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Research Article

Facile Postsynthesis of N-Doped TiO_2-SBA-15 and Its Photocatalytic Activity

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N-doped TiO_2-SBA-15 (denoted as N-TiO_2-SBA-15) material has been successfully synthesized by a two-step procedure. Firstly, TiO_2-SBA-15 was prepared by impregnating tetraisopropyl orthotitanate on SBA-15 and followed by calcination at 550°C. In the second step, TiO_2-SBA-15 was modified by doping nitrogen with the assistance of urea. The resulting material, N-TiO_2-SBA-15, was characterized by XRD, TEM, SEM, N_2 adsorption/desorption at 77 K, DR UV-Vis, and XPS. The results showed that N-TiO_2-SBA-15 material maintains its ordered hexagonal mesostructure and exhibits the absorption of visible region. The photocatalytic activity of N-TiO_2-SBA-15 sample was evaluated by the photodegradation of methylene blue under visible light.

1. Introduction

Heterogeneous photodegradation of organic pollutants with semiconductors has attracted much of the attention of researchers because of its efficiency and promises of economy [1, 2]. Among the semiconductor materials, TiO_2 has been investigated more widely due to its high photocatalytic efficiency, commercial availability, chemical stability, and environmental friendliness [3, 4]. However, its technological application seems to be limited by several factors such as relatively low surface area and the requirement of UV light. In order to overcome these limitations, a number of modifications have been tried.

Many efforts have been made on supporting TiO_2 on porous materials for increasing surface area of TiO_2 [5–7]. Among the various porous materials, SBA-15 silica has attracted great attention as an ideal catalytic support due to its large surface area, adjustable pore size ranging from 5 to 30 nm, ordered frameworks with the wall being in the thickness range of 3.1–6.4 nm, and transparency to UV radiation [8].

Over the past decades, in order to extend the useful spectral range into the visible region, metal-doped TiO_2 photocatalysts were intensively studied. However, metal-doped TiO_2 exhibits several drawbacks: thermal instability, electron trapping by the metal centers, and requirement of more expensive ion-implantation facilities [9, 10]. Recently, it was shown that the narrowing of band gap for TiO_2 can be better obtained by using anionic dopants rather than metal ions. In a breakthrough work, Asahi et al. showed that the substitution of oxygen atoms in TiO_2 by nitrogen atoms leads to the narrowing of the band gap by mixing the N 2p and O 2p states [11]. Since then, many synthetic strategies have been applied for doping of the TiO_2 with various nonmetal atoms such as N [12–25], C [26–29], B [30–33], S [34–37], P [38], F [39, 40], and I [41, 42].

These reports all showed that the doping can bring a significant enhancement for the photocatalytic activity of TiO_2 under visible light. Among the nonmetals, N is the most typical nonmetal dopant and has been intensively investigated so far. There are numerous publications on preparation of N-doped TiO_2 by various methods, including

