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Low-temperature hydrothermal synthesis of S-doped TiO_2 with visible light photocatalytic activity

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Abstract

A one-step low-temperature hydrothermal route was developed for the synthesis of S-doped TiO_2 photocatalysts from TiS_2 and HCl. Crystalline TiO_2 was formed and sulfur could be efficiently doped into the anatase lattice under hydrothermal conditions. When the initial TiS_2 concentration is increased, the content of S-dopant and optical absorption in the visible region also increase. The photocatalytic activity of the S-doped TiO_2 was evaluated through the degradation of 4-chlorophenol under visible light irradiation. Our results show that the S-doped TiO_2 prepared by this hydrothermal approach possesses much higher photocatalytic activity than that obtained by the traditional high-temperature thermal annealing method.

Keywords: Titanium dioxide; Sulfur; Doping; Photocatalyst; Visible light

1. Introduction

Titanium dioxide is the most widely used photocatalyst in environmental purification [1–10]. However, TiO_2 can only be activated by UV irradiation at around 360 nm ($E_g = 3.2\,eV$ for anatase). It is desirable to develop a photocatalyst that efficiently absorbs visible light, which occupies the main part of the solar spectrum. Many attempts have been made to prepare solar-driven photocatalysts by doping TiO_2 with transition metals [11–18] or by dye sensitization [19–25]. Their mechanisms are shown in Fig. 1. Another approach is to couple TiO_2 with narrow band gap semiconductors to achieve visible light photocatalytic activity [26–30].

Non-metal doping such as carbon [31–33], nitrogen [34–42], sulfur [43–49] have also been investigated. For example, Khan et al. [31] have shown efficient photochemical water splitting under visible light by a chemically modified TiO_2, in which carbon substitutes for some of the lattice oxygen. C-doped TiO_2 was also carried out by the oxidative annealing of TiC for decomposition of 2-propanol to CO_2 and acetone under visible light irradiation [32]. Kisch et al. [33] have also investigated the daylight photocatalysis by carbon-modified TiO_2.

Asahi et al. [34] reported theoretical calculations of the band structure of nitrogen-doped TiO_2 and its visible light photocatalytic degradation of acetaldehyde and methylene blue. They found that nitrogen atoms substituted the lattice oxygen sites and narrowed the band gap by mixing the N2*p* and O2*p* states. Reports by Hashimoto et al. demonstrated the visible-light-induced hydrophilicity [35] and photocatalytic decomposition of gaseous 2-propanol on nitrogen-doped TiO_2 [36]. They concluded that the lattice oxygen sites were substituted by nitrogen atoms and formed an isolated narrow band above the valence band and narrowed the band gap.

Umebayashi et al. [43–45] reported that S-doping shifted the absorption edge of TiO_2 to a lower energy, thereby exhibiting photocatalytic degradation of methylene blue under visible light irradiation. They suggested that sulfur was doped as an anion and replaced the lattice oxygen in TiO_2. On the contrary, reports by Ohno et al. [46–48] found that S atoms were incorporated as cations and replaced

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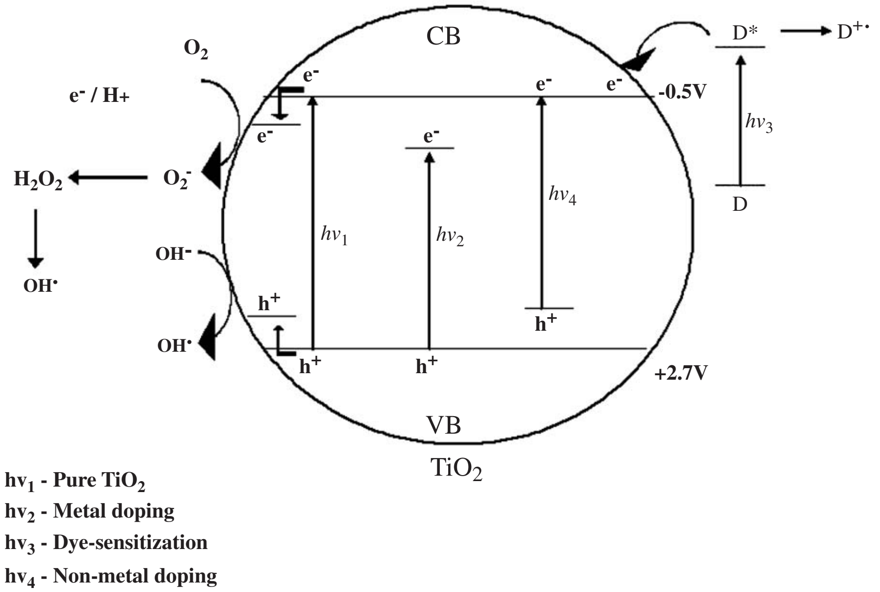

