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Fabrication and characterization of long-persistent luminescence/polymer ($Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}/PLA) composite fibers by electrospinning

Feng Ye [a], Shengjie Dong [b], Zhe Tian [a], Sijia Yao [a], Zhufa Zhou [a,*], Shumei Wang [a,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] Department of Orthopaedics, The First Affiliated Hospital of Soochow University, Suzhou 215006, PR China

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ABSTRACT

Long-persistent luminescence /polymer ($Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}/PLA) composite fibers have been fabricated via electrospinning method. The as-prepared one-dimensional fiber has been characterized by fluorescence microscope and distinct photographs have been obtained. The results show that the $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} particles (12 wt%, size 200 nm) are uniformly dispersed in the PLA fibers (diameter 2.5 μm). It was found that the composite fibers have an emission band from 430 nm to 650 nm that peaks at 537 nm and 452 nm. Similarly, its phosphorescent emission spectra have similar features of luminescence (emission band from 430 nm to 650 nm that peaks at 537 nm and 452 nm). The decay curves of the composite fibers present a similar attenuate tendency with $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} pure particles, but with lower intensity. The composite fiber has applications possibility in textile, display, optical detectors, indicator in the dark without electric energy which they never had before.

1. Introduction

Long-persistent luminescence (LPL) is an interesting phenomenon. The excitation energy can be stored by the LPL materials and then slowly released for several minutes even several hours after stoppage of the excitation. LPL materials such as rare earth metals doped alkaline-earth metal aluminate [1,2] have already been commercialized and been widely used in various applications such as emergency signs in the dark without electric energy. With the development of nanotechnology, rare earth metals doped alkaline-earth metal silicate LPL [3–5] materials represent a rapidly expanding field such as medical imaging and fluorescent probes for its excellent long-persistent luminescent property, chemical stability, and outstanding hydrolysis resistance [6,7]. $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} can emit yellow-green phosphorescence after stoppage of the excitation. Up to date, most of the LPL materials—big or small—are used in the form of powder. The report of LPL composite materials is lacking.

Electrospinning is an effective method to fabricate micro-scale fibers [8–10]. Recently, inorganic rare-earth metals doped luminescent fibers have drawn great attention due to their geometry advantage and excellent luminescence efficiency [11,12]. However, it is difficult to get wide range of application because of its hardness and fragility. Herein, we have fabricated $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+} particles and poly lactic acid (PLA)/$Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+} composite fibers by electrospinning [13]. The resulting product may possess new physical or chemical properties from the two components. It is expected that the one-dimensional composite fibers may have more wide applications in textile, optical detectors and *in vivo* imaging for their novel geometrical structure.

2. Experiments

In this study, analytical grade $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Si(OC_2H_5)_4$(TEOS) and guaranteed grade Eu_2O_3, Dy_2O_3 were used to synthesize precursor. Eu_2O_3 (0.0176 g) and Dy_2O_3 (0.0373 g) were dissolved in nitric acid (0.5 ml) and then mixed with the DI water (18 ml). $Mg(NO_3)_2{\cdot}6H_2O$ (2.564 g), $Ca(NO_3)_2{\cdot}4H_2O$ (4.652 g), TEOS (4.5 ml) and ethanol (5 ml) were added into above solution, and then pH was adjusted to 2 by adding nitric acid. The above mixture was stirred until the sol completely transformed to transparent gel. Subsequently, the gel was dried at 110 °C under reduced pressure for 24 h. The resulting opaque dry gel was then fired at 1200 °C for 2 h in a graphite reducing atmosphere (reduce Eu^{3+} to Eu^{2+}) to obtain LPL crystalline particles.

* Corresponding authors. Tel.: +86 0512 65880963; fax: +86 0512 65880089.
E-mail addresses: yefeng20131331@gmail.com (F. Ye), zhouzhufa@suda.edu.cn (Z. Zhou), wangshumei@suda.edu.cn (S. Wang).

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After above processes, the obtained particles of LPL were added in the dichloromethane and dimethylformamide (2:1 by volume) mixed solvent. The hydride suspension was dispersed with an ultrasonic vibrator for 1 h. Then, 1 g PLA (M_w = 100,000/g Sinopharm Chemical Reagent, China) was dissolved in 6 ml hydride suspension and stirred at room temperature for 1 h. In a possible short time, the above mixture was ejected through the stainless steel capillary to the surface of collector (a piece of aluminum foil) with a voltage of 12 kV. The ejected volume of spinning dope was controlled by electronic pump at 2 ml/h, and the distance between the capillary and collector was fixed at 20 cm. The fibers adhered to the collector were the target products. Schematic of fabrication process is shown in Fig. 1.

XRD data were collected on a Rigaku D/Mx diffractometer (Panalytical, Holland) using Cu Kα radiation (λ = 1.5406 Å). Morphology pictures were obtained by SEM (Hitachi, Japan) and TEM (Hitachi, Japan). The excitation and emission spectra data were recorded on a transient/steady state spectrofluorophotometer (Edinburgh, Britain). Fluorescence microscopic images were shot by fluorescence microscope (EVOS, America) at room temperature. The data of decay curves were measured by brightness meter (SR-2, China).

