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Short Communication

Luminescent Polyacrylonitrile(PAN) Electrospinning Nanofibers Encapsulating Silica nanoparticles carried Ternary Europium Complex

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A novel luminescent Polyacrylonitrile(PAN) nanofibre encapsulating silica nanoparticles carried ternary europium complex with α-thenoyltrifluoroacetone(htta) and 1,10-phenanthroline (phen) [$Eu(tta)_3phen$ (EuTP)] was obtained via electrospinning technique. Silica nanospheres carried Eu^{3+} complex achieved by sol-gel technique. The structural investigations by TEM and XRD indicated that europium complex behaves nanocrystals with diameter of ~20 nm that are embedded onto an amorphous nanoSiO_2 (~500 nm) surface. Luminescent spectra and fluorescent optical microscopic photograph of electrospinning fibers showed that introducing the europium complex in nanoSiO_2 can improve the luminescence properties and increase the compatibility between the pure complex and silica. Therefore, this kind of organic-inorganic hybrid materials could be a candidate applied to excellent optical devices.

Keywords: electrospinning; Polyacrylonitrile; Europium complex; Luminescence;

1. INTRODUCTION

Exploring new methods for fabricating materials with nanostructure have gained considerable attention over the last few decades because of their potential applications. Electrospinning has been found to be a simple, convenient, and versatile technique for generating fibers with diameters ranging from several micrometers to tens of nanometers[1-4]. Nanofibres with photoluminescence properties can provide us a wide range of applications in nanophotovoltaic devices, photodiodes, sensors, wave-guiding and all-optical switching[5].

Ternary europium complexes show a strong red fluorescence under a UV light excitation due to the “antenna effect” of ligands and f-f electron transition of Eu^{3+} ions[6]. However, pure complexes usually do not have good thermal and mechanical stabilities and processing ability, which restricts the complexes to promising extensive photophysical applications and limited practical uses. In order to dissolve these problems and to enhance the luminescent intensity of lanthanide complexes, new strategies were created. For example, lanthanide complexes can be incorporated into polymer, inorganic(such as SiO_2,TiO_2), or organic/inorganic hybrid matrixes, such as zeolites or mesoporous materials[7, 8], or organically modified silicates and/or copolymers[9-17] in previous researches. Silica matrix doped with different rare-earth ions are potential candidates for optical and electrochemical applications including biomedicine[18, 19], sensing areas[20, 21] and photoelectric imaging[22-24]. In our study, we choose silica as the matrix based on the fact that the particle size can be controlled according to stöber method[25], being beneficial for the photoelectric and electrochemical applications. The aim of this work is to obtain a kind of novel polyacrylonitrile nanofibres encapsulating nano-SiO_2 carried Eu^{3+} complex during electrospinning process.

2. EXPERIMENTAL SECTION

2.1 Preparation of nSiEuC

EuTP was prepared by referring to published papers[26, 27]. Anal.calcd. (found) for $C_{36}H_{20}Eu O_6N_2S_3F_9$ (Eu(tta)$_3$phen):C,42.72%(42.49),H,2.77%(2.46), N,2.86%(2.75), S,9.78% (9.44). nSiEuC (SiO_2:Eu(tta)$_3$phen) was synthesized according to the following procedure: purified EuTP(36mg, 0.03mmol) was dissolved completely into 0.5ml tetrahydrofuran~~,~~ the solution was added dropwisely into the mixture of ethanol, distilled water(the molar ratio of ethanol/H_2O was 3 to 2) under supersonic stirring for 30 minutes, and $NH_3{\cdot}H_2O$(0.1mol/l, 0.5-1cm^3) was added to the solution to adjust the pH value to about 6~7. Tetraethoxysilane(TEOS) was added dropwisely to the above mixture solution under magnetic stirring continuously for additional 3 hours. The precipitated products were washed with water, ethanol and then dried in a vacuum vessel to obtain the final nSiEuC white powder.

