SUPPLEMENTARY DATA

Versatility of One-pot, Single-step Synthetic Approach for Spherical Porous (Metal) Oxide Nanoparticles Using Supercritical Alcohols

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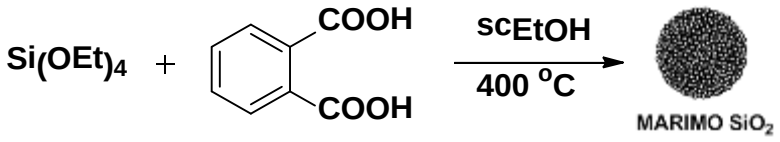
1. Synthesis of MARIMO SiO_2 nanoparticles in the presence of phthalic acid in supercritical EtOH



Scheme S1 Reaction of $Si(OEt)_4$ with phthalic acid in scEtOH at 400 ºC for 10 min and 0.28 g mL^{-1} EtOH density.

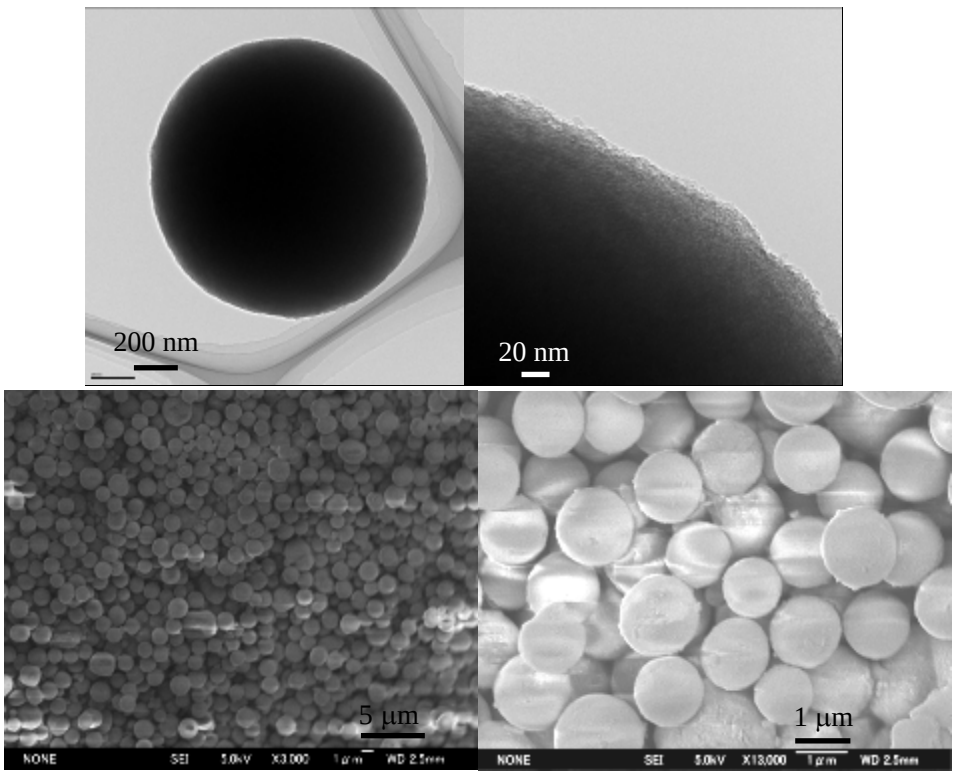


Fig. S1. TEM and FESEM images of MARIMO SiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} EtOH density in the presence of phthalic acid.

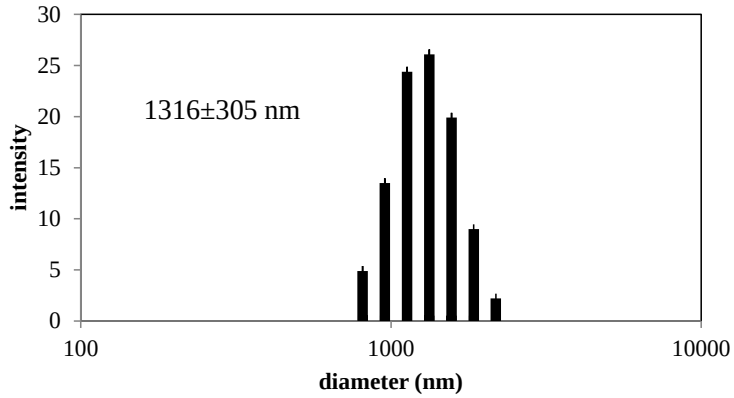


Fig. S2. DLS spectrum of MARIMO SiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} EtOH density in the presence of phthalic acid.

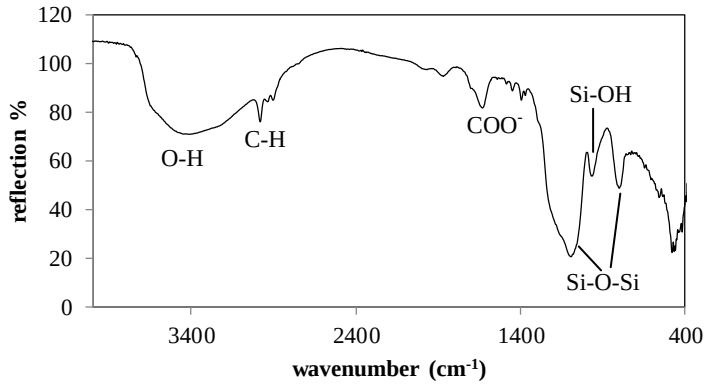
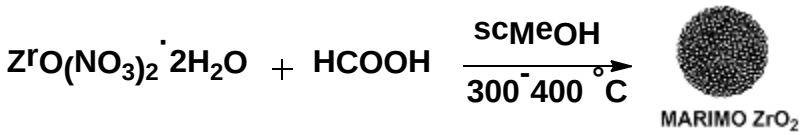


Fig. S3. FTIR spectrum of MARIMO SiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} EtOH density in the presence of phthalic acid.

2. Synthesis of MARIMO ZrO_2 nanoparticles in the presence of formic acid in supercritical MeOH



Scheme S2 Reaction of $ZrO(NO_3)_2 \cdot 2H_2O$ with formic acid in scMeOH at 300 or 400 °C for 10 min in 0.28 g mL^{-1} MeOH density.

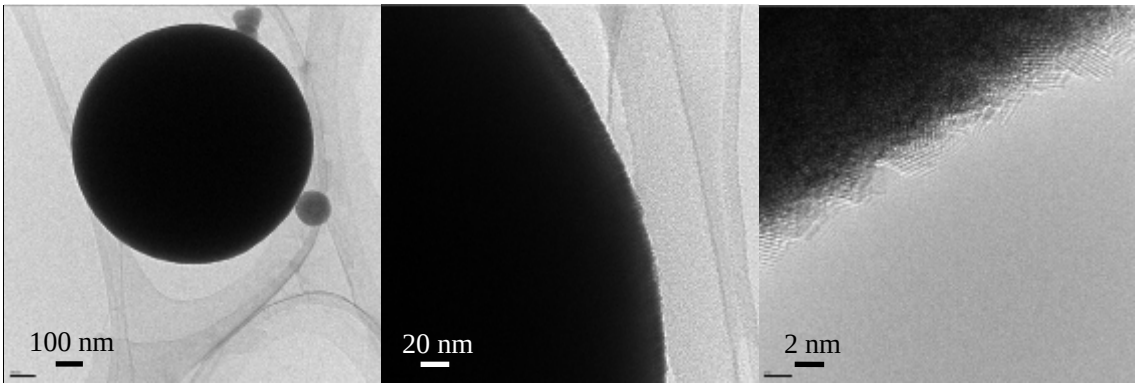


Fig. S4. TEM images of MARIMO ZrO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

