

Electrochemical and spectroscopy properties of NiPcMWCNTs modified electrode.

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ABSTRACT

A novel electrochemical sensor was developed based on Nickel phthalocyanine multi-walled carbon nanotubes NiPcMWCNTs composite coated on glassy carbon electrode GCE. The structure and morphology of the nanomaterials were characterized by UV/Vis spectroscopy, SEM, TEM, XRD and FTIR. The electrochemical characterization of the modified sensors was done using cyclic voltammetry CV and electrochemical impedance spectroscopy EIS. The cyclic voltammograms obtained for GCE, Ni/GCE, Pc/GCE, MWCNT/GCE, and NiPcMWCNT/GCE in $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ showed a pair of redox peaks. NiPcMWCNT/GCE electrode gave a higher current response of anodic peak current (I_{pa}) of 458 μA when compared to 25.0, 21.5, 35.6 and 58.1 μA for GCE, Pc/GCE, Ni/GCE, GCE/MWCNT respectively. A linear relationship between the peak current and the square root of the scan rate indicates that NiPcMWCNT is a typical diffusion-controlled electron transfer process. The EIS study of the electrodes revealed that NiPcMWCNT/GCE has the fastest electron transfer with a charge transfer resistance R_{ct} value of 0.07 k Ω which is lower than 0.53, 1.05, 0.99, and 0.34 k Ω for GCE, Pc/GCE, Ni/GCE, MWCNT/GCE respectively.

Keywords: Nickel nanoparticles, Phthalocyanine, Multiwalled carbon nanotube, Cyclic voltammetry, Electrochemical impedance spectroscopy.

INTRODUCTION

Carbon nanotubes CNTs have received wide attention in the field of nanotechnology due to their outstanding opto-electronic properties. Specifically, their biocompatibility, high reactivity, good conductivity and modifiable sidewall have made their application in sensors fabrication highly embraced in electroanalytical chemistry [1-2]. The success of such sensors has manifested in improved current response of biomolecules, inorganic compounds and some biological cells when CNTs are incorporated as part of a composite for the modification of an electrode. In addition, CNTs stand out as a sensing material as a result of their chemical stability, fast electron transfer kinetics and electrocatalytic activity towards a wide range of analytes in non-aqueous and aqueous media [2-3].

In recent years there is an emerging interest to synthesize magnetic nanoparticles of Fe, Co, and Ni due to their superior magnetic properties and potential uses in many fields including catalysis, memory storage devices and sensors. One of their recent applications is their role in the fabrication of carbon nanotubes (CNTs) [4]. Among the nanomaterials, cobalt and nickel nanoparticles (CoNPs, NiNPs) are one of the most efficient catalysts and have been widely used in many electrochemical fields and sensors [5]. In the last decade, because of their high electron transfer abilities, metal phthalocyanines have been utilized in many fields such as molecular electronics, electronic sensors, catalytic, catalysts, photonics, etc, [6]. MPs are thermally and chemically very stable and hence, can be used in adverse environment like high temperatures, acidic or basic conditions.

Recently, due to the changing world of advanced technology, the design of new environmentally friendly and easily accessible catalysts has been drawing much attention. Among these catalysts, metal phthalocyanines compounds stand out due to their symmetric macro ring as well as the physical and chemical entities [7-8].

MATERIALS AND METHODS

All chemicals used were of analytical-reagent grade. Field emission scanning electron microscopy (FESEM) images were obtained from high resolution scanning electron microscope (Zeiss Ultra Plus 55 HRSEM, Germany). Infrared spectroscopy data were obtained with Fourier transformed infrared spectrometer (Agilent Technology, Cary 600 series FTIR spectrometer, USA). UV-Vis experiments were performed with a UV-1901 UV-vis spectrophotometer (Agilent Technology, Cary series) using quartz cell with path length of 1.0 cm. 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. A 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ solution prepared in 0.1 M Phosphate buffer solution (PBS) of pH 7.0 was used as supporting electrolyte. Glassy carbon electrode (GCE) was used as the working electrode. All Experiments were performed at $25 \pm 1^\circ\text{C}$ with distilled water.

