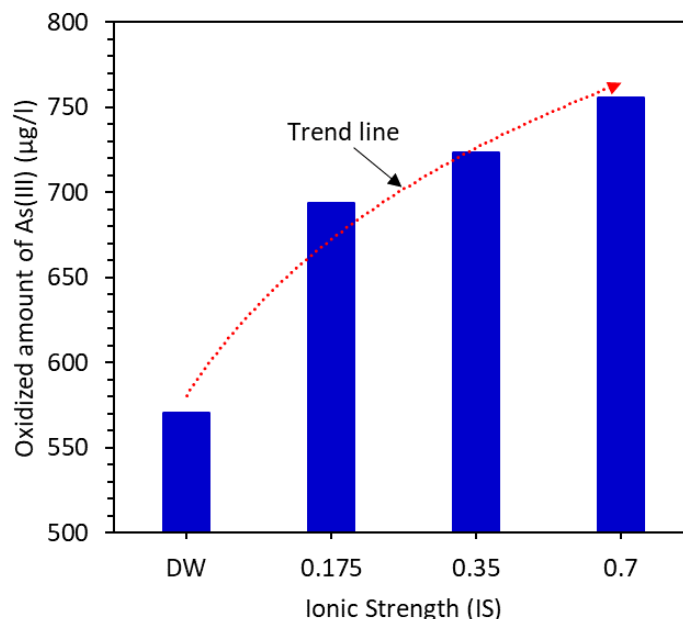


Figure 4. 13. Effect of ionic strength on the PCO of As(III) to As(V) [DW = deionised water, 0.175 IS = 25% synthetic seawater, 0.35 IS = 50% synthetic seawater and 0.7 IS = 100% synthetic seawater], [Conditions; 100 ml of As(III) = 1,000 µg/L, TiO₂ = 0.01 g, pH=7.4].

4.3.8 Photon flux absorption, penetration depth and quantum efficiency

In most experimental arrangements, the PCO rate will depend upon the intensity of the irradiation [65]. Therefore, determining the photon flux and quantum efficiency is necessary to understand the relationship between light input and reaction. This was achieved by determining the spectral output of our lamp, light intensity delivered to the suspension, and the proportion of light absorbed by the TiO₂ suspension.

The light was not perfectly monochromatic where the lamp showed a broad emission band in the UV region, centered at ~370 nm, and some sharp emission bands in the visible region at ~405 nm, ~430 nm, ~545 nm and ~580 nm. The counts/energy and cumulative counts/energy are presented in (Figure 4.14). By comparing the intensity of light capable of exciting the TiO₂ photocatalyst (*i.e.*, with wavelengths smaller than the bandgap of TiO₂ at ~387 nm) against the total intensity of light emitted by the lamp, our TiO₂ photocatalyst is capable of absorbing ~37% of emitted photons from the lamp (or rather, ~45% of the total energy emitted). The penetration depth describes the depth penetrated by the light before being absorbed. The overall emitted photon flux was determined, as described in chapter 3 (section 3.7), with the results shown in Figure 4.15.

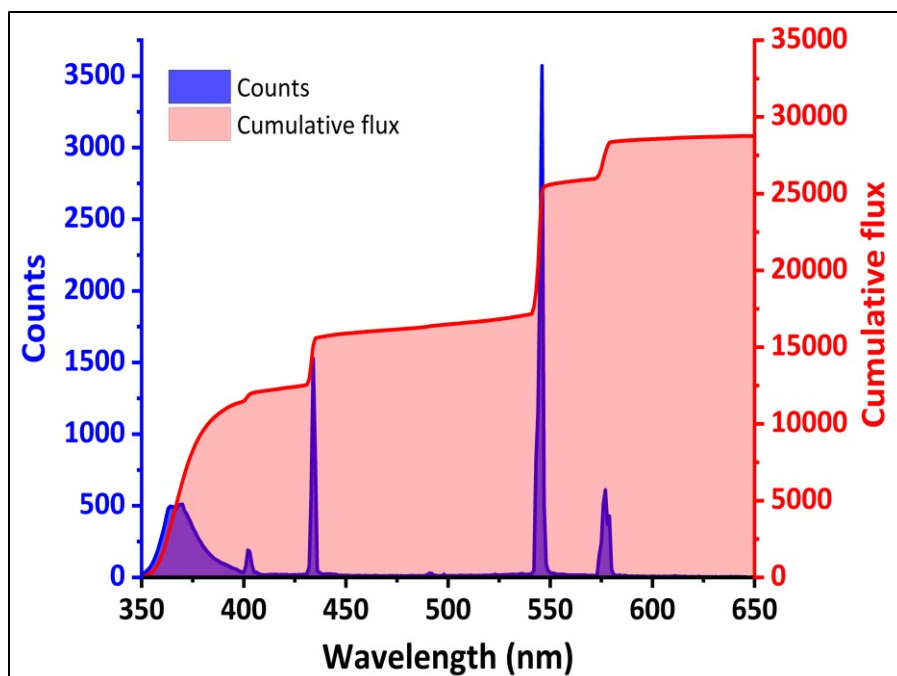


Figure 4. 14. Spectral output of the used UV lamp for our PCO experiments.

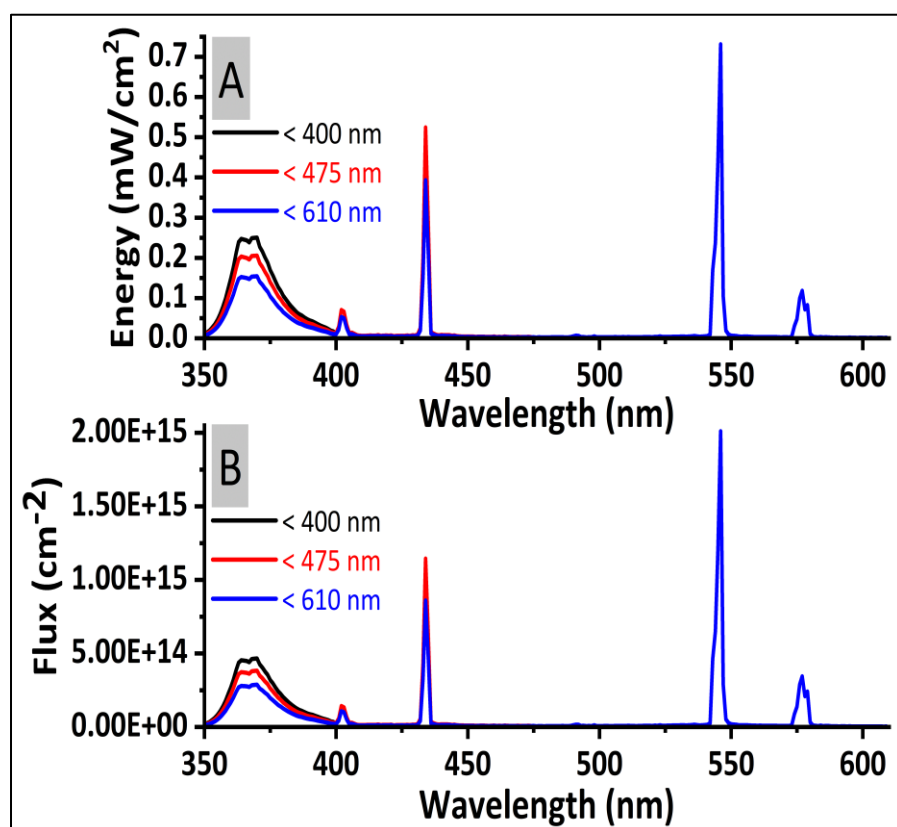


Figure 4. 15. Lamp Energy output using short pass filters(A), Emitted photon flux under applying different filters (B).

In order to calculate the flux absorbed with solution depth, the transmittance of the photocatalyst suspended in water ($\text{TiO}_2 = 0.01 \text{ g/ 100 ml}$) was firstly measured then used to determine the molar absorptivity at various wavelengths (350 - 400 nm) using eqn. 3.9 as presented in Figure 4.16.

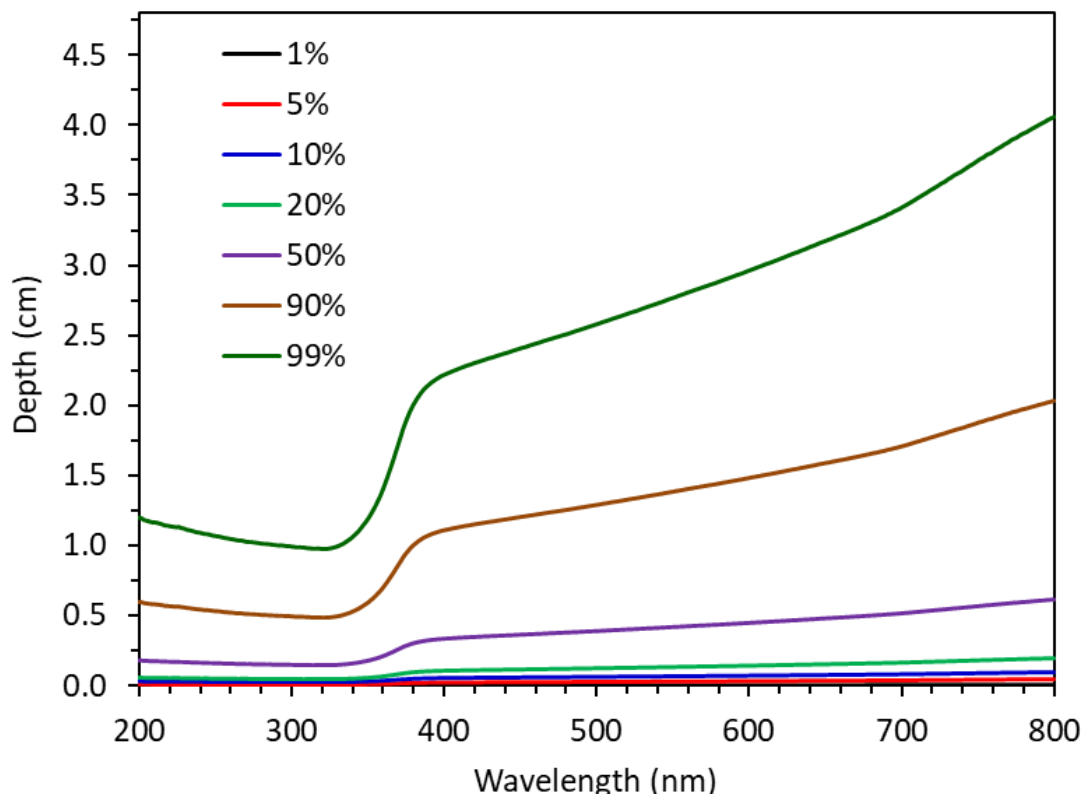


Figure 4. 16. Photon absorption (%) of 0.01g TiO_2 suspension in 100ml at different pathlengths (it is worth mentioning that this is based on absorbance values and a major component of which is due to scattering and reflection losses).

The photon flux absorbed at different penetration depths was then determined using eqn. 3.10 [171]. The results presented in Figure 4.17 shows that all UV light was absorbed upon travelling $\sim 2.0 \text{ cm}$ into the solution, with shorter wavelengths absorbed at shallower depths. Given that our reactions were carried out in vessels 5.6 cm deep, this indicates that the majority of incident UV light is absorbed nearest to the surface of the solution.

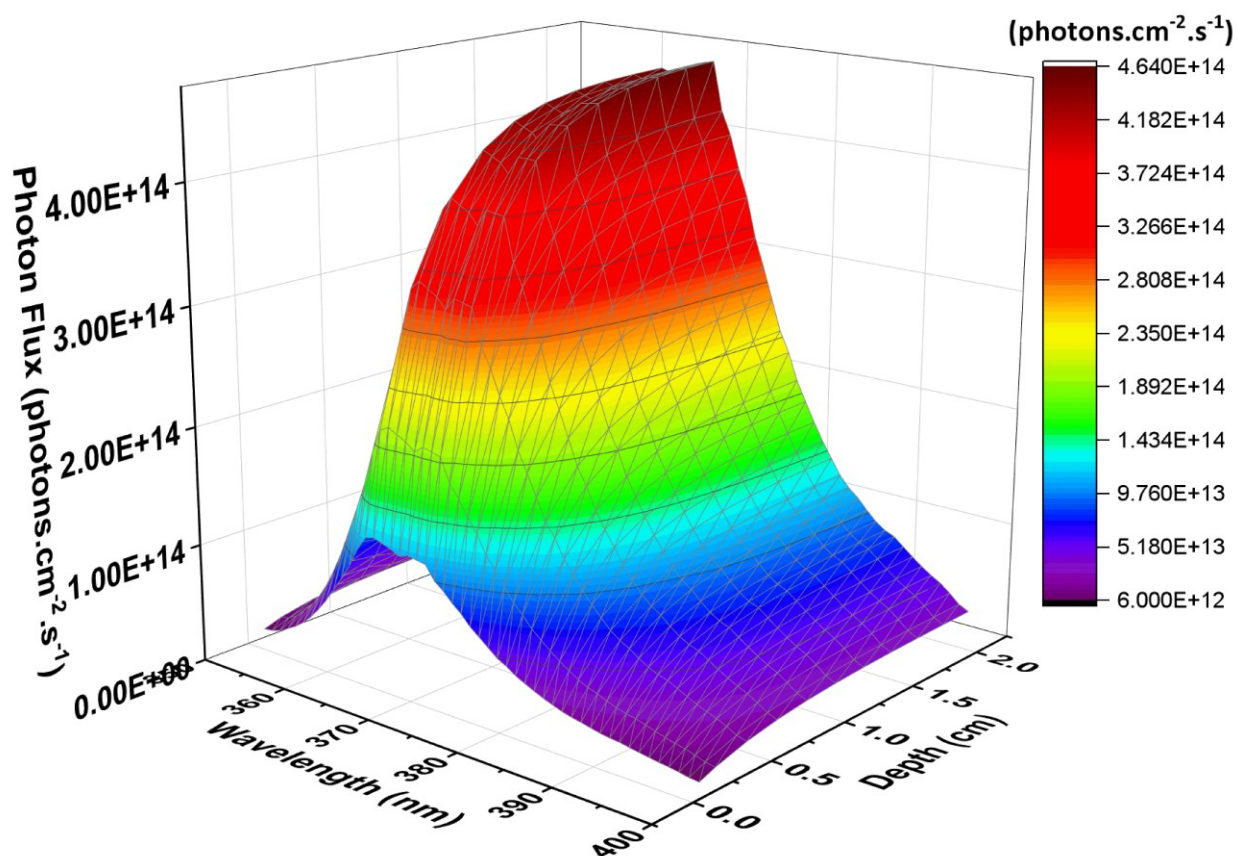


Figure 4. 17. Photon flux absorption and wavelength with penetration depth for TiO_2 photocatalyst at $\lambda < 400 \text{ nm}$ ($\text{TiO}_2 = 0.01 \text{ g/100 ml}$; optical bandgap of $\sim 387 \text{ nm}$).

The quantum efficiency (QE) expresses the ratio between the number of converted species and the number of photons absorbed by the photocatalyst [172,173]. Eqn. 3.11 was used to calculate ϕ (%) for the PCO experiments, and the findings summarised in Table 4.3. The results again confirm that HEPES buffer boosts the PCO of As(III) to As(V), and that using generated As(V) to evaluate the PCO yield results in an underestimation of activity. The literature contains very few studies where the ϕ of the PCO of As(III) is determined. In 2013, Ryu et al. [147], estimated a ϕ higher than 1 for the PCO of As (III) [$100 \mu\text{M}$ ($7492 \mu\text{g/l}$)] under 254 nm Irradiation at pH 7, where the reaction was kept under continuous purging of oxygen during the course of the reaction. This substantially higher ϕ , compared to the values found in this study, is due to a difference in reaction conditions, where harder UV light was used (which may have also contributed to a higher photolysis yield), higher As(III) concentrations, and continuous purging with oxygen that is known to promote the generation of H_2O_2 that boosts As(III) oxidation [147].

Table 4. 3: The quantum efficiency (QE) values for different PCO experiments of As(III) over TiO₂ (at pH = 7.4, after 2 hrs of irradiation).

Experimental details	(QE) %	Reaction conditions			
		Adsorption correction	Buffer	TiO ₂ (g/100 ml)	Species used in calculation
UV Photolysis	0.002± 0.0004	-	-	-	*
UV Photolysis	0.008± 0.009	-	HEPES	-	*
Buffer Effect	0.321 ± 0.061	Parallel	HEPES	0.01	Decrease in As (III)
Parallel Mode	0.164± 0.043	Parallel	-	0.01	Decrease in As(III)
Sequential mode	0.101± 0.046	Sequential	-	0.01	Decrease in As(III)
Parallel Mode	0.161± 0.031	Parallel	-	0.01	Generated As(V)

**Both decrease in As(III) and generated As(V) are equivalent.*

4.4 Conclusion

Herein, anatase TiO₂ was used as a model photocatalyst to development a robust, simple and accurate method for measuring the PCO rate of As(III) to As(V) and the quantum efficiency. The molybdenum blue spectrochemical method was used and cross checked against traditional methods of arsenic analysis (anodic stripping voltammetry and ICP-MS), and the results were in close agreement, demonstrating the high accuracy of our simple spectrochemical method in comparison to traditional, more complex methods.

A new correction method for adsorption was developed herein, where PCO experiments are run in parallel (one dark adsorption experiment and one UV irradiation experiment run in parallel).

This was found to be more accurate than the traditional method, where the PCO experiment is run sequentially (dark adsorption followed by UV irradiation).

Determination of the PCO rate is more accurate by measuring the changes in [As(III)] than changes in [As(V)], as As(V) has a greater preference to be adsorbed by TiO₂. This result was supported by evidence from XPS analysis, which showed that the adsorbed fraction on TiO₂, after the PCO reaction, is mainly As(V).

The calculated arsenic adsorption rates in the dark and under UV irradiation showed that adsorption under UV irradiation is ~23% higher than in the dark, which means that oxidation of As(III) to As(V) assists in its removal. The impact of light-induced photolysis was also measured, where our UV source was found to falsely increase the PCO yield by 3.1%. The effect of reaction medium was investigated, where the widely used HEPES buffer increased the PCO yield. In addition, the increase in ionic strength (namely chloride concentration) increases the PCO yield. The molar absorptivity and quantum efficiencies were determined for the PCO reactions studied herein, with values ranging from 0.002 ± 0.0004 to 0.32 ± 0.06 %, depending on the reaction conditions.

5 Synthesis and characterisation of the Sn-TiO₂@SnO₂ and SnO₂@Sn-TiO₂ heterophotocatalyst and their application in the PCO of As(III) using surface sensitive techniques.

5.1 Introduction

Metal oxides have been extensively studied as photocatalysts owing to their ability to generate excitation electron-hole (e^-h^+) pairs under ultraviolet (UV) exposure [174] and they drive a wide range of photocatalytic reactions (*e.g.* solar fuels production, organic and heavy metal pollutant remediation, bacterial disinfection). Amongst metal oxides, titanium dioxide (TiO₂) is the most widely investigated photocatalyst for water detoxification due to its photostability, cost-effectiveness, non-toxicity and abundance. However, the practical applications of TiO₂ are often hindered by its wide bandgap (anatase TiO₂ ~ 3.2 eV), which falls in the UV region of the electromagnetic spectrum and can only utilise $\sim 4-5\%$ of the solar spectrum. Another issue is the high recombination rate of e^-h^+ pairs formed upon photo-excitation which can reduce the quantum efficiency [175]. Several strategies have been investigated to overcome the limitations of the large bandgap of TiO₂ and fast charge recombination losses. One strategy is the doping with metals (*e.g.* Cu, Co, Ni, Cr, Mn and Fe) which leads to the formation of solid solutions and the development of new energy levels that lower the bandgap, introduce charge carriers and can reduce e^-h^+ recombination rates [75]. Another route is the doping of non-metals (*e.g.* C, N, S, B, P, F and I). Non-metal dopants do not introduce charge carriers and their role as recombination centers might be diminished. Nitrogen doping creates mixed N2p with O2p states in the valence band (N2p-O2p), causing the valence band maximum to lower in energy. Consequently, the bandgap is reduced, and visible light absorption is increased. In general, metallic dopants affect energy levels near the conduction band and non-metal dopants affect energy levels near the valence band [75].

A third strategy is to synthesise a heterostructure photocatalyst by coupling TiO₂ with another metal oxide semiconductor. Here, photocatalytic performance is improved through the tunable band structures and charge carrier transport across the interface between the two semi-

conductor phases. This approach increases charge carrier (e^-h^+) lifetimes and consequently increases solar light absorption and quantum efficiencies [75,176].

$\text{SnO}_2/\text{TiO}_2$ hetero-structure composites are particularly suited for coupling due to physical and structural similarities between both metal oxides. TiO_2 and SnO_2 have the same crystal symmetry (tetragonal) and have two molecular units per primitive unit cell ($Z=2$) [177]. Additionally, TiO_2 and SnO_2 exhibit structural similarities such as the cationic ionic radii ($\text{Ti}^{4+} = 0.605 \text{ \AA}$ and $\text{Sn}^{4+} = 0.69 \text{ \AA}$) [178]. Moreover, the bandgap of SnO_2 ($E_g \sim 3.5\text{--}3.6 \text{ eV}$) is higher than that of TiO_2 ($E_g \sim 3.0 \text{ eV}$ for rutile, $E_g \sim 3.2 \text{ eV}$ for anatase) and the conduction band (CB) of SnO_2 is more positive than that of TiO_2 [177]. For these reasons, one can form a heterojunction hybrid with intermixed electronic states between the two metal oxides [179]. In this heterojunction hybrid, SnO_2 functions as a sink for the photogenerated electrons which results in energy level (e^-h^+) separation and ultimately enhances the oxidation process [177,178].

While $\text{SnO}_2:\text{TiO}_2$ metal oxide bicomposite catalysts have been studied for applications in water treatment [180], batteries [181,182], solar cells [183] and water splitting [184–186], with improved performance versus pure TiO_2 , the present literature does not describe the effect of Sn doping on the final structure of the Sn-doped TiO_2 . Understanding that effect on structural features of the synthesised $\text{SnO}_2:\text{TiO}_2$ is important as this controls the properties and performance of the composite. Sn is considered safe up to considerably high concentrations limits (where according to WHO Technical Report Series, 930, the maximum tolerable daily intake is 2 mg/kg of body weight). Previous studies have shown the promising results of $\text{SnO}_2:\text{TiO}_2$ for the photodegradation of methylene blue (MB) [187,188], methylene green (MG) dye [174], methyl orange [189], rhodamine B [190], phenol [191], and photo reduction of Cr(VI) [192]. Thus, Sn-doped TiO_2 is a particularly promising photocatalyst for water treatment applications. Of particular interest is the application of a $\text{SnO}_2:\text{TiO}_2$ photocatalyst in the removal of arsenic from contaminated groundwaters, specifically the PCO of the toxic As(III). Arsenic is labelled as a first-class carcinogen by the International Agency for Research on Cancer (IARC) [193], and arsenic-contaminated waters pose a major threat to human health and the natural environment globally. Water contamination with arsenic derives from a combination of processes including both anthropogenic activities (e.g., burning fossil fuels and mining activities) and natural geochemical

processes (e.g., evaporation due to geothermal process and dissolution of arsenic-containing rocks) [70,194]. In the aquatic environment, arsenic predominantly exists in As(III) and As(V) oxidation states. The speciation of arsenic species is pH-dependent: As(III) exists as neutral H_3AsO_3 in neutral environment up to pH 8, while As(V) occurs as a mixture of anions (H_2AsO_4^- and HAsO_4^{2-}) over a wide range of pH (from 2 to 11). The oxidation state of arsenic controls its toxicity, mobility and treatment strategy [194,195]. The toxicity of As(III) is about 60 times that of As(V) [131]. Compared to As(V), As(III) is difficult to remove due to its high solubility and mobility (as it exists as uncharged H_3AsO_3) [193]. Consequently, to develop an effective arsenic treatment system (e.g. through adsorption), the pre-oxidation of As(III) to As(V) is crucial [196,197]. Whilst the oxidation of As(III) to As(V) under ambient conditions is thermodynamically favourable, the reaction kinetics are too slow for water treatment solution. Hence, different oxidation methods have been used, including the application of chemical oxidants O_3 , Cl_2 , H_2O_2 , [198,199]. The main issue with the use of such oxidants is the production of toxic disinfection by-products (DBPs) as well as their expense [193,194]. Alternatively, PCO using heterogeneous photocatalysts offers a potentially more eco-friendly and sustainable process for removing arsenite from contaminated drinking water [175].

Whilst TiO_2 has been shown to oxidise As(III), the energy efficiency of heterogeneous photocatalysts for water treatment are not well studied, hindering their real world application. Thus the Sn-doped TiO_2 is proposed as a way of improving light conversion efficiency and consequently making As(III) remediation via heterogeneous photocatalytic oxidation a favourable, competitive treatment option [200].

When investigating new photocatalysts for the photooxidation of As(III) a major challenge is the accurate determination of the PCO yield and, in turn, the accurate calculation of kinetic rate constants. This is challenging due to the simultaneous adsorption of As(III) and As(V). Previous studies have calculated the PCO yield and reaction kinetics using the decrease in aqueous As(III) [56,201] or the increase in generated As(V) in the solution [202,203] ignoring changes in the oxidation state of adsorbed arsenic. The precise calculation of the PCO kinetics should consider all the PCO products which include both aqueous As(V) and the surface adsorbed As(V).

5.2 Aims and objectives

Our objectives for this chapter are: (a) to identify the structure of Sn-doped TiO_2 and to determine how Sn doping content can affect the final structure of the composite catalyst, (b) to explore the application of Sn-doped TiO_2 for the PCO/adsorption of As(III) and (c) to investigate the PCO yield and reaction kinetics by considering both As(V) in solution and surface adsorbed As(V). To achieve these objectives, Sn-doped TiO_2 was firstly synthesised using a range of Sn:Ti ratios via a sol-gel synthesis. Secondly, the composite photocatalysts were characterized using a wide range of state-of-the-art spectroscopic and imaging tools, i.e. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS), energy dispersive X-ray analysis (EDX), Raman spectroscopy, scanning electron microscopy (SEM), HR-TEM, STEM and Fourier transform infrared spectroscopy (FTIR). The bandgap was calculated from diffuse reflectance spectra measuring in the UV-visible range and the valence band was analysed using XPS. The bandgap of TiO_2 was reduced by doping with different molar ratios of Sn. Based on findings from our physical characterisation, the process by which our heterostructured photocatalysts formed were postulated. Thirdly, the bicomposite showed an enhanced PCO compared with TiO_2 . The concentration of the remaining arsenic species [As(III) and As(V)] in solution and adsorbed to the photocatalyst were analysed along the course of the reaction. Finally, the PCO yield and kinetic rate constant were accurately calculated by considering the concentration of As(V) in the solution (using molybdenum blue UV/vis method) and the surface adsorbed As(V) (using XPS). It worth mentioning that our next paper will include further investigations such as the main oxidant, TAS investigations, pH, the effect of distance between the light source and the solution surface, the mass to solution ratio.

5.3 Results and discussion

5.3.1 Effect of Sn:Ti doping ratios on the structural control

Afterward the sol-gel (SG) method was used to dope TiO_2 with different molar ratios of Sn. SG synthesis yielded Sn-doped TiO_2 photocatalysts with improved photocatalytic oxidation efficiency, so it is considered in this study. In the first part of this chapter, a wide range of

characterisation techniques was used to investigate the SG synthesis controls (i.e. effect of Sn:Ti doping ratio) on the final structural and photocatalytic features of the Sn-doped TiO₂

5.3.1.1 XRD characterization

XRD studies confirmed the crystallinity of both undoped and Sn-doped TiO₂ samples (Figure 5.1). The main peaks in undoped TiO₂ were observed at $2\theta = 25.3, 37.8, 48.1, 54.2, 55.1$ and 62.7 which are assigned to the (101), (004), (200), (105), (211), and (204) Miller planes, respectively, of the reference anatase TiO₂ standard data (JCPDS 96-500-0224). After Sn doping, new peaks appear at $2\theta = (26.7, 34.4, 52.4^\circ)$ which become predominant as the Sn doping is increased. These peaks are often difficult to interpret due to the high similarity between the characteristic peaks of SnO₂ cassiterite and those of TiO₂ rutile [204]. Consequently, to provide an accurate interpretation of the XRD data, all data were modelled using X-ray diffraction pattern modelling software (GSAS-EXPGUI). A Le Bail refined model was fit to each XRD pattern. The models are presented in Appendix 9.3.1 (Figure 9.3 to Figure 9.8) and the results are summarised in Figure 5.1. The results show that these new peaks are attributed to the formation of a distinct cassiterite SnO₂ phase [95]. However, there was no anatase to rutile phase transformation after Sn-doping and TiO₂ maintains its anatase crystal structure, although some TiO₂ brookite impurities were detected with high levels of Sn doping (0.5Sn:1TiO₂ and 1Sn:1TiO₂) at 30.8 and 42.1 [205,206]. The height of the SnO₂ cassiterite peaks increases as the Sn:Ti ratio is increased, while the TiO₂ anatase height decreases.

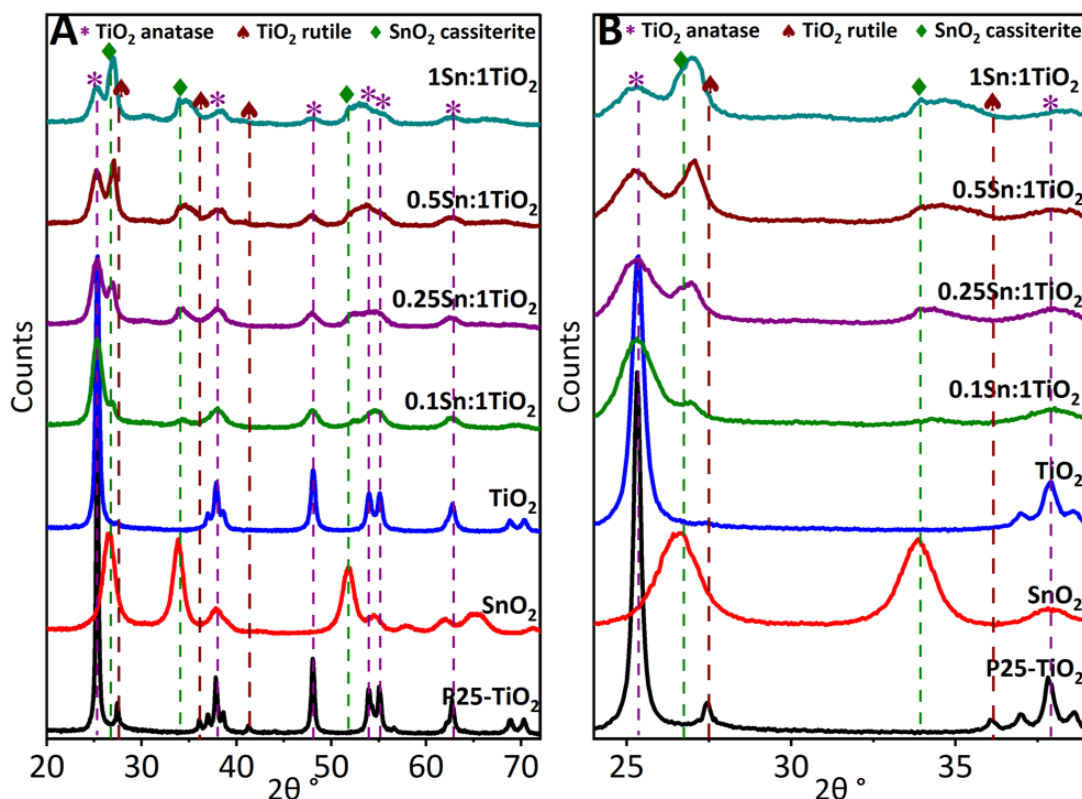


Figure 5. 1. XRD patterns for TiO_2 doped with different Sn molar [peaks are assigned based on GSAS modelling], A - shows the full range (20 to 70°) and B - A zoomed in section (25 to 40°) for ease of interpretation.

The masses and molar ratios of cassiterite SnO_2 and anatase TiO_2 were derived from the GSAS-EXPGUI model, as shown in Figure 5.2. For the samples 0.1Sn:1TiO_2 , 0.25Sn:1TiO_2 , 0.5Sn:1TiO_2 and 1Sn:1TiO_2 , the calculated molar ratios of $\text{SnO}_2 : \text{TiO}_2$ were 0.039, 0.11, 0.21 and 0.44 respectively (Figure 5.2A), which were less than the synthetic molar ratios. This may be due to the incorporation of Sn within the lattice structure of TiO_2 , as opposed to the segregation of the cassiterite SnO_2 phase, in addition to some losses during hydroxylation in the sol-gel synthesis. The $\text{SnO}_2:\text{TiO}_2$ mass percentages are shown in Figure 5.2B.

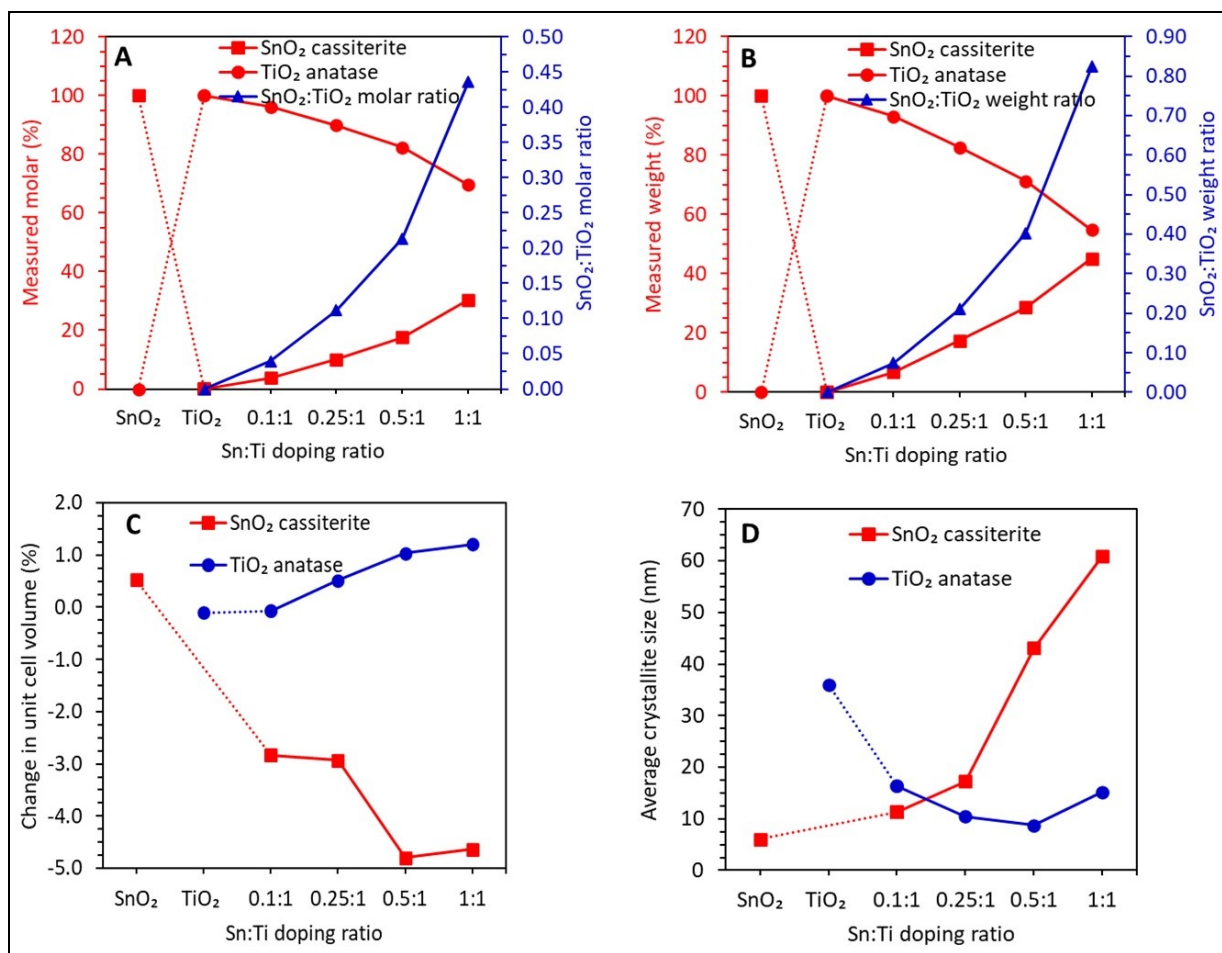


Figure 5.2. Summary of XRD modelling. A) The effect of Sn-doping on SnO₂:TiO₂ molar fraction, B) the effect of Sn-doping on SnO₂:TiO₂ weight fraction, C) the effect on mean cell volume (MCV) change versus anatase TiO₂ and cassiterite SnO₂ standards, and D) the average crystallite size.

The unit cell parameters derived from GSAS model show an expansion in the unit cell volume in the case of TiO₂, and a contraction in SnO₂ as the Sn-doping ratio is increased (Figure 5.2C and Appendix 9.3.1, Table 9.2). This change reaches a plateau in the 0.5Sn:1TiO₂ sample with a 1.3% increase in TiO₂ and a 4.8% decrease in SnO₂ unit cell size. This plateau may be a result of the solubility limits being reached in each phase (*i.e.* Sn-doping in TiO₂ and Ti-doping in SnO₂). The increase in the TiO₂ unit cell volume is strong evidence that Sn has been incorporated into the TiO₂ lattice structure [207] where Sn⁴⁺ ions are larger than Ti⁴⁺ and would thus cause a lattice expansion.

The average crystallite size was determined using a Scherrer analysis eqn. 5.1 (Figure 5.2D), showing that both TiO₂ and SnO₂ are nanocrystalline at all examined Sn fractions. The SnO₂ crystal grew with higher Sn doping from 11.2 nm in 0.1Sn:1TiO₂ to 60.9 nm in 1Sn:1TiO₂. In contrast, the

TiO₂ crystal size generally decreased from 36 nm in unmodified TiO₂ to 8.8 nm in 0.5Sn:1TiO₂ and then slightly increases to 15.2 nm in 1Sn:1TiO₂. This is shown by the broadness of TiO₂ anatase peaks after Sn-doping as shown in Figure 5.13. The inhibition in TiO₂ crystal growth in the doped samples is due to the electronegativity and size differences between Ti⁴⁺ (0.605 Å) and Sn⁴⁺ ion (0.69 Å) [208] which result in a distortion of the TiO₂ lattice structure during the substitution of some Ti⁴⁺ ion by Sn⁴⁺ to form Sn_xTi_{1-x}O₂ solid solution, which ultimately hinders TiO₂ crystal growth, making it more compact [209]. In addition, excess cassiterite SnO₂ may be distributed between TiO₂ crystals and retard the TiO₂ crystal growth. The slight enlargement in crystal size in the 1Sn:1TiO₂ sample may be due to the high SnO₂ content that causes the TiO₂ and SnO₂ phases to segregate, and in turn, increase the interplanar distance that enhances TiO₂ crystal growth [210].

