

Supplementary Information

Luminescent Meta-stable $Y_2WO_6:Ln^{3+}$ (Ln = Eu, Er, Dy, and Sm) Microspheres with Controllable Morphology via Self-assembled

Jiao Wang,^{a,b} Zhi-Jun Zhang,^a Jing-Tai Zhao,^{a,*} Hao-Hong Chen,^a Xin-Xin Yang,^a Ye Tao^c and Yan Huang^c

^a Key Laboratory of Transparent Opto-functional Inorganic Materials of Chinese Academy of Sciences, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, P. R. China

^b Graduate School of the Chinese Academy of Science, Beijing, 100039, P. R. China

^c Institute of High Energy Physics, Chinese Academy of Science, Beijing 100039, PR China

Table S1 Initial molar ratios and those measured by energy-dispersive X-ray spectroscopy (EDS) spectrum for different morphologies samples.

condition	morphologies	Initial molar ratios Y(Eu): W	Atomic %		Measured results Y(Eu): W
			Y (Eu)	W	
3	Core/shell	2	18.75	9.61	1.95
4	Waxberry-like	2	17.34	9.68	1.79
5	Nano-plane	2	17.05	8.51	2.00

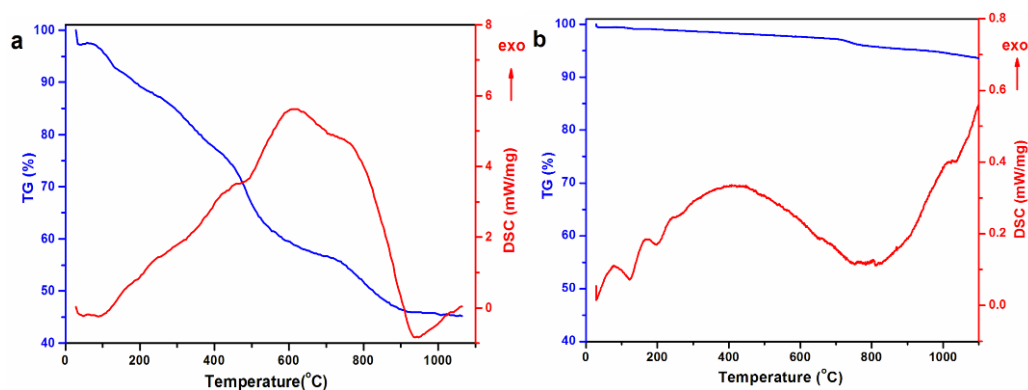


Fig. S1 Thermoanalytical data for (a) the sample prepared under typical synthesis condition without further heat treatment, and (b) the sample prepared under typical synthesis condition with further heat treatment at 500 °C for 6 hours. TG - blue line, DSC - red line. All the data were recorded at rate 10 °C/min in atmosphere.

Thermoanalytical data for the samples prepared under typical synthesis condition without (Fig. S1a) and with (Fig. S1b) further heat treatment shown in Fig. S1. Organic reagent (citrate anions will absorb

on the surface of the nano-particles and direct self-assembly) induced weight loss and exothermal effect at 200 ~ 800 °C range (Fig. S1a). Try to exclude the influence of organic reagent, sample synthesis under typical condition threat at 500 °C for 6 hours. The slight weight loss on the TG curve (Fig. S1b) may indicate some residual organic compound remained even treated under 500°C. The DSC curve indicated that this phase transition is one consequent process from 500 to 1100 °C, and the phase transition is associated with the transition of a completely disordered phase to partially ordered phase at about 800 °C. This slow thermal effect might be the indication of a long-range diffusion of atoms during the partial order to disorder transition.

