



Significantly boosted photoelectrochemical water splitting performance by plasmonic enhanced Hematite@MOF composite photoelectrodes

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ABSTRACT

Hematite as a catalyst for photoelectrochemical water splitting offers huge potential, due to its high chemical stability, great abundance, and low cost. However, the low water oxidation kinetics and poor charge transportation have hindered progress towards the manufacture of practical water splitting devices. To tackle these problems, a visible light responsive metal-organic framework (MOF) polyhedral zeolitic imidazolate (ZIF-67), and optimised plasmonic Ag nanorods were incorporated into hematite nanostructures to form a three-component heterojunction photoelectrode. The designed photoanode showed dramatically improved light harvesting in the visible range and enhanced charge transport. A mechanistic investigation allowed the deconvolution of the enhanced performance pathways. First, the Hematite@ZIF-67 core-shell p-n junction enables facile charge carrier transfer between ZIF-67 and hematite. In addition, ZIF-67 also provides active sites for water oxidation and boosts surface oxygen evolution reaction (OER) kinetics. Guided by finite-difference time-domain (FDTD) modelling, Ag nanorods with optimised aspect ratio were incorporated between ZIF-67 and hematite. The Ag nanorods facilitate broadband light absorption and surface charge injection, induced by near-field excitation enhancement and plasmonic resonance energy transfer (PRET) pathways. The design and addition of ZIF-67 and Ag nanorods result in superior performance for a hematite-based photoanode for photoelectrochemical (PEC) water oxidation.

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1. Introduction

Photoelectrochemical (PEC) water splitting has attracted attention as a means to address global concerns about energy supply. It converts solar energy to green hydrogen fuel, which can be used in a decarbonized hydrogen energy system [1,2]. Pioneers started research on PEC water splitting based on TiO₂ in the 1970s [3,4]. However, so far, no single semiconductor device has been commercialised. An energy conversion efficiency in excess of 10% under AM1.5 G radiation is a benchmark for commercialisation. Semiconducting oxides currently face challenges such as insufficient light absorption, poor charge separation, high charge recombination and high cost.

Hematite has been extensively explored for PEC water splitting.

As a semiconductor photoanode material, it offers the advantages of various simple synthesis routes, good stability in electrolytes under OER conditions, low cost, earth abundance and non-toxicity [5–7]. More importantly, hematite, with a band gap of 2.2 eV, fits in perfectly with the energetic requirement of the water splitting reaction (1.9–2.3 eV) and can theoretically absorb 40% of the solar spectrum [8,9]. However, hematite suffers from an extremely short hole diffusion length of 2–4 nm and poor water oxidation kinetics, which hinder the exploitation of hematite in industrial applications [10].

Recently, semiconducting oxides with enhanced performance in water splitting have been reported by integrating MOFs, hybrid inorganic-organic 3-dimensional (3D) materials constructed from metal nodes coordinated with organic linkers [11]. In the past decade, more than twenty thousand MOFs with different components, structures and functionalities have been studied, such as MILs, UiOs and ZIFs [11]. MOF photoanodes generally provide

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negligible photocurrent densities compared to traditional semiconductor oxides, owing to the low conductivity of MOF particles [12]. Nevertheless, MOF-semiconductor heterojunctions or composite structures have been investigated [13,14]. Zhan et al. [58] fabricated a ZIF-8@ZnO nanorod array structure and showed an enhanced selective photoelectrochemical response, which could be applied in sensors for H_2O_2 detection. However, in this study, ZIF-8 did not enhance visible-light harvesting.

In an ideal MOF-semiconductor hybrid PEC system, MOF should improve the light harvesting capability and charge separation efficiency. Yoon et al. prepared nanorods (NRs) containing a $\text{NH}_2\text{-MIL-125(Ti)/TiO}_2$ heterojunction, photoanodes formed from the material showed a 2.7 times photocurrent density enhancement, induced by promoted light harvesting and smart type-II band gap alignment [15]. Dong et al. fabricated electrodes of a $\text{Fe}_2\text{O}_3\text{:Ti/NH}_2\text{-MIL-101(Fe)}$ core/shell composite and reported a 2.3 fold photocurrent density boost to that of pristine Fe_2O_3 [16]. $\text{NH}_2\text{-MIL-101(Fe)}$ improved the light harvesting, charge separation and hole injection efficiency. Compared to the low water oxidation kinetics of hematite, Co-MOFs containing Co ion clusters could promote the oxygen evolution reaction [17]. Herein, visible light responsive MOFs like ZIF-67 have the potential to simultaneously improve light absorption, charge separation and surface oxygen evolution reaction. Several ZIF-67-related composites have been reported as photoanodes for visible-light-driven PEC water splitting, including ZnO/ZIF-67 [18], $\text{TiO}_2\text{/ZIF-67}$ [19], $\text{Co-MOF}/\alpha\text{-Fe}_2\text{O}_3$ [20], Co-MOF@TiFe [21], $\text{Ce-Fe}_2\text{O}_3\text{/ZIF-67}$ [22], $\text{Sn/Ti co-doped } \alpha\text{-Fe}_2\text{O}_3\text{/ZIF-67}$ [23], $\alpha\text{-Fe}_2\text{O}_3\text{/ZIF-67/PMS}$ [24] and $\text{Fe}_2\text{O}_3\text{/MIL-88B@ZIF-67}$ [25]. However, their incident-photon-to-current efficiencies (IPCE) at ~ 600 nm were below 2%, which indicates that the visible light absorption enhancement of the photoanode was very limited. In this study, the plasmonic nanostructure coupling strategy is employed to enhance the photoelectrode activity by plasmonic energy transfer from metal to hematite.

Plasmonic nanostructures of gold, silver, copper, and aluminium are the most common and effective plasmonic materials [26,27]. The plasmonic effect is a process in which the metal nanostructures absorb the incident light and temporarily store the energy in either localized surface plasmon resonances (LSPR) or surface plasmon polaritons (SPP) [26]. This energy can subsequently transfer non-radiatively or radiatively to surrounding media on a time scale from 1 fs to several ns [27]. There are three main mechanisms of plasmonic energy transfer from a metal to a semiconductor, including plasmon-induced resonance energy transfer (PRET), hot electron injection (HEI) and light scattering/trapping [2,28].

Binary hybrid plasmon-semiconductor composite photoelectrodes have been investigated [29]. To illustrate, Momeni et al. decorated Fe_2O_3 nanorods with silver nanoparticles and achieved a 2.5-fold increase in photocurrent, which was attributed to more efficient charge carrier separation and visible light sensitization by Ag nanoparticles [30]. In contrast, research on ternary semiconductor-metal-MOF structures is still in its infancy, despite its high potential. Dou et al. reported ZnO@M@ZIF-67 array composites for PEC water splitting with excellent catalytic performance [31]. Cui et al. prepared $\text{Ag/NH}_2\text{-MIL-125(Ti)/TiO}_2$ and measured a photocurrent density which was 4.42 times higher than that of pristine TiO_2 [32]. These works claimed the surface plasmon resonance (SPR) effect from metal nanoparticles contributed to the enhancement of PEC water splitting, yet the deconvolution of plasmonic effects was not discussed in detail. Thus, an effective strategy to improve the PEC performance of hematite is to integrate two or even three different materials to form a hybrid photoelectrode. In this study, a three-component composite, including a metal-organic framework (MOF), plasmonic Ag nanorods, and

hematite nanorods, are designed and fabricated to boost PEC water splitting performance.

Herein, ternary $\alpha\text{-Fe}_2\text{O}_3\text{:Ag@ZIF-67}$ composite photoelectrodes for PEC water splitting were designed and fabricated. The introduction of ZIF-67 improved the visible light absorption, charge-transport and surface reaction kinetics. Ag nanorods with various aspect ratios were synthesised. The introduction of Ag nanorods improved the surface charge transfer and generated a plasmonic effect. Type-II Ag nanorods with an aspect ratio of ~ 2.7 have a longitudinal plasmonic response in the visible to near-infrared (NIR) range and below the band edge of hematite, these may enhance the PEC performance via the HEI effect. While type-I Ag nanorods with an aspect ratio of ~ 1.8 have a longitudinal plasmonic response centred at ~ 480 nm. These Ag nanorods were chosen to promote light absorption and improve electron-hole pair generation, via PRET pathways. The photocurrent density of $\alpha\text{-Fe}_2\text{O}_3\text{:Ag-I@ZIF-67}$ was higher and increased by 2.8-fold, from 0.36 to 1.04 mA/cm^2 at 1.23 eV vs RHE. To gain insight into the enhanced performance, IPCE characterisation, together with modelling data, highlighted the plasmonic properties of the designed Ag nanorods and demonstrated a better energy transfer between silver and hematite/ZIF-67. PRET pathway to enhanced photocurrent density is the main pathway among those three widely proposed mechanisms. Finally, an energy diagram was proposed to illustrate the PEC water oxidation process.

2. Experimental section

2.1. Materials

Reagents were obtained as follows: Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), sodium nitrate (NaNO_3 , 99%), 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%), Cobalt (II) nitrate hexahydrate ($\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), hydrochloric acid (HCl, 37%) were bought from Sigma-Aldrich and used as received without further purification. FTO glass substrates (F doped SnO_2 coated glass) were purchased from Sigma-Aldrich and cut into 1.5 cm $\times$ 3.3 cm size.

