

Amperometric Determination of Hydrazine Based on Copper Oxide Modified Screen Printed Electrode

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Abstract: A low cost and commercial available screen printed electrode, copper oxide nanoparticles/carbon nanotube (CNT) modified screen printed electrode for electrocatalytic oxidation of hydrazine. For preparation of electrode copper oxide nanoparticles prepared by coprecipitation method and mixed manually with CNT dispersed in phosphate buffer solution (PBS). Cyclic voltammetry experiments shows oxidation of hydrazine was observed at 804 mV with an I_{pa} value of 970 μ A. The recorded amperometric current-time curves showed a linear dependence on the hydrazine concentration 5 μ M to 50 μ M with a detection limit of 5 μ M in response time < 5 s. This proposed modified exhibits a rapid, low cost and sensitive determination of hydrazine.

Keywords: Copper oxide nanoparticles, Co-precipitation method, XRD, SEM, Optical properties.

1. Introduction

There is continues growing demand for food quality and safety. In recent years, metal oxide nanoparticles contribute attention due to their unique optical, electronic, catalysis, mechanical, chemical and magnetic properties [1-8]. Copper oxide nanoparticles have been synthesized by various techniques like coprecipitation, sol-gel, thermal decomposition and spray pyrolysis [9-10]. Different types of nanomaterials like metal oxide nanoparticles, carbon nanotubes and quantum dots are used in biosensors because of their unique physical, chemical, magnetic and optical properties that enhance the specificity and sensitivity of detection of that particular analyte.

On the other hand, carbon nanotubes (CNT) have been used in the electrode fabrication due to high surface area and ability to mediate fast electron transfer [11-12]. In present work, copper oxide nanoparticles are prepared by coprecipitation method

and used in the fabrication of electrode for hydrazine detection. Since hydrazine is a carcinogenic, mutagenic and neurotoxin substance that affects the liver and brain of human beings [13]. Hydrazine (N_2H_4) and its by-products are commonly used as photography chemicals, pesticides, chemical blowing agents, intermediates in pharmaceutical industries [14-15]. In this work we synthesize a CuO/MWCNT modified screen printed electrode based electrochemical sensor for the detection of hydrazine as pesticide.

2. Experimental

2.1. Materials

Copper Sulphate Pentahydrate ($CuSO_4 \cdot 5H_2O$) was purchased from HiMedia Laboratories. Potassium chloride (KCl), sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4),

potassium ferrocyanide $K_4[Fe(CN)_6]$, potassium ferricyanide $K_3[Fe(CN)_6]$, sodium chloride (NaCl), multiwalled carbon nanotube (MWCNT) were purchased from CDH, New Delhi. All other chemicals were of analytical grade and used without further purification. The stock solutions of hydrazine were freshly prepared in phosphate buffer (pH 7.0).

2.2. Synthesis of CuO Nanoparticles

CuO nanoparticles were prepared by coprecipitation method. In this method, 0.1 M copper sulphate pentahydrate solution was prepared in double de-ionized water with continuous stirring to get a homogeneous solution. 0.2 M sodium hydroxide solution was added dropwise into the above solution with continuous stirring for 3 hrs. The resultant precipitates thus obtained were washed with double distilled water and after that with acetone. Precipitates were dried at 100 °C in oven for 5 hrs. Finally these were put into muffle furnace at 600 °C for 2 h and copper oxide nanoparticles were formed.

2.3. Fabrication of CuO/CNT Modified Screen Printed Carbon Electrode

Carbon nanotubes (CNT), nanoparticles (NP) and glutaraldehyde solution was prepared by mixing them vigorously in the ratio 5:3:2 to obtain homogeneous mixture. The above solution was then used for the fabrication process of the screen printed carbon electrode. The dot of SPCE i.e. working electrode was filled with above slurry using the pipette. Then the electrode was dried in the microwave oven at 70 °C for 5 minutes and left at room temperature for 24 h for the fixation of slurry on the working electrode dot of SPCE.

2.4. Characterization

The crystalline size of CuO nanoparticles was investigated by using X-ray diffraction (XRD) pattern, using D-8 Advance, Bruker diffraction, with monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscope (SEM) analysis was done through Hitachi S3700 SEM using an acceleration of 15 kV. The size of nanoparticles is calculated by SEM. The Cyclic Voltammetry (CV) and Chronoamperometry (CA) studies have been done using an Autolab Potentiostat/Galvanostat (Metrohm). The electrochemical measurements have been conducted on a three-electrode system using CuO/CNT/SPCE as the working electrode, a platinum (Pt) wire as the counter and saturated Ag/AgCl as a reference electrode in a phosphate buffer saline (PBS, pH 7.0, NaCl) containing 5 mM $[Fe(CN)_6]^{3-/4-}$ as a mediator.