Fig. 1. Mechanism of TiO_2 visible light photocatalysis.

Ti ions in the sulfur-doped TiO_2 photocatalyst. Previously, our group has also reported on the cationic doping of sulfur into TiO_2 to achieve a strong visible-light-induced antibacterial effect [49].

In the present work, we developed a simple and effective method for the synthesis of S-doped TiO_2 photocatalysts by low-temperature hydrothermal treatment of TiS_2 powder in HCl solution at 180 °C. Traditionally, sulfur doping was achieved under exotic reaction conditions such as thermal decomposition of thiourea (TU) [46–48,50] or thermal annealing of TiS_2 at 723–873 K [43,44,51,52]. The most attractive feature of our method is that TiS_2 is used as both a precursor of titanium dioxide and a sulfur source for the simultaneous crystallization and doping.

2. Experimental

In a typical procedure, titanium disulfide (Aldrich) was dissolved in HCl solution (1 M) to give a TiS_2 concentration of 0.1–2 M. The above TiS_2 solution was then placed in a 200-mL Teflon-lined stainless-steel autoclave until 80% of its volume was filled. The autoclave was maintained at 180 °C for 6 h and then air cooled to room temperature. After hydrothermal reaction, the samples were collected by centrifugation, gently washed with deionized water several times and dried in an oven at 100 °C.

3. Characterization

The X-ray diffraction (XRD) patterns, obtained on a Bruker D8 Advance X-ray diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å) at a scan rate of $0.05^\circ\ 2\theta\,\mathrm{s}^{-1}$, were used to identify the phase constitutions in samples and their crystallite size. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The crystallite size was calculated from X-ray line broadening analysis using the Scherrer formula [53]. The error range of the crystallite size is within ± 2 nm. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL 2010 transmission electron microscope operated with an 200-kV accelerating voltage and an energy-dispersive X-ray (EDX) instrument. The dopant concentration was analyzed by X-ray photoelectron spectroscopy on a PHI Quantum 2000 XPS System with a monochromatic Al$K\alpha$ source and a charge neutralizer. All the binding energies were referenced to the C1*s* peak at 284.8 eV of the surface adventitious carbon. UV-visible diffuse reflectance spectra were achieved using a UV-visible spectrophotometer (Cary 100 Scan Spectrophotometers, Varian, USA).

4. Photocatalytic activity measurements

The photocatalytic activities of the S-doped TiO_2 samples were measured by degradation of 4-chlorophenol in an aqueous solution. Oxygen was bubbled into the solution throughout the experiment. A 300 W tungsten halogen lamp with a 400 nm cutoff filter was used as visible light source. The photocatalyst (0.2 g) was suspended in a 200 mL aqueous solution of 2.5×10^{-4} M 4-chlorophenol. The concentrations of 4-chlorophenol and its degradation products were measured with a HPLC system (Waters Baseline 810) with a Waters 486 tunable UV absorbance detector. A Supelco LC-18-DB column (250 mm × 4.6 mm) was applied. The eluent consisted of a 40:60 methanol: water mixture, and the flow rate was 1 mL/min. The aromatic compounds were detected at 220 nm. Millipore discs were used to separate the catalysts before analysis of the solution.

