Efficient manganese luminescence induced by Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer in rare earth fluoride and phosphate nanocrystals

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Abstract

Manganese materials with attractive optical properties have been proposed for applications in such areas as photonics, light-emitting diodes, and bioimaging. In this paper, we have demonstrated multicolor Mn\(^{2+}\) luminescence in the visible region by controlling Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer in rare earth nanocrystals [NCs]. CeF\(_3\) and CePO\(_4\) NCs doped with Mn\(^{2+}\) have been prepared and can be well dispersed in aqueous solutions. Under ultraviolet light excitation, both the CeF\(_3\):Mn and CePO\(_4\):Mn NCs exhibit Mn\(^{2+}\) luminescence, yet their output colors are green and orange, respectively. By optimizing Mn\(^{2+}\) doping concentrations, Mn\(^{2+}\) luminescence quantum efficiency and Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer efficiency can respectively reach 14% and 60% in the CeF\(_3\):Mn NCs.

Introduction

The preparation of fluorescent nanomaterials continues to be actively pursued in the past decades. The potentially broad applicability and high technological promise of the fluorescent nanomaterials arise from their intrinsically intriguing optical properties, which are expected to pale their bulk counterparts [1-4]. Particularly, controllable energy transfer in the nanomaterials has been receiving great interest because it leads luminescence signals to outstanding selectivity and high sensitivity, which are important factors for optoelectronics and optical sensors [5].

Great efforts have been devoted to Mn\(^{2+}\)-doped semiconductor nanocrystals [NCs] due to their efficient sensitized luminescence [6,7]. When incorporating Mn\(^{2+}\) ions in a quantum-confined semiconductor particle, the Mn\(^{2+}\) ions can act as recombination centers for the excited electron-hole pairs and result in characteristic Mn\(^{2+}\) (4\(\text{T}_1\)-6\(\text{A}_1\))-based fluorescence. Compared with the undoped materials, the Mn\(^{2+}\)-doped semiconductor NCs often have higher fluorescence efficiency, better photochemical stability, and prolonged fluorescence lifetime. Therefore, such Mn\(^{2+}\)-doped NCs have recently been proposed as bioimaging agents [8,9] and recombination centers in electroluminescent devices [10,11]. They may even find applications in future spin-based information processing devices [12,13] and have been examined as models for magnetic polarons [14]. Moreover, as emission centers, Mn\(^{2+}\) ions can be used for the synthesis of long persistent phosphors [15,16], and white-light ultraviolet light-emitting diodes [17], when doped in inorganic host materials (such as silicate, aluminate, and fluoride).

Rare earth ions (such as Ce\(^{3+}\) and Eu\(^{2+}\)) have been commonly used as sensitizers to improve Mn\(^{2+}\) fluorescence efficiency in bulk materials [18-20]. Typically, the efficient room temperature [RT] luminescence were reported in the Mn\(^{2+}\), Ce\(^{3+}\) co-doped CaF\(_2\) single crystal and other matrices, which were assigned to the energy transfer from the Ce\(^{3+}\) sensitizers to the Mn\(^{2+}\) acceptors through an electric quadrupole short-range interaction in the formed Ce\(^{3+}\)-Mn\(^{2+}\) clusters [18]. However, a portion of isolated Ce\(^{3+}\) and Mn\(^{2+}\) ions which are randomly dispersed in the host usually causes a low Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer efficiency.

In this work, we have synthesized the CeF\(_3\):Mn and CePO\(_4\):Mn NCs and investigated the Ce-Mn energy transfer in these representative rare earth NCs. Upon UV light excitation, both the CeF\(_3\):Mn and CePO\(_4\):Mn show bright Mn\(^{2+}\) luminescence in the visible region. Their fluorescence output colors, however, are quite different owing to different host crystal structures. The optimum Mn\(^{2+}\) doping concentration has been found at which the Mn\(^{2+}\) luminescence quantum efficiency and
Ce$^{3+}$-Mn$^{2+}$ energy transfer efficiency peak at 14% and 60% in the CeF$_3$:Mn NCs, respectively.