2.2. Synthesis

2.2.1. Preparation of hematite nanorod arrays

Hematite nanorod arrays were grown on 1.5 cm $\times$ 3.3 cm FTO glass substrates via a hydrothermal method. Briefly, FTO glass substrates were ultrasonically cleaned in isopropanol, acetone and Milli-Q water, respectively. The non-conducting sides of the FTO glass pieces were covered by Kapton polyimide tape. In a typical synthesis, 4.050 g Iron (III) chloride hexahydrate, together with 8.499 g sodium nitrate were dissolved in a beaker containing 100 ml deionized (DI) water and stirred for 30 min. Then, 139 μl hydrochloric acid was added to the solution by pipette and further stirred for 5 min. Eight FTO substrates were vertically aligned in the beaker and fully immersed in the reaction solution. The beaker was transferred to an oven and heated for 4 h at 100 $^\circ\text{C}$. The samples were then cooled to room temperature. To obtain hematite nanorods, samples were annealed in air at 550 $^\circ\text{C}$ for 4 h, and further annealed at 800 $^\circ\text{C}$ for 10 min, followed by cooling down to room temperature. The colour of the samples changed from yellow to red, indicating the growth of hematite nanorod arrays on the FTO substrates.

2.2.2. Preparation of ZIF-67 coated hematite nanorod array

The as prepared hematite nanorod arrays were washed in DI water and dried in the air before usage. Typically, 0.1 g of pulverised 2-Methylimidazole (2-mim) powder was evenly covered onto the

surface of each α -Fe₂O₃ array sample. The samples were transferred to an oven and annealed at 155 °C for 1 h, followed by cooling down to room temperature. Next, the samples were washed carefully with methanol and dried in air. These steps above are surface modification processes. After the surface modification, each sample was set in a 100 mL autoclave, conducting side down.

2.328 g of Co(NO₃)₂·6H₂O and 2.627 g of 2-methylimidazole were dissolved in 50 ml methanol, respectively. Equal volumes of these organic and metal precursor solutions were poured into the autoclave and transferred to an oven, heated at 60 °C for 12 h. The obtained electrodes were thoroughly washed with methanol and DI water and dried at 80 °C overnight.

2.2.3. Preparation of α -Fe₂O₃@Ag@ZIF-67 photoelectrodes

After the surface modification with 2-mim, 50 μ l of Ag nanorod solution, prepared according to a template method [33], was drop cast onto the hematite nanorod arrays samples and dried in air. The drop casting process was repeated three times and then the electrode was dried at 60 °C in a vacuum prior to further use. The growth of ZIF-67 on α -Fe₂O₃@Ag was as described above.

2.3. Advanced characterisation

Powder X-ray diffraction (XRD) patterns were obtained with an MPD PANalytical diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K Alpha instrument with a monochromated Al K α radiation source ($h\nu = 1486.6$ eV). The UV–Visible–near-infrared (UV–Vis–NIR) spectra of the samples were recorded using a Cary 5000 UV–Vis–NIR spectrometer. The morphology and structure of the samples were characterized by scanning electron microscopy at 5 kV (Zeiss Auriga SEM) and transmission electron microscopy at 200 kV (JEOL 2100Plus TEM). Energy-dispersive X-ray spectroscopy (EDS) attached to the SEM and STEM was applied to acquire compositional information at the nanoscale.

All PEC water splitting performance studies were performed on an Ivium CompactStat.h workstation in the dark and under AM 1.5G full-spectrum solar light with a power density of 100 mW/cm² at room temperature. The Photoelectrochemical performance measurements were performed in a three-electrode configuration, with

the photoanode as the working electrode, an Ag/AgCl (3 M KCl) as the reference electrode and a platinum foil (1.5 cm $\times$ 1.5 cm) as the counter electrode. A 0.1 M NaOH solution (pH = 13) was employed as the electrolyte. The potential was converted to a value vs RHE using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197V$$

Electrochemical Impedance Spectroscopy (EIS) was performed by employing an AC amplitude of 10 mV to the open-circuit voltage of a sample in the frequency range from 10⁵ to 10^{−1} Hz. The IPCE measurement was conducted with a homemade IPCE measurement system. The system consists of the Newport monochromator, SRS SR830 DSP lock-in amplifier and a 100 W xenon lamp. The IPCE data was measured under the same three-electrode system with PEC measurements.

3. Results and discussion

3.1. Morphological characterisation

A novel three-component photoelectrode was designed based on α -Fe₂O₃@Ag@ZIF-67 ternary structure. As shown in Fig. 1, the hematite nanorod arrays were first prepared on FTO glass. Then, the surface of the hematite was functionalised and pre-prepared Ag nanorods were incorporated. Finally, the α -Fe₂O₃@Ag@ZIF-67 core-shell structure was prepared by the growth of ZIF-67 onto α -Fe₂O₃@Ag.

The morphology of samples at each intermediate stage was characterised by scanning electron microscopy (SEM). As shown in Fig. 2a and b, worm-like hematite nanorods are identified and the electrode can be considered as a nanorod array, though not all the nanorods are vertically grown on the substrate. In Fig. S1, the samples are homogeneous at the nanoscale resolution but show some grain boundary-like patterns at a larger scale. Fig. 2c and e provide the cross-section and top view of α -Fe₂O₃@ZIF-67 samples, respectively. It is shown that dodecahedral ZIF-67 nanoparticles are dispersed on top of the hematite nanorod arrays. Comparing Fig. 2a with 2d, the roughness of the surface increases after ZIF-67 coating, which indicates a possible core-shell structure between ZIF-67 and hematite. Furthermore, the TEM image (Fig. S2) and TEM-EDS mapping (Fig. S3) confirm a uniform coating of ZIF-67 on

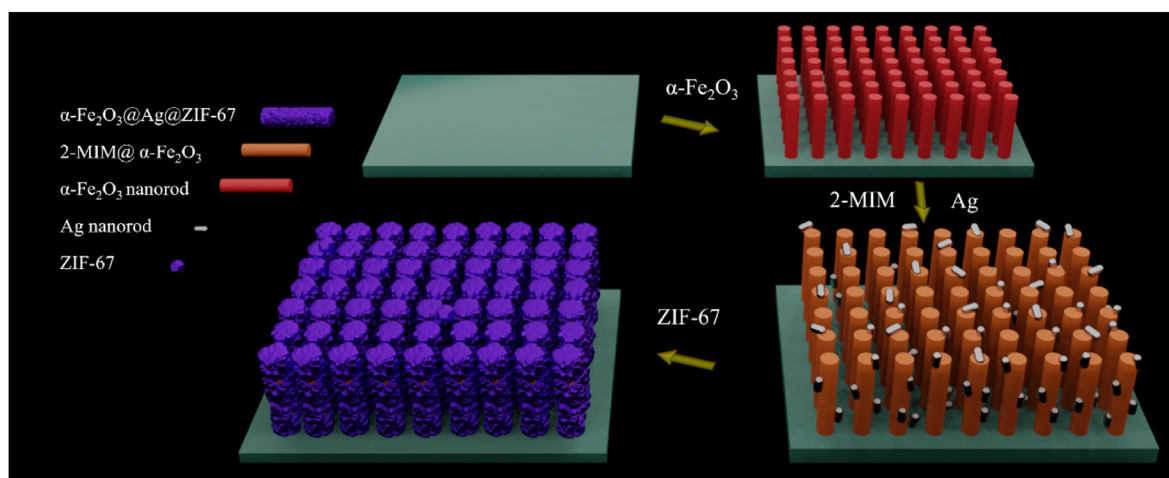


Fig. 1. Schematic workflow of α -Fe₂O₃@Ag@ZIF-67 photoanode for PEC water splitting. (i) FTO glass as substrate, (ii) growth of hematite nanorod arrays on FTO glass, (iii) hematite nanorod arrays were modified by 2-mim and then coated with pre-prepared silver nanorods, (iv) In-situ growth of ZIF-67 on α -Fe₂O₃@Ag, generated an outer layer of ZIF-67 packing α -Fe₂O₃@Ag and ZIF-67 nanoparticles on top of the composite nanorod arrays. The introduction of ZIF-67 significantly improves the charge carrier separation and transport. Ag nanorods provide plasmonic enhancement via PRET and light scattering.