RESULTS

Spectroscopic characterization

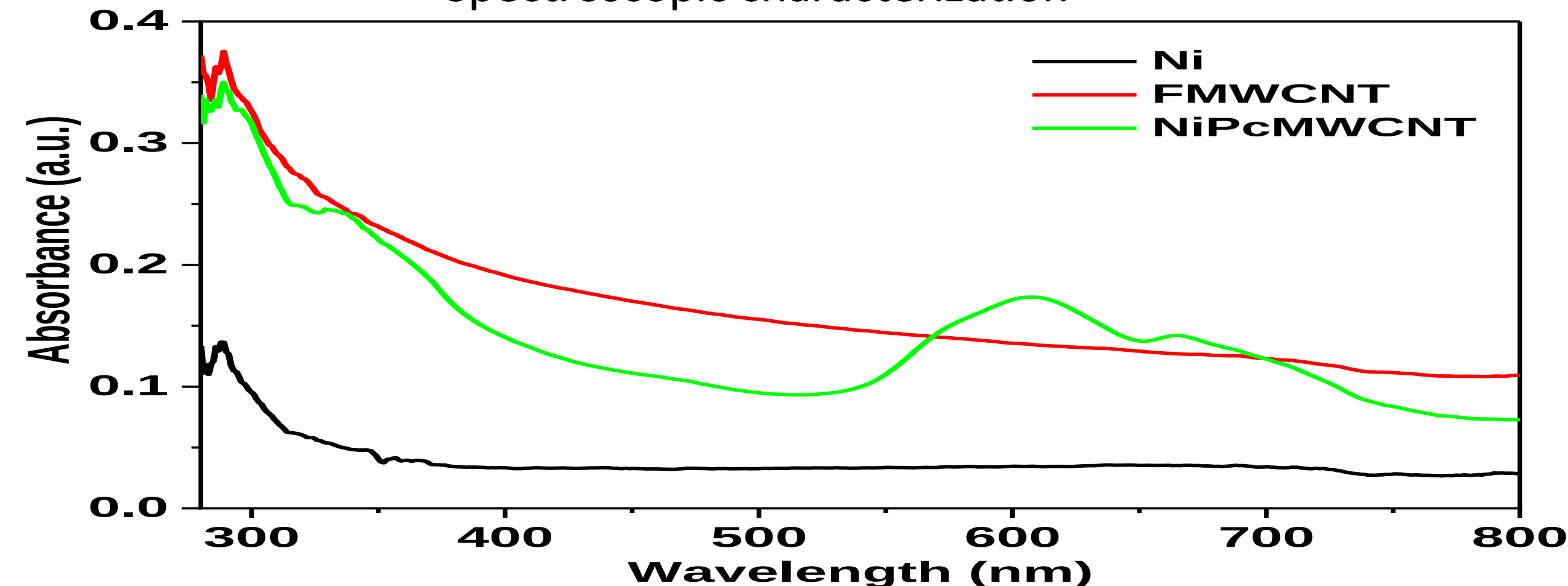


Fig. 1: UV-vis spectra of NiNps, fMWCNT and NiPcMWCNT nanocomposites.