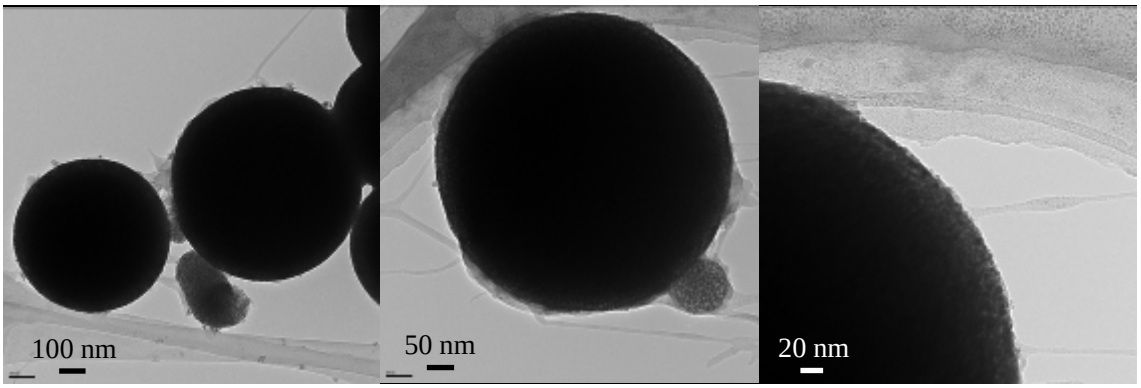


Fig. S5. TEM images of MARIMO ZrO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

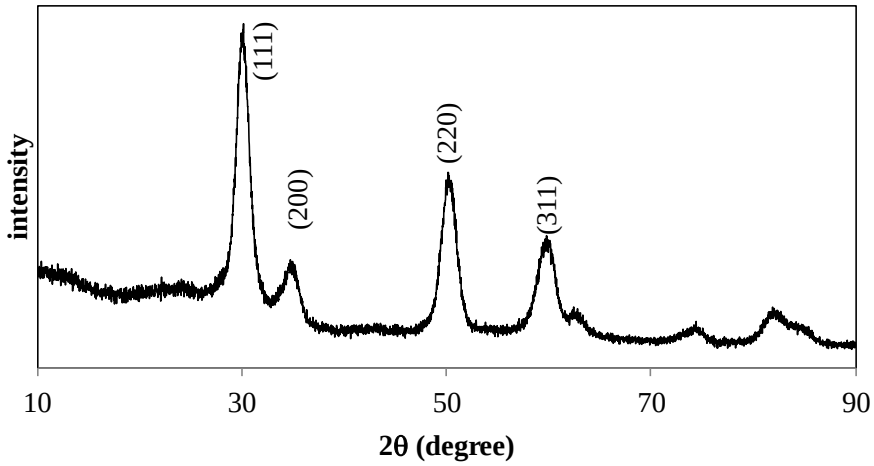


Fig. S6. XRD pattern of MARIMO ZrO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

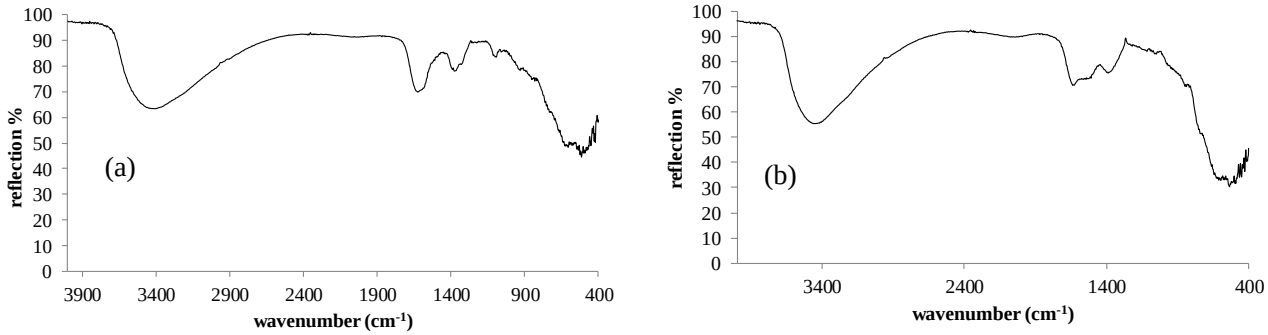


Fig. S7. FTIR spectra of MARIMO ZrO_2 nanoparticles prepared at (a) 300 °C and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

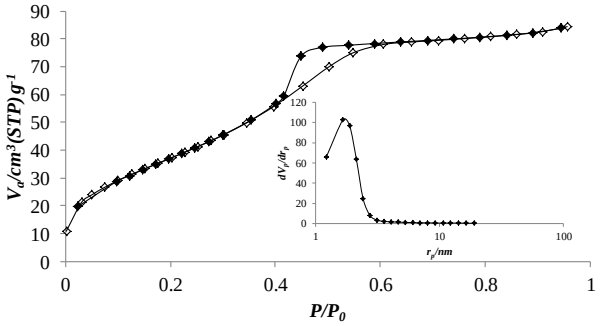


Fig. S8. Nitrogen adsorption–desorption isotherm and Barret Joyner Halenda (BJH) pore size distribution plots of MARIMO ZrO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

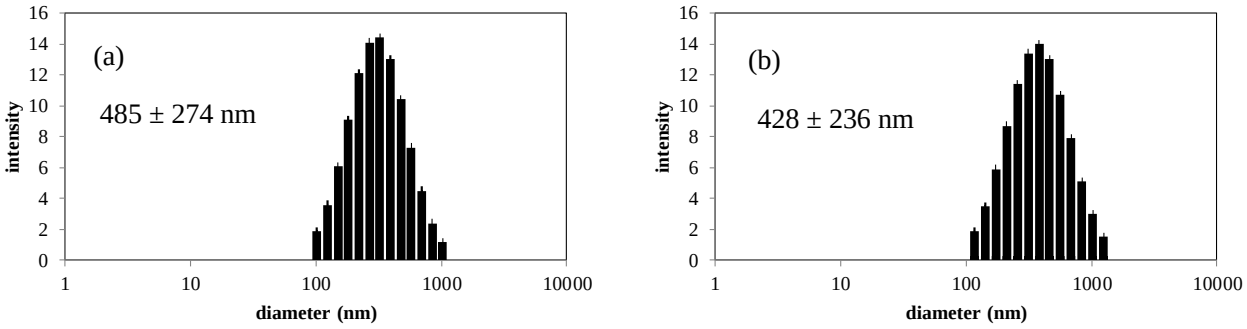
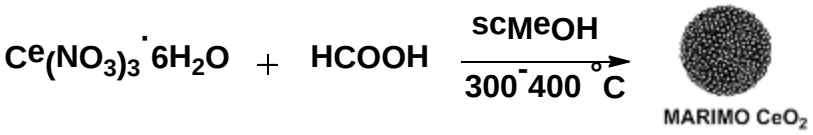


Fig. S9. DLS spectra of MARIMO ZrO_2 nanoparticles prepared at (a) 300 °C and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

3. Synthesis of MARIMO CeO_2 nanoparticles in the presence of formic acid in supercritical MeOH



Scheme S3 Reaction of $Ce(NO_3)_3 \cdot 6H_2O$ with formic acid in scMeOH at 300 or 400 ºC for 10 min in 0.28 g mL^{-1} MeOH density.

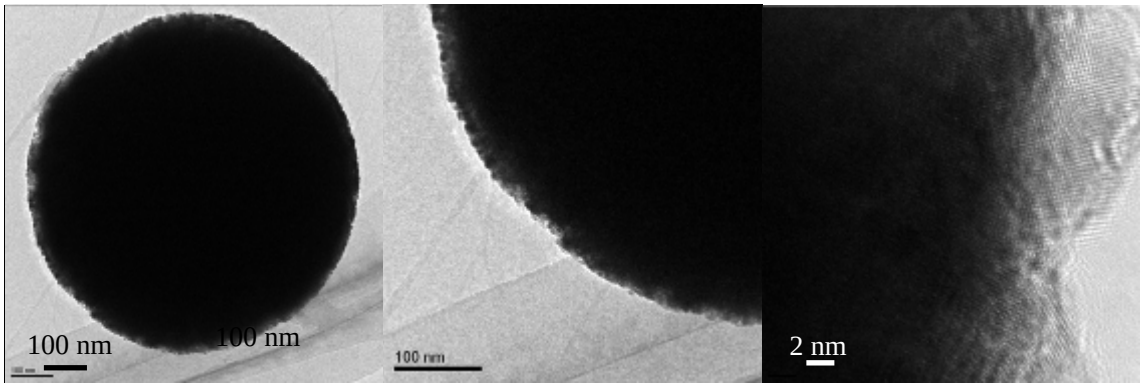


Fig. S10. TEM images of MARIMO CeO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