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (\text{Eqn. 5.1})$$

where 'D' is the average crystallite size, 'λ', the X-ray wavelength, θ, Bragg's angle, and 'β' the peak position and the FWHM (full-width at half maximum) the peak after correction for instrumental broadening

5.3.1.2 Raman spectroscopy characterization

Active Raman modes of anatase TiO₂ are observed at 144.6 (E_g), 196.1 (E_g), 396.23 (B_{1g}), 516.09 (A_{1g} and B_{1g}), 637.95 (E_g) cm⁻¹ (Figure 5.3) [211]. In 0.5Sn:1TiO₂ and 1Sn:1TiO₂ samples, some traces of Raman active modes of brookite TiO₂ impurities are detected at around 245 (A_{1g}), 320 (B_{1g}) and 360 cm⁻¹ (B_{1g}) [212]. Raman modes for the rutile TiO₂ phase are not observed, in agreement with XRD analysis. The peak for cassiterite SnO₂ at 632 cm⁻¹ overlaps with the anatase shift at 637.95 cm⁻¹ (E_g), which results in an indistinguishable peak. A systematic decline in the intensity of TiO₂ anatase peaks was seen with increasing Sn content, which may be due to an increased coverage of anatase surface with SnO₂ particles (which becomes more dominant with higher doping resulting in SnO₂ agglomerates) [190]. The addition of Sn results in a small blue-shift in the main anatase E_g vibrational band. This observation is attributed to a restriction in the phonon mode, resulting in an increase in the energy required for this vibration to occur [213]. Also, with the addition of Sn, an asymmetric broadness in the Raman peaks were observed,

especially at 144.6 cm^{-1} (E_g), that may be due to a decrease in average crystal size of TiO_2 , phonon confinement and structural defects due to the insertion of Sn into the TiO_2 host structure [214].

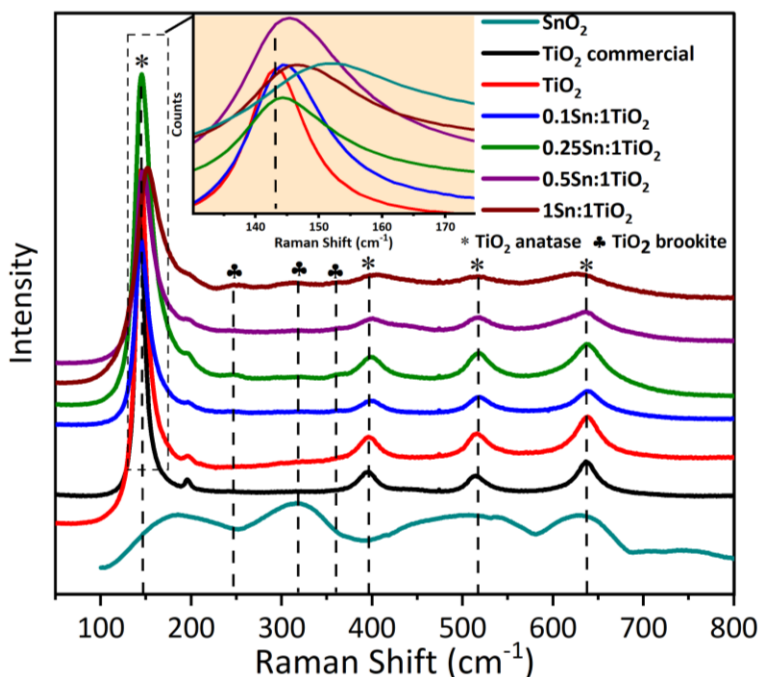


Figure 5. 3. The effect of diverse Sn-doping ratios on the Raman shift of dry powders of Sn-doped TiO_2 catalysts.

5.3.1.3 Determination of the bandgap and valance band

The determination of the bandgap energy is critical to assess the potential of generating the charge carriers [125,215]. The bandgap values were determined using the Tauc equation as shown in the materials and methods (chapter 3, section 3.4) by plotting the absorption coefficient against the photon energy. The bandgap is given by the interception of the two linear tangents according to Moss *et al.* [216]. The results shown in Figure 5.4 reveal that the bandgap of the pure TiO_2 and SnO_2 are $\sim 3.20\text{ eV}$ (Figure 5.4A) and $\sim 3.64\text{ eV}$ (Figure 5.4F), respectively. There is a steady decline in the bandgap values with increasing additions of Sn, where it decreased from $\sim 3.20\text{ eV}$ in the unmodified TiO_2 to $\sim 2.90\text{ eV}$ in $1\text{Sn}:1\text{TiO}_2$. These results are consistent with Tripathi *et al* [217]. The observed red shift in the bandgap (shift in the absorption edge slightly towards the visible light) is attributed to the internal strain due to the unit cell expansion which creates new energy levels [218]. This ultimately leads to charge transfer from

core to the surface of the catalyst's nanocrystals, and can improve the lifetime of photo-induced charge carriers [217].

The valence band edge energy was determined by XPS and reported in Figure 5.5. The valence band edge energy is determined with respect to the O1s orbital energy correction, in accordance with Scanlon *et al.* [219]. The results presented in Figure 5.5 show that there was a slight decrease in the valence band edge values in the Sn-doped catalysts compared to the bare TiO₂. However, optical results showed a narrowing of the bandgap. This indicates that a shift in the CB is most likely the cause of the change in bandgap. The CB values, calculated according to eqn. 5.2, showed that with increasing Sn-doping the CB became less negative, going from -0.30 V vs NHE in unmodified TiO₂ to -0.10 V vs NHE in 1Sn:1TiO₂. This alters the Fermi level positions (zero binding energy) and develops tunable oxygen vacancies energy states between the maximum valence band (MVB) and the minimum conduction band (MCB) [103,220].

$$E_{VB} + E_g = E_{CB} \quad (\text{Eqn. 5.2})$$

where E_{VB} , E_g and E_{CB} are the valence band, conduction band and conduction band energies.

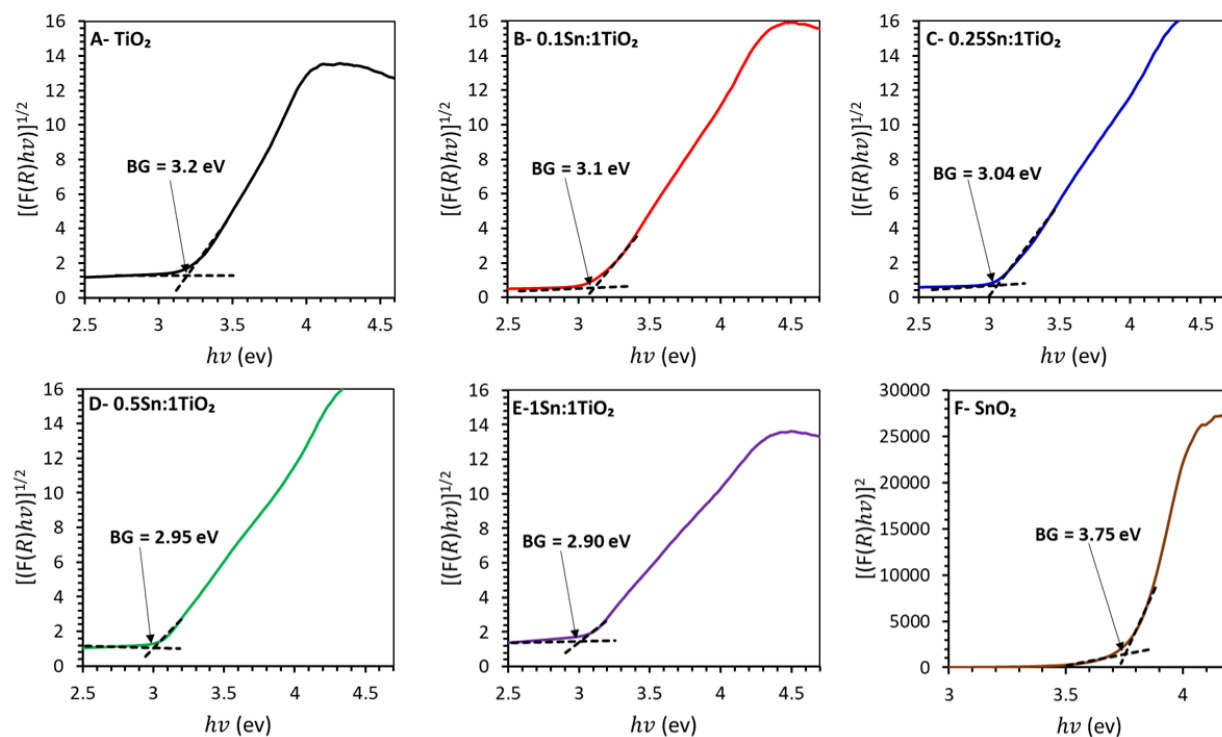


Figure 5. 4. Bandgap calculations from a Tauc plot of diffuse reflectance data of the dry catalyst (A - TiO₂, B - 0.1Sn:1TiO₂, C - 0.25Sn:1TiO₂, D - 0.5Sn:1TiO₂, E - 1Sn:1TiO₂ and F- SnO₂).

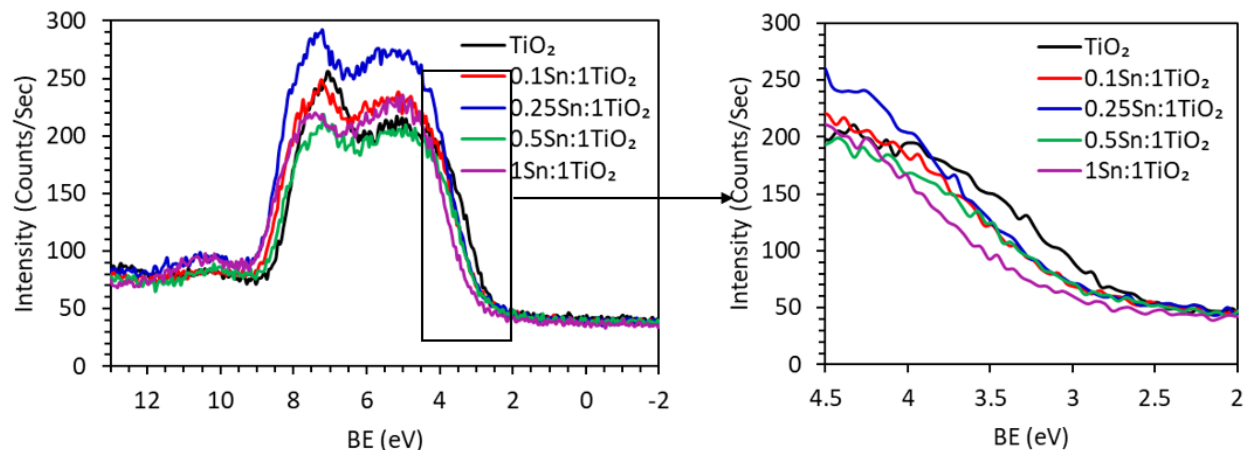


Figure 5. 5. XPS valence band edge analysis after applying $M-O^{2-}$ correction.

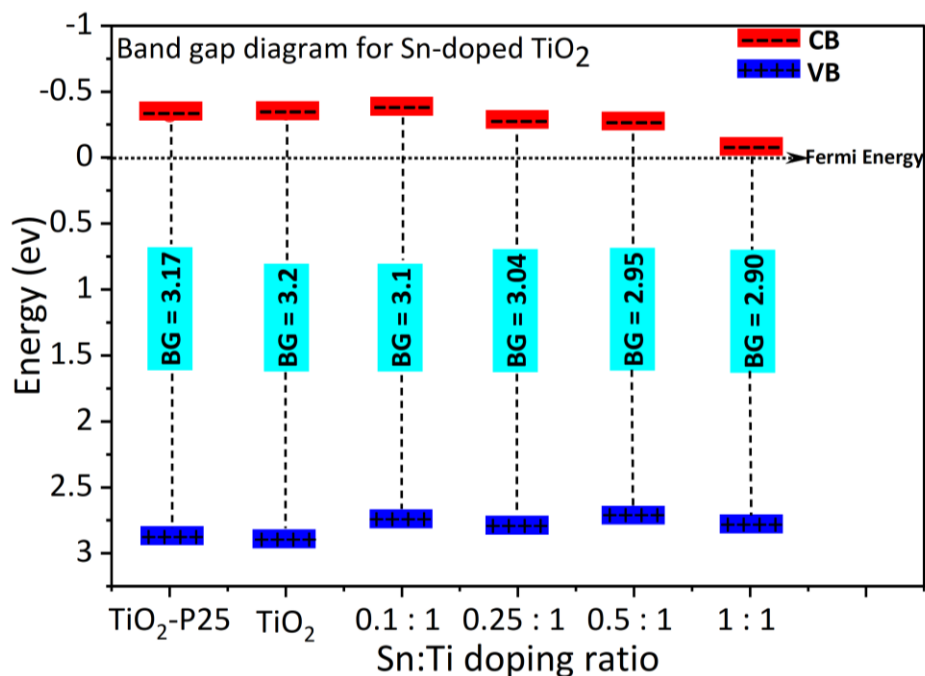


Figure 5. 6. Band energy analysis based on valence band edge determination from XPS and band gap determination from diffuse reflectance spectra.

5.3.1.4 The effect of Sn-doping on the surface and bulk elemental composition

The chemical composition of the near surface was studied using XPS. Survey spectra of the Sn-doped TiO_2 samples and their peak assignments are shown in Figure 5.7. The results show that the surface of the Sn- TiO_2 consists of Sn, Ti, O and C only.

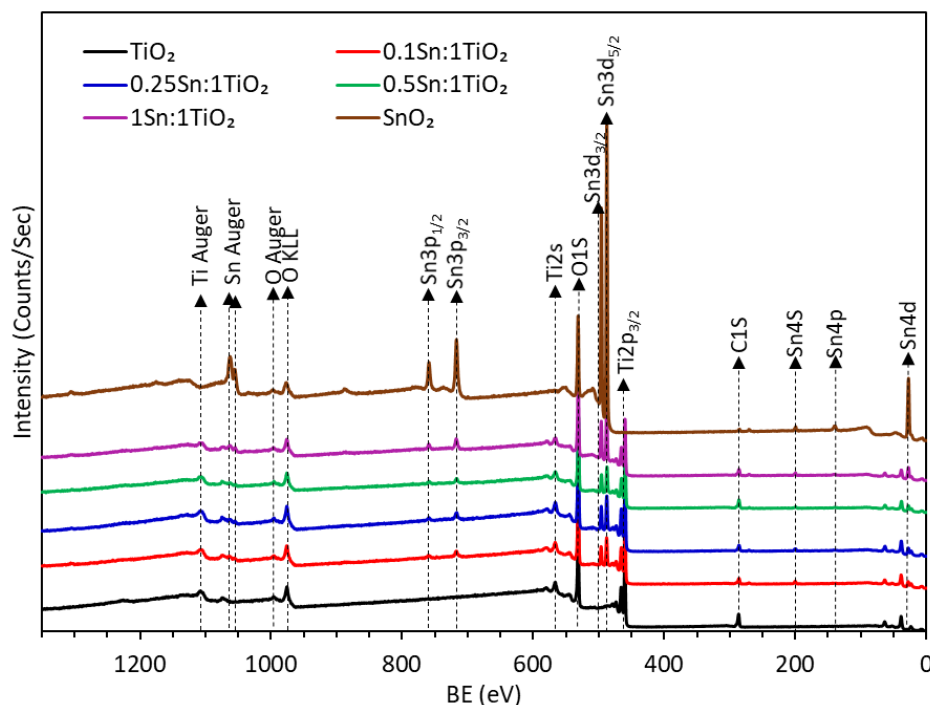


Figure 5. 7. XPS survey spectra showing the surface elemental composition.

Peak deconvolution using high-resolution scans and fitted by CASAXPS software are presented in Figure 5.8 to Figure 5.11. The detailed peak fitting of the composition and chemical states for each sample are presented in (Appendix 9.3.2). The fitted results show that Ti is present as Ti^{4+} and Sn as Sn^{4+} . There are chloride impurities in the Sn-doped samples which originate from the Sn precursor (SnCl_4). The respective binding energies of the Ti^{4+} $2p_{3/2}$ and Ti^{4+} $2p_{1/2}$ doublet increased with Sn doping, from 458.6 and 464.3 eV in unmodified TiO_2 to 459.0 and 464.7 eV in $1\text{Sn}:1\text{TiO}_2$. These changes in the binding energies are attributed to the shift in the Fermi level of the material, discussed in section (Section 5.4.3). The summary of the chemical composition of the surface environment of prepared catalysts was analysed using CASAXPS fitting software and are presented in Table 5.1 showing that the Sn:Ti ratios increased as Sn-doping increases. The Sn:Ti ratio intuitively increased with Sn-doping. This corroborates the findings from XRD and EDX (see below).

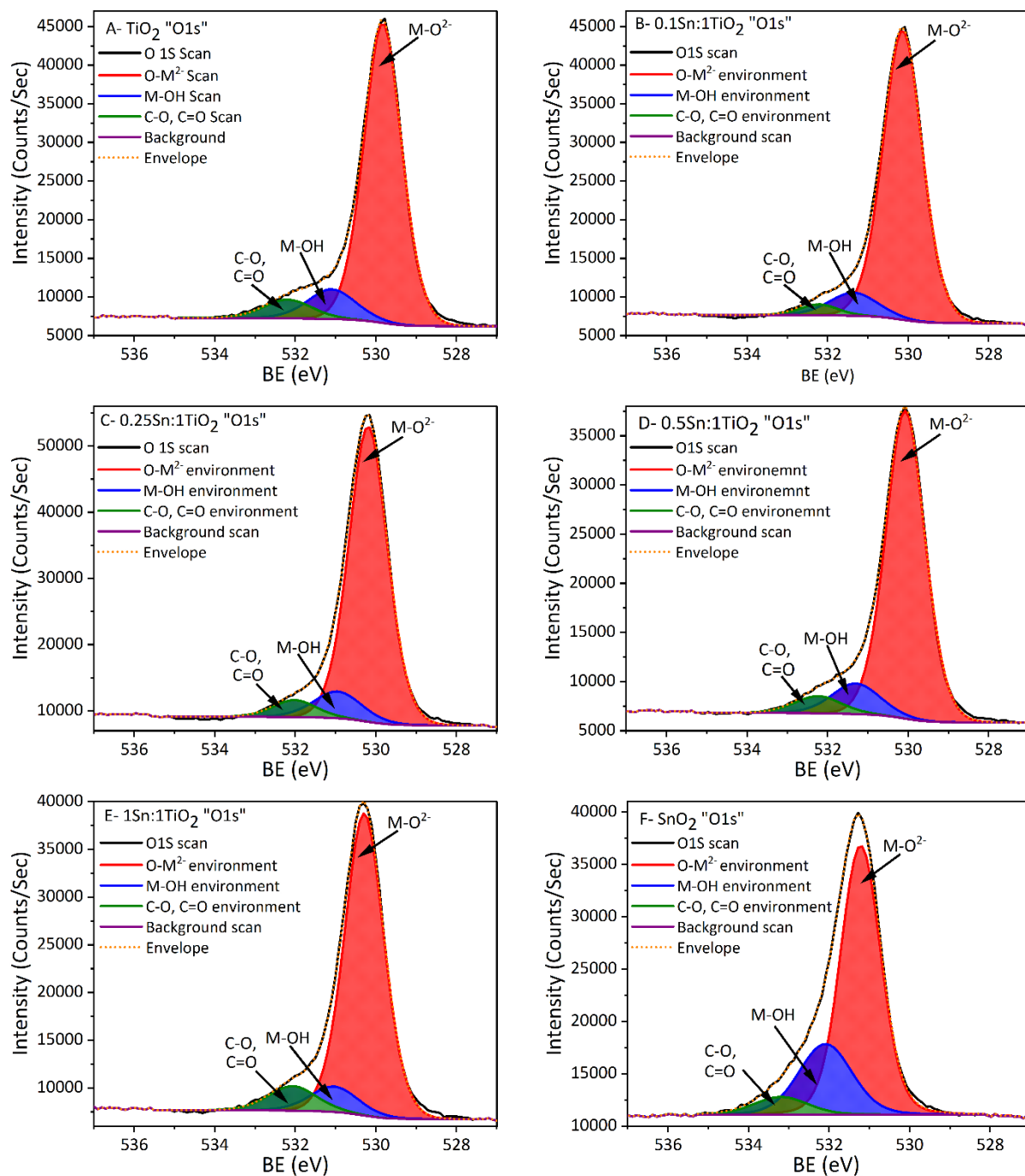


Figure 5. 8. High-resolution XPS of O1s peak in (A) TiO₂, (B) 0.1Sn:1TiO₂, (C) 0.25Sn:1TiO₂, (D) 0.5Sn:1TiO₂, (E) 1Sn:1TiO₂, (F) SnO₂.

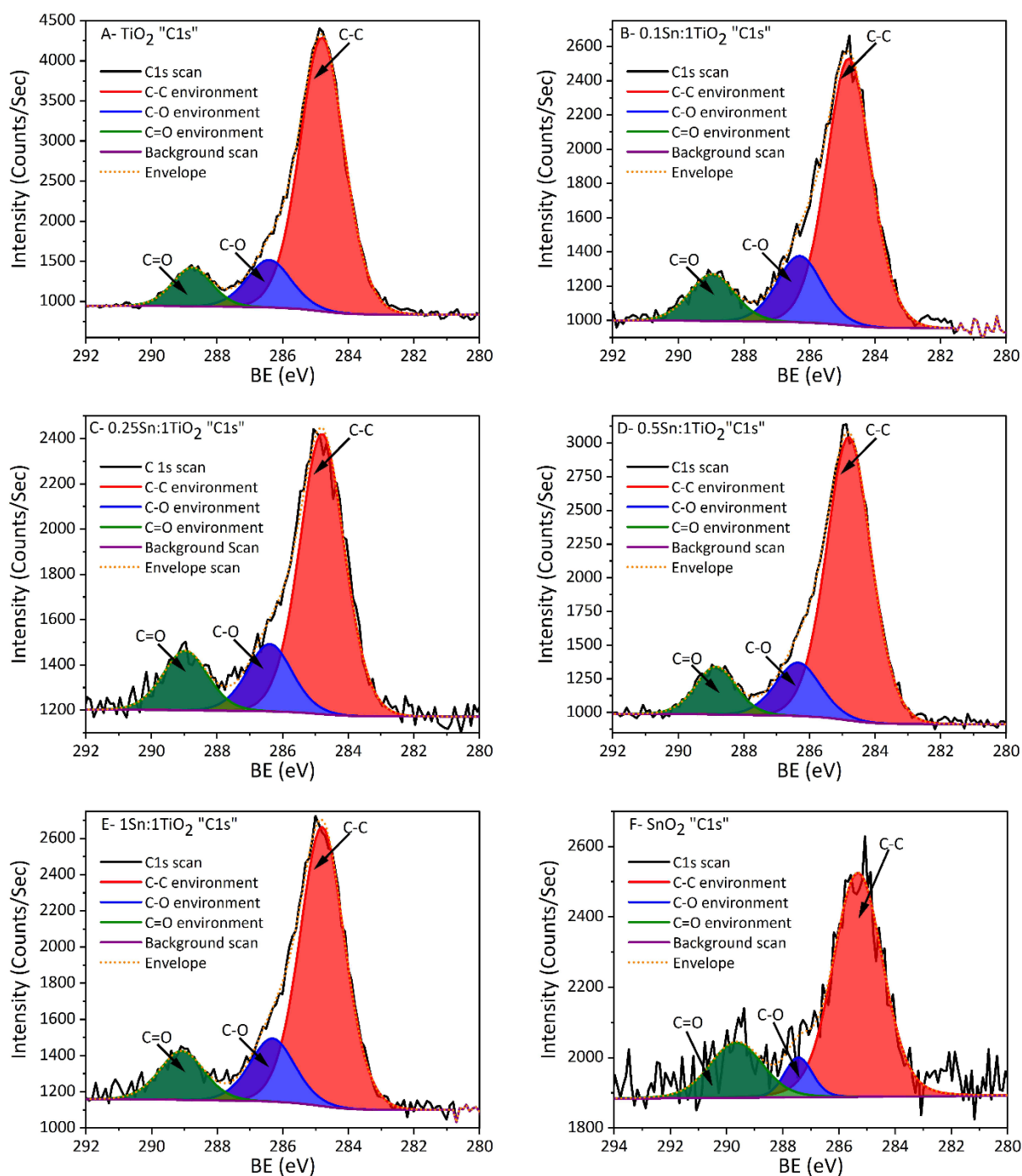
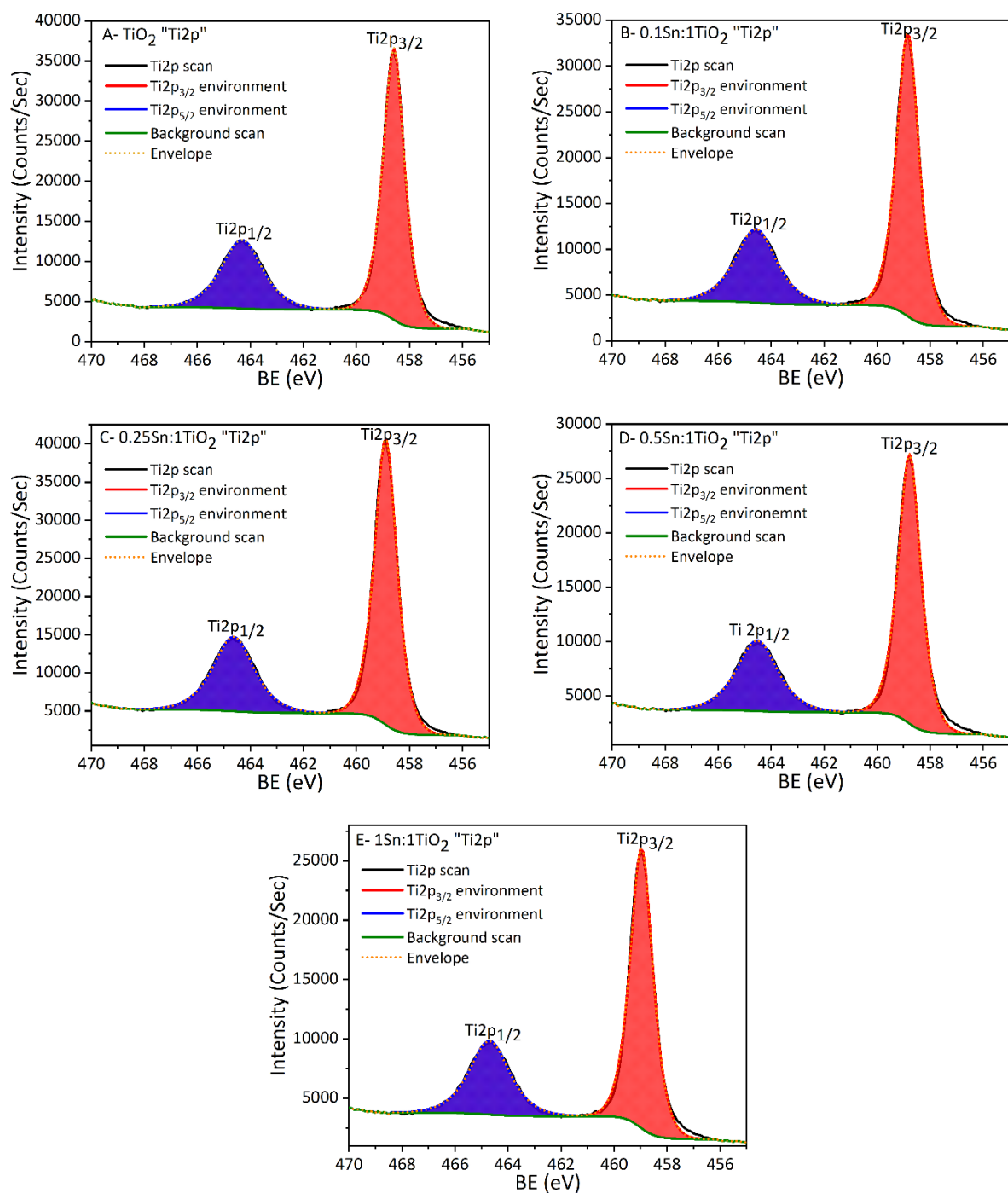


Figure 5. 9. High-resolution XPS of C1s peak in (A) TiO_2 , (B) 0.1Sn:1TiO_2 , (C) 0.25Sn:1TiO_2 , (D) 0.5Sn:1TiO_2 , (E) 1Sn:1TiO_2 , (F) SnO_2 .



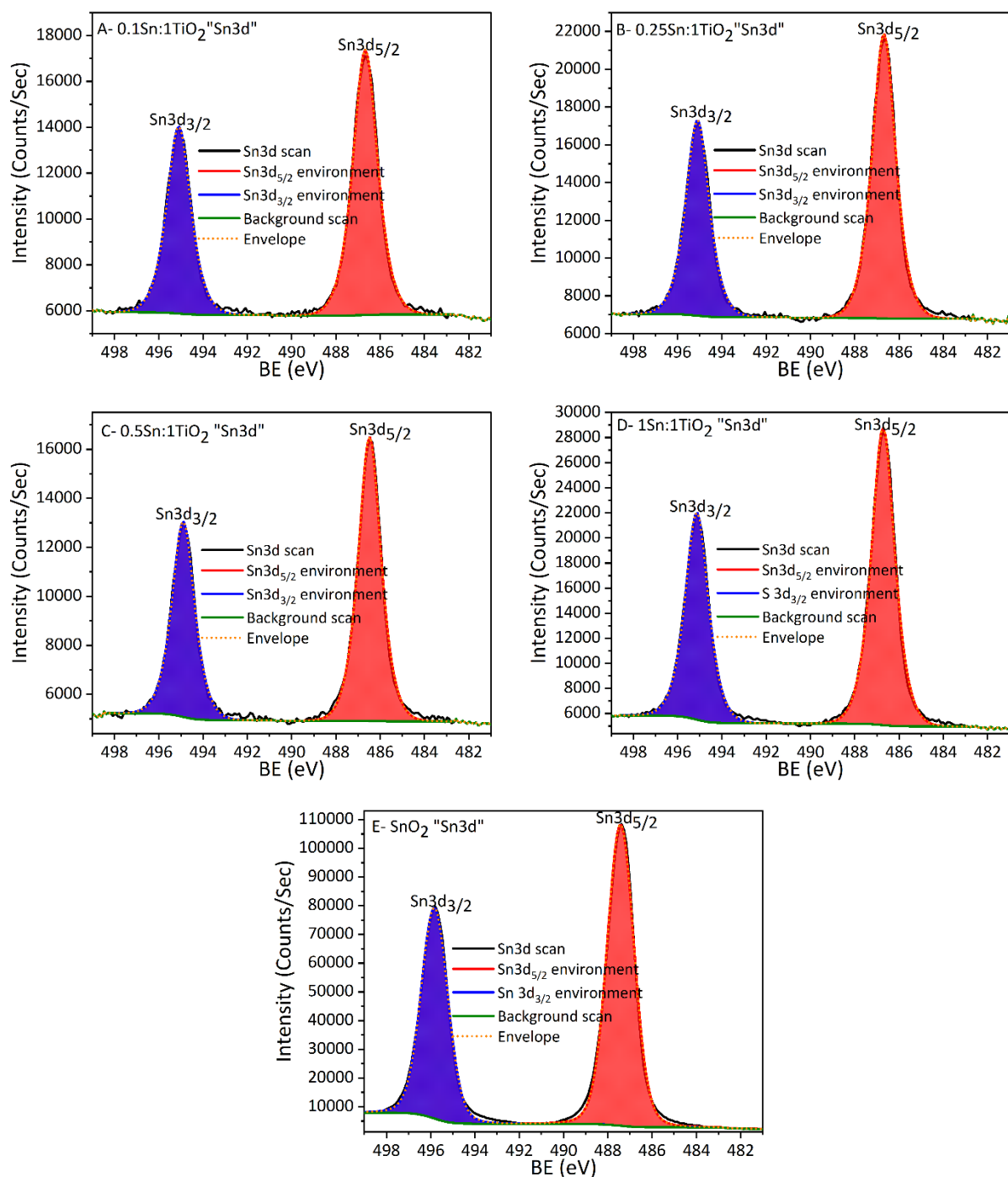


Table 5. 1: XPS analysis for the surface element environment and abundance (%).

Environment	Abundance (%)					
	TiO ₂	0.1Sn:1TiO ₂	0.25Sn:1TiO ₂	0.5Sn:1TiO ₂	1Sn:1TiO ₂	SnO ₂
C (C-C)	15.40	7.80	5.30	11.70	8.40	2.40
C (C-O)	2.60	1.90	1.30	2.20	1.90	1.20
C (C=O)	1.90	1.40	1.10	1.80	1.50	0.70
C (total)	20.00	11.10	7.70	15.70	11.80	4.30
Ti ⁴⁺ (TiO ₂)	20.70	22.00	22.70	19.70	18.30	0.00
Sn ⁴⁺ (SnO ₂)	0.00	3.80	4.10	3.90	8.10	37.00
O (M-O ²⁻)	49.20	54.30	54.50	50.40	50.00	43.50
O (M-OH)	6.20	5.30	6.10	6.20	5.10	10.60
O (C-O, C=O)	3.90	1.90	3.50	3.40	5.00	2.00
O (total)	59.30	61.50	64.10	60.00	60.10	56.20
Cl ⁻ (M-Cl)	0.00	1.60	1.40	0.70	1.70	2.50
Sn:Ti ratio	0.00	0.17	0.18	0.20	0.44	-

LEIS was used to characterise our Sn-doped TiO₂ materials. In this study, LEIS dynamic depth profiling is used to analyze the outermost surface atomic layers with 0.2-1 nm depth resolution [221]. The LEIS spectra were recorded using a 3 keV He⁺ and the spectra are presented in Figure 5.12. Interestingly, the results show that with increasing Sn-doping, the concentration of Sn in the outermost surface atomic layers decrease. This is attributed to a greater abundance of Sn in the core of the catalyst (in SnO₂ clusters) as opposed to the uppermost surface.

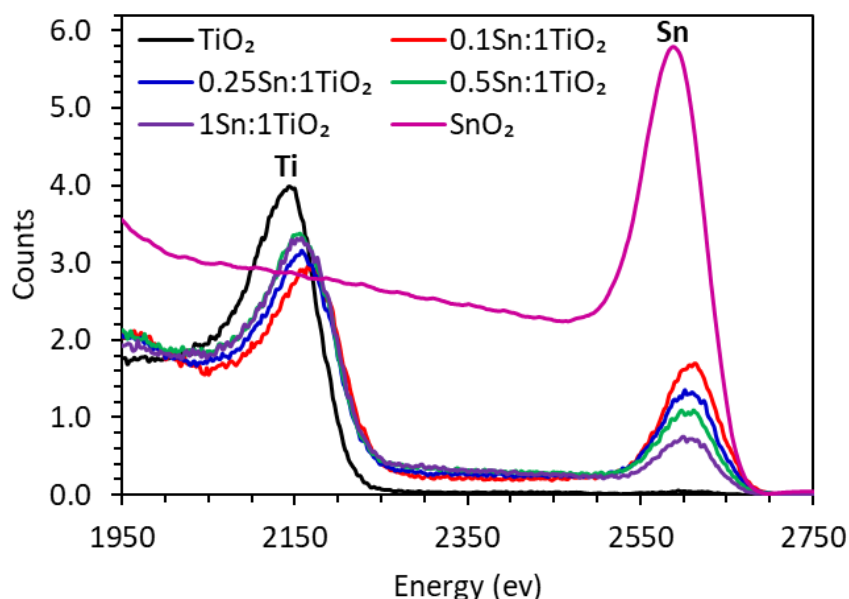


Figure 5. 12. LEIS spectra for TiO₂ doped with different Sn ratios.

Successive cycles of He ion sputtering with depth profiling were carried out with overall dose reaching $\sim 5.3 \times 10^{15}$ ions/cm² (calculated using eqn. 3.2). Each acquisition dose of 1×10^{15} (ions/cm²) is sufficient for sputtering one atomic layer and thereby the applied ion dose was enough for depth profiling down to 5 atomic layers. Similar to LEIS surface spectra results (Figure 5.12), the Sn:Ti ratio between the different catalysts shows a gradual decrease in the Sn:Ti ratio with increasing Sn-doping (Figure 5.13 and Figure 5.14). In each single sample, the data points (Figure 5.13) and the average Sn:Ti ratios (Figure 5.14) show a steady increase in Sn:Ti ratio when going into the deeper atomic layers. Therefore, Sn is more predominant in the core of the catalyst, despite the Sn doping level.

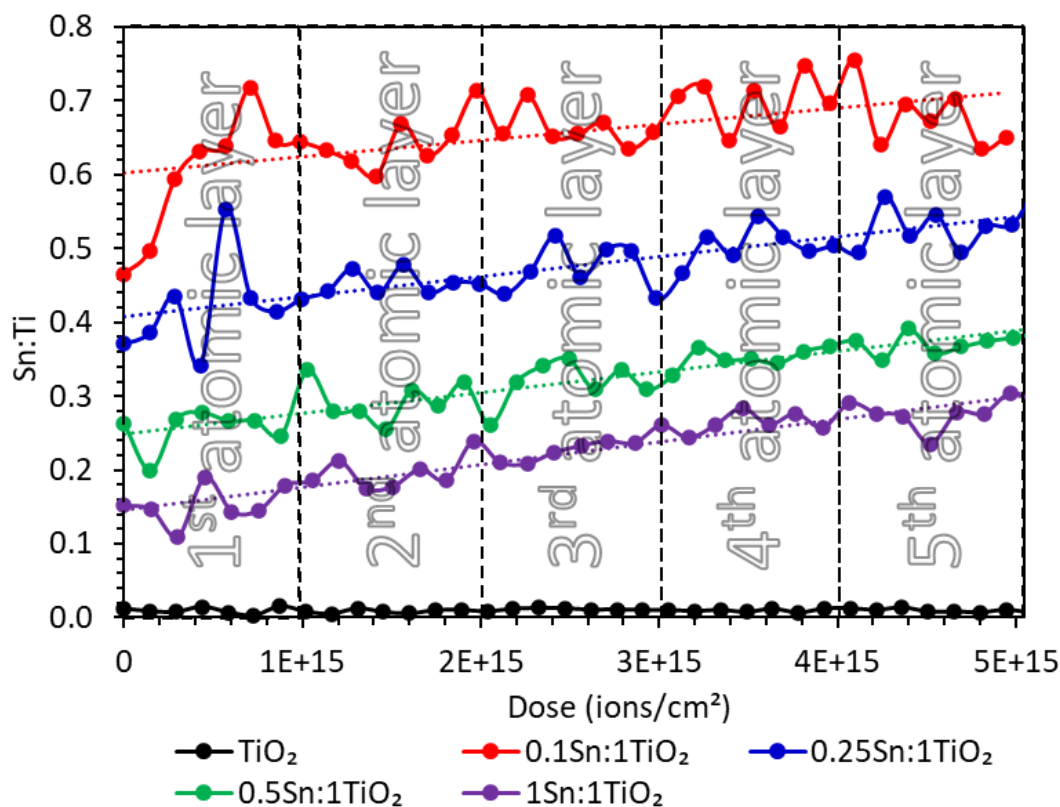


Figure 5. 13. LEIS depth profiling showing the effect of Sn doping on the Sn:Ti ratio in the outmost surface atomic layers [Each acquisition dose of 1×10^{15} (ions/cm²) sputters one atomic layer].

