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Supporting Information for

Tuning the Size and Shape of Colloidal Cerium Oxide Nanocrystals through Lanthanide Doping

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Experimental Section

Chemicals: Ceric ammonium nitrate (Ce(NH$_4$)$_2$(NO$_3$)$_6$, 99.9%, Sigma-Aldrich), Ytterbium(III) chloride hexahydrate (YbCl$_3$·6H$_2$O, 99.9%, Beijing Founde Star Science and Technology Co., Ltd China), Gadolinium (III) chloride hexahydrate (GdCl$_3$·6H$_2$O, 99.9%, Beijing Founde Star Science and Technology Co., Ltd China), Erbium(III) chloride hexahydrate (ErCl$_3$·6H$_2$O, 99.9%, Beijing Founde Star Science and Technology Co., Ltd China), Oleic acid (OA, 90%, Sigma-Aldrich), Octadecene (ODE, 90%, Sigma-Aldrich). These chemicals were used as received without further purification.

Instruments: The powder x-Ray diffraction (XRD) pattern was carried out on a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (λ=0.15418 nm). The 2θ angle of the XRD spectra was recorded at a scanning rate of 5 °/min. The size and morphology of colloidal CeO$_2$ powders were characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 microscope at an acceleration voltage of 200 KV. These as-prepared CeO$_2$ samples were dispersed in cyclohexane for further TEM test. One drop of diluted colloidal CeO$_2$ solution was allowed to be dried on the surface of the carbon-coated copper grid. Fourier transform infrared (FT-IR) spectra were measured on an IRPRESTIGE-21 spectrometer via the potassium bromide (KBr) pellet technique. In making the KBr pellets, 1 mg of CeO$_2$ sample was diluted with approximately 100 mg KBr powder. The FT-IR spectrum was collected in the spectral range of 500-3750 cm$^{-1}$. Measurement of upconversion luminescence was carried out under a regeneratively amplified 980 nm diode laser (Hi-Tech Optoelectronics Co. Ltd., Beijing). The emitted upconversion photoluminescence (PL) was collected by a lens-coupled monochromator (Zolix Instruments Co. Ltd., Beijing) of 2 nm spectral resolution with an attached photomultiplier tube (Hamamatsu CR131). All measurements were performed at room temperature, preserving the same geometry for the upconversion luminescence recording. Photographic images of colloidal nanocrystals CeO$_2$:Er$^{3+}$/Yb$^{3+}$ were taken by a digital camera (Lumix DMC-Fx520, Japan) without adding any filter. The composition of the nanoparticles was further determined by inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies 7500 Series).
Synthesis of CeO$_2$ nanoparticles: Appropriate safety measures are required to be taken to remove the overpressure caused by violent decomposition of Ce(NH$_4$)$_2$(NO$_3$)$_6$ at the temperature of about 220 °C. As a typical synthesis procedure, 1 mmol Ce(NH$_4$)$_2$(NO$_3$)$_6$ was added into a three-necked flask (100 mL) with 20 mmol OA and 20 mmol ODE, followed by vacuum degassing at 100 °C for 30 min to remove water and oxygen. Then the solution was heated to 340 °C at a temperature rate of 5 K·min$^{-1}$ under nitrogen protection. After maintaining at 340 °C for 60 min, the reaction was stopped and cooled down to room temperature. The CeO$_2$ NPs were precipitated by using an excess amount of ethanol, and then collected via centrifugation.

Synthesis of CeO$_2$:Yb$^{3+}$ nanoparticles: The synthetic procedure for the synthesis of colloidal CeO$_2$ nanoparticles doped 4, 7, 12, and 22 mol% Yb$^{3+}$ was exactly the same as that used for preparing CeO$_2$ NPs, except that a fixed amount of YbCl$_3$·6H$_2$O and Ce(NH$_4$)$_2$(NO$_3$)$_6$ were added into a three-necked flask at the same time. The total amount of YbCl$_3$·6H$_2$O plus Ce(NH$_4$)$_2$(NO$_3$)$_6$ is 1 mmol for the preparation of every single sample.