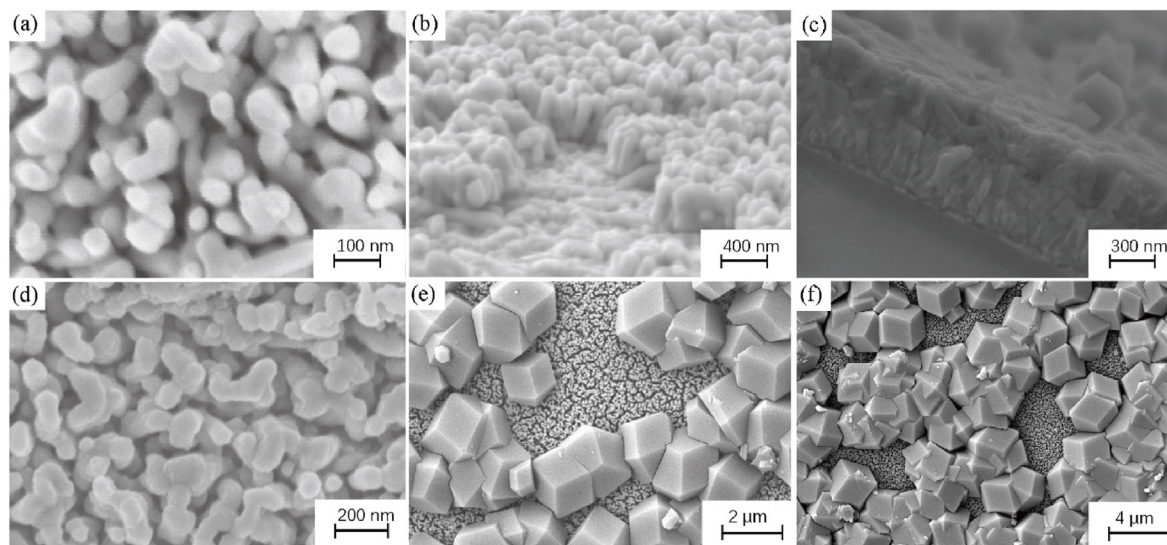


Fig. 2. Morphological characterisation for samples. SEM images of (a) hematite nanorods with high magnification, (b) side view of hematite nanorod array on FTO glass, (c) cross section view of α -Fe₂O₃@ZIF-67 on FTO glass, (d) α -Fe₂O₃@ZIF-67 with high magnification, (e) α -Fe₂O₃@ZIF-67 on FTO glass, (f) α -Fe₂O₃@Ag@ZIF-67 on FTO glass.

hematite nanorods. The thickness of MOF coating on the side of the hematite nanorod is 4.2 ± 1.5 nm (Fig. S4). On the other hand, Ag nanorods were small and placed between hematite and ZIF-67, thus could not be recognized in the SEM image (Fig. 2d). Therefore, α -Fe₂O₃@Ag@ZIF-67 samples were further characterised by TEM and STEM.

The dimension of Ag nanorods is displayed in Fig. 3a and b. The average aspect ratio of type-I Ag nanorods is ~ 1.8 and the dimensions are $26 \text{ nm} \times 46 \text{ nm}$. Due to the seed-mediated growth mechanism, type-I Ag nanorod sols contain some Ag nanospheres (Fig. 3a). The average aspect ratio of type-II Ag nanorods is ~ 2.7 and the dimension is $22 \text{ nm} \times 60 \text{ nm}$. The α -Fe₂O₃@Ag@ZIF-67 powders were scratched from FTO glass for TEM imaging. Fig. 3c–f and S5 show a random dispersion of dark small nanorods surrounding bigger nanorods and a thin layer of MOF around packing these nanorods. Fig. 3f, at higher magnification, focuses on the region within the red square of Fig. 3e, which is a spot constructed from Ag nanorods, hematite nanorods and ZIF-67 coating. The Ag nanorods are set between two hematite nanorods and were covered with a layer of ZIF-67. This thick composite structure blocks the possibility of generating a clear FFT pattern. Yet the TEM-EDS images present the element distribution of the composite samples (Fig. 3g–i). In Fig. 3g, Cobalt and silver are marked on the original morphological TEM image. The Ag nanorods, marked in yellow, are clear and show a random dispersion around central hematite nanorods, which agree with results from Fig. 3c and d. The homogeneous distribution of Co indicates a uniform coating of ZIF-67 on α -Fe₂O₃@Ag. Fig. 3h and i provide the distribution of Fe and O and suggest the larger nanorods are hematite. All the elements are identified in Fig. S6 and the Cu is ascribed to the TEM copper grid. Based on morphological characterisation, we conclude the successful fabrication of an α -Fe₂O₃@Ag@ZIF-67 core-shell structure.

3.2. Structural characterisation and optical properties

The phase structure of the prepared samples were characterised and confirmed by X-ray Diffraction Spectroscopy (XRD), shown in Fig. S7. Compared to the original FTO glass pattern, the characteristic diffraction peaks at 35.6° and 64.2° , corresponding to the (110)

and (300) planes of α -Fe₂O₃ (JCPDS No.33-0664), are observed in α -Fe₂O₃/FTO sample. Diffraction peaks at 7.3° , 10.4° , 12.7° , 16.3° and 18.0° could be assigned to the (011), (002), (112), (013) and (222) planes of ZIF-67 nanocrystals, are observed in both ZIF-67/FTO, α -Fe₂O₃@ZIF-67/FTO, α -Fe₂O₃@Ag@ZIF-67 samples. Despite the small amount of Ag nanorods, the diffraction peaks observed in the samples with silver nanorods (AgNRs) are unambiguous and are clear for the Fe₂O₃@Ag@ZIF-67 on FTO glass substrate (Fig. S8). Diffraction peaks at 38.18° , 44.25° , 64.72° , and 77.4° represent the (111), (200), (220), and (311) planes of AgNRs, demonstrating successful loading of AgNRs.

The PEC performance of photoanodes is determined by their optical properties, charge transport and surface charge transfer. The optical properties of the samples were characterised by UV–Visible absorption spectroscopy, as shown in Fig. 4a. Hematite nanorod arrays present a characteristic absorption peak centred at 450 nm and an absorption edge at ~ 550 nm. The indirect Fe *d-d* transitions ($\text{Fe}^{3+}_{3d} \rightarrow \text{Fe}^{3+}_{3d}$) are responsible for the absorption at ~ 550 nm. The absorption peak centred at 450 nm is attributed to direct transition between O^{2-} and Fe^{3+} ($\text{O}^{2-}_{2p} \rightarrow \text{Fe}^{3+}_{3d}$) [34]. For ZIF-67, the broad absorption in the near UV region (<450 nm) corresponds to a ligand-to-metal charge-transfer (LMCT) transition of the 2-methylimidazole ligand [35]. The visible absorption band, consisting of three peaks centred at 541 nm, 567 nm, and 587 nm, are attributed to the $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ *d-d* ligand field transition of tetrahedral coordinated Co(II) in a Td environment [36]. No peaks occur between 480 nm and 506 nm, indicating that within ZIF-67, there is no octahedrally coordinated Co(II).

Ag nanorods were chosen as a plasmonic component in this study. It has been reported that nanorods are more effective in light scattering than nanospheres, nanocubes and nanostars [2]. In particular, two batches of Ag nanorods were synthesised and loaded onto composite electrodes, the first with an aspect ratio of 1.8 and diameter of ~ 25 nm (type-I) and the second with an aspect ratio of 2.7 and diameter of ~ 22 nm (type-II). For type-I Ag nanorods, plasmonic responses are at 391 nm and 477 nm, corresponding to the transverse mode resonance and longitudinal resonance, respectively [37]. The longitudinal LSPR mode excited by incident photons polarized along the length direction tailor the

