Synthesis of Various MnF₂ Nanostructures with Single-Band Red Emission
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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 Er³⁺ ion in combination with Yb³⁺ 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 Er³⁺ ion from green to red is highly desired for the deep tissue imaging. On the other hand, some dopants, such as manganese ion (Mn²⁺), 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 Er³⁺ and Mn²⁺ ions. However, there are only a few reports on synthetic approach and UC luminescence property of MnF₂:Er³⁺/Yb³⁺ nanocrystals, especially with controllable size and morphology.

Materials and Methods: In a typical synthesis process, MnF₂ doped with 2 mol% Er³⁺ and 20 mol% Yb³⁺ was synthesized as follows: 3.12 mL of 0.2 M MnCl₂·4H₂O, 0.8 mL of 0.2 M YbCl₃·6H₂O and 0.08 mL of 0.2 M ErCl₃·6H₂O, and 4 mL of 0.6 M NH₄F 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 MnF₂ 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 MnF₂ crystal (JCPDS standard card no. 24-727). The SEM images show that the morphology of MnF₂ 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 MnF₂ nanoparticles are obtained. In the OA/ET ratio range of 0.5~1, well-dispersed sphere-like MnF₂ 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 Er³⁺/Yb³⁺ codoped MnF₂ nanoclusters, which is assigned to the ⁴F₉₂ → ⁴I₁₅₅ transition of Er³⁺ ions. The complete disappearance of green emissions of lower Er³⁺ concentration samples suggests an extremely efficient exchange-energy transfer process between the Er³⁺ and Mn²⁺ ions, which is mainly attributed to the close proximity and excellent overlap of energy levels of the Er³⁺ and Mn²⁺ ions in the host lattices.

Conclusions: In the present work, we have described a facile synthetic method for the preparation of MnF₂ nanostructures with Er³⁺ and Yb³⁺ 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 Er³⁺ ion and host Mn²⁺ 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 NaYF₄:Er³⁺/Yb³⁺ nanocrystals. The excellent optical properties make these interesting nanostructures promising in application as in vivo bioimaging.