Tuning PbS QDs Deposited onto TiO₂ Nanotube Arrays to Improve Photoelectrochemical Performances

Xiaoming Zhang , Bin Wang, Zhongqing Liu*

College of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, PR China

Abstract: The ability to anchor quantum dots (QDs) onto the inner channels of nanotube arrays affords the opportunity to engineer the electron and band structures for a variety of applications. During the successive ionic layer adsorption and reaction (SILAR) preparation, the deposition of PbS QDs had been tuned by adjusting the concentration ratio of sulfur and lead sources onto the TiO₂ nanotube array (TNA) support formed via anodic ionization. The photoelectrochemical properties of the PbS QD sensitized TNAs were optimized. The sample microstructure and photoelectrochemical properties were analyzed with X-ray diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), UV-visible diffuse reflectance spectroscopy (UV-Vis DRs), photoluminescence (PL), current–voltage characteristics (J – V), electrochemical impedance spectroscopy (EIS), transient photovoltage plots and Mott-Schottky curves. The size and distribution of the PbS QDs were tuned by varying the concentration ratio of sulfur and lead sources during the SILAR process. The band gap structure, flat band potential, lifetime and transport of the photo-induced charge carriers were subsequently modified. With a S/Pb concentration ratio of 5, the samples demonstrated the best photoelectrochemical characteristics with a peak photocurrent density of 8.24 mA cm⁻² and a corresponding photoconversion efficiency of 7.80%.

Keywords: SILAR; PbS QDs; S/Pb; Mott-Schottky; Transient photovoltage

1. Introduction

In 1971, Fujishima and Honda demonstrated that a photoelectrochemical cell composed of TiO_2 and Pt could split water into H_2 and O_2 upon light illumination [1]. This discovery illustrates the possibility of H_2 production by using solar energy. The great application potential in solving difficulties faced in energy supply crisis and environmental concerns of this field entices significant research interests around the world.

During the past four decades, the key scientific questions in this research area focus on expanding the light response range of TiO_2 and reducing photo-induced charge carrier recombination [2,3]. To achieve these goals, doping with transition metal or non-metal elements [4], surface deposition of noble metals [5,6], sensitization with dyes [7], and sensitization with narrow band gap semiconductor quantum dots (QDs) [8,9] have been investigated. Sensitization of TiO_2 with narrow band gap semiconductor QDs has become an effective method to provide tunable absorption band edges, and lower recombination rates because of accelerated charge separation via the heterojunction formed between the QDs and TiO_2 [10-12]. TiO_2 has taken forms in nanoparticles, nanotubes, nanorods, or nanofibers as the supports for QDs. Among them, the perpendicularly oriented upon the base, highly ordered TiO_2 nanotube arrays (TNAs) maintain one-dimensional carrier pathways for electrons and holes and are considered ideal support materials because of their superb photoelectrochemical characteristics, exhibiting immense application potentials in photocatalyzed decomposition of organic pollutants [13,14], solar cells [15,16], and sensors [17]. Lead chalcogenides such as PbS have been extensively studied as the sensitization materials for TiO_2 -based photoelectrodes because of its big exciton Bohr radius (18 nm), narrow band gap (0.41 eV), long exciton lifetimes (200–800 ns), highly degenerated first excited state, mirror-imaged conducting band and valence band, and matching energy and with TiO_2 [18,19]. In TiO_2 photoelectrodes using QDs as light harvesters, anodic charge transport is carried out by the wide band gap TiO_2 . Electrons are injected from QDs to TiO_2 , generating the photocurrent. Improved device efficiency may be attained via the accelerated exciton dissociation at the QDs/ TiO_2 interfaces, and charge injection into the anodic material [20]. Due to the quantum confinement effects, the light absorption, bandgap, and absorption band edges of the QDs are

closely related to the deposition amount, size, and distribution of the QDs. It is possible to manipulate the QD deposition process to adjust and optimize the photoelectrochemical performance of QD sensitized TiO_2 photoelectrodes.

