

## Characterization of a Nano-synthesised Cobalt Complex and its Electrocatalytic Properties towards Nitrite Oxidation

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We report on the synthesis of a nano cobalt complex potassium nitratopentacyanocobaltate (III) ( $K_3[Co(CN)_5NO_3]$ ) made by a simple green chemistry method. The synthesized complex was characterized using FTIR, UV-Vis, XRD, EDX, HRSEM and TEM techniques. Electron transfer behaviour of the  $[Co(CN)_5NO_3]^{3-}$  complex on an electrode support was investigated in a ferrocyanide/ferricyanide ( $Fe(CN)_6^{4-} / [Fe(CN)_6]^{3-}$ ) redox probe using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The EIS study in  $Fe(CN)_6^{4-} / [Fe(CN)_6]^{3-}$  redox probe showed that nano cobalt complex modified edge plane pyrolytic graphite electrode (EPPGE-Co) exhibit faster electron transfer with a charge transfer resistance of  $R_{ct} = 0.52 \Omega cm^2$  which was 12 times greater than that of the bare EPPGE ( $R_{ct} = 6.42 \Omega cm^2$ ). The equivalent circuit used demonstrated the pseudocapacitive and the lower capacitance of the EPPGE-Co electrode compared to the EPPGE. The EPPGE-Co showed an enhanced catalytic current (3 and 7 folds higher) in nitrite ( $NO_2^-$ ) and nitric oxide (NO) respectively, than the current at the bare EPPGE electrode. The nano cobalt complex was simple to prepare, environmental friendly and should be a potential catalyst for sensors, semiconductors and energy storage devices applications.

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**Keywords:** Nano cobalt complex; Electron transfer kinetics; Impedance spectroscopy; pseudocapacitance; Nitrite oxidation

### 1. INTRODUCTION

The use of Co metal and Co complexes in nanoscience and nanotechnology has been widely explored and documented especially nowadays where nanometer scale materials have attracted considerable attention due to their superior functional properties and a wide range of potential technological applications, including catalysis, optics, microelectronics, chemical sensors and

biological biosensors [1]. For example, pure cobalt and cobalt oxides nanoparticles (2–20 nm) have attracted research interest due to their unique quantum effects and have been put to use in laboratory and industrial applications, for example catalysis, biosensing, magnetics, fluids, optoelectronics and in data storage [2-7]. On the other hand, cobalt complexes have found few or limited applications possibly due to their weak electron transport properties which is usually exploited in industrial processes. More importantly, the synthesis of the nanosize-dimension of cobalt complexes, which will improve and confer on these complexes the potential for catalysis, has been a herculean task. However, there have been reports on the use of cobalt as alloy with other metals [8,9] or its nanocomposite with other conducting materials and polymers [10]. Some research work involving the use of cobalt complexes as either film or nanosize materials include methanol oxidation in fuel cells using cobalt phthalocyanine, [11,12]; ascorbic acid and dopamine oxidation using cobalt hexacyanoferrate films [13], detection of hydrogen peroxide on cobalt hexacyanoferrate nanoparticles (CoNP) modified electrode [14]; nanoscaled cobalt phthalocyanine-glucose oxidase biocomposite for glucose sensing [15], carbon/polyaniline/Co nanocomposite for oxygen reduction reaction in fuel cell [16] and as energy storage devices in supercapacitors [17].

Most of the documented reports have placed more emphases on sensing, catalysis and the energy storing capacities of cobalt complexes, rather than their electron transport behaviour that forms the basis for electrocatalysis. Therefore, due to no literature reports available on the synthesised cobalt complex to be discussed in this paper, nor any report on its nanosize dimension or its application in catalysis, we have used this as the basis to conduct this study.

Nitrite is an environmentally important molecule which is commonly used as an additive in the food industry [18], in manufacturing diazo dyes, textile industry, photography, in the manufacture of rubber chemicals, as components of fertilizers in agriculture [19] and as medicinal agents (as a vasodilator) [20]. The nitrite ion is an environmentally hazardous species because of its toxicity. When combined with blood pigments, it leads to the production of meta-haemoglobin which leads to oxygen depletion in the tissues [21,22]. Also, when combined with amines and amides in the stomach, highly carcinogenic *N*-nitrosamine compounds are produced [23]. Therefore, because of the potential environmental hazard of the nitrite ion, its detection and quantification has become very important to analytical and clinical scientists. Hence, its electrochemical detection was developed in this study since the method is cheap, convenient, saves time and gives reproducible results compared to conventional analytical techniques.

In this study, we have explored for the first time the surface electrochemistry of a nanosynthesised cobalt complex  $[\text{Co}(\text{CN})_5\text{NO}_3]^{3-}$  and its potential application in sensing and catalysis using nitrite as an analytical probe. The synthesised cobalt complex was used as an electron-transfer mediator to facilitate charge transfer between the nitrite and the base edge plane pyrolytic graphite electrode (EPPGE). The low charge transfer resistance, high catalytic current and the ease of preparation of the complex which is purely a Green Chemistry approach would not only make it environmentally friendly but as a potential material in the fabrication of sensors, electrical and energy storage devices.

## 2. EXPERIMENTAL

### 2.1 Materials and Reagents

$\text{KNO}_2$ ,  $\text{HNO}_3$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{K}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{Fe}(\text{CN})_4$  and other reagents were of analytical grade and were purchased from Sigma Chemicals. Phosphate buffer solutions (PBS) at various pHs were prepared using appropriate amounts of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , and the pH was adjusted with 0.1 M  $\text{H}_3\text{PO}_4$  or  $\text{NaOH}$ . Ultra pure water of resistivity 18.2 M $\Omega$ cm was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used throughout for the preparation of solutions.

