Supporting Information

Dispersible lanthanides organic hybrid nanoparticles: Synthesis, morphology and application

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Experimental

Materials

The rare earth oxides, Gd_2O_3 and Tb_4O_7 was purchased from Beijing Found Star Science Technology Co, Ltd. 1,2,4,5-Benzenetetracarboxylic acid (BTA) was synthesized by hydrolysis of 1,2,4,5-Benzenetetracarboxylic anhydride. $Gd(CH_3COO)_3 \cdot xH_2O$ was prepared by dissolving Gd_2O_3 in excess dilute acetic acid. $Tb(CH_3COO)_3 \cdot xH_2O$ was prepared by dissolving Tb_4O_7 in excess acetic acid and H_2O_2. Other commercial reagents were purchased from J&K Scientific Ltd. and used as received unless otherwise noted.

Characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed on a SHIMADZU XRD-6000 diffractometer (40 kV, 40 mA, increment =0.02°) using monochromatized Cu Kα radiation of wavelength λ= 1.54059 Å. Fourier-transform infrared (FT-IR) spectra were collected on a Nicolet 6700 spectrometer (using KBr

pellets) in the wavenumber range of 400–4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed on a TA Q500 from room temperature to 800 °C with a heating rate of 10 °C/min in an air flow. The hydrodynamic diameters of the nano CPs were measured by dynamic light scattering (DLS) using a particle size analyzer (Zetasizer Nano Serisse, Malvern Instruments) at 25 °C. The morphology of the samples were inspected using a scanning electron microscope (SEM, S-4800) at an acceleration voltage of 3 kV and transmission electron microscope (TEM, JEOL JEM-1230) with an accelerating voltage of 80 kV. The content of Gd^{3+} was determined by inductively coupled plasma spectroscopy (ICP, ICAP6300). Excitation and luminescence spectra of composite films were recorded on a spectrofluorophotometer (RF-5301PC, SHIMADZU).

Morphology-controllable synthesis of nano Gd-CPs

Nanometer-scaled Gd-CPs with spherical shape were synthesized via adding separately prepared 5 mL aqueous solution of $Gd(CH_3COO)_3 \cdot xH_2O$ (0.0881 g) into 5 mL ethanol solution of BTA (0.0636 g) at the ambient temperature. The solution turned milky almost immediately after mixing the two solutions and the suspension was then left to stand for 30 min at room temperature. The obtained white precipitate was isolated by filtration and washed with water and ethanol. The resulting solid was dried under vacuum. Using the same method, fibrous-like nanosized CPs were prepared by keeping the mixed solution at 80 °C for 1 h.

Triethylamine (TEA) with 0.58 or 1.44 molar ratio of [TEA]/[BTA] was added into the above-mentioned ethanol solution of BTA to get short stick-like CPs with different sizes. The precipitate was collected by repeated centrifugation, washed with a mixture of water and ethanol (v/v=1:1), and subsequently re-dispersed in mixed solvent of ethanol and water (v/v=1:1) via sonication. To investigate the effect of solvent on the morphology, we replaced ethanol with DMF while kept the other conditions unchanged. After the addition of TEA, all of the CPs were highly dispersible and could keep stable for a period of time no matter they were synthesized in ethanol or DMF. In order to disperse CPs better, the surface of CPs was modified

by adding 0.5 g polyvinylpyrrolidone (PVP, Mw=40 kDa) into the suspension and stirring for 16 h at room temperature. Thin films were prepared by coating glass slides with PVP-modified CPs using spin coating at the speed of 1500 r/min for 60 s. The film were dried at 96 °C for two hours.

Preparation of Tb-CPs composite films

Tb-CPs were prepared by 0.0886 g $Tb(CH_3COO)_3 \cdot xH_2O$ and BTA (0.0636 g) using the same method as above. In the presence of TEA ([TEA]/[BTA]=1.44), uniform nanoparticles were obtained and dispersed in water. Methyl cellulose (0.04 g) was added into the solution via strong stir for 2 h and sonication for 10 min. To fabricate composite films, the mixture was casted on glass, and finally air-dried at 70 °C.

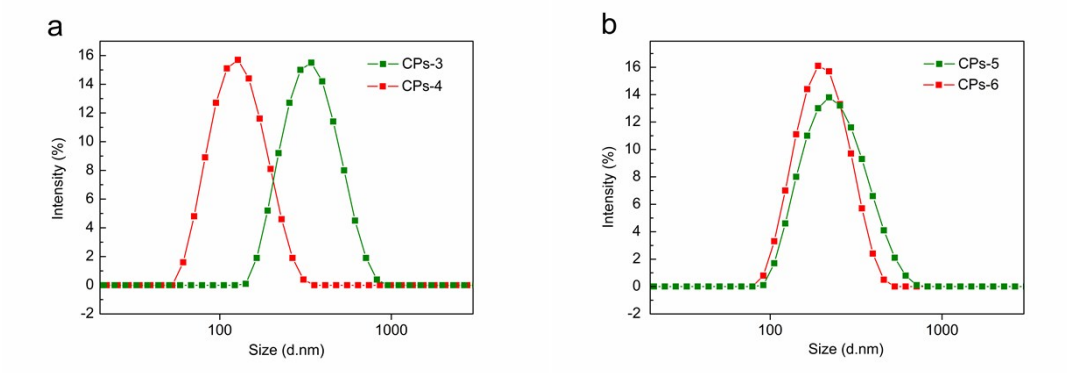

Fig. S1 DLS profiles of synthesized Gd-CPs with addition of TEA in a mixture of water with the solvent: a) ethanol; b) DMF.

a **b** **c**

Fig. S2 Photographs of CP-4 dispersed in a) water; b) DMF; c) ethanol.