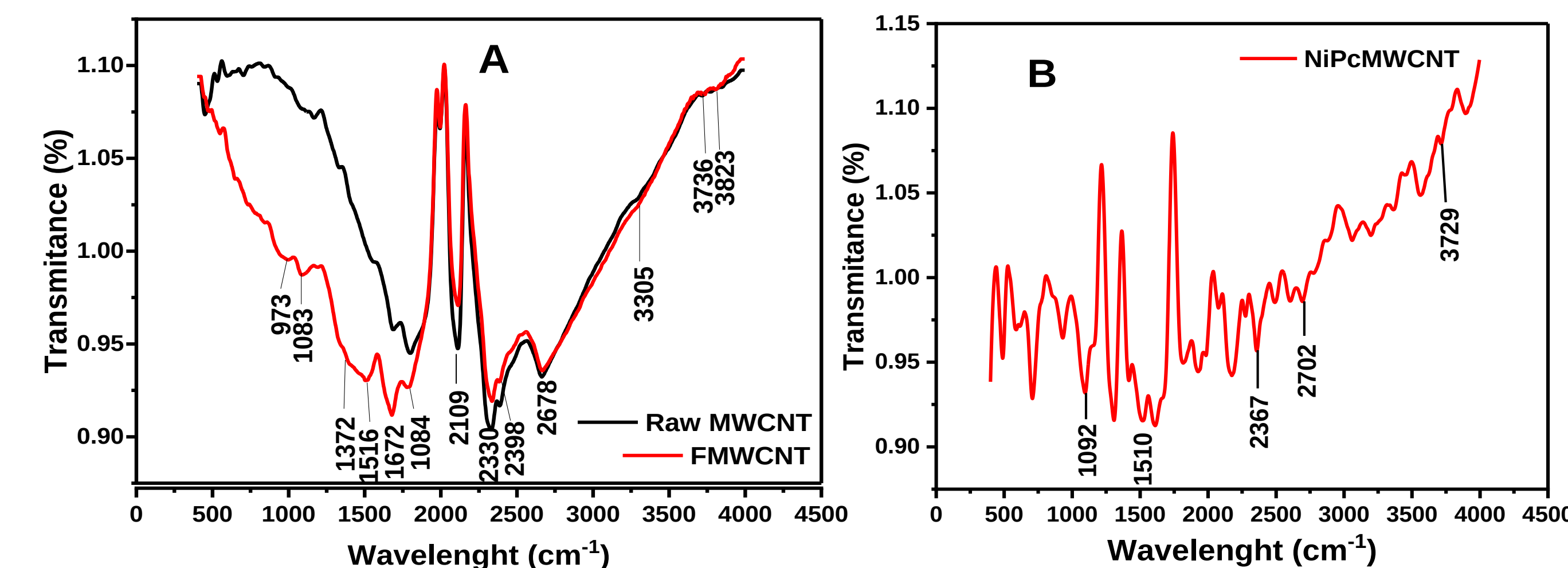


Fig. 2: FTIR spectra of (A) Raw MWCNT & fMWCNT (B) NiPcMWCNT nanocomposites.

