Electronic Supplementary Information

A solvent extraction route for CaF_2 hollow spheres

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Experimental Section

Materials. The extractant di-2-ethylhexyl phosphoric acid (D2EHPA) was supplied by Tianjin Beicheng Chemical Plant (China) and used without further purification. The extractant N1923 is a primary amine, having two carbon chains branched. It was obtained from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences and purified by distillation under 667 kPa at 175-205 °C.[1] The stock organic solutions were prepared by dissolving a certain amount of extractant in *n*-heptane.

Preparation of CaF_2 hollow spheres. A typical synthetic procedure for CaF_2 hollow spheres is as follows: 10 mL of 0.9 mol L^{-1} D2EHPA organic solution and 10 mL of 0.3 mol L^{-1} $Ca(NO_3)_2$ aqueous solution were mixed in an equilibrium tube and then shaken for 30min with a mechanical shaker. The separation of each phase was achieved by centrifugation for 5 min. D2EHPA organic solution loaded Ca^{2+} was obtained. The N1923 organic solution loaded F^- was prepared by shaking the mixture of 10 mL of 0.2 mol L^{-1} N1923 organic solution and 5 mL of 1.0 mol L^{-1} HF aqueous solution for 30min. The N1923 organic solution loaded F^- was then added dropwise to the D2EHPA organic solution loaded Ca^{2+} with a Ca^{2+}/ F^- molar ratio of 1:2. The mixed solutions were then maintained at a static condition under ambient air for 12 h in polytetrafluoroethylene (PTFE) vial. Finally, the as-obtained precipitates were collected by centrifugation, washed with ethanol (3 min in an ultrasonic water bath) and dried in vacuum at 60 °C for 12 h.

Bulk CaF_2 particles were prepared by mixing stoichiometric amounts of 0.3 mol L^{-1} $Ca(NO_3)_2$ and 1.0 mol L^{-1} HF aqueous solutions.

Characterizations. The samples were characterized by X-ray powder diffraction using a BRUKER D8 FOCUS X-ray diffractometer with Cu Kα radiation (λ= 1.5418Å). Scanning electron microscopy (SEM) images were taken on a Hitachi-S4800 electron microscope equipped with an energy-dispersive X-ray spectrometer operated at 15.0 keV. High-resolution transmission electron microscopy (HRTEM) images were acquired by a FEI Tecnai G2 F20 transmission electron microscope at 200 kV. Dynamic light scattering (DLS) measurements (Zetasizer 1000HS, Malvern Instruments) were carried out at a constant temperature of 25 °C. Each sample was filtrated through a 0.45 μm hydrophobic Millipore filter to remove any dust particles. N_2 adsorption-desorption isotherms were measured at the liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 instrument. Samples were degassed at 180

ºC overnight before measurements. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) model, and the pore size distributions were evaluated from the desorption branches of the nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) model. A redox titration method using $KMnO_4$ as the titrant was used to determine the Ca^{2+} concentration in the aqueous solution. The F^- concentration in aqueous solution was measured by ion-selective electrode with pHs-3C acidimeter (Shanghai Precision & Scientific Instrument, China). The concentrations of Ca^{2+} and F^- in the organic solutions were determined by difference.

References

1 H. F. Gai, Z. L. Gao, S. X. Sun, L. Q. Zheng, and J. L. Shen, *Acta Chim. Sin.*, 1987, **45**, 383.

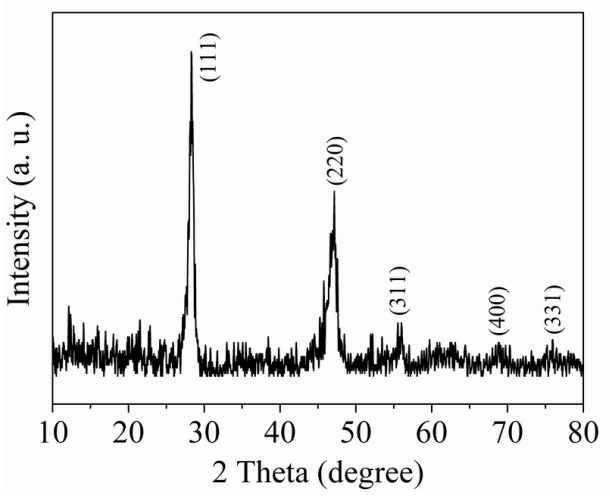

Fig. S1 XRD patterns of the as-obtained CaF_2 hollow spheres.

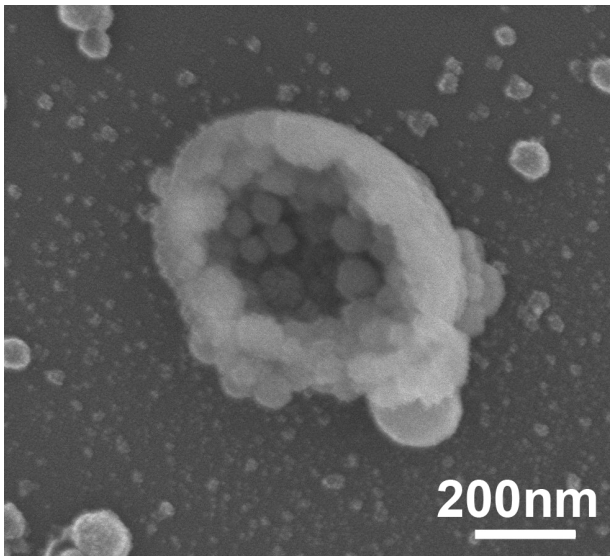

Fig. S2 SEM images of a broken CaF_2 hollow sphere.

