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Improved synthesis of copper oxide nanosheets and its application in development of supercapacitor and antimicrobial agents

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ABSTRACT

Copper oxide (CuO) nanosheets (NSs) have been synthesized using improved chemical bath deposition (CBD) method and used as energy materials in supercapacitor devices. The quality of CuO-NSs were investigated using different techniques such as, cyclic voltammetry, galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy. The structure, composition, and morphology of CuO-NSs were examined by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy dispersion spectrum (EDS). CuO-NSs device exhibited maximum specific capacitance about 564 Fg^{-1} at 5 mV/s. Antibacterial properties of CuO-NSs with *Bacillus subtilis* and *Salmonella typhimurium* have shown promising prospects for the development of antibacterial agents.

Introduction

From the last two decades, synthesis of transition metal oxides nanostructures has been a topic of a huge scientific curiosity for their characteristic properties and applications in batteries [1,2], solar cells [3], biomedicine [4], sensing [5] and antimicrobial activity [6]. Transition metal oxides materials are suitable to form of range of structural motifs, and are the key components of number of hybrids and composites nanomaterials. Copper oxides (CuO) that are in form of wires and nanosheets (NSs) have shown their role in reversible electrochemical properties that make them a potential candidate in fabrication of energy storage devices and supercapacitor [7,8]

Among different transition metal oxides, CuO is certainly an attractive choice to construct environmentally benign supercapacitor, since copper is abundant, and non-expensive [9–11]. However, previously reported CuO electrode shown reduced cyclability and low capacity, which are mainly caused by their low conductivity and large volume changes during charge/discharge cycles [12–14]. Currently, the preparation of ordered self-assembly of nanoscale building blocks into different architectures such as NSs and nanoclusters has become a hot topic in the field of nanoscience and technology.

In present investigation, we have focused on the ability to control the shape of nanocrystals by using a low-cost chemical method. CuO have been synthesized using various methods such as least square-support vector [15], impregnation method [16], precipitation method [17,18] and chemical bath deposition [19,20], SILAR method [21]. Among these methods, chemical bath deposition is facile, low-cost and versatile method to result good pseudocapacitive properties and antimicrobial activities of copper nanomaterials such as NSs as reported previously [22–26].

CuO-NSs were synthesized by improved chemical bath deposition method and used to investigate their properties by SEM/EDS and XRD to understand their mechanism, structure, morphology, composition and phase. Electrochemical performance of CuO electrode was improved by formation of large NSs from individual nanoscale building blocks. Enhancement of the surface area and well-ordered pores of NSs supported the adsorption and transportation of electrolytes. The antibacterial

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properties of CuO-NSs were tested by minimum inhibitory concentration (MIC) with minimum bactericidal concentration using well diffusion methods. CuO-NSs have demonstrated excellent antibacterial effectiveness against *Bacillus subtilis* (gram positive bacteria) and *Salmonella typhimurium* (gram negative bacteria).

Materials and methods

Synthesis of CuO thin films

CuO thin films have deposited using chemical bath deposition (CBD) technique. Briefly, aqueous solution of 0.1 M copper sulfate ($CuSO_4$) is used as a source of copper with aqueous ammonia as complexing agent. The resultant pH of solution after addition of ammonia was ~10. Well cleaned stainless steel substrate substrates, were dipped in the above bath and the bath was heated. When the bath attained the temperature of 343 K, the precipitation started in the bath. During the precipitation, heterogeneous reaction occurred on the stainless steel substrate and deposition of copper oxide took place on the substrate. Copper substrate coated with copper oxide thin films was removed after 45 min from the bath, washed with double-distilled water, dried in air and preserved in an airtight container. The formation mechanism of the 2D interconnected nanosheets (NSs) like CuO includes the following: nucleation, growth, and oriented attachment. The nucleation is strongly dependent on the amount of super saturation. In the nucleation stage, the super saturation is very high and electrostatic repulsive barriers are low, hence particles tend to aggregate. Reaction temperatures the nucleation rate and also enhances the growth progression. The adjoining nanoparticle grows along particular crystal orientation due to the oriented attachment and form 2D CuO-NSs nanostructure.

Characterization techniques

Structural arrangement of copper oxide (CuO) films was carried out with X-ray diffractometer (XRD) using Cu-K_α radiation (K = 1.54 Å). The film surface morphology was observed by field emission scanning electron micrograph (FE-SEM) and transmission electron microscopy (TEM) (FEI Tecnai).