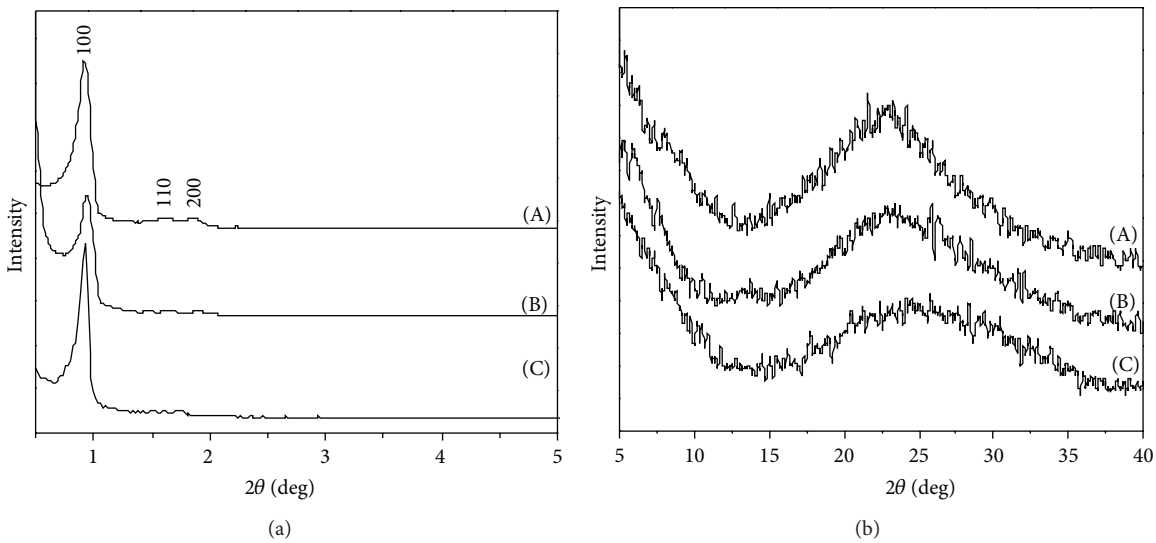


Figure 1: (a) Small-angle XRD patterns of the pure SBA-15 (A), TiO_2-SBA-15 (B), and N-TiO_2-SBA-15 (C); (b) Large-angle XRD patterns of the pure SBA-15 (A), TiO_2-SBA-15 (B), and N-TiO_2-SBA-15 (C).

sol-gel [13–20], sputtering [11, 12], ion-implantation [21], and plasma-enhanced chemical vapor deposition [22] methods. Beside NH_3 as a significant nitrogen source for the doping, urea has attracted considered attention as an alternative nitrogen source because of its useful characteristics such as environment-friendly and easy operation in doping [43–45]. The aim of our research study is to use urea as a nitrogen source to synthesize N-doped TiO_2 supported on SBA-15.

A combination of modified TiO_2 and SBA-15 can take advantage of both SBA-15 and TiO_2. In this paper, we report a facile preparation of N-doped TiO_2-SBA-15 using urea as a nitrogen source. The as-synthesized material showed visible-light response and potential application in photodegradation of methylene blue under visible light.

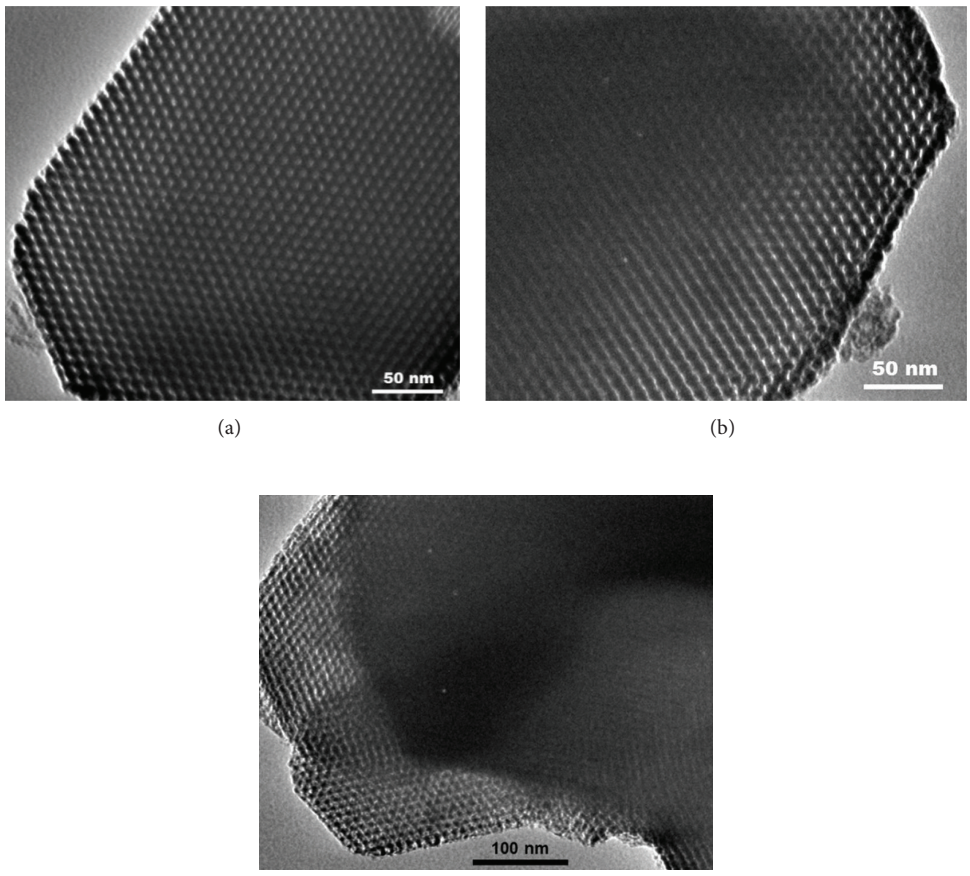
2. Experimental Section

2.1. Chemicals. Triblock copolymer Pluronic P123 ($HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$), tetraethyl orthosilicate (TEOS, $(C_2H_5O)_4Si$), methylene blue, and titanium isopropoxide ($Ti(C_3H_7O)_4$) were purchased from Merck. Hydrochloric acid and urea were purchased from Shanghai Chemical Company. All chemicals were used as received without any further purification.