Morphological characterization

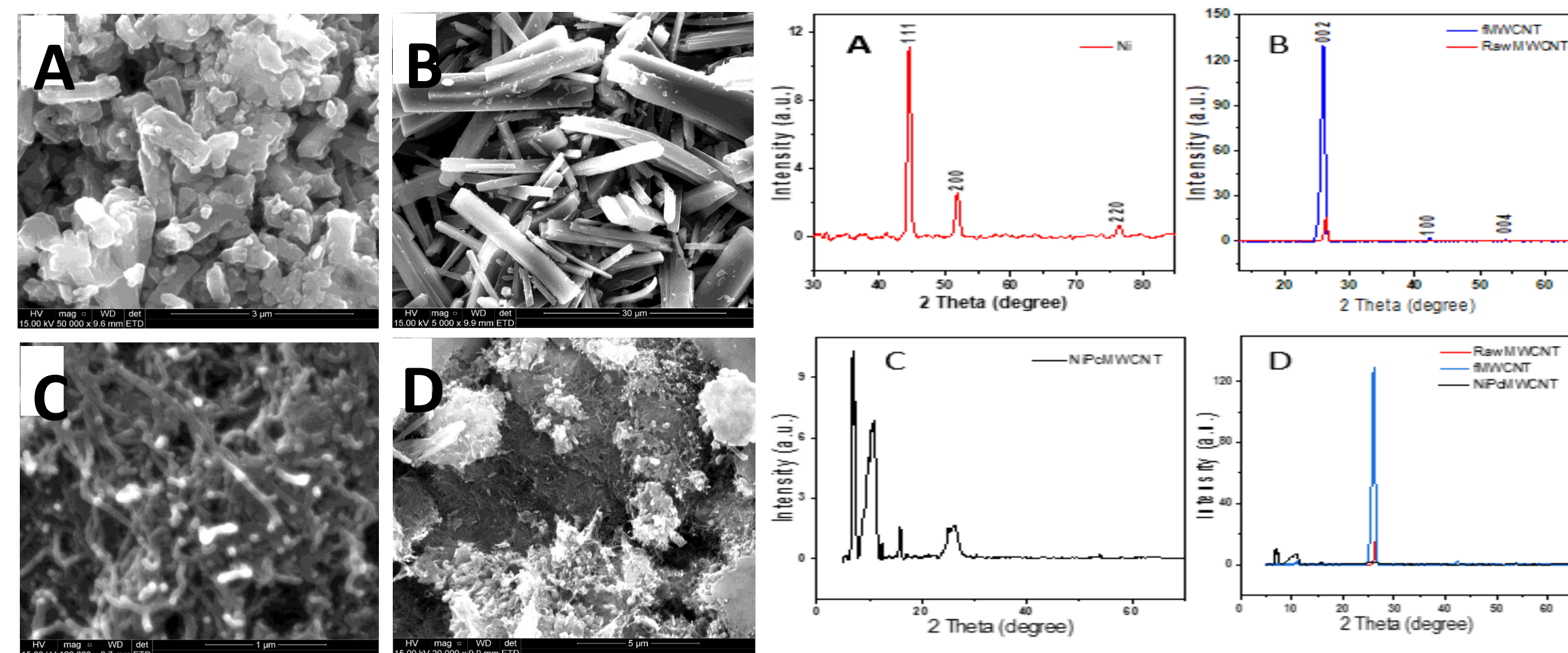


Fig. 3: SEM images of (A) NiNps, (B) Pc (C) fMWCNTs and (D) NiPcMWCNT nanocomposites

Fig. 4: XRD spectra of (A) NiNps, (B) Raw MWCNT & fMWCNT (C) NiPcMWCNT and (D) Raw MWCNT, fMWCNT & NiPcMWCNT nanocomposite

