Supplementary Information

Morphology-Dependent Fluorescence of Europium-Doped Cerium Oxide Nanomaterials

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Equation S1. Working Definition of theoretical Eu\(^{3+}\) doping percentage.

The theoretical Eu\(^{3+}\) concentration with regard to atomic percentage within each material ranges from 0% to 18% Eu\(^{3+}\) as calculated by Equation 1, and based on experimental reactant concentrations:

\[
%Eu = \frac{m M Eu^{3+}}{m M Eu^{3+} + m M Ce^{3+}}
\]  

(S1)

Figure S1. Diagram of electrospinning apparatus.

Figure S2. Representative SEM images of (a) unannealed 8% Eu-CeO\(_2\)/PVP nanowires, and (b) annealed 8% Eu-CeO\(_2\) nanowires.
Figure S3. Histograms of 8%-Eu-CeO$_2$ (a) nanorods length, (b) nanorods width, (c) annealed nanorods length (d) annealed nanorods width, (e) nanowire diameters, and (f) nanocube edge length.
Equation S2. Scherrer formula and associated definitions. Crystalline domain sizes are estimated by use of the Scherrer equation (Equation S2). Here $\tau$ is the crystalline domain size in nm, $K$ is the shape constant approximated to be 0.94, $\lambda$ is the wavelength of the incident x-rays (1.54178 Å for Cu Kα), $\beta$ is the full-width half-max of the CeO$_2$ (111) peak at 31° and, $\theta$ is the Bragg angle, or $\frac{1}{2}$ the 2$\theta$ x-ray angle.

$$\tau = \frac{K\lambda}{\beta \cos(\theta)} \quad (S2)$$

Figure S4. XRD spectra of 8% Eu-CeO$_2$ nanomaterials.

Table S1. Atomic percentage of Eu$^{3+}$ in CeO$_2$ nanorods, nanowires, nanocubes, and annealed nanorods, calculated without consideration to oxygen as determined by EDS analysis.

|          | Undoped | 2% Eu | 8% Eu | 15% |
|----------|---------|-------|-------|-----|
| Nanowire | 0.0 ± 0.0 | 2.4 ± 0.7 | 9.7 ± 1.7 | 16.2 ± 0.5 |
| Nanorod  | 0.2 ± 0.2 | 3.1 ± 1.0 | 7.9 ± 1.7 | 15.6 ± 0.7 |
| Annealed | 1.1 ± 0.9 | 3.1 ± 0.9 | 7.0 ± 0.9 | 15.7 ± 0.4 |
| Nanorod  | 0.2 ± 0.2 | 2.9 ± 1.0 | 6.8 ± 0.9 | 11.7 ± 0.3 |
Table S2. Atomic percentage of europium, cerium, and oxygen in CeO$_2$ nanorods, nanowires, nanocubes, and annealed nanorods as determined by EDS analysis.

|         | 0% Eu-CeO$_2$ | 2% Eu-CeO$_2$ | 8% Eu-CeO$_2$ | 15% Eu-CeO$_2$ |
|---------|---------------|---------------|---------------|---------------|
| Nanowire |               |               |               |               |
| % O     | 52.5 ± 6.8    | 51.4 ± 0.9    | 53.1 ± 4.3    | 51.1 ± 2.3    |
| % Ce    | 47.1 ± 4.8    | 46.0 ± 2.4    | 42.3 ± 3.8    | 41.1 ± 2.2    |
| % Eu    | 0.0 ± 0.0     | 1.15 ± 0.4    | 4.6 ± 0.9     | 7.9 ± 0.1     |
| Nanorod |               |               |               |               |
| % O     | 62.7 ± 7.2    | 68.6 ± 8.0    | 62.1 ± 5.5    | 60.5 ± 1.3    |
| % Ce    | 37.2 ± 7.2    | 30.5 ± 8.0    | 34.2 ± 4.6    | 32.2 ± 1.9    |
| % Eu    | 0.1 ± 0.1     | 0.9 ± 0.1     | 3.7 ± 0.9     | 7.3 ± 1.9     |
| Annealed Nanorod |   |               |               |               |
| % O     | 65.6 ± 6.7    | 57.8 ± 0.9    | 60.2 ± 1.9    | 56.3 ± 3.8    |
| % Ce    | 32.1 ± 6.9    | 40.9 ± 1.3    | 37.0 ± 2.1    | 36.7 ± 3.4    |
| % Eu    | 0.33 ± 0.3    | 1.3 ± 0.4     | 2.8 ± 0.4     | 6.9 ± 0.4     |
| Nanocube |               |               |               |               |
| % O     | 53.5 ± 0.9    | 51.9 ± 1.6    | 54.3 ± 3.6    | 55.8 ± 1.1    |
| % Ce    | 46.4 ± 0.9    | 46.7 ± 1.2    | 42.6 ± 3.7    | 39.0 ± 1.1    |
| % Eu    | 0.1 ± 0.1     | 1.4 ± 0.6     | 3.1 ± 0.2     | 5.2 ± 0.1     |

