

Electronic Supporting Information (ESI)

Template-free synthesis of TiO₂ microspheres with tunable particle size via a non-aqueous sol-gel process

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Experiment

1. Preparation

All the reagents were purchased from Sinopharm Chemical Reagent Co. and used as received without further purification. TiO₂ microspheres were prepared by a non-aqueous route using alcohols as solvent. The solvent was pure ethanol, pure methanol, or the mixture of ethanol and methanol. In a typical procedure, 1.3 ml titanium isopropoxide (TTIP) was dissolved in solvent (30 mL) to get a transparent solution. 0.35 mL of formic acid was mixed with the solution. In the solution, the molar ratio of formic acid/Ti is 2.1. The solution was sealed within a Teflon-lined autoclave (40 mL) which is filled about 80% of its capacity and heated at 150 °C under a solvothermal condition for 6 h. The solid products were collected by centrifugation, washed with ethanol several times, and then dried in air at 80 °C for 12 h. The samples prepared with various parameters, such as the reaction time, the temperature, the amount of formic acid and the amount of methanol, were carried out.

2. Characterization

Powder X-ray diffraction (XRD) was used to characterize the samples. Data were collected on an X-ray diffractometer (XRD-6000, Shimadzu) equipped with a monochromator of graphite for Cu K α radiation ($\lambda=1.54178 \text{ \AA}$) at a beam current of 40 mA. The morphologies and size distributions of the samples were investigated by using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) with cold field emitter. The size distribution of the sample was obtained on the basis of statistical analysis of at least 400 randomly selected objects in a FE-SEM image. Transmission

electron microscopy (TEM) was carried out on a Philips CM200 with accelerating voltage of 160 kV.

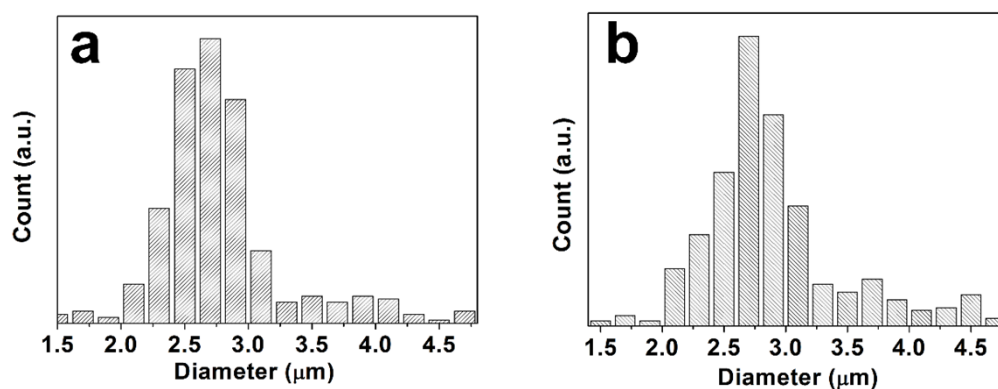


Figure S1. The size distribution of the microspheres prepared in ethanol for (a) 1 h and (b) 6 h.

