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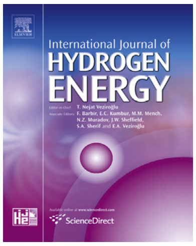

Effects of copper:aluminum ratio in CuO/Al_2O_3 nanocomposite: Electrochemical hydrogen storage capacity, band gap and morphology

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ABSTRACT

CuO/Al_2O_3 nanocomposites were successfully prepared via a thermal decomposition method using green tea extract as a precipitating agent. The biosynthesized CuO/Al_2O_3 nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), fourier transform infrared spectroscopy (FT-IR), X-ray energy dispersive spectroscopy (EDS), N_2 adsorption (BET), ultraviolet–visible (UV–Vis) spectroscopy and transmission electron microscope (TEM). Also, the electrochemical hydrogen storage properties of porous CuO/Al_2O_3 nanocomposites with various aspect ratio of Cu:Al were studied. The discharge capacity of CuO/Al_2O_3 nanocomposites at the first cycle with 2:1 ratio of each compartments obtained at 330 mAh/g while enhanced to 6750 mAh/g after 14 cycles.

Introduction

Hydrogen is an ideal and environmental friendly fuel to have a severe future impact on world energies. It is in fact a new energy carrier alternative to fossil fuels, due to its high conversion efficiency, polluting nature and non-recyclability [1]. The use of hydrogen for fuel cell represents one of the most environmentally sound methods for the production of electrical energy [2] due to its high efficiency, easy synthesis and the ability for implementation in a carbon-free emission cycle [3]. Hydrogen can be stored in various methods, such as physisorption of hydrogen on porous materials [4], compressed gas, in its liquid form and hydrogen intercalation in metals and complex hydrides [5]. Electrochemical hydrogen storage of porous materials is a more appropriate method, in comparison with the conventional hydrogen storage methods (i. e., at relatively low or high temperature and under relatively high pressure). In this method, the hydrogen is adsorbed in materials during electrochemical decomposition of an aqueous medium [6].

Recently, most of the research in electrochemical hydrogen storage has been focused on CNT [7], graphite [8], alloys [9], and hydride compounds [10]. In this work, we are trying to use new and cheaper materials with high capacity for hydrogen storage. To the best of our knowledge, there is no report on the porous CuO/Al_2O_3 nanocomposite in hydrogen

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storage technology. The CuO/Al_2O_3 nanocomposites has been used in various application such as catalyst-sorbent suitable for simultaneous SO_2 and NOx removal from flue gases [11], oxidation of methane [12], catalyst for the low-temperature water–gas shift reaction [13], photocatalysts [14], oxygen carriers for chemical-looping combustion [15], oxidation of carbon monoxide [16],etc. This paper presents a green, safe and economically reasonable synthesis technique for production of porous CuO/Al_2O_3 nanocomposites via a thermal decomposition method.

Experimental

Materials and physical measurements

All chemical reagents in our experiments were used in analytical grade without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffract meter using Ni-filtered Cu Ka radiation. Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. Scanning electron microscope (SEM) images were obtained on using Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The EDS analysis with 20 kV accelerated voltage was done. UV–Vis spectroscopy (diffuse reflectance) of the obtained was performed with a Shimadzu UV/3101 PC in a range between 200 and 700 nm. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The N_2 adsorption/desorption analysis (BET) was performed at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. Transmission electron microscope (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV.

Preparation of CuO/Al_2O_3 nanocomposite

All the chemical reagents for the synthesis of CuO/Al_2O_3 composites such as $Cu(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, methanol, were commercially available and employed without further purification. A mixed solution of metal nitrates was prepared by dissolving $Cu(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ in distilled water with the molar ratio of $Cu^{2+}/Al^{3+} = {}^{+}$ equal to 0.25:1 (S_a), 0.5:1 (S_b), 1:1 (S_c) and 2:1 (S_d). Separately 20 ml green tea extract was added. The previous reaction mixtures subsequently heated at 80 °C with continuous stirring for 1 h on a hot plate let the ions react. The solution was evaporated on a hot plate above 120 °C for dehydration. The samples finally calcined at 800 °C for 5 h.

Electrochemical system

The hydrogen storage capacity of the as prepared electrodes was measured using chronopotentiometry technique. The charge–discharge cycles were sat up in three-electrode system, Cu–CuO/Al_2O_3, Pt and Ag/AgCl as a working, counter and reference electrodes, respectively. The electrolyte solution was prepared using 6 M KOH dissolved in double distilled water. In this system, a constant current was applied between the working and counter electrodes and was measured the potential differences between the working and the reference electrodes were recorded. To prepare an electrode of CuO/Al_2O_3 composite, copper foam of nano size porosities was used as a substrate for the CuO/Al_2O_3 composites (Fig. 12). The CuO/Al_2O_3 composite (homogeneously dispersed) was prepared in ethanol for 20 min. A pure copper plate (1 × 2 cm^2) was coated by a thin layer of CuO/Al_2O_3 powders at 100 °C without using glue or a binder. In the charging process, the electrolyte dissociates around the working electrode and hydrogen in the solution migrates to the cathode and absorbed by CuO/Al_2O_3 nanocomposite. The opposite direction represents the discharging cycle; the hydrogen atoms migrate from the cathode under alkaline circumstance.

Results and discussion

The XRD patterns of various aspect ratios of CuO/Al_2O_3 nanocomposites prepared from the thermal decomposition are shown in Fig. 1. Fig. 1(a–d) shows the XRD patterns of

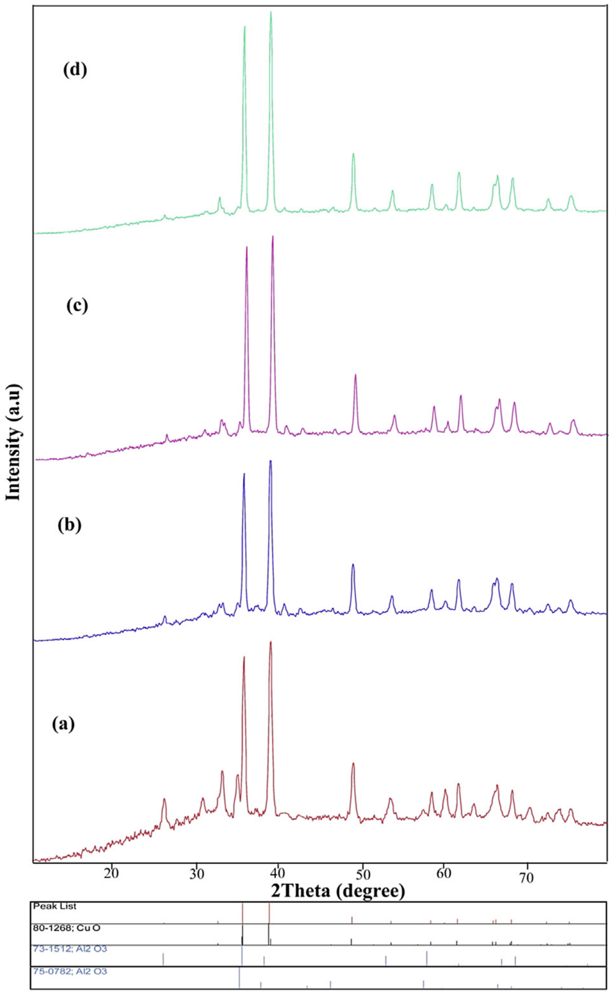

Fig. 1 – XRD patterns of CuO/Al_2O_3 nanocomposite (a) S_a, (b) S_b, (c) S_c and (d) S_d.