

Electronic Supplementary Information

A facile template-free route to fabricate highly luminescent mesoporous gadolinium oxides

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Experimental sections

Preparation of $\text{Gd}(\text{OH})\text{CO}_3\cdot\text{H}_2\text{O}$. The monodisperse $\text{Gd}(\text{OH})\text{CO}_3\cdot\text{H}_2\text{O}$ colloidal nanoparticles were prepared via a urea-based homogeneous precipitation process. A total of 5 mL of $\text{Gd}(\text{NO}_3)_3$ (1 M) and 10 g of urea [$\text{CO}(\text{NH}_2)_2$] were dissolved in deionized water. The total volume of the solution was about 250 mL. The above solution was first homogenized under magnetic stirring at room temperature for 2 h. The resultant solution was then reacted at 85 °C for 2.5 h in an oil bath. The obtained suspension was separated by centrifugation and collected after washing with deionized water and ethanol several times. Eu^{3+} -doped samples were obtained under the same conditions by replacing a fraction of $\text{Gd}(\text{NO}_3)_3$ by $\text{Eu}(\text{NO}_3)_3$.

Preparation of mesoporous $\text{Gd}_2\text{O}_3\cdot\text{Eu}$. Mesoporous gadolinium oxides (Gd_2O_3) were obtained by heating the as-prepared $\text{Gd}(\text{OH})\text{CO}_3\cdot\text{H}_2\text{O}\cdot\text{Eu}$ at 750 °C for 2 h with a heating rate of 2 °C min^{-1} .

Characterizations

The X-ray powder diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer (CuK α X-radiation at 40 kV and 50 mA) in the 2 θ range from 10° to 70° with

a scanning step of 0.02°. The transmission electron microscopy (TEM) observations were carried out using a JEOL 2200FS microscope. Samples for TEM investigations were prepared by first dispersing the particles in ethanol under assistance of ultrasonification and then dropping 1 drop of the suspension on a copper TEM grid coated with a holey carbon film. Fourier transform infrared (FT-IR) spectra (Mattson 5000) of the samples were measured in the range of 4000-500 cm^{-1} in transmission mode. The pellets were prepared by adding 0.8 mg of the sample powder to 80 mg of KBr. The powders were mixed homogeneously and compressed at a pressure of 10 KPa to form transparent pellets. Thermogravimetric analysis (TGA) of the as-prepared precursor was performed using a thermoanalyzer (Thermo Plus TG 8120, Rigaku). The data were recorded at a scan rate of 5 $^{\circ}\text{C min}^{-1}$ from room temperature to 800 $^{\circ}\text{C}$ in air. The N_2 adsorption-desorption isotherms were recorded at 77 K on a Micromeritics ASAP 2010. The samples were degassed at 523 K and 10^{-6} Torr for 10 h prior to measurement. The fluorescence spectra were recorded on a fluorescence spectrophotometer (F-7000, Hitachi) at room temperature. The slit widths of the excitation and emission were both 1.0 nm. The luminescence quantum yield was taken on Fluorescence SENS-9000 PL calibrated spectrometer equipped with an integrated sphere. Three measurements were made for each sample and the average value is reported. The method is accurate to within 5%.

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 (Gd+Eu):C:O molar ratio of about 1:1.01:5.10. Assuming that all the carbon was from CO_3^{2-} and considering molecular neutrality, the chemical formula of the as-prepared product may be expressed as $\text{Gd}(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O} \cdot \text{Eu}$. The results are consistent with the pioneering work of Matijevic *et al.* and the recent work by Lechevallier's group.

Table 1. Elemental content of as-prepared particles (mass %).

Gd	Eu	C	O
58.2%	3.7%	4.8%	31.6%

The FT-IR spectrum provides the insight into the chemical composition of the as-prepared precursor (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 $1350\text{--}1600\text{ cm}^{-1}$ (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} Upon calcination at 550°C , the characteristic absorptions of hydration water and hydroxyl groups almost disappear completely (Figure S1(b)), compared to that of the as-prepared $\text{Gd}(\text{OH})\text{CO}_3\cdot\text{H}_2\text{O}$. This indicates the occurrence of the dehydration in the temperature ranging from 200 to 550°C . Further calcination up to 800°C , the characteristic absorptions of CO_3^{2-} disappear due to the release of CO_2 molecules, and a new peak around 560 cm^{-1} was observed, which is the characteristic vibration of Gd-O bond of Gd_2O_3 . Therefore, a two-step thermal decomposition process finally leads to the formation of a new product, that is, gadolinium oxides Gd_2O_3 , as revealed also by XRD.