2.2 Solution of PAN-nSiEuC preparation and electrospinning process

The electrospinning solution was prepared by ~~first~~ dissolving PAN in N,N-dimethylformamide firstly at the concentration of 12 wt.%. The solution was stirring for three hours or so to get the homogeneous spinning solution and adding the spinning solution into a 10ml syringe to be fixed on the electrospinning setup.

Electrospinning process: the prepared solution was firstly placed into a 10ml plastic syringe with the inner diameter of the capillary of 0.8mm. During electrospinning process, a positive high voltage of 18kv was applied to the needle. A piece of aluminum foil was used as the collector plate and connected to the earth electrode. The distance between the aluminum plate and the tip of the needle was set at 9.5cm, and spinning operations were in open air and at normal temperature.

2.3 Measurements

The CHNS elemental analyses were carried out on a VarioEL analyzer. The morphology of nSiEuC was characterized by cold field emission SEM (JSM-6700F) and TEM (JEM-1200EX). The morphological structure and fluorescent optical microscopic images of electrospun fibers was characterized by scanning electronic microscope (SEM, JSM-6390LV) and OLYMPUS BX41 universal microscope, equipped with a UV lamp emitting in the wavelength range of 340nm-380nm. The excitation and emission spectra of samples were measured on a Cary Elipse fluorescent spectrometer(Agilent, inc.) equipped with a xenon lamp source. All the measurements were carried out at normal temperature.

3. RESULTS AND DISCUSSION

3.1 Structures of nanoSiO$_2$-carried ternary Europium complexes [nSiEuC]

The scanning electron micrographs of the nSiEuC hybrid materials in Fig.1A show that the particles are spherical and relatively uniform in size about ~500nm. It can be obviously observed in Fig.1B and its magnified image in the inset that many black spots about 5-10nm are doped in nano-SiO$_2$, which are originated from some europium complex clusters.

