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# Fabrication of transparent and luminescent CdTe/TiO<sub>2</sub> hybrid film with enhanced photovoltaic property

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## ABSTRACT

A novel strategy for fabricating surface modified quantum dots (QDs)/titania hybrid films with increased synergistic property is reported. Through electrostatic interaction, anionic CdTe QDs are wrapped with a cationic surfactant bearing hydroxyl groups at hydrophobic terminal, forming a surfactant-encapsulated QD complex particle with hydroxyl active sites on its periphery. The complex is covalently doped into titania matrix by means of a sol–gel approach of tetraethyl orthotitanate. In comparison to the well designed materials with inorganic core and shell nanostructure, the present study utilizes the inorganic core but organic shell, which can further alloy to titania supports evenly. The original luminescent property of QDs and the flexibility of titania sol–gel materials are well retained in the resulting hybrid films. The monodispersion of QDs in the matrices brings about high transparent titania films, leading to an enhanced photovoltaic effect and a visible region response for light excitation.

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## 1. Introduction

Semiconductor quantum dots (QDs) have attracted extensive attention in chemistry, biology, and materials science in the past decades because of their size tunability, wide excitation wavelength, and changeable luminescence [1–3]. For example, double-shelled ZnO/CdSe/CdTe nanocable arrays have been applied for photovoltaic applications [4]. To fabricate stable light emitting devices with these nanoparticles, many attempts focus on incorporating QDs into transparent host matrices [5,6]. Among the known diverse host materials, titania reveals to be the viable one [7]. The transparency, high refractive index, semiconductor feature and convenient processibility make titania sol–gel materials a suitable carrier for full use of the luminescent property of QDs. The perfect combination of QDs and TiO<sub>2</sub> is supposed to generate synergistic properties such as extended wavelength range of photovoltaic response [8] and amplified spontaneous emission effect in light emitting devices, solar cells and so forth [9].

Two important methods for fabricating QDs/TiO<sub>2</sub> hybrid materials are often used in recent researches [9,10]. By introducing metal salts or powder precursors into titania matrix in advance, QDs in-situ form and grow up upon consequent thermal treatment [11]. But, the yielded QDs normally have wide size distribution,

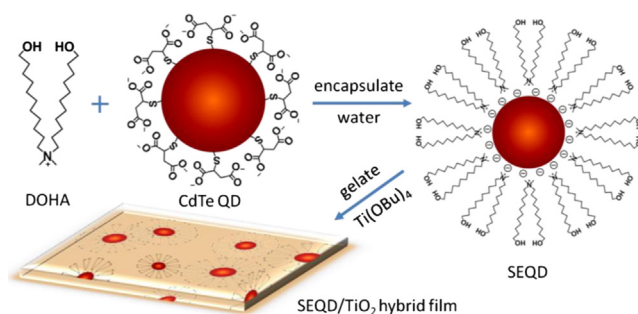
poor luminescence and low doping volume fraction, which restrict the application of QDs/TiO<sub>2</sub> hybrid as potential optical materials. Ligand exchange, as another typical and useful route, could decouple the synthesis of QDs from the preparation of titania matrix [12]. However, the composition and shape of QDs vary with the conditions [10], and the ligand exchange may cause serious quenching of luminescence, which is unfavorable for the purpose of light emission. Therefore, a general approach to create luminescent QDs/TiO<sub>2</sub> hybrid materials is still desired.

