Photoluminescence Characterization of Silicon Nanoparticles Hybridized Europium Complex *

RAN Guang-Zhao(冉广照)[1,3], BIAN Zu-Qiang(卞祖强)[2], LIU Shi-Feng(刘仕锋)[1], HUANG Chun-Hui(黄春辉)[2], QIN Guo-Gang(秦国刚)[1,3]**

[1]*School of Physics, State Key Laboratory for Mesoscopic Physics, Peking University, Beijing 100871*
[2]*Materials Chemistry and Applications, State Key Laboratory of Rare Earth, Peking University, Beijing 100871*
[3]*International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110015*

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A europium complex Eu (DBM)$_3$ TPPO (Eu tris(benzoylmethide)- (triphenylphosphine oxide)) and silicon nanoparticles have been hybridized. The hybridization can evidently change the photoluminescence (PL) characteristics of the Eu complex in the following aspects: under an excitation of 390 nm, the intensity of the PL peak at 611 nm due to the $^5D_0$–$^7F_2$ transition of the Eu^{3+} ions has been increased by 30%, and the integrated PL intensity in the visible range has been increased by nearly 3 times; the PL excitation efficiency beyond 440 nm has been improved evidently; the peak in the PL excitation spectrum shifts from 408 to 388 nm, and the PL decay time decreases from 2.07 to 0.96 μs. The experimental results indicate that in the PL process, the photoexcited energy may transfer from the silicon nanoparticles to the Eu^{3+} ions.

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Rare earth ions are well-known luminescence centres with sharp spectra and independent wavelengths on the environments.[1−3] However, they are generally difficult to be excited directly either by photons or carriers, instead, usually exited by energy transfer from the host matrix, or from the ligands if in the form of complexes.[4,5] It has been shown recently that the silicon nanoparticles (SNPs) embedded in the silicon oxide can excite the nearby rare earth ions efficiently by energy transfer in the PL processes and enhance the emission of the rare earth ions.[6−8] In this work, we dope the silicon nanoparticles (∼3 nm in sizes) into a europium complex, Eu (DBM)$_3$TPPO, to study the effect of the SNPs on the photoluminescence (PL) properties.

The synthesis method of Eu (DBM)$_3$TPPO was similar to that reported in Ref. [6]. The SNPs were produced by anode etching from a crystalline silicon wafer (boron-doped, 6–9 Ω·cm, (100)-oriented). The etching solution was the HF (40%) and H_2O_2 (40%) mixture (1:1 in volume), and the current density was 100 mA/cm^2. After the Eu complex and SNPs are prepared, 0.1 mg Eu (DBM)$_3$TPPO were first resolved in 1.0 ml xylene, followed by PL measurement, and then 0.1 mg SNPs was added in the Eu-complex solution, followed by a 30-min tender ultrasonic treatment. After PL measurement, another 0.1 mg SNPs were added in the same way. The hybrid was spin-coated on a silicon wafer for PL characterization. PL and PL excitation (PLE) spectra were measured on a spectrometer (JOBIN-YVON-SPEX FL-3), with excitation and emission slits of 0.25 mm. The PL decay time was measured on a homemade time-related single-photon counting lifetime spectrometer with a 0.2-ns resolution, and excited at 390 nm by a cavity-dumped frequency-doubled Ti: sapphire laser (Coherent, Mira 900). All the PL characterization was carried out at room temperature.

Figure 1 illustrates a high-resolution transmission electronic microscope image of the SNPs. The lattice fringes of the SNPs are seen clearly, and the sizes of the SNPs are around 3 nm indicated by the lattice fringes and by the scale bar.

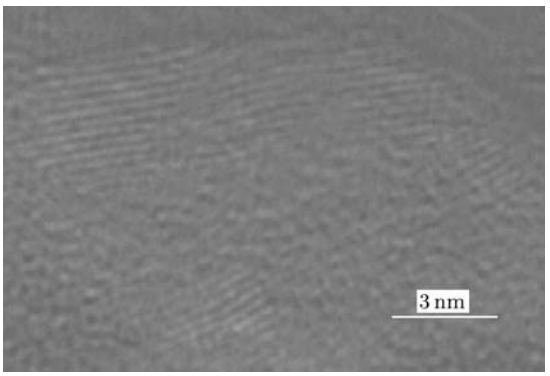


Fig. 1. A high-resolution transmission electronic microscope image of SNPs. The scale bar is 3 nm.

