

Effective Surface Modification of Titanate Nanosheets Using the Lamellar Self-assembly of a Cationic Amine Surfactant as a Template

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Titanate nanosheets with a lamellar mesostructure were developed using the lamellar self-assembly of cationic 1,12-dodecanediamine (DDA) as a template. An electrostatic interaction between negatively charged titanate nanosheets and positively charged DDA molecules was required to form layered titanate nanosheets. This approach leads to titanate nanosheet surface characteristics such as visible light absorption and high adsorption of hydrophobic organic compounds.

Two-dimensional metal oxide nanosheets have attracted much attention as a new class of nanoscale material because of their attractive features such as high surface area, protonic acidity, and favorable electron-transfer characteristics.^{1–5} Recently, metal oxide nanosheets have been developed using the lamellar phase of surfactant self-assembly as a template.⁶ Layered germanium oxide nanosheets with a lamellar mesostructure have been prepared by the hydrolysis and condensation of germanium alkoxide using a two-dimensional water layer in a lamellar phase of dodecylamine.⁶ This lamellar template preparation can produce metal oxide nanosheets over shorter times and at lower reaction temperatures than the general nanosheet preparation using the exfoliation of an inorganic layered compound^{1–5} or the intercalation of a surfactant into the inorganic layered compound.⁷ Therefore, the lamellar template preparation is an environmentally friendly method for the mass production of metal oxide nanosheets. An effective surface modification of these nanosheets is possible by this method because surfactant molecules cover the entire surface of nanosheets. In addition, a possible chemical interaction between the nanosheets and the surfactant molecules during the preparation is also expected. This approach offers a variety of opportunities to obtain desired chemical properties for the nanosheets by combining different kinds of nanosheets and surfactants. Although some papers have reported the preparation of titanate nanosheets and related nanostructures in surfactant solutions,^{8–10} layered titanate nanosheets with a lamellar mesostructure have not been obtained to date.

In this work, we developed layered titanate nanosheets with a lamellar mesostructure using the lamellar phase of 1,12-dodecanediamine (DDA) self-assembly as a template by a one-pot synthesis. We focused on the electrostatic interaction between nanosheets and surfactant molecules for the formation

of a stable lamellar mesostructure because of the negative charge of the titanate nanosheets. It is important to note that the obtained layered titanate nanosheets with a lamellar mesostructure show better visible light absorption and improved adsorption toward hydrophobic phenol compounds.

The preparation consists of self-assembly based on the interactions between titanium precursors and amine surfactants, as reported in the literature.^{8–10} In a typical experiment, tetraisopropyl orthotitanate (TIPT) was mixed with triethanolamine (TEOA) in a molar ratio of TEOA/TIPT = 4 to form a Ti(IV) compound, which is stable against hydrolysis at room temperature. A 1.0 M DDA aqueous solution was added to the Ti(IV) stock solution. The pH of the mixed solution was 10.5 after the addition of DDA and TEOA. The pH was adjusted to 8.0 or 12.0 by adding aqueous HCl or NH₄OH as necessary. The mixed solution was then transferred to a Teflon autoclave, aged at 373 K for 24 h and kept at 413 K for 96 h. The resulting solid products were centrifuged, washed with distilled water and ethanol to remove possible residual ions in the final products, and then dried at 353 K in air. The obtained sample was denoted Ti+DDA+TEOA.

The adsorption properties were evaluated using several organic compounds to investigate the adsorption behavior by changing the hydrophobicity of the organic compounds. The organic compounds used were phenol ($\log P_{ow} = 1.37$, P_{ow} is the distribution coefficient between octanol and the aqueous phase), 2-methylphenol (1.72), 4-ethylphenol (2.03), and 2-naphthol (2.36).¹¹ The samples were dispersed in an aqueous solution that contained these organic compounds at 303 K for over 2 h until an adsorption–desorption equilibrium was obtained. After centrifugation, the concentration of the organic compounds in the solution was estimated by measuring the absorbance with a UV spectrophotometer.

