

1 **Chemically modified multiwall carbon nanotube composite Electrodes: An**
2 **assessment of fabrication strategies**

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17 **Keywords:** multiwall carbon nanotubes, Electrodes, chemical sensors, Prussian
18 blue, glutathione

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20 **Acronyms:** MWCNT, multiwall carbon nanotubes; PB, prussian blue; GSH,
21 glutathione; SEM, scanning electron microscopy; EDX, Electron-dispersive X-ray
22 spectroscopy; PBMix, PB mixed with MWCNT; PBMod, PB modified with MWCNT;
23 PBCoat, PB coated on MWCNT electrode.

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25
26 **Abstract**

27 Chemically modified electrodes have been widely used to enhance electrochemical
28 monitoring of analytes that are not easily detected using traditional base conductive
29 materials. We have investigated different fabrication approaches to chemically
30 modify multi-wall carbon nanotube (MWCNT) composite electrodes with Prussian
31 blue. Composite Electrodes were made where Prussian blue was mixed with
32 MWNCTs, where Prussian blue was coated on MWCNT composite electrodes and
33 where MWCNTs were modified by generating PB on the surface of MWCNTs. Our
34 findings indicate that MWCNT modified PB electrodes provided good sensitivity for

the detection of glutathione and exceptional stability; whilst MWCNT coated PB electrodes provided excellent sensitivity but poor stability. Such findings provide important implications on the fabrication, suitability and use of chemically modified electrodes for electroanalysis.

1. Introduction

Chemically modified electrodes have been widely used as they offer the ability to tailor the physiochemical properties of the electrode in order to facilitate electrochemical reactions of analytes that may not display desirable properties with the base electrode material [1, 2]. These chemically modified electrodes have displayed significant improvements over the base electrode including the ability to provide selectivity for the detection of specific analytes, prevent electrode fouling, improve the electrochemical/electrocatalytic properties and reduce the over-potential required for oxidation/reduction of a given species [2-4].

In previous studies, various different fabrication strategies for the chemical modification of electrode have been employed. These methods include adsorption of the chemical agent/s on the electrode surface as a film, direct bonding of the chemical agent/s on the electrode surface and or mixing the chemical agent/s within the conductive material to create a composite electrode [2]. The first two approaches are widely used for solid electrodes and electrodes. Many studies have examined the use of Prussian blue (PB) to modify electrodes, these have shown how the electrocatalytic behaviour of the PB on the surface of the electrode facilitates electron transfer and provided enhanced sensitivity [5-7]. These studies all show differences in the sensitivity, selectivity and stability of the fabricated electrodes when monitoring the same analyte. These differences can be attributed to variations in the fabrication methods utilised for the different electrodes [5, 7-12].

Multi-wall carbon nanotubes (MWCNTs) have emerged as excellent electrochemical materials and have been widely used for sensor development [13]. One of the major issues with using nanotubes is the difficulty in incorporating this material within an electrode. Various approaches have been used including film coating of MWCNTs on solid electrodes, creating buckypaper or column and more commonly fabricating composite electrodes [14-16]. The latter type of fabrication has potential benefits as composite electrodes are known to offer enhanced electrochemical behaviour due to

various electroactive sites on the surface, which provide improved mass transfer [17-19].

In this study we have examined various approaches of chemically modified electrodes using multi-wall carbon nanotubes as the base electrochemical material. Composite electrodes were fabricated as they offer the ideal spatial dimension for tissue measurements and PB was utilised as the chemical agent to modify the MWCNT composite material. To assess the various chemically modified electrodes, glutathione (GSH) was utilised. GSH has been shown to require a greater over-potential for oxidation on conventional carbon based electrodes, and therefore many studies have been published utilising the catalytic activity of chemically modified electrodes to reduce the over-potential required for the oxidation of GSH and to facilitate monitoring of GSH [20-23]. Three different approaches of fabrication were compared for the detection of GSH. These involve a composite material made from a mix of PB powder with MWCNT, a composite material made from chemically forming PB in the presence of MWCNT and creating a film membrane of PB on a MWCNT composite electrode. Each of these approaches was compared to a control MWCNT composite electrode for their sensitivity and stability for the detection of glutathione.

