



Photoelectrochemical performance of cadmium sulfide quantum dots modified titania nanotube arrays



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ARTICLE INFO

Article history:

Received 6 September 2015
Received in revised form 29 October 2015
Accepted 24 November 2015
Available online 28 November 2015

Keywords:

Cadmium sulfide
Quantum dots
Titania nanotube arrays
Photoelectrochemistry
Photocurrent response

ABSTRACT

The cadmium sulfide quantum dots modified titania nanotube arrays (CdS QDs/TiO₂ NTAs) were prepared through a sequential sonication-assisted chemical bath deposition (CBD) process. The morphology and microstructure of CdS QDs/TiO₂ NTAs were characterized using scanning electron microscopy, transmission electron microscopy, X-ray diffraction spectroscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy and UV–vis diffuse reflectance spectroscopy. The photoelectrochemical performance of CdS QDs/TiO₂ NTAs was investigated under solar light illumination. The affecting parameters were studied including the nanotube length of TiO₂ NTAs, CBD cycles of CdS QDs and the annealing treatment of CdS QDs/TiO₂ NTAs. CdS QDs synthesized through 8 CBD cycles could uniformly cover on the tube walls of TiO₂ NTAs to form unique CdS QDs/TiO₂ NTAs with an open pore mouth. The appropriate annealing treatment at 400 °C for 60 min in N₂ atmosphere could improve the crystallinity of CdS QDs, and accordingly enhance the photovoltaic properties of CdS QDs/TiO₂ NTAs. Significantly, the nanotube length was the predominant factor affecting photoelectrochemical performance of CdS QDs/TiO₂ NTAs. The unannealed CdS QDs/TiO₂ NTAs with an optimal nanotube length of 12 μm achieved a short-circuit photocurrent density of 4.37 mA cm⁻², an open circuit photovoltage of 1.10 V and a top photoconversion efficiency of 3.56%. Comparatively, the annealed CdS QDs/TiO₂ NTAs with an optimal nanotube length of 4 μm achieved a short-circuit photocurrent density of 6.31 mA cm⁻², an open circuit photovoltage of 1.23 V and a top photoconversion efficiency of 4.18%. The suitable modification of crystalline CdS QDs could well improve the photoelectrochemical performance of TiO₂ NTAs photoanode.

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1. Introduction

Vertically oriented TiO₂ nanotube arrays (NTAs) prepared by the electrochemical anodization of titanium have received considerable attention in the photochemical and electrochemical fields [1–7]. The highly ordered TiO₂ NTAs offer large surface as active reaction sites and feature directive charge transport along the nanotube wall, which are beneficial to efficient photoelectrochemical application [8–11]. The nanoarray structure usually enables to improve photoelectrochemical performance of electrode materials [12–21]. However, it is well known that TiO₂ is n-type semiconductor material and has a wide bandgap of 3.0 eV for rutile phases and for 3.2 eV anatase phases, respectively. The properties restrict its utilization of the solar energy in limited UV region, which only accounts for only 4–5% of total solar energy [22]. Accordingly, great efforts have been made to shift the bandgap of TiO₂. TiO₂ is photosensitized with organic dyes to act as visible light absorbers. The highest efficiency of the dye sensitized solar cell has reached 11% [22]. In addition, the sensitization of TiO₂

can be accomplished through modifying with quantum dots (QDs) of narrow bandgap semiconductors, such as CdS, CdSe, PbS and Ag₂S, which can absorb light in the visible region [23–26]. These semiconductor QDs have large extinction coefficients and multiple electron–hole pairs per photon [27], which are contributive to a high photo-to-electrical conversion efficiency [28]. CdS semiconductor has a suitable bandgap of 2.42 eV which matches well with the solar visible spectrum. The bandgap of CdS QDs can be further modulated simply by controlling the sizes.

The photovoltaic properties of QDs sensitized TiO₂ photoanode in the energy conversion are affected by the light absorption and the charge transport at the interfacial layer between QDs and TiO₂. Any structural defect in the QDs, as well as mismatch between TiO₂ and QDs, can inhibit the efficient transfer of photogenerated electrons. The photovoltaic properties of CdS QDs sensitized TiO₂ NTAs photoelectrodes have been fully reported [29–32]. However, the previous research work mostly focused on the fixed nanotube length of TiO₂ NTAs to investigate the photoelectrochemical performance of CdS QDs/TiO₂ NTAs [33,34]. The microstructure correlation between TiO₂ NTAs and CdS QDs was seldom investigated. It is believed that the nanotube length of TiO₂ NTAs and the loading amount of CdS QDs could affect photovoltaic properties of CdS QDs/TiO₂ NTAs. The appropriate

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annealing treatment is also able to enhance the photoconversion efficiency of CdS QDs/TiO₂ NTAs.