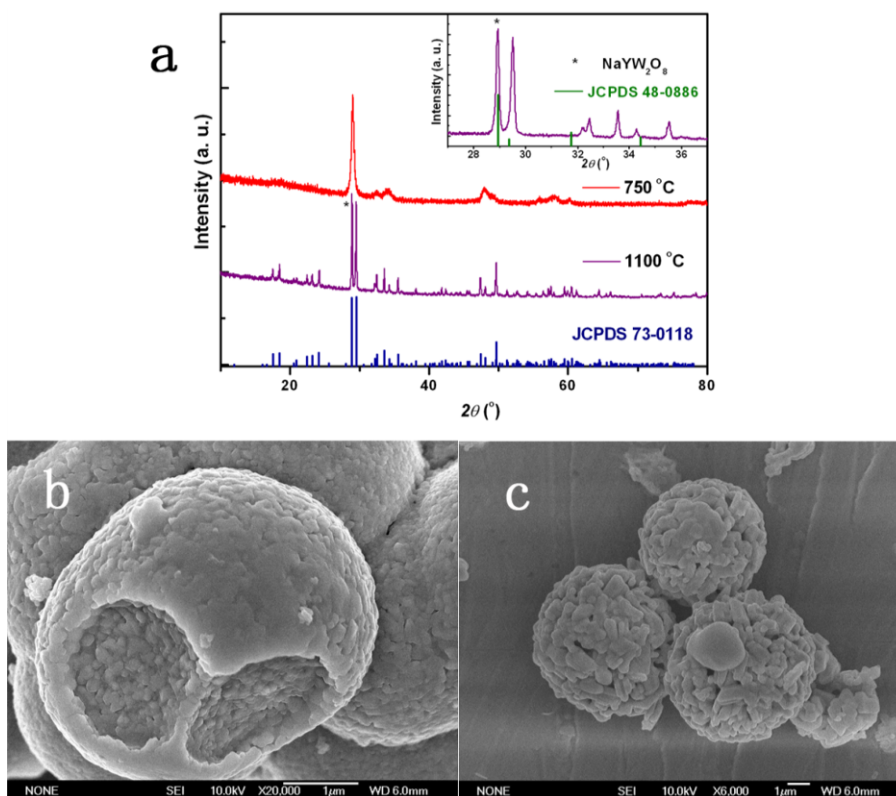


Fig. S2 XRD patterns of tetranonal (red) and monoclinic (purple) structure samples prepared used NaOH as starting material (Table 1, Condition 2) (a), and SEM micrographs of as-prepared samples annealing at 750 °C (b) and 1100 °C (c) for 10 h and 2 h, respectively.

The XRD patterns indicate that the as-samples are major T'-phase and M-phase Y_2WO_6 crystal structure. Based on the JCPDS file (N.O. 73-0118), for the (211) and (013) crystal planes of M-phase, the intensity of X-ray diffraction peaks should be similarly (marked with *). But the XRD pattern of as-prepared M-phase sample evident shows that the intensity of X-ray diffraction peak of (211) plane are higher than (013) plane. The inset in (a) shows that small amount of $(NaY)W_2O_8$ impurity (marked with *). SEM micrographs indicate that the samples are solid microspheres morphology. Due to HMTA was omitted from the synthesis procedure, there will no gas bubbles formed as soft templates for nanoparticle self-assembly, so citric acid direct the nanoparticles agglomerate into solid microsphere. This control experiment shows that HMTA plays a crucial role in the formation of the hollow microsphere, and citric acid directs

nanoparticles agglomerate ordered. But $(\text{NaY})\text{W}_2\text{O}_8$ impurity was undesirable, so we choose HMTA aqueous solution to dissolve H_2WO_4 . And prolong heat treatment at high temperatures only induce phase change and nanoparticles growth up dramatically, which will not influence the morphologies of samples (Fig. S2c).