2.2. Synthesis. The mesoporous silica SBA-15 was prepared according to the literature [46]. In a typical synthesis, 2 g of P123 was added to 62.5 g of 1.9 M HCl with stirring. 3.84 g of TEOS was added after the mixture was heated to 40°C. The reaction mixture was stirred for 20 h at 40°C and then aged in an autoclave at 100°C for 24 h. The solid products were separated by filtration and washed with distilled water for several times. The structure directing agent (P123) was removed by heating the samples at 550°C for 6 h in the air. The TiO_2-SBA-15 sample was prepared according to the following procedure. 0.5 g of SBA-15 was added to the solution of 0.75 g of $Ti(C_3H_7O)_4$ in 20 mmL of ethanol. After evaporation of the solvent with stirring at 40°C, the resulting solid was dried at 100°C for 12 h and then heated at 550°C for 5 h. The obtained solid was denoted as TiO_2-SBA-15. For the doping of TiO_2-SBA-15 with nitrogen, a mixture of TiO_2-SBA-15 and urea solution with the urea/TiO_2-SBA-15 ratio of 1 : 3 in weight was prepared. After evaporation of the solvent with stirring at 40°C, the resulting solid was dried at 100°C overnight and then calcined at 500°C for 1 h in the air. The resulting material was denoted as N-TiO_2-SBA-15.

2.3. Characterization. X-ray diffraction (XRD) patterns for the samples were measured on a Bruker D8 Advance diffractometer using CuKα radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were recorded on JEOL JEM-2100F and JEOL 5410, respectively. N_2 adsorption-desorption isotherms were obtained on ASAP 2010 at 77 K. Before the measurement, the samples were degassed at 100°C for 6 h. Diffuse-reflectance UV-Vis spectra were investigated on a Sinco S-4100 spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG Microtech Multilab ESCA 3000 spectrometer.

For the photocatalytic test, 100 mg of the catalyst was suspended in 50 mL of 100 mg/L methylene blue (MB) aqueous solution, and then the mixture was stirred for 2 h in dark to obtain the equilibrium adsorption. The reaction mixture was exposed to visible light from a 300 w lamp with a UV cutoff filter (>420 nm). After a given irradiation time, about 4 mL of the mixture was withdrawn and the catalysts were separated by centrifugation. The selected solutions were measured using a UV-Vis spectrophotometer (Jenway 6800).



(a) (b)

(c)

Figure 2: TEM images of the pure SBA-15 (a), TiO_2-SBA-15 (b), and N-TiO_2-SBA-15 (c).

3. Results and Discussion

3.1. Characterization of Catalysts. The small-angle X-ray diffraction patterns of pure SBA-15, TiO_2-SBA-15, and N-TiO_2-SBA-15 are shown in Figure 1(a). For the pure SBA-15, three resolved diffraction peaks with 2θ at 0.92°, 1.60°, and 1.84°, indexed as (100), (110), and (200) reflections, are clearly observed, indicative of a two-dimensional hexagonal lattice with high p6*mm* symmetry [43]. The other materials have an intensive reflection (100), indicating the presence of ordered hexagonal structure similar to the pure SBA-15 silica. However, the peak intensity, especially for (110) and (200) reflections, significantly decreases with the graft of TiO_2 and the doping of nitrogen. This is probably due to decreasing scatter contrast between the silica framework and TiO_2 inside the pores [47, 48]. From the 2θ values of the (100) reflections, the hexagonal lattice parameters are calculated and reported in Table 1.

The large-angle X-ray diffraction for N-TiO_2-SBA-15 was also studied to characterize the structure of TiO_2 grafted on SBA-15 (Figure 1(b)). Also shown are the patterns of SBA-15 and TiO_2-SBA-15. All patterns are similar in shape and show a broad peak centered at about 25° that may be due to amorphous SiO_2 of SBA-15. TiO_2 cannot be detected by XRD, indicating that TiO_2 may disperse homogeneously into nanoparticles on SBA-15.

