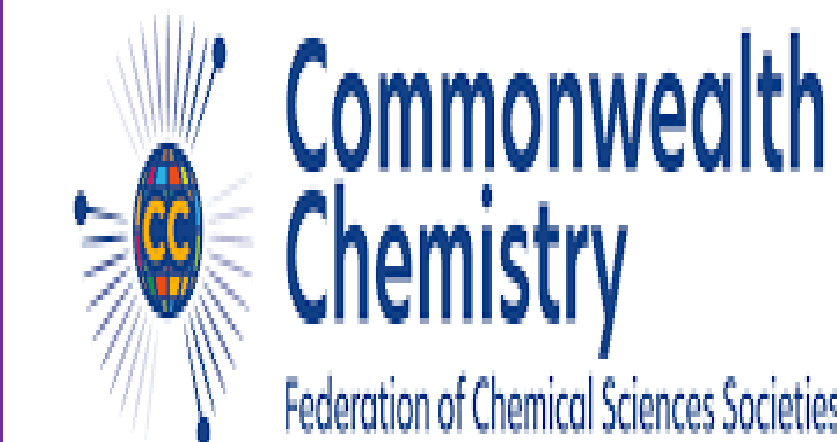




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Electrochemical characterization of metal oxide nanoparticles/MWCNT modified electrode

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Abstract

The electrochemical and sensing properties of glassy carbon electrode (GCE) modified with nanocomposites of metal oxide nanoparticles and functionalized multi-walled carbon nanotube (f-MWCNTs) were investigated. The metal oxide nanomaterials namely CuO-ZnO binary nanoparticles, ZnO and CuO nanoparticles, fMWCNTs and their nanocomposites (fMWCNTs/CuO, fMWCNTs/ZnO, fMWCNTs/CuO-ZnO) were characterized using fourier-transform infrared spectroscopy (FT-IR), x-ray diffraction spectroscopy (XRD), energy dispersive x-ray spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrochemical characterization of the composite modified GCEs done in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe via cyclic voltammetry (CV) revealed a higher anodic current response at GCE/fMWCNTs/CuO, suggesting a synergy between fMWCNTs and CuO for improved sensing. Keywords: Cyclic voltammetry, CuO, ZnO, multi-walled carbon nanotube, glassy carbon electrode

Introduction

The distinctive potential of stimulating faster kinetics of electron transfer between the active site of desired species and the electrode is notable in nanostructured metal oxides¹. Copper oxide (CuO), a p-type semiconductor, and Zinc oxide (ZnO), an n-type semiconductor both have their nanostructures demonstrating high specific surface area, excellent electrochemical activity, and many other interesting properties that make them great choices in sensor applications.

The high electrical conductivity and chemical stability characteristic of multi-walled carbon nanotube (MWCNT) also makes for its suitability and wide use in the field of electrochemical sensors². Integration of these metal oxide nanoparticles with the conducting carbon nanotubes has the potential of boosting the sensor performance tremendously by enhancing the charge transfer between analytes and the support matrices^{3, 4}. Electrode modifications with nanostructured metal oxides and carbon nanotubes have yielded electrochemical sensors of (i) excellent electrical conductivity, due to the swift electron transfer rates; (ii) enhanced catalytic activity, emanating from

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the reduction of over potentials of the redox reactions; (iii) improved selectivity with relevance to an array of chemical species in various samples, and (iv) high surface area, favouring the analyte aggregation hence improving sensitivity⁵.

Materials and Methods

All experiments were performed at room temperature $25 \pm 1^\circ\text{C}$. Chemicals used were of analytical-reagent grade. Infrared spectroscopy data were obtained with Fourier transformed infrared spectrometer (Agilent Technology, Cary 600 series FTIR spectrometer, USA). X-ray diffraction (XRD) study was performed on X-ray diffraction spectrophotometer (Bruker-AXS, Madison, Wisconsin). Electrochemical experiments were carried out using an AUTOLAB Potentiostat PGSTAT 302 (Eco Chemie, Utrecht, and the Netherlands) driven by the GPES software version 4.9. $[\text{Fe}(\text{CN})_6]^{3-/4-}$ prepared in phosphate buffer solution (PBS) of pH 7.4 was used as the redox probe at scan rate of 25 mVs^{-1} . Bare or modified glassy carbon (GCE) electrode was used as the working electrode.

