Journal of Alloys and Compounds 688 (2016) 769–775

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis and microstructure-dependent photoactivated properties of three-dimensional cadmium sulfide crystals

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ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form
28 June 2016
Accepted 10 July 2016
Available online 11 July 2016

Keywords:
Microstructure
Crystallite
Defect
Photoactivity

ABSTRACT

Networked rod-like and intersecting flake-like CdS crystallites with three-dimensional structures were synthesized using a thermal evaporation method. Both types of CdS crystallites had a hexagonal crystal for given growth conditions. The rod-like CdS crystallites contained many irregular CdS grains, whereas the flake-like CdS crystallites comprised many granular CdS grains with various sizes. Furthermore, the flake-like CdS crystallites were more defective than the rod-like CdS crystallites because they contained a larger number of grain boundaries and showed greater sulfur deficiency. Additionally, the flake-like CdS crystallites showed higher photocatalytic activity and photoelectrochemical performance. The substantial differences in the microstructure and optical properties between the two types of CdS crystallites explained the superior photoactivated properties of the flake-like CdS crystallites.

1. Introduction

Photoexcited electrons and holes play a crucial role in the photocatalytic and photovoltaic behavior of binary semiconductors. Most photoactivated properties of binary semiconductors require ultraviolet (UV) light for promoting interaction between the semiconductors and their environment. Because UV light accounts for only a small fraction of solar radiation, this limits the efficiency of these semiconductors when they are used in photoactivated devices [1–3]. Recently, because of their capability to use solar energy, sulfide semiconductors with visible light band gaps have attracted considerable attention for use in photoactivated devices [4–7]. Such sulfide semiconductors have satisfactory photoactivated properties under visible light irradiation and are crucial for the development of photocatalytic and photovoltaic devices. Among sulfide semiconductors, CdS has a band gap in the visible light region and shows high chemical stability at room temperature; moreover, it can be prepared using many synthesis methods. Accordingly, CdS is mostly used for harvesting solar light in photoactivated devices [8]. Several chemical and physical synthesis methods have been developed for synthesizing CdS with various morphologies and sizes [9,10]. Comparatively, highly crystalline CdS crystals synthesized using a thermal evaporation method are promising for integration into industrial semiconductor processes [11,12].

Semiconductors with a three-dimensional architecture are more suitable for photocatalytic and photovoltaic applications than those with a two-dimensional architecture. In semiconductors, the size of photogenerated electron–hole pairs and the efficient migration of the photogenerated carriers to the semiconductor surface for reaction with environmental species under illumination are highly correlated with the semiconductor microstructure and crystal quality [13]. Furthermore, the microstructure of three-dimensional semiconductors obtained using thermal evaporation methods is closely related to the process parameters [14]. For a given synthesis method, semiconductors with various degrees of photoactivity have been reported because the semiconductor crystal features change with the process parameters [15]. To design semiconductors for use in photoactivated devices, it is essential to understand the correlation between the structure and the photoactivity of semiconductors under the synthesis conditions. In this study, three-dimensional rod-like and flake-like CdS crystallites were synthesized using a thermal evaporation method, and their microstructure and photocatalytic and photoelectrochemical properties were investigated to understand their structure-dependent photoactivity.

2. Experimental procedures

CdS crystallites with various morphologies were grown on pure

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http://dx.doi.org/10.1016/j.jallcom.2016.07.108

glass and fluorine-doped tin oxide (FTO) glass substrates by thermal evaporation. The substrates used herein have a size of 1.5 cm × 2.5 cm and CdS powders (0.6 g; purity, 99.999%) were used as source material for thermal evaporation processes. The temperature for thermally evaporating the CdS source material is fixed at 900 °C and a constant supply of 50 sccm high purity argon gas was used as carrier gas in a horizontal quartz tube furnace. The rod-like CdS crystallites were obtained at the growth temperature of 600 °C and that for the flake-like CdS crystallites is 450 °C.

Sample crystal structures were investigated by X-ray diffraction (XRD; Bruker D2 PHASER) using Cu Kα radiation. The morphologies of the as-synthesized samples were characterized by scanning electron microscopy (SEM; Hitachi S-4800), and high-resolution transmission electron microscopy (HRTEM; Philips Tecnai F20 G2) was used to investigate the detailed microstructures of the samples. Room temperature dependent photoluminescence (PL; HORIBA HR800) spectra were obtained using the 325 nm line of a He–Cd laser. The optical transmittance spectra of the samples were recorded by using UV–visible spectrophotometer (Jasco V750). Photocatalytic activity of as-prepared samples were performed by comparing the degradation of 10^{-6} M aqueous solution of methylene blue (MB) containing various CdS samples as catalysts under visible light ($\lambda > 420$ nm) irradiation. The photoelectrochemical (PEC) properties were measured in a convenient three electrodes electrochemical system (SP-50 potentiostat/Galvanostat). A mixed aqueous solution composed of Na_2S (0.25 M) and Na_2SO_3 (0.35 M) were used as electrolyte. Work electrode was made of CdS crystallites on the conductive FTO glass. Ag/AgCl (1M KCl) electrode was used as a reference electrode and a platinum wire was used as a counter electrode. A 100W Xe arc lamp equipped with an ultraviolet light filter was used as the illumination source for photocurrent measurements.