Table 1: Structural, textural properties of the pure SBA-15, TiO_2-SBA-15, and N-TiO_2-SBA-15.

Material	S_{BET} (m^2/g)	Pore diameter (nm)	a (nm)	Wall thickness (nm)
SBA-15	689.8	7.5	11.1	3.6
TiO_2-SBA-15	529.4	6.6	10.9	4.3
N-TiO_2-SBA-15	462.6	6.0	11.1	5.1

The periodicity in the mesostructure of the three materials is confirmed directly by transmission electron microscopy (Figure 2). The TEM micrographs display that both the perpendicular and parallel channels relative to the longitudinal axis are observed, which confirms that the modified SBA-15 materials possess ordered, one-dimensional pore structure similar to that of the pure SBA-15. However, a gradual decrease in structural ordering from SBA-15 to TiO_2-SBA-15 to N-TiO_2-SBA-15 can be seen from the images of channels in Figure 2. A raw estimation from the TEM images presents that the pore-pore distances match the lattice parameters calculated from XRD data.

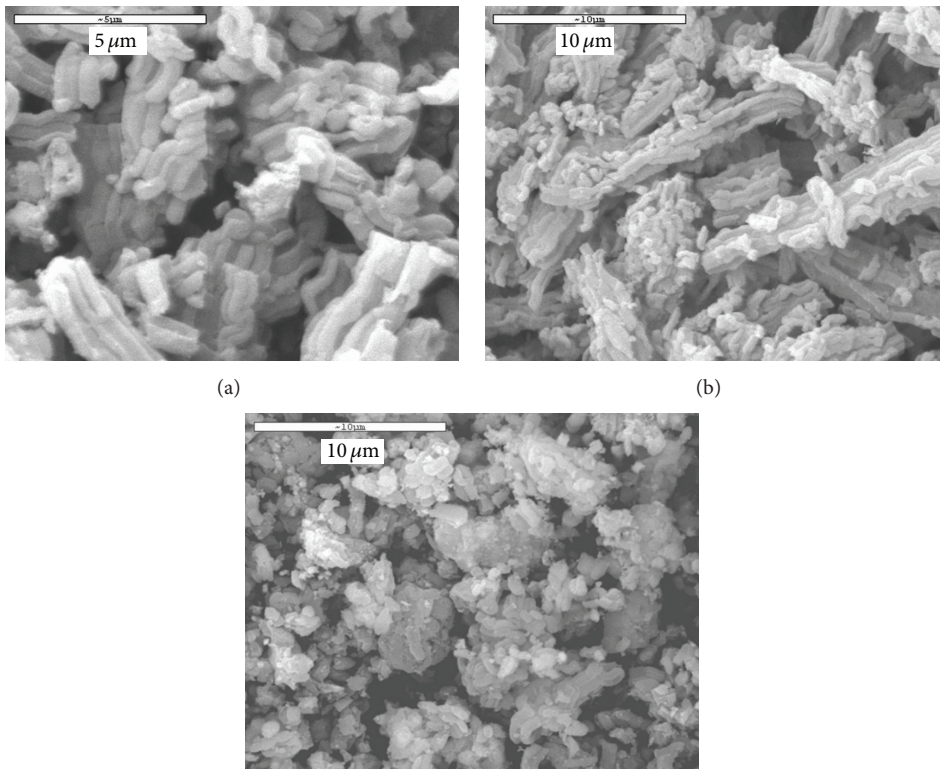


Figure 3: SEM images of the pure SBA-15 (a), TiO_2-SBA-15 (b), and N-TiO_2-SBA-15 (c).