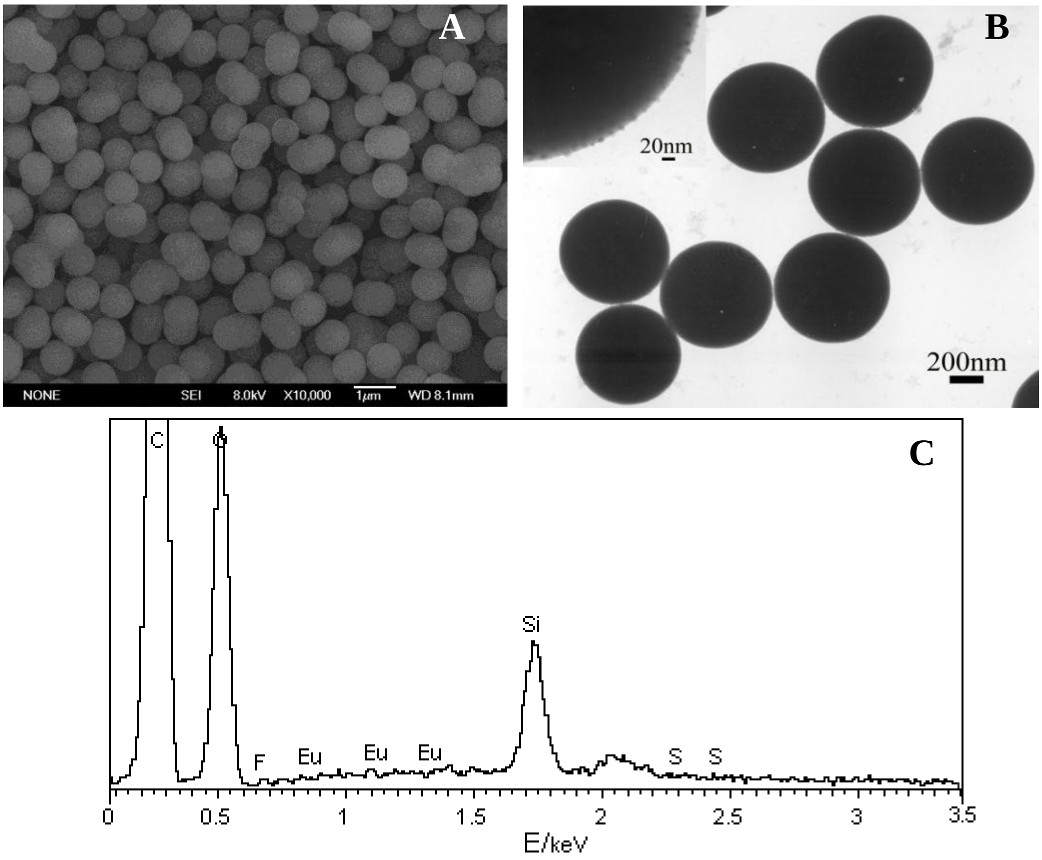

Figure 1. SEM (A) and TEM (B) the morphology of Eu^{3+} complex doped in nano-SiO$_2$ [SiO$_2$:Eu(tta)$_3$phen(nSiEuC)] hybrid nanoparticles. (C) EDS spectrum of nSiEuC.

As seen in Fig.1C, the existence of the rare-earth complex is embedded in the silica matrix that was examined by EDS measurements, O,Si,Eu,F,S were detected in a single particle, which indicates that Eu(tta)$_3$Phen(EuTP) complex are well doped in silica matrix, this also means the successful preparation of the hybrid nanospheres.

Powder X-ray diffraction patterns from 10 to 40° of nanoparticles are shown in Fig.2. Diffraction diagram in Fig.2a shows a single broad peak, indicating that powder nano-SiO$_2$ is amorphous. And diffraction diagram in 2b shows that europium complex is crystal according to our synthesis method. The nanoparticle nSiEuC in Fig.2c almost shows a broad peak like nano-SiO$_2$, even though different number and relative intensities compared with Fig.2b indicated that chemical bonding exist between nano-SiO$_2$ and Europium complex, rather than simple physical mixing. It must be said that only three corresponding diffraction peaks marked with * in the Fig.2b and Fig.2c, because of trace amount of domination of Europium complex.

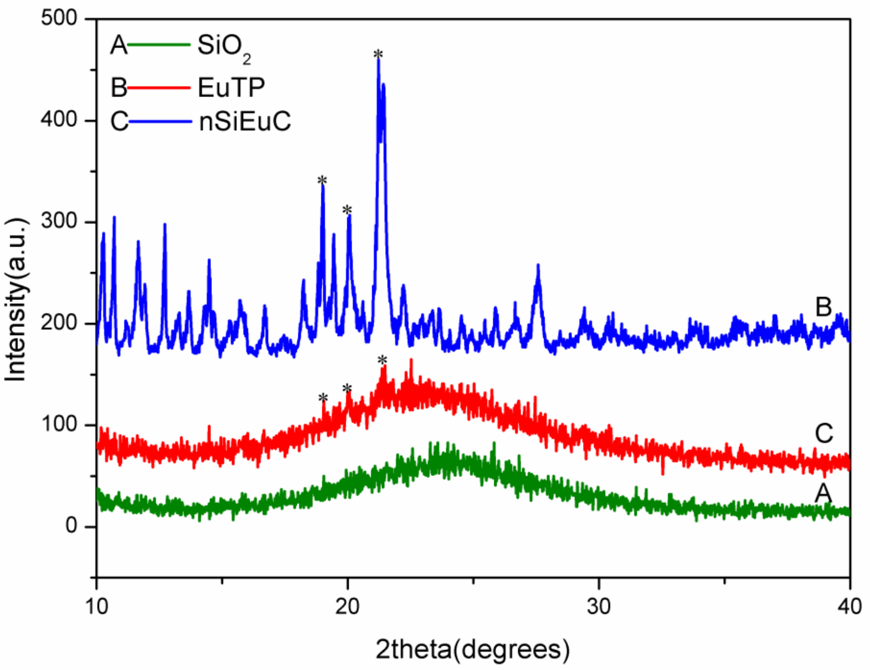

Figure 2. X-ray diffraction patterns of (a)SiO$_2$; (b)EuTP; (c)nSiEuC.