2. Experimental

2.1. Materials

Potassium chloride, Prussian blue, potassium ferricyanide, iron (III) chloride, glutathione and hydrochloric acid (Sigma-Aldrich, USA), epoxy resin and hardener (Robnor Resins Ltd, UK) were used as received. MWCNT-epoxy composites sensors were prepared from 30-50 nm diameter MWCNT with a length of 10-20 μm (CheapTubes, VT, USA).

2.2. Scanning Electron Microscope (SEM) and Electron-dispersive X-ray spectroscopy (EDX)

SEM was performed on a Carl Zeiss SMT Ltd SIGMA VP Field Emission Scanning Electron Microscope (FESEM) employing secondary electrons for the analysis. EDX was done with AZTEC software v2.2, created and provided by Oxford Instruments

Analytical Limited. The energy dispersive (ED) analysis we carried out using back-scattered electrons on powder samples.

2.3. Preparation of prussian blue modified MWCNT

1.00 g of MWCNTs were dispersed in an aqueous solution of an equi-volume mixture of 0.1 M FeCl_3 and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 10 mM HCl. This solution was then stirred for 30 minutes. The MWCNTs were filtered and washed with 10 mM HCl and distilled water in succession then allowed to dry. Final weight was approximately 1.40 g (28.5% PB).

2.4. Electrode fabrication approaches

Electrodes were made from are conductive MWCNTs, where epoxy resin was utilised as the non-conductive binder component to provide structural support. Four different approaches of electrode manufacture were attempted (see **Fig. 1**): (i) control electrode consisted of a ratio, by weight, of 15% MWCNTs: 85 % epoxy resin, (ii) PBMix electrodes that utilised a mixture of 15% MWCNTs : 6% PB : 79 % epoxy resin, (iii) PBMod electrodes were prepared by generating PB on the surface of MWCNTs, by placing MWCNTs in equi-volume mixture of 0.1 M FeCl_3 and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM HCl) for 30 minutes. This generated a material where MWCNTs were coated with PB. The PBMod electrode comprised of 21 % MWCNTs coated in PB : 79 % epoxy resin and the (iv) PBCoat electrodes were prepared by generated a film of PB on the surface of a control electrode. Control electrodes were dipped in to a equi-volume mixture of 0.1 M FeCl_3 and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM HCl) for 30 minutes. This generated a film coat of PB on the electrode surface.

For fabrication of the electrodes, the various composite materials were packed into a gel loading pipette tip (300 μm internal diameter) and an electrical connection was achieved by firmly inserting a copper wire into the composite material so as to minimise the thickness of the composite material and the resulting internal resistance of the final electrode. The composite material was 2 mm in thickness. The electrodes were then left for 48 hrs at room temperature in order to allow the composite electrodes to set.

Following this, so as to provide support to the electrode for easy handling, a glass capillary was inserted over the copper wire and adhered to the back to pipette tip with superglue, adhering the capillary and sealing the electrode. The electrode

surface was smoothed and polished with 0.3 and 0.05 micron alumina powder in succession for 30 seconds. The PBMix, PBMod and PBCoat electrodes were cycled between -0.2 and 1.2 V in 1 M KCl until steady CV response was obtained before being used.

2.5. Electrochemical measurements and electrode characterisation

All electrochemical measurements and data extraction were carried out using CHI 630B potentiostat (CH Instruments, Austin, TX) controlled using CH Instruments software. All studies were carried out with a three electrode system, which consisted of a Ag|AgCl (3 M KCl) reference electrode, a platinum wire auxiliary electrode and the various composite electrodes as the working electrode. The variability in the manufacturing of the composite electrodes was assessed using 1 mM ruthenium hexamine, an ideal one electron redox couple, in deoxygenated 1 M KCl through cyclic voltammetry (CV). Oxygen was purged from the electrolyte by bubbling through argon gas.

