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Influence of Cu^{2+} dopant in optical property of CdTe quantum dots and photoelectrochemical performance of CdTe:Cu^{2+}/TiO_2 nanotube arrays

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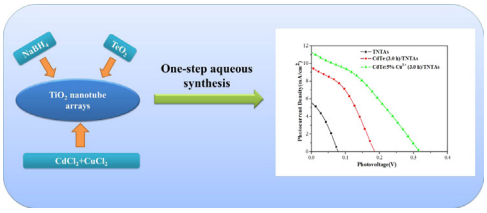
HIGHLIGHTS

- CdTe:Cu^{2+} quantum dots are synthesized using a one-step method in aqueous solution.
- The high quantum yields of the as-prepared quantum dots was calculated 52.1%.
- The tunable band gaps of obtained CdTe:5% Cu^{2+} QDs ranging from 2.28 to 2.13 eV.
- The photoelectric conversion efficiency of CdTe:5% Cu^{2+} (3.0 h)/TNTAs is 1.24%.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel one-step synthesis process was used to prepare CdTe:Cu^{2+}/TiO_2 nanotube arrays (TNTAs). X-ray powder diffraction and high-resolution transmission electron microscopy analyses confirmed that the obtained CdTe:Cu^{2+} quantum dots (QDs) possess cubic structures, which are approximately spherical, and a small particle size (2.95 nm). The photoluminescent and UV–visible absorption spectra of CdTe:Cu^{2+} QDs also display an obvious redshift, which was attributed to the replacement of Cd^{2+} with Cu^{2+}. Compared with that of the TNTAs and CdTe/TNTAs, the photoelectric conversion efficiency of CdTe:5% Cu^{2+}/TNTAs increased by 785.7% and 103.3%, respectively. The incident photo-to-current conversion efficiency of CdTe:5% Cu^{2+}/TNTAs was 50.6%, which indicated the potential use of QDs in photochemical solar cells.

1. Introduction

Quantum dots (QDs) have attracted considerable interest because of their outstanding optical, magnetic, and electronic properties, which are significantly different from those of their bulk form [1–5]. In direct synthesis of QDs in an aqueous solution with different types of thiols as stable agents, the products generally exhibit desirable characteristics, such as low toxicity, improved water solubility, and biological compatibility [6,7].

TiO_2 nanotube arrays (TNTAs) are promising photoanode materials for QD-sensitized solar cells (QDSSCs) with several advantages, such as high energy conversion efficiency, environmentally friendly effects, and tube length stability [8]. However, only UV, which constitutes 5% of solar light, can be effectively absorbed by TNTAs because of wide band gad (3.2 eV) [9]. To address this limitation, the surface of TNTAs is modified with narrow band gap semiconductors. CdTe QDs have a direct energy band gap of approximately 1.5 eV, which is near optimal to achieve high efficiency with an AM1.5 solar spectrum [10]. Furthermore, the electronic band structures of CdTe QDs and TNTAs facilitate the electron transfer from the photo-excited CdTe QDs to TNTAs, resulting in an amelioration of photoelectrochemical performance

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[11]. The photocurrent of TNTAs sensitized with CdTe QDs presented a 35 times improvement compared to that of a plain TNTAs [12]. The CdTe QDs/TNTAs showed better photoelectric properties than those of bare TNTAs [13]. The band gap of QDs can be tuned by synthesizing QDs in the presence of transition metal because doped QDs inherit the properties of host materials, thereby facilitating the development of new properties [14,15]. For example, a slight shift of energy gap from 2.68 eV (ZnSe) to 2.66 eV (ZnSe:Cu) was observed in Ali's study [16].

Unlike many methods to form QDs/TNTAs semiconductors, such as sol–gel method, electrochemical deposition, and succession layer adsorption and reaction, a novel technique is used to fabricate QDs/TNTA compound semiconductors in our study because most synthetic methods are energy and time consuming [17–20]. In the present study, the optical properties and band gap of thioglycolic acid (TGA)-capped CdTe:Cu^{2+} QDs were investigated. Furthermore, a new and simple method was adopted to sensitize TNTAs during a one-step CdTe:Cu^{2+} QDs synthesis process, which is conducted simultaneously with TNTA sensitization. The photoelectrochemical performance and mechanism of the CdTe:Cu^{2+}/TNTAs were studied.

2. Experimental

2.1. Materials and chemicals

CdTe:Cu^{2+} QDs and CdTe:Cu^{2+}/TNTAs were prepared through a one-step aqueous method using TeO_2 (99.99%), $NaBH_4$ (96.00%), $CdCl_2$ (99.00%), $CuCl_2 \cdot 2H_2O$ (99.00%), TGA (90.00%), CH_3COCH_3(99.50%), C_2H_5OH(99.70%), $C_3H_8O_3$(99.00%), Na_2SO_3 (98.00%), Na_2S (98.00%), and NH_4F (96.00%). All of the materials were analytical-grade. Deionized water was utilized throughout the experiment.

