High Performance Separation of Aerosol Sprayed Mesoporous TiO_2 Sub Microspheres from Aggregates via Density Gradient Centrifugation

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A comparison of as-prepared TiO_2 materials with typical reported TiO_2 materials (100-1000 nm) is shown in Table S1. Based on the information in the table, our work is the first to report a uniform mesoporous TiO_2 NPs in the range of 100-200 nm with a narrow size distribution and covers the entire size range from 10 nm to 1000 nm.

Experimental details:

A home-made atomizer was employed and air was used as carrier gas. The titanium precursor solution was made by dissolving 50 mmole $Ti(OBu)_4$ (97% from Sigma Aldrich), 60 mmole HCl, and 0.2 mole HOAc into approximately 60 mL ethanol. After strong stirring for two hours, 6.0 g of F127 ($EO_{106}PO_{70}EO_{106}$, $M_{W:}$ 12600) were added into the precursor solution. The solutions were stirred vigorously for one more hour before the aerosol spray process. During the spray process, the temperature of the furnace was kept at 400 °C. The volumetric flow rate of air was about 5 L (STP) /min, and the time of droplets in furnace was less than 5 s, which was enough for evaporation of ethanol. The dry powder was collected by using a 0.45 μm filer. These as-synthesized mesostructured hybrid spheres were then calcined at 350 °C (ramp rate 1 °C/min) in air for 5 hours to obtain mesoporous spheres.

The porous and crystal structures of the materials synthesized by aerosol technique without further fractionation were studied by using Nitrogen sorption, TEM, and XRD. The surface area of the sub-microspheres was 155 m^2/g with an average pore size of 6.4 nm. These were calculated from adsorption branch based on BJH model. WAXRD confirmed that anatase-phase, rather than rutile-phase, TiO_2 was formed. The average crystallized grain size was 10 nm as calculated by Scherrer Equation.

Table S1. Comparison of properties between various TiO_2 materials

Titania related materials	Crystal phase	Particle size: Mean size nm	Particle size: Standard Deviation nm	Pore size	Surface area m^2/g	References	Year
Spherical colloids	Anatase/Rutile	400	80	-	-	Visca[5(a)]	1979
Spherical colloids	-	350	<10	-	-	Barringer[5(b)]	1982
Spherical colloids	-	400-500	<10	-	-	Jean[5(c)]	1986
Spherical colloids	Anatase/Rutile	500 400 320 200	13.8 5.2 9.7 11.6	-	-	Jiang[2(c)]	2003
Rhombic nano crystal	Anatase	10	<0.1	-	-	Wu[5(d)]	2008
Nanoporous spheres	Anatase	200	<20	2 nm to 30 nm	244.6	Zhong[5(e)]	2007
Mesoporous beads	Anatase	830	40	14 nm	108	Chen[3(b)]	2009
Mesoporous spheres	Anatase	119 201	<30 <50	6.4 nm	155	As-Prepared	2009

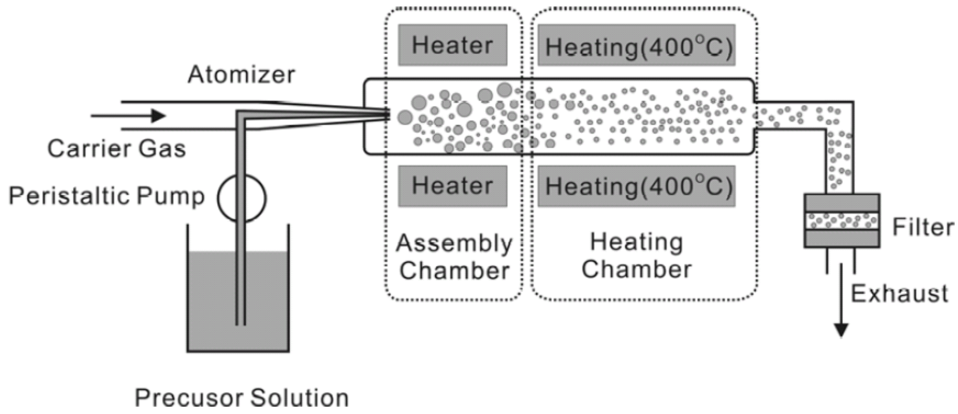

Figure S1. Schematic of the aerosol-assisted synthesis system.

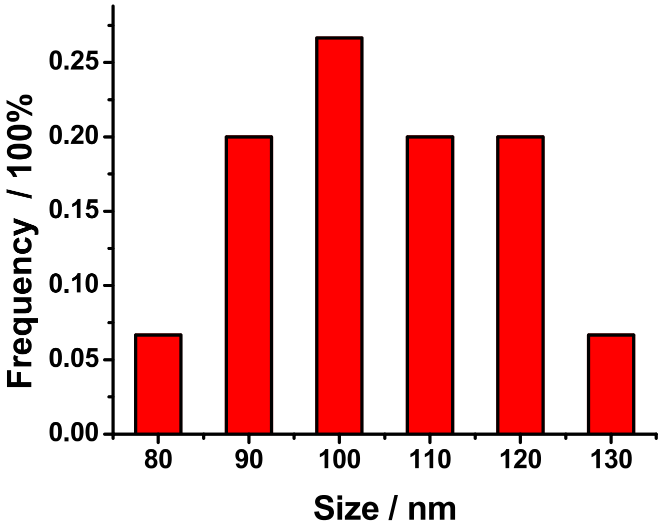

Figure S2. Size histogram of several fractions of TiO_2 nanospheres (TL114) separated after second-round centrifugation at 5000 rpm for 5 minutes. The calculation used about 20 particles in each fraction.

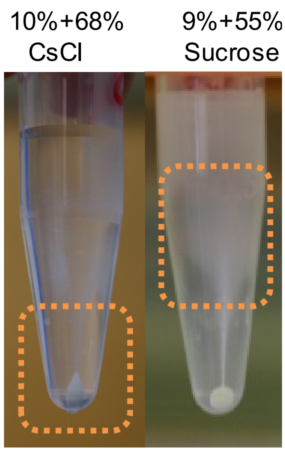

Figure S3. Digital camera images of differential centrifugation by using CsCl gradient and sucrose gradient, respectively