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Facile electrochemical growth of spinel copper cobaltite nanosheets for non-enzymatic glucose sensing and supercapacitor applications

Kusha Kumar Naik, Surjit Sahoo, Chandra Sekhar Rout*

School of Basic Sciences, Indian Institute of Technology, Bhubaneswar 751013, Odisha, India

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ABSTRACT

Herein, we report a facile and low-cost electrodeposition approach for the synthesis of Copper Cobaltite ($CuCo_2O_4$) nanosheets on indium doped tin oxide (ITO) coated glass substrates. The crystal structure and morphology of the material are characterized by X-ray diffraction, energy dispersive X-ray analysis, Raman spectroscopy, field-emission scanning electron microscopy and transmission electron microscopy. The synthesized $CuCo_2O_4$ nanosheets are composed of numerous nanoparticles and showed enhanced electrochemical activity for the glucose sensing and supercapacitor applications. The non-enzymatic glucose sensing performance of the nanosheets exhibits sensitivity of 8.25 $\mu A \mu M^{-1}$ cm^{-2}, linear range of detection of 5–110 μM and response time of 15 s towards glucose molecules. Similarly, supercapacitor fabricated using the $CuCo_2O_4$ nanosheets as the active electrode shows high specific capacitance of 100 F/g at a current density of 1 A/g with remarkable cycling stability.

1. Introduction

Self-assembled nanoparticles with ordered nanostructures promise new opportunities towards research in developing miniaturization of technology in the applied research field of electronic, optoelectronic, and magnetic devices [1]. The integration of nanoparticles into 2D and 3D structures have led to novel collective and enhanced intrinsic properties of the nanoparticles and have a tremendous application in the field of electronic devices such as sensors, energy storage devices and in organic transistor technology [2–6]. Self-assembly of nanoparticles is an important process where the building blocks spontaneously organize into ordered structures by thermodynamic process and other constraints, that can be manipulated by controlling the cooperative interaction between the nanoparticles [7–9]. In addition to that, nanomaterials prepared by the self-assembly process are expected to perform high electrochemical and bio-catalytic activities due to their enhanced electrochemical active surface area, large number of active sites and good electron transport property.

Mixed valence oxides of transition metals with spinel structure have great potential in various devices for technological applications in magnetic recording media, catalysis, lithium battery materials, supercapacitor and sensors and in applied research fields due to their remarkable intrinsic properties [10–13]. Recently, binary transition metal oxides have gained more attention for the supercapacitor and glucose sensing applications due to their superior conductivity and higher electrochemical activity compared to the individual metal oxides [14–17]. $CuCo_2O_4$ is a ternary material having spinel structure in which Cu cations occupy the tetrahedral sites while Co cations are evenly distributed to all the octahedral sites, and the anions (O^{2-}) tend to coordinate both the cations Cu^{2+} and Co^{3+} tetrahedrally and octahedrally respectively to form a close packed FCC structure [18]. In the $CuCo_2O_4$ spinel structure, the unfiled and unshared d–orbital electrons of both Cu and Co atoms arrange in the fascinating manner in a unit cell which lead to increase in its electrocatalytic activities [19,20].

Glucose is an electrochemically active compound and due to this reason, electrochemical based glucose sensors are found to be suitable for their effective detection and determination. Enzymeless amperometric glucose sensors have attracted attention for high repeatability, stability, life time and simple mechanism of detection compared to enzymatic glucose sensor [21]. A good glucose sensor demands highly sensitive, accurate and precise detection, fast response and excellent selectivity and stability [22]. To achieve these prevailing challenges, different nanostructures of metals, metal oxides, chalcogenides, nitrides and carbides have

* Corresponding author.
E-mail addresses: csrout@iitbbs.ac.in, csrout@gmail.com (C.S. Rout).

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been extensively examined for the fabrication of high performance glucose sensors for its use in blood sugar detection, pharmaceutical analysis, food processing and biotechnology industries [17]. $CuCo_2O_4$ nanosheets emerge as a potential candidate for glucose sensing applications due to the presence of numerous self-assembled nanoparticles with large surface area. Also, the presence of Cu and Co elements may provide abundant electrocatalytically active sites and excellent bio-catalytic activities for oxidation of glucose molecules [23,24]. The advantages of $CuCo_2O_4$ is due to its superior electrical conductivity than the individual metal oxide components such as copper oxide and cobalt oxide respectively [25,26].

Similarly, Supercapacitors have been emerged as one of the promising energy-storage device because of their long lifespan compared with secondary batteries, high capacitance and excellent reliability compared with conventional dielectric capacitors [27–29]. The performance of supercapacitors and glucose sensors not only largely depend on the electrochemical properties and electro-kinetics of the composed materials but also morphology of the nanostructures, electrolytes and desirable composition of active materials [15,30–32]. Herein, we report a facile electrochemical synthesis approach to grow $CuCo_2O_4$ nanosheets on conducting substrates with remarkable electrochemical performance for non-enzymatic glucose detection and supercapacitor applications. The synthesized electrode possesses sensitivity of 8.25 $\mu A \mu M^{-1}$ cm^{-2}, linear range of 5–110 μM and response time of 15 s towards glucose molecules detection. Similarly, the supercapacitor fabricated using the $CuCo_2O_4$ nanosheets as the active material exhibit high specific capacitance of 100 F/g at a current density of 1 A/g with remarkable cycling stability.

