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# Enhancing photoelectrochemical performance of $TiO_2$ nanotube arrays by CdS and $Bi_2S_3$ co-sensitization

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ABSTRACT

$TiO_2$ nanotube arrays ($TiO_2$ NTs) were prepared by a two-step anodization of titanium foils in ethylene glycol electrolyte. Then, CdS and $Bi_2S_3$ nanoparticles were deposited on $TiO_2$ NTs by an one-pot solvothermal method. The investigations of X-ray diffraction and scanning electron microscopy indicated that CdS and $Bi_2S_3$ nanoparticles grew uniformly on the surface of $TiO_2$ NTs. UV–vis absorption and photoelectrochemical measurements proved that the CdS and $Bi_2S_3$ co-sensitization significantly improved the visible light absorption, photocurrent response and photoelectrocatalytic removal of RhB and Cr(VI). In addition, the influence of $Cd^{2+}/Bi^{3+}$ concentration ratios on the photoelectrochemical performance of $TiO_2$ NTs-CdS/$Bi_2S_3$ was investigated in detail. The $TiO_2$ NTs-CdS/$Bi_2S_3$ (1:1) showed an optimal photoelectrochemical activity which could be attributed to the improvement of visible light response and charge separation derived from the coupling effect of CdS/$Bi_2S_3$ nanoparticles.



## 1. Introduction

Energy shortage and environment pollution have become two of the most serious obstacles limiting the sustainable development of human society [1–3]. Fortunately, as remarkable materials, $TiO_2$ nanotube arrays ($TiO_2$ NTs) show tremendous applications in solar cells and environmental protection due to their inherent advantages such as relatively low cost, stability, and non-toxicity [4,5]. However, owing to the large band-gap (3.2 eV), their activity is largely restricted to the UV region which only contributes to about 5% of the whole solar spectrum. Moreover, the large recombination chance of photo-induced electrons and holes greatly lowers the efficiency of $TiO_2$ NTs. Various attempts, such as transition metal cation doping [6], nonmetal doping [7] and surface modification with noble metal [8] and semiconductor [9], have been tried to improve the visible light response of $TiO_2$ NTs and inhibit the recombination of electron-hole pairs. Previous reports [10–12] indicated that the coupling of $TiO_2$ NTs with semiconductors with suitable energy band structures and band gaps could greatly enhance the charge separation, and simultaneously extend their light absorption to the visible light region. Among these narrow band-gap semiconductors, CdS is an attractive one because of its visible-light activity and excellent energy level matchability with $TiO_2$ NTs [13]. Our group prepared CdS nanoparticles to sensitize $TiO_2$ NTs by a successive ionic layer absorption and reaction method [14] and UV photodeposition [15], respectively. The as-prepared $TiO_2$ NTs/CdS showed excellent photoelectrochemical properties as photoelectrodes and photocatalysts. However, CdS nanoparticles are unstable under light irradiation, and this obstacle urgently needs to be resolved.

Previous work [16] showed that two sensitizers had more beneficial influences than a single one for enhancing the visible-light absorption and photoelectrochemical activities of $TiO_2$ NTs. Co-sensitization by two chalcogenide semiconductors, such as CdS/CdSe [17,18], CdS/PbS [19] and CdS/$Ag_2S$ [20] indicated that the hybrid sensitizers could form gradient band structures that could significantly improve the visible light absorption and photoelectrochemical performance. $Bi_2S_3$ is regarded as a promising material for solar energy utilization due to its narrow band gap (1.3 eV), which could absorb the whole visible light region contributing 45% of solar spectrum and determine its applicability as an optoelectronic material [21]. Yang [22] and Cai [23] prepared $Bi_2S_3$ nanoparticles deposited on the surface of $TiO_2$ NTs, and the $TiO_2$ NTs-$Bi_2S_3$ showed superior photoelectrochemical properties including the excellent photocatalytic degradation of dyes and photocurrent response. It was speculated that the hybrid of CdS and $Bi_2S_3$ may be advantageous in tackling photocorrosion of CdS, improving visible light response by $Bi_2S_3$, and enhancing electron

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transfer efficiency by CdS. Despite the co-sensitization made thus far in previous studies [17–20], noteworthily, up to now, there have still been very limited systematic studies on the multifunctional photoelectrochemical potentials of CdS and $Bi_2S_3$ co-sensitized $TiO_2$ NTs.

