Synthesis and Characterization of Visible-Light-Active TiO$_2$-Based Photocatalysts

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Abstract

TiO$_2$ has gained great popularity for environmental treatment and purification purposes; however, it shows poor absorption of visible light and requires ultraviolet (UV) light for activation. Here we have successfully synthesized a visible-light-active carbon and nitrogen co-doped TiO$_2$ catalyst. The catalyst was characterized by Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS). Results showed that the optical response of modified TiO$_2$ was extended to the visible light region. Nitrogen substituted for some of the lattice oxygen atoms and most of the carbon was in the form of elemental carbon. The photocatalytic tests indicated that the modified catalyst demonstrated higher visible-light activity for the degradation of methylene blue (MB) than TiO$_2$.

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Introduction

Titanium dioxide (TiO_2) has been widely used as photocatalysts for solar energy conversion and environmental application because of good photoactivity, high chemical stability, low cost, and non-toxicity. However, the application of pure TiO_2 was limited because poor absorption of visible light. Therefore, efforts have been directed toward expanding the optical response of TiO_2-based photocatalysts from UV to the visible light region. One method is introduction of allowed energy states in the band gap of TiO_2 by doping of transition metal ions such V, W, or Fe.[1,2,3,4] However, these doped materials are thermally unstable and the introduction of these ions can also increase the carrier recombination rate, resulting in low photocatalytic efficiency.[5,6] Another approach is to modify TiO_2 with nonmetal atoms such as S, C, or N. It was assumed that these nonmetal atoms either substituted oxygen atoms or titanium in the lattice of TiO_2 or formed impurity level between the conduction and valence band of TiO_2, thus increased the visible light sensitivity.[7,8,9,10,11] In this paper, we synthesized carbon and nitrogen co-doped TiO_2 photocatalysts by the sol-gel method and their photocatalytic activities will be tested by using methylene blue (MB) as a probe molecule, which has been widely used in textile industry and as a standard compound in a test of photocatalysts.

Experimental

Preparation 3.0 g urea (99.0-100.5%, Aldrich) was dissolved in 30 ml deionized water. While under vigorous stirring in water-ice bath, 8 ml titanium isopropoxide (97%, Aldrich) was added drop-wise. The mixture was stirred for 12 h and aged for 24 h. Water removal was accomplished by drying in air at 80 °C. The as-obtained samples was

calcined under NH_3 flow at 500 °C for 2 h then treated in air at 200 °C for 1 h, denoted as CN-TiO$_2$. For comparison purposes, pure TiO_2 was also prepared using the similar procedure without urea and the calcination was performed in air.

Characterization Raman spectrum is recorded using a Nicolet Nexus 670 Fourier transform IR (FT-IR) with a Raman module. X-Ray powder diffraction (XRD) patterns are obtained with a Bruker D8 diffractometer, using Cu Kα radiation (1.5406Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) data are recorded using a Perkin-Elmer PHI 5400 electron spectrometer. Binding energies for the samples are normalized with respect to the position of the C 1s peak resulting from adsorbed hydrocarbon fragments. Diffuse reflectance spectra (DRS) are recorded with a Cary 500 Scan UV-vis NIR spectrophotometer with an integrating sphere attachment for their diffuse reflectance in the range of 200-800 nm.

Results and discussion

Figure 1 showed Raman spectrum of CN-TiO$_2$. Four peaks at 148, 399, 519, and 638 cm^{-1} were observed. It was reported that six modes A_{1g} (519 cm^{-1}), B_{1g} (399 and 519 cm^{-1}), and E_g (144, 197, and 639 cm^{-1}) were Raman-active of anatase phase. Four modes A_{1g} (612 cm^{-1}), B_{1g} (143cm^{-1}), B_{2g} (826 cm^{-1}), and E_g (447cm^{-1}) were Raman-active of rutile. [12,13,14] Therefore, anatase was the predominant phase structure. An additional peak appeared at 320 cm^{-1} in the spectrum and this feature was contributed to the first-order scattering of a non-stoichiometric titanium nitride.[15] In order to better understand the change in the Raman spectra, the spectra at the range of 300-700 cm^{-1} were fitted. The fitted results were shown in the inset of Figure 1. In the fitting curves, two peaks at 460