RESULTS – CON'T

Electrochemical characterization of modified electrodes

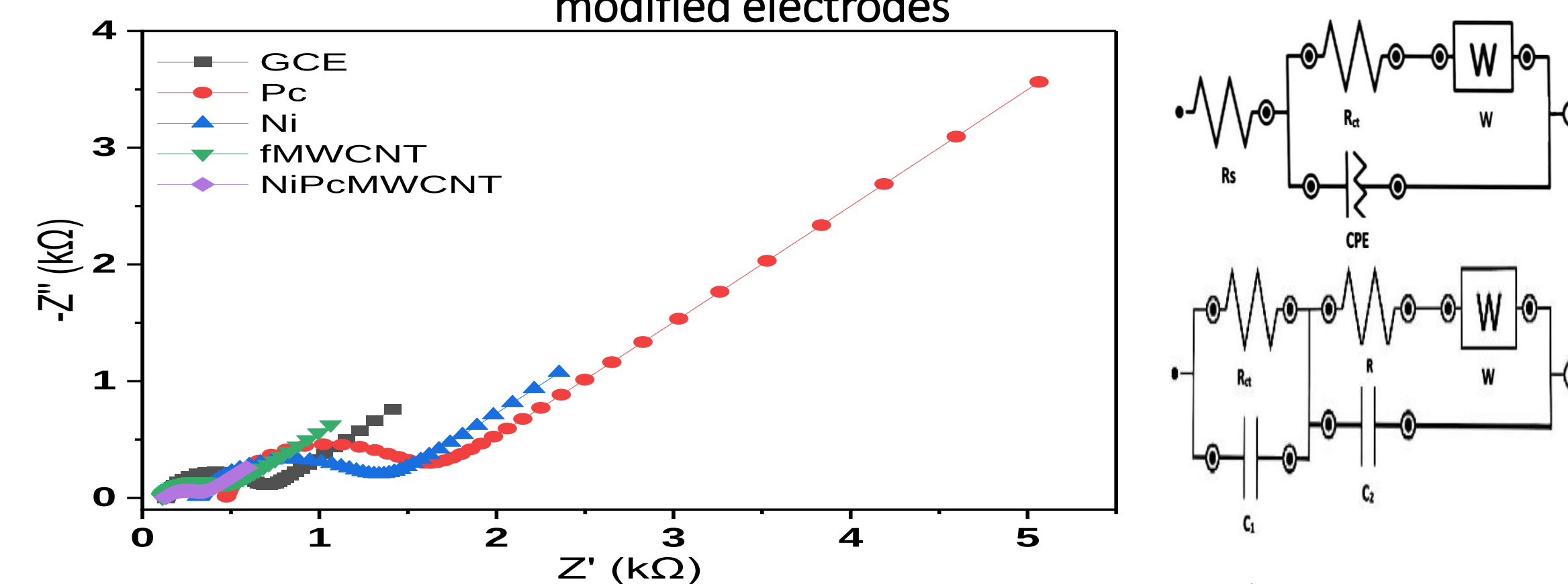


Fig. 5: (A) Obtained Nyquist plots for the modified electrodes in 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ solution at a fixed potential of 0.2 V (vs Ag/AgCl, sat'd KCl). (B & C) represents the circuit used in the fitting of the EIS data (B – GCE, Pc, Ni, fMWCNT & C- NiPcMWCNT modified electrode).

Electrode	Electrochemical impedance spectroscopy parameters					
	R_s (k Ω)	CPE (μF)	R_{ct} (k Ω)	W (mF)	n	χ^2
GCE	0.13(1.55)	3.26(14.68)	0.53(2.24)	1.17(3.39)	0.88(2.05)	0.1091
Pc	0.47(2.40)	0.77(31.62)	1.05(4.26)	0.25(3.37)	0.88(4.15)	0.2162
Ni	0.31(2.50)	5.58(23.15)	0.99(3.75)	0.83(5.80)	0.72(3.95)	0.1946
fMWCNT	0.11(1.43)	1.64(16.89)	0.34(3.59)	1.43(3.41)	0.83(2.80)	0.1746
NiPcMWCNT	0.35(0.73)	6.33(13.96)	0.074(5.54)	1.55(1.78)		0.0390

Table 1: Impedance data obtained for modified electrodes in 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ solution at a fixed potential of 0.2 V (vs Ag/AgCl, sat'd KCl) with the percent errors of data fitting in the parentheses are percent errors of data fitting.

