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How CdS nanoparticles can influence TiO_2 nanotube arrays in solar energy applications?

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ABSTRACT

In this study, titanium dioxide (TiO_2) nanotube array (TNA) films are fabricated via anodization of titanium (Ti) sheet. After annealing, the films consisted of well ordered, vertically oriented TNAs of 125 ± 6 nm diameter, 38 ± 3 nm wall thickness, and 2.9 ± 0.3 μm in length. Cadmium sulfide (CdS) nanoparticles are deposited on the synthesized TNAs by sequential-chemical bath deposition (S-CBD) method with different immersion cycle (n) to produce heterogeneous TNA/CdS-n (n = 10, 20 and 30) nanostructures. UV–visible absorption spectra of the samples revealed that the absorption edge of CdS modified TNAs was shifted to a higher wavelength with respect to the pure TNAs indicating band gap reduction of the TNA/CdS-n. Photocurrent response of the samples was changed with n, and the maximum photocurrent density (at steady state) of 28 ± 1 mA/cm^2 (or 70 ± 2 mA/W) was obtained for the TNA/CdS-20 photoanode which is about 30 times higher than one for the pure TNA under similar condition.

1. Introduction

Increasing human population and industrialization, global warming and ozone layer depletion a result of fossil fuels consumption are among major challenges for scientists, technologists and policy makers. Moreover, the rapid growth of many developing economies, the need for both clean and renewable sources of energy is unavoidable. One of the most interesting options is the wide-scale utilization of hydrogen (H_2) as a clean fuel and recyclable energy carrier [1]. Unfortunately, up to now, commercial H_2 production is mostly based on use of fossil fuels, leading to large CO_2 releases resulted in global warming. To reduce this problem, H_2 gas generated from water in solar radiation as a renewable energy sources such as H_2 production under photocatalytic water splitting over nanostructures has attracted many attentions in recent years [2,3].

The most well-known scientific contribution that triggered the development of this method was pioneered by Fujishima and Honda [4], describing photocatalytic water splitting in a photoelectrochemical (PEC) cell using a TiO_2 electrode. Up to now, many researchers have investigated water photoelectrolysis using various forms of semiconductors such as particulate [5,6] or thin films [7] photoanodes, which is interesting and also a challenging topic currently. But there are limited studies on detailed understanding of PEC measurements.

One of the semiconductors which have been extensively used in solar and PEC cells is Titanium dioxide [8–10]. Photoelectrochemical properties of nanostructured TiO_2 photoanodes have been studied intensively due to its excellent photochemical stability, well-known wide band gap semiconducting nature and high surface area of interface with electrolyte [11,12]. Since the first report on fabrication of highly ordered TiO_2 nanotube arrays (TNAs) by anodic oxidation as a controllable and cost-effective method in HF aqueous electrolyte in 2001 [13], a large number of researches have been published to improve the geometry of titania nanotubular structures for hydrogen sensing, photoelectrolysis, photocatalysis and dye-sensitized solar cells [8,14,15].

But, TiO_2 films can absorb only a very small UV portion (approximately 4%) of whole solar energy spectrum arriving at the earth's surface. For obtaining a more efficient light harvesting of TiO_2 nanotube, efforts such as doping with other elements (like Ta [16], Ni [17] and N [18,19]) and surface modification with narrow band gap semiconductors (e.g. CdS [20,21], Fe_2O_3 [22], PbS [23], ZnS [24], Ag_2S [25]) have been performed leading to successful increase in their photoresponse under visible light.

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Table 1
A brief review of the CdS synthesis methods on the TNA films and the obtained photoresponses.

CdS nanostructure	CdS growth method	Normalized photocurrent (mA/W)	Wavelength (nm)	Electrolyte	Bias voltage (V)[a]	Ref.
Nanoparticle (10–20 nm)	Electrodeposition	~25	>400	1 M Na_2S	0.5	[28]
Thin layer	Electrodeposition	~100	Xe lamp	1 M Na_2S	0.2	[29]
Nanoparticle (~10 nm)	S-CBD	48	Xe lamp	1 M Na_2S	0.2	[30]
Nanoparticle (2–10 nm)	S-CBD	56.5	>400	1 M Na_2S	0.0	[31]
Nanoparticle (~10 nm)	S-CBD	14.3	>300	0.1 M Na_2S	−0.4	[32]
Nanoparticle (~50 nm)	Sonoelectrodeposition	32	>400	1 M Na_2S	0.5	[33]
Quantum dot (~5 nm)	Sonoelectrodeposition	2.0 mA/cm^2[b]	>420	0.5 M Na_2S	0.0	[34]
Quantum dot (~5 nm)	Solvothermal	5.7 mA/cm^2[b]	>420	0.1 M Na_2S	0.0	[35]
Quantum dot (5–10 nm)	S-CBD	14.6	Solar simulator	0.5 M Na_2S; 2 M S; 0.2 M KCl	0.0	[36]
Nanoparticle	Sonication-assisted; S-CBD	41.6	Solar simulator	0.5 M Na_2S; 2 M S; 0.2 M KCl	0.0	[26]
Quantum dot (5.6 nm)	Electrostatic attractive interactions	~12 $\mu A/cm^2$[b]	>420	0.1 M Na_2SO_4	0.0	[37]
Nanoparticle (~30–50 nm)	S-CBD	70 ± 2	Xe lamp	0.1 M Na_2S	0.1	This work

[a] Bias voltage was measured vs. Ag/AgCl electrode.
[b] No light intensity (with unit of W/cm^2) was mentioned.

