La$_2$O$_2$CO$_3$:Tb$^{3+}$ one-dimensional nanorod with green persistent luminescence

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Trivalent terbium-doped oxycarbonate (La$_2$O$_2$CO$_3$:1%Tb$^{3+}$) one-dimensional nanorods are synthesized via a facile precipitation method. The average length of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ nanorods is 184.5 nm. Doping Tb$^{3+}$ ions led to several visible emission peaks at 486 nm, 542 nm, and 587 nm under excitation of 258 nm wavelength light. The green afterglow at 542 nm can be detected almost 600 s after ceasing the UV-light irradiation. It can be calculated that the La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ sample has one shallow trap depth ($E = 0.848$ eV) by measuring the thermoluminescence. All the results indicate that a simple precipitation method can synthesize a one-dimensional nanorod with green persistent luminescence.

Introduction

Persistent luminescent nanoparticles (PLNPs) are types of optical materials that have plenty of crystal defects as the charge-trappers. PLNPs can store charge carriers (electrons and holes) under excitation with ultraviolet (UV) radiation and then release subsequently for several seconds, minutes and even hours. PLNPs are playing an important role in multidisciplinary fields because of their broad applications, such as in safety signage, night-vision surveillance, latent fingerprint images, decoration and biomedicine.

Nowadays, only a few terbium doped bulk-phosphors such as Lu$_2$O$_3$:Tb$^{3+}$, SrAl$_2$O$_4$:Tb$^{3+}$ etc. have demonstrated their green afterglow. The synthesis method of these materials is a solid-state method, yet almost no successful chemical route can be traced to perfect the size, morphology and dispersion for PLNPs. However, the effective combination of nanostructure and rare earth doped persistent luminescent materials are the valid ways to expand the development of PLNPs in the multi-disciplinary fields.

For example, it had been reported that Tb(NO$_3$)$_3$·6H$_2$O was added to 100 mL of deionized water followed through vigorous stirring for 10 min. Secondly, NH$_4$OH (25 wt%) was purchased from Shanghai Aladdin Biochemical Technology Company, and NH$_4$OH (25 wt%) was purchased from Tianjin Zhiyuan Chemical Reagent Company, and anhydrous ethanol was purchased from Sinopharm Chemical Reagent Company. All chemicals were of analytical-grade reagents and were used directly without further purification.

Preparation of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$. The La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ nanorods were compounded by a precipitation method. Firstly, 0.01 mol of La(NO$_3$)$_3$·6H$_2$O and 0.0001 mol of Tb(NO$_3$)$_3$·6H$_2$O were added to 100 mL of deionized water followed through vigorous stirring for 10 min. Secondly, NH$_4$OH (25 wt%) was added to the mixture to reach the pH = 10. Finally, the mixture in a beaker, wrapped with a polyethylene film, was heated in a water bath at 90 °C for 2 h and heavily stirred and then cooled to room temperature. The precursor products La(OH)$_3$:1%Tb$^{3+}$ nanorods were obtained by washing the resulting precipitates with deionized water and anhydrous ethanol respectively for three times, and then dried at 80 °C for...
12 h in the oven. The final La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods were collected after annealing the precursor products at 600 °C for 3 h in the muffle furnace. The carbon atom maybe come from carbon dioxide in air atmosphere.

**Characterization**

The X-ray diffraction (XRD) (Cu/Kα) patterns of samples were recorded on a PANalytical X’Pert PRO X-ray polycrystal diffractometer. Transmission electron microscopy (TEM) images and scanning electron microscopy (SEM) images were obtained on a Thermo-Talos F200S and Hitachi-SU8220, respectively. Dynamic light scattering spectrum of samples was performed on a Malvern Instruments-Zetasizer Nano ZS at 25 °C. The dispersant is ethanol. Room temperature photoluminescence (PL), PL excitation (PLE) spectra, afterglow spectrum and decay curves of samples were monitored on a high-resolution spectrophotometer (UK, Edinburgh Instruments, FLS 980) equipped with a 500 W Xenon lamp as an excitation source, with a Hamamatsu R928P visible photomultiplier (250–850 nm).

