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Photoluminescence enhancement of ZrO_2/Rhodamine B nanocomposites

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For the first time, a ZrO_2/Rhodamine B (RhB) fluorescent nanocomposite material was synthesized by a simple heat refluxing method. The properties of the samples were characterized by transmission electronic microscopy, Fourier transformation infrared spectroscopy, UV-Vis spectroscopy and photoluminescence spectroscopy. The results showed that chemical bonds had formed between the surface atoms of ZrO_2 nanoparticles and RhB molecules. The PL intensity of ZrO_2/RhB nanocomposites was much higher than that of both RhB powders and ZrO_2 nanoparticles. In addition, the effect of the dye concentrations on the photoluminescence of the nanocomposites was also investigated.

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1. Introduction

ZrO_2 is a wide band-gap (5.0–5.5 ev) transition metal oxide with good mechanical, thermal, optical and electric properties [1], which can be widely used in the fields of ceramic technology, gas sensors, catalysts and optoelectrics [2–5], etc. In addition, ZrO_2 is an ideal catalyst or catalyst support, since it has redox properties as well as acidic and basic character [6]. So both the preparation and properties of ZrO_2 have been widely investigated. There are also many reports on ZrO_2 composites for their high wear resistance [7], high biological reactivity [8], high strength [9], high photocatalytic activity [10] and other interesting properties [11, 12] etc. To our knowledge, there have been no reports on ZrO_2/RhB nanocomposites till now. In this paper, we reported the results of the preparation and characterization of ZrO_2/RhB fluorescent nanocomposites by a simple heat refluxing method. It is expected that, the nanocomposites have promising applications in novel optoelectronic devices, solid-state lasers and sensors etc.

2. Experimental

2.1. Preparation of ZrO_2/RhB nanocomposites

The starting materials in our experiments are ZrO_2 nanoparticles (purchased from Mingri Nanometer Materials Co. Ltd., China) with average particle size of 40 nm (as shown in Fig. 1), RhB (purchased from ACROS ORGANIC, USA, 99+%) and deionized water.

Three aliquots of 1 g ZrO_2 nanoparticles was firstly added into three beaks, and then mixed with 20 ml RhB aqueous solution of 10^{-5}, 10^{-4} and 10^{-3} mol/l, respectively. All were stirred for 30 min, and then treated by the heat refluxing method at 80°C for 24 h. Thus obtained aqueous ZrO_2/RhB nanocomposite was filtrated for several times by deionized water to remove the excessive RhB molecules. At last, the nanocomposites were dried in an oven for 6 h at 50°C. The obtained samples were denoted as ZR1, ZR2 and ZR3, respectively.

2.2. Characterization

The photoluminescence spectra of the samples were obtained with a FLS 920 fluorescent spectrometer. The absorption spectra were recorded by UV-3500 spectroscopy. The morphology of the samples was observed on H-800 with the accelerating voltage of 150 kv. The FTIR spectra were collected on a NEXUS-670 spectrometer with the spectral resolution of 4.00 cm^{-1}. The samples were mixed with KBr with weight ratio of sample to KBr of 1:100 and pressed into pellet for characterization. All measurements were carried out at room temperature.

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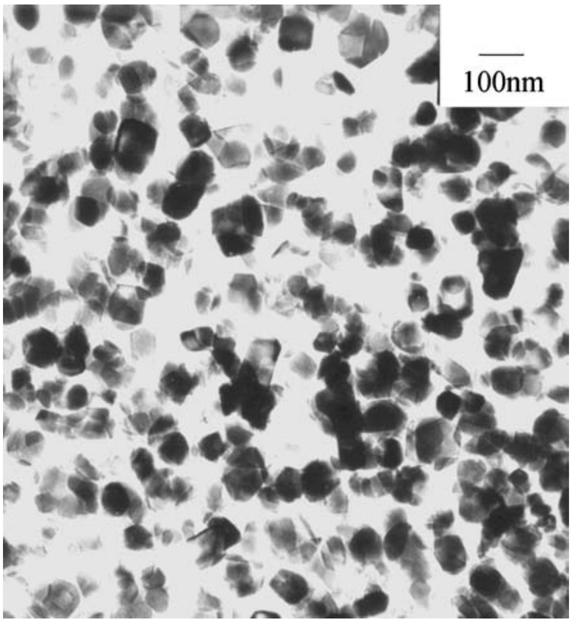

Figure 1 The TEM photo of ZrO_2 nanoparticles.

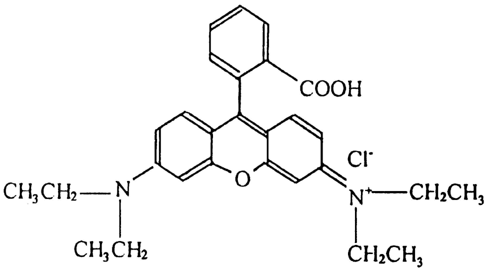

Figure 2 Schematic structure of RhB molecule.