5. Results and discussion

Fig. 2 shows the XRD patterns of the hydrothermally synthesized S-doped TiO_2 samples. The characteristic peaks correspond to the anatase TiO_2 with different crystal planes (JCPDS 21-1272) were detected. The average crystallite sizes for the S-doped TiO_2 samples are in the range of 6.5–8.2 nm (Table 1), as calculated by applying the Scherrer equation to the full-width at half-maximum of the (101) crystal plane of anatase TiO_2. It is clear that the crystallite sizes of the S-doped TiO_2 samples increase with the S-dopants. This suggests that the incorporation of sulfur leads to the crystal growth of the anatase TiO_2 during hydrothermal process, resulting in a larger crystallite size for the doped materials.

Fig. 3 shows the high-resolution XPS spectra of the S2*p* region of the S-doped TiO_2 with different S-contents. The sulfur atoms are all in the state of S^{2-}, with a peak at about 160–161 eV. It corresponds to the Ti–S bond formed when some of the oxygen atoms in the TiO_2 lattice are replaced by sulfur atoms. Umebayashi et al. [43–45] used theoretical calculations to depict the band gap narrowing when oxygen was replaced by sulfur in anatase TiO_2. They found that the sulfur dopant was in the anionic form when TiS_2 was used as the starting material. Similarly, in our case, most of the sulfur in TiS_2 was oxidized and the residual sulfur would naturally remain as S^{2-} dopant after the hydrothermal process. It should be noted that no peaks are found around 169 eV, which corresponds to the S^{6+} species. As stated in our previous study [49], the oxidation state of the S-dopant is dependent on the preparation routes. If titanium tetraisopropoxide and TU were used as the titanium and sulfur precursors, the substitution of Ti^{4+} by S^{6+} would be chemically more favorable than replacing O^{2-} with S^{2-} [46–49].

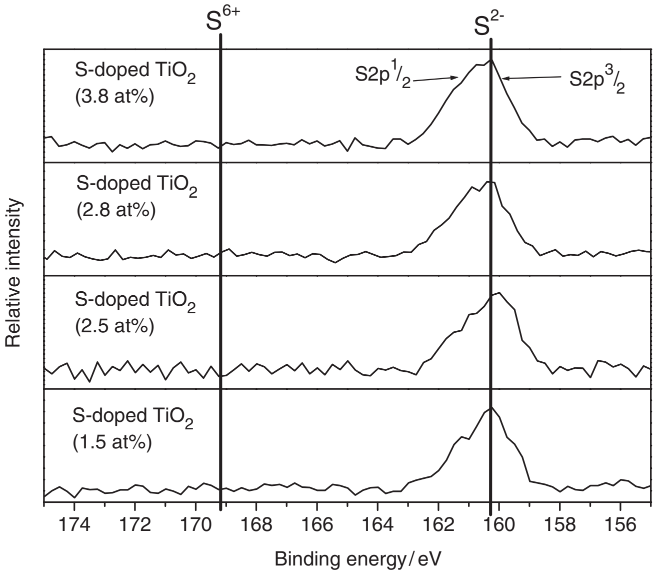

Fig. 3. High-resolution XPS spectra of the S2*p* region for the S-doped TiO_2 with different atomic percentages of sulfur.

