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Ultimately Simple One-pot Synthesis of Spherical Mesoporous TiO_2 Nanoparticles in Supercritical Methanol

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Mesoporous TiO_2 nanoparticles were synthesized using different carboxylic acids as organic additives in a very short reaction time (10 min) in supercritical methanol. Solid spherical mesoporous TiO_2 nanoparticles were obtained using phthalic acid, whereas hollow spherical mesoporous TiO_2 nanoparticles were obtained using formic acid.

Recently, mesoporous materials, such as zeolites,[1] metal organic frameworks (MOFs),[2] and metal oxides,[3] have received considerable interest in gas absorption, drug delivery, and substrate-size-controlled catalysis because of their unique properties of intrinsic large surface areas; they have also been utilized for the sustained release of absorbed materials. Dimension-controlled mesoporous nanospheres are particularly important for practical applications owing to their easy manipulation, effective catalyst recovery, excellent thermal stability, monodisperse nature, and enhanced light-harvesting properties.[4] We named these criteria of mesoporous spherical metal oxide particles as **m**esoporously **ar**chitected **r**oundly **i**ntegrated **m**etal **o**xide (MARIMO) nanoparticles, because their shapes are similar to those of *MARIMO* (*Cladophora aegagropila*) moss balls. One of the most important MARIMO nanomaterials should be titanium dioxide (TiO_2) nanoparticles because of their low toxicity and unique semiconductor properties, which enable their application as a photocell,[5] photocatalysts in chemical reactions,[4,6] and a drug or gene delivery system in biotechnology.[7] To obtain MARIMO TiO_2 nanoparticles, the classical hydrothermal, sol–gel, and self-assembly methods and their combinations have been employed. Moreover, these methods generally require complex multistep operations and long reaction times (several hours).[8] Recently, supercritical fluids such as supercritical water (SCW) and supercritical alcohol have been used as new reaction media to obtain size- and morphology-controlled inorganic–organic hybrid nanoparticles such as monodisperse nanoparticles in supercritical ethanol,[9] ZnO nanoparticles in supercritical methanol (scMeOH),[10] and SCW,[11] and CeO_2,[12] TiO_2,[13] and Fe_2O_3[14] nanoparticles in SCW in a very short reaction time (several seconds to several minutes).[15] However, little has been reported about the synthesis of MARIMO TiO_2 nanoparticles in supercritical fluids. In this research, we report the first ultimately simple one-pot synthesis of MARIMO TiO_2 nanoparticles in scMeOH in the presence of carboxylic acids as organic additives in a very short reaction time.

A mixture of titanium tetraisopropoxide, phthalic acid, and methanol ($Ti(O\textit{i}\text{-}Pr)_4$:carboxylic acid = 1:5 (mole ratio)) is treated at 300 or 400 °C for 10 min in a stainless steel SUS 316 batch-type reactor followed by sonication in methanol, decantation, and vacuum drying, affording white powdery products. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) clearly reveal that the particles obtained in both these reactions have nearly the same shape with porous surfaces, and their shapes resemble that of *MARIMO* (Figure 1). The two samples prepared at different reaction temperatures differ in their MARIMO particle sizes and component crystal sizes. The MARIMO particle size obtained at 300 °C is larger than that at 400 °C; however, the component crystal size at 300 °C is smaller than that at 400 °C. Dynamic light scattering (DLS) measurements indicate that the average sizes of the MARIMO TiO_2 nanoparticles obtained at 300 and 400 °C are 300.5 ± 159.6 and 263.7 ± 99.3 nm (Figure S4),[16] respectively, suggesting that the size of the MARIMO TiO_2 nanoparticles can be controlled easily by changing the reaction temperature. Low temperatures yielded large and dense MARIMO nanoparticles, whereas high temperatures yielded small and coarse MARIMO nanoparticles.

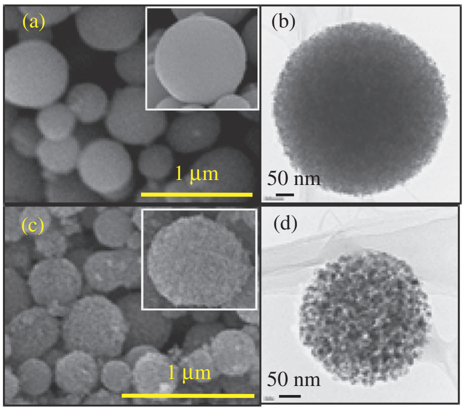


Figure 1. FE-SEM (a and c) and TEM (b and d) images of MARIMO TiO_2 nanoparticles obtained at 300 (a and b) and 400 °C (c and d) with phthalic acid in scMeOH.