In this paper, we reported a novel simultaneous loading of CdS/$Bi_2S_3$ nanoparticles on the $TiO_2$ NTs photoelectrode by using a solvothermal method. Such an advantageous combination of two metal sulfides leads to effective photocurrent and photoelectrocatalytic properties, and the as-prepared $TiO_2$ NTs-CdS/$Bi_2S_3$ would be exceedingly attractive for applications in solar cells and photocatalysts.

## 2. Experimental

### 2.1. Synthesis of CdS/$Bi_2S_3$ co-sensitized $TiO_2$ nanotube arrays

$TiO_2$ NTs were prepared by a two-step anodization of Ti foils, which was similar with our previous report [24]. The as-prepared $TiO_2$ NTs were annealed at 450 °C for subsequent solvothermal treatment. The $TiO_2$ NTs on Ti substrates were immersed into Cd $(Ac)_2$, $Bi(NO_3)_3$ and thiacetamide ethylene glycol solution with different $Cd^{2+}/Bi^{3+}$ concentration ratios. The total addition of metallic ions containing $Cd^{2+}$ and $Bi^{3+}$ was 0.3 mmol, and thiacetamide was fixed at 0.45 mmol. To prepare the hybrid sensitizers with various CdS and $Bi_2S_3$ ratios, concentration ratios of $Cd^{2+}/Bi^{3+}$ in 30 mL ethylene glycol were mixed with 2:1, 1:1 and 1:2, respectively. The mixture solution was filled in Teflon-lined autoclave with 50 mL Teflon cup, and maintained at 180 °C for 12 h. After the autoclave cooled down naturally, the samples were ultrasonically cleaned with ethanol and deionized water.

### 2.2. Characterization

The products were characterized by using XRD (D8 ADVANCE, Germany), SEM (Quanta 200 FEG, Japan), and DRS (UV-2550, Japan). Photoelectrochemical performances were measured with electrochemical system (CHI620E, China) in 0.1 M $Na_2S$ and 0.1 M $Na_2SO_3$ solution. The sample electrodes were illuminated by a solar simulator equipped with a 500 W Xe lamp (CEL-S500) with a visible-light filter (>400 nm).

### 2.3. Measure of the photoelectrocatalytic activity

The photoelectrocatalytic activities of these samples for the degradation of RhB were measured under irradiation by a 500 W Xe lamp (CEL-S500) equipped with an ultraviolet cutoff filter to provide visible light ($\lambda > 400$ nm). The sample was placed in the photoreactor as the working electrode and a platinum electrode served as the counter electrode. 0.1 M $K_2SO_4$ solution was used as supporting electrolyte, and the potential was fixed at 1 V. Before photodegradation, adsorption equilibrium for dye molecules on the catalyst surface was established by magnetic stirring in dark for 30 min. After visible-light irradiation for 20 min, the remaining dye concentration was determined with a UV 1700 UV–vis spectrophotometer by detecting the maximum absorption wavelength of RhB at 552 nm.

The photoelectrocatalytic reduction of Cr(VI) ions was performed similar with the photoelectrocatalytic degradation of RhB. 0.1 M NaCl solution was used as supporting electrolyte, and the potential was fixed at 0.5 V. A Cr(VI) solution of 25 mL with an initial concentration of 50 mg/L was exposed to visible light. After the photoelectrocatalytic experiment was initiated, 1 mL volumes of solution were periodically withdrawn from the reaction vessel, and the Cr(VI) concentration was measured using the diphenylcarbazide (DPC) method at 540 nm.

