

# Synthesis and applications of lanthanide-doped nanocrystals

## Abstract

Lanthanide ( $\text{Ln}^{3+}$ )-doped nanocrystals continue to receive significant interest due to the large number of applications in display devices, optical communication, solid-state lasers, catalysis, and biological labeling. It is well known that the  $\text{Ln}^{3+}$ -doped nanocrystals can exhibit unique optical properties such as long fluorescence lifetime, large Stokes shift, single to multicolor emission and good luminescence efficiency combined with high photochemical stability of the hosts. Nano-sized phosphorescent or optoelectronic devices usually exhibit novel properties, depending on their structures, shapes, and sizes, such as tunable wavelengths, rapid responses, and high efficiencies. In terms of the mechanism of luminescence, the luminescence of  $\text{Ln}^{3+}$  ions can be divided into down-conversion and up-conversion emission processes. The down-conversion process is the conversion of higher-energy photons into lower-energy photons, which often requires two main components, an inorganic matrix (known as the host) and activated  $\text{Ln}^{3+}$  doping ions (activators). Among all the  $\text{Ln}^{3+}$ -based host materials observed to date including oxides, phosphates, vanadates, oxides, and so on. The optical properties of  $\text{Ln}^{3+}$ -doped nanocrystals depend critically on the hosts in which the  $\text{Ln}^{3+}$  reside, and thus it is important to seek for suitable host matrices to achieve desirable luminescence of  $\text{Ln}^{3+}$ . In this review, we focus on the most recent advances in the development of the synthesis and applications of  $\text{Ln}^{3+}$ -doped nanocrystals.

**Keywords:** Lanthanide, Nanocrystals, Luminescence, Fluorescence resonance energy transfer

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**Abbreviations:**  $\text{Ln}^{3+}$ , Lanthanide; FRET, Fluorescence Resonance Energy Transfer; DOX, Doxorubicin; DSSCs, Dye Sensitized Solar Cells

## Introduction

In recent years, Lanthanide ( $\text{Ln}^{3+}$ )-doped nanocrystals have become promising alternatives to organic fluorophore because  $\text{Ln}^{3+}$  ions can exhibit unique luminescent properties, such as large anti-Stokes shifts, low auto fluorescence background, low toxicity and high penetration depth.<sup>1</sup> In terms of the mechanism of luminescence, luminescence of  $\text{Ln}^{3+}$  ions can be divided into down-conversion and up-conversion emission processes. The down-conversion process is the conversion of higher-energy photons into lower-energy photons,<sup>2</sup> which often requires two main components, an inorganic matrix (known as the host) and activated  $\text{Ln}^{3+}$  doping ions (activators). Hitherto, many types of inorganic compounds, such as oxides, fluorides, phosphates, and vanadates, have been widely used as host materials.

Nanosized phosphors or optoelectronic devices usually exhibit novel capabilities, depending on their structure, shape, and size, such as tunable wavelengths, rapid responsibilities, and high efficiencies. Thus, the development of a facile synthetic method toward high quality  $\text{Ln}^{3+}$ -doped nanocrystals with uniform size and shape appears to be of key importance for the exploration of new research and application fields.<sup>3-7</sup> So far, a large variety of chemical synthetic approaches such as thermal decomposition, high-temperature co-precipitation, hydrothermal synthesis, and sol-gel procedure, have been proposed to synthesize high-quality nanomaterials.<sup>8-10</sup> In this review, we focus on the most recent advances in the development of the synthesis and applications of  $\text{Ln}^{3+}$ -doped nanocrystals.

## Synthesis and application

**Synthetic Studies:** Over the past decade, monodispersed nanocrystals, which exhibit many interesting phenomena and

properties, have been extensively investigated for their scientific and technological applications. A unified approach, the LSS process, has been used to synthesize a large variety of nearly monodispersed  $\text{Ln}^{3+}$ -doped nanocrystals. Detailed explanations of the LSS process can be found in.<sup>11</sup>

Hydrothermal methods have been shown to be effective in the synthesis of nanowires, nanorods, and nanotubes.<sup>12</sup> In addition, the thermal decomposition method generally employs organo-metallic compounds as precursors, which decompose at an elevated temperature in a high boiling point organic solvent. One of the earliest examples of this approach was that Yan and co-workers synthesized highly LaF<sub>3</sub> triangular nano plates via the thermal decomposition of the metal trifluoroacetate ( $\text{La}(\text{CF}_3\text{COO})_3$ ).<sup>13</sup> So far, many groups still attempted to develop other synthetic strategies to yield  $\text{Ln}^{3+}$ -doped nanocrystals with different compositions, shapes and sizes.<sup>14</sup>