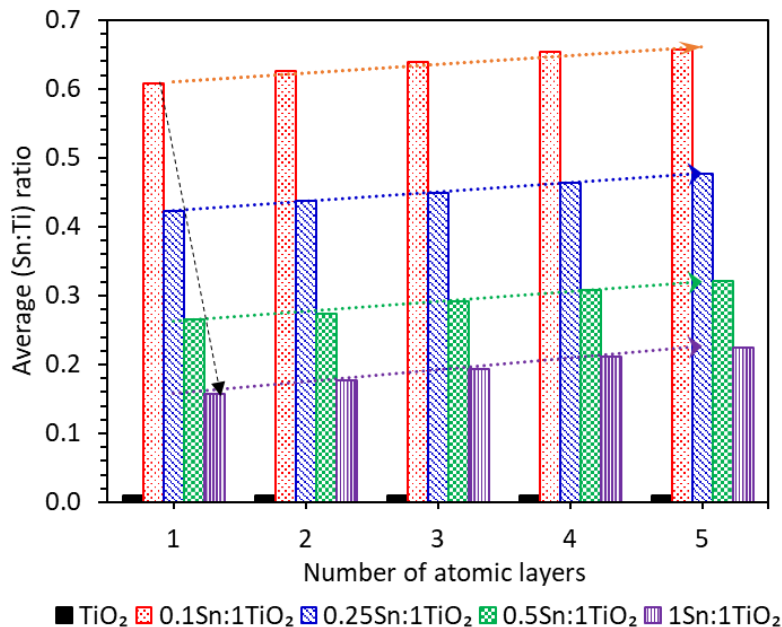


Figure 5. 14. Average Sn:Ti ratios in each individual atomic layer in different prepared samples (LEIS depth profiling data using ion dose = $\sim 5.3 \times 10^{15}$ ions/cm²).

A calibration curve of the Sn:Ti ratios was created from the LEIS spectra by plotting the peak signals of Sn (from Figure 5.12) vs the peak signal of Ti (from Figure 5.12) to assess possible matrix effects. The linearity of this curve with $R^2 = 0.99$ (Figure 5.15) implies that there is no matrix effect nor suppressing effect of the Sn signal and Ti signal on each other [222].

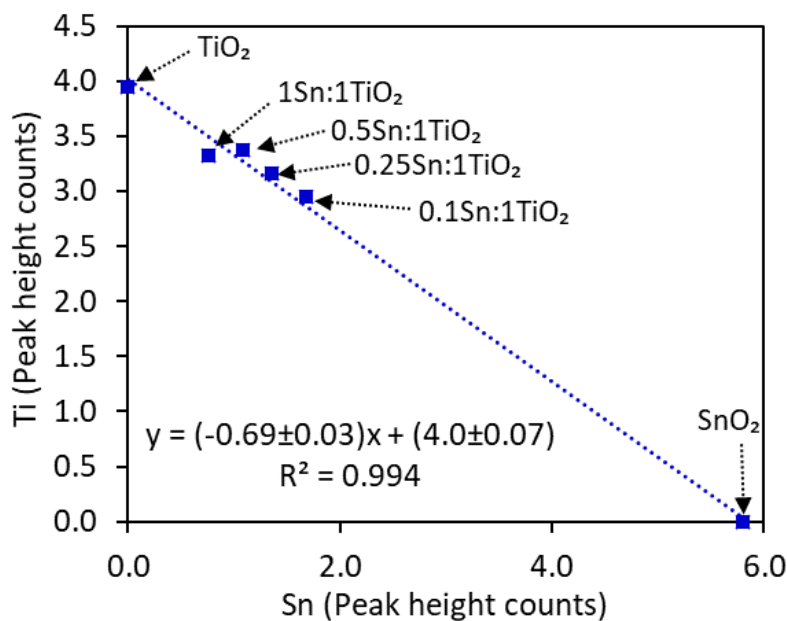


Figure 5. 15. Calibration plot based on the Sn and Ti LEIS peak spectra.

The Sn:Ti molar and mass ratios were determined using EDX analysis. The Sn:Ti ratio increased with the Sn-doping level, as shown in Figure 5.16. The molar ratios are smaller than the synthetic molar ratios, most likely due to some mass loss of Sn during synthesis. In general, the analytical values are in parallel with the calculated Sn:Ti ratios from XRD data (comparing the amount of anatase TiO_2 to cassiterite SnO_2 formed; but does not take into account the level of Sn doping into anatase TiO_2 and *vice-versa*).

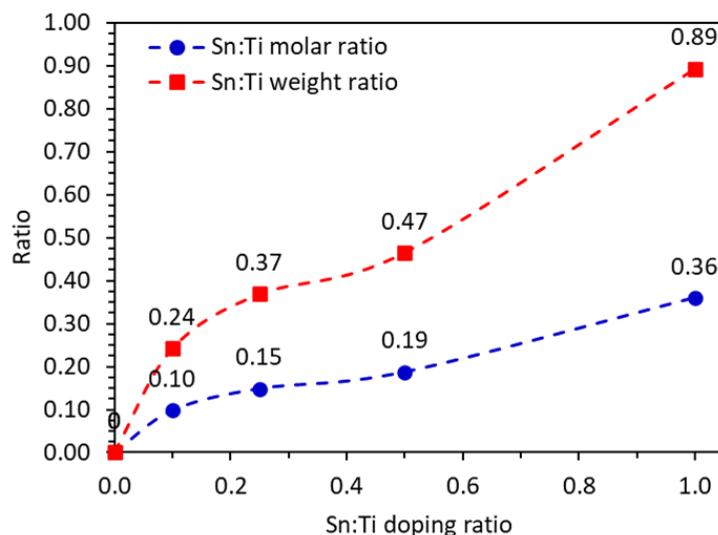


Figure 5. 16. Calculated molar and mass ratios based on EDX analysis

5.3.1.5 Investigation of surface morphology

HR-TEM figures are presented in Appendix 9.3.3. In TiO_2 sample only anatase d-spacings are observed with the prominent 101 peak. In the 0.1Sn:1TiO₂ sample, the anatase (101) peaks at a d-spacing of 3.56 Å are observed. One particle with a d-spacing of 3.35 Å matches the cassiterite (110) peak. In the 0.25Sn:1TiO₂ sample, only d-spacings related to the formation of anatase are observed. Discrete cassiterite crystals are not observed. d-spacing is observed at 3.01 Å, likely due to impurities. In the 0.5Sn:1TiO₂ sample, particles related to the presence of anatase crystals are observed (the majority showing the principle 101 peak at 3.56 Å) where Several cassiterite particles are observed including individual SnO₂ particles. For the 1Sn:1TiO₂ sample, the results are similar and cassiterite SnO₂ particles are detected amongst a mass of TiO₂ anatase particles. In the SnO₂ sample, only cassiterite is observed. A d-spacing of 3.36 Å is assigned to the principal peak of cassiterite at (110).

In S-TEM investigations (presented in Appendix 9.3.4), only Ti and O were detected in the TiO_2 sample, and the unit cell of each discrete phase is observed. In the $0.1\text{Sn}:1\text{TiO}_2$ sample, Ti, O and Sn are observed. In the $0.25\text{Sn}:1\text{TiO}_2$ sample, Ti, O and Sn are detected with pronounced delocalisation of Sn. The particles presented in this image show TiO_2 structures doped with Sn. This supports XRD data in that the TiO_2 crystals in this sample have expanded by 0.51%. For the $0.5\text{Sn}:1\text{TiO}_2$ sample, the Sn and Ti regions are well mixed. The STEM data alone does not to indicate the presence of Sn-doped TiO_2 or Ti-doped SnO_2 . This supports XRD data suggesting that SnO_2 crystals contract by 4.79% and TiO_2 crystals expand by 1.03 % due to Ti and Sn doping respectively. For the $1\text{Sn}:1\text{TiO}_2$ sample, we have a similar outcome to the $0.5\text{Sn}:1\text{TiO}_2$ sample. However, from the examined location, there are clearly some regions where Ti is present in far greater majority than Sn. This supports conclusions drawn from the XRD data that Ti more readily dopes SnO_2 structures. There is a much larger contraction in SnO_2 crystals compared to TiO_2 crystals, indicating a higher level of doping. Ti and Sn levels are more even, in line with XRD data, showing a 45: 55 % mixture of SnO_2 and TiO_2 phases are present. Only Sn and O were detected in the SnO_2 sample.

SEM micrographs of TiO_2 and $\text{Sn-TiO}_2:\text{SnO}_2$ samples (Figure 5.17) exhibit well dispersed spherical particles with variable size distribution with a diameter ranging from 50 to 200 nm, however the SnO_2 reference sample (Figure 5.17F) shows more aggregated particles with irregular edges. TiO_2 samples retained the porous morphology after Sn doping. The findings show that the particle sizes decreased after doping and aggregates as the Sn content increases [210]. These smaller particle sizes generate a larger surface area and provide more reaction points, which in turn increases the photocatalysis reaction rate [101].

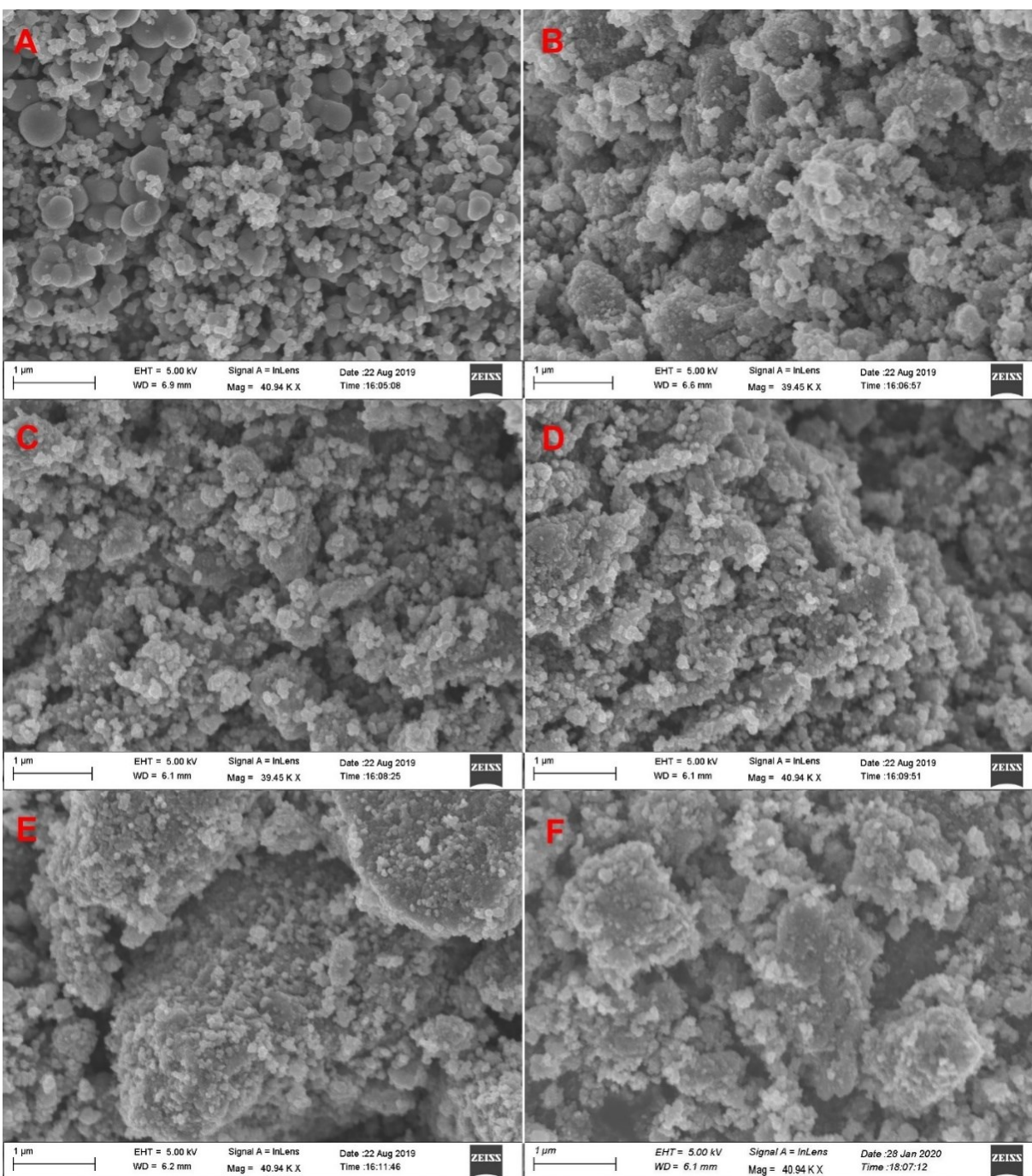


Figure 5. 17. SEM micrographs of different prepared catalysts [A- TiO₂, B- 0.1Sn:1TiO₂, C- 0.25Sn:1TiO₂, D- 0.5Sn:1TiO₂, E- 1Sn:1TiO₂, F- SnO₂].

5.3.1.6 Characterization of the surface bonding

Fourier transform infrared (FTIR) spectra are shown in Appendix 9.3.5. Despite the different Sn doping ratios, all the Sn-TiO₂ samples show a sharp band at 660 cm⁻¹, which is due to the Ti-O-Ti bond vibration [152]. Bands appearing at 400–650 cm⁻¹ are assigned to the stretching vibration

modes of Ti–O in the case of the undoped sample, and to both Sn–O and Ti–O–Sn bonds in Sn-doped samples. As observed in the FTIR spectrum of Sn-doped TiO₂ (Appendix 9.3.5), there is a shift in the wavenumber towards the higher energy spectrum. This is mainly because the Sn–O bond is longer than the Ti–O bond [223,224].

5.3.1.7 Proposed structure of the Sn doped TiO₂ photocatalyst

The core and the shell of the catalyst plays a vital role during the PCO process and the surface reactions. Based on the main characterization results summarised in Table 5.2, the following structure and control of the Sn:Ti doping ratios is proposed. As Sn-doping increases, SnO₂ content increases and tends to segregate and forms the core of the catalyst, while Sn-TiO₂ floats on the surface. At higher Sn-doping ratios, SnO₂ crystal size increases, confirming SnO₂ segregation and the mean cell volume (MCV) of the TiO₂ expands, confirming the insertion of Sn in TiO₂ lattice and the formation of Sn-TiO₂. The low Sn content at higher Sn-doping ratios is attributed to the floating shell Sn-TiO₂ and less likely from the core SnO₂, while higher Sn detected in the outermost surface at lower Sn-doping content is attributed to the SnO₂ shell as presented in Figure 5.18. The development of Sn-TiO₂ on the surface of the catalyst at high Sn doping (1Sn:1TiO₂) makes the catalyst more efficient, where Sn-TiO₂ is a more effective catalyst than the surface SnO₂ formed at low Sn doping levels.

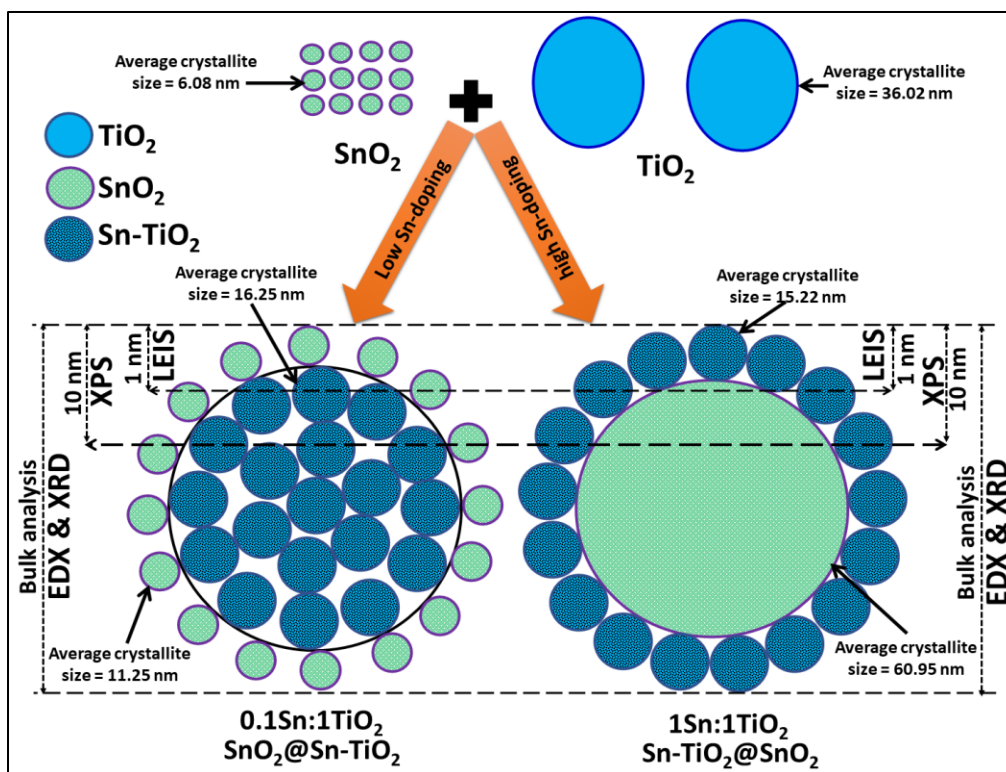


Figure 5. 18. Schematic diagram of the structure of the synthesised Sn-doped TiO₂ at low and high Sn-doping content through sol-gel synthesis.

Table 5. 2: Summary of characterisation findings derived from the various analytical techniques

Techniques	Low Sn-doping	High Sn-doping
	No expansion in TiO ₂ MCV; Sn-TiO ₂ formation unlikely.	Expansion in TiO ₂ MCV; Sn-TiO ₂ formation likely.
XRD	Smaller SnO ₂ average crystal size (~11 nm); SnO ₂ particles are more dispersed.	Larger SnO ₂ average crystal size (~61 nm); segregation of the SnO ₂ core more likely.
	Larger TiO ₂ average crystal size (~36 nm); TiO ₂ present as clusters	Smaller TiO ₂ crystal size (~15 nm).
EDX	Low Sn:Ti ratio.	High Sn:Ti ratio.
XPS	Low Sn:Ti ratio.	High Sn:Ti ratio.
LEIS	High Sn:Ti ratio.	Low Sn:Ti ratio.
SEM	Bigger particles, more segregated	Smaller particles, more aggregated
FTIR	Metal-O band at lower energy wavelength	Shift in Metal-O band at higher energy wavelength, confirming Sn-O formation

5.3.2 Photocatalytic oxidation (PCO) of As(III) over Sn-doped TiO₂

The second part of this chapter includes the investigations of the PCO activity of the synthesised sol-gel Sn-doped TiO₂ photocatalysts for the oxidation of As(III) to As(V) .

5.3.2.1 Effect of Sn doping content on the PCO of As(III)

Photocatalytic oxidation experiments were carried out using the sol-gel Sn-doped TiO_2 samples and the unmodified TiO_2 . The results show that Sn-doped TiO_2 samples have an improved PCO efficiency towards As(III) than the unmodified TiO_2 as presented in Figure 5.19. After 2 h, the percentage of As(III) oxidised was 31.8%, 61.9%, 72.3%, 78.2% and 71.4% for TiO_2 , 0.1Sn:1 TiO_2 , 0.25Sn:1 TiO_2 , 0.5Sn:1 TiO_2 and 1Sn:1 TiO_2 respectively. Sn-doping increased the oxidation yield by up to ~ 94 % to 145 % with respect to unmodified TiO_2 . This improvement in As(III) oxidation using the Sn-doped TiO_2 is attributed to two factors: (i) the reduction in the bandgap enables the doped catalyst to absorb more light in the UV region and (ii) reduced recombination of charge carriers due to charge transfer across the Sn- TiO_2 @ SnO_2 (or SnO_2 @Sn- TiO_2) heterojunction that forms upon the addition of Sn. This in turn, increases the lifetime of the positive hole in the valence band which drives the oxidation reaction. High Sn doping content is slightly more active than lower Sn-doping TiO_2 . This is attributed to the surface shell of Sn- TiO_2 formed at higher Sn content which is more effective in As(III) oxidation than the surface shell of SnO_2 that forms at lower Sn content. It worth noting that the prepared TiO_2 contains high carbon content as presented in Table 5.1 which can decrease its photocatalytic activity.

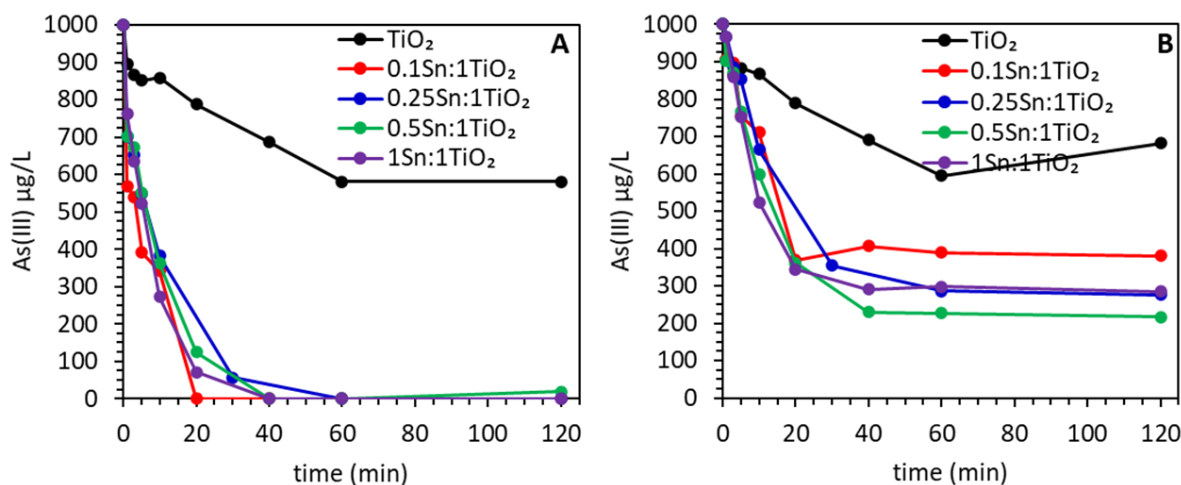


Figure 5. 19. A- PCO reaction using different TiO_2 and (0.1, 0.25, 0.5 and 1) Sn:1 TiO_2 . A- As(III) under UV reaction without adsorption correction $SD \pm 36$ ($SD\% = 3.6\%$) [based on a duplicate experiment], B- As(III) concentrations after adsorption correction (i.e., remaining As(III) in dark - remaining As(III) under UV irradiation); $SD \pm 23$ ($SD\% = 2.3\%$) [based on a duplicate experiment]. [Reaction conditions; 1000 $\mu\text{g/L}$ As(III), 0.1 g catalyst/L, pH 7.4].

5.3.2.2 Electron-hole separation as controlling factor in As(III) PCO

The development of n-n heterojunction in the Sn-doped TiO_2 [225] assists the electron-hole separation as shown in Figure 5.20 and eqn. 5.3 & eqn. 5.4. Since the VB of TiO_2 is energetically placed between the VB and CB of SnO_2 , and the Fermi level of TiO_2 is higher than that of SnO_2 the transfer of electrons from the CB of Sn-TiO₂ to the CB of SnO_2 is energetically favourable (*i.e.*, the CB of SnO_2 serves as a sink for the photogenerated electrons and therefore SnO_2 acts as a conductor of the conductance electrons). This creates an electron depletion layer in TiO_2 and an electron accumulation layer in SnO_2 which enhances electron transfer at the heterojunction interface between Sn-TiO₂ and SnO_2 . Therefore, the electron-hole recombination is hindered by this spatial separation of charge that increases their lifetime, and therefore, increases the likelihood of driving surface redox reactions that drive the oxidation of As(III) [94,177]. The main reaction pathways of the PCO of As(III) over Sn-doped TiO_2 are shown in Figure 5.21.

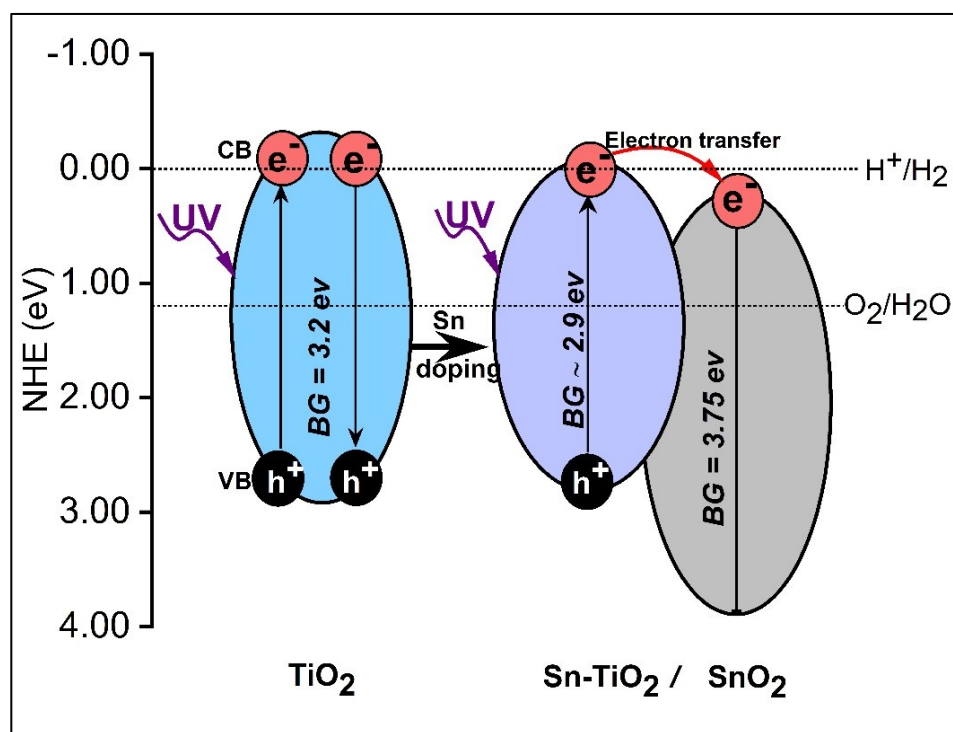
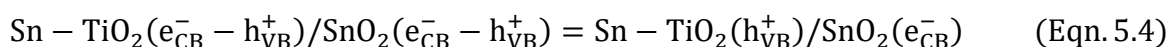
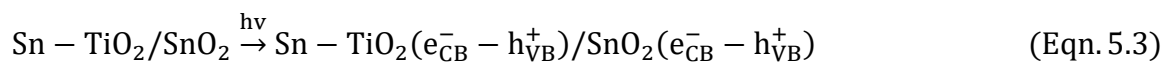


Figure 5. 20. Schematic diagram illustrating the effect of TiO_2 doping with Sn on the bandgap and charge separation.

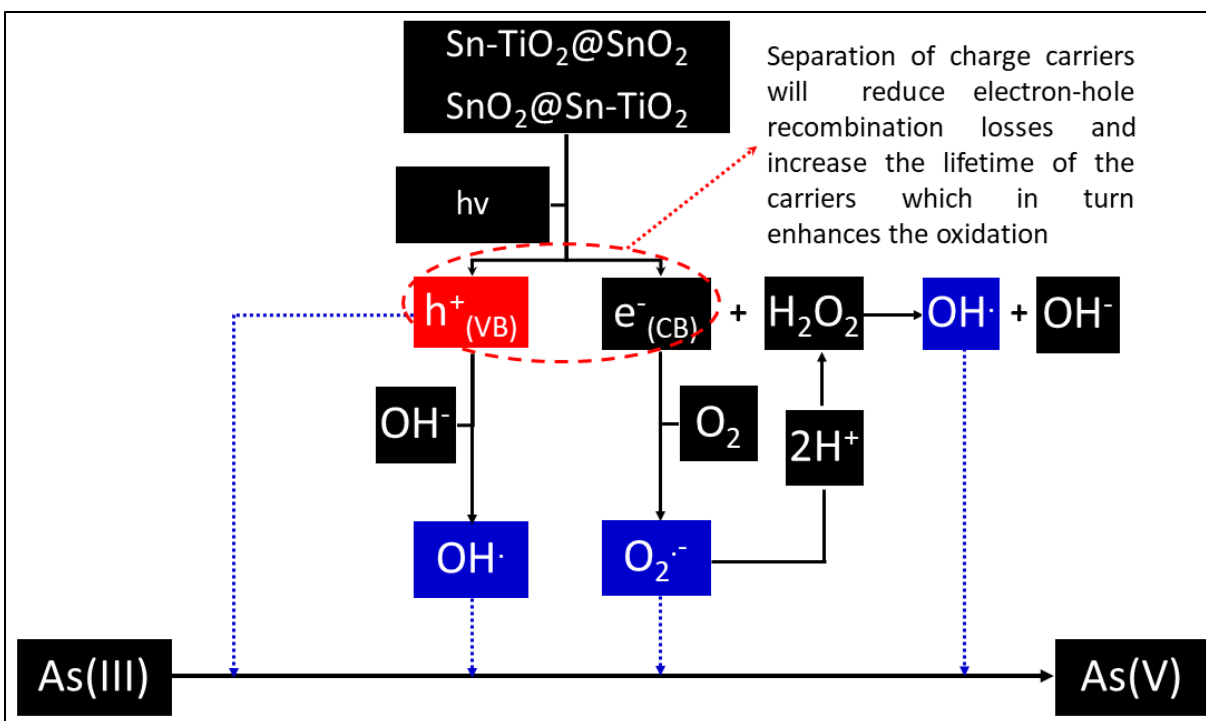


Figure 5. 21. Main reaction pathways of the PCO of As(III) over Sn-doped TiO₂ "Reactions are adapted from López-Muñoz et al [70].

5.3.2.3 Monitoring the surface adsorbed As(III) and As(V) using XPS throughout the PCO reaction

Under the experimental conditions used in this study (1 mg/L initial As(III), to represent natural contaminant levels), and 0.01 g/100 mL 1Sn:1TiO₂ [*i.e.* Sn-TiO₂@SnO₂]), a significant fraction of total arsenic is adsorbed). To gain a better understanding of the overall As(III) oxidation rate the surface-sensitive technique XPS was used to monitor changes in the oxidation state of adsorbed arsenic with time.

Under dark conditions, only As(III) was detected on the surface at ~1326.6 eV, [157,226] as shown in Figure 5.22A, while under UV irradiation both adsorbed As(III) and As(V) species were detected on the surface at ~1326.6 eV and 1327.9 eV respectively [157,226] (Figure 5.22B). The findings show that under UV irradiation, the fraction of the surface adsorbed As(V) formed 41.3% of the adsorbed amount after 1 min and continued to increase to 81.2% after 2 h. The reverse was true for the surface adsorbed As(III) which declined with time from 58.67% after 1 min to 18.8% after 2 h (Figure 5.23). These results suggest that the surface of the 1Sn:1TiO₂ has more preference towards As(V) adsorption than As(III). The decline of the surface adsorbed As(III) fraction on the

surface over time maybe due to one of the following mechanisms: 1) the surface adsorbed As(III) is displaced by the adsorption of As(V) from the solution with time due to the higher affinity of As(V) to be adsorbed, 2) some surface As(III) is desorbed into the solution, then oxidised and re-adsorbed as As(V) or 3) surface As(III) was oxidised on the surface to As(V) without being desorbed into the solution.

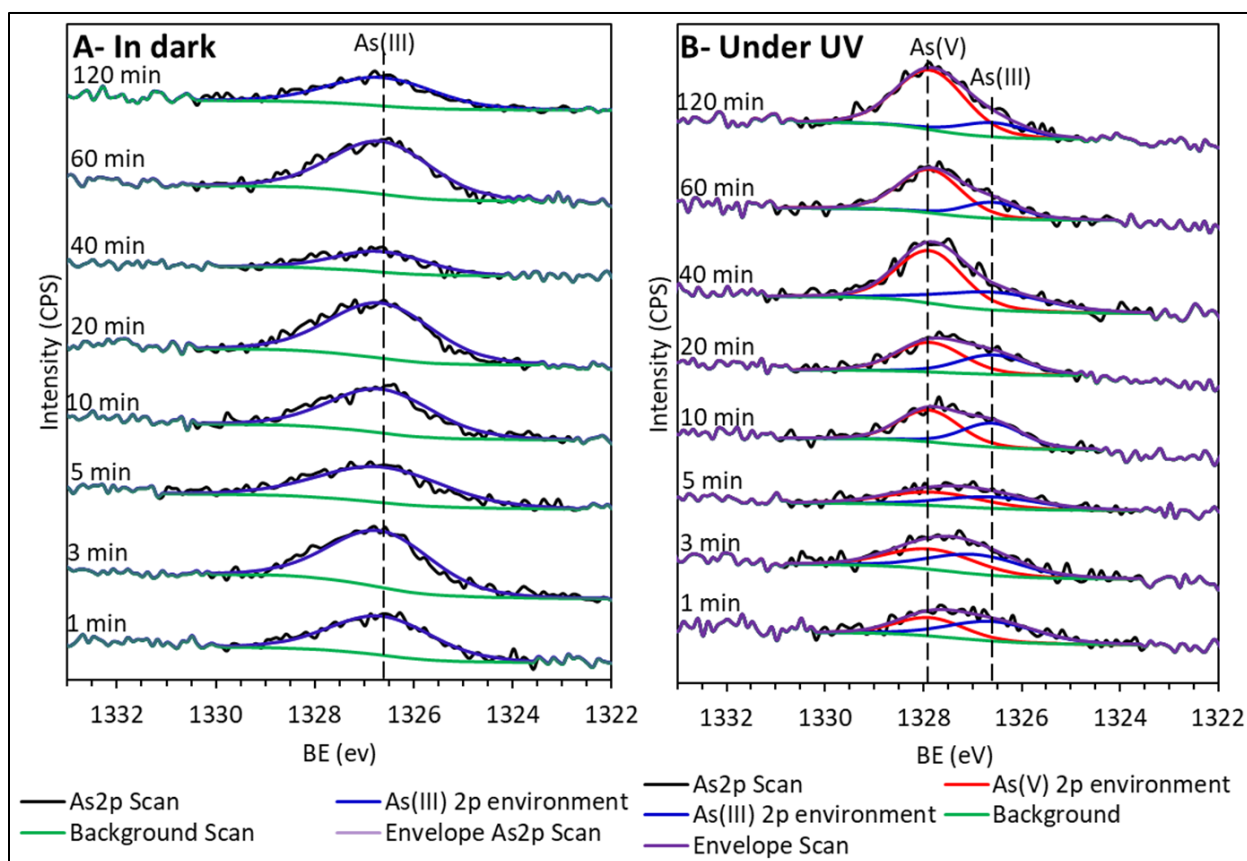


Figure 5. 22. XPS peak deconvolution of As₂p binding energy environment showing A- the adsorbed arsenic species in dark conditions, B- the adsorbed arsenic species under UV irradiation. The PCO experiment was performed using 0.1 g/L of 1Sn:1TiO₂ with 1000 µg/L As(III) at pH 7.4.

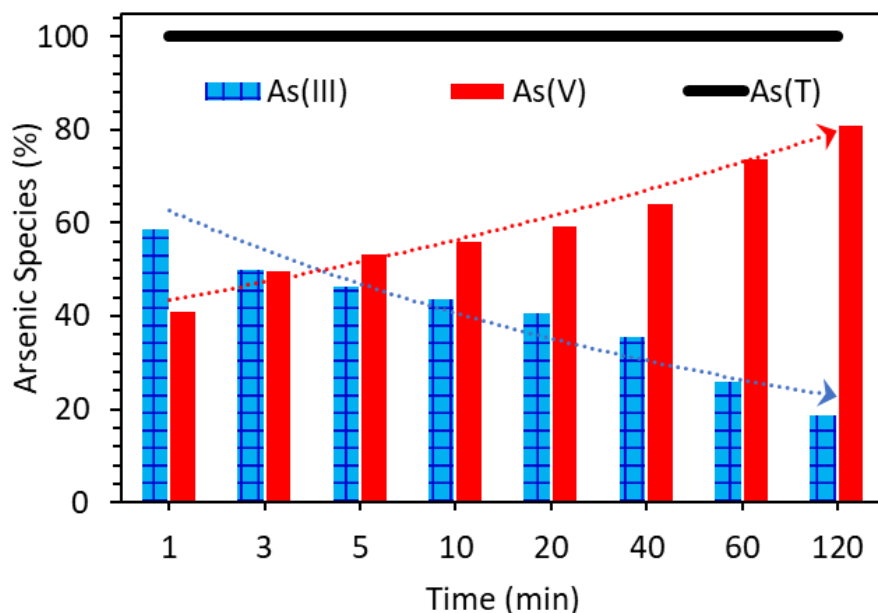


Figure 5. 23. The adsorbed percentages of different arsenic species relative to the total adsorbed amount at each time interval for 1Sn:1TiO₂. Percentages of arsenic species were measured using XPS and environment was modelled using CASAXPS software. The PCO experiment was performed under UV irradiation using 0.1 g/L (1Sn:1TiO₂) at pH 7.4.

