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Photocatalytic activity of titania hollow spheres: Photodecomposition of methylene blue as a target molecule

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Abstract

The submicrometers-sized titania hollow spheres have been synthesized by employing sulfonated-polystyrene latex particles as a template in sol–gel method. The hollow spheres have relatively smooth surface and dense arrangement of titanium dioxide layers. Photocatalytic activity of the hollow spheres was investigated by employing methylene blue (MB) as a target compound. It was observed that the particle size, size distribution, and crystallinity are important factors to get high photocatalytic activity for the decomposition of MB.

Keywords: Titania hollow spheres; Sol–gel method; Photocatalytic activity; Crystallinity; Methylene blue

1. Introduction

Titania nanoparticles have attracted much attention of scientists because of their photocatalytic activity for the decomposition of various environmental pollutants, such as NO_x in air, fertilizers in water [1–3], and also some organic dyes such methylene blue (MB), reactive blue, reactive orange, methyl red, congo red, eosin Y, etc. [4–11] Although titania has wide range of applications [12–21], its low absorption in visible region is a drawback from a view point of effective use of solar energy. Many studies have been carried out to extend the absorption to visible region, for example, by metal ion-implantation [22–24], by doping nitrogen atoms [25,26], sulfur atoms [27,28], or carbon atoms [29] into titanium dioxide nanoparticles.

One of promising candidates of solar energy–responsive photocatalysts is a hollow sphere. Even though there are very rare reports about photoactivity of titania hollow spheres, some researchers found that the hollow titania particle has a smaller band gap resulting in the absorption in longer wavelength region [30–32]. This fact has made the titania hollow spheres a promising photocatalyst that is able to use sunlight more efficiently to degrade organic pollutants in environments.

In a previous paper [33], we reported the synthesis of submicrometer-sized titania hollow spheres with tunable shell thickness and void volume by employing sulfonated-polystyrene (PS) latex particles as a template in sol–gel method. In the present paper, we studied their application to photocatalytic decomposition of MB, which is often used as a standard target compound in a test of photocatalysts, and also mixed into some fertilizers as a dye. The behavior of titania hollow spheres in photocatalytic decomposition of MB in aqueous medium was studied as a function of preparation method and their crystallinity. To our knowledge, this is the first report in which photocatalytic activities of titania *hollow* spheres are examined.

2. Experimental

2.1. Chemicals

MB (Sigma Aldrich, reagent grade) and commercially-available TiO_2 (Ishihara Sangyo, ST-01, diameter 7 nm)

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were used as received. Water was first distilled, and then purified with Milli Q ultra-filtration system.

2.2. Synthesis and characterization of titania hollow spheres

Synthesis of titania hollow particles was given in detail in the previous paper [33]. The hollow structures of titania particles were characterized by transmission electron microscopy (TEM). TEM images were obtained on a Hitachi H-800MU microscope, using an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) measurement was made on Shimadzu XRD-6100 instrument with CuKα radiation. UV–vis absorption spectra of the titania hollow spheres were observed with Jasco Ubest-50 spectrophotometer equipped with an integrating sphere.

2.3. Photocatalytic decomposition of methylene blue

0.0015 g of titania hollow spheres was dispersed into a 3 ml of an aqueous MB solution (4 ppm) and then irradiated with a 150 W xenon lamp equipped with UV-D33S band pass filter ($\lambda = 220$–440 nm) under continuous stirring. For comparison, the same procedure was also done for commercially-available titania particles TiO_2 (ST-01). The concentration of MB was determined from the absorbance at the wavelength of 664 nm.

3. Results and discussion

3.1. Characterization of titania hollow spheres

Fig. 1 shows examples of TEM images of titania hollow particles. The strong contrast between the dark edges and bright centers indicates the hollow structure of titania spheres. These TEM images also revealed that the utilization of sulfonated PS latex particles as a template has resulted in the formation of spherical shells with relatively smooth surface and dense arrangement of titanium dioxide nanolayers.

It was found that the shell thickness of the titania hollow spheres were able to be controlled by altering the concentration of titanium tetrabutoxide (TBOT) [33]. When the concentration of TBOT were 0.15, 0.20, 0.25, and 0.50 M, the shell thickness of the titania hollow spheres were approximately 9, 14, 17, and 23 nm, respectively. The void size of titania hollow spheres were approximately 147, 151, 155, and 159 nm for the TBOT concentrations of 0.15, 0.20, 0.25, and 0.50 M, respectively.

Fig. 2 shows an X-ray powder diffraction pattern for each sample. The X-ray diffraction pattern indicates that the crystallinity of the titania hollow spheres is mostly anatase after calcinations. It was observed that titania hollow spheres prepared using TBOT concentration of 0.20 M resulted in the formation of the finest anatase crystallinity.

