Visible-Light-Activated Nanoparticle Photocatalyst of Iodine-Doped Titanium Dioxide

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A novel class of visible-light-activated TiO_2 photocatalysts were prepared by direct hydrolysis of tetrabutyl titanate through iodine-doping. When calcination temperature is at 673 K, these nanoparticles (mean diameter of ∼5 nm) show stronger absorption in the 400−550 nm range with a red shift in the band gap transition and significantly higher photocatalytic activity than pure TiO_2 prepared by the same procedure and Degussa P-25 titania nanoparticles in aqueous phenol solution under visible light irradiation ($\lambda > 400$ nm). Furthermore, I-doped TiO_2 (673 K) still showed pronounced photocatalytic activity under UV and visible light irradiation.

1. Introduction

Semiconductor photocatalysis is one of the most efficient destructive technologies among advanced oxidation processes (AOPs), because it appears to utilize solar energy to lead to the total mineralization of most of the organic pollutants that exist in air and aqueous systems.[1] Among the most viable nanoparticles for photocatalysis is titanium dioxide because of its high oxidative power, photostability, low cost, and nontoxicity.[2] Unfortunately, because of its large band gap of 3.2 eV, it can be activated only under UV light irradiation of wavelength <387 nm. UV light constitutes only a small fraction (5%) of the solar spectrum,[3] so any improvement of the photocatalytic efficiency of TiO_2 by shifting its optical response to the visible range will have a profound positive effect.

For this purpose, an initial approach of doping TiO_2 with transition metals has been investigated extensively. However, the photocatalytic activity of metal doping is impaired by thermal instability[4] and an increase in carrier-recombination facilities.[5] Another option is using dye-sensitized TiO_2.[6] However, all of the known sensitizers are toxic and unstable in aqueous solution, thus making them unsuitable for application in photocatalysis. Very recently, some groups have reported several improved kinds of nonmetal-doped TiO_2. TiO_2 doping with F[7,8] and TiO_2 codoping with Cl and Br[9] all showed higher photocatalytic activity under UV irradiation, but the authors have not reported their photocatalytic activity under visible-light irradiation. Visible-light-activated TiO_2 doping with nonmetal atoms such as nitrogen,[10−15] carbon,[16,17] and sulfur,[18−21] and codoping with nitrogen and fluorine[22] all showed high photocatalytic activity under visible light owing to band gap narrowing.

Some iodine-doped materials such as mutiwall carbon nanotubes (MWNT),[23] ZnTe,[24] and CdTe,[25] have been reported. At the same time, Kuhn et al. have pointed out that iodine was promising for n-type doping.[26] To our knowledge, the visible-light nanoparticle photocatalyst of

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TiO_2 doping with iodine has not been reported. Herein we demonstrate the synthesis route, characterization, and photocatalytic properties of iodine-doped TiO_2 under visible-light irradiation and UV and visible-light irradiation.

2. Experimental Section

2.1 Sample Preparation. All chemicals were reagent grade and used without further purification. The synthesis of iodine-doped TiO_2 began with dissolving 1.32 g of iodic acid (HIO_3) in 50 mL of deionized water, then the dropwise addition of tetrabutyl titanate with continuous stirring of the mixture for 5 min. After this, this mixture was transferred to a culture dish (i.d. 120 mm) and dried at 100 °C for 3 h in an oven. Finally yellow nanocrystals were achieved through calcinating of the samples at 673, 773, and 873 K. We also obtained the pure TiO_2 without any doping using the same procedure calcined at 673 K for comparison.