5.3.2.4 Accurate determination of PCO reaction rates

The accurate determination of the PCO reaction rate is a challenge, due to the masking of aqueous As(III) and As(V) by their adsorption to the photocatalyst. This makes both aqueous As(III) and As(V) concentrations inaccurate indicators of the PCO yield [227]. To this end, for the accurate calculations, both aqueous and surface adsorbed As(V) were considered measured using the molybdenum blue UV/Vis method and XPS respectively (Table 5.3). The reaction rate was calculated based on the solution [As(V)], total produced [As(V)] “i.e. solution [As(V)] + surface [As(V)]” and the decline in the solution [As(III)] “i.e. [As(III)] in dark – [As(III)] under UV”. The first order kinetic model best fit the data as shown in Figure 5.24. The values of the calculated reaction rate (k) using 1Sn:1TiO₂ doping were 0.027 ± 0.003 , 0.055 ± 0.002 and $0.055 \pm 0.003 \text{ min}^{-1}$ based on solution [As(V)], total [As(V)]_[aq+surf] and the decline in solution [As(III)] respectively. These results highlight that the reaction rate is underestimated by nearly 50% when considering aqueous As(V) only and ignoring surface adsorbed As(V). Both reaction rate calculation based on [As(V)]_[aq+surf] and the decline in [As(III)] gave the same reaction rate, suggesting that these methods were accurate and cross-validate each other. Finally, calculation of the reaction rates

(based on the difference between the remaining [As(III)] in the dark and under UV) showed that using 1Sn:TiO₂ ($0.055 \pm 0.003 \text{ min}^{-1}$) was 7 times faster than the unmodified TiO₂ ($0.0075 \pm 6 \times 10^{-4} \text{ min}^{-1}$).

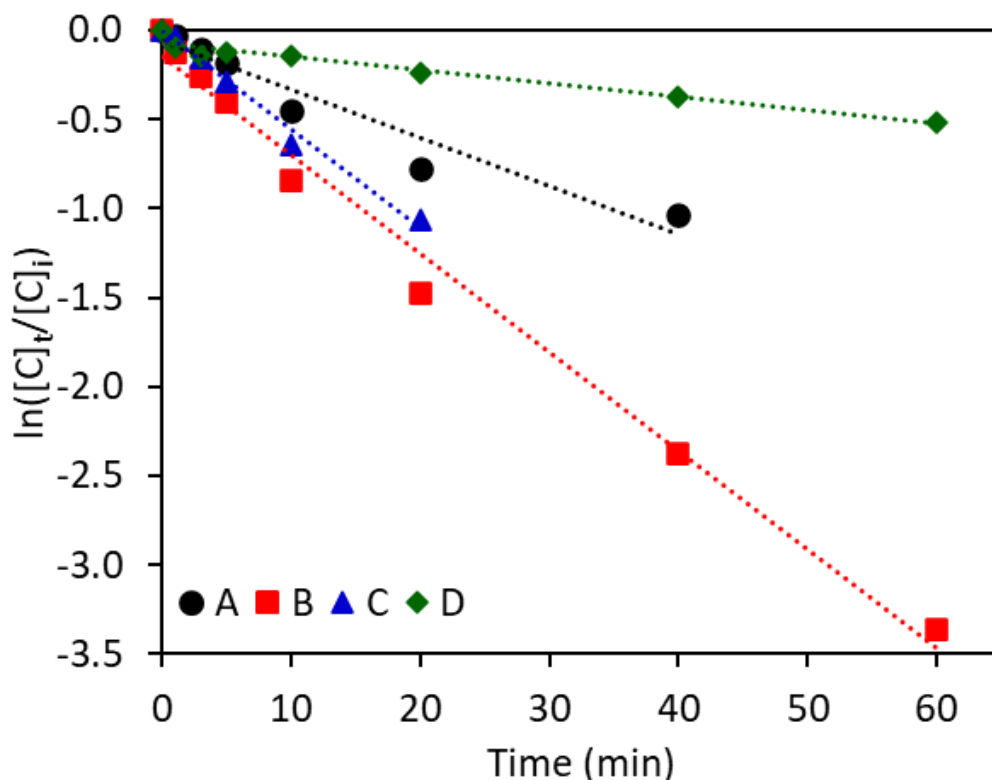


Figure 5. 24. First order kinetic plot of the PCO under UV irradiation based on concentration of solution As(V), total As(V) concentration. The PCO experiment was performed under UV irradiation using 0.1 g/L of 1Sn:1TiO₂ (or TiO₂) with 1000 µg/L As(III) at pH 7.4. A - PCO using 1Sn:1TiO₂, k is calculated based on [As(V)] generated in the solution, $y = (-0.0269 \pm 0.003)x - (0.0643 \pm 0.06)$, $R^2 = 0.930$. B - PCO using 1Sn:1TiO₂, k is calculated based on total [As(V)] (i.e. $[As(V)]_{\text{Surface}} + [As(V)]_{\text{Solution}}$), $y = (-0.0553 \pm 0.003)x - (0.144 \pm 0.064)$, $R^2 = 0.989$. C - PCO using 1Sn:1TiO₂, k is calculated based on the decline in solution As(III) (i.e. $[As(III)]_{\text{in dark}} - As(III)_{\text{under UV}}$), $y = (-0.055 \pm 0.0031)x - (0.0057 \pm 0.03)$, $R^2 = 0.988$. D - PCO using TiO₂, k is calculated based on the decline in solution As(III) (i.e. $[As(III)]_{\text{in dark}} - As(III)_{\text{under UV}}$), $y = (-0.007 \pm 0.0006)x - (0.0749 \pm 0.017)$, $R^2 = 0.956$.

Table 5. 3: Distribution of arsenic species in the solution and on the surface of 1Sn:1TiO₂ based on XPS analysis.

Time (min)	Fractions of Surface As species determined by XPS		Total adsorbed arsenic As(T) under UV	^a Surface adsorbed As(V) mg/L	^b Solution As(V) mg/L	^c Total As(V) yield	^d Decline in solution As(III)
	Surface As(III) %	Surface As(V) %					
0	0	0	0.00	0.00	0.00	0.00	1000.00
1	58.67	41.33	207.26	85.66	31.42	117.08	966.48
3	49.99	50.01	268.33	134.19	95.73	229.92	858.59
5	46.41	53.59	311.39	166.88	166.46	333.33	753.23
10	43.65	56.35	363.04	204.57	364.51	569.08	524.73
20	40.5	59.5	388.58	231.20	540.57	771.77	344.83
40	35.54	64.46	409.84	264.18	642.73	906.91	291.45
60	26.02	73.98	420.92	311.39	653.76	965.15	298.24
120	18.80	81.20	424.21	344.46	637.26	981.72	285.70

^a Surface adsorbed [As(V)] mg/L = surface adsorbed [As(V)] % / 100 * Total adsorbed Arsenic [As(T)].

^b Solution [As(V)] mg/L as measured by UV/Vis

^c Total [As(V)] yield = Surface [As(V)] + Solution [As(V)]

^d Decline in [As(III)] = [As(III)] in dark – [As(III)] under UV

5.3.2.5 Effect of Sn doping and PCO on arsenic adsorption

As previously mentioned, photocatalysis of As(III) is a preliminary step to enhance the adsorption of arsenic. In this part of the study, the adsorption efficiency of unmodified TiO₂ is compared to that of 1Sn:1TiO₂ (i.e. Sn-TiO₂:SnO₂). The amount of adsorption is calculated using eqn. 5.5.

$$\text{Adsorbed fraction} = [\text{As(Total)at initial time}] - [\text{As(Total)at time(t)}] \quad (\text{Eqn. 5.5})$$

The calculated results exhibited in Figure 5.25 show that Sn doping improves the adsorption efficiency. In the dark experiment, (1Sn:1TiO₂) shows 18.6 % more adsorption than unmodified TiO₂, which can be attributed to the higher adsorption affinity of SnO₂ compared to that of TiO₂. Also, under UV irradiation, 1Sn:1TiO₂ shows 32.5 % more adsorption than unmodified TiO₂, and 13.9% more adsorption than when examined in the dark. The enhanced adsorption under UV irradiation is due to the oxidation of As(III) to As(V), which can be more readily adsorbed.

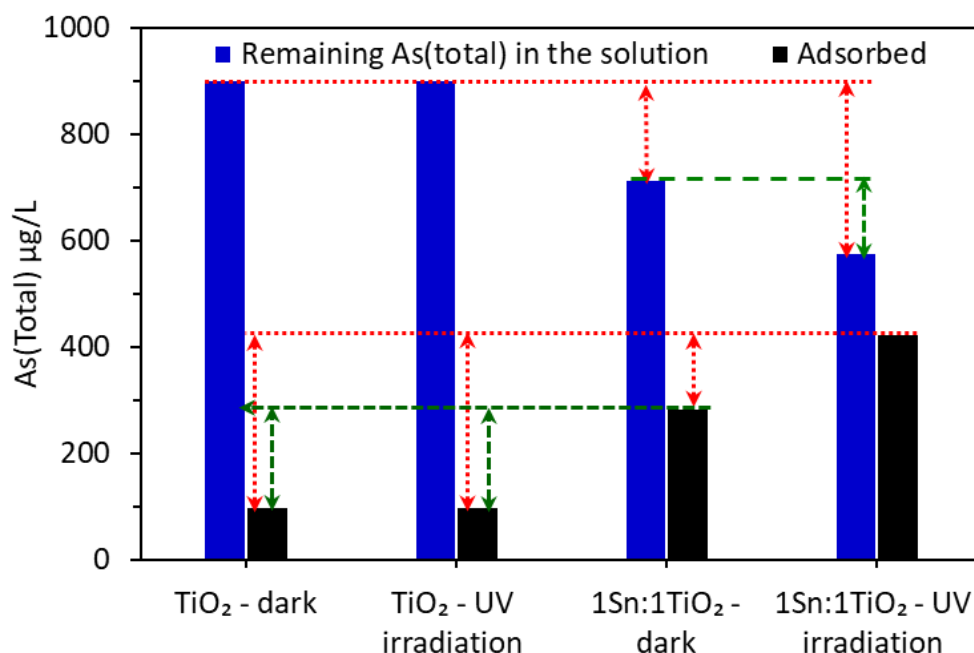


Figure 5. 25. Effect of Sn doping on the adsorbed fraction of As(III) at equilibrium (2 h). [the results based on a duplicate experiment with average SD ± 40.3 (4%)]. [Reaction conditions; 1000 $\mu\text{g/L}$ As(III), 0.1 g catalyst/L, pH 7.4].

5.3.2.6 PCO using thermal diffusion (TD) synthesised Sn-doped TiO₂

TiO₂ was doped using different molar ratios of Sn through thermal diffusion (TD) synthesis. A full characterisation of TD synthesis is presented in Appendix 9.4.

The PCO results of 10mg/L As(III) are presented in Appendix 9.5. The results indicate that TD doping was not effective to improve the PCO oxidation of anatase TiO₂, all TD synthesised samples give ~ 3.5 % oxidation which is very low compared to the SG synthesised 1S:1TiO₂ (82.9 % oxidation) and even anatase TiO₂ (24.7%). Therefore, TD prepared TiO₂ photocatalysts were not considered for further PCO experiments.

5.4 Conclusion

Herein, the effect of different Sn:Ti doping ratios on the formation of Sn-TiO₂ photocatalysts is studied and thoroughly the Sn and Ti oxide heterostructures that form is characterized. Then the application of the photocatalysts for the photocatalytic oxidation (PCO) of As(III) is explored. The concentration of Sn added during synthesis influences the structure and composition of the material formed. Characterisation using XRD, Raman, XPS, LEIS, EDX, HR-TEM, S-TEM, SEM and FTIR shows that at low Sn-doping levels (*i.e.* Sn:Ti = 0.1) SnO₂ forms the shell and TiO₂ forms the

core of the bicomposite catalyst (*i.e.* $\text{SnO}_2@\text{Sn-TiO}_2$ forms), whereas at high Sn-doping levels (*e.g.* Sn:Ti = 1) Sn-TiO_2 forms the shell and SnO_2 forms the core of the bicomposite catalyst (*i.e.* $\text{Sn-TiO}_2@\text{SnO}_2$ forms). Sn-doping reduced the bandgap and decreased the conduction band energy, improving electron-hole separation. The Sn and Ti oxide heterostructure photocatalysts provided ~30 – 46% higher oxidation yield than pure TiO_2 . Moreover, the PCO kinetic rate (k) was accurately determined by tracking the amount of arsenic species [As(III) and As(V)] at the surface and in solution. Determining k values based solely on aqueous As(V) underestimates the photocatalysis yield by ~50% because this neglects the surface adsorbed As(V). In contrast, determining k based on total $\text{As(V)}_{[\text{sol}+\text{surf}]}$ or the decline in aqueous As(III) give similar values, and therefore this rate is deemed more accurate. In addition to the PCO enhancement, the bicomposite photocatalyst with high levels of Sn-doping (Sn:Ti = 1; *i.e.* $\text{Sn-TiO}_2@\text{SnO}_2$) improves the total arsenic adsorption by 32.5 % compared to unmodified TiO_2 .

6 Photochemical processes and experimental parameters controlling the photocatalytic oxidation of As(III) over 1Sn:1TiO₂

6.1 Introduction

In the previous chapter I discussed the synthesis and characterisation of Sn doped TiO₂. In this chapter I will discuss the photophysics, photochemical mechanism and experimental parameters affecting and controlling the photocatalytic oxidation (PCO) of arsenite As(III) over Sn doped TiO₂.

The enhanced efficiency of light driven photocatalysis measured with core/shell materials has been ascribed to slow charge recombination rate [228]. Inorganic bicomposite photocatalysts such as 1Sn:1TiO₂ are understood to possess a heterojunction with improved photoinduced charge separation. Tracking the charge transfer kinetics and recombination rates at the heterojunction is vital to guide the development of future materials and its impact on photocatalytic efficiency. Transient absorption spectroscopy (TAS) is well established/recognised technique to track the migration of trapped photogenerated charges in sub microsecond time scales [229].

As(III) oxidation mechanism occurs via the transient species As(IV) which is readily oxidized by dissolved oxygen at rate constant of $1.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [230]. The mechanism of the PCO of As(III) has been studied in great detail for the TiO₂/UV system but the identification of the oxidant responsible for the rate limiting-step (i.e. As(III) $\rightarrow$ As(IV)) remains a controversial issue since no agreement has been attained over the exact identity of the major oxidant species, i.e. HO[•], HO₂[•]/O₂^{•-} radicals or h⁺_{VB} [70,231]. The possible effect/impact of the Sn dopant on the main oxidant remains also unknown and should be explored.

Experimental conditions have a strong control on oxidation yield and the quantum efficiency of the As(III) oxidation. This includes the distance between light source and solution surface, pH, initial concentration of arsenic, catalyst and the salinity of the water.

For the successful development of arsenic treatment plants, the oxidation mechanisms and the parameters controlling the PCO need to be understood as this controls the engineering process.

6.2 Aims and objectives

The aim of this chapter is to identify mechanisms and experimental parameters that control the PCO of As(III) over Sn doped TiO₂. The observative are to (i) identify the PCO mechanism of As(III) over 1Sn:1TiO₂, this includes TAS studies to identify of the effect of Sn doping on the charge carriers lifetime and recombination rates within the heterojunctions in the Sn-doped TiO₂. In addition to the investigation of the main oxidant during the oxidation process, (ii) study the control of experimental parameters including distance between the light source and the solution surface, salinity, pH, the photocatalyst mass to solution ratio and the As(III) concentration.

6.3 Results and discussion

6.3.1 Photochemical processes during the PCO of As(III)

The first part of this study deals with the mechanism of the photocatalytic oxidation of As(III) over 1Sn:1TiO₂ through tracking the lifetimes of the charge carriers using transient absorption spectroscopy (TAS) and the identification of main oxidant during the oxidation process.

6.3.1.1 Charge carrier's lifetime

Transient absorption spectroscopy (TAS) is a flash photolysis measurement used to monitor the transient behaviour of charge carriers in semiconductor photocatalysts [232]. TAS experimental setup is described in chapter 3, section 3.9. The measurement begins with a short ultra-bandgap pulse of energy (typically from a laser) which results in the formation of charge carriers. As these charge carriers absorb in the UV-visible-NIR, their dynamics can be followed by tracking changes in absorption in this region of the electromagnetic spectrum. TAS is used to study a wide range of metal oxide semiconductor photocatalysts. During the study of anatase TiO₂ nanopowders, a broad absorption spectrum in the visible is typically observed on the microsecond timescale after excitation [233], with recombination that follows power law decay kinetics with a half time of several milliseconds. The use of chemical scavengers during TAS measurements can reveal the regions of the transient absorption where electron and hole carriers primarily absorb, where in anatase TiO₂, electrons absorb most strongly at ~800 nm and holes absorb most strongly at ~ 500 nm [107]. To our knowledge, SnO₂ nanopowders have not previously been studied. Figures 6.1

A, 6.2 A, 6.3 A and 6.4 A show the results of the TAS measurements of the dry powders of SnO₂ and when suspended in various scavenger solutions.

The TAS experiments of powder samples only are shown in Figure 6.1. In the absence of any chemical substrates with which the photocatalyst can react, TAS monitors the intrinsic electron-hole recombination behaviour in these materials. For the SnO₂ sample, almost negligible transient absorption signals are observed, with only a slight bleach observed at 550 nm (*i.e.* a negative transient absorption signal, which arises when there is a loss in the ground state absorption). This bleach signal is attributed to shallow intra-bandgap defect states in SnO₂ (*e.g.* oxygen vacancy states), which trap photogenerated charge carriers up to the ~100 μ s. For anatase TiO₂, the typical transient absorption and recombination behaviour is observed, *i.e.*, a broad absorption seen across the visible and a recombination half-time of ~0.5 ms. For 1Sn:1TiO₂, similar transient absorption spectrum and recombination dynamics are observed. However, the initial transient absorption signal is ~ 2 times higher than that of anatase TiO₂, which demonstrated that early timescale (pre- μ s) electron-hole recombination is suppressed in the composite system and is evidence of enhanced spatial separation of charge carriers in this system. This suppression in the electron-hole recombination is due to one of the following reasons which have been proposed in the literature (i) (1) TiO₂ passivates the sites that enhance recombination on SnO₂, (2) the redox gradient due to lowering the conduction band causes a barrier that prevents the electrons in the core (SnO₂) to reach oxidized species at the shell, (iii) trapping the electrons in an electronic state between the core and the shell [228].

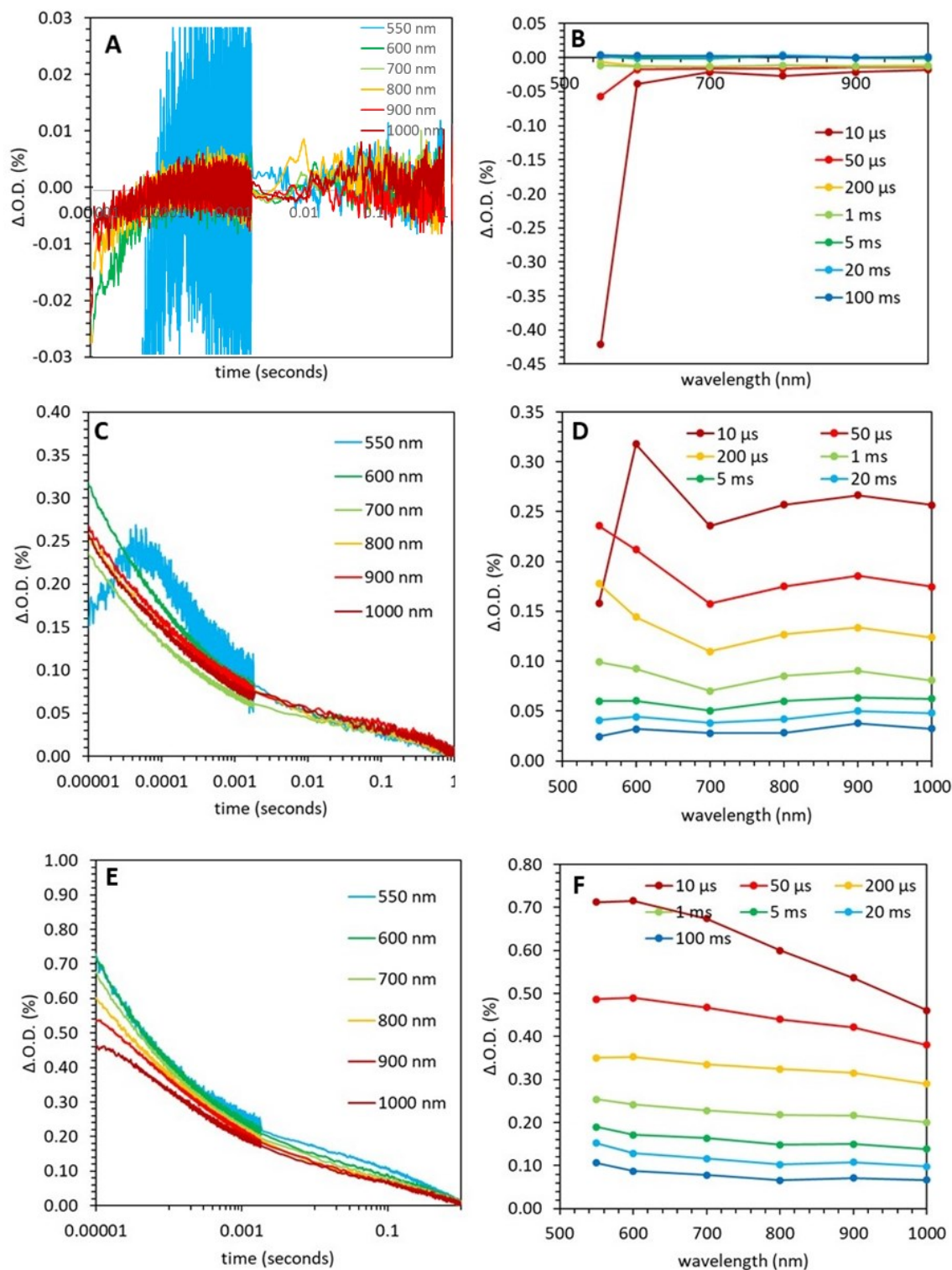


Figure 6. 1. Transient absorption spectroscopy of dry powders. The operating conditions were $\lambda_{exc} = 355 \text{ nm}$, $\sim 1.0 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 6 ns pulse width, laser repetition rate $\sim 1 \text{ Hz}$. Shown are changes in adsorption vs time for SnO_2 (A), TiO_2 (C) and $1\text{Sn}:1\text{TiO}_2$ (E) and changes in adsorption vs wavelength at select times for SnO_2 (B), TiO_2 (D) and $1\text{Sn}:1\text{TiO}_2$ (F).

TAS experiments of powders suspensions of in solutions with AgNO_3 (electron scavenger) are shown in Figure 6.2, it worth noting that the solution turns darker here due to Ag precipitation which perturbs the system. High signal to noise ratios is observed in these experiments due to the tendency of catalyst particles to settle during the measurements. For SnO_2 , no significant changes are observed for the transient decay dynamics, indicating a poor reaction of photogenerated electrons with AgNO_3 (*i.e.* no prolonged signal due to longer lived hole carriers was observed). In both our anatase TiO_2 and 1Sn:1 TiO_2 samples, similar yet marginal electron scavenging behaviour is observed, prolonging transient decay signals to the ~ 1 ms timescale. Compared to previous studies of more nanoparticulate TiO_2 , the increase in hole carrier lifetime is substantially lower, as lifetimes of up to ~ 1 s have previously been found [229]. Moreover, a minimal change in the transient absorption spectra is observed in these samples, which is indicative of a low quantum efficiency of this scavenging reaction in comparison to electron-hole recombination.

TAS experiments of powders suspensions with methanol (hole scavenger) are shown in Figure 6.3. SnO_2 shows no significant changes in the transient decay dynamics, indicating a poor reaction of photogenerated holes with methanol (*i.e.* no prolonged signal due to longer lived electron carriers is observed). A similar hole scavenging effect is observed in anatase TiO_2 , with transient decays showing halftimes of ~ 1 ms decays prolonged until ~ 10 ms. In contrast to observations with nanoparticulate TiO_2 , where lifetimes of up to ~ 1 s have previously been found [232], this increase in electron carrier lifetime is significantly lower. This results in minimal changes in the transient absorption spectra compared with powder experiments.

TAS experiments of powders suspensions in the presence of 1 ppm of As(III) is shown in Figure 6.4. A blue solution forms when molybdate is bound to As(V). SnO_2 shows no significant changes in the transient decay dynamics, indicating a poor reaction of photogenerated charges with As (III) to form As (V) (*i.e.* no change in colour due to the formation of a blue coloured complex was observed). Anatase TiO_2 shows a similar transient absorption behaviour to that in presence of methanol, but with an increased absorption in the blue region. This indicates of a marginal scavenging effect (*i.e.* a marginal scavenging of charge carriers in TiO_2 by As (III)). 1Sn:1 TiO_2

displays large changes in both transient decay kinetics and transient absorption spectra, with halftimes in the region of ~ 100 ms and a stark increase in absorption at ~ 700 nm. This is a strong indication that molybdate is reacting with As(V) *in situ* during the reaction, giving rise to an increase in transient absorption in the red. Importantly, as this transient absorption peak is observed on the time resolution of this measurement (~ 10 μ s), this indicates that the oxidation of As(III) to As(V), and the subsequent formation of the molybdate complex is rapid, and occurs on the pre- μ s timescale.

It worth noting that in TAS experiments, the power is very intense over the ns (e.g., in this study $\sim 167 \times 10^6$ mW/cm²). This is always the case for flash photolysis. The charge carrier behaviour will differ with more ambient continuous wave (CW) irradiation then one can do measurements at a range of laser power. This would show the intensity dependence and give an indication if the charge carrier behaviour will change at more ambient light levels.

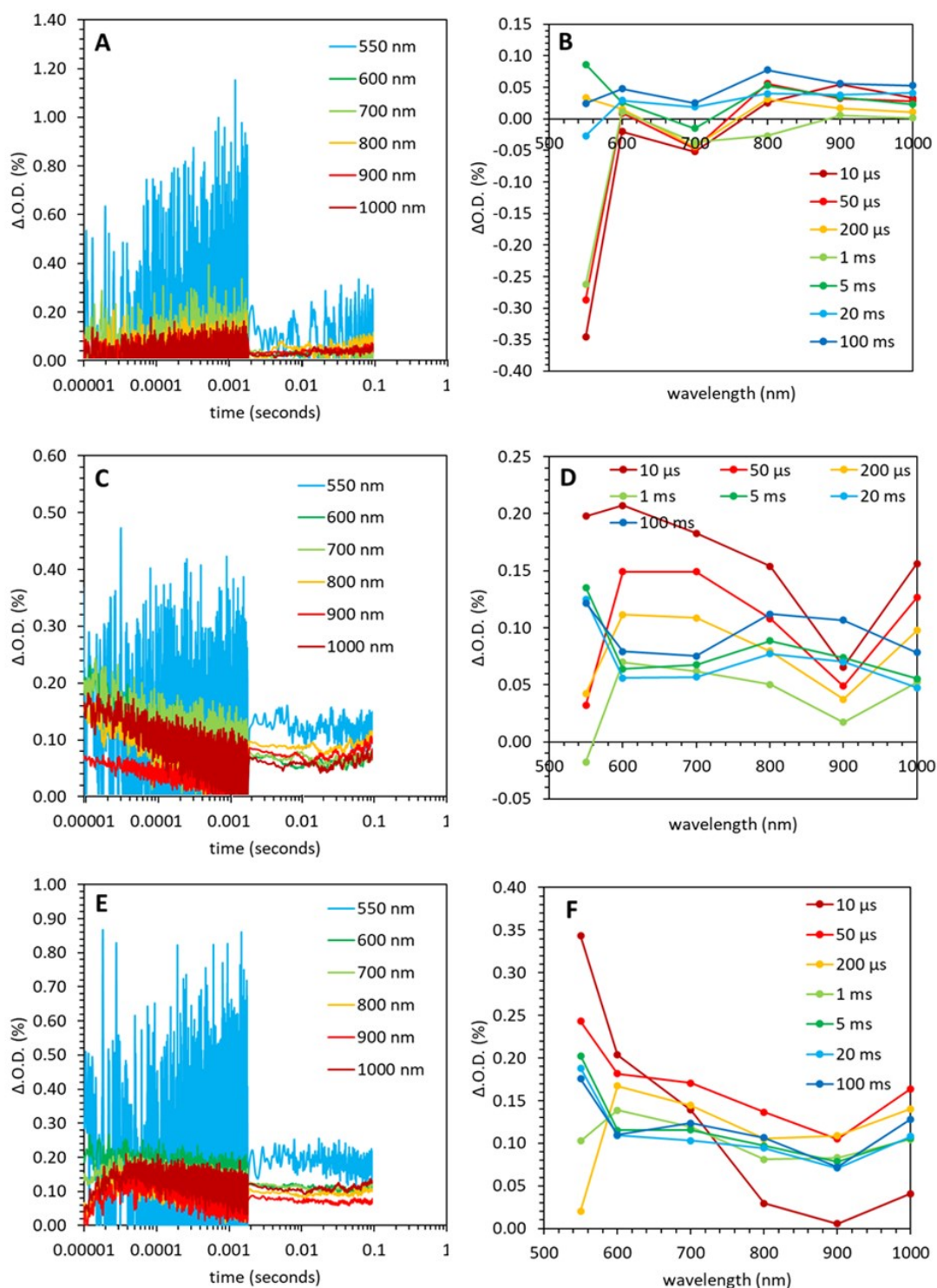


Figure 6. 2. Transient absorption spectroscopy of powders suspensions (1g/L) in an aqueous $AgNO_3$ electron scavenger solution (2 mM $AgNO_3$; pH 7.3 ± 0.1). The operating conditions were $\lambda_{exc} = 355$ nm, ~ 1.0 mJ cm $^{-2}$ pulse $^{-1}$, 6 ns pulse width, laser repetition rate ~ 1 Hz. Shown are changes in adsorption vs time for SnO_2 (A), TiO_2 (C) and $1Sn:1TiO_2$ (E) and changes in adsorption vs wavelength at select times for SnO_2 (B), TiO_2 (D) and $1Sn:1TiO_2$ (F).

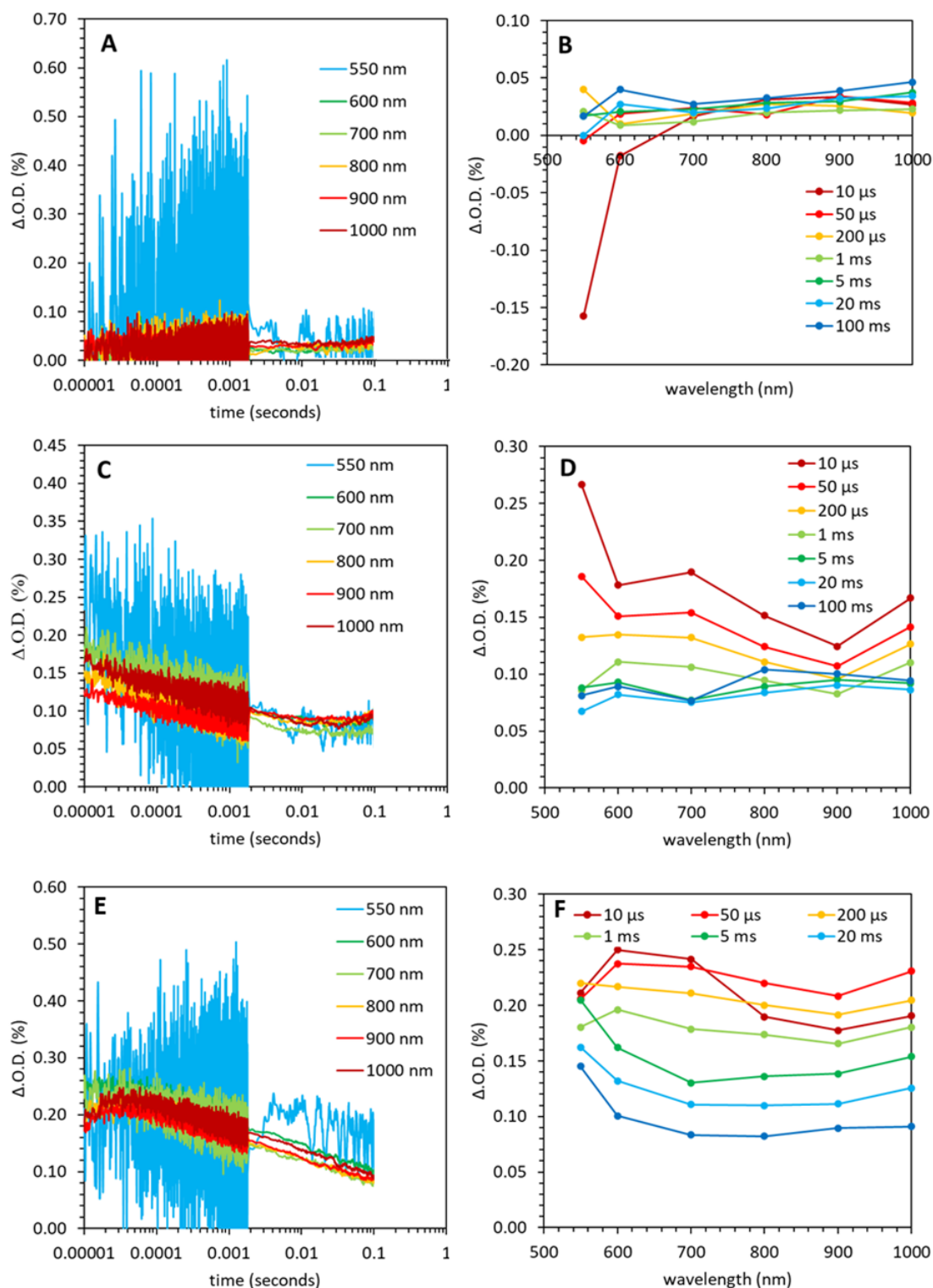


Figure 6. 3. Transient absorption spectroscopy of powders suspensions (1g/L) in pure methanol hole scavenger solution. The operating conditions were $\lambda_{exc} = 355 \text{ nm}$, $\sim 1.0 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 6 ns pulse width, laser repetition rate $\sim 1 \text{ Hz}$. Shown are changes in adsorption vs time for SnO_2 (A), TiO_2 (C) and $1\text{Sn}:1\text{TiO}_2$ (E) and changes in adsorption vs wavelength at select times for SnO_2 (B), TiO_2 (D) and $1\text{Sn}:1\text{TiO}_2$ (F).

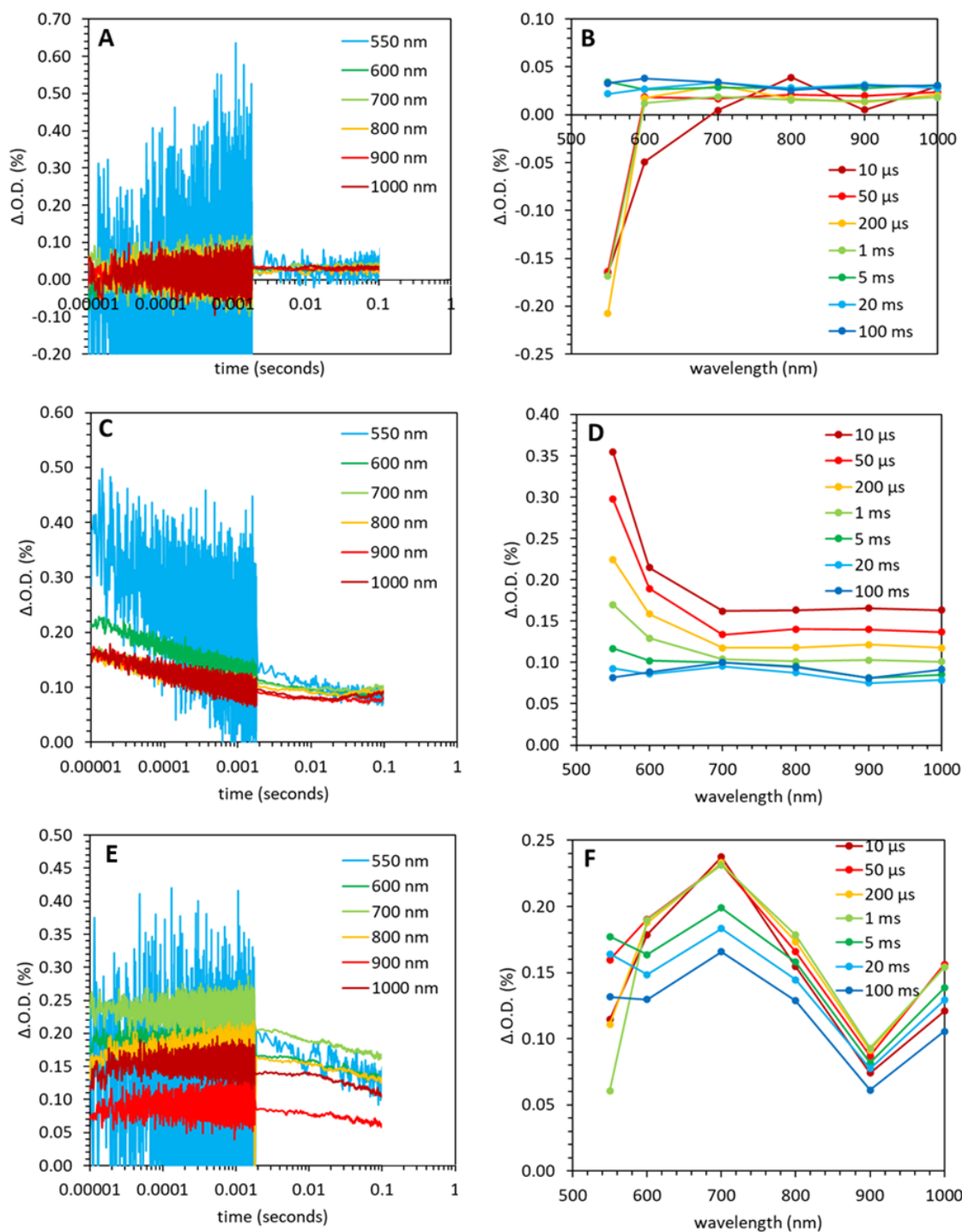


Figure 6. 4. Transient absorption spectroscopy of powders suspensions (1g/L) in an aqueous solution containing As (III) (1 ppm) and our molybdate complex that forms a blue coloured compound when bound to As (V). The operating conditions were $\lambda_{\text{exc}} = 355 \text{ nm}$, $\sim 1.0 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 6 ns pulse width, laser repetition rate $\sim 1 \text{ Hz}$. Shown are changes in adsorption vs time for SnO_2 (A), TiO_2 (C) and $1\text{Sn}:1\text{TiO}_2$ (E) and changes in adsorption vs wavelength at select times for SnO_2 (B), TiO_2 (D) and $1\text{Sn}:1\text{TiO}_2$ (F).