3. Results and discussion

Fig. 2 shows the schematic structure of RhB molecule. It is believed that, the functional groups that can form strong chemical bonds with the surface atoms of ZrO_2 nanoparticles should be groups containing N or O, which can be examined by FTIR spectroscopy. Fig. 3 presents the FTIR spectra of nanocomposites, ZrO_2 nanoparticles and RhB powder. From this figure, it is known that, the major absorption peaks of ZrO_2 (as shown in Fig. 3a) locate at 1631, 1450, 1405 and 1384 cm^{-1}. Whereas, the peaks at 1589, 1412, 1345, 1274, 1249 and 1180 cm^{-1} on spectrum (e) are attributed to the stretch vibration mode of C=C in benzene rings, bending vibration of CH_2 in $–N^+$ $(C_2H_5)_2$, vibration of C–N linked benzene ring, vibration of C–O of COOH, vibration of C–N in –N $(C_2H_5)_2$ group and asymmetry stretch vibration of C–O–C, respectively [13].

It also can be seen from Fig. 3 that, the characteristic peaks of RhB are gradually distinct with the increasing of the concentration of RhB solution, this fact implies that more RhB molecules are adsorbed on the surface of ZrO_2 nanoparticles. Compared with the curve (e), no apparent changes are found in the peaks at 1589 and 1180 cm^{-1}, whereas the peaks which link N atom (such as 1345 and 1249 cm $^{-1}$) and the vibration of C–O (1274 cm^{-1}) of –COOH obviously broaden, this fact indicates that the bonds have formed between RhB molecules and the surface atoms of ZrO_2 nanoparticles. The bonding of the surface atoms with N atom gives rise to the decrease of the charge concentration of N and makes the peaks link N broaden. At the same time, the peaks at 1706 and 1693 cm^{-1} attributed to the vibration of C=O [13] in COOH disappear in nanocomposites, indicating the C=O also forms bonds with the surface atoms, and thus caused the broaden of the peak of C–O. The IR spectra indicate that a complicated structure has formed in the ZrO_2/RhB nanocomposites.

In Fig. 4, we present the photoluminescence (PL) spectra of nanocomposites, which provides the evidence that chemical bonds have formed between the surface atoms of ZrO_2 nanoparticles and RhB molecules. It is clear that, the PL intensity of the sample ZR3 is much higher than that of ZrO_2 nanoparticles and RhB powder. The peak of the PL intensity of ZR3 is 60 times as strong as that of RhB powder. Besides, the peak wavelength (594 nm) of ZR3 shows a blue shift of 94 nm compared to that (688 nm) of

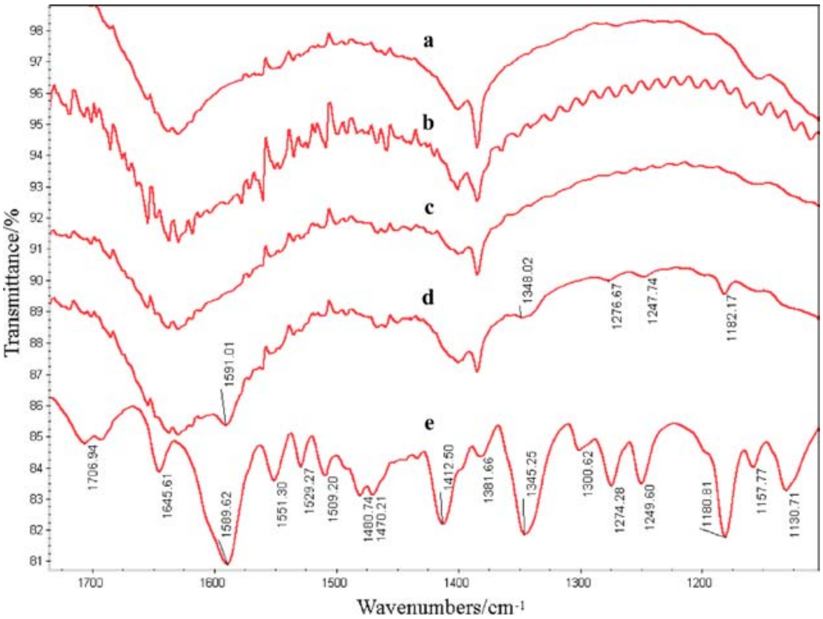

Figure 3 The IR spectra of ZrO_2 nanoparticles (a), nanocomposite ZR1 (b), ZR2 (c), ZR3 (d) and RhB powder (e).

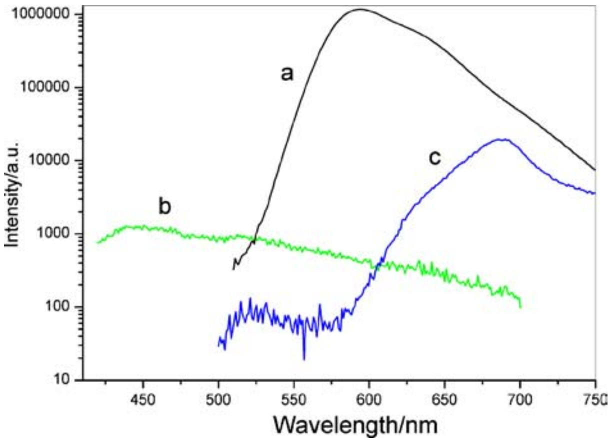

Figure 4 The PL spectra of (a) ZR3, (b) ZrO_2 nanoparticles and (c) RhB powder.