An inexpensive wet chemical means, the successive ionic layer adsorption and reaction (SILAR) method has been widely utilized in the surface deposition of semiconductor QDs [21,22]. In our previous work, we have studied the effects of surface hydroxylation and heat treatment on the photoelectrochemical properties of the TNA photoelectrodes prepared via the SILAR approach [23,24]. Fabrication of PbS QDs by the SILAR method resembles the ion association process in solution, i.e., Pb^{2+} ions are associated with S^{2-} ions and/or HS^- ions to form PbS deposits. During the PbS deposition onto TNAs, the process is more complicated than the situation in free space such as a true solution. Besides the influences of threshold distance between Pb^{2+} and S^{2-} ions and static force changes, the effects of space confinement of the nanotubes and resistance to mass transfer play an important role in the QD nucleation and growth. When depositing PbS via the SILAR route, the ion supersaturation degree of the process, solution dielectric constant, the relative mass transfer rates of Pb^{2+} and S^{2-} within the nanotubes change according to the variation of the lead versus sulfur concentration ratio. In this study, we tuned the deposition amount, size and distribution of PbS QDs by varying the concentration ratio of lead and sulfur sources during SILAR. We observed the subsequent changes in the bandgap, flat band potential, lifetime and transport of the photo-induced charge carriers. With an S:Pb ratio of 5, the peak photocurrent density reached 8.24 mA cm^{-2} , corresponding to a photoconversion efficiency of 7.80%.

2. Experimental

2.1 Preparation of PbS QD sensitized TiO_2 nanotube arrays

The detailed procedure and conditions of electrochemical anodization preparation of TiO_2 nanotube arrays are reported in our previous work [23–25]. The thermally crystallized TNAs were immersed in 5 g L^{-1} NaOH for 30 min. After rinse with water, the TNAs were immersed in 0.02 mol L^{-1} thioacetic acid (TGA) for 2 h. Using $\text{Pb}(\text{Ac})_2$ and Na_2S as the Pb and S sources, respectively, successive ion layer adsorption reaction (SILAR) was performed on TNAs. One SILAR cycle contained immersing in $\text{Pb}(\text{Ac})_2$ -rinse and drying- immersing in Na_2S -rinse and

drying step and each dipping time is set to 5 minutes. The PbS sensitized TNAs (PbS/TNAs) were prepared with five SILAR cycles. Different samples were prepared under the following conditions: (1) Using $2.0 \text{ mmol L}^{-1} \text{ Pb}(\text{Ac})_2$ solution as the Pb source, the Na_2S concentration was systematically varied to afford S:Pb ratios of 5, 10, and 15, respectively; (2) using $2.0 \text{ mmol L}^{-1} \text{ Na}_2\text{S}$ solution as the S source, the $\text{Pb}(\text{Ac})_2$ concentration was systematically varied to afford S:Pb ratios of 0.1, 0.2, and 1.0, respectively. The corresponding samples were labeled (x)PbS/TNAs, x indicates the concentration ratio of Na_2S and $\text{Pb}(\text{Ac})_2$ sources.

2.2 Characterization Techniques

XRD (Philips XPert pro MPD) analysis was conducted to provide the crystalline phase information of the samples. TEM (FEI Tecnai G2 F20 S-Twin) was applied to demonstrate the microscopic morphologies. FE-SEM (HITACHI S-4800) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford 51-XXM0019) was used to characterize surface morphology and element composition. Light response was observed by ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy (UV2100). PL (F-7000) was recorded to afford the dissociation properties of photoinduced charge carriers with an excitation wavelength of 300 nm.

2.3 Photoelectrochemical analysis

The photoelectrochemical analyses were performed on CHI650E electrochemical work station (Chenhua, Shanghai) at ambient temperature, including J – V , transient photovoltage, EIS, and Mott–Schottky analyses. The light source was AM1.5G (100 mW.cm^{-2}). The PbS/TNAs sample was used as the working electrode, a Pt tile as the counter electrode, SCE as the reference electrode, and $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$ as the supporting electrolyte.