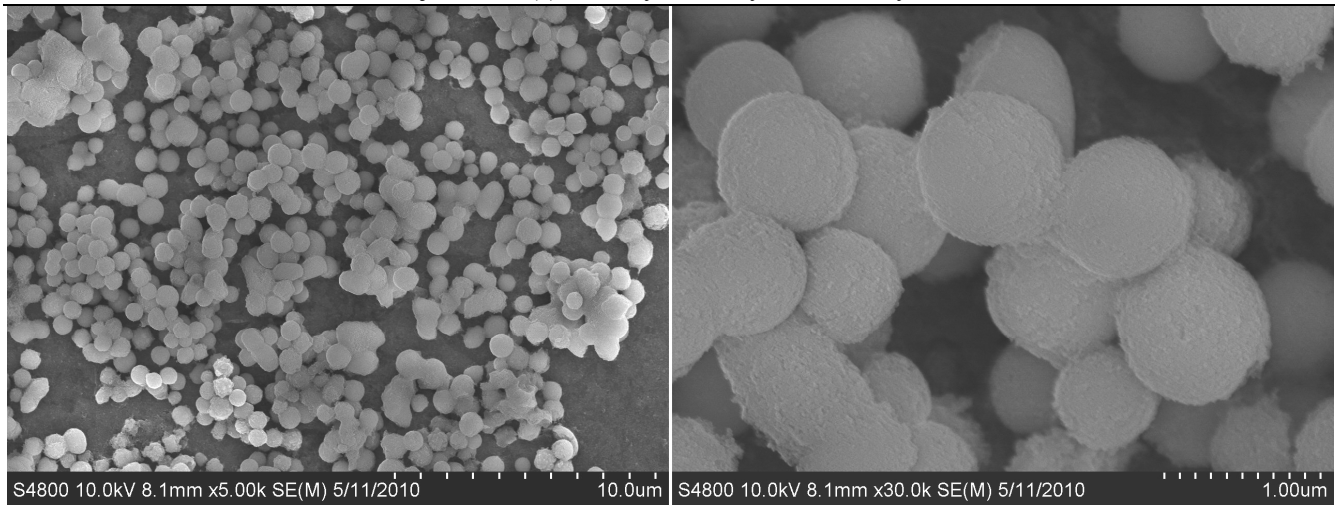

Fig. S3 SEM images of CaF_2 hollow spheres washed without sonication: (a) low- and (b) high-magnification SEM image.

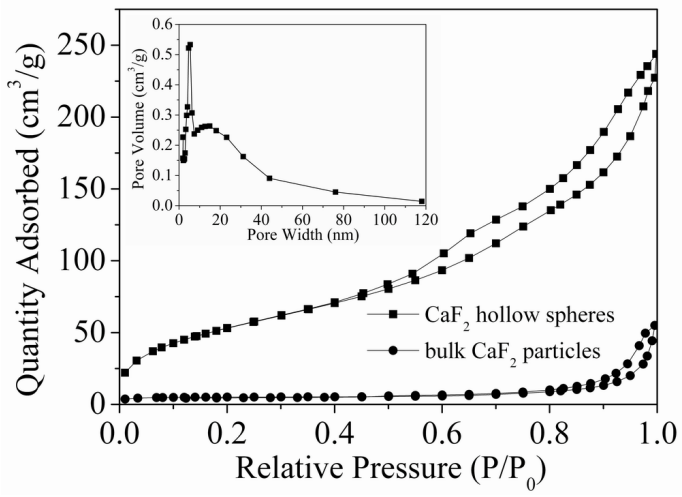

Fig. S4 N_2 adsorption/desorption isotherms; the inset is pore-size distribution curve of CaF_2 hollow spheres.

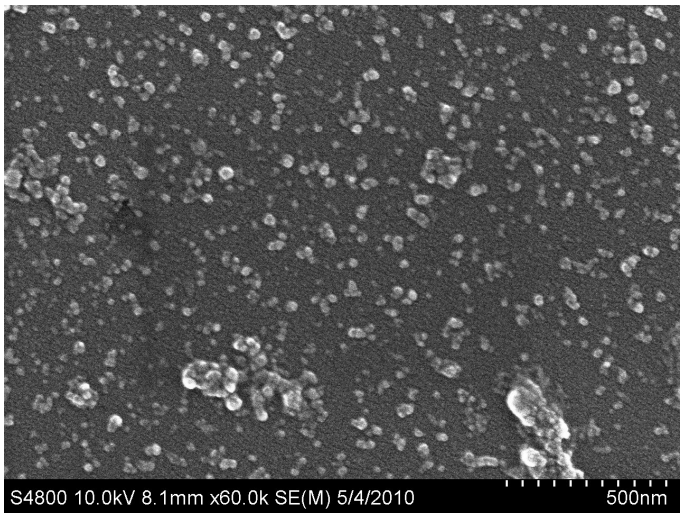

Fig. S5 SEM images of CaF_2 nanoparticles fabricated with equal molar of D2EHPA and N1923 organic solutions.