## Application exploration

The unique luminescent properties render  $\text{Ln}^{3+}$ -doped nanocrystals particularly useful in the fields of optical devices and biomedicine, such as displays, immunoassays, and anti-counterfeiting. Here, the application of typical  $\text{Ln}^{3+}$ -doped nanocrystals has been summarized in Table 1.<sup>2,8,12-21</sup>

Optical and magnetic materials have attracted much attention due to their importance in the fields of chemistry, biology, medical sciences, and biotechnology. By combination of magnetic-field-assisted biochemical separation and concentration technology, novel composite materials of  $\text{Fe}_3\text{O}_4$  and  $\text{Ln}^{3+}$ -doped nanocrystals have been applied to the sensitive detection of DNA.<sup>12</sup> In addition, by use of bioconjugated  $\text{Ln}^{3+}$ -doped nanocrystals as energy donor and bioconjugated gold nanoparticles as energy acceptor, a simple and sensitive Fluorescence Resonance Energy Transfer (FRET) biosensor for avidin has been successfully developed.<sup>13</sup> Recently,  $\text{Ln}^{3+}$ -doped nanocrystals were utilized as drug carriers and optical nanoprobe.<sup>14-16</sup>

For example, Doxorubicin (DOX), a commonly used anticancer drug, chemically conjugated to NaYF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> nanoparticles. The system demonstrates the ability to release DOX by cleavage of the hydrazone bond in mildly acidic environments, which is helpful to reduce the side-effect of chemotherapeutics.<sup>17</sup>

**Table 1** The applications of typical Ln<sup>3+</sup>-doped nanocrystals.

Samples		Application	
Core@shell	CeO <sub>2</sub> @Ce <sub>1-x</sub> Zr <sub>x</sub> O <sub>2</sub>	Catalysis	
Hydroxides	Ln(OH) <sub>3</sub>		
Oxides	Ln <sub>2</sub> O <sub>3</sub> and CeO <sub>2</sub>	Biology	
Fluorides	NaLuF <sub>4</sub> :Ln <sup>3+</sup> , NaYF <sub>4</sub> :Ln <sup>3+</sup> , LnF <sub>3</sub> , CaF <sub>2</sub> :Ln <sup>3+</sup> , LiLuF <sub>4</sub> :Ln <sup>3+</sup> , and BaF <sub>2</sub> :Eu <sup>3+</sup>		
	Orthophosphate		LnPO <sub>4</sub>
	Orthovanadates		YVO <sub>4</sub>
	Tungstate		BaWO <sub>4</sub> :Eu <sup>3+</sup>
Sulfide	Bi <sub>2</sub> S <sub>3</sub> :Eu <sup>3+</sup>	Solar cells and biology	

Recently, we successfully synthesized Pt/Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> composite nanotubes, which not only exhibited enhanced red luminescence under 255- or 468-nm excitation but could also be used to improve the efficiency of Dye Sensitized Solar Cells (DSSCs), resulting in an efficiency of 8.33%, which represents a significant enhancement of 11.96% compared with a solar cell without the composite nanotubes.<sup>19</sup>

## Conclusion

This review has described the Ln<sup>3+</sup>-doped nanocrystals with synthetic strategies and applications. By surface modification, Ln<sup>3+</sup>-doped nanocrystals can be used for a wide range of bio-applications such as bio-detection, cancer therapy, bio-labeling, fluorescence imaging, magnetic resonance imaging and drug delivery. Recently, some progress of the application in DSSCs has also been made. Though some achievements have been made, there still exist challenges, which hinder potential developments of practical applications in biology and in DSSCs. For example, the luminescence efficiency should be further increased, in order to further improve the efficiency of DSSCs.

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## Conflicts of interest

None.