3.2 Fluorescent Property of EuTP and nSiEuC

The fluorescent property of EuTP and nSiEuC are shown in Fig.3 and Fig.4. Fig.3 compared the excitation spectra of pure complex and naoparticles monitored at the maximum intensity of the $^5D_0 \rightarrow {}^7F_2$ transition. The broad excitation band was observed at lower wavelengths are representative of the efficient antenna effect between the ligands and the Eu^{3+} ions. The band at 320nm may be assigned to the $\pi \rightarrow \pi^*$ electron transition absorption in the α-thenoyltrifluoroacetone moiety, the other broad excitation band centered at 380nm is due to oxygen-europium charge transfer(CT). And the intensity of nSiEuC is higher than that of EuTP, this indicate that the site symmetry decreases in the nSiEuC because of the presence of silica medium[28].

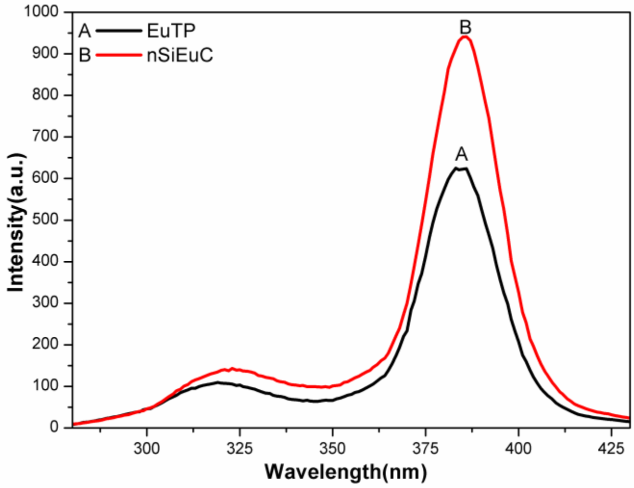

Figure 3. Excitation(λ_{em}=614nm) spectra for the transitions of Eu^{3+} ions in: (A)EuTP; (B)nSiEuC

Solid-state emission spectra of the samples were monitored with 614nm excitation wavelength. Both of the two spectra present the characteristic peaks at similar wavelengths in the range of 550-725nm associating with $^5D_0 \rightarrow {}^7F_J$ (J=0-4) transitions of Eu^{3+} ions. The results indicated that EuTP and nSiEuC nanoparticles show similar fluorescence properties, but the intensity of the nSiEuC improved obviously compared with the EuTP. In the emission spectra (Fig.4A and Fig.4B), the strongest peak at 614nm is due to the forced electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion, while the peaks near 580 and 591nm corresponding to the transitions of $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ (the allowed magnetic dipole transition)[29-31], respectively.

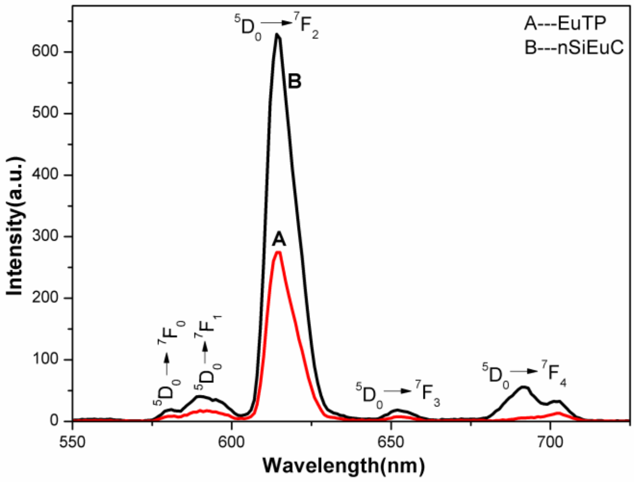

Figure 4. Emission(λ_{ex}=385nm) spectra for the transitions of Eu^{3+} ions in: (A)EuTP; (B)nSiEuC

As is well known, the magnetic dipole transitions $^5D_0 \rightarrow {}^7F_1$ are mostly independent on the ligand field and therefore can be used as an internal standard to account for the ligand differences[32].