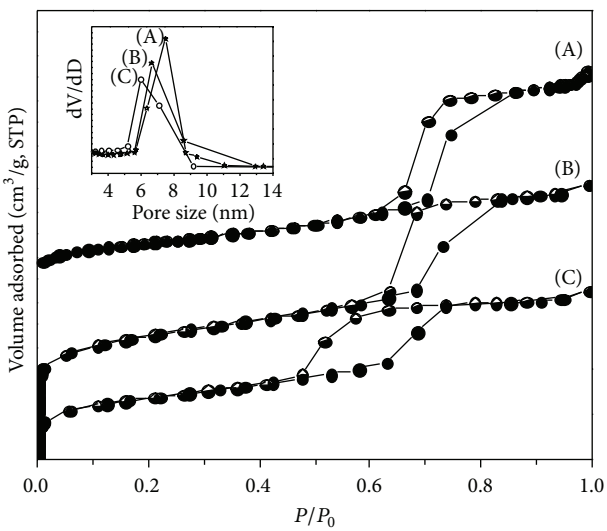


Figure 4: N_2 adsorption-desorption isotherms and pore size distribution (the inset) of the pure SBA-15 (A), TiO_2-SBA-15 (B), and N-TiO_2-SBA-15 (C).

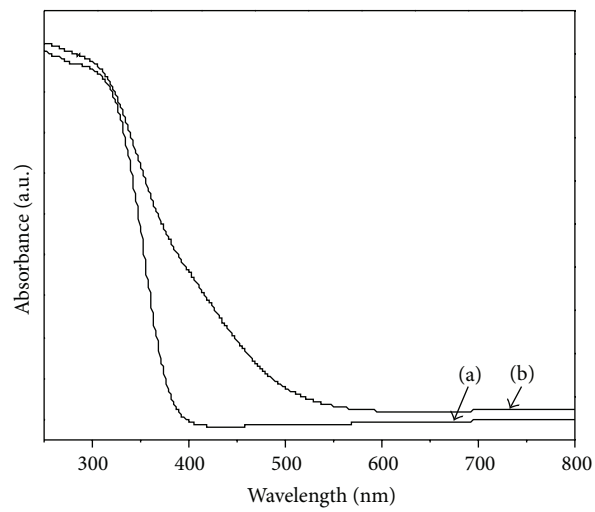


Figure 5: Diffuse reflectance UV-Vis spectra of TiO_2-SBA-15 (a) and N-TiO_2-SBA-15 (b).

The morphology of rope-like domains with a uniform size was obtained for the materials SBA-15 and TiO_2-SBA-15 (Figures 3(a) and 3(b)). A different shape can be seen from Figure 3(c) for N-TiO_2-SBA-15. The reaction between TiO_2 on SBA-15 and urea may result in breaking the rope-like domains of SBA-15. It can be seen from the TEM and SEM images of TiO_2-SBA-15 that TiO_2 nanoparticles disperse homogeneously on SBA-15 silica. This is further supported by the large-angle XRD patterns of TiO_2-SBA-15 without any peaks as mentioned above.

The N_2 adsorption/desorption isotherms at 77 K of the calcined SBA-15 and the modified SBA-15 samples are shown in Figure 4. Type IV IUPAC isotherms, characteristic of

