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Electronic Supporting Information

Gadolinium fluorides mesoporous microspheres: controllable synthesis, materials and luminescent properties

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1. Study on the leakage of Gd^{3+} ions and host degradation during delivery

It is very important to study the leakage of Gd^{3+} ions and host degradation during delivery, especially for the further utilizing $NaGdF_4$:Yb/Er microspheres for biomedical use. Firstly, we test the degradation characteristics of the sample by using the buffer solutions. The as-obtained $NaGdF_4$:Yb/Er spheres dispersed in the buffer solution (pH = 7.0) at 37 °C with slow stirring for a week. Then the dispersions were centrifuged and dried at 60 °C for 12 h for further characterization. From the results of XRD, SEM and EDS, it can be known that the product after immersion treatment is still $NaGdF_4$:Yb/Er with original morphology and structure.

Then the supernatant from the immersion treatment can be further analyzed for the leakage of Gd^{3+} ions. By adding appropriate amount of NaOH, turbid solution and $Gd(OH)_3$ precipitate cannot be found. ICP analysis also cannot detect the Gd^{3+} ions. It thus can be inferred that very little even none free Gd^{3+} ions can dissociate from the host. On the other hand, due to the complete translation of $Gd(OH)CO_3$ after the hydrothermal treatment at 160 °C for 8 h, the obtained NaGdF4:Yb/Er was quite stable and hardly dissociated in PBS at 37 °C.

2. Study on acid compatibility of $NaGF_4$:Yb^{3+}/Er^{3+} mesoporous spheres

To test the acid compatibility of $NaGF_4$:Yb^{3+}/Er^{3+} mesoporous spheres, it is very important to study the leakage of Gd^{3+} ions in acid environment. Firstly, we test the degradation characteristics of the sample by using the acid solutions. The as-obtained $NaGdF_4$:Yb^{3+}/Er^{3+} spheres dispersed in the buffer solution (pH = 4.0) at 37 °C with slow stirring for a week. Then the dispersions were centrifuged and dried for further characterization. From the results of XRD, SEM and EDS, it can be known that the product after immersion treatment is still $NaGdF_4$:Yb^{3+}/Er^{3+} with original morphology and structure. Then the supernatant from the immersion treatment can be further analyzed for the leakage of Gd^{3+} ions. By adding enough amount of NaOH, turbid solution and $Gd(OH)_3$ precipitate cannot be found. It can declare very little even none free Gd^{3+} ions can dissociate from the host.

3. Supporting figures

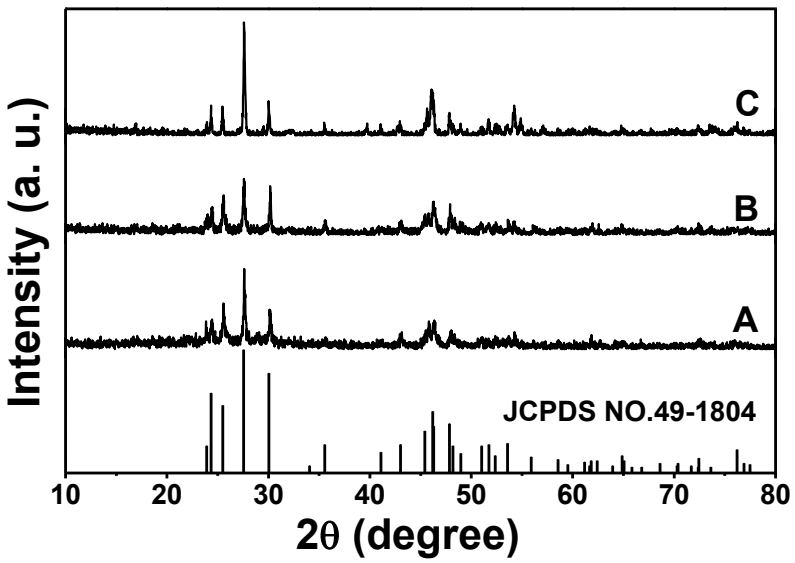

Fig. S1 XRD patterns of the product obtained at 160 °C for 8 h: (A) pure GdF_3, (B) GdF_3:2%Eu^{3+}, (C) GdF_3 annealed at 550 °C for 3 h and the standard data of GdF_3 (JCPDS No. 49-1804) as a reference.