2.2 Characterization. The X-ray diffraction (XRD) patterns were obtained on a D8-Advance Bruker-AXS diffractometer using Cu Kα irradiation. The phase content of the samples was determined from the integrated intensities of anatase (101), rutile (110), and brookite (121) peaks with the following formulas:

$$W_A = k_A A_A/(k_A + A_R + k_B A_B)$$

$$W_R = A_R/(k_A + A_R + k_B A_B)$$

$$W_B = k_B A_B/(k_A + A_R + k_B A_B)$$

where W_A, W_R, and W_B are the weight fractions of anatase, rutile, and brookite, respectively. A_A, A_R, and A_B represent the integrated intensities of anatase (101), rutile (110), and brookite (121) peaks, respectively. According to the literature,[27] $k_A = 0.886$ and $k_B = 2.721$. The average crystalline sizes of the samples are estimated from Debye−Sherer. A UV−vis spectrophotometer (Varian Cary 500 Scan) was used to obtain the absorption spectra of samples. The binding energies of Ti, I, O, and C were measured at room temperature using an X-ray photoelectron spectroscope (VG Scientific Micro lab 310F). The peak positions of each element were corrected by using that of C1s (285.0 eV). Bright field image and selective area diffraction (SAD) patterns were obtained from transmission electron microscopy (JEM 100 CX 11/SC17).

2.3 Photocatalysis of the Phenol Solution. The photocatalytic activity of the samples was evaluated by phenol degradation because phenol has no absorption in the visible region. A 1000-W Xe lamp was used as the light source and visible-light-activated photocatalytic activity of I-doped TiO_2 was tested with any irradiation below 400 nm removed by using a cutoff filter. The distance between light source and the surface of the solute was 100 cm, and the temperature of the phenol solution stirred by a magnetic stirrer in an open reactor was about 25 °C. The concentration of phenol was monitored by colorimetry[28] with a UNICO UV-2102 spectrometer. Finally, the decrease of total organic carbon (TOC), which confirmed the mineralization of phenol, was determined by a Multi N/C2000 TOC analyzer.

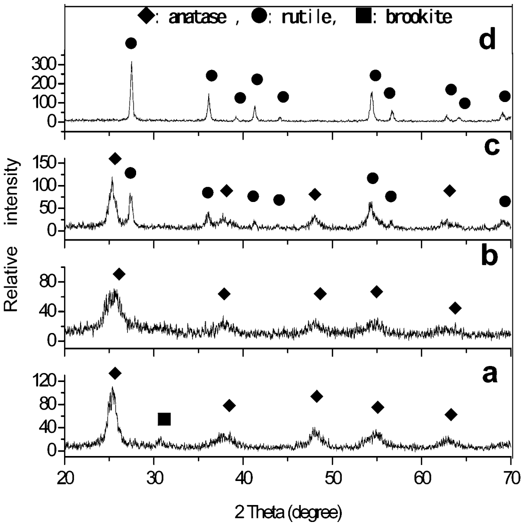

Figure 1. XRD patterns of pure TiO_2 (673 K) (a) and iodine-doped TiO_2 calcined for 2 h at 673 K (b), 773 K (c), and 873 K (d).

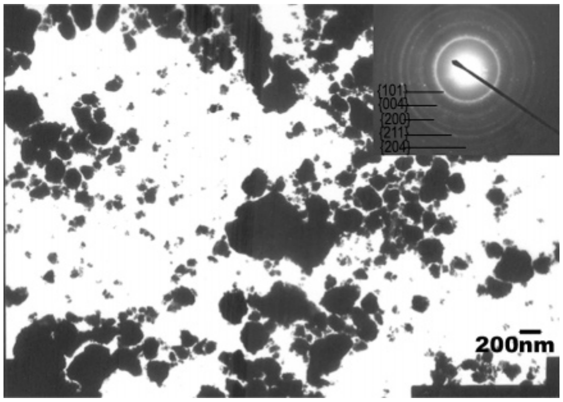

Figure 2. TEM bright field image and SAD (inset) of iodine-doped TiO_2 (673 K).

