

Synthesis and Characterization of Copper Oxide Nanoparticles and their Application as Electrode Modifiers

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Abstract: Nano-sized copper oxide (CuO) powder was synthesized through the method of wet chemical precipitation from Cu(NO₃)₂. The nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size analyzer and Fourier transform infra-red spectroscopy (FTIR). Two most prominent peaks in the XRD profile, around $2\theta = 35.9^\circ$ and 39.2° , which are combinations of double-reflections $\{(002) \text{ and } (-111)\}$ and $\{(111) \text{ and } (200)\}$, respectively, are characteristics of monoclinic CuO. The unit cell parameters determined from the analysis of XRD data were: $a = 4.6927$, $b = 3.4283$ and $c = 5.137$ Å, with $\alpha = \gamma = 90^\circ$ and $\beta = 99.546^\circ$. SEM pictures showed uniform distribution of ice-glass like crystalline particles, which are made up of smaller particles. Crystallite size estimation from XRD data using Debye-Scherrer formula produced average size of 34 nm for the nanoparticles. However, the particle size analyzer measured the average grain-size as 86 nm. Clearly, each grain of the nano-sized CuO seemed to be made up of roughly 16 crystallites. FTIR results showed expected peaks corresponding to Cu-O stretching. Further, the electrocatalytic properties of CuO nanoparticles as carbon paste electrode (CPE) modifier were investigated for the electrochemical oxidation of ascorbic acid, atenolol, diclofenac, dopamine, hydrazine and glucose using cyclic voltammetry. The results showed marked improvement of detection efficiency with CuO nanoparticles modified carbon paste electrode as compared to the response of the unmodified carbon paste electrode.

Keywords: Copper oxide; Nanoparticles; Voltammetry; Modified carbon paste electrode.

1. Introduction

Nano-sized and nanostructured transition metal oxides have attracted considerable attention from researchers in the recent years. Oxides such as ZnO, TiO₂ and Fe₃O₄, etc. are perhaps the most investigated inorganic materials due to their interesting physical and chemical properties. Copper (II) oxide, CuO, also known as cupric oxide is a p-type semiconductor with a bandgap of 1.2 – 1.9 eV. It is a black transition metal oxide with monoclinic crystal structure and many interesting characteristics, e.g., high thermal conductivity, photovoltaic properties, high stability and antimicrobial activity. Because of such useful properties, CuO has been investigated extensively for its wide range of potential applications, such as, in electrochemical cell, gas sensors, magnetic storage devices, field emitters and in catalysis [1].

Carbon paste electrodes (CPEs) are widely used for the electrochemical determinations of various biological and pharmaceutical species due to their low residual current and noise, ease of fabrication, wide anodic and

cathodic potential ranges, rapid surface renewal and low cost. Moreover, chemically modified carbon paste electrodes (CMCPEs) can be easily prepared by adding different substances to the bulk of CPEs in order to increase sensitivity, selectivity, and rapidity of determinations.

In the past few decades, nanoparticles of a variety of shapes, sizes and compositions exhibit excellent conductivity and fascinating catalytic properties, which make them suitable for constructing novel electrochemical sensors. Nanocomposites can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve reproducibility of the electrode response in the area of electroanalysis [2]. Appropriate modifications of the electrodes are generally required for improved performance and efficiency of electrochemical cells, in photovoltaics, and applications as sensors and detectors. CuO nanoparticles and nanostructures, in pure and in combination with other materials, have been proven to be interesting candidates for carbon paste electrode

modifiers [2-5]. A variety of methods have been reported for the preparation of nanocrystalline CuO particles, which include the sol-gel technique [1], sonochemical method [6], electrochemical method [7], microwave irradiation method [8], wet chemical/alcothermal method [9], solution-plasma method [10], etc.

In this report we present the synthesis of CuO nanoparticles using wet chemical precipitation (WCP) method, using $\text{Cu}(\text{NO}_3)_2$ and 1,10-phenanthroline as precursors, and ethanol/water mixture and NaOH as a reducing agents. Characterization of the synthesized CuO nanoparticles have been done by X-ray diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), thermogravimetric analysis (TGA) and particle-size analysis. Further, their potential application as electrocatalysts has been examined using them as carbon paste electrode modifiers by cyclic voltammetry (CV) for the detection of ascorbic acid, atenolol, diclofenac, dopamine, hydrazine and glucose.