**Results and discussions**

**Phase and crystal structure**

The X-ray diffraction (XRD) patterns of samples are described in Fig. 1a. The XRD patterns of the host La$_2$O$_2$CO$_3$ are in good agreement with the hexagonal La$_2$O$_2$CO$_3$ phase (JCPDS No. 37-0804) and no impurity peak was detected. When small amount of Tb$_{3+}$ doped in the host, the peak position remains unchanged but the main peak shape of the XRD patterns becomes wider. In La$_2$O$_2$CO$_3$, the La site (ionic radius: 0.127 nm, CN = 10) bonds to three category O atoms (three O sites: O$_1$, O$_2$, O$_3$), thus offering the applicable decahedron coordination LaO$_{10}$ to attach the rare-earth emitter Tb$_{3+}$ (ionic radius: 0.110 nm, CN = 9). Tb$_{3+}$ may replace La$_{3+}$ lattice site in this architecture based on the ionic radius and LaO$_{10}$ coordination configuration (Fig. 1b). It is possible that the peak of the doped sample is broadening owing to the substitution of the La$_{3+}$ by the relatively size Tb$_{3+}$.

**Morphology and texture**

The size and morphology of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods are investigated via scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As revealed in Fig. 2a, La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ sample is a kind of one-dimension rod-like nanomaterial with uniform dispersion. Additionally, the hydrodynamic size of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods is measured via dynamic light scattering (DLS). It confirms that size distribution follows a normal distribution with average length 184.5 nm. The polydispersity index (PdI) value (0.248) shows that the sample is moderately polydisperse (Fig. 2b). These results indicate that the precipitation method can successful compound well-dispersed PLNPs.

For further revealing the information on morphology and structural features of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods, the TEM and HRTEM also be measured. Fig. 3a and b display the typical TEM images of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods. It demonstrates that the diameter of nanorods is 15–20 nm and the length are 50–200 nm, which is in keeping with DLS result. Fig. 3c displays the HRTEM image of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorods. The lattice planes of nanorod are counted to be 2.0388 nm and 1.3299 nm, which belong to (110) and (211) crystallographic planes of La$_2$O$_2$CO$_3$, respectively. It indicates that La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ nanorod is polycrystalline while the different crystal

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**Fig. 1** XRD patterns (a) and crystal structure (b) of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ sample.

**Fig. 2** SEM image (a) and dynamic light scattering (DLS) spectrum (b) of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ sample.

**Fig. 3** TEM images (a and b), HRTEM image (c) and crystal diffraction spot image (d) of La$_2$O$_2$CO$_3$:1%Tb$_{3+}$ sample.
orientations can be found distinctly. The presence of indiscernible lattice fringes in La$_2$O$_2$CO$_3$ nanorod due to the formation of defects. The crystal diffraction spot image of a single nanorod (Fig. 3d) insinuates that nanorod is polycrystalline, which matches greatly with the HRTEM results.

Photoluminescent properties

The excitation and emission spectra are used to illustrate the photoluminescent property of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ nanorods (the doping content of 1% has been reported to be a suitable value for preparing Tb$^{3+}$-doped luminescent phosphors), as shown in Fig. 4a. An evident excitation peak at 258 nm can be measured when monitoring at 542 nm emission at room temperature. It can be assigned to the spin allowed inter-configurational 4f$^8$–4f$^5$5d$^1$ transition of Tb$^{3+}$.

The excitation and emission spectrum (a) and the energy levels diagram of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ sample are presented in Fig. 5a. It clearly reveals that the decay process includes a fast decay part and a slow decay process. A strong probability for both forced electric dipole and magnetic dipole transitions belongs to the strongest transition 5D$_4$ to 7F$_5$ of largest energy gap between the electron trap and the conduction band, the thermo-active energy of trap depths (in eV) denoting the energy gap between the electron trap and the conduction band, and $E_T$ is the ThL peak temperature in kelvin. The trap depth of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ is 0.848 eV.