Figure 2 shows the PL spectra of Eu (DBM)$_3$TPPO, the SNPs and their hybrids, all excited at 390 nm. The inset shows the molecular structure of Eu (DBM)$_3$TPPO. The sharp peak at 611 nm is the characteristic emission of Eu^{3+} due to the $^5D_0$–$^7F_2$ transitions. The PL spectrum of the SNPs has a broad band peaked at 610 nm, which overlaps that of the Eu complex. After adding the SNPs into

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** To whom correspondence should be addressed. Email: qingg@pku.edu.cn
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the Eu(DBM)$_3$TPPO, both the PL peak intensity at 611 nm and the PL integrated intensity for the hybrid increased, compared with the pure Eu complex. When the weight ratio of the Eu complex and SNPs is 1:1, the PL integrated intensity increased by more than 2 times, whereas the peak intensity increased slightly compared with the pure Eu complex. When their weight ratio is 1:2, the integrated intensity in the visible range increases by about 3 times, and the peak intensity by 30%. Further increase of SNPs does not lead to further PL enhancement. For clarity, this result has not been given.

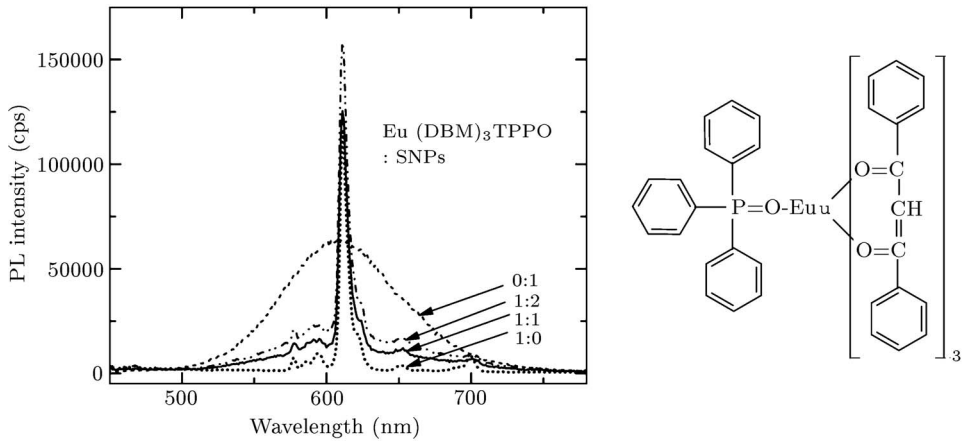


Fig. 2. PL spectra of SNPs, Eu(DBM)$_3$TPPO and their hybrid, all excited at 390 nm; as well as the molecular structure of the Eu(DBM)$_3$TPPO.

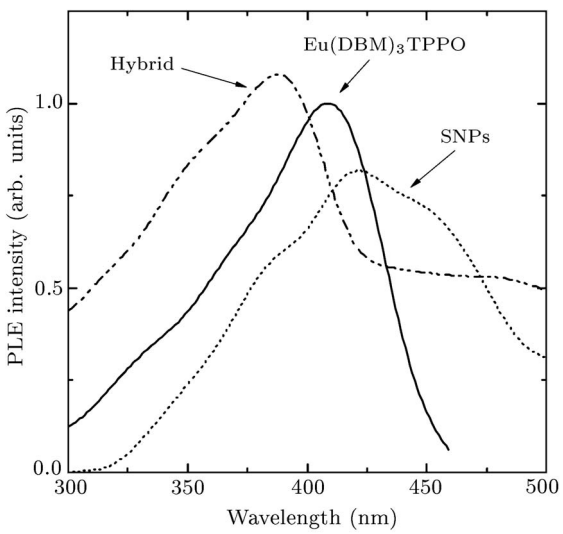


Fig. 3. PLE spectra for the SNPs, Eu (DBM)$_3$TPPO and their hybrid, all monitored at 611 nm.

Figure 3 shows the PLE spectra of the SNPs, the Eu (DBM)$_3$TPPO and their hybrid (2:1 in weight), all monitored at 611 nm. For the SNPs, the PLE spectrum has a broad band with a peak located at 422 nm; for the Eu complex, the PLE spectrum has a peak of 408 nm. However, after addition of SNPs into Eu (DBM)$_3$TPPO, the peak in the PLE spectrum shifts to 388 nm.