#### 2.1.1 Synthesis of potassium nitratopentacyanocobaltate (III) $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$ complex

The starting material,  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ , used in the synthesis of this new metal complex was prepared according to a reported literature procedure [24]. The procedure for the synthesis follows a simple Green Chemistry method and it is aimed at introducing a most stable  $\text{NO}_x$  group ( $\text{NO}_3^-$ ) and to improve the electronic properties of the molecule. The procedure is as follows:

$\text{KNO}_2$  (0.5g) was introduced slowly into a solution made by dissolving 1.5g of  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$  (golden yellow crystals) in distilled water (4 ml) and conc.  $\text{HNO}_3$  (4 ml). The resulting solution was vigorously stirred, warmed up to 40 °C and maintained at this temperature for approximately 25 mins after which the mixture was cooled to room temperature. Insoluble materials were filtered off and the clear filtrate was treated with cold absolute ethanol (35 ml) at 0 °C. The clean precipitate (white powder) obtained was filtered and washed with absolute ethanol and diethyl ether (200 ml). The product was then dried under vacuum (Yield: 0.65; 43%) and was identified to be  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$  based on its characterization by FTIR, UV spectroscopes and the XRD profiles. Similar methods in which precursors were treated with nitric acid have been reported for the syntheses and characterisation of nitrate derivatives of other transition metal complexes [25].

The resulting sample was characterised using high resolution scanning electron microscopy (HRSEM), transmission electron microscopy (TEM), and X-ray Diffractometry (XRD) with  $\text{CoK}\alpha$  radiation.

### 2.2 Equipment and Procedure

The edge plane pyrolytic graphite electrode (EPPGE) plate (5mm diameter) was purchased from Le Carbone (Sussex, UK). UV/Vis experiments were performed with a UV-Visible spectrophotometer, 100 Bio Varian Win UV (Australia). Infrared spectroscopy data were obtained using PerkinElmer GX 2000 FT-IR Spectrometer attached to a PerkinElmer Auto Image Microscope System equipped with liquid nitrogen cooled MCT detector. The samples were analyzed using KBr in the transmission mode. High resolution scanning electron microscope (HRSEM) images were obtained using the Zeiss Ultra Plus 55 HRSEM (Germany), while the energy dispersive x-ray spectra (EDX) were obtained from NORAN VANTAGE (USA) at the Microscopy and Microanalysis Laboratory of

the University of Johannesburg. The TEM experiment was performed using a Model JEOL JEM-2100F field emission transmission electron microscope, Tokyo (Japan). XRD analysis was done using a back loading preparation method. The sample was analysed using a PANalytical X'Pert Pro powder diffractometer (Netherlands) with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K $\alpha$  radiation. Electrochemical experiments were carried out using an Autolab Potentiostat PGSTAT 302N (Eco Chemie, Utrecht, Netherlands) driven by the GPES software version 4.9. Electrochemical impedance spectroscopy (EIS) measurements were performed with an Autolab Frequency Response Analyser (FRA) software between 10 kHz and 0.1 Hz using a 5 mV rms in 5 mM [Fe(CN) $_6$ ] $^{4-}$ /[Fe(CN) $_6$ ] $^{3-}$  solution (containing 0.1 M KCl) vs. Ag|AgCl in sat'd KCl). Ag|AgCl in saturated KCl and platinum wire were used as reference and counter electrodes, respectively, while EPPGE decorated with Co complex was used as the working electrode. All solutions were de-aerated by bubbling nitrogen prior to each electrochemical experiment. All experiments were performed at  $25 \pm 1$  °C.

### 2.3 Electrode modification procedure

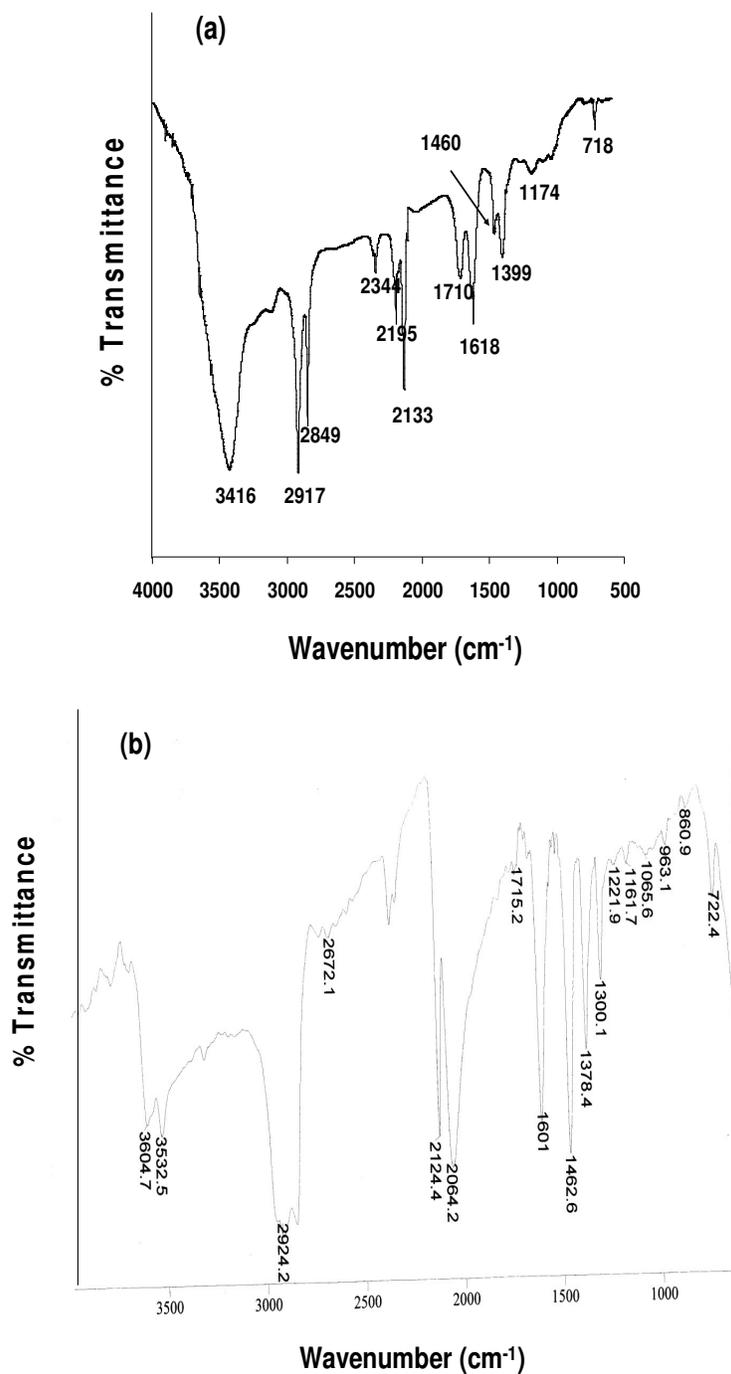
EPPGE surface was cleaned by gentle polishing in aqueous slurry of alumina nanopowder (Sigma-Aldrich) on a SiC-emery paper and then polished to a mirror finish on a Buehler felt pad. The electrode was then subjected to ultrasonic vibration in absolute ethanol to remove residual alumina particles that might be trapped at the surface. EPPGE-Co complex was prepared by a drop-dry method. Briefly, the Co complex (2.5mg) was weighed and dissolved in dimethylformamide (DMF) (1.0 ml). The suspension was sonicated at room temperature for an hour until the solid dissolved. The obtained solution (20  $\mu$ l) was drop-cast on the EPPGE and allowed to dry in the oven at 50 $^{\circ}$  C for 5mins. The modified electrode is denoted as EPPGE-Co complex. The morphology of the modified electrode was investigated with X-ray Diffractometry (XRD) using CoK $\alpha$  radiation and was further characterised using electrochemical techniques.

