



NICKEL-MAGNETITE/CARBON-NANOTUBE COMPOSITE: SYNTHESIS, CHARACTERIZATION AND SUPERIOR ELECTRO-OXIDATION PROPERTIES FOR SUGARS AND DETECTION OF THE METABOLITES

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Abstract:

Nickel and Copper magnetite Nanoparticles fabricated on acid functionalized carbon nanotubes have been synthesized by facile hydrothermal method. The nanocomposite modified glassy carbon electrode exhibit an enhanced electro oxidation properties and the ultrathin architecture of the nanocomposite leads to enhanced ionic diffusion and charge transport. The electrode delivers NiFe_2O_4 and CuFe_2O_4 current densities of as high $11.61 \mu\text{A}/\text{cm}^2$ and $10.56 \mu\text{A}/\text{cm}^2$ respectively. The electrocatalyst are highly active for electrocatalytic activity towards the glucose oxidation, with low overpotential values. Gluconolactone was determined as an intermediate metabolite by reverse-phase HPLC and UV-Visible spectroscopy with good precision. The electrocatalysts are highly resistant to intermediate poisoning and demonstrates long-term cyclic stability as well as compared to the bare ferrite electrodes. The as synthesized Nickel and Copper magnetite nanocomposite fabricated electrode can be used as Non-enzyme based glucose sensors with advantage of low cost and long-term durability.

1. INTRODUCTION

Glucose is the most naturally available aldose monosaccharide forms 80% of the available biomass and easily produced by plants via photosynthesis. The rapidly developing food technologies and processing in the fields of

additives and artificial sweeteners has imposed challenge of quality control and safety.¹ As a result, a quicker and accurate estimation of sugars and sugar based additives are currently of great importance towards human benefits. Electrocatalysis for the oxidation of sugars finds its importance in reliable and fast determination of glucose in areas such as clinical diagnostics,² biotechnology, environmental and food industry.³ Different approaches are available for precise monitoring of glucose including electrochemiluminescence,⁴ fluorescence,⁵ Raman spectroscopy,⁶ but extensive attention has attracted by electrochemical glucose sensor because of their fast response, time efficient, low cost and easy operation techniques. Previously enzyme based amperometric biosensors have been widely used such as Glucose oxidase⁷ for glucose detection due to its sensitivity and selectivity.⁸ However, enzyme –modified electrodes have disadvantages such as high cost, complicated immobilization process, instability, critical operation conditions. Therefore, development of non-enzymatic electrodes⁹ to resolve this problem is of great attention. Noble metals,¹⁰ metal alloys or composites electrodes,¹¹ metal nanoparticles,¹² metal oxides¹³ and several different electrocatalysts¹⁴ have been extensively investigated in sugar oxidation, electrocatalysis¹⁵, non-enzymatic glucose sensors, energy conversion and storage,¹⁶ and

photocatalysis.¹⁷ However, these electrodes have drawbacks such as low selectivity, high cost, surface poisoning from the adsorbed intermediates and chloride ions¹⁸ etc which greatly restricts their applications.

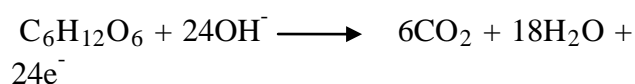
Nowadays, carbon nanotubes¹⁹ have been reported rapidly as an electrode material due to their unique properties such as high surface area, unique structures, excellent electrical conductivity, significant mechanical properties and high chemical stability²⁰ as a support of nanoparticles²¹ are of great interest for sensors and biosensors.²²

Thermodynamically, electro-oxidation of glucose is favorable, but slow reaction kinetics at conventional electrodes restricts its utilization for analytical purposes.²³

