

Enhancement of Sm³⁺ emission by SnO₂ nanocrystals in the silica matrix

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Abstract Silica xerogels containing Sm³⁺ ions and SnO₂ nanocrystals were prepared in a sol–gel process. The image of transmission electron microscopy (TEM) shows that the SnO₂ nanocrystals are dispersed in the silica matrix. The X-ray diffraction (XRD) of the sample confirms the tetragonal phase of SnO₂. The xerogels containing SnO₂ nanocrystals and Sm³⁺ ions display the characteristic emission of Sm³⁺ ions (⁴G_{5/2} → ⁶H_J (*J* = 5/2, 7/2, 9/2)) at the excitation of 335 nm which energy corresponds to the energy gap of the SnO₂ nanocrystals, while no emission of Sm³⁺ ions can be observed for the samples containing Sm³⁺ ions. The enhancement of the Sm³⁺ emission is probably due to the energy transfer from SnO₂ nanocrystals to Sm³⁺ ions.

Keywords Sm³⁺ ions · Emission · Sensibilization · SnO₂ nanocrystals · Silica matrix

Introduction

Sm³⁺ ions can exhibit strong emission in the orange spectral region. The silica gel has been known as an excellent host material for rare earth ions because of its high transparency, compositional variety and easy mass production [1]. Therefore, the silica gel containing Sm³⁺ ions has a potential application for high-density

optical memory [2, 3]. However, the Sm³⁺-doped gel cannot emit strong fluorescence [4]. It is necessary to introduce a sensitizer into the gel containing Sm³⁺ ions in order to obtain strong emission of Sm³⁺ ions.

Our previous study [5] showed that there existed the interaction between Eu³⁺ ions and CdS nanoparticles in the silica matrix. Furthermore, Franzo et al. [6], Brovelli et al. [7], Bang et al. [8] and Selvan et al. [9] investigated the energy transfer between Si, SnO₂, ZnO and CdS nanoparticles and rare earth ions. The present work aims to understand whether the SnO₂ nanocrystals can sensitize the Sm³⁺ emission in the silica matrix. The one-step synthesis of the silica xerogels containing SnO₂ nanocrystals and Sm³⁺ ions was described in a sol–gel process. The energy transfer from SnO₂ nanocrystals to Sm³⁺ ions was presumed to explain the enhancement of the Sm³⁺ emission in the silica matrix.

Experimental

All of reagents were commercially available and used without further purification. Double-distilled water was used as solvent. The silica xerogels containing SnO₂ nanocrystals (10 wt%) and Sm³⁺ ions (0.5 mol%) were prepared in the sol–gel process similar to the procedure described by Nogami et al. [1]. In a typical preparation, the tetraethyl orthosilicate (TEOS) (10 mL) was added in the flask containing ethanol (5 mL), HCl (0.1 mmol), and H₂O (3.25 mL). After the mixture was stirred for 0.5 h at room temperature, Sm(NO₃)₃ aqueous solution (0.1 mol L⁻¹, 2.25 mL) was introduced into the solution and stirred for another 0.5 h. Subsequently, SnCl₂ · 2H₂O ethanol solution

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(0.15 g mL⁻¹, 5 mL) was introduced into the sol. After stirred for 2 h, the sol was kept at 313 K for about 2 weeks to form gel. The sample was further dried in air to form the stiff xerogel. Finally, the xerogel was annealed in air at 700 °C for 5 h to obtain the silica xerogel having SnO₂ nanocrystals and Sm³⁺ ions.

The X-ray diffraction (XRD) of the silica xerogel having SnO₂ nanocrystals and Sm³⁺ ions was performed on a Rigaku D/Max 2550VB/PC X-ray diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm). The transmission electron microscopy (TEM) images were taken with a JEOL JEM-100CX electron microscopy. The absorption spectra were carried on a Unico UV-2102 PCS UV-vis spectrophotometer. The emission and excitation spectra were measured at room temperature with a Shimadzu RF-5301PC spectrophotometer.

Results and discussion

The TEM image of the silica xerogel containing Sm³⁺ ions and SnO₂ nanocrystals is shown in Fig. 1. It can be clearly observed that a lot of nanoscale particles are dispersed in the silica matrix. These particles ought to be assigned to SnO₂ nanocrystals (see the discussion below).

