Materials Research Express

PAPER

Shell thickness dependent photocatalytic activity of TiO₂/ZnS core-shell nanorod arrays

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Keywords: TiO₂/ZnS, nanorod arrays (NRAs), photocatalysis, core-shell

Abstract

Rutile TiO₂ nanorod arrays (NRAs) were first fabricated via solvothermal route using Ti foil as both substrate and titanium source, then TiO₂/ZnS core-shell heterostructure NRAs were synthesized by successive ionic layer adsorption and reaction (SILAR) method using the TiO₂ NRAs as a sacrificial template. The diameters of TiO₂ nanorods ranged from 20 to 200 nm, and the thickness of ZnS shell varied from 3 to 20 nm. The photocatalytic activities of the samples were compared by the degradation of rhodamine B (RhB) water solution under simulated sunlight irradiation. All TiO₂/ZnS NRAs exhibited higher photocatalytic activities than bare TiO₂ NRAs, and the optimal ZnS shell thickness of TiO₂/ZnS NRAs was 10 nm. Furthermore, TiO₂/ZnS NRAs possessed excellent reusability.

1. Introduction

With the increasing awareness of water contamination and shortages, constructing high quality and clean water is indispensable for environmental issues [1]. Nowadays, the technology of photocatalysis has attracted great attention because it can directly degrade organic pollutants into non-toxic products [2]. A large amount of semiconductor materials (such as TiO₂, ZnO, ZnS, Cds, ZnSe) are used to degrade contaminant [3–6]. Among various alternative photocatalysts, TiO₂ has drawn considerable scientific enthusiasm on account of its unique characteristics like low-cost, non-toxicity, stability and high photocatalytic activity [7, 8]. TiO₂ usually occurs in three distinct crystal phases, anatase, rutile and brookite, and the corresponding band gaps are 3.2, 3.0 and 3.4 eV, respectively [9, 10]. Among these crystalline structures, it is widely recognized that anatase TiO₂ shows higher photocatalytic activities than rutile and brookite TiO₂ [11]. Nevertheless, the relatively wide band gap of anatase TiO₂ limits its photocatalytic application because pure anatase TiO₂ only can be excited by ultraviolet (UV) light [12, 13]. Recently, rutile TiO₂ is reported to exhibit superior to anatase TiO₂ in the application of oxygen evolution from water [14]. In addition, the excitation wavelength of rutile extends into the sunlight below 410 nm due to the relatively small band gap of 3.0 eV. Thus, synthesizing rutile TiO₂ is still a topical subject in the field of photocatalysis.

The easy recombination of the electrons (e₋) and holes (h₊) is a representative shortcoming of conventional homogeneous photocatalysts. Coupling TiO₂ with other semiconductors to fabricate heterojunction photocatalyst is an efficient and popular way to enhance photocatalytic activity of pure TiO₂ [15]. Furthermore, heterogeneous photocatalysts are reported to exhibit the outstanding photocatalytic activity because of the higher e₋ and h₊ separation rate and longer carrier life time [16, 17]. ZnS is another excellent photocatalyst has received considerable concern due to its excellent properties such as relatively less toxic and high activity [18]. Several anatase-TiO₂/ZnS heterostructure composites in the form of powder are synthesized [19–21]. For example, Stengl et al. [22] reported that anatase TiO₂/ZnS power nanocomposites were prepared by homogeneous hydrolysis of thioacetamide in aqueous solution, which exhibited excellent photocatalytic activity to degrade the aqueous solution of Orange II dye under visible light. Furthermore, Talebi et al. [23] showed that
ZnS/TiO₂ hybrid photocatalyst was successfully synthesized using a chemical deposition method. And the results showed that the composite had outstanding degradation performance to the azo dye acid blue 113 in UV light. Compared with the film photocatalyst, photocatalyst in powder form is completely to the disadvantage of separating and recycling. Nowadays, rutile-TiO₂/ZnS heterostructure composites film is rarely studied. Thus, it is of great significance to fabricate TiO₂/ZnS heterostructure NRAs films with different ZnS shell thicknesses and compare their photocatalytic activities.

