



# Amperometric sensing of hydrogen peroxide using glassy carbon electrode modified with copper nanoparticles



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## ABSTRACT

In this paper, fabrication of glassy carbon electrode (GCE) modified with nano copper particles is discussed. The modified electrode has been tested for the non-enzymatic electrochemical detection of hydrogen peroxide ( $H_2O_2$ ). The copper nanoparticles (Cu NPs) were prepared employing a simple chemical reduction method. The presence of Cu NPs was confirmed through UV–visible (UV–vis) absorption spectroscopy and X-ray diffraction (XRD) analysis. The size and morphology of the particles were investigated using transmission electron microscopy (TEM). The electrochemical properties of the fabricated sensor were studied via cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The electrochemical sensor displayed excellent performance features towards  $H_2O_2$  detection exhibiting wide linear range, low detection limit, swift response time, good reproducibility and stability.

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## 1. Introduction

The abnormal production of hydrogen peroxide ( $H_2O_2$ ) in human body is a valuable biomarker of oxidative stress and inflammation [1–3]. The increase in the level of  $H_2O_2$  in breath levels is an indication of respiratory disorders such as asthma and pneumonia [4,5]. Other numerous chronic diseases such as diabetes, cancer, aging and atherosclerosis [6–8] are also associated with the excess production of  $H_2O_2$ . Apart from these, it also serves as an essential mediator in food, industry, medicine and environmental analysis [9]. Therefore, accurate and sensitive detection of  $H_2O_2$  has become an area of increased importance in recent years. Several analytical techniques such as fluorometry, titrimetry, spectrophotometry, electrochemical techniques and chemiluminiscence [10] have been employed for the determination of  $H_2O_2$ , but electrochemical methods have emerged as the preferred one due to its simplicity, rapid detection, good selectivity, high sensitivity and low cost [11]. To date, most of the electrochemical biosensors employ the use of enzymes immobilized on an electrode for the determination of  $H_2O_2$ , but employing enzymes poses several practical difficulties; for example, it requires a specific set of experimental parameters such as temperature and pH. The preparation process is quite costly; and on long-term usage, there is a possibility of

denaturation of the enzyme [12]. The current work reports the preparation of electrode modified with polymer stabilized Cu NPs for the non-enzymatic detection of  $H_2O_2$ .

Though metal nanoparticles in general, have aroused considerable interest due to their unique physical and chemical properties [13], copper nanoparticles (Cu NPs) have gained wide attention in electrochemical platforms owing to their advantages such as good electrical conductivity, cost effectiveness and simplicity in preparation methods. In addition, it exhibits excellent biocompatibility and catalytic properties [14–17]. It is also found that Cu NPs act as the catalytic centres and accelerate electron transfer resulting in better  $H_2O_2$  reduction [17–20]. Many biosensors based on nano copper [18,20,21], copper oxide [16] and copper hybrid composite materials [17,19,22,23] for  $H_2O_2$  reduction have been reported recently.

Selvaraju and Ramaraj [18] reported the preparation of nanostructured copper modified electrode for electrocatalytic reduction of  $H_2O_2$ . Qiu et al. [20] reported the use of dendritic copper nanostructures for  $H_2O_2$  reduction. Fabrication of a novel non-enzymatic  $H_2O_2$  sensor by dispersing Cu NPs onto polypyrrole (PPY) nanowires through electrochemical deposition method was reported by Zhang et al. [21]. A work on the preparation and characterization of non-enzymatic sensor based on  $Cu_2O/Cu$  nanocomposites for electrochemical detection of  $H_2O_2$  was reported by Luo et al. [16]. Bo et al. [19] used a simple and facile synthetic method for the preparation of copper sulfide nanoparticles on ordered mesoporous carbon. Ensafi et al. [22] reported a sensor using copper/porous silicon for the determination of  $H_2O_2$ .

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Baskar et al. [23] prepared copper–polymelamine composite material for  $\text{H}_2\text{O}_2$  sensing.

In this paper, we report the preparation of polyvinylpyrrolidone (PVP) stabilized Cu NPs (PSCN) by simple chemical reduction method. The formation of PSCN has been confirmed by UV–vis absorption spectroscopy (UV–vis) and X-ray diffraction (XRD) analysis. The size and shape of the nanoparticles were observed through field emission transmission electron microscopy (FETEM). The interaction between the polymer and Cu NPs was confirmed by FTIR spectroscopy. PSCN solution was then coated onto a glassy carbon electrode (GCE) to study its electrocatalytic response towards the reduction of  $\text{H}_2\text{O}_2$  by using cyclic voltammetry (CV) and chronoamperometry. The electrode modification process and charge transfer were characterized by electrochemical impedance spectroscopy (EIS). The performance of the biosensor is discussed in detail. The fabricated biosensor exhibited wide linearity with low detection limit (LOD) ( $3.45 \mu\text{M}$ ), excellent reproducibility and stability.

