Low-temperature S-doping on N-doped TiO₂ films and remarkable enhancement on visible-light performance

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ABSTRACT

Sulfur doping of nitrogen-doped TiO₂ nanograss array films was realized through facile thiourea solution immersion at a low temperature of 353 K. Doped nitrogen and sulfur atoms were found mainly in the interstitial form. Nitrogen doping (N-doping) and sulfur doping (S-doping) enhanced visible light absorption and decreased the band gap of undoped TiO₂ films from 3.10 to 3.01 and 2.81 eV, respectively. Furthermore, N-doped and N,S co-doping made the water absorbed on TiO₂ easier to chemically dissociate and generate hydroxide groups. N-doping favored to produce more O₂⁻ radicals and S-doping benefit to generate more OH⁻ radicals. Both OH⁻ and O₂⁻ active radicals played a significant role in the degradation of RhB. The photocatalytic activity of undoped TiO₂ films was increased by 2.5 times by N-doping through urea treatment. By further S-doping, the photocatalytic performance of N-doped TiO₂ films was enhanced by 4.0 times again.

1. Introduction

Doping with non-metallic ions is frequently used to enhance the visible light photocatalytic activity of titanium dioxide (TiO₂). Asahi and his coworkers [1] developed nitrogen doping (N-doping) to greatly increase the reactivity of TiO₂ under visible light. Subsequently, Umebayashi [2] and Ohno [3] improved the visible-light-responsive photocatalytic performance of TiO₂ with sulfur-doping (S-doping) nearly simultaneously. To further improve the visible light photocatalytic activity of TiO₂, researchers have also attempted the combined use of N-doping and S-doping [4–8]. Generally, N-doping using the nitrogen sources of nitrogen gas [1], ammonium salts [9,10], urea [11,12], ammonia gas [13] is performed at relatively high temperatures. On the other hand, S-doping with different sulfur sources including thiourea [14–17], benzyl disulphide [18], sulphates [19], methionine [20] and sulphuric acid [21] has to be performed at elevated temperatures.

Compared with nanoparticles, TiO₂ thin films have many advantages such as easy separation, high recovery and reuse, low fabrication and maintenance costs as well as relatively high specific area and excellent performance. Therefore, TiO₂ films are expected to be one form of the greatest potential photocatalysts in the application of organic sewage degradation, air purification and hydrogen production from photocatalytic water splitting. Wu and his coworkers [22] developed a chemical oxidation route to prepare TiO₂ nangrass array thin films on Ti foils. However, the films exhibited low visible light-driven photocatalytic activity although they showed relatively high performance under UV irradiation.

In this work, we prepared N-doped TiO₂ nangrass array films on Ti wire mesh through moderate chemical oxidation. To improve their visible light-driven photocatalytic activity, we carried out S-doping on N-doped TiO₂ nangrass array films with thiourea solution at a low temperature of 353 K. A facile and feasible route to improve visible-light-responsive photocatalytic activity was also developed. In future, N,S co-doped TiO₂ nangrass array films on Ti wire mesh with high photocatalytic activity could be directly used in air purification and organic sewage degradation.
2. Experimental

2.1. Preparation of TiO\textsubscript{2} nanograss array films

TiO\textsubscript{2} nanograss array films were prepared on Ti wire mesh of 100 mesh size with a wire diameter of 0.1 mm (purity: 99.8%, Kangwei Co., Ltd., China). The preparation procedure is as follows. First, Ti wire mesh was cut into small pieces of 6 cm × 5 cm and then the cut pieces of Ti wire mesh were cleaned in dilute hydrochloric acid, acetone and distilled water in sequential order using ultrasonic cleaning (40 kHz, Xinzi Co., Ltd., China). The cleaned pieces of Ti wire mesh were then dried in a drying oven at 333 K. Second, five cleaned pieces of Ti wire meshes were made available for a sealed glass pot containing a mixed suspension of 147 mL H\textsubscript{2}O\textsubscript{2} (30 wt.%, Reagent CO., Ltd., China), 3 mL HNO\textsubscript{3} (65° 68 wt.%, Sinopharm Chemical Reagent Co., Ltd., China) and 0.909 g urea powder (purity: 99%, Macklin Co., Ltd., China). The sealed glass pot was then kept in the drying oven at 353 K for 48 h. After that, pieces of Ti wire mesh were taken out for cleaning in distilled water with ultrasonic cleaning for five minutes. Finally, the as-prepared samples were calcined at 723 K holding for one hour to transform amorphous TiO\textsubscript{2} into anatase one. The heating rate was five K/min. The calcined samples were donated as U-80-48-450-1. To compare with control sample, undoped TiO\textsubscript{2} nanograss array films, the sample was prepared with the similar preparation procedure in absence of urea powder. The sample was labelled as 80-48-450-1.

