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Synthesis and Electric Field Response of Titanium Dioxide Nanoparticles Dispersed in Hydrophobic Solvents

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We present a novel synthesis method for producing stable titanium dioxide nanoparticles (<10 nm) dispersed in hydrophobic solvents using organophosphates. Our approach enables the control of nanoparticles' electric field responsiveness by altering the dispersing medium's composition, expanding their potential applications in electronics, photovoltaics, and photocatalysis.

In recent years, nanotechnology has made innovative advances across many fields of science and technology, with a particular focus on the synthesis and applications of nanoparticles. Among these, titanium dioxide (TiO₂) nanoparticles have been extensively used due to their excellent photocatalytic properties, chemical stability, and non-toxicity in applications ranging from photocatalysis¹ to solar cells^{2,3}. To fully harness the functionalities of nanoparticles, the size, dispersity, and responsiveness to specific external stimuli are crucial.

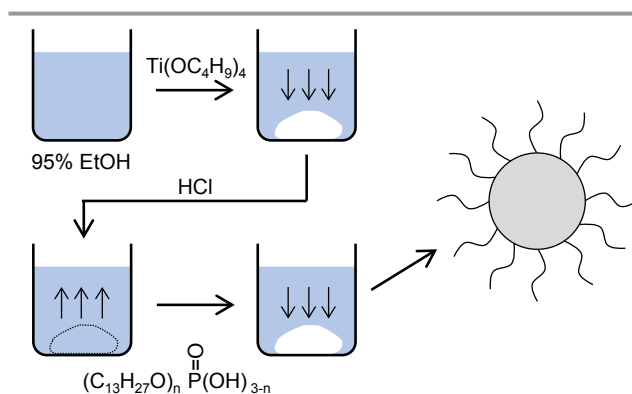
Particularly, nanoparticles with diameters less than 10 nm are expected to exhibit superior performance due to their large surface area⁴. However, nanoparticles generally tend to agglomerate more readily as their particle size decreases, making it exceedingly challenging to achieve monodispersity of nanoparticles with diameters less than 10 nm.

Nanoparticles that respond to electric fields have particularly important technological applications. These applications range from the precise manufacturing of electronic devices^{5,6} to environmental remediation technologies⁷. However, the response to electric field is significantly influenced by the ionization of hydroxyl groups on the TiO₂ surface, and achieving both dispersion in organic solvents and ionization remains a challenge, limiting their functionality.

In this study, we developed a new method for effectively

dispersing titanium dioxide nanoparticles with a diameter less than 10 nm in hydrophobic solvents and extensively evaluated their dispersion stability and responsiveness to electric fields. Our findings provide a foundation for pioneering new applications of titanium dioxide nanoparticles, expanding their application range, and contributing to the advancement of nanoparticle surface modification technologies.

There are various approaches to synthesize TiO₂ particles, and the bottom-up method is suitable for synthesis of well-dispersed nanoparticles. Hydrothermal synthesis^{8,9} and sol-gel synthesis¹⁰ are typical methods, but while these methods can easily synthesize particles of 10 nm or less, they are prone to aggregation. Aggregated nanoparticles are robust, and once aggregated, it is difficult to re-disperse them even with a dispersing agent. Ito *et al.* synthesized titanium dioxide nanoparticles that disperse well in organic solvents using a method called flushing¹¹, which is used in the production of inks. Flushing is a process in which a hydrated metal oxide sol synthesized in an aqueous solution is transferred into an organic solvent using a surfactant, but stable synthesis is difficult because the yield tends to change significantly with slight changes in temperature, water content, and the amount of surfactant. We improved this method and established a stable



Scheme 1 Schematic illustration of bottom-up method for synthesis of well-dispersed TiO₂ nanoparticle.