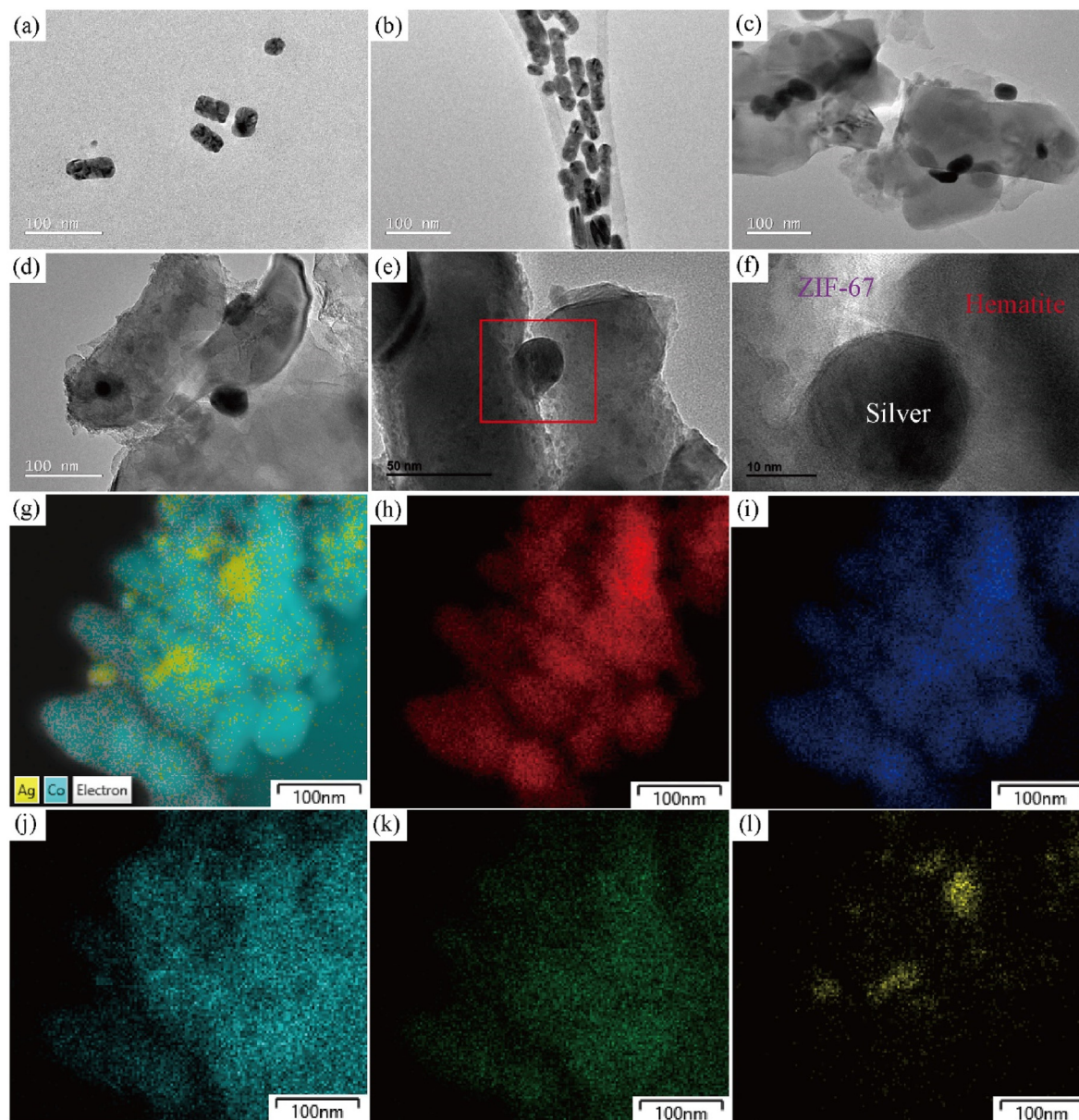


Fig. 3. Morphological characterisation for samples. TEM images of (a) type-I Ag nanorods (with silver nanospheres), (b) type-II Ag nanorods, (c–e) α -Fe₂O₃@Ag@ZIF-67. (f) Zoomed in image of Ag nanorod and hematite with ZIF-67 coating layer. (g) STEM image of α -Fe₂O₃@Ag@ZIF-67 with Ag and Co labelled. TEM-EDS images of (h) Fe, (i) O, (j) Co, (k) N, (l) Ag.

position of the long wavelength peak. For type-II Ag nanorods, the transverse and longitudinal LSPR is at 375 nm and 630 nm, respectively.

The light harvesting capabilities of α -Fe₂O₃, ZIF-67, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag@ZIF-67 were assessed by UV–Vis spectroscopy, shown in Fig. 4a and b. Compared with bare hematite, the introduction of ZIF-67 improves the light harvesting capability from the UV into the visible region (~600 nm), due to absorption from ZIF-67, shown in Fig. 4c. By incorporating Ag–I, an increased absorption profile in the spectral range from 450 nm to 560 nm is observed. A red shift of the longitudinal peak, originally centred at 477 nm has been found. The redshift occurs as the dielectric constant of hematite is higher than water, a typical plasmonic response of metal nanoparticles. Similarly, after loading Ag–II (AgNRs–II), the absorption profile in the visible (till~750 nm) region is enhanced, originating from the longitudinal plasmonic response centred at ~630 nm. Tauc plots (Fig. 4d) were constructed from the UV–Visible

absorption spectra. The band edges of α -Fe₂O₃, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@AgNR-I@ZIF-67, α -Fe₂O₃@AgNR-II@ZIF-67 are 2.31 eV, 2.19 eV, 2.11 eV and 2.07 eV, respectively. The shifted band edges of the three-component composite electrodes imply improved light harvesting in the visible region, leading to improved PEC performance.

X-ray photoelectron spectroscopy was conducted to investigate the composition and chemical state of α -Fe₂O₃@Ag@ZIF-67. High-resolution XPS spectra of Ag 3d, O 1s, C 1s, N 1s, Fe 2p, Co 2p are shown in Fig. 5. In the Ag 3d core level, the peaks of Ag(0) and AgO are difficult to recognize due to a tiny difference of 0.3 eV in binding energy, however, the Ag(0) 3d_{5/2} loss feature at 371.5 eV is clearly observable. Also in the Ag MNN spectrum, the auger peaks at 351.6 eV and 357.8 eV unambiguously confirm the existence of Ag(0) [38]. There is a tiny peak representing AgS, due to the functionalisation of AgNRs with thiolated- Polyethylene glycol (PEG). In the O 1s and C 1s spectra, the O–Fe band can be attributed to

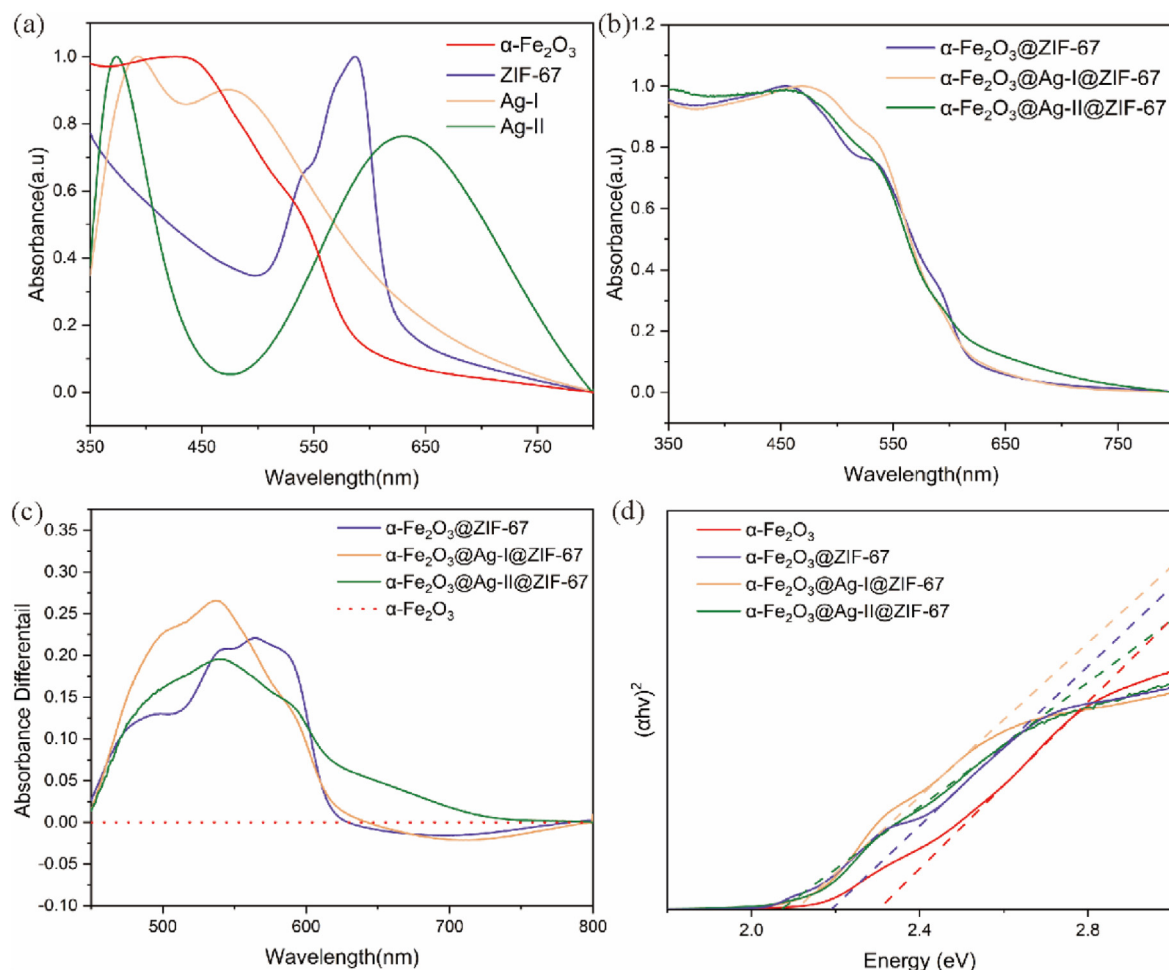


Fig. 4. Optical properties of samples. (a) Normalised UV–Vis spectra of α -Fe₂O₃, ZIF-67, Ag-I, Ag-II, (b) UV–Vis spectra of Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67, (c) Deviation value of the absorbance of samples Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67 from original hematite nanorod sample, (d) Tauc plots of α -Fe₂O₃, Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67.

hematite, while the C=O, C–O, and C–C are assigned to the ZIF-67 and PEG. The XPS spectra of N 1s indicate two bonds of pyrrolic N (400.3 eV) and N–Co (398.6 eV) in ZIF-67 [19]. As the Co LMM peaks overlap with Fe 2p, the original Fe 2p curved was modified to exclude the effect from Co LMM. The satellite peak at 718.8 eV clearly distinguishes Fe³⁺ from Fe²⁺. In summary, the results suggest the existence of Fe₂O₃ rather than FeO [39]. Though the Fe 2p core-level spectra of α -Fe₂O₃ and γ -Fe₂O₃ are almost the same [40], combining the results of XRD, demonstrates the existence of α -Fe₂O₃ phase in α -Fe₂O₃@Ag@ZIF-67 hybrids. The Co 2p XPS pattern shows 2p_{3/2} and 2p_{1/2} at 781.2 eV and 796.7 eV with a satellite peak at 786.1 eV, indicating the Co(II) state [41]. There is no obvious Co(III) signal in XPS patterns, as the satellite peak of Co(III) normally have a blue shift of 9–10 eV from the main Co 2p [36]. In addition, no Co–N_x features are recognized [42]. Therefore, cobalt mainly exists in the form of Co(II) in Co–N₄ of ZIF-67. All these results reveal the successful fabrication of α -Fe₂O₃@Ag@ZIF-67 composite photoanodes.