and 570 cm^{-1} were observed. The peak at 460 cm^{-1} was related to second-order acoustic mode of titanium nitride and peak at 570 cm^{-1} was related to transverse optical mode.[16] Consequently, nitrogen was doped and replaced oxygen atoms in the titanium oxide crystal lattice.
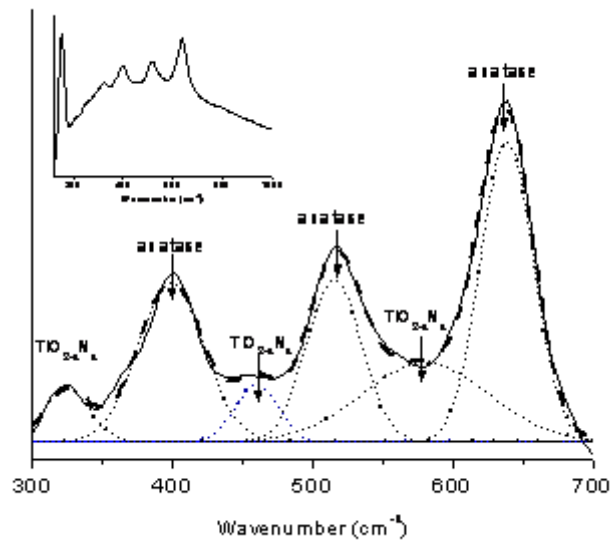
Figure 1 Raman spectra and fitting curves for CN-TiO$_2$

Figure 2 showed the XPS spectrum for CN-TiO$_2$. C 1s spectrum showed one strong peak at 284.6 eV and a weak shoulder around 288.5 eV. So most of the carbon incorporated in the TiO$_2$ matrix existed as elemental carbon and a small amount carbonate species existed on the surface. No peak at 281 eV resulting from Ti-C bond was observed, suggesting carbon did not substitute oxygen atom in the lattice of TiO$_2$. The N 1s spectra showed one peak at 396.2 eV and another at 399.5 eV. We attributed the peak at 396 eV to the presence of Ti-N bond resulting from substitution for oxygen sites by nitrogen atoms in the TiO$_2$ lattice, which was consistent with literatures.[17,18,19] The results also coincided

with Ramam data in Figure 1. The feature at 399.5 eV was assigned to the adsorbed NH_3 based on our preparation method.
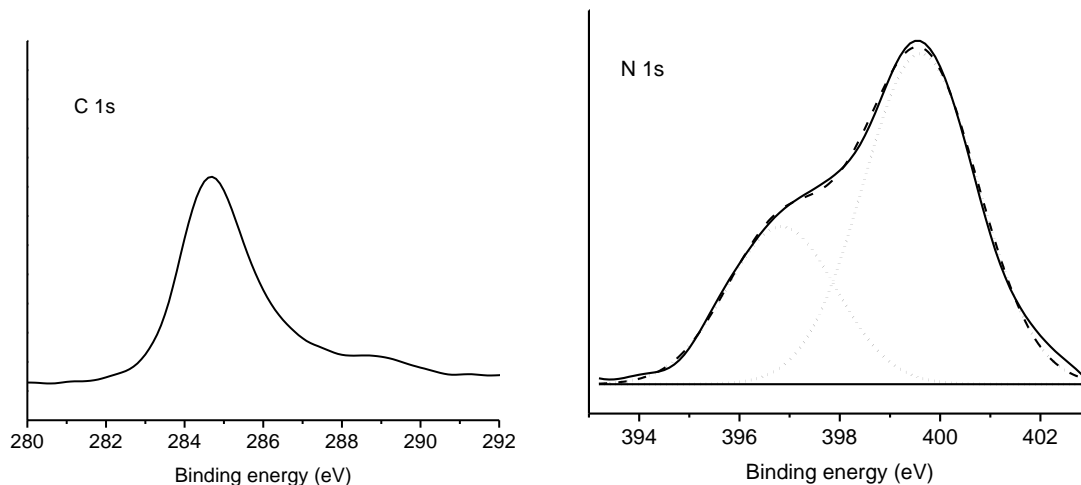

Figure 2 XPS spectra for C 1s, N 1s of of CN-TiO$_2$

Figure 3 showed the XRD patterns of CN-TiO$_2$ and TiO$_2$. Both samples only showed anatase phase ($2\theta = 25.3°$, representative of (101) anatase phase reflections). No other crystal phase (rutile or brookite) was detected. Compared with pure TiO$_2$, the peak position shifted toward higher 2θ value, which suggests that the crystal lattice of TiO$_2$ was distorted by the carbon or nitrogen dopants. From the full width at half maximum (FWHM) of the diffraction pattern, the particle sizes were calculated using Scherrer's equation: pure TiO$_2$ had the particle size of 14 nm and the values for doped TiO$_2$ are about 9 nm.
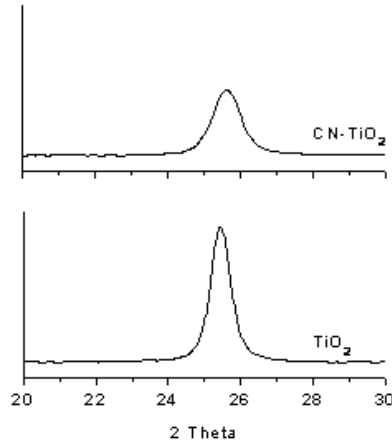
**Figure 3 XRD pattern of CN-TiO$_2$ and TiO$_2$**

