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Cadmium selenide-sensitized upright-standing mesoporous zinc oxide nanosheets for efficient photoelectrochemical H_2 production☆

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ABSTRACT

Cadmium selenide (CdSe)-sensitized upright-standing mesoporous zinc oxide (ZnO) nanosheets were prepared via a chemical bath deposition followed by annealing and electrochemical deposition of CdSe quantum dots (QDs). The CdSe QDs absorb visible photons under sunlight illumination, promoting electrons from the valence band to the conduction band of CdSe, which then quickly transfer to ZnO followed by the external load to the Pt counter electrode for water reduction. The as-prepared CdSe/ZnO nanosheets show promising photoelectrochemical activities for hydrogen generation.

1. Introduction

Photoelectrochemical (PEC) water splitting provides a promising means for renewable fuel production, which includes two photoelectrodes: a photocathode for water reduction and a photoanode for water oxidation [1–4]. Over the past few years, wide band gap low-dimensional semiconductor nanostructures including nanowires, nanotubes and nanosheets have been extensively studied in various PEC applications because of their outstanding chemical and electrical properties [5–11]. The low-dimensional nanostructure could effectively decouple the direction for light absorption and minority carrier diffusion, which greatly enhanced the photogenerated charge carrier separation and improved the performance of PEC devices. However, the wide band gap nature of those nanostructures severely limited the utilization of visible photons in the solar spectrum. Sensitization of narrow band gap semiconductors could effectively improve the light absorption in the visible solar spectrum and thus the overall performance of PEC devices [12–16].

In this work, we demonstrate a facile solution method for the preparation of CdSe QDs sensitized upright-standing mesoporous zinc oxide (ZnO) nanosheet arrays on transparent conductive fluorine-doped tin oxide (FTO) substrate. The CdSe QDs absorb visible photons under sunlight illumination, promoting electrons from the valence band to the conduction band of CdSe, which then quickly transfer to ZnO followed by the external load to the Pt counter electrode for water reduction. Under AM 1.5 G illumination, the optimized CdSe/ZnO nanosheet arrays exhibit a hydrogen production photocurrent density of 5.2 mA/cm^2, which is 3.4 times higher than that of the CdSe thin film and 63.8 times higher than that of ZnO nanosheets.

2. Experimental

2.1. Growth of ZnO nanosheet arrays

Porous ZnO nanosheet arrays were grown on fluorine-doped tin oxide substrate (FTO) via a chemical bath deposition (CBD) followed by a subsequent annealing [17]. In brief, 2.23 g of zinc nitrate hexahydrate and 10 g of urea were dissolved in 50 mL of deionized water at room temperature to prepare the growth solution. Pre-cleaned FTO substrates were placed at an angle against the wall of a beaker filled with the growth solution with conductive side facing down. The beaker was then sealed by parafilm and kept at 60 °C for 18 h. After reaction, the substrates were taken out, cleaned with deionized water and annealed at 300 °C for 1 h in air.

2.2. Sensitization with CdSe QDs

Electrochemical deposition was applied to sensitize ZnO nanosheets with CdSe QDs. The deposition solution was prepared

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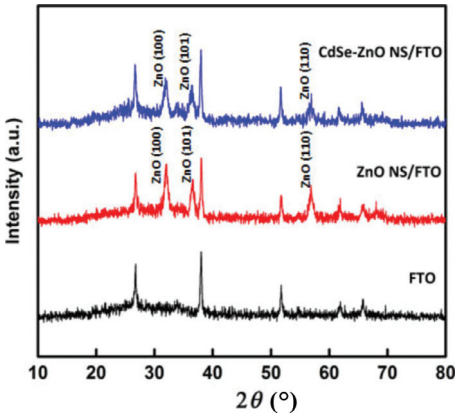

Fig. 1. XRD patterns of CdSe/ZnO nanosheets, ZnO nanosheets and FTO substrate.

by dissolving 92 mg of cadmium chloride and 20 mg of selenium in 50 mL of *N*,*N*-Dimethylformamide (DMF). The electrochemical deposition was conducted at 125 °C in a two-electrode configuration with ZnO nanosheets/FTO as the working electrode and Pt as the counter and reference electrode. A constant current of −0.7 mA was applied throughout the deposition. CdSe thin film electrodes were also fabricated with the electrochemical approach using the blank FTO substrates as the working electrodes during deposition.