3. Results and Discussion

3.1 Crystal Structure. Figure 1 shows that iodine-doped samples (673 K) are identified as pure anatase, but pure TiO_2 (673 K) is an anatase (67%)−brookite (33%) mixture. At 773 K, the iodine-doped TiO_2, though dominantly of the anatase form (60%), also contains some notable contribution from rutile phase (40%). When calcined at 873 K, the iodine-doped TiO_2 contains completely rutile structure. As estimated from Debye−Sherer, the iodine-doped TiO_2 (5 nm) calcined at 673 K has a smaller mean diameter compared to those of pure TiO_2 (8 nm) and P-25 powders (30 nm),[29] but the mean diameters of doped samples calcined at 773 K and 873 K are 33 nm and 34 nm, respectively. Shown in Figure 2 are the transmission electron microscopy (TEM) bright field image and selective area diffraction (SAD) pattern (inset) of the partly agglomerated iodine-doped TiO_2 (673 K). Nanostructures of iodine-doped samples (673 K) were confirmed also by SAD pattern to be of the anatase crystalline phase only.

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(28) A series of 5-mL phenol samples was obtained by filtering the solutions using a Millipore filter (0.45 mm). Then each sample was successively mixed with ammonia (0.5 mL, pH ≈ 10), 4-aminoantipyrine (1 mL, M/V = 2%), and $K_3Fe(CN)_6$ (1 mL, M/V = 8%), and then adding deionized water to 50 mL in a Cuvette. The phenol degradation was determined by measuring the absorption of these mixtures at the wavelength of 510 nm. The absorption was converted to the phenol concentration referring to a standard curve showing a linear behavior between the concentration and the absorption at this wavelength.

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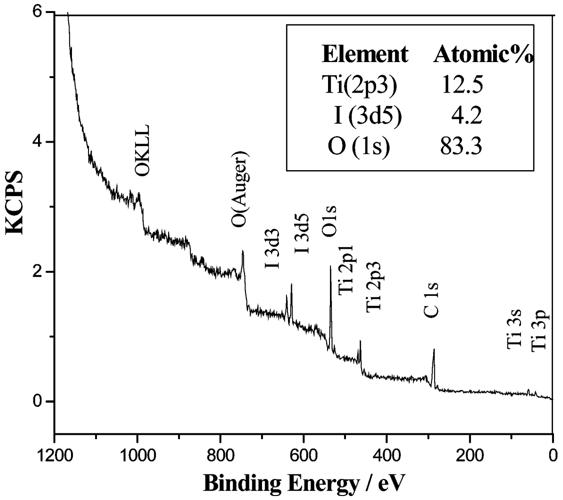

Figure 3. XPS spectrum of iodine-doped TiO_2 calcined at 673 K for 2 h.

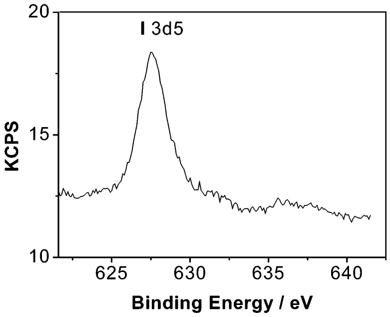

Figure 4. I3d5 high-resolution XPS spectrum of iodine-doped TiO_2 calcined at 673 K for 2 h.

3.2 XPS Studies. According to the X-ray photoelectron spectroscopy (XPS) survey spectrum (Figure 3) of iodine-doped TiO_2 (673 K), these nanoparticles contain only Ti, O, I, C. And binding energies for Ti2p3, O1s, I3d5, and C1s are 261.9, 533.2, 627.5, and 285 eV, respectively. The C element is ascribed to traces of non-hydrolyzed alkoxy groups,[30] the adventitious hydrocarbon from XPS itself, the residual carbon from precursor solution,[7] and adventitious element carbon.[31] But it is difficult to quantify because ^{13}C-MAS NMR could not be applied due to paramagnetic nature of the materials (no signal) and it is not possible to determine the C/H ratio of carbonaceous material.[30] However, there should be no contributions to photocatalytic activity of I-doped TiO_2 (673 K) because in solution phenol is efficiently mineralized only by I-doped TiO_2 (673 K), whereas the pure TiO_2 (prepared by the same procedure) is almost inactive under visible light irradiation (Figure 6). From the high-resolution XPS spectra (Figure 4), the single peak of binding energy of 627.5 eV of I3d5 cannot pertain to I3d5 of HIO_3 because this species decomposes at 573 K ($2HIO_3 = I_2 + {}^5/_2\ O_2 + H_2O$), and the I3d5 peak of HIO_3 would be located at 622 eV. It is unlikely to pertain to I3d5 of TiI_4, which will not exist above 673 K because its boiling point is 650 K. As confirmed by XRD and SAD, the iodine-doped TiO_2 (673 K) is in anatase phase without any contamination of the other phases of TiO_2. The shift of I3d5 may arise from I^{5+} substituting Ti^{4+} which is energetically favorable because they have equivalent ionic radius of 0.62 nm and 0.64 nm for I^{5+} and Ti^{4+}, respectively, and the distorted perovskite structure of HIO_3 is analogous to that of TiO_2.