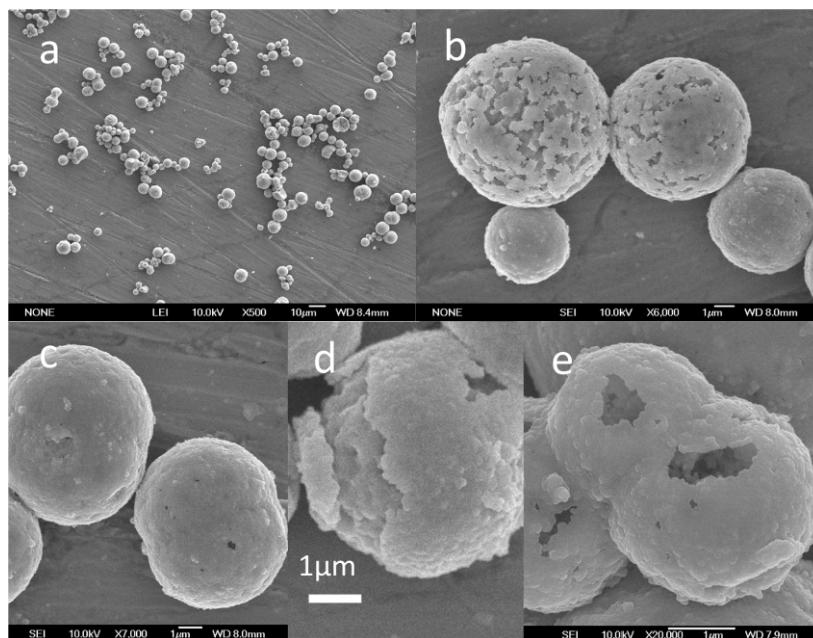


Fig. S3 FE-SEM micrographs of core/shell microspheres (750 °C for 6 hours, condition 3, Table 1).

The sizes of the core/shell microspheres shown in micrograph (a) are poly-dispersity. Fig. S3e, which indicates that there still small amount hollow microspheres in the samples, even through the core/shell sample are major in the samples. This also indicates that PVP and citric acid play crucial roles in the formation of the core/shell microspheres. And PVP micells filled with nanoparticles used as hard templates, and citric acid direct nanoparticles in the solution grow on the surface of hard or soft templates.

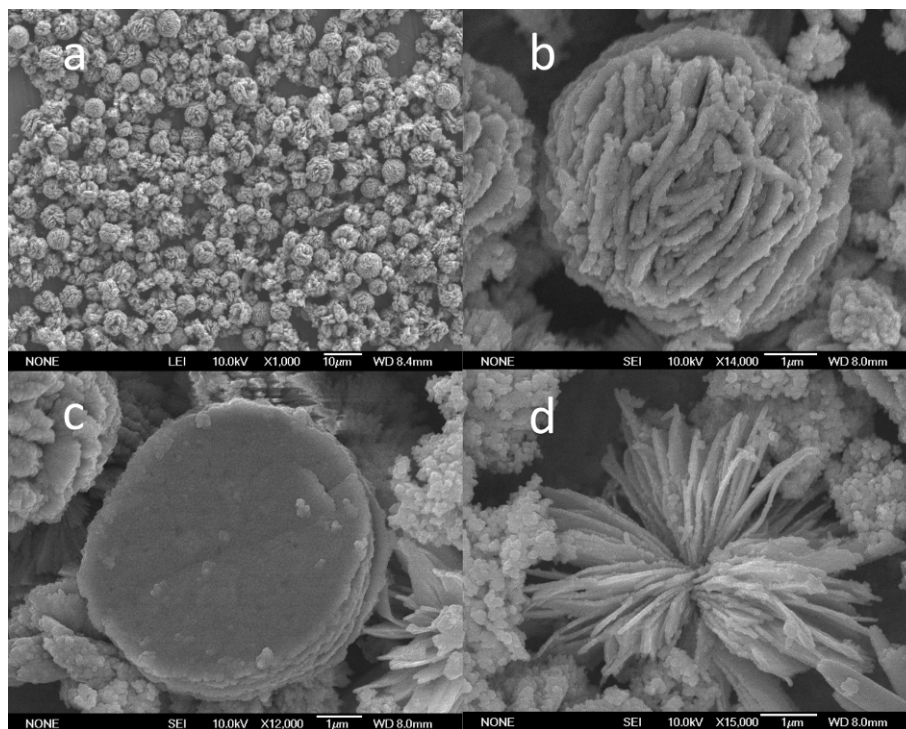


Fig. S4 FE-SEM micrographs of solid waxberry-like microspheres (750 °C for 6 hours, condition 4, Table 1).

Fig. S4a describes the typical panoramic FE-SEM image of as-prepared product, which indicates that the sizes of the as-prepared waxberry-like sample are nearly monodispersity. The surfaces of these microspheres are coarse and have many microstructures on them. Near-size PVP (K-30) micelles in the solution were used as soft templates during this synthesis process in condition 4. As can be seen from this low-magnification SEM image, the sample consists entirely of a large quantity of microspheres with diameters of 5 μm. All the samples constitute of nanoparticles. Fig. S4d show that small amount of samples are flower-like microstructure. This means nanoparticles inside and outside PVP micells aggregate in different way. The nanoparticles outside the PVP micells tend to self-assembled to reduce the surface energy as the way in condition 5 (Table 1, Fig 4d and Fig S4).

