



# Multi-wall carbon nanotube–NiO nanoparticle composite as enzyme-free electrochemical glucose sensor



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## ABSTRACT

We report a simple, solvent-free method to decorate multi-walled carbon nanotubes (MWCNTs) with nickel oxide nanoparticles (NiO-NPs). The as prepared NiO–MWCNT composite were characterised by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. The enzyme-free modified carbon paste electrode (CPE) was fabricated using as-synthesised composite material and investigated for glucose sensing. The 10% NiO–MWCNTs composites sensor showed excellent electro-catalytic activity towards direct glucose oxidation. The sensitivity of this sensor is found to be  $1696 \mu\text{A mM}^{-1} \text{cm}^{-2}$  and  $122.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$  and the limit of detection (LOD) was found to be 11.04 nM and 31  $\mu\text{M}$  for the linear response over glucose concentration ranging from 1–200  $\mu\text{M}$  to 0.5–9.0 mM, respectively. Furthermore, the 10% NiO–MWCNTs sensor also showed excellent anti-interference ability, high stability and good reproducibility. Hence, due to simple method of material preparation, easy sensor fabrication and excellent electro catalytic activity towards glucose oxidation, the 10% NiO–MWCNT/CPE is a potential material for the development of enzyme-free sensor for reliable glucose determination.

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## 1. Introduction

Development of an electrochemical method for glucose monitoring has gained significant attention in clinical diagnosis, biotechnology, food industry and so forth [1,2]. The enzyme based biosensor was successfully designed to estimate the glucose with high selectivity [3–5]. Though the enzyme based biosensor is more stable and commercialised, however they still show instability due to the factors like temperature, humidity, organic reagents, toxic chemicals, oxygen, etc. [6] which affects the sensitivity and reproducibility. These factors restrict the use of biosensors in continuous monitoring during fermentation processes or in human bodies. The major drawback with the enzymatic biosensor setup is interference of bio-molecules like dopamine (DA), ascorbic acid (AA) and uric acids (UA) on glucose detection. These limitations can be overcome by developing the non-enzymatic biosensors on direct electro-catalytic oxidation of glucose [7–14].

The recent literature studies, demonstrated that non-enzymatic electro-oxidation of glucose varies considerably depending on the

electrode material used [15–17]. Hence, development of novel electrode materials with high electrocatalytic activity and high stability for glucose attains major attention in developing the practical non-enzymatic sensor. Many different transition metals and their oxides (Pt, Co, Ni, Au,  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , NiO,  $\text{RuO}_2$ , etc.) have been explored as the electrode substrates toward the oxidation of glucose [18,19]. Among these, NiO materials are the best choice because of its excellent electrocatalytic properties, low toxicity and are relatively inexpensive for the construction of non-enzymatic glucose sensors [20,21]. Fleischmann et al. in 1971 reported that Ni acts as highly efficient electrocatalyst for glucose oxidation resulting from the redox couple of  $\text{Ni}^{3+}/\text{Ni}^{2+}$  in the alkaline medium [22]. Hence, extensive research was carried out on non-enzyme biosensors using Ni based nano-materials. There are many numbers of Ni based non-enzymatic glucose sensors constructed by modifying the substrate with nickel nanoparticles, nickel–carbon hybrids, Ni–CNT composite, Ni–graphene composites, etc. [23–27]. The recent developments in electrochemical sensor technology show significant increase in electrocatalytic activity for nano-materials as compared to the bulk materials [28,29].

Carbon nanotubes (CNTs) are helical tube like structures of graphitic-carbon sheets with high electrocatalytic properties, chemical stability, extremely high mechanical strength and greater surface area for glucose oxidation [30,31]. CNTs also serve as a good

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supporting material for heterostructure like metal and metal oxide catalyst and hence they find application in electrode modification to obtain high-performance sensors [32,33]. Many different methods for decoration of CNTs with metal oxide are reported such as, wet impregnation, ball-milling, sputtering, electro-deposition, etc. [34–37]. However, still uniform, bulk, simple and precise control of the decoration of CNTs remain challenging and only limited number of studies on NiO-modified CNT nano-composite for non-enzymatic glucose sensors were reported [36,37].

Herein, we report construction of enzyme-free glucose sensor based on nickel oxide nanoparticles (NiO-NPs) decorated multi-walled carbon nanotubes (MWCNTs) composites modified carbon paste electrode (NiO-MWCNT/CPE). To decorate the MWCNTs by NiO-NPs we followed a simple, rapid, solvent-free, economic and scalable route in which thermal decomposition of Ni formates without reducing agent. Nickel formate is used for the first time as a precursor for the decoration of NiO on MWCNTs. The weight percentage of precursor to MWCNTs was optimised to decorate uniform nanoparticles of size 15–25 nm on MWCNTs. This hybrid composite was characterised by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy. The composite material was applied to investigate the electrocatalytic oxidation of glucose. The sensor performance factors like sensitivity, selectivity, stability, linear range, limit of detection (LOD), interference effect and reproducibility of the proposed enzyme-free glucose sensor was systematically investigated and compared with other non-enzymatic reported glucose sensors. The best combination composite material was used to determine the glucose concentration in human blood serum and commercially available glucose samples.

