Supporting Information

Synthesis of porous upconverting luminescence α-$NaYF_4$:Ln microspheres and their potential application as carriers

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1-Characterization of the as-synthesized $Y(OH)CO_3{\cdot}H_2O$ and $Y(OH)CO_3{\cdot}H_2O@SiO_2$ particles

The FT-IR spectrum provides the insight into the chemical composition of the as-prepared sample (Figure S1). A strong and broad absorption bands peaking at 3400 cm^{-1} and a shoulder located at 1645 cm^{-1} are the characteristic absorption of water of hydration in the structure or surface adsorbed water and hydroxyl groups (OH^-).[1] The presence of carbonate anions in the molecular structure was confirmed by the appearance of absorption doublets in the region 1350–1600 cm^{-1} (ν_3 of CO_3^{2-}, peaking at ~1408 and 1504 cm^{-1}) and also by the occurrence of multiple absorptions ranging from 500 to 1000 cm^{-1} (ν_2 and ν_4 of CO_3^{2-}).[2,3] The elemental analysis quantifies the elemental components (mass %) of the as-prepared precursor. Elemental contents of the dried particles analyzed by the inductively coupled plasma (ICP) spectrophotometric method were listed in Table S1, yielding a Y:C:O molar ratio of about 1:1.03:5.18. Assuming that all the carbon was from CO_3^{2-} and considering molecular neutrality, the chemical formula of the as-prepared product

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may be expressed as $Y(OH)CO_3{\cdot}H_2O$. The results are consistent with the pioneering work of Matijevic *et al.* and the recent work by Lechevallier's group.[2,4]

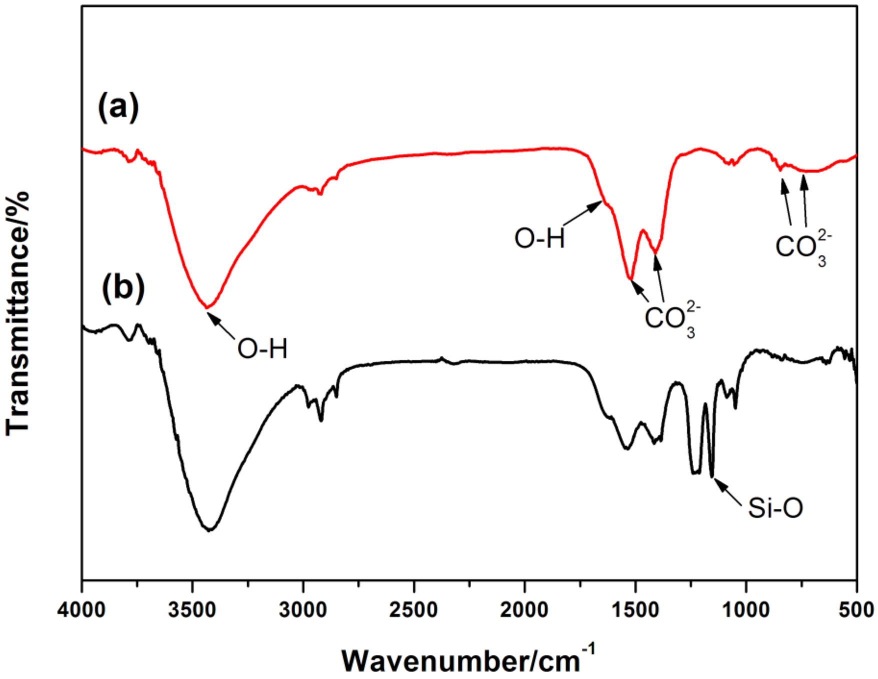


Fig. S1 FT-IR spectra of the as-prepared $Y(OH)CO_3{\cdot}H_2O$ (a) and $Y(OH)CO_3{\cdot}H_2O@SiO_2$ (b).