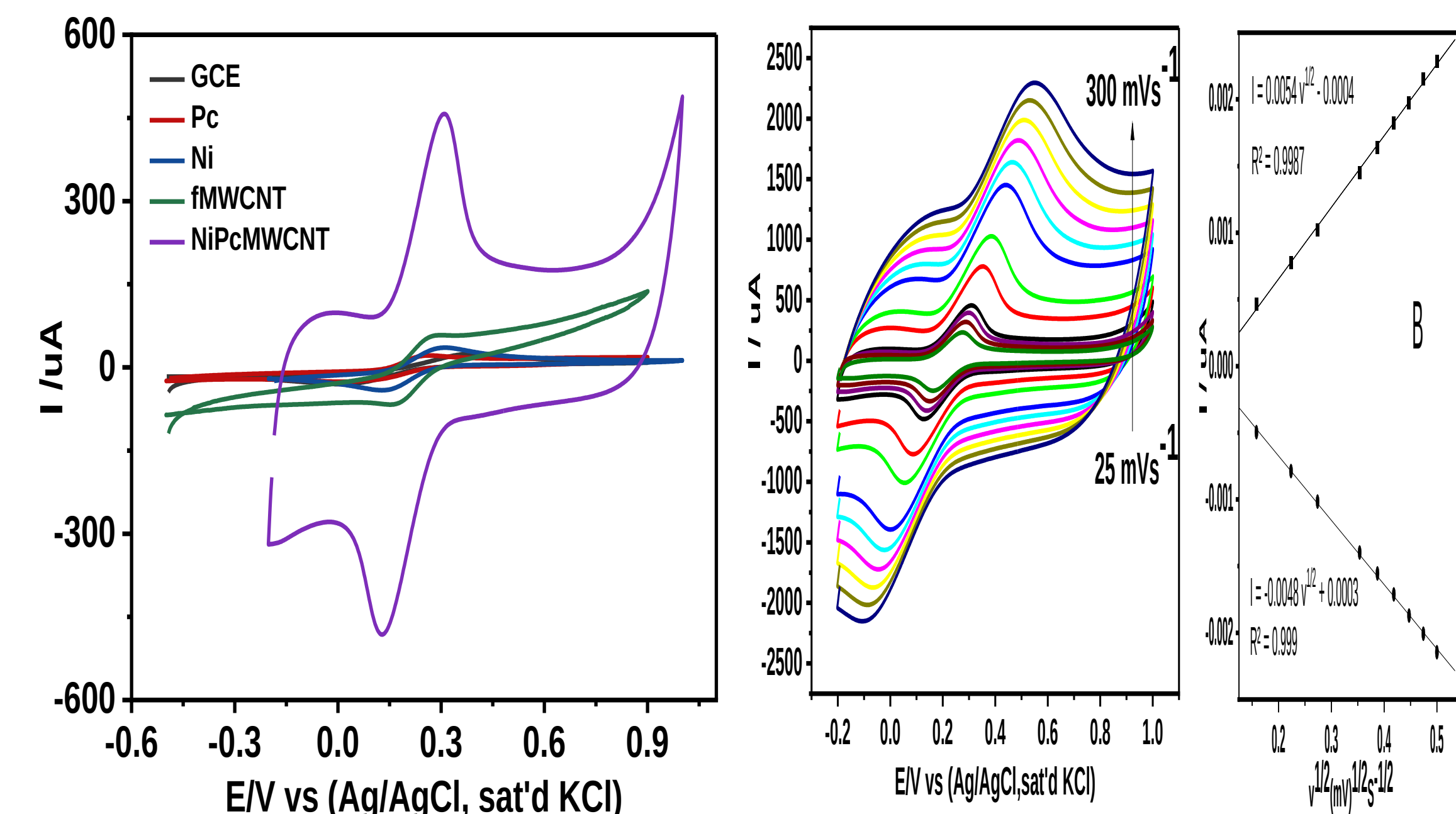


Fig. 6: Cyclic voltammograms for modified electrodes in 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ solution at a scan rate of 25 mVs⁻¹.

Fig. 7: Cyclic voltammograms of scan rate study for GCE-NiPcMWCNT modified electrode in 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ at a scan rate of 25 - 300 mVs⁻¹ (inner to outer) and B is the linear graph of the peak current and the square root of the scan rate.

RESULTS – CON'T

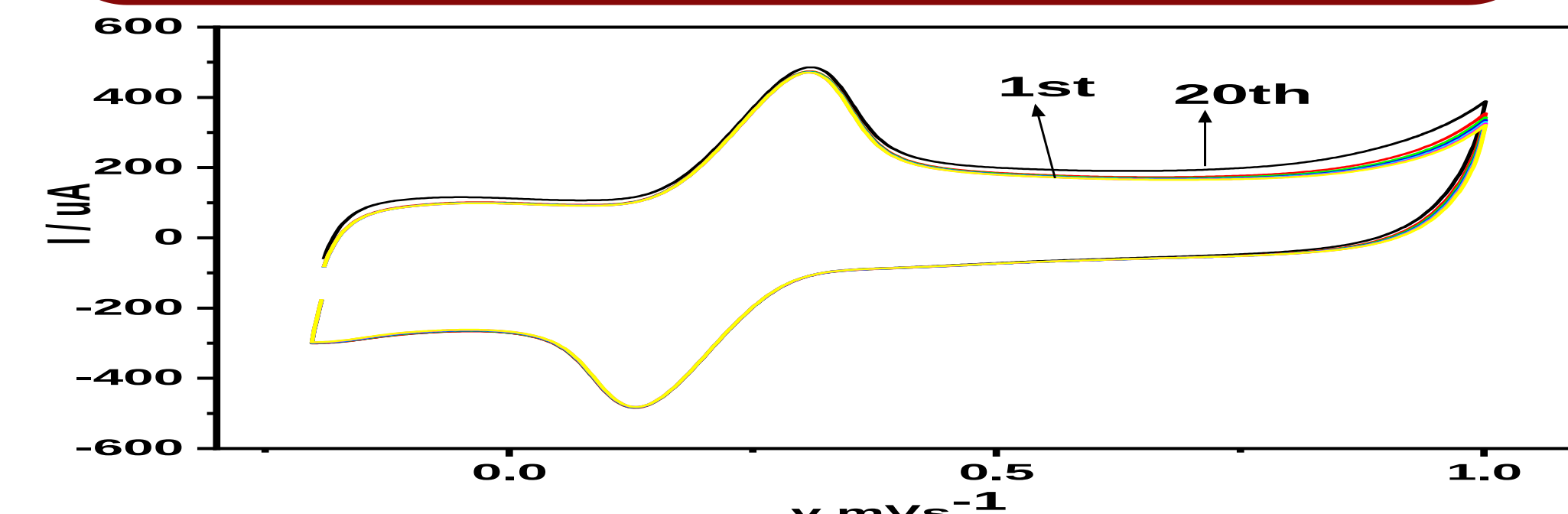


Fig. 8: Cyclic voltammograms of 20 scans of GCE-NiPcMWCNT modified electrode in 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ prepared in 0.1M PBS (pH 7) at a scan rate of 25 mVs⁻¹.