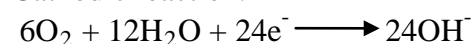
The current study focuses on the utility of the acid functionalized multi-walled carbon nanotubes fabricated Copper and Nickel magnetite for the modification of a glassy carbon electrode to improve its electro-activity towards glucose electro oxidation. The major advantages of this material include the uniform dispersion of metal oxide nanoparticles on the surface of CNTs, high porous, electrical conductivity as well as mechanically strong network structure of the resulting nanocomposite, contributes for high electrocatalytic activity by providing exceptionally larger active surface area which prevents the agglomeration and detachments from NPs, and facilitate faster mass and electron transfer within the nanocomposite system. In addition to electrocatalysis these materials find their promising applications in biomedicine,²⁴ environments,²⁵ catalysis,²⁶ and renewable energy-based applications.²⁷

In general the complete oxidation of glucose molecule in alkaline medium follows the chemical reactions as:

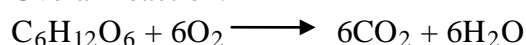
Anodic reaction:



Cathodic reaction:



Overall reaction:



In addition, electro-oxidation of glucose has two applications for practical use: (a) as human implantable devices i.e. in vivo applications for powering microelectromechanical²⁸ devices as glucose can be implemented in fuel-cell technology and (b) electrochemical sensors for diabetic checks in medical economy.

The applications of Ni/Cu-magnetite fabricated Nanocomposite materials are new and to our knowledge not reported till date in electrocatalysis.

2. EXPERIMENTAL SECTION

2.1.1. Instruments and Materials Characterizations

X - ray diffraction measurements were done using Rigaku Smart Lab XRD spectrometer with Cu K alpha radiation (1.5406 Å) in the range of 20 - 80 degrees. Raman spectroscopic studies were done using micro Raman spectrometer of Technos (Japan) using diode laser for excitation with 532 nm. Fine powders of samples were used for X-ray diffraction studies for phase identification using Bruker D8 DISCOVER instrument using Cu-target ($\lambda=1.5406$). Diffraction data has been analyzed with Diffraction. EVA supplied with Bruker's D8 DISCOVER for reference search patterns (ICDD) database PDF-2 release. The SEM measurements were carried out using a field emission instrument (LEO 1530VP). Samples for SEM analysis were prepared on carbon coated copper grids; the instrument used was ZEISS Libra 200FE scanning electron microscope operated at 200 kV and equipped with a field emission gun, an in-column filter (Omega filter), and a high-angle annular dark-field (HAADF) detector. All micrographs were taken with a 4K x 4K CCD camera and analyzed with the software package Digital Micrographs (Version 1.71.38, Gatan Company). The transmission electron microscopy (TEM) image was captured in a FEI Tecnai G2 20S Twin transmission electron microscope operated at 200 kV accelerating voltage. Cyclic voltammogram (CV) and Electrostatic impedance spectroscopy were measured by an electrochemical working station (SP-150, Biologic Science instrument). Cycle stability tests were carried out with a CH instruments electrochemical workstation instrument.

2.1.2. Materials

All chemicals used were analytical grade and used as received without further purification. Ferrous ammonium sulphates, ferric chloride, Copper chloride, Nickel chloride, were purchased from Himedia. Silver nitrate used was Merck grade. The water used throughout all experiments was as de-ionized water from Himedia. Glucose, ethanol, Polytetrafluoroethylene as a binder, Isopropanol, and potassium hydroxide were all Merck grade. The multi-walled CNTs (MWCNTs) were purchased (diameter 12.9 nm and length 3–12 mm) from Nanoshell Laboratories (Haryana, India).

