

Upconversion Luminescence of Monodisperse $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ Nanocrystals

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Fluorescent labeling materials have been attracting considerable interest for their biological applications.¹ However, conventional downconversion fluorescent materials, including organic dyes and semiconductor quantum dots, have their intrinsic limitations.^{1d,2} Furthermore, these downconversion fluorescent materials are excited by ultraviolet (UV) or short wavelength visible (vis) radiation, which have very limited penetration into tissues, strong autofluorescence, and potential cytotoxic and carcinogenic effects.³ To solve these problems above, the development of alternative biological luminescent labels through the use of up-converting rare-earth (RE) nanophosphors has been carried out and sparked considerable interest.⁴ It offers an attractive optical labeling technique in biological studies without many of the constraints associated with organic fluorophores and quantum dots. RE nanocrystals have sharp absorption and emission lines, high quantum yields, long lifetimes, and superior photostability.⁵ In particular, the upconversion (UC) technique utilizes near-infrared excitation rather than UV excitation, thereby significantly minimizing background autofluorescence, photobleaching, and photodamage to biological specimens. Up to now, many RE-doped nanomaterials have been prepared,⁶ and many strategies have been developed for their application in diagnostic and analytical pathology.⁷

Among various UC nanomaterials, fluorides are efficient hosts for UC luminescence of RE ions due to their appropriate energy phonons to produce strong UC fluorescence.⁸ Especially, NaYF_4 is acknowledged as the most efficient UC host material at present.⁹ Previous investigations have shown that the UC luminescence in RE doped NaYF_4 strongly depends on the phase and particle size.^{9,10} For example, the UC efficiency of green emission in hexagonal $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ is ~ 10 times stronger than that in cubic $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$, and again that of bulk cubic $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ is $\sim 10^2$ – 10^3 times stronger than that in nanosize cubic NaYF_4 .⁹ However, compared with the cubic sample, hexagonal NaYF_4 nanocrystals usually have larger particle sizes. Therefore, it is of vital importance to enhance the UC efficiency of the nanocrystals with a smaller size.

CaF_2 , a very important fluoride, has been used as an attractive host for phosphors with interesting up/down-conversion luminescent properties.¹¹ The edge of the fundamental absorption band in CaF_2 lies in the vacuum UV at ~ 12 eV. CaF_2 has a well-known fluorite structure, in which Ca^{2+} ions lie at the nodes in a face-centered lattice, while F^- ones lie at the centers of the octants.¹² In RE doped CaF_2 nanocrystals, the substitution of a cation requires a negative ion for compensation, and therefore, some interesting luminescence properties can be expected.

Herein, we successfully prepared sub-10 nm monodispersed $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals according to our reported liquid–solid-solution (LSS) strategy (Supporting Information).^{6e} These as-prepared nanocrystals not only can be transparently dispersed in cyclohexane but also present bright UC luminescence under 980 nm excitation. The UC luminescence properties of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$

nanocrystals were compared with those of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals. The results indicate that CaF_2 is a promising host material for producing desirable UC luminescence and has potential applications in fluorescent labels for biomolecules.

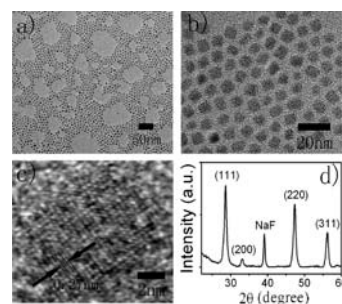


Figure 1. (a) TEM image of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals, (b) magnified image of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals, (c) HRTEM image of an individual $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystal, and (d) XRD pattern of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals.

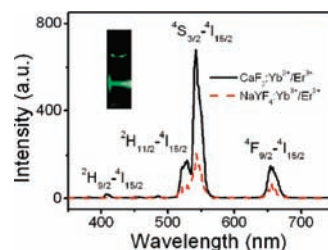


Figure 2. UC luminescence spectra of cubic $\text{CaF}_2:\text{Yb}^{3+}(20\%)/\text{Er}^{3+}(2\%)$ and cubic $\text{NaYF}_4:\text{Yb}^{3+}(20\%)/\text{Er}^{3+}(2\%)$ nanocrystals dissolved in cyclohexane excited with a 980 nm laser. Inset shows the luminescence photograph of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals dissolved in cyclohexane under 980 nm excitation.

Figure 1a,b show the transmission electron microscopy (TEM) images of the as-synthesized $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals. They are monodisperse, with a diameter of ~ 7 nm. The high-resolution transmission electron microscopy (HRTEM) image of a single nanoparticle is shown in Figure 1c. The measured lattice spacing is ~ 0.27 nm, corresponding to the distance of the {200} planes of the cubic CaF_2 . This image also reveals the single-crystal nature of the product. The corresponding XRD pattern is presented in Figure 1d, and the peaks matched very well with the standard cubic $\text{CaF}_2:\text{Yb}^{3+}(20\%)$ crystal structure data (01-087-0976 in the JCPDS database). In addition, excessive NaF was also found in the XRD pattern.

