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Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructured photocatalysts with the enhanced and stable photocatalytic activity under both ultraviolet and visible light irradiation were obtained by S-doping Ag$_2$O/TiO$_2$. 
Phase Transformation and Enhanced Photocatalytic Activity of S-doped Ag$_2$O/TiO$_2$ Heterostructured Nanobelts

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Ag$_2$O/TiO$_2$ nanobelts heterostructures have been found to possess a high ultraviolet photocatalytic activity, but poor cycling performance. After a S-doping treatment, the obtained Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructured nanobelts exhibited an enhanced and stable photocatalytic activity under both ultraviolet and visible light irradiation, which was exemplified by the photo-degradation of organic pollutants and photocurrent response measurements. Meanwhile, the crystal structure and phase transformation of Ag$_2$O, Ag$_2$S$_2$O$_7$ and Ag$_2$S were studied by XRD and XPS measurements.

Thus, in order to improve the stability of these photocatalysts, surface plasmon effects and core-shell structures have been used to prevent photo corrosion, as shown in the preparation of Ag/AgCl and Cu$_2$O/TiO$_2$ hybrid structures. Herein, we designed a new approach based on S-doping of Ag$_2$O on TiO$_2$ nanobelts to prepare Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructures that exhibited high and stable photocatalytic activity under both ultraviolet and visible light irradiation. The Ag$_2$S$_2$O$_7$ on the surface of Ag$_2$O can effectively protect Ag$_2$O from conversion to Ag. The crystal structure and phase transformation of Ag$_2$O, Ag$_2$S$_2$O$_7$ and Ag$_2$S were studied by X-ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Experimental

Chemicals. Titania P25 (a commercial TiO$_2$), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H$_2$SO$_4$), silver nitrate (AgNO$_3$), and sodium sulfide (Na$_2$S) were purchased from Sigma-Aldrich Co. LLC. All chemicals were used without further purification. Deionized water was used throughout all experiments. Synthesis of TiO$_2$ nanobelts with rough surface. TiO$_2$ nanobelts with a rough surface were synthesized through a simple hydrothermal procedure followed by an acid corrosion treatment. In a typical reaction, 0.1 g of TiO$_2$ powder (P25) was mixed with 20 mL of 10 M NaOH aqueous solution. The mixed solution was stirred and then transferred into a Teflon-lined stainless steel autoclave, heated at 180 °C for 48 h, and then air-cooled to room temperature. The obtained wet powder was washed thoroughly with deionized water followed by a filtration process. The obtained Na$_2$Ti$_2$O$_7$ nanobelts were immersed in 0.1 M HCl aqueous solution for 24 h and then washed thoroughly with distilled water to obtain the H-titanate (H$_2$Ti$_3$O$_7$) nanobelts. To roughen the surface, the obtained H$_2$Ti$_3$O$_7$ nanobelts were added into a 25 mL Teflon vessel, then filled with 20 mL 0.02 M H$_2$SO$_4$ aqueous solution and maintained at 100 °C for 12 h. Finally, the products were

Introduction

Titanium dioxide (TiO$_2$) as an efficient photocatalyst has been intensively investigated since Fujishima and Honda discovered photocatalytic splitting of water on TiO$_2$ electrodes in 1972. TiO$_2$ has been shown to be an excellent photocatalyst with long-term stability, low-cost preparation and a strong oxidizing power useful for the decomposition of unwanted organic compounds. However, this material is only active under UV excitation because of its large energy band gap of 3.2 eV (anatase). Considering the fraction of UV light is less than 5% in the total solar spectrum on the earth, it is crucial and of great challenge to develop efficient visible light-active photocatalysts. Thus band gap engineering of photocatalysts to induce absorption into the wide visible light region has been considered as a possible solution to this problem. Doping of anions such as N, H, and C into TiO$_2$ has been widely reported. In addition, the growth of TiO$_2$-based heterostructures, such as Ag$_2$O/TiO$_2$, Cu$_2$O/TiO$_2$, MoS$_2$/TiO$_2$, Fe$_2$O$_3$/TiO$_2$, and SrTiO$_3$/TiO$_2$ have been developed, aiming to enhance the photocatalytic efficiency by broadening their light-harvesting window to the visible range. At the same time, the efficiency of charge separation can be enhanced by coupling two semiconductor structures with matched energy levels, leading to the improved photocatalytic activity.