**Experimental section**

**Materials**
Reagents MnCl$_2$ (>99%), TbCl$_3$ (>99%), CeCl$_3$ (>99%), NH$_4$F (>99%), and H$_3$PO$_4$ (>85%) were obtained from Sino-pharm Chemical Reagent Co., Ltd. (Beijing, China). Poly-ethyleneimine [PEI] (branched polymer (-N(CH$_2$CH$_2$NH$_2$)CH$_2$CH$_2$-)$_x$ (-N(CH$_2$CH$_2$NH$_2$)CH$_2$CH$_2$-)$_y$) was purchased from Sigma-Aldrich (St. Louis, MO, USA). All reagents were used as received without further purification.

**Synthesis of CeF$_3$:Mn nanocrystals**
CeF$_3$ NCs were synthesized using a modified method reported previously [21]. In a typical procedure, $x$ mL of 0.2 M MnCl$_2$ and (0.2 - $x$) mL of 0.2 M CeCl$_3$ were added to 15 mL of ethanol with 5 mL of PEI solution (5 wt.%). After stirring for 30 min, an appropriate amount of NH$_4$F was charged. The well-agitated solution was then transferred to a Teflon-lined autoclave and subsequently heated at 200°C for 2 h. After cooling down, the product was isolated by centrifugation, washed with ethanol and deionized water several times, and dried in vacuum.

**Synthesis of CePO$_4$:Mn nanocrystals**
In a typical procedure, $x$ mL of 0.2 M MnCl$_2$ and (12-$x$) mL of 0.2 M CeCl$_3$ were mixed. The mixture was agitated for 10 min, then charged with 5 mL of 0.5 M H$_3$PO$_4$, and eventually placed under ultrasonic irradiation for 2 h. All ultrasonic irradiations were performed in a water bath with an ultrasonic generator (100 W, 40 kHz; Kunshan Ultrasonic Instrument Co., Shanghai, China). The particles were obtained by centrifugation, washed with ethanol and deionized water several times, and dried in vacuum.

**Physical and optical measurements**
The transmission electron microscopy [TEM] measurements were carried out on a JEOL 2010 HT transmission electron microscope (operated at 200 kV). X-ray diffraction [XRD] analyses were performed on a Bruker D8-advance X-ray diffractometer with Cu Kα irradiation ($\lambda = 1.5406$ Å). The absorption spectra were obtained with a Varian Cary 5000 UV/Vis/NIR spectrophotometer. The photoluminescence [PL] and PL excitation [PLE] spectra were recorded by a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp as the excitation source.

**Results and discussion**

**Morphology and structure**
Both the CeF$_3$:Mn and the CePO$_4$:Mn NCs were synthesized by effective hydrothermal processes. The prepared CeF$_3$:Mn NCs are shaped as hexagonal plates with average sizes of ~25 nm, as shown by the TEM image in Figure 1a. Figure 1b demonstrates CePO$_4$:Mn nanowires with an average diameter of ~8 nm and an average length of ~400 nm.

Figure 2 shows XRD spectra of CeF$_3$:Mn and CePO$_4$:Mn NCs. The XRD pattern of the CeF$_3$:Mn NCs shows that all the peak positions are in good agreement with the literature data of the hexagonal CeF$_3$ crystal, and the peak positions exhibited by the CePO$_4$:Mn NCs are well indexed in accord with the hexagonal CePO$_4$ crystal, revealing high crystallinity of these two kinds of products.

**Absorption spectra**
As shown in Figure 3, the CeF$_3$:Mn NCs exhibit four absorption peaks located at 248, 235, 218, and 205 nm, which are attributed to the electronic transitions from the ground state to different 5$d$ states of the Ce$^{3+}$ ions. The above absorption peaks’ wavelength of the CeF$_3$:Mn NCs are in good agreement with those reported for...
CeF$_3$ bulk crystals [22]. The CePO$_4$:Mn NCs exhibit two absorption bands with peaks at 256 and 273 nm [23]. The two bands are overlapped because the excited state is strongly split by the crystal field [24]. We note that the Mn$^{2+}$ $^6A_{1g}(S)-^4E_g(D)$ and $^6A_{1g}(S)-^4T_{2g}(D)$ absorption transitions from 310 to 350 nm [18] in these NCs are not obvious due to the much weaker Mn$^{2+}$ absorption ability and low Mn$^{2+}$/Ce$^{3+}$ ratio in the host.