The thermogravimetric analysis (TGA) curve of the as-prepared sample was shown in Figure S2. The weight loss of $Y(OH)CO_3{\cdot}H_2O$ undergoes a three-step process. The first one (25-170°C) is due to the desorption of water molecules adsorbed at the particles surface due to the storage in air. The second weight loss (170-550°C) is related to the removal of water molecules due to the dehydration of hydrated compounds and the self-condensation of hydroxyl groups (O-H).[4,5] The third one (550-750 °C) originates from the release of CO_2 molecules.[4,5]

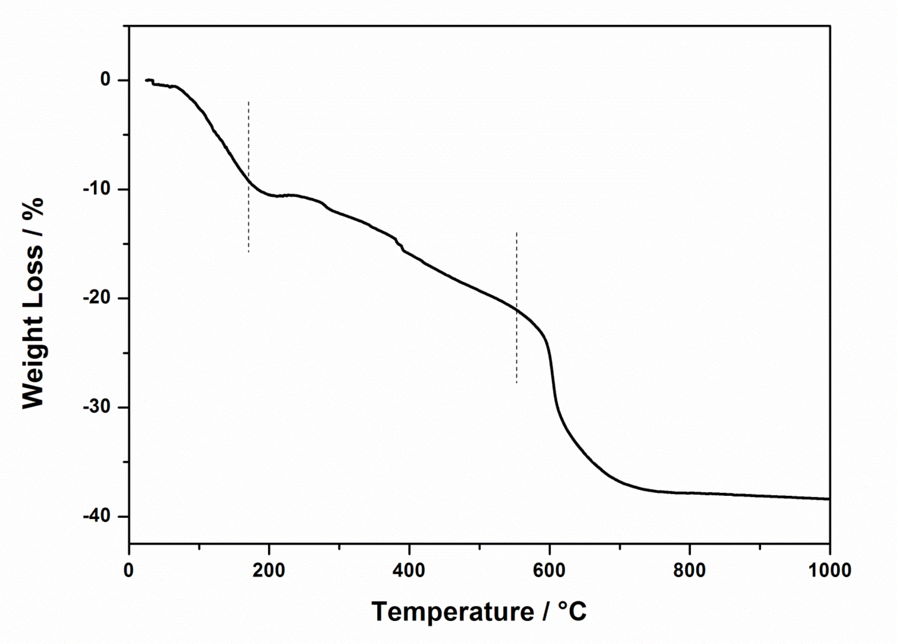


Fig. S2 Thermogravimetric analysis curve of the precursor Y(OH)CO_3·H_2O measured in air.

Table S1. Elemental content of as-prepared particles (mass %).

