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RAPID COMMUNICATION

Enhanced photoelectrochemical and photocatalytic performance of TiO_2 nanorod arrays/CdS quantum dots by coating TiO_2 through atomic layer deposition

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Abstract
TiO_2 nanorod arrays/CdS quantum dots/ALD-TiO_2 nanostructures were fabricated as photocatalyst and its related properties were investigated comprehensively. Enhanced photoelectrochmical properties are observed and the degradation rate of methyl orange under visible light is enhanced by *ca.*156% compared to the nanorod arrays/CdS quantum dots, which is due to the enhancement of the separation of electrons-holes induced by the introduction of the ultrathin TiO_2 top layer. Moreover, the stability of the TiO_2 nanorod arrays/CdS quantum dots is increased by the ALD-TiO_2 coating. These results suggest that the design of TiO_2 nanorod arrays/CdS quantum dots/ALD-TiO_2 nanostructures gives a promising strategy to improve the photoelectrochemical and photocatalytic properties in solar energy conversion, along with reduced photo-corrosion in the semiconductor-semiconductor heterojunction.

Introduction

As one of the environmentally friendly photocatalytic materials, titanium dioxide (TiO_2) has been studied widely

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since the investigation of the photocatalytic splitting of water was performed by Honda in 1972.[1] Compared with WO_3, Fe_2O_3, and ZnO, TiO_2 is the most competitive candidate due to its low-cost, photo-stability, chemical inertness, nontoxicity as well as good photocatalytic activity.[2] However, widespread applications of TiO_2 are limited owing to its wide band gap, that is, *ca.* 3.2 eV and 3.0 eV for anatase and rutile, respectively, which suggests that the photoresponse of TiO_2 is confined within the ultraviolet (UV) light range (i.e., using less than *ca.* 5% of the solar energy).[3] To enhance the energy conversion efficiency, one of the strategies is to extend its photoresponse activity to the visible light, which is the main component of the solar spectrum (*ca.*45%).[4] Accordingly, various tries/attempts have been carried out such as doping with impurities,[5] coupling with dyes, [6] and sensitizing with other semiconductors, [7]. Recently, narrow band gap semiconductors such as PbS,[8] CdSe,[9] ZnS,[10] and CdS, [11] have been successfully utilized as a sensitizer for TiO_2 nanostructures, which exhibits excellent photoresponse enhancement in visible light. For instance, CdS has a band gap of *ca.* 2.5 eV with its conduction band more negative than that of TiO_2.[12] Under irradiation of the visible light, the electrons generated in CdS could be transferred to TiO_2, thus the photon-induced electrons and holes are confined in TiO_2 and CdS, respectively. CdS quantum dots (QDs) have advantages of high extinction coefficient, good stability and spectral tunability。More importantly, it can be grown directly on TiO_2 by electrodeposition,[13] chemical bath deposition (CBD),[14] Chemical Vapor Deposition[15] and successive ion layer adsorption and reaction (SILAR).[11] The sole disadvantage of CdS QDs is that the exited electrons and holes of CdS QDs can be trapped by the surface states in ambient conditions, leading to the degradation of photostability and photocatalytic efficiency. Hence, it is essential to suppress the recombination of electrons and holes, and thus to enhance the photostability of CdS and increase the photocatalytic efficiency.[16] One of the effective methods to decrease the surface recombination velocity is to deposit a surface coating on CdS QDs.[17] Atomic layer deposition (ALD) is a coating technique which can passivate the surface states to decrease the surface recombination velocity.[18] Its layer-by-layer deposition allows for highly conformal coating even on the dense and rough surface of certain nanostructures. It is noteworthy that ALD has had success in preventing anodic corrosion in other nanostructured system.[19,20]

On the other hand, the fabrication of one dimensional (1-D) nanostructures, such as nanotubes, nanowires, nanobelts and nanorods, has been proved to be a promising way to enhance the solar energy conversion efficiency of TiO_2 since some desirable characteristics, such as large surface areas, longer charge carrier diffusion lengths and low reflectivity, can be obtained readily.[21] Additionally, 1-D nanostructures can be grown by the oblique angle deposition (OAD)[22], which is a simple way to produce large area, uniformed and aligned nanorod arrays (NRAs) with controlled porosity.

In this work, a TiO_2 NRAs/CdS QDs/ALD-TiO_2 heterojunction is reported. The TiO_2 NRAs were fabricated by oblique angle deposition (OAD) technique, while the CdS QDs and the ultra-thin TiO_2 film were deposited successively by using SILAR and ALD, respectively. Excellent photocatalytic property and stability were achieved in this structure, which predicts potential application in solar energy conversion.

Experimental

TiO_2 nanorod arrays fabrication

Ti NRAs were deposited on planar Si substrates and transparent F-doped SnO_2 (FTO) substrates (20 Ω per square) by the oblique angle deposition technique (OAD) described elsewhere,[23] and Si substrates were used for scanning electron microscopy (SEM) and Raman measurements. Prior to deposition, the substrates were ultrasonically cleaned sequentially in acetone and ethanol 15 min each, and then rinsed in deionized(DI) water for another 5 min. The system was pumped down to a vacuum level of 4×10^{-8} Torr, and then Ti thin film was deposited on the substrate at a deposition rate of 0.5 nm s^{-1}, of which the thickness was monitored by a quartz crystal microbalance. To produce films with aligned Ti nanorods, the incident beam of the Ti flux was set at *ca.* 85° from the normal of the substrate at room temperature. After which the Ti films were oxidized in a tube furnace in order to obtain TiO_2 NRAs. The Ti films were heated up to 450 °C for 2 h at a ramp of 5 °C min^{-1} at atmosphere so that the resultants are of crystalline with good photocatalytic active.

CdS QDs deposition on TiO_2 nanorod arrays

CdS QDs were deposited on TiO_2 nanorods through a Successive Ionic Layer Adsorption and Reaction (SILAR) method with slight modification as previously reported.[11] Briefly, the TiO_2 NRAs substrates were successively exposed to $Cd(Ac)_2$ and Na_2S solutions to deposit CdS nanocrystallites. The TiO_2 NRAs were immersed in $Cd(Ac)_2$ (0.05 M) solution for 30 s, followed by rinsing with DI water and then immersed in Na_2S solution (0.05 M) for another 30 s, after which the resultant was rinsed clearly with DI water. This SILAR process was repeated for several times until the desired thickness of CdS nanocrystallites was achieved.

ALD of TiO_2

ALD of TiO_2 was performed in a custom-built reactor, and the substrate temperature was maintained at 150 °C during the ALD process. The precursor, four dimethylamino titanium, was kept at 110 °C and water at 40 °C. N_2 was used as carrier and purge gas. To ensure sufficient penetration of the precursors into the whole nanorods, a soak step was employed, which is similar to that adopted in previous report.[24] First, four dimethylamino titanium was pulsed for 250 ms and allowed to soak for additional 5 s, and then, the chamber was evacuated for 20 s (purge step). Next, H_2O was pulsed for 5 ms and allowed to soak for additional 3 s, followed by a 20 s purge step. This process was marked one ALD cycle, and repeated until the desired deposition of TiO_2 was fulfilled.