Inorganic Chemistry
COMMUNICATION
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Rare-Earth-Doped Bifunctional Alkaline-Earth Metal Fluoride Nanocrystals via a Facile Microwave-Assisted Process

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Supporting Information

ABSTRACT: Rare-earth-doped magnetic–optic bifunctional alkaline-earth metal fluoride nanocrystals have been successfully synthesized via a facile microwave-assisted process. The as-prepared nanocrystals were monodisperse and could form stable colloidal solutions in polar solvents, such as water and ethanol. They show bright-green fluorescence emisson. Furthermore, Gd^{3+}-doped ones exhibit paramagnetic behavior at room temperature and superparamagnetic behavior at 2 K.

Bifunctional nanoparticles in possession of magnetism and luminescence have drawn much attention because of their great potential applications especially for biological research, like bioimaging[1] and cell labeling.[2] Generally, such bifunctional nanoparticles are often obtained by physically assembling magnetic nanocrystals (NCs) with luminescent quantum dots (QDs) or organic pigment molecules by the following silane hydrolysis process to form multicomponent silica nanocomposites.[3] In addition to the strategy of magnetic-core/luminescent-shell structure, heterostructure particle pairs are also successfully applied to achieve bifunctions.[4] However, in all cases, the prepreparation of several kinds of high-quality NCs as building blocks is indispensable, which makes the steps rather laborious. In addition, the large use of toxic Cd ions based on QDs and organic pigments may cause severe environment pollution and be harmful for human bodies.

Another valuable way to achieve bifunctions is by the direct doping of the fluorescent rare-earth (RE) ions accompanied by the magnetic RE ones into a single-component substrate.[5] Such a combination could not only simplify the preparation process and the structures of the products but also considerably reduce the influence of the magnetic components on the luminescence because of the small weight ratios of magnetic ions. Fluorides are efficient hosts for RE-doped NCs because of their low phonon energies (~350 cm^{-1}) and high chemical stability.[6] As an important category of fluorides, alkaline-earth metal fluorides (MF_2) have been used as an attractive host for phosphors with interesting up/down-conversion luminescent properties.[7] Recently, many methods involving thermal decomposition,[8] microemulsion,[9] and hydrothermal treatment[10] have been explored to prepare MF_2 NCs. However, they were all performed under a quite high temperature for several hours. Compared to the traditional methods, microwave-assisted synthesis can significantly promote the temperature shortly and reduce the reaction time, which is feasible for the rapid preparation of nanomaterials. It has been identified as successful in the preparation of RE-doped $BaYF_5$ NCs with good optical properties in our previous work.[11] However, it would be interesting to extend the study and determine if the magnetic–optic bifunctional MF_2 NCs can be prepared in one step and one pot. To the best of our knowledge, the microwave-assisted synthesis of RE-doped MF_2 NCs, combining both optical and magnetic properties, has not been reported until now.

Herein we present the rapid microwave-assisted synthesis of RE-doped MF_2 NCs, which show magnetic–optic bifunctional properties. The as-prepared NCs are monodisperse and ultrasmall in a size range of 3–5 nm and could form stable colloidal solutions in polar solvents, such as water and ethanol. Experimentally, amounts of 1 mmol of alkaline-earth metal acetates [$M(CH_3COO)_2$, M = Ca, Sr, and Ba], in addition to amounts of $Tb(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Gd(NO_3)_3 \cdot 6H_2O$, were dissolved in 13 mL of ethylene glycol (EG), and then the resulting solutions were added into stoichiometric amounts of 7 mL of NH_4F/EG solution. After vigorous stirring, the solution was transferred into the microwave reactor and reacted for 10 min at a defined temperature and then cooled to room temperature naturally (for detailed information, see the Supporting Information). The products were collected by centrifugation, washed with ethanol several times, and finally dispersed in ethanol.

The high-resolution transmission electron microscopy (HRTEM) and TEM images of RE-doped (Ce^{3+}, Tb^{3+}, and Gd^{3+}) MF_2 (M = Ca, Sr, and Ba) NCs [abbreviated as MF_2:(x%–y%–m%), where x, y, and m are in calculated molar values and correspond to Ce^{3+}, Tb^{3+}, and Gd^{3+}, respectively] in Figures 1 and S1 in the Supporting Information show that the MF_2 NCs are uniform and monodisperse with average sizes of 3.5, 3.1, 4.9, and 3.1 nm, respectively. The TEM images (Figure S2 in the Supporting Information) reveal that no obvious differences in their sizes were observed while the dopant ratios were changed in these NCs. The interplanar spacing of all of the NCs should be indexed to the (220) planes of MF_2, and the slight changes of the spacings compared with pure MF_2 were caused by the incorporation of RE ions into the MF_2 NCs.[12] The doping amount of RE ions was verified by energy-dispersive X-ray (EDX) spectroscopy and ICP analysis (Figure S3 and Table S1 in the Supporting Information). From the X-ray diffraction (XRD) patterns in Figure S4 in the Supporting Information, it can be seen that all of the samples are in the pure face-centered-cubic (fcc) phase (space group: *Fm*3*m*), showing three high-intensity peaks of (111), (220), and (311) planes.