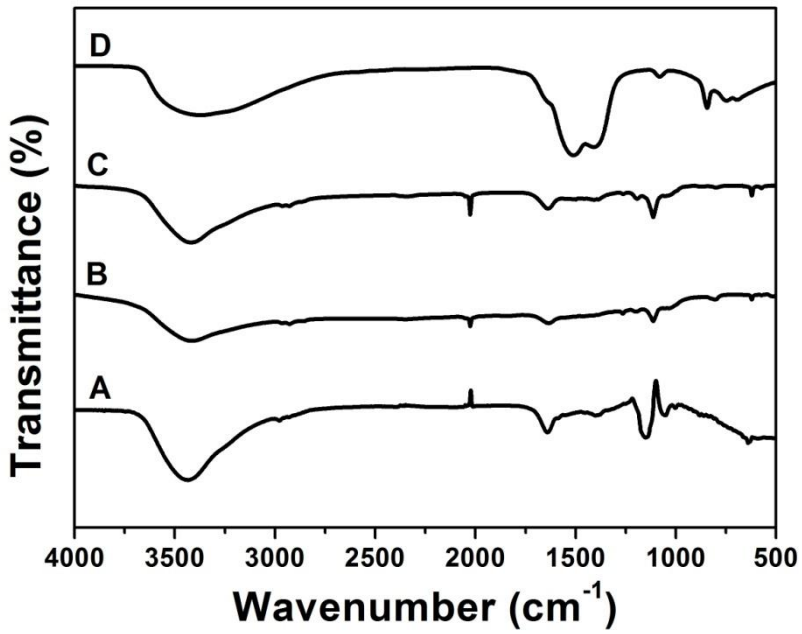

Fig. S2 FT-IR spectra of GdF_3 (A), $Na_5Gd_9F_{32}$ (B), $NaGdF_4$ (C) and $Gd(OH)CO_3$ (D).

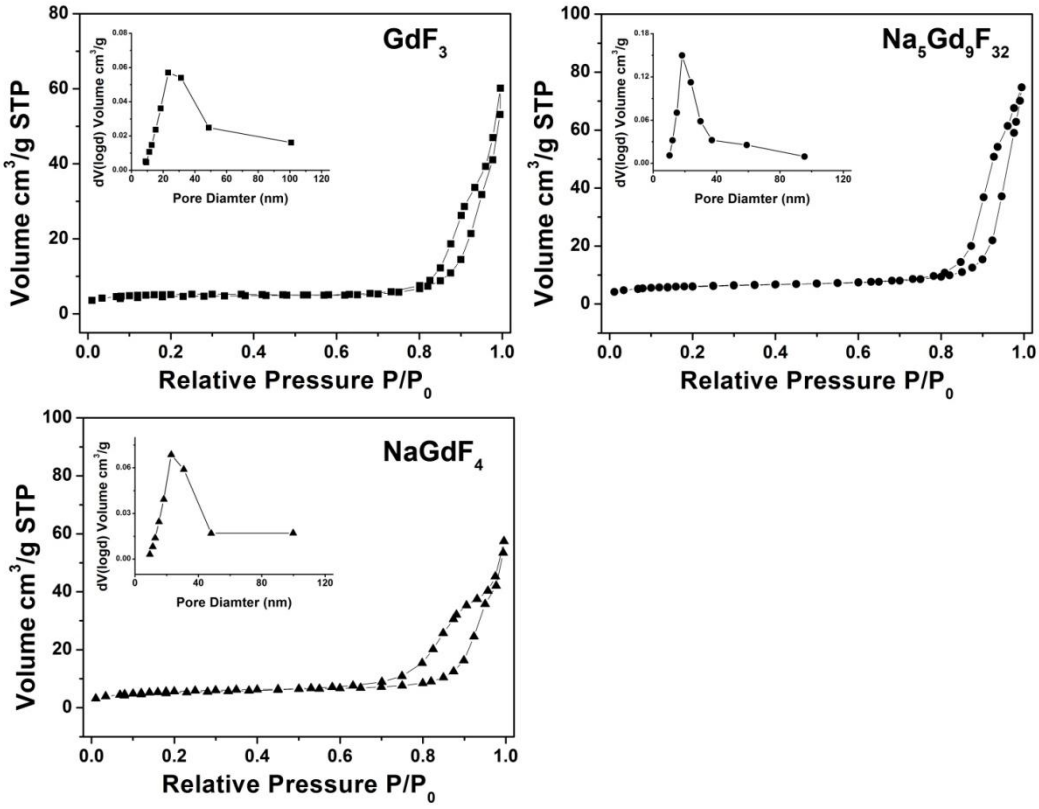

Fig. S3 N_2 adsorption/desorption isotherms and corresponding pore size distribution (insets) of GdF_3, $Na_5Gd_9F_{32}$ and $NaGdF_4$ mesporous microspheres.

