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Three-dimensional CdS nanostructure for photoelectrochemical sensor

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ABSTRACT

Cubic CdS nanoparticles and hexagonal CdS nanowalls were fabricated directly on Cd foils via a modified composite hydroxide mediated approach. The phase transition of CdS nanocrystals from cubic to hexagonal phase can be controlled by varying the water content in the hydroxide melts. The metal Cd foils serves as both Cd source and substrate in the formation of the CdS nanostructures. The surface morphology and phase structure were characterized by scanning electron microscope, energy dispersive X-ray spectrometer and X-ray diffraction. The obviously enhanced photoelectrochemical performances of the hexagonal nanowalls were found under the illumination of the simulated sunlight in comparison with that of the cubic CdS nanoparticles. The surface morphology plays a vital role in its photoelectrochemical behaviors due to the different specific surface area and charge transport, indicating such three-dimensional hexagonal CdS nanostructure has prominent advantages in photoelectrochemical applications.

1. Introduction

In recent years, three-dimensional (3D) nanostructrures have attracted much attention as fundamental building blocks for the development of next generation devices, which have high performance and novel functionalities. The photoelectrochemical cells based on TiO_2 nanoparticle porous films, is a well-known example of a 3D nanostructured solar cell [1]. Aligned nanostructure arrays are regarded as an ideal architecture to photovoltaic applications because they provide a direct pathway for charge transport as well as a high junction area [2–5]. Various kind of metallic electrodes modified with 3D nanomaterial, such as zinc oxide nanowires [6], carbon nanotubes (CNTs) [7–9], gold nanoparticles [10] and Ag–Pd bimetallic nanostructure [11], have been used for electrochemical sensors for their capability to provide strong electrocatalytic activity and stability, and to minimize surface fouling. Furthermore, to improve the connection of modified materials with metallic electrodes and to reduce the contact resistance between nanomaterials and electrode, nanomaterials growing directly on metal electrodes have been explored. He et al., have reported a hydrogen peroxide sensor made from the $BaTiO_3$ nanocubes that are prepared directly on Ti foils [12]. The Cu_2S nanowires grown vertically on Cu foil have also been synthesized [13].

The unique properties of nanostructured semiconductors have led to an intensive study for construction of new type devices, catalyst and biosensors with the enhanced properties [14]. As an important fundamental material, CdS has attracted great interest due to its wide-ranging applications as field effect transistors [15], photocatalysts [16], photovoltaics [17] and optical switches [18]. To date, substantial efforts have been devoted to enhancing its performance by modifying the surface morphology and structure [17,18]. Of all the morphologies, 3D single-crystalline CdS nanostructure has been demonstrated to have high absorption of light [17]. Therefore, well controlled morphology in the synthesis of nanomaterials, especially 3D CdS nanostructures, is significant for future development in nanotechnology. However, there have been only a few reports on the synthesis of this novel nanostructures, especially of single crystalline structure [18–22], and some synthetic efforts have been focused on mesoporous metal chalcogenides using structure-directing methods including soft and hard templates [21,22]. Recently, template-free synthetic routes for CdS nanowire arrays have been reported. Aligned CdS nanowire arrays have been fabricated directly on a Cd foil via a simple solvothermal method by Qian et al. [23], in which ethylenediamine serves as the solvent. Lu's group has successfully fabricated well-aligned plain CdS and ternary $Cd_{1-x}Zn_xS$ nanowire arrays via a metal organic chemical vapor deposition process [24]. Although all these methods have their own advantages, most of them involve organic templates or solvents which are environmentally unfriendly [22–24] and some of them involve high vacuum and high temperature which need sophisticated equipment [24]. Here, we report a novel and convenient route to synthesize 3D CdS nanostructures by the modified composite hydroxide mediated (M-CHM) approach without any templates or organic solvents. The CHM approach is a new strategy that provides a one-step, convenient, low-cost, environment

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friendly and possibly mass production route for synthesizing nanostructures of functional materials [25]. It was found that different phase structures and morphologies of products can be obtained with a small amount of water added in the melts [26,27]. Here, we synthesized cubic CdS nanoparticles and hexagonal nanowall arrays by M-CHM. The phase transition from cubic to hexagonal phase can be controlled by varying water content in the melts, and the morphologies of the CdS nanocrystals are controlled simultaneously. The energy gap (Eg) of the CdS nanocrystals was calculated from the optical diffuse reflectance spectrum. The influence of surface morphology and phase structure on the Eg has been investigated. Photoluminescence (PL) measurements manifest the optical properties of the 3D CdS nanostructures. The photoelectrochemical (PEC) properties are also investigated and discussed.

2. Experimental

Cadmium foils (99.85%) are 1 cm^2 and 0.5 mm in thickness. NaOH, KOH and $NaS{\cdot}9H_2O$ are of reagent grade. In a typical reaction, an amount of 5 g mixed NaOH and KOH with Na/K ratio of 51.5:48.5 was placed in a 25 mL Teflon vessel and, 2 mL, 5 mL, 7 mL, 10 mL, 15 mL or 20 mL deionized water also was put into the vessel. One mmol $NaS{\cdot}9H_2O$ was added into the vessel. Cd foils were sonicated in deionized water and ethanol in succession, and dried in air and then put into the vessel. The vessel in the autoclave was then placed in a furnace preheated to 180 °C for 24 h. Afterwards, the autoclave was allowed to cool to room temperature, and the resultant cadmium foil covered with yellow product (CdS) was taken from the solution, rinsed with distilled water several times, and dried in air at 60 °C for 1 h.