Received: March 17, 2011
Published: May 09, 2011

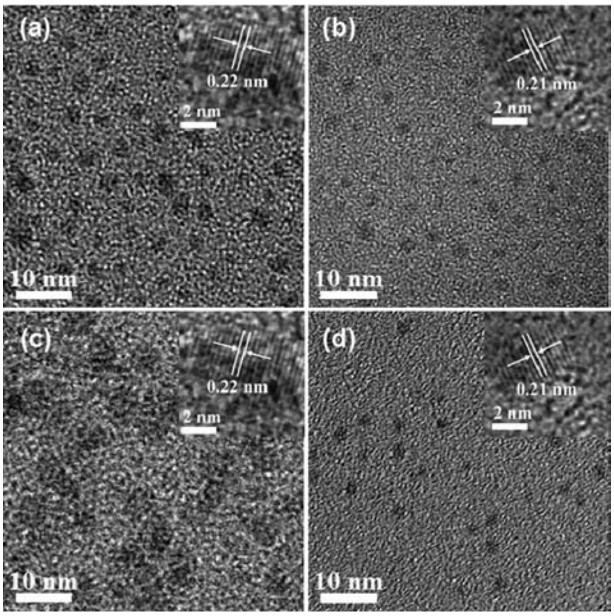

Figure 1. HRTEM images of (a) CaF_2:(5%-5%), (b) SrF_2:(5%-5%), (c) BaF_2:(5%-5%), and (d) SrF_2:(5%-5%-20%) NCs.

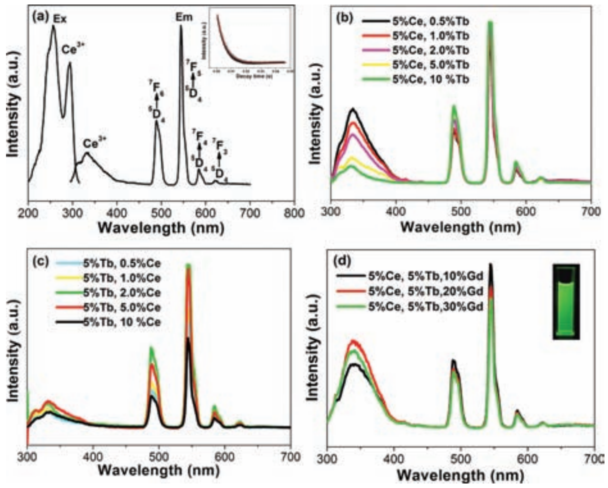

Figure 2. (a) PL spectra of SrF_2:(5%-5%) NCs (inset: decay curve of Tb^{3+} luminescence). PL spectra of (b) SrF_2:(5%-*y*%), (c) SrF_2:(*x*%-5%) (*x* or *y* = 0.5, 1, 2, 5, and 10), and (d) SrF_2:(5%-5%-*m*%) NCs (*m* = 10, 20, and 30) (inset: photograph of the luminescence under excitation of ultraviolet light). All of the samples are in ethanol solutions (10 mM).

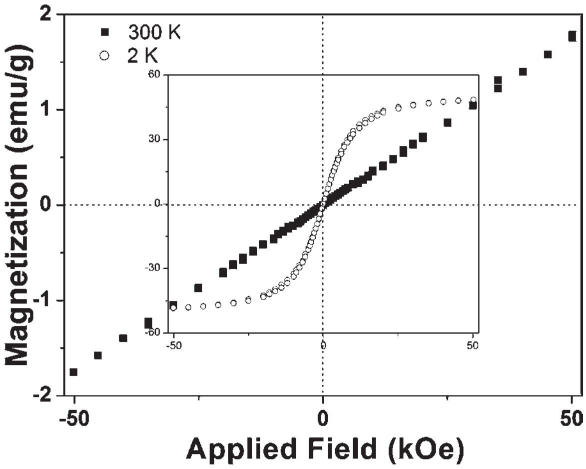

Figure 3. Magnetization curves of the SrF_2:(5%-5%-20%) NCs at 300 and 2 K.

It should also be pointed out that there is no additional phase observed in our cases.