## References

- Zheng W, Huang P, Tu DT et al. Lanthanide,-doped Up conversion Nano,-Bioprobes: Electronic Structures Optical Properties and Biodection. *Chem Soc Rev.* 2015;44(6):1379,-1415.
- Huang P, Zheng W, Zhou SY et al. Lanthanide,-Doped LiLuF<sub>4</sub> Up conversion Nanoprobes for the Detection of Disease Biomarkers. *Angew Chem Int Ed.* 2014;53(5):1252,-1257.
- Zijlmans H, Bonnet J, Burton J et al. Detection of Cell and Tissue Surface Antigens Using Up,-Converting Phosphors: A New Reporter Technology. *Anal Biochem.* 1999;267(1):30,-36.
- Qin W, Zhang D, Zhao D et al. Near,-Infrared Photo catalysis Based on YF<sub>3</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup>/TiO<sub>2</sub> core/shell Nanoparticles. *Chem Commun.* 2010;46(13):2304,-2306.
- Rijke F, Zijlmans H, Li S et al. Up,-Converting Phosphor Reporters for Nucleic Acid Microarrays. *Nat Biotechnol.* 2001;19(3):273,-276.
- Lim S, Riehn R, Ryu W et al. In Vivo and Scanning Electron Microscopy Imaging of Upconverting Nanophosphors in Caenorhabditis Elegans. *Nano Lett.* 2006;6(2):169,-174.
- Chen Z, Chen H, Hu H et al. Versatile Synthesis Strategy for Carboxylic Acid,-Functionalized Upconverting Nanophosphors as Biological Labels. *J Am Chem Soc.* 2008;130(10):3023,-3029.
- Wang F, Liu XG Recent Advances in the Chemistry of Lanthanide,-Doped Upconversion Nanocrystals. *Chem Soc Rev.* 2009;38(4):976,-989.
- Wang C, Tao HQ, Cheng L et al. Near,-infrared Light Induced in Vivo Photodynamic Therapy of Cancer Based on Upconversion Nanoparticles. *Biomaterials.* 2011;32(26):6145,-6154.
- Zhang C, Sun L, Zhang Y et al. Rare Earth Upconversion Nanophosphors: Synthesis, Functionalization and Application as Biolabels and Energy Transfer Donors. *Journal of Rare Earths.* 2010;28(6):807,-819.
- Wang X, Zhuang J, Peng Q et al. A General Strategy for Nanocrystals Synthesis. *Natures.* 2005;437:121,-124.
- Wang GF, Peng Q, Li YD Lanthanide,-Doped Nanocrystals: Synthesis, Optical,-Magnetic Properties, and Applications. *Acc Chem Res.* 2011;44(5):322,-332.
- Zhang YW, Sun X, Si R et al. Single,-Crystalline and Monodispersed LaF<sub>3</sub> Triangular Nanoplates from Single,-Source Precursor. *J Am Chem Soc.* 2005;127(10):3260,-3261.
- Liu YS, Tu DT, Zhu HM et al. Lanthanide,-doped Luminescent Nanoprobes: Controlled Synthesis, Optical Spectroscopy, and Bioapplications. *Chem Soc Rev.* 2013;42:6924,-6958.
- Wang L, Li Y Luminescent Nanocrystals for Nonenzymatic Glucose Concentration Determination. *Chemistry.* 2007;13(15):4203,-4207.
- Yang PP, Gai SL, Lin J Functionalized Mesoporous Silica Materials for Controlled Drug Delivery. *Chem Soc Rev.* 2012;41(9):3679,-3698.
- Li ZX, Barnes JC, Bosoy A et al. Mesoporous Silica Nanoparticles in Biomedical Applications. *Chem Soc Rev.* 2012;41(7):2590,-2605.
- Xue XJ, Wang F, Liu XG Emerging Functional Nanomaterials for Therapeutics. *J Mater Chem.* 2011;21(35): 13107,-13127.
- Dai YL, Yang DD, Ma YA, Kang XJ, Lin J, et al. Doxorubicin Conjugated NaYF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> Nanoparticles for Therapy and Sensing of Drug Delivery by Luminescence Resonance Energy Transfer. *Biomaterials.* 2012;33(33):8704,-8713.
- Wang YP, Qu Y, Pan K, Wang GF, Li YD Enhanced photoelectric conversion efficiency of dye sensitized solar cells via the incorporation of one dimensional luminescent BaWO<sub>4</sub>: Eu<sup>3+</sup>. *Chem Commun.* 2016;52(74):11124,-11126.
- Yu MQ, Su JM, Wang GF, Li YD Pt/Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> composite nanotubes: Enhanced photoluminescence and application in dye,-sensitized solar cells. *Nano Research.* 2016;9(8):2338,-2346.