Influence of nanoenvironment on luminescence of Eu$^{3+}$ activated SnO$_2$ nanocrystals

Paramita Saha Chowdhury, Sujata Saha, Amitava Patra*

Sol–Gel Division, Central Glass and Ceramic Research Institute, Jadavpur, Kolkata 700 032, India

Received 22 May 2004; accepted 22 June 2004 by C.N.R. Rao

Available online 28 July 2004

Abstract

The emission intensity of the peak at 612 nm ($^5D_0 \rightarrow ^7F_2$) of the Eu$^{3+}$ ions activated SnO$_2$ nanocrystals (doped and coated) is found to be sensitive to the nanoenvironment. We have compared the luminescence efficiencies of the nanocrystals of SnO$_2$ doped by Eu$_2$O$_3$ with those of SnO$_2$ coated by Eu$_2$O$_3$ and we found that the intensities are significantly higher in coated nanocrystals. Furthermore, it is clear from luminescence intensity measurements that Eu$^{3+}$ ions occupy low symmetry sites in the Eu$_2$O$_3$ coated SnO$_2$ nanocrystal. The analysis suggests that the radiative relaxation rate is higher in Eu$_2$O$_3$ coated SnO$_2$ nanocrystals than Eu$_2$O$_3$ doped SnO$_2$ nanocrystals due to the asymmetric environment of Eu$^{3+}$ ions in coated samples. © 2004 Elsevier Ltd. All rights reserved.

PACS: 76.30.Kg; 78.55.−m; 73.61.Tm; 74.25.Gz

Keywords: A. Rare-earth ions; B. Photoluminescence; C. Nanocrystalline

In the new millennium, there has been a growing interest in the study of nanoparticles doped with rare-earth ions for photonic and bio-photonic applications [1–4]. Recently, attention has been paid in the properties of wide-band gap oxide quantum dot (QD) semiconductors such as SnO$_2$ for their size dependent linear and non-linear optical properties [5–7]. A few papers [6–8] have been recently reported on rare-earth ions containing SnO$_2$ nanoparticles, which is the topic of the manuscript. They may find wide ranging applications such as micro-lasers, multicolor display and luminescent labels. Combining the promising optical properties of rare-earth ions and nanoparticles, in the form of coatings or thin films is important in fabrication of optical devices such as multicolor display and microlasers. In case of rare-earth ions, the electronic f–f transitions involve electrons which are localized in atomic orbital of the ions. Therefore, no size-dependent quantization effect from confinement of delocalized electrons is found of these transitions. However, confinement effects of semiconductor nanoparticles create photogenerated carriers may have an interaction with f-electrons which has important manifestations in influencing the optical properties. Thus, a nanostructure controls either by judiciously choosing the nanoenvironment of the species to be excited or by utilizing a nanoconfined structure that can be utilized to manipulate the excitation dynamics. Nanoscopic interactions play key roles in controlling the excitation dynamics. The efficiency of a nanomaterial is often limited by the band-to-band recombination and non-radiative surface recombination rates. Bhargava et al. [9] showed strong orange luminescence from Mn$^{2+}$ ions doped in ZnS nanoparticles. They discussed the enhanced luminescence which occurs through the recombination of photogenerated carriers confined in nanoparticles and subsequent energy transfer to ions. Therefore, it is expected the efficient energy transfer is possible if the emission energy of the nanoparticle matches with the excitation energy of the rare-earth ion in the...
rare-earth doped semiconducting nanoparticles. No report has been found on the study of energy transfer from SnO2 nanocrystals to Eu$^{3+}$ ions doped in and coated on SnO2 nanocrystals for comparison, to our knowledge. It is believed that the energy transfer efficiency may be different because of their difference in nanoenvironment. Therefore, it is very important to study the photoluminescence of Eu$^{3+}$ ions doped in and coated on SnO2 nanocrystals.