3. Results and discussion

Fig. 1(a)–(c) show SEM micrographs of networked rod-like CdS crystallites formed on a substrate. The crystallites contain many CdS segmental crystals with irregular morphologies. The surface of the rod-like CdS crystallites is rough and dense, and no pores are evident. Furthermore, the crystallites have a diameter in the range of approximately 0.4–1.1 μm and are tangled together to form a net-like structure. Fig. 1(d)–(f) depict SEM micrographs of flake-like CdS crystallites. These crystallites are vertically aligned and intersect each other. Their thickness is in the range 0.7–1.2 μm, and they contain many granular grains of various sizes, ranging from 0.15 to 0.9 μm. Moreover, the diameter of the flake-like CdS crystallites is in the order of tens of micrometers. Notably, because the constituent granular CdS grains were of various sizes, clear and numerous grain boundaries were observed on the surface of the crystallites. Because the granular grains in some local regions of the flake-like CdS crystallites were not densely packed, some tiny pores were also observed on the surface of the crystallites.

Fig. 2 shows XRD patterns of CdS crystallites with various morphologies. In addition to the Bragg reflection centered at approximately 37.8°, which originates from the FTO glass substrate, the other Bragg reflections are attributable to the hexagonal CdS phase (JCPDS no. 06-0314). No other impurity phases were detected, showing that the pure CdS phase was formed. The sharp and distinct Bragg reflections of the CdS prepared through the thermal evaporation of CdS powders indicated the formation of highly crystalline CdS. Notably, the rod-like CdS crystallites showed a more intense peak for the (002) plane compared with the intensity for the other crystallographic planes; however, this crystallographic feature was not observed for the flake-like CdS crystallites. The surface energies of the facets of hexagonal CdS crystals have been shown to predominantly determine the crystal morphology during crystal growth under various conditions [16]. The peak intensities of the non-*c*-axis crystallographic planes CdS(100) and CdS(101) are greater than that of CdS(002) for the flake-like CdS crystallites, possibly indicating that granular CdS grains tend to laterally cluster and form flake-like CdS crystallites under the growth conditions maintained in the current study.

Fig. 3(a) shows the low-magnification TEM image of CdS segmental crystals scraped from the rod-like CdS sample. An irregular surface feature is evident. The rod-like segments confirm that many irregularly shaped CdS crystals aggregated with a specific orientation during crystal growth, resulting in the crystals having a high aspect ratio. The diameters of the CdS segmental

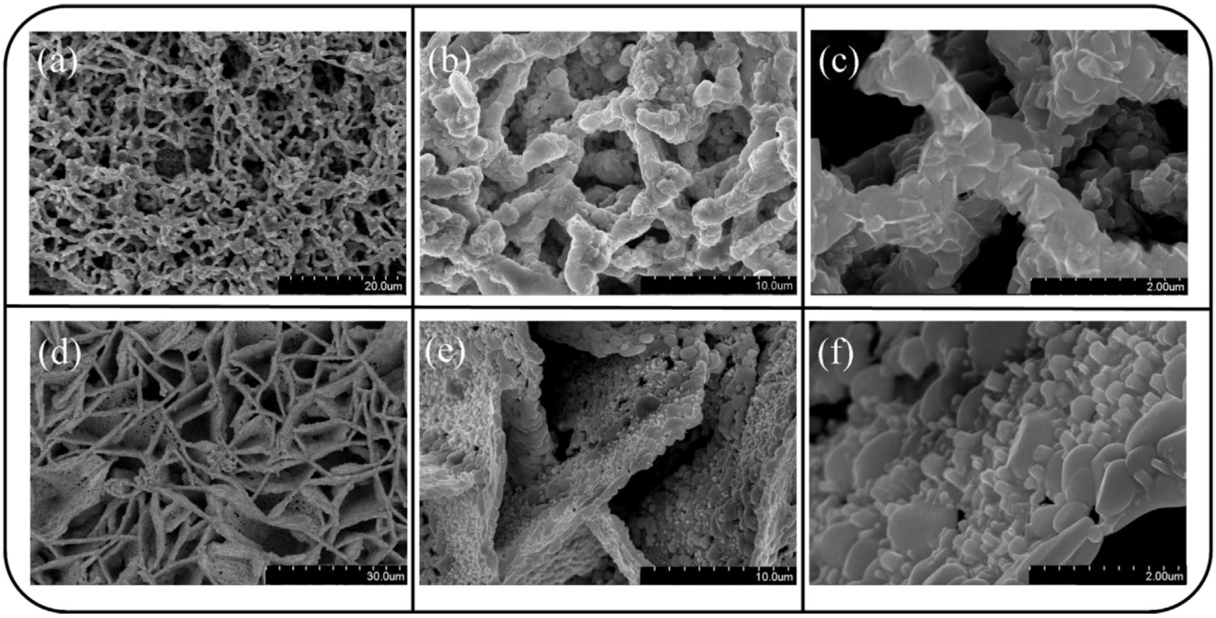

Fig. 1. (a)–(c) SEM micrographs of rod-like CdS crystallites with various magnifications. (d)–(f) SEM micrographs of flake-like CdS crystallites with various magnifications.