6.3.1.2 Identification of the main oxidant species during the PCO

Photocatalytic reactions are complex. The initial step of As(III) oxidation is the generation of oxidant species, such as h^+_{VB} , $HO^\bullet$, and $HO_2^\bullet/O_2^{\bullet-}$ as presented in Table 6.1 (eqn. 6.1 to eqn. 6.14). Typically, one reaction is rate-limiting of the photocatalytic oxidation process (i.e., As(III) $\rightarrow$ As(IV)) as presented in (eqn. 6.15 to eqn. 6.18).

To determine the main oxidant during the photooxidation, experiments are conducted in the presence of several scavengers including silver nitrate ($AgNO_3$) as electron scavenger (e^-_{CB}), ascorbic acid as hole scavenger (h^+_{VB}), and isopropanol, Rebamipide Anhydrous, DMSO, as hydroxyl radical ($HO^\bullet$) scavenger, SOD and P-benzoquinone as superoxide scavenger.

As shown in Figure 6.5 and table 6.1, in the control experiment without a scavenger, the efficiency of the PCO of As(III) to As(V) is 62% ($k = 0.008 \pm 1.9 \times 10^{-4} \text{ min}^{-1}$). Using $AgNO_3$ as an electron scavenger improves the oxidation rate by 85.2% ($k = 0.015 \pm 8.9 \times 10^{-4} \text{ min}^{-1}$). This enhanced oxidation rate is because $AgNO_3$ captures electrons and hinders the e^-h^+ recombination which eventually increases the lifetime of the positive hole in the valence band and thus more hydroxyl radical are generated [234], (eqn. 6.4). In addition, in 1Sn:1TiO₂, the CB edge is located at ca. 0.51 V (at pH 7), which gives CB electrons a mildly reducing control. In most PCO processes, molecular oxygen dissolved in water serves as an acceptor of CB electrons ($E_1(O_2/O_2^-) = 0.33 \text{ V}$). The presence of alternative electron acceptors such as Ag^+ may accelerate the photocatalytic processes even in the absence of O_2 [235]. $AgNO_3$ as electron scavenger also reduces the accumulation of the photogenerated electrons on the surfaces of the 1Sn:1TiO₂. Since electrons react preferentially with Ag^+ and precipitate, this stops the subsequent production of $HO_2^\bullet/O_2^{\bullet-}$ (see eqn. 6.7 & eqn. 6.8) [236], and therefore $AgNO_3$ inhibits As(III) photooxidation by $O_2^{\bullet-}$ (see eqn. 6.17 and eqn. 6.18). Although $AgNO_3$ inhibits the photooxidation of As(III) by the $O_2^\bullet$ pathway, the overall oxidation increases. This result implies that superoxide ($O_2^{\bullet-}$) is not the main oxidant during the PCO of As(III) over 1Sn:1TiO₂ while the hydroxyl radical ($HO^\bullet$) and the positive hole (h^+_{VB}) have a dominant role in the oxidation of As(III).

Ascorbic acid as a hole (h^+_{VB}) scavenger dramatically reduces the PCO efficiency of As(III) to 2.3% ($k = 0.0015 \pm 1.4 \times 10^{-4} \text{ min}^{-1}$, Figure 6.5). This result implies that the photooxidation process is

mostly driven by the valence holes (h^+_{VB}) and/or its subsequent reaction that forms hydroxyl radical $HO^\bullet$ (eqn. 6.4).

To explore the contribution of $HO^\bullet$ in the oxidation, isopropanol, Rebamipide anhydrous and DMSO were used as $HO^\bullet$ scavenger. The PCO efficiency is reduced to 21% ($k = 0.004 \pm 3.6 \times 10^{-4} \text{ min}^{-1}$), 30% ($k = 0.003 \pm 2.6 \times 10^{-4} \text{ min}^{-1}$) and 23% ($k = 0.003 \pm 2.9 \times 10^{-4}$) in case of Isopropanol, Rebamipide anhydrous and DMSO, respectively (Figure 6.5). The use of superoxide scavengers, SOD and p-benzoquinone reduced the oxidation yield to 35.25% ($k = 0.004 \pm 1.7 \times 10^{-4}$) and 48.93% ($k = 0.006 \pm 4.3 \times 10^{-4}$) respectively. This implies that the hydroxyl radical ($OH^\bullet$) scavengers suppress oxidation process more than the superoxide scavengers.

The results summarised in Table 6.2 conclude that in our system, hydroxyl radical ($HO^\bullet$) is the main oxidant followed by direct oxidation by the positive hole, this can be supported by the fact that the rate constant for the reaction of $HO^\bullet$ and valence hole with As(III) is around 3 times faster than its reaction with $O_2^{\cdot-}$ (see eqn. 15 to 6.17) [63]. Finally, there are some minor oxidation pathways through superoxide (eqn. 6.17 and 6.18), generated hydrogen peroxide (eqn. 6.19) and dissolved oxygen (eqn. 6.20 and 6.21).

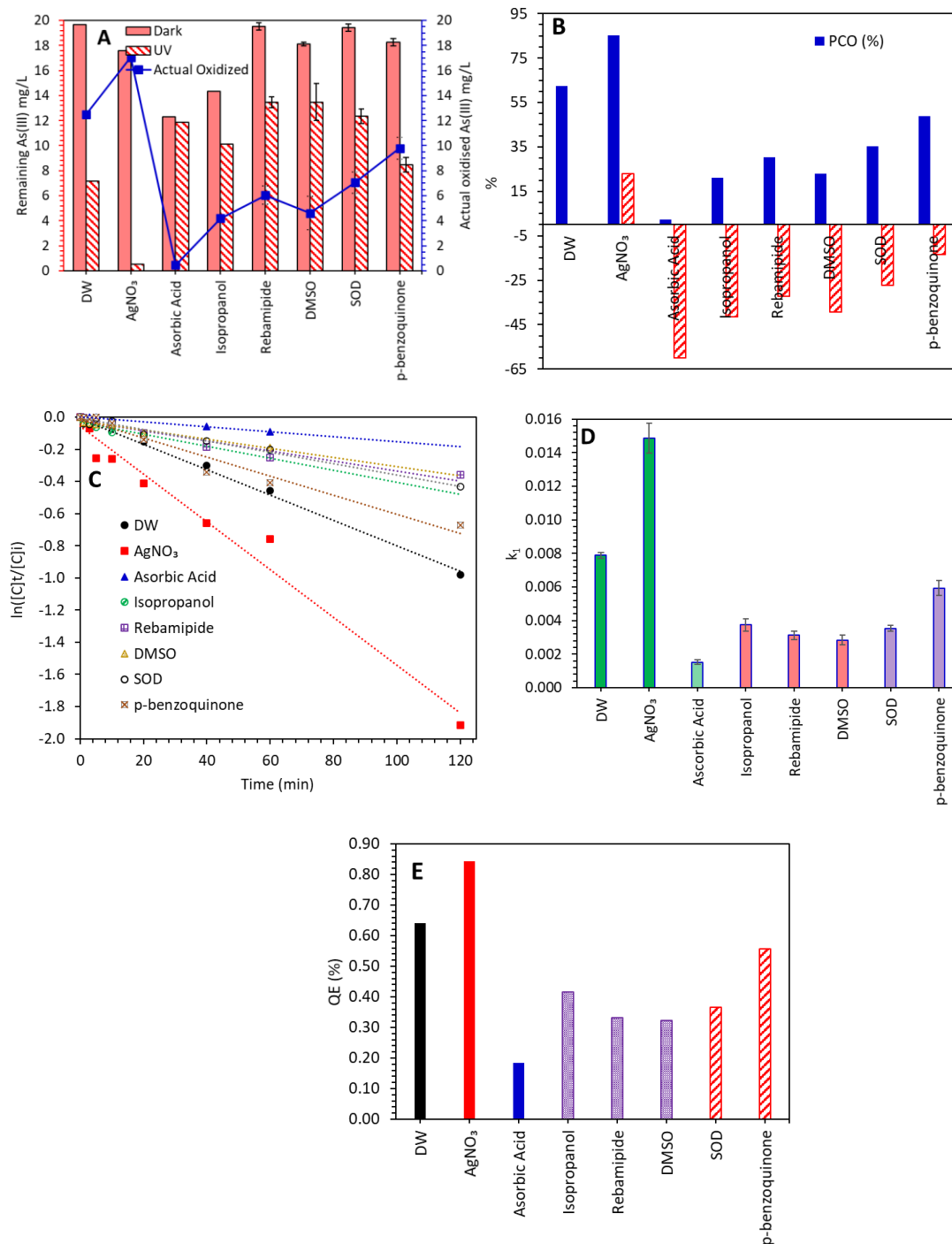


Figure 6. 5. Effect of scavengers on the PCO of As(III) in deionized water, in the presence of 2 mM AgNO₃ as electron (e^-_{CB}) scavenger, 2 mM ascorbic acid as hole scavenger, isopropanol, 67.4 μ M Rebamipide anhydrous and (10%, i.e 1.4M) DMSO as hydroxyl radical and (0.25 mM) SOD and (2mM) p-benzoquinone as superoxide (O_2^-) scavenger. [As(III) = 20 mg/L, 100 ml, pH 7.4, 0.01 g 1Sn:1TiO₂, t= 120 min]. A- Remaining As(III) under UV and in dark after 2 hrs , B- the change in the PCO percentage in presence of different scavengers, C- First order kinetic plot, D- First order kinetic rates ,E- Quantum efficiency (QE%) in presence of different scavengers.

Table 6. 1: Charge carriers generation and possible As(III) photooxidation pathways

Eqn.	Reaction	Rate (k)	Reference
<i>Charge Separation and generation of charge carriers</i>			
6.1	$\text{TiO}_2 \xrightarrow{h\nu} e_{\text{CB}}^- + h_{\text{VB}}^+$	$k = 10^{15} \text{ s}^{-1}$	[237]
6.2	$e_{\text{CB}}^- + h_{\text{VB}}^+ \rightarrow \text{heat (Charge recombination)}$		[238]
6.3	$\text{H}_2\text{O} + h_{\text{VB}}^+ \rightarrow \text{OH}^- + \text{H}^+$		[63]
6.4	$\text{OH}_{\text{ads}}^- + h_{\text{VB}}^+ \rightarrow \text{OH}^\cdot$		[238]
6.5	$\text{H}_2\text{O}_2 + \text{OH}^\cdot / h_{\text{VB}}^+ \rightarrow \text{HO}_2^\cdot + \text{H}_2\text{O}$		[239]
6.6	$\text{O}_2^- + e_{\text{CB}}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$		[239]
6.7	$\text{H}_2\text{O}_2 + e_{\text{CB}}^- \rightarrow \text{OH}^\cdot + \text{OH}^-$		[239]
6.8	$\text{O}_2 + e_{\text{CB}}^- \rightarrow \text{O}_2^-$	$k = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	[63]
6.9	$\text{O}_2^- + \text{H}^+ \leftrightarrow \text{HO}_2^-$		
6.10	$\text{HO}_2^- + \text{HO}_2^- \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2$		
6.11	$\text{O}_2^- + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$		
6.12	$\text{HO}_2^- + \text{O}_2^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2$		
6.13	$2\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[240]
6.14	$\text{H}_2\text{O}_2 + \text{OH}^\cdot \rightarrow \text{O}_2^- + \text{H}_2\text{O} + \text{H}^+$	$k = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	[241]
<i>Arsenite oxidation</i>			
<u>Hydroxyl radicals as an oxidant</u>			
6.15	$\text{As(III)} + \text{OH}^\cdot \rightarrow \text{As(IV)} + \text{OH}^-$	$k = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[63]
<u>Positive hole as an oxidant</u>			
6.16	$\text{As(III)} + h_{\text{VB}}^+ \rightarrow \text{As(IV)}$	$k = 8.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	[239,242]
<u>Superoxide as an oxidant</u>			
6.17	$\text{As(III)} + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{As(IV)} + \text{H}_2\text{O}_2$	$k = 3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	[239]
6.18	$\text{As(IV)} + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{As(V)} + \text{H}_2\text{O}_2$		
<u>Other possible oxidation reactions</u>			
6.19	$\text{As(III)} + \text{H}_2\text{O}_2 \rightarrow \text{As(V)} + 2\text{OH}^-$	$k = 15.3 \text{ M}^{-1} \text{ s}^{-1}$	[239,242]
6.20	$\text{As(III)} + \text{O}_2 \rightarrow \text{As(IV)} + \text{O}_2^-$		
6.21	$\text{As(IV)} + \text{O}_2 \rightarrow \text{As(V)} + \text{O}_2^-$	$k_5 = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[239]
<u>Possible surface processes</u>			
6.22	$2\text{As(IV)}_{\text{ads}} \rightarrow \text{As(III)}_{\text{ads}} + \text{As(V)}_{\text{ads}}$	$k = 8.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	[242]
6.23	$\text{As(III)}_{\text{ads}} \leftrightarrow \text{As(III)}_{\text{aq}}$		[243]
6.24	$\text{As(V)}_{\text{ads}} \leftrightarrow \text{As(V)}_{\text{aq}}$		[243]
<u>Possible reduction processes</u>			
6.25	$\text{As(IV)} + e_{\text{CB}}^- \rightarrow \text{As(III)}$	$k = 2.0 \times 10^8 \text{ s}^{-1}$	[239]

Table 6. 2: Effect of scavengers on the PCO of As(III)

	DW	ECB	HVB	OH ⁻ scavenger			O ₂ scavenger	
	non	AgNO ₃	Ascorbic Acid	Isopropanol	Rebamipide Anhydrous	DMSO	SOD	p-benzoquinone
Oxidation % (after 2 hrs)	62.4 3	85.25	2.33	21.01	30.25	23.10	35.25	48.93
Change in Oxidation %		36.55	-96.27	-66.35	-51.55	-63.00	-43.53	-21.62
k ₁	0.008	0.015	0.002	0.004	0.003	0.003	0.004	0.006
SE	1.9 x 10 ⁻⁴	8.9 x 10 ⁻⁴	1.4 x 10 ⁻⁴	3.6 x 10 ⁻⁴	2.6 x 10 ⁻⁴	2.9 x 10 ⁻⁴	1.7 x 10 ⁻⁴	4.3 x 10 ⁻⁴
QE*(%)	0.64	0.84	0.18	0.42	0.33	0.32	0.37	0.56
RSS	0.00	0.07	0.00	0.00	0.01	0.00	0.00	0.02
Pearson's r	-1.00	-0.99	-0.98	-0.97	-0.98	-0.97	-0.99	-0.98
R ²	1.00	0.97	0.95	0.94	0.95	0.94	0.98	0.96

* QE is the quantum efficiency.

6.3.2 Control of experimental parameters on PCO efficiency

In this part of the study, the control of experimental parameters including distance between the light source and the solution surface, salinity, pH, the photocatalyst mass to solution ratio and the As(III) concentration on the PCO efficiency are discussed

6.3.2.1 Effect of distance between the light source and the solution surface on the PCO efficiency

The distance between the light source and the solution surface is critical during the PCO as it has a strong influence on the light intensity and the photon flux arriving the solution. And therefore on quantum efficiency (QE%). First, the lamp power has been measured at different distances using Thorlabs GmbH power meter while using short light pass <400 nm based on the bandgap values. The lamp power was then converted to the photon flux and the QE(%) was calculated for different distances. Following this, the As(III) oxidation rates at optimum (QE) was determined. The results shown in Figure 6.6. indicate that the incident light intensity at the solution surface decreases from 7.40 to 0.59 mW.cm⁻² as the distance between the lamp and solution surface

increases from 1.8 to 22 cm. As a result, the photon flux arriving the solution surface decreases from 1.38×10^{16} (at 1.8 cm) to 1.10×10^{15} (at 22 cm) $\text{flux.cm}^{-2}.\text{s}^{-1}$.

At longer distances between the lamp and the solution surface, the oxidation yield and the PCO rate (k) decreases from $0.016 \pm 8.5 \times 10^{-4}$ (1.8 cm) to $0.0019 \pm 8.5 \times 10^{-4}$ at (22cm) decrease (Figure 6.7). At shorter distance there are excess photons which generate excess e^-h^+ pairs which generate high concentrations of radicals. However, this plenty of e^-h^+ pairs at shorter distances are the main reason for high oxidation rate, most of these e^-h^+ pairs undergo e^-h^+ recombination.

As the distance increases from 1.8 to 22 cm, the quantum efficiency (QE%) increases from 0.37 % (at 1.8 cm) to 1.07% (at 22 cm) as shown in Figure 6.7. The reason of the lower QE at shorter distances is stronger lamp power and hence excess of photons which generate excess of e^-h^+ pairs while the arsenite concentration remains constant which results in high e^-h^+ pairs to As(III) ratio. Therefore, most of e^-h^+ pairs undergo recombination without being consumed in the oxidation process, leading to the lower QE observed. In the other hand, at longer distance, less photons are arriving at the catalyst surface and generate thus less e^-h^+ pairs (i.e. low e^-h^+ pairs to As(III) ratio) therefore, most of positive holes are utilised in oxidation and the recombination loss becomes lesser.

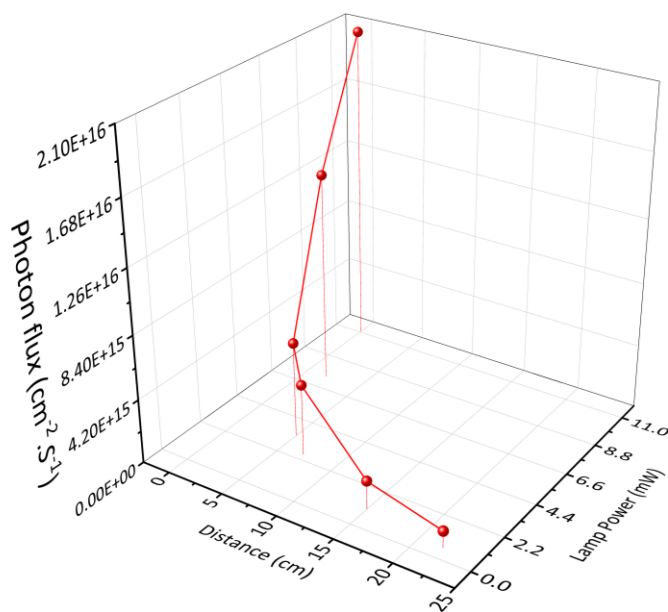


Figure 6. 6. Effect of distance between the lamp and the solution surface on the lamp power and the photon flux yield.

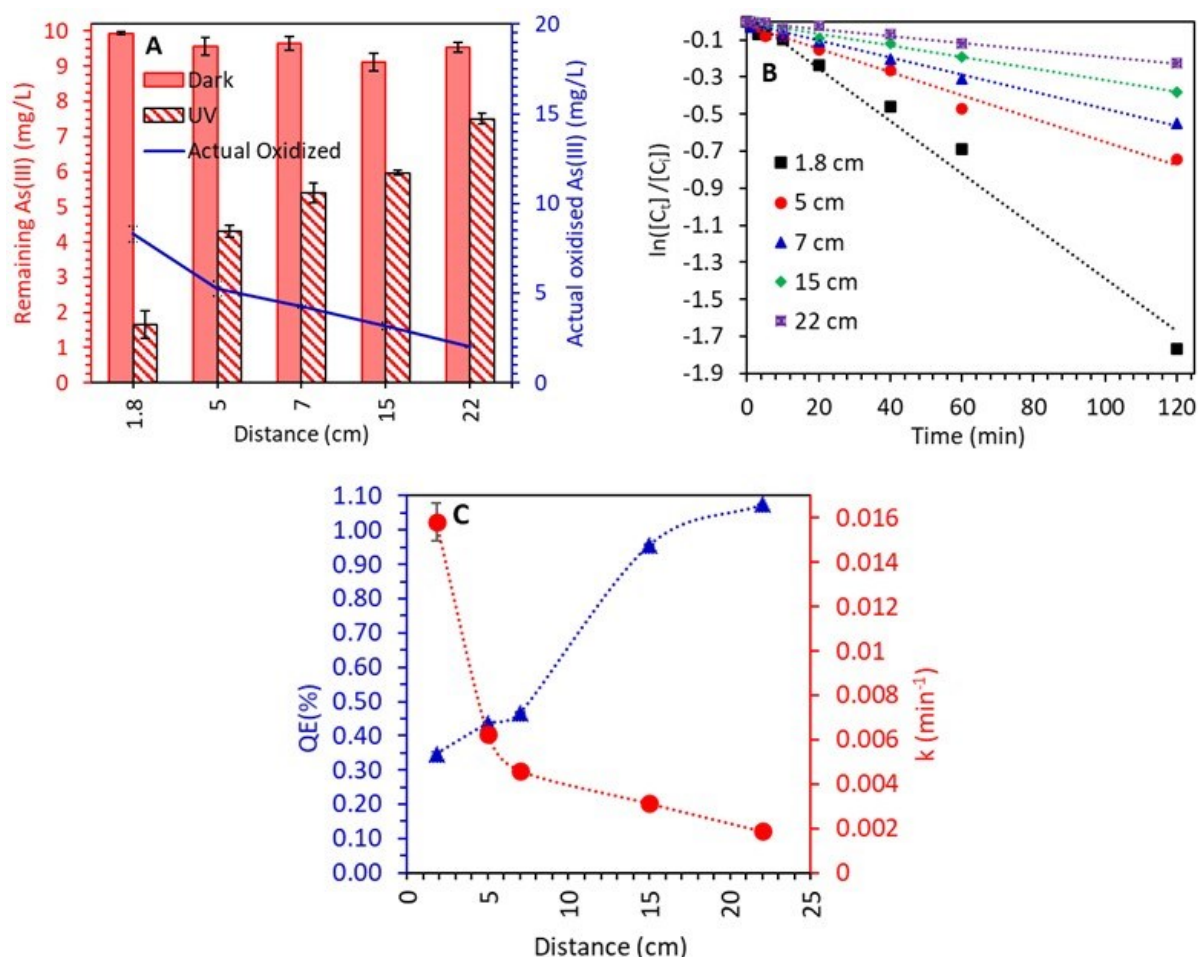


Figure 6. 7. Effect of distance between the light source and the solution surface on the PCO efficiency of arsenite As(III). A- Remaining As(III) under UV and in dark and the actual oxidised As(III) after 2 hrs, B- First order kinetic plot, C- The quantum efficiency (QE%) versus the kinetic rate (k_1).

6.3.2.2 Effect of salinity on the PCO efficiency

The effect of salinity on the PCO of arsenite was studied. To this end, artificial seawater was prepared and diluted to a specific ionic strength. The results shown in Figure 6.8 indicate that the PCO rates declines slightly from $0.014 \pm 2.7 \times 10^{-4} \text{ min}^{-1}$ (in control experiment using distilled water) to $0.006 \pm 6.67 \times 10^{-4} \text{ min}^{-1}$ (in IS = 0.7 M). Unlike the enhanced effect of salinity using TiO_2 in chapter 4 (section 4.7.2), high salinity suppressed the photocatalytic oxidation for 1Sn:1TiO₂. This is because of as the SnO₂ fraction in the prepared 1Sn:1TiO₂ photocatalyst makes is a stronger adsorbent compared to TiO₂. 1Sn:1TiO₂ adsorbs the seawater salts and reduces

significantly reduces the possibility of exposing er of As(III) to catalyst surface in seawater and ultimately supresses photocatalytic oxidation efficiency [244].

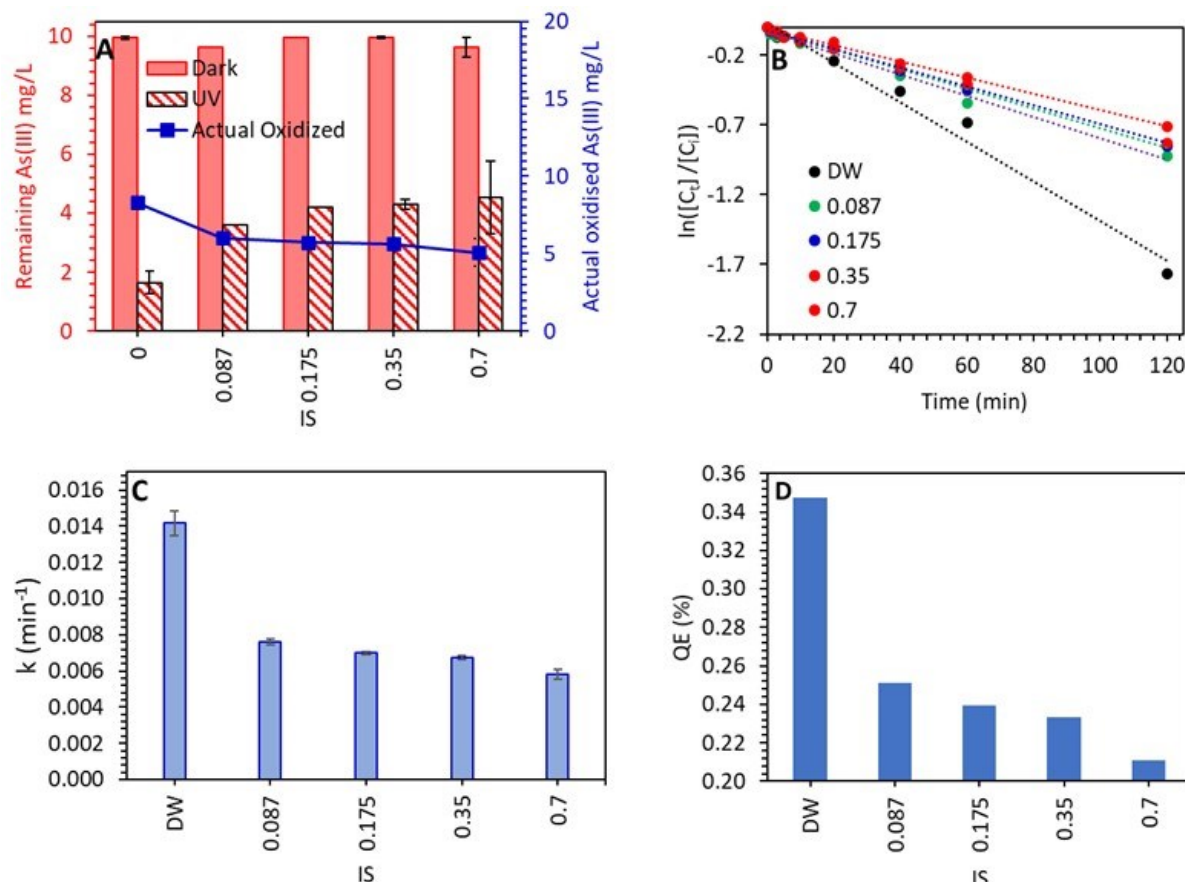


Figure 6. 8. Effect of seawater ionic strength on the PCO of arsenite As(III). A- Remaining As(III) in solution under UV and in dark and the oxidised As(III) after 2 hrs, B- First order kinetic plot, C- First order kinetic rates (k), D- The quantum efficiency (QE%), seawater was prepared according to ASTM D1141-98 method.

6.3.2.3 Effect of pH on PCO efficiency

pH is an important control parameter of the photocatalytic oxidations efficiency because it controls the distribution of the As(III) species. The experimental solution pH ranged from 2.8 to 9.2 at the beginning and between 2.7 to 7.6 at the end of the experiment (Figure 6.9 A).

The results shown in Figure 6.9 present the oxidative conversion of As(III) over 1Sn:1TiO₂ at pH 2.76, 3.4, 4.9, 7.4 and 9.2 after irradiation for 2 hr. The PCO efficiency is 43%, 58%, 67%, 82% and 93% respectively. The oxidation rate using 1Sn:1TiO₂ improves with increasing pH (2.8 to 9.2) particularly in the mildly acidic to alkaline range. This is possibly due to several factors that control the As(III) to As(V) redox reactions. During the PCO of As(III) to As(V), three distinct process occur:

(1) As(III) adsorbs to the surface of 1Sn:1TiO₂; (2) As(III) is oxidised to As(V) at the surface; (3) As(V) is adsorbed from the surface of 1Sn:1TiO₂. The adsorption/desorption process of As(III) and As(V) is strongly dependant on the solution pH. In acidic pH, 1Sn:1TiO₂ has a stronger affinity towards As(V) but in alkaline pH, As(III) can be strongly adsorbed and oxidized. Therefore, steps (1) and (3) during the oxidation reaction are limited at acidic pH and enhanced at alkaline pH [7]. In addition, higher pH promotes the generation of more OH[•] radicals; thus eventually enhances the PCO of As(III) to As(V) [245].

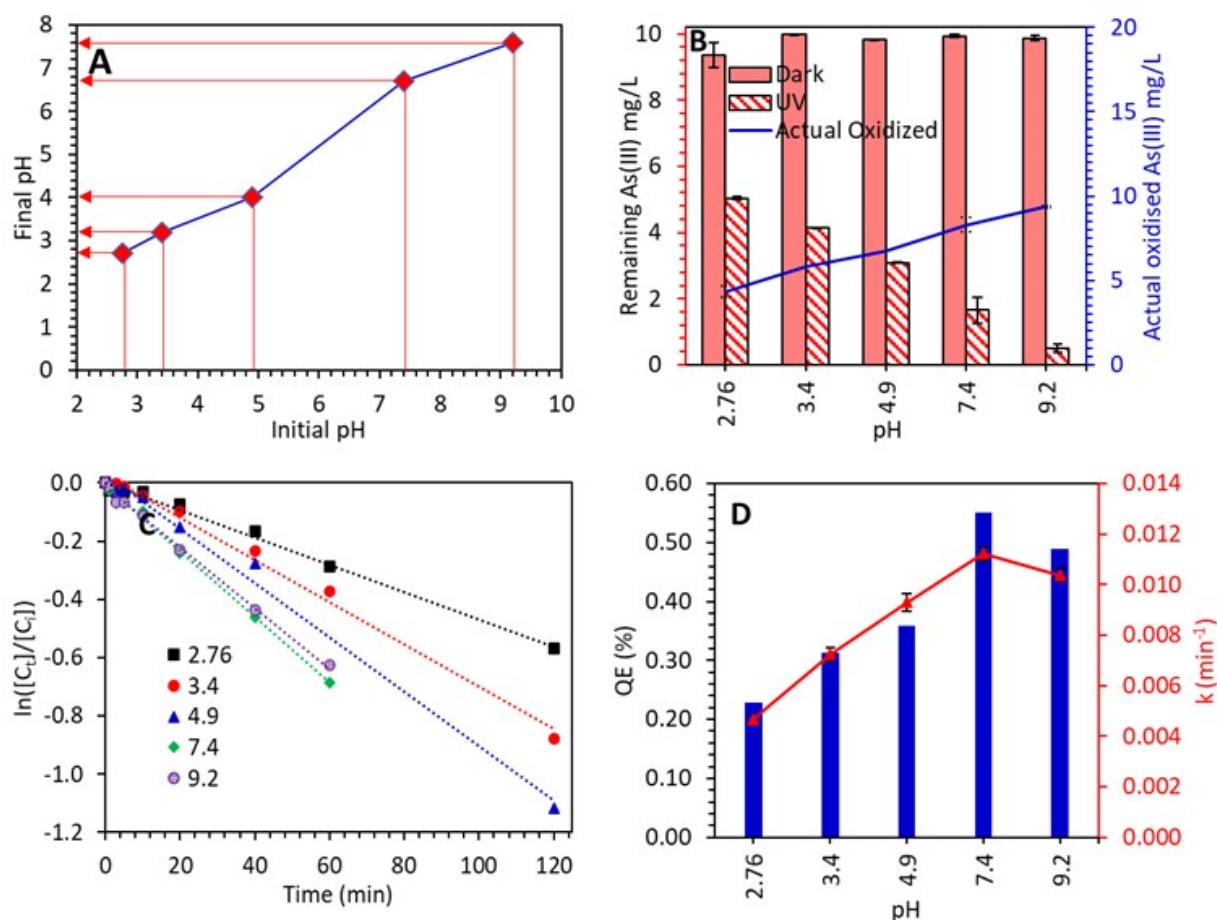


Figure 6. 9. Effect of pH on the PCO of arsenite As(III). A- Change in pH after conducting the PCO experiment, B- Remaining As(III) under UV and in dark and the actual oxidised As(III) after 2 hrs, C- First order kinetic plot, D- First order kinetic rates (k), D- The quantum efficiency (QE%).

6.3.2.4 Effect of 1Sn:1TiO₂ mass to solution ratio on PCO efficiency

Figure 6.10 shows the effect of increased catalyst loading ranging between 0.02 and 0.4 g/L on PCO of 10 mg/L As(III). The PCO increases from 40 % ($k = 0.008 \pm 1.36 \times 10^{-4}$) at 0.02 /L to 96 ($k = 0.028 \pm 10.6 \times 10^{-4}$) at 0.2 g/L then it began to decrease to 92% ($k = 0.022 \pm 10.6 \times 10^{-4}$) at 0.4g/L.

The increase of the PCO rate observed with sorbent loading ranging between 0.02 and 0.2 g/L is explained with more active sites available at the photocatalyst surface, which in turn increases the number of hydroxyl radicals [246]. The decrease observed of the PCO rate with sorbent loading ranging between 0.2 and 0.4 g/L is possibly due to the high saturation of the solution with the catalyst which in turn possibly results in (1) agglomeration of the catalyst decreasing the surface area, (2) increase of the settling down rate of the photocatalyst which is sparingly soluble in water, (3) excessive concentration of the suspended photocatalyst in the solution causes more light scattering because of the optical hindrance [247]. All these factors cause a slowdown in the oxidation rate (Figure 6.10 C) and a reduction or plateauing of the quantum efficiency (Figure 6.10 D) at high 1Sn:1TiO₂ concentration.

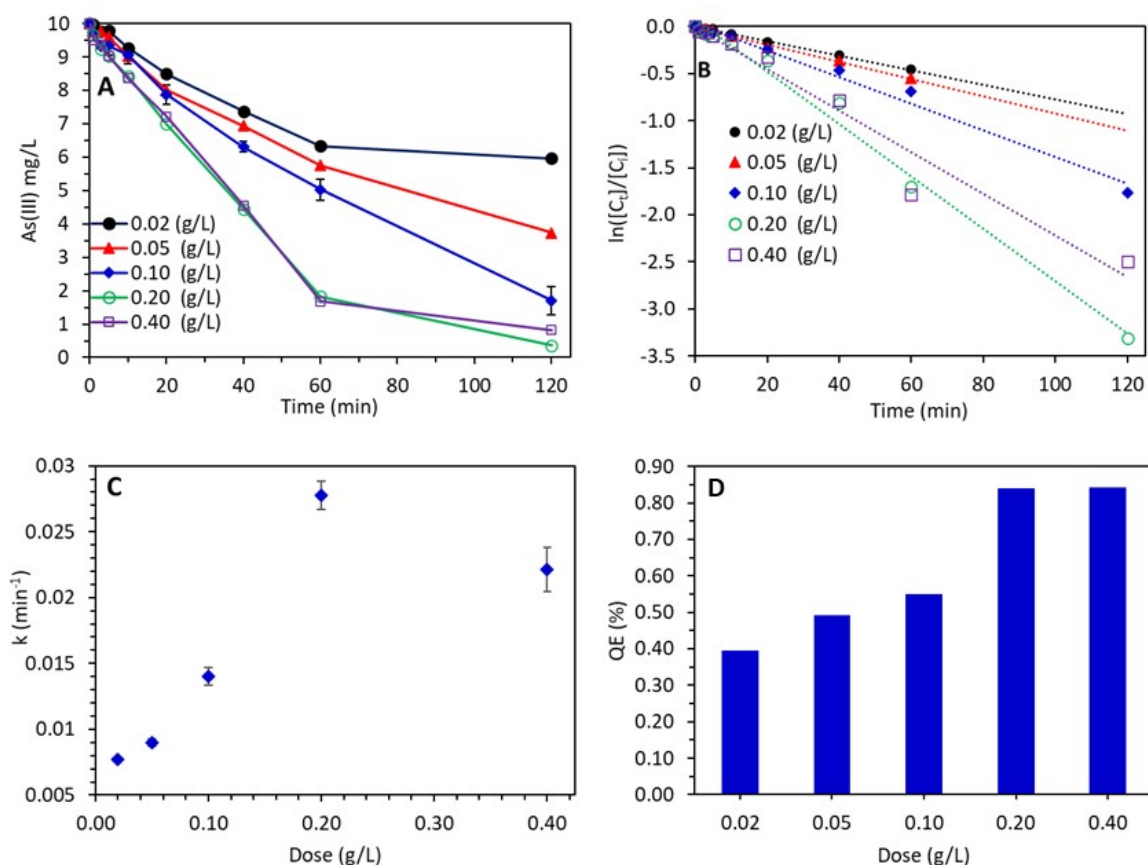


Figure 6. 10. Effect of mass to solution ratio on the PCO of As(III). A- As(III) in solution after correcting for adsorption, B- First order kinetic plot, C- Rate constant vs dose, D) Quantum Efficiency (QE%). The experiments were performed using 100 ml of 10 mg/L As(III), pH 7.4 adjusted with using 1 M HCl and 1 M NaOH, catalyst dose (0.02, 0.05, 0.1, 0.2, 0.4 mg/l). Error bars represent the $\pm$ SD.

6.3.2.5 Effect of initial As(III) concentration on the PCO efficiency

The effect of the initial As(III) concentration on the PCO process was studied for the concentration range 1 to 100 mg/L. Figure 6.11 shows the effect of As(III) concentration over time on the PCO of As(III) over 1Sn:1TiO₂. Figure 6.11 (B and C) show that the PCO oxidation rate constant decreases as initial concentrations increases from $0.056 \pm 0.0034 \text{ min}^{-1}$ at 1 mg/L to $0.002 \pm 9.3 \times 10^{-5} \text{ min}^{-1}$ at 100 mg/L. The oxidation rate decreases when [As(III)] increases because the ratio between the active sites on 1Sn:1TiO₂ to As(III) ions becomes smaller resulting in high competition between As(III) ions to bind to the unoccupied sites.

The results presented in Figure 6.11C shows that there is a direct relationship between the quantum efficiency (QE) and the initial concentration of arsenite which increases from 0.22% at 1 mg/L to 1.08 % at 100 mg/L. This is because quantum efficiency is proportional to [As(III)] as expected from Langmuir Hinshelwood kinetics.

