

Supplementary Information

A vesicle-aggregation-assembly approach to highly ordered mesoporous γ -alumina microspheres with shifted double-diamond networks

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Experimental Section

Chemicals.

Monomethoxy poly(ethylene oxide) (Mw 5000 g/mol) was purchased from Aldrich. 2-Bromoisobutyryl bromide (98%) was obtained from Acros. N,N,N',N'',N'''-pentamethyldiethylenetriamine (98%) was supplied by J&K China Chemical Ltd. Methyl methacrylate (CP), copper bromide (CP), aluminum isopropoxide (CP), 4-nitrophenol (AR), sodium borohydride (AR), H₂AuCl₄·4H₂O (AR), triethylamine (AR), ethylenediamine (AR), hydrochloric acid (37 wt%), tetrahydrofuran (AR), dichloromethane (AR), anhydrous diethyl ether (AR), acetic acid (AR), alcohol (AR), petroleum ether (60-90 °C) and neutral alumina (FCP, 200-300 mesh) were purchased from Sinopharm Chemical Reagent Co., Ltd. Monomer methyl methacrylate was purified by neutral alumina column to remove the polymerization inhibitor before used. CuBr was washed with acetic acid and alcohol for three times, respectively, and then dried under vacuum. Other chemicals were used as received without any further treatment. Millipore water was used in all experiments.

Synthesis of PEO₁₁₃-Br.

The macroinitiator monomethoxy poly(ethylene oxide)₁₁₃ with a bromic terminal group (PEO₁₁₃-Br) was synthesized by acylation of monomethoxy poly(ethylene oxide) (PEO₁₁₃) with 2-bromoisobutyryl bromide. Typically, PEO₁₁₃ (40 g) and triethylamine (7.3 mL) were mixed in dichloromethane (100 mL) under stirring. After 2-bromoisobutyryl bromide (3.24 mL) was quickly added into the above solution, the resultant solution in the sealed flask was kept stirring in an oil bath under 30 °C for 48 h. Then the solution was washed with water (80 mL) for two times, concentrated, and dripped into a large amount of anhydrous diethyl ether to precipitate PEO₁₁₃-Br. The product PEO₁₁₃-Br was collected by filtration and dried under vacuum.

Synthesis of PEO₁₁₃-*b*-PMMA₃₃₅.

Diblock copolymer poly(ethylene oxide)₁₁₃-*block*-poly(methyl methacrylate)₃₃₅ (PEO₁₁₃-*b*-PMMA₃₃₅) was prepared by an atom transfer radical polymerization (ATRP) method. Firstly, PEO₁₁₃-Br (2.5 g) and N,N,N',N'',N'''-pentamethyldiethylenetriamine (230 μL) were added into a mixed solution containing tetrahydrofuran (THF) (30 mL) and methyl methacrylate (MMA) (30 mL). Then the reaction solution in the sealed bottle was bubbled with argon for 30 min before copper bromide (75 mg) was added under argon atmosphere quickly. After bubbling for another 30 min, the resealed bottle was placed in an oil bath at 60 °C for 3 h under stirring. Afterwards, the resultant viscous solution was quickly taken out from the oil bath, cooled down to room temperature, diluted with dichloromethane and exposed to the air with stirring before it was filtered through a neutral alumina column to remove the copper complex using dichloromethane as an eluent. After the filtrate was concentrated under vacuum, PEO₁₁₃-*b*-PMMA₃₃₅ was precipitated in petroleum ether, collected by filtration and dried under vacuum.

Loading of Au Nanoparticles.