2. Experimental

Synthesis of CuO nanoparticles:

NaOH was obtained from ACE (South Africa), 1,10-phenanthroline from Saarchem (South Africa), ethanol from Laboratory & Analytical Suppliers Co. (Pty) Ltd (South Africa), glucose from Merck-Schuchardt (Germany), $\text{Cu}(\text{NO}_3)_2$ from NT Laboratory Suppliers (Pty) Ltd (South Africa), ascorbic acid from Merck Chemicals (South Africa), hydrazine, atenolol,

dopamine and diclofenac were from Fluka. All reagents were used as received and ultra-pure water was used throughout. Stock solutions of 0.01 M solutions of ascorbic acid, atenolol, diclofenac, dopamine, hydrazine and glucose were prepared and diluted as required. Phosphate buffer of pH 7 (supporting electrolyte was prepared from stock solution of 0.1 M disodium hydrogen phosphate and 0.1 M HCl. $\text{Cu}(\text{NO}_3)_2$ 3 mM and 1,10-phenanthroline 6 mM were prepared in 1:1 ethanol/water mixture. 2 M NaOH aqueous solution was then added to the solution under magnetic stirring and heating. The alkaline solution was transferred into an autoclave. The autoclave was then sealed and maintained at 160 °C for 24 h. The solution was then cooled to room temperature, the black precipitates were filtered, washed with water and absolute ethanol for several times and then dried in an oven at 50 °C.

Figure 1 shows the synthesis route and reactions for the preparation of CuO nanoparticles. In reaction R1, water displaces the nitro group because it is a stronger ligand, resulting in a blue complex of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The same is true for reaction R2 [11]. 1, 10-phenanthroline is an organic compound that enhances formation of individual nanowires, a flower of nanowires agglomerated together would otherwise result if it was not used. It does not take part in the chemical synthesis of the reaction.

Instruments:

X-ray diffraction measurements were executed with a Shimadzu D6000 Diffractometer (from Shimadzu,

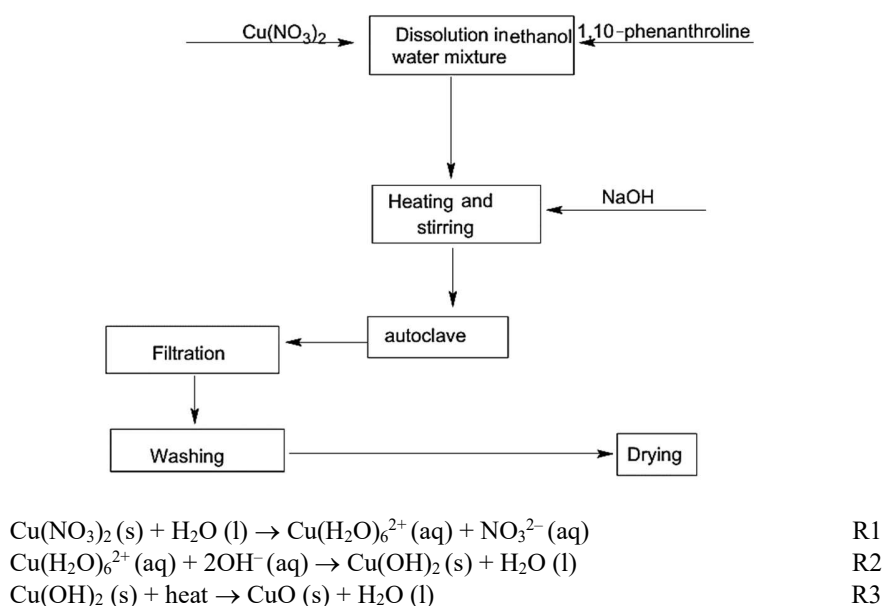


Figure 1. Synthesis route of CuO nanoparticles and chemical reactions.

Japan) using Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 20° to 60° . Scanning electron microscopy (SEM) was carried out on a Zeiss crossbeam series with Gemini FESEM unit. Fourier transform infra-red (FTIR) spectroscopy was carried out with Shimadzu FTIR, run from 400 cm^{-1} to 4000 cm^{-1} using diffuse reflection method, and KBr pellet was used for background measurement. Thermogravimetric analysis (TGA) was carried out with SDT 2960 Simultaneous DSC-TGA, TA Instruments from 24°C to 700°C at a ramp of $10^{\circ}\text{C}/\text{min}$. Particle size analysis was performed using Microtrac/Nanotrac TM150, which employs optical light scattering of particles suspended in water. Cyclic voltammetry measurements were done using BAS 100B Electrochemical Analyzer [Bio-analytical Systems (BAS), USA] and a one component glass cell vial with a three electrode configuration. Electrodes used were platinum wire counter electrode, Ag/AgCl (3M NaCl) reference electrode and CuO modified and unmodified CPE working electrode. The pH of the buffer solutions was measured with a Hanna Instruments digital pH meter.

