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Fabrication of hollow N-doped TiO_2 photocatalyst by spray-induced hydrolysis

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Hollow particles of nitrogen doped TiO_2 were fabricated by a newly developed method based on the spray-induced hydrolysis. An aqueous solution of urea was sprayed into a titanium tetraisopropoxide (TTIP) / hexane solution, inducing the rapid hydrolysis of TTIP at the interface between the droplets of urea solution and TTIP solution. The resultant hollow particles were converted to N-doped TiO_2 with anatase crystal structure by heat treatment. The absorption ability of visible light was remarkably improved by nitrogen doping. The hollow N-doped TiO_2 particles showed higher photocatalytic activity estimated by the decomposition of methylene blue (MB) compared to undoped TiO_2 particles.

Key-words : Hollow particle, Photocatalyst, TiO_2, Spray, Nitrogen doping

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1. Introduction

TiO_2 is the most popular photocatalyst and its application for environmental purification, hydrogen production, and dye-sensitized solar cell has been studied. For the practical use of TiO_2 photocatalyst, the morphology control is an important issue. Generally, the smaller the particle size is, the higher the photocatalytic activity is due to the larger surface area. Therefore the synthesis and photocatalytic activity of TiO_2 nanoparticles are actively studied. However, nanoparticles have difficulties in separation and recovery after used for photocatalytic reaction in a liquid phase. From this viewpoint, micron-sized hollow particle is one of the desirable morphologies because it has relatively high surface-to-volume ratio and is more easily recovered than nanoparticle. TiO_2 based hollow particles have been prepared by a variety of methods such as solid-templating method,[1] low-temperature hydrothermal method,[2] aerosol-assisted method,[3] and their high photocatalytic activities were reported.

Another important problem in utilizing TiO_2 as a photocatalyst is its large band gap (3.2 eV for anatase and 3.0 eV for rutile). Owing to the large band gap, only UV light in the wavelength range shorter than 400 nm is available for photocatalytic reaction by TiO_2. One of the solutions is doping of TiO_2 with nitrogen atom to enhance the absorption of visible light.[4] It is known that nitrogen doping of TiO_2 could be easily achieved by the impregnation of TiO_2 with nitrogen-containing organic compounds such as urea[5),6] and guanidine,[7] followed by the thermal decomposition of the organic compounds.

Recently, we developed a simple method for fabricating hollow TiO_2 particles, named "spray-induced hydrolysis".[8),9] In this method, water is sprayed into an organic phase containing titanium tetraisopropoxide (TTIP). It is expected that rapid hydrolysis of TTIP and the subsequent condensation near the interface of the water droplet–organic phase leads to the formation of a solid shell. Here, water-soluble chemicals might be easily encapsulated inside the particle if their aqueous solutions were substituted for water. Based on this idea, the fabrication of N-doped TiO_2 hollow particles was attempted by the spray-induced hydrolysis. The process consists of two steps: (1) TiO_2 hollow capsules containing urea are prepared by spraying its aqueous solution into a TTIP solution. (2) The crystallization of TiO_2 shell and the decomposition of urea are simultaneously induced by heat treatment. The advantage of this method is that the formation of hollow structure and introduction of nitrogen source can be accomplished in a single step. The photocatalytic activity of the N-doped TiO_2 hollow particles under visible-light irradiation was investigated by using the photocatalytic decomposition of methylene blue (MB) in an aqueous solution as the test reaction.

2. Experimental procedure

2.1 Preparation of samples

All the chemicals were provided by Wako Pure Chemical Industries, Ltd., and were used as supplied. The synthetic procedure of the N-doped TiO_2 hollow particles is as follows. An aqueous solution of urea (0.2 or 1.0 mol L^{-1}) was atomized by a two fluid nozzle (ATOMAX, AM6–IS) with N_2 as the carrier gas (0.2 MPa gauge). The droplets were introduced into a stirred solution of TTIP in hexane (0.5 mol L^{-1}, 50 mL). The distance from the tip of the nozzle to the solution surface is fixed at 20 cm. Spraying for several seconds resulted in the production of white precipitates. The precipitates were recovered by filtration, washed with hexane, and then dried at 363 K for 1 d. The white powder was heat-treated in air at 673 K for 2 h, and finally the yellow powder was obtained. The products prepared with urea concentrations of 0.2 mol L^{-1} and 1.0 mol L^{-1} were named as HP–02 and HP–1, respectively. For comparison, the undoped sample was also prepared with the same procedure except using distilled water as a spray liquid and was named as HP–0.

