

# Synthesis of dendrimer-protected TiO<sub>2</sub> nanoparticles and photodegradation of organic molecules in an aqueous nanoparticle suspension

Yuko Nakanishi<sup>a</sup>, Toyoko Imae<sup>a,b,\*</sup>

<sup>a</sup> Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

<sup>b</sup> Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

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## Abstract

Dendrimer-protected TiO<sub>2</sub> nanoparticles were synthesized by hydrolysis of TiCl<sub>4</sub> in solutions of poly(amido amine) dendrimers (64 terminals) under cooling. The morphology of dendrimers surrounding TiO<sub>2</sub> nanoparticles depended on the terminal groups (amine, carboxyl, hydroxy) of dendrimers. The size (4.4–6.7 nm) of dendrimer-protected TiO<sub>2</sub> nanoparticles was slightly smaller than that (7.5 nm) of bare TiO<sub>2</sub> nanoparticles. The photodegradation of 2,4-dichlorophenoxyacetic acid revealed that dendrimer-protected TiO<sub>2</sub> nanoparticles are more active as a photocatalyst than TiO<sub>2</sub> nanoparticles without protectors. This suggests that the dendrimer acts as a reservoir of photoreacting reagents besides acting as a protector of nanoparticles.

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## 1. Introduction

Titanium dioxide, TiO<sub>2</sub>, which can be utilized as photoelectrochemical solar cells and photocatalysts [1,2], has been investigated extensively [3–15]. Of great importance is the understanding of the photochemical behavior of TiO<sub>2</sub> dispersion in aqueous media because of their ecofriendly application to the detoxification of polluted water environments [3,11–14]. However, such systems are not sufficiently well established, since TiO<sub>2</sub> colloids are not stably dispersed in water, unless adequate stabilizers are utilized.

Ultrafine particles, nanoparticles, have extremely large surfaces, and this property is related to the particle characters. The potential applications of nanoparticles, includ-

ing the construction of nanodevices, catalysts, and ultrathin films, are mainly affected by the size and surface character of the particles. The synthesis of metal and metal sulfide nanoparticles protected by dendrimers has been reported [16–39]. However, no one has reported the preparation of dendrimer-protected metal oxides, as far as we know. In the present work, we synthesized water-dispersed TiO<sub>2</sub> nanoparticles by using dendrimers as protectors. We used poly(amido amine) (PAMAM) dendrimers with 64 terminal groups [40–42] and compared the dependence of the formation of TiO<sub>2</sub> nanoparticles on the type of terminal groups (amine, carboxyl, and hydroxyl groups). We also examined the photocatalytic activity of dendrimer-protected TiO<sub>2</sub> nanoparticles in water and compared it with that of bare TiO<sub>2</sub> nanoparticles. As a photodegradation reagent, we selected 2,4-dichlorophenoxyacetic acid, which was used for the determination of methodology on the photocatalyzed degradation [14].

\* Corresponding author. Fax: +81-52-789-5912.

E-mail address: [imaie@nano.chem.nagoya-u.ac.jp](mailto:imaie@nano.chem.nagoya-u.ac.jp) (T. Imae).

## 2. Experimental

### 2.1. Reagents

Fourth-generation amine-terminated PAMAM (G4 PAMAM-NH<sub>2</sub>) dendrimer (10 wt% methanol solution), 4.5th-generation carboxylate-terminated PAMAM (G4.5 PAMAM-COONa) dendrimer (5 wt% methanol solution), and fourth-generation hydroxy-terminated PAMAM (G4 PAMAM-OH) dendrimer (10 wt% methanol solution) were purchased from Aldrich Chemical Co. Titanium tetrachloride (TiCl<sub>4</sub>) and 2,4-dichlorophenoxyacetic acid were purchased from Wako Chemical Co. and Merck Achuchardt, respectively. The other reagents were of analytical grade. The chemicals were used without further purification. The methanol dendrimer solutions were evaporated under nitrogen gas atmosphere, and the residues were dissolved in water. Ultrapure water (Millipore Milli-Q) was used throughout all experiments.

