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Article

Facile synthesis of S-doped reduced TiO_{2-x} with enhanced visible-light photocatalytic performance

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ABSTRACT

A different approach to synthesize visible-light-active sulfur (S)-doped reduced titania (S-TiO_{2-x}) using thiourea dioxide as both the S source and reductant was developed. The structure, morphology, and optical and electronic properties of the as-prepared S-TiO_{2-x} samples were examined by multiple techniques, such as X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, Brunauer-Emmett-Teller and photocurrent measurements, and electrochemical impedance spectroscopy. The photocatalytic activity of S-TiO_{2-x} was evaluated by photodegradation of organic Rhodamine B under visible-light irradiation. The degradation rate of Rhodamine B by S-TiO_{2-x} obtained by calcination was about 31, 2.5, and 3.6 times higher than those of pure TiO_2 , pristine TiO_{2-x} , and S-doped TiO_2 , respectively. In addition, the as-prepared S-TiO_{2-x} exhibited long-term stable photocatalytic performance in the degradation of Rhodamine B under visible-light illumination. This report reveals a new approach to prepare stable and highly efficient solar light-driven photocatalysts for water purification.

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1. Introduction

Since the discovery of photocatalytic water splitting on titania (TiO_2) single-crystal electrodes by Fujishima et al. in 1972 [1], photodegradation of toxic organic pollutants in wastewater using solar light as an energy source has been considered to be one of the most promising directions to solve global environmental problems. Although numerous novel compounds with various photocatalytic activities have been developed, TiO_2 has remained a leading catalyst in the photocatalytic degradation of organic pollutants because it is effective, photo and chemically stable, non-toxic, and readily available [2]. However, the wide band gap and quick recombination of photogenerated elec-

tron-hole pairs of TiO_2 impede its practical applications. Therefore, band-gap engineering of TiO_2 is needed to use it as a high-efficiency photocatalyst under visible-light illumination for antibacterial applications [3,4].

Nonmetal-doped TiO_2 has received much attention because the incorporation of nonmetals into TiO_2 can extend its photoresponse from the ultraviolet (UV) to the visible region [5–8]. The introduction of doping agents as anions or cations to substitute Ti or/and O in the lattice of TiO_2 could narrow the TiO_2 electronic band gap or create localized electronic states in the band gap, which could improve its visible-light absorption and result in high visible-light photocatalytic activity. Among non-metal dopants, sulfur (S) has received particular attention be-

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cause of its high thermal stability and ability to enhance visible-light photocatalytic activity. S-doped TiO_2 photocatalysts have been prepared using S-based compounds including TiS_2 , thiourea, elemental S, CS_2 , and dimethyl sulfoxide as the S source [9–13]. However, these precursors are either expensive or highly toxic. Therefore, it is worth seeking safe and cheap S sources for use in S-doped TiO_2 photocatalysts.

Recently, Ti^{3+} self-doping of TiO_2 (TiO_{2-x}) has emerged as an effective approach to trigger the visible-light activity of TiO_2 [14,15]. In TiO_{2-x} , electronic transitions originating from the Ti^{3+} -induced states in the band gap are known to contribute to its photoabsorption. Meanwhile, Ti^{3+} endows TiO_2 with good electronic conductivity, which is important to improve its photoelectric conversion efficiency [16,17], and enhance its visible-light photocatalytic activity [18,19]. Various attempts have been made to synthesize TiO_{2-x} photocatalysts [20–24], but most methods involve complicated experimental conditions and multistep processing. In situ reduction treatment using a short processing time and mild conditions to prepare TiO_{2-x} photocatalysts with high photocatalytic and photoelectrochemical performance is still challenging [18]. In our previous work, we used an oxidation-based method to prepare TiO_{2-x} nanomaterials in aqueous solution using the water- and air-stable industrial raw material TiH_2 as the Ti source [25,26]. Hydrogen peroxide was used as an oxidizing agent to give different states of precursor gels, after which different treatment methods were used to produce TiO_{2-x} nanoparticles.