## 3. Results and discussion

The typical powder XRD patterns of pure $TiO_2$ NTs and $TiO_2$ NTs-CdS/$Bi_2S_3$ are shown in Fig. 1. As shown in Fig. 1a, the annealed sample demonstrates a distinct XRD pattern that confirms the formation of crystalline $TiO_2$ with anatase phase (PDF no. 21-1272). One can also observe signals from the underlying Ti substrate (PDF no. 44-1294). After the solvothermal deposition, new diffraction peaks situated at 26.51°, 28.18 °, 43.68 °, 51.82 °, and 28.61°, 31.80 °, 32.94 °, 46.46° are observed, which are due to (0 0 2), (1 0 1), (1 1 0), (1 1 2) lattice planes of hexagonal CdS (PDF no. 41–1049) and (2 1 1), (2 2 1), (3 0 1), (4 3 2) lattice planes of orthorhombic $Bi_2S_3$ (PDF no. 17-0320), respectively. In addition, the relative intensities of CdS and $Bi_2S_3$ nanoparticles in $TiO_2$ NTs-CdS/$Bi_2S_3$ are consistent with the concentration ratio of $Cd^{2+}$ and $Bi^{3+}$ ions, and the $TiO_2$ NTs-CdS/$Bi_2S_3$ (1:1) sample demonstrates the balanced diffraction peak intensities of CdS and $Bi_2S_3$ nanoparticles. The XRD results reveal the effective deposition of CdS and $Bi_2S_3$ nanoparticles on $TiO_2$ NTs, and the detailed morphologies of $TiO_2$ NTs-CdS/$Bi_2S_3$ samples are further confirmed by SEM results.

SEM images demonstrate the pure $TiO_2$ NTs and $TiO_2$ NTs-CdS/$Bi_2S_3$ prepared with different $Cd^{2+}/Bi^{3+}$ concentration ratios. Fig. 2a and b show the typical SEM images of $TiO_2$ NTs, and the average outer diameter and wall thickness of these nanotubes are about 160 nm and 25 nm, respectively. Fig. 2d–l show SEM images and corresponding EDS of $TiO_2$ NTs-CdS/$Bi_2S_3$ prepared with $Cd^{2+}/Bi^{3+}$ concentration ratios at 2:1, 1:1 and 1:2, respectively. As shown in these typical SEM images, CdS and $Bi_2S_3$ nanoparticles on $TiO_2$ NTs-CdS/$Bi_2S_3$ (2:1) and $TiO_2$ NTs-CdS/$Bi_2S_3$ (1:2) lead to aggregations on the tubular surface. However, the $TiO_2$ NTs surface becomes extensively coated with a relatively uniform distribution of CdS and $Bi_2S_3$ nanoparticles with an average diameter of 21 nm on $TiO_2$NTs-CdS/$Bi_2S_3$ (1:1), and the solvothermal deposition process doesn't damage the ordered $TiO_2$ NTs tubular structure (Fig. 2h).

The UV–vis diffuse reflectance spectra of the pure $TiO_2$ NTs and $TiO_2$ NTs-CdS/$Bi_2S_3$ prepared with different $Cd^{2+}/Bi^{3+}$ concentration ratios are presented in Fig. 3. The spectrum from $TiO_2$ NTs (Fig. 3a) shows that $TiO_2$ NTs primarily absorb UV light with a wavelength below 387 nm, which is ascribed to the intrinsic band gap (3.2 eV) of $TiO_2$, and the weak absorption in visible-light region after 700 nm could be attributed to the scattering of visible light caused by pores or cracks during the annealing progress [25]. After the solvothermal co-deposition of CdS and $Bi_2S_3$ nanoparticles, absorption edges of $TiO_2$ NTs-CdS/$Bi_2S_3$ are significantly shifted toward the visible light region, and the visible light response ranges are dramatically extended along with the increasement of

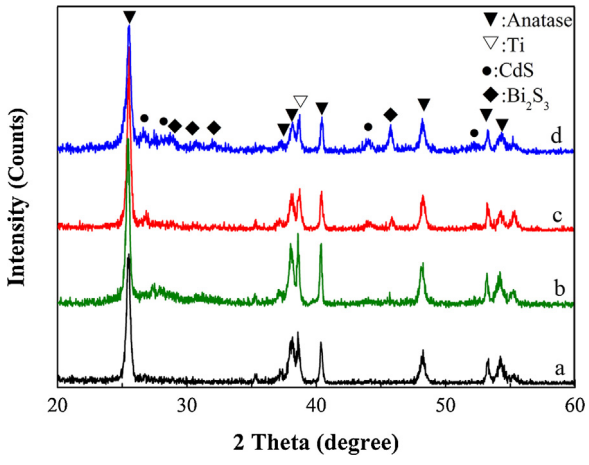


**Fig 1.** XRD patterns of $TiO_2$ NTs (a), $TiO_2$ NTs-CdS/$Bi_2S_3$ (2:1) (b), $TiO_2$ NTs-CdS/$Bi_2S_3$ (1:1) (c) and $TiO_2$ NTs-CdS/$Bi_2S_3$ (1:2) (d).