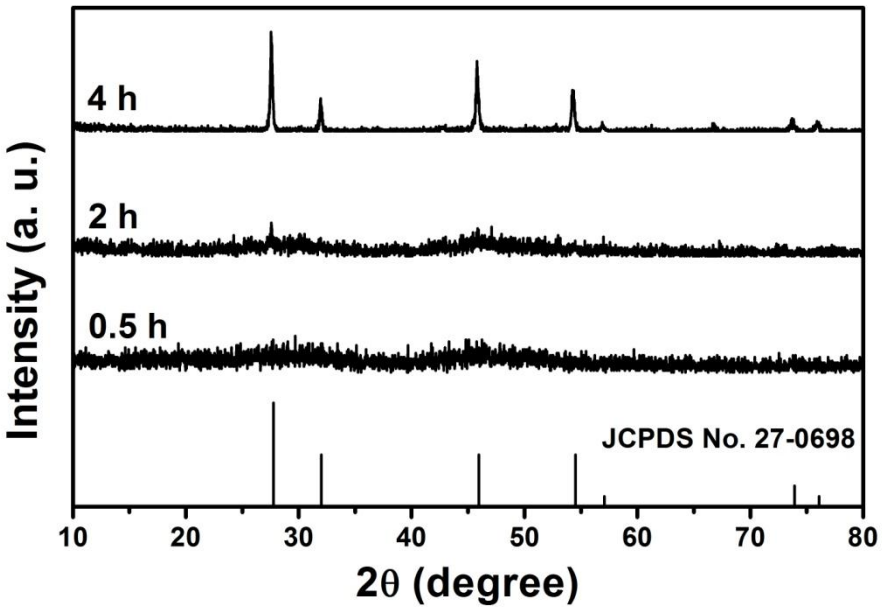

Fig. S4 XRD patterns of $Na_5Gd_9F_{32}$ prepared at 160 °C for different reaction time, and the standard data of $Na_5Gd_9F_{32}$ (JCPDS No. 27- 0698) as a reference.

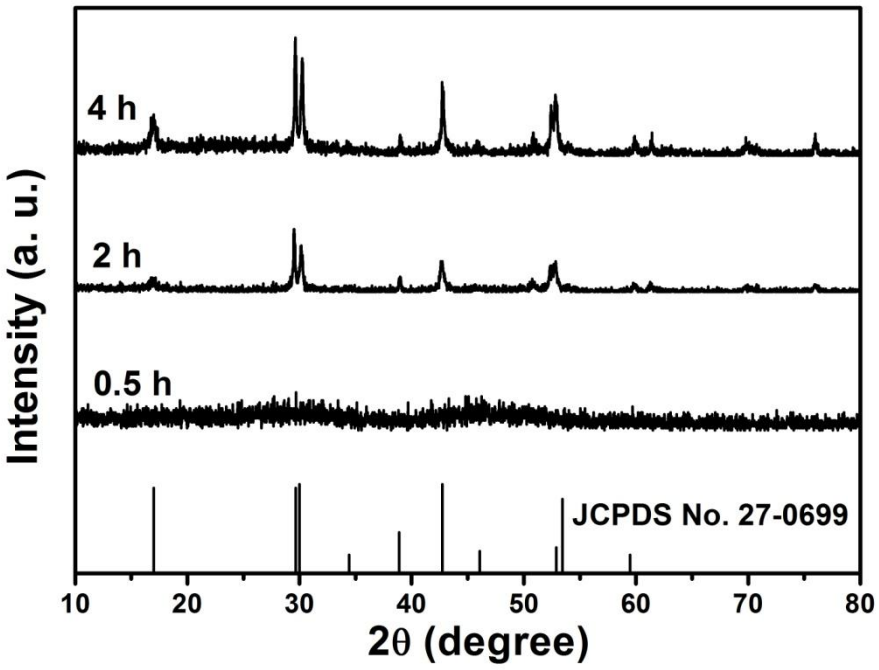

Fig. S5 XRD patterns of the obtained $NaGdF_4$ with 6.4 mmol $NaBF_4$ and 3.2 mmol NaOH at 160 °C for different reaction time, and the standard data of $NaGdF_4$ (JCPDS No. 27-0699) as a reference.

