Synthesis and tunable photoresponse for core-shell structured NaGdF₄:Yb,Er@SiO₂@Eu(TTA)₃Phen nanocomplexes

Yao Li a, Jiqing Jiao a,b, Peipei Yan a, Lihua Liu a, Jiuxing Wang a, Yao Wang a, Linjun Huang a, Jixian Liu a, Laurence A. Belfiore a,b, Jianguo Tang a,b,⁎

a Institute of Hybrid Materials, National Center of International Joint Research for Hybrid Materials Technology, National Base of International Sci. & Tech. Cooperation, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, PR China
b Department of Chemical and Biological Engineering, Colorado State University, Fort Collins, CO 80523, USA

Abstract
Highly monodispersed core-shell structured NaGdF₄:Yb,Er@SiO₂@Eu(TTA)₃Phen(2-Thenoyltrifluoroacetone (TTA), 1,10-Phenanthroline monohydrate (Phen))) nanospheres were synthesized via two-step process. These nanospheres with diameter of 13 nm were encapsulated in SiO₂ shell via micro-emulsion preparation. The ligand-sensitized Eu complexes attached to the outer surface of SiO₂. The green (542 nm) and red (610 nm) light were excited by NIR and UV illumination, respectively. Thus, tunable photoresponse was possible in the core-shell structured hybrid nanocomposites. Under upconversion process, 5-fold increase at 542 nm and a 14-fold increase at 660 nm could be achieved under 980 nm laser, respectively.

Keywords:
Lanthanide ion
Luminescence
Core-shell
Photoresponse
Complexes

Lanthanide ion doped upconversion (UC) nanoparticles have recently emerged as an important class of luminescence materials, owing to their potential applications in biological imaging [1], photodynamic therapy [2], 3D displays [3,4], and solar energy conversion [7]. Compared with organic chromophores (organic dyes) and quantum dots (QDs), UC nanoparticles have high detection sensitivity [5], high light penetration depth [6,7], no photobleaching and blinking [8]. Generally, UC nanoparticles are composed of hosts, activators and sensitizers. Among UC nanoparticles, rare earth (RE) fluorides are considered to be a promising and most efficient host lattice which includes NaYF₄ and NaGdF₄. The lowest excited level (6P7/2) of Gd³⁺ is located in the ultraviolet spectral region, which is far higher than most excited levels of other lanthanide ion. And Gd³⁺ is widely known as the ideal paramagnetic relaxation agent for its large magnetic moments and electron relaxation at the nanosecond time scale, which makes it useful as a contrast agent for magnetic resonance imaging [9,10].

Since UC luminescence was first proposed, its synthesis [11], phase control [12], luminescent properties and biocompatibility [13] of nanoparticles have been extensively studied. However, the UC emission under different excitation. Thus, the water-soluble UCNPs@SiO₂@EuTP nanospheres display red and green color emissions for core-shell nanostructure of NaGdF₄:Yb,Er@SiO₂@Eu(TTA)₃Phen (UCNPs@SiO₂@EuTP) nanospheres. The prepared UCNPs were coated by SiO₂. Then Eu(TTA)₃Phen which could be excited by down-conversion (DC) process was introduced onto the silica surface. The detail experiment was found in Supplementary Material. The TTA ligand absorbs the ultraviolet light and transfers energy to Eu³⁺ ions. The UC excitation wavelength is in the infrared and the Eu(TTA)₃Phen excitation wavelength is in the ultraviolet, respectively. SiO₂ not only does improve hydrophilicity of nanoparticles but also it combines the DC and UC process. Notably, the water-soluble UCNPs@SiO₂@EuTP nanospheres display red and green color emission under different excitation. Thus, the water-soluble nanoparticles would have potential medical application in bioimaging, magnetic resonance imaging and solar energy conversion.

Recently, various core-shell structures including homogeneous structures [16,17] and heterostructures have been designed. The shell can preserve the optical integrity of the nanoparticles and sufficiently minimize surface quenching induced losses [18]. Recently, Ren et al. reported the tunable multicolor UC by lanthanide-doped NaGdF₄ nanorods [19]. Su’s group had reported the NaYF₄/Fe₃O₄@SiO₂@Tb(DBM)₃·2H₂O/SiO₂ luminomagnetic microspheres with core–shell structure [20]. And its size is approximately 200 nm. It’s still a formidable challenge to develop multifunctional and small size UC nanoparticles.