Electron spin resonance (ESR) is an effective and direct characterization to analysis varied behaviours of defects. The ESR test result of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ sample is measured (Fig. 5b). It can be seen an ESR signal at $g = 2.0$, which is close to free electrons generating from oxygen vacancies ($V'_0$). $V'_0$ is a common electron-trap in oxide long afterglow phosphors. The terbium ions in the La$_2$O$_2$CO$_3$ host lattice would substitute the La$^{3+}$, which acted as hole-traps.

The afterglow decay curve of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ sample is presented in Fig. 5a. It clearly reveals that the decay process includes a fast decay part and a slow decay process. A strong afterglow at 542 nm appear at the initial stage of fast decay while a long afterglow duration almost 600 s after ceasing the UV-light irradiation support the existing slow decay. The color of the sample is yellow-color possibly due to the existence of extra tetravalent terbium ions (Tb$^{4+}$). Particularly, no feature fluorescence of Tb$^{4+}$ are found in Fig. 4a, because it may play the role of ion impurities. It is well-known that the generation of long persistent luminescence is primarily attributed to the capture of excited electrons via creating traps in the host lattice. The ThL curve can provide vital information about the number, depth and density of traps, which are advantageous to reveal the possible afterglow mechanism. Therefore, ThL curve of La$_2$O$_2$CO$_3$:1%Tb$^{3+}$ sample is measured (Fig. 5b). Samples were excited at $T_{exc}$ by 254 nm light for 20 min, the heating rate of 2 K s$^{-1}$. ThL spectrum consists a broad band locating at 424 K. The depths and densities of traps can be estimated by the following equations:

$$E = T_{thl}/500$$

where $E$ is the thermo-active energy of trap depths (in eV) denoting the energy gap between the electron trap and the conduction band, and $T_{thl}$ is the ThL peak temperature in kelvin.

The Tb ions with a positive net charge (Tb$^{4+}$) acted as electron-traps. Meanwhile, a charge compensation is coming out owing the unequally charges possibly. It means a simultaneous creation of a La$^{3+}$ vacancy ($V'_0$), which acted as hole-traps.

Based on experimental results of afterglow properties, doping Tb$^{3+}$ ions not only acted as an activator but also formed
point defects (Tb$_{La}^{+}$). The Tb$^{3+}$ impurities not only changed the sample’s color, but also created electron-traps (Tb$_{La}^{-}$) and hole-traps (V$_{La}^{-}$). A possible diagrammatic drawing of La$_2$O$_2$CO$_3$:1% Tb$^{3+}$ afterglow mechanism is shown in Fig. 5d. To explain, the Tb$^{3+}$ energy levels are putted between the conduction band (CB) and valence band (VB). The band gap of La$_2$O$_2$CO$_3$ is 5.83 eV. During ultraviolet (UV) light irradiation ( ), most of the excited electrons and holes are transferred through the CB and VB to the luminescence centers of Tb$^{3+}$ respectively ( ). However, some of the excited electrons and holes will be captured by electron-traps (V$_{el}^{-}$, Tb$_{La}^{-}$, Tb$_{La}^{+}$) from CB or hole-traps (V$_{ho}^{-}$) from VB through non-radiative transition respectively ( ). Then, the stored electrons and holes can escape from the traps by the proper thermal activation, and the released energy be transferred to Tb$^{3+}$ ions via the VB and CB ( ). Then the afterglow of Tb$^{3+}$ ( ) is appearing.

Conclusions

In this paper, the La$_2$O$_2$CO$_3$:1% Tb$^{3+}$ PLNPs have been synthesized via a facile precipitation method. The morphology and texture of La$_2$O$_2$CO$_3$:1% Tb$^{3+}$ sample display uniform dispersion and rod-like shape. The strongest emission peak locates at 542 nm which attributes to $^3$D$_4$ to $^7$F$_{5}$ transition. The green afterglow at 542 nm can be detected almost 600 s after ceasing the UV-light irradiation. ThL measurement reveals that La$_2$O$_2$CO$_3$:1% Tb$^{3+}$ sample possesses one shallow trap depth calculated to be 0.848 eV. The results show that the one-dimensional nanorods with green long afterglow can be successfully synthesized via a simple precipitation method.

Conflicts of interest

There are no conflicts to declare.

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