Intermolecular interactions provide a sort of flexible forces in supporting assembly of QDs. An amphiphilic approach was reported in fabricating QDs/TiO<sub>2</sub> hybrid materials effectively [13]. The hydrophobically covered polymer can avoid ligand exchange and protect luminescence of QDs effectively. Unfortunately, this method is mainly applicable to hydrophobic alkyl chain stabilized QDs rather than those synthesized from water solution. To overcome these disadvantages and realize convenient incorporation of carboxylic acid stabilized QDs into titania matrix, we herein propose a strategy combining the electrostatic modification of CdTe QDs and the titania sol–gel process to fabricate stable QDs/TiO<sub>2</sub> transparent hybrid film with high luminescence and enhanced photovoltaic property (Scheme 1) [14]. In comparison to the known parallel orientated materials with inorganic core and shell nanostructure that can avoid grain boundaries along the radial direction [15,16], the present study utilizes CdTe inorganic core but organic alkyl chain shell, which can both decrease the energy level alignments and make the nanoparticles conveniently incorporate into supports evenly. The introduced cationic surfactant bearing hydroxyl

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**Scheme 1.** Schematic drawing for the preparation of surfactant encapsulated QD (SEQD)/TiO<sub>2</sub> hybrid film.

groups at hydrophobic terminal (DOHDA) connecting both QDs and titania matrix is proved to play an important role in making QDs in monodispersion and the hybrid film in high transparency [17–19]. Because a simple electrostatic interaction is used, the present method is applicable for all kinds of QDs with a charged surface for the fabrication of titania hybrid materials.

## 2. Experimental

A detailed procedure for sample preparation is described in [Supplementary material](#). Simply, the CdTe QDs were prepared by refluxing the precursor solution at 100 °C under open-air conditions and the particle size was tuned by controlling refluxing time. The surfactant dimethyldi(11-hydroxydecyl)ammonium bromide, DOHDA, was synthesized following the literature and the detailed procedures are described in [Supplementary material](#) [17]. The detailed characterizations indicate the expected chemical structure and satisfied purity. The surfactant encapsulated QD (SEQD) was prepared according to following procedures. To a 30 mL of DOHDA water solution in concentration of 30 mmol L<sup>-1</sup> 20 mL of CdTe water solution was added with concentration ca.  $3 \times 10^{-3}$  mmol L<sup>-1</sup>, estimated from UV–vis absorption spectrum [20]. After stirring for 30 min, the resulting precipitate was filtered and washed with deionized water several times. The precipitate was dried in vacuum for 5 h, giving the pure product SEQD. The SEQD/TiO<sub>2</sub> hybrid film was then fabricated according to the following procedure. Typically, to a 0.1 g of SEQD in 10 mL of ethanol 1.0 g of Ti(OBu)<sub>4</sub> was added, and the mixture was stirred vigorously under refluxing until homogenization appeared. The solution was concentrated to ca. 2–3 mL. For the samples for spectral and photovoltaic measurements, the above resulting sol was then cast onto the quartz slides, silicon wafers, and/or ITO plates through spin coating under a suitable speed, aged and dried in air for about 2 days, giving the samples of hybrid thin films in micrometer thickness level containing ca. 5–20% of SEQD in weight, depending on the preparation conditions.

## 3. Results and discussion

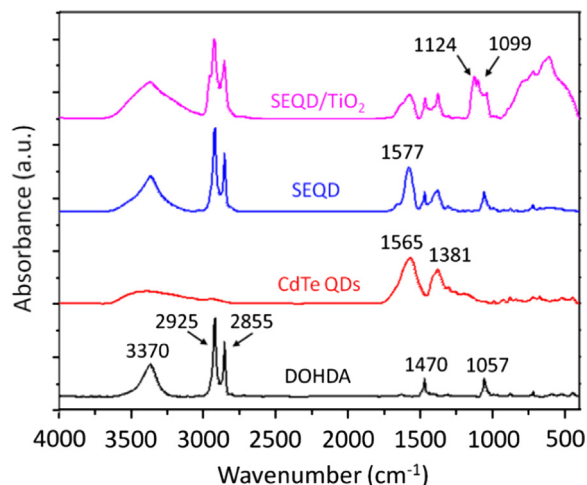
The narrow and symmetrical emission band in the spectrum (Fig. S1a) indicates the narrow size distribution and less electronic defects in the obtained CdTe QDs [21]. Since mercaptosuccinate acid (MSA, pK<sub>a1</sub> = 3.12, and pK<sub>a2</sub> = 4.52) on CdTe nanoparticles ionize at neutral condition [22,23], the cationic surfactant DOHDA can combine with carboxylic anions on the surface of QDs through electrostatic interaction. Due to the increased hydrophobicity, the obtained surfactant-encapsulated QD (SEQD) complex precipitates in water, as shown in Fig. S2. UV–vis spectra reveal no luminescent