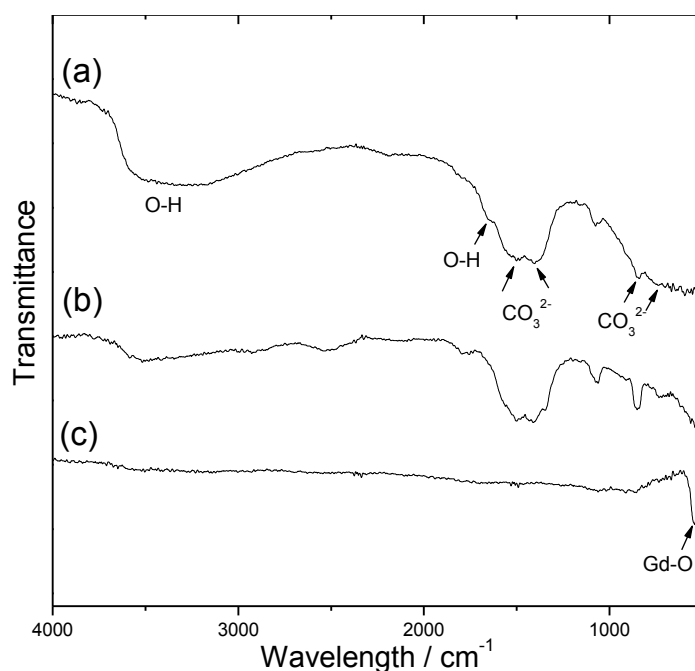


Figure S1. FT-IR spectra of the as-prepared $\text{Gd}(\text{OH})\text{CO}_3\cdot\text{H}_2\text{O}:\text{Eu}$ (a) and the samples calcinated at 550°C (b) and 750°C (c), respectively.

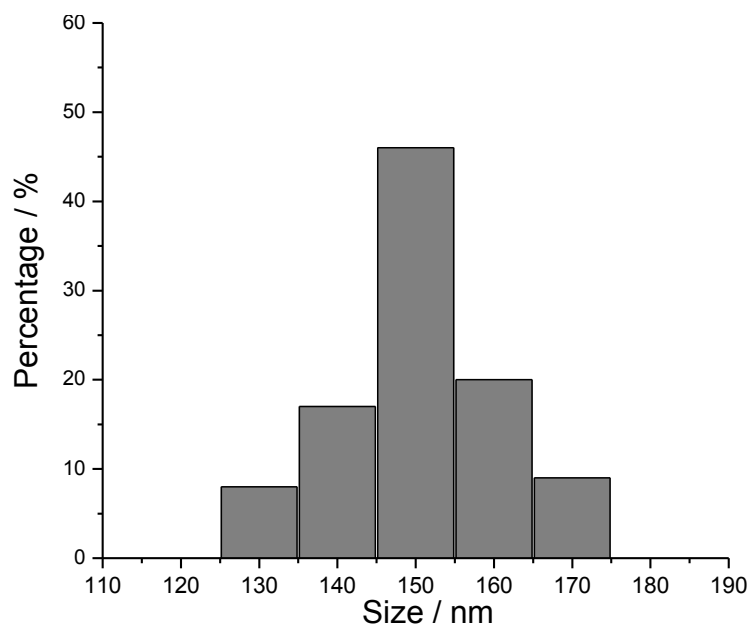


Figure S2. The size distribution plot of as-prepared Gd(OH)CO₃·H₂O:Eu particles based on the analysis of 100 particles from TEM observations

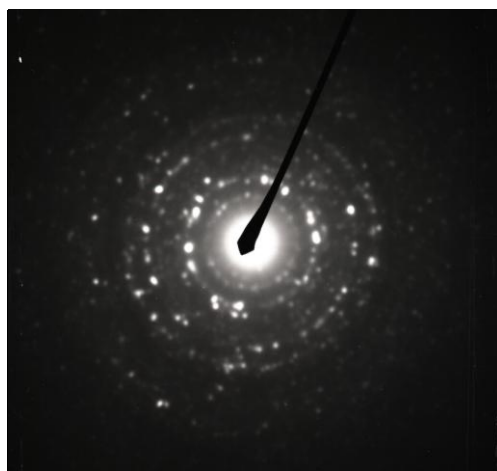


Figure S3. Electron diffraction pattern of mesoporous Gd₂O₃:Eu.

