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Degradation of methylene blue in aqueous dispersion of hollow titania photocatalyst: Optimization of reaction by peroxydisulfate electron scavenger

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Abstract

The submicrometer-sized titania hollow spheres have been synthesized by employing sulfonated polystyrene latex particles as a template in sol–gel method. Photocatalytic activity of the hollow spheres was investigated by focusing on the effect of electron scavengers in the photocatalytic decomposition of methylene blue (MB). Photocatalytic activities of titania hollow spheres were significantly enhanced by the addition of peroxydisulfate as an electron scavenger. The rate constant for photodecomposition of MB was increased more than two times by the addition of peroxydisulfate. The significant increase in the photodecomposition rate seems to be related to electrons scavenging as well as production of additional oxidizing species. It was found that the optimum concentration of peroxydisulfate was 10 mM. Further increase in the concentration of peroxydisulfate is not recommended due to the saturation of reaction rate by the excess amount of SO_4^{2-} species.

Keywords: Titania hollow spheres; Sol–gel method; Photocatalytic activity; Electron scavenger; Methylene blue; Peroxydisulphate

1. Introduction

Photocatalytic process, which utilizes TiO_2 semiconductor photocatalyst, has received increasing attention because of its low cost, relatively high chemical stability of the catalyst, and the possibility of using sunlight as a source of irradiation [1–21]. The process is initiated by UV irradiation of the semiconductor to excite an electron from the valence band (VB) to the conduction band (CB) resulting in formation of a high energy electron–hole pair. The highly oxidative valence band hole ($E^0 = 2.8$ V) may directly react with the surface-sorbed organic molecule (R) to form R^+ or indirectly via the formation of $^\bullet$OH radicals [1,22]. The reaction of the photogenerated holes with hydroxyl ions and water molecules adsorbed on the surface of TiO_2 yields hydroxyl radicals [23,24]. The resulting hydroxyl radicals, being very strong oxidizing agents, can oxidize most of organic compounds [25].

In photocatalytic reaction of TiO_2, the major energy-wasting step is the electron–hole recombination [26]. Hence the prevention of electron–hole recombination is very important in the photocatalytic reaction. This can be achieved by adding proper electron donor (or acceptor) to the system [27]. Inorganic oxidants such as IO_4^-, $S_2O_8^{2-}$, BrO_3^-, ClO_3^-, H_2O_2 can be used as additives to increase the photodegradation rates of organic substrates. The addition of these electron acceptors (i.e. electron scavengers) enhances the degradation rate by several ways such as: (i) preventing the electron–hole recombination by accepting the conduction band electron, (ii) increasing the hydroxyl radical concentration, and (iii) generating other oxidizing species (e.g., $SO_4^{\bullet-}$) to accelerate the rate of intermediate compound oxidation [26,28,29]. It is known that the electron scavengers should fulfill a criterion that they dissociate into harmless by-products and lead to formation of $^\bullet$OH or other oxidizing agents. Peroxydisulphate ($S_2O_8^{2-}$) seems to fit these conditions [30]. Furthermore, peroxydisulfate is known to be more efficient than hydrogen peroxide (H_2O_2) in the treatment of waste water [31,32].

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In previous papers [33,34], we reported the synthesis of submicrometer-sized titania *hollow* spheres with tunable shell thickness and void volume, and their photocatalytic activity by employing methylene blue (MB) as a model target molecule, which is widely used as a standard target compound in a test of photocatalysts. In the present paper, we studied optimization of the photocatalytic activity by utilizing peroxydisulfate as an electron scavenger. The effects of peroxydisulfate on photocatalytic decomposition of MB were studied as a function of preparation method of titania hollow spheres and the concentration of peroxydisulfate.

Although a lot of papers have been published on the photocatalytic activities of *dense* titania, there still were rare works on *hollow* particles and a few works on *hollow-like* particles [35–37]. Shchukin et al. carried out similar experiments for titania particles filled with polymer gel inside the particles [35]. Titania particle coated on hollow glass microbeads were examined in the photoassisted oxidation of ethanol to acetaldehyde [36,37]. However, these hollow-like titania particles seem to be different from real titania hollow spheres because polymer gels or glass beads inside the titania particles could affect the properties of the particles. In this sense, this and previous works [34] are the first papers which report photocatalytic activities of titania hollow particles.