3. Results and discussion

3.1 Sample Characterization

Figure 1 shows the XRD patterns of samples (0.2,1,5)PbS/TNAs. It is shown that (0.2)PbS/TNAs and (1)PbS/TNAs have very similar XRD patterns. Diffraction peaks of {200} and {220} facets PbS are clearly visible. Sample (5)PbS/TNAs does not show evident {200} or {220} diffractions, possibly due to low concentration or small size of the PbS QDs [19]. Figure 2 illustrates the FE-SEM images of the samples. From Figure 2a, the pristine TNAs

show smooth tube walls and openings, with the outside diameter of about 100 nm and the wall thickness of 10 nm. After the SILAR treatment (Fig. 2b,c), there are a significant number of nanoparticles accumulating at the tube openings, increasing the surface roughness of the wall and reducing the opening size. Even though containing much less QD deposition around the tube openings compared to (0.2)PbS/TNAs and (1)PbS/TNAs, sample (5)PbS/TNAs shows apparent particle accumulation and high roughness around the openings compared to pristine TNAs. In Table 1, the EDS results of samples (0.2,1,5)PbS/TNAs illustrate that the PbS QD deposition reaches the maximum when $x = 1$, followed by $x = 0.2$, while PbS QDs are the least when $x = 5$. It is worth noticing that when $x = 0.2$ or 1, the S/Pb atomic ratio is 0.94 or 0.73. The PbS QDs are n-type semiconductors [26]. But when $x = 5$, the S/Pb ratio becomes 1.17, indicating p-type semiconductor materials [26]. Figure 3 presents the TEM images of samples (1,5)PbS/TNAs, and the histograms of PbS QD size distribution. From Figures 3a–c, (1)PbS/TNAs holds greater PbS QDs and a wide distribution, with those in the range of 6–10 nm around 70%. In comparison, (5)PbS/TNAs has smaller PbS QDs with a narrow distribution, primarily around 2–3 nm (>80%). The less concentration of smaller PbS QDs in (5)PbS/TNAs correlates well with obscure XRD diffraction peaks of this sample.

Due to the quantum size effect, the band gap of PbS quantum dots is changed. The band gaps (E_r) of the nanoscale semiconductor materials were calculated using Brus equation [27]:

$$E_r = E_g + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r} \quad (1)$$

where r is the particle radius, here defined as mean radius of PbS QDs; m_e^* and m_h^* are effective masses of electrons and holes, respectively; ϵ_0 and ϵ_r are the vacuum permittivity and the relative permittivity of QDs material, respectively; and h and e are the Planck constant and basic charge, respectively. E_g is the band gap of the bulk PbS, 0.41 eV. According to the calculation, the band gaps of PbS QDs in (1,5)PbS/TNAs are 0.565 and 1.975 eV, respectively. The conduction band levels (E_{CB}) were estimated by using the following equation [28]:

$$E_{CB} = X - 4.5 - 0.5E_r \quad (2)$$

where X is the absolute electronegativity of the semiconductor, expressed as the geometric mean of the Sanderson electronegativity of the constituent atoms. For the QDs of the same

semiconductor, E_{CB} is only related to E_r . Therefore, the band gap edge position of sample (5)PbS/TNAs is 0.71 eV higher than that of (1)PbS/TNAs. It is beneficial for the separation of photo-induced excitons at the PbS QDs and TiO₂ interface, and the fast injection of electrons from PbS QD conduction band to TiO₂ conduction band.