2.2. Preparation of TNTAs

Similar to the procedure of our previous work [20], high-purity Titanium foil (0.35 mm-thick foils, 99.6% purity) was cut into 1.0 cm × 3.5 cm strips. The strips were ultrasonically cleaned in acetone, ethanol, and deionized water for 15 min each. The TNTAs were fabricated by anodic oxidation at 45 V for 8 h in an electrolyte containing $C_3H_8O_3$ (volume ratio of 1:5) and NH_4F (0.5 wt%) with a titanium strip anode and a lead oxide electrode as the cathode. After oxidation, the samples were annealed at 450 °C for 3 h in air at a heating rate of 1 °C/min and naturally cooled afterwards.

2.3. One-step aqueous synthesis of CdTe:Cu^{2+}/TNTAs

Similar to the reported method [20], moderate $CuCl_2 \cdot 2H_2O$ (0.02 M) solution was added before TGA to 100 mL CdTe (0.02 M) solution under stirring. The pH of the mixture solution was adjusted to 11 by the dropwise addition of 1 M NaOH solution. Annealed TNTAs were loaded into a three-necked flask. The molar ratio of (Cd + Cu)/Te was adopted from Ref. [6]. TeO_2 and $NaBH_4$ were added to the original solution under stirring. The resulting solution was placed in a three-neck flask attached to a condenser and heated to 110 °C to reflux at different times.

2.4. Characterization

The absorption spectra were recorded with a UV-2501PC spectrometer. PL measurements were performed with an RF-5301 fluorescence spectrometer at an excitation wavelength of 326 nm. QY was determined using rhodamine B (QY = 0.65) as performed in [21,22]. X-ray powder diffraction (XRD) patterns were recorded with a Rigaku D/max-IIIA diffractometer with Cu Kα radiation (λ = 1.54060 Å) at room temperature. The morphology of the solution was characterized by scanning electron microscopy (Quanta 250) coupled with an energy-dispersive spectrometer and a high-resolution transmission electron microscopy (HRTEM) system (H-7650). Photoelectrochemical measurements were conducted in a solution containing 0.7 M Na_2SO_3 and 0.5 M Na_2S with Pt as the counter electrode and Ag/AgCl as the reference electrode. Photocurrent–voltage (*J–V*) measurements were performed with a computer-programmed Keithley2400 Source Meter at room temperature under 100 mW/cm^2 irradiation with Zolix SS150 solar spectrum simulation. Incident photo-to-current conversion efficiency (IPCE) was measured by a Zolix electrochemical station utilizing a Zolix LSH-X150 150 W Xenon lamp with a monochromator. All measurements were conducted at room temperature.

3. Results and discussion

3.1. Characterizations of CdTe:Cu^{2+} QDs

3.1.1. Effect of Cu^{2+} ions on the PL and absorption of CdTe QDs

Fig. 1A shows the PL spectra (solid line) of CdTe and CdTe:5% Cu^{2+}QDs refluxed 0.5 h with normalized intensity and the

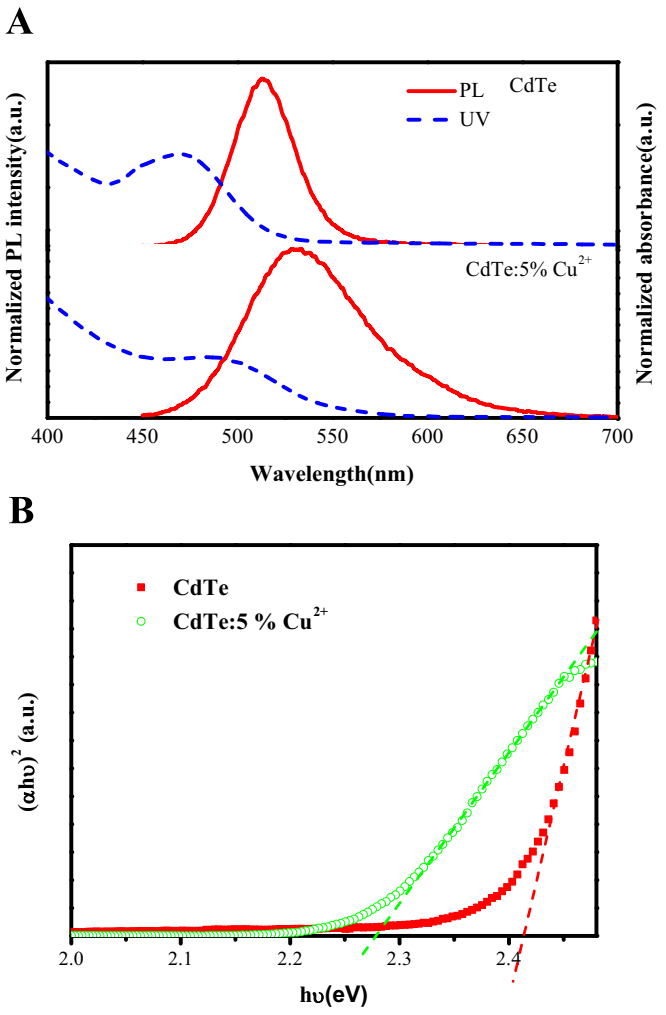

Fig. 1. (A) UV–vis absorption (dashed line) and PL spectra (solid line) of CdTe and CdTe: 5%Cu^{2+} QDs; (B) Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the CdTe and CdTe: 5%Cu^{2+}QDs.