An aqueous solution (0.05 M) of SnCl$_4$ · 5H$_2$O was prepared by dissolving the salt in de-ionized water. 15 ml of this aqueous solution was then slowly added to the supporting solvent consisting of 5% by volume Span 80 in cyclohexane (solution: cyclohexane was 1:4, v/v) to achieve emulsified droplets. Precipitation of the emulsified droplets resulted from controlled addition of a base after which centrifugation (6000 rpm, 30 min) allowed for facile particle collection. The particle was then washed twice with acetone and then twice with methanol. After preliminary drying at 60 °C for 12 h in a vacuum oven, annealing of the as-prepared gel particles was carried out at 400, 700 and 1000 °C in air for 1 h. For the Eu$_2$O$_3$ doped SnO$_2$ nanoparticles, the required amount (for 1.0 mol% Eu$_2$O$_3$) of Eu(NO$_3$)$_3$ · 6H$_2$O was added to the aqueous solution of SnCl$_4$ · 5H$_2$O and then followed the same procedure. To prepare Eu$_2$O$_3$ coated nanoparticle, 400 °C annealed pure SnO$_2$ particles were ultrasonically dispersed in water and then the aqueous solution of Eu(NO$_3$)$_3$ · 6H$_2$O (1.0 mol% Eu$_2$O$_3$) and base were added into it. The resulting product was then centrifuged and washed as above. Finally, the dried gel particles were annealed out at 700 and 1000 °C in air for 1 h. The crystalline phases of annealed powders were identified by X-ray diffraction (XRD) using a Philips model PW-1730, powder X-ray diffractometer using a Cu K$_\alpha$ source (1.5418 Å radiation). Crystallite sizes ($D$, in Å) were estimated from the Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of Cu K$_\alpha$ radiation, $\beta$ is the corrected half-width of the diffraction peak, $\theta$ is the angle and $K$ is equal to 0.9.

The excitation and emission spectra of SnO$_2$: Eu$^{3+}$ ions (coated and doped) were measured using a Perkin–Elmer LS55 Luminescence Spectrometer. All measurements were done at room temperature, using solid sample holder. All samples were excited at 265 nm (bandwidth (Ex) = 10 nm, bandwidth (Em) = 10 nm), under same conditions. X-ray diffraction patterns of the pure SnO$_2$ annealed at 400, 700 °C annealed Eu$_2$O$_3$ coated SnO$_2$ and Eu$_2$O$_3$ doped SnO$_2$ are shown in Fig. 1(a)–(c), respectively. In case of 400 °C annealed pure SnO$_2$ nanocrystals (Fig. 1(a)), the $2\theta$ values are ~26.8, 34.3 and 52.3°, which are identified for t-SnO$_2$ particles were ultrasonically dispersed in water and SnO$_2$ are shown in Fig. 1(a)–(c), respectively. In case of Eu$_2$O$_3$ coated samples were excited at 265 nm (bandwidth (Ex) = 0.9), using solid sample holder. All measurements were done at room temperature, using solid sample holder. All samples were excited at 265 nm (bandwidth (Ex) = 10 nm, bandwidth (Em) = 10 nm), under same conditions. X-ray diffraction patterns of the pure SnO$_2$ annealed at 400, 700 °C annealed Eu$_2$O$_3$ coated SnO$_2$ and Eu$_2$O$_3$ doped SnO$_2$ are shown in Fig. 1(a)–(c), respectively. In case of 400 °C annealed pure SnO$_2$ nanocrystals (Fig. 1(a)), the $2\theta$ values are ~26.8, 34.3 and 52.3°, which are identified for t-