Thiourea dioxide is an organosulfur compound that is used in reductive bleaching in textiles and as an antioxidant in organic synthesis [27]. Thiourea dioxide is a strong reductant and has high thermal stability. In addition, compared to other S sources, thiourea dioxide is cheap and easy to use. We were therefore inspired to explore a facile, effective, and environmentally friendly route to synthesize S-doped TiO_{2-x} using thiourea dioxide as both the S source and reductant. In this study, pristine TiO_{2-x} and S-doped TiO_{2-x} are prepared by a hydrothermal or calcination method using thiourea dioxide as the S source and reductant. The relationship between the structure and photocatalytic performance of the products obtained from different methods are studied in detail. Rhodamine B (RhB) dye is used as a model pollutant to evaluate the photocatalytic activity of the samples.

2. Experimental

2.1. Sample preparation

All chemicals were reagent grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. Double-distilled water was used throughout the experiments.

The precursor gel preparation process was similar to that described in our preliminary study, except that yellow precursor gel was obtained by controlling the oxidation time [25,26]. To obtain the pristine TiO_{2-x} -H, the wet gel was hydrothermally treated at 180 °C for 20 h. To prepare the S-doped TiO_{2-x} photocatalyst, thiourea dioxide (0.2 g) was added to the precursor

gel and its pH was adjusted to 8 using NaOH solution. The mixture was then hydrothermally treated at 180 °C for 20 h. The obtained bluish-gray sample was denoted as S- TiO_{2-x} -H. Half of the precursor gel was dried in air, mixed with thiourea dioxide (0.2 g), and then calcined at 500 °C for 3 h. The obtained gray-blue sample was denoted as S- TiO_{2-x} -T (Fig. 1). For comparison, pristine S-doped TiO_2 (denoted S- TiO_2 -T) nanoparticles were prepared according to ref. [10].

2.2. Characterization

An X-ray diffractometer (XRD; Rigaku, D/max-2500VPC) was employed to characterize the crystalline phases of the final products using Ni-filtered $\text{Cu-K}\alpha$ radiation from 20° to 70° at a scan rate of 0.02° s^{-1} . A transmission electron microscope (TEM; JEOL-2100) was used to observe the morphologies of the products. An X-ray photoelectron spectrometer (XPS; ESCA 3000) with a monochromatic Al $\text{K}\alpha$ X-ray source (1486.6-eV photons) was used to characterize the chemical state of elements in the as-prepared samples. The C 1s signal at a binding energy of 284.6 eV was used as a reference. UV-Vis diffuse reflection spectra (DRS) were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer at room temperature from 200 to 800 nm. Fine BaSO_4 was used as the reflectance standard. The Brunauer-Emmett-Teller (BET) specific surface areas of the powders were determined by nitrogen adsorption-desorption measurements at 77 K in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). Mass spectra (MS) were collected on an electrospray ionization mass spectrometer (Bruker ESQUIRE 3000). The total organic carbon (TOC) content of the samples after degradation for different times was measured with a Shimadzu TOC-VCPH analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a MAGNA 550 FT infrared spectrometer for samples embedded in KBr pellets.

2.3. Photoelectrochemical measurements

The transient photocurrent responses of the samples were performed with a standard three-electrode setup using a CHI 660E electrochemical station (Chenhua Instrumental Co., China). Each photoelectrode was prepared by spin coating a mixture of sample (0.01 g) in ethanol Nafion solution (5 wt%, 0.05 mL) on a 1.0 cm^2 fluorine-doped tin oxide glass substrate and drying at 100 °C for 2 h. The as-prepared photoelectrodes were used as working electrodes; Ag/AgCl and platinum wire were

Fig. 1. Overview of the formation of different samples.

used as reference and counter electrodes, respectively. Na_2SO_4 aqueous solution (0.2 mol/L) was used as the electrolyte. A 300-W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd., China) coupled with a filter ($\lambda > 400$ nm) was used as the visible-light source. The transient photocurrent responses of the photoelectrodes were measured using typical on-off cycles under visible-light irradiation. Electrochemical impedance spectroscopy (EIS) measurements of the samples were performed in the dark or under illumination at open-circuit potential over a frequency range of 10^4 –1 Hz. All experiments were carried out under ambient conditions.