residues retaining in filtrate, indicating that the QDs are fully precipitated by controlling the addition of DOHDA cation.

IR spectra of SEQD in Fig. 1 exhibit the typical vibrations of both DOHDA and CdTe QDs. The broad band at wavenumber over 3300 cm<sup>-1</sup> is obviously derived from terminal OH groups. The absorption bands at 2925, 2855, and 1470 cm<sup>-1</sup> can be well attributed to anti-symmetric ( $\nu_{as}$ ), symmetric ( $\nu_s$ ) stretchings and bending mode ( $\delta$ ) of methylene chains. The peak at 1057 cm<sup>-1</sup> can be clearly assigned to the vibration of C–O bond ( $\nu_s$ ) by comparing to the spectrum of DOHDA. In comparison to the vibrations of  $\nu_{as}$  (C=O) and  $\nu_s$  (C=O) at 1565 and 1381 cm<sup>-1</sup> sourcing from MSA stabilizer on CdTe QDs, the former vibration band becomes narrower and shifts to 1577 cm<sup>-1</sup> in SEQD. As the band of carbonyl group is sensitive to the chemical environment [24], this result implies the successful formation of strong electrostatic interaction between DOHDA and CdTe QDs. In addition, the appearance of precipitate supports the electrostatic combination because both isolated components are soluble in aqueous solution. Importantly, as shown in Fig. S1b, SEQD maintains characteristic photophysical property of CdTe QDs, as confirmed in the following part.

The SEQD full of hydroxyl group on its surface makes the subsequent sol–gel reaction with Ti(OBu)<sub>4</sub> covalently favorable [17–19]. As the hydrolysis of precursor and the condensation of –OH groups in SEQD and Ti–OH take place concurrently [12,17–19], the chemical binding is believed to form between SEQD nanoparticles and TiO<sub>2</sub> hybrid film upon the sol–gel reaction. The characteristic vibrations belonging to DOHDA and CdTe QDs are found in IR spectra of SEQD/TiO<sub>2</sub> hybrid distinctly (Fig. 1), confirming the successful incorporation of SEQD into titania matrix. Besides, the absorption band centered at 1099 cm<sup>-1</sup>, assigned to  $\nu$  (Ti–O–Ti) vibration, indicates the formation of titania frameworks, while the band at 1124 cm<sup>-1</sup> assigned to  $\nu$  (Ti–O–C) confirms the covalent bonding of SEQD with titania matrix [25,26]. It should be mentioned that the residue band absorption ascribed to C–O bond implies the incomplete reaction of surface –OH groups on SEQD though it is difficult to evaluate the content.

The sol–gel hybrid films display high transparence, revealing the well dispersion and small size distribution of SEQD dopant in titania matrices. TEM observations in Fig. 2a and b confirm the homogeneous dispersion of SEQD in mixed solvent of ethanol and water before condensation reaction. The chemical immobilization of SEQD in titania matrix also does not trigger obvious aggregation in hybrid film. TEM image in Fig. 2c demonstrates that CdTe QDs distribute in separate black spots with diameter ranging from 3.0–3.5 nm throughout the sample film. The SEQD/TiO<sub>2</sub> hybrid



**Fig. 1.** IR spectra of DOHDA, CdTe QDs, SEQD and SEQD/TiO<sub>2</sub> (10%) hybrid film in KBr.

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