### 2.2. Measurements

The pH of solutions was measured with an IWAKI GRASS pH meter. Ultraviolet–visible (UV–vis) absorption spectrum measurements were carried out with a Shimadzu UV 2200 spectrometer using a quartz cell (10-mm path). The absorbance was collected for the background absorbance of the solvent. Fourier transform infrared (FT-IR) absorption spectra in the region 4000–700 cm<sup>-1</sup> were recorded on a Bio-Rad FTS 575C FT-IR instrument. Specimens were prepared by casting a droplet of a solution on a CaF<sub>2</sub> window and drying. Fluorescence was measured with a HITACHI F-4010 fluorometer with a 10-mm-path cell.

The morphology of the particles was visualized on a Hitachi H-7000 transmission electron microscope (TEM) equipped with a CCD camera attachment and operated at 100 kV. Specimens were prepared by casting a droplet of solution on a copper grid, which was coated with a thin carbon film, and drying.

All measurements were performed at room temperature (~25 °C).

### 2.3. Synthesis of nanoparticles

TiO<sub>2</sub> nanoparticles were prepared by hydrolysis of TiCl<sub>4</sub> in aqueous dendrimer solutions. Liquid TiCl<sub>4</sub> (4.1 × 10<sup>-2</sup> cm<sup>3</sup>) cooled at -20 °C was slowly added, under vigorous stirring, to an aqueous dendrimer solution (10 cm<sup>3</sup>), which was maintained at ~0 °C. The pH of the dendrimer solution was adjusted by adding HCl or NaOH prior to the synthesis of TiO<sub>2</sub> nanoparticles. The number ratio of dendrimer terminal and Ti ion was 1:1. Dialysis (Viscose membrane, presoaked in distilled water and then thoroughly rinsed prior to use) against 1000 cm<sup>3</sup> of water was repeated for 2 days in order to remove nonreacted dendrimers and ions. TiO<sub>2</sub> particles without protective dendrimer were also prepared for comparison.

### 2.4. Photodegradation

Photoirradiation to an aqueous suspension (10 cm<sup>3</sup>) of TiO<sub>2</sub> nanoparticle containing 2,4-dichlorophenoxyacetic acid (3.0 mM) was carried out under atmosphere, using a HOYA EX250 UV light source with a 250-W Hg lamp (below 320 nm). The reaction of 2,4-dichlorophenoxyacetic acid was evaluated from the fluorescence intensity at an emission wavelength of 357 nm under excitation at 254 nm.

## 3. Results and discussion

### 3.1. Formation of dendrimer-protected TiO<sub>2</sub> nanoparticles

The hydrolysis of TiCl<sub>4</sub> was carried out in water with and without dendrimers, and the reacted solutions were dialyzed. UV spectra of inner dialysis solutions treated with and without G4.5 PAMAM-COONa dendrimer are shown in Fig. 1. An absorption band of the TiO<sub>2</sub> particle at 260 nm, which was observed in a solution without dendrimer, appeared as a shoulder of a strong absorption band of the dendrimer around 200 nm in a solution with dendrimer. Similar UV spectra were observed for solutions with other two dendrimers. FT-IR spectra (not shown) of inner dialysis solutions treated with different dendrimers displayed, in common, the characteristic bands of the dendrimers at 3229 (amide A), 3076 (amide B), 2964 (ν<sub>as</sub>,CH<sub>2</sub>), 1648 (amide I), and 1550 cm<sup>-1</sup> (amide II). An additional band at 1723 cm<sup>-1</sup>, which originated from carboxyl group, was appeared in a case of G4.5 PAMAM-COONa dendrimer. Both UV and IR spectra indicate the coexistence of TiO<sub>2</sub> particles and dendrimers in the inner dialysis solutions.

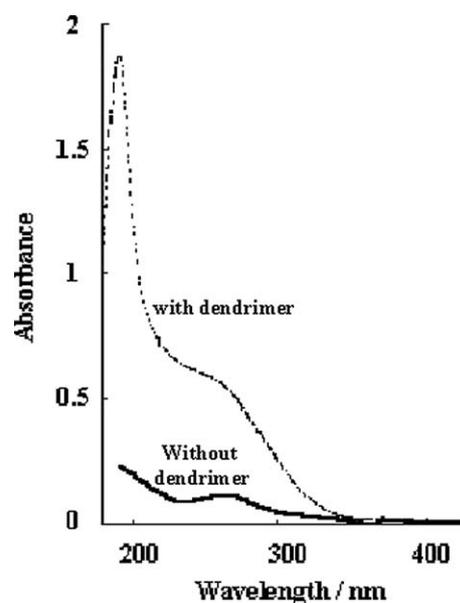


Fig. 1. UV spectra of an inner solution of dialysis after hydrolysis reaction of TiCl<sub>4</sub> in the presence and absence of G4.5 PAMAM-COONa dendrimer at pH 10.

