Template-free Hydrothermal Synthesis of High Surface Area Nitrogen-doped Titania Photocatalyst Active under Visible Light

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(Received January 11, 2005; CL-050040)

The nanofibrous ammonium titanate $(NH_4)_2Ti_3O_{7-x}N_x$ was hydrothermally synthesized by a new method proposed here from titanium oxysulfate precursor in a NH_4OH solution under hydrothermal conditions at 393 K without any extra templates. The calcination of the as-synthesized material at 673 K produced nitrogen-doped titania ($TiO_{2-x}N_x$) with anatase phase, which absorbed visible light and had an extremely high surface area ($377\,m^2g^{-1}$). This material showed an excellent photocatalytic activity in decomposition of 2-propanol under visible light irradiation.

Titanium dioxide TiO_2 is an efficient photocatalyst[1] with a wide variety of practical applications exploiting its strong oxidation activity,[2] disinfection capability,[3] and superhydrophilicity.[4] However, TiO_2 is active only under UV light ($\lambda < 400\,nm$) because of its large band-gap energy of ca. 3.2 eV (for anatase crystalline phase). Since the fraction of UV in solar spectrum is less than 4%, photocatalysts responding to visible light are in great demand to utilize the main part of solar spectrum (46%) for large scale outdoor facilities, and for indoor applications under weak interior lighting, Hence, development of visible-light-active photocatalytic materials has recently become a subject of extensive research. Recently, Asahi et al.[5] have demonstrated that doping of TiO_2 with nitrogen renders it visible-light photocatalytic activity. The induced visible-light activity has been attributed to the narrowing of band gap due to hybridization of N 2p and O 2p orbitals,[5] or formation of an isolated narrow N 2p band above the valence band.[6]

Most of previous reports on nitrogen-doped metal oxide photocatalysts including the original report by Asahi et al. employed high-temperature nitridation of an oxides or its precursor in gaseous ammonia in order to introduce N into oxide lattice.[5,6] This highly reductive treatment usually results in crystals with many defects.[7] Recently, a few liquid-phase synthetic methods of $TiO_{2-x}N_x$ have also been proposed. Thus, hydrothermally prepared titanate nanotubes were protonated, immersed into aqueous NH_4OH, and calcined in air.[8] Alternatively, anatase nanocolloid solution was treated with an alkylammonium salt at room temperature.[9] In the present study, we report a new synthetic method of $TiO_{2-x}N_x$ (anatase) based on mild, template-free hydrothermal reaction in an aqueous ammonia solution at 393 K followed by calcination at 673 K. Nitrogen is introduced into titanium oxide in situ during the hydrothermal reaction from the ammonia solution. The material showed a very high surface area ($377\,m^2\,g^{-1}$), absorbed visible light ($\lambda \geq 420\,nm$), and was active for the photocatalytic decomposition of 2-propanol under visible light irradiation.

Titanium oxysulfate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$, Aldrich) was used as a titanium source in this study, in which TiO_2 content was 33.6 wt %. In a typical synthesis, into a uniform aqueous slurry of titanium oxysulfate powder, an aqueous ammonia solution (28–30 wt %, J.T. Baker) was added slowly. The molar composition of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$, NH_4OH, and H_2O in the mixture was 1:15:50. The mixed solution was transferred into a Teflon-lined autoclave and statically heated in an oven at 393 K for 3 days. After the hydrothermal treatment, the formed white precipitates were filtered out, washed thoroughly with deionized water until the pH of the washing solution reached around 7 and then subsequently washed with absolute ethanol. The wet products were dried in an oven at 353 K for 24 h to obtain white titanate powders. These titanate intermediate products were calcined at 673 K for 4 h in air flow to obtain yellowish titanium oxynitride powders.