Here, TiO₂/ZnS heterostructure NRAs with different ZnS shell thicknesses were fabricated via a solvothermal method followed by the successive ionic layer adsorption and reaction (SILAR) technique. Their geometrical morphologies, microstructures and optical properties were investigated by XRD, SEM, TEM, XPS, and UV-Vis DRS. The photocatalytic properties were investigated by the degradation of RhB under simulated sunlight irradiation. Furthermore, the possible mechanism of the photocatalytic process was put forward.

2. Experimental section

2.1. Preparation

TiO₂/ZnS NRAs were synthesized by two steps. In the first step, rutile TiO₂ NRAs grew on Ti foil via solvothermal method. Typically, Ti foil with dimensions of 1 cm × 1 cm was put into a 30 mL Teflon-lined autoclave with HCl (0.4 mol L⁻¹), and this system was maintained at 200 °C for 12 h. After free cooling, the rutile TiO₂ NRAs were obtained by washed the Ti foil with deionized water and absolute ethanol several times. In the second step, the as-prepared TiO₂ NRAs were separately dipped into 0.1 mol L⁻¹ Zn(NO₃)₂ aqueous solution and 0.1 mol L⁻¹ Na₂S aqueous solution for 3 min with slowly shaking. At each soaking interval, the sample was rinsed completely with deionized water. This process was defined as a SILAR cycle. Different ZnS shell thicknesses of TiO₂/ZnS core-shell structure was obtained by repeated SILAR cycle for 2, 4 and 6 times. For convenience, the corresponding samples were called as TiO₂/ZnS-2, TiO₂/ZnS-4 and TiO₂/ZnS-6, respectively.

2.2. Characterization

The crystal structure and phase component were investigated using X-ray diffraction (XRD, Rigaku-D/max-2500 diffractometer, Japan), operated at 40 kV and 40 mA. The geometrical morphologies and microstructures were determined by a field emission scanning electron microscope (FE-SEM, JEOL 7800 F, Japan) and transmission electron microscope (TEM, FEI Tenai G2 F20, USA). The elemental compositions and chemical status were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi A1440 system, USA). All binding energies were calibrated by C 1 s peak at 284.1 eV. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were obtained on a spectrometer (Perkin-Elmer Lambda 900, USA) using magnesium oxide as a standard. The radical species were detected by electron spin resonance (ESR) spectrometer (Brucker, A300). The optical properties were detected by photoluminescence spectra (PL, Renishaw inVia micro-PL spectrometer) at room temperature.

2.3. Photocatalytic test

The photocatalytic activities of the samples were assessed by means of the photocatalytic degradation of rhodamine B (RhB) aqueous solution under simulated solar light. The light source was provided by a 300 W Xe lamp (CEL-HXF300). The initial concentration of RhB aqueous solution is 2 mg L⁻¹. In a typical procedure, the as-prepared sample (1 cm × 1 cm) was placed on the bottom of a vessel containing 4 ml of RhB aqueous solution. Before simulated solar light irradiation, the reaction system was placed in the dark for 30 min to achieve the adsorption–desorption equilibrium between RhB molecules and photocatalyst. At regular interval, the absorbance spectrum of RhB aqueous solution was monitored by a UV-Vis spectrophotometer (UV-5800PC, China). For comparison, the blank experiment was executed in the absence of photocatalyst under the identical condition.