**Photoluminescence properties**

Figure 4a schematically depicts the Ce$^{3+}$-Mn$^{2+}$ energy transfer process in the CeF$_3$:Mn NCs, which efficiently induces a bright green luminescence under UV irradiation at RT. The RT PL emission spectra (with excitation wavelength $\lambda_{ex} = 260$ nm) of the CeF$_3$:10%Mn NCs contain not only the strong Mn$^{2+}$ emission at 498 nm but also the Ce$^{3+}$ emission at 325 nm. As known, the Mn$^{2+}$ $^6A_{1g}(S)-^4E_g(D)$ and $^6A_{1g}(S)-^4T_{2g}(D)$ absorption transition is respectively at 325 and 340 nm [18]; both of these absorption bands are overlapped by the Ce$^{3+}$ emission. This overlap facilitates the energy transfer from Ce$^{3+}$ to Mn$^{2+}$, resulting in the characteristic $^4T_{1g}(G)-^6A_{1g}(S)$ emission of Mn$^{2+}$ [25,26]. Such Ce$^{3+}$-Mn$^{2+}$ energy transfer is induced by the electric dipole-quadrupole interaction between the Ce$^{3+}$ sensitzers and Mn$^{2+}$ acceptors [19]. Furthermore, in Figure 4a, only the RT excitation peak ascribed to the Ce$^{3+}$ 4f-5d transition can be observed at 260 nm, while the Mn$^{2+}$ characteristic peaks cannot be witnessed because the Mn$^{2+}$ absorption transitions are forbidden by spin and parity for electric dipole radiation as $T > 200$ K [27]. Since the RT Mn$^{2+}$ luminescence is very difficult to be found in the transition-metal concentrated materials like MnF$_2$ [27], the Ce$^{3+}$-Mn$^{2+}$ energy transfer offers an efficient route for obtaining Mn$^{2+}$ RT luminescence in nanomaterials.

Similarly, the Ce$^{3+}$-Mn$^{2+}$ energy transfer process in the CePO$_4$:10%Mn NCs triggers an orange luminescence under UV irradiation (Figure 4b). The emission spectra of the CePO$_4$:Mn upon excitation at 260 nm contain both the Ce$^{3+}$ emission at 355 nm and the Mn$^{2+}$ orange emission around 575 nm arising from the $^4T_{1g}(G)-^6A_{1g}$
14% as the doped Mn\(^{2+}\) molar concentration increases which the Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer also results in the CeF\(_3\):Mn NCs increases significantly and reaches NCs. We note that the CePO\(_4\):Mn NCs synthesized are [19,34]. In our CeF\(_3\):Mn NCs, the Ce\(^{3+}\)-Mn\(^{2+}\) clusters action distance for the short-range energy transfer. We note that the highest QE we obtained is similar to that of the Ce, Tb co-doped LaF\(_3\) NCs reported previously [32]. The Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer efficiency (\(\eta_{ET}\)) was estimated from the emission intensity ratio \(I_{\text{Mn}}/(I_{\text{Ce}} + I_{\text{Mn}})\) when the sample solutions were sufficiently diluted and the energy loss caused by the re-absorption effects between different particles could be neglected [31,33]. As shown in Figure 5a, a high \(\eta_{ET}\) of 60% is observed in the CeF\(_3\):Mn NCs while the Mn\(^{2+}\) doping concentration is over 10%. We note that the \(I_{\text{Mn}}\) is much weaker than the \(I_{\text{Ce}}\) in the previously reported Mn,Ce co-doped CaF\(_2\) and other bulk materials because of a portion of randomly dispersed Ce\(^{3+}\) and Mn\(^{2+}\) ions beyond the interaction distance for the short-range energy transfer [19,34]. In our CeF\(_3\):Mn NCs, the Ce\(^{3+}\)-Mn\(^{2+}\) clusters are easily formed and result in the efficient Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer.