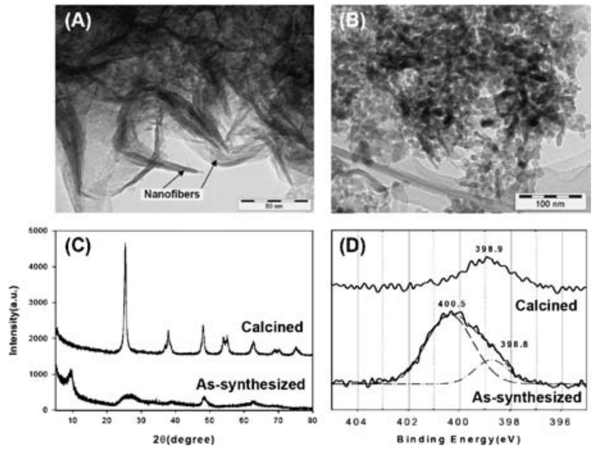

Figure 1. (A), (B) TEM images of as-synthesized samples , and the calcined sample of (A), respectively; (C) X-ray diffraction (XRD) patterns of each samples; (D) X-ray photoemission spectra (XPS) in the N 1s core level region of each samples.

As shown in Figure 1, the as-synthesized sample shows the curled nanofibrious morphology. According to XRD analysis shown in Figure 1C, this intermediate phase is a poorly crystalline titanate.[10] The peak around $2\theta \approx 10^\circ$ indicates that the titanate has a layered structure[10] with an interlayer distance of ca. 0.8 nm. Chemical analysis of this intermediate solid product indicates that it containes nitrogen corresponding to a molecular formula of $(NH_4)_2Ti_3O_{7-x}N_x$ ($x = 0.2$). The presence of ammonium ion was confirmed by an infrared analysis. Upon calcination in air at 673 K, gaseous ammonia was released and the sample turned to yellow. Figure 1B shows that the majority of the sample has particulate morphology, although some parts preserve the fibrous morphology. The XRD pattern of the final product is that of anatase TiO_2, with a high crystallinity. Together with the result of chemical analysis, the molecular formula could be determined to be $TiO_{2-x}N_x$ ($x = 0.07$). Thus, highly crystalline $TiO_{2-x}N_x$ has been synthesized via this simple two-step process. In this process, NH_4OH has played duel roles; as a hydrolyzing agent for $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ during the hydrothermal reaction, and as a source of nitrogen for $(NH_4)_2Ti_3O_{7-x}N_x$ and $TiO_{2-x}N_x$. The above proposed formulae should be further verified by confirming chemical states of nitrogen in these solids. As shown in Figure 1D, a detailed N 1s core region of as-synthesized intermediate sample exhibits a broad and skewed peak extending from 397 to 403.5 eV, which could be deconvoluted into two peaks centered at 400.5 and 398.8 eV. These peaks could be assigned to N species in ammonium ion and the one coordinated to Ti in the titanate structure, respectively.[11] The presence of the latter is considered as a signature of Ti–N coordination with high photocatalytic activity under visible light.[11] In contrast, the calcined sample in Figure 1D displays a broad, but nearly symmetric peak centered at 398.9 eV. This indicates that only N species coordinated to Ti is present in the structure of $TiO_{2-x}N_x$. From the deconvoluted profile of N 1s core region in the uncalcined sample, the amount of nitrogen coordinated to Ti accounts for ca. 1.65 atom %. This amount is well matched with the amount of nitrogen (1.8 atom %) coordinated to Ti in the calcined sample. Thus, during the calcination process, ammonium group is released from the titanate structure and only the Ti-coordinated nitrogen remains in anatase structure, forming $TiO_{2-x}N_x$.

