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Electronic Supplementary Information (ESI)

Hydrolysis-resistant yttrium alkoxide rhombic dodecahedrons prepared by a facile hydrothermal method

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EXPERIMENTAL SECTION

Chemicals and Materials. RE oxides Y_2O_3 (99.99 %) and NaOH (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nitric acid (65–68 %) was purchased from Sichuan Xilong Chemical Industry Co., Ltd. Ethylene glycol was purchased from Tianjin Tianli Chemical Reagent Ltd. All chemicals were used without further purification.

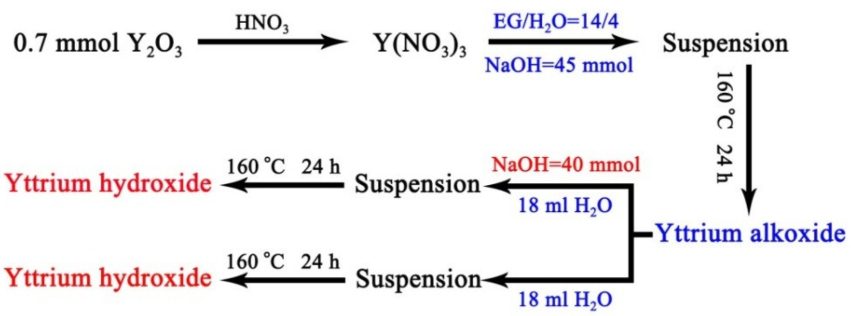
Synthesis of rhombic dodecahedrons. In a typical synthesis of microstructured rhombic dodecahedrons, 0.7 mmol Y_2O_3 was dissolved in 3 mL of nitric acid heated at 70 °C. The superfluous nitric acid was driven off by constant heating. The obtained rare earth nitrate was dissolved in 2 mL of deionized water in a baker equipped with a stirring bar, followed by adding 14 mL of ethylene glycol under continuous magnetic stirring. A solution containing 45 mmol sodium hydroxide in 2 mL deionized water was added to the baker in 30 min under stirring. The total volume of solution is kept at 18 mL no matter how much ethylene glycol used. After additional agitation for 30 min, the final solution was transferred to a 25 mL Teflon-lined stainless autoclave and heated at 160 °C for 24 h. When the autoclave was cooled to room temperature naturally, the precursors were collected by centrifugation, washed several times with deionized water and ethanol and dried at 60 °C in air. The synthesis yield of the yttrium alkoxide is >80%. The products were annealed in air at 800 °C with a heating rate of 5 °C/min.

For the synthesis of Eu^{3+} doped Y_2O_3 rhombic dodecahedrons, 0.67 mmol Y_2O_3 and 0.033 mmol Eu_2O_3 was dissolved in 3 mL of nitric acid heated at 70 °C. The molar ratio of Y and Eu is 95:5. All other steps were the same as for undoped Y_2O_3 rhombic dodecahedrons.

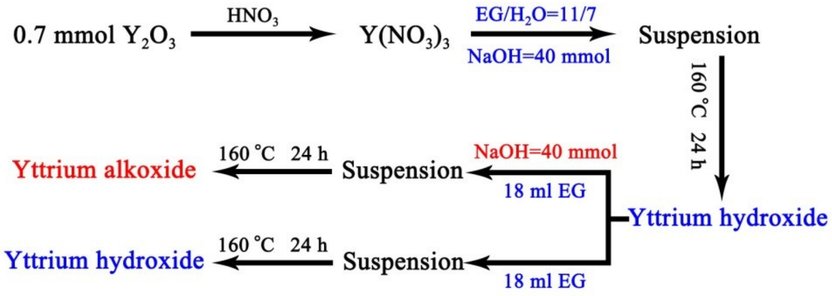
Synthesis of yttrium hydroxide. In a typical synthesis of yttrium hydroxide, 0.7 mmol Y_2O_3 was dissolved in 3 mL of nitric acid heated at 70 °C. The superfluous nitric acid was driven off by constant heating. The obtained rare earth nitrate was dissolved in 1 mL of deionized water in a baker equipped with a stirring bar, followed by adding 14 mL of ethylene glycol under continuous magnetic stirring. A solution containing 70 mmol sodium hydroxide in 3 mL deionized water was added to the baker in 30 min under stirring. The volume ratio of EG/H_2O is 14/4. After additional agitation for 30 min, the final solution was transferred to a 25 mL Teflon-lined stainless autoclave and heated at 160 °C for 24 h. When the autoclave was cooled to room temperature naturally, the precursors were collected by centrifugation, washed several times with deionized water and ethanol and dried at 60 °C in air.