## 2. Materials and methods

### 2.1. Materials

Copper(II) sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) were obtained from Merck (Mumbai, India). Sodium borohydride ( $\text{NaBH}_4$ ), polyvinylpyrrolidone (PVP K 40) and nafion were purchased from Sigma–Aldrich (USA).  $\text{H}_2\text{O}_2$  (30% w/v) is from SD Fine Chemicals (Mumbai, India). The chemicals used were of analytical grade. All glassware was washed with non-ionic detergent and aqua regia. Prior to use, they were rinsed with deionised water and oven dried.

### 2.2. Methods

Cu NPs were synthesized by reducing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $\text{NaBH}_4$  and were stabilized into PVP. In a typical synthesis,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1 mM, 25 mL) was added drop by drop into  $\text{NaBH}_4$  solution (2 mM, 50 mL) with rapid stirring. The solution turned into brownish orange colloid resulting from borohydride-assisted reduction of copper [24]. After the reaction, the Cu NPs thus formed were

immediately introduced into PVP (0.015 mM, 25 mL) followed by vigorous magnetic stirring to prevent the aggregation of the nanoparticles.

### 2.3. Instrumentation and measurements

UV–vis absorption spectra were recorded in the range of 300–800 nm using a Jasco V-630 spectrophotometer in a quartz cuvette with 1 cm optical path length. The morphology of the particles was characterized using a JEM 2100 F, JEOL field emission transmission electron microscope operated at 200 kV. XRD patterns were recorded on a XPERT-PRO diffractometer using Cu  $\text{K}\alpha$  (30 mA, 40 kV) radiation source with  $\lambda = 1.540 \text{ \AA}$ . FTIR spectra were performed on a PerkinElmer Spectrum BX II spectrometer.

All electrochemical measurements (CV, chronamperometry and EIS) were carried out in a three-electrode cell at room temperature using a CHI 600 D electrochemical workstation (CH instrument) with platinum wire as the counter electrode and Ag/AgCl (saturated with KCl) as the reference electrode. The PSCN modified GCE (3 mm diameter) served as the working electrode.

### 2.4. Preparation of the modified electrode

Prior to preparation, the GCE was successively polished using 1, 0.3 and 0.05  $\mu\text{M}$  alumina slurry followed by thorough rinsing with deionized water. 10  $\mu\text{L}$  of polymer stabilized nano-Cu solution prepared in the present work was pipetted onto the GCE and dried. Then 5  $\mu\text{L}$  of 0.05% nafion was dropped onto the surface of the modified electrode. The electrochemical measurements were carried out in 0.02 M PBS (pH 7).

## 3. Results and discussion

### 3.1. Optical and structural studies

UV–vis absorption spectrum of freshly prepared Cu NPs stabilized by PVP is shown in Fig. 1. The surface plasmon resonance (SPR) band of Cu NPs could be observed between 500 and 600 nm depending on size, shape, solvent and capping agent involved in the synthesis [25,26]. The presence of sharp and narrow surface plasmon band at 577 nm (Fig. 1) confirms the formation of Cu NPs [26–29]. Without polymer protection, the surface plasmon band of Cu NPs gets red-shifted to 591 nm

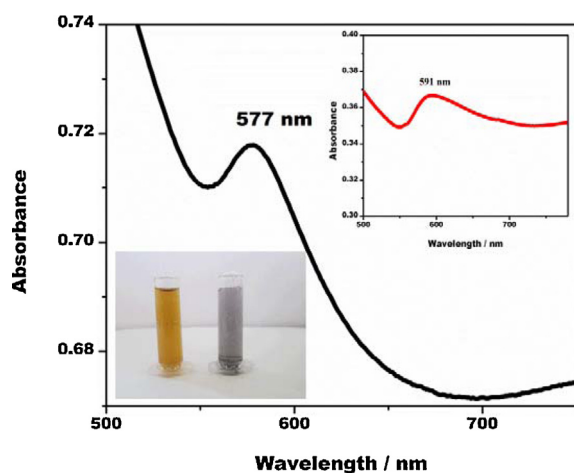


Fig. 1. UV–vis absorption spectrum of the solution containing PVP stabilized Cu NPs. Inset (top right) shows UV–vis absorption spectrum of unstabilized Cu NPs and its corresponding photograph is shown in the inset (bottom left). (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

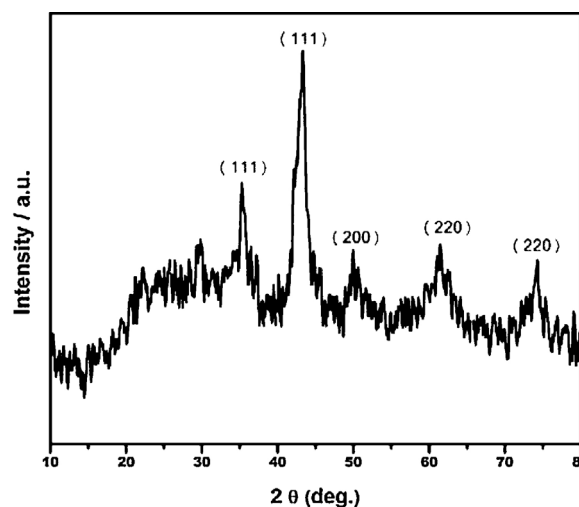


Fig. 2. XRD pattern of PVP stabilized Cu NPs.

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