Herein, we report a tunable photoresponse for core-shell nanostructure of NaGdF₄:Yb,Er@SiO₂@Eu(TTA)₃Phen UCNPs@SiO₂@EuTP nanospheres. The prepared UCNPs were coated by SiO₂. Then Eu(TTA)₃Phen which could be excited by down-conversion (DC) process was introduced onto the silica surface. The detail experiment was found in Supplementary Material. The TTA ligand absorbs the ultraviolet light and transfers energy to Eu³⁺ ions. The UC excitation wavelength is in the infrared and the Eu(TTA)₃Phen excitation wavelength is in the ultraviolet, respectively. SiO₂ not only does improve hydrophilicity of nanoparticles but also it combines the DC and UC process. Notably, the water-soluble UCNPs@SiO₂@EuTP nanospheres display red and green color emission under different excitation. Thus, the water-soluble nanoparticles would have potential medical application in bioimaging, magnetic resonance imaging and solar energy conversion.

Generally, UCNPs are insoluble in water and have narrow excitation wavelength range, thus their application had been limited. In order to address the above problems, the core-shell structure was designed

E-mail addresses: jiqiao@googlemail.com (J. Jiao), tang@qdu.edu.cn (J. Tang).
Firstly, the oleic acid stabilized UCNPs were synthesized according to a previously reported procedure [21]. Subsequently, water-soluble UCNPs were obtained by coating a thin layer of amorphous silica onto the UCNPs via a microemulsion method. After coating with silica, the nanospheres were dispersible in ethanol with excellent chemical and photochemical stability. Finally, Eu(TTA)$_3$Phen complexes were introduced to the surface of silica via Van Der Waals forces. UCNPs@SiO$_2$@EuTP nanospheres with core-shell structure was synthesized at last. Thus, water-soluble UC nanospheres with tunable photoresponse can be synthesized.

The uniform nanospheres (NaGdF$_4$:Yb,Er) with diameter about 13 nm are shown in Fig. 1(b) and (c). The corresponding HRTEM image (inset of Fig. 1(c)) reveals the clear lattice fringes with interplanar spacing of 0.30 nm, which was ascribed to the (110) plane of $\beta$-NaGdF$_4$. After coating SiO$_2$, UCNPs@SiO$_2$ is still well dispersed (Fig. 1(d)) and the thickness of the silica shell is about 6 nm (inset of Fig. 1(e)).

**Fig. 1.** (a) The fabrication of the UCNPs@SiO$_2$@EuTP nanospheres. (b) and (c) TEM images of UCNPs. (d) and (e) TEM images of UCNPs@SiO$_2$. (f) and (g) TEM images of UCNPs@SiO$_2$@EuTP with different magnifications. Inset is HRTEM images. UCNPs: NaGdF$_4$:Yb,Er.
The nanospheres modified with Eu(TTA)₃Phen complexes still have good dispersibility (Fig. 1(f)). And the diameter of UCNPs@SiO₂@EuTP is about 25 nm.

The XRD pattern of as-obtained oleic acid stabilized UCNPs is illustrated in Fig. 2a. And all the diffraction peaks can be indexed to the hexagonal $\beta$-NaGdF₄ (JCPDS card no. 27-0699) and no other impurity phase was detected. Hexagonal $\beta$-NaGdF₄ belongs to the space group ($P6_3/m$) with unit-cell parameters ($a = 6.02$ Å, $c = 3.60$ Å) [13]. And diffraction peaks of NaGdF₄ can be clearly observed, corresponding to typical peak of (100), (110), (101), (201) and (211) crystal planes. The XRD patterns of UCNPs@SiO₂ (Fig. 2b) and UCNPs@SiO₂@EuTP (Fig. 2c) indicate the amorphous silica structure peak at $2\theta = 22^\circ$ besides the characteristic peaks of NaGdF₄, indicating the successful coating of SiO₂ shell.