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2.2 Characterization

The morphologies of the resultant particles were observed by a field emission scanning electron microscope (FE–SEM, JEOL Ltd., JSM–6340FS, operated at 15 kV). X-ray diffraction (XRD) analysis was performed using Rigaku Co., Multiflex/CE diffractometer (Cu Kα radiation, λ = 0.154 nm, operated at 40 kV and 40 mA). The UV-vis diffuse reflectance spectra were measured using Shimadzu UV 2500PC equipped with an integrating sphere. The presence of nitrogen atoms in TiO_2 was confirmed by X-ray photoemission spectroscopy (XPS, Shimadzu Co., ESCA–3400, Mg Kα radiation, operated at 10 kV and 20 mA).

2.3 Photocatalytic activity

Methylene blue was purchased from Wako Pure Chemical Industries, Ltd. 0.01 g of sample powder was suspended in a 20 mL of a MB aqueous solution (2 ppm) in a glass vessel. The suspension was kept in the dark for 0.5 h under stirring, and then was irradiated with a 100 W halogen lamp (Moritex, MHAA–100W). The particles quickly settled down by gravity when the stirring was stopped and a small portion of MB solution could be easily sampled for the concentration analysis. The concentration of MB was estimated by the absorbance at the wavelength of 664 nm using Shimadzu UV 2500PC spectrometer.

3. Results and discussion

3.1 Characterization of N-doped hollow particles

Figure 1(a) shows typical examples of SEM images of HP–1. A large number of spherical particles are observed (Fig. 1(a)). The diameters of the particles are in the range of microns to several tens of microns. The SEM image of fractured particle indicates the formation of hollow particle with the shell thickness of ca. 15–25% of its outer radius (Fig. 1(b)). No significant difference is seen between the morphologies of N-doped HP–1 and undoped HP–0 (Fig. 1(c), (d)).

The XRD patterns of samples are shown in **Fig. 2**. It is confirmed that all the samples have anatase crystal structure, which is known to exhibit higher photocatalytic activity compared to rutile phase. It is concerned that the incorporation of nitrogen in TiO_2 may disarray its crystal structure. The size of crystallite was calculated as an estimate of crystallinity by Scherrer's equation from the sharpness of (101) diffraction peak for each sample. The sizes are 17 nm for HP–1, 16 nm for HP–02 and 19 nm for HP–0, respectively. Although the crystallinity is slightly reduced, the negative effect of the nitrogen doping on the crystal structure of TiO_2 is small.

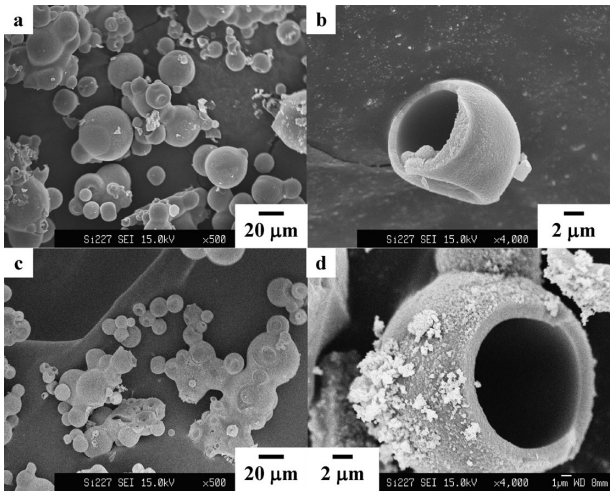

Fig. 1. SEM images of N-TiO_2 and TiO_2 hollow particles. (a) Overview and (b) hollow structure of HP–1. (c) Overview and (d) hollow structure of HP–0.