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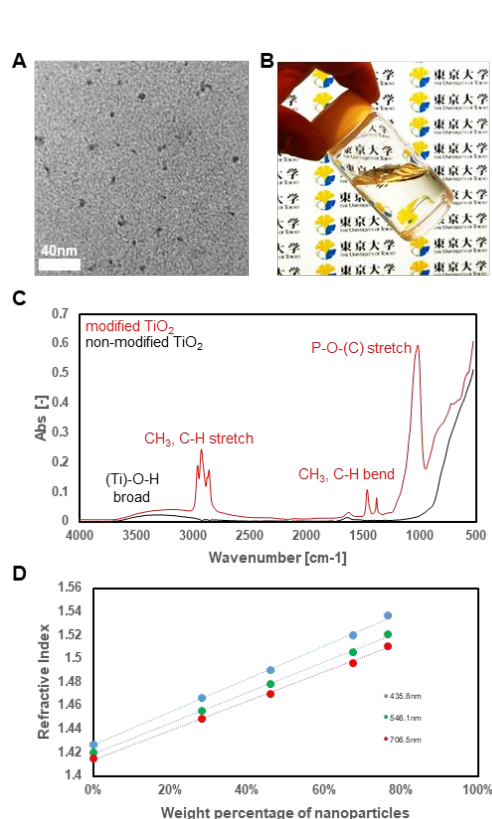


Figure 1 (A) TEM image of nanoparticles. (B) Photo of high concentration dispersion (3.24 g/1 g solvent). (C) FT-IR spectrum of organophosphate-modified TiO_2 nanoparticles. (D) Relation between the refractive index and the weight fraction of nanoparticles.

and reproducible nanoparticle synthesis method as described below and in Scheme 1.

Titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$, TTB, 80 mmol) was added dropwise to 800 mL of 95% ethanol. TTB was hydrolysed immediately, resulting in a white precipitate. After 1 h of stirring, hydrochloric acid was added, the precipitate peptized and clear solution was obtained. At this point, the solute was considered to be titanium dihydroxide oxide: $\text{TiO}(\text{OH})_2$ rather than dense TiO_2 . When isotridecyl acid phosphate ($\text{PO}(\text{OH})_3 \cdot \text{n}(\text{C}_{13}\text{H}_{27}\text{O})$, $\text{n}=1$ or 2 , 8 mmol) was added dropwise to this solution, $\text{TiO}(\text{OH})_2$ reacted with the phosphate portion, forming micelles with the carbon chains facing outward, and precipitation was formed. The precipitate was filtered and dried overnight at room temperature. When the resulting powder was added to toluene at 1 g/mL, it dispersed spontaneously and became a transparent solution without ultrasonication. Finally, titanium dioxide nanoparticle powder was obtained by refluxing in toluene, dehydrating, and then reprecipitating with large amounts of ethanol, washing with ethanol twice, and drying.

The obtained nanoparticles spontaneously dispersed when added to a hydrophobic solvent such as toluene, hexane and octyl acetate, and became a transparent solution without ultrasonication, indicating that particles in the solvent were dispersed well. On the other hand, if the filtered solids were directly heated instead of toluene refluxing, they did not disperse at all. To synthesize stably dispersible nanoparticles in

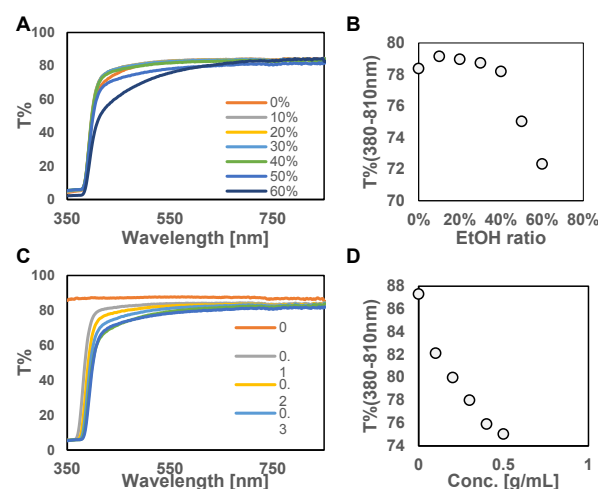


Figure 2. (A) Transmittance spectra of nanoparticle dispersions (0.5 g/mL) with different EtOH ratio. (B) Relationship between visible light (380–810 nm) transmittance and EtOH ratio. (C) Transmittance spectra of nanoparticle dispersions in 50% EtOH with different concentration. (D) Relationship between visible light (380–810 nm) transmittance and concentration.

hydrophobic solvents, it is important to dehydrate them in a monodispersed state in hydrophobic solvents.