Y	C	O
47.9%	6.7%	44.2%

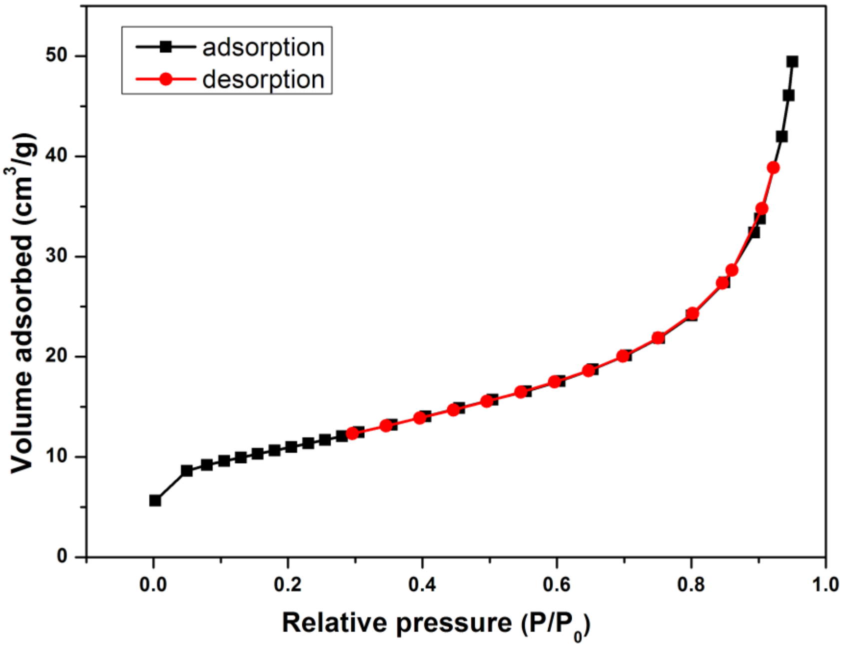


Fig. S3 Nitrogen adsorption-desorption isotherms of as-prepared precursor Y(OH)CO_3@SiO_2.

2-XRD of the product obtained by the reaction of bared Y(OH)CO_3 microspheres with NH_4F and $NaNO_3$

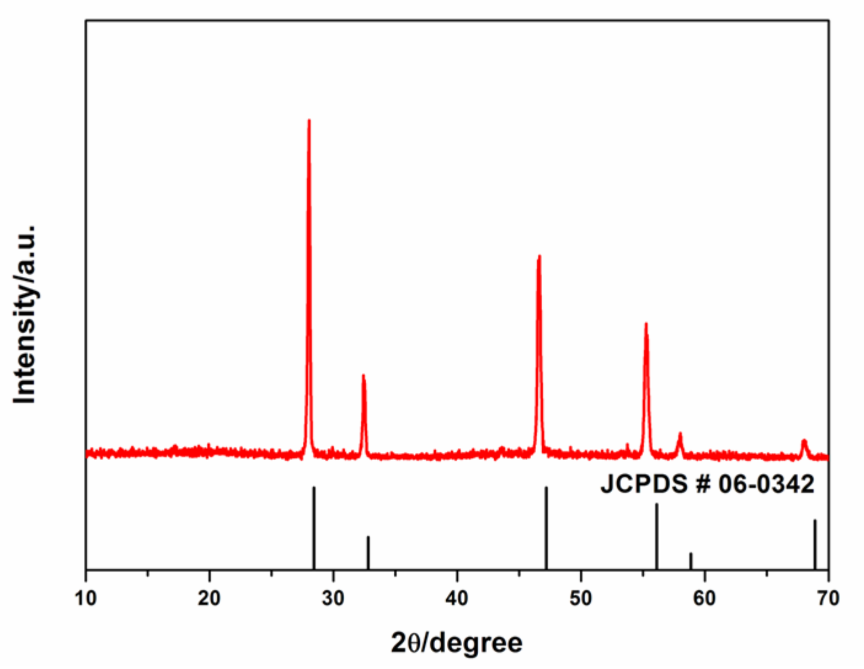
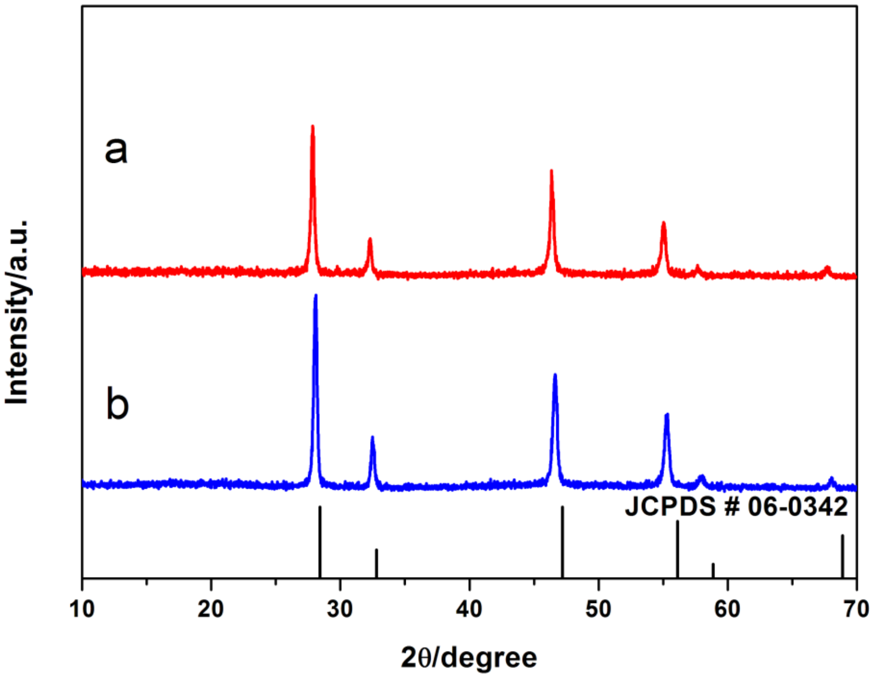