Crystal structures of the obtained MARIMO nanoparticles were determined by powder X-ray diffraction (XRD) (Figure 2).[16] The diffraction peak patterns of the two MARIMO nanoparticles clearly indicate that they have good crystallinity and that their crystal structures correspond to JCPDS 21-1272 (anatase) TiO_2. The observed lattice spacing of MARIMO TiO_2 nanoparticles by high-resolution transmission electron microscopy (HRTEM) is 0.35 nm, which corresponds to that of anatase (101) planes (Figures S1b and S1d).[16] Thus, calcination is not necessary in our reaction for anatase formation because of the inherent high temperature of scMeOH.

The Brunauer–Emmett–Teller (BET) specific surface areas of the MARIMO TiO_2 nanoparticles obtained at 300 and 400 °C are 210.9 and 100.9 $m^2\,g^{-1}$, respectively, which are larger than

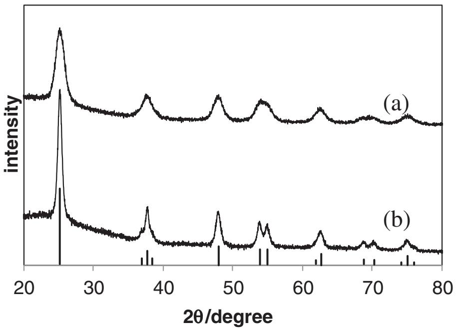


Figure 2. Powder X-ray diffraction patterns (graphite-monochromatized Cu Kα radiation) of the synthesized TiO_2 nanoparticles with phthalic acid at (a) 300 and (b) 400 °C for 10 min and with a 0.28 g mL^{-1} methanol density.

some of the reported mesoporous TiO_2 nanoparticles and commercially available P25 TiO_2 nanoparticles.[17] The nitrogen adsorption–desorption isotherm spectra of two MARIMO nanoparticles obtained at 300 and 400 °C were classified as type IV and type II, indicating that the particles have meso- and macropores, respectively (Figure S5).[16]

To examine the existence of organic residue on the surface of the MARIMO TiO_2 nanoparticles, Fourier transform infrared (FTIR) reflection spectra were measured (Figure S7).[16] The broad peaks at 3700–3000 cm^{-1} represent hydrogen-bonded O–H stretching on the surface of TiO_2 and/or absorbed H_2O. The absorptions appearing at 1562 and 1415 cm^{-1} observed for both particles obtained at 300 and 400 °C correspond to absorptions of carboxylate (COO^-) groups (Figure S7),[16,18] indicating that phthalic acid is attached onto the surface of the MARIMO TiO_2 nanoparticles. As a reference, the TiO_2 nanoparticles synthesized in scMeOH without organic acid exhibit only a broad peak at 3700–3000 cm^{-1} (OH hydrogen bonds) in the FTIR spectra (Figure S10).[16] Thermogravimetric (TG) analysis under N_2 gas flow showed that weight losses of the MARIMO TiO_2 nanoparticles synthesized in the presence of phthalic acid at 300 and 400 °C are 12.0% and 11.5%, respectively, indicating that the MARIMO TiO_2 nanoparticles contain a maximum of ca. 12 wt % organic materials such as phthalic acid and methanol (Figure S6).[16]

To elucidate the role of organic acids in MARIMO formation, reaction conditions were altered. First, when the reaction was performed in scMeOH at 400 °C without organic acid, randomly aggregated nanoparticles were obtained (Scheme S2 and Figure S9).[16] A reaction performed in SCW instead of scMeOH in the presence of phthalic acid at 400 °C resulted in monodisperse single-crystal TiO_2 nanoparticles (Scheme S3 and Figure S12).[16] Thus, a combination of organic acid and scMeOH is indispensable to afford MARIMO TiO_2 nanoparticles. Next, to elucidate the effect of organic acids on MARIMO structures, several carboxylic acids, such as benzoic acid, acetic acid, formic acid, maleic acid, and fumaric acid, were introduced in the reaction under similar reaction conditions. All reactions afforded white powdery products, whose crystal structures were determined to be anatase phase by XRD (Figures S14, S19, S22, and S27).[16] FE-SEM images of these materials obtained in the presence of benzoic acid and formic acid clearly indicate that they belong to the family of the MARIMO TiO_2 nanoparticles (Figures 3a and 3c). To our astonishment, however, in the case of formic acid, an almost complete, beautiful spherical hollow structure of the MARIMO nanoparticles was confirmed by TEM (Figure 3d). Moreover, in the cases of acetic acid and benzoic acid, mixtures of solid and hollow MARIMO structures were obtained (Figures 3b and S20[16]). On the other hand, in the cases of fumaric and maleic acids, several MARIMO TiO_2 aggregates were obtained under similar reaction conditions (Figure 4). Based on these results, it can be inferred that organic acids are key materials for construction of the MARIMO structure.