TEM observation showed that particles of about 10 nm in diameter were obtained (Figure 1A). The nanoparticles were well monodispersed and no aggregation was observed. Powder FT-IR also confirmed that organophosphate was immobilized on the surface of the nanoparticles (Figure 1C). The broad peak around 3400 cm^{-1} and the large peak below 1000 cm^{-1} are TiO_2 -derived peaks, while the C-H stretching peak at 2900 cm^{-1} , the C-H bending peak at 1450 cm^{-1} , and the P-O peak at 1050 cm^{-1} are organophosphate-derived peaks. The absence of (P)-O-H stretching peak ($2525\text{--}2725\text{ cm}^{-1}$) suggests P-O-Ti bond formation. Both samples exhibited a broad peak in the range of $3000\text{--}3600\text{ cm}^{-1}$ corresponding to O-H groups on TiO_2 surface, indicating that hydroxyl groups remained on the surface even after modification with organic phosphates. The presence of these residual O-H groups allows the particle surface to acquire charges through dissociation, enabling it to respond to an applied voltage. The nanoparticles were able to remain transparently dispersed state even at very high concentration: 3.24 g TiO_2 nanoparticle in 1 g octyl acetate (Figure 1B). Furthermore, this dispersion was extremely stable so that it remained clear even 6 months after preparation. As shown in Figure 1D, the refractive index of the colloidal solution is linearly correlated with the weight fraction of nanoparticles, increasing by more than 0.1 at 75 wt% dispersion in octyl acetate. At higher concentrations, the viscosity also increased, resulting in a decrease in fluidity.

The ionization of hydroxyl groups on the surface of nanoparticles provides the driving force when voltage is applied. However, when dispersed only in nonpolar solvent such as hexane, toluene, octyl acetate, the nanoparticles were hardly ionized, so a polar solvent such as ethanol must be mixed with the dispersant. Figure 2A–D shows the visible light transmittance of the dispersion in a mixture of polar and non-

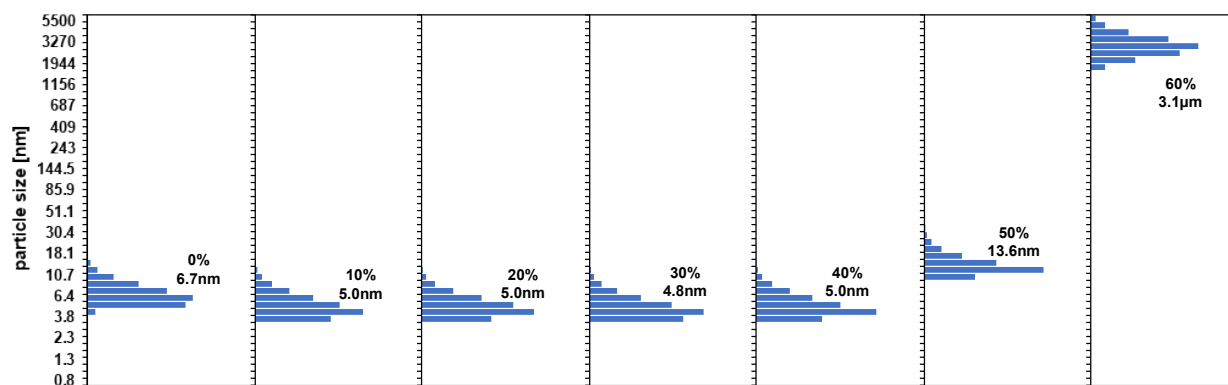


Figure 3 DLS measurements of 0-60% ethanol dispersions.

polar solvents. When ethanol (polar solvent) was mixed with octyl acetate (non-polar solvent), the dispersion was kept transparent up to 40%, but became slight milky at 50%. The dispersion with 60% ethanol was obviously milky, indicating that aggregation occurred (Figure 2A, B and S1).

When the nanoparticles were dispersed in 50% ethanol, aggregation of nanoparticles occurred even at low concentrations (Figure 2D,E). Therefore, the aggregation of nanoparticles does not depend on the particle concentration, but only on the composition ratio of mixed solvent. The particle size distribution of the colloidal dispersion was also measured by DLS as shown in Figure 3. The particle size in solution with ethanol was smaller than that without ethanol, corresponding to the dispersion in pure octyl acetate. This is probably the result of solvation of both hydrophilic hydroxyl groups and hydrophobic hydrocarbon groups of the modifier on the particle surface. In 50% ethanol solvent, a few nanoparticles aggregated to form secondary particles, and in 60% ethanol, the aggregation became larger. This result is in good agreement with transmittance measurements and visual observations.