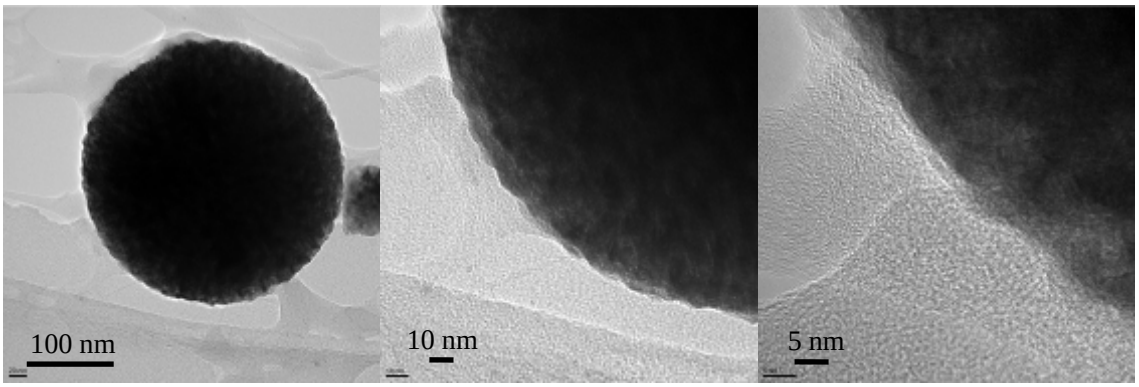


Fig. S11. TEM images of MARIMO CeO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

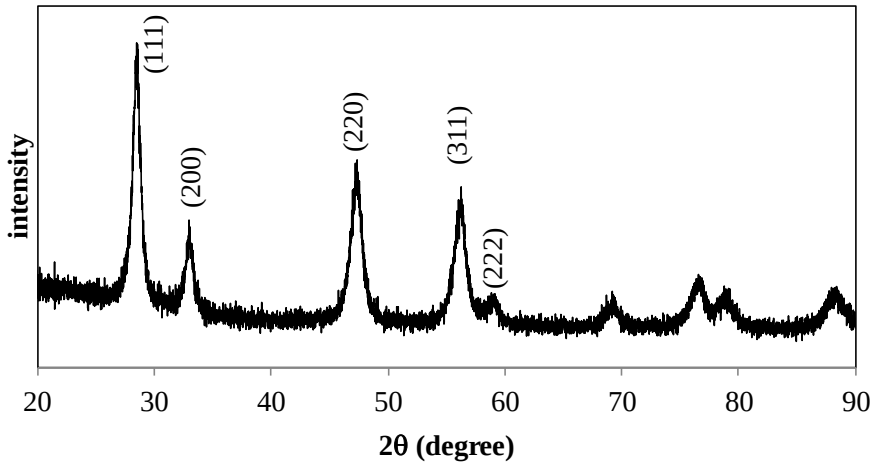


Fig. S12. XRD pattern of MARIMO CeO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

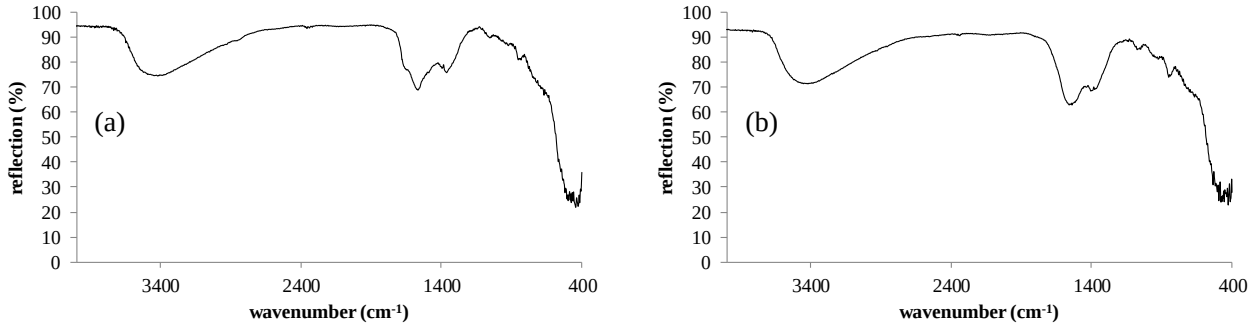


Fig. S13. FTIR spectra of MARIMO CeO_2 nanoparticles prepared at (a) 300 °C and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

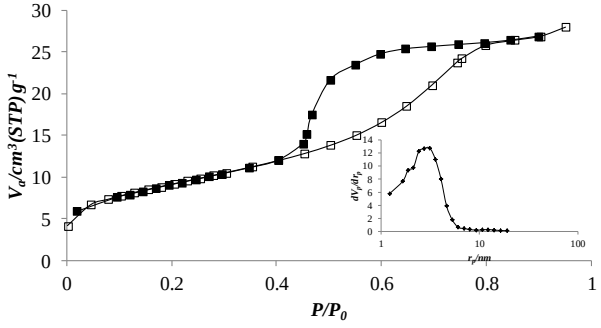


Fig. S14. Nitrogen adsorption–desorption isotherm and BJH pore size distribution plots of MARIMO CeO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

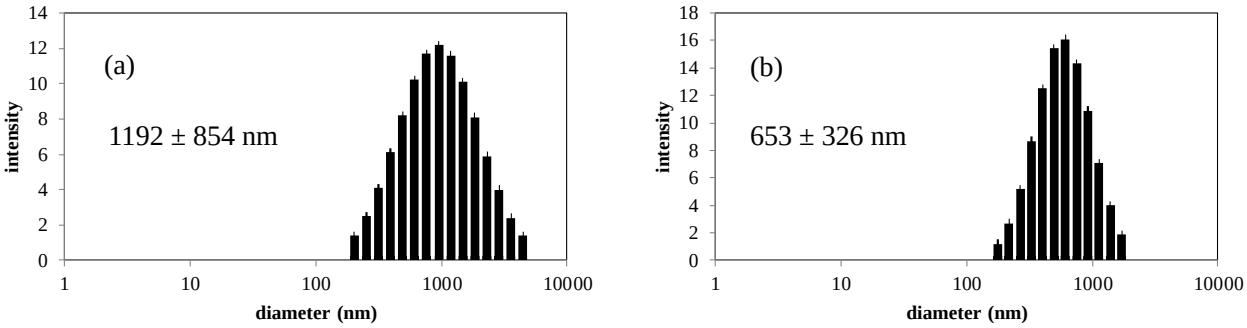


Fig. S15. DLS spectra of MARIMO CeO_2 nanoparticles prepared at (a) 300 °C and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

4. Synthesis of MARIMO ZnO nanoparticles in the presence of formic acid in supercritical MeOH

Scheme S4 Reaction of $Zn(OCOCH_3)_2 \cdot 2H_2O$ with formic acid in scMeOH at 300 or 400 ºC for 10 min in 0.28 g mL^{-1} MeOH density.

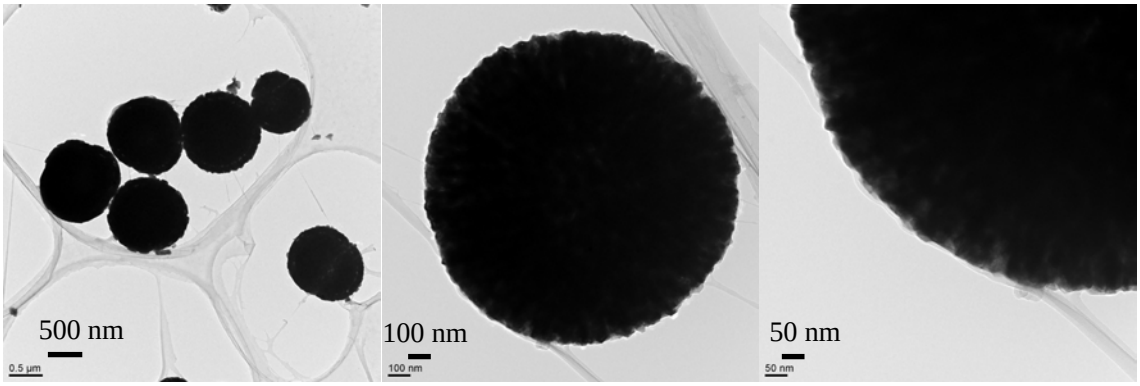


Fig. S16. TEM images of MARIMO ZnO nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