3.3. Evaluation of PEC water splitting performance

The main factors that determine the performance of a photoanode are light harvesting efficiency, charge-transport efficiency

and surface charge-transfer efficiency. The designed three-component nanocomposites were tested for PEC water splitting under full spectrum illumination. Fig. 6a shows linear sweep voltammetry (LSV) curves of the samples including α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67 as well as control samples of α -Fe₂O₃ and α -Fe₂O₃@ZIF-67. α -Fe₂O₃@ZIF-67 presents a photocurrent density of 0.61 mA/cm² at 1.23 eV vs RHE while the bare hematite nanorod array only shows a current density of 0.36 mA/cm². From UV–Vis spectra results (Fig. 4b), α -Fe₂O₃@ZIF-67 presents enhanced light absorption capability across the UV to the visible region, until ~600 nm.

To gain further insight, IPCE measurements for α -Fe₂O₃ and α -Fe₂O₃@ZIF-67 were conducted, shown in Fig. 6b (red and blue curves). The red curve indicates that though it is generally accepted that hematite is a low band-gap material, its visible light harvesting capability is not promising. In addition, the blue curve indicates that the increased photocurrent mainly came from the UV region (<450 nm). The enhanced incident photon-to-electron conversion rate in the spectral range between 550 and 600 nm is relatively low. The applied bias to photon current conversion efficiency (ABPE) of the samples was also studied (Fig. S9). The α -Fe₂O₃@ZIF-67 sample exhibits an elevated photoconversion efficiency of 0.09% at 0.97 V vs RHE, which is significantly higher than that of α -Fe₂O₃ (0.04%) at

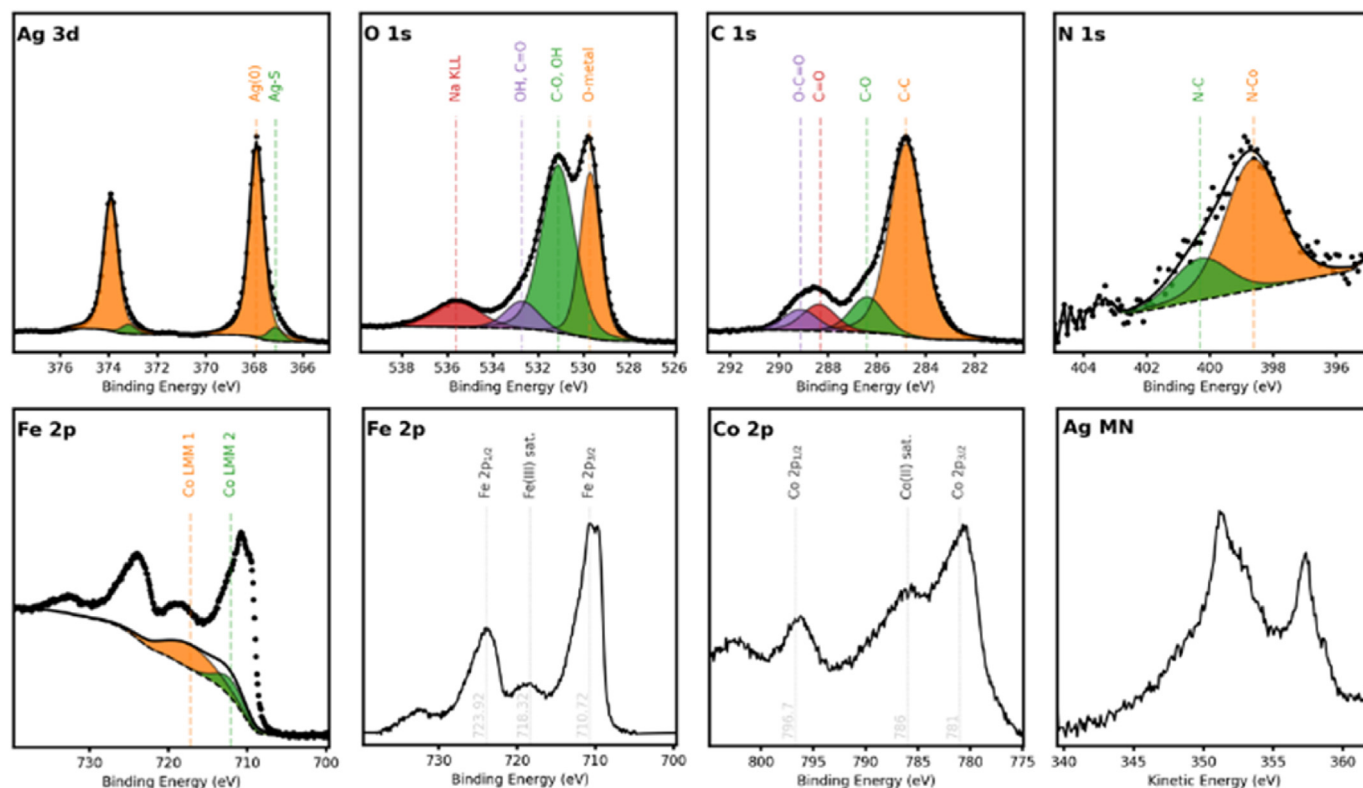


Fig. 5. High resolution XPS spectra of α -Fe₂O₃@Ag@ZIF-67 at binding energies corresponding to Ag 3d, O 1s, C 1s, N 1s, Fe 2p (with and without Co signal), Co 2p and Ag MN.

0.99 V vs RHE. We further characterise the charge transport and surface charge transfer properties of the samples to investigate the origins of the enhancement on ABPE.

The charge transport ability of the α -Fe₂O₃@ZIF-67 sample was further investigated via characterisation of transient time (Fig. 6c and d), Mott-Schottky (M – S) plots (Fig. 7c) and bulk charge separation (Fig. 7f). The ZIF-67 exhibits a prominent positive effect that extends the transient time from 1.6 s to 16.1 s, which means holes could travel much further before any recombination occurs. In the Mott–Schottky plots, Fig. 7a–c, the conductivity type of a semiconductor can be confirmed by the slope of the tangent line. The positive slope of α -Fe₂O₃ and negative slope of ZIF-67 indicate that α -Fe₂O₃ is an n-type semiconductor and ZIF-67 is a p-type semiconductor, respectively [43]. The “inverted V” M – S curve in Fig. 7c confirms the generation of the p–n junction between α -Fe₂O₃ and ZIF-67. The built-in electric field at the p–n junction boundary favours the charge carrier separation and transportation. It helps to drive photogenerated electrons from ZIF-67 to α -Fe₂O₃. The calculated bulk charge separation efficiency also implies that with ZIF-67 coating, the charge separation was improved, which can be attributed to the p–n junction field effect. The intercept of the tangential line and X-axis reveals the flat band position. There is a negative shift in the flat-band potential from α -Fe₂O₃ to α -Fe₂O₃@ZIF-67 resulting from the generation of the p–n junction. This negative shift could increase the band bending and elevate the driving force for the charge separation.

Electrochemical impedance spectra (EIS) were measured to investigate the charge transfer behaviour at the electrolyte/electrode interface (Fig. 7d). In general, the process in the high frequency region is kinetic control and in the low frequency region is mass transfer control. The diameter of the semicircle represents the electron-transfer resistances (R_{ct}). The diameter of the impedance semicircle of α -Fe₂O₃@ZIF-67 is smaller than that of α -Fe₂O₃

indicating a better charge carrier mobility at the interface. The R_{ct} reduces from 1209.0 to 789.1 Ω . Co-MOF was reported to store holes at the interface [20]. In the water oxidation process, these surface-trapped holes are first to be consumed, followed by holes in the valence band, inducing a boosted interfacial charge transfer rate.

The hole injection efficiency, η_{inj} was also measured (Fig. 7e) to identify the surface charge transfer performance and the equation is given by:

$$\eta_{inj} = J_{H_2O} / J_{Na_2SO_3}$$

where J_{H_2O} is the photocurrent density of the photoanode in 0.1 M NaOH solution and $J_{Na_2SO_3}$ is the photocurrent density in 0.1 M NaOH solution with 0.1 M Na₂SO₃.

After coating with ZIF-67, the charge injection (charge-transfer) efficiency has been improved. The hole injection efficiency of α -Fe₂O₃@ZIF-67 at 1.23 eV vs RHE is 71.2%, which is higher than that of hematite (62.7%).