Shown in Fig. 3 are UV–vis absorption spectra of the calcined hollow spheres and TiO_2 dense particles (TiO_2-R). The TiO_2-R particles have pure anatase crystallinity and an average diameter from several tens to hundreds nanometers. The pure anatase crystallinity of TiO_2-R was confirmed by XRD measurements (data not shown). UV–vis absorption spectrum of commercially-available titania (ST-01) is also shown for comparison. The onset wavelength (λ_{onset}) in the spectrum of TiO_2-R particles (spectrum b) is about 380 nm, while the λ_{onset} of the hollow spheres (spectrum a) shifts toward longer wavelength region to some extent. The λ_{onset} in the spectrum of the ST-01 sample (spectrum c) is much more blue-shifted in comparison to that of TiO_2-R spectrum. This phenomenon is mainly due to the quantum-size effect which occurs on the ST-01 sample. The buff color observed for the hollow spheres is well consistent with these results.

There are two possibilities regarding the red shift in the absorption spectrum of the hollow spheres. The first possibility is the oxygen defects that probably occurred during formation of TiO_2 particles. The effects of oxygen defects for extending the TiO_2 activity to visible region was reported by Martyanov and co-workers[34]. The second possibility is that C and/or S atoms, which were originated from sulfonated PS latex particles, will make the TiO_2 hollow spheres to act as C- or S-doped TiO_2 photocatalysts [23–25]. The exact reason is currently unclear, and will be elucidated in future works.

3.2. Photocatalytic activity of titania hollow spheres

Photocatalytic activities of titania hollow spheres, TiO_2-R, and commercially-available ST-01 have been

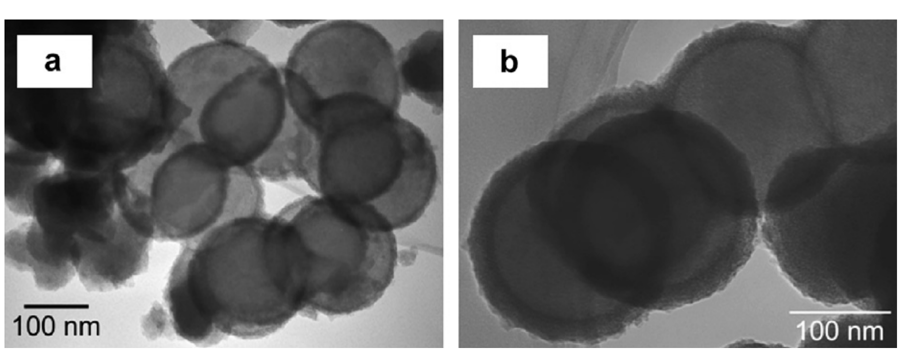

Fig. 1. TEM images of titania hollow particles. TBOT concentration: 0.20 M (a) and 0.50 M (b).

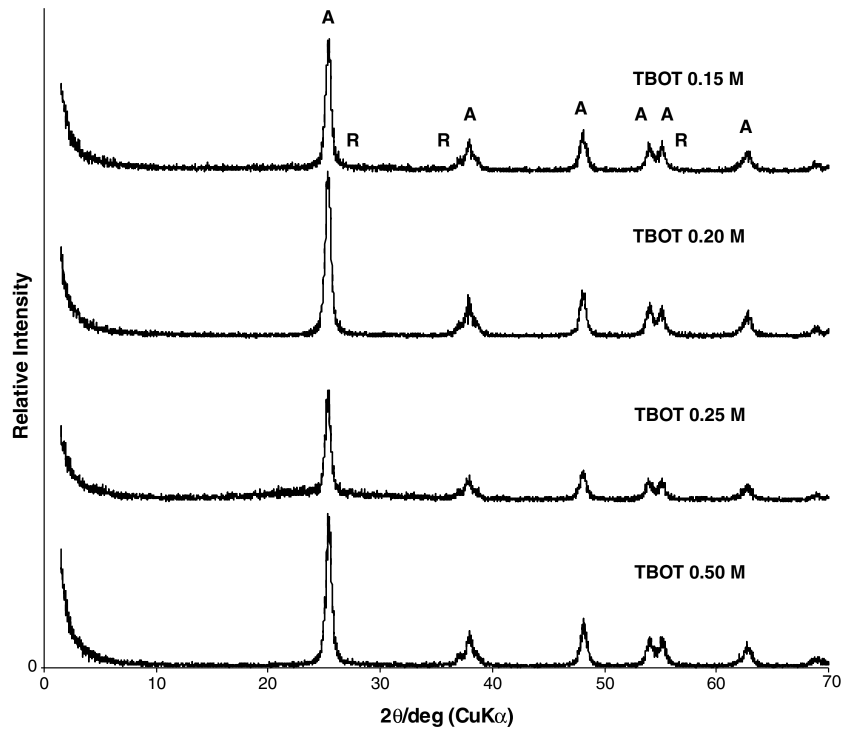

Fig. 2. X-ray powder diffraction patterns of titania hollow spheres prepared using different concentration of TBOT (peak assignment: A, anatase; R, rutile).