## 3. RESULTS AND DISCUSSION.

### 3.1 Spectroscopy and microscopy characterization

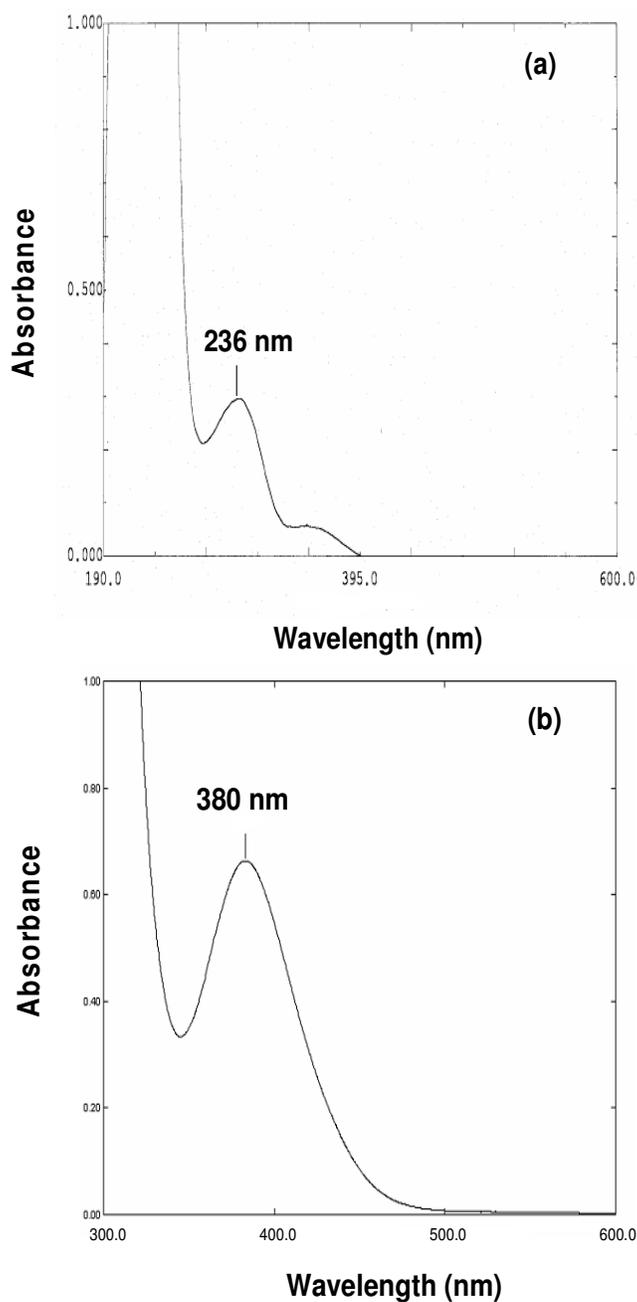
Figure 1 shows the comparative FTIR spectra of the synthesized complex (a) (K $_3$ [Co(CN) $_5$ NO $_3$ ]) and the starting material (b) (K $_3$ [Co(CN) $_5$ N $_3$ ]). The new band appearing at 1399 cm $^{-1}$  for [Co(CN) $_5$ NO $_3$ ] $^{3-}$  complex is the N=O stretching vibration of the NO $_2^-$  or NO $_3^-$  formed during the acid treatment of the K $_3$ [Co(CN) $_5$ N $_3$ ] indicating that the starting material had been successfully modified. The band at 1460 cm $^{-1}$  common to both compounds is due to the Co-C stretching vibration. The prominent peak at 1601 cm $^{-1}$  in the precursor was attributed to C=N stretches and diminished in the complex due to the modification process. This led to a growing peak at 1710 cm $^{-1}$  in [Co(CN) $_5$ NO $_3$ ] $^{3-}$  complex and the peak is attributed to C=O of trace COOH acidic group probably formed during acid treatment. More importantly in this study, the growing peak at 1710 cm $^{-1}$

confirmed the introduction of oxygen atoms in the complex. The bands at 2133, 2195 and 2344  $\text{cm}^{-1}$  confirm the presence of  $\text{C}\equiv\text{N}$  stretching vibration in the complex. The intense band at 3416  $\text{cm}^{-1}$ , common to both spectra is ascribed to the O-H group of adsorbed moisture during sample preparation.



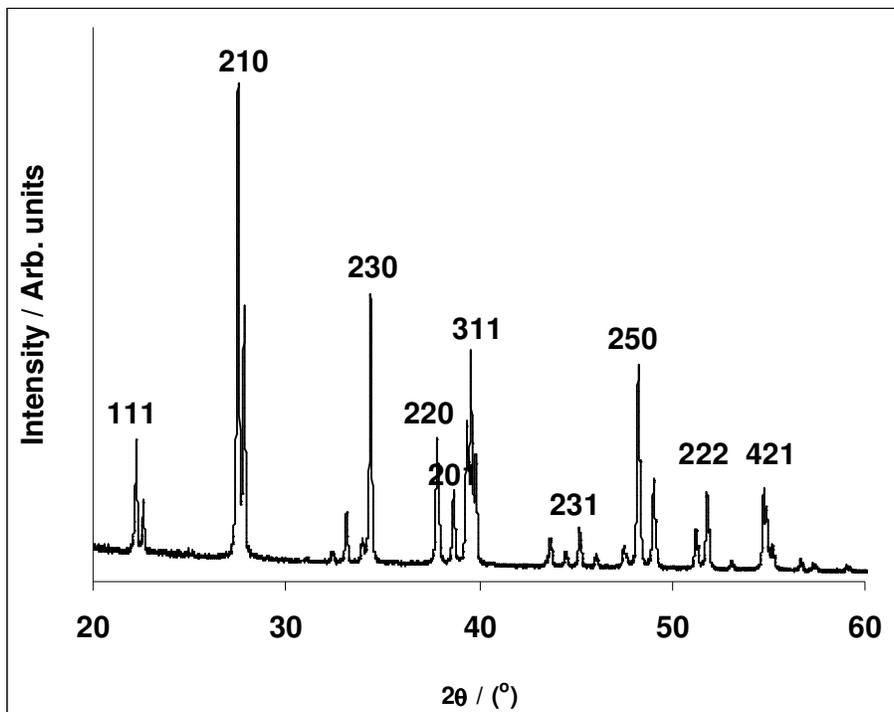
**Figure 1.** FTIR spectra of (a)  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$  and (b)  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ .

UV-vis absorption spectroscopy experiments were performed to further show the successful modification of the starting material. Figure 2 compares the UV-vis spectra of (a)  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$  and (b)  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ . The  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$  has a sharp absorption band at 236 nm which is less than the absorption band at 380 nm for  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ . The difference can be attributed to the introduction of  $\text{NO}_3^-$  group whose UV-Vis absorption band in water is in the range of 220 to 301 nm, where 220 and 301 nm represent its very intense and weak intense bands respectively [26].



**Figure 2.** UV/Vis spectra of (a)  $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_3]$  and (b)  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ .

The XRD spectrum (Fig. 3) gave Co characteristic peaks at  $2\theta = 22.2, 27.5, 33.7, 37.6, 38.8, 39.2, 45.3, 48.0, 51.6$  and  $56.1$ , corresponding to Miller indices (111), (210), (230), (220), (201), (311), (231), (250), (222) and (421), indicating a cubic crystal structure of the  $K_3[Co(CN)_5NO_3]$  complex.



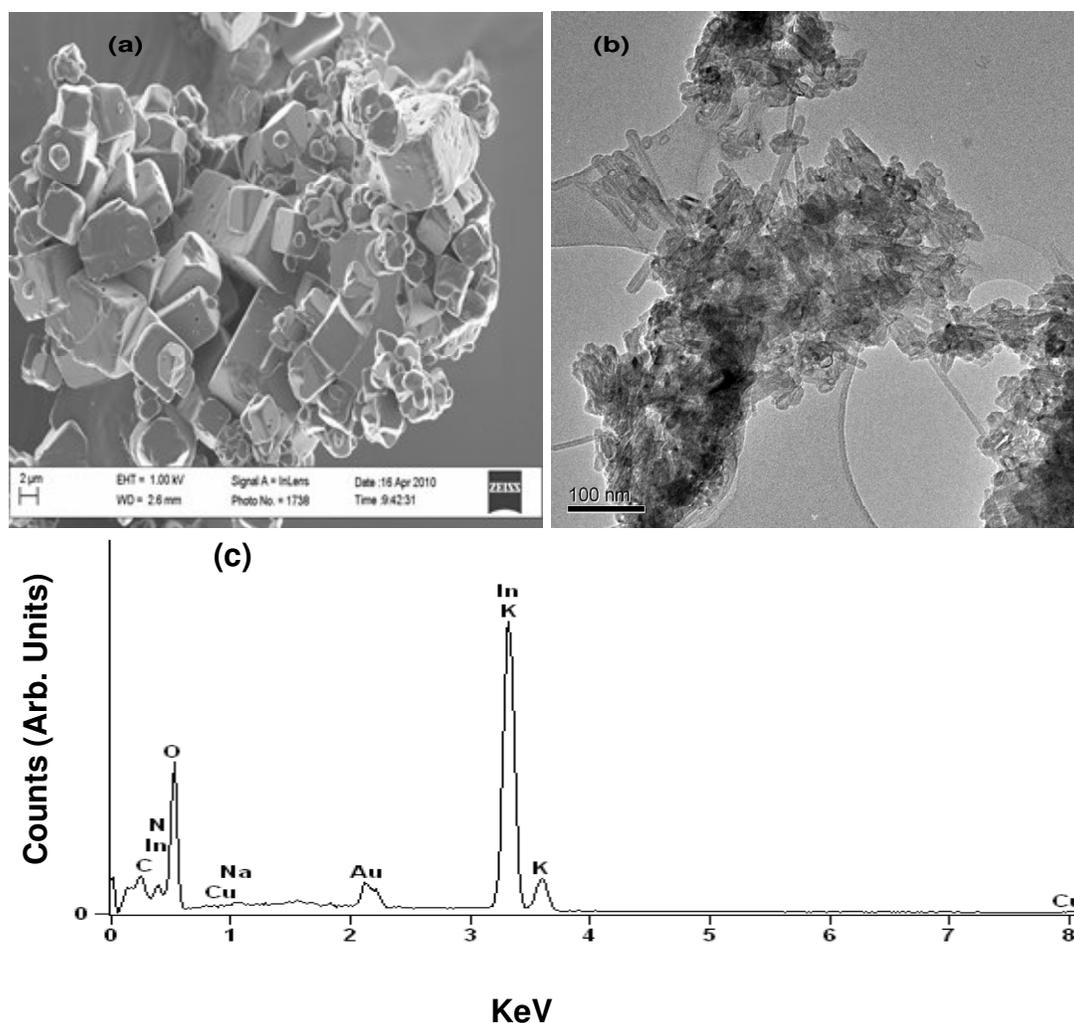
**Figure 3.** XRD spectrum of synthesised  $K_3[Co(CN)_5NO_3]$  complex

From Debye-Scherrer formula [27]:

$$d = \frac{K\lambda}{B\cos\theta} \quad (1)$$

where  $d$  is the average crystal size;  $K$  is a constant (0.89);  $\lambda$  is the wavelength (1.78901 nm) used;  $B$  is the full width at half maximum of the peak,  $\theta$  is the Bragg's angle of the XRD peak, the average crystal size of the complex was estimated to be  $\sim 18$  nm.