Figure 2 shows the UC luminescence spectrum of the as-prepared $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals in cyclohexane under 980 nm excitation. The spectral peaks correspond to the following transitions: $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (~ 410 nm), $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (~ 524 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (~ 541 nm), and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (~ 654 nm). It is obvious that the

dominant emission is located in the green luminescence range. The eye-visible green UC fluorescence photo of the transparent colloidal solution of the $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals in cyclohexane is shown in the inset of Figure 2.

To evaluate if CaF_2 is an efficient UC host material, the UC luminescence properties of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals were compared with those of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals. The TEM images and XRD patterns of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals with different morphologies, sizes, and phases are shown in Figures S1 and S2 in the Supporting Information. Obviously, the mean sizes of hexagonal nanocrystals are much larger than that of the cubic sample. Under 980-nm excitation, the hexagonal $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals as well as cubic $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals with more than 10 nm in size can exhibit much stronger UC luminescence than the $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals. However, in comparison with the sub-10 nm $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals, the emission intensities of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals are slightly stronger (Figure 2), indicating that CaF_2 is a promising host material for producing desirable UC luminescence. Of course, many factors might be responsible for the UC luminescence properties of RE-doped nanocrystals, such as crystal structure, size, shape, and the number of ions surrounding RE ions, on which no final conclusion has yet been reached.

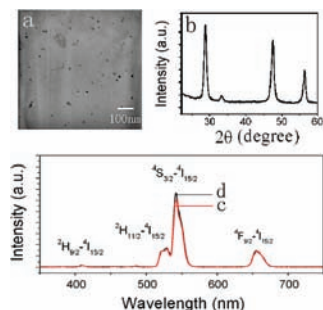


Figure 3. TEM image (a) and XRD pattern (b) of the oxidized sample. Normalized UC spectra of (c) hydrophilic $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ in water and (d) hydrophobic $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ in cyclohexane under 980 nm excitation.

We expect that these monodispersed $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals can be further employed as multichannel luminescent probes in biological applications.¹³ Then, Lemieux–von Rudloff reagent¹⁴ was used to oxidize oleic acid ligands and convert the hydrophobic into hydrophilic. After Lemieux–von Rudloff oxidation, oleic acid ligands on the surface of UC nanoparticles were converted to azelaic acids ($\text{HOOC}(\text{CH}_2)_7\text{COOH}$), which have been examined with Fourier transform infrared and NMR spectroscopy by Chen et al.¹⁵ These oxidized nanophosphors could be well-dispersed in water with the help of free carboxylic acid groups on their surface.¹⁵ The TEM image of the sample is shown in Figure 3a. The corresponding XRD pattern of sample is shown in Figure 3b. Obviously, the peak of excessive NaF disappeared. Figure 3c shows the UC luminescence spectrum of the oxidized $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals in water. For comparison, the UC luminescence spectrum of the corresponding nanocrystals before oxidizing is also shown (Figure 3d). The relative intensity of the green to the red slightly decreases after oxidation, which could be attributed to the change of ligands on the surface.¹⁵

In addition, the UC mechanisms and power dependent intensities of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals are discussed. The relative intensity of ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ as well as ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ to

${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ gradually increased with increasing excitation power, which was discussed in the Supporting Information.¹⁶

In conclusion, monodispersed $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals have been prepared via a facile wet chemical technology. These as-prepared nanocrystals not only can be transparently dispersed in cyclohexane but also can be converted into water-soluble by oxidizing oleic acid ligands with the Lemieux–von Rudloff reagent. Under 980 nm excitation, the colloidal solutions of the as-prepared sample in cyclohexane and the oxidized sample in water both present bright green UC luminescence. The UC luminescence properties of $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals were compared with those of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals with different phases and particle sizes. The results indicated that CaF_2 is a promising host material for producing desirable UC luminescence. In addition, these luminescent properties show that these water-soluble $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals have potential applications in biological labeling and imaging.

Acknowledgment. This work was supported by NSFC (90606006 and 10979032), the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2006CB932300).