In this study, the microstructure correlation between TiO₂ NTAs and CdS QDs was focused to investigate photoelectrochemical performance of the CdS QDs/TiO₂ NTAs. The nanotube length and microstructure of TiO₂ NTAs were controlled by adjusting the anodization parameters. A sequential sonication-assisted CBD process was used as a feasible method to introduce CdS QDs into TiO₂ NTAs with different nanotube length. The loading mass and microstructure of CdS QDs were controlled by adjusting the CBD cycles. The well-designed CdS QDs/TiO₂ NTA photoelectrode was obtained by optimizing the nanotube length of TiO₂ NTAs in relevance with the loading mass and annealing treatment of CdS QDs. The photocurrent response and photoconversion efficiency of CdS QDs/TiO₂ NTAs were expected to be improved by controlling nanotube length, CBD cycles and annealing treatment.

2. Experimental section

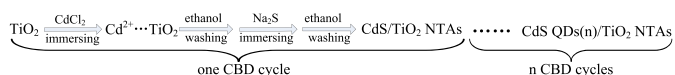
2.1. Materials

Titanium foil (Ti, 0.1 mm thickness, 99.6% purity, Good fellow), cadmium chloride (CdCl₂, 99.0%, Kanto Chemical Co., Ltd.), ammonium fluoride (NH₄F, 99%, Sigma-Aldrich), sodium sulfide (Na₂S, 99.0%, Sigma-Aldrich), and ethylene glycol (EG, 99.0%, Sinopharm Chemical Reagent Co., Ltd.) were used as received.

2.2. Synthesis of CdS QDs/TiO₂ NTAs

TiO₂ NTAs were synthesized through the electrochemical anodization process in a two-electrode configuration using a cathode of platinum (Pt) foil and an anode of Ti foil, which was ultrasonically cleaned with acetone, deionized water and ethanol sequentially. The short TiO₂ NTAs with a tube length of 1 μm were fabricated at 30 V for 2 h at 25 °C using water solution with 0.5 M H₃PO₄, 0.15 M HF and 8.0 M EG. Alternatively, the long TiO₂ NTAs a tube length of 4, 12 and 25 μm were fabricated at 60 V for 1 h, 2 h, and 5 h at 25 °C using EG solution with 0.07 M NH₄F and 0.5 M H₂O. The anodic TiO₂ samples were crystallized through a two-stepped annealing process in an air environment, which involved 300 °C for 30 min and then 450 °C for 2 h with a programming rate of 5 °C min⁻¹.

CdS QDs/TiO₂ NTAs were synthesized by depositing CdS QDs on crystalline TiO₂ NTAs through a sequential sonication-assisted CBD process [16]. The following schematic diagram illustrated the preparation process of CdS QDs(n)/TiO₂ NTAs.



Typically, the bare TiO₂ NTAs were immersed in 0.2 M CdCl₂ ethanol solution at 50 °C for 5 min and rinsed sufficiently with ethanol. It was then dipped in a 0.2 M Na₂S methanol solution for 5 min and rinsed sufficiently with ethanol again. Such an immersing procedure was denoted as one CBD cycle. The CdS QDs could be formed through 3, 5, 8, 10 CBD cycles. The obtained CdS QDs(n)/TiO₂ NTAs with n CBD cycles were then treated at a controlled temperature of 300, 400 or 500 °C for 0, 30, 60, or 90 min in N₂ atmosphere. To avoid the oxidation of CdS during a directly annealing process, the as-prepared CdS QDs/TiO₂ NTAs conducted the drying pretreatment at 50 °C for 2 h in a vacuum condition to remove air and water contained in the nanotubes, and then conducted the annealing treatment in N₂ atmosphere.