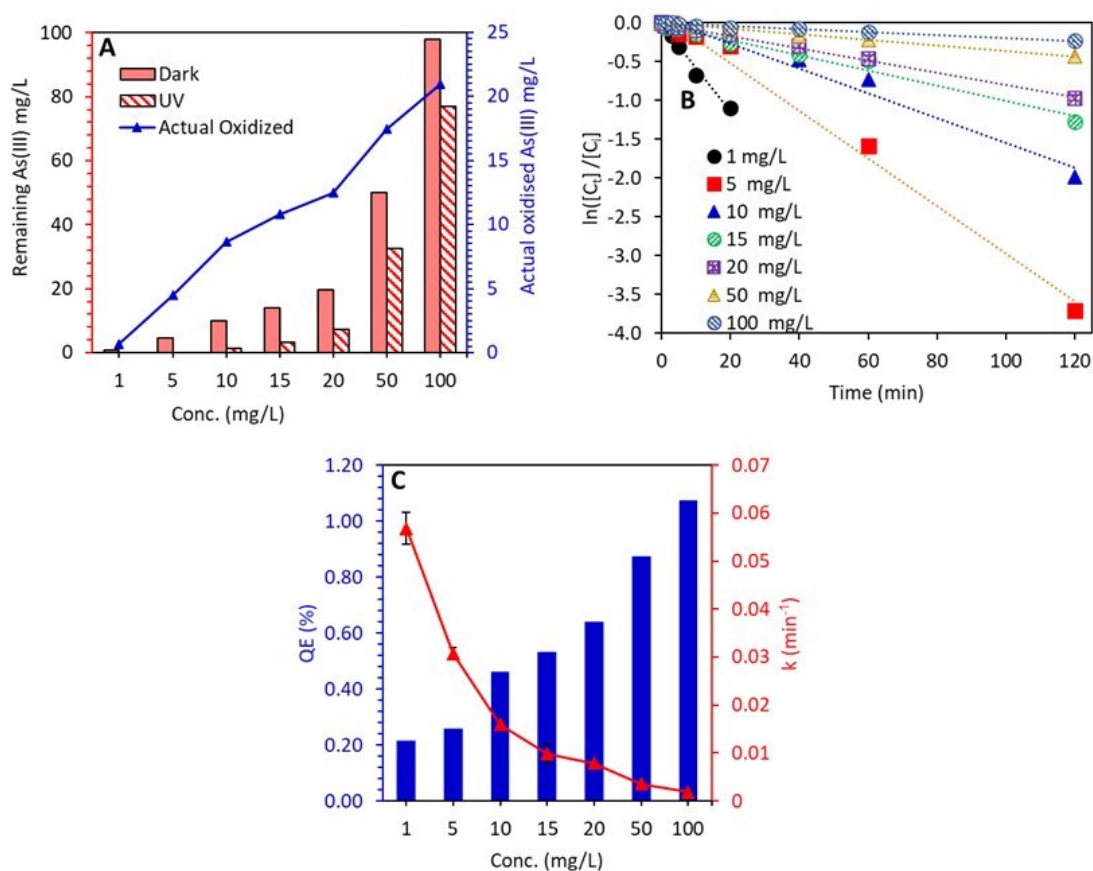


Figure 6. 11. Effect of As(III) concentration on the PCO of arsenite As(III). B- Remaining As(III) in solution under UV and in dark and the oxidised As(III) after 2 hrs, C- First order kinetic plot, D- First order kinetic rates (k_1) and the quantum efficiency (QE%).

6.4 Conclusion

The PCO mechanism of As(III) over 1Sn:1TiO₂ was studied through TAS experiments and showed a long-lived charge carrier in the 1Sn:1TiO₂ photocatalyst. Compared to anatase TiO₂ the initial transient absorption signal was ~3 times higher, suggesting early timescale (pre-μs) suppression in the electron-hole recombination in 1Sn:1TiO₂ and evidence of enhanced spatial separation of charge carriers. This can be one of the main reasons for improved PCO over 1Sn:1TiO₂ photocatalyst. The main oxidant during the oxidation process, was investigated using different scavengers. HO• scavengers Isopropanol, Rebamipide anhydrous and DMSO reduce the PCO to 21% ($k = 0.004 \pm 3.6 \times 10^{-4} \text{ min}^{-1}$), 30% ($k = 0.003 \pm 2.6 \times 10^{-4} \text{ min}^{-1}$) and 23% ($k = 0.003 \pm 2.9 \times 10^{-4}$) respectively. Compared to HO• scavengers, Superoxide scavenger such as SOD and p-benzoquinone show a little suppression in the oxidation where the oxidation was reduced to 35% ($k = 0.004 \pm 1.7 \times 10^{-4}$) and 49% ($k = 0.006 \pm 4.3 \times 10^{-4}$) respectively. This implies that the hydroxyl radical (OH•) was the main oxidant beside the as a hole (h^+_{VB}) (ascorbic acid scavenger) which reduces the oxidation of As(III) to 2.3%.

The controls of experimental parameters on the PCO rates were studied. A negative relationship was observed between rate and increasing distance between light source and solution surface, salinity and As(III) concentration was observed and a positive relationship with pH. The QE correlates positively with increase in the distance between light source and solution surface, pH and As(III) concentration, but negatively with increase in salinity. The 1Sn:1TiO₂ photocatalyst mass to solution ratio improved PCO rates until 0.2 g/L and beyond this mass it showed a negative impact on both oxidation rates and QE.

7 Discussion and future work

7.1 Discussion

This thesis investigated doping of TiO_2 with different molar ratios of Sn to prepare a multifunctional photocatalyst-sorbent material, for the treatment of arsenic(III) contaminated waters. The study includes three main experimental objectives as follows:

- An accurate determination of PCO rates of arsenite (As(III)) to arsenate (As(V)) using TiO_2 . This was achieved by accounting different surface processes that can affect the PCO yield, such as adsorption of both arsenic species on the surface of the catalyst, the contribution of direct photolysis, and the composition of the reaction media. In addition to the surface processes, other factors were studied such as the effect of used analytical techniques, and which arsenic species concentration should be used during the calculations of the oxidation rates. To that end, anatase TiO_2 was used as model photocatalyst and characterized using XRD, SEM, FTIR and XPS. Arsenic species were analysed using molybdenum blue spectrochemical method and cross calibrated with anodic stripping voltammetry (ASV) and ICP-MS. The results after cross calibration were close enough to demonstrate the accuracy of the spectrochemical molybdenum blue method. The directly adsorbed fraction of As was corrected by running two experiments in parallel, one in the dark and one under UVA irradiation. XPS investigation showed that a considerable amount of the oxidised As(V) was adsorbed to the catalyst surface and so masked from the analysis of the aqueous As(V) . Therefore, relying on only the produced As(V) in the solution underestimated the PCO yield and give a falsely underestimated oxidation rate over TiO_2 by 7.1% due to the high affinity of As(V) to be adsorbed to the TiO_2 surface. Alternatively, the decline in As(III) concentration (as opposed to the rise in As(V) concentration) gives a more accurate measure of the PCO rate. The impact of UV light-induced photolysis enhance the PCO of 1 mg/L As(III) by 3.1% . The effect of reaction medium was investigated, where the widely used HEPES buffer and the medium ionic strength increased the PCO yield. The PCO increased the As(III) adsorption over TiO_2 by ~23% compared to adsorption in dark due to the oxidation of As(III) to As(V) which can be easily adsorbed than As(III) . Photophysics has been studied to calculate the

quantum efficiency (QE) of the PCO reactions. QE (%) values varied from 0.002 ± 0.0004 to 0.32 ± 0.06 %, depending on the reaction conditions.

- A central theme of this thesis was to investigate the effect of TiO_2 doping with different molar ratios of Sn and application of the produced bicomposite photocatalyst to remediate As(III) from contaminated water. The study shows that the added concentration of Sn during the synthesis influences the structure and efficiency of the formed Sn doped TiO_2 photocatalyst. Characterisation using XRD, Raman, XPS, LEIS, EDX, HR-TEM, S-TEM, SEM and FTIR shows that at low Sn-doping levels (*i.e.* Sn:Ti = 0.1), SnO_2 forms the shell and Sn- TiO_2 forms the core of the bicomposite catalyst (*i.e.* $\text{SnO}_2@\text{Sn-TiO}_2$ forms), whereas at high Sn-doping levels (*e.g.* Sn:Ti = 1), Sn- TiO_2 forms the shell and SnO_2 forms the core of the bicomposite catalyst (*i.e.* $\text{Sn-TiO}_2@\text{SnO}_2$). Sn-doping reduced the bandgap and decreased the conduction band energy, improving electron-hole separation. The Sn doped TiO_2 heterostructure photocatalysts showed ~ 30 – 46% higher oxidation yield than pure TiO_2 . The calculation of the PCO kinetic rate (k) based solely on aqueous As(V) undervalues the photocatalysis yield by ~50% because this ignores the surface adsorbed As(V) which is a photocatalysis product. Therefore, the accurate k values should be determined by either considering both aqueous As(V) and surface adsorbed As(V) or tracking the decline in aqueous As(III) which gave similar values. The bicomposite photocatalyst with high levels of Sn-doping (Sn:Ti = 1; *i.e.* $\text{Sn-TiO}_2@\text{SnO}_2$) enhances the total adsorbed arsenic by 32.5 % compared to the unmodified TiO_2 .
- The transient absorption spectroscopy (TAS) technique was used to study the PCO of As(III) over 1Sn:1 TiO_2 experiments. TAS results exhibited a long-lived charge carrier in the 1Sn:1 TiO_2 photocatalyst which in turn helped the charge separation. Compared to anatase TiO_2 the initial transient absorption signal was ~3 times higher, suggesting early timescale (pre- μs) suppression in the electron-hole recombination in 1Sn:1 TiO_2 and evidence of enhanced spatial separation of charge carriers. This can be one of the main reasons for improved PCO over the synthesised 1Sn:1 TiO_2 photocatalyst. Different scavengers were used to investigate the main oxidant during the oxidation process. Hydroxyl radical ($\text{HO}^\bullet$) scavengers such as Isopropanol, Rebamipide anhydrous and DMSO reduce the PCO to 21%

($k = 0.004 \pm 3.6 \times 10^{-4} \text{ min}^{-1}$), 30% ($k = 0.003 \pm 2.6 \times 10^{-4} \text{ min}^{-1}$) and 23% ($k = 0.003 \pm 2.9 \times 10^{-4}$) respectively whereas a lower suppression in the oxidation rates were observed while using the superoxide scavenger such as superoxide dismutase (SOD) and p-benzoquinone which reduced the oxidation to 35% ($k = 0.004 \pm 1.7 \times 10^{-4}$) and 49% ($k = 0.006 \pm 4.3 \times 10^{-4}$) respectively. This suggests that the main oxidant was the hydroxyl radical ($\text{HO}^\bullet$) beside the as a hole (h^+_{VB}) (ascorbic acid scavenger) which reduces the oxidation of As(III) to 2.3%. The controls of experimental parameters on the PCO rates exhibited a negative relationship between the rate and distance between light source and solution surface, salinity and As(III) concentration. A positive relationship was observed between the rate and pH. The quantum efficiency (QE) correlates positively with longer distances between light source and solution surface, pH and As(III) concentration, but negatively correlates with salinity extent. The 1Sn:1TiO₂ photocatalyst mass to solution ratio improved PCO rates until 0.2 g/L and beyond this mass it showed a negative impact on both oxidation rates and QE.

7.2 Recommendations and outlook

The benchmark TiO₂ photocatalyst has been extensively studied for water treatment over the last four decades. TiO₂-based photocatalytic oxidation (PCO) has been identified as a promising and competitive approach for water treatment in the near future. However, there is a barrier between the laboratory successful studies and the practical implementation. Therefore, further research in TiO₂-based photocatalysis is necessary to mitigate these problems, the key areas for future studies are suggested as follows:

- The large-scale design should be considered in the bench studies to translate these studies to industrial world. For example, the studies should focus on the photocatalyst improvement as well as the design of an innovative reactor design.
- Application of the solar irradiation in the TiO₂-based photocatalytic water treatment system is yet to be designed and demonstrated.
- The industrial partners should be encouraged to adopt and pull the successfully modified TiO₂-based photocatalysis from academics to niche applications.

- TiO_2 photocatalyzed reactions are non-selective oxidations because it is controlled by a free radical mechanism which produce large amounts of waste. Therefore, more studies should focus on development of a selective photocatalyst system that can only oxidize hazardous pollutants (e.g., arsenic) and avoid the non-toxic component and essential elements in drinking.
- The previous studies are mainly centred around the batch experiments which suffers from problems of the photocatalyst separation. Thus, future studies should focus on the development of a prototype that allows both the photocatalytic oxidation and simple photocatalyst separation.

8 Conclusions and evaluation

Objectives and key findings from the research are outlined as follows.

1. To identify the processes and parameters that control the determination of As(III) PCO rates and the quantum efficiency (QE), and to develop guidelines for best practice.
 - 1.1. For the first time, the study showed that the choice of analytical technique is not critical provided that rate constants are calculated based on the depletion of As(III) in solution and after correction of the directly adsorbed As(III).
 - 1.2. Correction of the directly adsorbed As(III) at each time interval is best done by running parallel experiments (one under UV and one in dark) instead of running a sequential experiment (i.e. running the experiment in the dark then turning on the UV lamp). These findings are supported by XPS analysis of the oxidation state of TiO₂-sorbed As.
 - 1.3. Photolysis by the light source itself and the chemical composition of the solution (i.e. presence of HEPES and ionic strength) can significantly increase As(III) oxidation rates. This needs to be corrected for.
 - 1.4. The quantum efficiency (QE) for this oxidation of As(III) by TiO₂ is low and in the region of 0.1 to 0.2 %.
2. To Improve the photocatalytic efficiency of TiO₂ through doping with Sn and to study effects on the structure of the composite catalyst.
 - 2.1. For the first time, the characterisation indicated that the composition of the catalyst's core and shell depends on the molar ratio of Sn-doping. At low doping ratios (0.1Sn:1TiO₂), SnO₂ tends to 'float' on the surface of TiO₂ and form the shell of the catalyst (SnO₂@Sn-TiO₂), whereas at higher Sn doping ratio (1Sn:1TiO₂) the formation of a Sn-TiO₂ shell alongside clusters of SnO₂ in the core of the catalyst (Sn-TiO₂@SnO₂) is observed..
 - 2.2. The bandgap shifts the conduction and valence band edge energies and reduces the bandgap, where the smallest bandgap was 2.87 eV in the 1Sn:1TiO₂ sample.

3. To apply Sn-doped TiO₂ to the PCO of As(III) and subsequential removal of As
 - 3.1. The bicomposite catalysts (Sn-TiO₂@SnO₂ and SnO₂@Sn-TiO₂) improves the PCO performance of TiO₂ by ~ 30% to 46% pending on the Sn-doping ratio. This increase is due to the reduction of the bandgap energy (2.87 eV) and to the improved electron-hole separation.
 - 3.2. Highly Sn-doped TiO₂ samples are more efficient in oxidising As(III) due to the development of the Sn-TiO₂ shell that was more effective in oxidising As(III) than the SnO₂ shell that formed in less Sn-doped samples.
 - 3.3. For the first time, the PCO kinetic rate was accurately determined by tracking and mounting the concentration of the oxidation states of both adsorbed arsenic (using XPS) and the arsenic remaining in solution (spectrophotometry). The pseudo-first order kinetic rate constant (k) is $0.055 \pm 0.002 \text{ min}^{-1}$. The determination is based on tracking the concentration states of arsenic adsorbed and remaining in solution using XPS and spectrophotometry.
4. To identify the PCO mechanism of As(III) over 1Sn:1TiO₂. This includes TAS study and to identify of the effect of Sn doping on charge carrier's lifetime and recombination rates within the heterojunctions in the Sn-doped TiO₂. In addition, to scavenger experiments to define the main oxidant during the PCO process.
 - 4.1. TAS experiments of 1Sn:1TiO₂ were conducted for the first time and showed a long-lived charger carrier in the 1Sn:1TiO₂ photocatalyst compared to TiO₂ and SnO₂. This can be one of the main reasons that is responsible for the improved PCO over 1Sn:1TiO₂ photocatalyst. Compared to TiO₂ the initial transient absorption signal was ~3 times higher than that of our anatase TiO₂, which showed that early timescale (pre-μs) suppression in the electron-hole recombination in this 1Sn:1TiO₂ system and is evidence of enhanced spatial separation of charge carriers.
 - 4.2. The main oxidant during the oxidation process was investigated using different scavengers. HO• scavengers such as isopropanol, rebamipide anhydrous and DMSO reduce the PCO to 21 % ($k = 0.004 \pm 3.6 \times 10^{-4} \text{ min}^{-1}$), 30% ($k = 0.003 \pm 2.6 \times 10^{-4} \text{ min}^{-1}$) and 23% ($k = 0.003 \pm 2.9 \times 10^{-4}$) respectively. Superoxide scavenger such as superoxide

dismutase (SOD) and p-benzoquinone show little suppression of the oxidation, i.e. to 35.25% ($k=0.004 \pm 1.7 \times 10^{-4}$) and 48.93% ($k=0.006 \pm 4.3 \times 10^{-4}$) respectively. This implies that the hydroxyl radical ($\text{OH}\cdot$) is the main oxidant along with a hole (h^+_{VB}) (ascorbic acid scavenger) which reduces the oxidation of As(III) to 2.3%.

5. To study the control of experimental parameters on the PCO of As(III) over 1Sn:1TiO₂
 - 5.1. The PCO decreases with increasing the following factors; a) distance between the light source and the solution surface, b) salinity, c) initial As(III) concentration and d) pH.
 - 5.2. The QE increases with increasing a) distance between light source and solution surface, b) pH and c) initial As(III) concentration but decreases with increasing salinity.
 - 5.3. PCO and QE using 1Sn:1TiO₂ increase with increasing mass to solution ratio until 0.2g/L but decrease beyond.

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9 Appendix

9.1 Physical characterisation of the anatase TiO_2 photocatalyst

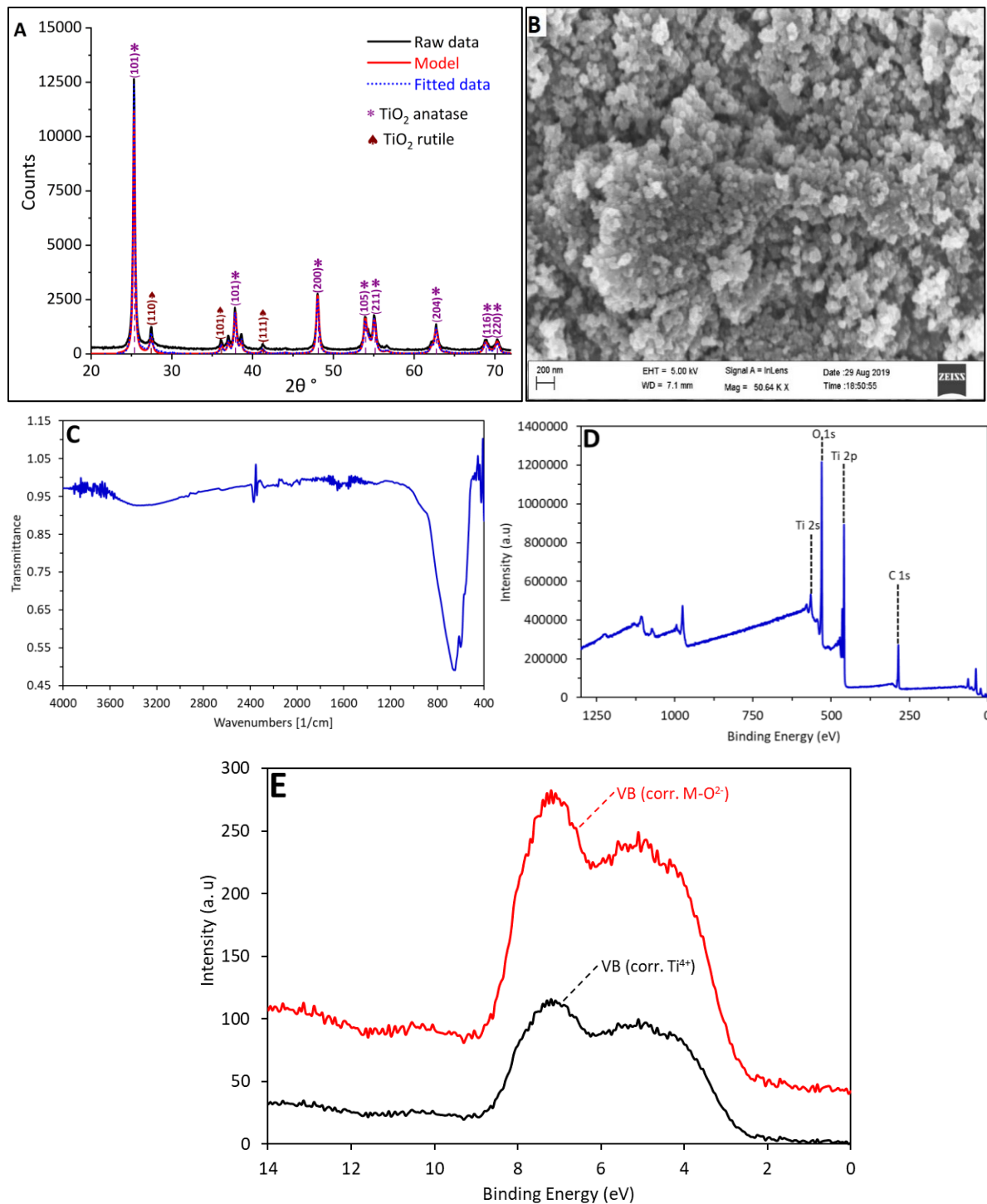


Figure 9. 1. TiO_2 characterization [A-XRD, B-SEM, C-FTIR, D-XPS surface survey, E- XPS Valence band analysis]

Table 9. 1. XPS Surface analysis of metal abundance in TiO₂

Name	Position	Environ.	Ref.	Raw Area	RSF	Real Area	Abundance
C 1s	284.8	C-C	[248]	11820.7	0.18	65308	23.4
C 1s	286.44	C-O	[248]	2092.38	0.18	11560	4.1
C 1s	288.62	C=O	[248]	1758.31	0.18	9714	3.5
O 1s	529.75	M-O ²⁻	[249]	52142.7	0.45	116912	41.9
O 1s	531.7	M-OH	[250]	8367.17	0.45	18760	6.7
O 1s	533.01	C-O, C=O	[251]	4132.43	0.45	9266	3.3
Ti 2p 3/2	458.56	TiO ₂	[249]	39937	0.84	47431	17.0
Ti 2p 1/2	464.29	TiO ₂	-	19004	-	-	-

9.2 Correction of directly adsorbed As(III), parallel versus sequential methods

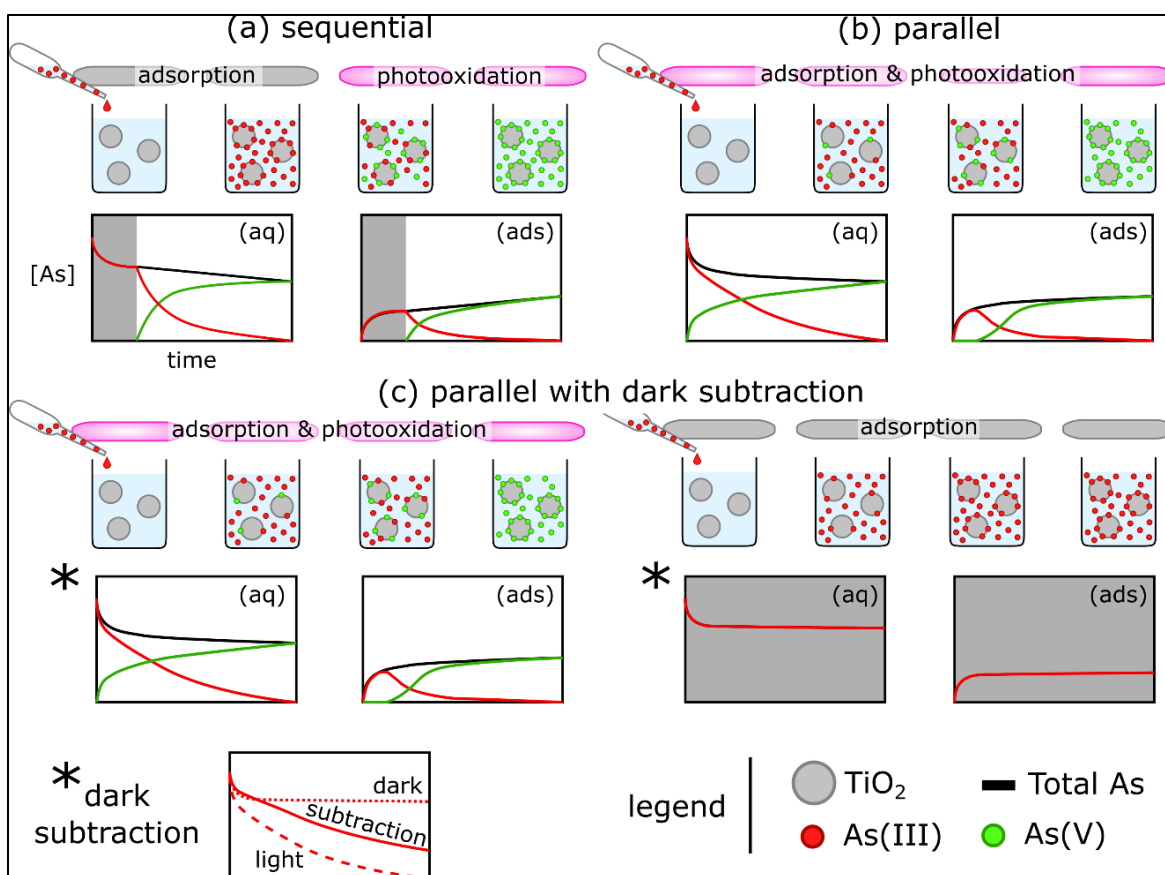


Figure 9. 2. Correction of the directly adsorbed As(III) using sequential and parallel method.

9.3 Sol-Gel (SG) synthesis method

9.3.1 XRD characterisation

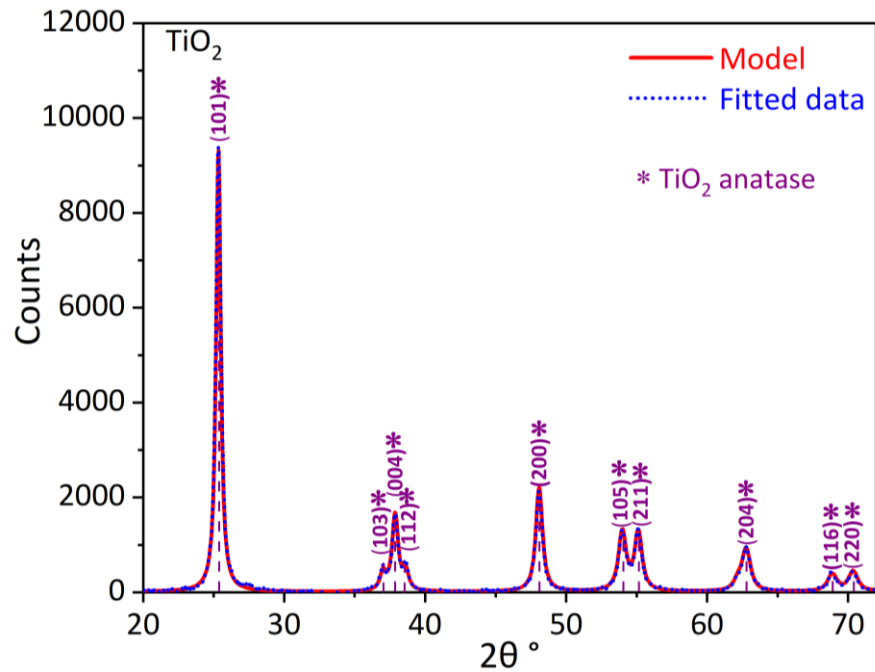


Figure 9. 3. XRD pattern of TiO_2 showing phase analysis using GSAS.

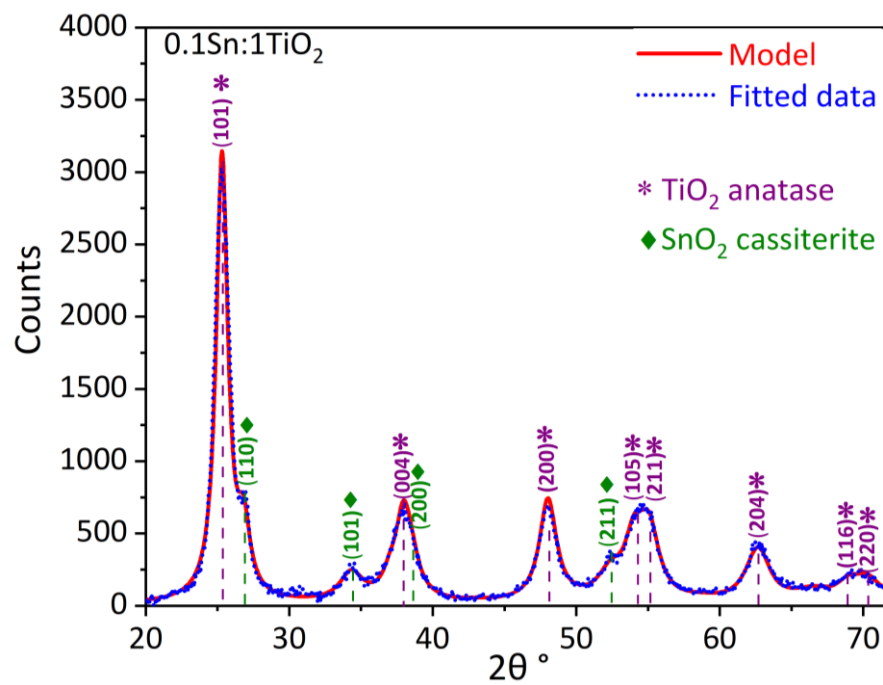


Figure 9. 4. XRD pattern of $0.1\text{ Sn} :1\text{ TiO}_2$ showing phase analysis using GSAS.

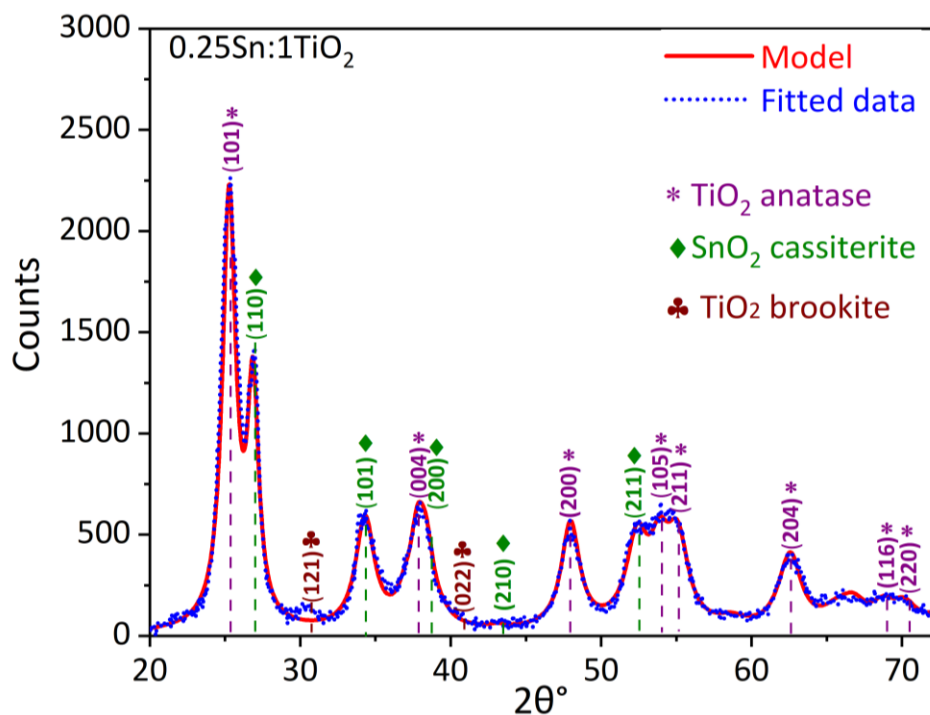


Figure 9. 5. XRD pattern of 0.25 Sn :1 TiO₂ showing phase analysis using GSAS.

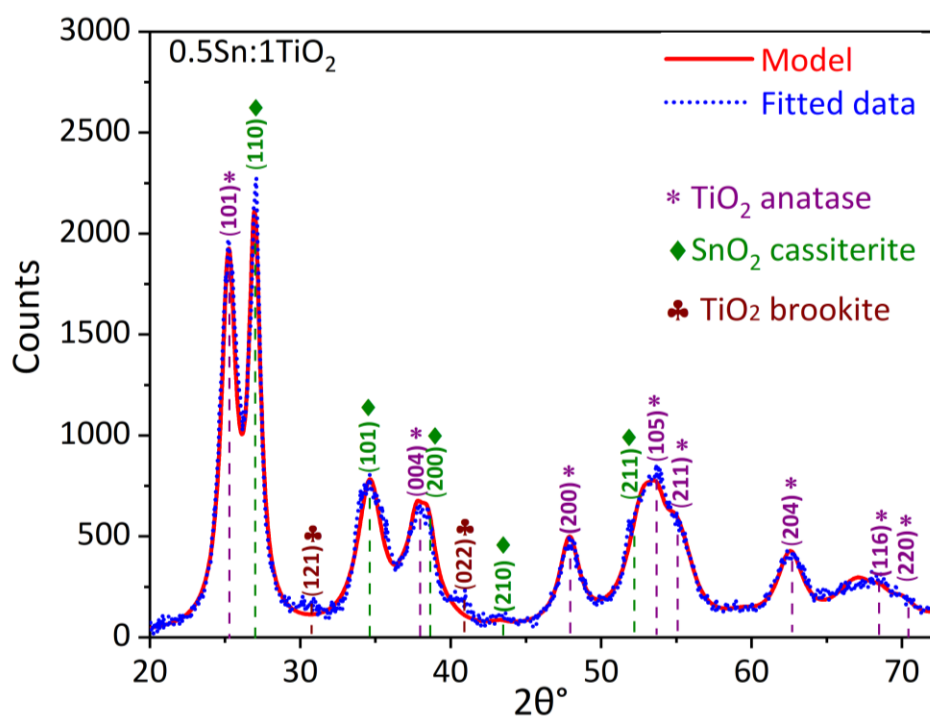


Figure 9. 6. XRD pattern of 0.5 Sn :1 TiO₂ showing phase analysis using GSAS.

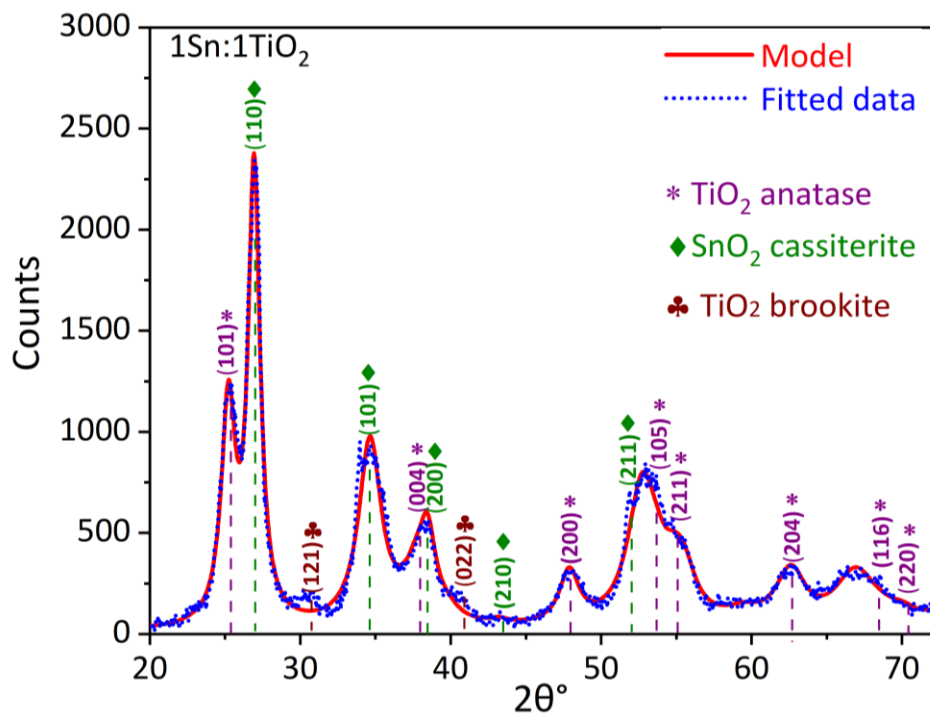


Figure 9. 7. XRD pattern of 1Sn:1TiO₂ showing phase analysis using GSAS.

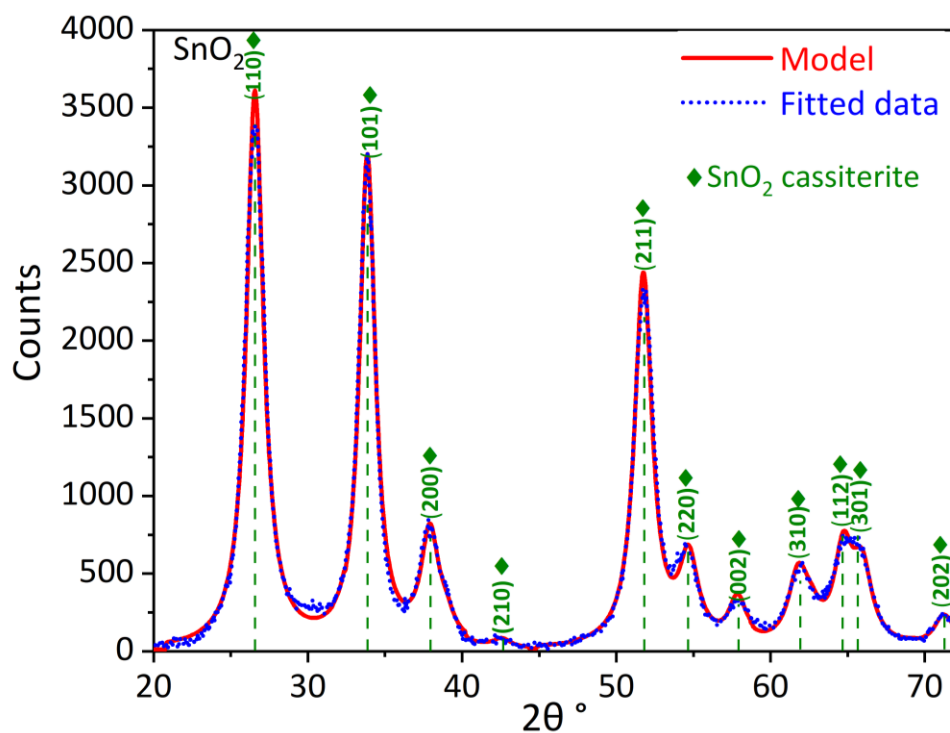


Figure 9. 8. XRD pattern of SnO₂ showing phase analysis using GSAS.