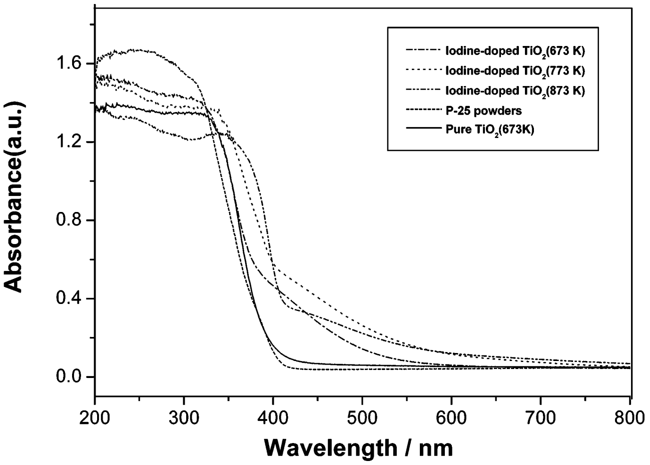

Figure 5. UV−Vis absorption spectra of P-25 powders (Degussa), pure TiO_2 (673 K), and iodine-doped TiO_2 powders before reaction.

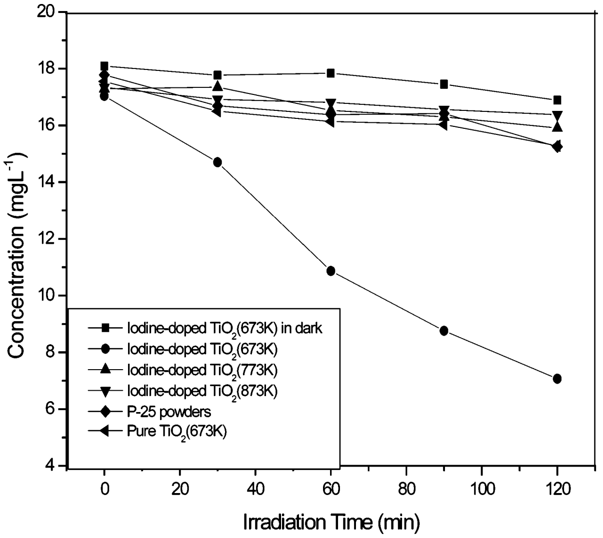

Figure 6. Comparison of the photocatalytic degradation of phenol in the presence of I-doped TiO_2, P-25 powders, and pure TiO_2 nanoparticles (673 K) under visible light irradiation (λ > 400 nm) and absorption of phenol on I-doped TiO_2 (673 K) in dark.

3.3 UV−Vis Absorption Spectroscopy. Optical absorption spectra of the iodine-doped TiO_2 powders, pure TiO_2 powders (673 K), and Degussa P-25 powders before reaction are shown in Figure 5. The absorption measurements of iodine-doped TiO_2 samples show drastic and stronger photoabsorption in the range of wavelengths from 400 to 550 nm compared to P-25 and pure TiO_2 because of the yellow color of iodine-doped TiO_2 and white color of P-25 and pure TiO_2, although P-25 has the predominance of photoabsorption at wavelengths <325 nm. The absorption edge of iodine-doped TiO_2 (673 K), TiO_2 (773 K), TiO_2 (873 K), P-25, and pure TiO_2 (673 K) occurs at 415, 441, 424, 408, and 391 nm, respectively, and accordingly the band gap energy is estimated to be about 2.99, 2.81, 2.92, 3.04, and 3.17 eV, respectively.[32] This shows that doping with iodine can shift