The second hydro/solvothermal reaction .

The yttrium alkoxide (raw material) was synthesized following the steps above. The pre-synthesized $Y_{10}O_2(OCH_2CH_2O)_{13}\cdot 5H_2O$ was added into 18 mL of an aqueous solution containing NaOH (40 mmol) under stirring. The mixture was constantly stirred for 30 min before being transferred to a Teflon-lined stainless steel autoclave of a 25 ml capacity. The autoclave was placed in a preheated electric oven that was maintained at 160 °C for 24 h. Similarly, the $Y_{10}O_2(OCH_2CH_2O)_{13}\cdot 5H_2O$ was added into solution only containing 18 mL deionized water as a contrast, and the rest remains exactly the same. The detailed steps are shown in schematic blew.



The yttrium hydroxide was synthesized through the hydrothermal method mentioned above with minor modifications. The NaOH content is 40 mmol NaOH and the EG/H_2O volume ratio is 11/7. The pre-synthesized yttrium hydroxide was added into the solution containing NaOH (40 mmol) and EG (18 mL) under stirring. The mixture was constantly stirred for 30 min before being transferred to a Teflon-lined stainless steel autoclave of a 25 ml capacity. The autoclave was placed in a preheated electric oven that was maintained at 160 °C for 24 h. Similarly, the $Y(OH)_3$ was added into solution only containing 18 mL EG as a contrast, and the rest remains exactly the same. The detailed steps are shown in schematic blew.



Characterization

XRD was performed to determine the structure of the samples using a BRUKER D8 advanced X-ray diffractometer with Cu Ka irradiation. Thermogravimetric and differential scanning calorimetric (TG–DSC) data were recorded through STA (NETZSCH, STA449 F3 Jupiter®) at a heating rate of 3 °C/min to 900 °C with a continuous flow of air. Fourier transform infrared spectroscopy (FT-IR) spectra were measured by a JASCO FT/IR-470 plus infrared spectrophotometer with the KBr pellet technique. Scanning electron microscopy (SEM) characterization was performed on a Hitachi TM-3000 scanning electron microscope. The FESEM images were obtained by Carl Zeiss Merlin Compact and FEI Quanta 600 FEG field emission scanning electron microscope equipped with an energy-dispersive spectrometer (EDS). Elemental analyses were carried out on a Vario EL III (Elementar Analysensysteme, Germany). Room temperature PL emission of the powder samples were measured using a Hitachi F-7000 fluorescence spectrophotometer and the xenon lamp was used as the excitation source.

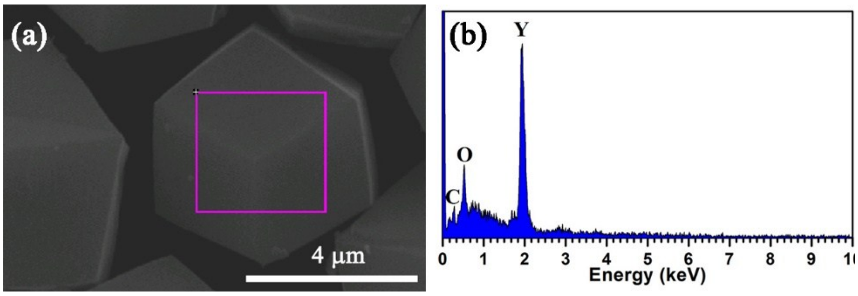


Fig. S1 the EDS of precursor after hydrothermal process.

