Supporting information

Evidence of Trivalent Europium Incorporated in Anatase TiO₂ Nanocrystals with Multiple Sites

Wenqin Luo,^{†,‡} Renfu Li,^{†,‡} Guokui Liu,[§] Mark R. Antonio,[§] and Xueyuan Chen^{†,*,**}

Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China, State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China and Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Figure S1. The enlarged emission spectra of Eu³⁺ ions at Site II ($\lambda_{\text{exc.}}=470.7$ nm) and Site III ($\lambda_{\text{exc.}}=472.1$ nm). The 0-0 line of Eu³⁺ at Site II is clearly observed. The inset shows the weak emissions from ⁵D₁ to ⁷F_J (J=0,1,2) multiplets. All spectra were measured at 10 K.

[†]Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

[‡] State Key Laboratory of Structural Chemistry, China.

[§] Argonne National Laboratory.

* Corresponding author. Phone and fax: +86-591-8764-2575. E-mail: xchen@fjirsm.ac.cn.

Figure S2. Influence of the annealing temperature on the emission intensities of $^5D_0 \rightarrow ^7F_2$ transitions of Eu^{3+} at different sites in $\text{Eu}^{3+}:\text{TiO}_2$ (2 at.%) nanocrystals. Multiple sites can be observable for the sample annealed at a temperature up to 700°C. However, only Site I can be observed if annealed above 700°C. The above facts indicate that Eu^{3+} ions at Sites II and III in the samples annealed at high temperature are unstable, and may be expelled from the lattice to the disordered grain or surface sites.

TG-DTA experiments: Thermogravimetric-differential thermal analyses (TG-DTA) were conducted on a Netzsch STA449C thermal analysis system with pure air flow of 20 cm³/min. The sample was heated at a rate of 10°C/min.

Figure S3. TG-DTA curves of the as-prepared $\text{Eu}^{3+}:\text{TiO}_2$ ($x=2,4,6$ at.%) nanoparticles. The exothermic peaks at approximately 400, 520, and 560°C correspond to the crystallization temperatures for samples with Eu^{3+} contents of 2 at.%, 4 at.% and 6 at.% respectively.

Figure S4. XRD patterns of $\text{Eu}^{3+}:\text{TiO}_2$ ($x=1,2,4,6$ at.%) nanoparticles annealed at 400°C. The higher Eu^{3+} contents the worse crystallinity of the sample was observed, and the sample of $\text{Eu}^{3+}:\text{TiO}_2$ (6 at.%) exhibits amorphous structure, which indicates a higher crystallization temperature required for its heat-treatment

Figure S5. TEM images of the as-prepared $\text{Eu}^{3+}:\text{TiO}_2$ (2 at.%) nano-aggregates. The inset is the SAED spectrum of a spherical aggregate, showing the amorphous structure before annealing.