3. Results and Discussion

3.1. XRD Analysis

The XRD pattern exposed the single phase monoclinic structure and orientation of the fabricated CuO NPs powder. The major peaks at 2θ values of 32.54°, 35.54°, 35.56°, 38.72°, 38.94°, 46.20°, 53.44°, 58.36°, 61.50° and 65.76° are indexed as (110), (002), (-111), (111), (200), (-112), (020), (202), (-113), (022) which are in good agreement with the CuO NPs obtained from the respective "JCPDS" (Joints Committee on Powder Diffraction Standards) card No (80-1917). No other extra peaks are obtained. The average particle size of CuO was found to be 33.4 nm by using Debye Scherrer equation ($D = K\lambda/\beta_{1/2} \cos \theta$), Fig. 1.

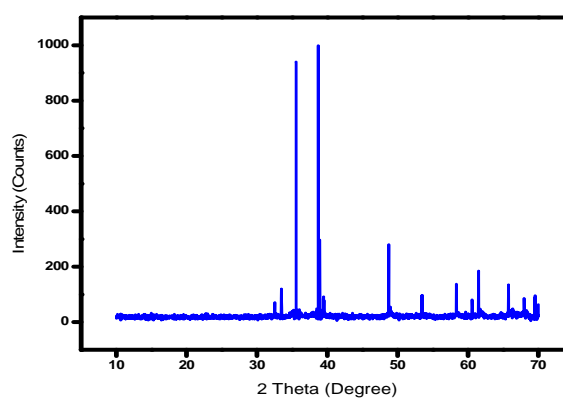


Fig. 1. XRD spectra of copper oxide nanoparticles.

3.2. SEM Analysis

The surface morphology of synthesized copper oxide NPs shows the magnification of 10 μm (Fig. 2). It clearly shows the leaf like structure and the morphology of NPs indicates an average diameter of 10-100 nm.

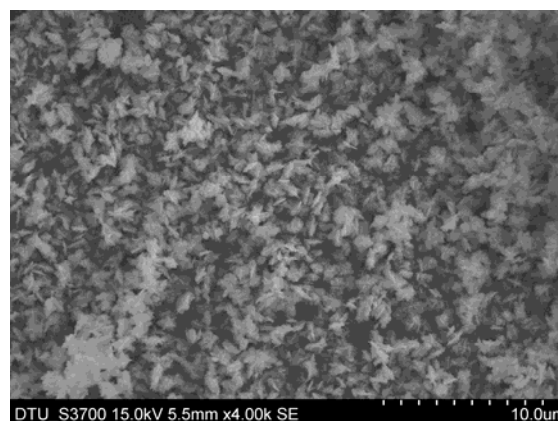


Fig. 2. SEM image of copper oxide NPs.

3.3. FTIR Spectroscopy

Fig. 3 shows the FTIR spectra of copper oxide nanoparticles by co-precipitation method. The absorption peak lies between 1000-400 cm^{-1} i.e. the absorption peaks correspond to stretching and bending vibration of metal-oxygen bonds.

The peak of OH stretching vibration in between 3600 and 3400 cm^{-1} and also exhibits only three vibrations at 635, 532 and 474 cm^{-1} for the stretching vibrations of CuO NPs and confirming the formation of pure CuO NPs.

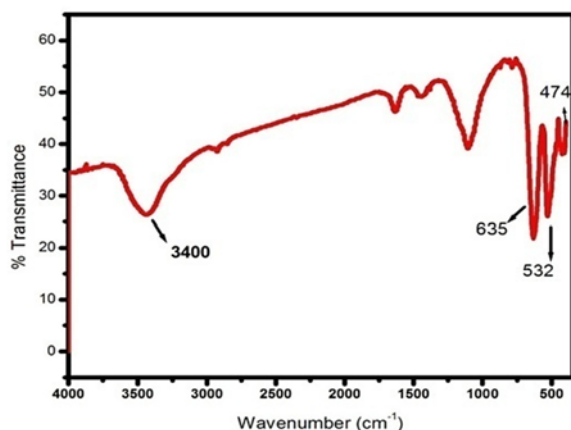


Fig. 3. FTIR image of copper oxide NPs.

3.4. Electrochemical Studies

3.4.1. Cyclic Voltammetry

Fig. 4(a) shows the cyclic voltammograms of 0.5 mM hydrazine in 0.1 M PBS (pH 7.0) measured on CuO/CNT modified SPCE. After the modification of SPCE with CuO/CNT shows the higher anodic peak - 804 mV with I_{pa} value of 970 μA . The observed modified CV graph is responsive towards the hydrazine.

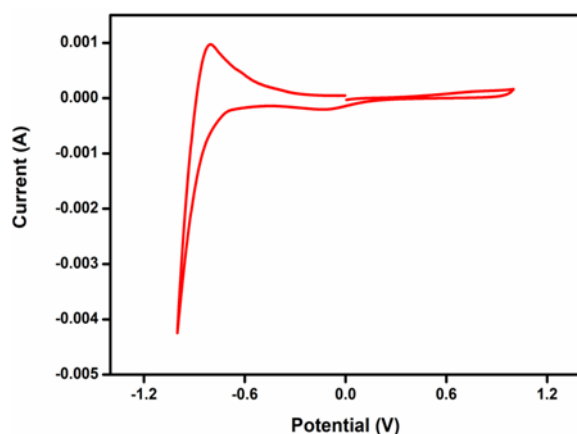


Fig. 4(a). Cyclic Voltammograms of 0.5 mM hydrazine in 0.1 M PBS (pH 7.0) with scan rate of 100 mV/s obtained at CuO/CNT modified SPC.