Among the semiconducting surface modifiers, CdS (with $E_g \sim 2.4$ eV) is more attractive because of its low cost and simple preparation process. Recent studies on the PEC properties of the CdS modified TNA are summarized in Table 1. Among the various CdS synthesis methods, S-CBD as a solution-based method due its low cost was attended by other researchers [26,27].

In this work, free-standing TNA films have been prepared by anodic oxidation of a Ti foil in NH_4F organic electrolyte. Subsequently, the TNA films have been modified with various amounts of CdS nanoparticles using sequential-chemical bath deposition (S-CBD). The optical properties, crystalline structure and surface chemical state of the annealed TNA films have been determined using appropriate analytical techniques. In addition, a comprehensive study on electrochemical and photoelectrochemical properties of the CdS modified TNAs has been performed for further understanding the function of CdS for the first time. Moreover, an optimum amount of CdS immersion cycle number was determined leading to maximum photocurrent density. A higher photoresponse of the TNA/CdS is accomplished as compared to other published reports by using simillar S-CBD method (see Table 1 for details). Furthermore, the effect of CdS deposition process cycles on trap state and photovoltage variation of TNA/CdS films has been also investigated.

2. Materials and methods

Vertically oriented TiO_2 nanotube array films have been synthesized by using two-step anodization of titanium sheets (99.5% purity, 0.5 mm thickness) in electrolyte solution contained deionized (DI) water and ethylene glycol with ratio 10:90 with 0.1 M NH_4F and small amount of 1 M H_3PO_4 (for reducing the pH to 5.6) [25]. The anodization was carried out at 60 V for 200 min (80 min for first step and 120 min for second step). During the anodization, samples were sonicated for about 30 s between the steps. Crystalline TNAs were formed by annealing the anodized Ti sheet in air at 500 °C for 80 min with heating rate of about 10 °C min^{-1} [38]. TiO_2 particulate films (PF) have been also prepared by TiO_2 nanoparticle paste4SHARIFSOLAR, PST-20T, with the average size of 30 nm) by doctor blade method. Then, the PFs have been annealed in 500 °C for 80 min for comparision. The average thicknesses of the PFs were about ~50 μm.

CdS nanoparticles were deposited on surface on the synthesized TNAs by S-CBD method using the following procedure: The samples were successively immersed in four different beakers for 20 s each; the first beaker contained 0.1 M $Cd(NO_3)_2$ aqueous solution, another contained 0.1 M Na_2S, and the other two contained distilled water to rinse the samples from the excess of each precursor solution. The immersion cycle was repeated for different cycles (n) to synthesized TNA/CdS-n and PF/CdS-n (n = 10, 20, 30). After each rinsing, the samples washed out with DI water to remove loosely bounded CdS and after several cycles, the color of the film became a strong yellow to orange as also observed by other researchers [26,27].

The morphology of the prepared films and their surface chemical composition were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi-S-4160) and X-ray photoelectron spectroscopy (XPS), using monochromatic AlK_α radiation source (1486.6 eV), respectively. All binding energy values were calibrated by fixing the C(1s) core level to the 284.6 eV. All of the peaks were deconvoluted using SDP software (version 4.1) with 80% Gaussian–20% Lorentzian peak fitting. The accuracy in binding energy measurements was ±0.1 eV. The elemental composition of the nanotube array films is also analyzed by Energy Dispersive X-Ray Spectroscopy (EDS, Philips XL-30 ESEM). Moreover, optical absorption spectra of the samples were investigated by UV–visible diffuse reflectance spectroscopy (DRS) from 200 to 1000 nm wavelength with resolution of 1 nm. X-ray diffraction (XRD) analysis with CuK_α radiation source (λ = 1.5410 Å), was also employed to determine crystallinity and phase formation of the annealed samples.

PEC properties of the synthesized TNA/CdS-n thin film photoanodes such as photocurrent density response (J) and open circuit voltage (V_{oc}) were studied using 0.1 M Na_2S (pH = 13.2) solution as electrolyte. It is well-known that Na_2S electrolyte solution is an efficient hole scavenger for CdS in which the electrodes are stable [28,39]. All PEC measurements were carried out using three-electrode configuration galvanostat/potentiostat (Autolab PGSTAT302) with a Pt counter electrode and Ag/AgCl reference electrode. The working electrode (TNA/CdS-n thin film photoanodes) was illuminated with solar like light source (Xenon short arc lamp (OSRAM 5000 W HBM/OFR)) during a voltage sweep from −0.6 to 1.0 V (versus Ag/AgCl) with a constant sweep rate of 1 mV/s. To perform the measurements at room temperature, a glassy IR filter has been placed in front of the lamp. The photocurrent dynamics of the electrode was recorded according to changes in response to sudden switching on and off at constant input power of 400 mW/cm^2 at a bias voltage of 0.1 V (vs. Ag/AgCl). The incident photon to current efficiency (IPCE) of the samples was also investigated as a function of incident wavelength (λ) at constant illumination intensity.