Figure 4 depicts the PL decay spectra monitored at the PL peak wavelength of 611 nm in a semi-logarithmic coordinate for the Eu complex and the hybrid (Eu complex : SNPs = 1 : 2 in weight). Each curve can be fitted quite well by a simple exponent function with decay time of 2.07 and 0.96 μs, respectively. The PL decay time of the hybrid decreases evidently compared with that of the Eu complex.

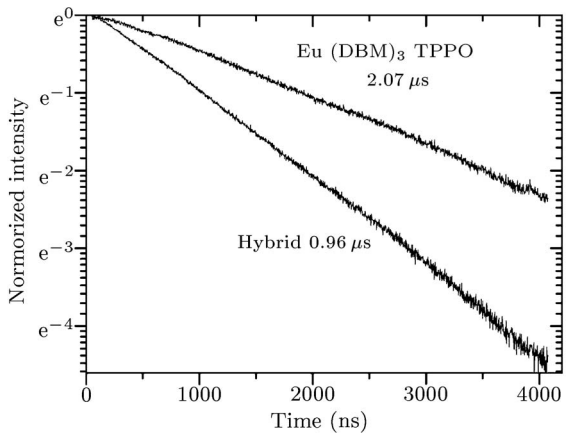


Fig. 4. PL decay spectra of the Eu(DBM)$_3$TPPO before and after the hybridization with the SNPs in a semi-log coordinate, monitored at 611 nm.

We now explain the changes of the PL characteristics tentatively. The SNPs have active and relatively large surfaces. Most of Eu-complex molecules in the solution will be physically absorbed on the surfaces of the added SNPs: that is, most of the Eu-complex molecules are hybridized with the SNPs. However, we cannot rule out the existence of a small quantity of separate Eu-complex molecules or SNPs in the solution.

Because both the peak at 611 nm and the full width

of the half maximum for the PL spectra of the hybrid are the same as those of the Eu complex, the photoemission after hybridization is believed to occur mainly in the Eu ions. For the PL from the SNPs, the photoemission occurs mainly in the luminescence centres in the silicon oxide layers, which were formed by the oxidation in air, on the SNP surfaces.[9,10] The PL quench for the SNPs may be attributed to some new nonradiative centres introduced by hybridization, and the energy transfer from the SNPs to the Eu complex, which also equals a nonradiative process for the SNPs. The residual solvent molecules of xylene, and the interfacial states of Eu complex/SNPs generally act as nonradiative centres.

The evident shift of the peak in the PLE spectrum indicates that the excitation process of the Eu complex has been modified by the hybridization with SNPs. Firstly, an alternative excitation channel to the Eu ion in the complex may be opened: the photoexcited carriers with suitable energy in the SNPs may excite the ligands by energy or charge transfer first, and then excite the Eu ion. On the other hand, the energy transfer channel from SNPs directly to Eu ions could not be ruled out when the excitation energy is appropriate. The ionization potential of the lowest unoccupied molecule orbit is about 3.6 eV for the Eu-complex,[11] and the conduction bands of the SNPs are also around this level if considering that the band gaps of the SNPs have been widened due to quantum confinement. This is a precondition of the energy transfer between the SNPs and Eu complex. Secondly, the photoabsorption energies of the ligands may have been increased by the addition of SNPs due to the dilution effect, which makes the PLE peak shift to a shorter wavelength.[12]

Equation (1) is conventionally used to describe the relationship of the measured PL decay time τ_{pl}, the radiative lifetime τ_r, and nonradiative lifetime τ_{nr}.[13,14]

$$\frac{1}{\tau_{pl}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}. \qquad (1)$$

From Eq. (1), the decrease of the PL decay time is mainly due to the decrease of the nonradiative lifetime, which means the increase of the nonradiative recombination. In addition to the two nonradiative processes mentioned above, the energy back-transfer from the Eu complex to the silicon nanoparticles is also a possible nonradiative channel for recombination of the Eu complex.

In summary, the PL characteristics of the Eu complex, Eu $(DBM)_3TPPO$, could be evidently changed by hybridizing with SNPs. The blue shift of the PLE peak and the decrease of the PL decay time after hybridization may be explained by the photoexcited energy transfer from the SNPs to the Eu ions via the ligands or directly and the increase of the nonradiative recombination probability.

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