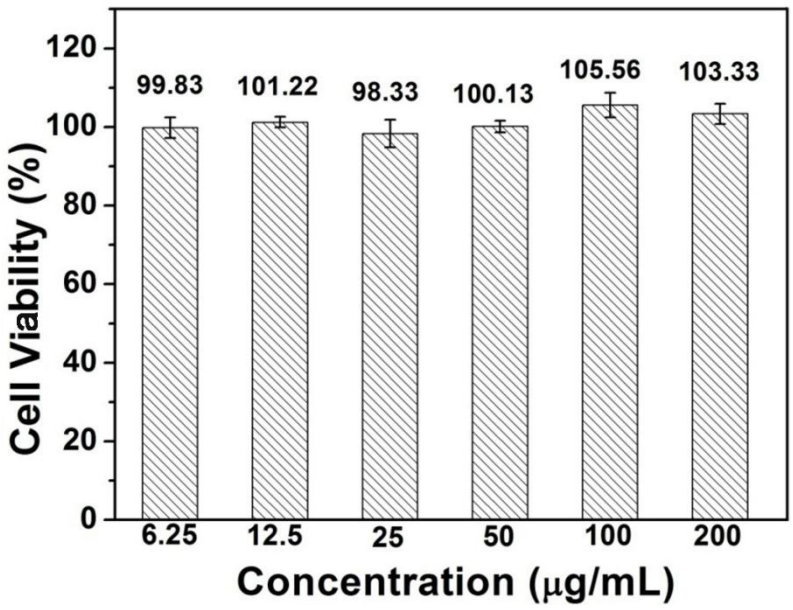

Fig. S6 The biocompatibility of β-$NaGdF_4$:Yb/Er mesoporous microspheres analyzed using the MTT assay. L929 fibroblast cells were incubated with the samples for 24 h.

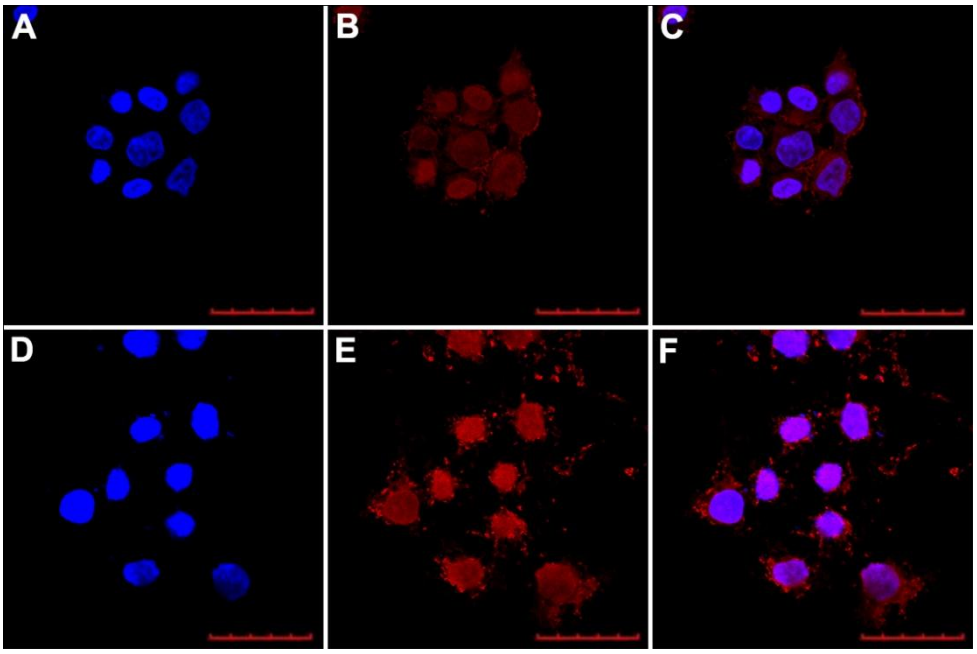

Fig. S7 Confocal laser scanning microscopy (CLSM) images of HeLa cells incubated with β-$NaGdF_4$:Yb/Er for 30 min (A–C) and 3 h (D–F) at 37 °C. For each series, images from left to right can be classified to the nuclei of respective cells (blue, being dyed by Hoechst 33324), DOX fluorescence in cells (red), and the merged images of both above. All scale bars are 50 mm.