

Preparation of siloxy focal dendron-protected TiO₂ nanoparticles and their photocatalysis

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Abstract

TiO₂ nanoparticles were synthesized at ~0 °C by hydrolyzing [(CH₃)₂CHO]₄Ti in 1-propanol solutions of poly(amido amine) dendrons with a siloxy focal point and long alkyl chain spacers. Transmission electron microscopic photographs showed that TiO₂ nanoparticle was 1–5 nm in size and protected by dendrons, when prepared at a mixing ratio 1:10 of Ti ion and dendron. At higher contents of Ti ion, TiO₂ nanoparticles aggregated up to a maximum size of 90 nm, depending on the dendron generation (first to third). It was confirmed from X-ray photoelectron spectroscopy that Si–O–Ti covalent bond was formed in dendron-protected TiO₂ nanoparticles. The ability of dendron-protected TiO₂ nanoparticles as a photocatalyst for the photodegradation of 2,4-dichlorophenoxyacetic acid was higher than that of nonprotected nanoparticle and superior at higher generation. It was suggested that the dendrons protecting TiO₂ nanoparticle have enough void volume to conserve guest molecules and behave effectively as a reservoir of guest molecules.

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1. Introduction

Titanium dioxide has attracted much attention in the fields of photocatalysis and solar system [1,2], and basic researches have been reported toward their applications [3–12]. To acquire effective photocatalysts in decomposing pollutants in air and solutions, TiO₂ materials must be fabricated with large surface areas and greatly porous structures (preferred in nanoscale) in order to contact efficiently with pollutants. So far, large numbers of studies have been done to achieve various TiO₂ nanomaterials with large surface area such as thin films [3,5–8,11,12], nanotubules [4,9] and nanoparticles [13–23], consisting of nanocrystals. Especially, TiO₂ nanoparticles, which were dispersed in water, have the application to the detoxification of water pollution environment [24–28]. However, such system is not sufficiently established, since the dispersibility of TiO₂

nanoparticles in water is low [29] because of the hydrophobicity of nanoparticles.

Size of TiO₂ nanoparticles is essential for the stable dispersion of nanoparticles in medium. The TiO₂ nanoparticles with small sizes were synthesized by the oxidation of TiCl₄ [13–15,19] or the hydrolysis of tetraisopropyl orthotitanate (titanium isopropoxide) [16–18,20–24] and utilized for the examination of photophysical property [13], relaxation dynamics [14], and photoluminescence [15]. The synthesized and commercial TiO₂ nanoparticles were also used for the photocatalytic degradation of phenol [20], surfactant [24], dyes [25–27], and 2,4-dichlorophenoxyacetic acid [28]. Using medium-soluble protectors enables the preparation of medium-dispersible TiO₂ nanoparticles. Dodecylbenzenesulfonate-capped TiO₂ nanoparticles were synthesized and their optical and photochemical properties were examined in nonaqueous solvents [22].

Poly(amido amine) (PAMAM) dendrimers are a useful protector and stabilizer for water-dispersible metal nanoparticles [30]. In the previous work, we synthesized water-dispers-

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ible TiO₂ nanoparticles by using fourth generation (G4) PAMAM dendrimers as a protectant [30]. The resultant dendrimer-protected TiO₂ nanoparticles stably dispersed in water. These nanoparticles were more active in water as a photocatalyst than TiO₂ nanoparticles without protector. On the other hand, the interaction of PAMAM dendrimer with metal or metal oxide nanoparticles is not necessarily strong. Amine-terminated PAMAM dendrimers covering a gold nanoparticle were easily replaced by dodecanethiol [30].

In order to prepare water-dispersible TiO₂ nanoparticles protected by advantageous dendritic polymer, in the present work, TiO₂ nanoparticles were synthesized by using a dendron protector, which has a siloxy focal point and long alkyl (hexyl, C6) chain spacers. Then the siloxy group is able to form covalent bond with TiO₂ nanoparticles through Si–O–Ti bond. The photocatalytic activity of dendron-protected TiO₂ nanoparticles in water was also examined and compared with that of dendrimer-protected TiO₂ nanoparticles.

2. Experimental

2.1. Reagents

3-Aminopropyl triethoxysilane was purchased from Aldrich Chemical Co. Methylacrylate, hexamethylene diamine, tetraisopropyl orthotitanate ($[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$), and tetraethyl orthosilicate (TEOS) were products from Tokyo Chemical Industry Co. 2,4-Dichlorophenoxyacetic acid (2,4-DPA) was obtained from MERK Achuchardt. The other reagents were of analytical grade. The chemicals were used without further purification. Ultrapure water (Millipore Milli-Q) was utilized throughout all experiments.