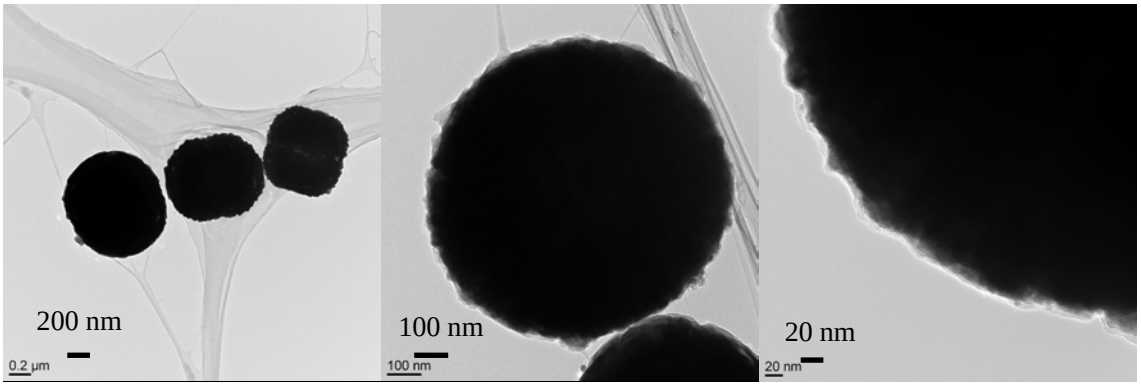


Fig. S17. TEM images of MARIMO ZnO nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

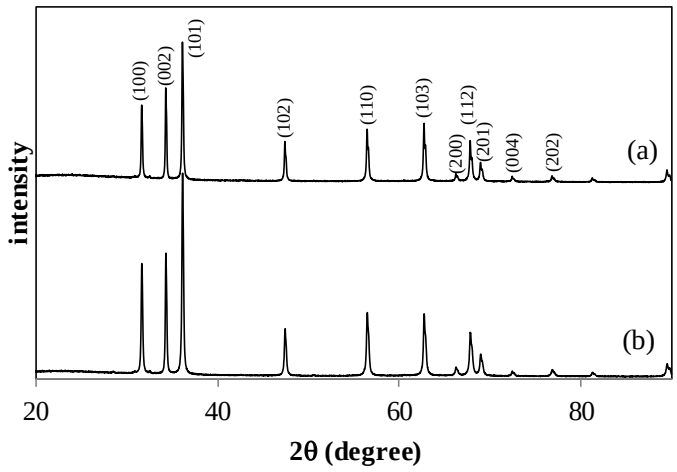


Fig. S18. XRD patterns of MARIMO ZnO nanoparticles prepared at (a) 300 °C and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

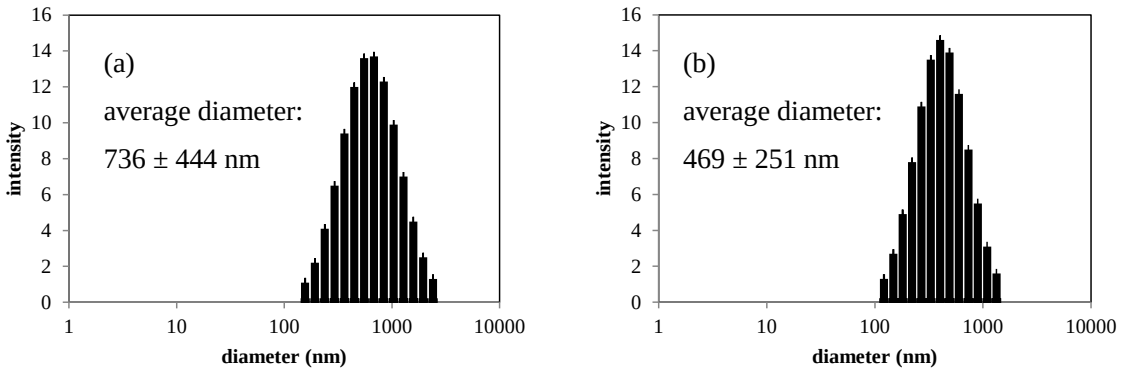
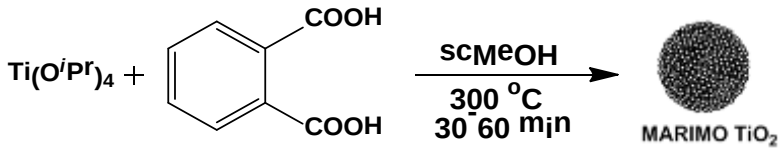


Fig. S19. DLS plots of MARIMO ZnO nanoparticles prepared at (a) 300 and (b) 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of formic acid.

5. Synthesis of MARIMO TiO_2 nanoparticles in the presence of phthalic acid in different reaction times in supercritical MeOH



Scheme S5 Reaction of Ti(O^iPr)$_4$ with phthalic acid in scMeOH at 300 ºC for 30 or 60 min in 0.28 g mL^{-1} MeOH density.

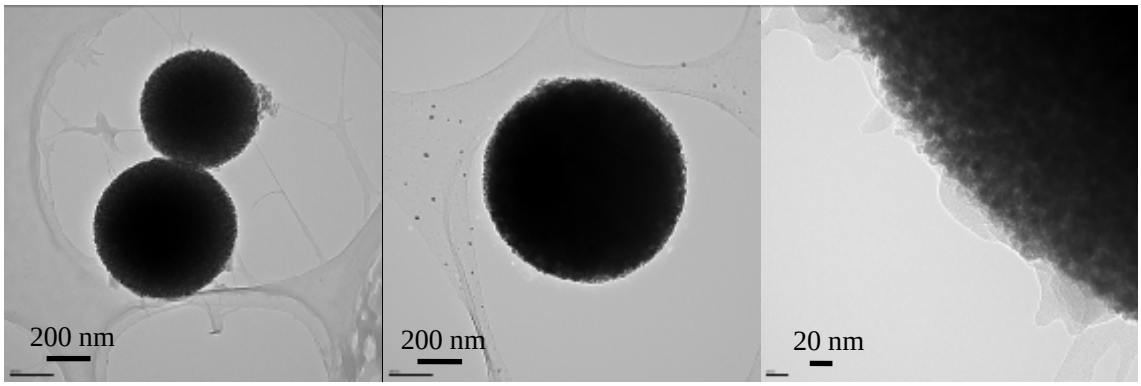


Fig. S20. TEM images of MARIMO TiO_2 nanoparticles prepared at 300 °C for 30 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid.

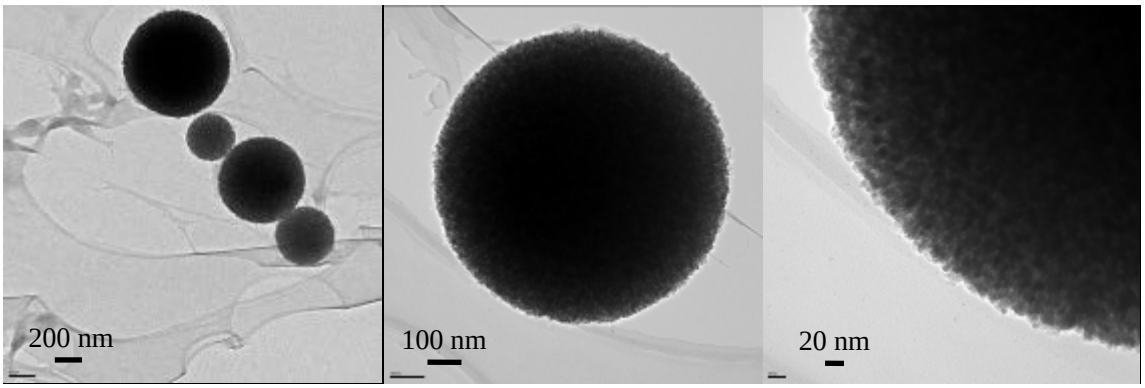


Fig. S21. TEM images of MARIMO TiO_2 nanoparticles prepared at 300 °C for 60 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid.

