Supporting Information

for

Facile fabrication of Rare-earth doped Gd_2O_3 hollow spheres with upconversion luminescence, magnetic resonance and drug delivery properties

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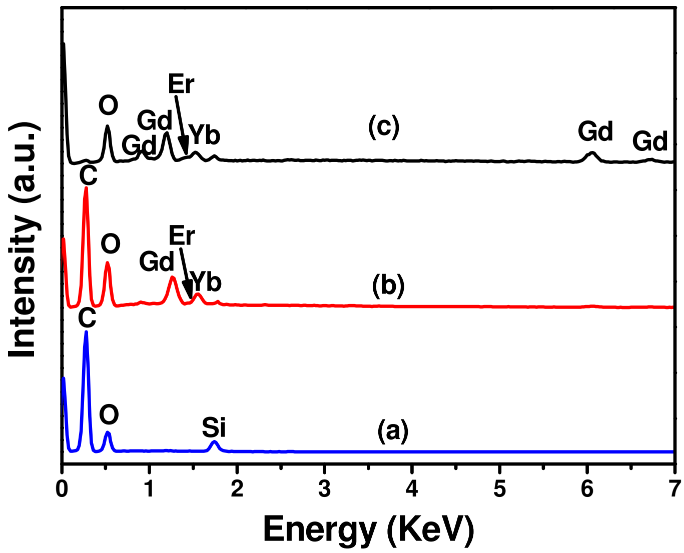

Figure S1. EDX spectra of (a) HTC spheres, (b) core-shell structured composite and (c) Gd_2O_3 hollow spheres.

The EDX analysis as shown in Figure S1a reveals that the element compositions of the hydrothermal carbon (HTC) template are carbon (C) and oxygen (O). The weak signals for silica (Si) come from silica substrate. Figure S1b confirms the presence of C, O, gadolinium (Gd), ytterbium (Yb) and erbium (Er) in the core-shell structured precursor, indicating that these lanthanide ions are effectively adsorbed by the HTC template and form a amorphous $Gd(OH)CO_3$: Yb/Er shell of the precursor. After annealing at 800 °C for 2 h, the as-obtained oxide hollow spheres are composed of O, Gd, Yb and Er elements, and the C element cannot be detected (Figure S1c). This result implies that the HTC templates have been removed completely and the precursor shell has converted to crystalline Gd_2O_3 during the calcination process, which is in good accordance with the XRD results.

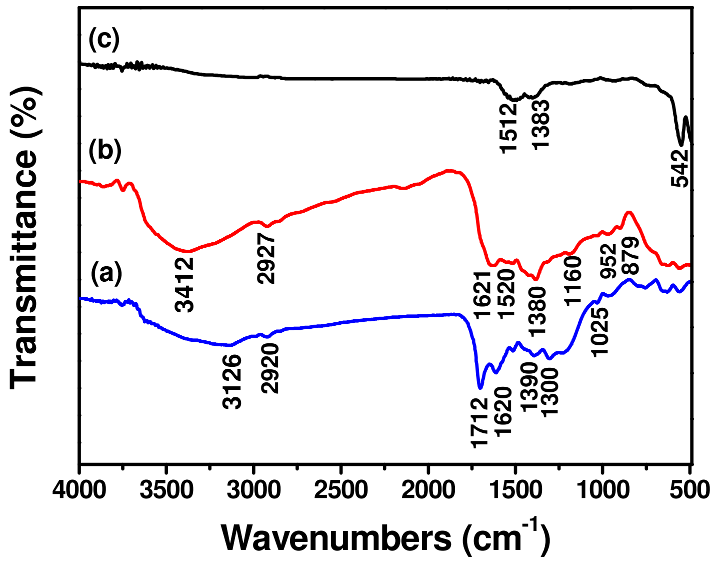

Figure S2. FT-IR spectra of (a) HTC spheres, (b) core-shell structured composite and (c) Gd_2O_3 hollow spheres.

The FTIR spectra were used to identify the functional groups of the as-obtained HTC template, the core-shell-structured precursor, and the Gd_2O_3 product. The FTIR spectrum of the HTC template (Figure S2a) shows the characteristic absorption bands of hydrothermal carbon, which are similar to some in the literature. The absorption bands at about 3126 (1620), 2926 (1390), 1712 and 1025 cm^{-1} are assigned to the vibrations of -OH, $-CH_3$, -COOH and C-O-C groups,[1] respectively. The FT-IR spectrum of the precursor is similar to that of the HTC templates expect the absorption band at 1721 and 1520 cm^{-1} (Figure S2b). It can be seen that the absorption band centered at 1721 cm^{-1} nearly disappears, which may be due to the coating of the $Gd(OH)CO_3$ nanoparticles on the surfaces of HTC spheres. The new band at 1520 cm^{-1} assigned to the vibration of CO_3^{2-} groups indicates the existence of the amorphous $Gd(OH)CO_3$ shell.[2] After calcination at 800 °C for 2 h, the absorption bands of the HTC template nearly disappear, and a new band centered about 542 cm-1 can be detected (Figure S2c), which can be attributed to the Gd-O stretching frequencies of the Gd_2O_3 product.[3] The FT-IR result provides additional evidence that the HTC template can be effectively removed during the calcination process, which agrees well with the XRD and EDX results.