Figure 2 exhibits the XRD pattern of the silica xerogel containing Sm³⁺ ions and SnO₂ nanocrystals. The broaden peak ($2\theta = 22^\circ$) is the characteristic one for amorphous SiO₂ (JCPDS 29-0085). There exist eight peaks at 26.5°, 33.7°, 37.8°, 51.4°, 54.6°, 61.5°, 65.0°, 65.8°, respectively, which can be indexed to (110), (101), (200), (211), (310), (112), (202), and (312) planes of tetragonal phase of SnO₂ based on the data

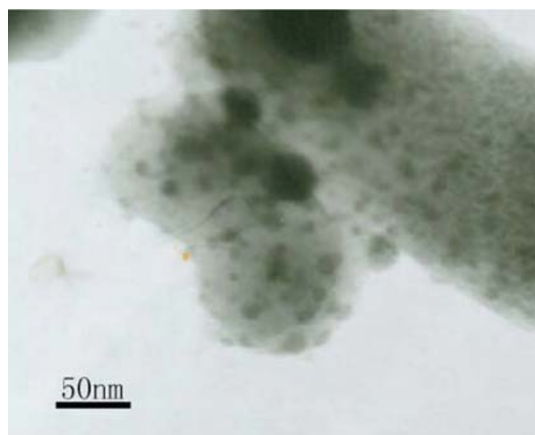


Fig. 1 TEM image of the silica xerogel containing Sm³⁺ ions (0.5 mol%) and SnO₂ nanocrystals (10 wt%)

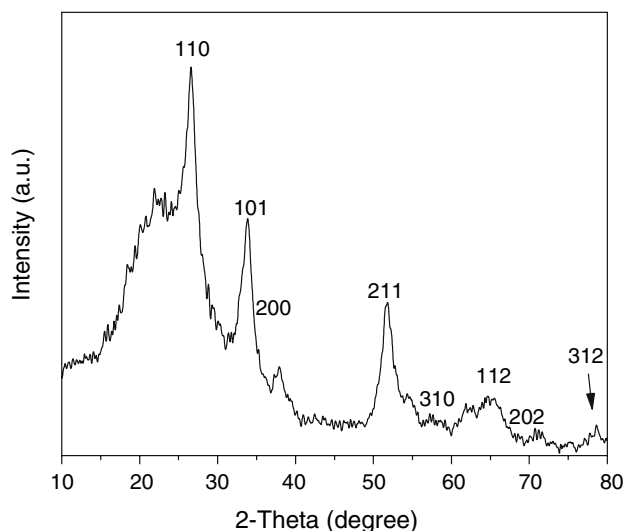


Fig. 2 XRD pattern of the silica xerogel containing Sm³⁺ ions (0.5 mol%) and SnO₂ nanocrystals (10 wt%)

from Powder Diffraction File No. 41-1445. The result indicates that the SnO₂ nanocrystals stabilized by the silica matrix have a rutile-type structure. In combination with the TEM image, it can be deduced that the SnO₂ nanocrystals are indeed introduced in the silica xerogel.

From the UV-Vis spectrum of the silica xerogel containing Sm³⁺ ions and SnO₂ nanocrystals (Fig. 3), it can be observed that there exists a relatively steep shoulder around 300 nm, which may be assigned to the direct electron transition of the SnO₂ nanocrystals [10]. Furthermore, the shoulder red-shifts with increasing

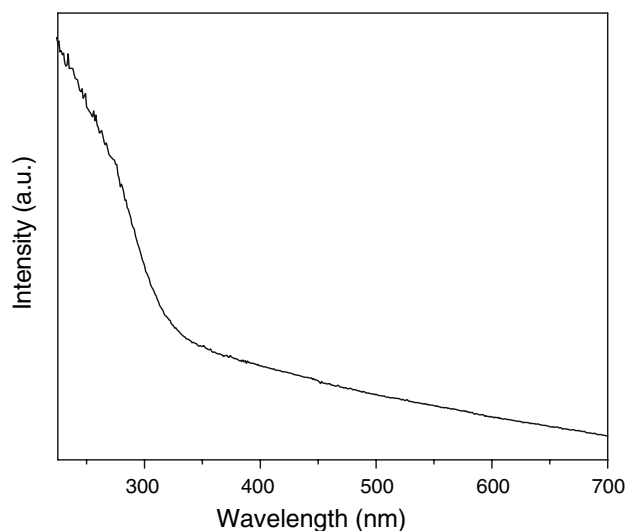


Fig. 3 UV-Vis spectrum of the silica xerogel containing Sm³⁺ ions (0.5 mol%) and SnO₂ nanocrystals (10 wt%)