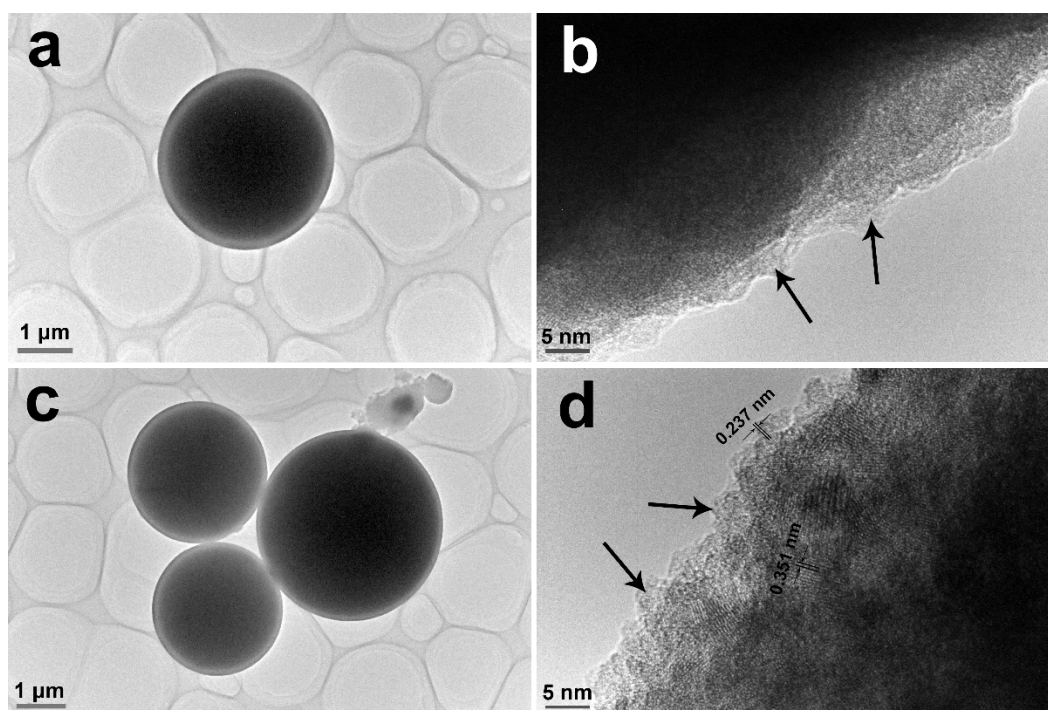


Figure S2. TEM images of the samples prepared in ethanol for (a and b) 1 h, (c and d) 6 h.

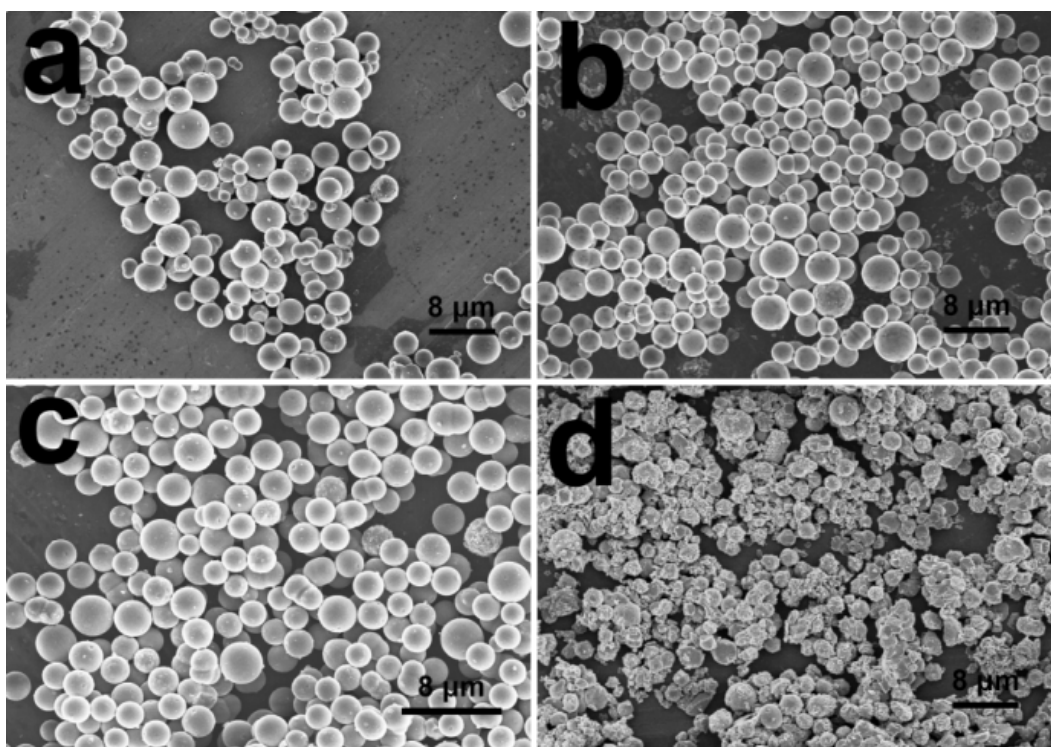


Figure S3. FE-SEM images of the samples prepared in ethanol with various molar ratio of formic acid/Ti: (a) 1.8, (b) 2.4, (c) 2.7, (d) 3.0.

Fig. S3 shows FE-SEM images of the samples prepared in ethanol with various molar ratio of formic acid/Ti. In Fig. S3a, the samples prepared with formic acid/Ti = 1:1.8 are composed of some aggregated microspheres. In Fig. S3b-c, highly dispersed microspheres with smooth surfaces are obtained in the samples prepared with formic acid/Ti = 2.4 and 2.7. In Fig. S3d, the sample prepared with formic acid/Ti = 3 show irregular spherical morphology. According to Fig. S3, well-defined TiO₂ microspheres are formed when the molar ratio of formic acid/Ti is about 2.