Figure 1 shows XRD patterns of Ti+DDA+TEOA prepared at different pH values. In the higher angle region at $2\theta > 20^\circ$, the peaks of the Ti+DDA+TEOA prepared at pH 8.0 comes from the TiO₂ anatase phase (JCPDS file No. 21-1272). In contrast, some peaks were observed at $2\theta = 25.3, 48.1,$ and 62.7° for the Ti+TEOA+DDA prepared at pH 10.5 or 12.0. The peaks at $2\theta = 48.1$ and 62.7° seem to correspond to the 20 and 02 reflections of the lepidocrocite titanate phase^{8,10,12} and the very small peak at $2\theta = 25.3^\circ$ corresponds to the 101 reflection of the TiO₂ anatase phase. In the lower angle region at $2\theta < 20^\circ$, a sharp peak at $2\theta = 9.6$ was observed for the Ti+DDA+TEOA

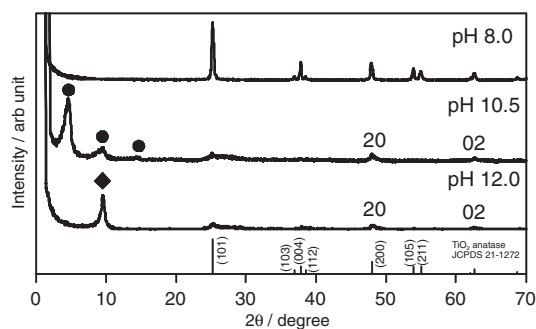


Figure 1. XRD patterns of the Ti+DDA+TEOA prepared at different pH values.

prepared at pH 12.0. This peak corresponds to layered pairs with an interlayer spacing of 0.92 nm for lepidocrocite titanate.^{10,12} This result is almost the same as that of reported titanate nanosheets.⁸ In contrast, three peaks at $2\theta = 4.7, 9.0,$ and 14.0° were observed for the Ti+DDA+TEOA prepared at pH 10.5. These peaks indicate the formation of a strictly ordered lamellar phase with an interlayer spacing of 1.8 nm.

A remarkable difference was found for the mesostructure in the Ti+DDA+TEOA prepared at pH 10.5 and 12.0. The formation of the lamellar mesostructure is related to DDA self-assembly and to the nature of the titanate crystal structure. From our previous in situ measurements of small-angle X-ray scattering using synchrotron radiation, an ordered lamellar mesostructure was found to form at the liquid–liquid interface when amine surfactants such as dodecylamine and 1,12-dodecanediamine were brought into contact with water.^{6,13} Therefore, the hydrolysis and condensation of TIPT are expected to occur in the two-dimensional water layer in the lamellar phase. Considering the crystal structure, a two-dimensional sheet structure of an anionic TiO_6 framework is constructed containing cations in a layered titanate structure.¹² Lepidocrocite titanate was present in both the samples that were prepared at pH 10.5 or 12.0 (Figure 1). For the Ti+DDA+TEOA that was prepared at pH 12.0, ammonium ions function as natural cations during the formation of the layered titanate. On the other hand, no cations other than the amine surfactants were included in the Ti+DDA+TEOA prepared at pH 10.5. According to our previous work, positively charged DDA molecules exist as $\text{H}_2\text{N}(\text{CH}_2)_{12}\text{NH}_3^+$, which becomes hydrophobic and creates a lamellar phase when the pH of the solution is adjusted to 10–11.¹³ Therefore, we assume that positively charged DDA molecules work as cations during the formation of the layered titanate in the Ti+DDA+TEOA prepared at pH 10.5 upon the hydrolysis and condensation of TIPT that was modified with TEOA. Thus, DDA molecules play an important role in the lamellar template for nanosheet formation and in the cations for the formation of the lepidocrocite titanate crystal.