The electric field response of nanoparticles in colloidal dispersions can be evaluated by electroconductivity measurements as shown in Figure 4. When nanoparticles were dispersed only in octyl acetate, no ionization occurred and conductivity was extremely low. The addition of ethanol raised the ionization and conductivity (Figure 4A). The isoelectric point of titanium oxide nanoparticles is between pH 3 and 5¹², and they tend to ionize and acquire a negative charge in organic solvents close to neutrality. However, in non-protic solvents, proton cannot exist stably, resulting in no ionization. The addition of protic polar solvents can promote the dissociation of O-H groups on the surface of titanium oxide, stabilizing the surface charge of the particles, result in the improvement of higher responsivity to electric fields. Concentration dependence of the conductivity in 50% ethanol showed that the conductivity increased up to a nanoparticle concentration of 0.2 g/mL, but did not increase thereafter (Figure 4B).

The electrical conductivity Λ_0 of the electrolyte solution can be obtained by the Nernst-Einstein equation¹³ (1)

$$\Lambda_0 = \frac{F^2}{RT} (v_+ z_+^2 D_+ + v_- z_-^2 D_-) \quad (1)$$

where F is Faraday constant, v_{\pm} is the concentration, z_{\pm} is the valence, and D_{\pm} is the diffusion coefficient. The diffusion coefficient of a particle can also be obtained from the Stokes-Einstein equation¹⁴ (2)

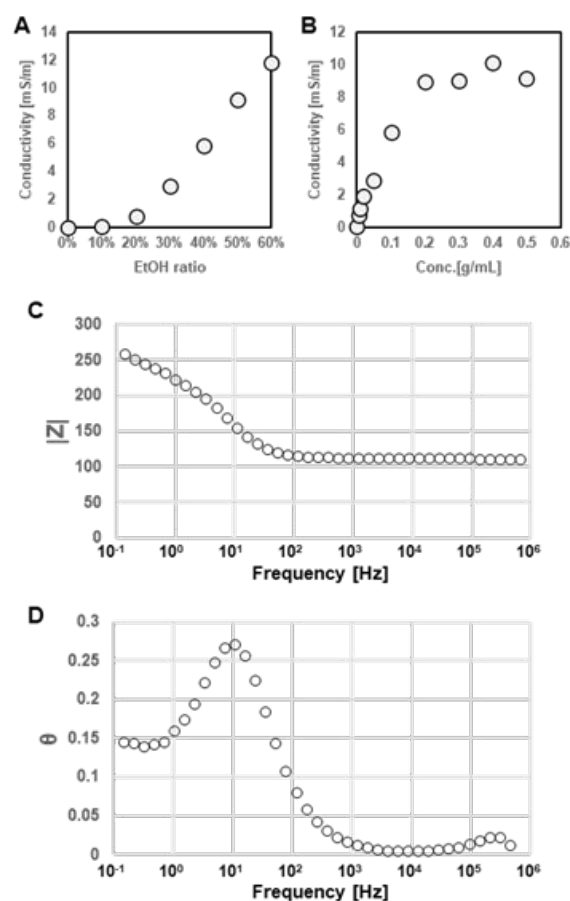


Figure 4. The electric field response of nanoparticles: Conductivity at 1250 Hz versus EtOH ratio (A) and that versus concentration (B). Bode plot of 0.2 g/mL, 50% ethanol dispersion: $|Z|$ (C) and phase θ (D) versus frequency. Resistance increases below 100 Hz, with θ peak around 10 Hz.

$$D = \frac{k_B T}{6\pi\eta r} \quad (2)$$

where k_B is Boltzmann's constant, r is the radius of nanoparticle, and η is the viscosity. Since Equation (1) is only an estimate in a strong electrolyte, the actual conductivity Λ can be described as in (3) using the ionization ratio α .

$$\Lambda = \alpha\Lambda_0 \quad (3)$$

The dispersion viscosity was adequately low in the concentration range measured in this study, so it was possible to assume that there was no difference in the diffusion coefficient. Therefore, the increase in conductivity with ethanol addition can be associated with the increase in ionization ratio. Conductivity reached the plateau above 0.2 g/mL probably due to the saturation of ionization.