To acquire N, S co-doped TiO\textsubscript{2} nanograss array films, we put sample U-80-48 in a sealed glass pot containing thiourea solution with a concentration of 1 mol/L (purity: 99%, Alfa Aesar Co., Ltd., China). The sealed glass pot was then kept in a drying oven at 353 K for 48 h. Second, the prepared samples were calcined at 723 K holding for one hour with the same heating rate. Finally, the prepared samples were cleaned in distilled water with ultrasonic cleaning. The samples were described as U-80-48-S-24-450-1.

2.2. Characterization

The crystal composition of all the prepared samples was analyzed with X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) using Cu-K\textalpha\textsubscript{x} irradiation. Phase types of the prepared samples were characterized using a laser confocal Raman spectrometer (inVia, Renishaw, England) with an excitation wavelength of 532 nm. The morphology of the as-prepared samples was observed with scanning electron microscope (SEM) (Sigma 300, Zeiss, Germany). The light absorption was monitored by UV–vis diffuse reflectance spectroscopy (UV 3600Plus, Shimadzu, Japan). The surface elements and their chemical valence were analyzed using X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher Scientific, USA). Hydroxyl radicals (OH\textsuperscript{•}) and superoxide radicals (O\textsuperscript{2−}) in the darkness and under the irradiation of Xe lamp (> 420 nm) were examined by an electron spin resonance (EPR) (A300, Bruker, Germany).

2.3. Photocatalytic activity evaluation

The photocatalytic activity of the as-prepared samples was evaluated by means of degradation of rhodamine B (RhB) dye in aqueous solution under visible light irradiation. The evaluation procedure is as follows. The pieces of the prepared sample (80-48-450-1, U-80-48-450-1 and U-80-48-S-24-450-1) of 6 cm × 5 cm were cut into small ones with the dimension of 3 cm × 2.5 cm. Sample 80-48-450-1, U-80-48-450-1 and U-80-48-S-24-450-1 with the dimension of 3 cm × 2.5 cm were placed at the bottom of three glass beakers with a volume of 50 mL, respectively. 20 mL RhB solutions with an initial concentration of about 10 mg/L were then poured into the three beakers separately. Before photocatalytic activity evaluation, these beakers were kept in the darkness for 30 min to achieve adsorption-desorption equilibrium. One 300 W Xe lamp with a reaching optical power density of 45 mW/cm\textsuperscript{2} was used as the light source. An optical filter was used to cut off the light with the wavelength less than 420 nm. Meanwhile, a beaker containing 20 mL same RhB solutions was also prepared to observe the self-degradation of RhB under visible light irradiation. The concentration of RhB solutions was monitored with a UV–vis spectrophotometer (DR 3900, Hach, USA) every 30 min. To study the photocatalytic activity of the as-prepared samples during photodegradation recycle use of RhB, recycle tests were carried out. The evaluation condition is the same as the above description.

3. Results and discussion

Fig. 1a shows the XRD patterns of the as-prepared samples. We could see intensive diffraction peaks of titanium as well as weak peaks of anatase TiO\textsubscript{2} at about 25° of 2theta. The formed anatase TiO\textsubscript{2} films should be rather thin, which led to the weak diffraction peak of anatase
TiO₂. Fig. 1b shows the Raman spectra of the as-prepared samples. Four peaks at 149, 402, 519 and 637 cm\(^{-1}\) appeared in all the samples. The above four peaks correspond to \(E_{g}\), \(B_{1g}\), \(B_{1g}\) \(E_{g}\) phononic mode of anatase TiO₂, respectively [23]. Fig. 2 shows the morphology of the as-prepared samples observed by SEM. We could see films like cracked tree bark covered the Ti wires (Fig. 2a–b). From Fig. 2c, we could observe that the thickness of the films was no more than five microns. In the magnified images (Fig. 2d), nanograss arrays of TiO₂ could be observed. Meanwhile, we could see that the nanograss arrays became compact after urea treatment. The trend became more obvious (Fig. 2d–f) after thiourea treatment. That is to say, urea and/or thiourea treatment had great influence on the morphology of TiO₂ nanograss array films. From Figs. 1–2, we could confirm that anatase TiO₂ nanograss array films formed in the chemical oxidation and followed calcination.