Electrode preparation and electrochemical measurements

The electrochemical performance was analyzed using CHI-660-D Electrochemical workstation. The electrochemical measurements were carried out using three electrode cell configurations with CuO as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode with Na_2SO_4 as an electrolyte. The cyclic voltammetry measurements of the CuO electrode was performed at different scan rates in a potential window of 0.0 to 0.7 V. The charge–discharge characterization was performed at different current densities within a potential window of 0.0 to 0.7 V.

Preparation materials and methods for antimicrobial activity of CuO-NSs

Nutrient agar, agar (Type 1) and sodium chloride was purchased from Hi-media, which are used for maintenance and growth of bacterial cultures. The microorganisms used in this study are *B. subtilis* NCIM 2010 and *S. typhimurium* NCIM 2501. Nutrient agar was used to grow these bacterial cultures and these cultures are stored in refrigerator. The sample was prepared in DMSO solvent in two concentrations such as 50 μg/ml and 500 μg/ml. A positive control of streptomycin (50 μg/ml) and solvent control were also kept with the samples. The bacterial suspension was prepared in 0.85% saline which was spread on the plates of nutrient agar to form a lawn of bacterial growth. The wells of 6 mm were prepared and 50 μl of test and control samples were poured into each well. Then the plates were kept in refrigerator for 20 min for diffusion of respective sample in the plate and then they were incubated at 37 °C for 24 h.

Results and discussion

Structural and morphological studies

Fig. 1 shows the XRD pattern of CuO-NSs thin film deposited by chemical bath deposition method. All the peaks of CuO-NSs can be indexed to the monoclinic crystal system CuO (JCPDS card no. 45-0937). The peaks were observed at 2θ = 32.99°, 35.83°, 38.96°, 48.63°, 53.57°, 58.07°, 61.41°, 66.29°, 68.58° and 75.81° which correspond to (1 1 0), (1 1 1), (1 1 1), (−2 0 2), (0 2 0), (2 0 2), (−1 1 3), (0 2 2), (2 2 0) and (0 0 4) Bragg's reflections of monoclinic structure of CuO respectively (JCPDS:80–1916). No characteristic peaks of any impurities were detected, suggesting that high quality of CuO NPs was prepared. The crystallite size has been estimated from the XRD pattern using the Scherrer's equation [27]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where k = 0.9 is the shape factor, λ is the X-ray wavelength of Cu K_α radiation (1.54 Å), θ is the Bragg diffraction angle, and β is the FWHM of the respective diffraction peak. The crystallite size corresponding to the highest peak observed in XRD was found to be 20 nm. The presence of sharp structural peaks in XRD patterns and crystallite size less than 100 nm suggested the nanocrystalline nature of CuO-NSs as reported earlier [28]

The morphology, size and nanostructure of the products were investigated in feature from side to side by field-emission scanning electron microscopy (FE-SEM). Fig. 2(a and b) shows the FE-SEM image of CuO thin film deposited by chemical bath deposition method. Fig. 3a shows the TEM images of 15–20 nm CuO-NSs and also coincides with the particle size calculated from XRD. Fig. 3b shows the NSs with regulars pacing of clear lattice planes and the length of NSs ranges from 90 to 140 nm. This lattice spacing is found to be 0.2 nm which corresponds to (1 1 1) planes of monoclinic structure of CuO-NSs. Inset of Fig. 3 shows the energy dispersive spectra of the CuO-NSs. It confirms the existence of copper oxide in thin films.

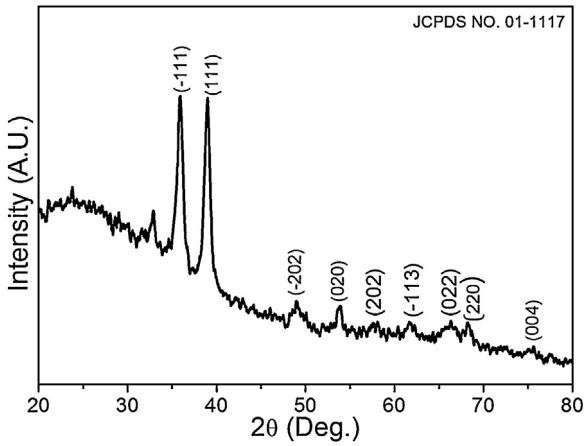

Fig. 1. Shows the XRD pattern of the CuO nanosheet materils.