In Fig. 4(b) the scan rate experiments were also performed in 0.1 M PBS (pH 7.0) containing 0.5 mM hydrazine at the different scan rates in a range of 5, 10, 20, 50 and 100 mVs^{-1} . The observed scan rate dependent CV graph represents that the increase in the scan rate, current values also increases which shows that the oxidation process is diffusion controlled. In Fig. 4(b) linear relationship is observed between anodic current (I_{pa}) and $v^{1/2}$, which proves the diffusion-controlled kinetics. According to Randles-Sevcik equation the number of electrons is 2.

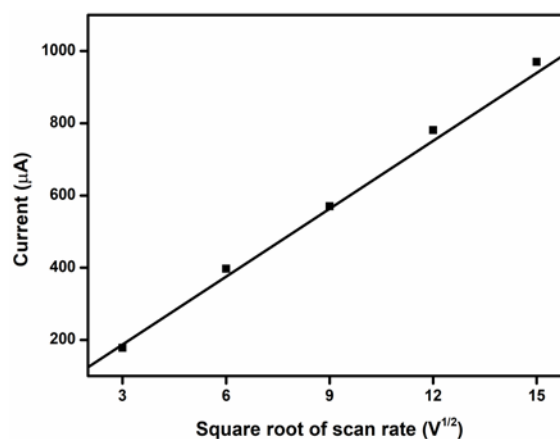


Fig. 4(b). Different scan rates (5, 10, 20, 50, 100 mV/s) of modified electrode of 0.5 mM hydrazine in 0.1 M PBS.

3.4.2. Chronoamperometry

Amperometric experiments were performed using the CuO/CNT modified screen printed electrode. Fig. 5 (a) shows the response of the modified SPE on the successive addition of hydrazine i.e. 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μM in 0.1 M PBS (pH 7.0) solution at constant potential of 0.45 V. The fabricated sensor shows the current response increase after the addition of hydrazine. Fig. 5(b) depicts the plot between current vs hydrazine concentration. From the graph it is clear that with increase the concentration of hydrazine the value of current increases and that greatly shows the linear relationship. The sensitivity of the fabricated hydrazine sensor was 70.72 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$. The relationship between the hydrazine concentration and anodic peak current showed a linear regression of $I_{pa} (\mu\text{A}) = 17.68 (\mu\text{M}) + 95.4$ with correlation coefficient (R^2) of 0.998. The detection limit of fabricated hydrazine sensor was found to be 5 μM and the response time was <5 sec.

4. Conclusions

In the present work CuO nanoparticles were prepared by coprecipitation method. The above synthesized nanoparticles were characterized by several techniques. The electrooxidation behavior of

CuO/MWCNT SPCE showed optimal response (<5 s), good sensitivity ($70.72 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$) and low detection limit $5 \mu\text{M}$ and long term stability. This proposed electrode was used for rapid determination of hydrazine in clinical and pharmaceutical samples.

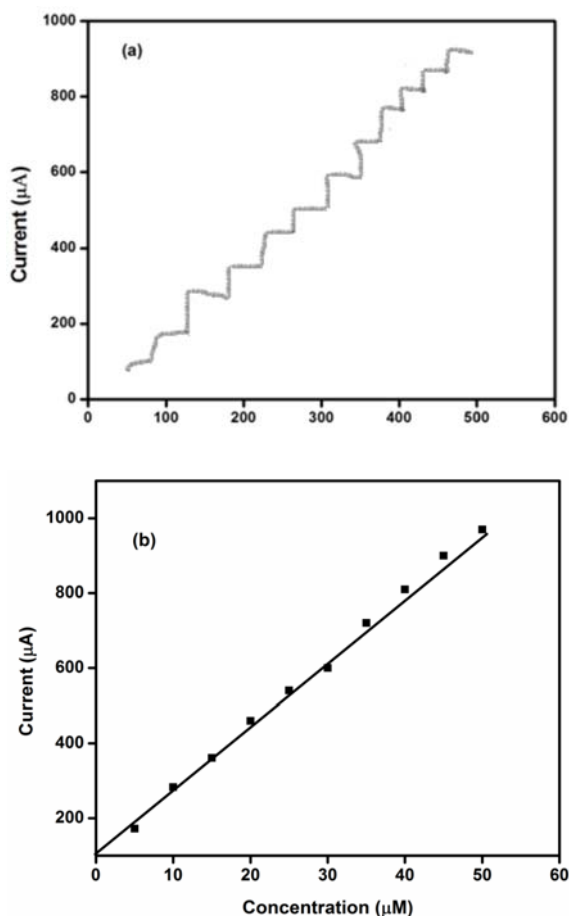


Fig. 5. (a). Successive addition of hydrazine 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μM in 0.1 M PBS (pH 7.0) solution at constant potential of 0.45 V (b) current versus concentration graph.

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