2.3. Characterization and measurement

The morphological characterization and elemental analysis were conducted using a field emission scanning electron microscope (SEM,

JSM-6700F, JEOL. Ltd., Japan), transmission electron microscope (TEM, JEM-2100, JEOL. Ltd., Japan) and energy dispersive X-ray (EDX) spectroscopy. The crystalline structure characterization was conducted using X-ray diffraction (XRD, D/MAX 2500 V, Rigaku Corporation, Japan). UV-visible spectrum was conducted for absorption bandgap analysis using UV-visible diffuse reflectance spectroscopy (UV-vis DRS) equipped with a SA-13.1 diffuse reflector (S-4100, Scinco Co., Ltd., South Korea).

The photoelectrochemical measurement was carried out in a 100 mL quartz cell using the electrochemical workstation (CHI760, CH Instruments, USA) equipped with a three-electrode configuration, which included of a working electrode of CdS QDs/TiO₂ NTAs, a counter electrode of Pt foil and Ag/AgCl reference electrode. The electrolyte was 1.0 M Na₂S aqueous solution. The working electrodes conducted a potential sweep from -1.3 to 0 V at the rate of 10 mV s⁻¹, which were illuminated by a simulated solar light source with an intensity of 100 mW cm⁻².

3. Results and discussion

3.1. Morphological characterization

The SEM and TEM measurements of TiO₂ NTAs and CdS QDs/TiO₂ NTAs were conducted for morphological microstructure characterization (see Fig. 1). The cross-section view images show that TiO₂ NTAs exhibited the different tube length of 1, 4, 12 and 25 μm, respectively. The top-surface view images show that short TiO₂ NTAs had an independent tube wall structure and long TiO₂ NTAs had a tightly connected tube wall structure. Both of them revealed regularly arranged tube alignment structure (see Fig. 1(A–F)). Fig. 1(G–J) shows top-surface view and cross-section view images of the CdS QDs/TiO₂ NTAs, which were prepared by 8 and 10 CBD cycles of CdS on TiO₂ NTAs. In view of CdS QDs(8)/TiO₂ NTAs, the tube walls of TiO₂ NTAs were extensively covered with uniform CdS QDs. Its pore mouth still kept open. Comparatively in view of CdS QDs(10)/TiO₂ NTAs, the pore mouth of TiO₂ NTAs was completely sealed by CdS QDs. It indicates that the deposition amount of CdS QDs could be well adjusted by controlling CBD cycles. The increase of CBD cycles of CdS QDs could cause the decrease of TiO₂ nanotube diameter and gradually covered all nanotube pores. The excessive deposition of CdS QDs resulted in the complete block of TiO₂ nanotubes eventually. TEM image shows that the CdS QDs could well attach on TiO₂ nanotube walls and keep a uniform dispersion characteristic (see Fig. 1(K)). So, the nanotube length and microstructure of TiO₂ NTAs could be well controlled by simply adjusting the anodization parameters. The sequential sonication-assisted CBD process was proven as a feasible method to introduce CdS QDs into TiO₂ NTAs with different nanotube length. The loading mass and microstructure of CdS QDs could be well controlled by simply adjusting the CBD cycles.

The EDX spectroscopy measurement of the CdS QDs/TiO₂ NTAs was carried out to identify the element composition (see Fig. 2). The characteristic peaks at 4.52, 0.52, 3.78, and 3.14 keV were attributed to the elements of Ti, O, Cd, and S, respectively. The quantitative analysis result reveals that the atomic ratio of Cd to S was close to 1. It indicates that CdS QDs was well formed and deposited on the TiO₂ NTAs substrate. The atomic ratio of Cd to Ti was increased from 0.036 for CdS QDs(3)/TiO₂ NTAs, 0.094 for CdS QDs(8)/TiO₂ NTAs to 0.103 for CdS QDs(10)/TiO₂ NTAs, presenting the more loading amount of CdS QDs of CdS QDs(n)/TiO₂ NTAs with an increase of CBD cycles.

The XRD spectroscopy measurement of TiO₂ NTAs and CdS QDs/TiO₂ NTAs was carried out to analyze the crystal phase. Fig. 3(A) shows XRD patterns of TiO₂ NTAs and CdS QDs/TiO₂ NTAs before and after annealing treatment at 400 °C for 60 min. The characteristic diffraction peaks appeared at 2θ = 25.4, 37.8, and 48.18 were regarded as an attributive indicator of anatase TiO₂ (see curve a). The new peaks emerged at 2θ = 26.55, 30.75, 44.04, and 52.16 were corresponding to the (002), (101), (110), and (112) crystal planes of CdS, respectively (see curve b and c). Fig. 3(B) shows the magnified XRD patterns of CdS QDs/TiO₂

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