Previously we developed a new system of Ag$_2$O/TiO$_2$ nanobelts, which can effectively suppress hole-electron recombination under UV light irradiation. Ag$_2$O nanoparticles are found to act as efficient electron absorbing agents under UV light irradiation and as an efficient photosensitiser under visible light irradiation. Subsequently, many studies on the synthesis of Ag$_2$O photocatalysts have been reported, such as Ag$_2$O, Ag$_2$O/ZnO, Ag$_2$O/Br$_2$O$_3$, Ag$_2$O/TIO$_2$, Ag$_2$O/Ag$_2$CO$_3$, Graphene Oxide/Ag$_2$O and g-C$_3$N$_4$/Ag$_2$O. In our work, we found that Ag$_2$O/TiO$_2$ heterostructures possess a high photocatalytic activity, but poor cycling performance, as Ag$_2$O may be reduced into Ag by photogenerated electrons. Thus, in order to improve the stability of these photocatalysts, surface plasmon effects and core-shell structures have been used to prevent photo corrosion, as shown in the preparation of Ag/AgCl and Cu$_2$O/TiO$_2$ hybrid structures. Herein, we designed a new approach based on S-doping of Ag$_2$O on TiO$_2$ nanobelts to prepare Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructures that exhibited high and stable photocatalytic activity under both ultraviolet and visible light irradiation. The Ag$_2$S$_2$O$_7$ on the surface of Ag$_2$O can effectively protect Ag$_2$O from conversion to Ag. The crystal structure and phase transformation of Ag$_2$O, Ag$_2$S$_2$O$_7$ and Ag$_2$S were studied by XRD and XPS measurements.

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isolated from the solution by centrifugation and sequentially washed with deionized water for several times, and dried at 70 °C for 10 h. By annealing the acid-corroded H₂TiO₇ nanobelts at 600 °C for 2 h, anatase TiO₂ nanobelts with a rough surface were obtained.

**Synthesis of Ag₂O/TiO₂ nanobelt heterostructures.** The formation process of Ag₂O/TiO₂ nanobelt heterostructures (50 wt% of Ag₂O) was described as follows. Typically, 0.2 g of the acid-corroded TiO₂ nanobelts prepared above was dispersed in 50 mL of distilled water, and 0.29 g of silver nitrate (AgNO₃) was dissolved into the above suspension. The mixture was stirred magnetically for 30 min to establish the adsorption equilibrium. 50 mL of a 0.2 M NaOH aqueous solution was slowly dropped to the above mixture of AgNO₃ and TiO₂. The amount of NaOH was more than sufficient to completely consume all the added AgNO₃, and the final pH of reaction solution was 14. Finally, TiO₂ nanobelts coated by Ag₂O nanoparticles was collected after centrifugation and washed with deionized water for several times, then dried at 50 °C for 12 h.

**Synthesis of S-doped Ag₂O/TiO₂ nanobelts heterostructures.** 0.2 g of the Ag₂O/TiO₂ nanobelt heterostructures (50 wt% of Ag₂O) prepared above was dispersed in 50 mL of distilled water, then stirred magnetically for 30 min. A calculated amount of an aqueous solution of 0.01 M sodium sulfide (Na₂S) was slowly added into the above suspension under magnetic stirring. The color of the suspension was found to gradually change from yellow to black. S-doped Ag₂O/TiO₂ nanobelts were produced and collected after centrifugation and sequentially washed with deionized water for several times, then dried at 50 °C for 12 h. The different components of heterostructures were controlled by adding different amount of sulfur. 0 mg, 8.4 mg, 16.8 mg and 33.6 mg of Na₂S were added into the above aqueous solution of 0.2 g Ag₂O/TiO₂, respectively. The obtained heterostructures were denoted as S₁ (Ag₂O/TiO₂), S₂ (Ag₂O/Ag₂S₇/TiO₂), S₃ (Ag₂S₇/TiO₂) and S₄ (Ag₅S/TiO₂), respectively.