The element contents of the precursor were measured for several times. The element contents of precursor are characterize by EDS, CHN element analysis, and TG-DSC. The elements involved in the hydrothermal reaction are C, H, O, N, Na and Y. Firstly, the kind of elements in precursor is verified by EDS. The nitrogen and sodium elements do not exist. The contents of carbon and hydrogen are characterize by CHN element analysis. The mass fraction of carbon and hydrogen were 17.4 wt.% and 3.39 wt.% respectively. The content of yttrium element is calculated from the data of TG-DSC. After calcining at 900 °C, the yttrium alkoxide is decomposed into Y_2O_3 and the percent of residual mass is 67 wt.%. So the yttrium mass fraction was 49.62 wt.%. Now, the total content of C, H and Y is 70.41 wt.%. Therefore, the content of oxygen element is 29.59 %. Based on the results above, the elemental composition of the precursors can be expressed by the general formula $Y_2C_{5.2}H_{12.8}O_{6.65}$. The monohydric alkoxides are unstable and easy to hydrolyse. [1] The product exhibits outstanding high stability not only in alcohol but also in water, which confirms the absence of $[OCH_2CH_2OH]^-$. Besides, the absorption peak associated with the vibration band of Y-O-Y centred at 564 cm^{-1} shows up in the IR spectrum of $Y_2C_{5.2}H_{12.8}O_{6.65}$, which confirms the existence of Y-O-Y bond. The Y-O-H bond located at 742 cm^{-1} is not found in the IR spectrum of $Y_2C_{5.2}H_{12.8}O_{6.65}$ illuminating the absence of OH^-. In conclusion, the formula of this new compound may be $Y_2O_{0.4}(OCH_2CH_2O)_{2.6}{\cdot}H_2O$.

Table S1 the element content of precursor.

Element	wt %	at %
Y	49.62	7.68
C	17.4	20.01
H	3.39	46.78
O	29.59	25.53

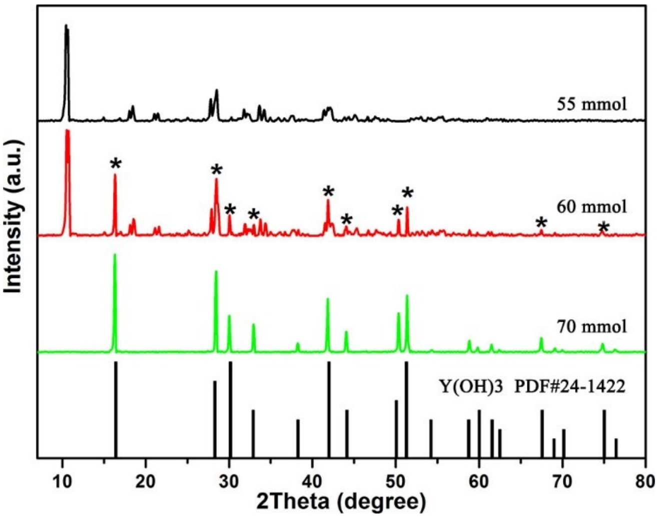


Fig. S2 XRD spectrum of precursor prepared with different amounts of NaOH.

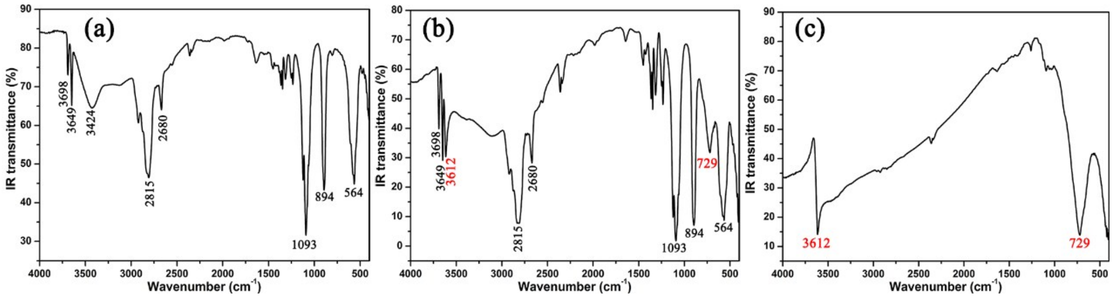


Fig. S3 FT-IR spectrum of precursor prepared with different amounts of NaOH. (a) 55 mmol; (b) 60 mmol; (c) 70mmol.