DISCUSSION

The spectroscopy and morphological characterization of the nanocomposites were successfully synthesised as shown in Figures 1-4.

The EIS fitted data in table 1 revealed that the GCE-NiPcMWCNT electrode has the lowest charge transfer resistance R_{ct} value and this suggests that it has the fastest electron transfer as compared to the other modified electrodes.

In Figure 6, a very high current response was obtained with the GCE-NiPcMWCNT electrode as compared to others and the magnitudes of both anodic and cathodic peak currents response of GCE-NiPcMWCNT electrode increase linearly with the increasing scan rate as illustrated by figure 7, suggesting a diffusion control process. The high current response of the GCE-NiPcMWCNT electrode may be due to the great surface area of fMWCNT and Pc, and electrical conductivity of the NiNps and fMWCNT.

A slight current drop (4.3%) was exhibited by the GCE-NiPcMWCNT electrode as shown in figure 8, suggesting the stability of the electrode towards 5 mM $\text{Fe}(\text{CN})_6^{4-/-}$ solution.

CONCLUSION

This study has described a successful fabrication of a GCE electrode with NiNps, fMWCNT and NiPcMWCNT nanocomposite. GCE- NiPcMWCNT, exhibited a better current response than the Bare, NiNps and fMWCNT.

REFERENCES

- Campidelli, S.; Ballesteros, B.; Filoramo, A.; Diaz, D. D. a.; de la Torre, G.; Torres, T.; Rahman, G. A.; Ehli, C.; Kiessling, D.; Werner, F., Facile decoration of functionalized single-wall carbon nanotubes with phthalocyanines via "click chemistry". *Journal of the American Chemical Society* 2008, 130 (34), 11503-11509.
- Zhu, L.; Yang, R.; Zhai, J.; Tian, C., Bi enzymatic glucose biosensor based on co-immobilization of peroxidase and glucose oxidase on a carbon nanotubes electrode. *Biosens Bioelectron* 2007, 23(4), 528-35.
- Li, Z.; Chen, J.; Pan, D.; Tao, W.; Nie, L.; Yao, S., A sensitive amperometric bromate sensor based on multi-walled carbon nanotubes/phosphomolybdic acid composite film. *Electrochimica Acta* 2006, 51 (20), 4255-4261.
- Zhou, R.; Jose, F.; Gopel, W.; Ozturk, Z. Z.; Bekaroglu, O. (1996). Phthalocyanines as Sensitive Materials for Chemical Sensors. *Appl. Organomet. Chem.* 10, 557-577.
- Campidelli, S.; Ballesteros, B.; Filoramo, A.; Diaz, D., de la Torre, G.; Torres, T.; Rahman, G. M. A.; Aminur, E.C.; Kiessling, D.; Werner, F.; Sgobba, V.; Guld, D.M.; Cioffi, C.; Prato, M., Bourgojn, J-P. (2008). Facile decoration of functionalized single-wall carbon nanotubes with phthalocyanines via "Click Chemistry". *J. Am. Chem. Soc.* 2008, 130, 11503-11509.
- Keichi, S.; Eiko, O. (2009). Syntheses and Functional Properties of Phthalocyanines. *Materials*, 2, 1127 - 1179.
- Ece, S.; Zekeriya, B. (2015). Co(II) and Fe(II) Phthalocyanines: synthesis, investigation of their catalytic activity towards phenolic compounds and electrochemical behaviour. *J. Applied Organometallic Chemistry*, DOI 10.1002/aoc.3304.
- De La Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T., Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. *Chemical Reviews* 2004, 104 (9), 3723-3750.

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