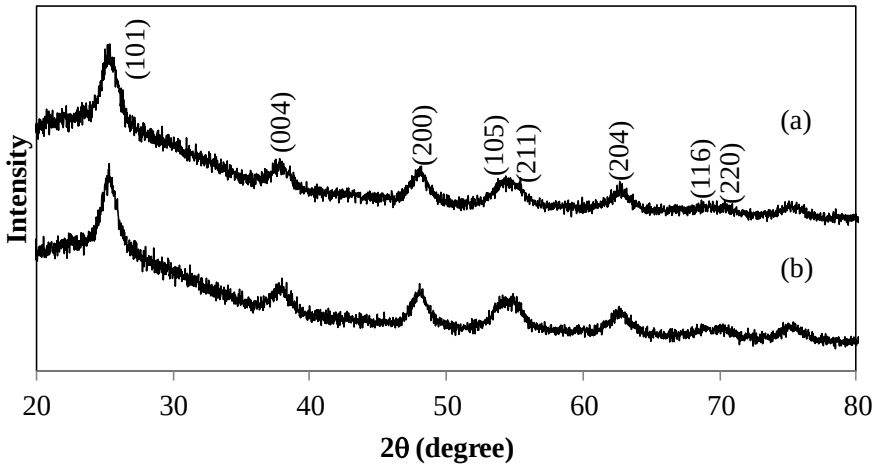
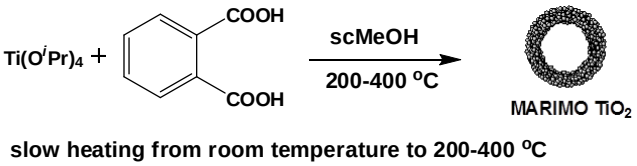


Fig. S22. XRD pattern of MARIMO TiO_2 nanoparticles prepared at 300 °C for (a) 30 min and (b) 60 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid.

6. Synthesis of hollow MARIMO TiO_2 nanoparticles in the presence of phthalic acid in supercritical MeOH with slow heating

The reaction was performed under the conditions of 200-300 ºC, 10 min, and 0.28 g mL^{-1} MeOH density with slow heating (ca. 2.0, 5.4, and 10.0 ºC/min) from room temperature (Scheme S5). Then, the reaction was quenched by putting the reactor into ice-water bath or slow cooling (5.4 ºC/min) to room temperature.



Scheme S5 Reaction of Ti(O^{i}Pr)$_4$ with phthalic acid in scMeOH at 200-400 ºC for 10 min in 0.28 g mL^{-1} MeOH density with slow heating.

6.1 Reaction of $Ti(O^iPr)_4$ with phthalic acid in scMeOH at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density with slow heating (5.4 °C/min).

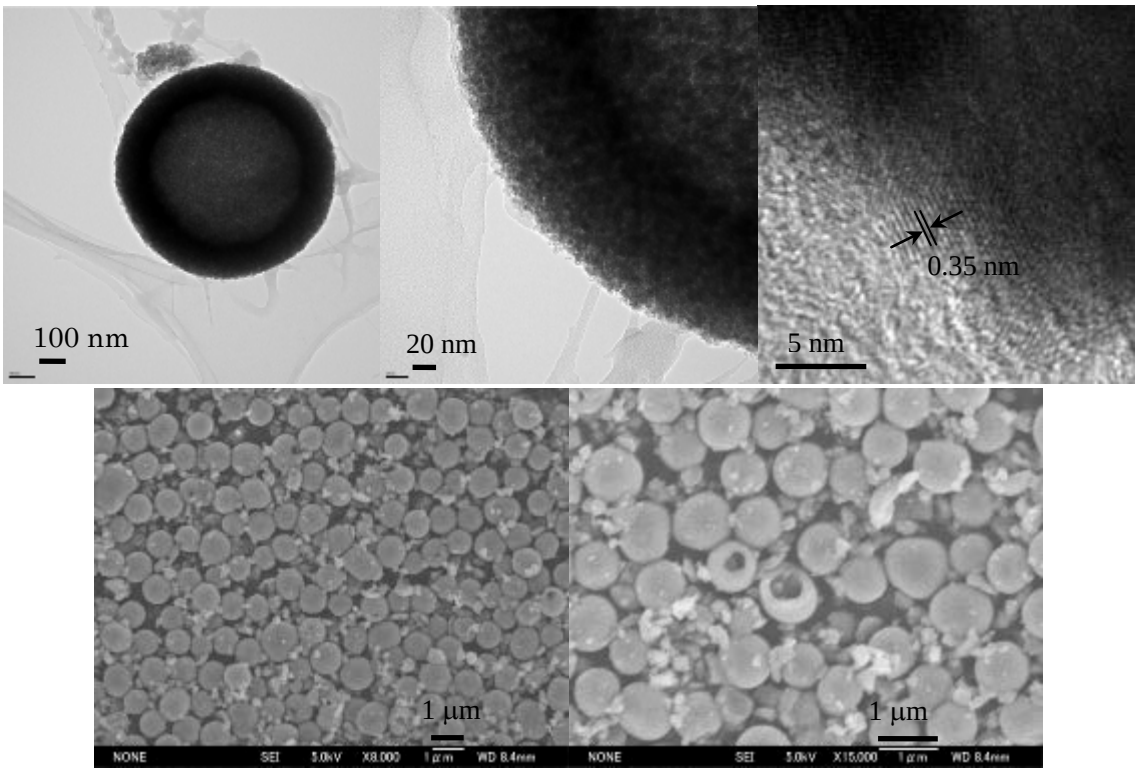


Fig. S23. TEM and FESEM images of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid (slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min).

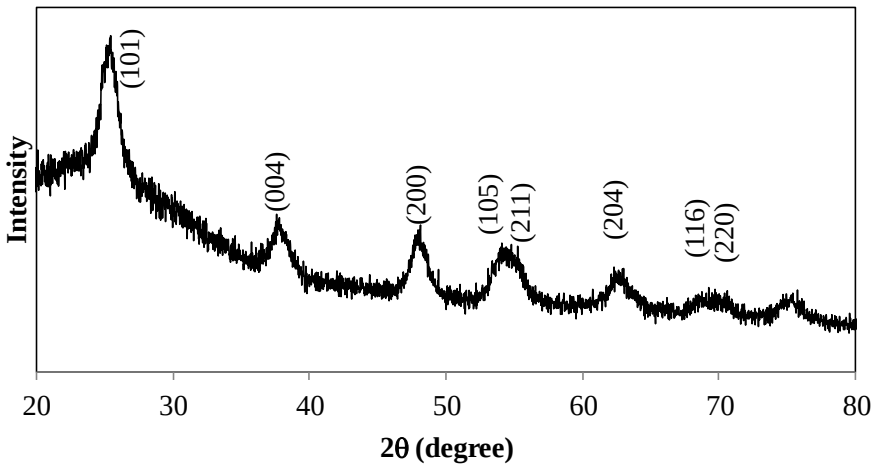


Fig. S24. XRD patterns of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid with slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min.

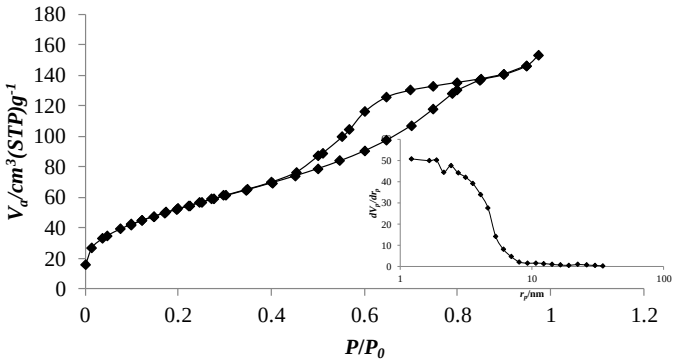


Fig. S25. Nitrogen adsorption–desorption isotherm and BJH pore size distribution plots of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid. (slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min).