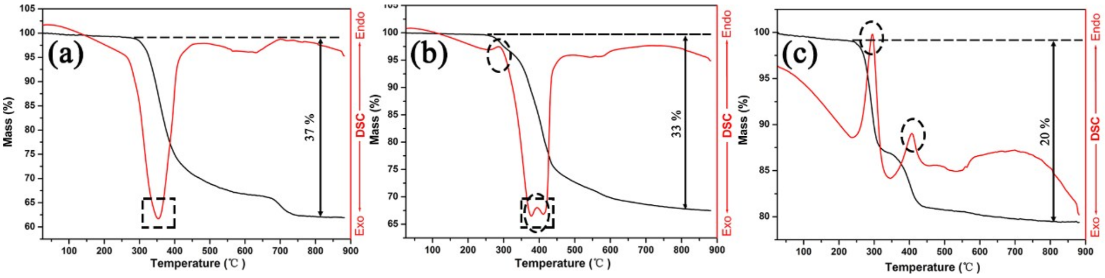


Fig. S4 TG-DSC curves of precursor prepared with different amounts of NaOH. (a) 55 mmol; (b) 60 mmol; (c) 70mmol.

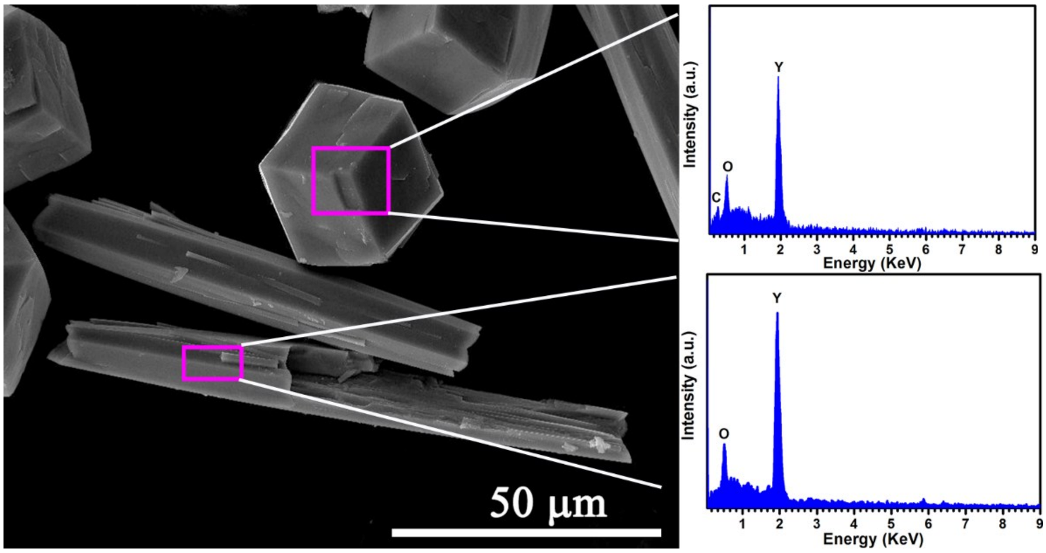


Fig. S5 EDX spectrum of precursor prepared with 60 mmol NaOH.

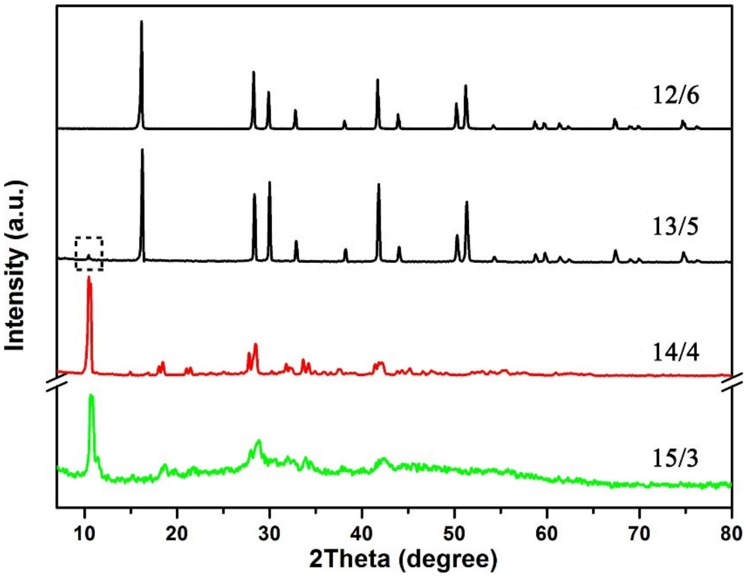


Fig. S6 XRD spectrum of precursor prepared with different EG/H_2O volume ratios.