This efficiency is generally affected by surface traps and surface reaction kinetics. Surface charge recombination is a major loss mechanism in hematite-based photoanodes [44]. The inert surface of hematite is covered by ZIF-67. The passivation of the surface traps can potentially suppress the surface charge recombination. Yet, the effect of ZIF-67 coating on the surface traps requires further investigation. Herein, ZIF-67 acts as a passivation layer on the hematite and reduces the surface electron-hole recombination rate [45]. Besides, the large surface area and inherent porous nature of the MOF favour the surface redox reaction [46]. Co²⁺-based materials have been reported as surface catalysts [44]. The charge-separation state of ZIF-67 contains a long-lived intermediate state [35]. From Fig. S10, it is evident that the ZIF-67 coating results in a cathodic shift of the onset potential from 0.740 V (vs. RHE) to 0.697 V (vs. RHE). The improvement of the surface catalysis gives

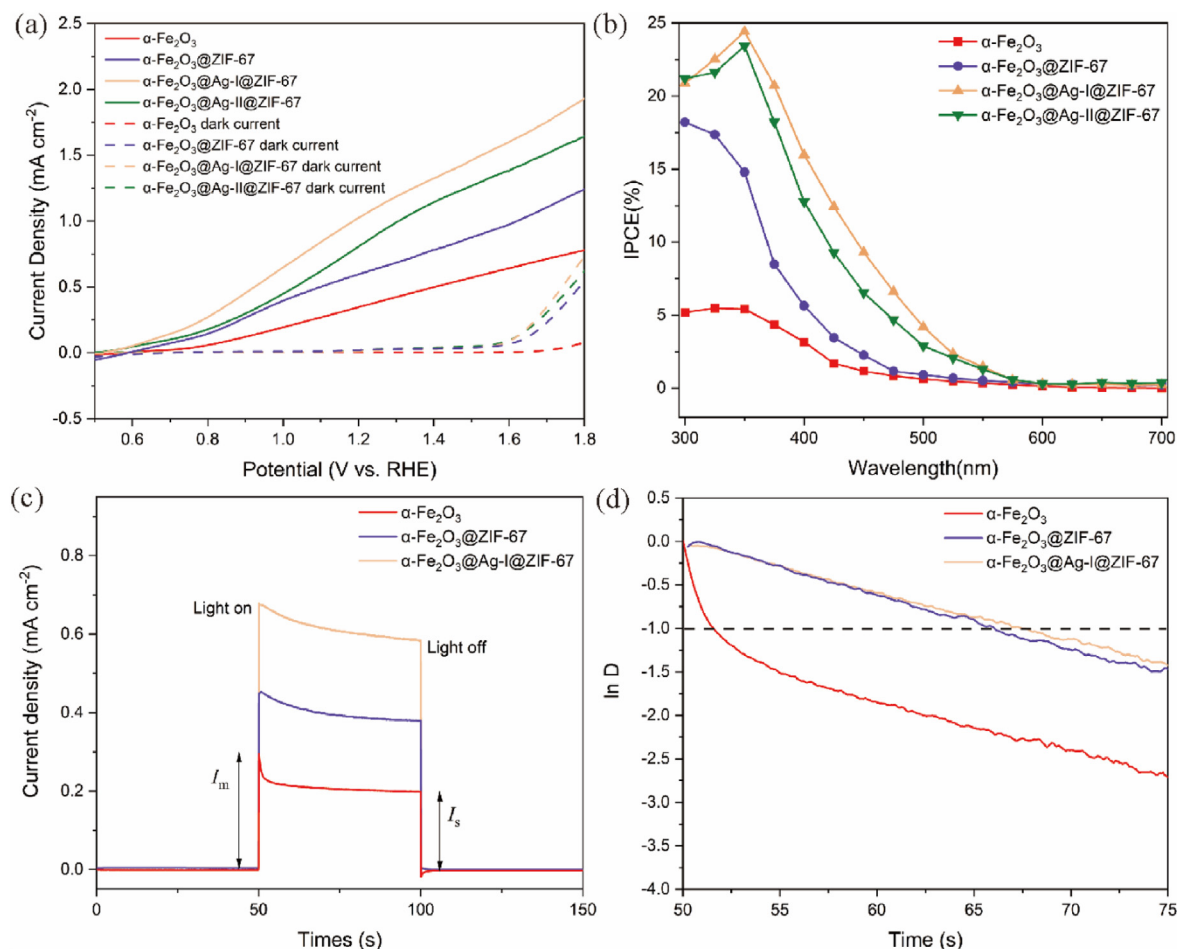


Fig. 6. PEC water splitting performance evaluation. (a) Linear sweep voltammetry (LSV) curves of photoanodes: α -Fe₂O₃, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67. (b) IPCE curves of measured at 1.23 V (vs. RHE). of the photoanodes: α -Fe₂O₃, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67, α -Fe₂O₃@Ag-II@ZIF-67. (c) Transient photocurrent decay of α -Fe₂O₃, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67 under illumination at an applied potential of 1 V vs RHE. (d) Transient decay times of the α -Fe₂O₃, α -Fe₂O₃@ZIF-67, α -Fe₂O₃@Ag-I@ZIF-67 samples.

rise to the cathodic shift of the onset potential. The passivation of the surface trapping states may also contribute to this cathodic shift, which requires further investigation in the future.

Therefore, the ZIF-67 coating improves the PEC performance in several aspects. The construction of α -Fe₂O₃@ZIF-67 P-N junction improved the bulk charge separation efficiency. The ZIF-67 shell reduces the surface charge transfer resistance and improves the surface charge separation efficiency. As mentioned in 3.2, ZIF-67 also improve the light-harvesting, especially the light absorption in the visible light range. Though the IPCE results indicate that the visible light photons absorbed did not dominate the enhancement in the photocurrent density. Additionally, the ZIF-67 also brings a negative shift of the onset potential and plays a catalytic role.

Significantly, α -Fe₂O₃@Ag-II@ZIF-67 and α -Fe₂O₃@Ag-I@ZIF-67 photoanodes both show enhanced photocurrent densities of 0.86 mA/cm² and 1.04 mA/cm² at 1.23 eV vs RHE, respectively. That is up to ca. 3-fold increase in the photocurrent density, compared to α -Fe₂O₃ photoelectrode. Such enhanced PEC water splitting performance is mainly attributed to the plasmonic effect induced by AgNRs. To gain further insight into the enhanced efficiency of PEC water splitting, IPCE measurements for both plasmonic samples, i.e., α -Fe₂O₃@Ag-I@ZIF-67 and α -Fe₂O₃@Ag-II@ZIF-67, were carried out, as shown in Fig. 6b. The IPCE results show a better photon-to-electron transfer efficiency from 300 nm to 600 nm. In addition, the α -Fe₂O₃@Ag-I@ZIF-67 photoanode slightly outperforms the α -

Fe₂O₃@Ag-II@ZIF-67 photoelectrode, with 6-fold enhancement of IPCE at 500 nm.

Such enhanced PEC water splitting performance is mainly attributed to the plasmonic effect induced by AgNRs. It has been widely accepted that plasmonic energy in a metal can be transferred to a semiconductor through three major mechanistic pathways: (1) light scattering/trapping, (2) plasmon-induced resonance energy transfer (PRET), and (3) hot electron injection (HEI). The LSPR extinction of AgNRs, consists of both absorption and scattering cross-sections. The light scattering contribution is significant in the LSPR band for AgNRs, which will be further discussed in the simulation section. Hence when AgNRs are integrated with α -Fe₂O₃, incident light can be scattered by AgNRs to further penetrate α -Fe₂O₃ arrays, leading to an increased light absorption [47]. Consequently, this scattering effect induced by AgNRs enhances the light absorption and charge separation in the α -Fe₂O₃@ZIF-67 composite photoanodes. Elevated photon conversion efficiency above the band gap region could also be a result of PRET. In PRET, the plasmonic energy in AgNRs is non-radiatively transferred to α -Fe₂O₃@ZIF-67 semiconductors via the dipole-dipole interaction in the near-field, generating electron-hole pairs in the semiconductor [48]. PRET efficiency is strongly dependent on the distance between metal and semiconductor as well as the spectral overlap between the plasmonic resonance band and the semiconductor's absorption band [49–51]. In this study, AgNR-I displays better spectral overlap

