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LETTER

Acid-mediated sol–gel synthesis of visible-light active photocatalysts

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Photocatalysis by visible light has received a great deal of attention ever since titanium oxide was first discovered to exhibit photocatalytic activity under ultraviolet radiation in 1970s [1, 2]. To equip titanium oxide with visible light activity, cationic doping by transition metal elements has been extensively investigated [3–7]. The problems with the photocatalysts so prepared are their low conversion efficiency of photo-generated carriers and poor thermal instability [8, 9]. After Asahi et al. [10] found N-doped TiO_2 synthesized by sputtering methods showed remarkable visible-light absorption, other methods in doping nitrogen and other anions into TiO_2 have also been reported subsequently [11–18]. For example, Umebayashi [15] et al. succeeded in synthesizing S anion doped TiO_2 by oxidation annealing of titanium disulfide. Khan et al. [16] prepared C-doped TiO_2 by controlled combustion of titanium metal in a natural gas flame. Sivalingam et al. [17] also succeeded in preparation of C-doped TiO_2 by combustion method. However, studies on TiO_2 doped with more than one kind of anion are seldom reported in literature.

Here we report the synthesis of nitrogen- and carbon-doped titanium oxide photocatalysts from a concentrated nitric acid and titanium tetrabutanoxide. Nitric acid is often used as a hydrolysis catalyst or peptizing agent in hydrolytic preparation of oxides such as titanium oxide [19–25]. In this case, the amount of nitric acid added to the oxide precursor is typically very small and the primary role of nitric acid is believed to enhance the crystallization of the oxide precipitates [19, 20]. By systematically increasing the amount of nitric acid, we found that nitric acid not only provided a source for nitrogen dopant but also assisted the introduction of carbon into the anatase lattice. The titanium oxides so doped were catalytically active to visible light illumination. Compared to the published methods [10–18], such a nitric acid based synthesis pathway offers a much simpler method for obtaining visible-light active photocatalysts.

Different volumes of concentrated nitric acid (65–68%) were first added into 28 ml absolute alcohol, followed by adding 14 ml titanium tetrabutanoxide [$Ti(C_4H_9O)_4$] into it. The mixture of 3 ml distilled water and 14 ml ethanol was then drop-wise added into the above solution with vigorously stirring by magnetic stirrer. The resulting transparent yellowish sol solution was stirred for 1 h to complete the hydrolysis activity. The sol was subsequently dried in an oven at 70 °C for 1 day. The xerogels were grounded and calcined at 300 °C in air for 1 h. The solid products were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV–vis spectroscopy.

Photocatalytic activity was determined by measuring the decomposition rate of methylene blue (MB) in neutral water solution under the irradiation of an 18 W fluorescent reading lamp (containing less than 5% ultraviolet light at 366 nm). The lamp was placed above the reaction vessel, 7.5 cm away from the surface of the test solution in a 100 ml beaker, resulting in an illumination intensity of 3.35 mW/cm^2. The initial concentration of MB was 1.0×10^{-5} mol/l and the catalyst loading was 1 mg/ml. Vigorous stirring was used to make sure the uniformity of

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the solution. After the solution was equilibrated for 30 min, 5 ml aliquots were withdrawn at various reaction times and centrifuged at 4000 rpm for 20 min. The supernatants were collected for the absorbance measurement by UV–vis spectrophotometer.

X-ray powder diffraction pattern of the gel after 70 °C drying is shown in Fig. 1. Without nitric acid, the gel was amorphous. When the volume of concentrated nitric acid increased to 1 ml, strong diffraction peaks appeared, indicating that crystallization had improved with the acid addition, as previously reported [19, 20]. From the width of the diffraction peak, the grain size of the anatase was estimated from the Sherrer's equation to be about 3.4 nm for the dry gel. After the gel was calcined at 300 °C for 1 h, the grain size grew slightly to 4.1 nm with BET-specific surface area of 267.3 m^2/g.