2. Experimental section

2.1. Material synthesis

$CuCo_2O_4$ nanosheets were synthesized on indium tin oxide (ITO) coated glass substrate by chrono-amperometric technique of the electrodeposition method. The electrodeposition process was carried out in a three electrodes configuration set-up consisting of glass cell with deposition bath; Pt wire as counter electrode, Ag/AgCl as reference electrode and ITO/glass substrate as working electrode. At first 0.01 M of copper sulphate (CuO_4S) was dissolved in 10 ml de-ionized (DI) water in the glass cell followed by addition of 0.02 M cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$). After complete dissolution of the electrolytes, 0.01 M of potassium chloride (KCl) was added as a supporting electrolyte to increase the conductivity of the solution. After that, the three electrodes set-up kept in the glass cell was supplied with a voltage of −1.1 V to the three electrodes through a potentiostat (Technoscience instruments, Bangalore) for 180 s and the temperature of the deposition bath was maintained at 70 °C throughout the deposition process. At 70 °C under the applied potential, the dissolved metal ions (Cu^{2+}, Co^{2+} and OH^-) diffused and drived by the driving force towards the substrate. In the interface of the substrate, the migrated ions striped, reacted with each other and nucleated to form $CuCo_2O_4$ nanoparticles. Then, the nucleated nanoparticles further interconnected with each other thermodynamically and nanosheets of the nanoparticles formed on the working electrode. After completion of the deposition process, the deposited film was rinsed several times by DI water to remove the presence of KCl salt and the film was dried at room temperature. The as-prepared electrode with the deposited film was calcined at 500 °C for 6 h and a dark grey coloured film of $CuCo_2O_4$ nanosheets was obtained.

2.2. Material characterization

The crystallinity of the as-synthesized material was checked by X-ray diffraction (XRD) patterns obtained by a Bruker D8 advanced diffractometer using Cu-K_α radiation (λ = 1.54184 Å). Morphology, composition and distribution of the as-prepared samples were examined by FESEM (MERLIN Compact with GEMINI I electron column, Zeiss Pvt. Ltd, Germany) equipped with energy dispersive X-ray spectroscopy (EDAX). Raman spectrometer with a laser excitation wavelength of 488 nm was used to obtain the Raman spectrum of the $CuCo_2O_4$ nanosheets. The high resolution transmission electron microscopy (HRTEM, JEM- 2100) was performed with an acceleration voltage of 200 kV.

2.3. Glucose sensing measurement

Glucose sensing measurements were performed by the electrochemical method i.e by cyclic voltammetery (CV) and chrono amperometric (CA) techniques in a three electrodes configuration with $CuCo_2O_4$ nanosheets acting as the active materia. For CV experiment, 10 ml of NaOH (0.1 M) solution was taken in the glass cell and a linear potential of 0–0.75 V was applied to the electrodes for the detection of glucose species (0.5 M) present in the electrolyte. At first, CV of $CuCo_2O_4$ nanosheets in the absence of glucose was performed and then CVs at different scan rates and at different concentrations of glucose molecules were recorded in the same potential range. Similarly, for CA experiments, 140 ml of NaOH solution was taken in a separate glass cell and a potential of 0.3 V was applied to the electrodes to observe the step like current response of different concentrations of glucose molecules in the electrolytes. To perform the selectivity of the sensor, CA measurement was performed with the addition of 10 μM interfering molecules; uric acid (UA), dopamine (DA), ascorbic acid (AA), lactic acid (LA) and maltose in the rotating electrolyte.

2.4. Supercapacitor measurement

Supercapacitor performances of the $CuCo_2O_4$ nanosheets were carried out in 6 M aqueous KOH electrolyte. The cyclic voltammetery (CV) and charge-discharge (CD) measurements were carried out at different scan rates and at different current densities by keeping the fixed potential window of 0.6 V (−0.1 V–0.5 V) vs Ag/AgCl reference electrode and Pt as counter electrode at room temperature. The specific capacitance (C_{sp}) was calculated from cyclic voltammetery curves using the following equation;

$$C_{sp} = \frac{\int I(v)dv}{ms2\left[V_f - V_i\right]} \quad (1)$$

Where the integral part in the numerator gives the area under the CV curve, m is the mass of the sample deposited on the Ni foam surface, s is the scan rate and $[V_f – V_i]$ is the potential window (V_f and V_i are the final and initial potential values respectively). From the charge/discharge curves, specific capacitance of the material was calculated by using the following equation;

$$C_{sp} = \frac{I}{m\left(\frac{dV}{dt}\right)} \quad (2)$$

Where I is the discharge current, m is the mass of the sample deposited on the Ni foam surface and dV/dt is the slope of the discharge curve. To calculate the energy density (E_d) and power density (P_d) of the $CuCo_2O_4$, following equations were used;

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