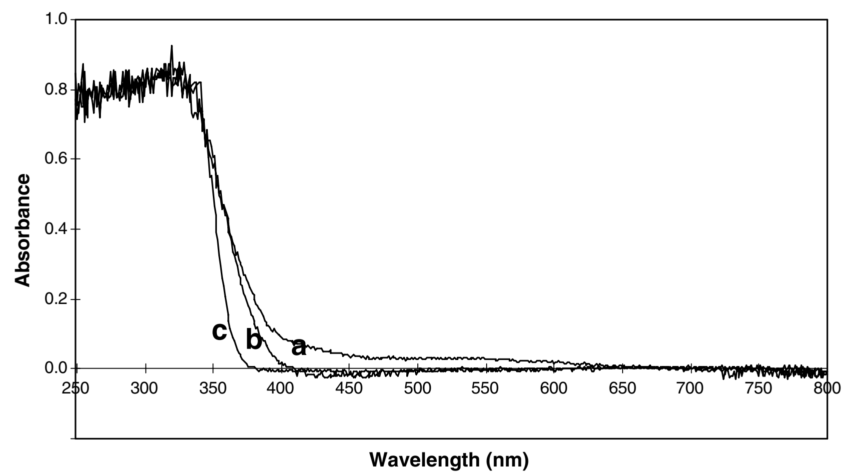

Fig. 3. UV–vis integrating spheres spectra of (a) calcined titania hollow spheres, (b) dense titania particle (TiO_2-R), and (c) commercially-available titania (ST-01).

investigated. Fig. 4 depicts the results on the photocatalytic decomposition of MB. The period *A* in Fig. 4 is the initial time (30 min for all the samples) during which the mixture of titania and MB in water was stirred in the dark. The period *B* denotes the time for the mixture to be exposed to UV irradiation. It is evident from Fig. 4 that there is no photooxidation in the dark. Only after the irradiation started, the decomposition of MB was initiated. It seems that almost all of MB molecules were decomposed during 180 min in the sample of (a), (b), and (d). The titania hollow spheres for 0.20 M TBOT concentration have the highest photoactivity. This seems to be due to the fact that this sample contains the highest anatase crystallinity as shown in Fig. 2. In addition to the content of anatase crystallinity, the uniformity size of the particles and the degree of aggregation are likely to be responsible for the enhanced photocatalytic activity for MB decomposition. The commercially-available ST-01 sample has lower photoactivity compared to the hollow particles, though the average size of ST-01 (diameter: 7 nm) is much smaller than that of the hollow spheres. This lower photoactivity of ST-01 seems to be attributed to their absorption characteristics. In the

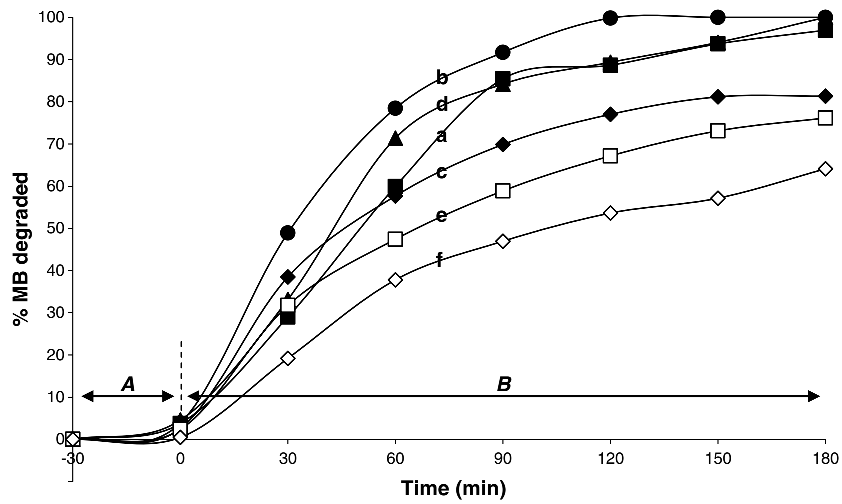

Fig. 4. Photocatalytic decomposition of MB on titania hollow spheres, prepared using TBOT concentration of (a) 0.15 M, (b) 0.20 M, (c) 0.25 M, and (d) 0.50 M. Photocatalytic decomposition of MB was also carried out on (e) TiO_2-R and (f) ST-01.