**Characterizations.** X-ray powder diffraction (XRD) patterns of the catalysts were recorded with a Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 0.15406 nm). A HITACHI S-4800 field emission scanning electron microscope (FE-SEM) was used to characterize the morphologies and size of the synthesized Ag₂O/TiO₂ samples. The chemical composition was investigated via energy-dispersive X-ray spectroscopy (EDS). High resolution transmission electron microscopic (HRTEM) images were acquired with a JOEL JEM 2100 microscope. UV-Vis absorption spectra were recorded with a UV72600 spectrophotometer (UV72600, Shimadzu) with an integrating sphere attachment and BaSO₄ as the reference. The absorbance was recorded with a UV72102PC spectrophotometer (UV72102PC). The different samples were repeatedly used for six times with same experiment conditions to test the photocatalytic stability.

**Results and discussion**

![Figure 1. The XRD patterns of (a) Ag₂O/TiO₂, (b) Ag₂O/Ag₂S₇/TiO₂, (c) Ag₂S₇/TiO₂ and (d) Ag₅S/TiO₂ nanobelt heterostructures.](image-url)
prepared Ag contrast. with rough surface by SEM equipment due to the low Ag Ag up to hundreds of micron, which as shown in Figure S1. The corroded nanobelts show a width of 50 to 200 nm, and length of Ag nanobelts heterostructures of only composed of Ag, Ti and O elements. After sulfu Ag nanoparticles can’t be distinguished from the TiO nanoparticles on TiO virtually unchanged as shown in Figure 2b-d, indicating the obscure interfaces on the surface of TiO nanoparticles with Ti and O signals (Figure 3c). In addition, the obscure interfaces on the surface of AgO nanoparticles were observed in HRTEM image of S2 (AgO/AgS2O7/TiO2) as shown in Figure S3, which implied that the AgS2O7 was possibly formed by sulfur diffusion into the interior AgO nanoparticles.

The morphological and microstructural details of the as-prepared AgO/TiO2, AgO/AgS2O7/TiO2, AgS2O7/TiO2 and AgS/TiO2 nanobelt heterostructures were then investigated by SEM and HRTEM measurements. Figure 2a shows a typical SEM image of the as-prepared AgO/TiO2 nanobelts. The acid corroded nanobelts show a width of 50 to 200 nm, and length of up to hundreds of micron, which as shown in Figure S1. The Ag2O nanoparticles on TiO2 nanobelts exhibited a narrow size distribution with a small size of 5 to 20 nm. However, the Ag2O nanoparticles can’t be distinguished from the TiO2 nanobelts with rough surface by SEM equipment due to the low contrast.4,11 Energy dispersive X-ray spectroscopy (EDS) analysis (Figure 2e) reveals that the Ag2O/TiO2 nanobelts are only composed of Ag, Ti and O elements. After sulfur doping, the morphologies of the nanobelt heterostructures of Ag2O/AgS2O7/TiO2, AgS2O7/TiO2 and AgS/TiO2 remained virtually unchanged as shown in Figure 2b-d, indicating the nanoparticles on TiO2 nanobelts are very stable. EDS analysis reveals that the sulfur content of the heterostructures increased with the doping contents, which were shown in Figure 2e.