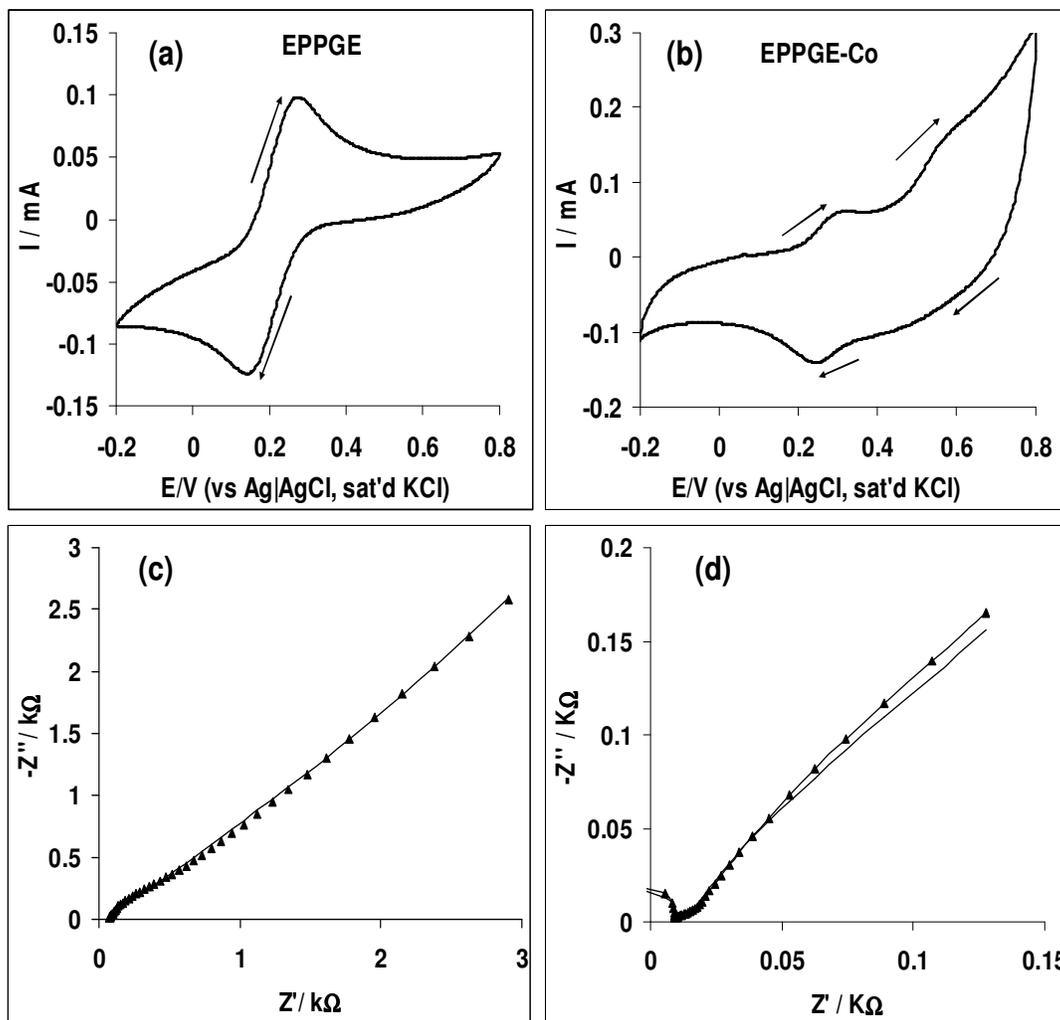
Figure 4a and 4b show the SEM and the TEM images of the Co complex. Both images showed crystal shaped particles connected together as clusters or aggregates. From the TEM image, the average size of the complex was estimated to be 25 nm after calibrating the scale on the TEM image using the UTHSCSA Image Tool for windows version 3.0. The EDX profile (Fig. 4c) confirmed the presence of K, C, N, and O. The prominent oxygen peak clearly suggests successful modification to  $NO_3^-$ . The absence of the Co peak might probably be as a result of the screening effect of the attached ligands or the bulky size of the complex. The Au peak is attributed to trace metal impurities during preparation.



**Figure 4.** (a) HRSEM image, (b) HRTEM image and (c) EDX spectrum of of  $K_3[Co(CN)_5NO_3]$  complex.

### 3.2 Electrochemical characterization

Figure 5 is the comparative cyclic voltammograms (CV) of the bare EPPGE (a) and the EPPGE-Co complex (b) in 5 mM  $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$  redox probe solution (in PBS pH 7.0). The peaks in the 0 – 0.4 V region are due to the  $Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$  redox couple while the one at the 0.4 – 0.7 V region is ascribed to the Co(II)/Co(III) redox process. The peak around 0.4 – 0.7 (Fig. 5b) is absent in bare EPPGE (Fig. 5a) therefore indicating the successful modification of the electrode with the Co complex. The enhanced current response of EPPGE-Co electrode (200 μA) in the redox probe over bare EPPGE (100 μA) also implies the electroactive and charge transfer nature of the Co complex. It could also mean that the synthesized Co complex may act as a potential catalyst towards the electrocatalytic oxidation or reduction of some notable and important biologically and environmentally challenging molecules. This result is in agreement with other reports on chemically modified electrodes where enhanced current was noted in comparison with the bare electrode [28-31]