Ti+DDA and Ti+TEOA were synthesized to examine the role of DDA or TEOA molecules for the nanosheet formation. Figure S1 in Supporting Information¹⁴ shows XRD patterns of Ti+DDA and Ti+TEOA. The crystal structure of both samples was anatase phase. A small peak at $2\theta = 4.8^\circ$ was observed in Ti+DDA indicating the formation of a lamellar mesostructure. Figure 2 shows SEM images, a TEM image, and selected area electron diffraction (SAED) patterns of the obtained samples

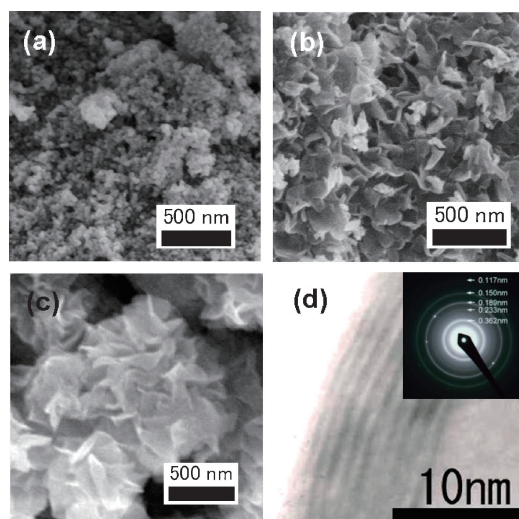


Figure 2. SEM image of (a) Ti+TEOA and (b) Ti+DDA. (c) SEM image and (d) TEM image of Ti+DDA+TEOA, inset: SAED patterns.

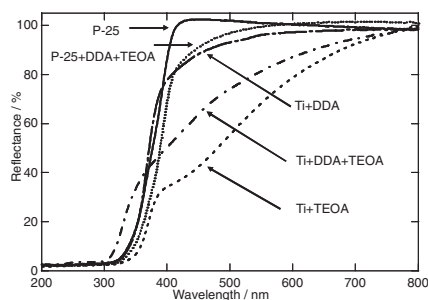


Figure 3. UV–visible diffuse reflectance spectra of the obtained samples.

prepared at pH 10.5. Spherical nanoparticles with a diameter of ca. 50 nm were observed in Ti+TEOA (Figure 2a). On the other hand, flaky forms with a thickness of 10–20 nm were observed in Ti+DDA (Figure 2b) and Ti+DDA+TEOA (Figure 2c). Multilayer structures were also observed in Ti+DDA+TEOA and the interlayer spacing of this layered structure was estimated to be 1.0–1.5 nm (Figure 2d). This value corresponds to that calculated for the lamellar structure using the low-angle XRD patterns. The SAED patterns were composed of a series of diffraction rings (inset of Figure 2d). The ring spacing of 0.362 nm corresponds to the 101 reflection of the anatase phase of TiO_2 . The other ring spacings of 0.233, 0.189, 0.150, and 0.117 nm correspond to the 11, 20, 02, and 22 indices for the lepidocrocite titanate structure, respectively.^{8,10,12}

To characterize the layered titanate nanosheets with a lamellar mesostructure, the optical properties and adsorption toward several phenol compounds were determined. Figure 3 shows the optical properties of the samples that were prepared at pH 10.5 as determined by UV–visible diffuse reflectance spectroscopy. Degussa P-25 was used as a standard TiO_2 sample and is shown for comparison. In the shorter wavelength region ($\lambda < 400$ nm), the onset of Ti+DDA+TEOA absorption was observed at around 300 nm and this is significantly shifted toward shorter wavelengths compared with the bulk TiO_2 crystals with an onset around 320 nm. The band gap energy

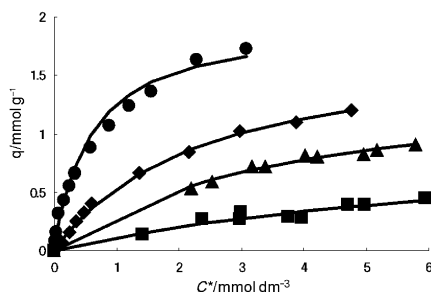


Figure 4. Adsorption isotherms of several phenols in the aqueous phase with Ti+DDA+TEOA, ●: 2-naphthol, ◆: 4-ethylphenol, ▲: 2-methylphenol, ■: phenol.