Preparation of unmodified and CuO nanoparticles modified CPE:

Unmodified CPE was prepared by hand mixing 2.0 g carbon powder with a few drops of mineral oil. After mixing in an agate mortar, the resulting paste was packed into a 3 mm diameter cavity of a syringe and electrical contact was established via a copper wire. The electrode surface was gently smoothed by rubbing against a glass block. A 15% CuO modified CPE was prepared from 0.30 g CuO nano-particles, 1.7 g graphite and few drops of mineral oil in the same manner as above. The same procedure was used to regenerate the surface of the electrodes.

Cyclic voltammetry procedure:

10 cm^3 of the supporting electrolyte i.e., 0.1M

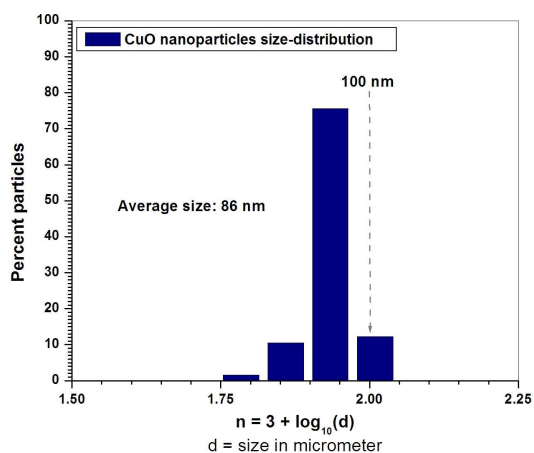


Figure 3. Particle size distribution of CuO nanoparticles.

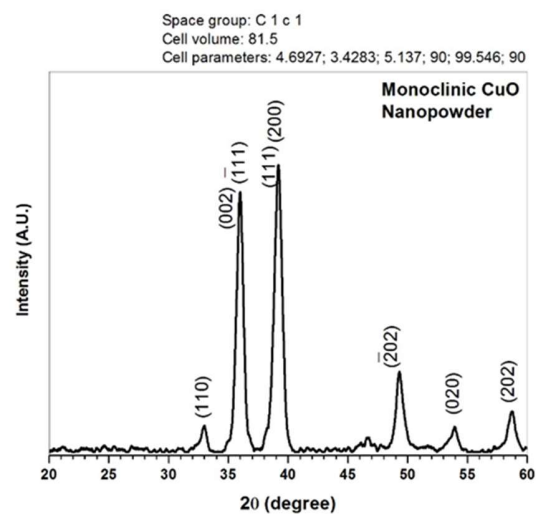


Figure 2. X-Ray Diffraction spectrum of CuO nanopowder.

phosphate buffer pH 7.0 was placed in the electrochemical cell, stirred for 30 seconds and CV of the supporting electrolyte was run from 0 mV to 600 mV and back. Thereafter the electrolyte was spiked with the solution of the electroactive compound that is intended for the study, stirred and CV was run in the same potential range. All measurements were done at room temperature.

3. Results and Discussion

X-ray diffraction analysis of CuO nanopowder:

X-ray diffraction pattern of nano-sized CuO is shown in figure 2. A detailed Reitveld analysis of XRD data to determine the crystal structure was also performed using FullProf Software Suite [12]. The two most prominent peaks around $2\theta = 35.9^{\circ}$ and 39.2° , which were identified as combinations of double-reflections $\{(002) \text{ and } (-111)\}$ and $\{(111) \text{ and } (200)\}$, respectively, are characteristics of CuO. Further the acceptable FullProf solution after several trials produced monoclinic unit-cell with Cc space group and cell parameters: $a = 4.6927 \text{ \AA}$, $b = 3.4283 \text{ \AA}$, $c = 5.137 \text{ \AA}$, $\alpha = 90^{\circ}$, $\beta = 99.546^{\circ}$ and $\gamma = 90^{\circ}$. These results are in very good agreement with the already reported single crystal data for CuO [13]. It is also noteworthy that the actual peaks recorded for the CuO nanopowder are apparently shifted approximately by $+0.3^{\circ}$ of 2θ value, which may be tentatively attributed to the strains within the crystallites.

Particles size analysis:

Average crystallite size of 34 nm for the CuO nanoparticles was estimated using Debye-Scherrer method. FWHM of the Gaussian best-fit to prominent peaks in the XRD data was used in the formula.

