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Interface optimization of ZnO nanorod/CdS quantum dots heterostructure by a facile two-step low-temperature thermal treatment for improved photoelectrochemical water splitting

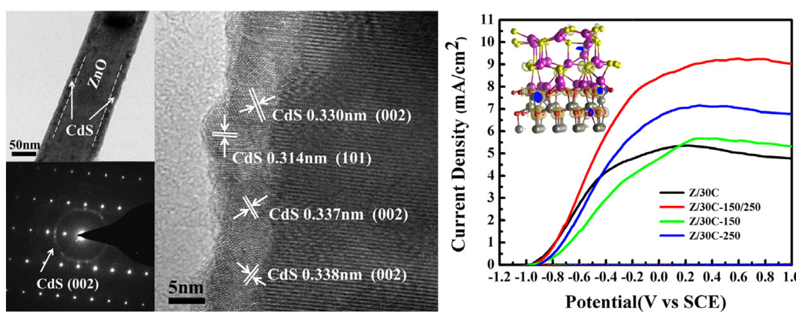
Qun Nie [a,b,1], Liang Yang [b,1], Chang Cao [a,b], Yamei Zeng [b], Guizhen Wang [b], Caizhuang Wang [c], Shiwei Lin [a,b,*]

[a] State Key Laboratory of Marine Resource Utilization in South China Sea, Hainan University, Haikou 570228, PR China
[b] College of Materials and Chemical Engineering, Hainan University, Haikou 570228, PR China
[c] Ames Laboratory-U. S. Department of Energy, and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA

HIGHLIGHTS

- A facile low-temperature thermal treatment is proposed for interface modification.
- PEC performance can be dramatically improved by the two-step annealing process.
- Interface optimization by the thermal treatment plays a key role in PEC enhancement.
- First-principles calculation supports the importance of interface modification on improving photoelectric properties.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and efficient low-temperature thermal treatment process has been demonstrated to dramatically improve the photoelectrochemical (PEC) performance of ZnO nanorod/CdS quantum dots heterostructure. The ZnO/CdS heterojunction was sequentially fabricated by atomic layer deposition, hydrothermal method and successive ionic layer adsorption-reaction method. In contrast to the traditional annealing usually conducted in muffle furnace at high temperature, a two-step low-temperature thermal treatment has been first carried out just on a hot plate at 150 °C for 10 min and then 250 °C for another 10 min, which significantly enhanced the PEC performance of the ZnO/CdS photoanodes. The optimal photocurrent density and the corresponding photoconversion efficiency can reach 9.16 mA cm^{-2} (0.4 V_{SCE}) and 4.03% under a standard simulated illumination condition (AM 1.5 G, 100 mW cm^{-2}), which improved 75% and 44% as much as those of the unheated sample. The incident photon-to-current efficiency (IPCE) is raised up to 95% at 350 nm. These are one of the best results ever reported on the similar ZnO/CdS photoanodes. Systematic PEC experiments attribute the enhancement to the optimized interface between ZnO and CdS by the thermal treatment which can promote charge carrier separation and transportation. Further theoretical calculation confirms the importance of the interface modification on improving the photoelectric properties. The two-step low-temperature thermal treatment thus presents a facile method for the design and optimization of high-performance PEC photoelectrodes.

1. Introduction

Recently, one-dimensional (1D) nanostructure arrays have attracted increased attention among various nanostructures for

* Corresponding author at: College of Materials and Chemical Engineering, Hainan University, Haikou 570228, PR China.
E-mail address: linsw@hainu.edu.cn (S. Lin).
[1] Contributed equally to this work.

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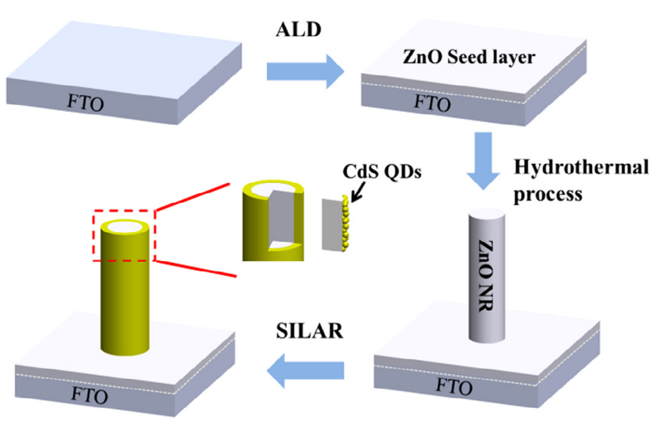
using as photoelectrodes in photoelectrochemical (PEC) cells [1–4]. The 1D nanostructure arrays, such as nanorods (NRs), nanotubes (NTs), and nanowires (NWs), not only have large specific surface areas, but also exhibit a fast electron transport pathway with a low recombination rate. Metal-oxides semiconductor based photoanodes, for instance, TiO_2 [5], ZnO [4], become the first choice as they are stable, environment-friendly and inexpensive. However, due to the wide bandgap of TiO_2 (~3.2 eV) and ZnO (~3.37 eV), they can only be active under ultraviolet irradiation. Specially, ZnO has superior electron mobility which is nearly two orders of magnitude higher than TiO_2 [6]. The higher electron mobility leads to lower recombination of photogenerated electrons and holes in ZnO, and effectively improves the quantum efficiencies of photoanodes. Thus, 1D ZnO nanostructure has a great potential for applications in PEC cells and dye-sensitized solar cells [7,8].

