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Self-calibrating optic thermometer based on dual-emission nanocomposite

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ABSTRACT

A new approach to optical thermometers with high sensitivity was developed herein by using In_2O_3 quantum dots (QDs) emission as temperature detecting signal and Eu^{3+} ions emission as reference one. Originated from the diverse thermal quenching behavior between the defect-related emission of In_2O_3 QDs and 4f-4f transitions of Eu^{3+} ions, fluorescence intensity ratio of In_2O_3 to Eu^{3+} in nanocomposite exhibited excellent temperature sensing property in the range from 303 K to 543 K. The maximum absolute and relative temperature sensitivity can reach as high as 4.43×10^{-2} K^{-1} and 0.89% K^{-1}, respectively. We believe that this work exploits an effective pathway for developing other innovative optical thermometers.

1. Introduction

Recently, self-calibrating optical thermometer based on fluorescence intensity ratio (FIR) technique has attracted great attention due to its fast response, high-spatial resolution, and noninvasive operation. It is favorable for operation in electromagnetically and thermally harsh environments, as well as detection for fast moving objects [1–3]. To date, varieties of luminescent materials have been employed as optical thermometers, such as semiconductor QDs, organic dyes, polymers, metal-organic frameworks (MOFs), and rare earth (RE^{3+}) ions doped phosphors [4–8], etc. Among them, QDs are gaining attentions because of their excellent photostability, broad excitation profiles, large absorption cross sections, high photoluminescence (PL) quantum yields, and tunable emission energies [9].

Generally, QDs present a simple PL spectrum with a single broad band [10]. In order to utilizing FIR technique, dual-emission from two thermally coupled substates within QDs were induced by careful engineering of doping and/or layering [4,11,12]. One such example arose from $Zn_{1-x}Mn_xSe$/ZnCdSe core/shell nanocrystals [9,13]. However, the sensor sensitivity, an important parameter in determining the performance of temperature sensor, is proportional to the energy gap of the corresponding thermally coupled energy levels [14]. Small energy gap is necessary for realizing large absolute temperature sensitivity (S_a), but is harmful to the relative temperature sensitivity (S_r), and vice versa [1]. In addition, QDs-based optical thermometers suffer from limited working range of temperature response, high environmental sensitivity, poor temperature sensitivity and thermal stability [9,12,15,16]. Therefore, searching for new types of QD-based optical thermometers with wide operating temperature range, high sensitivity and stability is of immense importance.

Herein, we show a strategy for developing high-performance luminescent temperature material via dual-emission from wide band gap semiconductor In_2O_3 QDs and Eu^{3+} ions co-doped aluminosilicate glass. In this nanocomposite, the excitonic emission of QDs is expected to decrease quickly with increase of temperature owing to the strong electron phonon coupling [17,18]. In contrast, the optical transitions within the $4f^n$ configuration of RE^{3+} ions are insensitive to temperature because the 4f orbitals are shield from the surroundings by the filled $5s^2$ and $5p^6$ ones [2]. These features indicate the possibility to perform optical thermometry with superior temperature sensitivity and signal discriminability based on the diverse temperature dependent luminescence from QDs and Eu^{3+} ions.

When used as temperature sensor, unlike powders, the transparent nanocomposite can decrease light scattering, improve spatial resolution and temperature sensitivity, as well as attach

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easily to the target surface [3,11,19]. More importantly, the incorporation of QDs into glass matrix provides many advantages, such as protection of QDs from the environment, ease of processability, good thermal, chemical and physical stability, and retaining the favorable optical property of the colloidal solution of QDs [15,19]. Therefore, the obtained composite has many potential applications such as temperature monitoring in highly corrosive media, electrical power stations, oil refineries and building fire detection. Considering the thermal inertia of glass, the obtained nanocomposite is not suitable to measure the temperature of the fast-moving object. In this work, In_2O_3 QDs and Eu^{3+} co-doped transparent nanocomposite was successfully fabricated by a melt quenching method. Temperature dependent luminescence of In_2O_3 QDs and Eu^{3+} ions co-doped nanocomposite was systematically investigated to explore their possible application in optical thermometry.

2. Experimental section

The precursor glass was fabricated with the following composition (in mol%): $18Na_2O$-$10CaO$-$12Al_2O_3$-$56.9SiO_2$-$3In_2O_3$-$0.1EuO_{1.5}$. The mixed chemicals were melted in a covered alumina crucible at 1520 °C for 30 min. The melt was then poured into a 300 °C preheated copper mold and cool down naturally to room temperature to relinquish the inner stress. The obtained glass slice was cut into 5 × 5 mm^2 square coupons and heat-treated from room temperature to 660 °C at a heating rate of 10 °C/min without isothermal holding to form transparent nanostructured composite (denoted as NC0).