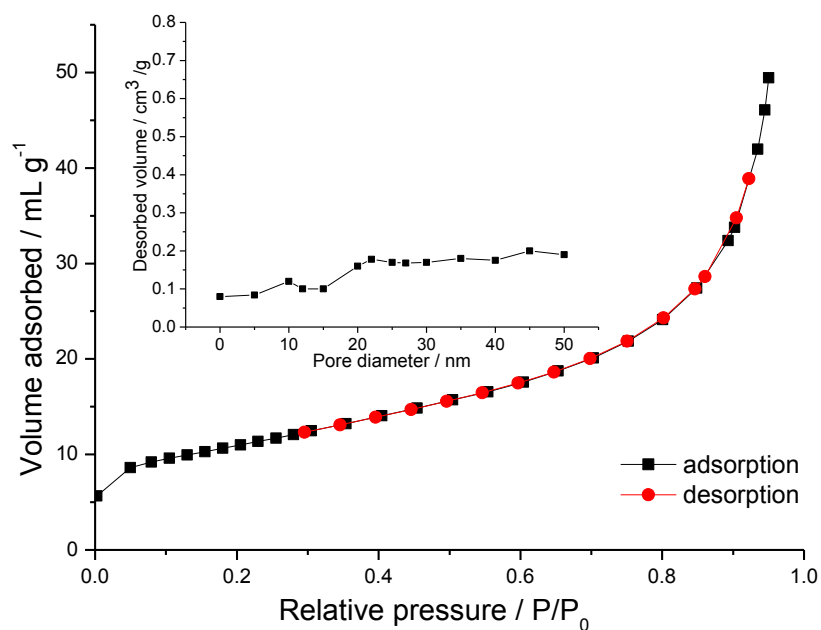


Figure S4. Nitrogen adsorption-desorption isotherms of as-prepared precursor Gd(OH)CO₃·H₂O:Eu. The inset shows the corresponding pore diameter distribution curve.

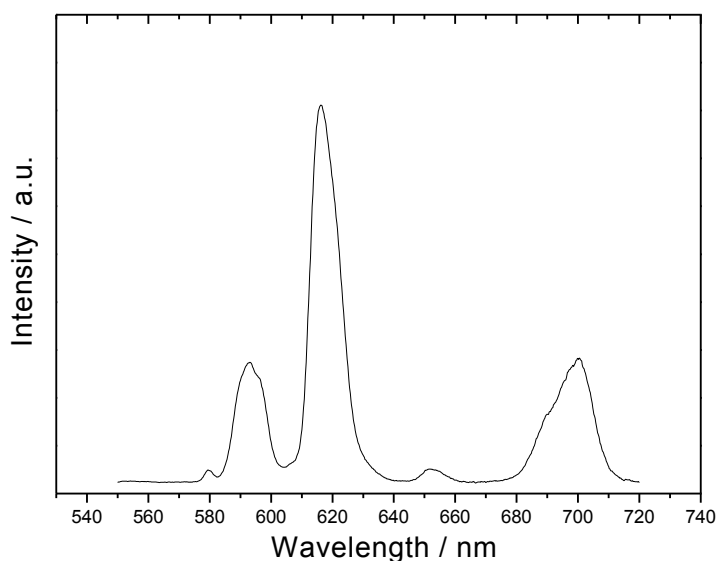


Figure S5. Emission spectrum of as-prepared Gd(OH)CO₃·H₂O:Eu upon excitation at 254 nm.

References

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2. W. Matijevic and W. Hsu, *J. Colloid. Interface Sci.* 1987, **118**, 506.
3. K. Makamoto, *Infrared spectra of inorganic and coordination compounds*. New York: John Wiley & Sons; 1963.