Table S3. Binding energies and areas from fitted Ce 3d XPS spectra for 8% Eu-CeO$_2$ nanomaterials and undoped CeO$_2$ nanorods.

|    | u  |  u' |  u'' |  u''' | v  |  v' |  v'' |  v''' |
|----|----|-----|------|-------|----|-----|------|-------|
| CeO$_2$ Nanorod |     |     |      |       |    |     |      |       |
| Binding Energy (eV) | 881.89 | 884.87 | 888.27 | 897.89 | 900.53 | 903.45 | 906.73 | 916.33 |
| Integrated Area    | 8259.7 | 4762.6 | 3694.8 | 5993.1 | 5153.2 | 2168.8 | 2296.6 | 4336.1 |
| Eu-CeO$_2$ Nanorod |     |     |      |       |    |     |      |       |
| Binding Energy (eV) | 881.86 | 884.69 | 888.20 | 898.0 | 900.61 | 903.20 | 906.70 | 916.37 |
| Integrated Area    | 6423.7 | 4434.9 | 3933.5 | 5752.9 | 4034.0 | 2161.2 | 2336.1 | 3710.6 |
| Eu-CeO$_2$ Annealed Rod |    |     |      |       |    |     |      |       |
| Binding Energy (eV) | 881.95 | 884.92 | 888.35 | 897.74 | 900.53 | 903.45 | 906.97 | 916.17 |
| Integrated Area    | 5561.9 | 1863.9 | 3506. | 5379.1 | 3551.2 | 938.2 | 2143.31 | 3898.86 |
| Eu-CeO$_2$ Nanowire |     |     |      |       |    |     |      |       |
| Binding Energy (eV) | 881.9 | 884.6 | 888.2 | 897.9 | 900.4 | 902.4 | 906.9 | 916.1 |
| Integrated Area    | 26655 | 4786 | 4835 | 16583 | 8056 | 1108 | 1442 | 8279 |
| Eu-CeO$_2$ Nanocube |     |     |      |       |    |     |      |       |
| Binding Energy (eV) | 882.00 | 883.50 | 888.04 | 898.10 | 901.03 | 903.89 | 907.11 | 916.46 |
| Integrated Area    | 2287.95 | 1838.26 | 1834.6 | 3172.9 | 1720.34 | 293.87 | 902.894 | 2021.89 |
Table S4. Binding energies and integrated areas from fitted O 1s XPS spectra for 8%-Eu-CeO$_2$ nanomaterials and undoped CeO$_2$ nanorods.

|                      | $O_\alpha$ | $O_\beta$ |
|----------------------|------------|------------|
|                      | Binding Energy (eV) | Integrated Area | Binding Energy | Integrated Area |
| CeO$_2$ Nanorod      | 528.95     | 5017.1     | 531.40       | 1055.4 |
| Eu-CeO$_2$ Nanorod   | 528.99     | 4282.6     | 531.39       | 1478.6 |
| Eu-CeO$_2$ Annealed Nanorod | 528.69     | 4454.6     | 531.32       | 1234.8 |
| Eu-CeO$_2$ Nanowire  | ~529.3     | 15639.2    | ~531.99      | 2460.4 |
| Eu-CeO$_2$ Nanocube  | 529.16     | 4657.9     | 532.04       | 500.4 |

Figure S5. XPS spectra of Ce 3d (a) CeO$_2$ nanorod, (b) 8% Eu-CeO$_2$ nanocubes, (c) 8% Eu-CeO$_2$ nanowires, and O 1s of (d) CeO$_2$ nanorods, (e) 8% Eu-CeO$_2$ nanocubes, and (f) 8% Eu-CeO$_2$ nanowires.
Figure S6. FT IR spectra of cerium oxide nanorods before and after annealing at 600°C.

Figure S7. Normalized absorbance spectra of 8 at% Eu-CeO$_2$ nanowires (75 μg/mL), nanorods (260 μg/mL), nanocubes (112 μg/mL), and annealed nanorods (188 μg/mL).
Figure S8. UV-Vis absorbance with varying Eu$^{3+}$ concentration for CeO$_2$ (a) nanowires, (b) nanorods, (c) nanocubes, and (d) annealed nanorods.

Figure S9. Excitation spectrum for nanocubes measuring emission at 590 nm.

Table S5. Asymmetry ratio of 8% Eu-CeO$_2$ nanorods with increasing annealing temperature with excitation at 375 nm.

| Annealing Temperature | Unannealed | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|-----------------------|------------|--------|--------|--------|--------|--------|
| Asymmetry Ratio       | 1.99       | 2.49   | 2.29   | 2.32   | 2.23   | 2.19   |