3. Results and discussion

Figure 1 shows the XRD patterns of Ti foil, pure TiO₂ and TiO₂/ZnS NRAs. All diffraction peaks in figure 1(a) belong to Ti (JCPDS card No. 87-0713) foil. Besides some diffraction peaks originating from Ti foil, all characteristic peaks in figure 1(b) correspond well to rutile TiO₂ (JCPDS card No. 21-1276) without other impurity. No obvious characteristic peaks assigning to ZnS in figures 1(c) and (d) are detected, indicating that the quantities of ZnS are small in both TiO₂/ZnS-2 and TiO₂/ZnS-4 NRAs. However, three diffraction peaks separately at about 28.9°, 48.1° and 57.1° in figure 1(e) originating from the (111), (220) and (311) planes of
cubic ZnS (JCPDS card No. 80-0020) are found, suggesting that the quantities of ZnS in TiO$_2$/ZnS-6 is higher than TiO$_2$/ZnS-2 and TiO$_2$/ZnS-4 NRAs.

Figures 2(a) and (b) display the SEM images of bare TiO$_2$ NRAs. According to figures 2(a) and (b), rodlike TiO$_2$ with smooth surface grow in large-scale on the surfaces of Ti substrate. In addition, TiO$_2$ nanorods have a rectangular profile, and the diameters range from 20 to 200 nm. Figs. c-h show the SEM images of TiO$_2$/ZnS NRAs obtained by different SILAR cycle times. Compared to bare TiO$_2$ nanorods, all TiO$_2$/ZnS nanorods have rough surfaces because some ZnS nanoparticles attach to the surfaces of TiO$_2$ nanorods. Furthermore, the diameters of the TiO$_2$ nanorods increase gradually with the increasing of SILAR cycle times, indicating that the ZnS shell thickness increases gradually with the increasing of SILAR cycle times. It is worth noting that the surfaces of TiO$_2$ nanorods are not covered completely with ZnS nanoparticles in TiO$_2$/ZnS-2 NRAs, whereas the whole surfaces of TiO$_2$ nanorods in TiO$_2$/ZnS-6 NRAs are covered with an exceedingly dense ZnS shell layer.

Figures 3(a), (c), (e) and (g) display the TEM images of individual TiO$_2$, TiO$_2$/ZnS-2, TiO$_2$/ZnS-4 and TiO$_2$/ZnS-6, respectively. These nanorods have an average length of about 400 nm. In addition, bare TiO$_2$ nanorod exhibits a smooth surface, while the outlines of all TiO$_2$/ZnS nanorods are gruff. This is consistent with the SEM results in figure 2. The HRTEM image (figure 3(b)) of TiO$_2$ shows the lattice spacing of 0.325 nm and 0.295 nm, which separately correspond well to (110) and (001) facets of rutile TiO$_2$. This result indicates that TiO$_2$ nanorod grow along (001) direction. The evident lattice fringes with interplanar distance of 0.312 nm and 0.191 nm (in figures 3(d), (f) and (h)) are separately coincident with the (111) and (220) planes of cubic ZnS, confirming the formation of TiO$_2$/ZnS core-shell structure. In addition, TiO$_2$ nanorods of TiO$_2$/ZnS-2 are not covered thoroughly with ZnS nanoparticles, which is agreement with the SEM observation in figure 2(d). According to figures 3(d), (e) and (g), the average thickness of ZnS shell in TiO$_2$/ZnS-2, TiO$_2$/ZnS-4 and TiO$_2$/ZnS-6 is approximately 3, 10 and 20 nm, respectively.