UV Vis diffuse reflectance spectra can be used to characterize the optical absorption properties of the samples. As shown in Figure 4a, in (1,5)PbS/TNAs, characteristic band for tetrahedrally coordinated titanium appears at about 390 nm, attributed to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer, corresponding to electronic excitation from the VB to the CB of TiO₂. A slightly enhanced absorption was observed in the (5)PbS/TNAs than the (1)PbS/TNAs ranging from 380 nm to 700 nm. The PL spectra have been widely used to study the transfer behavior of the photo-induced electrons and holes in semiconductor materials to reflect the separation and recombination of charge carriers [29]. The markedly lower PL intensity for (5)PbS/TNAs indicates that it may possess an enhanced photocatalytic activity than (1)PbS/TNAs, as seen in Figure 4(b).

3.2 Photoelectrochemical analysis

Figure 5 displays the Tafel polarization plots of samples (1,5,10)PbS/TNAs under AM1.5 illumination. The recorded electrode potentials were ± 80 mV deviated from the corresponding equilibrium potential (open circuit potential). When using Na₂S and Na₂SO₃ mixed solution as the supporting electrolyte, photo-induced holes are transported to the interfacial double layer between PbS and the electrolyte solution under light illumination and the external field, and captured by S^{2-} and/or SO_3^{2-} via the following reaction [30]:

When there exist differences between the ionic transport rates, hole donating rates, and the electrochemical reaction rates, electrode polarization occurs. Anodic polarization produces positive migration of the electrode potentials. In Figure 5, the right side of the dashed line represents the anodic polarization curves, whose current density magnitude demonstrating the rates of the electrode reaction. It is observed that under the same overpotential, sample (5)PbS/TNAs has the largest polarization current density amongst the three samples, pointing to high photoelectrochemical performance.

Mott-Schottky plot provides accurate information of the samples such as donor

concentration N_d or acceptor concentration N_a , and the flat band potential E_{fb} . Fig. 6 shows the Mott-Schottky curves of samples (x)PbS/TNAs ($x=0.1,0.2,1,5,10,15$). In the linear parts of the curves, the slopes of the tangent lines are all positive, representing n-type semiconductors. The relationship between donor concentration N_d and flat band potential E_{fb} of n-type semiconductors can be expressed by the following equation [31,32]:

$$(C/A)^{-2} = \frac{2}{eN_d\epsilon\epsilon_0} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (4)$$

here, N_d is the donor concentration, ϵ is the relative permittivity of the semiconductor (48 for anatase TiO_2), ϵ_0 is the permittivity of vacuum), E is the applied bias potential, and A is the electrode area. The extension of the Mott-Schottky curve to $1/C^2 = 0$ results in the flat band potential E_{fb} . The flat band potentials of the samples relative to SCE are tabulated in Table 2. Under flat band conditions, the flat band potential of a semiconductor is equal to the Fermi energy. The flat band potential plays an important role on the photoelectrical reactions. The more positive the Fermi energy, the greater the chemical potential gradient from the electrolyte to the semiconductor, the greater the curvature of the semiconductor energy band, which in turn implies faster charge carrier dissociation and transfer at the interface between the semiconductor and the electrolyte. According to Table 2, the E_{fb} of the (5)PbS/TNAs is the most positive in the all samples. It suggests that at the interface between the semiconductor and the electrolyte, sample (5)PbS/TNAs has the greatest energy band curvatures and accordingly embraces faster charge carrier dissociation and transfer at that semiconductor and electrolyte interface than do the other samples.

The electrochemical impedance spectroscopy (EIS) can provide information on the electrode kinetics model and the electrochemical processes on the electrode surface [33]. The radius of the Nyquist curve represents the magnitude of device resistance. The EIS plots of the samples under AM1.5 illumination are presented in Fig. 7, with the equivalent circuit shown as the inset. Here, R_s represents the resistance of the electrolyte solution, R_1 and C_1 the resistance and capacitance of electric double layer between electrode surface and electrolyte solution, R_2 and C_2 the charge transfer impedance and capacitance inside the porous membrane electrode of photo generated carries. The simulated values of each corresponding device in the equivalent circuit are listed in Table 3. Compared to the corresponding R_1 of the samples, the

much larger R_2 values suggested that in PbS QD sensitized TiO₂ nanotube array electrodes, charge carriers transport is controlled by the transfer inside the electrode. For the (5)PbS/TNAs, the smallest value of R_2 and time constant ($\tau_2 = R_2 \times C_2$) indicates the greatest transport efficiency and fastest separation and transfer rates of the photoinduced charge carriers in all samples.