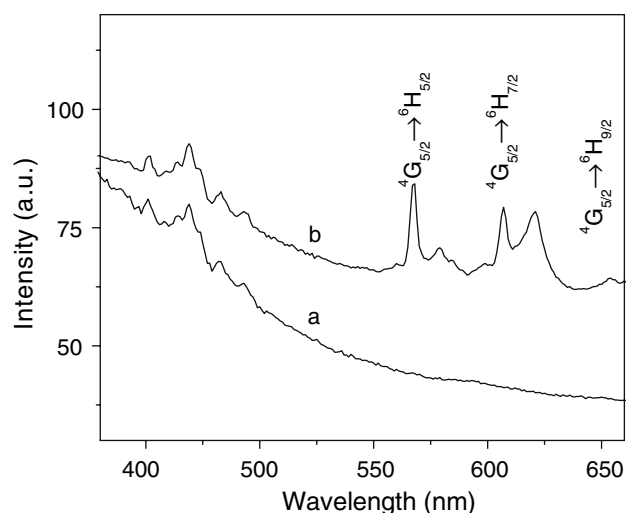
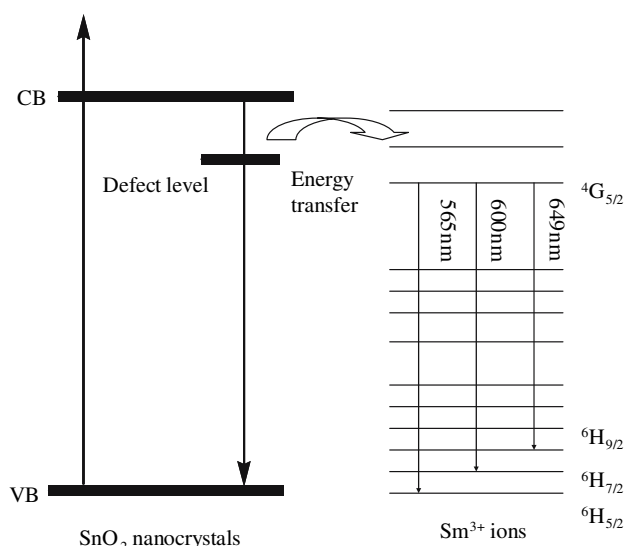


Fig. 4 Emission spectra of the silica xerogels containing Sm^{3+} ions (0.5 mol%) (a), and Sm^{3+} ions (0.5 mol%) and SnO_2 nanocrystals (10 wt%) (b), excited at 335 nm

the amount of SnO_2 nanocrystals (not shown here), suggesting that the size of SnO_2 nanocrystals increases. These results further confirm that the SnO_2 nanocrystals are incorporated in the silica matrix, and the network of silica and SnO_2 is not formed.

Figure 4 shows the emission spectra of the silica xerogels under the excitation of 335 nm (3.7 eV) corresponding to the energy gap of the SnO_2 nanocrystals. The peaks before 500 nm should be ascribed to the emission of silica gels. No characteristic emission of Sm^{3+} ions can be observed for the silica xerogel containing Sm^{3+} ions (curve a), while the sample containing SnO_2 nanocrystals and Sm^{3+} ions shows strong characteristic emission of Sm^{3+} ions (curve b). The emission peaks are assigned to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$ ($J = 5/2, 7/2, 9/2$) transitions of Sm^{3+} ions [11]. These results indicate that the SnO_2 nanocrystals can sensitize the emission of Sm^{3+} ions in the silica matrix. Meanwhile, it is possible that there exists effective energy transfer between SnO_2 nanocrystals and Sm^{3+} ions in the silica matrix. The SnO_2 nanocrystals may act as light-harvesting antennas to sensitize emission of Sm^{3+} ions.

