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Microwave assisted synthesis of copper oxide and its application in electrochemical sensing

S Felix[1], **R Bala Praveen Chakkravarthy**[2] **and A Nirmala Grace**[1*]
[1]Centre for Nanotechnology Research, VIT University, Vellore – 632 014, Tamil Nadu, India.
[2] Research & Advanced Engineering Division (Materials), Renault Nissan Technology & Business Center India (P) Ltd., Chennai - 603 002, Tamil Nadu, India.
[*]Corresponding author's e-mail:balapraveen2000@yahoo.com, anirmalagladys@gmail.com

Abstract. Copper oxide nanopowders were prepared using copper acetate as the precursor and polyethylene glycol (PEG) as stabilizer in ethanol medium. The mixture containing copper acetate, sodium hydroxide and PEG was irradiated with microwave and nanometric copper oxide particles were formed within 8 min. The prepared nanoparticles were characterized using x-ray diffraction, UV-vis spectroscopy and scanning electron microscopy. The average particle size was found to be ~ 4 nm. This was used to modify glassy carbon electrode with PVDF & DMF as binder and used for sensing of carbohydrates (glucose and sucrose) and H_2O_2. The copper oxide nanoparticles showed excellent sensitivity in the range of 0.1 mM to 1 mM when choronoamperometry was carried out at 0.6 V Vs. Ag/AgCl. The observed sensitivity is much higher when compared with conventional micron sized copper oxide particles.

1. Introduction

Metal oxides are versatile materials with electrical conductivities ranging from insulating to metallic, optical transmission from opaque to transparent, magnetic susceptibility from para to ferromagnetic, etc., [1]. In recent years research focus has been increasing in producing nanostructured metal oxides for a variety of applications like transparent conductors, super paramagnetic materials, battery materials, catalysts etc., Compared with the bulk metal oxide materials, nanoscale metal oxides have many advantages due to their extremely reduced size and large surface to volume ratio provided the crystallinity is maintained [2]. Diabetes is a worldwide public health problem. An important clinical test for diagnosing diabetes is accurate measurement of blood glucose level. Many types of glucose sensors are known, viz., chemiluminence, fluorescence and optic sensors [3, 4]. Sucrose is the important carbohydrate in most of the drinks and foods. Fast, simple and efficient electrochemical method used to determine sucrose in food industry [5]. Hydrogen peroxide (H_2O_2) can induce functional and morphological disturbances and because of its extreme toxicity in cells can cause cancer and its detection is important to clinical, industrial, and environmental analyses. Although technologies such as titrimetry, fluorescence, and absorption spectra have been used to detect H_2O_2 and new sensors based on electrochemical technology have proven simple to use and highly sensitive for real-time detection [6]. Electrochemical sensors have many advantages compared to the optical methods like relatively low cost, high selectivity and sensitivity, and ease of integration with electronic systems.

CuO is a p-type semiconductor and its narrow band gap 1.24 eV makes it suitable for applications in gas sensors, magnetic storage media, lithium batteries and solar cells due to its photoconductive and photochemical properties. The properties of CuO are closely related to its crystal size, orientation and morphology [7]. Microwave irradiation as a heating method has found a number of applications in chemistry. The microwave solvothermal synthesis is popular as it is faster, simpler and efficient in energy for metal oxide nanopowder synthesis. Good phase purity is also reported when microwaves are used [8, 9]

In this work CuO nanoparticles were synthesized by microwave irradiation method in ethanol medium. The prepared CuO nanoparticles were characterized by using XRD, UV-vis spectroscopy and SEM. The electrocatalytic activity of CuO nanoparties with modified electrodes towards the glucose, sucrose and hydrogen peroxide sensing in 0.1 M NaOH was investigated using cyclic voltammetry and chronoamperometry. It was found that sucrose can also be sensed using these modified electrodes with comparable sensitivity to that of glucose, thus opening avenues to use it as a chemical oxygen demand sensor.