2.4. Photocatalytic activity measurements

The photocatalytic activities of the pure TiO_2 , pristine S-TiO_2 , TiO_{2-x} , $\text{S-TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$ were evaluated by measuring the degradation of RhB in aqueous solution under visible-light irradiation. The optical system for the photocatalytic reaction included a 300-W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd) with a UV cutoff filter (UVCUT 400, Beijing Trusttech Co., Ltd.). For each photodegradation experiment, sample (40 mg) was suspended in RhB aqueous solution (80 mL, 10 mg/L) in a customized quartz reactor. The suspension was magnetically stirred in the dark for 30 min to achieve adsorption/desorption equilibrium prior to photocatalytic reaction. The change of RhB concentration was measured with a visible spectrophotometer throughout the photocatalytic process.

3. Results and discussion

3.1. Catalyst characterization

The crystal structure and crystalline phase of a sample greatly affect its photocatalytic and photoelectrochemical properties. XRD measurements were carried out to investigate the crystal identity and effect of S and Ti^{3+} doping on the crystal structures of the samples. Fig. 2 shows XRD patterns of the obtained samples. The diffraction peaks at $2\theta = 25.3^\circ$, 36.9° , 37.8° , 48.0° , 53.9° , 54.9° , 62.6° , 68.6° , 70.2° , and 75.0° correspond to the (101), (103), (004), (200), (105), (211), (204), (116), (220), and (215) planes of anatase TiO_2 (JCPDS 21-1272), respectively, and the sharp diffraction peaks reveal the high crystallinity of TiO_2 . The full width at half maximum (FWHM) of the (101) peak at $2\theta = 25.3^\circ$ was measured for each sample. The FWHM of $\text{TiO}_{2-x}\text{-H}$, $\text{S-TiO}_2\text{-T}$, $\text{S-TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$ are 0.76, 0.57, 0.95, and 0.47, respectively. Based on the Scherrer formula, the crystallite sizes of $\text{TiO}_{2-x}\text{-H}$, $\text{S-TiO}_2\text{-T}$, $\text{S-TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$ are 11.4, 15.3, 9.2, and 18.5 nm, respectively. The crystallite sizes of the samples obtained by the hydrothermal treatment are smaller than those of the samples obtained by heat treatment. In addition, the diffraction peak intensities of the samples obtained by calcination are higher than those of the samples obtained by hydrothermal treatment. Higher crystallinity may promote photocatalytic performance. Furthermore, no other peaks originating from impurities or other phases such as rutile TiO_2 or TiH_2 were observed in the

Fig. 2. XRD patterns of $\text{TiO}_{2-x}\text{-H}$, $\text{S-TiO}_2\text{-T}$, $\text{S-TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$.

XRD patterns, indicating that the samples were pure anatase TiO_2 .

The morphologies of the samples were observed by TEM and high-resolution TEM (HRTEM); the results are presented in Fig. 3. Fig. 3(a) shows a typical TEM image of the pristine TiO_{2-x} nanoparticles, which are rice-like, similar to our previous reports [25,26]. The pristine $\text{S-TiO}_2\text{-T}$ sample is composed of irregular particles with smooth surfaces (Fig. 3(b)). When thiourea dioxide was used as the S source and reductant, the subsequent processing method affected the morphology of the product. When hydrothermal treatment was used, the obtained $\text{S-TiO}_{2-x}\text{-H}$ consisted of polygonal particles with smooth surfaces (Fig. 3(c)). When the dried mixture of gel and thiourea dioxide was heat treated at 500°C for 3 h ($\text{S-TiO}_{2-x}\text{-T}$), the resulting sample was composed of irregular particles with slight sintering (Fig. 3(d)). The average diameters of the samples were around 12, 14, 11, and 20 nm for $\text{TiO}_{2-x}\text{-H}$, $\text{S-TiO}_2\text{-T}$, $\text{S-TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$, respectively. The HRTEM images of $\text{S-TiO}_{2-x}\text{-T}$ and $\text{S-TiO}_{2-x}\text{-H}$ contained a lattice fringe spacing of 0.351 nm, corresponding to the (101) lattice plane of anatase TiO_2 (Fig. 3(e) and (f)). In addition, the electron diffraction results (insets in Fig. 3(a)–(d)) indicated that all samples were highly crystalline, consistent with the XRD results.