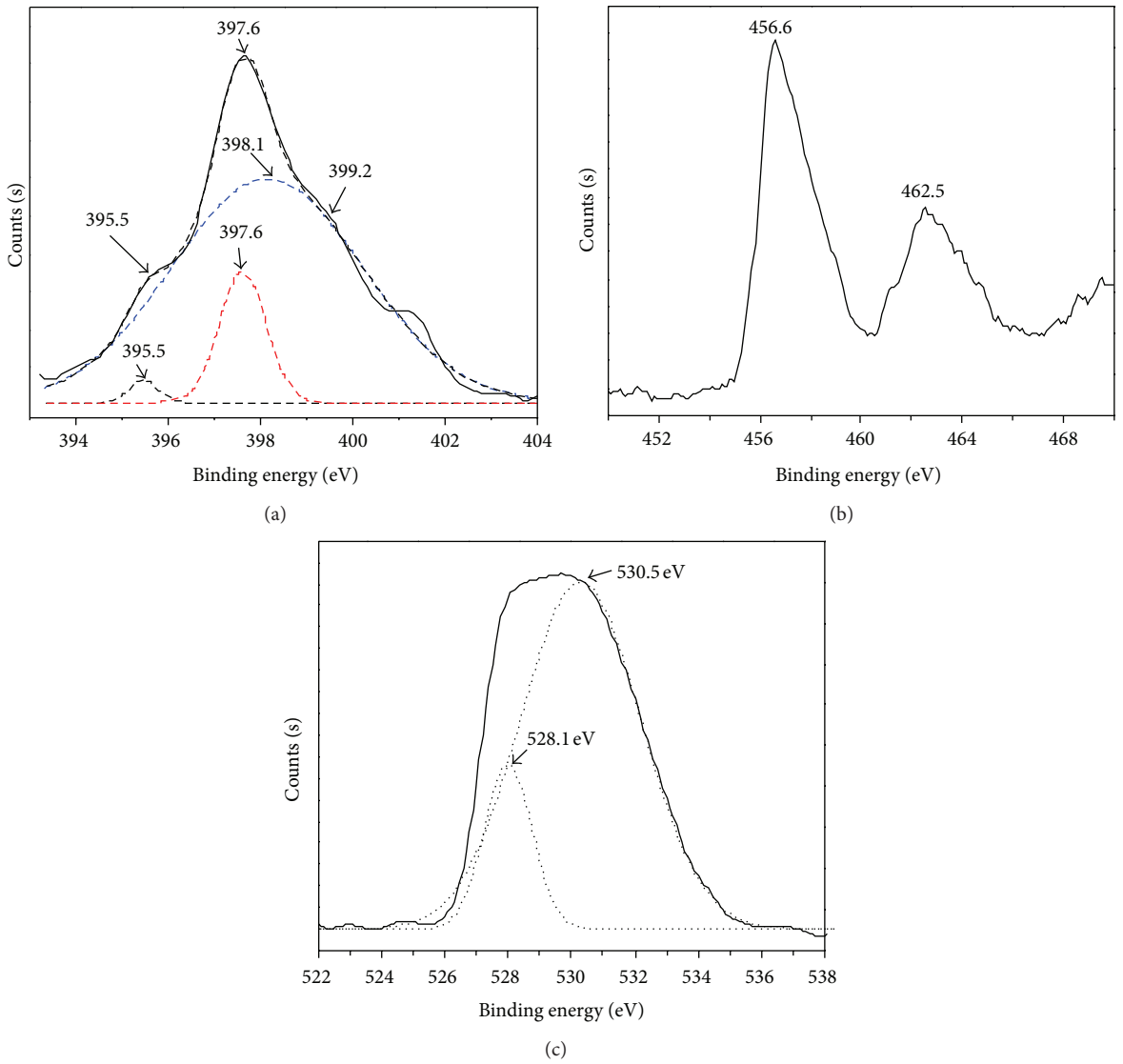


Figure 6: XPS spectra of N 1s (a), Ti 2p (b), and O 1s (c) for N-TiO_2-SBA-15.

capillary condensation in mesopores, are found for all samples. However, their shapes are different with a capillary condensation of N_2 occurring over a slightly lower P/P_0 range when going from SBA-15 to TiO_2-SBA-15 to N-TiO_2-SBA-15. The pore-size distribution of the materials is shown in the inset of Figure 4. It can be seen that pore diameters of about 7.5, 6.6, and 6.0 nm for SBA-15, TiO_2-SBA-15, and N-TiO_2-SBA-15, respectively, were obtained. A decrease in specific surface area and pore size was observed in order of the following materials: SBA-15, TiO_2-SBA-15, and N-TiO_2-SBA-15. However, the wall thickness increased in the same order of the materials. These results can be attributed to the fact that TiO_2 particles are attached to the wall of SBA-15 in TiO_2-SBA-15 and some TiO_2 particles are exfoliated from the wall to block the pores in N-TiO_2-SBA-15 when TiO_2-SBA-15 reacted with urea. The summary data on structural, textural properties of the three materials obtained from the N_2 adsorption/desorption isotherms are shown in Table 1.

The doping of TiO_2 on SBA-15 with nitrogen was further supported by the diffuse reflectance UV-Vis spectroscopy. Figure 5 shows that TiO_2-SBA-15 exhibits a strong absorption in UV region corresponding to the band to band transition. Compared with TiO_2-SBA-15, the sample N-TiO_2-SBA-15 possesses a tailing absorption extending out to approximately 600 nm, which is a typical absorption feature of N-doped TiO_2. The absorption in visible light for the sample N-TiO_2-SBA-15 may come from the narrowing band. The band gap value was calculated from the diffuse reflectance measurements to be 2.89 eV.

