

## Bifunctional Highly Fluorescent Hollow Porous Microspheres Made of BaMoO<sub>4</sub>:Pr<sup>3+</sup> Nanocrystals via a Template-Free Synthesis

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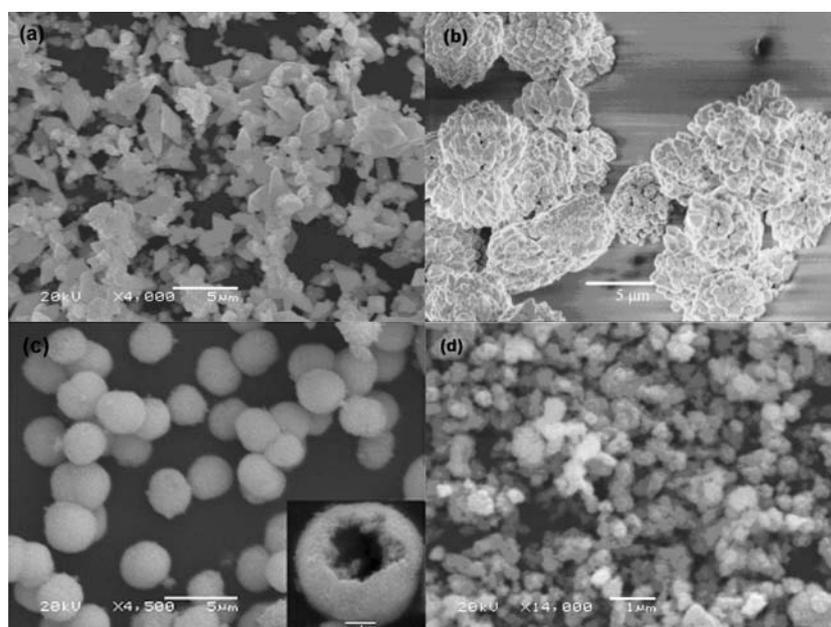
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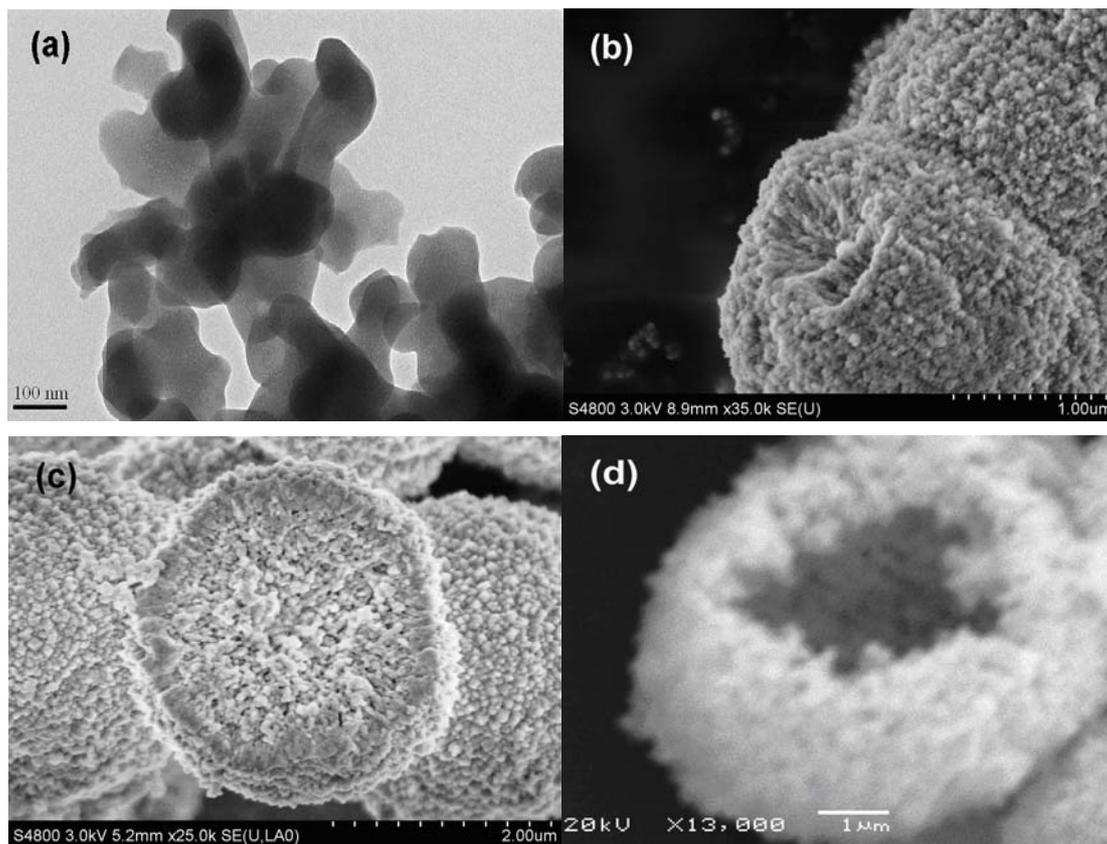
**SI-1.** The influence of the amount of citric acid on the kinetic growth of BaMoO<sub>4</sub> crystals and the formation of BaMoO<sub>4</sub>:Pr<sup>3+</sup> hollow microspheres (without changing the amount of other reactants).