To investigate the chemical composition and elemental states of the samples, XPS analysis was performed. The C 1s, Ti 2p, S 2p, and O 1s spectra of the samples are presented in Fig. 4. The C 1s spectra of the samples all contained one peak at 284.6 eV and a shoulder at around 286.3 eV, which are assigned to C–C bonds and C–O bonds, respectively (Fig. 4(a)). This possibly originates from environmental species introduced during the measurement [5,28]. We did not observe the formation of C–Ti bonds because there were no bands at about 282 eV, which indicates carbon that was not doped into TiO_2 .

Fig. 4(b) depicts the high-resolution Ti 2p XPS spectra of the

Fig. 3. TEM images of $\text{TiO}_{2-x}\text{-H}$ (a), $\text{S-TiO}_2\text{-T}$ (b), $\text{S-TiO}_{2-x}\text{-H}$ (c), and $\text{S-TiO}_{2-x}\text{-T}$ (d). HRTEM images of $\text{S-TiO}_2\text{-T}$ (e) and $\text{S-TiO}_{2-x}\text{-H}$ (f).

Fig. 4. High-resolution C 1s (a), Ti 2p (b), S 2p (c), and O 1s (d) XPS spectra of the TiO_2 -based samples.

samples. The $\text{S-TiO}_2\text{-T}$ displays two peaks centered at 458.8 and 464.5 eV, which can be ascribed to the binding energies of $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ in TiO_2 , respectively [10,29]. For $\text{TiO}_{2-x}\text{-H}$ and S-TiO_{2-x} , the peaks were shifted to lower binding energies relative to the TiO_2 peaks. This shift should be related to Ti^{3+} self-doping effects [30,31]. The magnitude of the shift to lower binding energy depended on the sample, indicating that the

concentration of Ti^{3+} in the samples is different. Following hydrothermal treatment of the precursor gel or mixture of the gel and thiourea dioxide, the Ti^{3+} concentration was higher than that of the sample obtained by heat treatment in air. It should be emphasized that Ti^{3+} is essentially a defect site that captures a hole to prolong the electron-hole separation lifetime by suppressing the recombination of electron-hole pairs.

Fig. 4(c) shows the high-resolution XPS data for the S 2*p* region. The TiO_{2-x}-H sample did not display a peak, meaning this sample did not contain S. For the samples obtained by adding thiourea dioxide, the presence of S was confirmed by a peak at 168.8 eV. Generally, a peak at about 168.6 eV can be ascribed to S⁶⁺ substituting Ti atoms in the lattice of TiO₂ [10,32]. In addition, no peaks were detected around 160–163 eV in the S 2*p* spectra, which correspond to Ti–S bonds formed via substitution of O atoms in the TiO₂ lattice by S atoms. Generally, the substitution of Ti⁴⁺ by S⁶⁺ is energetically more favorable than replacing O²⁻ with S²⁻ [11,32]. The formation of cationic S-doped TiO₂ could create a charge imbalance in the photocatalyst lattice; the extra positive charge is probably neutralized by hydroxide ions [12]. This effect has the potential to suppress the recombination of electrons and holes, leading to improved photocatalytic activity [9,33].

The O 1*s* spectra in Fig. 4(d) reveal that the TiO₂-based samples displayed a main peak corresponding to the oxygen groups in the lattice. The spectra could be resolved into two peaks at about 529.8 and 531.2 eV, which are ascribed to Ti–O and surface hydroxyl species, respectively. The peaks in the spectra of TiO_{2-x}, S-TiO_{2-x} were shifted to lower energy than those of the other samples because of the formation of oxygen vacancies in the TiO₂ lattice. The peak from chemisorbed –OH at a binding energy of 531.2 eV represents surface defects (oxygen vacancies). These defects can trap holes to promote electron-hole separation and suppress the recombination of electron-hole pairs, consequently enhancing catalytic activity. Meanwhile, the abundant adsorbed –OH on the photocatalyst surface can potentially trap holes to form oxidative hydroxyl radicals (•OH), which are important for advanced oxidation of organic pollutants [21].