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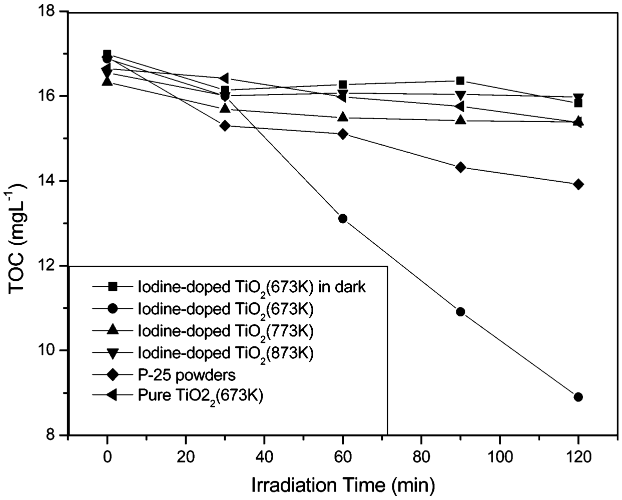

Figure 7. Comparison of the decreasing TOC in the presence of iodine-doped TiO_2, P-25 powders, and pure TiO_2 nanoparticles (673 K) under visible light irradiation (λ > 400 nm) and the change of TOC with I-doped TiO_2 (673 K) in dark.

the absorption edge of TiO_2 to the visible light range and narrow the band gap.

3.4 Photocatalytic Activity. Figure 6 shows the decrease of concentration of phenol in the 720 mL solution (pH = 4.5) under wavelengths >400 nm and absorption of phenol on I-doped TiO_2 (673 K) in dark. There was no obvious change of concentration of phenol with I-doped TiO_2 (673 K) in dark in 120 min. The iodine-doped TiO_2 (673 K) shows significantly higher photocatalytic activity compared to undoped TiO_2 nanoparticles (P-25 and pure TiO_2 calcined at 673 K), as it achieves a reduction of about 59% of the phenol concentration, but P-25 and pure TiO_2 are reduced only 14% and 13% in 120 min. However, iodine-doped samples (773 K) show very low photocatalytic activity and iodine-doped samples (873 K) have no photoactivity at all. Shown in Figure 7 is the observed decrease of TOC, and achieving 47% confirmed that phenol had been not only degraded but also mineralized efficiently upon the iodine-doped TiO_2 nanoparticles calcined at 673 K.

Figure 8 shows that under UV and visible light irradiation the decrease of concentration of phenol can be greatly enhanced in all photocatalytic reaction systems compared with the experiments carried out under visible light and there was very little phenol volatilized. The iodine-doped TiO_2 (673 K) has almost the same high photocatalytic activity as P-25 powders. After illumination for 60 min phenol was almost degraded completely in I-doped TiO_2 (673 K) and P-25 powders systems. Shown in Figure 9, upon I-doped TiO_2 (673 K) TOC achieves 93% which has a significantly higher degree of phenol mineralization than pure TiO_2 (53%) under UV and visible light irradiation, though P-25 has the highest degree of phenol mineralization (98%) in 120 min.