Au nanoparticles were loaded onto the ordered mesoporous γ -alumina *via* an impregnation-reduction approach. Firstly, ethylenediamine (115 μ L) was added into 0.10 g/mL $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ aqueous solution (2.0 mL) under stirring until a transparent orange solution was formed. Then alcohol (16 mL) was added to precipitate the $\text{Au}(\text{en})_2\text{Cl}_3$ complex, and the complex was separated by centrifugation, washed with alcohol for two times, and dried under vacuum at 40 $^\circ\text{C}$ for 1 day. $\text{Au}(\text{en})_2\text{Cl}_3$ (10 mg) was dissolved in water (5.0 mL), and the pH value was modified to 10 with NaOH aqueous solution (5.0 wt%). The mesoporous γ -alumina obtained after calcination at 900 $^\circ\text{C}$ in air (60 mg) was dispersed in the above solution under stirring for 1 h. The sample was separated by centrifugation, washed with water quickly, and dried under vacuum at 40 $^\circ\text{C}$ for 2 days. The sample was reduced with H_2/Ar (5.0 %) stream at 150 $^\circ\text{C}$ for 1 h, resulting in the Au/mesoporous γ -alumina composites.

Catalytic Reduction of 4-nitrophenol.

The reduction of 4-nitrophenol was carried out in a quartz cuvette and monitored by using a UV-vis spectroscopy at 25 $^\circ\text{C}$. Typically, 0.2 mM 4-nitrophenol aqueous solution (1.0 mL) was mixed with 0.1 M sodium borohydride aqueous solution (2.0 mL). Subsequently, 200 μ L of Au/mesoporous γ -alumina composites aqueous solution (0.2 mg/mL) was added, and the mixed solution was quickly subjected to UV-vis measurements for monitoring the absorption changes during the reaction in the range of 200-600 nm at 3 min intervals.

Measurements and Characterization.

^1H NMR spectrum was recorded on a Varian Mercury Plus 400 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal reference. The molecular weight distribution of the diblock copolymer PEO-*b*-PMMA was estimated by an Agilent 1100 gel permeation chromatography (GPC) system using THF as the eluent against polystyrene standards with a RID detector. Field-emission scanning electron microscopy (FESEM) images were taken by a Hitachi S4800 scanning electron microscope. Samples were directly dispersed onto conductive tapes attached on a sample holder for direct observation under vacuum. Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100F microscope (Japan) operated at 200 kV. The samples for TEM measurements were suspended in ethanol and dropped onto Cu grids. To load the as-made Al^{3+} -based gel/PEO₁₁₃-*b*-PMMA₃₃₅ composites, the Cu grids were mixed with composites and then fetched out for the tests. To obtain more detailed information during the solvent evaporation induced vesicle-aggregation-assembly process, cryo-transmission electron microscopy (cryo-TEM) images were taken on a FEI Tecnai G20 microscopy (Netherlands) operated at 200 kV, and the samples for cryo-TEM tests were made on a Vitrobot specimen-making machine by quickly freezing the reactant solution-loaded Cu grids with liquid nitrogen. Thermogravimetric analysis (TGA) experiments were conducted on a PerkinElmer TGA 4000 analyzer. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$).

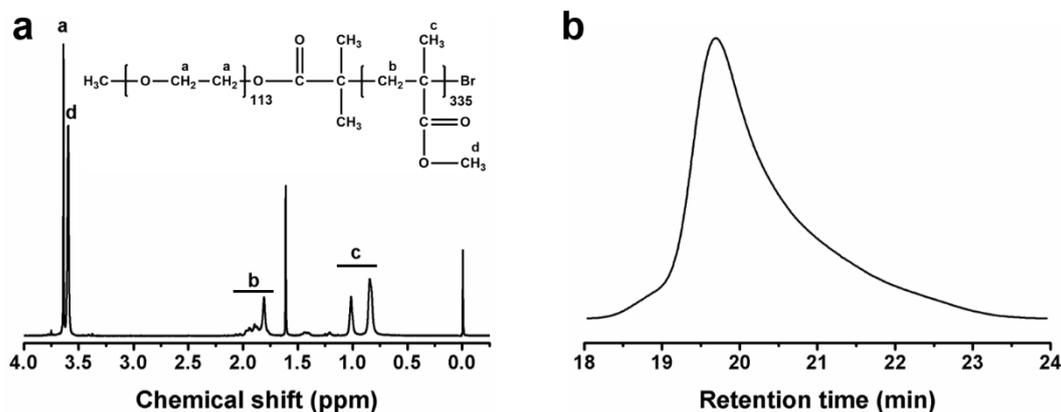


Fig. S1 (a) The ^1H NMR spectrum (400 MHz, CDCl_3) and (b) GPC plot of the block copolymer $\text{PEO}_{113}\text{-}b\text{-PMMA}_{335}$. The molecular weight of the PMMA block (M_{PMMA}) was determined by the formula:

$$\frac{M_{\text{PEO}}}{M_{\text{PMMA}}} = \frac{(I_a + d - I_c) \times 44/4}{I_c \times 100/3}$$

so the number of repetitive units calculated from M_{PMMA} is about 335. The polydispersity index (PDI) is 1.31, according to the GPC tests.

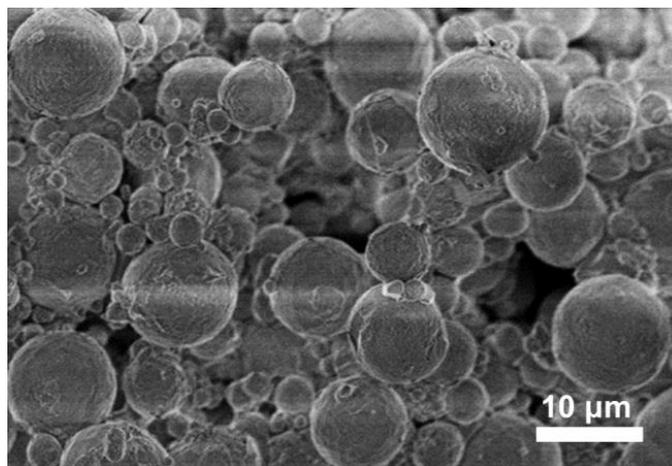


Fig. S2 The FESEM image of as-made Al^{3+} -based gel/PEO-*b*-PMMA composite microspheres prepared by the vesicle-aggregation-assembly approach.

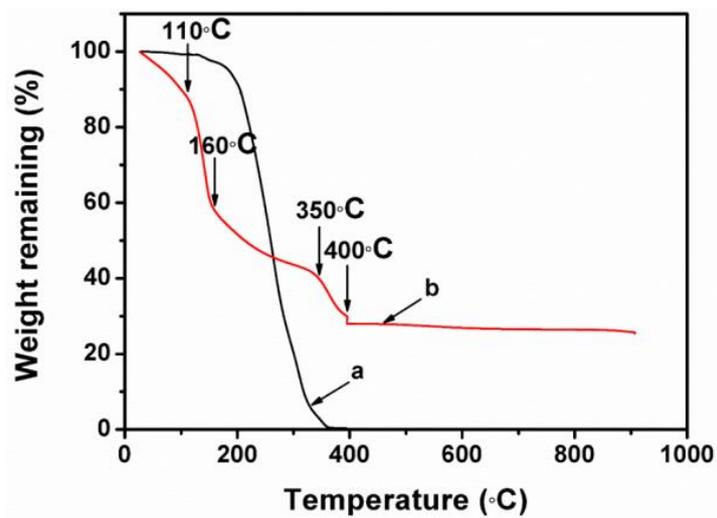


Fig. S3 TGA curves of (a) the diblock copolymer PEO-*b*-PMMA and (b) as-made Al³⁺-based gel/PEO-*b*-PMMA composites following the same ramping rate and holding time as that of mesoporous alumina obtained after calcination at 900 °C in air.