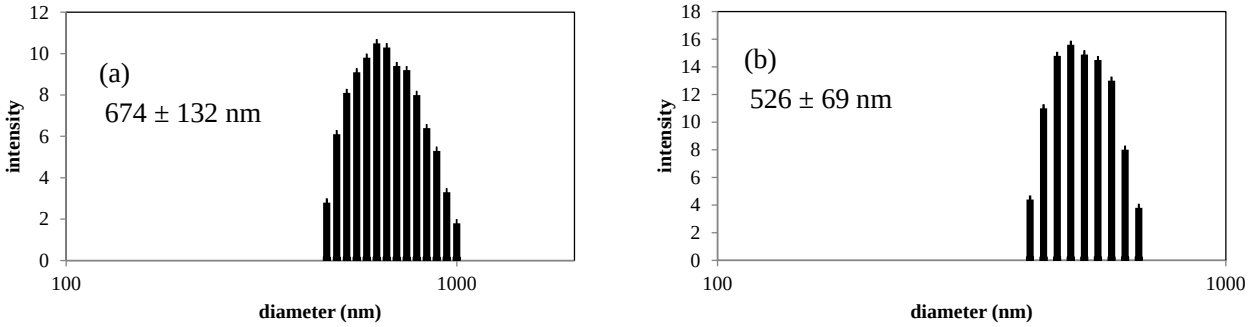


Fig. S26. DLS spectra of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid; (a) slow heating: 5.4 °C/min and the reaction was quenched by ice water and (b) slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min.

6.2 Reaction of $Ti(O^iPr)_4$ with phthalic acid in scMeOH at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density with slow heating (5.4 °C/min).

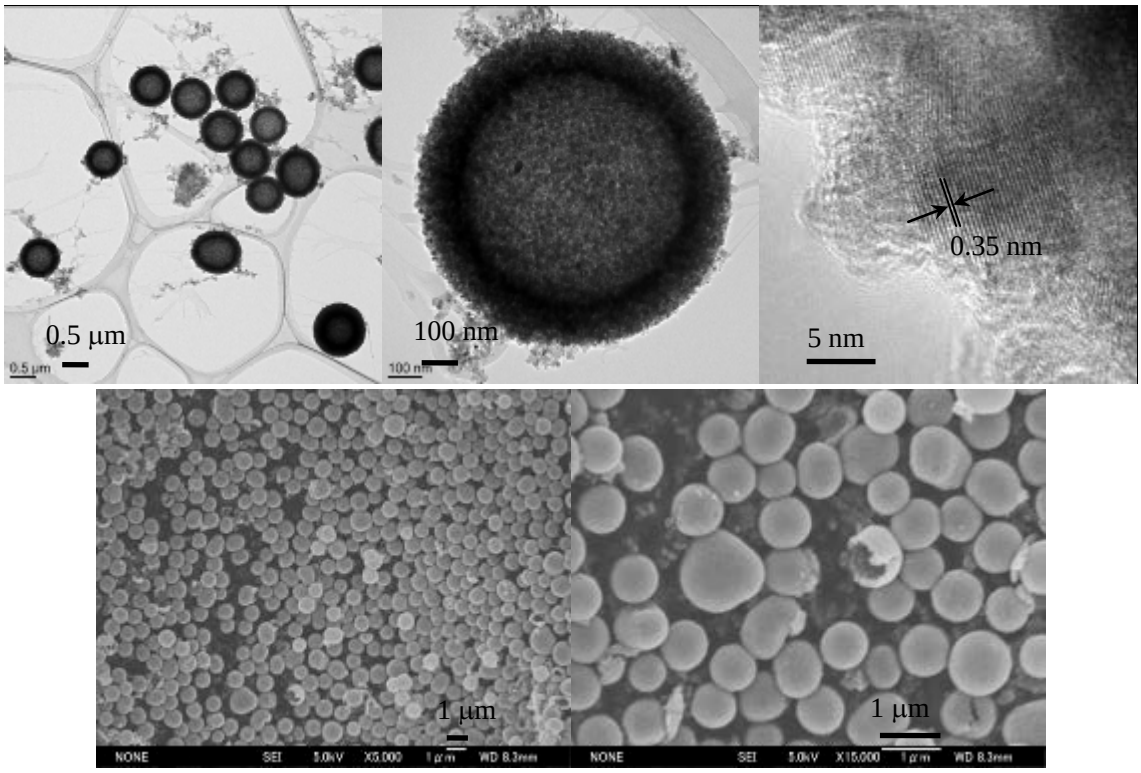


Fig. S27. TEM and FESEM images of MARIMO TiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid. (slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min)

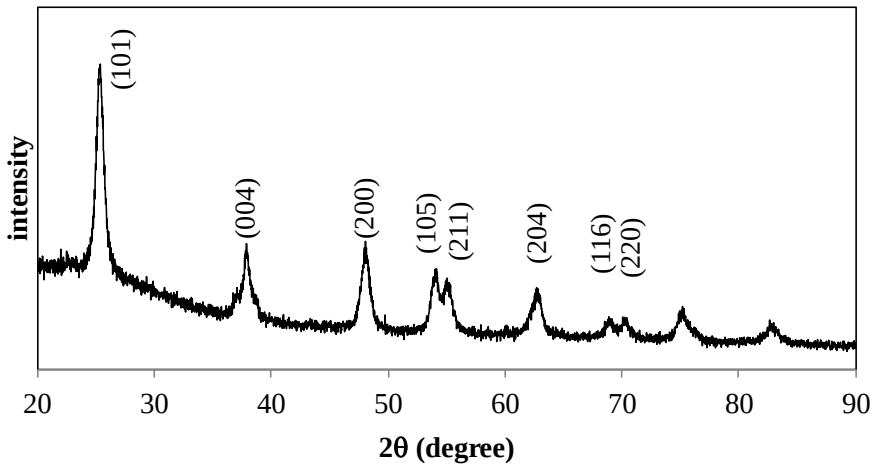


Fig. S28. XRD pattern of MARIMO TiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid. (slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min)

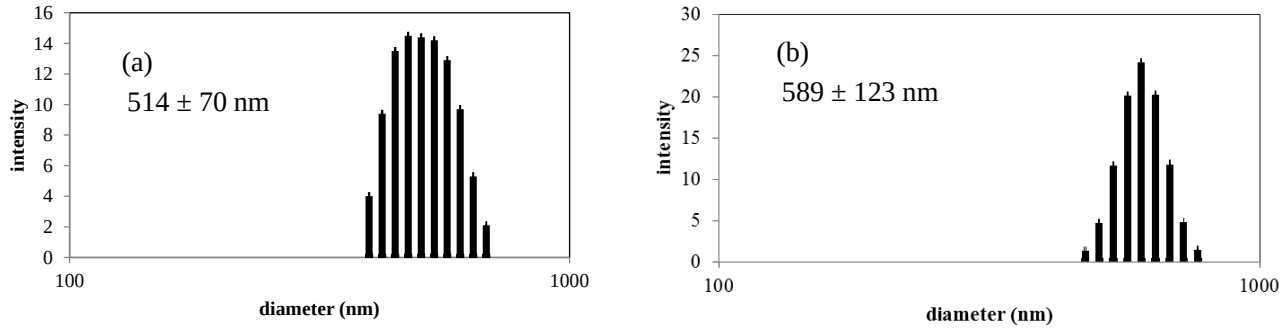


Fig. S29. DLS spectra of MARIMO TiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid, (a) slow heating: 5.4 °C/min and the reaction was quenched by putting the reactor into ice-water bath; (b) slow heating: 5.4 °C/min and slow cooling: 5.4 °C/min.

6.3 Reaction of $Ti(O^iPr)_4$ with phthalic acid in scMeOH at 200 °C for 10 min and 0.28 g mL^{-1} density with slow heating (5.4 °C/min).