2.1.3. Preparation of Cu/Ni-Ferrite/CNT Nanocomposite

A general preparation of acid functionalized MWCNT, in-situ ferrites synthesis and Cu/Ni-Ferrite/CNT nanocomposite is described as follows: Pure CNTs (5.0 g) were dispersed in a solution of conc. HNO_3 (4.0 mL) and conc. H_2SO_4 (16.0 mL). The suspension was ultra sonicated for 3 h at room temperature. Later pure water (100mL) was added and further sonicated for 10 min. Then the suspension was washed several times thoroughly with water till the neutral pH is attained and dried at 50 °C overnight to get the $-\text{COOH}$ functionalized CNTs. The synthesis of Magnetite-CNT was performed by first adding ferrous ammonium sulphate hexahydrate (392.1 mg) and ferric chloride (324.4 mg) in 1: 2 ratio to distilled water (50.0 mL) containing 2.0 g of $-\text{COOH}$ functionalized CNTs. The resultant mixture was sonicated for 30 min at room temperature. Then, NH_4OH aq (15 mL) solution was added slowly while sonicating until the complete precipitation formed. The resulting powder was washed several times with water to get the neutral pH. The free flowing powder was dried for 24 h to get the magnetite functionalized CNTs. Similarly NiFe_2O_4 and CuFe_2O_4 -CNTs were prepared.

2.1.4. Electrode modification

To prepare working electrode, 5 mg of the catalyst and 10 μl of 5 wt% Polytetrafluoroethylene solution were dispersed in ml water-isopropanol solution (50:50 v/v)

mixed solvent, followed by sonication at least 30 minutes. Finally, the catalyst slurry was drop cast on a precleaned glassy carbon electrode and dried at the room temperature. The typical catalyst loading was found to be 0.38 mg cm^{-2} . All the Electrochemical measurements were performed in a standard three-electrode system using a CHI 660D an electrochemical workstation. A glassy carbon electrode coated with active material was used as working electrode along with saturated calomel electrode (SCE) and Pt wire as reference and counter electrode respectively. The glucose electro-oxidation were examined with the CuFe_2O_4 and $\text{NiFe}_2\text{O}_4/\text{CNT}$ nanocomposite using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements with different scan rates within the potential window from -0.2 V to 0.8 V (vs. SCE) in N_2 saturated alkaline solution of glucose in 0.5 M KOH.

3. RESULTS AND DISCUSSION

Electrochemical properties and electrocatalytic activity for Glucose oxidation

To understand the electrocatalytic properties of all the materials towards glucose oxidation, cyclic voltammetry analyses were performed. Fig. 1 shows the CV behaviors of the different electrodes coated with composites and bare ferrites of Glucose in 0.5M KOH solution recorded the redox peaks in the potential range of -0.2-0.8V in alkaline medium. As shown in the fig.1 small current for glucose oxidation were observed at the electrodes due to the electrocatalytic response of glucose oxidation. In comparison with copper magnetite nanocomposite, Nickel magnetite nanocomposite exhibited lower anodic peak potentials and enhanced redox current (fig.1), indicating facilitated redox processes in nickel nanocomposite. When the Nickel nanocomposite electrode was used, a substantial negative shift of the anodic peak potential and dramatic increase of current signal was observed. The variation of concentrations of Glucose was accompanied by the significant shift in anodic peak current toward higher value and anodic peak potential toward lower values, indicating that the electron transfer mechanism involve in the redox process. The oxidation

process of glucose at the Ni nanocomposite electrode (curve in Fig.1) starts at +0.20V with a shoulder peak at +0.40V. In contrast, the Glucose oxidation at Cu nanocomposite electrode starts at +0.26V with a shoulder peak at +0.41V. The increase in the anodic peak current may be attributed to a higher electrical

conductivity of Ni composite due to proper fabrication of CNT and magnetite at the surface, while decrease in anodic peak current could be understood by lower conductivity content and enrichment of surface nanoparticles in Cu composite.

