Enhanced Visible Light Photocatalytic Activity of Mesoporous Anatase TiO₂ Codoped with Nitrogen and Chlorine

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Anatase mesoporous titanium dioxide codoped with nitrogen and chlorine (N-Cl-TiO₂) photocatalysts were synthesized through simple one-step sol-gel reactions in the presence of ammonium chloride. The resulting materials were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflection spectrum (UV-vis DRS). XRD results indicated that codoping with nitrogen and chlorine could effectively retard the phase transformation of TiO₂ from anatase to rutile and the growth of the crystallite sizes. XPS revealed that nitrogen and chlorine elements were incorporated into the lattice of TiO₂ through substituting the lattice oxygen atoms. DRS exhibited that the light absorption of N-Cl-TiO₂ in visible region was greatly improved. As a result, the band gap of TiO₂ was reduced to 2.12 eV.

The photocatalytic activity of the as-synthesized TiO₂ was evaluated for the degradation of RhB and phenol under visible light irradiation. It was found that N-Cl-TiO₂ catalyst exhibited higher visible light photocatalytic activity than that of P25 TiO₂ and N-TiO₂, which was attributed to the small crystallite size, intense light absorption in visible region, and narrow band gap.

1. Introduction

Titanium dioxide (TiO₂) is known as a semiconductor with various kinds of application in solar energy conversion, gas sensors, air purification, and waste water treatment due to its cheapness, nontoxicity, and strong oxidation power [1–6]. However, anatase TiO₂ can only be excited by UV light with wavelengths less than 388 nm, which only accounts for a small part of the solar spectrum [7]. In order to effectively extend the light absorption to visible region and enhance the photocatalytic activity, many attempts have been made, such as dye sensitization, noble metal deposition, coupling of TiO₂ with a narrow semiconductor and doping of TiO₂ with foreign ions. Among these, doping of TiO₂ with foreign ions has been an effective and feasible approach to improve the visible light response and photocatalytic activity [8–13]. Recently, many researches indicate that TiO₂ doping with two different species into the lattice could further enhance the visible light photocatalytic activity. Sun et al. [14] synthesized C-S-codoped TiO₂ by the hydrolysis of tetrabutyl titanate in a mixed aqueous solution containing thiourea and urea. Lv et al. [15] prepared C-N-codoped TiO₂ nanoparticles with visible light photocatalytic activity. Xu and Zhang [16] reported an enhanced photocatalytic activity of the C-Cl-codoped TiO₂ powders towards the degradation of RhB under visible light irradiation. Although such reports demonstrated successful fabrication of relative high photocatalytic activity, they still suffered from some deficiencies due to the discharge of poisonous gases, troublesome procedure during the reaction process.

In this study, N-Cl-codoped TiO₂ photocatalyst (N-Cl-TiO₂) has been synthesized through simple one-step sol-gel reactions in the presence of ammonium chloride. N and Cl elements were incorporated into the lattice of TiO₂ through...
substituting the lattice oxygen atoms. As expected, the N-Cl-codoped TiO₂ catalyst exhibited higher visible light response and photocatalytic activity than that of P25 TiO₂ and N-TiO₂. Further, the activity-enhanced mechanism was also discussed in detail.

2. Experimental

2.1. Synthesis of Materials. Typically, a solution consisting of 10 mL absolute EtOH, 12 mL dilute HNO₃ (1:5, volume ratio between HNO₃ and DI water), and the desired amount of ammonium chloride was added dropwise into a solution containing 40 mL absolute EtOH and 10 mL Ti(OBu)₄ within 120 min under vigorous stirring. After being aged for 6 h at room temperature, the TiO₂ precursor was received by drying the wet gel in an oven for 36 h. Finally, the N-Cl-codoped TiO₂ sample was obtained by calcining the precursor at 623 K for 4 h with a heating rate of 3 K·min⁻¹. For comparison, pure TiO₂ and N-TiO₂ catalysts were synthesized as the reference according to the previous work of our groups [17].

2.2. Characterization of Materials. X-ray diffraction (XRD) patterns were collected on Model D/MAX-III B diffractometer equipped with Cu Kα radiation source (λ = 0.15406 nm). An accelerating voltage of 40 kV and an emission current of 30 mA with a scanning rate of 5°·min⁻¹ were employed, respectively. Transmission electron microscopy (TEM) was taken on a JEOL JEM-2010 EX instrument operated at an accelerating voltage of 200 kV. High-resolution transmission electron micrograph (HRTEM) was obtained by employing a FEI TECNAI G2 S-TWIN with a 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) was performed on a Model PHI-5700 ESCA apparatus with Al Kα X-ray source. All the binding energies (BE) were referenced with the adventitious carbon (binding energy = 284.6 eV). The ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) of the as-synthesized TiO₂ samples was recorded with a Model Shimadzu UV-2550 spectrophotometer.

