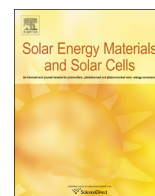




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Fabrication of metal sulfide porous foams via electrodeposition and galvanic replacement reaction



P. Shahbazi, A. Kiani*

Department of Chemistry, Faculty of Science, University of Isfahan, Isfahan, Iran

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ABSTRACT

A simple and non toxic method is reported for fabrication of metal sulfide foams such as Cu_2S , Ag_2S and CdS . The presented method is mainly based on the electrochemical fabrication of metal foam and galvanic replacement reaction. Cu_2S and Ag_2S foams are synthesized by immersing as-fabricated Cu and Ag foams in aqueous sulfide solution. Furthermore, another method is used for fabrication of Ag_2S foam based on immersing of as-prepared Cu_2S foam in AgNO_3 solution. Electrodeposition of CdS on as-fabricated Cu foam electrode is performed potentiostatically using a two electrode setup in an aqueous solution of CdSO_4 , EDTA, and $\text{Na}_2\text{S}_2\text{O}_3$. The synthesis process is rapid and convenient. The as-fabricated foams were characterized through XRD, BET, SEM and EDX analysis. The obtained data reveal fabrication of Cu_2S , Ag_2S and CdS foams with porous and ramified walls and high surface area. The applicability of as-fabricated Cu_2S in the photodegradation of methylene blue is reported, as a proof of concept. The proposed approaches demonstrate a practical route toward preparation of porous metal sulfide foams via electrodeposition and galvanic replacement.

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1. Introduction

Photocatalysts are known as a type of semiconductor materials which have been attracted a great deal of attention due to their potential in environmental purification [1–4] and hydrogen energy production [5–7]. As a result of fast development of nanotechnology a great deal of efforts has been devoted to the synthesis and characterization of nano and micro sized semiconductor structures [8–10]. Nanoporous foam materials represent a very promising type of structured materials having a number of interesting and unique properties [11–13] especially in heterogeneous catalysis [14–16]. Metal foams can be deposited electrochemically from a metal ion solution [17]. Direct electrochemical fabrication of 3-D foam of Cu metal, using hydrogen bubbles as a dynamic and effective template; with highly porous ramified (dendritic) walls have been reported [18].

Following on our previous work on the fabrication of Ag and Pd (noble metal) foam coated electrodes, [19,20] we present the indirect fabrication of metal sulfide foams based on electrochemical deposition of a scarified Cu foam and galvanic replacement reaction. The groups of Adzic and Kokkinidis was first utilized the galvanic replacement reaction for preparation of metallic and bimetallic electrocatalysts [21–27]. In this study; the main goal is

the fabrication of metal sulfide foams. Since foam materials have porous and ramified walls with high surface area, we decided to introduce a new, simple and fast method for fabrication of semiconductor foams.

2. Experimental section

2.1. Chemicals and apparatus

All reagents were of analytical grade and used without any further purification. Solutions were made with twice distilled water. All electrochemical experiments were performed using a Potentiostat & Galvanostat (Autolab, PGSTA, Eco Chemie, Netherlands). An Ag|AgCl|KCl (3 M) electrode and a platinum wire served as the reference and counter electrodes, respectively. The working electrodes used throughout this work were constructed with small pieces of high-purity Cu sheets (Merck). Scanning electron microscopy (SEM), Energy dispersive X-ray (EDX) spectroscopy and XRD were used to characterize the morphology and performing the elemental qualitative analysis of the as-fabricated electrodes. The phase and crystallographic structure of the products were characterized by XRD using the D8ADVANCE (Japan). The X-ray diffractometer was equipped with nickel-monochromatized Cu $K\alpha$ radiation ($\lambda=0.154$ nm). The photocatalytic activity of the Cu_2S foam, $\text{Cu}_2\text{S}/\text{Au}$ foam and Cu_2S sheet (with the geometrical

* Corresponding author. Tel.: +98 313 7932742; fax: +98 313 6689732.

E-mail address: a.kiani@chem.ui.ac.ir (A. Kiani).

surface of 3.5 cm²) was evaluated based on the photodegradation process of methylene blue (0.025 mM), one of the most frequently reported dyes in photocatalytic studies.

Brunauer–Emmett–Teller (BET) specific surface areas of Cu₂S, Ag₂S and CdS foams, were measured by nitrogen adsorption isotherms recorded on a Micromeritics ASAP 2020 volumetric adsorption system using N₂ adsorption data at relative pressure from 0.05 to 0.25.

Absorbance measurements, initial and the residual concentrations of the dye were evaluated using a spectrophotometer (A Carry UV–vis–NIR (Cary 500, Version 8.01)). The spectra were recorded in the range of 380–800 nm. The photocatalytic efficiency was calculated based on the calibration curve, drawn at the maximum absorption wavelength experimentally registered at $\lambda=665$ nm. The resulting solution was irradiated with a 200 W xenon lamp (power density ~ 0.09 W/cm²) equipped with a UV filter. A static cylindrical flask was positioned at equal distances (5 cm) for each sample. So it was used as photodegradation reactor. For a given time interval and during the reaction process, 4 mL of the mixture solution was pipetted into a quartz cell (path length 1.0 cm), and its absorption spectrum was measured using a UV–vis spectrophotometer at ambient temperature for an optical absorbance measurement. The UV–vis diffused reflectance spectra (UV–vis DRS) were obtained from UV–vis Spectrophotometer, JASCO, V-670 with an integrated sphere reflectance accessory. BaSO₄ was used as a reference material. UV–vis absorption spectra were recorded in the spectral range of 190–900 nm.

