Research Article

Fabrication and Photocatalytic Property of One-Dimensional SrTiO$_3$/TiO$_{2-x}$N$_x$ Nanostructures

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One-dimensional SrTiO$_3$/TiO$_{2-x}$N$_x$ nanostructures were prepared by the hydrothermal method and investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) measurements. The photocatalytic activities of the prepared samples were evaluated by photodegrading the methylene blue (MB) solution. According to the characterizations, the intermediate product of SrTiO$_3$/titana tenotubes was presented after hydrothermal processing of the TiO$_{2-x}$N$_x$ nanoparticles with the mixed solution of NaOH and Sr(NO$_3$)$_2$. The final product of SrTiO$_3$/TiO$_{2-x}$N$_x$ nanorods was obtained after calcining the intermediate. As compared to the TiO$_{2-x}$N$_x$ nanoparticles, the absorption performance of SrTiO$_3$/titana tenotubes or SrTiO$_3$/TiO$_{2-x}$N$_x$ nanorods was depressed, instead of improving it. The mechanisms of the absorption property changes were discussed. The SrTiO$_3$/TiO$_{2-x}$N$_x$ nanorods presented better photocatalytic activity than the TiO$_{2-x}$N$_x$ nanoparticles or nanorods. However, due to overmuch adsorption, the SrTiO$_3$/titana tenotubes gave ordinary photocatalytic performances.

1. Introduction

TiO$_2$ has been extensively investigated for several decades in photocatalysis and photovoltaic areas. Anatase-type TiO$_2$ has attracted great interest as one of the most promising photocatalysts due to its impressed advantages such as high degradation capability, chemical stability, and low cost. However, the application potential of TiO$_2$ photocatalyst is restricted for its low quantum efficiency which is mainly caused by its low light absorption efficiency and high photogenerated charge carrier recombination rate. One-dimensional (1D) nanostructures can facilitate transport of charge carriers and minimize the loss of charge carriers at grain boundaries [1–3]. Hence, the charge carrier recombination of TiO$_2$ is expected to be held back by fabricating 1D nanostructure. Another efficient method to increase the charge separation efficiency of TiO$_2$ is modifying the photocatalyst with some other semiconductors because of the charge carrier transfer between valence or conduction band of two different semiconductors [4–6].

Recently, TiO$_2$ photocatalyst was reported to be modified by various materials such as graphene [7], Fe$_5$O$_4$ [8], C$_{60}$ [9], CdS, and Bi$_2$S$_3$ [10], by which the photocatalytic activity of TiO$_2$ was enhanced. Moreover, to further improve the photogenerated charge carrier separation rate, some semiconductors were coupled with prepared 1D nanostructures (such as nanotube, nanofiber, and nanorod). Zhai et al. reported high photoactivities in the visible light responsive graphene/titana tenotubes photocatalysts fabricated by hydrothermal method [11]. Yi et al. fabricated the silver nanoparticles, decorated nanobranched TiO$_2$ nanofibers, and presented that the photocatalytic degradation rates of silver loaded on nanobranched TiO$_2$ nanofibers were 1.6 and 1.7 times as those of pure TiO$_2$ nanofibers in the presence of methylene blue and methyl orange, respectively [12].

Cubic-perovskite-type SrTiO$_3$, a multimeatallic oxide semiconductor with a band gap of 3.4 eV comparable to TiO$_2$, has drawn considerable interest because of its applications in storage batteries, thermoelectric property, solar cell, and photocatalysis [13–16]. SrTiO$_3$ is a good candidate for coupling TiO$_2$ and improving the photocatalytic performance of the photocatalyst because its conduction band edge is more negative than TiO$_2$. Due to the potential differences between
the band edges of these two semiconductors, the photogenerated electrons transfer from the conduction band of SrTiO$_3$ to that of TiO$_2$. Conversely, the photogenerated electrons transfer from the conduction band of SrTiO$_3$ to that of TiO$_2$. Then the photogenerated charge carriers can be efficiently separated by these processes, resulting in the enhancement of the photocatalytic property in the photocatalyst. Recently, some research work about SrTiO$_3$/TiO$_2$ photocatalysts has been reported [17–19]. On the other hand, it has been extensively reported that N-doping could obviously improve the photocatalytic activity of TiO$_2$ [20, 21]. In this work, we fabricated one-dimensional SrTiO$_3$/TiO$_2$-$x$N$_x$ nanostructures by the hydrothermal method. The photocatalytic activity for the degradation of methylene blue (MB) solution in the N-doped TiO$_2$ was greatly enhanced after coupling with SrTiO$_3$.