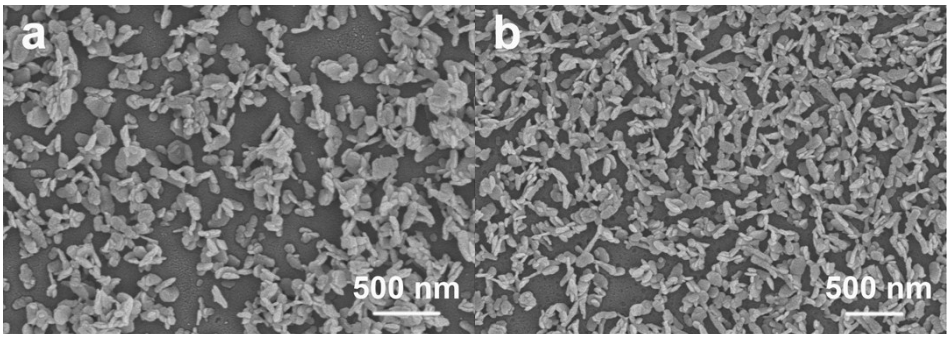

Fig. S3 SEM images of synthesized Gd-CPs with addition of TEA in DMF/water mixture: a) CP-5; b) CP-6 (Table 1).

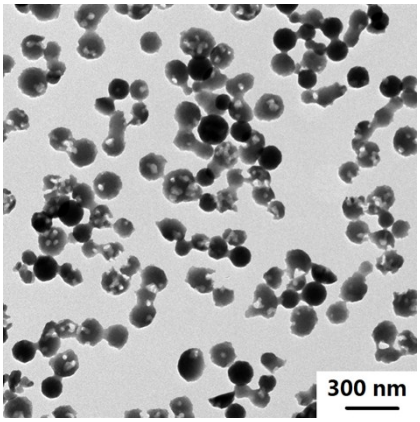

Fig. S4 TEM image of CP-5 synthesized in DMF and water.

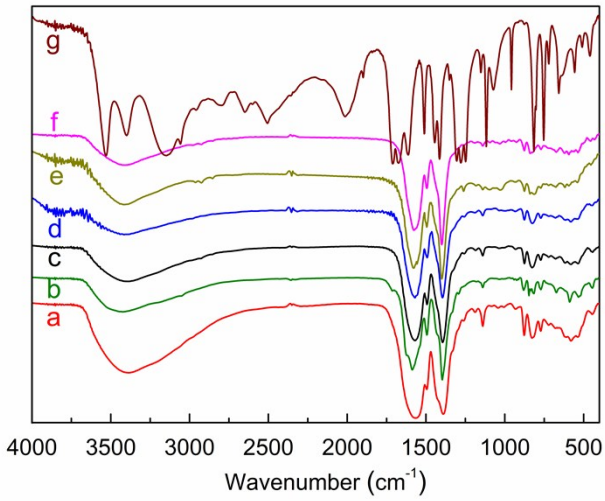

Fig. S5 FT-IR spectra of BTA (g) and the Gd-CP samples: a) CP-1; b) CP-2; c) CP-3; d) CP-4; e) CP-5; f) CP-6 as listed in Table 1.

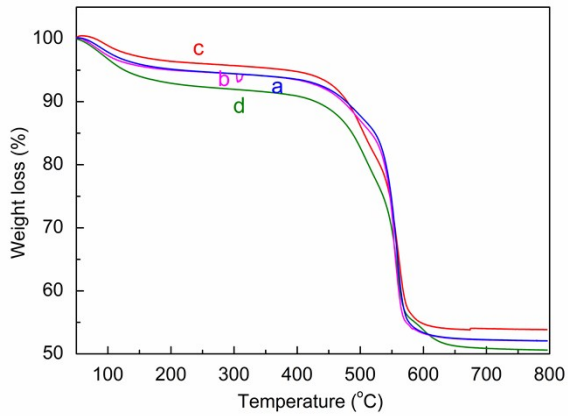

Fig. S6 TGA curves of the Gd-CP samples: a) CP-3; b) CP-4; c) CP-5; d) CP-6 as listed in Table 1.