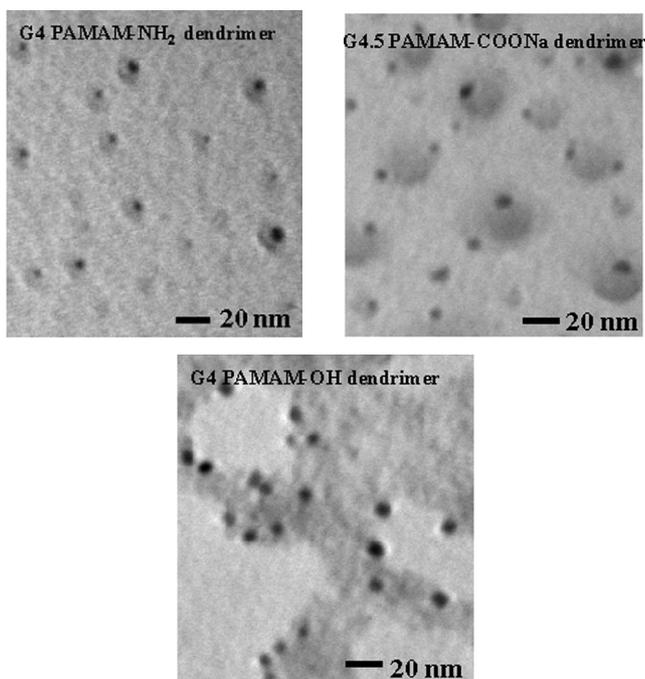


Fig. 2. TEM photographs of inner solutions of dialysis after hydrolysis reaction of  $\text{TiCl}_4$  in the presence of dendrimers at pH 10.

The morphologies of particles were observed by TEM (see Fig. 2). TEM photographs, where spherical  $\text{TiO}_2$  nanoparticles appeared as deep dark spots and light dark spheres were dendrimers, showed the formation of the dendrimer-protected  $\text{TiO}_2$  nanoparticles.  $\text{TiO}_2$  nanoparticles were located in a center of surrounding G4 PAMAM- $\text{NH}_2$  dendrimers.  $\text{TiO}_2$  nanoparticles existed in a G4.5 PAMAM- $\text{COONa}$  dendrimer or in aggregates of the dendrimers. Otherwise, coexisting with G4 PAMAM- $\text{OH}$  dendrimer,  $\text{TiO}_2$  nanoparticles were in gel-like aggregates of dendrimers. These results indicate that the protection of the  $\text{TiO}_2$  particles depends on the dendrimer. The terminal groups of the dendrimer may play an important role.

The sizes of  $\text{TiO}_2$  particles prepared were evaluated from TEM photographs. The size distribution of 300 particles is shown as histograms in Fig. 3, from which the average diameters were calculated. Those of  $\text{TiO}_2$  nanoparticles without dendrimer were  $14.7 \pm 4.7$  nm at pH 2,  $7.8 \pm 4.7$  nm at pH 7, and  $7.5 \pm 5.4$  nm at pH 10. The particle sizes depended on the pH of the aqueous solution before the addition of  $\text{TiCl}_4$ . The average sizes of dendrimer-protected  $\text{TiO}_2$  particles prepared at pH 10 were  $4.4 \pm 5.0$  nm for G4 PAMAM- $\text{NH}_2$  dendrimer,  $5.0 \pm 5.8$  nm for G4.5 PAMAM- $\text{COONa}$  dendrimer, and  $6.7 \pm 6.0$  nm for G4 PAMAM- $\text{OH}$  dendrimer. It can be referred that sizes of dendrimer-protected  $\text{TiO}_2$  nanoparticles are slightly smaller than that of bare  $\text{TiO}_2$  nanoparticle and depend slightly on the terminal groups of dendrimers. It should be noticed that the suspensions of dendrimer-protected  $\text{TiO}_2$  nanoparticles are stable and did not precipitate even over several months, in contrast to the suspensions of bare  $\text{TiO}_2$  nanoparticles. The reason is that the dendrimer