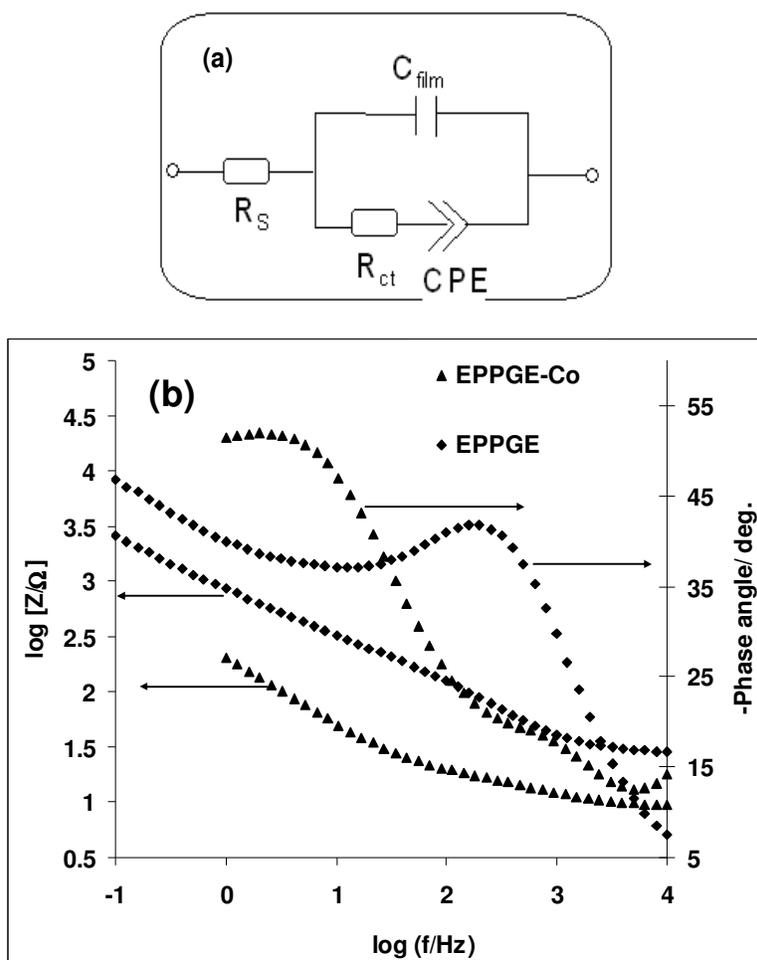


**Figure 5.** Comparative cyclic voltammograms of the (a) bare EPPGE and (b) EPPGE-Co in 5 mM  $\text{Fe}(\text{CN})_6^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$  redox probe (scan rate;  $50 \text{ mVs}^{-1}$ ). (c) and (d) are their respective Nyquist plot in 5 mM  $\text{Fe}(\text{CN})_6^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$  redox probe at a fixed potential of 0.20 V vs Ag|AgCl sat'd KCl. The square data points are experimental while the solid lines in the spectra represent non-linear squares fits

In order to further understand the electronic behaviour of the EPPGE-Co complex modified electrode, we carried out an EIS study in  $\text{Fe}(\text{CN})_6^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$  solution at the equilibrium potential of the redox couple ( $E_{1/2} = 0.3 \text{ V}$ ). The impedance technique is a very sensitive technique which gives insight into the mechanism of the electron transport between the electrode/electrolyte interfaces. The Nyquist plots for the bare EPPGE (Fig. 5c) and EPPGE-Co complex (Fig. 5d) are presented.

The EIS data was satisfactorily fitted with the equivalent circuit represented in Figure 6a wherein  $C_{dl}$  or  $C_{film}$  describes the true capacitance of the electrode, while  $Q$  or  $CPE$  also known as the constant phase element, indicates the porous nature of the modified electrodes,  $R_s$  is the solution/electrolyte resistance,  $R_{ct}$  denotes the charge-transfer resistance. From the fitting of the

experimental data, the following parameters were obtained. Bare EPPGE:  $R_s(29.79 \Omega)$ ,  $C(6.93 \mu\text{F})$ ,  $R_{ct}(6.24 \Omega\text{cm}^2)$ ,  $Q(0.5073 \text{ mF})$  and  $n(0.4757)$ ; and EPPGE-Co:  $R_s(8.59 \Omega)$ ,  $C(15.52 \mu\text{F})$ ,  $R_{ct}(0.52 \Omega\text{cm}^2)$ ,  $Q(1.578 \text{ mF})$  and  $n(0.6390)$ . The  $R_{ct}$  value determines the kinetic of electron transport at the electrode; hence it is the most crucial data for determining the surface electrochemistry of the Co complex, or of a modified electrode. The lower its value, the higher the charge transfers at the electrode and vice versa. Thus, the low  $R_{ct}$  ( $0.52 \Omega\text{cm}^2$ ) for the EPPGE-Co electrode was 12 times lower than that of the bare EPPGE ( $R_{ct} = 6.24 \Omega\text{cm}^2$ ), suggesting faster electron transport possibly as a result of the porous, nanosized and the large electroactive surface area created by the Co complex on the EPPGE-Co electrode. The larger surface area allows for easy contact and faster charge transfer between the electrolyte and the base EPPGE, therefore lowering the resistance to charge transfer. This result further confirms the enhanced or high current response observed for the CV of EPPGE-Co modified electrode compared to the bare electrode. The result was in agreement with the impedance behaviour of other modified electrodes reported in the literature [32,33].