2.6. Amperometric measurements of glutathione (GSH)

In order to assess the performance of the various electrode fabrication strategies, the response towards the detection of glutathione was examined in 1 M KCl using amperometric i-t curves. To test the sensitivity of each electrode type additions of glutathione at a concentration range from 50 μ M to 1 mM were added to a stirred solution of PBS buffer at 100 second intervals after a 200 second settling period. In order to assess the stability of each type of electrode the response of 1 mM GSH was carried out after 1, 7, 14, 30 and 60 days after fabrication. The response was compared to the initial response. All measurements were carried out at 0.5 V vs Ag|AgCl reference electrode. Data were statistically compared using a 2-way ANOVA.

3. Results and Discussion

3.1. Physical characterisation of the materials

For the various strategies utilised for the formation of the four different chemically modified electrodes, three different types of material were utilised as the conductive element. The control electrode consisted of a plain MWCNTs composite (**Fig. 2A**), the composite for PBMix electrodes utilised a mixture of MWCNTs and PB (**Fig. 2B**) and the composite for PBMod electrodes contained Prussian blue modified MWCNT(**Fig. 2C**). The characterisation of the various materials and chemical composition was carried out. **Fig. 2D-F** displays the SEM images of the control, PBMix and PBMod MWCNT materials in order to compare their physical appearance, whilst **Fig. 3A-C** displays the elemental composition of each of the materials. In all samples a peak for Pt was observed which was due to background interference of the holder in which the sample was placed for analysis. The elemental presence of Fe was utilised to confirm the presence of PB within the various samples. The control material has no specific metal impurities suggesting that pre-treatment of the MWCNT has removed all metal contaminants and is composed of bundles of carbon nanotubes as expected (**Fig. 2D**). When MWCNT are mixed with PB, large agglomerate bundles of MWCNTs are accompanied by smooth PB spheres (**Fig. 2E**). The elemental analysis showed the presence of a signal for Fe in **Fig 3B** indicative that PB is present in this material. However other sections of the material show much lower composition of PB and the elemental analysis is much closer to that of the base MWCNT material. This clearly indicates the heterogeneity of this material as sections would be dense in PB and other would not be. When looking at the SEM image of the PBMod material (**Fig. 2F**), the MWCNT strands seems to be coated over the external surface of the individual stands and on some strands there are the presence of nano-sized particles of PB on the carbon nanotube surfaces. There is a clear difference in the PBMod SEM when compared to the MWCNT alone, suggestive that PB has coated the surface of the MWCNTs. Unlike the PBMix material the PBMod material retains a relatively identical elemental composition throughout the material and displays a signal for Fe arising from the presence of the PB coating the surface of the MWCNTs (**Fig 3C**).

3.2. Assessment of the behaviour of the various types of PB-MWCNT composite electrodes

Initially the reproducibility of the MWCNT epoxy composite electrodes was assessed to investigate the variation in-between electrodes. The variation between different MWCNT control electrodes was examined by comparing the behaviour of 1 mM ruthenium hexamine at ten different electrodes. Ruthenium hexamine displayed a mean cathodic peak potential (E_{pc}) of -221.4 ± 6.4 mV, a mean anodic peak potential (E_{pa}) of -135.0 ± 4.4 mV, a mean cathodic peak current (I_{pc}) of 323.4 ± 23.4 nA, a mean anodic peak current (I_p) of 293.3 ± 25.3 nA and a mean peak separation (ΔE) of 86.4 ± 10.4 mV ($n=10$) at these electrodes.

The initial exploration of the behaviour of these electrodes towards GSH was performed through cyclic voltammetry using 10 mM GSH to highlight the electrochemical behaviour of the various electrodes fabricated.