Since XPS powder analysis is subject to surface contamination, sol gel film samples were used for XPS measurements. Prior to XPS analysis, Ar-ion beam was used to sputter clean the film surface to a depth of 5 nm. Multiple high-resolution spectra of C1s and N1s are plotted in Fig. 2 for the film calcined at 300 °C for 1 h. The C1s spectrum contained two strong peaks at 284.6 and 281 eV. The peak at 284.6 eV is assigned to graphitic or hydrogenated C–C bonding [26]. The other peak at 281 eV is very close the binding energy of C in Ti–C bond [27], at 281.8 eV. Therefore, this peak is believed to result from carbon atoms bonded to Ti in the TiO_2 lattice in either interstitial or substitutional sites. In the N1s spectrum, two peaks at the binding energies of 400, and 396 eV were observed. While the peak at 400 eV is from N–O bond [13], the peak at 396 eV is assigned to Ti–N in substitutional form in TiO_2 lattice [10]. From the relative peak intensities, the C and N concentrations in TiO_2 lattice were estimated to be 1.1% and 0.4%, respectively. Such levels of C and N dopants are very similar to those in carbon-doped TiO_2 [16, 17] and nitrogen-doped TiO_2 [10–18].

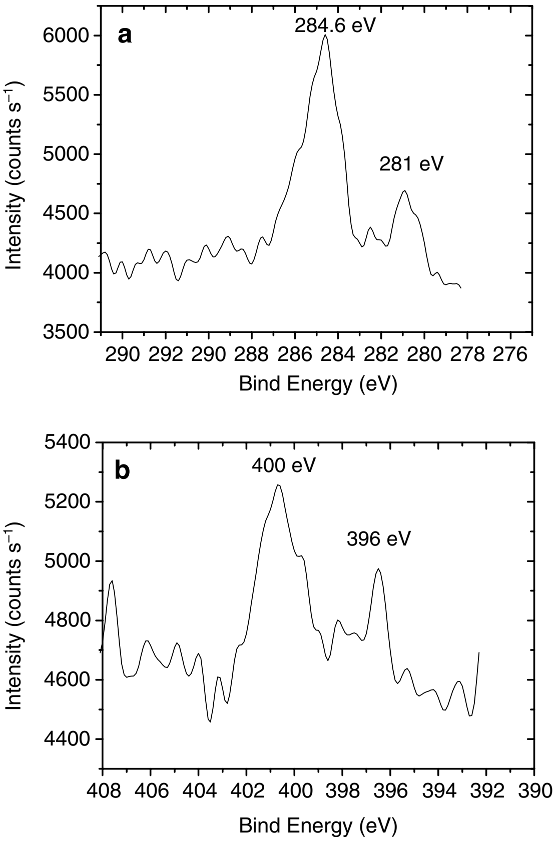

Fig. 2 XPS spectra of doped titanium oxide made from 1 ml concentrated HNO_3, calcined at 300 °C: **a**. C 1s and **b**. N 1s.

The optical absorption of the C- and N-doped TiO_2 is shown in Fig. 3 along with the spectrum for a pure TiO_2 obtained from a commercial source (Sachtleben hombikat UV100). Compared to the pure TiO_2 with an absorption onset at 380 nm, the synthesized powders exhibited strong visible light absorption with an absorption edge beyond 600 nm.

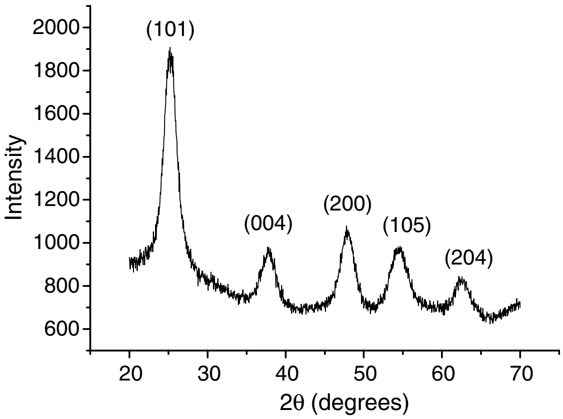

Fig. 1 X-ray diffraction pattern of dried gel synthesized with concentrated HNO_3