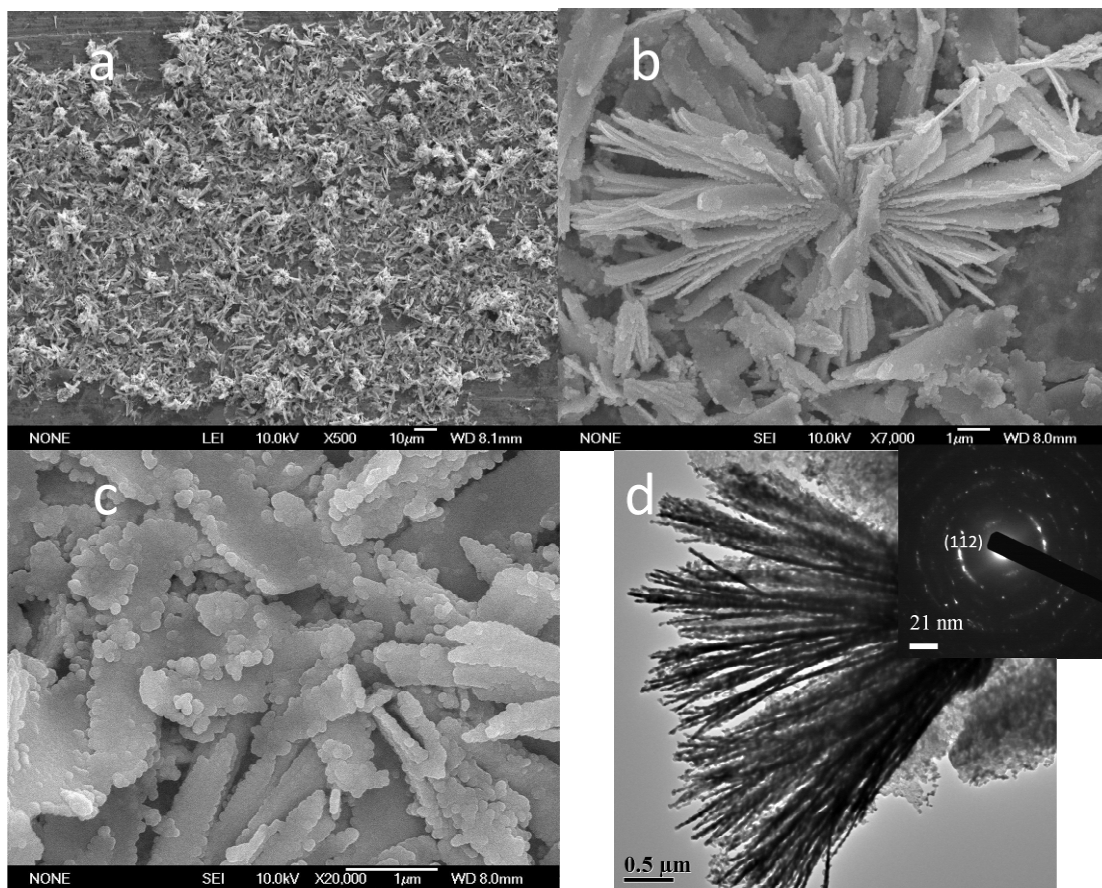


Fig. S5 (a-c) FE-SEM and (d) TEM micrographs of T'-type Y₂WO₆:Eu (5 mol%) flower-like microspheres and inserted SAED pattern (750 °C for 6 hours, condition 5, Table 1).

Fig. S5a describes the typical panoramic FE-SEM image of as-prepared Y₂WO₆:Eu (5 mol%), which indicates that the as-prepared sample is flower-like or nanoplane. All the samples constitute of nanoparticles. This means the nanoparticles tend to self-assembled to reduce the surface energy. An inserted selected-area electron diffraction (SAED) pattern recorded on the flower-like microsphere shows its polycrystalline structure. Meanwhile, this SAED pattern suggesting that the tiny nanoparticles have a strong tendency to self-assemble via an oriented manner after aggregation. For T'-type crystal structure, (112) plane is close packed plane of atoms.