2. Materials and Methods

2.1. Sample Preparation. Anatase nanocrystalline TiO$_2$ was synthesized by a simple sol-gel method as our previous work described [22]. Different amounts of Sr(NO$_3$)$_2$ were dissolved in 40 mL of 10 mol/L NaOH solution. Then 0.78 g N-TiO$_2$ powder was dispersed into the mixture solution to form a suspension which was heated at 180$^\circ$C for 24 h under hydrothermal condition in a PTFE-lined stainless steel vessel. The observed sediment at the bottom of the vessel was washed with 0.1 mol/L HCl solutions until pH is less than 7, followed by washing with DI water and drying at 80$^\circ$C in air overnight. The dried powder was milled and calcined at 400$^\circ$C under air for 2 h. SrTiO$_3$/N-TiO$_2$ samples with different ratios of SrTiO$_3$ were then prepared.

2.2. Characterization and Measurements. X-ray diffraction (XRD) patterns were recorded on a DX-2500 diffractometer (Fangyuan, Dandong) with Cu K$\alpha$ radiation with $\lambda = 0.1541\text{\AA}$ nm. Transmission electron microscopy (TEM) measurements were carried out on a JEOL-2010 TEM at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded on an Axis Ultra system with monochromatic Al K$\alpha$ X-rays (1486.6 eV) operated at 45 W and 15 kV with a background pressure of approximately 5.0 $\times$ 10$^{-9}$ Torr. A survey spot size and 40 eV pass energy were used for the analysis. Emitted photoelectrons perpendicular to the sample surface were collected. The binding energy of all investigated elements was referenced by the C 1s peak at 284.8 eV of the surface adventitious carbon, respectively. The diffuse reflection spectra were obtained on an UV-vis spectrophotometer (Varian Cary 5000) using BaSO$_4$ as the reference standard and were converted to the absorbance data through the Kubelka-Munk method.

Photocatalytic experiments were carried out in an inner-irradiation-type reactor. A cylindrical reaction cell was used to contain the reaction solution, and a 500 W long-arc xenon lamp surrounded with a water cooling system was fixed in the center of the reaction cell. 30 mg of photocatalyst was suspended in 200 mL of a methylene blue (MB) solution (10 mg/L) under stirring magnetically. The mixture was kept in the dark for 30 minutes to establish an adsorption-desorption equilibrium before the light radiation. The amount of MB in the solution was determined on the basis of its characteristic optical absorption at 665 nm using a visible light spectrophotometer (Model: 723C) based on Lambert-Beer’s law.

3. Results and Discussion

3.1. Crystal Structure and Morphology. The XRD patterns of the uncalcined and calcined samples are presented in Figure 1. The main diffraction peaks at about 9.1, 24.3, 28.0, and 48.3$^\circ$ in the patterns of the uncalcined samples (Figures 1(a), 1(b), and 1(c)) are designated to the protogenic titanate phase [23]. Additionally, with the increase of the Sr/Ti ratio, the intensity of the diffraction peaks contributed by SrTiO$_3$ at about 32.3, 46.4, 57.5, and 67.6$^\circ$ gradually increases. From Figures 1(d), 1(e), and 1(f), it can be found that main crystalline phases in the calcined samples involve the anatase and SrTiO$_3$ phase. Figure 2 shows the morphologies of the uncalcined and calcined samples. From the TEM results as shown in Figures 2(a), 2(b), and 2(c), it is found that the uncalcined samples are all composed of nanotubes with lengths about 200–300 nm and diameters about 10 nm. After the calcination, the nanotubes in the uncalcined samples morph into nanorods with diameters of 510 nm and different lengths as Figures 2(d), 2(e), and 2(f) show.