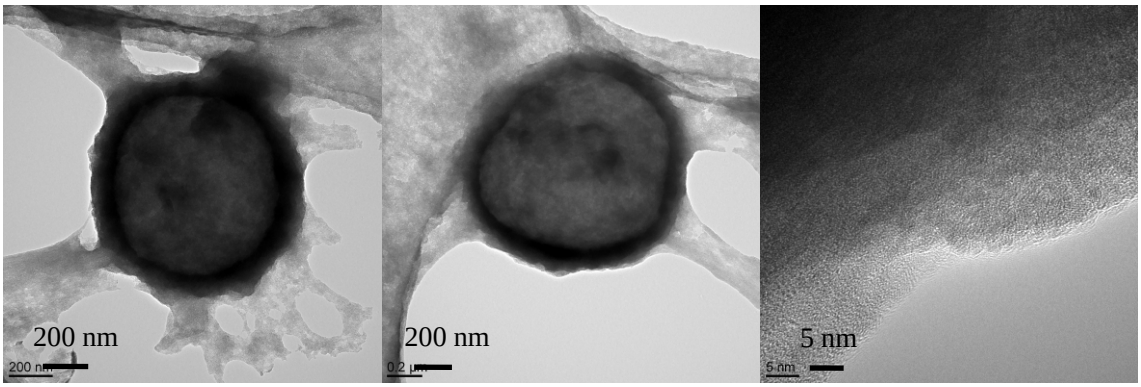


Fig. S30. TEM images of MARIMO TiO_2 nanoparticles prepared at 200 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid (slow heating: 5.4 °C/min and the reaction was quenched by putting the reactor into ice-water bath).

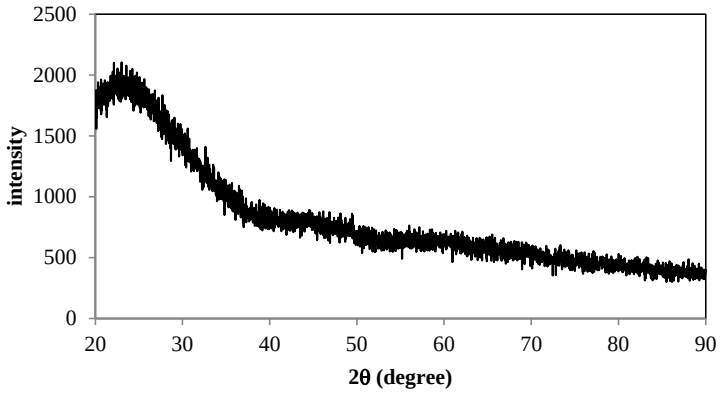


Fig. S31. XRD pattern of MARIMO TiO_2 nanoparticles prepared at 200 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid (slow heating: 5.4 °C/min and the reaction was quenched by putting the reactor into ice-water bath).

6.4 Reaction of $Ti(O^iPr)_4$ with phthalic acid in scMeOH at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density with slow heating (2 and 10 ºC/min).

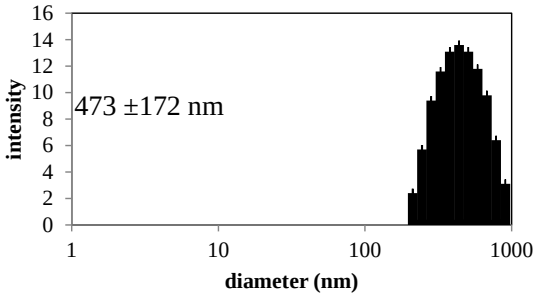


Fig. S32. DLS spectrum of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid (slow heating: 2 °C/min and the reaction was quenched by putting the reactor into ice-water bath).

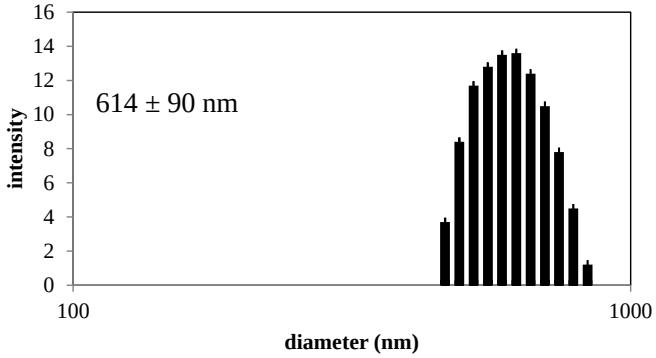
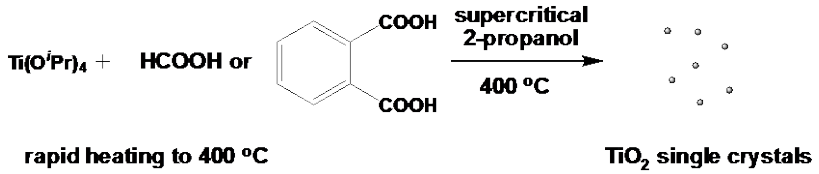


Fig. S33. DLS spectrum of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid (slow heating: 10 °C/min and the reaction was quenched by putting the reactor into ice-water bath).

7. Effect of reaction media

The reaction was performed in supercritical 2-propanol in the presence of HCOOH or phthalic acid under the conditions of 400 ºC, 10 min, and 0.28 g mL^{-1} 2-propanol density (Scheme S6).



Scheme S6 Reaction of Ti(O^iPr)$_4$ with phthalic acid in supercritical 2-propanol at 400 ºC for 10 min in 0.28 g mL^{-1} 2-propanol density.

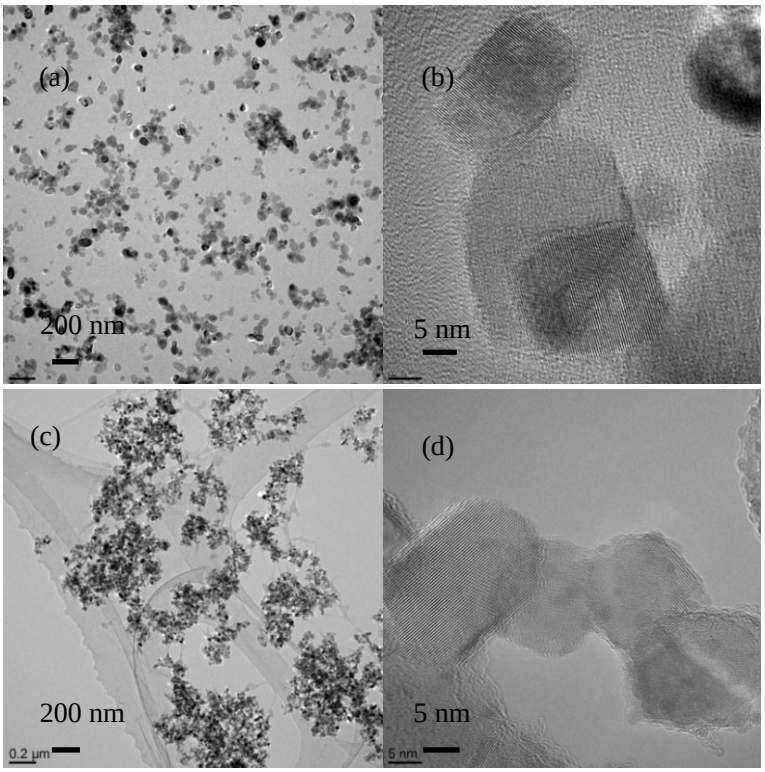


Fig. S34. TEM images of prepared TiO_2 nanoparticles at 400 °C for 10 min in 0.28 g mL^{-1} 2-propanol density, (a and b) in the presence of phthalic acid; (c and d) in the presence of HCOOH.

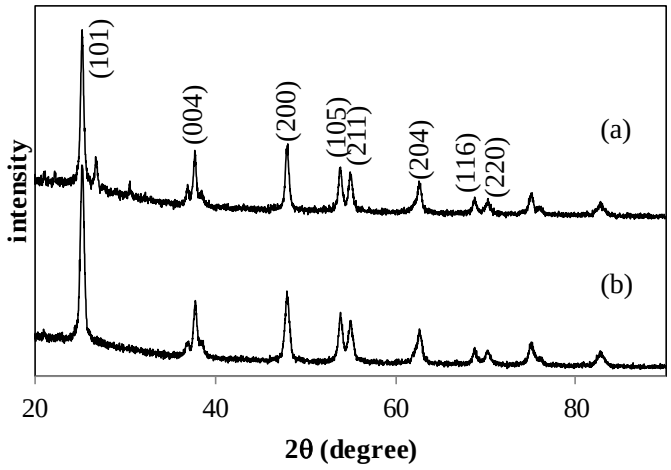
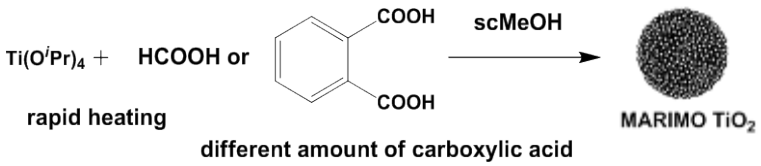


Fig. S35. XRD patterns of TiO_2 nanoparticles prepared at 400 °C for 10 min in 0.28 g mL^{-1} 2-propanol density, (a) in the presence of phthalic acid; (b) in the presence of HCOOH.