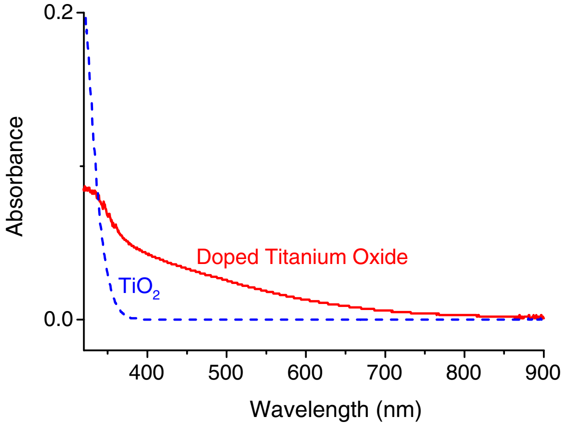

Fig. 3 UV–vis absorption spectra of $TiO_{2-X-Y}C_XN_Y$ and the commercial TiO_2

The photocatalytic activities of the C- and N-doped titanium oxides are shown in Fig. 4. For comparison, the photodegradation curve for undoped TiO_2 (Sachtleben hombikat UV100) is also presented along with the control case where no photocatalyst was used. Compared to the control experiment, the undoped TiO_2 showed a slight photocatalytic activity under the irradiation of the fluorescent lamp. By comparison, the synthesized TiO_2 showed strong photodegradation activity. More than 81% methylene blue was decomposed after 60 min reaction.

While the use of carbon or nitrogen separately as anionic dopant in TiO_2 to achieve visible-light catalytic activity has been previously reported [10–18], the results above have shown that carbon and nitrogen can coexist in TiO_2 to extend the photoabsorption and photocatalytic activity of TiO_2 well into the visible regime. The synthetic pathway for introducing C and N required addition of nitric acid mixed with alcohol to a common titanium oxide precursor. In this process, nitric acid apparently reacted with alcohol to produce C–N complexes that bind well to the titanium ion. It is not clear whether C and N dissociate from each other during subsequent reaction. Compared to other methods of anionic doping, such as the flame combustion method for introducing C dopant [16, 17] and co-sputtering for N-doping [10–15], the addition of nitric acid is simpler and easier to control, and requires no special nitrogen precursor.

It should be noted that other acids may be also be used in place of nitric acid to gain visible-light activity from titanium oxide. Lettmann [28] et al. prepared carbon-containing visible-active catalysts with different alkoxide precursors and hydrochloric acid without intentional addition of any dopants. They also obtained visible-active photocatalyst by simple calcination of an alcoholic suspension of titanium dioxide. However, the photocatalytic activity disappeared when the sintering temperature rose to 400 °C.

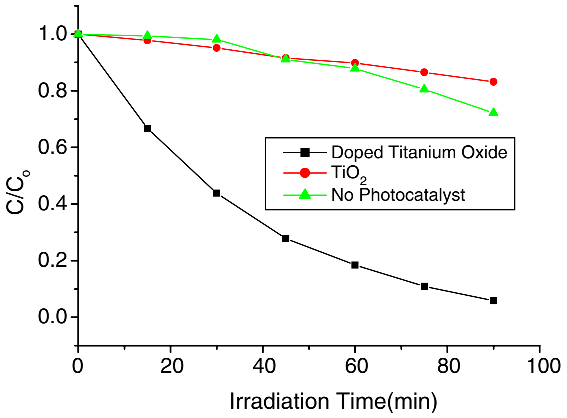

Fig. 4 Comparison of the photocatalytic decomposition of methylene blue in the presence of doped and undoped titanium oxide nanoparticles

In summary, titanium oxide photocatalysts were prepared by sol–gel method using nitric acid as a chelating agent. Following calcination, the oxides were found to contain both carbon and nitrogen as the dopants. The doped oxide absorbed visible light up to 700 nm and rapidly degraded methylene blue by visible light illumination.

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