2. Experimental procedure

2.1. Chemicals

Copper acetate, sodium hydroxide, ethanol and polyethylene glycol (PEG) were purchased from S. D. fine-chemicals. D-(+)-glucose, Sucrose, H_2O_2, N, N-Dimethyl formamide and polyvinyllidene fluoride were purchased from Sigma Aldrich.

2.2. Synthesis of CuO nano particles by Microwave irradiation method

1.59 g of $Cu(CH_3COO)_2$ was dissolved in 50 mL ethanol and mixed with 0.016 g of NaOH added to 50 mL ethanol. 5 g PEG was then dissolved in the solution mix. The mixture was placed in a domestic microwave oven (Sanyo, EM-G3686WY) and irradiation was carried out in ambient air for a total of 8 min at 80 % power. The solution mixture boils in about 10 s of microwave irradiation. Therefore, it was cooled in an ice bath after every 10 s and heating was continued till. Therefore, it was cooled in an ice bath after every 10 s and heating was continued till. The dark-green precipitate was formed at the end of the reaction. After cooling to room temperature the precipitate was centrifuged, washed with de-ionized water repeatedly and finally with absolute ethanol, dried in a hot air oven at 100 º C for 3 h. The final product (dark brown in color) was collected for characterization [9].

2.3. Characterization of CuO nanoparticles

The phase purity and crystallinity of the prepared nanoparticles was determined by XRD (D8 Advanced, Bruker diffractometer, Germany). The optical absorbance of the powder characterized in the wavelength between 200 to 800 nm using UV-Visible spectrophotometer (Shimadzu, UV-3600, china). The surface morphology and size of CuO nanoparticles were investigated using Scanning Electron Microscope (JEOL SM 840, Spain) and Electrochemical studies were carried out using an electrochemical analyzer (CHI 660C, CH Instruments, Switzerland).

2.4. Electrode modification and electrochemical measurements

The glassy carbon working electrode had a nominal diameter of 3 mm; it was polished with 0.05 micron alumina powder mixed with deionized water before testing and washed thoroughly with acetone and de-ionized water. 3 mg of CuO was dispersed in 150 µL (PVDF&DMF) solution in the ratio of 1:50 and then sonicated for 10 min. 10 µL of above dispersion was coated on the surface of glassy carbon electrode and dried at room temperature for 5 h. This gave a stable electrode with copper oxide immobilized on it. Electrochemical measurements were performed using a conventional three electrode system with CuO modified glassy carbon as the working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. During chronoamperometry measurements, the voltage was maintained at 0.6 V and the current was observed after successive addition of (1000 µL of 5.4 $mg\,cm^{-3}$) glucose to the electrolyte solution with constant stirring. The same condition was followed for sucrose at a constant potential of 0.6 V in a successive addition of sucrose to the electrolyte under stirring condition. In case of hydrogen peroxide, the concentration was varied from 0.5 mM to 10 mM with a constant stirring at 0.6 V.

3. Results and Discussion

3.1. XRD-analysis

XRD analyses were used to study the phases and crystalline nature of CuO nanoparticles as shown in figure 1. All diffraction peaks located at values between 30º and 65º (35.51, 38.71, 48.81 and 58.41) can be attributed to the Miller indexes of the (-1 1 1), (2 0 0), (-2 0 2) and (2 0 2) planes of monoclinic CuO, according to (JCPDS 89-5895). The size of the nanoparticles was calculated by Debye-Scherrer formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where λ is the wavelength of x-rays (Cu kα = 1.54178 Å), β is the full width half maximum value in terms of radians, θ refers to diffraction angle, the calculated particle size was 4 nm.