Table 9. 2. Calculation of the lattice parameters, mean cell volume, molarity, and average crystallite size using GSAS model.

	Standards			TiO ₂	0.1Sn:1TiO ₂		0.25Sn:1TiO ₂		0.5Sn:1TiO ₂		1Sn:1TiO ₂		SnO ₂
Phase	Anatase	Rutile	Cassiterite	Anatase	Anatase	Cassiterite	Anatase	Cassiterite	Anatase	Cassiterite	Anatase	Cassiterite	Cassiterite
a	3.785	4.594	4.736	3.785	3.789	4.700	3.793	4.694	3.798	4.675	3.799	4.681	4.745
±a	0.00003	0.0001	0.0002	0.0001	0.0004	0.002	0.0007	0.0012	0.0009	0.0009	0.0014	0.0009	0.0004
b	3.785	4.585	4.736	3.7845	3.7886	4.700	3.7932	4.6942	3.798	4.675	3.799	4.685	4.745
±b	0.00003	0.0001	0.0002	0.0001	0.0005	0.002	0.0007	0.0012	0.0009	0.0009	0.0015	0.0009	0.0004
c	9.5124	2.953	3.185	9.504	9.487	3.141	9.519	3.1467	9.542	3.112	9.553	3.108	3.189
±c	0.00012	0.0001	0.0003	0.0007	0.0026	0.004	0.0035	0.0018	0.0045	0.0019	0.0102	0.0015	0.0004
V	136.261	62.071	71.431	136.118	136.169	69.402	136.961	69.34	137.668	68.006	137.907	68.12	71.804
wt.%	100	100	100	100	93.1	6.9	82.587	17.413	71.29	28.71	54.825	45.175	100
mol.%	100	100	100	100	96.221	3.779	89.950	10.051	82.412	17.588	69.606	30.394	100
V% change	-	-	-	-0.105	-0.068	-2.840	0.5135	-2.927	1.032	-4.794	1.208	-4.635	0.523
wRp	-	-	-	0.076	0.067		0.0731		0.079		0.086		0.065
LX	-	-	-	22.045	48.857	70.598	76.261	46.071	90.62	18.43	52.19	13.03	130.534
τ (nm)	-	-	-	36.023	16.254	11.249	10.413	17.237	8.763	43.088	15.216	60.945	6.084
Ref.	[252]	[252]	[253]										

Where the average crystallite size of Sn-doped TiO₂ samples was calculated using Scherer's equation [174] [Eq. (S1)].

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (Eq. S1)$$

where 'D' is the average crystallite size, 'λ', the X-ray wavelength, θ, Bragg's angle, and 'β' the peak position and the FWHM (full-width at half maximum) the peak after correction for instrumental broadening

9.3.2 XPS characterisation

Table 9. 3. TiO₂ Surface environment analysis based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF*	Real Area	Abundance
TiO ₂	C 1s	284.8	C-C	[248]	5988	0.18	33081	15.4
	C 1s	286.4	C-O	[248]	1024	0.18	5656	2.6
	C 1s	288.8	C=O	[248]	743	0.18	4105	1.9
	Cl 2p3/2	198.6	-		0	0.29	0	0.0
	Cl 2p1/2	200.5	-		0	-	-	-
	O 1s	529.8	M-O ²⁻	[249]	47049	0.45	105491	49.2
	O 1s	531.1	M-OH	[250]	5903	0.45	13236	6.2
	O 1s	532.2	C-O, C=O	[251]	3718	0.45	8336	3.9
	Sn 3d5/2	-	-		0	2.34	0	0.0
	Sn 3d3/2	-	-		0	-	-	-
	Ti 2p3/2	458.6	TiO ₂	[249]	37297	0.84	44295	20.7
	Ti 2p1/2	464.3	TiO ₂	-	17938	-	-	-

*(RSF) Relative Sensitivity Factors.

Table 9. 4. Surface environment analysis of the 0.1Sn:1TiO₂ based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF	Real Area	Abundance
0.1Sn:1TiO ₂	C 1s	284.8	C-C	[248]	2735	0.18	15112	7.8
	C 1s	286.3	C-O	[248]	680	0.18	3758	1.9
	C 1s	289.0	C=O	[248]	481	0.18	2655	1.4
	Cl 2p3/2	198.4	M ⁺ Cl ⁻	[254]	875	0.29	3026	1.6
	Cl 2p1/2	200.1	M ⁺ Cl ⁻		434	-	-	-
	O 1s	530.1	M-O ²⁻	[249]	46924	0.45	105211	54.3
	O 1s	531.4	M-OH	[250]	4582	0.45	10273	5.3
	O 1s	532.2	C-O, C=O	[251]	1679	0.45	3766	1.9
	Sn 3d5/2	486.7	SnO ₂	[255]	17348	2.34	7414	3.8
	Sn 3d3/2	495.1	SnO ₂	[256]	11911	-	-	-
	Ti 2p3/2	458.8	TiO ₂	[249]	35812	0.84	42532	22.0
	Ti 2p1/2	464.6	TiO ₂		16805	-	-	-

Table 9. 5. Surface environment analysis of the 0.25Sn:1TiO₂ based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF	Real Area	Abundance
0.25Sn:1TiO ₂	C 1s	284.8	C-C	[248]	2174	0.18	12011	5.3
	C 1s	286.4	C-O	[248]	521	0.18	2878	1.3
	C 1s	289.0	C=O	[248]	460	0.18	2543	1.1
	Cl 2p _{3/2}	198.5	M ⁺ Cl ⁻	[254]	895	0.29	3097	1.4
	Cl 2p _{1/2}	200.1	M ⁺ Cl ⁻		335	-	-	-
	O 1s	530.2	M-O ²⁻	[249]	54988	0.45	123291	54.5
	O 1s	531.0	M-OH	[250]	6201	0.45	13903	6.1
	O 1s	532.0	C-O, C=O	[251]	3532	0.45	7920	3.5
	Sn 3d _{5/2}	486.7	SnO ₂	[255]	21621	2.34	9240	4.1
	Sn 3d _{3/2}	495.1	SnO ₂	[256]	14745	-	-	-
	Ti 2p _{3/2}	458.9	TiO ₂	[249]	43322	0.84	51452	22.7
	Ti 2p _{1/2}	464.6	TiO ₂		20320	-	-	-

Table 9. 6. Surface environment analysis of the 0.5Sn:1TiO₂ based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF	Real Area	Abundance
0.5Sn:1TiO ₂	C 1s	284.8	C-C	[248]	3687	0.18	20373	11.7
	C 1s	286.4	C-O	[248]	694	0.18	3837	2.2
	C 1s	288.9	C=O	[248]	559	0.18	3088	1.8
	Cl 2p _{3/2}	198.4	M ⁺ Cl ⁻	[254]	347	0.29	1202	0.7
	Cl 2p _{1/2}	200.0	M ⁺ Cl ⁻		164	-	-	-
	O 1s	530.1	M-O ²⁻	[249]	39107	0.45	87684	50.4
	O 1s	531.3	M-OH	[250]	4773	0.45	10701	6.2
	O 1s	532.2	C-O, C=O	[251]	2610	0.45	5852	3.4
	Sn 3d _{5/2}	486.5	SnO ₂	[255]	16055	2.34	6861	3.9
	Sn 3d _{3/2}	494.9	SnO ₂	[256]	10990	-	-	-
	Ti 2p _{3/2}	458.8	TiO ₂	[249]	28801	0.84	34206	19.7
	Ti 2p _{1/2}	464.5	TiO ₂		13601	-	-	-

Table 9. 7. Surface environment analysis of 1Sn:1TiO₂ based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF	Real Area	Abundance
1Sn:1TiO ₂	C 1s	284.8	C-C	[248]	2705	0.18	14946	8.4
	C 1s	286.3	C-O	[248]	612	0.18	3381	1.9
	C 1s	289.1	C=O	[248]	473	0.18	2613	1.5
	Cl 2p _{3/2}	198.6	M ⁺ Cl ⁻	[254]	888	0.29	3074	1.7
	Cl 2p _{1/2}	200.2	M ⁺ Cl ⁻		456	-	-	-
	O 1s	530.3	M-O ²⁻	[249]	39648	0.45	88896	50.0
	O 1s	531.0	M-OH	[250]	4085	0.45	9160	5.1
	O 1s	532.1	C-O, C=O	[251]	3950	0.45	8857	5.0
	Sn 3d _{5/2}	486.7	SnO ₂	[255]	33705	2.34	14404	8.1
	Sn 3d _{3/2}	495.1	SnO ₂	[256]	23285	-	-	-
	Ti 2p _{3/2}	459.0	TiO ₂	[249]	27402	0.84	32544	18.3
	Ti 2p _{1/2}	464.7	TiO ₂		12708	-	-	-

Table 9. 8. Surface environment analysis of SnO₂ based on the peak fitting of XPS high resolution scans.

Sample	Name	Position	Environ	Ref	Raw Area	RSF	Real Area	Abundance
SnO ₂	C 1s	284.8	C-C	[248]	873.119	0.18	4824	2.4
	C 1s	285.78	C-O	[248]	446.958	0.18	2469	1.2
	C 1s	289.25	C=O	[248]	235.252	0.18	1300	0.7
	Cl 2p3/2	198.92	M ⁺ Cl ⁻	[254]	1443.64	0.29	4995	2.5
	Cl 2p1/2	200.49	M ⁺ Cl ⁻		784.543	-	-	-
	O 1s	530.98	M-O ²⁻	[249]	38577.4	0.45	86496	43.5
	O 1s	532.02	M-OH	[250]	9436.4	0.45	21158	10.6
	O 1s	533.5	C-O, C=O	[251]	1784.19	0.45	4000	2.0
	Sn 3d5/2	487.14	SnO ₂	[255]	171885	2.34	73455	37.0
	Sn 3d3/2	495.56	SnO ₂	[256]	115444	-	-	-
	Ti 2p3/2	-	TiO ₂	[249]		0.84	0	0.0
	Ti 2p1/2	-	TiO ₂			-	-	-

9.3.3 Investigation of Surface morphology using HR-TEM

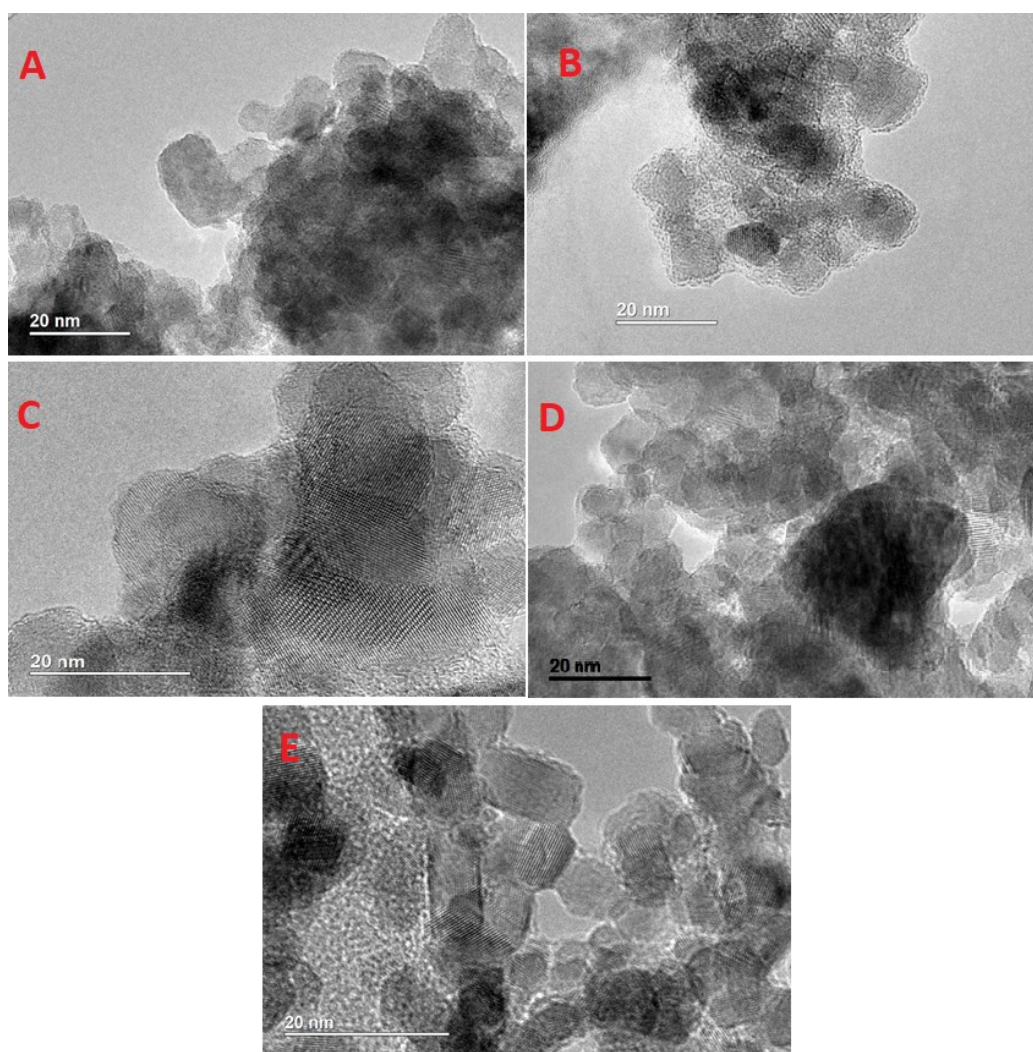


Figure 9. 9. HRTEM images of A-TiO₂-SG, B- 0.1Sn:1TiO₂, C- 0.25Sn:1TiO₂, D- 0.5Sn:1TiO₂, E-SnO₂.

9.3.4 Investigation of Surface morphology using S-TEM

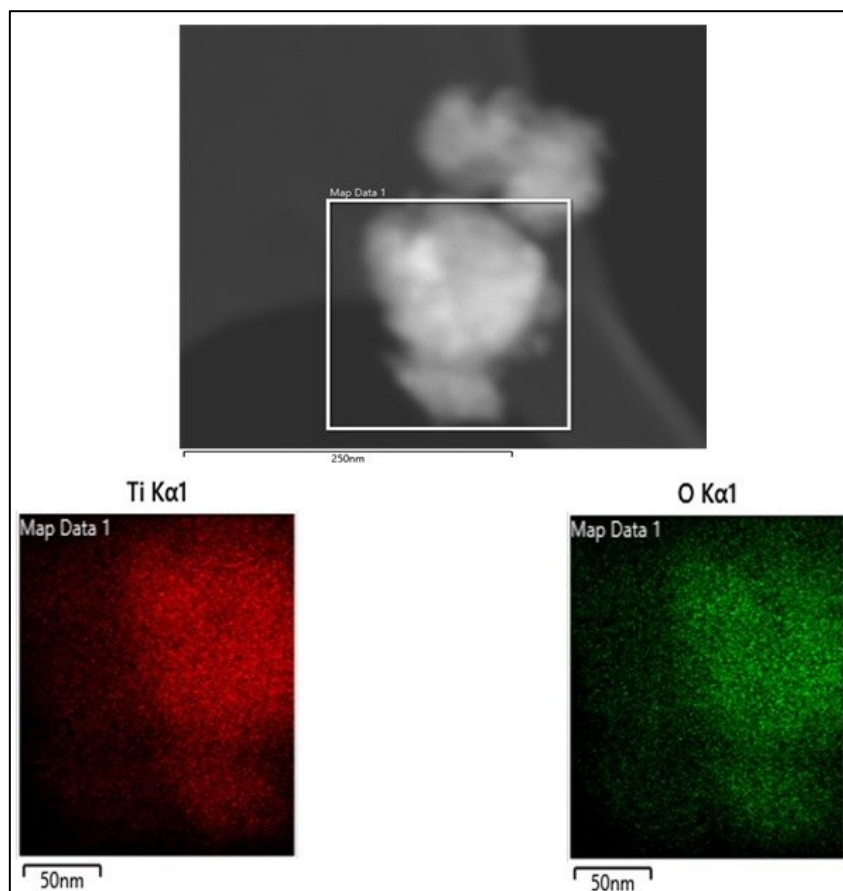


Figure 9. 10. S-TEM elemental mapping analysis of TiO_2 SG

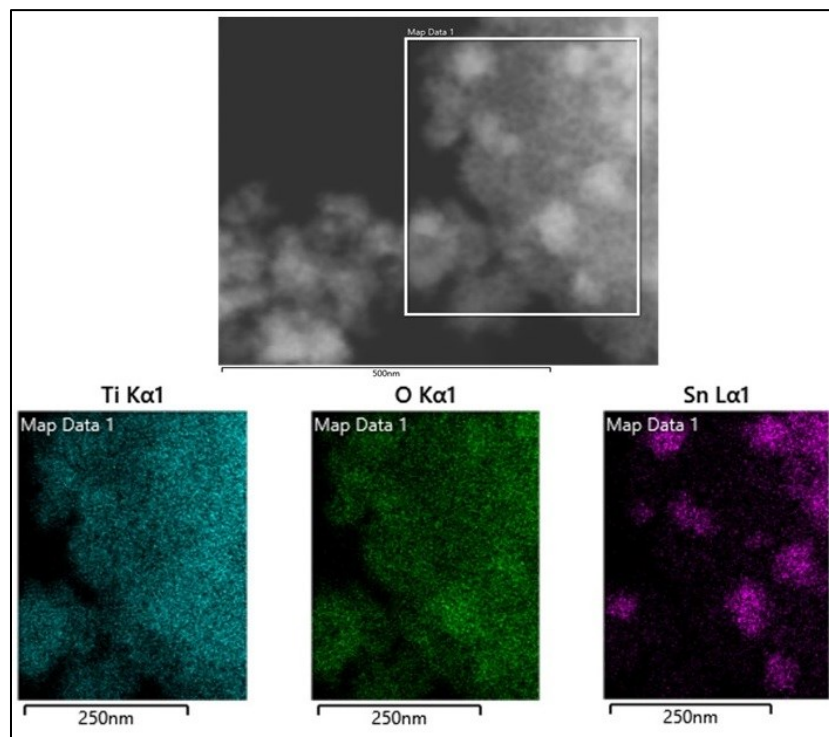


Figure 9. 11. S-TEM elemental mapping analysis of $0.1\text{Sn}:1\text{TiO}_2$.

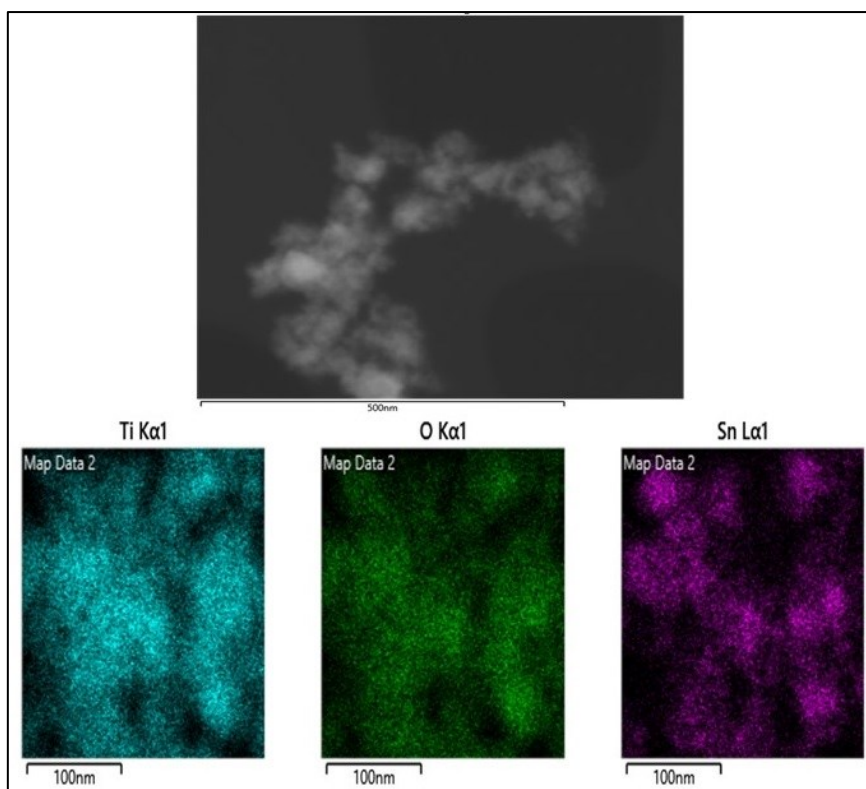


Figure 9. 12. S-TEM elemental mapping analysis of $0.25\text{Sn}:1\text{TiO}_2$.

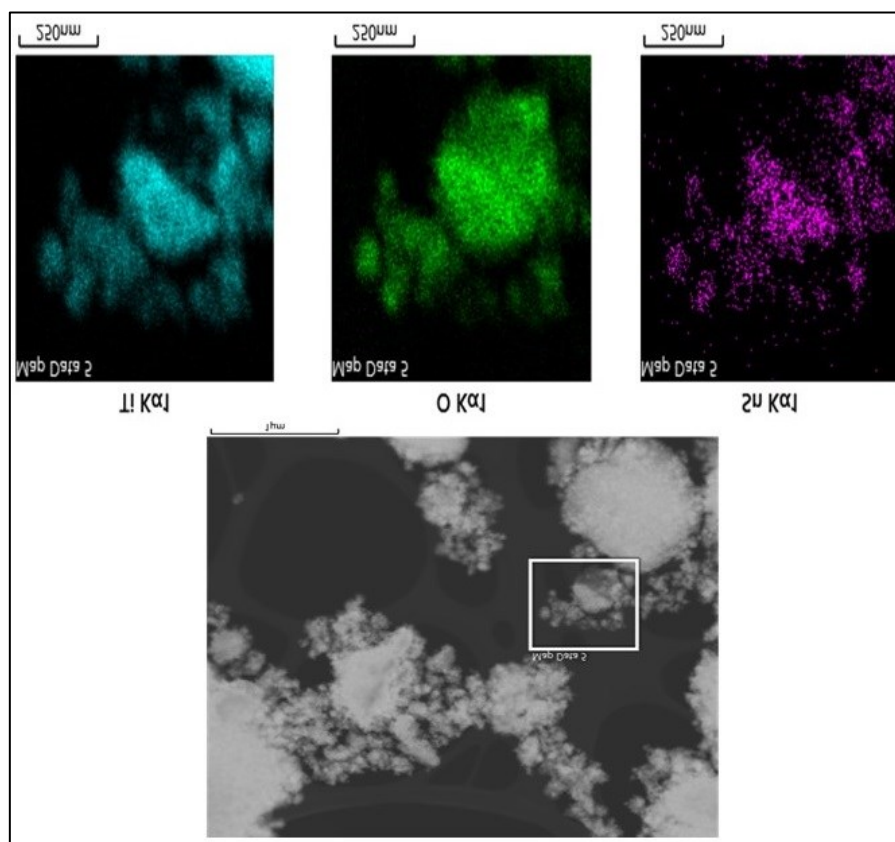


Figure 9. 13. S-TEM elemental mapping $0.5\text{Sn}:1\text{TiO}_2$.

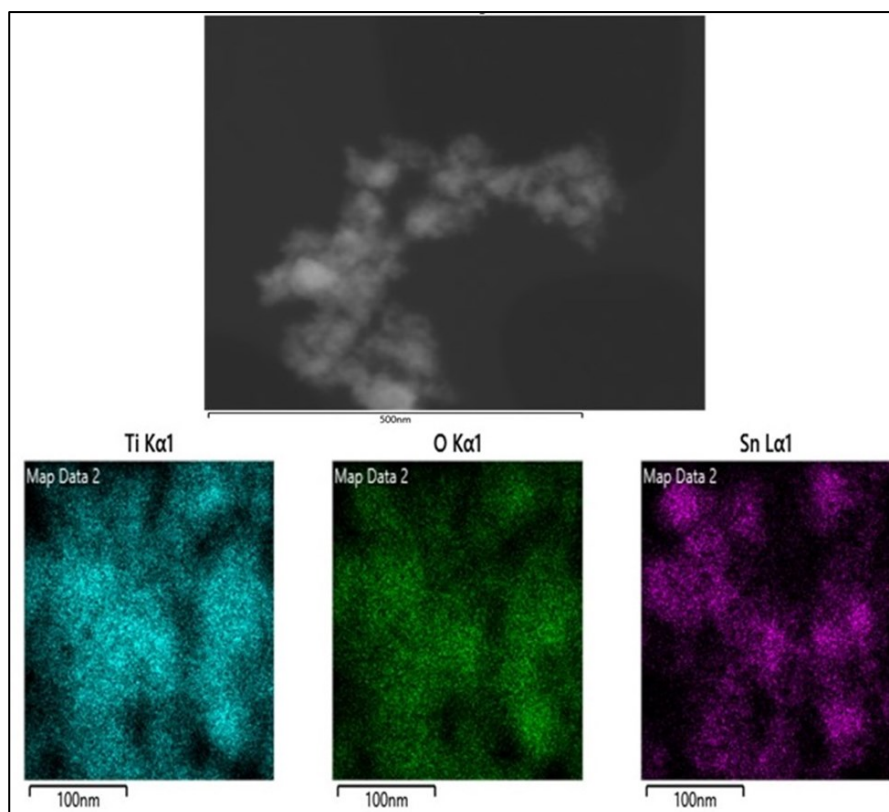


Figure 9. 14. S-TEM elemental mapping analysis of SnO_2 .

9.3.5 Characterization of the surface functional groups

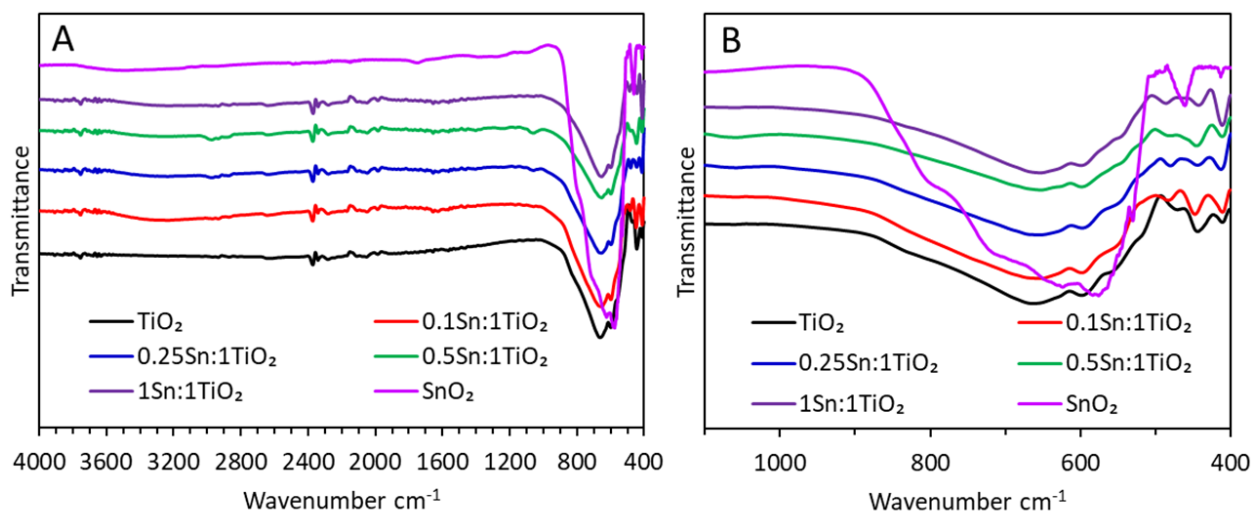


Figure 9. 15. FTIR spectrum of the prepared Sn doped TiO_2 photocatalysts.

Table 9. 9. Observed shift in the functional groups wavelength of TiO_2 after Sn doping.

	TiO_2	0.1Sn:1 TiO_2	0.25Sn:1 TiO_2	0.5Sn:1 TiO_2	1Sn:1 TiO_2
Wavenumber	410.11	410.35	413.44	412.1	411.83
	443.29	447.23	444.77	446.25	443.91
	470.18	482.89	480.91	481.41	486.46

9.4 Thermal diffusion (TD) synthesis method

9.4.1 XRD characterization

XRD was performed for the Sn:TiO₂ synthesized through the thermal diffusion method. The results shown in Figure 9.16 exhibit the characteristic peaks of rutile TiO₂ at $2\theta = 27.4, 36, 39.2, 41.13, 43.93, 54.23, 56.55, 63.6, 64, 69.6, 72.25^\circ$ for all Sn:TiO₂ doping ratios.

Commercial TiO₂ anatase was used as a starting material, and the results show that after TD there was a complete anatase-to-rutile phase transformation. The reason beyond this is the used high calcination temperatures (973 K and 1,173 K) which promotes the anatase-to-rutile transformation because of the thermodynamic meta-stability of the anatase phase which possess a higher surface energy and smaller crystals compared with the rutile phase [101].

Usually, the phase transition occurs in a temperature range 400-1200° C depending on the synthesis conditions time, surface area, impurities, and the presence of dopants. The anatase-to-rutile transformation is an irreversible nucleation and growth process, which is not instantaneous because of its time dependent reconstructive nature [257].

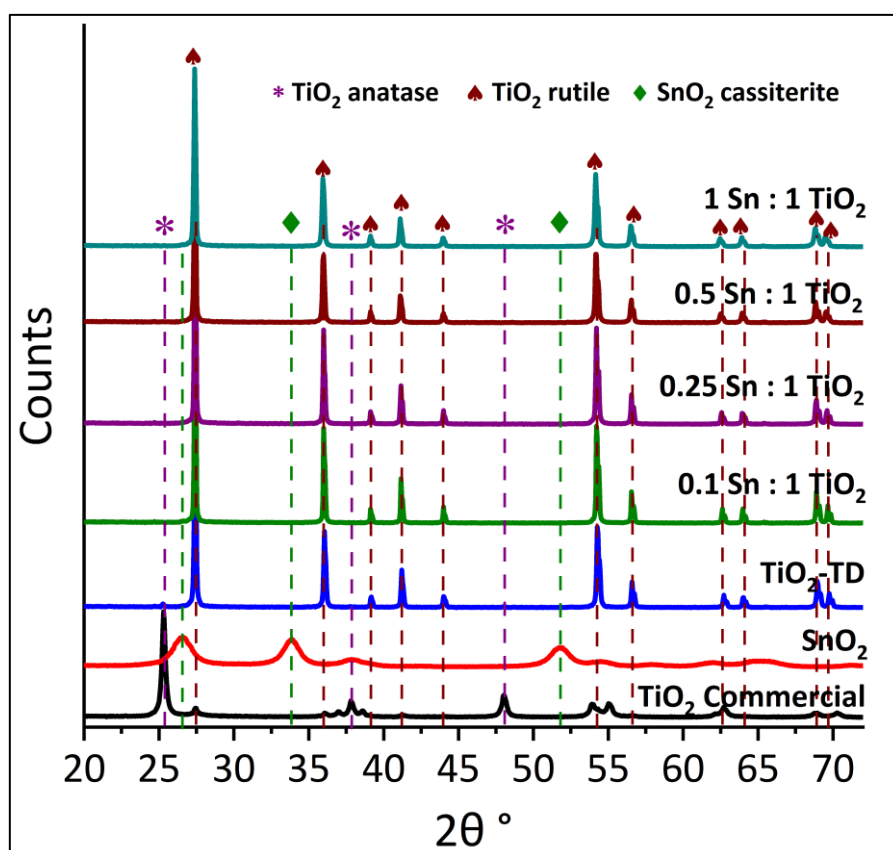


Figure 9. 16. XRD patterns for thermal-diffusion synthesized Sn-TiO₂ samples and the precursor commercial TiO₂ anatase.

Unlike the SG synthesis, modelling of XRD data using GSAS-EXPGUI software showed that cassiterite SnO_2 wasn't formed, the modelling further proved the complete phase transformation of anatase TiO_2 to rutile TiO_2 . The narrow sharp peaks (Figure 9.3) suggest formation of larger crystals than the anatase TiO_2 starting material, and larger crystals than those formed in the SG samples. This observation was further proven by the crystal size calculation using GSAS-EXPGUI modelling (Fig. 8.4), which show a rise in the crystal size after doping through thermal treatment. In the Sn TD samples, the calculations show a general decline in crystal size at higher Sn^{4+} doping content, whereas the average unit cell volume expanded up to 1.45% in the 1:1 Sn/Ti sample, confirming the influence of Sn incorporation inside the rutile TiO_2 lattice. This expansion in the unit cell volume is similar to that occurred in the SG synthesis (1.3%). Unlike the SG samples, a separate SnO_2 cassiterite phase was not observed in the TD samples, and hence no lattice parameters for this phase were derived.

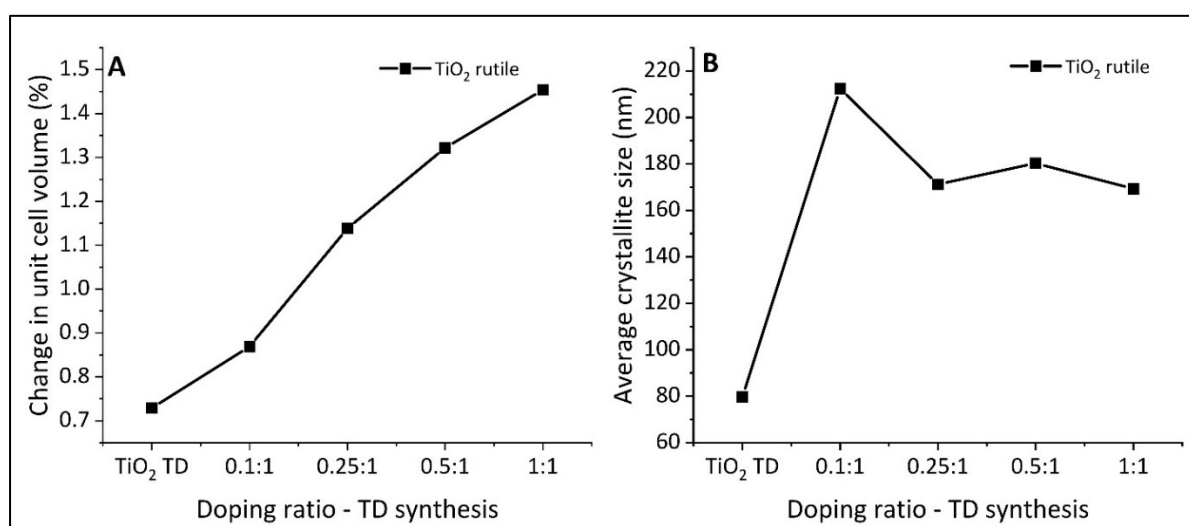


Figure 9. 17. Average crystal size and change in unit cell volume in the thermal diffusion synthesized Sn- TiO_2 .

9.4.2 Raman spectroscopy characterization for TD Sn doped TiO_2

In TD synthesis, Raman spectra (Figure 9.5) confirms the anatase to rutile phase transformation, where no anatase peaks were observed, while the fundamental vibrational symmetry modes of TiO_2 rutile were observed at 143.23 , 237.8 cm^{-1} , 442.4 cm^{-1} and 610.33 cm^{-1} [188]. The characteristic band of SnO_2 cassiterite at 632 wasn't observed, in line with XRD findings, suggesting a $\text{Ti}_x\text{Sn}_x\text{O}_2$ solid solution was formed [188]. A red shift of the 143.23 cm^{-1} rutile band was observed in the TD series, which is possibly caused by a particle size increase or oxygen vacancies due to higher calcination temperature [211].

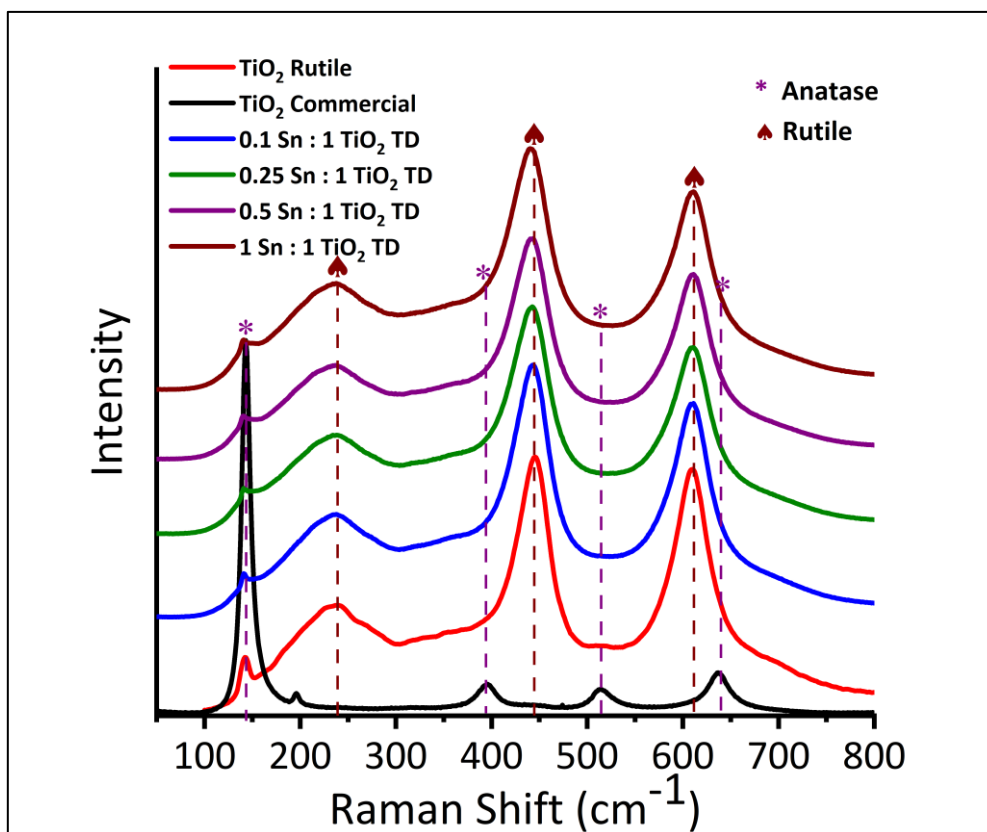


Figure 9. 18. Raman shift for TD prepared catalysts.