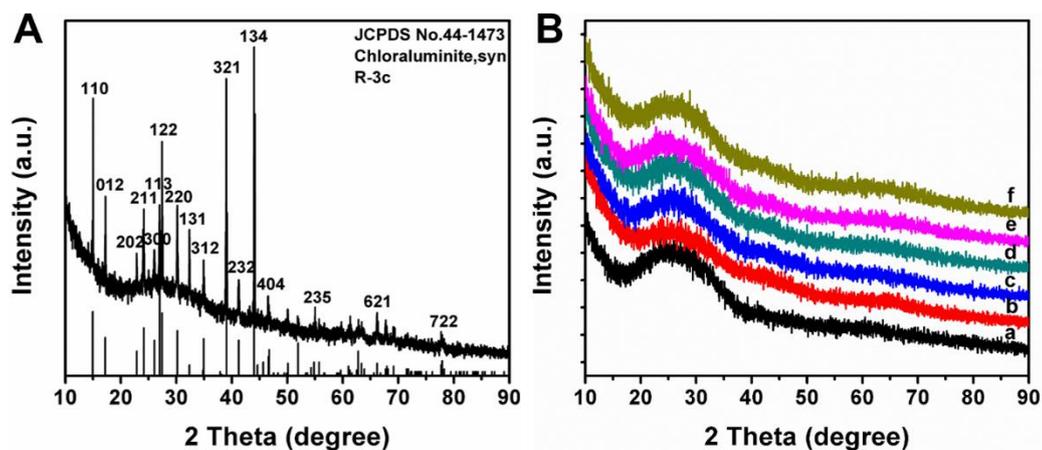


Fig. S4 Wide-angle XRD patterns of the intermediate products obtained after the as-made Al^{3+} -based gel/PEO-*b*-PMMA composites were calcined from 25 °C to (A) 100 °C, (B) (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C and (f) 350 °C with a ramp rate of 1 °C/min in air. The wide-angle XRD pattern shown in B(a) is corresponded to the glass substrate used as a sample support for a reference.

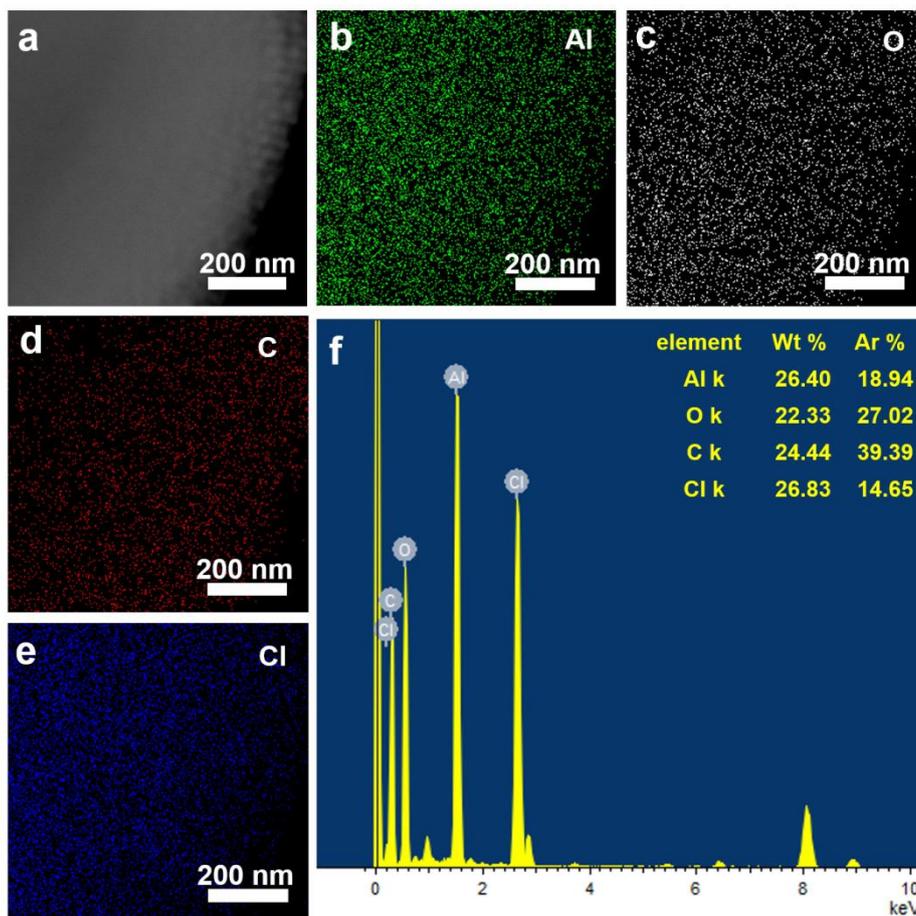


Fig. S5 (a) The dark-field scanning transmission electron microscopy (STEM) image, (b-e) the corresponding element mapping images (element Al, O, C and Cl) and (f) the energy dispersive X-ray (EDX) spectrum of the as-made Al^{3+} -based gel/PEO-*b*-PMMA composites prepared by the vesicle-aggregation-assembly approach. The table inserted in (f) shows the chemical composition of the selected area.