The photoluminescence (PL) spectra of SrF_2:(5%-5%) NCs in Figure 2a were first taken for example. When it was monitored with Tb^{3+} emission (545 nm), there were only two bands of 257 and 291 nm originating from the 4f−5d transitions of Ce^{3+} in the excitation (Ex) spectrum (Figure 2a),[13] indicating the energy transfer from Ce^{3+} to Tb^{3+} ions.[14] The emission (Em) spectrum shows the characteristic peaks of Tb^{3+} ($^5D_4$−^7F_J at 489, 545, 585, and 625 nm) accompanied by a broad peak of Ce^{3+} (300−350 nm). Thus, most of the energies of excited Ce^{3+} ions should be transferred to Tb^{3+} ions and only a small part released by themselves.[15] Similar PL spectra have also been observed in the cases of CaF_2 and BaF_2 NCs as the substrates (Figures S5 and S6 in the Supporting Information). The inset of Figure 2a shows the luminescence decay curve of SrF_2:(5%-5%) NCs, which can be well fitted to a single-exponential function as $I(t) = I_0 \exp(-t/\tau)$ (I_0 is the initial emission intensity at $t = 0$, and τ is the 1/e lifetime of the emission center). Consequently, the lifetime is determined to be 5.13 ms, related to the typical luminescence of Tb^{3+} ions.[16]

A series of PL emission spectra of SrF_2:(5%-*y*%) and SrF_2:(*x*%-5%) (excited at 250 nm) are presented in Figure 2b,c. It can be seen in Figure 2b, similar to the other hosts for Ce^{3+} and Tb^{3+} ion pairs,[17] that the energy transfer from Ce^{3+} to Tb^{3+} is enhanced when the Tb^{3+} molar ratio is increased from 0.5% to 10%, resulting in a decrease of the Ce^{3+} emission and an increment of the Tb^{3+} emission. However, the spectra in Figure 2c of SrF_2:(*x*%-5%) NCs show that the characteristic emissions of Tb^{3+} first rise at lower concentrations of Ce^{3+} ions (*x* = 0.5 and 1) and the intensity reaches a maximum when *x* = 2, but they suddenly begin to decrease with the continuous increment of the Ce^{3+} ratios. This phenomenon is likely caused by the PL quenching effect between the RE ions. Also, a similar energy migration to a second Ce^{3+} ion at the ground state in other systems has been firmly observed.[18]

In the following work, SrF_2:(Ce^{3+}−Tb^{3+}) NCs were then doped with Gd^{3+} ions to get tridoped samples. It is shown in Figure 2d that when *x* = *y* = 5, along with the increment of Gd^{3+} ratios from 10% to 30%, the tridoped NCs give PL emissions similar to those of the SrF_2:(Ce^{3+}−Tb^{3+}) NCs. The results indicate that the introduction of Gd^{3+} ions only leads to a slightly decreased PL intensity of the samples. Besides, the Gd^{3+}-doped NCs exhibit excellent magnetic properties. The magnetization curves of SrF_2:(5%-5%-20%) NCs at 300 and 2 K are shown in Figure 3. It can be seen that the NCs are paramagnetic at room temperature. This originates from the intrinsic magnetic moment of Gd^{3+} ions with a noninteracting and localized nature.[19] However, at 2 K the NCs are superparamagnetic with saturation magnetization values of about 50 emu g^{-1}. The result is consistent with the previous report.[20]

In conclusion, RE-doped alkaline-earth metal fluoride NCs have been synthesized via a microwave-assisted method. The as-prepared NCs show characteristic emissions of RE ions, that is, Ce^{3+} 5d−4f and Tb^{3+} $^5D_4$−^7F_J (*J* = 6, 5, 4, and 3) transitions. A series of PL emission spectra indicate that Ce^{3+} acts an effective energy transfer medium in these host materials. After further introduction of Gd^{3+} ions, the tridoped NCs exhibit spectral characteristics similar to those of MF_2:(Ce^{3+}–Tb^{3+}) NCs, which also possess magnetic properties simultaneously. These bifunctional NCs synthesized in this work could form stable colloidal solutions in water or ethanol and may have great potential for biological applications. Additionally, this synthesis procedure is less time-consuming without using any assistant and/or template reagents and may be expected to be a general method for the rapid synthesis of other RE-doped fluoride NCs.

ASSOCIATED CONTENT

Ⓢ Supporting Information. TEM images of SrF_2 NCs doped with various contents of trivalent RE ions, EDX spectra and XRD patterns of CaF_2:(5%-5%), SrF_2:(5%-5%), BaF_2:(5%-5%), and SrF_2:(5%-5%-20%) NCs, excitation and emission spectra of CaF_2:(5%-5%) and BaF_2: (5%-5%) NCs in an ethanol solution, TEM images of RE-doped MF_2 NCs, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

The authors are grateful for financial aid from the National Natural Science Foundation of China (Grants 21071140 and 20901075) and the National Natural Science Foundation for Creative Research Group (Grant 20921002).

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