2.3. Material characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu-$K\alpha$ radiation ($\lambda = 0.154$ nm). Field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) were conducted on a JEOL-JSM-6700F microscope. High-resolution TEM images were obtained on JEOL JEM-2100F. The absorption spectra were acquired using ultraviolet (UV)–visible spectroscopy (Shimadzu UV-2450).

2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were conducted in a quartz electrochemical cell in a three-electrode configuration. The as-prepared electrode was used as the working electrode with Pt plate and Ag/AgCl as the counter and reference electrode, respectively. The electrolyte contained 0.2 M Na_2S aqueous solution. The light source was a 150 W Xe lamp with AM 1.5 G illumination (100 mW/cm^2).

3. Results and discussion

Fig. 1 shows the XRD patterns of CdSe sensitized ZnO nanosheet arrays grown on FTO substrate. Three sets of different patterns are discernible, which are assigned to the fluorine-doped tin oxide resulting from the FTO substrate, wurtzite ZnO and CdSe, respectively [18–20]. The ZnO nanosheets grow perpendicularly on the FTO substrate with an average sheet thickness of around 20 nm (Fig. 2(a)–(c)). The film thickness of ZnO nanosheets is tunable

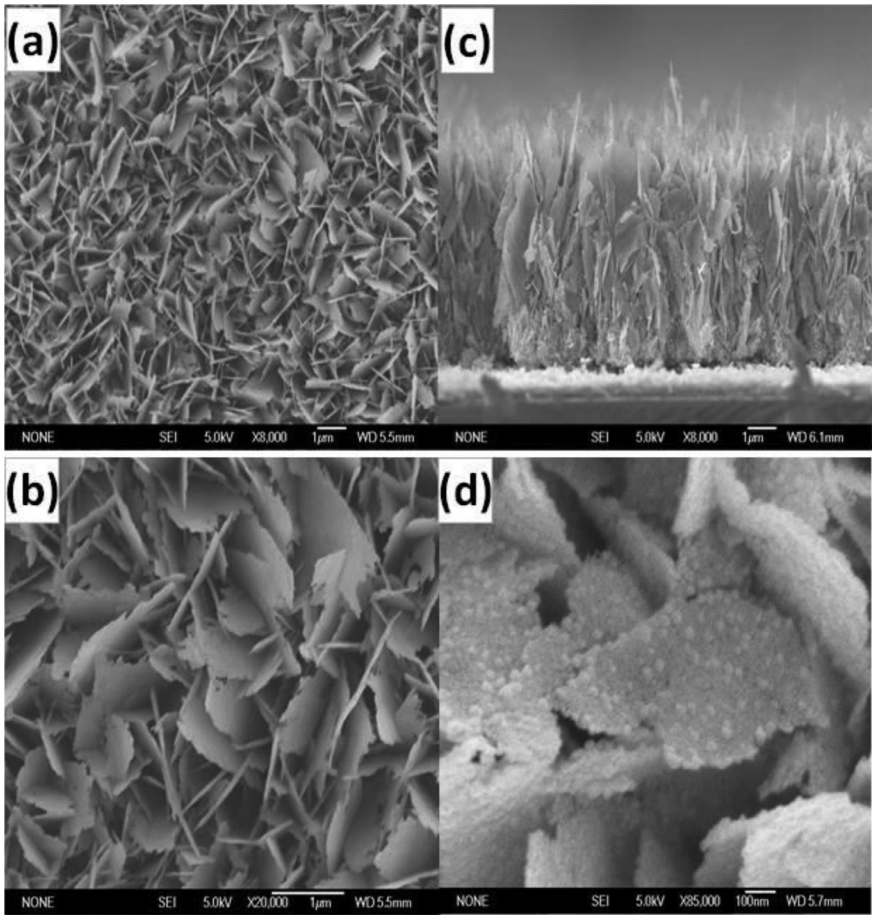

Fig. 2. SEM images of (a) ZnO nanosheets viewed from the top at low magnification, (b) ZnO nanosheets viewed from the top at high magnification, (c) cross-sectional view, and (d) CdSe sensitized ZnO nanosheets.