Chemical states of the doped nitrogen in N-TiO_2-SBA-15 were investigated by XPS. It can be seen from Figure 6(a) that a shape peak around 397.6 eV and two shoulders around 395.5 and 399.2 eV, respectively, for N 1s were found. After fitting the peaks, three peaks at 395.5, 397.6, and 398.1 eV were observed. The binding energy at 395.5 eV can come from replacing the oxygen in the crystal lattice of TiO_2 by nitrogen. The peak

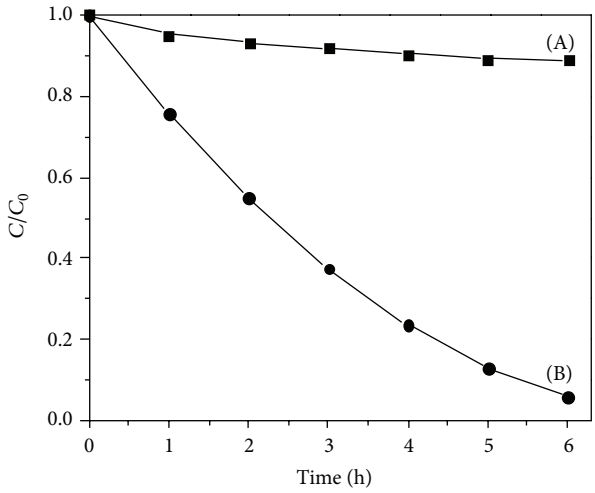


Figure 7: Photocatalytic degradation of methylene blue on TiO_2-SBA-15 (A) and N-TiO_2-SBA-15 (B) with initial methylene blue concentration of 100 mg/L under visible light.

at 397.6 eV is attributed to the nitrogen anion incorporated in the TiO_2 in N-Ti-O bond. And the strong peak at 398.1 eV can be assigned to the nitrogen in the Ti-O-N site of the N-TiO_2 matrix. These results are consistent with the previous reports [49–51] and will be supported further by the XPS data of Ti 2p and O 1s below. The N content of 3.37% in mol for N-TiO_2-SBA-15 was obtained from the XPS data.

Compared to Ti-N, a relatively higher binding energy at 397.6 eV for N-Ti-O may be explained by the high electronegativity of oxygen leading to the reduction of electron density on the nitrogen [52]. This is further supported by the result of XPS spectrum for Ti 2p (Figure 6(b)). Two XPS peaks at 456.6 eV and 462.5 eV corresponding to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, were obtained. The Ti $2p_{2/3}$ peak for pure TiO_2 should be at 458.8 eV [53]. A decrease in the binding energy of Ti $2p_{3/2}$ after nitrogen doping may come from the electronic interaction of Ti with anions in N-TiO_2, which is different from that of TiO_2. The lower electronegativity of nitrogen compared to oxygen may lead to a transfer of partial electron from the N to the Ti. Therefore, the electron density around the anion decreases, resulting in the increase in electron density around the cation [54]. This indicates the substitution of oxygen atoms in TiO_2 by nitrogen atoms. The incorporation of nitrogen in TiO_2 can be further confirmed by the binding energy of O 1s. As shown in Figure 6(c), the peak at 530.5 eV may be attributed to the presence of Ti-O-N bonds [52].

3.2. Photocatalytic Test. The photocatalytic activity of the samples was determined by the degradation of methylene blue in water under visible light. Figure 7 shows the variation of methylene blue concentration (C/C_0) with irradiation time over the two catalysts. For the N-TiO_2-SBA-15 catalyst, it can be seen that the concentration of methylene blue decreases rapidly in the initial three hours and slowly in the later period. Methylene blue can be effectively degraded in the presence of N-TiO_2-SBA-15, and the degradation efficiency reaches about 90% in 6 h irradiation. For comparison, the photodegradation of methylene blue for the sample TiO_2-SBA-15 under the same conditions is also shown in Figure 7. An insignificant catalytic activity of about 3–5% is obtained for the sample without nitrogen doping.

4. Conclusion

The visible-light-sensitive nitrogen-doped TiO_2-SBA-15 material was synthesized by a two-step process. TiO_2 nanoparticles with homogeneous dispersion on the SBA-15 silica were treated with urea to form nitrogen-doped TiO_2-SBA-15 material. The absorption of visible light for the material comes from the partial substitution of the oxygen in TiO_2 by nitrogen atoms. The nitrogen-doped TiO_2-SBA-15 material exhibits a good photocatalytic activity for the degradation of methylene blue in the aqueous solution under visible light.

Acknowledgment

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