Figure 2. Typical SEM images of (a) Ag2O/TiO2, (b) Ag2O/AgS2O7/TiO2, (c) AgS2O7/TiO2 and (d) AgS/TiO2 nanobelt heterostructures with different magnifications, (e) EDS results of the different heterostructures.

HRTEM images of the samples further confirm the formation of a heterostructure between TiO2 nanobelt and AgS2O7 nanoparticles (Figure 3). After a Na2S aqueous solution was added into the mixed aqueous solution of AgO/TiO2 nanobelts, AgS2O7 nanoparticles were found to be tightly attached on the surface of TiO2 nanobelt, forming AgS2O7/TiO2 heterostructures (Figure S2), which may be propitious to electron transfer between the two phases. Measurements of the lattice fringes showed an interplanar distance of ca. 0.35 nm and 0.14 nm, corresponding to the (101) plane of anatase TiO2 and the (220) plane of Ag2S2O7, respectively. Energy dispersive X-ray spectrometry (EDS) mapping analysis of S3 sample also confirmed that AgS2O7 nanoparticles, composed of Ag, S, and O elements, were dispersed on the surface of TiO2 nanobelt.

The electronic states of the Ag and S elements in S-doped AgO were then studied by XPS measurements. The results are shown in Figure 4. The Ag 3d5/2 electrons of AgO/TiO2 can be identified at 368.1 eV, which is characteristic of Ag+ (Figure 4a). The asymmetric peaks for Ag3d5/2 and Ag3d3/2 suggest that the AgO nanoparticles might have undergone partial surface reduction from photoelectrons of TiO2 nanobelts. From sample S2 to sample S4, the binding energy of the Ag 3d5/2 electrons was found to shift to 367.8, 367.9 and 368 eV, respectively, in
good agreement with the expected values for Ag bound to sulfur, indicating the increasing degree of sulfur doping.\textsuperscript{31} XPS measurements of the S 2p electrons display similar results (Figure 4b). For the Ag$_2$O/TiO$_2$ sample, no S signal was observed. After sulfur doping, obvious signals can be observed for the S 2p electrons in the S2, S3 and S4 samples. For instance, for the S2 and S3 samples, in addition to S 2p electrons at 162.9 and 161.7 eV, S 2p electrons can also be at 168.7 and 167.7 eV, indicating the formation of Ag$_2$S$_2$O$_7$. After being completely vulcanized (S4), the S$_2^+$ peaks disappeared, consistent with the complete conversion from Ag$_2$S$_7$O$_2$ to Ag$_2$S. In comparison with the results of Ag$_2$S, the S 2p peaks for Ag$_2$S$_7$O$_2$ shift by about 0.7 eV from 161.0 eV to 161.7 eV, which could be attributed to the S-O bonding effect. These XPS results suggest that the S-doping process might involve a change of the S valence state from S$^2_-$ (Na$_2$S$_2$) to S$^\text{O}_7$ (Ag$_2$S$_2$O$_7$), and then to S$^2_-$(Ag$_2$S).

![Figure 5](image5.png)

**Figure 5.** (a) Photocatalytic activity and (b) stability under UV light irradiation of (S1) Ag$_2$O/TiO$_2$, (S2) Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, (S3) Ag$_2$S$_7$O$_2$/TiO$_2$ and (S4) Ag$_2$S/TiO$_2$ nanobelts and TiO$_2$ nanobelts.

To evaluate the photocatalytic activity, we examined the decomposition of MO in water under UV light irradiation as a function of time. For comparison, the decomposition over (S1) Ag$_2$O/TiO$_2$, (S2) Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, (S3) Ag$_2$S$_7$O$_2$/TiO$_2$ and (S4) Ag$_2$S/TiO$_2$ was carried out under the same experimental conditions. As shown in Figure 5, the Ag$_2$O/TiO$_2$ heterostructures exhibited the highest photocatalytic activity in MO degradation under UV irradiation. With increasing irradiation time, the decomposition of the MO dye progressed steadily and completed in 8 min of UV irradiation. The degradation activity of Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$ heterostructures was much higher than those of the Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S/TiO$_2$ and TiO$_2$ nanobelts, and slightly lower than that of Ag$_2$O/TiO$_2$. The results suggest that the photocatalytic activity of the heterostructures decreased with the increase of the sulfur content.