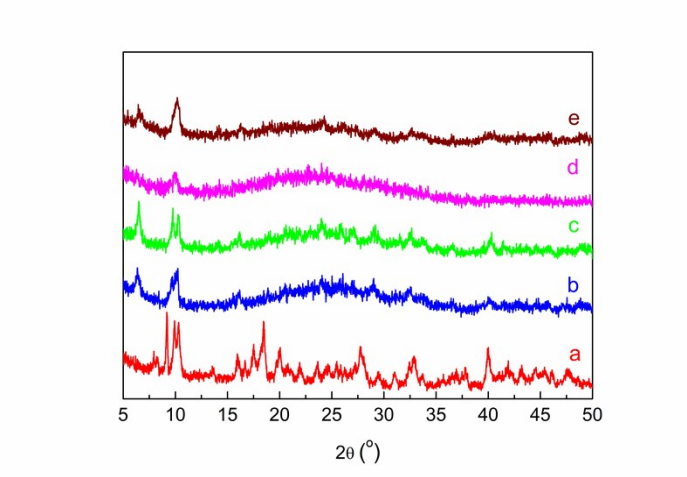

Fig. S7 XRD patterns of the Gd-CP samples: a) CP-2; b) CP-3; c) CP-4; d) CP-5; e) CP-6.

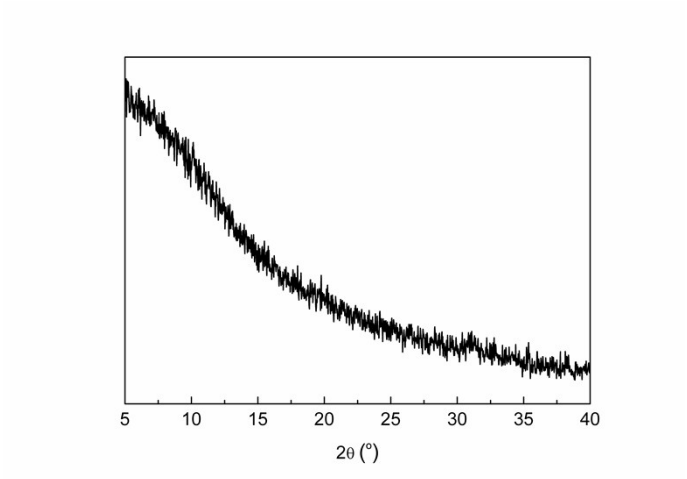

Fig. S8 XRD patterns of CP-1 synthesized at room temperature.

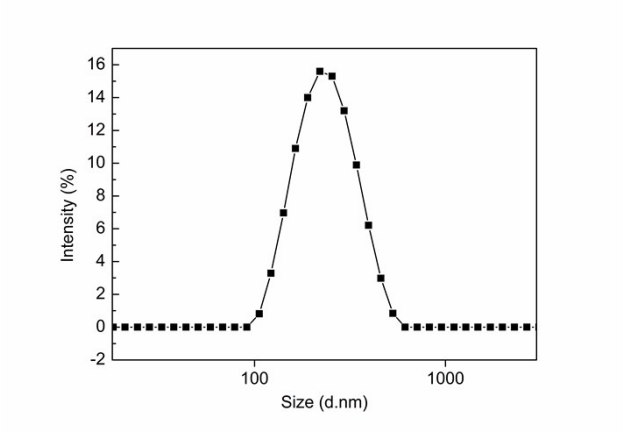

Fig. S9 DLS profile of Tb-CP.

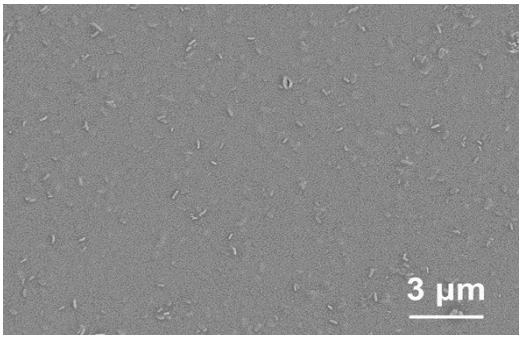

Fig. S10 SEM image of the surface of the Tb-CP/MC composite film.

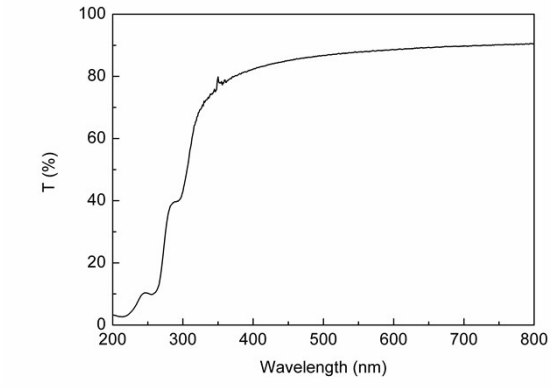

Fig. S11 Transmittance of the composite film. No scattering is found between 350 and 800 nm. Considering the particle sizes around 250 nm, we conclude no obvious particle aggregation in the film.

Table S1. Average hydrodynamic size and particle distribution index of CP-4 with and without PVP coating.

without coating		with coating	
d. (nm)	PDI	d. (nm)	PDI
256.5	0.169	256.6	0.093
259.7	0.112	261.5	0.049
255.6	0.140	258.7	0.097

Experiments of DLS measurements (Table S1) show the narrower size distribution, i.e. smaller PDI values, of the CP particles with PVP coating, which confirms higher homogeneity and better dispersion.