The morphology, size and phase of the UCNPs@SiO₂@EuTP had been demonstrated by TEM and XRD. And the corresponding elemental components of the UCNPs@SiO₂@EuTP were detected by the energy dispersive X-ray spectroscopy (EDS) analysis. The structure of the UCNPs@SiO₂@EuTP can be confirmed by the position of the element distribution. From the HRTEM image and the elemental mapping, the distribution of elements is mostly concentrated on the UCNPs@SiO₂@EuTP nanoparticles (Fig. 3(a–d)). In particular, the Gd is located in the core of the nanospheres and the Eu is at the edges with SiO₂ layer, which prove that UCNPs@SiO₂@EuTP was the core-shell nanostructure. Other elements of the UCNPs are also located in the core of nanoparticles.
In order to further examine the core-shell nanostructure, the line-scanning had been performed (Fig. 3e). With the changing of the location, the distribution of elements also changed as showed in Fig. 3f, which further confirmed the core-shell nanostructure of the composites. Obviously, the Eu(III) complexes were also proved to be existed in the surface of SiO$_2$ layer. Based on the above discussion, the Eu(III) complexes and UCNPs are combined in a core-shell system by the silica. In addition, the FTIR spectra of UCNPs, UCNPs@SiO$_2$ and UCNPs@SiO$_2$@EuTP were determined, respectively (Fig. S2).

It's well known that NaGdF$_4$ has been thought as an ideal host material for UC luminescence. Under 980 nm laser excitation, the bright green emissions can be achieved by doping Yb$^{3+}$/Er$^{3+}$ in NaGdF$_4$. Under the excitation of NIR laser, the typical UC luminescent spectra of UCNPs, UCNPs@SiO$_2$ and UCNPs@SiO$_2$@EuTP are shown in Fig. 4a. As can be observed from Fig. 4b, the emission peak of UC nanospheres in 410, 523, 542 and 660 nm, which was corresponded to the energy level transition of Er$^{3+}$. As a sensitizer, Yb$^{3+}$ strongly absorbed the excitation irradiation and then transfers the excitation energy to the emitters. Yb$^{3+}$ absorbs the energy 980 nm and transfers into Er$^{3+}$. And then Er$^{3+}$ returns from the excited state to the ground state. The dominant green emissions ranging from 515 to 530 nm and from 530 to 550 nm were assigned to the $^4I_{15/2} \rightarrow ^4I_{15/2}$ and $^4I_{15/2} \rightarrow ^4I_{15/2}$ transitions, respectively. And the blue and red emission (410 and 660 nm) were attributed to the $^2H_{9/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions, respectively. For UC emission intensity, it's shown that the emission intensity of UCNPs had been enhanced largely after the coated silica (Fig. 4a). Here, 542 and 660 nm light are used as the target. Compared with bare UCNPs, the emission intensities of the green and red emission of UCNPs@SiO$_2$ were enhanced by about 7 and 12 times, respectively (Fig. 4c). The silica was coated on the surface of the nanospheres, and the surface quenching of the UC nanospheres was suppressed. Therefore, UC emission intensity was improved. Compared with UCNPs@SiO$_2$, the emission intensity of UCNPs@SiO$_2$@EuTP was decreased. But it's approximately 5 and 14 times stronger than that of UCNPs (Fig. 4c). Weaken UC emission intensity may be attributed to the fact that Eu(III) complexes block the absorption of Yb$^{3+}$ ions to 980 nm.

**Fig. 4.** (a) UC luminescence of UCNPs, UCNPs@SiO$_2$ and UCNPs@SiO$_2$@EuTP under excitation of 980 nm laser. The inset is photographs of UC of UCNPs@SiO$_2$@EuTP. (b) is the mechanism of UC processes. (c) Enhanced UC emission for various structures. (d) Pump power dependence of the 542 and 660 nm emission of UCNPs@SiO$_2$@EuTP. (e) Excitation, emission spectrum and photograph of downconversion of UCNPs@SiO$_2$@EuTP. (f) Energy level diagram of Eu$^{3+}$. 