Time response to electric field is also an important parameter for precise manufacturing. By measuring the frequency dependence of impedance to obtain a Bode plot, we estimated the speed of nanoparticle migration. Bode plot of 0.2 g/mL in 50% ethanol dispersion, measured at an amplitude of 0.1 V, showed a constant resistance from 1 MHz to 100 Hz, but below 100 Hz, the $|Z|$ increased (Figure 4C). The phase had a peak around 10 Hz, suggesting that the movement of nanoparticles by an electric field took about 0.1 second (Figure 4D). Since the migration speed of charged particles is proportional to the number of charges and the strength of the electric field, the migration speed can be controlled by the applied voltage.

In summary, we have successfully synthesized TiO_2 nanoparticles with diameters less than 10 nm that stably disperse in hydrophobic organic solvents. Furthermore, we have enhanced the nanoparticles' response to electric fields by mixing ethanol as polar solvent in dispersant in order to promote ionization of OH groups on TiO_2 surface. We believe that these findings will contribute to the advancement of precision manufacturing in various fields, including photocatalysis, optical modulation, electronics, and medical application.

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Data availability

The data supporting this article have been included as part of the Supplementary Information.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- He, X.; Wang, A.; Wu, P.; Tang, S.; Zhang, Y.; Li, L.; Ding, P. *Sci. Total Environ.* 2020, 740, 140694. DOI: 10.1016/j.scitotenv.2020.140694.
- Green, M. A.; Ho-Baillie, A.; Snaith, H. J. *Nat. Photonics* 2014, 8, 506–514. DOI: 10.1038/nphoton.2014.134.
- Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* 2010, 110 (11), 6595–6663. DOI: 10.1021/cr900356p.
- Li, D.; Song, H.; Meng, X.; Shen, T.; Sun, J.; Han, W.; Wang, X. *Nanomaterials* 2020, 10(3), 546. DOI: 10.3390/nano10030546.
- Wang, Y.; Miao, Z.; Zheng, S.; Chen, J.; He, Z. *Coatings* 2023, 13(4), 783. DOI: 10.3390/coatings13040783.
- Chien, Y.-A.; Chang, T.-F. M.; Chen, C.-Y.; Yamane, D.; Ito, H.; Machida, K.; Masu, K.; Sone, M. *Electrochem.* 2020, 1(4), 25. DOI: 10.3390/electrochem1040025.
- Rosolymou, E.; Spanou, S.; Zanella, C.; Tsoukleris, D. S.; Köhler, S.; Leisner, P.; Pavlatou, E. A. *Coatings* 2020, 10(8), 775. DOI: 10.3390/coatings10080775.
- Chae, S. Y.; Park, M. K.; Lee, S. K.; Kim, T. Y.; Kim, S. K.; Lee, W. I. *Chemistry of Materials* 2003, 15 (17), 3326–3331. DOI: 10.1021/cm030171d.
- Yang, J.; Mei, S.; Ferreira, J. M. F. *Materials Science & Engineering C-Biomimetic and Supramolecular Systems* 2001, 15 (1-2), 183–185. DOI: 10.1016/s0928-4931(01)00274-0.
- Sugimoto, T.; Zhou, X. P.; Muramatsu, A. *Journal of Colloid and Interface Science* 2002, 252 (2), 339–346. DOI: 10.1006/jcis.2002.8454.
- Ito, S.; Siragane, K.; Kuwahara, T. *Journal of Japan Society of Colour Material* 1984, 57 (6), 305–308. DOI: https://doi.org/10.4011/shikizai1937.57.305.
- Borghi, F.; Vyas, V.; Podesta, A.; Milani, P. *PLOS ONE* 2013, 8, e68655. DOI: 10.1371/journal.pone.0068655.
- France-Lanord, A.; Grossman, J. C., *Phys. Rev. Lett.* 2019, 122, 136001. DOI: 10.1103/PhysRevLett.122.136001.
- Koddermann, T.; Ludwig, R.; Paschek, D., *ChemPhysChem* 2008, 9, 1851–1858. DOI: 10.1002/cphc.200800102.

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The data supporting this article have been included as part of the Supplementary Information.