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Electrochemical sensing platform based on CuO@CeO$_2$ hybrid oxides

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ABSTRACT

Advanced functional materials were synthesized to obtain catalytic compositions of CuO@CeO$_2$ hybrid oxides (xCuO@CeO$_2$, $x = 5–25$ wt%) by means of precipitation/impregnation method. Morphological characteristics of the materials were studied through FTIR, XRD, SEM, EDX, TEM and PSD analyses. Glassy carbon (GC) modified with these materials was used as a sensing platform. Electrochemical impedance spectroscopy (EIS) was carried out to assess the electrical properties; cyclic voltammetry was performed to investigate the redox nature of the catalysts. The redox properties of the materials were in accordance with EDX analysis. Application study for glucose and methanol electro oxidation was also carried out via cyclic voltammetry. All the prepared samples proved to be potential materials for electro analysis applications, however 10CuO@CeO$_2$ was found to exhibit highly improved available surface area, lowest charge transfer resistance (via EIS), and hence better potentiality as electro catalyst. 10CuO@CeO$_2$ composition mediated a fast electron transfer response for both the model analytes. Oxidation of methanol was shown to be of diffusion control nature and was rendered electro catalytic as evaluated through current function versus scan rate plots. The optimized material possessed significant sensitivity of 37.68 μA mM^{-1} cm^{-2} with a wide detection range (2–26 mM) for glucose electroxidation.

1. Introduction

Chemically modified electrodes (CMEs) have attracted considerable interest over the past two decades. In comparison with an ordinary solid electrode, a chemically modified electrode provides a high rate for electrode reaction and exhibits a higher selectivity and sensitivity for determination of different analytes [1]. One interesting research direction is the development of chemically modified electrodes with a catalytic response. One of the techniques for the preparation of CMEs with catalytic properties consists of applying a thin film of inorganic materials to the surface of the electrode. Noble metals are classical catalytic materials used in this regard however; various types of metal oxides and their composites are also being explored for this purpose being cost-effective and easy to use [2].

Cerium oxide is known for its wide range of applications in catalysis, corrosion prevention, electrochemical cells, photo catalysis, UV absorbers, biomaterials, microelectronics, optical devices, thermal coatings, and glass abrasives [3]. CeO$_2$ is unattractive as an electro catalyst, because of its insulating nature [4,5]. CuO is an important p-type semiconductor with a narrow bandgap (1.2 eV) and an eccentric band structure has been extensively investigated for its application in solar energy cells, electronics, gas sensors, biosensors, magnetic storage media, optical switch, batteries and heterogeneous catalysis [6,7].

Fabrication of multi-component hybrid nanostructures is of vital importance because their two phase interface could provide a rich environment for redox reactions, which are beneficial for enhancing catalytic performance [8]. CeO$_2$ supported CuO may be regarded as a promising electrocatalytic system because it combines highly active components, CuO and CeO$_2$. CuO@CeO$_2$ solids has been widely applied as active catalytic materials in water gas shift (WGS) reactions, soot oxidation, preferential CO oxidation and methanol reforming [9–12].

In this study, we exploited the potential of these oxidative catalysts as prospective electrocatalysts. We demonstrated that these catalysts are practicable for electro analysis.

2. Materials and methods

2.1. Chemicals

Cerium nitrate nonahydrate ($Ce(NO_3)_3 \cdot 9H_2O$), copper nitrate hexahydrate ($Cu(NO_3)_3 \cdot 6H_2O$), ammonia solution, D-glucose ($C_6H_{12}O_6$), methanol, potassium hydroxide (KOH), sulphuric acid (H_2SO_4), potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]\ 3H_2O$), potassium chloride (KCl), absolute ethanol, Nafion® and deionized water (18.2 MΩ cm) were used throughout the experiments. All

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the chemicals were purchased from Sigma-Aldrich and used as supplied without further purification.

2.2. Instrumentation

The crystal structure and phase purity of catalyst samples was determined by X-ray diffraction (PANalytical X'PERT High Score's diffractometer with a Cu Kα radiation, operating in the range of (20–70°). FTIR spectra of the catalyst samples were recorded on Nicolet 5PC, Nicolet Analytical Instrument, in the range of 4000–400 cm^{-1}. Surface morphology of the samples was evaluated by scanning electron microscopy (JEOL-JSM-6490A) equipped with energy dispersive X-ray microanalysis (EDX) to determine the elemental composition of the samples. Transmission electron microscopy (TEM) images were obtained on JEOL JEM-2011 electron microscope operating at 200 kV. Particle size analysis was carried out on a Malvern Instruments Mastersizer 2000.

The electrochemical measurements including cyclic voltammetry and chronoamperometry were performed at room temperature on potentiostat interface 1000 by Gamry. A standard three-electrode cell system equipped with modified glassy carbon as working electrode (with 0.07 cm^2 surface area), a platinum wire as an auxiliary electrode, and a saturated calomel electrode (SCE with 3 M KCl) as reference electrode, was used for collecting cyclic voltammetric data. All solutions were prepared in freshly deionized water and 10 mL of supporting electrolyte was utilized for each electrochemical measurement. Prior to each measurement, the solutions were purged with Ar.

Gamry interface 1000 was also used for electrochemical impedance spectroscopy (EIS) measurements at a DC bias of 0.25 V with a signal of 5 mV over the frequency range of 0.1 to 100 kHz.