Yet, the photocatalytic stability of the heterostructures under UV light irradiation was enhanced with S doping. Experimentally, the photocatalysts were used repeatedly for six times after separation via membrane filtration, and the activity was evaluated and compared, as shown in Figure 5b. One can see that the Ag$_2$O/TiO$_2$ photocatalyst was unstable for repeated use under UV irradiation with a marked decrease of the photocatalytic activity after each repetition. For instance, the photocatalytic degradation efficiency of MO was only 65% after six times. However, the S-doped samples of Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S/TiO$_2$ photocatalysts all exhibited stable photocatalytic performance under UV light irradiation. There is no obvious decrease of the removal rate of MO after six cycles for 96 min.

![Figure 6](image6.png)

**Figure 6.** (a) Visible-light photocatalytic activity and (b) stability of TiO$_2$ nanobelts, (S1) Ag$_2$O/TiO$_2$, (S2) Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, (S3) Ag$_2$S$_7$O$_2$/TiO$_2$ and (S4) Ag$_2$S/TiO$_2$.

![Figure 7](image7.png)

**Figure 7.** UV-vis absorbance spectra of TiO$_2$ nanobelts, (S1) Ag$_2$O/TiO$_2$, (S2) Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, (S3) Ag$_2$S$_7$O$_2$/TiO$_2$ and (S4) Ag$_2$S/TiO$_2$.

The visible-light photocatalytic activities of TiO$_2$ nanobelts, Ag$_2$O/TiO$_2$, Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$ and Ag$_2$S/TiO$_2$ were also evaluated by photocatalytic degradation of MO aqueous solution under visible light irradiation, which were shown in Figure 6. Due to the large band gap energy (3.2 eV for anatase), TiO$_2$ nanobelts can absorb UV light with wavelengths shorter than 400 nm. So, TiO$_2$ nanobelts showed only a low photocatalytic activity under visible-light irradiation, and the degradation was only 12% in 150 min. In contrast, the Ag$_2$O/TiO$_2$, Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$ and Ag$_2$S/TiO$_2$ heterostructured catalysts all showed apparent visible-light photocatalytic activity. Figure 7 depicts the UV-vis absorbance spectra of the different samples. One can see that Ag$_2$O, Ag$_2$S$_7$O$_2$ and Ag$_2$S might act as efficient visible-light sensitizers leading to improved visible light photocatalytic activity of the TiO$_2$ nanobelts. For instance, Ag$_2$O/TiO$_2$ nanobelts display strong light absorption in both UV and visible regions of 250-1200 nm. After sulfur doping, the obtained Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$ showed similar absorption in the same range of 250 nm to 1200 nm but with a blue shift. As for Ag$_2$S/TiO$_2$, the absorption peak between 500 and 600 nm disappeared, and the absorbance was significantly reduced at wavelength greater than 1000 nm. Note that the photocatalytic activity of Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$ heterostructure was better than those of Ag$_2$O/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$ and Ag$_2$S/TiO$_2$. This might be accounted for by energy band matching that has been found to play an important role in enhancing photocatalytic activity. The degradation rate of MO by Ag$_2$O/Ag$_2$S$_7$O$_2$/TiO$_2$ reached 81% in 150 min. The corresponding degradation rates of MO under the same conditions in the presence of Ag$_2$O/TiO$_2$, Ag$_2$S$_7$O$_2$/TiO$_2$ and
Ag$_2$S/TiO$_2$ were 55%, 62% and 24%, respectively. To investigate the photocatalytic stability under visible light irradiation, the same samples were repeatedly used for six times, which were shown in Figure 6b. All the heterostructured photocatalysts, (S1) Ag$_2$O/TiO$_2$, (S2) Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$, (S3) Ag$_2$S$_2$O$_7$/TiO$_2$ and (S4) Ag$_2$S/TiO$_2$, exhibited very stable photocatalytic activity under visible-light irradiation. There is no obvious decrease on the removal rate of MO after six cycles (for 900 min). Of these, Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructured nanobelts exhibited the best photocatalytic performance under both UV and visible light irradiation.