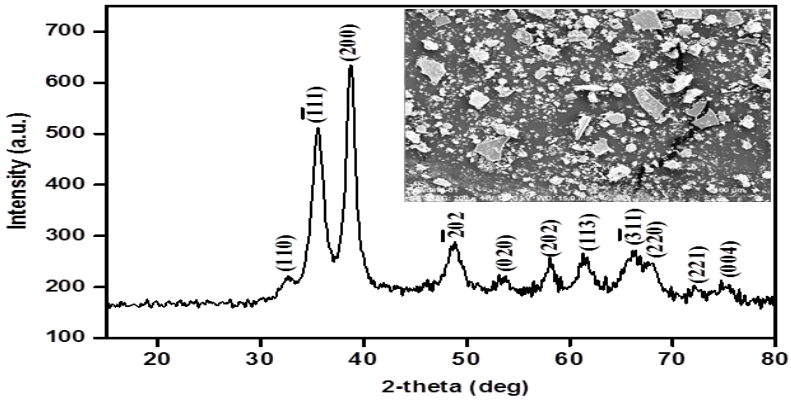

Figure 1. XRD patterns and SEM images (Inset) of synthesized copper oxide nanoparticles.

3.2. Optical properties

The UV-vis spectrum was used to determine the optical absorption properties of CuO nanoparticles. Figure 2 shows the UV-Vis absorption spectrum of CuO nanoparticles. A broad absorption peak at 297 nm confirmed that the band gap is due to the intrinsic transition of the CuO.

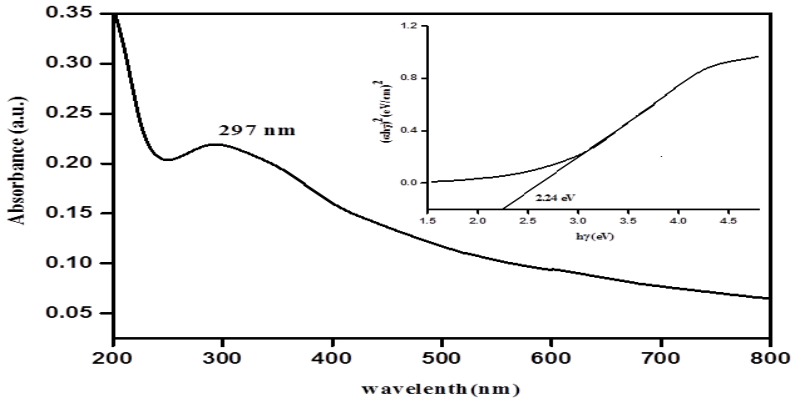

Figure 2. UV–vis absorption spectrum of monoclinic CuO. *Inset:* shows the plots of $(\alpha E_{photon})^2$ vs. E_{photon}.

The energy gap of these nano materials were estimated with Tauchi's equation [12] for direct transition in semiconductors given by

$$(\alpha h\gamma) = c(h\nu - Eg) \quad (2)$$

Where hγ, α, c, Eg are respectively incident photon energy, absorption co-efficient, constant and the energy gap. The plot drawn using $(\alpha h\gamma)^2$ on the y-axis against photon energy (E=hγ) on the x-axis show the value of the band gap given by the x-intercept as shown in figure 2 (inset), is 2.24 eV. The blue-shift behavior of the peak position in comparison with that of the bulk CuO (1.85 eV) [13] could be attributed to the enhancement of the quantum confinement effect resulting from the decrease in the size of the nanoparticles [12-14].

3.4. Electrochemical characterization

The sensing behavior of the modified electrode was observed at an applied potential of 0.6 V with successive addition of carbohydrates (glucose, sucrose) ranging from 50 µM to 1000 µM in 0.1 M NaOH solution using chronoamperometry. The first addition of glucose was made after 150 s with 50 µL added to the electrolyte. Then, 50 µL was added at 210 s. After that 100 µL was added once in every 60 s. A near linear behavior was observed. The sensitivity was calculated as 17.2 µA/mM and it gives a linear amperometric response in the glucose concentration from 100 µM to 1000 µM of glucose.