• Co-precipitation synthesis of the metal oxide nanoparticles

• Spectroscopy studies
• Morphological studies

• Nanocomposite preparation
• Modification of the electrode by drop & dry method

• GCE/f-MWCNT/MO
• Electrocharacterization & catalysis

Results

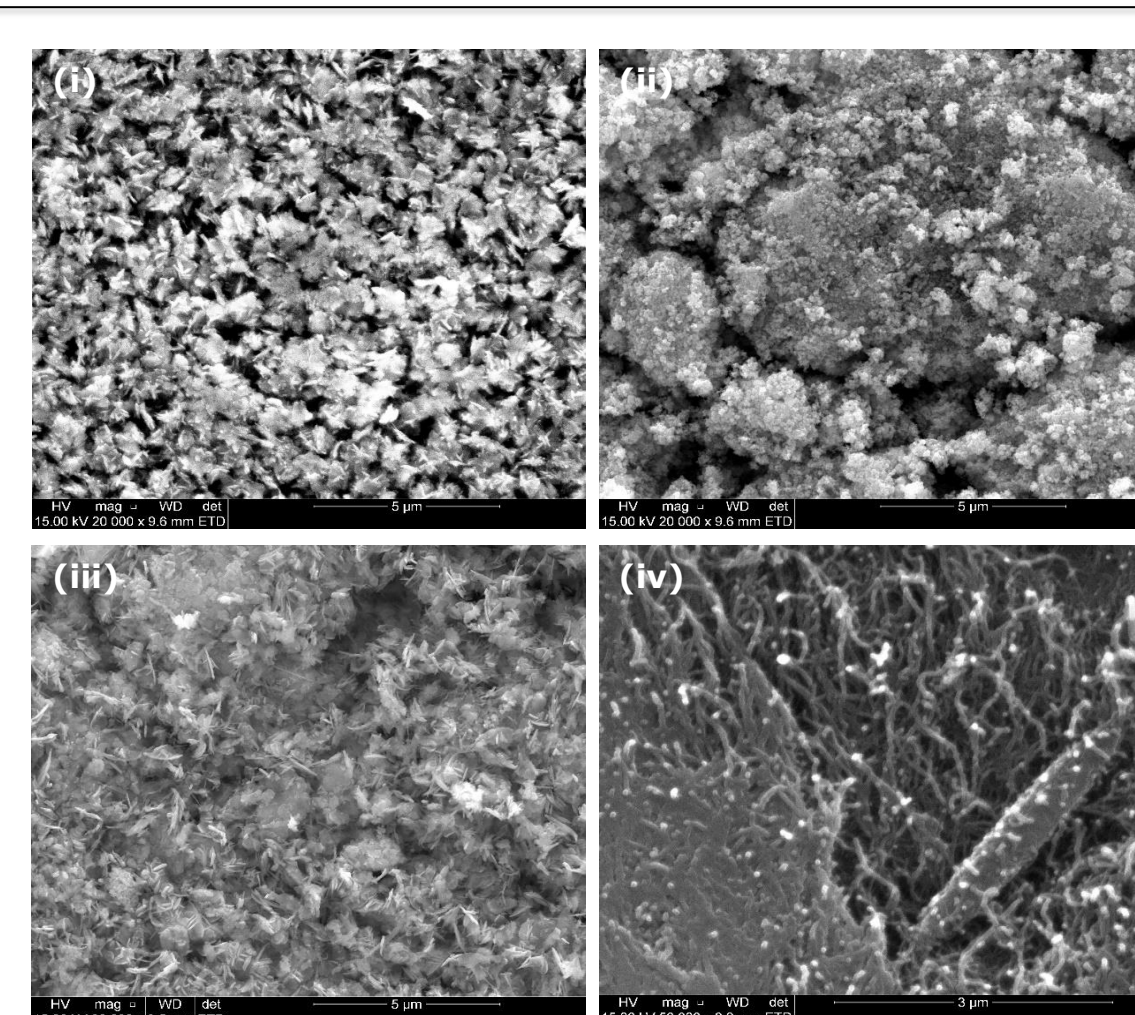


Figure 1a: SEM images of (i), CuO (ii), ZnO (iii), CuO - ZnO nanoparticles and (iv), functionalized MWCNT.