To identify the crystallization phase, X-ray diffraction (XRD) analyses was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu $K_{\alpha 1}$ radiation (λ = 0.1546 nm). The microstructure of the sample was studied using a transmission electron microscope (TEM, JEM-2010). TEM specimen was prepared by directly drying a drop of a dilute ethanol dispersion solution sample pieces on the surface of a carbon coated copper grid. The excitation and emission spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorimeter. Temperature-recycle measurement was performed on a temperature controlling stage (THMS600). Three samples with the same components were prepared. And each sample was measured three times to gain reproducible results.

3. Results and discussion

Three samples with the same components were colorless and transparent, and the results were reproducible. As shown in Fig. 1a, XRD patterns demonstrate the amorphous feature of NC0. The high resolution TEM (HRTEM) images show that NC0 sample (Fig. 1b) displays several 2–3 nm near-spherical amorphous In_2O_3 QDs among glass matrix, which has been investigated in detail in our previous work [20–22]. To facilitate the discussions in following sections, we first display the room temperature PL spectrum of NC0. As shown in Fig. 2, the broad emission band with maxima at 490 nm for NC0 originates from the carrier recombination between the valence band (VB) and the oxygen deficiencies induced defect states (DS) formed in the midst of In_2O_3 band gap [17,20]. The sharp emission peaks at 578 nm, 588 nm, 613 nm, 654 nm, and 704 nm can be assigned to the spin-forbidden inter-shell f-f electron transitions of Eu^{3+} ions, i.e., from the first excited level ($^5D_0$) to the ground state multiplets $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$, respectively.

To explore the possible application of the prepared nanocomposite in optical thermometer, temperature-dependent PL spectra of In_2O_3 QDs and Eu^{3+} ions co-doped NC0 sample were measured in the range of 303–543 K, as shown in Fig. 3. With

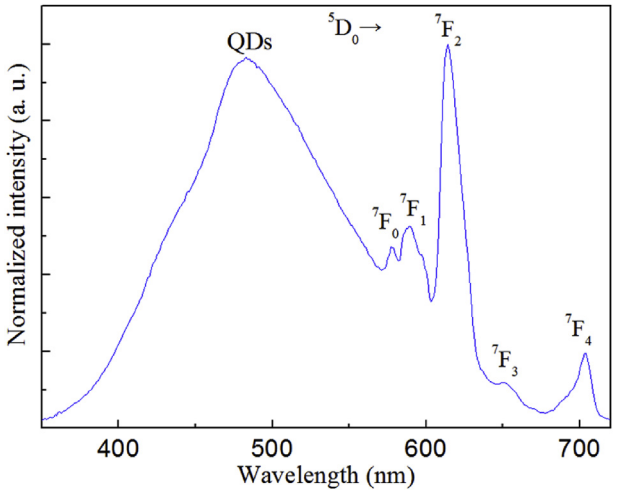

Fig. 2. Room temperature PL spectrum of In_2O_3 QDs and Eu^{3+} ions co-doped NC0 sample excited at 278 nm.

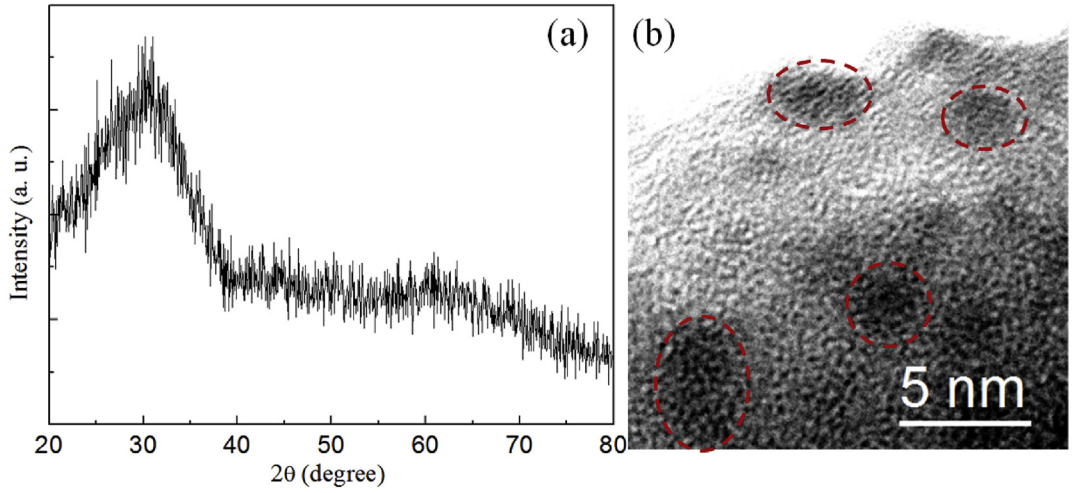

Fig. 1. (a) XRD pattern and (b) HRTEM image of In_2O_3 QDs and Eu^{3+} ions co-doped NC0 sample.