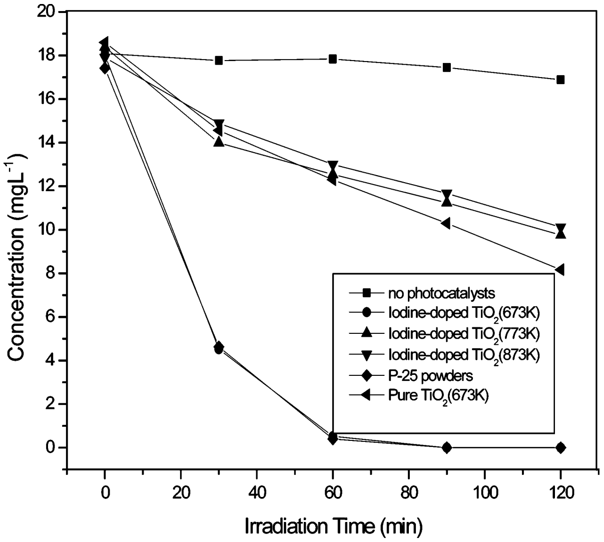

Figure 8. Comparison of the photocatalytic degradation of phenol in the presence of iodine-doped TiO_2, P-25 powders, and pure TiO_2 nanoparticles (673 K) and the change of concentration of phenol with no photocatalyst under UV and visible light irradiation.

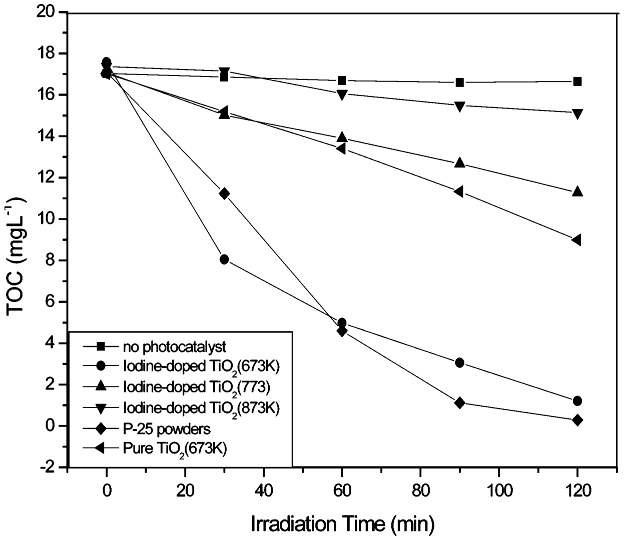

Figure 9. Comparison of the decreasing TOC in the presence of iodine-doped TiO_2, P-25 powders, and pure TiO_2 nanoparticles (673 K) and the change of TOC with no photocatalyst under UV and visible light irradiation.

The superior photocatalytic activity of the I-doped TiO_2 (673 K) can be perfectly demonstrated by illumination experiments both in visible light irradiation and in UV and visible light irradiation. This indicates that UV makes a great contribution to photocatalytic activity of I-doped TiO_2 (673 K); it can be related to their absorption spectra presented in Figure 5, because I-doped TiO_2 (673 K) showed stronger absorption not only in the 400−500 nm but also in the 200−400 nm range compared to the pure TiO_2 (673 K). Apart from band gap narrowing, one possible reason for this photocatalytic activity enhancement of iodine-doped TiO_2 (673 K) is that a certain amount of Ti^{3+} surface states/cation vacancies have been generated to maintain the electroneutrality by I^{5+} substituting Ti^{4+}. The existence of surface state of Ti^{3+} can slow down the recombination of the electron−hole pairs.[7] The other reason may be owing to its entire anatase phase and smaller mean diameter compared to doped TiO_2 (773 K and 873 K). The crystal phase is a crucial factor for photocatalytic activity of TiO_2.[33] It is commonly believed that anatase is the active phase in photocatalytic reactions, but pure rutile normally shows no activity at all.[34] In addition, iodine-doped TiO_2 (673 K) with small particle size needs

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less time for photogenerated carriers to diffuse from the inner region of the photocatalyst to its surface, thus accelerating the separation of photogenarated electrons and holes.

4. Conclusions

A novel visible-light-activated photocatalyst of iodine-doped TiO_2 was synthesized by direct hydrolysis of tetrabutyl titanate. Iodine-doped TiO_2 exhibited stronger absorption in the visible light range with a red shift in the band gap transition. Iodine-doped TiO_2 (673 K) with entire anatase phase and 5-nm mean diameter shows significantly high photocatalytic activity in aqueous phenol solution under visible light irradiation ($\lambda > 400$ nm) and UV and visible light irradiation.

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