![Figure 8](image)

**Figure 8.** Photographs (a) and time-dependent photocurrent response (b) of the ITO photoelectrodes composed of the different heterostructured photocatalysts at a bias voltage of 0.5 V. All the photocurrent intensities were unified correction with dark current. The scale bar of Y-Axis in Figure 8b is 0.5 mA/cm$^2$.

To further understand the effects of heterostructures and S-doping on the photocatalytic activity, we studied the photo-induced charge transfer properties of the S-doped Ag$_2$O/TiO$_2$ heterostructures. Photocurrent response of the different heterostructures were recorded under UV and visible-light irradiation ($\lambda > 420$ nm). Figure 8a shows the photographs of different photoelectrodes. The rich colors indicate different energy band structures of the S-doped Ag$_2$O/TiO$_2$ heterostructures that might affect photo absorption. Figure 8b show the photocurrent-time curves for S-doped Ag$_2$O/TiO$_2$ heterostructures under several on/off light irradiation cycles. All samples generate photocurrents with a reproducible response to on/off cycles under UV light irradiation, demonstrating effective charge transfer and electron collection for the photoelectrodes. However, only pure TiO$_2$ nanobelts were fast in generating photocurrent with a reproducible response to on/off cycles. The S-doped Ag$_2$O/TiO$_2$ heterostructures show longer photo-response time, implying the slow charge transfer process, which was possibly due to the heterostructured interface and the random order together of S-doped Ag$_2$O/TiO$_2$ nanobelts. However, sample S1 (Ag$_2$O/TiO$_2$) exhibited the highest photocurrent, which is consistent with the UV photocatalytic activity of S-doped Ag$_2$O/TiO$_2$ heterostructures (Figure 5). Under visible-light irradiation, pure TiO$_2$ nanobelts show only a negligible photocurrent, whereas all S-doped heterostructures showed apparent photocurrents, even higher than those under UV light irradiation, such as S2 (Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$). The high current density demonstrates that the photo-induced electrons and holes of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ prefer to separate and further transfer to the ITO glass due to the heterostructures built between Ag$_2$O, Ag$_2$S$_2$O$_7$ and TiO$_2$.

![Figure 9](image)

**Figure 9.** A schematic view for electron-hole separation and energy band matching of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructure under UV and visible light irradiation.

On the basis of above results, a possible mechanism of high and stable photocatalytic activity of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructure under UV and visible light irradiation was proposed (Figure 9). Standard density functional theory (DFT) was used to calculate the electronic structure of Ag$_2$S$_2$O$_7$ herein, which has not been reported up to now. The atomic unit cell structure, band structure and electronic density of states for Ag$_2$S$_2$O$_7$ were shown in Figure S4 and S5. The band gap of $\sim$2.24 eV for Ag$_2$S$_2$O$_7$ was obtained. In addition, the conduction and valence band positions were determined by using the following empirical equation$^{32}$,

$$E_{CB} = X - 0.5E_g$$

where $E_{CB}$ denotes the conduction band edge potential, $X$ is the geometric mean of the Mulliken electronegativity of the constituent atoms, $E_g$ is the energy of free electrons on the hydrogen scale (about 4.5 eV) and $E_g$ is the band gap. The X values for TiO$_2$, Ag$_2$O and Ag$_2$S$_2$O$_7$ are 5.81 eV, 5.29 eV and 6.02 eV, respectively,$^{34}$ and the corresponding Eg values are 3.2 eV, 1.2 eV, and 2.24 eV. Thus, the positions of the conduction band edge ($E_{CB}$) at the point of zero charge are estimated to be -0.29 eV, 0.19 eV, and 0.26 eV, respectively, as illustrated in Figure 9.