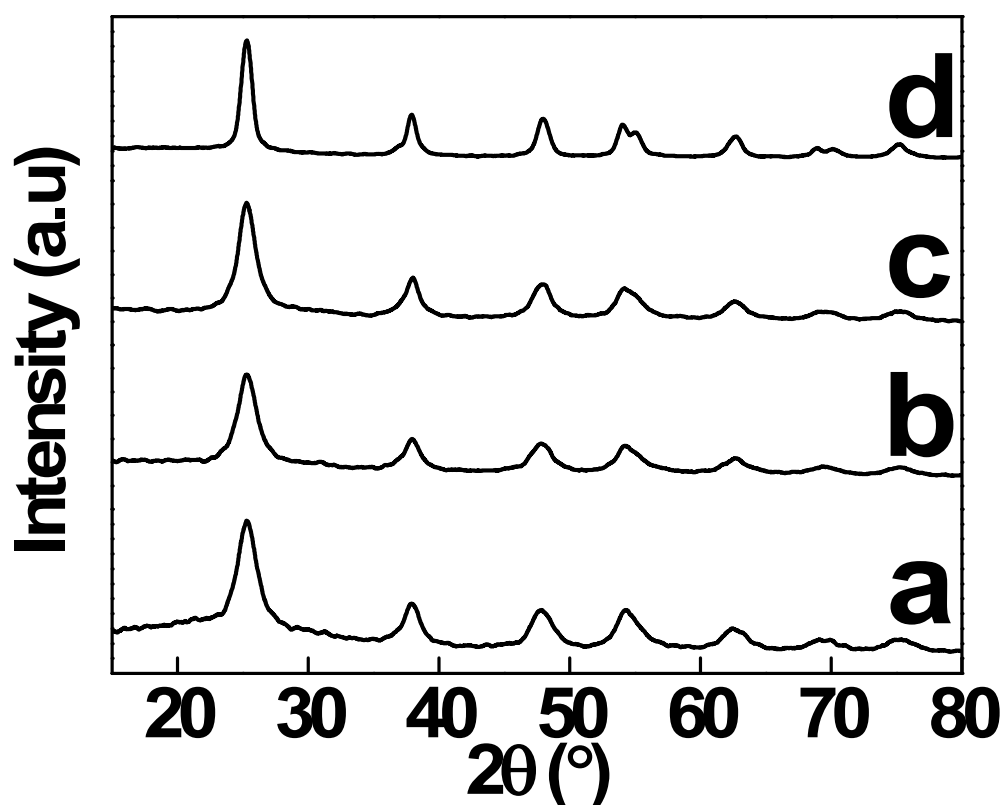


Figure S4. XRD patterns of the samples prepared in ethanol with various molar ratio of formic acid/Ti: (a) 1.8, (b) 2.4, (c) 2.7, (d) 3.0.

Fig. S4 shows XRD patterns of the samples prepared in ethanol with various molar ratio of formic acid/Ti. All the diffraction peaks of the samples are assigned to anatase. No impurity peaks are observed in the samples, indicating that highly crystalline anatase is synthesized by the facile non-aqueous route. In the curve a, the sample prepared with formic acid/Ti = 1.8 has relatively low crystallinity about 80% and the crystal size estimated by Debye-Scherrer equation is about 4.8 nm. In the curve b-d, the crystal sizes of the sample prepared with formic acid/Ti = 2.4, 2.7 and 3 are 4.7, 5.3 and 9 nm, respectively, indicating that the crystal size increases as the amount of formic acid increases.