Fig. 4A shows the behaviour of the control MWCNT electrodes ($n = 3$), where slight increases in the current were observed in the presence of 10 mM GSH (~ 4 -6 nA at 0.6 V). However the control MWCNT electrode displayed no clear oxidation peak/s in the short potential window. In **Fig. 4B**, the PBMix electrodes show a clear oxidation and reduction of the Fe(II) ions in the PB. This response is increased in the presence of 10 mM GSH (~ 5 -7 nA at 0.3 V). This response indicates that PB acts to facilitate electron transfer of GSH. For the PBMod electrodes (**Fig. 4C**) there are large oxidation and reduction peaks for the Fe(II) ion in the PB. In the presence of 10 mM GSH, PBMod electrodes displayed an increase in the observed current at 0.3 V. Although visually this response looks smaller than that of the other electrodes, due to the different scales employed, the current increase is ~ 100 -150 nA. This indicates the activity of this oxidised state of PB towards the oxidation of GSH to GSSH. Finally the PBCoat electrodes are shown in **Fig. 4D**. The oxidation peak and reduction peak of the Fe(II) ion in the PB film membrane are slightly smaller than on the PBMod electrodes but shows a similar shape. PBCoat electrodes displayed the greatest increase in the observed current (~ 300 -400 nA) in 10 mM GSH at 0.3 V. This result would indicate the film coverage of the PB on the PBMod electrode is less than that on the PB coat electrode.

While both PBMod and PBMix possess the same percentage composition of PB and MWNCTs their electrochemical behaviour is significantly different. PBMix electrodes show lower currents for the PB present relative to the PBMod electrodes. Due to the different preparations for the combined material the PBMod material possesses a greater surface area of PB, better connection between PB and the MWCNT and a

more homogenous mixture compared to that of the PBMix material. This may explain the difference observed between the electrochemical behaviour of PB in the PBMod and PBMix material. The PBCoat electrode showed the greatest response which may be due to greater coverage of the PB film on the electrode surface compared to the PBMod electrodes. It is more likely that there would be overlapping deposits of PB on the PBCoat electrodes, whilst there are most likely hotspots on the surface of the PBMod electrode. However the Fe(II) ion response of the PB is similar in both the PBMod and PBCoat electrodes which is suggestive that the amount of PB is similar, however the locations vary as on the PBCoat all the PB is on the surface of the electrode, whilst on the PBMod the PB is dispersed throughout the composite material and only a fraction is at the electrode solution interface.

3.3. Assessment of the sensitivity and stability of various PB-MWCNT composite electrodes for the detection of GSH

In order to examine the catalytic ability of the various PB modified electrodes, studies were carried out with GSH to examine electrode sensitivity and stability responses. For all measurements a potential of 0.5 V was chosen to oxidise PB into the correct redox state for it to then oxidise GSH. This potential was chosen such that is significantly more positive than the $E_{1/2}$ for the 1st redox couple (~ 0.26 V) on all electrodes, to ensure that effectively all of the PB is in its catalytically-active oxidised state while remaining at negative enough potentials to avoid influences from the 2nd oxidised state of prussian blue, $E_{1/2}$ of ~ 0.9 V (vs Ag/AgCl). **Fig. 5A** displays the amperometric response for examples of the four different electrodes with successive additions of GSH ranging from 50 μ M to 1 mM.

MWCNT control electrodes display insignificant changes in the observed current on addition of GSH with a sensitivity of 0.01 ± 0.01 pA μ M⁻¹ ($n = 3$, **Fig. 5B**). There was a significant increase in the current at the PBMix electrodes on addition of GSH with a sensitivity 0.21 ± 0.01 pA μ M⁻¹ ($p < 0.001$, $n = 3$, **Fig. 5B**) when compared to control electrodes. PBMod electrodes displayed a much more prominent increase in the observed current with the addition of GSH with a sensitivity of 2.05 ± 0.06 pA μ M⁻¹, which was significantly greater than that of both the PBMix and control electrodes ($p < 0.001$, $n = 3$, **Fig. 5B**). The PBCoat electrodes displayed a response was

significantly greater than that of the PMod electrode ($p < 0.001$, $n = 3$, **Fig. 5B**). The observed current sensitivity was $3.26 \pm 0.13 \text{ pA } \mu\text{M}^{-1}$ on the PCoat electrode, which was also significantly greater than that of both the PMix and control electrodes ($p < 0.001$, $n = 3$).