Figure 4 showed the diffuse reflectance spectra of CN-TiO$_2$ and TiO$_2$. The band gap energies were calculated according to the following equation, E$_g$ = hc/λ, where E$_g$ is the band gap energy (eV), h is the Planck's constant (4.135667×10^{-15} eV·s), c is the light velocity (3×10^8 m/s), and λ is the wavelength (nm) of absorption onset. Therefore, the band gap energies are 3.05 and 2.12 eV for TiO$_2$ and CN-TiO$_2$, respectively. As expected, the optical response of CN-TiO$_2$ was extended into visible light because of narrower band gap, resulting from doped nitrogen and carbon.
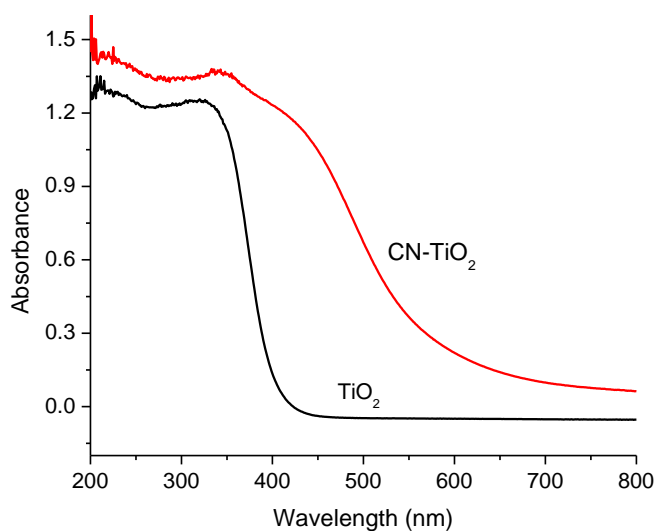
Figure 4 Diffuse reflectance spectra of TiO_2 and CN-TiO_2

Photocatalytic degradation of MB 30 mg of catalyst was suspended in 100 ml aqueous methylene blue dye solution (10 mg/l), contained in a water-jacketed reactor and its temperature was kept at 25 °C. The suspension was kept in the dark for 60 min to establish the adsorption-desorption equilibrium. Then the suspension was irradiation under visible light (>420 nm). Samples were withdrawn periodically and centrifuged and analyzed for the degradation of MB using a UV-vis Cary 500 Spectrophotometer. MB has the maximum absorbance at 664 nm and that was taken as a way for following up the MB degradation. Figure 5 depicts the results of degradation of MB in the presence of CN-TiO_2 and TiO_2 under visible light irradiation. It was clear that CN-TiO_2 showed much higher activity in the presence of visible light than pure TiO_2, which exhibited little activity as expected. If we assumed that the degradation of MB was the first order reaction ($dC/dt = -K \cdot C$), then the rate constant K for CN-TiO_2 was about 17.5 times

higher than that for TiO_2. So doping C and N was an effective way to improve the visible-light-induced activity of TiO_2 for the degradation of MB.
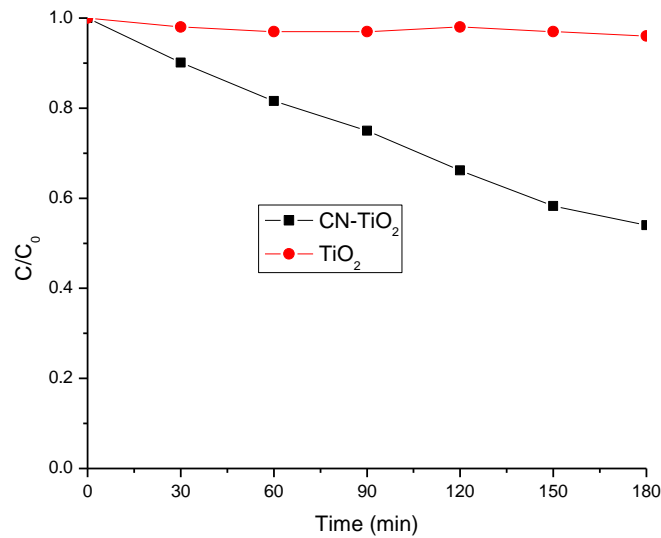
Figure 5 Degradation of MB on CN-TiO_2 and TiO_2 under visible light irradiation

Conclusions

Carbon and nitrogen co-doped TiO_2 catalysts were successfully synthesized by a facile method. Characterization results suggested that nitrogen substituted some of the oxygen atoms in the lattice of TiO_2. Carbon species existed in both elemental and carbonate forms. The co-doped TiO_2 showed higher activity than pure TiO_2 for the degradation of MB under visible light irradiation. The high activity was related to the several beneficial effects associated with the introduction of carbon and nitrogen.

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