Figure 4 shows XPS spectra of TiO$_2$/ZnS-4 NRAs. The survey spectrum in figure 4(a) reveals the presence of C 1s, Ti 2p, O 1s, Zn 2p and S 2p signal peaks. It is well known that the C 1s peak is attributed to adventitious carbon-based contaminant [24]. Figures 4(b)–(e) show the high resolution XPS spectra of Ti 2p, O 1s, Zn 2p and S 2p. The Ti 2p high-resolution spectrum in figure 4(b), two typical peaks located at 458.2 eV and 463.9 eV correspond to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively, indicating the existence of Ti$^{4+}$ state in TiO$_2$ [19]. Figure 4(c) presents that the O 1 s peak can be fitted into two peaks. One peak at 529.3 eV originates from crystal lattice oxygen of TiO$_2$ [25], and the other peak at 531.1 eV is related to the oxygen from hydroxyl group or water on the sample surface [26, 27]. Figure 4(d) exhibits the Zn 2p XPS spectra. There are two sharp peaks at 1021.0 eV and 1044.2 eV can be assigned to the characteristic peaks of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ [28]. As shown in figure 4(e), two shake-up peaks are noted at 161.2 eV and 162.3 eV, corresponding to the characteristic peaks S 2p$_{3/2}$ and S 2p$_{1/2}$ [29], respectively. In a word, the XPS result further demonstrates that Ti, O, Zn and S elements exist simultaneously in TiO$_2$/ZnS-4 NRAs.

Figure 5(a) represents the UV-Vis DRS of TiO$_2$, and all TiO$_2$/ZnS NRAs. Bare rutile TiO$_2$ NRAs can absorb the wavelengths shorter than 410 nm because of its intrinsic band gap. Meanwhile, the band gap of ZnS (3.6 eV) is larger than that of TiO$_2$. For TiO$_2$/ZnS NRAs, the absorption edges exhibit a slightly blue shift with the increasing of ZnS shell thickness. Compared to pristine TiO$_2$ NRAs, the absorption in the visible range of all TiO$_2$/ZnS NRAs is enhanced. In addition, the absorption in the visible light region increases with the increasing
of ZnS shell thickness. When the ZnS content of TiO$_2$/ZnS-4 is low, TiO$_2$ will combine and mix well with ZnS through heterogeneous nucleation, resulting in a strong recombination effect between TiO$_2$ and ZnS. However, as the proportion of loaded ZnS increases, TiO$_2$/ZnS-6 are not uniformly coated with ZnS, but the agglomeration of ZnS on the surface of TiO$_2$ is most obvious. Thus, the absorption for TiO$_2$/ZnS-4 at 400-700 nm is higher than that of TiO$_2$/ZnS-6. Similar phenomena have been found in two wide band gap heterostructure composites, such as TiO$_2$/AgCl [30] and TiO$_2$/ZnO [31]. This phenomenon is possible due to the mid band gap defects [31]. The band gap energy ($E_g$) value is calculated on the basis of the formula: 
\[ \alpha h\nu = (h\nu - E_g)^n \] [32]. As shown in figure 5(b), the $E_g$ values of TiO$_2$, TiO$_2$/ZnS-2, TiO$_2$/ZnS-4 and TiO$_2$/ZnS-6 are 3.02, 3.03, 3.05 and 3.07 eV, respectively. This indicates that these $E_g$ values of TiO$_2$/ZnS core-shell heterostructure NRAs strongly depend on the ZnS shell thickness.

Photoluminescence (PL) spectroscopy is an important technique for detecting charge carrier recombination and defects. Figure 6 shows the PL spectra of TiO$_2$, TiO$_2$/ZnS-2, TiO$_2$/ZnS-4, and TiO$_2$/ZnS-6. The PL broad signal peak of TiO$_2$ at 560 nm may result from the Ti$^{4+}$ ion adjacent to the oxygen vacancy [33]. In addition, with the increase of ZnS shell thickness, the PL emission intensity of all TiO$_2$/ZnS increases, indicating that the recombination of charge carriers is enhanced. The potential cause of this strength enhancement is the sulfur vacancy or defects. This means that the sulfur vacancy produces a mid-gap defect state in ZnS, which can be used
as the trapping and concentration of electrons, and the hole improves the separation efficiency of photogenic carriers [33–35]. Furthermore, the photocatalytic activity is improved.

Figures 7(a) and (b) separately shows the photocatalytic degradation curves of RhB over time with pure TiO2 and TiO2/ZnS-4 under simulated sunlight. As shown in figure 7(a), the concentration of RhB aqueous solution changes very slowly when pure TiO2 as photocatalyst. However, the main absorption peak at 550 nm weakens gradually after 120 min when the TiO2/ZnS-4 NRAs are used as photocatalyst, as displayed in figure 7(b).