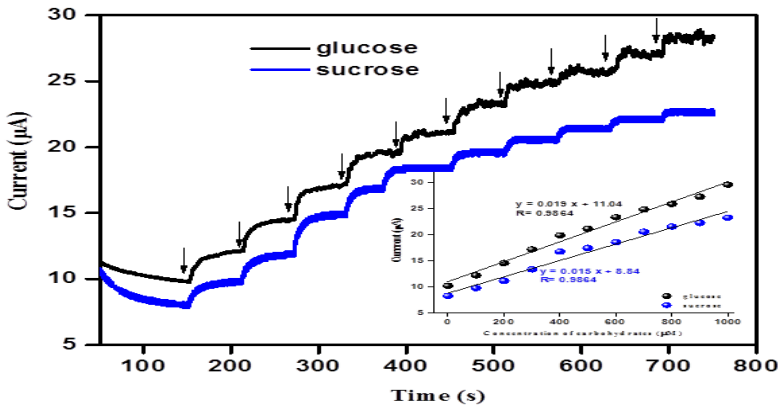

Figure 3. Choronoamperometry response of glucose and sucrose with glassy carbon modified with CuO in 0.1 M NaOH solution at a regular interval of 60 s. *Inset (right)* the corresponding calibration plot of net current vs. concentration.

The linear regression equation for glucose detection was calculated from net current, which is defined as the the total current minus the blank current i.e. current at ~145 s, $I_{glucose}$ =0.019x + 11.04C with R = 0.9864. Figure 3 displays the chronoamperometric behavior of sucrose with 50 µL sucrose added after 150 s. A fast, stable and stepwise increase in current was observed at 0.6 V. The sensitivity was calculated in the case of sucrose as 10.482 µA/mM. The linear regression equation is $I_{sucrose}$ =0.015x + 8.84C with R=0.9864. These values are comparable to those in the literature for copper oxide nanostructure [15, 16] and its sensitivity was calculated to be 6.53 µA/mM. Figure 4 (Inset) showed a poor linear range denoting a slow electron transfer speed and adsorption of the intermediate product produced during the glucose oxidation process. The same condition is followed for H_2O_2. But in the case of H_2O_2 concentration varying from 0.5 mM to 9 mM, a step current change occurred with its linear regression equation I(µA)=0.503x + 2.423, R = 0.9986. In general, insufficient stability of

enzyme electrode is the result of the loss and deactivation of enzyme. The fabrication of carbohydrate sensors has the advantages like long term stability, low detection limit, reproducibility, simplicity and inexpensive [15-16] Figure 4 showed that the step response is distorted at higher concentrations. At higher concentrations, the detection is not diffusion limited and more side reactions are possible. Therefore, it may be concluded that this electrode detects better when the concentration of the peroxide is less than 10 mM.

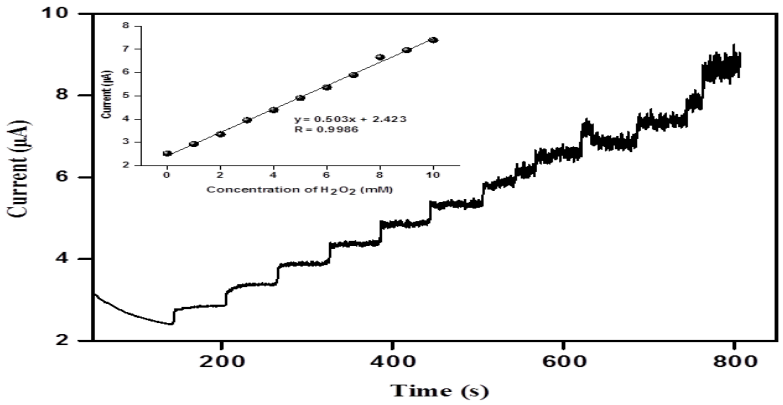

Figure 4. Amperometric response for the detection of H_2O_2. *Inset* shows the corresponding calibration plot.

4. Conclusions

CuO nanoparticles were successfully synthesized by microwave irradiation with phase purity and high crystallinity as seen by XRD; its optical properties and morphological studies were analyzed by UV-Vis spectroscopy and SEM analysis respectively. Using these nanoparticles, a sensitive amperometric electrochemical sensor for detecting glucose, sucrose and hydrogen peroxide is demonstrated.

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