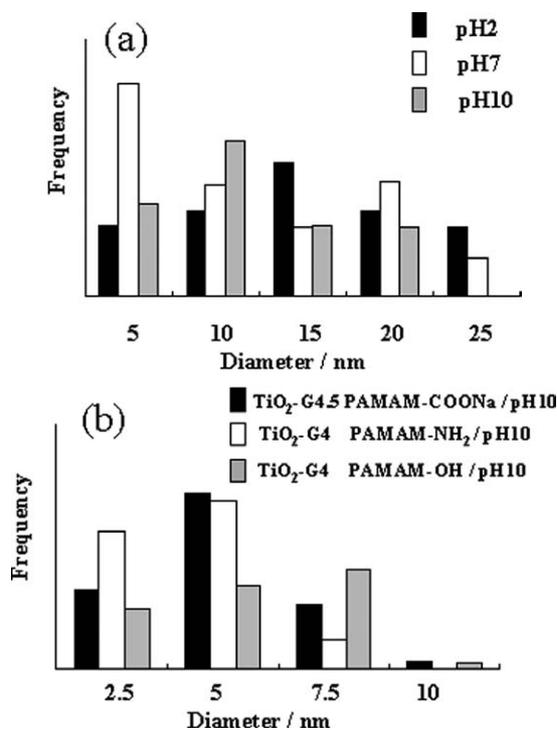


Fig. 3. Size histograms of  $\text{TiO}_2$  nanoparticles without (a) and with (b) dendrimer.

coating prevents the aggregation of  $\text{TiO}_2$  nanoparticles. The formation of stable particles with similar small sizes has been reported for dendrimer-protected metal nanoparticles [18–32,37–39].

### 3.2. Photodegradation of 2,4-dichlorophenoxyacetic acid in aqueous suspensions of $\text{TiO}_2$ nanoparticles

Time-dependent fluorescence spectra of 2,4-dichlorophenoxyacetic acid (2,4-DPA) under UV light irradiation in an aqueous suspension of  $\text{TiO}_2$  nanoparticles protected by G4.5 PAMAM- $\text{COONa}$  dendrimer are shown in Fig. 4. An emission band at 357 nm (at excitation of 254 nm) decreased with time, indicating the degradation of 2,4-DPA due to photocatalytic oxidation by  $\text{TiO}_2$ .

The degradation of 2,4-DPA monitored by the intensity  $I_{357 \text{ nm}}(t)$  at an irradiation time  $t$  of an emission band at 357 nm and normalized by the intensity  $I_{357 \text{ nm}}(0)$  at zero time is plotted in Fig. 5. Degradations in suspensions of  $\text{TiO}_2$  nanoparticles and in water were compared. The 2,4-DPA was degraded in  $\text{TiO}_2$  suspensions but not in the absence of  $\text{TiO}_2$ . The degradation data obeyed well to a  $\text{TiO}_2$ -assisted photocatalytic oxidation process via a first-order kinetics of  $-d[2,4\text{-DPA}]/dt = kt$ , with rate constants of  $k = 3.2 \times 10^{-3}$  and  $9.8 \times 10^{-3} \text{ min}^{-1}$  for particles without and with dendrimer, respectively.

Comparison of the decomposition rate of 2,4-DPA reveals that  $\text{TiO}_2$  nanoparticle protected by dendrimer is more efficient as a photocatalyst than  $\text{TiO}_2$  nanoparticle without protector. It is expected that the dendrimer protecting the

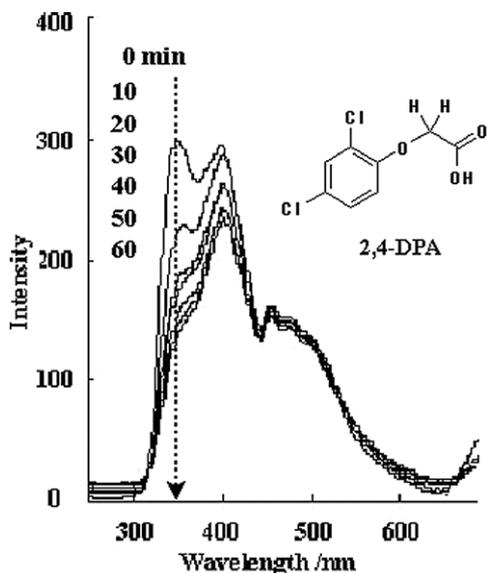


Fig. 4. Time-dependent fluorescence spectra of 2,4-DPA under the irradiation of UV light in an aqueous suspension of TiO<sub>2</sub> nanoparticles protected by G4.5 PAMAM-COONa dendrimer at pH 10.