The electric dipole transition $^5D_0 \rightarrow {}^7F_2$, so-called hypersensitive transition, is sensitive to the symmetry of the coordination sphere[33, 34]. Therefore, the above results indicate that the presence of silica generally increases the fluorescent intensity of the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition of Eu^{3+} ions. When the complexes are incorporated into the networks of silica matrix, which have a high surface effective on the fluorescence properties, the distortion of symmetry around the europium complex embedded in silica matrix results in the polarization of Eu^{3+} ions, which increases the probability for the forced electronic dipole transitions.

3.3 Red-fluorescence hybrid nanofibers

Fig.5 shows the morphology and fluorescent optical microscopic photograph of PAN electrospinning nanofibres. As shown in Fig.5A, the relatively uniform and super-long hybrid nanofibers exhibiting bead free smooth surface with diameter of 160±30nm averagely were achieved. Note that the polymer concentration is a key factor influencing the viscosity of the spinning solution, which plays an significant role in the procedure of electrospinning. Fig.5B show the red-fluorescence emission photograph of hybrid nanofibers. The color of the luminescent hybrid nanofibres is bright and the luminescence is strong, excited with a UV lamp emitting in the wavelength range of 340nm-380nm by a fluorescence optical microscopy. The red luminescence was originated from Eu^{3+} complex [EuTP] apparently, which indicates that the nSiEuC was successfully encapsulated in PAN nanofiber matrix.

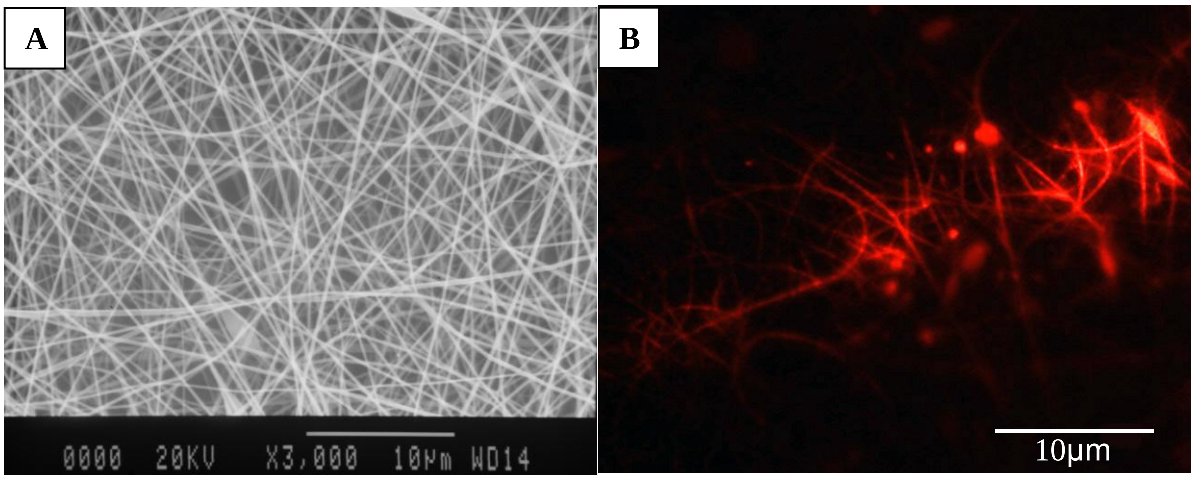

Figure 5. (A) SEM image and (B) Fluorescent optical microscopic photograph of PAN electrospinning nanofibres on a piece of aluminium foil.

4. CONCLUSIONS

Luminescent PAN nanofibers successfully encapsulating nano-SiO_2 carried Eu^{3+} complex was achieved through electrospinning technique. The fluorescence property of nSiEuC was studied in comparison with that of the EuTP complex, and the emission intensity was increased after incorporation with the silica matrix. The fluorescent optical microscopic photograph indicated that the nSiEuC was successfully embedded in PAN nanofibers. Due to the ideal morphology, good fluorescent properties and its photoelectric conversion performance, this kind of novel hybrid nanofibres will have important potential application in optical, electrochemical and nano materials.

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