Synthesis of Various MnF2 Nanostructures with Single-Band Red Emission

Z. Bai[1] and N. Hashemi[1]
[1]Iowa State University, Ames, IA

Introduction: Recently, the use of upconversion (UC) phosphors as fluorescent labels for the sensitive detection of biomolecules has attracted great attention. The most efficient UC phosphor currently known is based on Er^{3+} ion in combination with Yb^{3+} ion as a sensitizer, which exhibits a green emission (~ 550 nm) as well as a red emission (~ 660 nm). As is known, the red emission is preferred to be used as a probe for in vivo imaging since the red emission could afford the deeper tissue penetration than the green emission. Therefore, tuning the emission of Er^{3+} ion from green to red is highly desired for the deep tissue imaging. On the other hand, some dopants, such as manganese ion (Mn^{2+}), have been recognized as effective elements which can decrease the short-wavelength green emission and enhance the long-wavelength red emission because of the energy transfer between Er^{3+} and Mn^{2+} ions. However, there are only a few reports on synthetic approach and UC luminescence property of MnF_2:Er^{3+}/Yb^{3+} nanocrystals, especially with controllable size and morphology.

Materials and Methods: In a typical synthesis process, MnF_2 doped with 2 mol% Er^{3+} and 20 mol% Yb^{3+} was synthesized as follows: 3.12 mL of 0.2 M $MnCl_2 \cdot 4H_2O$, 0.8 mL of 0.2 M $YbCl_3 \cdot 6H_2O$ and 0.08 mL of 0.2 M $ErCl_3 \cdot 6H_2O$, and 4 mL of 0.6 M NH_4F were added to a beaker containing the mixture of oleic acid (OA) and ethanol (ET) under vigorous stirring. The sum amount of oleic acid and ethanol was fixed to 24 mL, and the OA/ET ratio varied to 0:24 mL, 4:20 mL, 8:16 mL, 12:12 mL, 16:8 mL, 20:4 mL, and 24:0 mL according to the experiment requirements. After mixing for 10 min, the resulting mixture was transferred to a 40 mL Teflon-lined autoclave, sealed and heated at 110~200 °C for 12 h. The final products were collected by means of centrifugation, washed with ethanol and deionized water for several times to remove any possible remnants.

Results and Discussion: The XRD patterns of MnF_2 nanostructures synthesized by different OA/ET volume ratios at the reaction temperature range of 140 °C reveal that all the diffraction peaks of the samples correspond to the tetragonal MnF_2 crystal (JCPDS standard card no. 24-727). The SEM images show that the morphology of MnF_2 nanocrystals is very sensitive to the OA/ET volume ratios. When the OA/ET ratio is lower than 0.2, the morphology does not change, and only aggregated MnF_2 nanoparticles are obtained. In the OA/ET ratio range of 0.5～1, well-dispersed sphere-like MnF_2 nanoclusters could be obtained by the self-assembly of the nanoparticles. When the OA/ET ratio is higher than 5, the nanoparticles are developed into nanolanterns via Ostwald ripening. Upon excitation at 980 nm, single-band UC emission at 656 nm are detected for Er^{3+}/Yb^{3+} codoped MnF_2 nanoclusters, which is assigned to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions. The complete disappearance of green emissions of lower Er^{3+} concentration samples suggests an extremely efficient exchange-energy transfer process between the Er^{3+} and Mn^{2+} ions, which is mainly attributed to the close proximity and excellent overlap of energy levels of the Er^{3+} and Mn^{2+} ions in the host lattices.

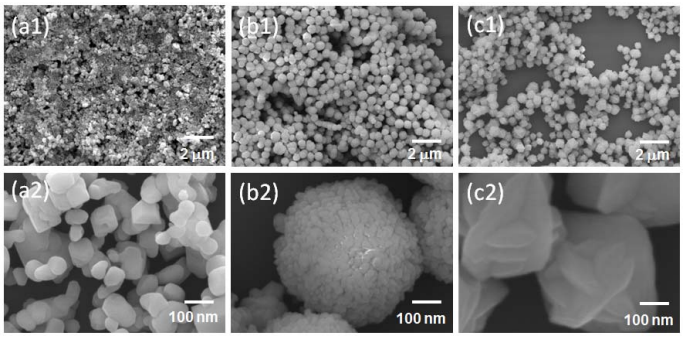

Figure 1. Low-resolution and high-resolution SEM images of MnF_2 nanocrystals synthesized by various volume ratio of oleic acid to ethanol: (a) 0:24 mL; (b) 12:12 mL; (c) 24:0 mL.

Conclusions: In the present work, we have described a facile synthetic method for the preparation of MnF_2 nanostructures with Er^{3+} and Yb^{3+} ions homogeneously incorporated in the host lattice. Various morphologies, such as nanoparticle, nanocluster and nanolantern, can be obtained with controllable sizes from 200 nm to 1.5 μm. As a result of efficient energy transfer between the dopant Er^{3+} ion and host Mn^{2+} ion, remarkably pure single-band UC emissions were generated in the red spectral region. The achieved red emission is two times stronger than that of $NaYF_4$:Er^{3+}/Yb^{3+} nanocrystals. The excellent optical properties make these interesting nanostructures promising in application as in vivo bioimaging.

References: Z. Bai, H. Lin, J. Johnson, S. C. Rong Gui, K. Imakita, R. Montazami, M. Fujii, N. Hashemi, J. Mater. Chem. C 2014, 2, 1736.