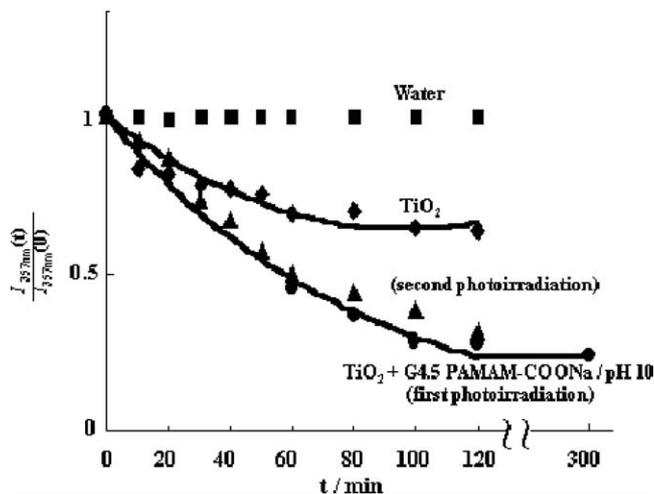


Fig. 5. Degradation of 2,4-DPA monitored by intensity  $I_{357\text{ nm}}(t)$  at an irradiation time  $t$  of an emission band at 357 nm normalized by the intensity  $I_{357\text{ nm}}(0)$  at zero time.

TiO<sub>2</sub> nanoparticle behaves as a reservoir of 2,4-DPA; that is, a guest molecule is trapped in the interior of a dendrimer before oxidation. It is assumed that this trapping ability of the dendrimer promotes the decomposition. The suspension was reused for the decomposition of 2,4-DPA. The degradation result is included in Fig. 5. The process was identical with the first route, indicating no damage of the suspension on the first irradiation.

The suspension of TiO<sub>2</sub> nanoparticles containing 2,4-DPA changed from opalescent to light yellow after UV irradiation for 2–3 h but generated no precipitation, indicating photoreaction. The UV spectra of dendrimer-protected TiO<sub>2</sub> nanoparticles without 2,4-DPA were invariable and presented no new UV bands after UV irradiation. No change

of UV absorption band of dendrimer after UV irradiation was observed as well for a dendrimer solution without TiO<sub>2</sub> nanoparticles and a mixed suspension of dendrimer with bare TiO<sub>2</sub> nanoparticle. Therefore, the dendrimer is not decomposed by the radical reaction of TiO<sub>2</sub> nanoparticles and is not removed from TiO<sub>2</sub> particle. However, it is inferred that the intermediate of the 2,4-DPA photodegradation is absorbed on the TiO<sub>2</sub> particle.

#### 4. Conclusions

In this study, dendrimers were used as a stabilizer of TiO<sub>2</sub> nanoparticles in order to anticipate the increasing stability of nanoparticles in water. The synthesis of dendrimer-protected TiO<sub>2</sub> nanoparticles was performed by the hydrolysis of TiCl<sub>4</sub> in a cold solution of dendrimers. The morphology of dendrimer-protected TiO<sub>2</sub> nanoparticles was dependent on the terminal groups of poly(amido amine) dendrimers. The size of dendrimer-protected TiO<sub>2</sub> nanoparticles was as small as 4.4–6.7 nm, while that of bare TiO<sub>2</sub> nanoparticles was 7.5 nm. The photodegradation of 2,4-dichlorophenoxyacetic acid was more active in a suspension of dendrimer-protected TiO<sub>2</sub> nanoparticles than in a suspension of bare TiO<sub>2</sub> nanoparticles. As a result, dendrimers affected in the reinforcement of the photocatalytic activity of TiO<sub>2</sub> nanoparticles, besides in the stabilization of the particles, due to the trapping activity of the dendrimer. This result proves the concept that dendrimers may be “monomolecular micelle.”

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