Y. Li et al. / Scripta Materialia 152 (2018) 1–5
To further determine the UC mechanism, the excitation power-dependent UC emissions of green, and red were investigated. For the unsaturated UC process, the output UC luminescent intensity \(I_{UC}\) is proportional to the infrared excitation \(I_{IR}\) power [23].

\[
I_{UC} = f(I_{IR})
\]

(1)

where \(I_{UC}\) is the fluorescent intensity, \(I_{IR}\) is the pump laser intensity, and \(n\) is the number of pump photon required. Furthermore, the value of \(n\) can be obtained from the slope of the fitted line of the plot of \(\log I_{UC}\) versus \(\log I_{IR}\). The slope \(n\) values were 3.45 and 2.99 for 542 and 660 nm emissions in the UCNPs@SiO\(_2\)@EuTP (Fig. 4d), which indicated that the green and red emissions were multi-photon processes [24].

\(\text{Eu(TTA)}_3\text{Phen}\) was bound to UCNPs by the silica. Therefore, UCNPs@SiO\(_2\)@EuTP has DC luminescent. The excitation and emission spectra of the UCNPs@SiO\(_2\)@EuTP nanospheres were studied, respectively (Fig. 4e). The emission spectrum was monitored at 610 nm, while the excitation spectrum was measured with 380 nm as the excitation wavelength. It can be seen that the narrow emission peaks observed in the emission spectrum (Fig. 4a) at 590, 610 and 650 nm of the nanospheres are assigned accordingly to transitions from the \(\text{D}_0\) level to the \(\text{F}_2\) (\(J = 1, 2, 3\) ) levels, of which the \(\text{D}_0 \rightarrow \text{F}_2\) emission is the most prominent one (Fig. 4f). These emission peaks correspond exactly to the emission peaks of Eu\(^{3+}\), which further illustrates the presence of Eu[III] complexes [25].

Fig. S3 shows the CIE 1931 chromaticity diagram. As can be observed in the diagram, the UC of all the samples is concentrated in the green area. And the downconversion of UCNPs@SiO\(_2\)@EuTP was depicted and can be viewed in the red region. From the photograph (inset of Fig. 4a and e), the emission of UC and DC is also green and red, respectively. Silica not only combines UCNPs and Eu(TTA)\(_3\)Phen, but also effectively separates rare earth ions so that the UC and DC luminescence can carry out independently. By the core-shell structure, the UCNPs@SiO\(_2\)@EuTP has a good performance of UC and DC. Therefore, the tunable photo-response could be obtained. Due to the presence of rare earth ions, especially Gd\(^{3+}\) ions, UCNPs@SiO\(_2\)@EuTP exhibits paramagnetism (Fig. S4).

In summary, the water-soluble UCNPs@SiO\(_2\)@EuTP nanospheres were successfully synthesized via two-step process. The nanospheres were characterized by XRD, HAADF and EDS mapping images and FTIR measurements. FTIR analysis indicated the presence of –OH on the surface of nanospheres. So, the UCNPs@SiO\(_2\)@EuTP has water solubility and better dispersibility. EDS mapping analysis proved that the nanospheres are a core-shell nanostructure. The core-shell nanostructure not only enhances the UC emission intensity, but also combines the DC and UC. The emission intensities of the green and red emission of UCNPs@SiO\(_2\)@EuTP were about 5 and 14 times than that of bare UCNPs, respectively. Under the excitation of 980 nm and 380 nm, the UCNPs@SiO\(_2\)@EuTP can emit bright eye-visible green and red light, respectively. Therefore, the tunable photo-response of UCNPs@SiO\(_2\)@EuTP nanospheres by core-shell nanostructure were obtained. Besides UC and DC emission, the UCNPs@SiO\(_2\)@EuTP also exhibits paramagnetic properties at 300 K. It is expected that the multifunction UCNPs@SiO\(_2\)@EuTP may have potential applications in bioimaging, magnetic resonance imaging and solar energy conversion.

The work was financially supported by the National Natural Science Foundation (No. 51403114, 51473082, 51373081 and 51273096), Natural Science Foundation of Shandong Province (BS2014CL025), China Postdoctoral Science Foundation (No.2014M56053), Qingdao Postdoctoral Applied Research Project, Qingdao Applied and Basic Research Fund (14-2-4-62-jch) and Postdoctoral Innovation Fund of Shandong Province (201402015), the National One-Thousand Foreign Expert Program (WQ20123700111), the Program for Introducing Talents of Discipline to Universities (“111” plan), 1st level discipline program of Shandong Province of China, and State Key Project of International Cooperation Research (2016YFE0110800).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scriptamat.2018.03.045.

References