It is well known that the energy transfer occurs unless the energy gap of the donor is equal to that of the acceptor in resonance condition. The emission band centered at 400 nm of SnO_2 nanocrystals in the SiO_2 gel which is ascribed to the electron transition mediated by defect levels [12] overlaps the dominating absorption line at 404 nm of Sm^{3+} ions [13]. Therefore, it is possible that the energy transfers from SnO_2 nanocrystals to Sm^{3+} ions. The proposed mechanism of the energy transfer between SnO_2



Scheme 1 Schematic diagram of energy transfer between SnO_2 nanocrystals and Sm^{3+} ions

nanocrystals and Sm^{3+} ions is shown in Scheme 1. When the sample is excited, the energy is harvested by the SnO_2 nanocrystals and transmitted from the defect levels of the SnO_2 nanocrystals to the Sm^{3+} ions. The excited Sm^{3+} ions emit the characteristic fluorescence via radiative relaxation. The surface states of the SnO_2 nanocrystals play an important role in the energy transfer. In our materials, these defect sites would be at the interface between the nanocrystals and the silica matrix. The results reported previously [14] shows that the energy transfer is not observed for SnO_2 nanoparticles doped with rare earth ions. Furthermore, the Sm^{3+} ions cannot be doped into the lattice of SnO_2 nanoparticles in our experiments because the size of Sm^{3+} ions (0.096 nm) is much bigger than that of Sn^{4+} ions (0.076 nm). Meanwhile, the energy transfer between SnO_2 nanoparticles and Sm^{3+} ions absorbed on the SnO_2 nanoparticles are not observed. Therefore, it is reasonable to deduce that the energy transfer takes place between the SnO_2 nanocrystals and the Sm^{3+} ions near the nanocrystals.

The excitation spectra of the silica xerogel containing Sm^{3+} ions and SnO_2 nanocrystals are monitored at 567 nm, 606 nm and 654 nm, respectively, as shown in Fig. 5. It can be seen that the sample displays a broad peak at 325 nm and a narrow peak at 404 nm for all of emission. The narrow peak can be assigned to the direct excitation of the Sm^{3+} ions, and the broad peak corresponds to the electron transition in the SnO_2 nanocrystals [15]. This result further confirms that the energy can transfer from the SnO_2 nanocrystals to the Sm^{3+} ions when the sample is excited.

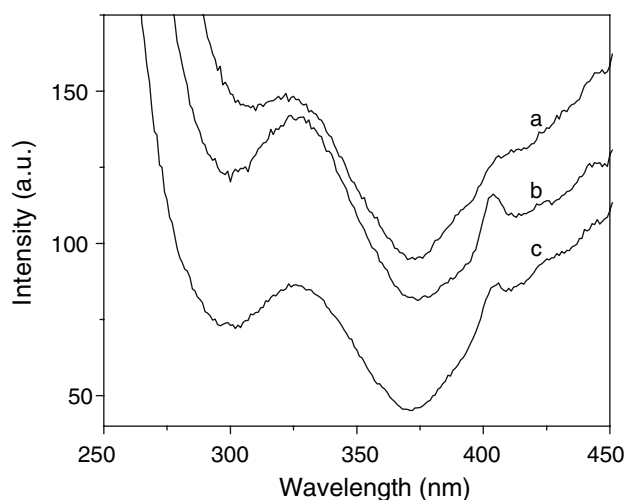


Fig. 5 Excitation spectra of the silica xerogel containing Sm^{3+} ions (0.5 mol%) and SnO_2 nanocrystals (10 wt%). Curve a, monitored at 567 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$); curve b, monitored at 606 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$); curve c, monitored at 654 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$)

Conclusion

The SnO_2 nanocrystals can sensitize the emission of the Sm^{3+} ions in the silica matrix. Meanwhile, there exists possible energy transfer between the SnO_2 nanocrystals and the Sm^{3+} ions near the nanocrystals. The surface states of the SnO_2 nanocrystals play an important role in this process.

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