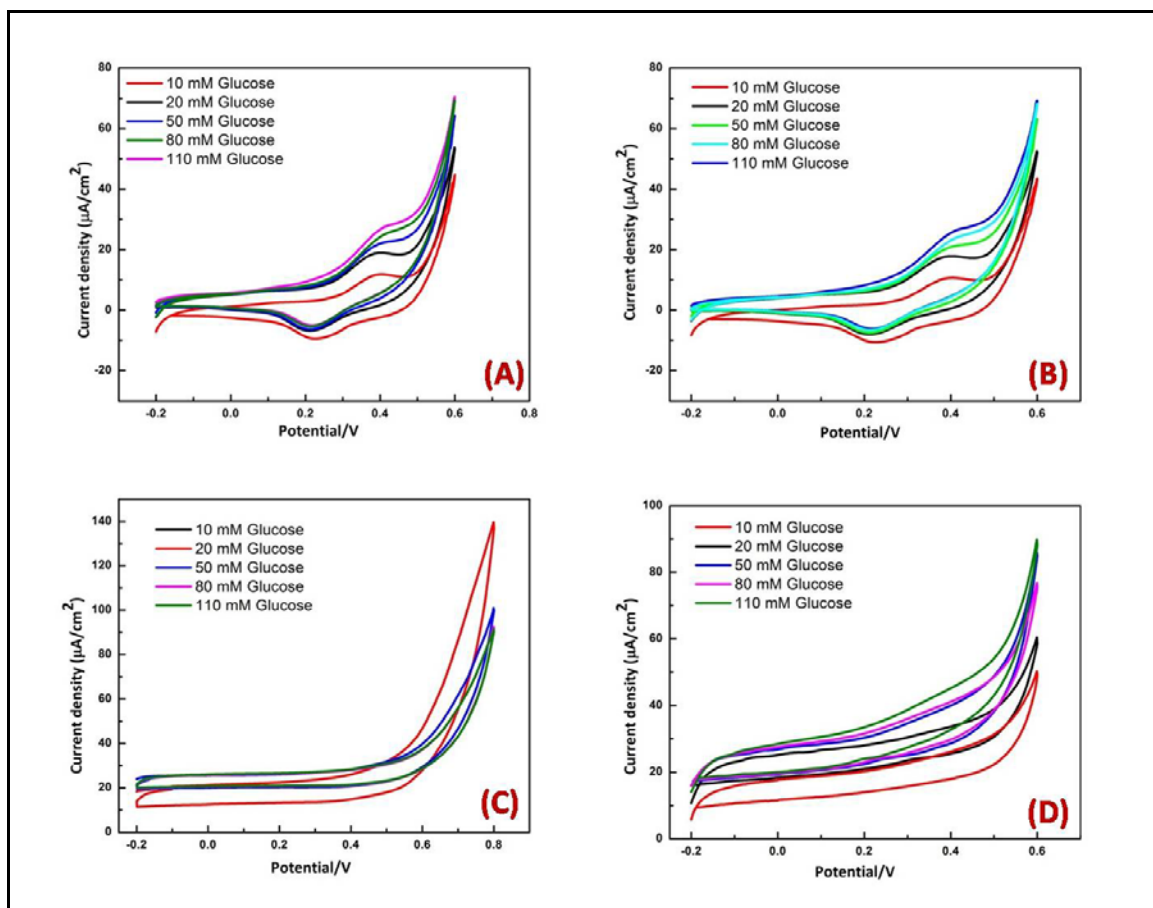


Figure 1 Current-Voltage curves of electrocatalysts at different concentrations of Glucose (A) NiFe₂O₄ nanocomposite, (B) CuFe₂O₄ nanocomposite (C) NiFe₂O₄ nanoparticles and (D) CuFe₂O₄ nanoparticles.

Further, to confirm the electrocatalytic properties of the nanocomposites the complete electrochemical investigations were also performed for the bare NiFe₂O₄ and CuFe₂O₄ nanoparticles (Fig.1 (C) & (D)).

In addition to the variations in concentrations, the influence of scan rates on the current response for the anodic current of glucose oxidation was also studied, and the results are shown in fig. S1. At both the electrode, the currents of the oxidation peaks increased with the increase of scan rate, and the current of the peaks showed linear response to the scan rate.