These results indicate that the PCoat electrode has the greatest sensitivity between the examined materials with the PMod electrode displaying slightly smaller sensitivity in comparison. This would indicate the film coating offers better sensitivity than mixing of chemical modifiers in electrode fabrication. PMod material was approximately 8.5 times more sensitive than the PMix material, suggesting that just mixing the chemical modifier is not sufficient and that it requires a more effective dispersal and/or shorter range electrochemical interaction between the MWCNT and PB. This interaction between the PB and the conductive material must be in direct contact as this provided enhanced current, however with the PCoat there is random distribution between the PB and the conductive MWCNT, thus varying interactions in the material

The stability of the various PB electrode fabrication strategies was assessed. Measurements were made at various times over a 60 day period. **Fig 5C** shows the normalised to initial current response for the four electrode fabrication strategies. There was no significant difference in the stability of the response between the control MWCNT electrode, the PMix and PMod electrodes. After 60 days, there was a $20.0 \pm 2.7 \%$ loss in response on the PMix electrode and $13.3 \pm 1.5 \%$ loss in the current response on the PMod electrode. However, the PCoat electrode displayed significantly decreased response over the duration of the study, where after 60 days the current response decreased by $97.3 \pm 1.5 \%$ loss. There was a significant reduction in the stability of the PCoat electrode when compared to the PMix, PMod and Control electrodes ($n=3$, $p<0.001$).

These results indicate that mixing or chemical modification of the conductive material for fabrication of chemically-modified electrodes provides far greater stability than film coated electrodes. There is a significant reduction in the stability of the film electrode even after a single day of storage, which suggests that coating of PB as an electrode fabrication approach is ideally suited for single use measurements. This may be due to the fact that the PB layer in the PCoat electrode is more exposed to the external

environment during measurements and storage and thus is more likely to degrade in comparison to the PBMix and PBMod electrodes where the PB is trapped within the epoxy composite electrode

Overall the varying strategies of fabrication of chemically-modified electrodes can provide significant differences in sensor performance and this study indicates that mixing chemical agent/s within the electrode material or film coating of chemical agent/s on the electrode surface can reduce the sensitivity or stability, respectively.

4. Conclusions

Our results indicate that different approaches to fabricate chemically modified electrodes can offer varying electrochemical properties. Our findings show that film coating of PB on MWCNT composite electrodes offer enhanced sensitivity for the detection of GSH but greatly reduced stability compared to other modification methods and thus offer potential as single use electrochemical sensors. Using a chemical reaction to generate PB on MWCNT to make composite electrodes provided good sensitivity, though less than the coating method, along with excellent stability. Taken together these properties would allow for the fabrication of long-term use electrochemical sensors. Mixing PB with MWCNT to make composite electrodes offer significantly reduced sensitivity but good stability. The use of these fabrication strategies will provide scope for the production of electrodes intended for varying applications.

Acknowledgements

We would like to thank Andrew Flint and Jon Salvage for support during SEM and elemental analysis measurements. AFM, MA and BAP would like to thank BBSRC (BB/K013807/1) for funding.

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FIGURES

Figure 1. Schematic diagrams of the various fabrication strategies utilised for formation of the chemically modified electrode.

