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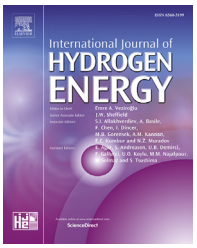

Surface modification of ZnO microrod arrays films by ion-exchange approach and their photoelectrochemical performances

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ABSTRACT

ZnO microrod arrays films with the surface modification by two steps ion-exchange approach have been investigated as photoanodes in photoelectrochemical (PEC) cells. X-ray diffraction, Raman, scanning electron microscope, energy dispersive X-ray detector, UV–vis techniques and PEC measurement have been used in the pristine and surface modified ZnO microrod films. The results show that ZnS and CdS layer can be deposited on ZnO microrod surface through a two steps ion-exchange procedure. What's more, it is found that ion-exchange method is a simple approach to adjust CdS content on the samples surface via changing experimental temperature. Consequently, the PEC property of films can be improved through optimizing CdS content on the ZnO microrods surface. In this experiment, it is found that the optimized condition for preparing film is 70 °C (first step) and 100 °C (second step). These results suggest that surface tuning via ion-exchange method should represent a viable strategy to further improve the efficiency of ZnO microrods photoanodes.

Introduction

Photoelectrochemical (PEC) water splitting is a promising approach to convert solar energy into chemical energy or electric energy, although the solar energy conversion efficiency is still low [1]. To improve the efficiency of PEC system for solar driven water splitting, numerous semiconductor materials, especially metal oxides, such as TiO_2, WO_3, ZnO, α-Fe_2O_3, and $BiVO_4$ have been developed as high-performance photoelectrodes in PEC water splitting system [2–6].

Among all of existing potential semiconductors, zinc oxide-ZnO is one of the most favorable materials due to its excellent electron mobility and ease of crystallization and anisotropic growth [7–10]. However, single ZnO is only UV light response. Considering that UV light consists of only a small portion (~4%) of the solar spectrum, the energy conversion efficiency for PEC water splitting using ZnO as the photoelectrode is very low, which is limited to largely by ZnO's wide band gap [11]. To address this challenge, various synthesis and modification strategies have been attempted to fabricate efficient ZnO photoelectrodes [12–17]. For example,

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Mao and coworkers designed ZnO nanoforest film to achieve high photocurrent density of 0.919 mA cm^{-2} [18]. Wang and coworkers have employed to broaden the light responding region of ZnO by ion doping method [19].

Recently, there has been growing interest in the use of one-dimensional nanostructured ZnO film photoelectrodes [20,21], especially in combination with narrow band gap semiconductors to form heterostructure [22–28], mainly because their design reduces the transport distance and enlarge the light absorption region. However, nanoscale structures are also associated with significant disadvantages, such as an increased the number of surface recombination sites and a reduced space-charge region [29].

In this study, ZnO microrod film was fabricated, and its surface was modified by ZnS and CdS with ion-exchange approach, a facilitative and low cost method. ZnS and/or CdS could be controllably deposited on the ZnO microrod surface by adjusting experimental temperature. Although the PEC activities were demonstrated to be enhanced by surface modification, our attention was mainly focused on the effects of temperature on CdS content of composite films and then PEC activities, rather than just the photocurrent density value itself. Therefore, in this study, PEC, Raman and EDX characterization were used to examine how the ion-exchange temperature influences CdS content of composite films, which correlated PEC performance to light energy absorption of photoelectrode.

Experiments

Preparation of ZnO microrods sample

All of samples at present experiment were directly grown on fluorine-doped tin oxide (FTO) surface. For synthesis of ZnO microrod arrays film, the hydrothermal approach described by Lionel [30] was used. In a typical condition, firstly, FTO substrates were ultrasonically cleaned and then dried in stream of nitrogen. The cleaned FTO glass was then placed in aqueous solution contained $Zn(NO_3)_2$ $6H_2O$ and $C_6H_{12}N_4$ (0.1 M). Finally, the desirable ZnO microrod arrays film was obtained after hydrothermal process at 90 °C for 6 h.

Fabrication of surface modified ZnO microrod arrays samples

A two steps ion-exchange method was developed to gain ZnS and/or CdS modified ZnO microrod films [31]. For the first ion-exchange step, the prepared ZnO microrod films were put into aqueous solution contained 0.05 M Na_2S and maintained for 24 h at different temperature of 30–90 °C. Consequently, ZnO composite films with different thickness of ZnS layer on the surface were obtained. For the second ion-exchange step, The prepared ZnO/ZnS microrod arrays films were put into aqueous solution of 0.1 M $Cd(NO_3)_2$ and kept for 12 h at different temperature of 60–120 °C. Finally, the samples were rinsed by de-ionized water after anneal 400 °C for 1 h under N_2 atmosphere. This two steps ion-exchange approach was designed in that ZnO, ZnS and CdS have different solubility product constant in aqueous solution. They are 6.8×10^{-17}, 3.6×10^{-23} and 7.94×10^{-27} for ZnO, ZnS and CdS, respectively. In that condition, ZnS layer can be deposited on the ZnO microrod surface by anion exchange and then CdS layer was synthesized on the ZnS surface by cation exchange. Ion-exchange time, reaction temperature and definition of sample abbreviation are listed in the Table 1 in detail.

Characterization

Glancing angle X-ray diffraction (GAXRD) analysis was performed using Xpert PRO diffractometer PANalytical, using Cu K irradiation ($\lambda = 15.4184$ nm) to determine the structure and phase of the samples. The chemical components and states of the samples were measured by using Raman spectrometer (Jobin Yvon LabRAM HR) with 514.5 nm irradiation. UV–vis spectroscopy of the microrods films on FTO was performed using a Hitachi U-4100 UV–vis–near-IR spectrophotometer. The size and morphology of samples were observed on a scanning electron microscope (JEOL JSM-6700FE). An energy-dispersive X-ray spectrometer (EDX), attached on the scanning electron microscope was used to determine chemical component of samples.

Photoelectrochemical study

PEC performance testing of samples was performed in a traditional three electrodes system. The prepared samples as working electrodes were placed on a special designed clip. The working electrode exposed in electrolyte was round in shape and the area was fixed at 0.785 cm^2. A large sheet of platinum was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference electrode. The electrolyte was aqueous solution of 0.5 M Na_2SO_3. The photocurrent of samples were recorded by the potentiostat 273 A under 100 mW cm^{-2} chopped light illumination.

Results and discussion

Crystal phase of samples

The structure information of all samples is firstly characterized by XRD and result is presented in Fig. 1. From the XRD data, it can be seen that the diffraction of peaks are ascribed to hexagonal structure ZnO [32]. The seven peaks in the patterns are well indexed to (112), (103), (110), (102), (101), (002) and (100) facet of ZnO with hexagonal structure. Further observation of the XRD patterns of samples except ZnO-4, the strongest intensity of peak is at 34.4° assigned to the diffraction of (002) facet of ZnO with hexagonal structure, which have been reported by other researchers and imply that the ZnO microrod obtained at this experiment grow along [002] direction [33]. Nevertheless, the intensity of XRD peaks from ZnO-4 are different from other samples, indicating that morphology of ZnO-4 may be changed during the ion-exchange procedure which will be discussed in the SEM section. In addition, no ZnS and/or CdS characteristic peak is found for all samples after two steps ion-exchange procedure, which maybe refer to the content of ZnS and/or CdS in the samples. As we all know, XRD technique has content threshold. If the content of ZnS

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