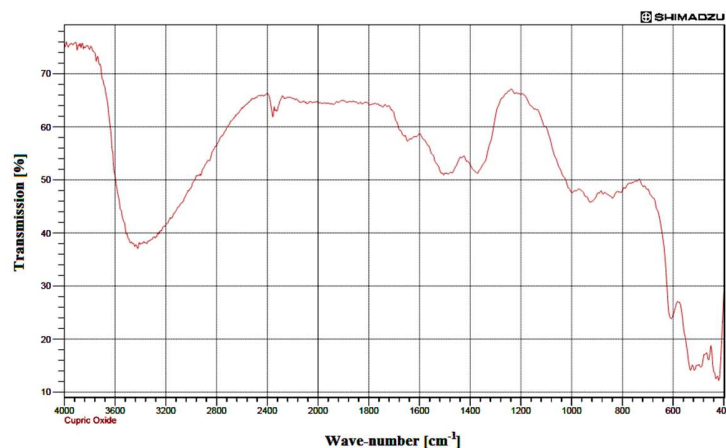


Figure 5. IR spectrum of CuO nanoparticles.

Though this method has its own limitations, it immediately gives a rough estimation of the size without much effort. Since the X-rays penetrate through the surface of the particles, what is measured here is the size of small crystallites within the grains that diffract X-rays coherently [14].

On the other hand, the grain-size was measured on a particle size analyzer. A solution of copper oxide was prepared with pure water and agitated in an ultrasonic bath to obtain an evenly dispersed solution. Instrument was set to zero using the solvent (water) then the CuO solution was filled in the cell and measured. Distribution of grain-size obtained is shown in figure 3. The mean grain size of CuO nanoparticles was determined to be 86 nm by the particle size analyzer, which measures the average diameter of the grains using light as a probe. Obviously, light cannot penetrate through the surface and therefore, this method gives the size of individual grains that could possibly be made up of several crystallites.

A comparison of volumes created by the two sizes reveals that apparently each grain consists of approximately 16 crystallites, on an average.

Scanning electron microscopy:

SEM pictures at two different magnifications are shown in figure 4. Highly crystalline, broken glass like structures are clearly visible in the pictures. The observed white spots in the SEM pictures are presumably traces of 1,10-phenanthroline left after washing. Moreover, the energy dispersive X-ray spectroscopy (EDX) carried out on the same machine established the composition of the nanoparticles as CuO.

FTIR and TGA:

Figure 5 shows the FTIR spectrum of CuO nanoparticles. Characteristic peaks of CuO range from around 400 cm^{-1} to 1000 cm^{-1} . Peaks around 420 cm^{-1} ,

500 cm^{-1} and 610 cm^{-1} can be assigned to Cu–O stretching along $[-202]$ Cu–O direction. Small sharp peak around 450 cm^{-1} is attributed to Cu–O stretching along $[202]$ direction. The peak around 2300 cm^{-1} can be assigned to CO_2 stretching, which could have been entrapped in the sample holder during packing. The broad peak around 3500 cm^{-1} is due to O–H stretch and bending from adsorbed water.

Thermogravimetric analysis of 8.4 mg of CuO nanoparticles was run from $24\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ at a ramp of $10\text{ }^\circ\text{C}/\text{min}$ (picture not shown). It shows that in the

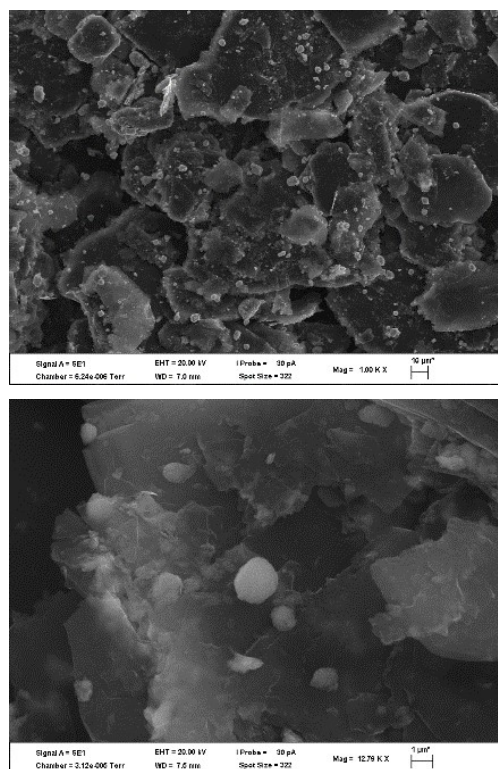


Figure 4. SEM pictures of CuO nano-particles.