The UV-vis diffuse reflectance spectra of samples are shown in **Fig. 3**. HP–0 can absorb only UV light, in accordance with the usual adsorption spectrum of TiO_2 anatase. In contrast, N-doped samples show improvement in absorbance of visible light in the range of 400–600 nm. The increase in the absorbance strongly depends on the urea concentration in the spray solution. **Figure 4** shows the N 1s and O 1s XPS spectra of N-doped samples. The peak around 399 eV demonstrates the existence of nitrogen in each N-doped sample. The atomic contents of nitrogen were estimated to be 0.37% for HP–1 and 0.16% for HP–02, showing the increase with the increased urea concentration in the spray solution. These spectrometric results indicate the successful incorporating of nitrogen in TiO_2 and promise the high photocatalytic activity of the N-doped particles.

3.2 Photocatalytic activity

As confirmed from the above results, the hollow particles of N-doped TiO_2 with high visible light absorption ability could be produced. The photocatalytic activities of the hollow particles were investigated using the photocatalytic decomposition of MB. **Figure 5** shows the temporal change in the MB concentration catalyzed by each sample under irradiation of halogen lamp. The

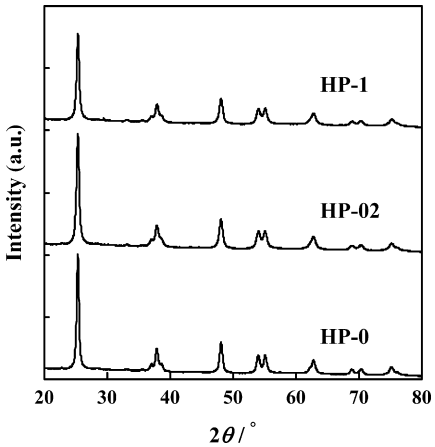

Fig. 2. XRD patterns of N-TiO_2 and TiO_2 hollow particles. All the peaks are corresponding to those of anatase crystal phase.

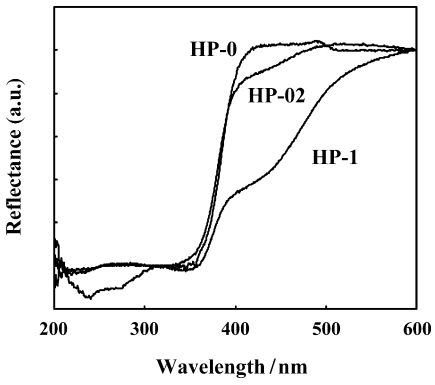

Fig. 3. UV-vis diffuse reflectance spectra of N-TiO_2 and TiO_2 hollow particles.

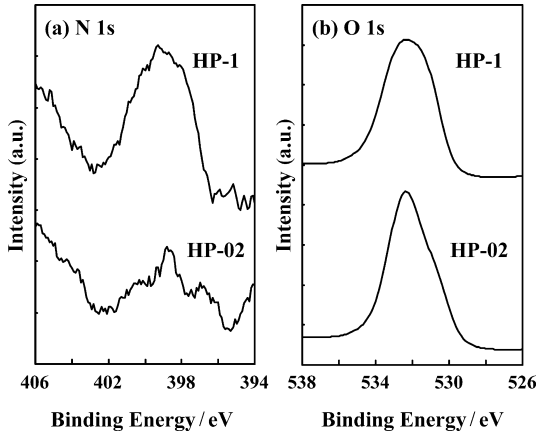

Fig. 4. (a) N 1s and (b) O 1s XPS spectra of N-TiO_2 hollow particles.