**Quantum efficiency and energy transfer efficiency**

The Mn\(^{2+}\) luminescence quantum efficiency (\(\eta_{QE}\)) was determined by comparing the Mn\(^{2+}\) emission intensity of the CeF\(_3\):Mn aqueous solution with a solution of quinine bisulfate in 0.5 M H\(_2\)SO\(_4\) with approximately the same absorption at an excitation wavelength of 260 nm [30]. It is important that all the sample solutions were sufficiently diluted (absorption value of 0.03 at 260 nm) to minimize the possible effects of reabsorption and other concentration effects [31].

Quantum efficiency (\(\eta_{QE}\)) and Ce\(^{3+}\)-Mn\(^{2+}\) energy transfer efficiency (\(\eta_{ET}\)) vs. molar percent of Mn\(^{2+}\) in CeF\(_3\):Mn NCs in the presence of different Mn\(^{2+}\) concentrations (Figure 5b). Upon doping with the increasing concentrations of Mn\(^{2+}\), both the \(\eta_{QE}\) and \(\eta_{ET}\) increase firstly, and the \(\eta_{QE}\) reaches the peak at 0.6% when the Mn\(^{2+}\) doping concentration is 10%. It is worth noting that both the \(\eta_{QE}\) and \(\eta_{ET}\) in the CeF\(_3\):Mn NCs are higher than those in the CePO\(_4\):Mn NCs. Compared with phosphates, fluorides normally have lower vibrational energies, which can decrease the quenching of the excited state of rare earth ions [35] and result in higher quantum efficiency. Besides, the energy transfer efficiency between the sensitzers and acceptors is influenced greatly by the interaction distance of these dopant ions [19,36]. Here, the less energy transfer efficiency in CePO\(_4\):Mn is probably attributed to the larger interaction distance between the Ce\(^{3+}\) and Mn\(^{2+}\) ions. A further increase of the quantum efficiency and energy transfer efficiency is possible by applying an undoped inorganic shell as a protective layer.
Conclusions
The sensitized Mn$^{2+}$ luminescence has been realized based on the Ce$^{3+}$-Mn$^{2+}$ energy transfer in the prepared Mn$^{2+}$-doped rare earth NCs. The $^{4}T_{1g}(G) ightarrow ^{6}A_{1g}(S)$ characteristic emission of Mn$^{2+}$ reveals green luminescence in CeF$_3$:Mn and orange luminescence in CePO$_4$:Mn, resulting from the crystal field differences of these two hosts. We worked out that the highest Mn$^{2+}$ luminescence quantum efficiency can reach 14% and 0.6% in the CeF$_3$:Mn and CePO$_4$ NCs, respectively. Our results may find applications in the manipulations of the Ce$^{3+}$-Mn$^{2+}$ energy transfer for redox switches [37] and broadly impact areas such as photonics, light-emitting diodes, and bioimaging based on manganese materials.

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Authors’ contributions
YD carried out the photoluminescence property studies and drafted the manuscript. LBL participated in the revision of the manuscript. ML and DF He participated in the synthesis of the nanocrystals. LX and PW contributed to characterization of the nanocrystals. XYF conceived of the study, and participated in its design and coordination. All authors read and approved the final manuscript.