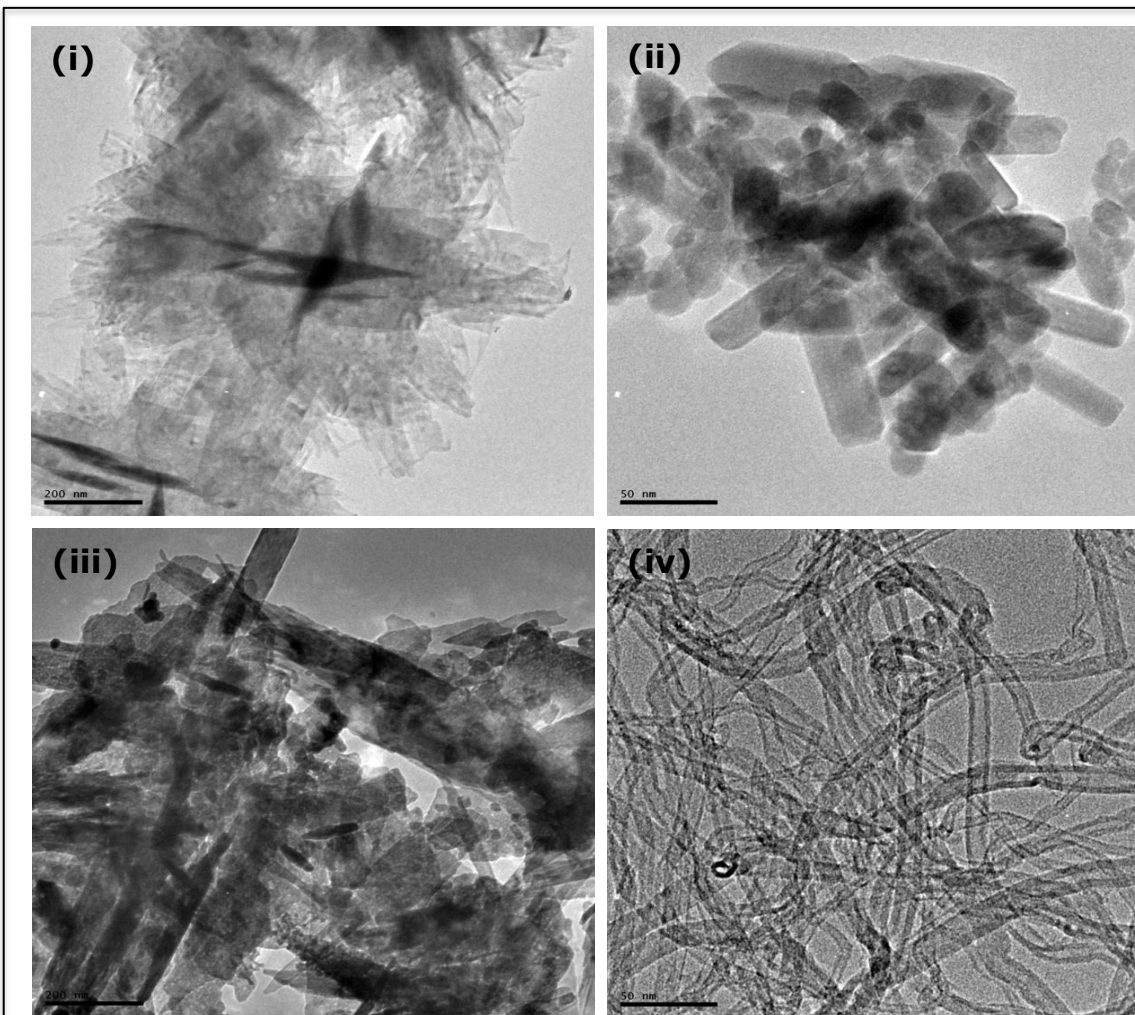


Figure 1b: TEM images of (i), CuO (ii), ZnO (iii), CuO - ZnO nanoparticles and (iv), functionalized MWCNT.