2.3. Synthesis of CeO_2 support and $CuO@CeO_2$ catalysts

CeO_2 substrate was prepared by simple precipitation reaction as reported earlier by I.-T. Liu et al. [6]. Active metal oxide, CuO, was loaded via impregnation method using copper nitrate precursor [13]. Five CuO loads, 5%, 10%, 15%, 20%, and 25% by weight, were prepared by impregnation onto pre-dried CeO_2 substrate using required volume of copper nitrate hexahydrate solution. All the samples were soaked overnight, dried in oven for 1 h and further calcinated at 500 °C for 2 h. Successful impregnation with respect to variation in wt% of CuO on CeO_2 was achieved as physically indicated by change in color tones (khaki–slate gray) of the as-synthesized catalysts.

2.4. Electrode modification

Prior to surface modification glassy carbon (GC) electrode was polished to a mirror finish using 0.3 μm alumina slurry and was then rinsed thoroughly with deionized water. In order to remove any loose alumina particles, electrode was ultra-sonicated in deionized water for 1 min and was dried thoroughly at room temperature. The working surface of the clean GC electrode was dampened with 2 μL of pure ethanol and 0.1 mg of finely ground catalyst sample was carefully dropped onto it, this was followed by drop casting 2 μL of 0.5% Nafion solution. The electrode was then allowed to air dry for 30 min. The prepared modified GC/$CuO@CeO_2$/Nafion electrode was used for acquiring electrochemical data. Pre-conditioning steps (10 cycles) were performed before each electrochemical measurement in respective potential windows in order to reduce background current and obtain a steady voltammogram.

3. Results and discussion

3.1. FTIR and XRD analysis of $CuO@CeO_2$ powders

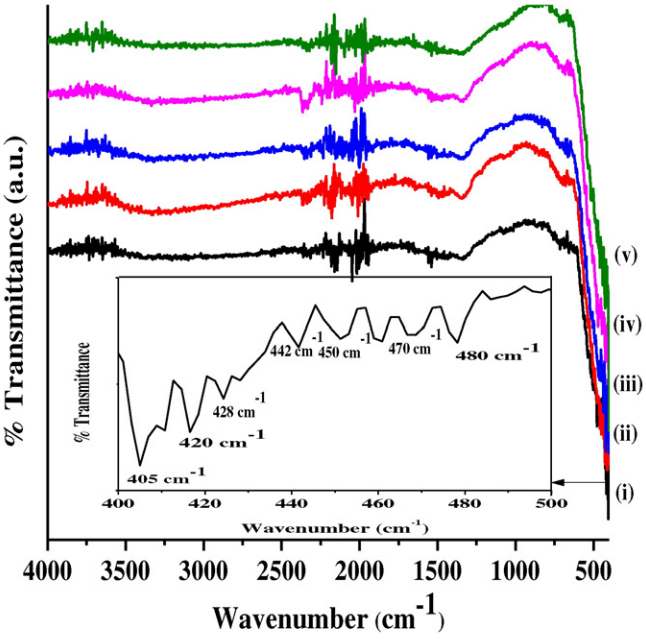

Fig. 1. Comparison of FTIR spectra of (5–25 wt%) $CuO@CeO_2$ catalysts, (i) 5 wt% (ii) 10 wt% (iii) 15 wt% (iv) 20 wt% (v) 25 wt% CuO loading.

Typical stretching vibrations of Cu–O bond, were observed in the FTIR spectra of all of the loaded catalysts at around 480– 400 cm^{-1} (highlighted in inset of Fig. 1), implying that CuO has been successfully incorporated into ceria matrix [13–15]. Vibrational bands observed at 450 cm^{-1} are due to stretching modes of Ce–O bond in CeO_2 [16].

Fig. 2 shows the X-ray diffraction patterns of $CuO@CeO_2$ catalysts along with the typical peaks for crystalline CeO_2 observed at $2\theta = 28.5°, 33.0°, 47.5°· 56.4°, 69.5°$ and 76.8°. All the XRD reflection peaks for CeO_2 could be exactly indexed on the basis of a cubic fluorite cell indicating that pure CeO_2 was synthesized.

The XRD patterns for supported catalyst samples (5% loading) shown in Fig. 2 (ii) is dominated by diffraction lines of cubic CeO_2 without any lines for CuO, showing that low contents of CuO are highly dispersed on CeO_2 substrate. As the loading of CuO is increased from

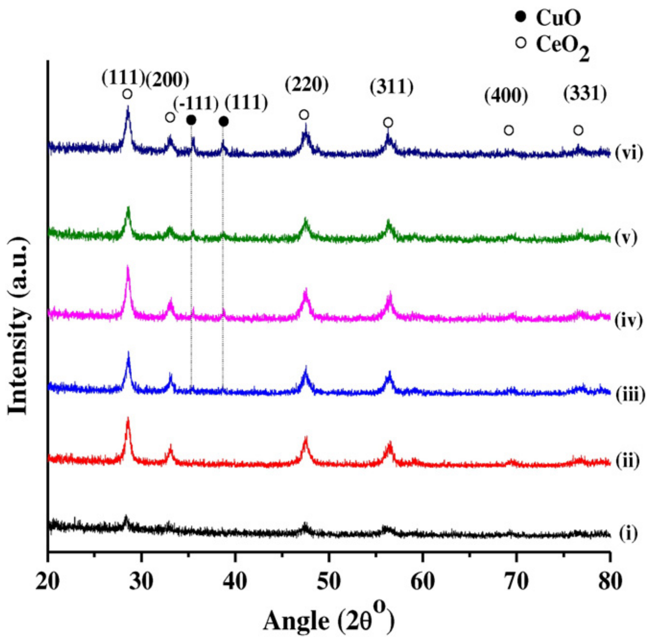

Fig. 2. XRD patterns for pure CeO_2 substrate (i) and 5-25 wt% $CuO@CeO_2$ catalysts, (ii) 5 wt% (iii) 10 wt% (iv) 15 wt% (v) 20 wt% (vi) 25 wt% CuO loading.