The influence of urea and thiourea treatment on the optical properties of the as-prepared samples is illustrated in Fig. 3. From Fig. 3a, all the three samples absorbed light in the entire visible light region. It shows the urea treatment did not enhance the visible light absorption of anatase TiO₂. Compared with the urea-treated sample (U-80-48-450-1), further thiourea treatment enhanced the visible light absorption of sample U-80-48-450-1 and extended its absorption edge. Meanwhile, the corresponding Tauc plots is illustrated in Fig. 3b. The band gap values of sample 80-48-450-1, U-80-48-450-1 and U-80-48-S-24-450-1 were estimated to be 3.10, 3.01 and 2.81 eV, respectively. Therefore, we could confirm that N-doping through urea treatment and S-doping through thiourea treatment indeed improved the visible light absorption of TiO₂ nanograss array films. The band gap narrowing should ascribe to N-doping and N, S co-doping. From the angle of increasing...
quantum efficiency of visible light utilization, the enhanced visible light absorption and band gap narrowing show special great significance.

X-ray photoelectron spectroscopy (XPS) was used to examine the bonding and status of the dopants in the as-prepared samples. Fig. 4 shows the XPS spectra of Ti 2p, O 1s, N 1s and S 2p of the as-prepared samples. For the Ti 2p spectra (Fig. 4a), they could not be divided into two or more peaks. Peaks at 458.8, 458.9, 464.5, 464.6, and 464.7 eV are observed. The first two peaks corresponded to Ti4+ 2p3/2, which has been confirmed by others’ works [24,25]. On the other hand, the last three ones should belong to Ti4+ 2p1/2 [26]. Binding energies at around 457.4 eV of standard Ti 2p3/2 are not observed, which means Ti3+ did not form in the TiO2 nanograss array films during their preparation. Therefore, we safely concluded that element Ti exists in the form of Ti4+ in the as-prepared TiO2 films.

For the O 1s in Fig. 4b, binding energies at 530.2 and 532.2 eV were detected. They should originate from Ti–O bond in TiO2 [27] and hydroxyl groups adsorbed on the TiO2 surface [28]. After urea treatment, the corresponding binding energies showed a positive shift to 530.9 and 532.8 eV, respectively. The two binding energies should assign to Ti–O bond [30] and hydroxyl groups on the surface [29], respectively. After further thiourea treatment, three peaks at 530.0, 531.0 and 532.6 eV of binding energy were observed. They are confirmed to correspond to Ti–O bond [30], hydroxyl groups [31] and O–H bonding [32], respectively. In addition, we also noted that urea and/or thiourea treatment remarkably enhanced the XPS signal of absorbed hydroxyl groups or H2O on the surface of TiO2 films. It suggests that the treatment made it easier for hydroxyl groups to be absorbed on the surface of TiO2 films.

For the N 1s spectra in Fig. 4c, one XPS peak at 399.8 eV of binding energy was detected in sample U-80-48-450-1 and U-80-48-S-24-450-1. Jagadale and his coworkers [32] believed that the peak of N 1s ranging from 398.8 to 400.8 should assign to the electron binding energy of Ti–N–O. Peaks ranging from 398-402 eV are related to the interstitial N [33,34]. The peak ~ 397 eV reflects the formation of N–Ti–O linkages, indicating the substitution of N ion for O ion [35]. In present work, only one peak at 399.8 eV was found, which indicates that the doped nitrogen in sample U-80-48-450-1 and U-80-48-S-24-450-1 should exist in the interstitial form. The result is well consistent with the conclusion of Smirniotis et al. [36–39]. They used urea as the nitrogen source to dope TiO2 through single-step flame spray pyrolysis and discovered that the doped nitrogen atoms mainly occupied interstitial positions in TiO2 lattice. For the S 2p (Fig. 4d), no signals were detected in sample 80-48-450-1 and U-80-48-450-1. On the other hand, two XPS peaks at 164.5 and 168.9 eV were discovered. It was reported that 168.9 eV represented the universal binding energy of S6+ (such as SO42−) [40–42]. The peak is thought to relate to the Ti-O-S bonds, suggesting sulfur doped TiO2 in the form of interstitial ones. In addition, sulfur should be available in the form of interstitial S6+ forming Ti-O-S bonds. The result is also similar to previous literature [43]. The second fitted peak located at 164.5 eV is assigned to S 2p 1/2 due to orbit coupling [44]. Therefore, we could confirmed the doped sulfur should exist in the interstitial S6+ form.