Open circuit potential decay curves are used as effective indicators of kinetics of the charge carrier recombination or separation. In Na₂S and Na₂SO₃ electrolyte, processes of electron injection into TiO₂, hole capturing by S²⁻ and/or SO₃²⁻ ions, and charge recombination in the form of S_n²⁻ or S₂O₃²⁻ accumulation become equilibrated when the PbS QD sensitized TNAs are illuminated with continuous light. Open circuit potential arrives at a steady state value. The accumulated electrons recombine with the photo-induced holes during light-off, causing open circuit potential decay. The response time correlates to the electron lifetime. Zaban et al. propose that open circuit potential V_{OC} and response time τ_n has the following relationship [34,35]:

$$\tau_n = \frac{k_B T}{e} \left(\frac{dV_{OC}}{dt} \right)^{-1} \quad (5)$$

here, k_B is the Boltzmann constant, e is the electron charge, T is the absolute temperature (298 K), t is time, and V_{OC} is the open circuit voltage at time t . Figure 8a demonstrates the relationship between the open circuit potential and time when the samples were exposed from light-on to light-off (each point taken in one μ s). The corresponding columnar diagrams comparison of the response time (τ_n) values at the switch-off instant is shown in Figure 8b. At the instant from light-on to light-off, the response time (τ_n) of the (5)PbS/TNAs is 0.312 s, the greatest among all samples. Hence, the photo-induced electrons had longer lifetimes and faster separation and transfer rates in the (5)PbS/TNAs photoelectrode than do the other samples.

The results of Mott-Schottky plots, EIS and transient photovoltage curves are in well agreement with the previous analyses of XRD, TEM, UV-Vis and PL, indicating that (5)PbS/TNAs should reveal the best photoelectrochemical performance, in the light of its largest interfacial energy band bending degree, lowest charge transfer impedance and longest lifetime of photo-induced carries, enhanced light absorption and decreased PL emission among all samples. To validate the conjecture, the J - V characteristics of the samples were conducted.

As shown in Fig. 9a, it can be seen that photocurrent densities of all samples attain to peak values at about -0.7 V vs. SCE. According to the J - V curves, the corresponding photoconversion efficiency η was calculated by the following equation [24,36]:

$$\eta(\%) = j_p \left[\frac{(E_{rev}^0 - |E_{app}|)}{I_0} \right] \times 100 \quad (6)$$

In Eq. 6, j_p is the photocurrent density, $j_p E_{rev}^0$ is the total power output, $j_p |E_{app}|$ is the electrical power input, I_0 is the power density of the irradiated light (100 mW cm^{-2}), and E_{rev}^0 is the standard reversible potential (1.23 V vs. NHE). The applied potential is obtained $E_{app} = E_{means} - E_{aoc}$, where E_{means} is the electrode potential (vs. SCE) of the working electrode at which the photocurrent is measured under light irradiation, and E_{aoc} is the electrode potential (vs. SCE) of the same electrode in an open circuit under the same conditions. As expected, the peak photocurrent density of the (5)PbS/TNAs is the greatest, attaining to 8.24 mA cm^{-2} and accordingly giving the greatest photoconversion efficiency of 7.80% in all samples.