Fig. 1. Powder X-ray diffraction patterns of SnO$_2$ nanocrystals obtained after heating at different temperatures, (a) pure SnO$_2$ at 400 °C, (b) 1.0 Eu$_2$O$_3$ coated at 700 °C and (c) 1.0 Eu$_2$O$_3$ doped at 700 °C.
almost matching with the excitation band (392 nm) of Eu\(^{3+}\) ions. Here, we see the decrease in overall intensity of the SnO\(_2\) emission drastically when the intensity of the 612 nm peak grows. This indicates that the emission energy of SnO\(_2\) is consumed for the excitation of Eu\(^{3+}\) ions. The emission spectrum of Eu\(_2\)O\(_3\) doped sample (Figs. 2(b) and 3(b)) lies between the spectra of pure SnO\(_2\) and Eu\(_2\)O\(_3\) coated SnO\(_2\) nanocrystals. However, the emission spectrum for coated sample always lies in below (Figs. 2(c) and 3(c)). Therefore, we can say from this observation that the energy transfer from SnO\(_2\) to Eu\(^{3+}\) ions is more in coated samples than doped samples. It is known [9] that the enhanced luminescence occurs through the recombination of photo-generated carriers confined in nanoparticles and subsequent energy transfer to rare-earth ions. The energy transfer efficiency from nanocrystal to Eu\(^{3+}\) ions is estimated accordingly \( n_{et} = 1 - III_0 \), where \( I_0 \) is the total emission intensity of pure SnO\(_2\) nanocrystals without europium and \( I \) corresponds to the emission intensity of SnO\(_2\) nanocrystals in presence of europium (either doped or coated). The calculated energy transfer efficiencies for doped and coated samples are 0.59 and 0.76 for 700 °C and 0.77 and 0.85 for 1000 °C annealed samples, respectively. This result further proves that the energy transfer from SnO\(_2\) nanocrystals to Eu\(^{3+}\) ions is more in Eu\(_2\)O\(_3\) coated samples (700 and 1000 °C annealed) than doped samples. The most dramatic effect is seen when we compare the intensity of the 612 nm peak for the Eu\(_2\)O\(_3\) coated and doped SnO\(_2\) nanoparticles. At the same experimental conditions, namely, Eu\(_2\)O\(_3\) concentration, annealing temperature, same wavelength excitation with same bandwidth, we have compared the luminescent efficiencies of the nanocrystals of SnO\(_2\) doped by Eu\(_2\)O\(_3\) with those of SnO\(_2\) coated by Eu\(_2\)O\(_3\) and we found that the intensities are significantly higher in coated nanocrystals (Figs. 4 and 5). The difference in nanoenvironments between doped and coated samples will account for the intensification of the luminescence intensity. In europium, the \((^5D_0 \rightarrow ^7F_1)\) (590 nm) transition is mainly magnetically allowed (a magnetic-dipole transition) and is independent of the site symmetry at which europium ion is situated, while \((^5D_0 \rightarrow ^7F_2)\) (612 nm) transition is a hypersensitive forced electric-dipole transition being allowed only at low symmetries with no inversion center [10]. Thus, the intensity ratio \( I_{612}/I_{590} \) serves as an effective spectroscopic probe of the site symmetry in which europium is situated, i.e. the higher the ratio, the lower the site symmetry. The intensity ratio values are 2.60 and 1.49 for 700 °C annealed coated and doped nanocrystals, respectively, and the values are 2.57 and 1.47 for 1000 °C annealed coated and doped samples, respectively. From these results, it is clear that Eu\(^{3+}\) ions occupy low symmetry sites in Eu\(_2\)O\(_3\) coated samples than Eu\(_2\)O\(_3\) doped SnO\(_2\) nanoparticles. It indicates that the crystal field of Eu\(^{3+}\) ions is different in coated and doped samples, which may be due to different coordination numbers. The lowering the site symmetry of the ion will cause to the increase in transition probabilities of Eu\(^{3+}\) ions in SnO\(_2\) nanocrystals. It should be remembered that the f–f transitions of Eu\(^{3+}\) ions are forbidden in the absence of a magnetic field due to the lack of dipole transitions, but when the magnetic field is applied, the transitions become allowed due to the Zeeman effect.
transitions arising from forced electric dipole which are parity forbidden and become partially allowed when the ion is situated at low symmetry site. Such situation allows intermixing of the f states with higher electronic configuration and as a result the optical transition probability increases, i.e. the radiative emission rate increases [10]. The existences of europium ions in low symmetry sites, 5D0 levels decay mostly radiatively to the 7F2 level and an overall increase in intensity is observed with changing the structure from symmetric to asymmetric. It is well known that the quantum efficiency is given by

\[
\eta = \frac{1}{R_\text{R}} \left( \frac{1}{R_\text{R}} + \frac{1}{NR_\text{R}} \right),
\]

where \(R_\text{R}\) and \(NR_\text{R}\) are the radiative and non-radiative surface recombination, respectively. The term \(R_\text{R}\) depends basically on the environment and symmetry while the term \(NR_\text{R}\) depends basically on the surface states or defect centers. Therefore, radiative emission rate can be modified by changing nanoenvironment and it is clear from the emission intensity of Eu\(^{3+}\) ions that the radiative relaxation rate is higher in coated samples than doped samples due to asymmetric environments of Eu\(^{3+}\) ions. All these reasons will explain the significant increase in the luminescence intensity with changing the nanoenvironment.

In summary, we have demonstrated the luminescence efficiencies of Eu\(^{3+}\) ions of the coated SnO\(_2\) nanocrystals are significantly higher than for doped samples. We believe that semiconducting nanocrystals coated with optically active luminescence centers may create new opportunities in the study and application of multicolor displays.

Acknowledgements

Authors thank Dr H. S. Maiti, Director of CGCRI for his constant encouragement and active co-operation to carry out the work. The Department of Science and Technology (NSTI, No.SR/S5/NM-05/2003) and CSIR (OLP9002 and CMM0022) are acknowledged for financial support.

References