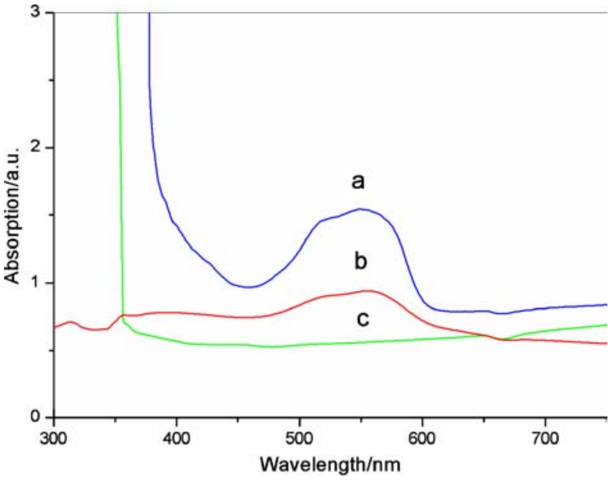

Figure 5 The absorption spectra of (a) nanocomposites, (b) RhB powder and (c) ZrO_2 nanoparticles.

RhB powder, and it is also different from that of ZrO_2 nanoparticles. In addition, from the absorption spectra of the samples (shown in Fig. 5), it can be seen that, no characteristic absorption peaks of ZrO_2 nanoparticles are found in the range of 350–800 nm. However, when RhB molecules are adsorbed on the surface of ZrO_2 nanoparticles, a new absorption peak appears in the range of 450–650 nm, and its position is almost the same as that of RhB powder. This fact reveals that the PL of the nanocomposite mainly originates from the RhB molecules. In addition, from the above results of IR spectra, it is known that, no new absorption bands are observed in nanocomposites, which implies that formation of new luminescent compounds on the surface of the ZrO_2 nanoparticles was excluded from consideration. This fact further reveals that the PL of nanocomposites does not originate from ZrO_2 nanoparticles but from RhB molecules adsorbed on the surface of ZrO_2 nanoparticles.

On the other hand, it is well known that the luminescence of a dye depends strongly on its concentration in solution. The PL intensity becomes weaker when the molecules become too concentrated. This means that more the dye molecules dispersed, more the luminescence is efficient. From the above results, it is known that, the RhB molecules are adsorbed on the surface of ZrO_2 nanoparticles, so the interaction between the RhB molecules decreases and a good dispersion of dye molecules is obtained, and as a result, the peak wavelength of nanocomposites shows a blue shift and the corresponding PL intensity improved [14].

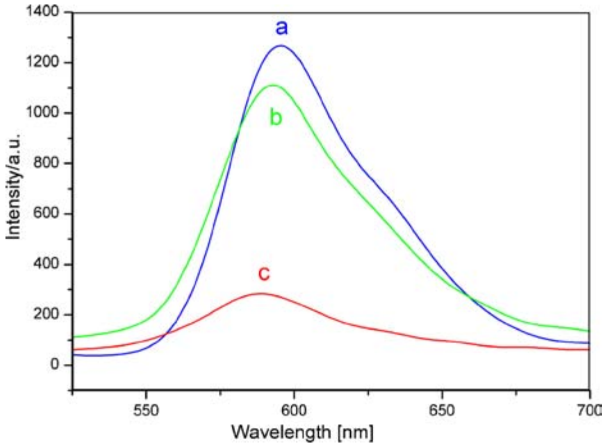

Figure 6 The PL spectra of nanocomposites ZR3 (a), ZR2 (b) and ZR1 (c).

In order to investigate the effect of the dye concentrations on the PL of nanocomposites, Fig. 6 presents the PL spectra of nanocomposites ZR3, ZR2 and ZR1. It can be seen that, the peak wavelength of nanocomposites exhibits a red shift (589–595 nm) and the PL intensity increases with the increasing of the concentrations of the dye in our experiments. This is simply related to the presence of more RhB molecules in the nanocomposites, when the samples are treated with more concentrated solutions. At low concentrations, RhB molecules can be sufficiently adsorbed on the surface of ZrO_2 nanoparticles. Whereas at high concentrations, more and more RhB molecules are adsorbed on the surface of ZrO_2 nanoparticles (this means that more and more RB molecules are contributed to the PL intensity), the interaction between them makes the peak wavelength red-shifted [14].

4. Conclusions

The ZrO_2/RhB nanocomposites can be synthesized by the heat refluxing method. The FTIR spectra proved that chemical bonds had formed between the surface atoms of ZrO_2 nanoparticles and RhB molecules, and thus, the dispersion of RhB molecules was improved and the interaction between RhB molecules was reduced accordingly. As a result, the PL intensity of nanocomposites enhanced. The PL of the nanocomposites was also affected by the dye concentrations. The results suggest a new simple approach for preparation of novel luminescent materials, and the nanocomposites may find many applications in the fabrication of optoelectronic devices, solid-state lasers and flat panel displays, etc.

Acknowledgements

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