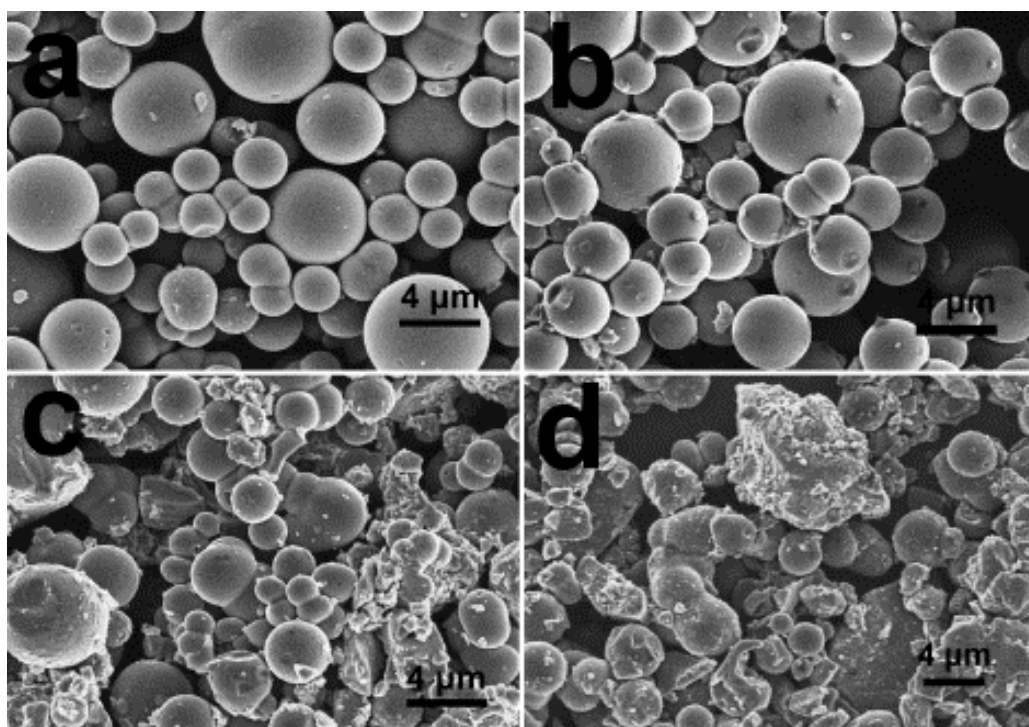


Figure S5. FE-SEM images of the samples prepared in ethanol at various temperatures: (a) 140 °C, (b) 160 °C, (c) 170 °C and (d) 200 °C.

Fig. S5 shows FE-SEM images of the samples prepared in ethanol at various temperatures. In Fig. S5a-b, the microspheres are formed in the samples prepared at 140 °C and 160 °C. In Fig. S5c, some objects with irregular shape and aggregated microspheres are observed in the sample prepared at 170 °C. In Fig. S5d, large objects with irregular shape appear in the sample prepared at 200 °C. According to Fig. S5, well-defined TiO₂ microspheres can be prepared at 150 °C and high temperature is unfavorable for the formation of well-defined TiO₂ microspheres.

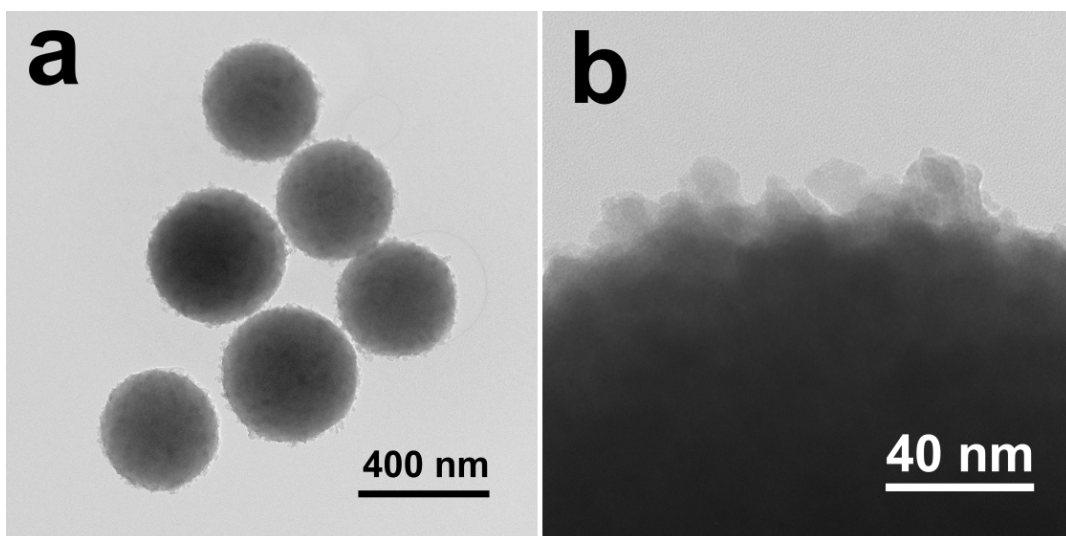


Figure S6. TEM images of the sample prepared with 30 ml methanol, (a) low magnification, (b) high magnification.