Supporting Information Available: Experiment procedures, Population and photoluminescence processes, and Figure S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Holmes, K.; Lantz, L. *Methods Cell Biol.* **2001**, *63*, 185. (b) Michalet, X.; Pinaud, F.; Bentolila, L.; Tsay, J.; Doose, S.; Li, J.; Sundaresan, G.; Wu, A.; Gambhir, S.; Weiss, S. *Science* **2005**, *307*, 538. (c) Medintz, I.; Uyeda, H.; Goldman, E.; Mattoussi, H. *Nat. Mater.* **2005**, *4*, 435. (d) Wang, F.; Tan, W.; Zhang, Y.; Fan, X.; Wang, M. *Nanotechnology* **2006**, *17*, R1.
- (2) Miyawaki, A.; Sawano, A.; Kogure, T. *Nat. Cell Biol.* **2003**, *5*, S1.
- (3) (a) Yan, H.; He, R.; Johnson, J.; Law, M.; Saykally, R.; Yang, P. *J. Am. Chem. Soc.* **2003**, *125*, 4728. (b) König, K. *J. Microsc. (Oxford, U. K.)* **2000**, *200*, 83.
- (4) Wang, F.; Liu, X. *Chem. Soc. Rev.* **2009**, *38*, 976.
- (5) (a) Li, P.; Peng, Q.; Li, Y. *Adv. Mater.* **2009**, *21*, 1. (b) Mahalingam, V.; Vetrone, F.; Naccache, R.; Spgehini, A.; Capobianco, J. *Adv. Mater.* **2009**, *21*, 1.
- (6) (a) Heer, S.; Lehmann, O.; Haase, M.; Güdel, H. *Angew. Chem.* **2003**, *115*, 3288. (b) Stouwdam, J.; Raudsepp, M.; van Veggel, F. *Langmuir* **2005**, *21*, 7003. (c) Meiser, F.; Cortez, C.; Caruso, F. *Angew. Chem.* **2004**, *116*, 6080. (d) Wang, L.; Li, P.; Li, Y. *Adv. Mater.* **2007**, *19*, 3304. (e) Wang, X.; Zhuang, J.; Peng, Q.; Li, Y. *Nature* **2005**, *437*, 121. (f) Liu, J.; Li, Y. *Adv. Mater.* **2007**, *19*, 1118. (g) Kömpe, K.; Borchert, H.; Storz, J.; Lobo, A.; Adam, S.; Möller, T.; Haase, M. *Angew. Chem.* **2003**, *115*, 5672. (h) Sivakumar, S.; van Veggel, F.; May, P. *J. Am. Chem. Soc.* **2007**, *129*, 620.
- (7) (a) Wang, L.; Yan, R.; Huo, Z.; Wang, L.; Zeng, J.; Bao, J.; Wang, X.; Peng, Q.; Li, Y. *Angew. Chem.* **2005**, *117*, 6208. (b) Diamante, P.; van Veggel, F. *J. Fluoresc.* **2005**, *15*, 543. (c) Wang, L.; Li, Y. *Nano Lett.* **2006**, *6*, 1645. (d) Lim, S.; Riehn, R.; Ryu, W.; Khanarian, N.; Tung, C.; Tank, D.; Austin, R. *Nano Lett.* **2006**, *6*, 169. (e) Sivakumar, S.; Diamante, P.; van Veggel, F. *Chem.–Eur. J.* **2006**, *12*, 5878.
- (8) Yan, R.; Li, Y. *Adv. Funct. Mater.* **2005**, *15*, 763.
- (9) (a) Krämer, K.; Biner, D.; Frei, G.; Güdel, H.; Hehlen, M.; Lüthi, S. *Chem. Mater.* **2004**, *16*, 1244. (b) Heer, S.; Kömpe, K.; Güdel, H.; Haase, M. *Adv. Mater.* **2004**, *16*, 2102.
- (10) (a) Feng, W.; Sun, L.; Zhang, Y.; Yan, C. *Small* **2009**, *5*, 2057. (b) Mai, H.; Zhang, Y.; Sun, L.; Yan, C. *J. Phys. Chem. C* **2007**, *111*, 13721.
- (11) (a) Chase, L. *Phys. Rev. B* **1970**, *2*, 2308. (b) Bensalah, A.; Mortier, M.; Patriarche, G.; Gredin, P.; Vivien, D. *J. Solid State Chem.* **2006**, *179*, 2636. (c) Rao, D.; Prasad, J.; Prasad, P. *Phys. Rev. B* **1983**, *28*, 20. (d) Sun, X.; Li, Y. *Chem. Commun.* **2003**, *34*, 1768.
- (12) (a) Hull, A. *Phys. Rev.* **1921**, *17*, 42. (b) Baker, J.; Davies, E. *J. Phys. C: Solid State Phys.* **1975**, *8*, 1869.
- (13) Zhang, T.; Ge, J.; Hu, Y.; Yin, Y. *Nano Lett.* **2007**, *7*, 3203.
- (14) Lemieux, R.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701. (b) Higashimura, T.; Sawamoto, M.; Hiza, T.; Karaiwa, M.; Tsuchii, A.; Suzuki, T. *Appl. Environ. Microb.* **1983**, *46*, 386.
- (15) Chen, Z.; Chen, H.; Hu, H.; Yu, M.; Li, F.; Zhang, Q.; Zhou, Z.; Yi, T.; Huang, C. *J. Am. Chem. Soc.* **2008**, *130*, 3023.
- (16) (a) Pollnau, M.; Gamelin, D.; Lüthi, S.; Güdel, H.; Hehlen, M. *Phys. Rev. B* **2000**, *61*, 3337. (b) Bai, X.; Song, H.; Pan, G.; Lei, Y.; Wang, T.; Ren, X.; Lu, S.; Dong, B.; Dai, Q.; Fan, L. *J. Phys. Chem. C* **2007**, *111*, 13611. (c) Vetrone, F.; Boyer, J.; Capobianco, J. *J. Appl. Phys.* **2004**, *96*, 661.

JA906732Y