**Fig. S1** (a) 0g citric acid; (b) 1.0507g citric acid; (c) 2.1014g citric acid; (d) 4.2028g citric acid

It can be seen from Fig. S1 that the self-assembly of BaMoO<sub>4</sub>:Pr<sup>3+</sup> hollow microspheres can be readily formed with an appropriate amount of citric acid and the sizes of BaMoO<sub>4</sub>:Pr<sup>3+</sup> hollow microspheres and BaMoO<sub>4</sub>:Pr<sup>3+</sup> crystals will decrease with the increasing of amount of citric acid.

SI-2.



**Fig. S2** TEM and SEM images of BaMoO<sub>4</sub>:Pr<sup>3+</sup> intermediate products at hydrothermal reaction time of (a) 0 h, (b) 0.5 h, (c) 4 h, and (d) 8 h.

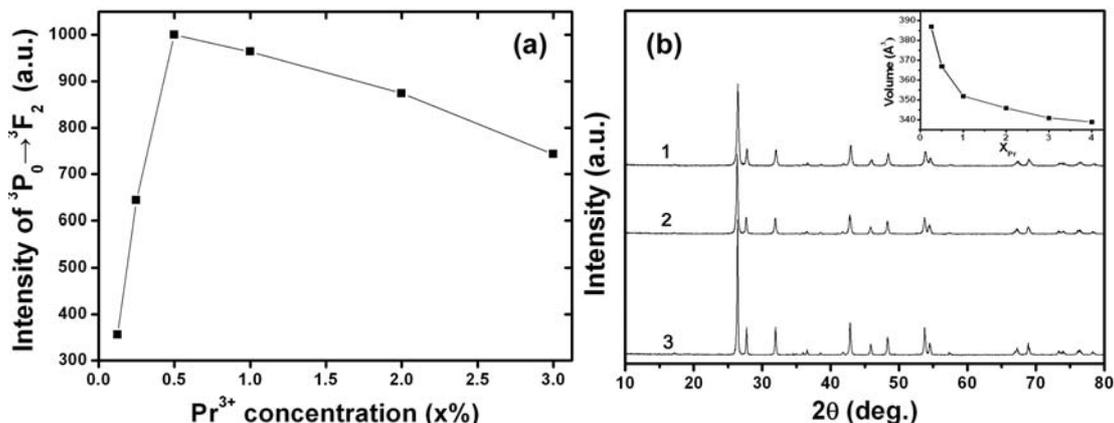
In order to reveal the formation mechanism of the BaMoO<sub>4</sub>:Pr<sup>3+</sup> hollow microspheres, time-dependent shape evolution experiments were performed by intercepting intermediate products in different hydrothermal reaction stages of 0, 0.5, 4, and 8 h. Figure S2 is a series of TEM and SEM images showing morphological evolution of the BaMoO<sub>4</sub>:Pr<sup>3+</sup> microspheres. Our time-dependent experiments reveal that only BaMoO<sub>4</sub>:Pr<sup>3+</sup> solid microspheres were obtained in the initial short reaction time of 0.5 h. The solid nature of the microspheres can be proved by the SEM images of an individual sphere in Figure S2b, which is composed of dense nanoparticles. With increasing reaction time to 4 h, microspheres with hollow structure are the main products. Figure S2c shows a single microsphere with a small interior, which is also composed of nanoparticles. This result indicates that the microspheres undergo a hollowing process when the reaction time is prolonged. Compared with the microspheres in Figure S2b, the constructed nanoparticles (Figure S2c) are less dense. When the reaction time is further prolonged to 8 h, perfect hollow microspheres are formed, as shown in Figure S2d. During this process of hollow structure formation, the diameters of the intermediate products intercepting in different reaction stages of 4 and 8 h do not change much, which is similar to what has been observed in the preparation of TiO<sub>2</sub><sup>[1]</sup> and F-doped TiO<sub>2</sub><sup>[2]</sup> hollow nanospheres. On the basis of above controlled experiments, it is possible to interpret