Fig. 5 shows the EPR spectra of OH• and O2•− reactive oxidizing species generated in the surface of the as-prepared samples in darkness and under visible light irradiation. As showed in Fig. 5a, characteristic quartet peaks of DMPO–OH• adducts with the intensity ratio of 1:2:2:1 were observed. In darkness, OH• signals in undoped sample (80-48-450-1) were not detected, while they were discovered in N-doped and N, S co-doped sample (U-80-48-450-1 and U-80-48-S-24-450-1). Water would physically adsorb on the surface of TiO2 and part of them might...
chemically dissociate to form H\(^+\) and OH\(^-\), which received the support of the above XPS results (Fig. 4b). The chemically dissociated OH species on the surface of TiO\(_2\) were captured by DMPO trapping reagent, which formed the EPR signals. The DMPO- OH\(^-\) signals for N, S co-doped TiO\(_2\) is more intensive than those for undoped and N-doped TiO\(_2\) in darkness. It is a clear indication that water is easier to chemically dissociate on the surface of N, S co-doped TiO\(_2\). Water dissociation and hydroxyl formation on the surface of TiO\(_2\) have been recorded [45]. The water dissociation and hydroxyl formation favor the photo-generated hole transfer and thereby the formation of OH\(^-\) radicals. Under visible light irradiation, intensive DMPO- OH\(^-\) peaks could be found for all the samples. That indicates that OH\(^-\) radicals were generated. Compared with undoped and N-doped TiO\(_2\) sample, N, S co-doped TiO\(_2\) samples could generate more intensive peaks of the OH\(^-\) radicals. It demonstrates that S-doping could make N-doped TiO\(_2\) generate more OH\(^-\) radicals under the irradiation of visible light.

For O\(_2^-\) radicals (Fig. 5b), no evident EPR peaks were observed for all the samples in darkness. Characteristic peaks of DMPO- O\(_2^-\) were found for all the samples under visible light irradiation although the signals were not rather strong. It states clearly that O\(_2^-\) reactive radicals were generated in the surfaces of undoped TiO\(_2\), N-doped TiO\(_2\) and N, S co-doped TiO\(_2\). Compared with the undoped TiO\(_2\) films, N-doped TiO\(_2\) could form a lot more O\(_2^-\) radicals. N, S co-doped TiO\(_2\) could generate little more O\(_2^-\) radicals compared to N-doped TiO\(_2\). In conclusion, S-doping could generate more OH\(^-\) radicals while N-doping could produce O\(_2^-\) radicals. In other words, N-doping had little influence on...
production of OH radicals and S-doping had little impact on O2⁻ radicals. Therefore, we believe radical as well as changed under the irradiation of visible light (Fig. 6). It states that the doping and S-doping made the water absorbed on the surfaces of TiO2 co-doping enhanced the photocatalytic activity of undoped TiO2.

4. Conclusions

Sulfur doping of nitrogen-doped TiO2 nanosheet films through facile thiourea solution immersion at a temperature as low as 353 K was successfully carried out. Doped nitrogen and sulfur mainly existed in the form of interstitial ions. Subsequent sulfur doping did not exert an impact on doped nitrogen. N-doping and N, S co-doping decreased band gap from 3.10 to 3.01 and 2.81 eV by N-doping and N-S co-doping. The XRD patterns and Raman spectra depicted that the formation of radical. N-doping and N-S co-doping decreased while that of N, S co-doped TiO2 films hardly decreased. It indicates the N, S co-doped TiO2 films possessed stable photocatalytic performance, which could ensure their long service time.

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References