Synthesis of CeO$_2$:Er$^{3+}$/Yb$^{3+}$ nanoparticles: The synthetic procedure for the synthesis of colloidal CeO$_2$ nanoparticles doped with 2 mol% Er$^{3+}$, and 4 mol% Yb$^{3+}$, 7 mol% Yb$^{3+}$, 12 mol% Yb$^{3+}$, and 22 mol% Yb$^{3+}$ was exactly the same as that used for preparing CeO$_2$ NPs, except that a fixed amount of YbCl$_3$·6H$_2$O, ErCl$_3$·6H$_2$O, and Ce(NH$_4$)$_2$(NO$_3$)$_6$ were added into a three-necked flask at the same time. The total amount of YbCl$_3$·6H$_2$O, ErCl$_3$·6H$_2$O, and Ce(NH$_4$)$_2$(NO$_3$)$_6$ is a constant of 1 mmol for synthesizing every single sample. The CeO$_2$:Er$^{3+}$/Yb$^{3+}$ NPs were dissolved in cyclohexane for further optical measurements.

Synthesis of CeO$_2$:Gd$^{3+}$ nanoparticles: The synthetic procedure for the synthesis of colloidal CeO$_2$ nanoparticles doped 4, 7, 12, and 22 mol% Gd$^{3+}$ was exactly the same as that used for preparing CeO$_2$ NPs, except that a fixed amount of GdCl$_3$·6H$_2$O and Ce(NH$_4$)$_2$(NO$_3$)$_6$ were added into a three-necked flask at the same time. The total amount of GdCl$_3$·6H$_2$O plus Ce(NH$_4$)$_2$(NO$_3$)$_6$ is a constant of 1 mmol for synthesizing every single sample.

**Figure S1** (A) Digital photograph of synthesized CeO$_2$ nanocrystals dissolved in cyclohexane, which displays the colloidal ability of CeO$_2$ nanoparticles. (B) FT-IR transmission spectra of the pure CeO$_2$ nanoparticles. As one can see in Figure S1B, there is a broad band peaked at 3403 cm$^{-1}$, which characterizes the stretching vibration mode of the O-H of the COO-H group. Two peaks with maxima at 2927 cm$^{-1}$ and 2853 cm$^{-1}$ can be assigned to the asymmetric ($v_{as}$) and symmetric ($v_s$) stretching vibration of methylene (CH$_2$) in the long alkyl chain of the oleic acid molecule, respectively. In addition, the =C-H stretching mode is located at 3008 cm$^{-1}$ in the FTIR spectrum. The peaks with maxima at about 1552 cm$^{-1}$ and 1463 cm$^{-1}$
belongs to the asymmetric ($v_{as}$) and symmetric ($v_s$) stretching vibration of the carboxylic group (-COOH), respectively. It can be concluded from Figure S1 that the oleic acid is coordinated to the surface of CeO$_2$ nanoparticles as an overlayer. This can also be suggested from the fact that these resulting CeO$_2$ nanocrystals can be easily dispersed into nonpolar solvent, e.g., cyclohexane, to form transparent solution, as shown in Figure S1A.