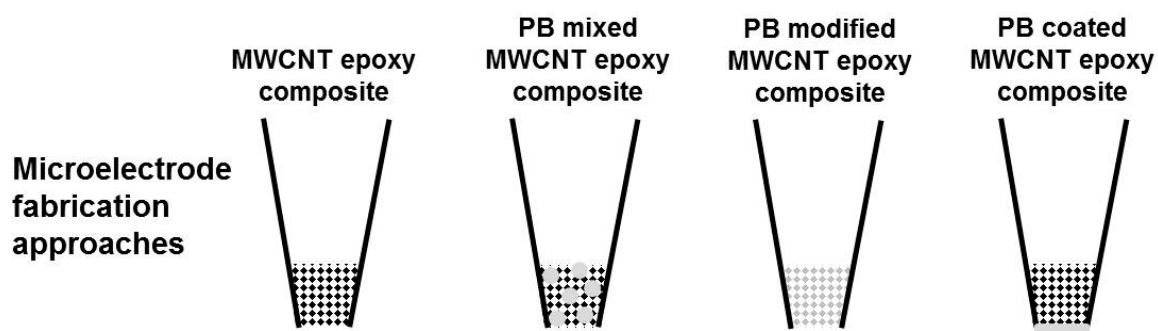


Figure 2. Characterisation of multi-wall carbon nanotube (MWCNT) materials consisting of Prussian blue (PB). Schematic diagrams of the material are shown in A-C based on the SEM images obtained in D-F. Data is shown for the MWCNT material alone (A & D), a mixture of MWCNT with PB (B & E) and MWCNT modified with PB (C & F). The arrows indicate the presence of the PB particles/spheres on within the two materials and the star symbol indicates the large agglomerate bundles of MWCNTs.

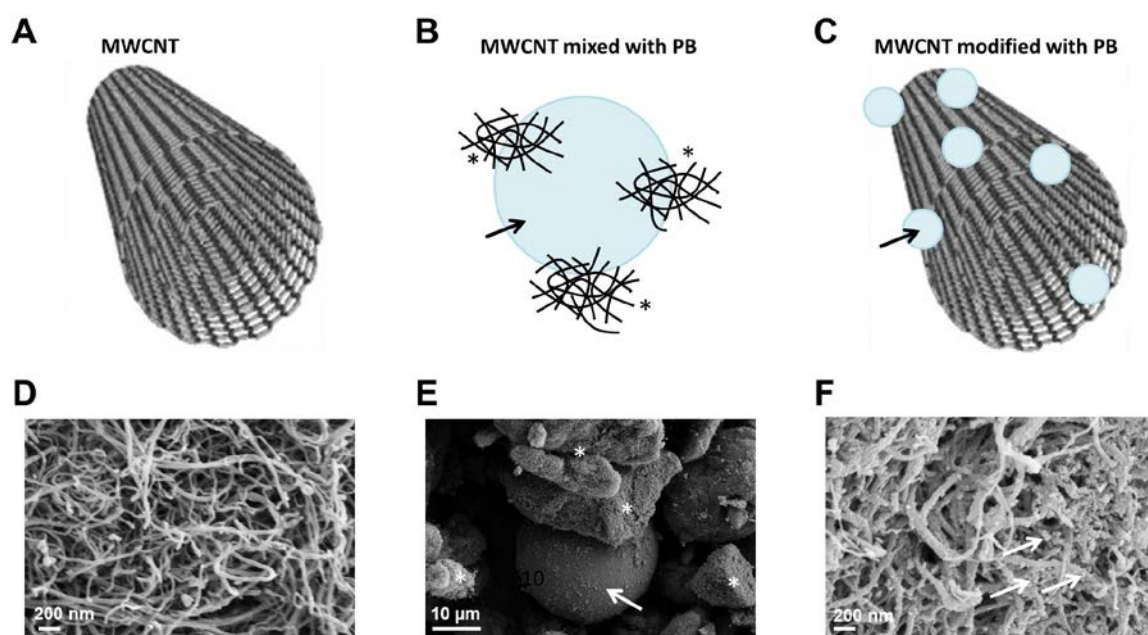


Figure 3. Elemental analysis of the different chemically modified materials. The base MWCNT material is shown in (A). MWCNT mixed with prussian blue is shown in (B) and the MWCNT modified with PB is shown in (C).