2.2. Fabrication of semiconductor foam

The Cu foam is fabricated based on method reported in the literature [19,28]. Briefly, high-purity Cu sheets (Merck, thickness 0.01 cm) were cleaned by immersing in acetone and dilute HCl through a period of sonication. The Cu sheet was cut into smaller pieces and was secured to the bottom of a Teflon cell with an O-ring that defined the electrode area as 0.43 cm². This smooth Cu sheet was used as the substrate for deposition of Cu foam. The electrodeposition of Cu foam was performed by applying constant current to electrochemical cell, containing 0.4 M CuSO₄+1.5 M H₂SO₄ aqueous solution (without stirring or N₂ bubbling). Gas bubbles were produced at the Cu surface during electrochemical deposition step. The growth of Cu foam was accompanied by gas evolution at all times until the electrochemical deposition was terminated.

2.3. Fabrication of Cu₂S foam

For fabrication of Cu₂S foam, the as-prepared Cu foam was simply immersed in 0.5 M Na₂S solution for 1800 s.

For fabrication of Cu₂S/Au foam, the as-prepared Cu foam was simply immersed in an aqueous solution of 0.3 Mm HAuCl₄ for 120 s and then the electrode was simply immersed in 0.5 M Na₂S solution for 1800 s.

The as-fabricated Cu foam was washed with distilled water and incubated at room temperature under a 5 mM aqueous solution of AgNO₃ for 720 s. In this step the solution was purged with Ar during the galvanic replacement process. Then the electrode was immersed in 0.5 M Na₂S solution for 43,200 s. In another approach the as-prepared Cu foam is first immersed in Na₂S solution for 1800 s then the fabricated Cu₂S foam is immersed in AgNO₃ solution for 3600 s.

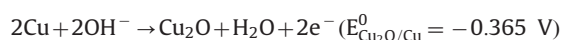
In order to fabricate CdS foam, first as-prepared Cu foam was immersed in an electrodeposition bath of an aqueous solution of 0.05 M CdSO₄, 0.1 M EDTA, and 0.5 M Na₂S₂O₃. The electrochemical cell consists of two electrodes; one of them is Cu foam serving as working electrode and the other is a Pt wire serving as the

counter electrode. A potential of -1.0 V was applied to the electrochemical cell for about 2700 s. The pH of the electrodeposition bath was adjusted 5.4 by using of a NaOH aqueous solution [29]. Finally, a thin yellow film of CdS was electrodeposited on the Cu foam electrode.

3. Result and discussion

3.1. Cu₂S foam

The Cu foam is fabricated based on method reported in the literature [20,28]. Then the as-fabricated Cu foam is simply immersed in a solution of 0.5 M Na₂S for 1800 s. The possible reactions which resulted in the conversion of Cu foam to Cu₂S foam could be summarized as [30,31]:



The morphology of the fabricated electrodes was observed by means of SEM. Fig. 1 depicts the 3D structures of Cu₂S foam at different magnifications. Total view of SEM images shows that Cu₂S foam has a porous structure with ramified and dendrite walls. The magnified SEM image (Fig. 1b) of the Cu₂S foam shows that it has the average pore size of about 15.7 μm . Analysis of the interior of these holes shows the size and shape of the agglomerates of Cu₂S grains from which the walls were constructed (Fig. 1c and d). The SEM images exhibit an obvious size and morphology depending on the preparation condition of the metal sulfide foams. By contrast, there are some remarkable points between SEM images of Cu₂S and Cu foams [20]. The overall macroscopic features of the Cu₂S foam are similar to those of the Cu foam (SEM images are not shown) [20]. Both of these structures have a highly porous structure with ramified walls. However, the details which are apparent in the more magnified images (Fig. 1d) reveal that there are some difference between shape and the way of agglomerating of particles of Cu₂S and Cu foams. It is shown in the more magnified image that one collection of Cu₂S particles has a special shape as cauliflower. The related differences would be due to the presence of S in Cu₂S. But as reported in our previous work Cu particles join together one by one to form the branches of the ramified (dendritic) walls.

Energy dispersive X-ray (EDX) spectroscopy was used to characterize the surface composition of the obtained Cu₂S foam (Fig. 2). Elemental analysis data given from EDX spectroscopy for Cu and Cu₂S foams were listed in Table 1. EDX results show that Cu₂S foam is composed of Cu and S and the amount of loaded S is only about 20.03 wt% of Cu foam after being immersed in Na₂S solution for 1800 s. X-ray diffraction spectroscopy was used to characterize the surface composition of the as-fabricated Cu₂S foam. As it could be seen in Fig. 3, the XRD pattern shows two main peaks for Cu and Cu₂S. The peaks at 2θ values of 43.40, 50.5 and 74 are related to Cu (no. 04-0836). The peaks at 2θ values of 37.2, 46, 48.5 and 53.5 correspond to beta-Cu₂S (no. 26-1116). As the substrate is made of Cu one could expect more intense peaks for Cu compare to those of Cu₂S or chalcocite, which is only formed at the surface. So the peak at 37.2, 46, 48.5 and 53.5 are rather weak. XRD analysis indicated a crystalline structure with hexagonal form for as-fabricated Cu₂S foam.

3.2. Ag₂S foam

The Ag₂S foam is fabricated in two ways. In the first approach, Ag foam was prepared via galvanic replacement of Cu by Ag [20]

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