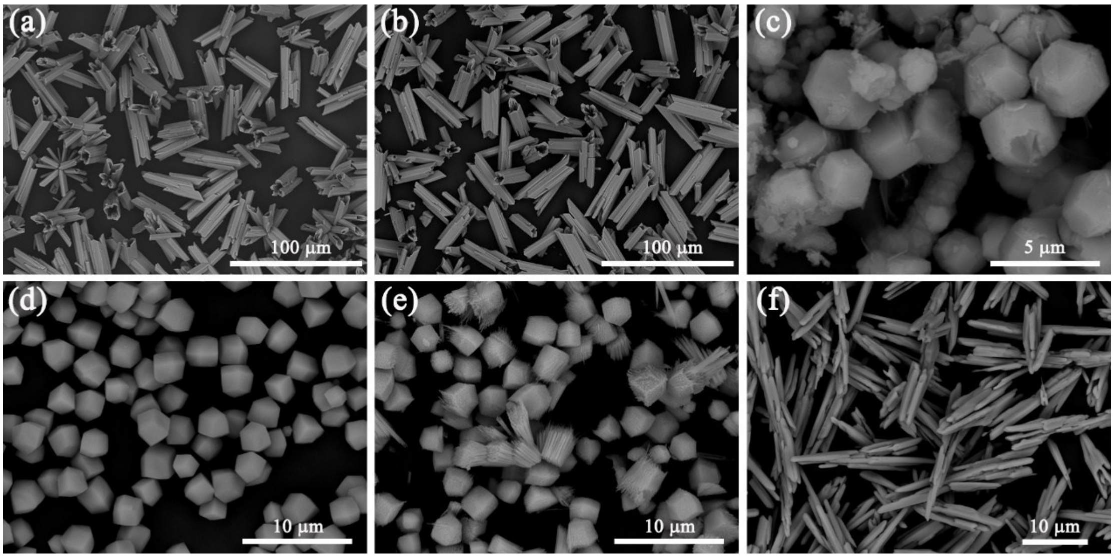


Fig. S7 SEM images of precursors prepared before and after the second hydro/solvothermal reaction. (a) $Y(OH)_3$ before the second solvothermal reaction, (b) after the second solvothermal reaction in the solution containing 18 mL EG, the product is still $Y(OH)_3$ (c) after the second solvothermal reaction in the solution containing 18 mL EG and 40 mmol NaOH, the product changes into yttrium alkoxide (d) yttrium alkoxide before the second hydrothermal reaction, (e) after the second hydrothermal reaction in the solution containing 18 mL H_2O, the product changes into $Y(OH)_3$ (f) after the second hydrothermal reaction in the solution containing 18 mL H_2O and 70 mmol NaOH, the product changes into $Y(OH)_3$.