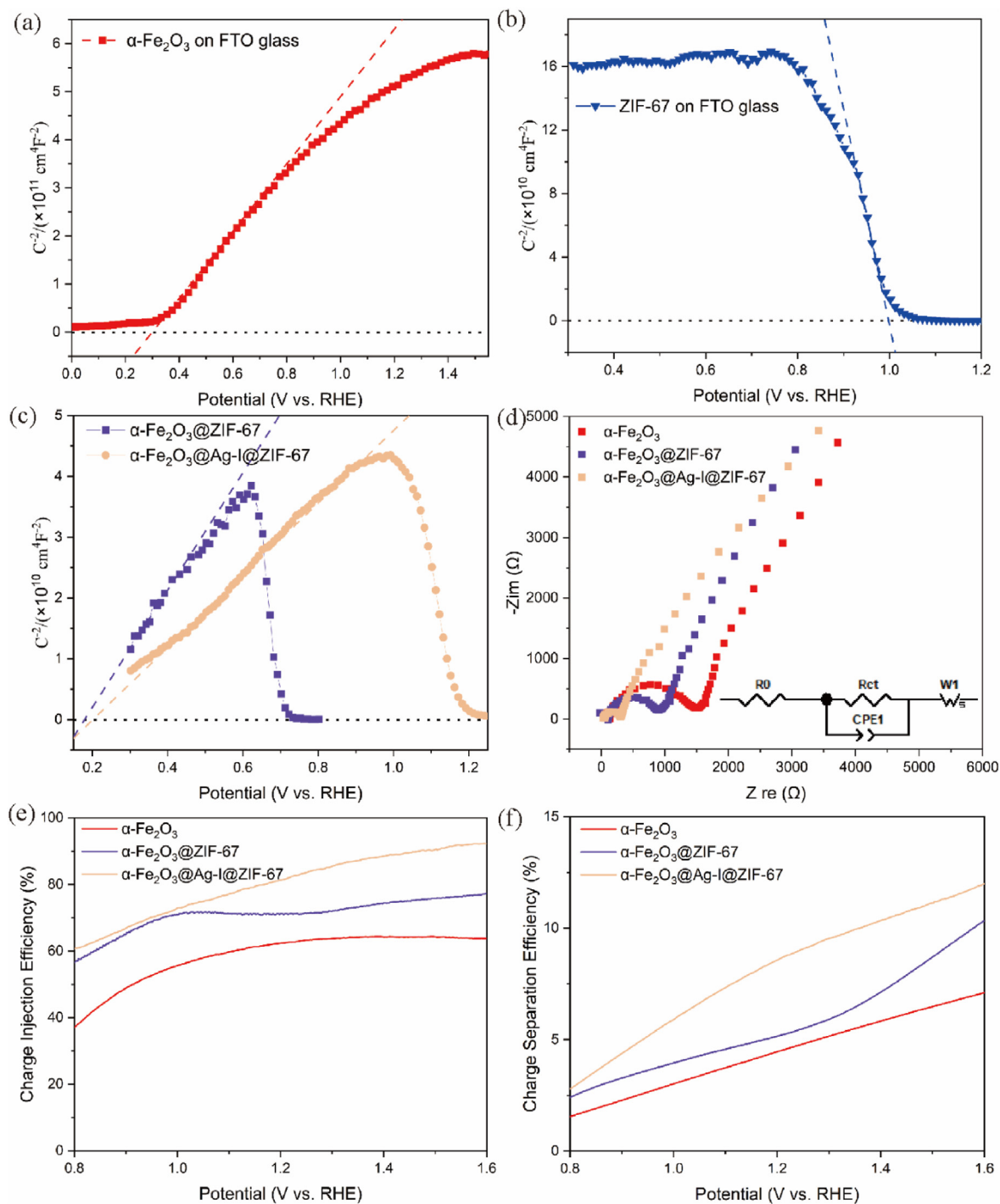


Fig. 7. PEC water splitting performance evaluation. Mott-Schottky plots of (a) $\alpha\text{-Fe}_2\text{O}_3$, (b) ZIF-67, (c) $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$ and $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ samples. (d) Nyquist Plot of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$, $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ samples, with the equivalent circuit. (e) Hole injection efficiency of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$, $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ samples. (f) Bulk charge separation efficiency of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$, $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ samples.

with $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$. The longitudinal plasmonic resonance band of AgNR-I is positioned above the band gap of hematite, in contrast, that of AgNR-II is far below the band gap of hematite. Consequently, $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ exhibits better performance than $\alpha\text{-Fe}_2\text{O}_3@Ag-II@ZIF-67$.

In summary, PRET, a coherent energy transfer process, is the main mechanism for enhanced performance in PEC water splitting. The third mechanistic pathway of HEI could occur below the band gap region [52,53]. After careful examination, there is a tiny,

enhanced photocurrent at 650 nm, shown in Fig. 6b. However, this increase is negligible, which means that HEI does not account for the elevated photocurrent in $\alpha\text{-Fe}_2\text{O}_3@Ag-I@ZIF-67$ photoelectrodes. In addition, HEI generally works more efficiently in smaller nanoparticles and our PEG-ligand further hinders the direct hot electron transfer [53].

For charge transport characterisation, in M – S plot Fig. 7c, there is no evident difference in the flat band position after the introduction of Ag nanorods to $\alpha\text{-Fe}_2\text{O}_3@ZIF-67$. The bulk charge

efficiency is improved with the implementation of the Ag nanorods. Due to LSPR, the Ag nanorods change the spatial distribution of the electromagnetic field and enhance the electromagnetic field near themselves. The photoexcitation of these regions is boosted given that the charge carrier generation rate is proportional to $|E|^2$ [48]. As these Ag nanorods are placed between the hematite and ZIF-67, more photon-induced electron-hole pairs are generated and separated by the E-field of the p-n junction efficiently. Consequently, the overall bulk charge separation efficiency is improved. The transient time slightly increases from 16.1 s to 17.6 s, probably because Ag nanorods improve the conductivity of the composite photoanode (Fig. 6d).

The surface charge-transfer efficiency was also studied, as shown in Fig. 7e. The hole injection efficiency of α -Fe₂O₃@Ag-I@ZIF-67 at 1.23 eV vs RHE is 82.6%, which is higher than that of hematite (62.7%) and α -Fe₂O₃@ZIF-67 (71.2%), respectively. The charge injection efficiency is further elevated after adding silver, which could be attributed to the surface catalytic effect of Ag nanorods. After the implementation of Ag nanorods, the onset potential shifts from 0.697 V (vs. RHE) to 0.659 V (vs. RHE) (Fig. S10). This indicates that Ag nanorods also play a catalytic role. Both AgNRs and ZIF-67 improve the charge transfer at the electrode/electrolyte interface.

In addition, the EIS of α -Fe₂O₃@Ag-I@ZIF-67 (Fig. 7d) displays the smallest radius of the semicircle as expected, compared with that of the hematite and α -Fe₂O₃@ZIF-67 samples. The R_{ct} further reduces to 254.0 Ω . It is reported that the introduction of metal NPs improves the overall conductivity of photoanodes and accelerates the transfer of charge [32]. The fitted Nyquist plot of α -Fe₂O₃@Ag-I@ZIF-67 is presented in Fig. S11.

The ABPE of the α -Fe₂O₃@Ag-I@ZIF-67 and α -Fe₂O₃@Ag-II@ZIF-67 samples were also measured (Fig. S9). The α -Fe₂O₃@Ag-I@ZIF-67 sample presents the best photoconversion efficiency of 0.15% at 0.95 V vs RHE. This can be attributed to the improved light harvesting efficiency, charge transport and surface charge transfer efficiency from the implementation of Ag nanorods and the construction of the α -Fe₂O₃@ZIF-67 p-n junction.

Fig. S12 shows the stability of the α -Fe₂O₃@Ag-I@ZIF-67 photoanode in 0.1 M NaOH solution for 1 h. The stability photoanode is

relatively stable, as MOFs based photoanodes suffer from instability in PEC water splitting catalysis [22]. Besides that, no significant change has been observed in the crystal structure from the XRD pattern collected after the multiple PEC measurement (Fig. S13).

In Fig. 8, the energy band structures of the designed three-component photoanode is proposed. Based on the results and the diagram above, the working mechanism of the ternary composite system is deconvoluted. ZIF-67 is split into a doublet, a narrow band gap corresponding to the Co cluster and a broader band gap from absorption of ligand, respectively. As mentioned above, hematite and ZIF-67 generate a p-n junction and the built-in electric field drives photogenerated electrons to move from ZIF-67 to α -Fe₂O₃. When a bias of 1.23 eV vs RHE is applied to the photoanode, all the fermi levels would have a positive (downward) shift. Considering the porous structure and Highest Occupied Molecular Orbital (HOMO) position of ZIF-67, an oxygen evolution reaction could occur both at hematite and ZIF-67. While energetic electrons could move from silver/ZIF-67 to hematite, and further transfer to the cathode. The transport of electrons from ZIF-67 to hematite is expedited by the electric field of the p-n junction. The introduction of ZIF-67 improves the light harvesting, charge-transport and surface charge transfer processes. The generation of the core-shell structure of α -Fe₂O₃@ZIF-67 p-n junction shifts the fermi level position, improving the surface catalysis. The addition of Ag nanorods generates plasmonic effects and improves the overall conductivity of the photoanode and accelerates surface transfer of charge. It is noteworthy that the majority of the plasmonic energy on silver transfers to the hematite via the PRET mechanism.

3.4. FDTD simulation

The localised electrical field distribution of a single AgNR was modelled using finite-difference time-domain (FDTD) simulation. The geometry of the nanorod was modelled as a cylinder with two hemi-spheres at the top and the bottom rather than a simple cylinder. The plane wave was set to propagate along the z-axis while the long axis of the cylinder was set to be vertical to the XZ plane to investigate the longitudinal plasmon resonance peaks. It was reported that Ag nanorods generally presented two absorption peaks

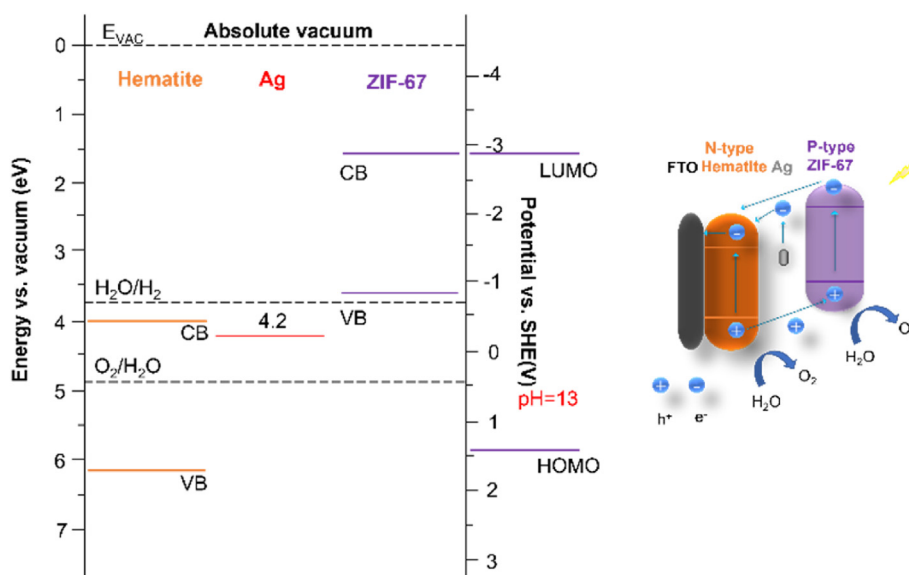


Fig. 8. Schematic Energy diagram of α -Fe₂O₃@Ag@ZIF-67 samples. The ZIF-67 and the α -Fe₂O₃ generate a p-n junction and favours photogenerated electrons transport from p-type ZIF-67 to n-type α -Fe₂O₃. Energetic electrons from silver nanorods also move to hematite and further transfer to the cathode passing FTO glass. OER occurs both at the hematite and the ZIF-67.

with one near-UV peak due to the transversal resonance mode and another peak from the longitudinal resonance [54]. The peak position could be tailored readily by tuning the aspect ratio of Ag nanorods [37]. In particular, the longitudinal plasmonic peak could be tuned from the visible to near-IR region [55].