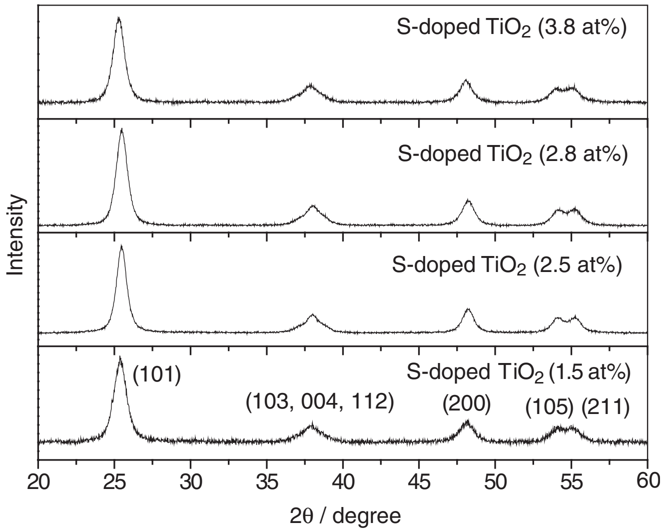

Fig. 2. XRD patterns of the S-doped TiO_2 photocatalysts with different atomic percentages of sulfur dopants.

Table 1
Sulfur content, crystal size and visible light photocatalytic activity of S-doped TiO_2

S-doped TiO_2 prepared from[a]	Sulfur content (at%)[b]	Crystal size (nm)[c]	% 4-chlorophenol degraded[d]
0.1 M TiS_2	1.5	6.5	51
0.5 M TiS_2	2.5	7.5	71
1 M TiS_2	2.8	7.9	86
2 M TiS_2	3.8	8.2	88

[a] Initial concentration used in the hydrothermal process.
[b] Measured by XPS.
[c] Determined by the Scherrer equation.
[d] Measured after 6 h of visible light irradiation.

Transmission electron microscopy (TEM) and EDX spectroscopy provide information on the morphology, crystallinity and chemical composition of the samples. The HRTEM image of the S-doped TiO_2 (Fig. 4a) shows spherical particles with an average size of approximately 6–7 nm, which is in good agreement with the XRD results. The well-resolved lattice fringes in Fig. 4b allow an accurate measurement of crystallographic spacing and identification of the observed crystallites. The measured fringe spacing of 3.5 Å matches well with the distance between the (101) crystal planes of anatase TiO_2 [54,55]. Chemical composition analysis using EDX spectroscopy (Fig. 5) illustrates that the hydrothermally prepared sample is mainly composed of Ti and O, with a trace amount of sulfur dopant.

Fig. 6 shows the UV-vis diffuse reflectance spectra of the pure TiO_2 (P25) and S-doped TiO_2 powders with different sulfur contents. Noticeable shifts of the absorbance shoulder from 400 nm to the visible light region are

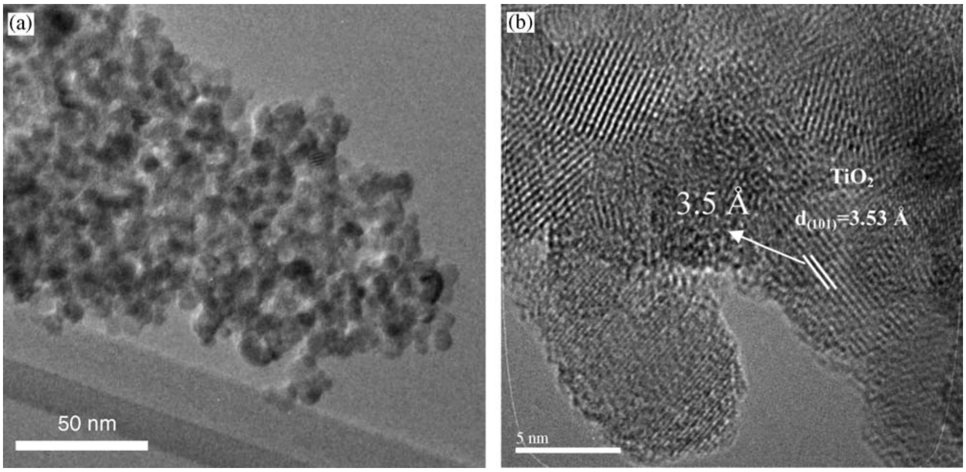

Fig. 4. (a) TEM images of the hydrothermally synthesized S-TiO_2. (b) HRTEM micrograph at 200 kV of the S-doped TiO_2 sample.