shift that is caused by exciton confinement in anisotropic 2-D crystallites is determined by crystallite dimensions and, therefore the shift toward a shorter wavelength is predominantly governed by the sheet thickness.¹⁵ This indicates the formation of a two-dimensional nanosheet structure for Ti+DDA+TEOA. Furthermore, in the longer wavelength region ($\lambda > 400$ nm), Ti+DDA+TEOA shows light absorption in the visible region. This result is obviously different from that obtained for previous titanate nanosheets.⁸ In addition, visible light absorption has not been reported for organically modified layered niobate nanosheets prepared using the intercalation of a surfactant into an inorganic layered compound.⁷ To investigate the bonding state of the Ti, O, and N atoms, XPS was carried out (Figure S2 in Supporting Information¹⁴). A small peak attributed to Ti–N bonding was observed around 396 eV indicating the possible formation of nitrogen-doped lepidocrocite titanate^{4,5} in Ti+DDA+TEOA. The optical properties of Ti+DDA, Ti+TEOA, and P-25+DDA+TEOA which was synthesized using mixture of P-25, DDA, and TEOA in hydrothermal solution were determined (Figure 3). There was a little shift toward longer wavelength for the absorption edge in P-25+DDA+TEOA and Ti+DDA compared with P-25. In contrast, Ti+TEOA gave a larger wavelength shift for the absorption edge in the visible region. We assume that the modification of TIPT with TEOA would affect the formation of nitrogen-doped titanate nanosheets in Ti+DDA+TEOA. Therefore, the lamellar template preparation gives nitrogen-doped titanate nanosheets at the relatively low temperature of 413 K and this is advantageous because the general preparation of nitrogen-doped metal oxide nanosheets needs heat treatment at temperatures higher than 673 K.^{4,5}

Figure 4 shows the relationship between the adsorbed quantity, q (mmol g^{-1}), for Ti+DDA+TEOA, and the equilibrium concentration, C^* (mmol dm^{-3}), of several phenol compounds in the aqueous phase. As shown by the solid lines, all the experimental data were correlated using a Langmuir type equation. The adsorption quantities increased as follows: phenol, 2-methylphenol, 4-ethylphenol, and 2-naphthol, which corresponds to an increase in hydrophobicity. The maximum adsorption quantity q_∞ of 2-naphthol was determined by a Langmuir plot. Table 1 shows the BET specific surface area and q_∞ of 2-naphthol of the obtained samples. The value of q_∞ on Ti+DDA+TEOA was found to be around 100 times higher than that of P-25 despite the fact that the BET specific surface area of Ti+DDA+TEOA was only 2 times larger than that of P-25. Relatively high q_∞ value was also obtained for Ti+DDA. A

Table 1. The BET specific surface area and q_∞ of 2-naphthol of the obtained samples

Sample	BET specific surface area / $\text{m}^2 \text{g}^{-1}$	q_∞ of 2-naphthol / mmol g^{-1}
P-25	54	0.02
Ti+TEOA	63	0.13
Ti+DDA	40	1.38
Ti+DDA+TEOA	104	1.98

lamellar mesostructure was observed in Ti+DDA+TEOA and Ti+DDA in the XRD result (Figure S1 in Supporting Information¹⁴). These results suggest that organic compounds can be solubilized into the lamellar mesostructure by a hydrophobic interaction between the solutes and the two-dimensional hydrophobic spaces that consist of alkyl chains in the lamellar phase. Previous reports discussed the adsorption of hydrophobic organic compounds into samples that included a surfactant phase,^{11,16} which supports our results. Thus, the layered titanate nanosheets showed better adsorption toward hydrophobic organic compounds.

In summary, we developed layered titanate nanosheets with a lamellar mesostructure using the lamellar phase of cationic DDA molecules. Effective surface modifications leading to visible light absorption and the adsorption of hydrophobic phenol compounds were achieved. The obtained nanosheets are expected to be used as photocatalysts or photovoltaic devices because of their unique surface properties.

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