Results

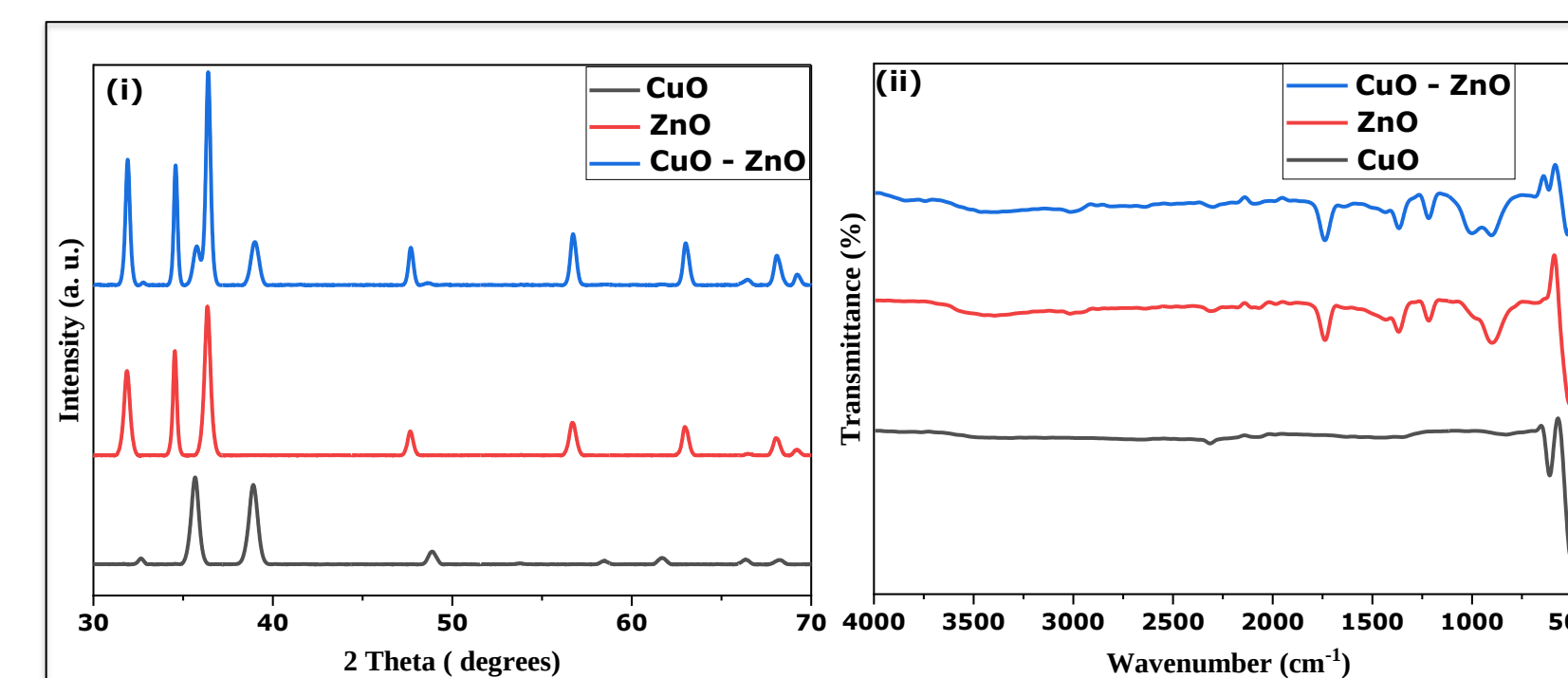


Figure 2: The (i) XRD and (ii) FTIR spectra of CuO, ZnO and CuO - ZnO

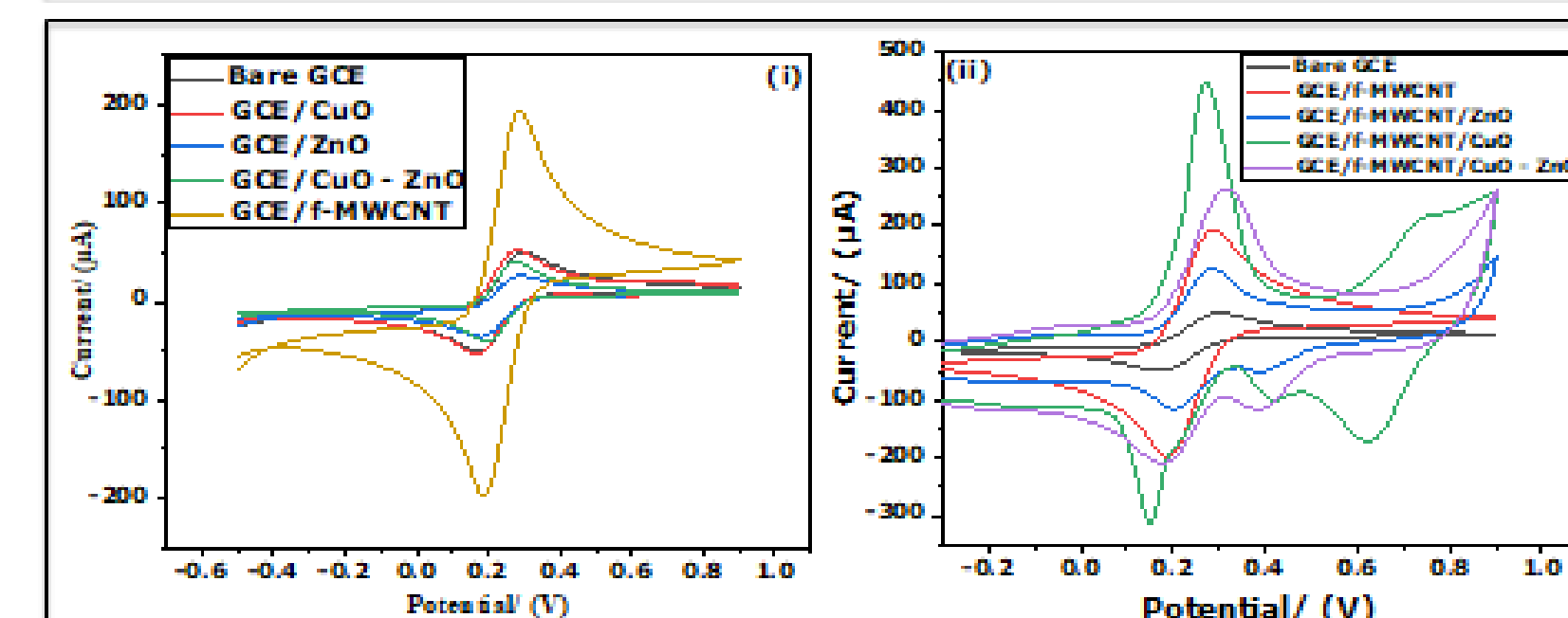


Fig. 4: Cyclic Voltammograms of (i) GCE, GCE-MO and GCE-MWCNT (ii) GCE, GCE-MWCNT and GCE-MWCNT-MO in 10mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution prepared in 0.1M PBS at scan rate 25 mVs^{-1} . (MO: (a) CuO, (b) ZnO and (c) CuO-ZnO nanoparticles)