3. Results and discussion

3.1. Phase analysis of $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} particles

XRD measurements are performed to identify the crystalline phases synthesized by the sol–gel process. The obtained $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+} particles sample that consists of tetragonal structured as a unique phase (lattice constants a = 7.837 Å and c = 5.010 Å) is shown in Fig. 2. The diffraction peaks can be indexed to a pure tetragonal structured $Ca_2MgSi_2O_7$ (JCPDS card No. 35-0592, a = 7.833 Å and c = 5.007 Å). No characteristic peaks of Eu^{2+} and Dy^{3+} are observed in samples for the low dosage (Eu^{2+} 1%, Dy^{3+} 2%) and the extremely high dispersion. No impurity peaks are detected in the scanning rang, which indicates that the Eu^{2+} and Dy^{3+} were completely incorporated into $Ca_2MgSi_2O_7$. The ions radii of Eu^{2+}, Dy^{3+}, Ca^{2+}, Mg^{2+}, Si^{4+} are 1.09 Å, 0.98 Å, 0.99 Å, 0.65 Å, and 0.42 Å, respectively. Since Eu^{2+} and Dy^{3+} have

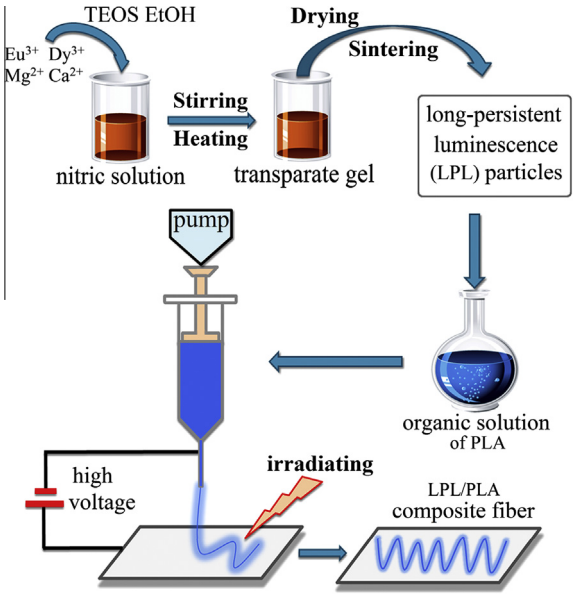

Fig. 1. Process diagram of the preparation of $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}/PLA composite fibers.

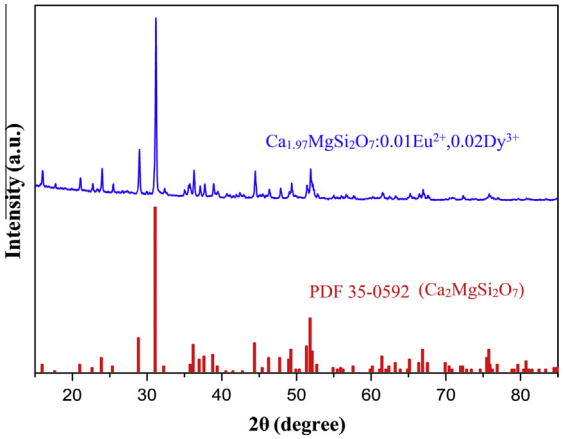

Fig. 2. XRD patterns of $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+} particles sample and JCPDs card No. 35-0592.

similar radius with Ca^{2+}, it can be deduced that they occupy Ca^{2+} site in lattice to form a more stable tetragonal structure [14,15]. As reported by Pawar et al. [16], the doped Eu^{2+} most possibly occupies defect of V''_{Ca} and forms Eu^{X}_{Ca}. The small amount of doped rare earth ions has virtually no effect on the phase structure of $Ca_2MgSi_2O_7$ and does not cause any significant lattice distortion.

3.2. Morphologies of composite fiber

Fig. 3 shows the SEM images of the $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+}/PLA composite fibers. Fig. 3a and b shows that the composite fibers are randomly oriented and have uniform fiber shape. The complicated process of electrospinning is influenced by many factors, such as the concentration of polymer, strength of electric field, the mixing rate of the particles, temperature and the humidity of ambient. Therefore, the morphologies and microstructure of the electrospun fibers are not perfectly identical after process. The morphological surface of the composite fiber is smooth. Because the fibers slightly shrink following the evaporation of the liquid phase, the particles that are close to the surface of fiber are uniformly exposed. Fig. 3c shows the tiny and uniform wrinkle distributed on surface of fibers due to the evaporation of the liquid phase in fibers.

Fig. 4 shows the TEM images (a, b) of $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+}/PLA composite fibers and TEM image of pure PLA fiber (c). As shown in Fig. 4a and b, as-prepared $Ca_2MgSi_2O_7$:Eu^{2+}, Dy^{3+} particles (size: from 50 nm to 2 μm) were embedded into the fibers (diameter: 3 μm). Different shapes of the particles are randomly distributed in the fibers. As shown in Fig. 4c, any shadow can be observed. Pure PLA fibers are uniform from the inside out.

3.3. Luminescent properties of $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+}/PLA composite fibers

Photoluminescence was measured to investigate the luminescence properties of the composite fibers, and Fig. 5a shows the fluorescent emission spectra (A, λ_{ex} = 378 nm, f = 400 nm) of $Ca_{1.97}MgSi_2O_7$:0.01Eu^{2+}, 0.02Dy^{3+}/PLA and the phosphorescent emission spectra collected after removing the exciting light for 1 min (B). The fluorescent emission spectra consist of a broad emission band at the scope of collection, and signals can be collected from 430 nm to 650 nm significantly with emission maximum at 452 nm and 537 nm. Fluorescence of the sample is originated from the energy transition between the $4f^6 5d$ excited state and the $4f^7$ ground state of the Eu^{2+} ions [14,17]. It also implies that there