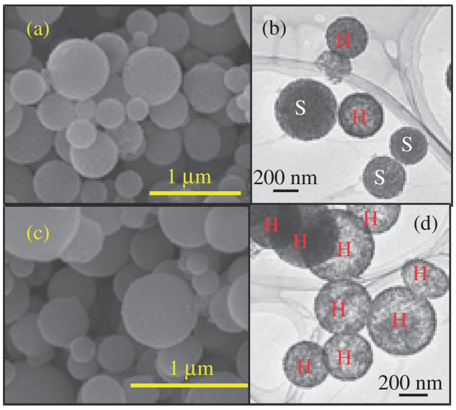


Figure 3. FE-SEM (a and c) and TEM (b and d) images of MARIMO TiO_2 nanoparticles prepared in the presence of different carboxylic acids at 400 °C for 10 min with a 0.28 g mL^{-1} MeOH density; (a) and (b) benzoic acid, (c) and (d) formic acid. S: solid MARIMO; H: hollow MARIMO.

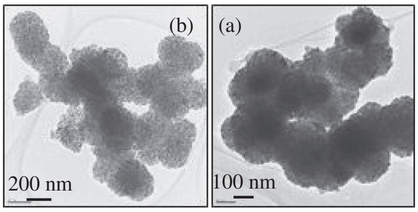
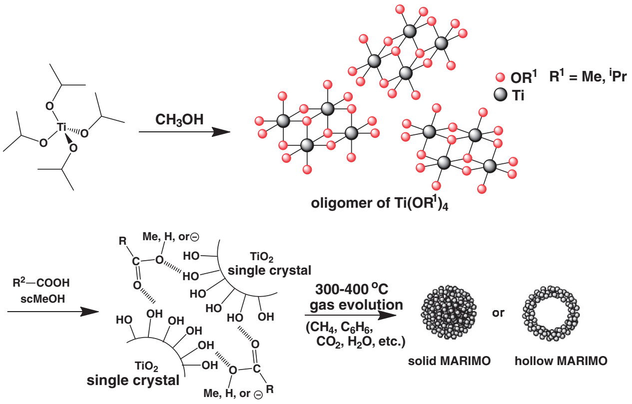


Figure 4. TEM images of prepared mesoporous TiO_2 nanoparticles with fumaric acid (a) and maleic acid (b) in scMeOH at 400 °C for 10 min with a 0.28 g mL^{-1} MeOH density.

With respect to the formation mechanism for the MARIMO TiO_2 nanoparticles in scMeOH, a carboxyl-group-assisted mechanism is plausible (Scheme 1). First, in a methanol solution, some of the isopropyloxy groups of Ti(O*i*-Pr)$_4$ can be substituted by the methoxy groups to form a primitive titanium alkoxide oligomer.[19] Next, the carboxyl groups would interact with the surface of the primitive oligomer to connect some of them with each other. When the reaction mixture is heated, esterification of acids with methanol proceeds easily to generate water. The titanium alkoxide oligomers bearing carboxylic acids react with water to form TiO_2 crystals;[8c] simultaneous decomposition of these carboxylic acids should occur to evolve gaseous products such as CH_4, C_6H_6, H_2, CO_2, and H_2O. The resulting TiO_2 aggregates grow and swell to form a mesoporous structure with solid MARIMO and/or hollow MARIMO nanoparticles. Hollow MARIMOs can be produced



Scheme 1. Formation mechanism of carboxylic-acid-assisted mesoporous TiO_2 nanoparticles in supercritical methanol.

more rapidly and with greater gas evolution from formic acid, which more effectively swells the primitive TiO_2 aggregates. This is because H_2 and CO_2 can be easily generated from formic acid in comparison to other carboxylic acids.

In summary, the MARIMO TiO_2 nanoparticles with large surface areas were successfully synthesized by an ultimately simple one-pot synthesis in the presence of carboxylic acids as organic additives in scMeOH in a very short reaction time (10 min). The particle size and surface area can be controlled by the reaction temperature. The morphologies of the MARIMO TiO_2 nanoparticles changed from solid to hollow using phthalic acid and formic acid, respectively, as organic additives. Interesting mesoporous TiO_2 nanoparticle aggregates were also obtained with maleic and fumaric acid under similar reaction conditions in scMeOH. The solid and hollow MARIMO TiO_2 nanoparticles can have applications in several areas, such as photocatalysis, drug delivery, solar cells, and so on.

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16 Detail is shown in Electronic Supporting Information (ESI). Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

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