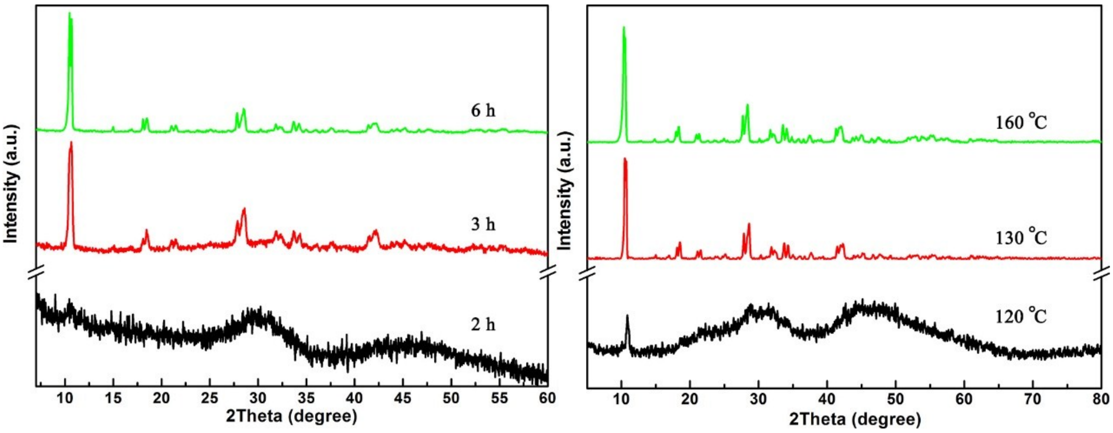


Fig. S8 XRD spectrum of precursor after different hydrothermal time (left) and different hydrothermal temperature (right).

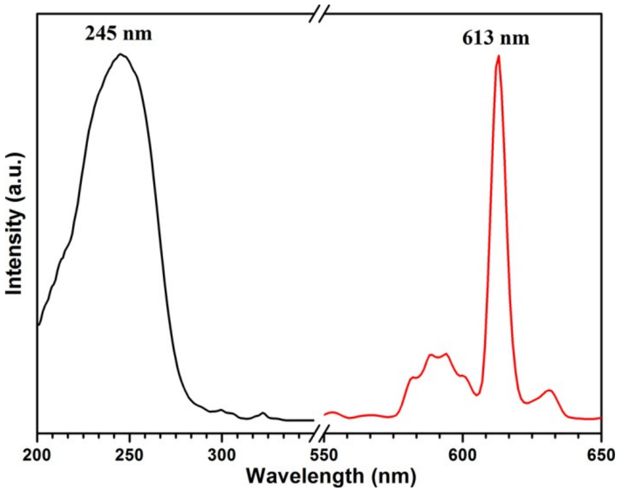


Fig. S9 the photoluminescence excitation and emission spectra of Y_2O_3:Eu .

By monitoring the characteristic emissions of Eu^{3+} ions at 613 nm, the PL excitation spectrum were obtained. The charge transform band (CTB) between O^{2-} and Eu^{3+} ions of Y_2O_3:Eu transformed from yttrium alkoxide is centered at 245 nm. Upon exciting at 245 nm, the emission spectra show the characteristic emission bands of Eu^{3+} ions. The strongest red emission at 613 nm arises from the forced electric dipole $^5D_0 \rightarrow {}^7F_2$ transitions of the Eu^{3+} ions.

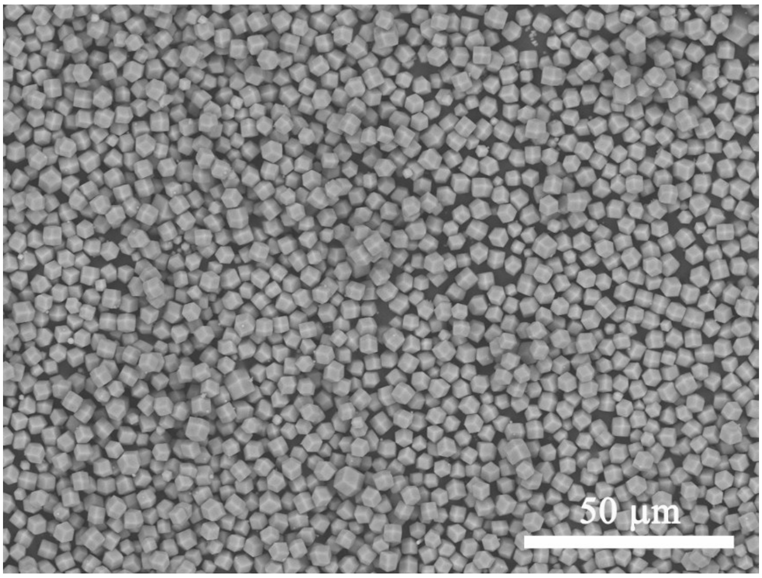


Fig. S10 SEM image of the precursors synthesized with 45 mmol NaOH and 14/4 EG/H_2O at 160 °C for 24 h. The image with low magnification confirms the good uniformity of RDs.

References

[1] R. Y. Dan Wang, N. Kumada, and N. Kinomura, *Chem. Mater.*, 1999, **11**, 2008-2012.