Under UV light irradiation, TiO$_2$ nanobelts were excited to produce h$^+$ and e$. Ag$_2$O nanoparticles on the surface of TiO$_2$ nanobelts captured electrons effectively due to the more positive conduction band of Ag$_2$O than that of TiO$_2$. The obtained electrons reacted with Ag$_2$O nanoparticles with the narrow band gap (1.2 eV) to produce Ag nanoparticles. The Ag$_2$O nanoparticles as electron acceptors prevent electrons and holes from recombination, and the holes efficiently oxidize organic compounds, and thus the photocatalytic activity is enhanced, but the catalysts were unstable. After sulfur doping,
the obtained Ag$_2$S$_2$O$_7$ on the surface of Ag$_2$O nanoparticles can effectively prevent deformation of the crystal structure. Ag$_2$S$_2$O$_7$ has the appropriate energy structure, energy band matching with that of Ag$_2$O, which can capture electrons from the conduction band of Ag$_2$O, but not be reduced by the photogenerated electrons of TiO$_2$ due to wide band gap of Ag$_2$S$_2$O$_7$ (~2.24 eV). However, compared with Ag$_2$O/TiO$_2$, the photocatalytic activity of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ was slightly decreased due to the reduced content of Ag$_2$O. So, the relatively high- and stable UV photocatalytic activity of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ was obtained by the sulfur doping due to the protective effect and energy band structure of Ag$_2$S$_2$O$_7$.

Under visible light irradiation, Ag$_2$O, Ag$_2$S$_2$O$_7$ and Ag$_2$S can be excited to produce holes ($h^+$) and electrons ($e^-$) due to the narrow band gap (1.2 eV, 2.24 eV and 0.92 eV, respectively), leading to apparent visible photocatalytic activity. Compared with Ag$_2$O/TiO$_2$ and Ag$_2$S$_2$O$_7$/TiO$_2$, Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructure possessed the best visible photocatalytic activity. The results were mostly attributed to the heterostructure and energy band matching of Ag$_2$O and Ag$_2$S$_2$O$_7$. The lifetime of the excited electrons and holes was prolonged in the transfer process between heterostructure, thus the photocatalytic reaction was enhanced. As electron excitation did not occur in TiO$_2$ by visible light irradiation, Ag$_2$O and Ag$_2$S$_2$O$_7$ were stable in the system of Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$. These characteristics led to the emergence of the Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructures as the best photocatalyst among the series.

Conclusions

Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ nanobelt heterostructures were synthesized by S doping of Ag$_2$O/TiO$_2$ nanobelts. The crystal structure and phase transformation of Ag$_2$O, Ag$_2$S$_2$O$_7$, and Ag$_2$S were studied by XRD and XPS measurements. XPS studies indicated that the sulfuration process involved various valence states of the S element, from S$^{2-}$ (Na$_2$S) to S$^+$ (Ag$_2$S), then to S$^{2+}$ (Ag$_2$S). Within the present experimental context, the Ag$_2$O/Ag$_2$S$_2$O$_7$/TiO$_2$ heterostructured nanobelts exhibited the high and stable photocatalytic activity both under ultraviolet and visible light irradiation. UV-vis absorption spectra showed that Ag$_2$O, Ag$_2$S$_2$O$_7$, and Ag$_2$S served as effective visible-light sensitizers that led to improved visible light photocatalytic activity of the TiO$_2$ nanobelts. The results might be accounted for by energy band matching among Ag$_2$O, Ag$_2$S$_2$O$_7$, and TiO$_2$ as well as by the structure restriction effects.

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