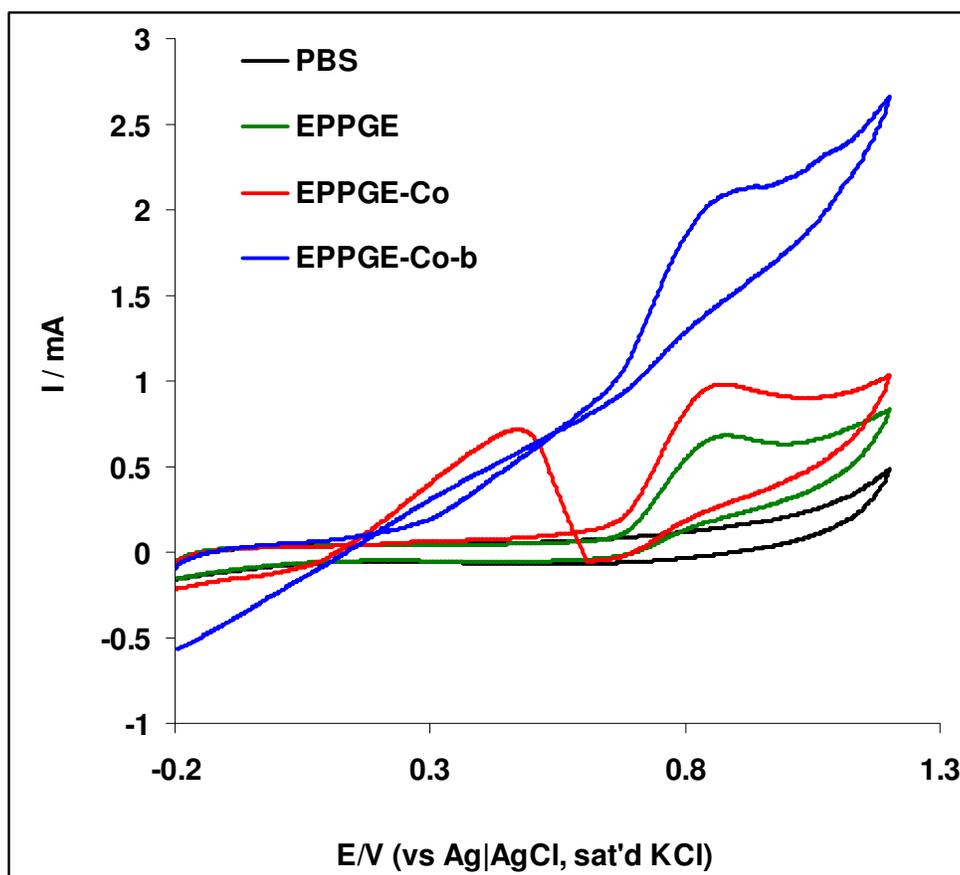


**Figure 6.** (a) is the circuit used for fitting the impedance data in 5(a) and (b) above. (b) Bode plots of -phase angle/ deg. vs  $\log(f/\text{Hz})$  and plots of  $\log|Z/\Omega|$  vs  $\log(f/\text{Hz})$  for EPPGE and EPPGE-Co electrodes in  $5 \text{ mM Fe}(\text{CN})_6^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$  redox probe.

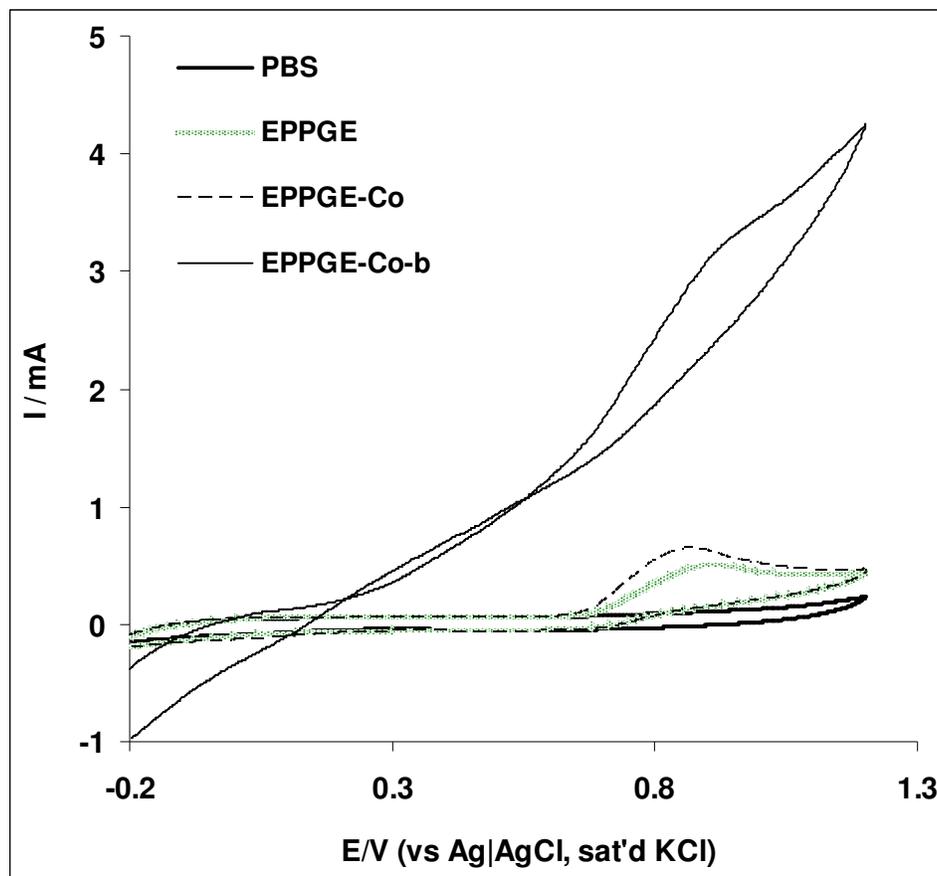
The Bode plots of  $-\text{phase angle}$  vs  $\log f$  (Fig. 6b) at high frequency region (2.3 Hz) gave phase angles of  $42^\circ$  for EPPGE and  $22^\circ$  for EPPGE-Co. Apart from these values being lower than the expected  $90^\circ$  of an ideal capacitive behaviour, the lower phase angle for the EPPGE-Co electrode also implies lower capacitance, further confirming the mediating capability of the nano Co complex in facilitating fast electron transport on the bare electrode. The result also confirms the pseudocapacitive behaviour of the synthesized Co complex on the modified electrode. The plot of  $\log |Z|$  vs  $\log f$  (Fig. 6b) also gave a slope value of  $-0.597$  ( $R^2 = 1.000$ ) for EPPGE and  $-0.441$  ( $R^2 = 0.9983$ ) for EPPGE-Co suggesting lower pseudocapacitance of EPPGE-Co electrode compared to EPPGE. A slope value of  $-1$  is expected for a pure capacitive behaviour.

### 3.3 Electrocatalysis using nitrite as a probe

Figures 7 and 8 present the current responses of the modified electrodes in  $10^{-2}$  M  $\text{NO}_2^-$  in PBS pH 7.4 and pH 3.0 (as NO) [34], respectively.



**Figure 7.** Comparative current response of EPPGE and EPPGE-Co electrodes in pH 7.4 PBS containing  $10^{-2}$  M  $\text{NO}_2^-$ . EPPGE-Co and EPPGE-Co-b are modified from Co suspended in ethanol and DMF respectively.



**Figure 8.** Comparative current response of EPPGE and EPPGE-Co electrodes in pH 3.0 PBS containing  $10^{-2}$  M NO. EPPGE-Co and EPPGE-Co-b are modified from Co suspended in ethanol and DMF respectively.

The occurrence of the  $\text{NO}_2^-$  and NO signals (absent in PBS electrolyte alone) at their respective pH solutions signify electro-catalysis. EPPGE-Co (modified from 2.5 mg of Co complex suspended in ethanol) gave improved current response over the bare EPPGE suggesting the enhanced catalytic properties of the modified electrode as a result of the presence of the Co complex (Figs. 7 and 8). However, the current response of the EPPGE-Co-b (modified from 2.5 mg of Co complex suspended in DMF) towards  $\text{NO}_2^-$  and NO was approximately 2 and 5 times higher than EPPGE-Co; and 3 and 7 times higher than bare EPPGE (Figs. 7 and 8), and at lower onset potentials of catalysis (0.31 V) compared to 0.67 V recorded for EPPGE and EPPGE-Co.

