Improving photoelectrochemical performance on quantum dots co-sensitized TiO$_2$ nanotube arrays using ZnO energy barrier by atomic layer deposition

Min Zeng [a], Xi Zeng [b], Xiange Peng [a], Zhuo Zhu [a], Jianjun Liao [a], Kai Liu [a], Guizhen Wang [a], Shiwei Lin [a,*]

[a] Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, College of Materials and Chemical Engineering, Hainan University, Haikou 570228, China
[b] College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming, 650500, China

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ABSTRACT

PbS and CdS quantum dots (QDs) have been deposited onto TiO$_2$ nanotube arrays (TNTAs) in turn via a sonication-assisted successive ionic layer adsorption and reaction method. This method could uniformly decorate TNTAs with QDs, avoiding QDs aggregation at the mouth of TiO$_2$ nanotube. The loading amounts of QDs on TNTAs could be controlled by adjusting the TNTAs length. Under one sun illumination, the QDs co-sensitized TNTAs (TNTAs/QDs) with the length of about 2.4 μm displayed the highest photocurrent of 4.32 mA cm^{-2}, which is 27 times higher than that of the bare TNTAs. Introduction of a thin ZnO energy barrier by atomic layer deposition (ALD) between the TNTAs and QDs can further improve the photocurrent of TNTAs/QDs. And the TNTAs/QDs with 10 ALD cycles of ZnO interlayer exhibits the highest photocurrent of 5.24 mA cm^{-2} and best photoconversion efficiency of 4.9%, a more than 20% enhancement over the bare TNTAs/QDs. Such enhanced photoelectrochemical performance may be ascribed to the increased amounts of QDs on the TNTAs due to the introduction of ZnO interlayer. The benefits of ALD layers play a crucial role in development and optimization of high-performance photoelectrodes in the near future.

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1. Introduction

As the increasingly serious problems of fossil resources depletion and environmental pollutions, photoelectrochemical (PEC) splitting of water into hydrogen by semiconductor materials absorbing solar energy has become one of the attractive strategies to relieve energy crisis. Among various materials used as photoelectrodes, TiO$_2$ is one of the most promising semiconductor materials, because of its high photocatalytic and photoelectrical activities [1]. Since the discovery of breaking down of water on a TiO$_2$ electrode by Fujishima and Honda [2], a wide variety of TiO$_2$ architectures have been fabricated, including nanoparticles [3], nanotube arrays [4], hollow spheres [5], mesoporous spheres [6], hollow porous nanosheets [7], nanowires [8], nanoflowers [9], nanorods [10], and interconnected architectures [11]. Especially, the aligned one dimensional nanotubes demonstrate superior optical absorption and efficient photoexcited charge transport properties due to its unidirectional electric channel and decreased grain boundaries [12,13]. However, pure TiO$_2$ was rarely used as photoelectrode, since its poor photocatalytic activity in the visible light region limited by its inherent large band gap of 3.2 eV. Aiming at this issue, tremendous efforts have been made. One effective strategy is transition metal or nonmetal element doping [10,14]. While the other effective way is sensitizing TiO$_2$ with smaller band-gap materials, such as dyes or semiconductor quantum dots (QDs) [15,16].

Herein, PbS/CdS was chosen as co-sensitizers to modify the TiO$_2$ nanotube arrays (TNTAs). Although PbS and CdS co-sensitized TiO$_2$ photoelectrode has been extensively studied, researchers are still seeking for new preparation methods [17] or constructing heterojunctions [18] to further improve the PEC performance. Moreover, the low coverage of QDs sensitizer was found to account for the low efficiency [19]. Therefore, an important key to improve PEC performance is to elevate the loading of QDs on TNTAs. One commonly utilized way of depositing QDs is solution method such as chemical bath deposition [20], cyclic voltammetry electrochemical deposition [21] and successive ionic layer adsorption and reaction [22], where the amounts of QDs can be improved by increasing the deposition cycles. Much recently, the amounts of QDs was further increased by improving the hydrophilicity of TiO$_2$ [23].

* Corresponding author. Tel.: +86898 66290185; fax: +86 898 66290185.
    E-mail address: linsw@hainu.edu.cn (S. Lin).

In this paper, we applied ZnO layer by atomic layer deposition (ALD) to adjust the QDs loading amounts on the TNTAs with different lengths. In most previous reports, however, the ZnO layer was used as an inherent energy barrier in dye-sensitized solar cells or QDs-sensitized solar cells to suppress charge recombination at the electrode/electrolyte interface. And it was mostly prepared by a thermal chemical vapor deposition [24], successive ionic layer adsorption and reaction [25], RF magnetron sputtering [26], sol–gel [27], precipitation [28], hydrothermal [29], and ultrasonic spray pyrolysis methods [30], but these methods cannot precisely control the thickness of ZnO. In comparison, the ALD technique in our work could prepare a uniform and conformal ZnO coating layer over the TNTAs at the nanoscale. Only 1.5 nm ZnO layer between the TNTAs and QDs, which is much thinner than those of 30 nm and even 2 μm used in the literature [30,31], was needed to apparently improve the photocurrent. Although ZnO layers deposited between sensitizer and TNTAs have been reported in solar cells [25,32,33], researchers rarely discussed the effect of ZnO thickness on the loading of QDs. We report hereby the influence of ZnO thickness on the QDs loading, microstructure variation and PEC performance.

2. Experimental

2.1. Synthesis of TiO2 nanotube arrays

Vertically oriented TNTAs were grown on Ti foils by anodic oxidation, which is similar to our previous report [21]. Briefly, the Ti foils were firstly chemical polished and ultrasonically cleaned, then biased at 25 V for 3, 5, 7 and 9 h, respectively. 0.27 M NH_4F solution consisting of deionized water and glycerol (1,2,3-propanetriol) with volumetric ratio of 1:1 was used as electrolyte. The anodized samples were ultrasonically cleaned in alcohol for 3 min to remove the surface debris. The as-anodized TNATs were then annealed at 450 °C for 3 h and 45 min with a heating rate of 2 °C min^{-1} under air ambient.