8. Effect of carboxylic acid amount



Scheme S7 Reaction of Ti(O^{i}Pr)$_4$ with different amount of HCOOH or phthalic acid in scMeOH at 300 ^{o}C for 10 min in 0.28 g mL^{-1} MeOH density.

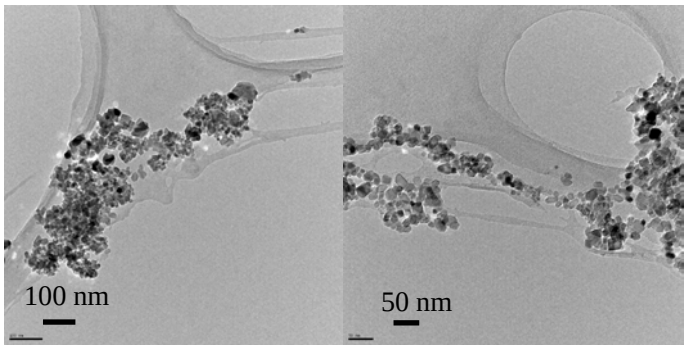


Fig. S36. TEM images of TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in scMeOH without carboxylic acid.

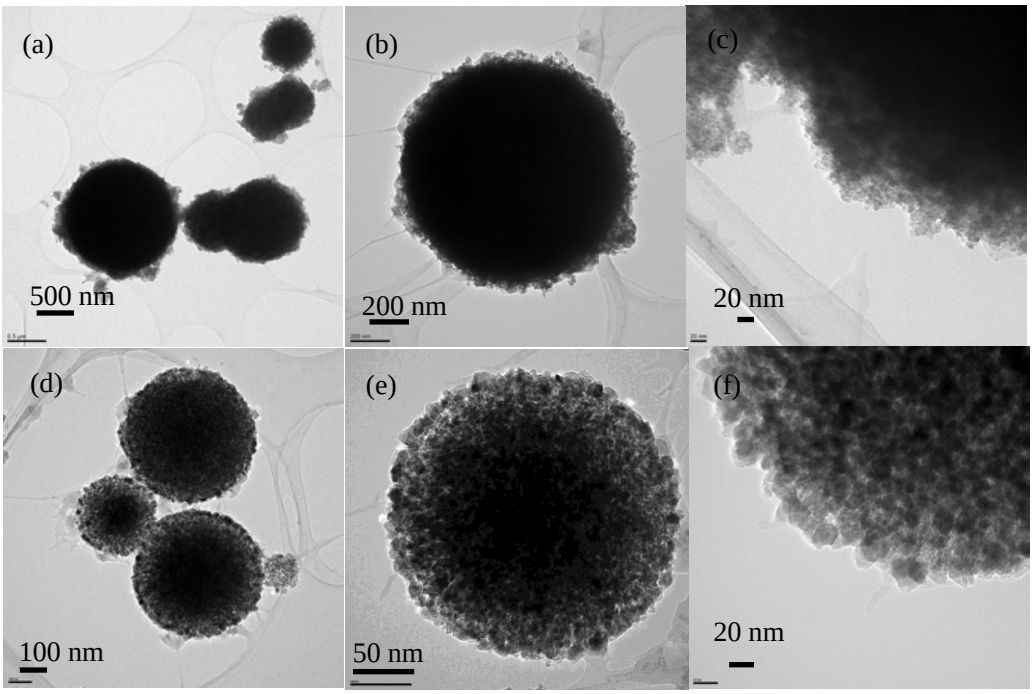


Fig. S37. TEM images of TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in scMeOH in the presence of HCOOH, (a, b, and c) Ti(O^{i}Pr)$_4$:HCOOH = 1:1; (d, e, and f) Ti(O^{i}Pr)$_4$:HCOOH = 1:10.

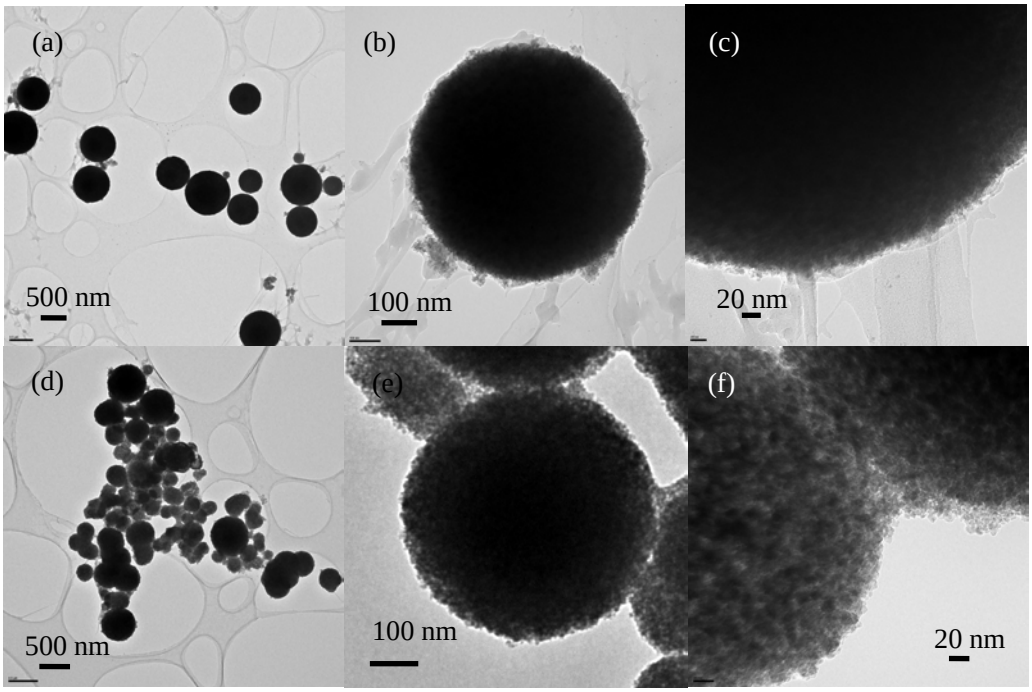


Fig. S38. TEM images of TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in scMeOH, (a, b, and c) $Ti(O^iPr)_4$:phthalic acid = 1:1; (d, e, and f) $Ti(O^iPr)_4$:phthalic acid = 1:10.

9. Photocatalytic reaction by MARIMO TiO_2 nanoparticles

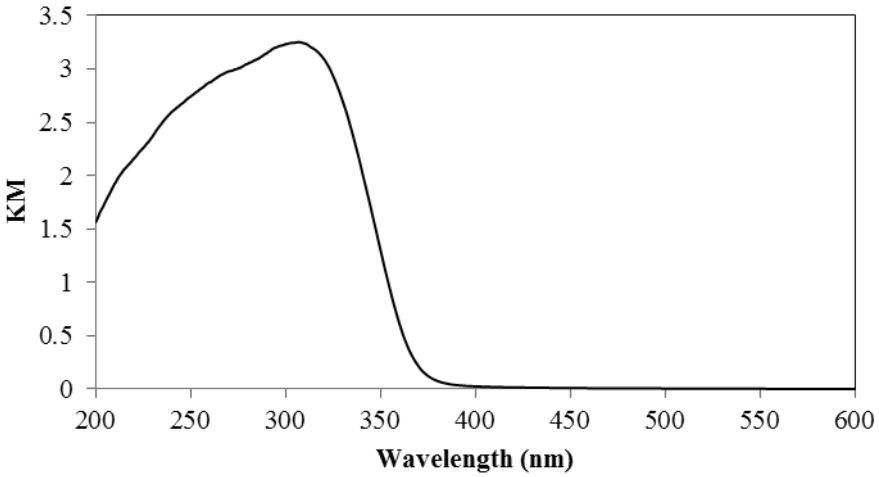


Fig. S39. UV-vis spectrum of MARIMO TiO_2 nanoparticles prepared at 300 °C for 10 min in 0.28 g mL^{-1} MeOH density in the presence of phthalic acid.