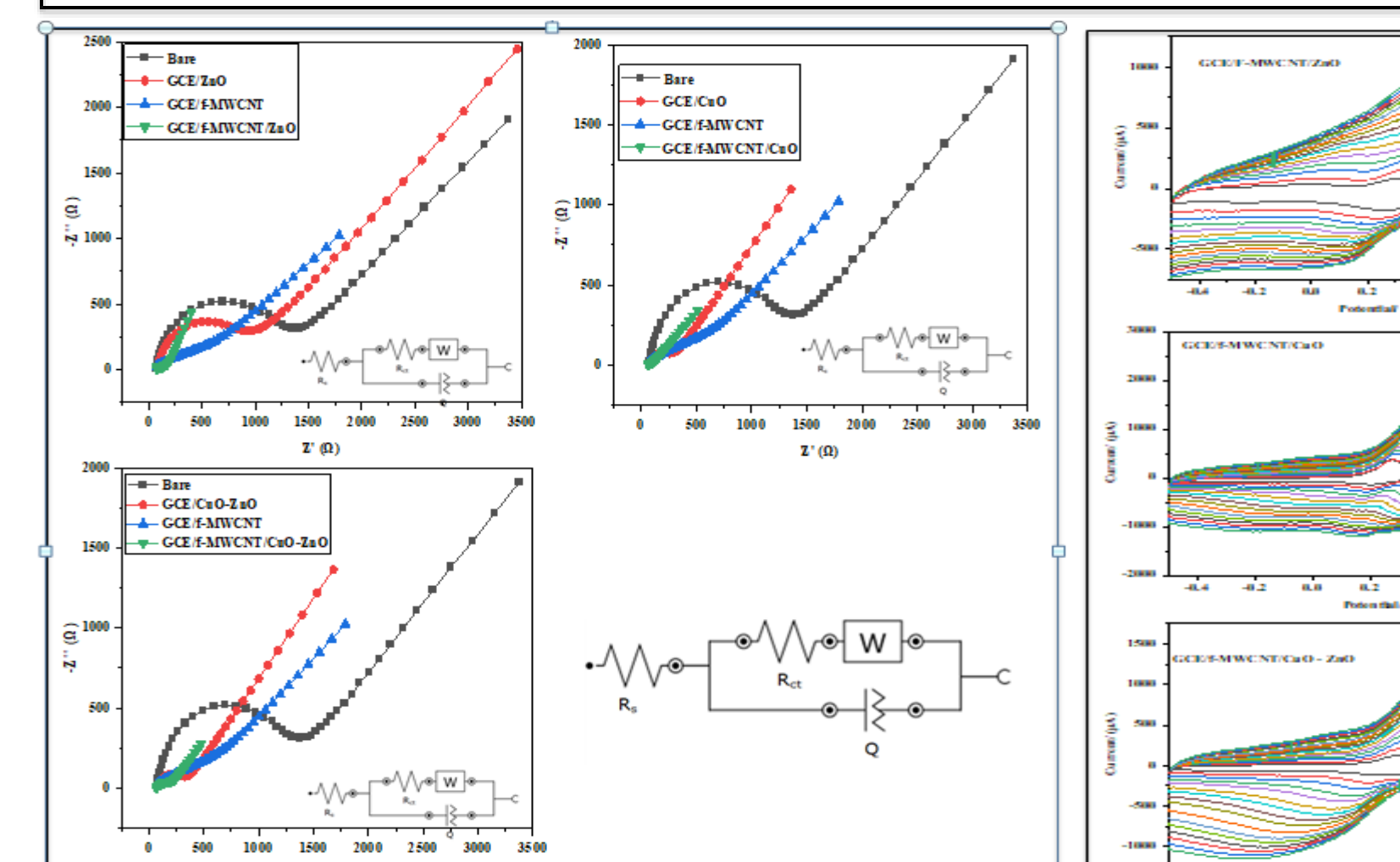


Figure 5: Nyquist plots of the electrochemical impedance spectroscopy data for the bare GCE, GCE/MO, GCE/f-MWCNT and GCE/f-MWCNT/MO electrodes in 10mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution (PBS pH 7.0) at a fixed potential of 0.2 V (vs. Ag/AgCl, saturated KCl) with the circuit description used in fitting the EIS data of all the electrodes.

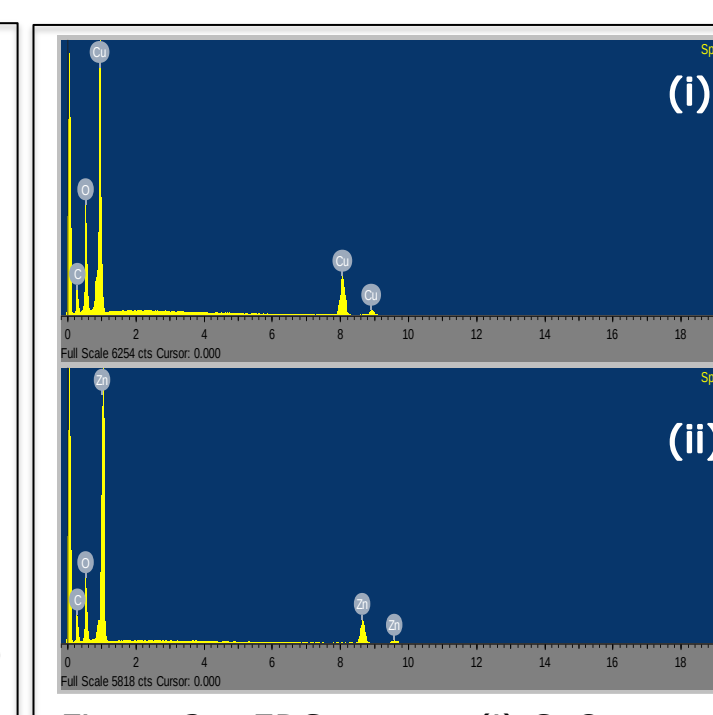


Figure 3a: EDS spectra (i) CuO and (ii) ZnO nanoparticles.