2.2. Preparation of ZnO barrier layer on TNTAs

ZnO thin layers were deposited on TNTAs by ALD at 145 °C in a hot-wall flow-type ALD reactor, using diethyl zinc (DEZ) and deionized water as the Zn and O precursors, respectively. Nitrogen was used as a carrier and purging gas. The ALD sequence was composed of 0.03 s pulse of DEZ with 5 s exposure, 20 s purging, 0.2 s pulse of H_2O with 5 s exposure, and 20 s purging, which was referred to as one ALD cycle. The growth rate per cycle was about 1.5 Å/cycle, calculated by High-resolution transmission electron microscopy (HRTEM) analysis. Various ZnO ALD cycles n (n = 0, 5, 10, 30 and 70) were carried out on the surface of TNTAs. The TNTAs electrode deposited with n cycles ZnO was denoted as TNTAs/nc ZnO.

2.3. TNTAs/nc ZnO decorated with PbS and CdS QDs

CdS and PbS QDs were loaded over the TNTAs/nc ZnO by successive ionic layer adsorption and reaction method. Typically, the process involved dipping the substrates into a 0.02 M Pb(NO$_3$)$_2$ methanol solution for 2 min, simultaneously conducting sonication for 15 s, rinsed with methanol and then dipped in a 0.02 M Na2S solution of methanol and deionized water (V:V = 1:1) for another 2 min, simultaneously sonicated for 15 s, followed by rinsing it with methanol. All these processes formed one cycle and repeated for 5 times to obtain an appropriate coverage on the surface of TNTAs/nc ZnO. Successively, the TNTAs/nc ZnO loaded with PbS QDs was sensitized with CdS QDs. The precursors were a 0.05 M Cd(NO$_3$)$_2$ ethanol solution and a 0.05 M Na2S solution which was the same as above. The procedures of CdS sensitization were the same as for PbS QDs except for the precursors and also repeated for 5 times. Finally,

the PbS and CdS co-sensitized TNTAs/nc ZnO electrode was covered with 2 cycles ZnS protecting layer to reduce electron recombination [34]. The photoelectrode was referred to as TNTAs/nc ZnO/QDs. In addition, we also prepared another configuration TNTAs/QDs/nc ZnO, whereas no improved photocurrent was achieved.

2.4. Characterization

The morphology of the films were imaged using a field emission scanning electron microscopy (FESEM, FEI Nova nanoSEM 450) equipped with a detector for energy dispersive spectroscopy (EDS). High-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100) was carried out to study the distribution of QDs and the thickness of ZnO layer. The crystalline structures of the films were investigated through an X-ray diffractometer with Cu Kα (XRD, Bruker D8). The absorbance and reflectance spectra were recorded using a spectrophotometer (UV, Purkinje TU-1901) with BaSO$_4$ as a reference.

2.5. Photoelectrochemical measurements

The photoelectrochemical (PEC) performance of the photoanode was characterized by an electrochemical workstation (Zennium, Zahner) in a three-electrode electrochemical cell. The working electrode was mounted in a stainless steel electrode holder with a specific area of 1 cm^2 measured. A Pt wire and a saturated calomel electrode (SCE) were the counter and reference electrodes, respectively. 0.2 M Na_2SO_3 and 0.1 M Na_2S aqueous solution with a volumetric ratio of 1:1 (pH 12.2) served as the supporting electrolyte throughout all the experiments. The linear sweep voltammograms (LSV) were measured in a potential range from −1.1 to +1 V (vs. SCE) both in dark and under one sun illumination (AM 1.5 G, 100 mW cm^{-2}), produced by a 500 W xenon lamp equipped with an AM 1.5 filter (Aulight, CEL-S500). The light intensity was measured with a digital power meter. The transient photoresponse was obtained under a white LED lamp (dominant wavelength: 565 ± 112 nm), and the light intensity was 80 mW cm^{-2}. The electrochemical impedance spectroscopy (EIS) measurement was carried out at open circuit voltage under one sun illumination, with a 10 mV amplitude perturbation and the frequency range was 100 kHz to 100 mHz conditions. Mott-Schottky analysis was conducted from −1 V (vs. SCE) to 0.8 V and with a scan rate of 30 mV s^{-1} in the dark. The frequency and amplitude perturbation were 1 kHz and 10 mV, respectively. All PEC tests were performed under ambient conditions.

3. Results and discussion

Fig. 1 depicts the optical properties and PEC performance of QDs sensitized TNTAs with various anodization times. For the TNTAs anodized for 3, 5, 7, 9 h, the nanotubes lengths are about 1.5, 1.7, 2.4, 2.8 μm, respectively, as determined by SEM images (not shown here). The UV–vis diffuse reflection spectra of the TNTAs before and after QDs deposition are displayed in Fig. 1(a). The peaks in the visible region for the pure TNTAs are due to the incorporated fluorine in the TiO$_2$ film [35]. QDs deposited on TNTAs enhance their visible-light absorption. The absorption edges of the TNTAs/QDs electrodes show an apparent red-shift relative to the corresponding pristine TNTAs. Furthermore, with increasing anodization time, the absorption edges of the electrodes before and after QDs assembly both show a red-shift with increasing anodization time.

Fig. 1(b) indicates the LSV curves of the TNTAs/QDs with various anodization times under one sun illumination and in dark. The dark currents were found to be negligible. The photocurrent density increases with increasing anodization time up to 7 h, which is probably ascribed to the increased photons harvested by more