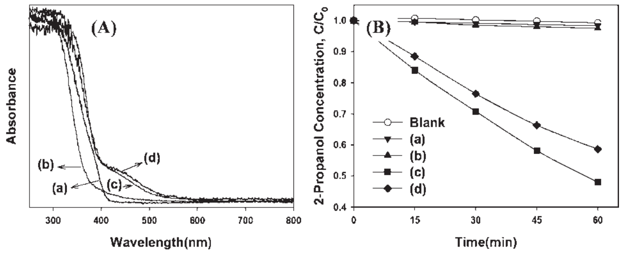

Figure 2. (A) UV–vis–diffuse reflectance (DR) spectra and (B) photocatalytic activity under visible light ($\lambda \geq 420$ nm) for the samples: (a) TiO_2 Degussa P25, (b) as-synthesized titanate, (c) calcined sample, and (d) $TiO_{2-x}N_x$ synthesized by Asahi et al.'s method.[5]

Figure 2A shows the UV–vis–DR spectra of $(NH_4)_2Ti_3O_{7-x}N_x$ and $TiO_{2-x}N_x$, which are compared with those of Degussa P25 and a $TiO_{2-x}N_x$ prepared by Asahi et al.'s method.[5] The $(NH_4)_2Ti_3O_{7-x}N_x$ sample exhibits an absorption edge at 340 nm, corresponding to band gap energy of 3.65 eV. This absorption value is significantly lower than that of Degussa P25 (380 nm, 3.26 eV). Neither sample absorbs visible light. Upon calcination of $(NH_4)_2Ti_3O_{7-x}N_x$ at 673 K, the obtained $TiO_{2-x}N_x$ shows a main absorption edge at 400 nm and, in addition, a shoulder that extends above 500 nm. This absorption spectrum is very similar to that obtained from $TiO_{2-x}N_x$ prepared by Asahi et al.'s method. It is interesting to note that this visible light sensitization effect is much stronger for anatase phase than for the titanate phase, although the degree of N-doping coordinated to Ti is almost the same for two samples.

Figure 2B shows the photocatalytic activity for the decomposition of 2-propanol under visible light irradiation ($\lambda \geq 420$ nm). The light source was a 500-W-mercury arc lamp with a cut-off filter under 420 nm and 0.1 g of catalysts deposited on glass substrate were used in a gas-phase photocatalytic reaction in a 500-mL Pyrex glass reactor with an initial concentration (C_0) of 2-propanol of 1000 ppm. Degussa P25 and uncalcined titanate do not exhibit the photocatalytic activity under the visible light. This is expected because these materials do not absorb visible light. However, both $TiO_{2-x}N_x$ samples showed photocatalytic activity. Interestingly, $TiO_{2-x}N_x$ prepared by the present method exhibits higher activity than $TiO_{2-x}N_x$ prepared by Asahi et al.'s method, although both samples show similar visible light absorption behavior. Although the reason for this difference in activity is not clear at this time, one evident feature of our sample is its high surface area. Our $TiO_{2-x}N_x$ has an extremely high surface area of over 377 m^2g^{-1}. Furthermore, the material also maintains good crystallinity as shown in Figure 1C, in spite of the high surface area. In comparison, $TiO_{2-x}N_x$ prepared by Asahi et al.'s method shows a surface area of ca. 100 m^2g^{-1}. The difference in nitridation method (liquid phase vs gas phase) might also have contributed to the activity difference.

In summary, a new method is proposed to synthesize $TiO_{2-x}N_x$ with an excellent photocatalytic activity under visible light. A salient feature of the process is the use of NH_4OH as a hydrolyzing agent of hydrothermal reaction as well as a nitrogen source for doping. Nitrogen is introduced to TiO_2 lattice in situ during the hydrothermal reaction, leaving out the postsynthesis nitridation step. The process involves nanofibrous $(NH_4)_2Ti_3O_{7-x}N_x$ as a synthetic intermediate. Our raw material titanium oxysulfate is the intermediate product in commercial TiO_2-manufacturing processes, and it is cheaper than using crystalline titania or titanium alkoxides in conventional sol–gel methods. The extremely high surface area while maintaining a good crystallinity of $TiO_{2-x}N_x$ synthesized in this work is a highly desired property for photocatalysis.

This work has been supported by the Brain Korea-21 Program and the Research Center for Energy Conversion & Storage, the Research Center for Nanocatalysis and the Hydrogen Energy R&D Center.

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Published on the web (Advance View) April 2, 2005; DOI 10.1246/cl.2005.660