**Figure S2** displays the XRD patterns of the CeO$_2$ nanocrystals. (A) Standard data of cubic CeO$_2$ (JCPDS 65-2975), (B) CeO$_2$: 0 mol%Yb$^{3+}$, (C) CeO$_2$: 4 mol%Yb$^{3+}$, (D) CeO$_2$: 7 mol%Yb$^{3+}$, (E) CeO$_2$: 12 mol%Yb$^{3+}$ and (F) CeO$_2$: 22 mol%Yb$^{3+}$. As illustrated in Figure S2, the positions of all the XRD peaks correspond well to the standard JCPDS 65-2975 cubic pattern of CeO$_2$, and no peaks from other phases or impurities are observed. This demonstrates that all the nanoparticles are highly crystalline in nature and have cubic structures. In addition, the unchanged peak positions in the XRD patterns illustrate that the lattice parameters are the same for all the CeO$_2$:Yb$^{3+}$ samples, suggesting that the Yb$^{3+}$ ions enter the host lattice in the way of replacing cationic Ce$^{4+}$ ions rather than by occupying interstitial sites, or else, the lattice parameters will change significantly due to the strong cumbic interactions between interstitial ions and lattice ions.
Figure S3. The energy dispersive spectroscopy (EDS spectra) of the 0, 4, 7, 12, 22 mol% Yb$^{3+}$ doped CeO$_2$ nanocrystals. As one can see, there is no detection of Yb$^{3+}$ ions in Figure S3(a), and the atomic content of Yb$^{3+}$ ions increase gradually from Figure S3(b) to Figure S3(e), correlating well with the use of the content of Yb$^{3+}$ precursors (Consult Figure 1). As all the synthetic procedure are exactly the same when preparing all the CeO$_2$ nanoparticles, the results here in Figure S3(a)-(e) give clear evidence that the evolution of size and shape in Figure 1 (a)-(e) indeed is induced by the doping of Yb$^{3+}$ ions. Quantitatively, the practical percentage of catonic content of Yb$^{3+}$ ions (conunted on cations displayed in Figure 3) was calculated to be about 0, 3, 5, 15, and 33 mol%, which generally is in good agreement with CeO$_2$ nanoparticles doped with 0, 4, 7, 12, 22 mol% Yb$^{3+}$ ions counted on cationic precursors. Also, such observation is in accordance with the results measured by inductively coupled plasma mass spectrometry (ICP-MS) (Supporting Information, Table S1). The practical large increase in the content of Yb$^{3+}$ ions might can illustrate the anomalous large increase in the size from 13 nm to 65 nm (consult Figure 1).
Figure S4. Histograms of the particle size for CeO$_2$ nanopowders doped with (A) 0 mol\% Yb$^{3+}$, (B) 4 mol\% Yb$^{3+}$, (C) 7 mol\% Yb$^{3+}$, (D) 12 mol\% Yb$^{3+}$, and (E) 22 mol\% Yb$^{3+}$ ions. These data were obtained from the TEM images of more than 200 CeO$_2$:Yb$^{3+}$ nanocrystals, which displays the increase in the size of the CeO$_2$: Yb$^{3+}$ nanoparticles with the increment of Yb$^{3+}$ ions doping. The average sizes for nanoparticles with relative content of Yb$^{3+}$ ions of 0 mol\%, 4 mol\%, 7 mol\%, 12 mol\% and 22 mol\% were found to be about 4.3 (with a standard deviation of 1.1), 4.2 (with a standard deviation of 1.2), 8.1 (with a standard deviation of 2.3), 13.1 (with a standard deviation of 3.5), and 67.4 (with a standard deviation of 13), respectively.
Table S1. Compositions of the nanoparticles measured by inductively coupled plasma mass spectrometry (ICP-MS). These results correlate well with that in Figure S3 and Figure S8 in the supporting information.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial doped [Ln (^{3+})] (at. %)</th>
<th>Doped [Ln (^{3+})] in NCs (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2):4%Yb</td>
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<td>16.53</td>
</tr>
<tr>
<td>CeO(_2):4%Gd</td>
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<td>5.20</td>
</tr>
<tr>
<td>CeO(_2):12%Gd</td>
<td>12</td>
<td>8.06</td>
</tr>
<tr>
<td>CeO(_2):22%Gd</td>
<td>22</td>
<td>17.39</td>
</tr>
</tbody>
</table>

Figure S5. Upconversion photoluminescence spectra of CeO\(_2\): Yb/Er nanocrystals dissolved in cyclohexane excited with a 980 nm diode laser of 20 W/mm\(^2\). The inset shows the intensity ratio of the red at 660 nm to the green at 550 nm as a function of Yb\(^{3+}\) ion concentration. As one can see, the green at 550 nm and the red emission at 660 nm arise from radiative decays from the \(^4\)S\(_{3/2}\) and \(^4\)F\(_{9/2}\) to the ground state of Er\(^{3+}\) ions, respectively.\(^{17a,17b}\) As compared with CeO\(_2\):Er\(^{3+}\) nanocrystals, upconversion PL in nanoparticles CeO\(_2\):Er\(^{3+}\)/Yb\(^{3+}\) show a great enhancement due to the energy transfer \(^4\)I\(_{15/2}\)(Er)+\(^2\)S\(_{5/2}\)(Yb) \(\rightarrow\) \(^4\)I\(_{13/2}\)(Er)+\(^2\)F\(_{7/2}\)(Yb) from Yb\(^{3+}\) to Er\(^{3+}\) ions.\(^{17b}\) This is a direct evidence of Yb\(^{3+}\) ions in the lattice, as Yb\(^{3+}\) ions has much larger cross section than Er\(^{3+}\) ions and can efficiently sensitize Er\(^{3+}\) ions. It is reported that the...
intensity ratio of the red to the green upconversion PL increases with the concentration of Yb$^{3+}$ ions in the crystal lattice due to also an increased rate of energy back-transfer process $^4S_{3/2}(Er)+^2F_{7/2}(Yb) \rightarrow ^4I_{13/2}(Er)+^2F_{5/2}(Yb)$. In addition, the changes in the intensity ratio of the red to the green upconversion PL not only further verifies the existence of Yb$^{3+}$ content in the crystal lattice, but also shows an increase in the atomic content of Yb$^{3+}$ ions in the nanocrystals. This correlates well with the observation of an increase in the content of Yb elements revealed by EDS (Figure S3) and ICP-MS (Table S1).