Fig. 9 presents the scattering and absorption cross-section spectra of AgNR-I and AgNR-II, respectively. The enhancement factors of the localized electric fields at the longitudinal resonance bands of AgNR-I and AgNR-II are also calculated.

Comparing Fig. 9a and b, AgNR-II has a larger extinction cross-section than AgNR-I. Longer nanorods normally have stronger extinction peaks [56]. The scattering-to-extinction ratios of AgNR-I and AgNR-II are 0.23 and 0.24. This means both AgNR-I and AgNR-II have a dominant absorption cross-section while light scattering effect is not that strong. Yet they both show more prominent scattering than silver nanospheres (Fig. S14, scattering-to-extinction ratio = 0.13), which agrees with Wu's report [2].

It is clear that the simulated Ag nanorods are subject to LSPR effects and yield on-resonance dipolar electric-field enhancement.

At their longitudinal resonance bands, both AgNR-I and AgNR-II shows up to 30-fold enhancement around the two tips of the rods.

The hot spots come from the mesh resolution problem (0.5 nm). As the diameter of the nanorods are only 22 and 26 nm, the tips of the rods are not perfectly spherical surfaces under simulation.

The calculated longitudinal resonance peak of AgNR-I is at 507 nm and that peak of AgNR-II is at 628 nm. The UV–Vis spectra results show peaks at 477 nm and 630 nm, respectively. The moderate difference is acceptable and could come from the plasmon coupling between adjacent Ag nanorods [57]. The results show a red shift of the longitudinal resonance peak with increasing aspect ratio of Ag nanorods, which has been well explored by our research group [33]. This could act as a guidance to design Ag nanorods with optimised longitudinal resonance band for better PRET enhancement [37,56].

As mentioned in the UV–Vis spectra discussion, a red shift of the peak position of AgNR-II occurs based on the original value of 630 nm because of the change in the dielectric constant of surrounding medium. Even though AgNR-II could yield strong field enhancement at the peak position, the degree of spectra overlap between Ag and α -Fe₂O₃/ZIF-67 is low, compared to AgNR-I. This is a critical condition for effective PRET mechanistic enhancement pathway. Consequently, a better overall PEC water splitting

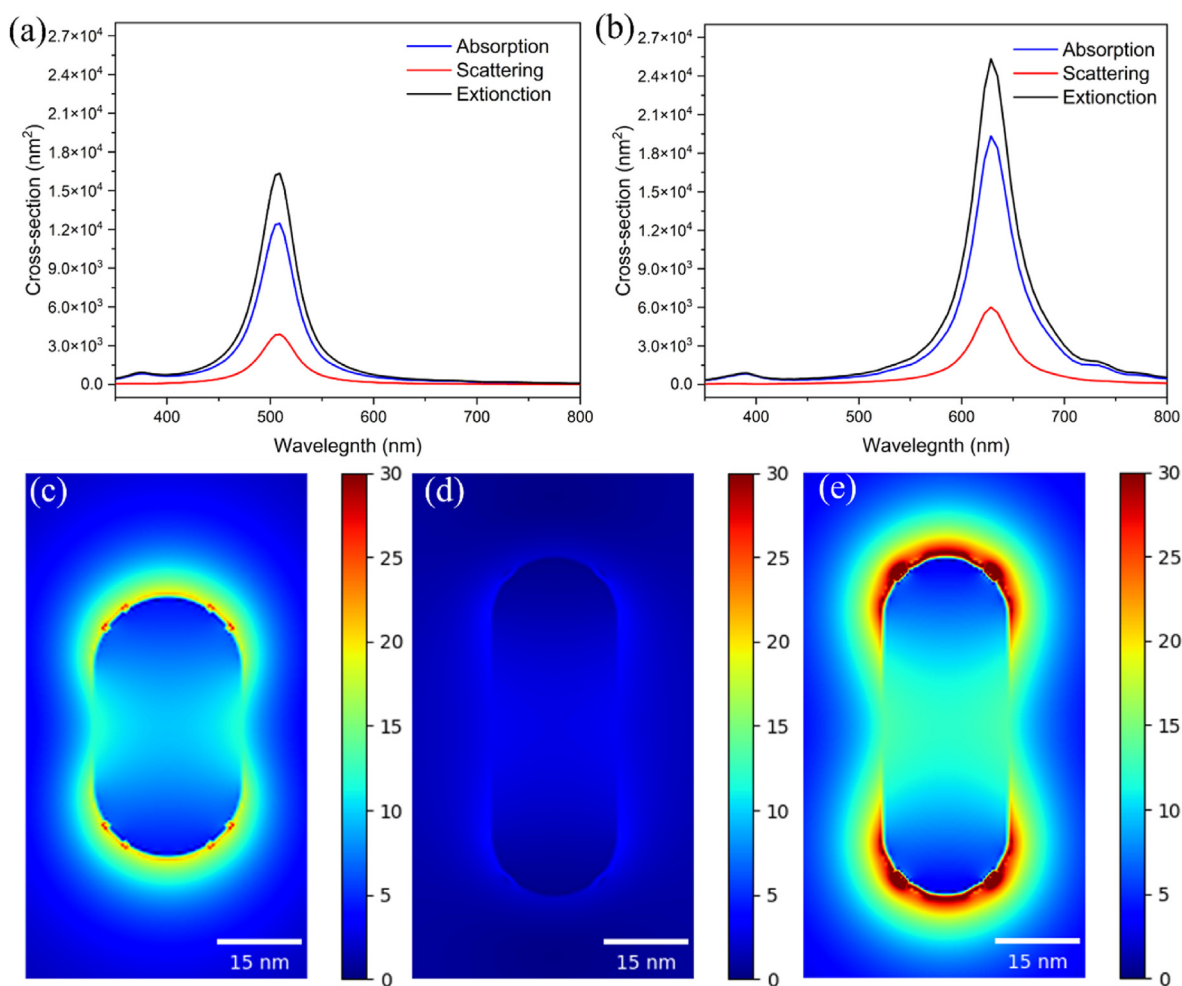


Fig. 9. FDTD simulation results of far-field spectra and near-field enhancement ($|E/E_0|$) distribution properties of AgNR-I and AgNR-II: Absorption and Scattering cross-section of (a) AgNR-I (26 × 46 nm), (b) AgNR-II (22 × 60 nm) in aqueous solution. AgNR-I and AgNR-II have similar scattering cross-section. The scattering component is more prominent for AgNR-I while AgNR-II has roughly the same absorption and scattering cross-section at the longitudinal resonance peak. -Calculated localised electric field by longitudinal resonance of (c) AgNR-I at wavelength of 507 nm, (d) AgNR-II at wavelength of 507 nm, (e) AgNR-II at wavelength of 628 nm. The figure provides an XY cross-sectional view. The incident wave vector k is perpendicular to the plot plane and the polarization direction is parallel to the long axis of the nanorods. Both AgNR-I and AgNR-II have the highest localised electric field enhancement (~20–30 times) around the two tips of the rods at their longitudinal resonance peak (507 nm and 628 nm). Considering the band edge of hematite ~500 nm, the electrical field enhancement of AgNR-II is less than 5 times.

performance was observed in α -Fe₂O₃@AgNR-I@ZIF-67 photoelectrodes.

4. Conclusions

In conclusion, a ternary semiconductor-plasmonic-MOF composite photoanode was designed for photoelectrochemical water splitting. A *c.a.* 3-fold photocurrent density enhancement was achieved. The boosted performance was attributed to two main routes: 1) improved electron-hole pair separation and charge transport induced by ZIF-67; 2) plasmonic enhanced photon to electron conversion efficiency induced by both PRET and light scattering mechanisms by incorporating AgNRs. This work provides an excellent example of ternary semiconductor-plasmon-MOF structures for photoelectrochemical water splitting and could be widely adapted to solar energy conversion and storage applications.

Author contributions

Chengyu Ji: Conceptualization, Data curation, Formal analysis, Validation, Investigation, Methodology, Software, Writing – original draft. **Jiamin Xu:** Investigation. **Qianfan Jiang:** Software. **Gwilherm Kerhervé:** Investigation. **Haochen Zhou:** Investigation. **Xiaoru Li:** Investigation. **Sixing Tang:** Investigation. **Pankaj Sharma:** Investigation, Writing – review & editing. **D. Jason Riley:** Supervision, Writing – review & editing. **Fang Xie:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtadv.2023.100361>.

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