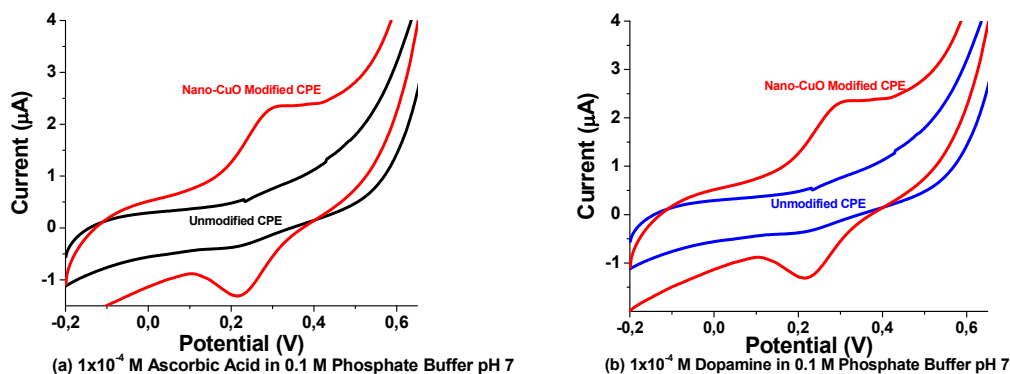


Figure 6. Detection of 1×10^{-4} M ascorbic acid (a) and 1×10^{-4} M dopamine (b) with unmodified CPE and CuO nanoparticle modified CPE, respectively.

temperatures range of 80 – 140 °C, the percentage weight loss with temperature is about 1.0 %. This can be attributed to loss of adsorbed water and ethanol, 2.0 % weight loss around 260 – 340 °C with is attributed to loss of hydroxyl ions. Weight percentage remains fairly constant above 500 °C, thus most impurities were lost at this temperature. The total weight loss is about 3 %. It can therefore be concluded that CuO nanoparticles are stable at elevated temperatures.

Electrochemical response of CuO nanoparticles modified CPE:

The electrochemical responses of CuO nanoparticles modified electrode were studied for the detection of ascorbic acid, atenolol, diclofenac, dopamine, hydrazine and glucose using cyclic voltammeter. Figure 6 shows the cyclic voltammograms of 1×10^{-4} M ascorbic acid (a) and 1×10^{-4} M dopamine (b) with unmodified CPE and CuO nanoparticles modified CPE, respectively, at a scan rate of 50 mV s^{-1} in 0.1 M phosphate buffer of pH 7. As can be seen from the voltammograms, At the unmodified carbon paste electrode, ascorbic acid and dopamine do not show detectable oxidation peaks while each of them show well undefined cathodic peaks. When 15% CuO nanoparticles modified CPE was used as the working electrode, both compounds gave well defined anodic and cathodic peaks with measurable currents, respectively. Similar voltammograms were also obtained for atenolol, diclofenac, hydrazine and glucose (figures are not shown).

It can be observed that the detection of these compounds improves with the use of CuO nanoparticle modified CPE relative to the unmodified CPE. The observed anodic and cathodic currents for all the studied compounds prove the electrocatalytic properties of the synthesized CuO nanoparticles.

4. Conclusions

Synthesis, characterization and application as a carbon paste electrode modifier of nano-sized copper oxide (CuO) powder has been reported. Prominent XRD peaks around $2\theta = 35.9^\circ$ and 39.2° , which are combinations of double-reflections $\{(002) \text{ and } (-111)\}$ and $\{(111) \text{ and } (200)\}$, respectively, have been identified as the characteristics of monoclinic CuO, with unit-cell parameters estimated as: $a = 4.6927$, $b = 3.4283$ and $c = 5.137 \text{ \AA}$; $\alpha = \gamma = 90^\circ$, $\beta = 99.546^\circ$. Moreover, the crystallite size calculated from XRD data through Debye-Scherrer method produced average size of 34 nm for the nanoparticles. The average grain-size measured on particle size analyzer however was 86 nm. Therefore it was concluded that each grain of the nano-sized CuO was apparently made up of nearly 16 crystallites. Uniform distribution of ice-glass like crystalline particles was visible in SEM pictures, which were agglomerations of smaller particles. FTIR results confirmed the stretching of Cu-O bonds as expected. Finally, the electrocatalytic properties of CuO nanoparticles as carbon paste electrode modifier were also investigated for the electrochemical oxidation of ascorbic acid, atenolol, diclofenac, dopamine, hydrazine and glucose using cyclic voltammetry. The results showed significant improvement of detection efficiency in the carbon paste electrode modified with CuO nanoparticles, as against the response of unmodified carbon paste electrode.

5. References

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