The photocatalytic performance of TiO₂-based catalysts is strongly determined by their optical absorption properties [18]. The UV-vis DRS for the pure TiO₂, pristine TiO_{2-x}-H, S-TiO₂-T and S-TiO_{2-x} samples are presented in Fig. 5. Pure TiO₂ shows an absorption edge at ~389 nm, corresponding to a band-gap energy of ~3.19 eV, which means that pure TiO₂ cannot be excited by visible light. Compared with that of the pure TiO₂, the corresponding UV-vis spectrum of S-TiO₂-T is red shifted with an absorption tail from 400 to 550 nm. The red shift and absorption tail are attributed to the introduction of S atoms into the lattice of TiO₂ [10]. The absorption intensity of TiO_{2-x}-H in the visible region is higher than that of pure TiO₂. The strong absorption of TiO_{2-x}-H in the visible region is attributed to the presence of Ti³⁺ [25,26]. For the S-TiO_{2-x} sample, the absorption edge is red shifted and the absorption intensity increases in the visible region compared with the behavior of pure TiO₂. The red shift and strong absorption in the visible region are attributed to the characteristics of S-doping and the presence of Ti³⁺. The formation of doping states can lower the electron transition energy from the valence band (VB) to the conduction band (CB) and thus lead to a red shift of the absorption edge. The photoabsorption capacities of the samples in the visible region indicate that they may have potential for photocatalytic decomposition of contaminants under visible-light irradiation. Moreover, the absorption intensity in the visible

Fig. 5. UV-vis diffuse reflectance spectra obtained for pure TiO₂, TiO_{2-x}-H, S-TiO₂-T and S-TiO_{2-x} samples.

range depends on the sample, further indicating that S-doping or the coexistence of S and Ti³⁺ in the photocatalysts benefits their visible-light absorption.

3.2. Photoelectrochemical properties

Photocurrent measurements can provide direct values to determine the separation efficiency of photoinduced electrons and holes and estimate the electronic interaction in photoanodes. The higher the photocurrent, the better the electron-hole separation efficiency [34]. The transient photocurrent response results for different samples (Fig. 6(a)) indicate that the pure TiO₂ photoanode only generates a low photocurrent under visible-light illumination, which can be readily explained by its poor visible-light absorption properties and high photogenerated electron-hole recombination rate. The pristine TiO_{2-x}, S-TiO₂, and S-TiO_{2-x} photoanodes exhibit higher photocurrents than that of pure TiO₂. When the light source was turned off, the current rapidly decayed, indicating that the current completely originated from the activity of the photoanode and that charge transport was very fast [35]. The arc radius in a Nyquist plot reflects the charge-transfer resistance at the photoelectrode/electrolyte interface [36]. A smaller arc radius indicates higher charge transfer efficiency [34]. In Fig. 6(b), each semicircle represents an individual sample, and the arc radii of the obtained S-doped and/or Ti³⁺ self-doped samples are smaller than that of pure TiO₂. These smaller radii indicate more effective separation of the photogenerated electron-hole pairs and faster interfacial charge transfer in the samples with S and/or Ti³⁺.

3.3. Photocatalytic performance

The photocatalytic activity of the sample was evaluated by RhB degradation tests under light irradiation from a 300-W Xe lamp coupled with a filter ($\lambda > 400$ nm). The concentration change and temporal evolution of the spectra of RhB in the presence of different sample are shown in Fig. 7. Fig. 7(a) reveals that the concentration of RhB gradually decreases during

Fig. 6. Transient photocurrent responses (a) and Nyquist plots (b) of the different photoelectrodes.

Fig. 7. (a) Photocatalytic degradation of RhB over the different samples under visible-light irradiation. (b) Kinetic linear simulation curves for the degradation of RhB over different samples. (c) Real-time absorption spectra of RhB during photocatalytic degradation over S-TiO_{2-x} -T. (d) Recyclability of TiO_{2-x} -H and S-TiO_{2-x} -T in the photocatalytic degradation of RhB.

visible-light illumination. The S-TiO_{2-x} sample has higher photocatalytic activity than those of pristine TiO_{2-x} and S-TiO_2 samples. The Langmuir-Hinshelwood pseudo first-order kinetics model was used to quantitatively investigate the reaction kinetics

of RhB degradation by the obtained samples. The sequence of RhB degradation rate constants was $\text{S-TiO}_{2-x}\text{-T} > \text{S-TiO}_{2-x}\text{-H} > \text{TiO}_{2-x}\text{-H} > \text{S-TiO}_2 > \text{pure TiO}_2$ (Fig. 7(b)). The rate constants of the catalytic degradation of RhB over pure TiO_2 , pristine