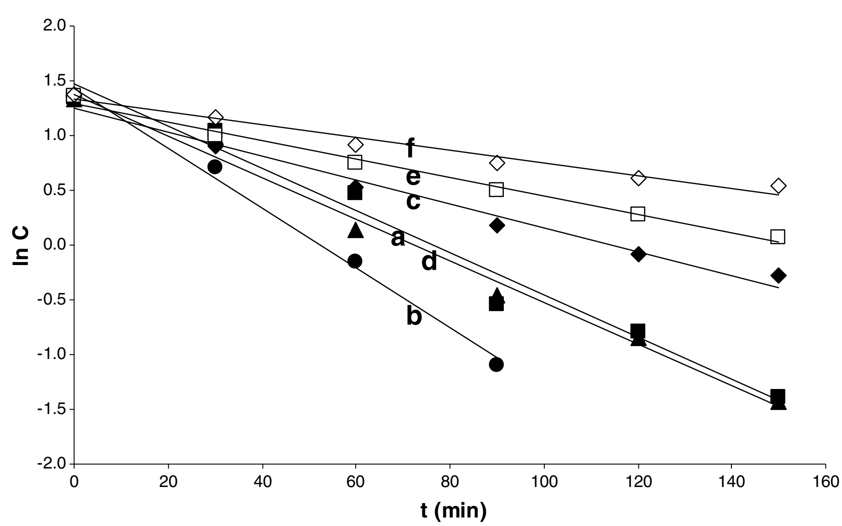

Fig. 5. Plots of the concentration of MB remained in the solution against irradiation time of UV. The titania hollow spheres were prepared using TBOT concentration of (a) 0.15 M, (b) 0.20 M, (c) 0.25 M, and (d) 0.50 M. The same plots are also shown for (e) TiO_2-R and (f) ST-01.

photodegradation experiment, we used 150 W xenon lamp together with UV-D33S band pass filter ($\lambda = 220$–440 nm). In this system, maximum light intensity is located around $\lambda = 370$ nm, while the ST-01 shows strong absorption in the region lower than 370 nm as clearly shown in Fig. 3.

For quantitative analysis of the decomposition reaction of MB, we employed a first-order kinetic model:

$$-\mathrm{d}C/\mathrm{d}t = k_{\mathrm{obs}}C$$

where k_{obs} is the observed rate constant for the photodecomposition reaction. From this equation, we obtain:

$$\ln C = -k_{\mathrm{obs}}t + \ln C_0$$

The relative concentration of MB remained in the solution is plotted against irradiation time in Fig. 5. The linearity between $\ln C$ and t is fairly good for all samples, suggesting that the present reaction is the first-order kinetics. From the slope of the line, the rate constants were calculated (Table 1). It is clear from Table 1 that the highest photoactivity was obtained for the sample (b) ($k_{\mathrm{obs}} = 2.74 \times 10^{-2}$ ppm min^{-1}). There is a strong correlation between the photocatalytic activity and content of anatase crystallinity in the titania hollow spheres. It is currently

Table 1
Observed rate constants (k_{obs}) for photodecomposition of MB

Photocatalyst sample	k_{obs} /10^{-2} ppm min^{-1}
(a) Hollow TiO_2 (0.15 M TBOT)	1.92
(b) Hollow TiO_2 (0.20 M TBOT)	2.74
(c) Hollow TiO_2 (0.25 M TBOT)	1.10
(d) Hollow TiO_2 (0.50 M TBOT)	1.90
(e) TiO_2-R	0.85
(f) ST-01	0.58

unclear why the highest content of anatase form was obtained for the sample (b). The reason will be investigated in future works.

4. Conclusions

Submicrometer-sized titania hollow spheres with tunable shell thickness and void volume have been synthesized by employing sulfonated-polystyrene latex particles as a template in conjunction with the sol–gel method. The UV–vis absorption spectra of these hollow samples showed a red shift of absorption edge compared to dense TiO_2particles (TiO_2-R) and commercially-available TiO_2 particles (ST-01). Photocatalytic decomposition of MB carried out in aqueous medium showed that the highest photocatalytic activity was given by titania hollow spheres which was prepared using 0.20 M TBOT ($k_{obs} = 2.74 \times 10^{-2}$ ppm min^{-1}). Photocatalytic activity of commercially-available ST-01 was lower than that of the hollow particles. This seems to be due to its poor response to the selected wavelength region of Xe-lamp irradiation used in this experiment. Particle size, size distribution, and crystallitnity of titania hollow particles were shown to be important factors in order to get high photocatalytic activity in the decomposition of MB in water.

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