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

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Abstract Silica xerogels containing Sm^{3+} ions and SnO_2 nanocrystals were prepared in a sol–gel process. The image of transmission electron microscopy (TEM) shows that the SnO_2 nanocrystals are dispersed in the silica matrix. The X-ray diffraction (XRD) of the sample confirms the tetragonal phase of SnO_2 . The xerogels containing SnO_2 nanocrystals and Sm^{3+} ions display the characteristic emission of Sm^{3+} ions (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$ (J = 5/2, 7/2, 9/2)) at the excitation of 335 nm which energy corresponds to the energy gap of the SnO_2 nanocrystals, while no emission of Sm^{3+} ions. The enhancement of the Sm^{3+} emission is probably due to the energy transfer from SnO_2 nanocrystals to Sm^{3+} ions.

Keywords Sm^{3+} ions \cdot Emission \cdot Sensibilization \cdot SnO₂ nanocrystals \cdot Silica matrix

Introduction

 Sm^{3+} 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 Sm^{3+} ions has a potential application for high-density

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

Our previous study [5] showed that there existed the interaction between Eu^{3+} 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 Sm^{3+} ions and SnO_2 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 SnO_2 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 Sm^{3+} ions (0.5 mol%) and SnO_2 nanocrystals (10 wt%)



Fig. 2 XRD pattern of the silica xerogel containing Sm^{3+} ions (0.5 mol%) and SnO_2 nanocrystals (10 wt%)

from Powder Diffraction File No. 41-1445. The result indicates that the SnO_2 nanocrystals stabilized by the silica matrix have a rutile-type structure. In combination with the TEM image, it can be deduced that the SnO_2 nanocrystals are indeed introduced in the silica xerogel.

From the UV–Vis spectrum of the silica xerogel containing Sm^{3+} ions and SnO_2 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 SnO_2 nanocrystals [10]. Furthermore, the shoulder red-shifts with increasing



Fig. 3 UV-Vis spectrum of the silica xerogel containing Sm^{3+} ions (0.5 mol%) and SnO_2 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 SnO₂ nanocrystals. The peaks before 500 nm should be ascribed to the emission of silica gels. No characteristic emission of Sm³⁺ ions can be observed for the silica xerogel containing Sm³⁺ ions (curve a), while the sample containing SnO₂ nanocrystals and Sm³⁺ ions shows strong characteristic emission of Sm³⁺ ions (curve b). The emission peaks are assigned to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$ (J = 5/2, 7/2, 9/2) transitions of Sm³⁺ ions [11]. These results indicate that the SnO₂ nanocrystals can sensitize the emission of Sm^{3+} ions in the silica matrix. Meanwhile, it is possible that there exists effective energy transfer between SnO₂ nanocrystals and Sm³⁺ ions in the silica matrix. The SnO₂ nanocrystals may act as light-harvesting antennas to sensitize emission of Sm³⁺ 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 Sm³⁺ ions is shown in Scheme 1. When the sample is excited, the energy is harvested by the SnO₂ nanocrystals and transmitted from the defect levels of the SnO₂ nanocrystals to the Sm³⁺ ions. The excited Sm3+ ions emit the characteristic fluorescence via radiative relaxation. The surface states of the SnO₂ 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 SnO₂ nanoparticles doped with rare earth ions. Furthermore, the Sm³⁺ ions cannot be doped into the lattice of SnO2 nanoparticles in our experiments because the size of Sm³⁺ ions (0.096 nm) is much bigger than that of Sn^{4+} ions (0.076 nm). Meanwhile, the energy transfer between SnO₂ nanoparticles and Sm³⁺ ions absorbed on the SnO₂ nanoparticles are not observed. Therefore, it is reasonable to deduce that the energy transfer takes place between the SnO₂ nanocrystals and the Sm³⁺ ions near the nanocrystals.

The excitation spectra of the silica xerogel containing Sm³⁺ ions and SnO₂ 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 Sm³⁺ ions, and the broad peak corresponds to the electron transition in the SnO₂ nanocrystals [15]. This result further confirms that the energy can transfer from the SnO₂ nanocrystals to the Sm³⁺ ions when the sample is excited.



Fig. 5 Excitation spectra of the silica xerogel containing Sm³⁺ ions (0.5 mol%) and SnO₂ nanocrystals (10 wt%). Curve a, monitored at 567 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$); curve b, monitored at 606 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$); curve c, monitored at 654 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$)

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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