that the Ostwald ripening process is the main growth mechanism of the formation of  $\text{BaMoO}_4:\text{Pr}^{3+}$  hollow microspheres.

[1] Hua Gui Yang and Hua Chun Zeng, *J. Phys. Chem. B*, **2004**, 108, 3492-3495.

[2] Jia Hong Pan, Xiwang Zhang, Alan Jianhong Du, Darren D. Sun, and James O. Leckie, *J. Am. Chem. Soc.*, **2008**, 130, 11256–11257.

### SI-3.



**Fig. S3** (a) The dependences of emission intensity on  $\text{Pr}^{3+}$  concentration of the  $\text{Ba}_{1-x}\text{MoO}_4:x\text{Pr}^{3+}$  hollow microspheres and (b) the XRD patterns of the  $\text{Ba}_{1-x}\text{MoO}_4:x\text{Pr}^{3+}$  hollow microspheres at (1)  $x_{\text{Pr}}=0.0025$ , (2)  $x_{\text{Pr}}=0.01$ , and (3)  $x_{\text{Pr}}=0.03$  prepared by under hydrothermal condition at 160 °C. Inset shows the evolution of the unit cell volume versus the  $\text{Pr}^{3+}$  fraction (%).

There are two important factors to influence the luminescent properties of  $\text{BaMoO}_4:\text{Pr}^{3+}$  hollow microspheres composed of nanocrystals: the  $\text{Pr}^{3+}$  doping concentration and crystal defects.

We analyzed the influence of doping content of  $\text{Pr}^{3+}$  on its luminescence performance, and obtained the optimal condition for the formation of red phosphors. The intensity of the  ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$  transition of the  $\text{Ba}_{1-x}\text{MoO}_4:x\text{Pr}^{3+}$  is shown in [Figure S3a](#) as a function of the  $\text{Pr}^{3+}$  concentration. The emission intensity reaches its maximum at a  $\text{Pr}^{3+}$  concentration of 0.5%, and decreases quickly with increasing concentration owing to the concentration quenching effect.

The corresponding XRD patterns in [Figure S3b](#) indicated that all samples crystallized in a pure tetragonal phase of  $\text{BaMoO}_4$  with high crystallinity as doping is increased. The structural refinements of XRD data for  $\text{Ba}_{1-x}\text{MoO}_4:x\text{Pr}^{3+}$  nanocrystals show that for  $x \leq 0.04$ , the cell volume decreases linearly with  $x$ . In other words, the  $\text{Pr}^{3+}$  content dependence of the cell volume follows the trend in the inset of [Figure S3b](#). When the  $\text{Pr}^{3+}$  concentration is increased beyond  $x = 0.03$ , the cell volume don't have apparent changes, which implies that the solubility of  $\text{Pr}^{3+}$  in  $\text{BaMoO}_4$  nanocrystals is ultimately saturated. For the present nanocrystals, the lattice volume reduction may come from the doping effects. As  $\text{Pr}^{3+}$  substitutes in  $\text{Ba}^{2+}$  sites of  $\text{BaMoO}_4$ , a lattice contraction is expected because the ionic radius of  $\text{Pr}^{3+}$  in 8-coordination is 1.01 Å, which is slightly smaller than that of 1.34 Å for  $\text{Ba}^{2+}$ .