Figure 7(c) shows the adsorption characteristics and photocatalytic activities of different photocatalysts under simulated sunlight. After achieving the adsorption-desorption equilibrium in the dark, the adsorption abilities of the samples show the following order: TiO2/ZnS-6 > TiO2/ZnS-4 > TiO2/ZnS-2 > TiO2. Namely, the adsorption abilities increase with the increasing of ZnS shell thicknesses. However, the adsorption quantities of RhB on the photocatalysts are negligible compared to the degradation quantities of photocatalytic treatment. According to the photocatalytic result, blank experiment indicates that the self-photolysis of RhB can be omitted. Furthermore, the photocatalytic performance of all TiO2/ZnS NRAs exhibit dramatic increase compared with bare TiO2. In the time of 120 min, only 41.1% of RhB aqueous solution is decomposed by the bare TiO2, while TiO2/ZnS-2, TiO2/ZnS-4 and TiO2/ZnS-6 separately decomposed 81.7%, 98.0% and 95.6%.

The value of rate constant (k) of RhB degradation is calculated by the following equation on the basis of the pseudo-first-order model, \(-\ln(C_t/C_0) = kt\) [36]. Where \(C_0\) is initial RhB concentration, and \(C_t\) is the

![Figure 3. TEM and HRTEM images of (a, b) TiO2, (c, d) TiO2/ZnS-2, (e, f) TiO2/ZnS-4 and (g, h) TiO2/ZnS-6 NRAs.](image)
concentration after at t time. Figure 7(d) displays the k value of the samples. Among all the employed photocatalysts, TiO2/ZnS-4 NRAs show the maximum k value, which is about 7.3 times than that of bare TiO2 NRAs.

In order to probe the role of reactive species of TiO2/ZnS-4 NRAs during the photocatalytic reaction, the trapping experiment is carried out. Three scavengers, including benzoquinone (BQ), sodium oxalate (SO), and tert-butyl alcohol (BuOH), are added in the photocatalytic process to trap superoxide anion radical (·O2−), photogenerated holes (hvb+), and hydroxyl radical (·OH), respectively [37]. The concentration of scavengers in the RhB aqueous solution is 2 mmol l−1. According to figure 8, the photocatalytic activity of TiO2/ZnS-4 is distinctly suppressed after adding three scavengers, illustrating that ·O2−, hvb+, and ·OH participate in the photocatalytic reaction. However, the decline of degradation rate by adding SO is the biggest. Therefore, the hvb+ is the dominant active species for the degradation of RhB.

To further demonstrate the active species present in the process, electron spin resonance (ESR) measurement with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was applied with water or methanol for DMPO−O2− and DMPO−OH [38, 39]. As presented in figures 9(a) and (b), no any ESR signals of DMPO−O2− and DMPO−OH are noticed in the dark, while theirs typical four-peak are detected under simulated solar light illumination. These results indicate that ·O2− and ·OH radicals are generated and would participate in the degradation process. Furthermore, the results of the ESR analysis are consistent with the capture experiments.