3.2. XPS Measurements. Figure 3 shows the XPS spectra of O 1s, N 1s, Ti 2p, and Sr 3d for the SrTiO$_3$/TiO$_2$-$x$N$_x$ with the Sr/Ti ratio of 5%. After fitting the result of O 1s XPS, it can be found that two peaks centered at 529.8 eV and 531.2 are observed in the O 1s XPS peak, attributing to bulk oxygen bonded to titanium and surface hydroxyl oxygen in TiO$_2$, respectively [22, 24]. From Figure 3, a similar broad peak from 397 eV to 403 eV is displayed in the XPS pattern of N.
Is state with our previous work where the broad N Is peak in the XPS pattern of the (Y, N)-codoped TiO$_2$ was attributed to the formation of the O–Ti–N (substitutional N) and Ti–O–N (interstitial N) structures in the lattice of TiO$_2$ during the nitridation process [22]. The XPS result of N Is also indicates that N still exists in the lattice of TiO$_2$ after the hydrothermal process. As shown in Figure 3, two peaks at 458.6 and 464.6 eV are observed in the spectrum of Ti 2p, which corresponds to the $2p_{3/2}$ and Ti $2p_{1/2}$ states of Ti$^{4+}$, respectively [22]. By fitting the XPS result of Sr 3d, two peaks at about 133.0 and 134.7 eV are revealed, assigning to the Sr 3d electronic states in the SrTiO$_3$ perovskite material and SrO complexes, respectively [24–26].

3.3. UV-Vis Spectroscopy. Figure 4 shows the UV-vis spectra of the uncalcined and calcined samples. It can be observed that all the absorption spectra in Figure 4 exhibit typical absorption behavior of the wide band gap oxide semiconductor, having an intense absorption band with a steep edge. From the spectra, the absorption edges of the uncalcined (SrTiO$_3$/titanate) samples with the Sr/Ti ratio of 0%, 1%, 2%, and 5%, respectively, lie at 390.9, 392.5, 408.4, and 396.7 nm as shown in Figure 4 (curves (a)–(d)). The absorption edges of the calcined (SrTiO$_3$/TiO$_{2-x}$N$_x$) samples with the Sr/Ti ratio of 0%, 1%, 2%, and 5%, respectively, lie at 424.5, 408.9, 418.8, and 402.1 nm (see curves (e)–(h) in Figure 4). Compared with the absorption edges of uncalcined samples, the absorption edges of the calcined samples shift slightly toward lower energy, respectively, which can be attributed to the differences of band structure and morphologies between titanate nanotubes and anatase nanorods. On the other hand, slight red shifts can be observed in the SrTiO$_3$/titanate samples after decorating titanate with SrTiO$_3$. However, different absorption edge blue shifts occur in the SrTiO$_3$/TiO$_{2-x}$N$_x$ samples as compared to the undecorated TiO$_{2-x}$N$_x$. The origins of absorption edge shifts after the decoration of SrTiO$_3$ are still under discussion. It is known that the N-doping in TiO$_2$ nanoparticles can result in obvious visible photocatalytic activity because the band narrowing and oxygen vacancies caused by the N-doping can greatly extend the optical absorption range to visible light region. The inset of Figure 4 shows the absorption spectrum of the TiO$_{2-x}$N$_x$.
nanoparticles which reveals that the absorption edge lies at 426.0 nm, and a broad absorption shoulder is observed from 380 to 550 nm. According to the calculational results by Dong et al. [27], the highest localized state for the substitutional N state is 0.14 eV above the top of the valence band and 0.73 eV for the interstitial N state. N-doping simultaneously favored the formation of oxygen vacancy whose electronic states are located 0.8 eV below the conduction band minimum. Herein, in our opinion, the absorption edge at 426.0 nm can be attributed to the electron transition from the substitutional N states to the conduction band, and the absorption shoulder is contributed by the electron transition between the valence (or conduction) band and the oxygen vacancy (or interstitial N) states. It should be noted that the absorption shoulder is not presented in the spectra of the uncinalned or calcined samples, indicating the decrease or vanishing of oxygen vacancies and interstitial N after the hydrothermal process.

