

Synthesis and Applications of Lanthanide-Doped Nanocrystals

Abstract

Lanthanide (Ln³⁺)-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 Ln³⁺-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 Ln³⁺ 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 Ln³⁺ doping ions (activators). Among all the Ln³⁺-based host materials observed to date including oxides, phosphates, vanadates, oxides, and so on. The optical properties of Ln³⁺-doped nanocrystals depend critically on the hosts in which the Ln³⁺ reside, and thus it is important to seek for suitable host matrices to achieve desirable luminescence of Ln³⁺. In this review, we focus on the most recent advances in the development of the synthesis and applications of Ln³⁺-doped nanocrystals.

Keywords: Lanthanide; Nanocrystals; Luminescence; Fluorescence resonance energy transfer

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Abbreviations: Ln³⁺: Lanthanide; FRET: Fluorescence Resonance Energy Transfer; DOX: Doxorubicin; DSSCs: Dye Sensitized Solar Cells

Introduction

In recent years, Lanthanide (Ln³⁺)-doped nanocrystals have become promising alternatives to organic fluorophore because Ln³⁺ ions can exhibit unique luminescent properties, such as large anti-Stokes shifts, low auto fluorescence background, low toxicity and high penetration depth [1]. In terms of the mechanism of luminescence, luminescence of Ln³⁺ 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 [2], which often requires two main components, an inorganic matrix (known as the host) and activated Ln³⁺ 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 Ln³⁺-doped nanocrystals with uniform size and shape appears to be of key importance for the exploration of new research and application fields [3-7]. 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 [8-10]. In this review, we focus on the most recent advances in the development of the synthesis and applications of Ln³⁺-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 Ln³⁺-doped nanocrystals. Detailed explanations of the LSS process can be found in [11].

Hydrothermal methods have been shown to be effective in the synthesis of nanowires, nanorods, and nanotubes [12]. 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 LaF₃ triangular nano plates via the thermal decomposition of the metal trifluoroacetate (La(CF₃COO)₃) [13]. So far, many groups still attempted to develop other synthetic strategies to yield Ln³⁺-doped nanocrystals with different compositions, shapes and sizes [14].

Application exploration

The unique luminescent properties render Ln³⁺-doped nanocrystals particularly useful in the fields of optical devices

and biomedicine, such as displays, immunoassays, and anti-counterfeiting. Here, the application of typical Ln³⁺-doped nanocrystals has been summarized in Table 1 [2,8,12-21].

Table 1: The applications of typical Ln³⁺-doped nanocrystals.

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

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 Fe₃O₄ and Ln³⁺-doped nanocrystals have been applied to the sensitive detection of DNA [12]. In addition, by use of bioconjugated Ln³⁺-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 [13]. Recently, Ln³⁺-doped nanocrystals were utilized as drug carriers and optical nanoprobe [14-16]. For example, Doxorubicin (DOX), a commonly used anticancer drug, chemically conjugated to NaYF₄:Yb³⁺/Tm³⁺ 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 [17].

Recently, we successfully synthesized Pt/Y₂O₃:Eu³⁺ 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 [19].

Conclusion

This review has described the Ln³⁺-doped nanocrystals with synthetic strategies and applications. By surface modification, Ln³⁺-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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