The excellent photocatalytic activity of TiO2/ZnS NRAs is attributed to the synergetic effect between TiO2 and ZnS. As shown in figure 10, there are two possible paths for the transfer the photogenerated charge carriers.
in TiO$_2$/ZnS heterostructure. Under simulated solar light illumination, ZnS is excited by UV light to yield e$_{cb}^-$ and h$_{vb}^+$, while TiO$_2$ is excited by the sunlight below 410 nm to produce e$_{cb}^-$ and h$_{vb}^+$. Subsequently, the e$_{cb}^-$ will drift from ZnS to TiO$_2$ because of the more negative potential of the conduction band (CB) for TiO$_2$ [40]. Similarly, the h$_{vb}^+$ will transfer from TiO$_2$ to ZnS due to the lower potential of the valence band (VB) of ZnS, as shown the mechanism I in figure 10. Nevertheless, the CB potential of TiO$_2$ is lower than that of O$_2$/·O$_2$$^-$ (-0.33 eV) [41]. Thus, the e$_{cb}^-$ in the CB of TiO$_2$ cannot reduce O$_2$ to yield ·O$_2$$^-$·. Similarly, H$_2$O cannot be oxidized to generate ·OH by h$_{vb}^+$ in the CB of ZnS because of the more positive potential of OH$^-$/·OH (2.7 eV) and H$_2$O/·OH (2.4 eV). According to the trapping experiments of reactive species, h$_{vb}^+$, ·OH and ·O$_2$$^-$ are involved during the photocatalytic reaction. Therefore, the photocatalytic process follows the typical Z-scheme mechanism, as shown mechanism II in figure 10. In this case, the e$_{cb}^-$ in ZnS tends to reserve in the CB of ZnS, and the h$_{vb}^+$ in TiO$_2$ keep in the VB of TiO$_2$. Meanwhile, the e$_{cb}^-$ in the CB of TiO$_2$ combines with the h$_{vb}^+$ in VB of ZnS. This is the typical Z-scheme mechanism [41]. Therefore, the recombination of e$_{cb}^-$ and h$_{vb}^+$ in both TiO$_2$ and
ZnS is limited efficiently and the lifetime of charge carrier in TiO$_2$/ZnS is prolonged. Consequently, TiO$_2$/ZnS heterostructure NRAs display higher photocatalytic activity than that of bare TiO$_2$ NRAs, and the optimal thickness of ZnS shell is 10 nm. TiO$_2$/ZnS-2 NRAs show weak photocatalytic activity not only because the ZnS shell layer is thin but also because the surfaces of TiO$_2$ nanorods are not covered completely with ZnS nanoparticles. In the case of TiO$_2$/ZnS-6 NRAs, the excessively thick ZnS shell not only restrains the TiO$_2$ absorption of UV light but also hinders the migration of charge carriers between ZnS and TiO$_2$.

The reusability of photocatalyst is very important for its large-scale processes. The repeated photocatalytic experiments are carried out using TiO$_2$/ZnS-4 as photocatalyst, and the results are shown in figure 11. After each recycling, the photocatalyst only is washed with distilled water and without any treatment for next experiment.
Figure 9. ESR spectra of radicals trapped by DMPO in the presence of TiO$_2$/ZnS-4 in the dark and under simulated solar irradiation: DMPO–O$_2^-$ (a), DMPO–OH (b).

Figure 10. Photodegradation of RhB and schematic diagram of the energy band structure of TiO$_2$/ZnS heterostructure.

Figure 11. Repeated photocatalytic experiments of TiO$_2$/ZnS-4 NRAs.
According to figure 11, a small decrease in the photocatalytic activity of TiO$_2$/ZnS–4 is found, indicating that the photocatalyst has a good lifetime during the degradation process.

4. Conclusions

Core-shell structure TiO$_2$/ZnS NRAs with different ZnS shell thicknesses were successfully prepared using rutile TiO$_2$ NRAs as precursor which were fabricated by solvothermal route on Ti foil. Under simulated sunlight irradiation, all TiO$_2$/ZnS NRAs displayed higher photocatalytic activities of than pristine TiO$_2$ NRAs. The photocatalytic performances of TiO$_2$/ZnS NRAs obeyed Z-scheme mechanism. Among all TiO$_2$/ZnS NRAs, the thickness ZnS shell of 10 nm had the highest photocatalytic activity and good reusability.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No. 61378085, 51608226, 21776110, 21878119) and the Thirteenth Five-Year Program for Science and Technology of Education Department of Jilin Province (Item No. JJKH20191017KJ).

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