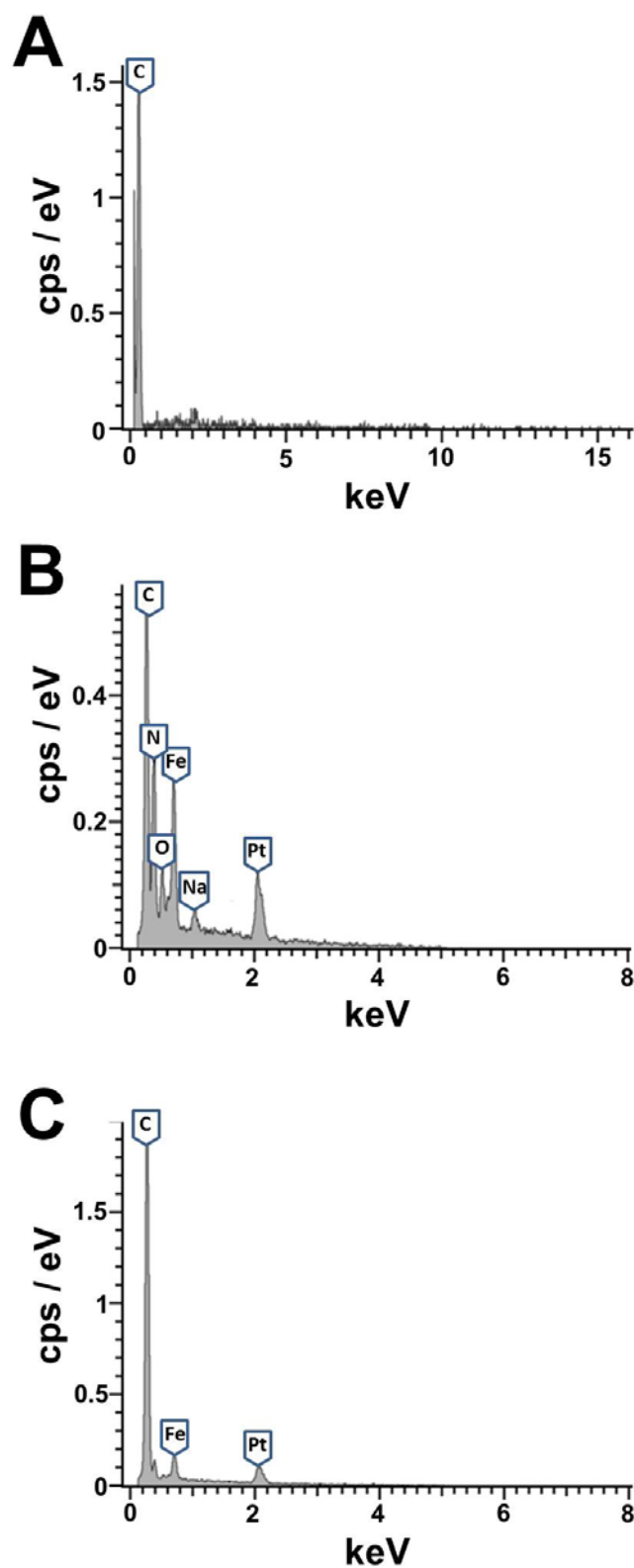


Figure 4. Cyclic voltammograms of the various fabricated PB modified MWCNT composite electrodes. The response of the control MWCNT composite electrode is shown in A, the PBMix composite electrode consisting of MWCNTs mixed with PB is shown in B, the PBMod MWCNT composite electrode is shown in C and the PBCoat electrode was shown in D where PB was film coated on the electrode surface. Measurements were carried out in the presence and absence of 10 mM glutathione (GSH) in 1 M KCl. Cyclic voltammograms were carried out using a Ag|AgCl (3 M KCl) reference electrode at scan rate 100 mVs⁻¹. Note: The change in scale from A and B in nA to C and D in μ A.