Before the electrode fabrication, the CdS foil was polished by abrasive paper on one side and a copper wire was attached to it by silver paste. Then, the CdS foil was covered with epoxy resin leaving an open area of 1 cm^2 on which CdS nanostructure grows.

The crystallographic structures of the samples were investigated by X-ray diffraction (XRD, BDX3200). The morphology and dimension of each sample was examined by scanning electron microscope (SEM, TESCAN, VEGA2) and high resolution transmission electron microscopy (HRTEM, JEOL-2100). The elemental analyses of the samples were conducted with an energy dispersive X-ray spectrometer (EDS). The reflection spectrum was carried out using a computer aided double-beam spectrophotometer (UV-vis-NIR, Hitachi 4100). Photoluminescence (PL) spectra were measured at room temperature by SPEX Flurolog-2 spectrofluorometer. The PEC properties were measured using a CHI660D workstation (CHI Co.), in a standard three-electrode system with the as-prepared sample as the working electrode, a Pt foil as the counter electrode, and a Ag/AgCl (saturated KCl) as the reference electrode, respectively, under the irradiation of the simulated sunlight (CHF-XM-500W) at intensity of 100 mW/cm^2. The light intensity was calibrated by a photometer (FZ-A). The electrolyte was 0.5 M NaS solution. All the experiments were carried out under ambient conditions.

3. Results and discussion

The samples prepared at temperature of 180 °C for 24 h with 2 mL, 5 mL, 7 mL, 10 mL, 15 mL or 20 mL water are denoted by S-a, S-b, S-c, S-d, S-e and S-f, respectively. The morphologies and elemental compositions of the samples are shown in Fig. 1. Fig. 1a shows SEM image of S-a, which reveals particles growing on the substrate with size of 100 nm–1 μm. When the water content

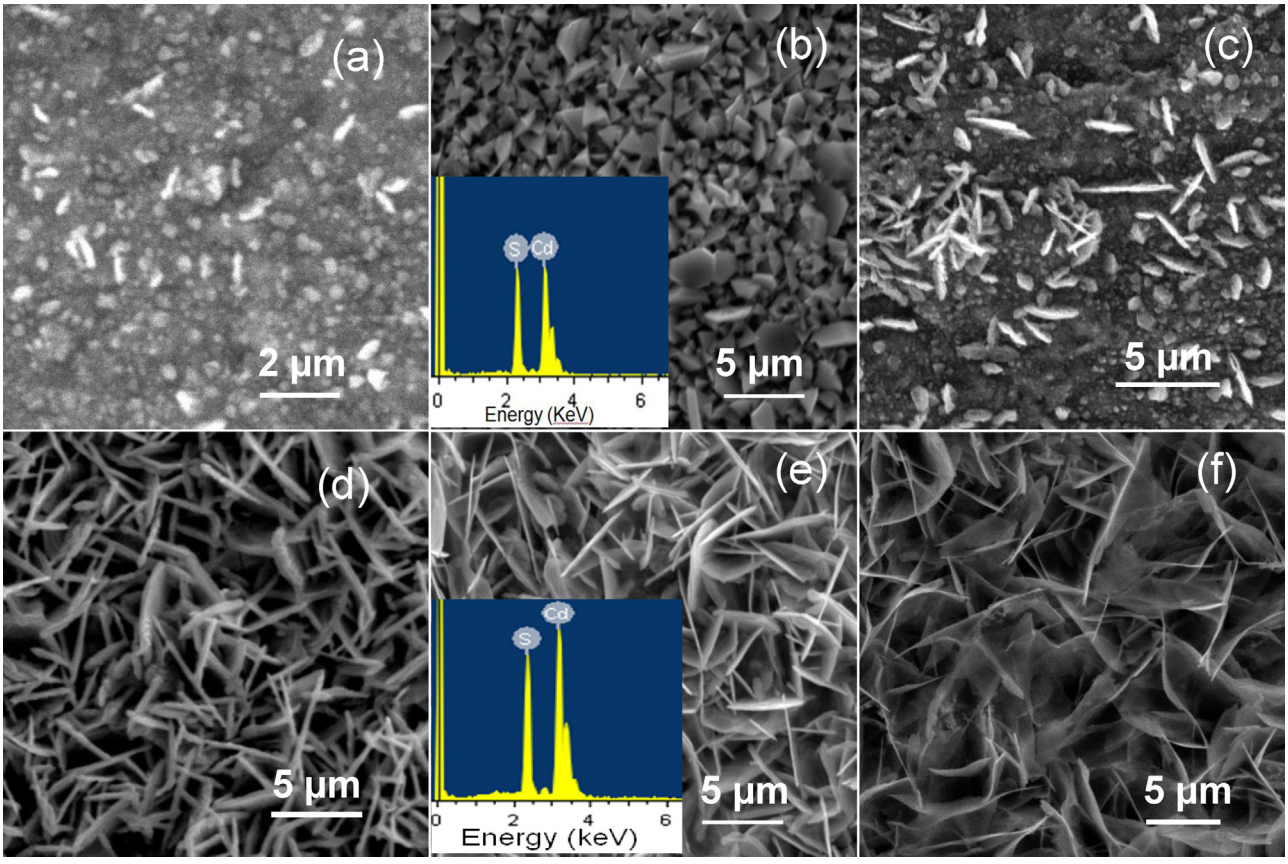

Fig. 1. SEM images of CdS nanocrystal grown on Cd foils with 5 g composite hydroxide and different amount of water as the medium: 2 mL water (a), 5 mL water (b), 7 mL water (c), 10 mL water (d), 15 mL water (e), 20 mL water (f). Insets are the corresponding EDS recorded from the samples.