4. Conclusions

PbS QDs had been deposited onto TiO_2 nanotube arrays using the successive ionic layer adsorption and reaction (SILAR) preparation. By adjusting the concentration ratio of sulfur and lead sources during the preparation, the deposited amount, size and distribution of the PbS QDs had been tuned accordingly. The photoelectrochemical properties such as light absorption, band gap bending, lifetime of the photo-induced charge carriers, and the carrier transport within the porous membrane electrode of the PbS QD sensitized TNAs were optimized. With a S/Pb concentration ratio of 5, the sample demonstrated the best photoelectrochemical characteristics with a peak photocurrent density of 8.24 mA cm^{-2} and a corresponding photoconversion efficiency of 7.80%. The results offer a feasible method for the preparation of QD sensitized photoelectrodes via SILAR with controlled photoelectrochemical properties.

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Graphical Abstract

The deposition of PbS QDs was tuned by varying S/Pb ratio in during SILAR. The peak photoconversion efficiency of PbS/TNAs reached to 7.80%.

Figure captions

Figure 1 XRD patterns of of the (x) PbS/TNAs ($x=0.2,1,5$).

Figure 2 SEM images of (a) pristine TNAs,(b) (0.2) PbS/TNAs, (c) (1) PbS/TNAs and (d) (5) PbS/TNAs.

Figure 3 TEM images and size distribution histograms of PbS QDs of the (X) PbS/TNAs($x=1,5$). (a),(b) and (c) (1) PbS/TNAs, (d),(e)and (f) (5) PbS/TNAs.

Figure 4 Uv-Vis diffuse absorbance spectra (a) and PL spectra (b) of the (x) PbS/TNAs($x=1,5$).

Figure 5 Tafel plots of the (x) PbS/TNAs($x=0.2,1,5,10$).

Figure 6 Mott–Schottky curves of of the (x) PbS/TNAs($x=0.1,0.2,1,5,10,15$).

Figure 7 EIS plots of the (x)PbS/TNAs($x=0.1,0.2,1,5,10,15$). The insets are the equivalent circuits.

Figure 8 V_{oc} decay profiles of the (x)PbS/TNAs ($x=0.1,0.2,1,5,10,15$) when the light is on to off. The insets are columnar diagrams of the response time at light switch off moment of the light.

Figure 9 Current-voltage characteristics (a) and photo conversion efficiency (b) of the (x) PbS/TNAs($x=0.1,0.2,1,5,10,15$).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1 Chemical composition of the samples from EDS analysis

Element	(0.2)PbS/TNAs		(1)PbS/TNAs		(5)PbS/TNAs	
	Weight(%)	Atomic(%)	Weight(%)	Atomic(%)	Weight(%)	Atomic(%)
O	36.52	64.78	31.28	60.02	44.60	71.24
Ti	56.66	33.57	57.19	36.66	52.27	28.13
S	0.96	0.80	9.54	1.41	2.77	0.34
Pb	5.86	0.85	1.99	1.91	0.36	0.29
Total	100	100	100	100	100	100

Table 2 The flat potentials of the samples prepared by different S/Pb ratios

Sample	S/Pb=0.1	S/Pb=0.2	S/Pb=1	S/Pb=5	S/Pb=10	S/Pb=15
E_{fb}/V	-0.684	-0.562	-0.871	-0.354	-0.497	-0.581

Table 3 Simulated values of devices in equivalent circuits of the samples

Sample	R_s ($\Omega \cdot \text{cm}^2$)	R_1 ($\Omega \cdot \text{cm}^2$)	R_2 ($\Omega \cdot \text{cm}^2$)	C_1 ($\text{F} \cdot \text{cm}^{-2}$)	C_2 ($\text{F} \cdot \text{cm}^{-2}$)
(0.1)PbS/TNAs	2.813	0.829	400.1	0.0227	0.00881
(0.2)PbS/TNAs	3.075	0.577	97.99	0.00972	0.00496
(1)PbS/TNAs	3.625	3.112	328.7	0.0370	0.0114
(5)PbS/TNAs	2.859	0.851	95.6	0.00664	0.00358
(10)PbS/TNAs	3.175	0.603	214	0.0121	0.00526
(15)PbS/TNAs	2.501	0.00609	230.5	0.0186	0.00609