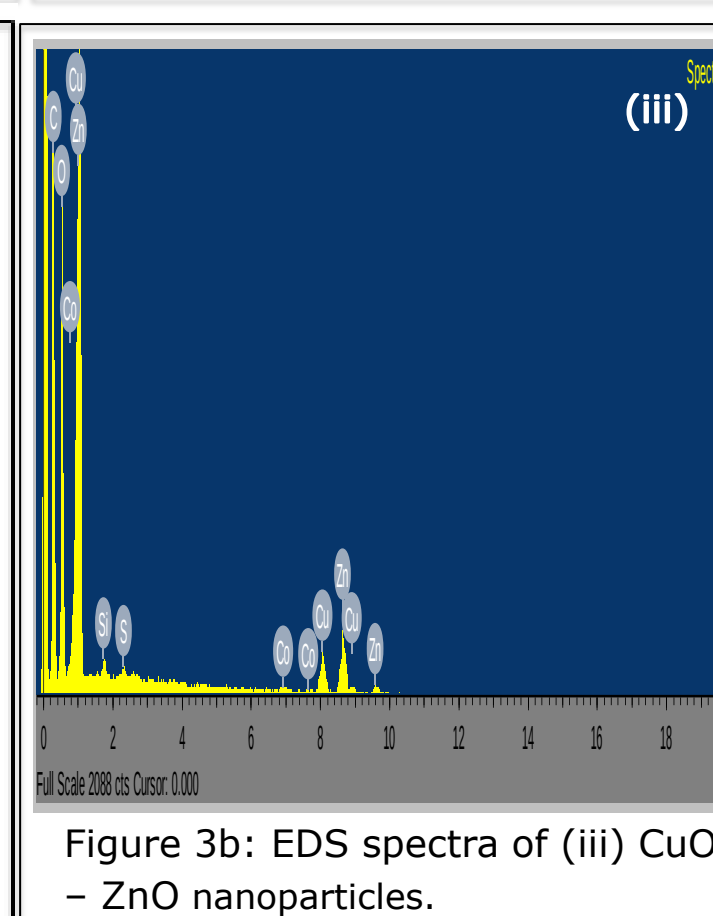


Figure 3b: EDS spectra of (iii) CuO - ZnO nanoparticles.

Discussion

The synthesis of the nanoparticles were confirmed by morphological and spectroscopy characterization as shown in Figures 1a-3b.

The GCE/f-MWCNT/CuO electrode as observed in the cyclic voltammogram (fig. 4) exhibited the highest current response ($448.09 \mu\text{A}$). The ionic interaction between MWCNT and the metal oxides is evident as their integration resulted in a huge increase in the current response as against bare GCE ($49.7 \mu\text{A}$)

Discussion

and the individual nanoparticles ($52.46 \mu\text{A}$, $26.29 \mu\text{A}$, $40.51 \mu\text{A}$, $194.15 \mu\text{A}$) CuO, ZnO, CuO-ZnO, and f-MWCNT respectively.

Redox peaks were observed in all the electrodes with peak-potential separations (ΔE_p) of 0.12V and 0.13V for GCE/f-MWCNT/CuO and GCE respectively.

The Nyquist plots in fig. 5 show lower R_{ct} for all nanocomposite modified electrodes with GCE/fMWCNT/CuO having the lowest R_{ct} value (24.1Ω) against (1211Ω) for the bare GCE implying that electron transport is faster in the GCE/f-MWCNT/CuO electrode compared to other electrodes (data not shown).

The conductivity of the MO nanoparticles, MWCNTs' electronic nature, and large surface area as well as the high electrocatalytic activity of the nanostructure enhanced electron transport at the GCE-MWCNT-MO modified electrodes⁶.

Conclusion

The characterization of metal oxide nanoparticles and their nanocomposite with MWCNT has been described in this work. The metal oxide/MWCNT modified glassy carbon electrodes improved sensing for electrochemical detection was established. All GCE/fMWCNT/MO demonstrated remarked improved sensing as compared to the bare with the GCE/fMWCNT/CuO exhibiting the most improved sensing.

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