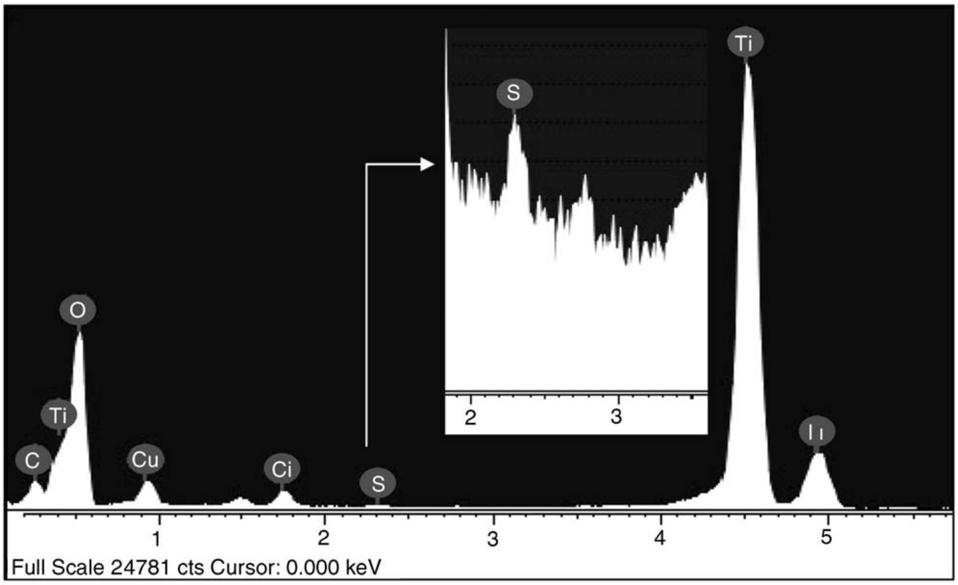

Fig. 5. EDX microanalysis spectra of the S-doped TiO_2 sample. The X-ray excitation energy for S is at about 2.3 keV.

observed for the S-doped TiO_2. Moreover, the absorbance increases with the atomic percentage of S-dopant. These results reveal that the sulfur dopants are indeed incorporated into the lattice of TiO_2, thus altering its crystal and electronic structures.

The photocatalytic activity of the samples were evaluated by degradation of 4-chlorophenol in aqueous solution under visible light irradiation. In Fig. 7 and Table 1, the photocatalytic activities of the samples prepared with different S-content are shown. It is not surprising that the visible light photocatalytic activity is strongly dependent on both the concentrations of TiS_2 and the S-dopant. When the concentration of TiS_2 for the hydrothermal process increases, the sulfur content detected by XPS also increases. As shown in the UV-vis spectra, the sulfur content in the doped TiO_2 greatly influences the visible light absorption of TiO_2, hence the visible light photocatalytic activity. This result is in good agreement with our previous report on the visible-light-driven disinfection effect of S-doped TiO_2 photocatalyst, in which the bactericidal activity increased with the doped sulfur content [49].

Fig. 8 shows that pure TiO_2 cannot degrade 4-chlorophenol when irradiated by visible light. Moreover, samples prepared by simply mixing TiO_2 and TiS_2 powders together are just as ineffective. The S-doped TiO_2 samples, however, exhibit significant photocatalytic activity under the same conditions. The sample prepared from TU can degrade 66% of the 4-chlorophenol in 6 h while the sample obtained by our hydrothermal method is even more effective at 86% degradation in 6 h. The substitutional doping of sulfur exhibits strong absorption of visible light because the *p* states of S contribute to band gap narrowing by mixing with the O2*p* states of TiO_2 [43,45,47]. Low-temperature hydrothermal synthesis is preferred over