$\text{TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$ were 0.002, 0.025 and 0.017 min^{-1} , respectively, while those of $\text{S-TiO}_{2-x}\text{-H}$ and $\text{S-TiO}_{2-x}\text{-T}$ were 0.043 and 0.062 min^{-1} , respectively. The photocatalytic efficiency of $\text{S-TiO}_{2-x}\text{-T}$ was improved 31-, 2.5-, and 3.6-fold compared with that of pure TiO_2 , pristine $\text{TiO}_{2-x}\text{-H}$, and $\text{S-TiO}_{2-x}\text{-T}$ samples under visible-light irradiation. The higher catalytic performance of $\text{S-TiO}_{2-x}\text{-T}$ compared with that of the other samples is attributed to the introduction of S into the lattice of TiO_2 and presence of Ti^{3+} , both of which narrow the bandgap of TiO_2 and enhances the rate of photogenerated electron transfer.

The photodegradation process of RhB by the samples was investigated by monitoring the change in its absorbance under visible-light irradiation. The time-dependent UV-Vis spectra of RhB solution during the degradation reaction over the $\text{S-TiO}_{2-x}\text{-T}$ sample is depicted in Fig. 7(c). The characteristic absorption band of RhB at 553 nm decreased substantially as irradiation time extended, suggesting that complete decolorization of RhB solution was realized. Because RhB is quite stable under photolysis conditions, decomposition of RhB was caused by photocatalytic degradation over $\text{S-TiO}_{2-x}\text{-T}$ [37].

The stability of a photocatalyst is important for its practical application. Recycling experiments were carried out for the photocatalytic degradation of RhB by the $\text{S-TiO}_{2-x}\text{-T}$ and pristine TiO_{2-x} samples (Fig. 7(d)). After reuse six times, no marked loss in photocatalytic performance was observed, clearly showing that these photocatalyst samples had high stability and good potential for practical application.

To further confirm the photocatalytic degradation of RhB, MS was used to investigate the photodegraded species in solution after photocatalysis. Fig. 8 suggests that the organic spe-

Fig. 8. Mass spectra of the RhB solution before photocatalysis (a), and after 10 (b) and 30 min (c) of photocatalysis by $\text{S-TiO}_{2-x}\text{-T}$ under visible-light irradiation.

Fig. 9. Changes in TOC in the reaction systems containing $\text{TiO}_{2-x}\text{-H}$ and $\text{S-TiO}_{2-x}\text{-T}$ photocatalysts during visible-light photocatalytic degradation of RhB.

cies in water undergo structural degradation during the course of photocatalysis. After 30 min, the remaining species in solution are mainly small molecules.

In addition, in the photodecomposition process of dye wastewater, it is important to evaluate the mineralization ability of catalysts. In our reaction system, the mineralization ability of RhB dye by the prepared $\text{TiO}_{2-x}\text{-H}$ and $\text{S-TiO}_{2-x}\text{-T}$ photocatalysts was evaluated by monitoring the changes in TOC. As illustrated in Fig. 9, the TOC removal reached 63% and 73% in the suspensions containing $\text{TiO}_{2-x}\text{-H}$ and $\text{S-TiO}_{2-x}\text{-T}$ photocatalysts, respectively after 40 min under visible-light irradiation. This result further confirms that $\text{S-TiO}_{2-x}\text{-T}$ has the highest photocatalytic performance among these photocatalysts.

Furthermore, to eliminate the possibility that the enhanced photocatalytic activity of our samples mainly resulted from their enhanced physisorption, FT-IR spectra of the $\text{S-TiO}_{2-x}\text{-T}$ sample were collected before and after the photodegradation of RhB. As illustrated in Fig. 10, the FT-IR spectra of $\text{S-TiO}_{2-x}\text{-T}$ before and after degradation one or five times were similar. Therefore, the visible-light photodegradation on $\text{S-TiO}_{2-x}\text{-T}$ is caused by the degradation of RhB molecules. These results also indicate that $\text{S-TiO}_{2-x}\text{-T}$ has good stability.