To explore the potential as efficient electrocatalysts and ion transport properties of glucose electro-oxidation on as-prepared Cu/Ni-magnetite nanocomposite modified electrodes, electrochemical impedance spectroscopy (EIS) were conducted comparing with the bare ferrite nanoparticles (Fig. 2) The electron transfer resistance (R_{ct}), which is known to dictate electron transfer kinetics of redox probe at the electrode/solution interface, was measured. R_{ct} of Ni is smaller than that of Cu and also with the bare ferrites, suggesting a synergism effect of Cu sites and Fe sites (in the anodic response mechanism) and high surface area in the

presence of the CNTs, which facilitates the electron transfer during redox processes. These results agree with the CV study, where the lower anodic potential peaks and higher anodic current peaks were observed.

Figure 2 shows impedance Nyquist plots of the samples. The top-right inset is the amplifier region and bottom right inset shows the fitted equivalent circuit for the measured impedance data. The high-frequency intercept of the semicircle on the real axis shows the series resistance (R_s), and the diameter of the

semicircle corresponds to the charge-transfer resistance (R_{ct}) of the Faradaic process. Moreover, the impedance spectrum of the NiFe_2O_4 nanocomposite electrode reveals a smaller semicircle arc, which indicates that its R_{ct} is lower than that of the bare NiFe_2O_4 electrode and even lower than that of CuFe_2O_4 nanocomposite, suggesting that the NiFe_2O_4 nanocomposite has a higher electrochemical activity.

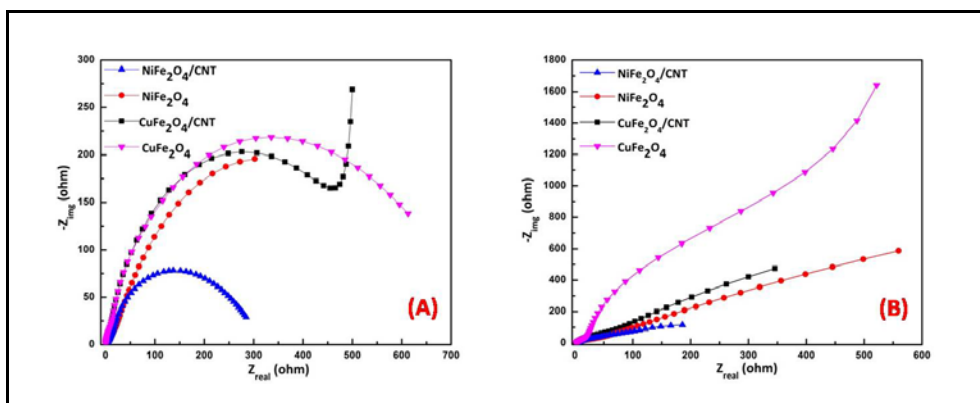


Figure 2 EIS spectra of the electrodes (A) amplifier region (B) Charge-transport impedance (Nyquist plot), respectively for NiFe_2O_4 and CuFe_2O_4 nanocomposite.

Cyclic stability of all the materials were also carried out as shown in the fig. for 100 cycles, which explained the stable nature of the material with respect to the continuous current response (fig. S2).

Further, to clarify the antifouling ability of the nanocomposite by chloride ions and other intermediates poisoning¹⁷ the nanocomposite electrode were probed by performing CV measurements in the solution with high concentration of chloride ions (i.e. replacing 0.5M KOH with 0.5M NaCl + 0.5 M KOH as the electrolyte). Upon addition of high chloride concentrations the current response of Cu/Ni composite electrode towards glucose oxidation showed no featureless CV curve and the anodic potential/current response remains unchanged (fig. S3), confirming the Cu/Ni composite

electrodes are good resistant to surface fouling and can be used for glucose electro-oxidation catalyst as well as sensor.

In order to explore the rate-determining step, a Tafel plot of E vs. $\log I$ was drawn using the data of the low current region part of the current-voltage curve for 0.05 M solution of glucose (fig. 3). The slope values observed in the current study are much higher (200mV/decade and 280mV/decade for NiFe_2O_4 nanocomposite and CuFe_2O_4 nanocomposite respectively), which indicates that the rate determining step may not be a single electrochemical step, but more likely the combination of two steps (one chemical and other electrochemical).