2. Experimental

2.1. Chemicals

Titanium tetrabutoxide (TBOT, 97.0%, Sigma–Aldrich), ethanol (99.5%, Wako), methylene blue (MB, Sigma–Aldrich, reagent grade), potassium peroxydisulfate (KPS, Aldrich, reagent grade), and commercially available TiO_2 (Ishihara Sangyo, ST-01, diameter 7 nm) were used as received. Water was first distilled, and then purified with Mili-Q ultra-filtration system.

2.2. Synthesis and characterization of titania hollow spheres

Synthesis of titania hollow particles was described in detail in the previous paper [33]. For comparison, the TiO_2 dense particles (TiO_2–R) were synthesized in the similar way to that of titania hollow particles in the absence of latex template particle. The structures of titania particles were characterized by transmission electron microscopy (TEM). TEM images were obtained with 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 Cu$K\alpha$ radiation. UV–vis absorption spectra were recorded on Jasco Ubest-50 spectrophotometer equipped with an integrating sphere.

2.3. Photocatalytic decomposition of methylene blue

1.5 mg of titania hollow spheres was dispersed into a 2.5 ml of an aqueous MB solution (4 ppm). Then, known amount of KPS was added in order to give peroxydisulfate concentrations of 5, 10, 15, and 20 mM. The solution was 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 titania dense particle (TiO_2–R) and commercially available titania particles TiO_2 (ST-01). Control experiments were carried out for all photocatalysts in the absence of peroxydisulfate. The concentration of the residual target molecule (MB) was determined from the absorbance at 664 nm.

3. Results and discussion

Fig. 1 shows examples of TEM images of titania hollow spheres which were fabricated by utilizing sulfonated PS latex in a sol–gel method. The utilization of sulfonated PS latex particles has resulted in the formation of uniform spherical shells with relatively smooth surface and dense arrangement of titanium dioxide nano-layers [33].

It was observed that the shell thickness of the titania hollow spheres are controllable by altering the concentration of titanium tetrabutoxide (TBOT) [33]. The shell thickness were approximately 9, 14, 17, and 23 nm according to the TBOT concentrations of 0.15, 0.20, 0.25, and 0.50 M, respectively. The void sizes were approximately 147, 151, 155, and 159 nm corresponding to the TBOT concentrations of 0.15, 0.20, 0.25, and 0.50 M, respectively. The X-ray diffraction pattern revealed that the crystallinity of the titania hollow spheres was mostly anatase after calcinations [33,34]. It was observed that titania

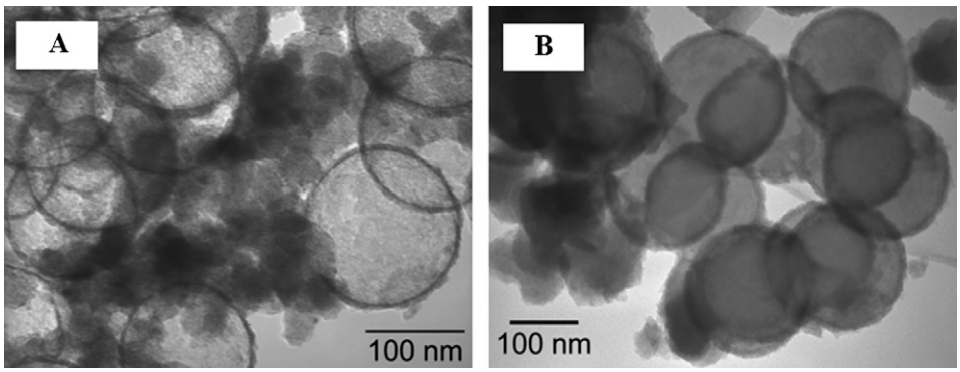

Fig. 1. TEM images of titania hollow particles. TBOT concentration: 0.15 (a) and 0.25 M (b).