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References
1. Duan XF, Huang Y, Cui Y, Wang JF: Nature 2001, 466:409.
2. Deng H, Liu C, Yang SH, Xiao S, Zhou ZK, Wang QQ: Crystal Growth and Design 2008, 8:4432.
3. Nam JM, Stoeva SI, Mirkin CA: Journal of the American Chemical Society 2004, 126:5932.
4. Yu XF, Chen LD, Li Y, Li M, Xie MY, Zhou L, Wang QQ: Advanced Materials 2008, 20:4118.
5. Keefe MH, Benkstein KD, Hupp JT: Coordination Chemistry Reviews 2000, 205:301.
6. Suyver JF, Wuister SF, Kelly JJ, Meijerink A: Nano Letters 2001, 1:429.
7. Norris DJ, Yao N, Charnock FT, Kennedy TA: Nano Letters 2001, 1:3.
8. Lee DH, Wang W, Gutu T, Jeffries C, Rorrer GL, Jiao J, Chang CH: Journal of Materials Chemistry 2011:3633.
9. Pradhan N, Battaglia DM, Liu Y, Peng X: Nano Letters 2007, 7:312.
10. Howard WE, Sahni O, Alt PM: Journal of Applied Physics 1982, 53:639.
11. Chen ZQ, Lian C, Zhou D, Xiang Y, Wang M, Ke M, Liang LB, Yu XF: Chemical Physics Letters 2010, 448:73.
12. Yang H, Holloway PH: Journal of Physical Chemistry B 2003, 107:9705.
13. Efros AL, Rashba EI, Rosen M: Physical Review Letters 2001, 87:206601.
14. Qu F, Hawrylak P: Physical Review Letters 2005, 95:217206.
15. Wang XJ, Jia DD, Yen WM: Journal of Luminescence 2003, 102-103:34.
16. de Chemont QM, Chaneac C, Seguin J, Pellel P, Malteyrean S, Jolivet JP, Gouvier D, Bessodes M, Scherman D: Proceedings of the National Academy of Sciences 2007, 104:9266.
17. Yang WJ, Luo L, Chen TM, Wang NS: Chemistry of Materials 2005, 17:3883.
18. Caldiño UG: Journal of Physics: Condensed Matter 2003, 15:5821.
19. Caldiño UG: Journal of Physics: Condensed Matter 2003, 15:2821.
20. Caldiño UG, Muñoz AF, Rubio JD: Journal of Physics: Condensed Matter 1990, 2:6071.
21. Yu XF, Li M, Xie MY, Chen LD, Li Y, Wang QQ: Nano Research 2010, 3:51.
22. Wojtowicz AJ, Balcerzyk M, Berman E, Lempicki A: Physical Review B 1994, 49:14880.
23. Wang Z, Quan Z, Lin J, Fang J: Journal of Nanoscience and Nanotechnology 2003, 5:1532.
24. Rivotski K, Meyssamy H, Kornowski A, Haase M: Journal of Physical Chemistry B 2000, 104:2824.
25. Oczkiewicz B, Twardowski A, Dermanian M: Solid State Communications 1987, 461:107.
26. Xue J, Ye Y, Medina F, Martinez L, Lopez-Rivera SA, Gjist W: Journal of Luminescence 1998, 78:173.
27. Hernández I, Rodriguez F: Journal of Physics: Condensed Matter 2007, 19:556200.
28. Hernández I, Rodriguez F, Hochheimer HD: Physical Review Letters 2007, 99:027403.
29. Volkov Yu F, Tormilin SV, Lukinykh AN, Lizin AA, Orlova AI, Kitaev DB: Radiochemistry 2002, 44:319.
30. Melhus WH: Journal of Physical Chemistry 1961, 65:229.
31. Dhami S, Dernello AJ, Rumbles G, Bishop SM, Phillips D, Beeby A: Photochemistry and Photobiology 1995, 61:341.
32. Xie MY, Yu L, He H, Yu XF: Journal of Solid State Chemistry 2009, 182:597.
33. Bourjct JC, Fong FK: Journal of Chemical Physics 1974, 60:34.
34. Paulose M, Jose G, Thomas V, Unnikrishnan NV, Warrier MKR: Journal of Physics and Chemistry of Solids 2003, 64:871.
35. Zhang YY, Sun X, Si R, You LP, Yan CH: Journal of the American Chemical Society 2005, 127:3260.
36. Dexter DL: Journal of Chemical Physics 1953, 21:836.
37. Li M, Yu XF, Yu WY, Zhou J, Peng XN, Wang QQ: Journal of Physical Chemistry C 2009, 113:20271.

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