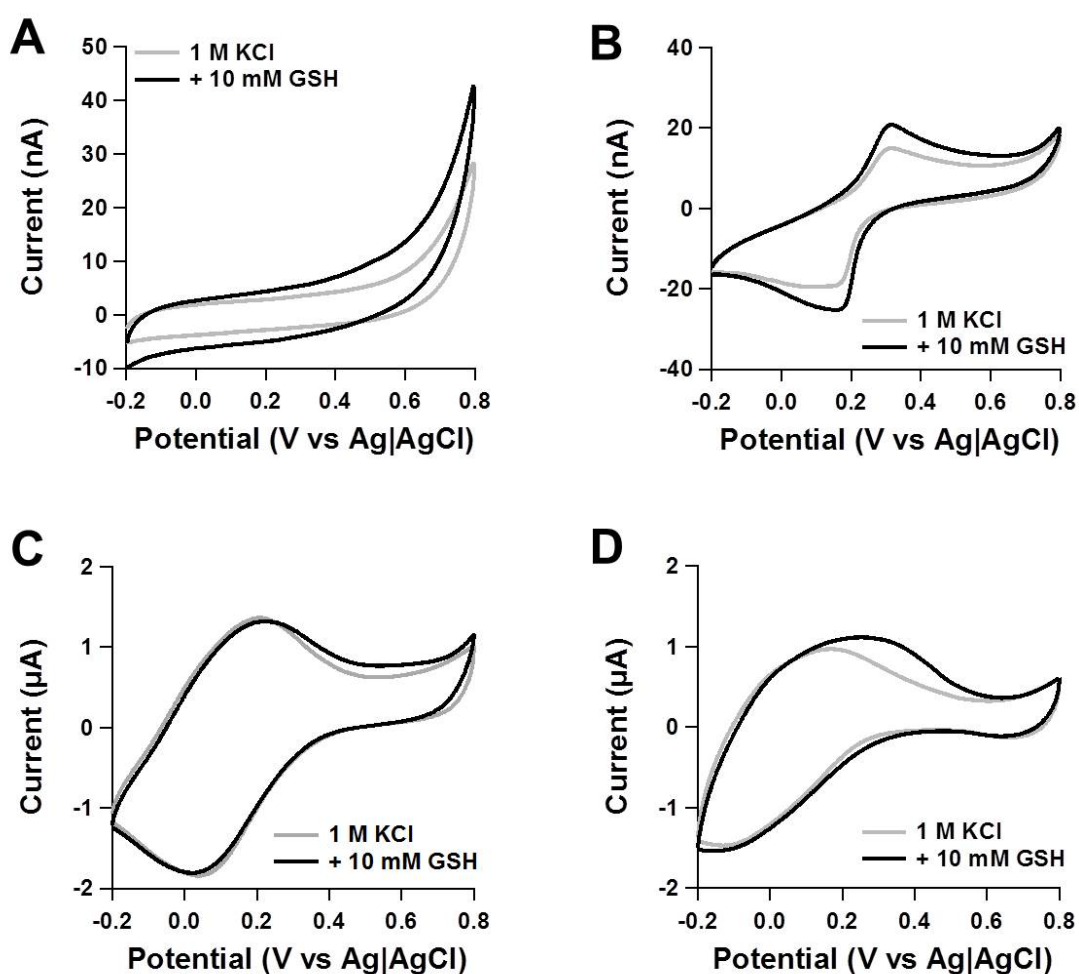


Figure 5. Amperometric responses of glutathione on the various PB modified MWCNT composite electrodes. For assessment of the selectivity of the various electrodes measurements were carried out in varying concentration of glutathione. Representative traces of the four electrodes is shown in A, where varying concentration of glutathione were added every 100 s. All measurements were carried out at 0.5 V vs Ag|AgCl. In B, the calibration response from multiple measurements is shown. The stability of the various electrodes was assessed in 500 μ M glutathione and the responses for day 1, 7, 14, 30 and 60 are shown in C. All data shown as mean $\pm$ sd, n=3.