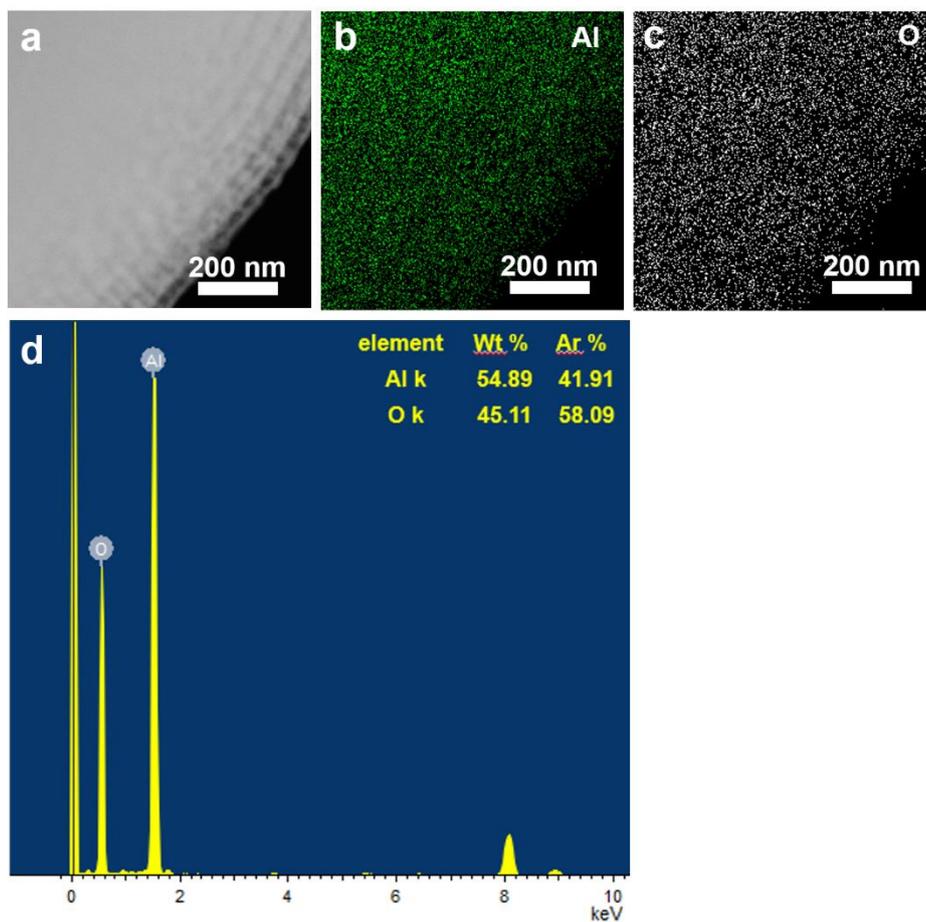


Fig. S6 (a) The STEM image, (b, c) the corresponding element mapping images (element Al and O) and (d) the EDX spectrum of the ordered mesoporous alumina microspheres obtained after calcination at 900 °C in air. The table inserted in (d) shows the chemical composition of the selected area.