3.4. Photocatalytic Activity. The photocatalytic activities of the prepared samples were evaluated by monitoring the degradation of MB solution, where the concentration of MB was obtained from the linear relation between the absorbance and the concentration of MB solution. Figure 5 displays the degradation rate of MB as a function of light irradiation time without any photocatalyst (the blank test) and over the photocatalysts of TiO$_2$-xN$_x$ nanoparticles, TiO$_2$-xN$_x$ nanorods, and SrTiO$_3$/TiO$_2$-xN$_x$ nanorods with different amounts of SrTiO$_3$ and SrTiO$_3$/titanate nanotube with 5% Sr/Ti ratio. Firstly, the TiO$_2$-xN$_x$ nanorods sample presents a similar photocatalytic performance with the sample of TiO$_2$-xN$_x$ nanoparticles even though the photoabsorption efficiency of the former is obviously lower than that of the latter. According to the C/C$_0$ values of these two samples after 30 of minutes dark reaction, the adsorption capability of the TiO$_2$-xN$_x$ nanorods is better than that of the nanoparticles. Moreover, as described above, the charge carrier recombination of TiO$_2$ is expected to be held back by fabricating 1D nanostructure. The above two factors are both positive to the photocatalytic activity of TiO$_2$-xN$_x$ nanorods. Secondly, the photocatalytic property of TiO$_2$-xN$_x$ nanorods was greatly enhanced after the decoration of SrTiO$_3$, as shown in Figure 5. With the increase of the amount of SrTiO$_3$, the photocatalytic properties of the SrTiO$_3$/TiO$_2$-xN$_x$ samples are improved gradually. Here, the visible light photodegradation experiments using a light source with a UV cut were also performed which revealed that there was almost no visible light photocatalytic activity in the samples of SrTiO$_3$/TiO$_2$-xN$_x$. This result is expected; after all, the decoration of SrTiO$_3$ cannot enhance the visible light absorption in the TiO$_2$-xN$_x$ photocatalyst. As described above, SrTiO$_3$ is a good candidate for coupling TiO$_2$ to improve the photocatalytic performance of the photocatalyst because the photogenerated charge carriers can be efficiently separated after the modification of SrTiO$_3$. As a result, better photocatalytic properties were presented in the composite samples than the sample of TiO$_2$-xN$_x$. Lastly, as Figure 5 shows, the photocatalytic activity of the SrTiO$_3$/titanate nanotubes is obviously inferior to the other samples even though its adsorption capability is best among all the samples. From the C/C$_0$ values of all the samples after the dark reaction, the adsorption capability of the nanotubes is obviously more prominent than the other samples. Generally, the better adsorption capability will indicate a better photocatalytic performance in a type of photocatalyst. However, overmuch adsorbed degrading dye will cover the photocatalytic active sites existing on the photocatalyst surface which is detrimental to the photocatalytic activity of photocatalyst. Herein, in our opinion, overmuch adsorption on the nanotubes surface causes the decrease of photocatalytic property in the SrTiO$_3$/titanate sample.
4. Conclusions

In summary, SrTiO$_3$/TiO$_{2-x}$N$_x$ nanostructures were fabricated by the hydrothermal method and characterized by XRD, TEM, XPS, and UV-vis DRS measurements. After hydrothermal processing of the TiO$_{2-x}$N$_x$ nanoparticles with the mixed solution of NaOH and Sr(NO$_3$)$_2$, SrTiO$_3$/titane nanotubes were obtained and presented ordinary photocatalytic performances even though their adsorption properties were greatly improved, indicating that overmuch adsorption is detrimental to the photocatalytic activity of photocatalysts. After calcining the SrTiO$_3$/titane nanotubes, SrTiO$_3$/TiO$_{2-x}$N$_x$ nanorods were produced and showed greatly enhanced photocatalytic activities even though their optical absorption performances were depressed as compared to the TiO$_{2-x}$N$_x$. The mechanisms about the absorption and photocatalytic properties in the prepared samples were discussed in detail.

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References