2.3. Evaluation of Photocatalytic Activity. The experiments were carried out in a 100 mL quartz photochemical reactor and the visible light source was provided from a side of the reactor, by a 350 W Xe-arc lamp equipped with a UV-cutoff filter (λ > 420 nm). In each run, 20 mg TiO₂ catalyst was added into 20 mL RhB solution of 10 mg·L⁻¹. Prior to photoreaction, the solution was magnetically stirred in the dark for 30 min to establish the equilibrium of adsorption-desorption. At given time intervals, the samples after filtration and centrifugation were analyzed by a T6 UV-vis spectrometer. In addition, the photodegradation of uncolored phenol was similar to that of RhB, and the concentration was determined by the colorimetric method of 4-aminoantipyrine at the wavelength of 510 nm.

3. Results and Discussion

3.1. XRD and TEM Analysis. Figure 1 showed the XRD patterns of the pure and N-Cl-codoped TiO₂ samples. It can be seen that pure TiO₂ contained anatase (JCPDS. No 21–1272) and trace of rutile (JCPDS. No 21–1276). However, N-Cl-TiO₂ consisted of anatase as a unique phase (JCPDS. No 21–1272), indicating that codoping with nitrogen and chlorine could effectively retard the formation of rutile. In addition, no XRD peaks relate to the dopants were detected. One reason was that the concentration of the dopants was so low that it cannot be detected by XRD. The other was that the dopants were incorporated into the lattice of TiO₂ through substituting oxygen atoms or located in the interstitial sites. Further, as seen from the inset of Figure 1, the diffraction peak position of N-Cl-codoped TiO₂ shifted to lower angle in comparison with the pure TiO₂, suggesting that oxygen atoms in the lattice of anatase in codoped TiO₂ sample may be substituted by the dopants. Further, the average crystallite sizes of the as-synthesized samples can be calculated by applying the Debeye-Scherrer formula [18] on the anatase (101) diffraction peaks:

\[
d = \frac{K\lambda}{\beta \cos \theta},
\]

where d is the crystallite size, λ is the wavelength of X-ray radiation (in our test, λ = 0.15418 nm), K is a constant (K = 0.89), β is the full width at half-maximum, and θ is the diffraction angle. The calculated d values were 10 and 5 nm for pure and N-Cl-codoped TiO₂, respectively. Thus, we can conclude that codoping with N and Cl elements could effectively retard the phase transformation of TiO₂ from anatase to rutile and growth of the crystallite size.

The crystal structure and grain size of N-Cl-codoped TiO₂ sample were also evaluated with TEM and HRTEM. Figure 2 showed the TEM and HRTEM images of mesoporous N-Cl-TiO₂ photocatalyst. As shown in Figure 2(a), many spherical aggregates of nanoparticles were observed with the nanoparticles at about 5–10 nm in crystallite sizes. However, an obvious agglomerative phenomenon was observed. As shown in Figure 2(b), the lattice fringes of nanocrystals revealed the lattice spacing of 0.352 nm, which
was in good accordance with the anatase (101) lattice fringes of 0.352 nm [19].