Figure S6. (A-D) Photographs of upconversion PL in colloidal CeO$_2$ nanoparticles doped with 2 mol% Er$^{3+}$, and (A) 4 mol% Yb$^{3+}$, (B) 7 mol% Yb$^{3+}$, (C) 12 mol% Yb$^{3+}$, and (D) 22 mol% Yb$^{3+}$ dissolved in cyclohexane under excitation at 980 nm with a power density of about 20 W/mm$^2$. As the excitation of 980 nm falls into the “biological transparent window” of tissues, this can allow their potential use as viable contrast agents for autofluorescence-insensitive in vitro and in vivo multiplex imaging. Multicolor upconversion PL in Figure S6 suggests that the simple method demonstrated for tuning the size and shape of CeO$_2$ can also be extended to control the upconversion color output, which is important for their biomedical applications.
Figure S7. TEM images of resulting CeO$_2$ nanoparticles doped with (A) 4 mol% Gd$^{3+}$, (B) 7 mol% Gd$^{3+}$, (C) 12 mol% Gd$^{3+}$, and (D) 22 mol% Gd$^{3+}$ ions. As one can see, the size of CeO$_2$ nanoparticle increases with the increment of the Gd$^{3+}$ ion concentration. Detailed analysis of size distribution is described in Figure S10.
Figure S8. The energy dispersive spectroscopy (EDS spectra) of the 4, 7, 12, 22 mol% Gd$^{3+}$ doped CeO$_2$ nanocrystals (consult Figure S7). As one can see, the atomic content of Yb$^{3+}$ ions increase gradually from Figure S8(a) to Figure S8(d), correlating well with the use of the content of Gd$^{3+}$ precursors. Also such an increase are in good agreement with the experimental results measured by ICP-MS in Table S1.

Figure S9 Displays the XRD patterns of the CeO$_2$ nanocrystals. (A) CeO$_2$: 4 mol%Gd$^{3+}$, (B) CeO$_2$: 7 mol% Gd$^{3+}$, (C) CeO$_2$: 12 mol% Gd$^{3+}$ and (D) CeO$_2$: 22 mol% Gd$^{3+}$. As illustrated in Figure S9, the positions of all the XRD peaks have not peaks from other phases or impurities are observed. This demonstrates that all the nanoparticles are highly crystalline in nature and have cubic structures.
Figure S10. Histograms of the particle size for CeO$_2$ nanopowders doped with (A) 4 mol% Gd$^{3+}$, (B) 7 mol% Gd$^{3+}$, (C) 12 mol% Gd$^{3+}$, and (D) 22 mol% Gd$^{3+}$ ions. These data were obtained from the TEM images of more than 200 CeO$_2$: Gd$^{3+}$ nanocrystals, which displays the increase in the size of the CeO$_2$: Gd$^{3+}$ nanoparticles with the increment of Yb$^{3+}$ ions doping. The average sizes for nanoparticles with relative content of Gd$^{3+}$ ions of 4 mol%, 7 mol%, 12 mol% and 22 mol% were found to be about 4.4 (with a standard deviation of 1.0), 8.0 (with a standard deviation of 2.9), 13.9 (with a standard deviation of 3.3), and 48.7 (with a standard deviation of 10.1), respectively.