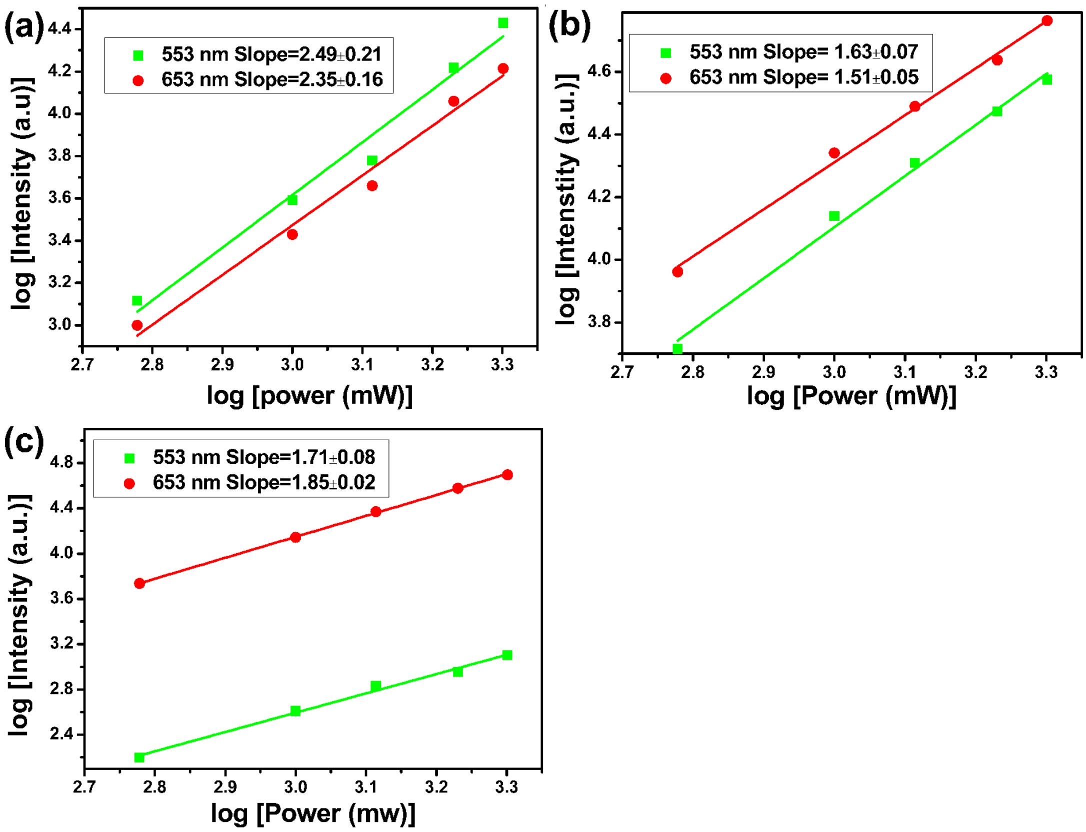

Figure S3. The double logarithmic plots of emission intensity versus excitation laser power show power dependence of upconversion process in (a) Gd_2O_3: Yb/Er (18/2 %), (b) Gd_2O_3: Yb/Er (30/2 %) and (c) Gd_2O_3: Yb/Er (40/2 %) hollow nanospheres, respectively.

To investigate the fundamental UC mechanism of sample, the pumping power dependence of the fluorescent intensity was investigated. For an unsaturated UC process, the emission intensity (I_f) will be proportional to some power (n) of the infrared excitation (P) power: [4]

$$I_f \propto P^n \qquad (1)$$

Where n is the number of infrared photons absorbed per visible photon emitted. Figure S3 shows the power dependence of the UC emission intensities: n = 2.49, 1.63, and 1.67 for the $^4S_{3/2} \rightarrow ^4I_{15/2}$ (green) emissions, respectively; n =2.35, 1.51, and 1.85 for the $^4F_{9/2} \rightarrow ^4I_{15/2}$ (red) emission, respectively. This means that two pumping photons are required to populate the Er^{3+}: $^2S_{3/2}$, $^4F_{9/2}$ emitting levels.

References and Notes for Supporting Information

1. Hu, B.; Wang, K.; Wu, L. H.; Yu, S.H.; Antonietti, M.; Titirici, M. M. **2010**, *22*, 813-828.

2. Martinez-Rubio, M. I.; Ireland, T. G.; Fern, G. R.; Silver, J.; Snowden, M. J. *Langmuir.* **2001**, *17*, 7145-7149.

3. Jia, G.; You, H. P.; Liu, K.; Zheng, Y. H.; Guo, N.; Zhang, H. J. *Langmuir*. **2010**, *26*, 5122-5128.

4. Wang, G. F.; Peng, Q.; Li, Y. D. *J. Am. Chem. Soc.* **2009**, *131*, 14200-14201.