3.2. XPS Analysis. In order to investigate the chemical states of the N-Cl-codoped TiO2 sample, XPS was conducted and shown in Figure 3. As seen from Figure 3(a), a single peak at binding energy of 399.6 eV was observed, which was attributed to the presence of substitutional N in O–Ti–N bond [20, 21], indicating that some lattice oxygen were substituted by nitrogen atoms, which correlated with the visible light photocatalytic activity of doped TiO2. As shown in Figure 3(b), two peaks at 197.7 and 199.3 eV seen from the Cl2p core-level XPS spectrum were observed. The strong peak at 197.7 eV was assigned to Cl− ions physically adsorbed on the surface of codoped TiO2 [22], while the minor peak located at 199.3 eV might be assigned to the Cl incorporated into the lattice of TiO2 [16], indicating that nitrogen and chlorine were incorporated into the lattice of TiO2 through substituting the lattice oxygen atoms.
3.3. DRS Analysis. Generally speaking, narrower band gap of a semiconductor corresponds to a higher photocatalytic activity. In order to investigate the optical absorbance property of pure and N-Cl-codoped TiO$_2$ samples, ultraviolet-visible diffuse reflection spectra were conducted and shown in Figure 4. In addition, band gap energies were also calculated according to the Kubelka-Munk function [23], which was shown in the insert in Figure 4. Noticeably, both as-synthesized TiO$_2$ samples showed a typical absorbance spectrum with an intense transition in the UV region of the spectra, corresponding to the band gap energy of 3.2 eV from the intrinsic band gap of pure anatase. However, the light absorption edge of N-Cl-codoped TiO$_2$ sample was greatly red-shifted to the visible light region, demonstrating a decrease in the band gap energy, which was responsible for the impurity level (formed from hybridization of N2p and Cl2p levels) in the band gap of TiO$_2$. After calculating, the band gap energy of N-Cl-codoped TiO$_2$ was 2.12 eV. As a result, the N-Cl-codoped TiO$_2$ should most probably possess excellent visible light photocatalytic activity for organic degradation.

3.4. Mechanism Analysis. Based on the above analysis, a possible photocatalytic mechanism was proposed and shown in Figure 5. Nitrogen and chlorine were incorporated into the lattice of TiO$_2$ through substituting lattice oxygen atoms. Thus, a new impurity level was formed from the hybridization of N2p and Cl2p levels between the valence band and conduction band of TiO$_2$. As shown in Figure 5, pure TiO$_2$ exhibited a relatively low visible photocatalytic activity for the degradation of pollutants due to its wide band gap (3.2 eV, process A). After codoping with nitrogen and chlorine elements, electrons can be promoted from the impurity level to the conduction band of TiO$_2$ (process B), thereby enhancing the separation efficiency of photoinduced charge carriers. As a result, more departed photoinduced electrons and holes can participate in the photocatalytic reactions. Further, the process of visible light photocatalytic oxidation of phenol can be described as followed:

Firstly, electrons and holes were generated under visible irradiation.

$$\text{N-Cl-TiO}_2 + h\nu \rightarrow h_{VB}^+ + e_{CB}^- (2)$$

Then, the departed electrons and holes can react with the absorbed O$_2$ and H$_2$O molecules, respectively, forming the main active species (such as ·O$_2$ and ·OH) responsible for the degradation of organic pollutants, such as RhB and phenol in our case. Eventually, organic pollutants were mineralized into small molecules, such as CO$_2$ and H$_2$O

$$\text{O}_2(\text{ads}) + e_{CB}^- \rightarrow \cdot\text{O}_2^-$$

$$h_{VB}^+ + \text{H}_2\text{O}(\text{ads}) \rightarrow \cdot\text{OH} + \text{H}^+$$

$$\cdot\text{O}_2^- + 2\text{H}^+ + e_{CB}^- \rightarrow \cdot\text{OH} + \text{OH}^- (3)$$

$$h_{VB}^+ + \text{OH}^- \rightarrow \cdot\text{OH}$$

$$\cdot\text{OH} + \text{Organic} \rightarrow \cdot\cdot\cdot \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

3.5. Photocatalytic Activity. The photocatalytic activities of the TiO$_2$ samples were evaluated by photocatalytic degradation of RhB and phenol under visible light irradiation.
The photocatalytic activity of P25 TiO2 and N-TiO2 was also supported by the National Natural Science Foundation of China for The authors wish to gratefully acknowledge the financial support by National Natural Science Foundation of China for light absorption in visible region, and narrow band gap. was mainly attributed to the small crystallite size, intense light absorption in visible region, and narrow band gap energy.

4. Conclusions

Based on the above analysis, the following conclusions can be drawn: (1) N-Cl-codoped TiO2 catalyst with high visible light photocatalytic activity has been successfully synthesized through simple one-step sol-gel reactions in the presence of ammonium chloride. (2) TiO2 doping with N and Cl could effectively retard the phase transformation of TiO2 from anatase to rutile and growth of crystallite size. (3) N and Cl elements were incorporated into the lattice of TiO2 through substituting some oxygen atoms, which could form a new impurity level between the valence band and conduction band of TiO2. (4) Codoping with N and Cl could greatly improve the photosresponse of TiO2, thereby reducing the band gap. (5) The enhanced activity of N-Cl-codoped TiO2 was mainly attributed to the small crystallite size, intense light absorption in visible region, and narrow band gap.

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