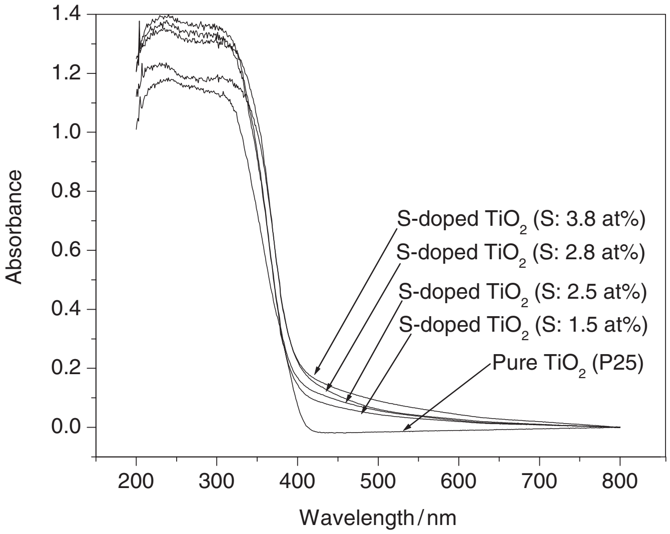

Fig. 6. UV-vis diffuse reflectance spectra of pure TiO_2 and S-doped TiO_2 with different sulfur contents.

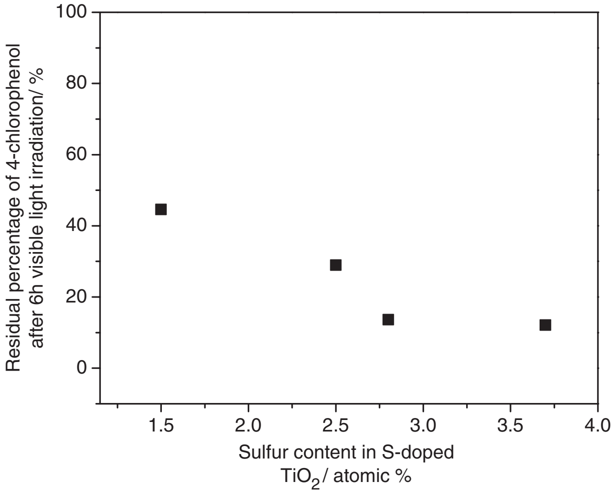

Fig. 7. Residual percentage of 4-chlorophenol after 6 h of visible light irradiation as a function of sulfur content of the S-doped TiO_2 photocatalyst.

the more traditional high-temperature processes for the preparation of TiO_2 particles [56], because excessive crystal growth can be avoided and samples with high specific surface area are readily obtained.

6. Conclusion

We have succeeded in preparing S-doped TiO_2 photocatalysts by using a simple one-step hydrothermal approach. This approach can efficiently dope sulfur atoms into the lattice of anatase TiO_2. The products show much improved visible light photocatalytic activity that will be useful in the design of solar-driven photocatalytic treatment systems.

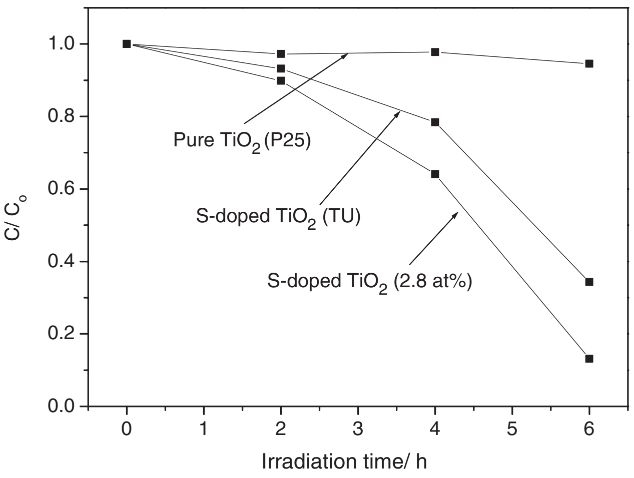

Fig. 8. Photodegradation of 4-chlorophenol for the pure TiO_2 and S-doped TiO_2 prepared by different methods under visible light irradiation ($\lambda > 400$ nm).

Acknowledgments

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