## 2. Experimental

### 2.1. Materials

All the chemicals are of analytical grade and were used without further purification.

D-(+)-glucose, dopamine (DA), L-ascorbic acid (AA), uric acid (UA) and graphite powder were purchased from Sigma-Aldrich, India. Stock solutions of all the reagents were prepared using double distilled water. The MWCNTs were synthesised by catalytic vapour deposition (CVD) technique and purified by reported procedure from our research group [38]. Nickel formate was prepared by refluxing nickel acetate and formic acid. The microcrystalline precipitate was obtained on cooling which was filtered and dried at 100 °C. The formation of nickel formate was confirmed by XRD.

### 2.2. Reagent preparation

The stock solution of 1.0M NaOH was prepared using double distilled water, from which 0.05 M to 0.3 M NaOH solution was prepared. All the analyte samples freshly prepared every day just before the analysis. The analyte sample stock solution (10 ml) was prepared using double distilled water such as, glucose (0.9 g, 0.4995 M), ascorbic acid (AA) (0.85 g, 0.4826 M) and dopamine (DA) (0.95 g, 0.4826 M). The uric acid (UA) (0.84 g, 0.4996 M) is insoluble in water and hence it is dissolved in 0.05 M NaOH solution just before the experiment.

### 2.3. Synthesis of NiO nanoparticles decorated MWCNTs

MWCNTs were dry mixed with different weight ratio (5%, 10% and 15%) of nickel formate with respect to MWCNT using a mortar and pestle until the formation of homogeneous mixture under ambient conditions. The solid mixture was then transferred to a

quartz boat and heated in an air atmosphere at 380 °C for 2 h. The products were then collected as the final NiO-NPs decorated MWCNT samples, namely 5%, 10% and 15% NiO-MWCNT composites.

### 2.4. Preparation of NiO-MWCNT modified carbon paste electrodes

Carbon paste electrodes (CPE) were prepared by mixing of the weighed amounts of graphite powder and paraffin (5:1). The resulting carbon paste was packed into the cavity of Teflon tube (3 mm internal diameter). The electrical contact was established using a copper wire inserted into the Teflon tube to the cavity filled with carbon paste which was smoothed over weighing paper until a smooth shiny surface was obtained. Similarly, NiO-MWCNT modified CPE was prepared using bulk modification method by mixing graphite powder, NiO-MWCNT composites and silicone oil in the optimised ratio of 75:25:5 (w/w), respectively. The modified electrode was named as 5% NiO-MWCNT/CPE, 10% NiO-MWCNT/CPE and 15% NiO-MWCNT/CPE for 5%, 10% and 15% NiO-MWCNT composites, respectively. For comparison purpose, only NiO-NPs/CPE and MWCNT/CPE was also constructed under identical conditions.

### 2.5. Measurements and apparatus

The crystal nature of the material was recorded by X-ray diffraction using JEOL JDX 8P model diffractometer at room temperature with a Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at a scan rate of 2° min<sup>-1</sup>. The surface morphology of the sample was characterised by FESEM on Carl Zeiss ULTRA 55 and TEM on a Philips CM200 electron microscope. Cyclic voltammetry (CV) and amperometry analysis were performed to investigate the electrocatalytic properties of the as prepared NiO-MWCNT modified electrodes. The electrochemical experiments were performed using a SP-150, Bio-Logic Science instruments with the three electrode configuration at room temperature. The NiO-MWCNTs modified CPE was employed as working electrode, a calomel as reference electrode and a platinum wire as counter electrode, respectively.

## 3. Results and discussion

The morphology and surface area of material used in electrode modification plays significant role in determining the sensitivity of sensor. Higher catalytic activity was obtained with NiO-MWCNT composites. Fig. 1(a) illustrates the FESEM images of the pure MWCNTs whereas as Fig. 1(b)–(d) represents the FESEM images of the NiO-NPs decorated MWCNT composites. As the precursor load increases from 5% to 15%, the nature of NiO particles formed on the surface of MWCNTs also differs. The uniform NiO-NPs decorated MWCNTs observed in 5% and 10% samples (Fig. 1b and c), wherein, 5% shows least NiO-NPs decoration due to less precursor load. Even though the 15% sample (Fig. 1d) shows the dense NiO particles decoration on MWCNTs, is not free from the agglomeration of NiO particles due to excess precursor load. Hence, among these NiO-MWCNT composites, the 10% NiO-MWCNT composite shows maximum and uniform NiO-NPs decorated MWCNTs with least or no agglomerated particles and are considered to be the optimized ratio.

Fig. 2a and b shows the TEM images of the 10% NiO-MWCNT and 15% NiO-MWCNT composites. It is observed that in 10% NiO-MWCNT the NiO-NPs are homogeneously dispersed on the sidewalls of the MWCNTs without aggregation. The particle size appears to be 2–25 nm with a mean value of ~15 nm. In 15% NiO-MWCNT, although the NiO-NPs are homogeneously dispersed, due to the excess precursor load the NiO particles agglomerates and forms macro particle.

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