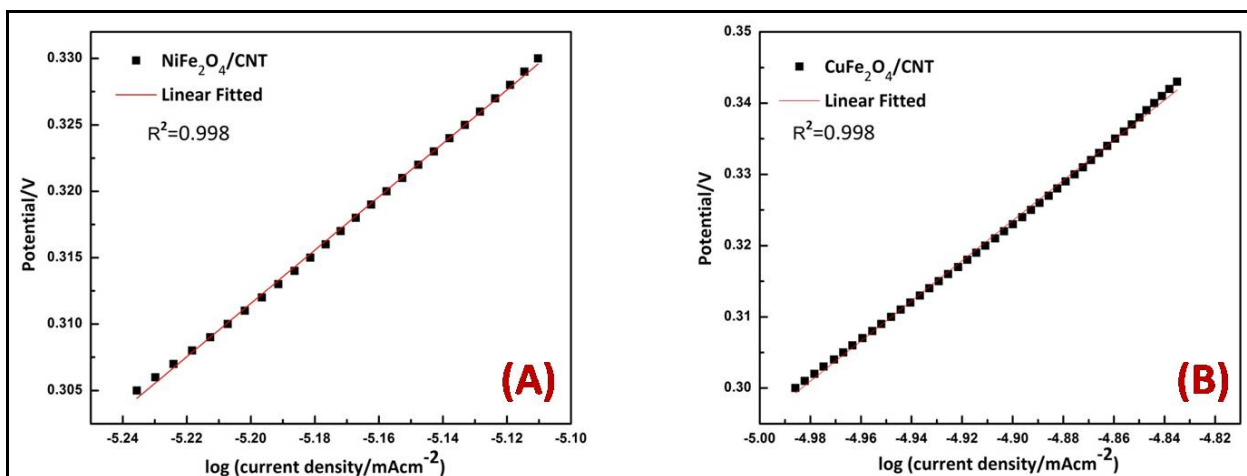


Figure 3 Tafel plots of the respective catalysts (A) NiFe₂O₄ nanocomposite, (B) CuFe₂O₄ nanocomposite

Electro-oxidation products of glucose such as Gluconolactone,²⁹ methanoates and oxalates³⁰ are well reported. A characteristic spectrum with a trough near 300 nm (Fig S6) and HPLC chromatogram (fig S7) was observed which confirms the intermediate product as Gluconolactone which has a similar spectral limit for maltose and maltodextrin like similar components.

The mechanistic detail of electro oxidation of Glucose to gluconate is shown in figure S5. The proposed mechanism is based on previous reports on noble electrodes³¹⁻³³. The fundamental aspect of this investigation is to understand the oxidative peak in the cyclic voltammetry for its implication in glucose sensing and characteristic detection of the metabolites after electro oxidation of glucose.

4. CONCLUSIONS

We have successfully fabricated and developed a glucose electro-oxidation nanocomposite based on Ni and Cu magnetite on acid functionalized MWCNTs by hydrothermal protocol. Compared to the bare ferrite electrodes, the nanocomposites display high electrocatalytic activity towards the glucose oxidation, showing lower overpotential and high anodic current response. Gluconolactone was determined by reverse-phase HPLC and UV-Visible spectroscopy with good precision. Meanwhile, the catalysts are highly resistant to intermediate poisoning and demonstrates long-term cyclic stability as well. Thus, to the best of

our knowledge the current nanocomposites are new for the electro-oxidation of glucose and can be proved as an efficient, low cost, and exhibits promising application in non-enzymatic glucose sensor. The study represents the basis of upcoming ferrite and CNTs based nanocomposites for potential clinical investigations.

ACKNOWLEDGMENTS

This work was financially supported by Department of Science and Technology (DST), Government of India, New Delhi is duly acknowledged.

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