Fig. S4 XRD pattern of the product formed through the reaction of the as-prepared bared Y(OH)CO_3 microspheres with NH_4F and $NaNO_3$ solutions by a hydrothermal process.

3- Characterizations of porous α-$NaYF_4$ annealed at 250 °C (XRD and TEM).



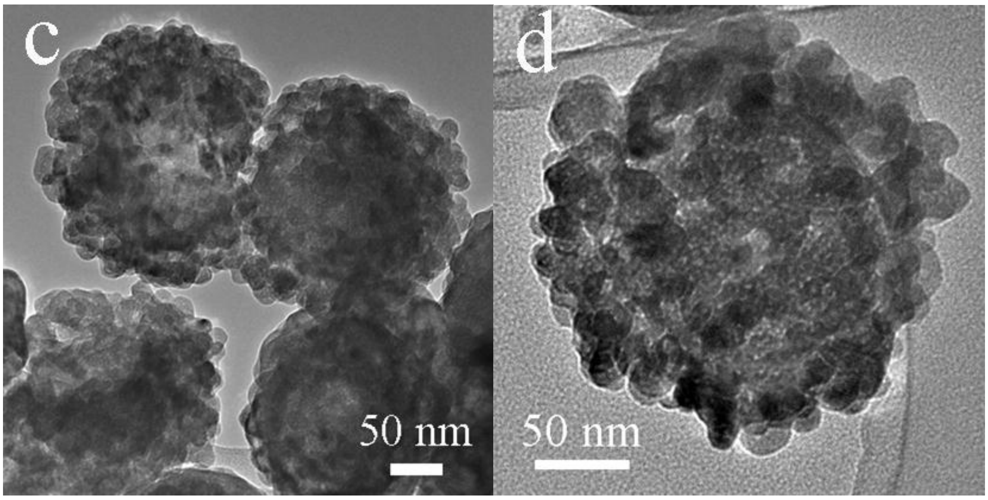


Fig. S5 XRD (b) and TEM (c, d) patterns of α-$NaYF_4$ annealed at 250 °C for 2 h. The XRD (a) as-synthesized α-$NaYF_4$ and the standard data of cubic $NaYF_4$ (JCPDS # 06-0342) are also shown.

References

1 L. Moscardini D'Assuncao, I. Giolito and M. Ionashiro, *Thermochim. Acta.*, 1989, **137**, 319

2 E. Matijevic and W. P. Hsu, *J. Colloid. Interface Sci.*, 1987, **118**, 506.

3 K. Makamoto, *Infrared spectra of inorganic and coordination compounds.* 1963 (New York: John Wiley & Sons).

4 S. Lechevallier, P. Lecante, R. Mauricot, H. Dexpert, J. Dexpert-Ghys, H. Kong, G. Law and K. Wong, *Chem. Mater.*, 2010, **22**, 6153.

5 W. Di, S. K. P. Velu , A. Lascialfari , C. X. Liu , N. Pinna , P. Arosio , Y. Sakka and W. Qin, *J. Mater. Chem.*, 2012, **22**, 20641.