To solve the absorption limit under the sunlight irradiation, various methods have been reported to extend the wavelength response of ZnO to visible region, such as coupling with noble metal nanoparticles (Au, Ag) [4,9], doping metal or non-metal ions [10,11], loading co-catalyst (MoS_2) [12–14] or new type catalyst (BiOI, BiOBr, g-C_3N_4) [15–17], or depositing narrow bandgap quantum dots (QDs) such as CdS, CdSe, PbS, etc [18,19]. Among these, CdS is regarded as the most suitable sensitizer for ZnO because of the similar lattice and narrow bandgap (~2.4 eV), which could absorb more visible light and effectively separate the photogenerated electrons and holes. On the other side, CdS can be easily obtained by chemical bath deposition method. For example, ZnO/CdS [20,21], ZnO/CdS/$ZnFe_2O_4$ [22], ZnO/CdS/CdSe [18,23], ZnO/CdS/$CuInS_2$ [24], and ZnO/CdS/RGO [25] have been used as various kinds of surface modification on the photoanodes to improve the PEC performance. Besides the application of the as-prepared CdS QDs, most of the composite photoelectrodes were annealed in furnace at 400–600 °C to improve the crystalline structure under nitrogen or argon atmosphere owing to the easy oxidation of CdS [20,22,26,27]. To the best of our knowledge, however, few works have presented a low-temperature thermal treatment in atmosphere below 250 °C. Such low-temperature treatment is of great significance not only for the preparation of PEC photoelectrodes using flexible organic substrates whose melting temperatures are usually lower than 250 °C, but also for understanding the physics of interface modification to improve the PEC behavior.

In this study, we combined 1D ZnO, as the electron acceptor to facilitate charge transport, and CdS QDs, as the light absorber, to form a heterostructure photoelectrode. The 1D ZnO was synthesized by conventional hydrothermal process and CdS QDs were prepared by successive ionic layer adsorption-reaction (SILAR) method (Scheme 1). Here, we first report a two-step low-temperature thermal treatment process to optimize the interface between ZnO nanorods and CdS QDs. After the thermal treatment,



Scheme 1. Fabrication process of ZnO nanorods sensitized with CdS quantum dots.

the PEC properties of the ZnO/CdS heterojunction show a great improvement. Systematic experimental investigation as well as theoretical simulation has been conducted to demonstrate the importance of interface modification on the enhancement of PEC performance. The two-step low-temperature thermal treatment has been demonstrated to be a facile and effective method to optimize the interface of heterojunction by increasing the QDs crystallinity, improving the degree of preferential orientation of CdS grains on ZnO nanorods and optimizing the lattice match to facilitate the carrier transfer.

2. Experimental section

2.1. Fabrication of ZnO nanorods

In a typical synthesis, the 1D ZnO NRs were prepared on F-doped SnO_2 coated glass (FTO; Wuhan Geao; 10 Ω per square) by a hydrothermal process. The FTO substrate was successively washed in acetone, alcohol and deionized water for 20 min each. Comparing with the traditional sol-gel method, the uniform and controllable ZnO seed film was deposited on FTO substrate by atomic layer deposition (ALD) [5]. Deionized water and diethyl zinc (DEZ) were used as O and Zn precursors, respectively. One ALD cycle of ZnO deposition consisted of 0.2 s pulse of H_2O, 3 s exposure to H_2O, 0.03 s pulse of DEZ, 3 s exposure to DEZ and then purge with nitrogen. After deposition, the thickness of ZnO seed film formed was about 30–40 nm. Next, 0.05 M zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 0.05 M hexamethylenetetramine ($(CH_2)_6N_4$, HMT) were mixed (molar ratio = 1:1) in a beaker and magnetically stirred for 10 min. The FTO substrates covered with ZnO seed film were placed with the conductive side down into hydrothermal synthesis reactor filled with the precursor mixed above and kept at 95 °C for 4 h. The as-prepared 1D ZnO NRs were then washed with deionized water and dried by N_2.

2.2. Deposition of CdS QDs

A simple SILAR method was used to deposit CdS QDs on ZnO NRs [28]. To complete a SILAR cycle, the ZnO NRs films were successively soaked in 0.2 M $Cd(NO_3)_2$ ethanol solution for 30 s, and then in 0.2 M Na_2S solution which was made up of methanol and deionized water (V:V = 1: 1) for 30 s. The samples with 10, 20, 30, 40 cycles of CdS deposition were referred to as Z/10C, Z/20C, Z/30C and Z/40C NRs, respectively. After coating CdS QDs, ZnS was deposited on the surface of the ZnO NRs/CdS QDs to form a protective layer. Because of its wide bandgap and higher conduction-band minimum than CdS, ZnS overlayer could also weaken the photogenerated carrier recombination. The ZnO NRs/CdS QDs will have great stability and efficiency after coating a ZnS protective layer [2,29]. For the deposition of ZnS by a SILAR method, $Zn(NO_3)_2$ (0.1 M) and Na_2S (0.1 M) were acted as Zn^{2+} and S^{2-} source, respectively. The as-prepared ZnO/CdS samples were sequentially dipped in the cation and anion precursors for 2 min each and for 2 cycles. A two-step low-temperature thermal treatment was then conducted on a hot plate (IKA, RCT basic, Germany) to anneal the ZnO/CdS NRs photoelectrodes at 150 °C for 10 min and then at 250 °C for another 10 min (referred to as Z/C-150/250). For the purpose of comparison, we also heated the samples either at 150 °C for 20 min (Z/C-150) or at 250 °C for 20 min (Z/C-250) on the hot plate.

2.3. Characterization

The optical properties of the films were obtained by an UV–vis spectrometer (PURKINJE TU-1901, China) using $BaSO_4$ as a