Fig. 10. FT-IR spectra of $\text{S-TiO}_{2-x}\text{-T}$ (1) before, and after degradation one (2) and five (3) times.

3.4. Proposed mechanism for the enhanced photocatalytic performance

It is widely recognized that photocatalysts with larger specific surface areas can supply more surface active sites for the adsorption of reactant molecules, resulting in enhanced photocatalytic performance. To study the effect of specific surface area on the photocatalytic activity of the samples, their BET specific surface areas were determined using nitrogen adsorption–desorption measurements. The samples were degassed at 170 °C prior to these measurements and BET surface areas were calculated from the linear part of each BET plot; the results are shown in Fig. 11. The calculated specific surface areas of pristine TiO_2 -H, S- TiO_2 -T, S- TiO_2 -x-H, and S- TiO_2 -x-T are 46.06, 44.00, 55.78 and 43.32 m^2/g , respectively. Considering their similar specific surface areas, it can be concluded that surface area is not the critical factor determining the efficiency of these photocatalysts.

The high photocatalytic performance of S- TiO_2 -x-T mainly originates from S doping in the Ti–O–Ti crystalline structure, but other factors also have contribute to its enhanced photocatalytic performance. First, calcination led to higher crystallinity than did hydrothermal treatment, lowering the content of defect-based recombination centers for photogenerated electrons and holes. Generally, the recombination of photogenerated electrons and holes occurs in crystal defects. Therefore, the photocatalytic and photoelectrochemical activities of TiO_2 are expected to increase if its defect density is decreased by annealing at high temperature [21]. Second, S-doping of TiO_2 -x resulted in a red shift of the absorption edge, leading to the visible-light photosensitivity of the S- TiO_2 -x samples [10]. When S atoms were doped into the lattice of TiO_2 -x by substituting the Ti^{4+} sites to form Ti–O–S bonds, an intermediate energy level was generated in TiO_2 -x located above the O 2p VB, narrowing the energy gap of TiO_2 -x and shifting its optical absorption from the UV region to the visible [12]. Third, the introduction of Ti^{3+}

Fig. 11. N_2 adsorption-desorption isotherms and corresponding BET surface areas of photocatalyst samples.

Fig. 12. Schematic illustration of the visible-light photocatalytic mechanism of the S- TiO_2 -x-T photocatalyst.

into TiO_2 can form a local state at the bottom of the CB, endowing the reduced TiO_2 -x with visible and infrared light absorption ability [38]. In addition, as a kind of defect, Ti^{3+} can act as an electron capture agent, increasing the electrical conductivity of the photocatalyst and accelerating the transfer of electrons and holes [39]. Based on the above experimental results and analysis, the proposed mechanism of the enhanced photocatalytic activity of the S- TiO_2 -x-T sample is displayed in Fig. 12.

Under visible-light irradiation, electrons are transported from the intermediate energy level located above the VB to the local state located below the CB. The electrons in the local state can transfer to the CB of TiO_2 . Holes in the intermediate energy level are captured by $-\text{OH}$ and H_2O to form $\bullet\text{OH}$, and the electrons in the local state and CB react with the O_2 molecules dissolved in water to form $\bullet\text{O}_2^-$. These $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ species are able to degrade RhB molecules in solution. Meanwhile, the photogenerated holes also have strong oxidation ability and can directly degrade RhB, thereby contributing to the high visible-light photocatalytic activity of the S- TiO_2 -x sample.

4. Conclusions

S- TiO_2 -x photocatalysts were synthesized using thiourea dioxide as both the S source and reductant. The subsequent treatment method (hydrothermal or calcination) affected the crystallinity and particle size of the photocatalyst and thus its photocatalytic properties. S-doping of TiO_2 -x resulted in a red shift of the absorption edge, and the introduction of Ti^{3+} in TiO_2 formed a local state at the bottom of the CB, so S- TiO_2 -x absorbed visible light. In addition, Ti^{3+} acted as an electron capture agent, increasing the electrical conductivity of the photocatalyst and accelerating the transfer of electrons and holes. Compared with pure TiO_2 , pristine TiO_2 -x and S-doped TiO_2 , the S- TiO_2 -x photocatalysts showed evidently enhanced photoactivity for the degradation of RhB under visible-light irradiation. This work provides a new method to develop stable and efficient visible-light-driven photocatalysts to degrade organic pollutants.