2.2. Synthesis of dendrons

Generation 1–3 (G1–G3) siloxy focal C6-PAMAM dendrons with amine terminals were synthesized from 3-aminopropyl triethoxysilane by repeating two steps of Michael addition and amidation, as described elsewhere [32]. On a Michael addition reaction, methylacrylate in methanol was added dropwise into a methanol solution of 3-aminopropyl triethoxysilane or full-generation dendron under nitrogen atmosphere. On an amidation reaction, hexamethylene diamine in methanol was added dropwise to a methanol solution of a Michael addition product (a half-generation dendron) under nitrogen atmosphere. Both reaction mixtures were stirred at room temperature for one day. Then the excess solvent and unreacted compounds were removed by vacuum distillation to give a yellow oil-like product.

2.3. Synthesis of nanoparticles

TiO₂ nanoparticles were prepared by the hydrolysis of $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ in 1-propanol. Liquid $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ (0.01 cm³) and G1–G3 siloxy focal C6-PAMAM dendron were mixed, at various mixing ratios of Ti ion and dendron, in 1-propanol (5 cm³) cooled at ~0 °C. The mixed solution was dropwise added, under vigorous stirring, to water (10 cm³)

maintained at ~0 °C. The dialysis by water (1000 cm³) in a Viscose membrane (presoaked in water and then thoroughly rinsed prior to use) was repeated for two days in order to remove the unreacted chemicals. For comparison, TiO₂ nanoparticles were also prepared in absence of protective dendron or in addition of TEOS instead of dendron.

2.4. Measurements

Microscopic observation was performed on a Hitachi H-7000 transmission electron microscope (TEM) equipped with a CCD camera attachment, operating at 100 kV. Fourier transform infrared (IR) absorption spectra in the region of 4000–700 cm⁻¹ were recorded on a Bio-Rad FTS 575C instrument. X-ray photoelectron spectroscopic (XPS) measurement was carried out on a Shimadzu ESCA-3300 spectroscopy. The X-ray source ($\text{MgK}\alpha$, 1253.6 eV) was operated at 10 kV and 30 mA. Specimens were exposed in argon for overnight to purge contamination. Specimens were prepared on substrates by casting a droplet of solutions and drying. The substrates were a CaF₂ window for IR spectroscopy and a copper grid coated with a thin carbon film for TEM and XPS. Fluorescence was measured on a HITACHI F-4010 fluorometer with a quartz cell (10 mm path). Ultraviolet-visible absorption spectra were measured on a Shimadzu UV 2200 spectrometer using a quartz cell (10 mm path). The absorbance was calibrated by the background absorbance of the solvent. All measurements were performed at room temperature (~25 °C).

2.5. Photodegradation and solubility

Aqueous suspensions of TiO₂ nanoparticles containing 2,4-DPA (3.0 mM) were photoirradiated by using a HOYA EX250 UV light source with a 250 W Hg lamp (below 320 nm). The degradation of 2,4-DPA was monitored by the intensity $I_{357\text{ nm}}(t)$ of an emission band at 357 nm, at an irradiation time t , which was normalized by the intensity $I_{357\text{ nm}}(0)$ at zero time. The excitation wavelength was at 254 nm.

Solubility was determined by shaking aqueous dendron solutions with excess powder of 2,4-DPA for two days. After filtering out the insoluble powder, ultraviolet-visible absorbance of 2,4-DPA was measured and the solubility per dendron was calculated by using an extinction coefficient of 2,4-DPA.

3. Results and discussion

3.1. Morphology and size distribution of TiO₂ nanoparticles

Morphologies of TiO₂ nanoparticles prepared with G1 dendron at 1:1 and 1:10 mixing ratios of Ti ion and dendron ($[\text{Ti}^{4+}]:[\text{dendrimer}]$) were observed on a TEM. As seen in Fig. 1a, TiO₂ nanoparticles at 1:1 were spherical particles with sizes less than 90 nm as well as those without dendrons (Fig. 1c). On the other hand, TiO₂ nanoparticles prepared at 1:10 were fairly small (<5 nm) and surrounded by dendrons (Fig. 1b). TiO₂ nanoparticles were also synthesized at different mixing ratios of Ti ion and G3 dendron. Their TEM photographs are

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