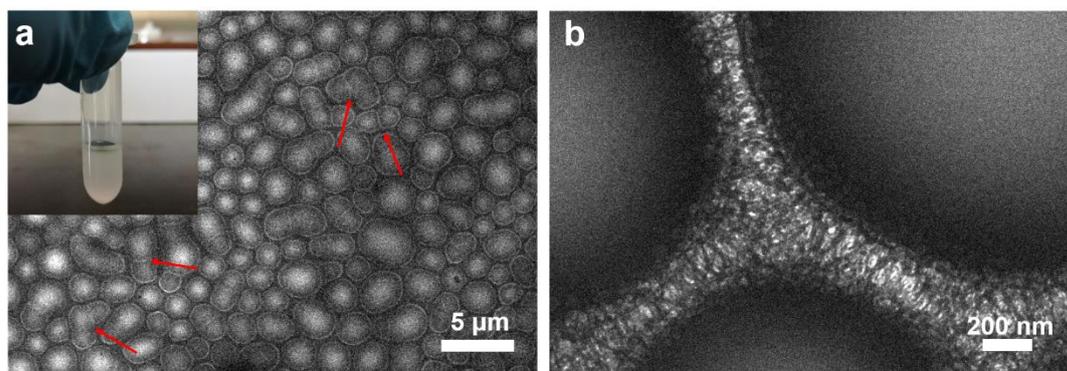


Fig. S7 Cryo-TEM images of the intermediate reaction solution taken from (a) a large area and (b) a local area after the evaporation of the reaction solvents at room temperature for 2 h. The inset in (a) shows the optical photograph of the intermediate reaction solution.

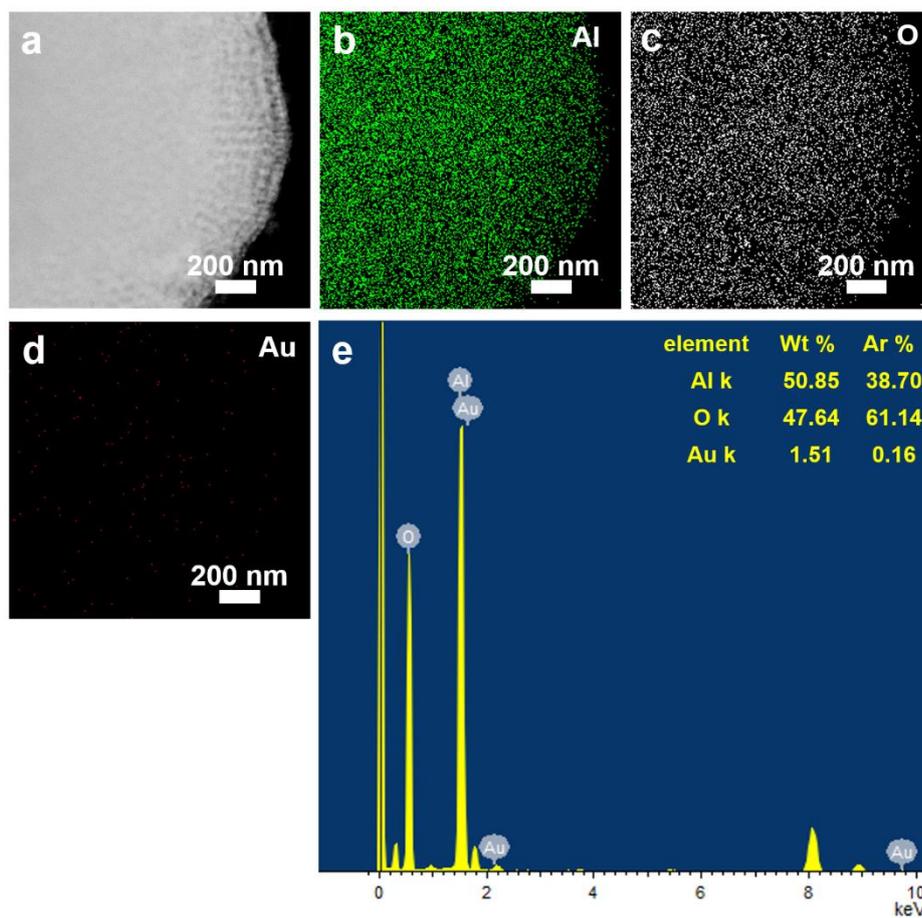


Fig. S8 (a) The STEM image, (b-d) the corresponding element mapping images (element Al, O and Au) and (e) the EDX spectrum of the Au/mesoporous γ -alumina composites after loading Au nanoparticles by an impregnation-reduction approach. The table inserted in (e) shows the chemical composition of the selected area.