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Graphical Abstract

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Facile synthesis of S-doped reduced TiO_{2-x} with enhanced visible-light photocatalytic performance

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Sulfur-doped reduced titania photocatalysts were synthesized via hydrothermal treatment or calcination using thiourea dioxide as both the sulfur source and reductant. The photocatalysts absorbed visible light and displayed excellent visible-light photocatalytic performance.

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S掺杂的还原态TiO_{2-x}的制备及其可见光催化性能

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摘要: 作为一种稳定、价廉的光催化剂, TiO₂被广泛应用于各种污染物的降解; 但是, 较大的宽禁带(~3.2 eV)和较低电子迁移率不仅使TiO₂很难吸收可见光, 而且光生电子和空穴的复合几率高, 从而导致TiO₂的总体光电效率不高. 因此, 设计能够被可见光激发、并具有快速光生电子传输的TiO₂一直是研究热点. 研究表明, Ti³⁺自掺杂的TiO₂ (还原态TiO_{2-x})不仅能够被可见光激发, 而且使TiO₂具有良好的电子导电性, 从而有利于提高TiO₂的光电转换效率. 另外, 非金属元素的掺杂能够减小TiO₂的禁带宽度, 使TiO₂能够响应可见光并具有良好的可见光催化性能, 其中S元素的掺杂被广泛研究.

目前, S掺杂纳米TiO₂的制备通常采用TiS₂, 单质S, 硫脲、二甲亚砜等为S源, 但这类原料通常价格昂贵或者具有一定的毒性, 因而实际应用受到限制. 而制备Ti³⁺自掺杂TiO₂的方法大都是基于“还原法”, 在真空或强还原性气氛如H₂, CO中加热TiO₂, 或采用高能粒子(电子、氩离子)轰击. 在实际应用中, 这些方法存在步骤多、条件苛刻、反应时间长和设备昂贵等不足. 而且, 还原法反应通常发生在颗粒的表面, 形成的Ti³⁺很容易被空气和水中的溶解O₂氧化, 降低材料的稳定性. 虽然在温和的液相中还原Ti⁴⁺可用于制备Ti³⁺掺杂的TiO₂, 但是由于反应过程中有副产物生成, 需要进行后续处理才能得到纯的Ti³⁺自掺杂TiO₂. 因此, 设计一种简单的制备S掺杂还原态TiO_{2-x}光催化剂仍具有十分重要的意义.

前期我们采用H₂O₂氧化TiH₂得到不同状态的前驱体凝胶, 然后进行不同方式的后续处理得到Ti³⁺自掺杂的纳米TiO₂. 本文以TiH₂和H₂O₂反应得到的黄色前驱体凝胶为Ti源, 以价格低廉、无毒、稳定的二氧化硫脲为S源和还原剂, 采用不同的方法制备了S掺杂的还原态TiO_{2-x}光催化剂. 本文初步研究了在凝胶中加入二氧化硫脲后进行水热处理, 以及将干燥的凝胶粉末与二氧化硫脲混合热处理对所得产物的影响. 并与纯的TiO₂、还原态TiO_{2-x}和S掺杂TiO₂的光吸收、电化学、光催化性能进行对比研究. 采用X射线衍射、透射电子显微镜、高分辨透射电子显微镜、X-射线光电子能谱、紫外-可见漫反射光谱、比表面分析和电化学工作站等技术对产物的结构、形貌和光电性能进行了表征. 以罗丹明B(RhB)溶液为模拟废水, 考察样品的可见光催化性能. 结果表明, 不同的后续处理方式不仅影响S掺杂TiO_{2-x}的结晶性和形貌, 而且影响产物的光吸收性能和电子传输性能, 从而使不同条件下所得产物的可见光催化性能不同. 其中, 采用热处理方式得到的S掺杂TiO_{2-x}样品在可见光下降解RhB的速率分别是纯的TiO₂, TiO_{2-x}和S掺杂TiO₂的31, 2.5和3.6倍, 而且样品具有良好的循环稳定性.

关键词: Ti³⁺自掺杂; 二氧化钛; 硫掺杂; 二氧化硫脲; 可见光催化

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