9.4.3 Bandgap of the TD Sn doped TiO₂

The results shown in Figure 9.6 revealed that the band gap of the anatase and rutile TiO₂ were 3.2 eV and 3 eV respectively. There was a steady decline in the bandgap values on Sn doping content increases where it decreased from 3.2 eV (in pure TiO₂) to 2.92 eV (in 1 Sn: 1TiO₂). This red shift in the bandgap (shift in the absorption edge slightly towards the visible light) can be attributed to the internal strain due to the unit cell expansion which led to creation of new energy levels [218]. A significant shift in the VB edge (Figure 9.6) with Sn doping was observed with increasing Sn doping ratio which results in in a more positive valence. This alters the fermi level positions (zero binding energy) and develop tunable oxygen vacancies energy states between the maximum valence band (MVB) and the minimum conduction band (MCB) [103,220].

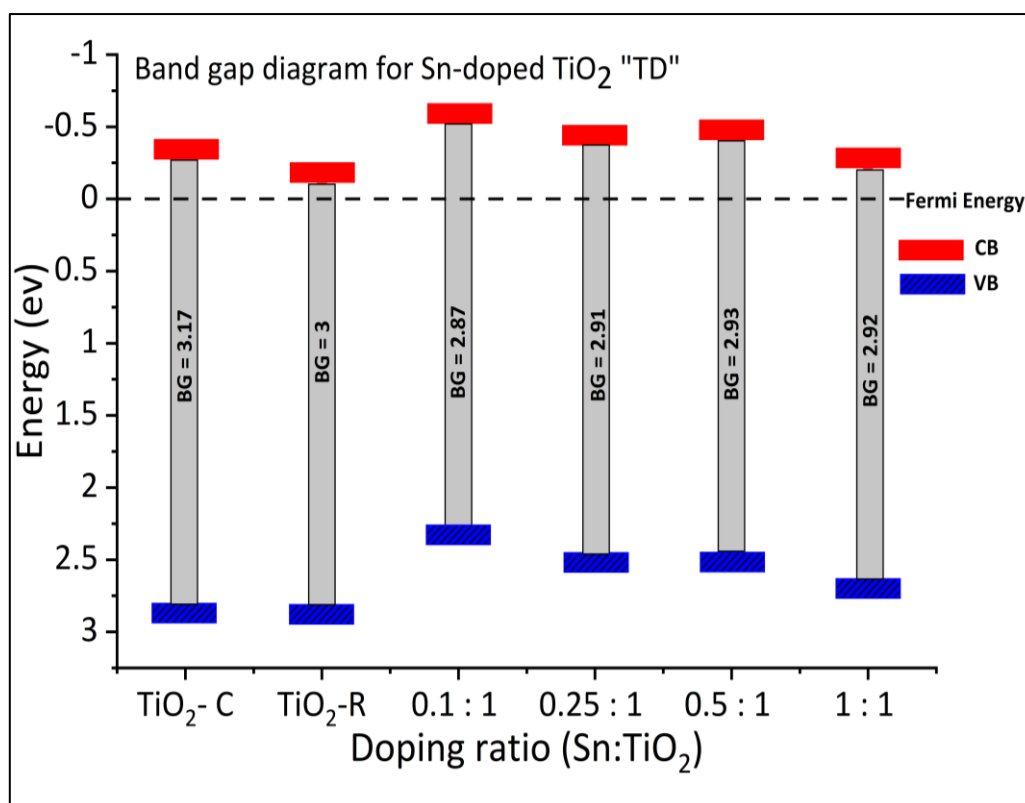


Figure 9. 19. XPS valence band edge analysis for TD synthesised photocatalysts.

9.4.4 XPS Surface analysis for TD Sn doped TiO

The chemical composition of the surface was studied using X-ray photoelectron spectroscopy (XPS) clearly deduced that all prepared catalyst surface consists of Sn, Ti, O and C atoms only (Figure 9.7), Sn peaks are less intense in the TD synthesis compared to SG synthesis in chapter 5. This is mainly attributed to the Sn loss because of the high synthesis temperature. The high-resolution peak deconvolution of the surface atoms was fitted using CASA software for each sample as presented in Figure (8.8 to 8.11).

However, in the TD synthesis the binding energies of the Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2} doublet slightly decreased respectively from 458.56 and 64.29 eV (in the commercial TiO₂) to 458.5, 464.26 eV in (1Sn:1TiO₂). These slight changes in the binding energies is probably due to the shift in the Fermi levels.

The chemical composition of the surface environment of prepared catalysts was analysed using CASAXPS fitting software and the summarised in Table 9.10. Sn:Ti ratio was found to increase with the doping ratios and the oxidation state of Sn and Ti were Sn⁴⁺ and Ti⁴⁺.

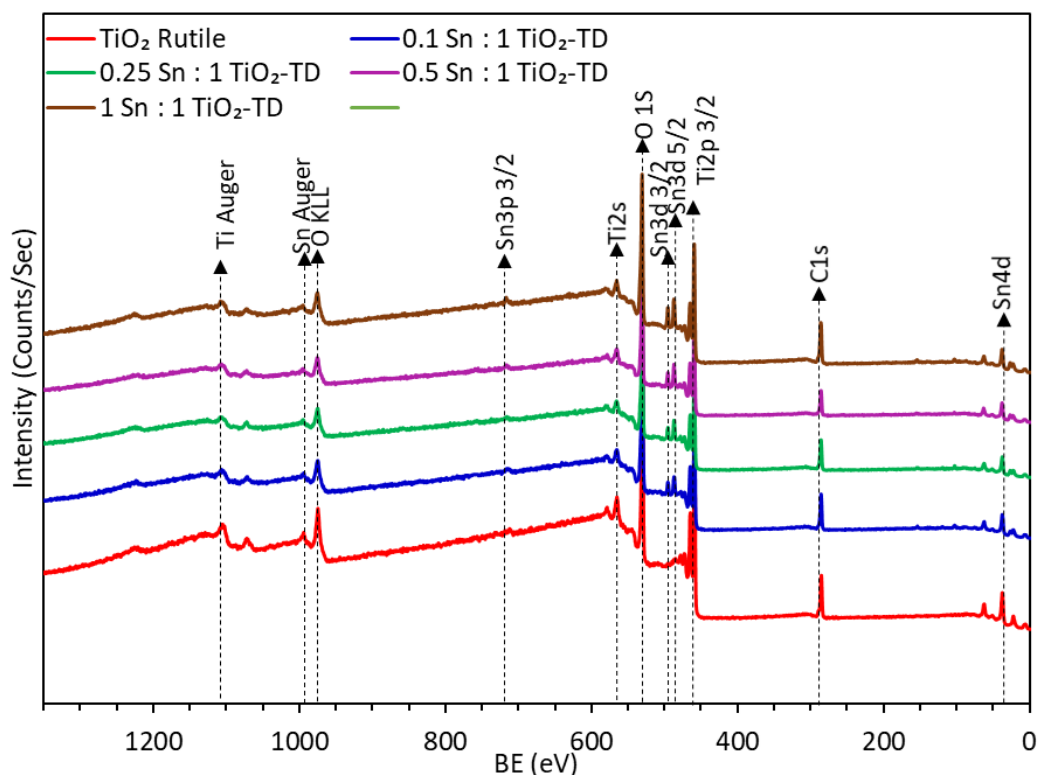


Figure 9. 20. XPS survey spectra showing the surface elemental composition.

Table 9. 10. XPS surface environment analysis of thermal diffusion synthesised photocatalysts.

	Abundance, %					
	TiO ₂ - Comm	TiO ₂ Rutile	0.1 Sn : 1 TiO ₂ -TD	0.25 Sn : 1 TiO ₂ -TD	0.5 Sn : 1 TiO ₂ -TD	1 Sn : 1 TiO ₂ -TD
C (C-C)	23.4	16.5	19.5	19.6	17.1	23.0
C (C-O)	4.1	2.9	2.9	2.9	2.3	4.8
C (C=O)	3.5	2.8	1.5	1.2	1.1	2.4
C (total)	31.0	22.2	23.9	23.7	20.4	30.2
Ti ⁴⁺ (TiO ₂)	17.0	19.0	16.6	16.9	18.1	14.4
Sn ⁴⁺ (SnO ₂)	0.0	0.2	1.2	1.4	1.8	1.7
O (M-O ²⁻)	41.9	50.7	45.4	46.2	48.7	38.8
O (M-OH)	6.7	6.1	7.5	6.9	4.1	8.8
O (C-O, C=O)	3.3	1.8	5.3	4.9	6.9	6.2
O (total)	52.0	58.7	58.2	58.0	59.7	53.7
Cl ⁻ (M-Cl)	0.0	0.0	0.0	0.0	0.0	0.0
As (As ³⁺)	0	0	0	0	0	0
Total	100.0	100.0	100.0	100.0	100.0	100.0
Sn/Ti	0.00		0.07	0.08	0.10	0.11

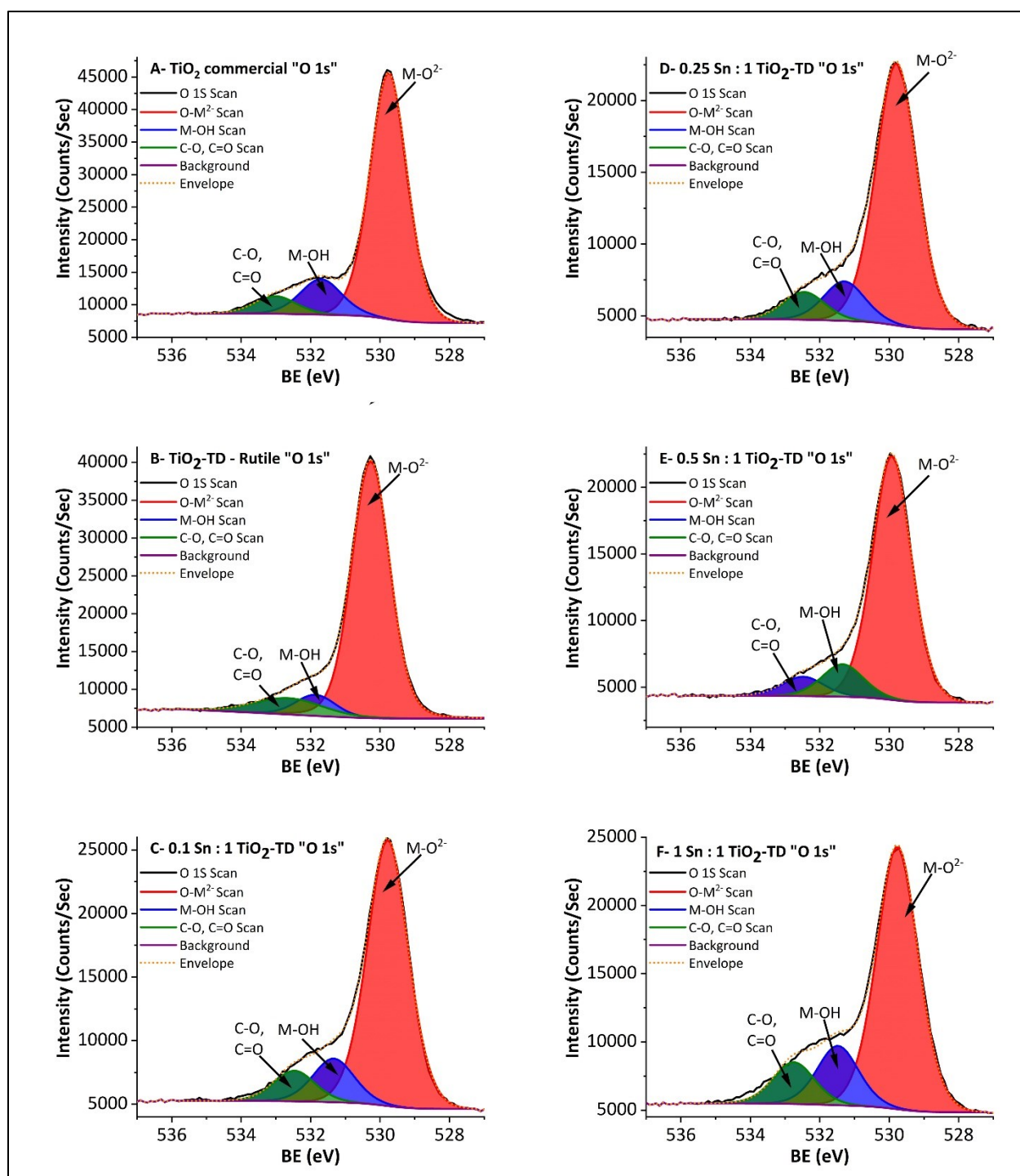


Figure 9. 21. High-resolution XPS of O1s peak in (A) TiO₂, (B) 0.1Sn:1TiO₂, (C) 0.25Sn:1TiO₂, (D) 0.5Sn:1TiO₂, (E) 1Sn:1TiO₂, (F) SnO₂ (Thermal diffusion synthesis).

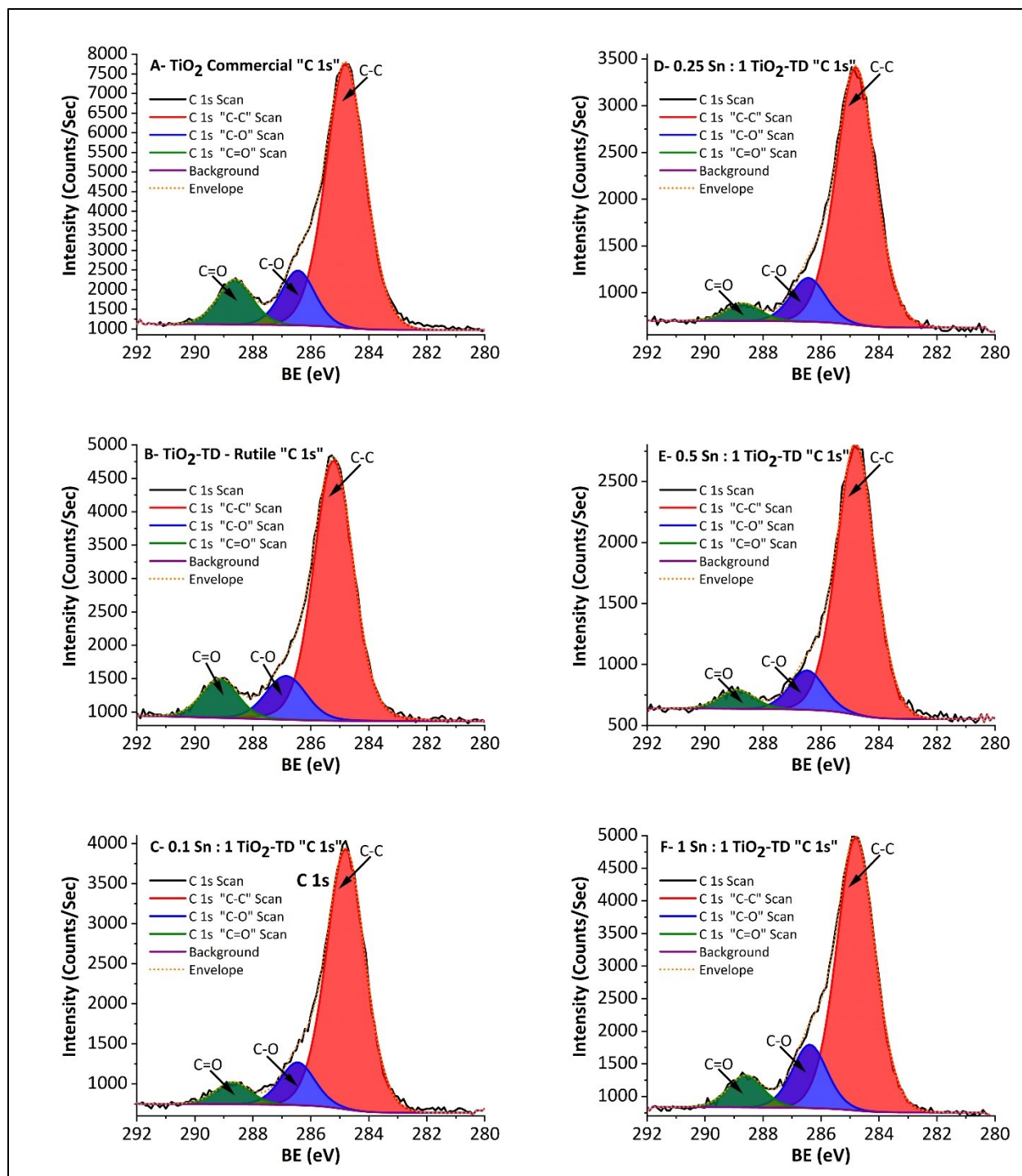


Figure 9. 22. High-resolution XPS of C1s peak in (A) TiO₂, (B) 0.1Sn:1TiO₂, (C) 0.25Sn:1TiO₂, (D) 0.5Sn:1TiO₂, (E) 1Sn:1TiO₂, (F) SnO₂ (Thermal diffusion synthesis).

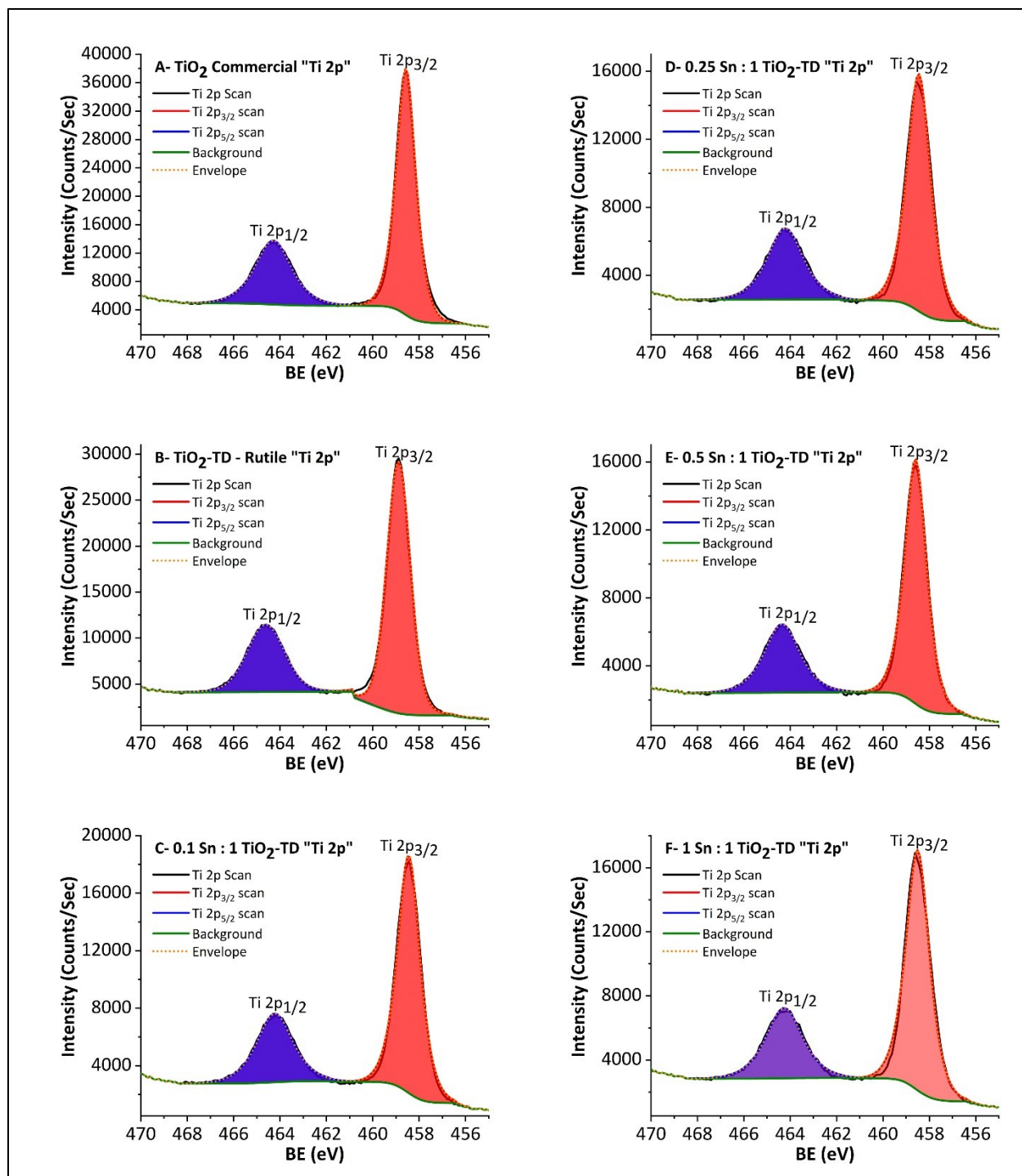


Figure 9. 23. High-resolution XPS of Ti2p peak in (A) TiO₂, (B) 0.1Sn:1TiO₂, (C) 0.25Sn:1TiO₂, (D) 0.5Sn:1TiO₂, (E) 1Sn:1TiO₂, (F) SnO₂ (Thermal diffusion synthesis).

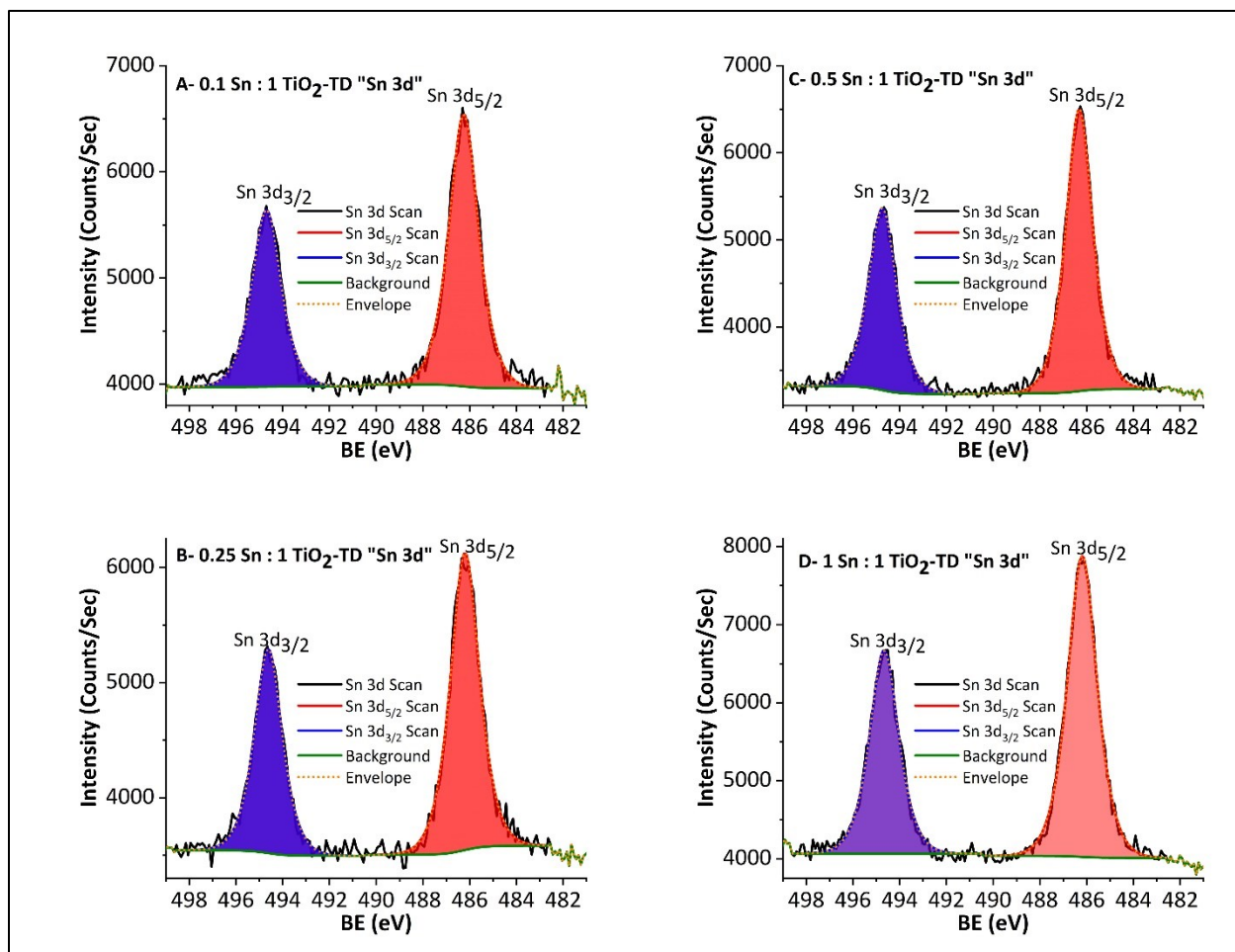


Figure 9. 24. High-resolution XPS of Sn3d peak in (A) TiO_2 , (B) $0.1\text{Sn}:1\text{TiO}_2$, (C) $0.25\text{Sn}:1\text{TiO}_2$, (D) $0.5\text{Sn}:1\text{TiO}_2$, (E) $1\text{Sn}:1\text{TiO}_2$, (F) SnO_2 (Thermal diffusion synthesis).

9.4.5 Outermost surface analysis

LEIS spectra for TD Synthesis (Figure 9.25) show that as the amount of surface Sn increases as the Sn:Ti doping ratio increases. Surface stoichiometries for Sn and Ti in different doped samples were calculated from LEIS measurements using the relative ratios of the peak areas corrected for scattering cross-sections.

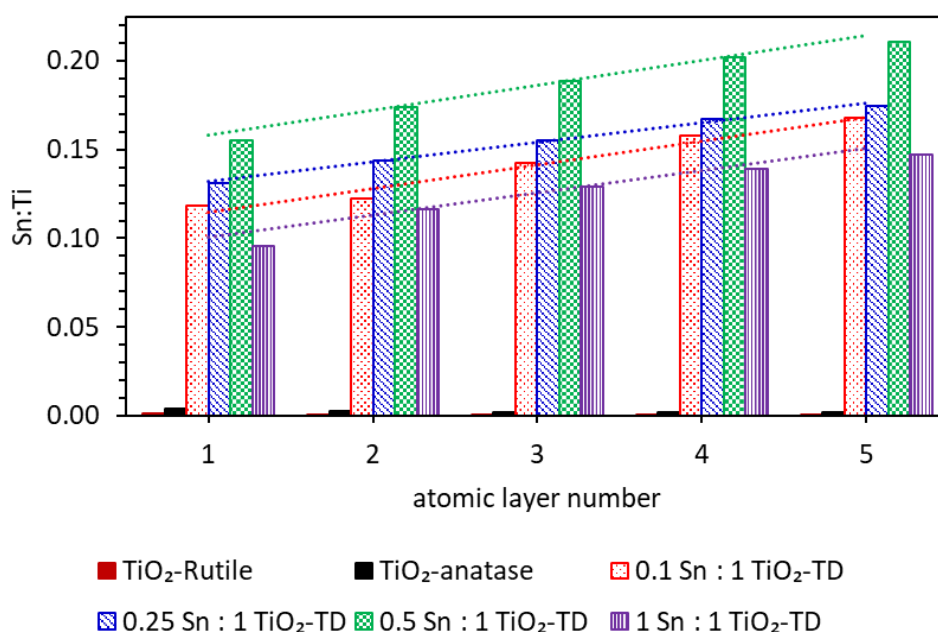


Figure 9. 25. Average Sn:Ti ratios in each individual atomic layer in different prepared samples (LEIS depth profiling data using ion dose = $\sim 5.3 \times 10^{15}$ ions/cm²) (in thermal diffusion).

9.4.6 Surface bulk analysis

Figure 9.26 shows the elemental Sn:Ti molar and mass ratios obtained by EDX analysis for the thermal diffusion synthesis. Like the SG synthesis, the Sn:Ti mass ratios is higher than the molar ratios and generally it is less than the calculated amounts during preparation. Interestingly, the SG method exhibits a higher doping yield than the TD synthesis, where for Sn_{0.1, 0.25, 0.5, 1}:Ti₁ doping the values were Sn_{0.098, 0.149, 0.188, 0.366}:Ti₁ in case of SG, and Sn_{0.022, 0.031, 0.048, 0.06}:Ti₁ in the case of TD. The lower doping ratios from the TD method is attributed to the high annealing temperature used, which may cause SnCl₄ to evaporate during synthesis.

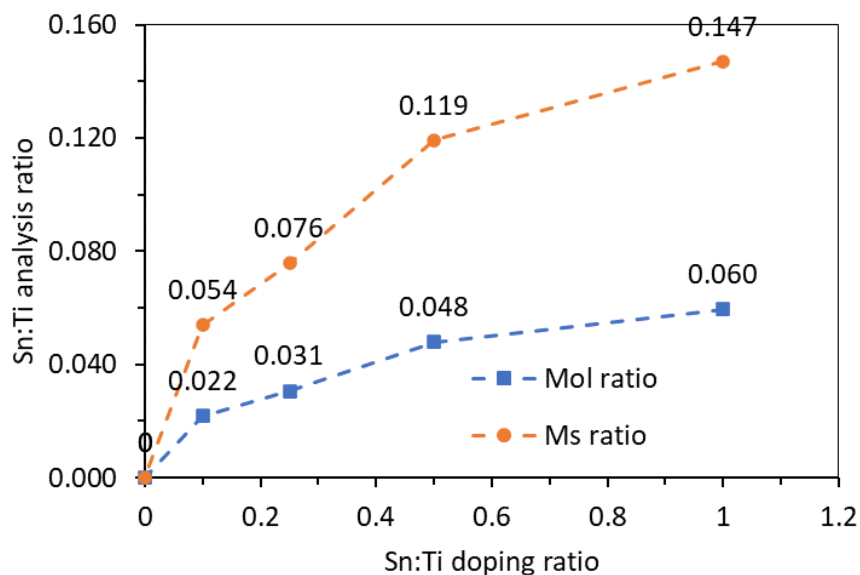


Figure 9. 26. Calculated molar and mass ratios in TD synthesis using EDX analysis

9.4.7 Investigation of Surface morphology

In the TD synthesis method, the main findings in SEM micrographs in Figure 9.27 reveal the commercial TiO_2 Fig. has well segregated spherical particles with diameter range (20 to 100 nm). After thermal treatment, the resulted rutile TiO_2 retained the well dispersed spherical particles with a slightly bigger particle size with diameters around 150 nm. The Sn doping resulted in aggregation and particles with irregular sizes and edges.

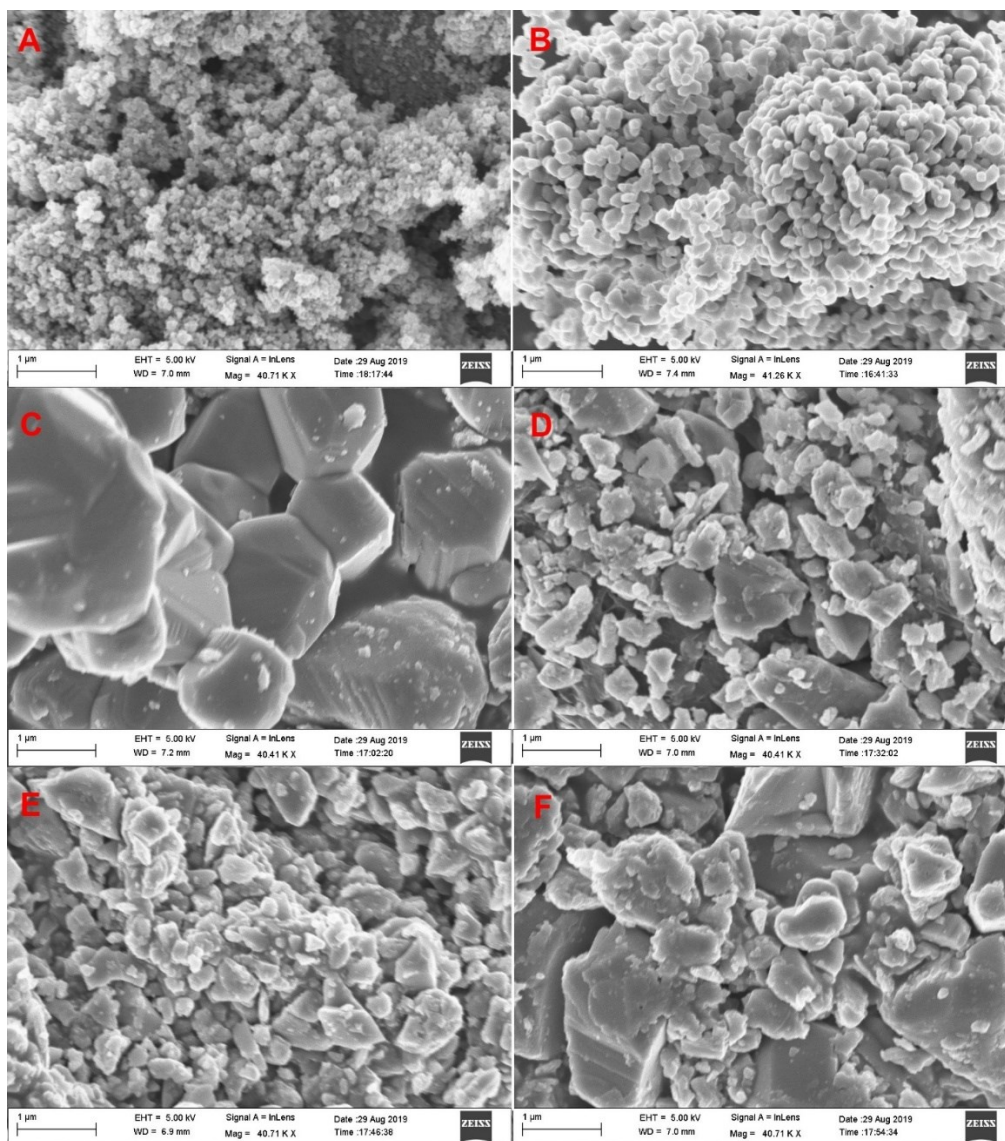


Figure 9. 27. SEM micrographs for thermal diffusion synthesized sample [A- TiO_2 commercial, B- TiO_2 rutile, C- 0.1 Sn : 1 S- TiO_2 , D- 0.25 Sn : 1 S- TiO_2 , E- 0.5 Sn : 1 S- TiO_2 , F- 1 Sn : 1 S- TiO_2].

9.4.8 characterization of the surface functional groups

FTIR spectra of TD samples (Figure 9.28) show a change in the lattice peaks ($400\text{--}600\text{ cm}^{-1}$), which are attributed to the change in crystal structure from anatase to rutile TiO_2 .

After heating at 1260°C , the number of bands at $400\text{--}600\text{ cm}^{-1}$ decrease, and shift in position, indicating a qualitative change in $\nu(\text{Ti-O-Ti})$ stretching vibration energy. It supported the fact of complete of anatase-to-rutile phase transformation [258].

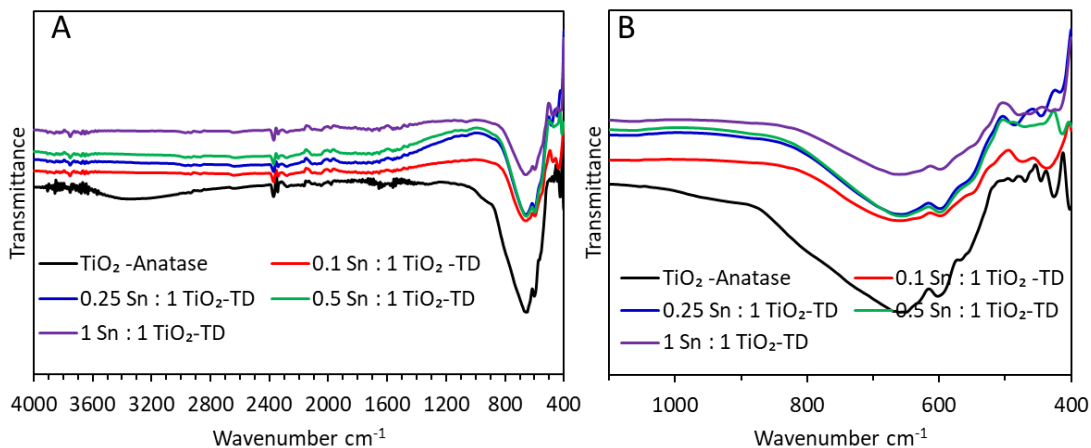


Figure 9. 28. FTIR of Sn-TiO₂ samples synthesized through thermal diffusion method.

9.5 PCO of As(III) over Sn doped TiO₂ via TD method

Compared with anatase TiO₂, the PCO of As(III) over Sn doped TiO₂ via thermal diffusion method do not show an improvement in the oxidation yield where the oxidation % are 24.7, 10.0, 10.7, 3.6, 3.0, 3.8, 3.7 and 82.9 for anatase TiO₂, SnO₂, rutile TiO₂, 0.1Sn:1TiO₂-TD, 0.25Sn:1TiO₂-TD, 0.5Sn:1TiO₂-TD, 1Sn:1TiO₂-TD and 1Sn:1TiO₂-G respectively

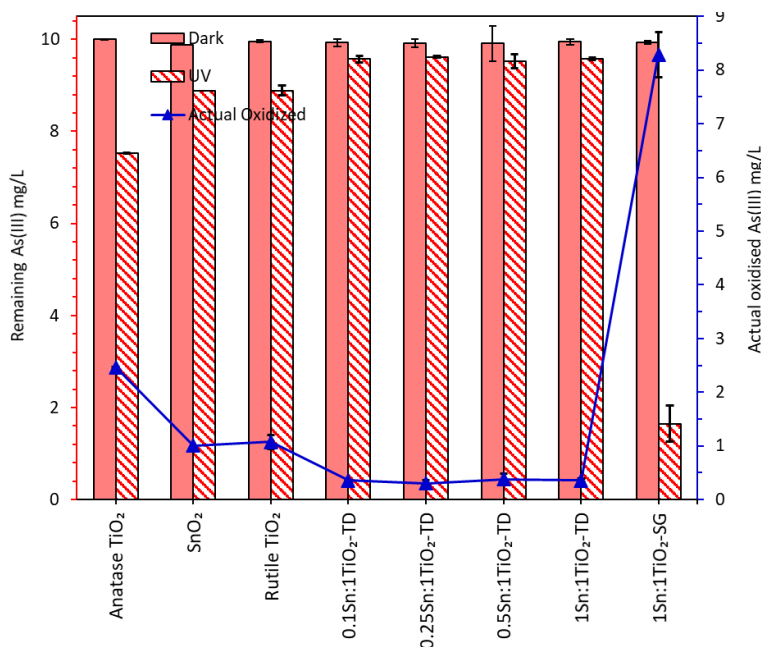


Figure 9. 29. PCO of As(III) over anatase TiO₂, SnO₂ and Sn doped TiO₂ via thermal diffusion method showing the decrease in As(III) in dark and under UV, (0.5 g/L of photocatalyst with 10 mg/L As(III) at pH 7.4, sample volume= 100 ml, distance between light to solution surface = 1.8 cm), Error bars represents the standard deviation.