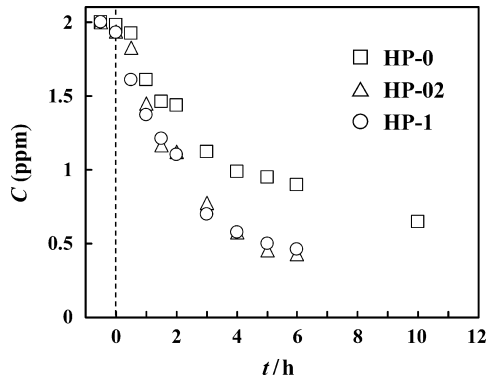

Fig. 5. Results of the photocatalytic decomposition of MB by N-TiO_2 and TiO_2 hollow particles. The irradiation of halogen lamp starts at $t = 0$.

slight decrease of MB concentration during initial 0.5 h without irradiation ($t < 0$) is due to the adsorption of MB on TiO_2 particles. After the irradiation starts ($t > 0$), the MB concentration decreases with time due to the photocatalytic decomposition. N-doped particles show obviously higher photocatalytic activity than that of undoped HP–0, demonstrating the improvement of visible-light response of TiO_2 photocatalyst by nitrogen doping.

The qualitative analysis of photocatalytic decomposition rate of MB was attempted. For simplicity, the first order kinetics was employed to obtain the observed rate of reaction k_{obs}.

$$\frac{dC}{dt} = -\frac{W}{V}k_{obs}C \qquad (1)$$

Here C, W, V and t are MB concentration, weight of photocatalyst, volume of MB solution and reaction time, respectively. From Eq. (1), the following relation is obtained.

$$\ln (C/C_0) = -(W/V)k_{obs}t \qquad (2)$$

Here C_0 is initial MB concentration. From this equation, k_{obs} can be estimated. As shown in **Fig. 6**, ln (C/C_0) and t shows a good linear relationship in the initial stage of reaction. From the slope of fitting lines, k_{obs} are estimated as 0.088 $cm^3\ g^{-1}\ s^{-1}$ for HP–0 and 0.17 $cm^3\ g^{-1}\ s^{-1}$ for HP–02 and HP–1. The rate of decomposition was nearly doubled by nitrogen doping.

Interestingly, the activities of HP–02 and HP–1 are almost the same, despite the huge difference in absorbance of visible light (Fig. 3). The cause of this tendency is still unexplained. The doping of nitrogen certainly enhanced the visible light absorption.

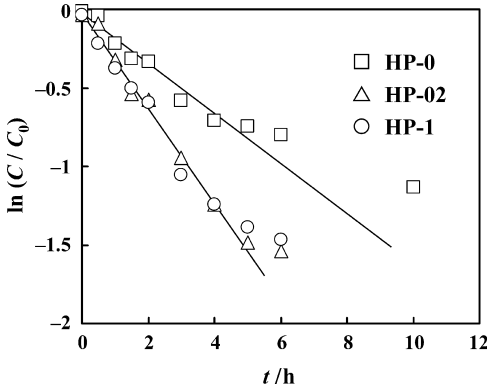

Fig. 6. Plots of logarithm of MB concentration against the irradiation time. The solid lines are fitting lines according to Eq. (2).

However, the excessive substitution of nitrogen for oxygen in TiO_2 might impair the photocatalytic activity of TiO_2. These results suggest the presence of the optimal content of nitrogen in TiO_2 that is controllable by the urea concentration. The analysis and optimization of the nitrogen content in TiO_2 hollow particle will be the issues in the future work.

4. Conclusion

A new and simple process for fabricating spherical hollow N-doped TiO_2 particles based on spray-induced hydrolysis was developed. The feature of this method is that the formation of hollow structure and the encapsulation of nitrogen source are simultaneously accomplished in the first step. In the second step, thermal decomposition of urea inside the capsules and crystallization of TiO_2 shells are induced together by heat treatment, resulting in the formation of N-doped TiO_2 hollow particles. The N-doped TiO_2 hollow particles showed highly enhanced absorption ability of visible light, which strongly depend on the urea concentrations of spray solutions.

Photocatalytic activities of N-doped TiO_2 hollow particles were also improved compared to undoped TiO_2, although no clear dependency on urea concentration was seen between the tested two samples.

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