The improved response at the EPPGE-Co-b electrode could be that the DMF interacts through ionic bonding with the Co complex, increasing its uniform dispersion, stability and larger surface area for  $\text{NO}_2^-$  and NO diffusion through the catalyst. Cobalt and other modified electrodes have been reported to give enhanced response towards electro-oxidation of nitrite on graphite substrates [28,30,35,36].

#### 4. CONCLUSION

Successful synthesis of a nano cobalt complex potassium nitropentacyanocobaltate (III) ( $K_3[Co(CN)_5NO_3]$ ) was achieved and confirmed using different spectroscopic and microscopic techniques. The cyclic voltammogram of the  $[Co(CN)_5NO_3]^{3-}$  complex on EPPGE in  $[Fe(CN)_6]^{3-}$  redox probe gave an enhanced current suggesting that the complex was electroactive and facilitated charge transfer. The EPPGE-Co complex electrode exhibited faster electron transfer (lower  $R_{ct} = 0.52 \Omega cm^2$ ) than the bare EPPGE ( $R_{ct} = 6.42 \Omega cm^2$ ). The EPPGE-Co electrode showed enhanced catalytic current (3 and 7 folds higher) with nitrite ( $NO_2^-$ ) and nitric oxide (NO) respectively than the current at the bare EPPGE electrode. This study provides a basis for future applications of the Co complex for sensors and energy storage devices.

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#### References

1. A. Salimi, R. Hallaj, S. Soltanian, *Biophys. Chem.*, 130 (2007) 122.
2. J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, *Phys Rev B*, 51 (1995) 11527.
3. K. Tanabe, *Mater. Lett.*, 61 (2007) 4573.
4. Y. Yu, G. Ji, J. Cao, J. Liu, M. Zheng, *J. All. Comp.*, 471 (2009) 268.
5. Z. Zheng, L. Huang, Y. Zhou, X. Hua, X. Ni, *Solid State Sciences*, 11 (2009) 1439.
6. Y. Shan, L. Gao, *Mater. Chem. Phys.*, 103 (2007) 206.
7. S. Thota, A. Kumar, J. Kumar, *Mater. Sci. Engin. B*, 164 (2009) 30.
8. Vinay Gupta, Toshikazu Kawaguchi, Norio Miura, *Mater. Res. Bulletin*, 44 (2009) 202.
9. J. Ahmed, S. Sharma, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *J. Coll. Interface Sci.*, 336 (2009) 814.
10. S.M. Yao, K. Xi, G.R. Li, X.P. Gao, *J. Power Sources*, 184 (2008) 657.
11. Y. Lu, R.G. Reddy, *Int. J. Hydrogen Energy*, 33 (2008) 3930.
12. Y. Lu, R.G. Reddy, *Electrochim. Acta*, 52 (2007) 2562.
13. Y. Shi, B. Zhou, P. Wu, K. Wang, C. Cai, *J. Electroanal. Chem.*, 611 (2007) 1.
14. M. Yang, J. Jiang, Y. Yang, X. Chen, G. Shen, R. Yu, *Biosensors and Bioelectronics*, 21 (2006) 1791.
15. K. Wang, J-J. Xu, H-Y. Chen, *Biosensors and Bioelectronics*, 20 (2005) 1388.
16. W. Martı́nez Milla´na, T. Toledano Thompsona, L.G. Arriagab, Mascha A. Smit, *Int. J. Hydrogen Energy*, 34 (2009) 694.
17. J. Chen, K. Huang, S. Liu, *Electrochem. Commun.*, 10 (2008) 1851.
18. C.A. Caro, F. Bedioui, J.H. Zagal, *Electrochim. Acta*, 47 (2002) 1489.
19. N.S. Bryan, *Free Radical Biol. Med.*, 41 (2006) 691.
20. E.T. Reichert, S.W. Mitchell, *Am. J. Med. Sci.*, 159 (1980) 158.
21. D. Zheng, C. Hu, Y. Peng, S. Hu, *Electrochim. Acta*, 54 (2009) 4910.
22. W.J.R. Santos, P.R. Lima, A.A. Tanaka, S.M.C.N. Tanaka, L.T. Kubota, *Food Chem.*, 113 (2009) 1206.
23. Z.H. Wen, T.F. Kang, *Talanta*, 62 (2004) 351.
24. T. Flor, J. Casabó., *Inorg. Met. Org. Chem.*, 16 (1986) 795.

25. P. B Critchlow, S.D. Robinson, *Inorg. Chem.*, 17 (1978) 1896.
26. M. Bravo, A.C. Olivieri, B. Oelckers, J. Chil. Chem. Soc., 54 (2009) 93.
27. Y-K. Sun, M. Ma, Y. Zhang, N. Gu, *Coll. Surf. A: Physicochem Eng Aspects*, 245 (2004) 15.
28. A.S. Adekunle, J. Pillay, K.I. Ozoemena, *Electrochim. Acta*, 55 (2010) 4319.
29. A.S. Adekunle, K.I. Ozoemena, *Electrochim. Acta*, 53 (2008) 5774.
30. A.S. Adekunle, K.I. Ozoemena, *Int. J. Electrochem. Sci.*, 5 (2010) 1972.
31. S-Q. Liu, W-H. Sun, L-C. Li, H. Li, X-L. Wang, *Int. J. Electrochem. Sci.*, 7 (2012) 324.
32. X. Che, R. Yuan, Y. Chai, J. Li, Z Song, W. Li, X. Zhong, *Coll. Surfaces B: Biointerfaces*, 84 (2011) 454.
33. A.S. Adekunle, K.I. Ozoemena, *J. Electroanal. Chem.* 645 (2010) 41.
34. C. Yang, Q. Lu, S. Hu, *Electroanalysis*, 18 (2006) 2188.
35. A.S. Adekunle, B.B. Mamba, B.O. Agboola, K.I. Ozoemena, *Int. J. Electrochem. Sc.*, 6 (2011) 4388.
36. A. Salimi, R. Hallaj, H. Mamkhezri, S.M.T. Hosaini, *J. Electroanal. Chem.*, 619–620 (2008) 31.