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Effect of Eu doping concentration on the morphologies and optical properties of ZnO film prepared by ultrasonic spray pyrolysis

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Abstract In this paper, we report a new and simple method to prepare different concentrations in molarities Eu-doped ZnO films on the ITO glass substrates by ultrasonic spray pyrolysis. The morphologies, crystal structures and optical properties were investigated by using scanning electro microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL). The SEM images show that the morphologies of Eu doping concentrations 3 and 9 at.% of ZnO films are lamellae. When the Eu doping concentration in molarities is 6 at.%, the morphology of films are graininess and dense, particle diameter is about 200–250 nm. The XRD results indicate that when the Eu doping concentration is 6 at.%, the structure of Eu-doped ZnO films have better hexagonal polycrystalline structure, and characteristic diffraction peak of Eu_2O_3 was appeared at $2\theta = 50.47°$. The PL spectra of different concentrations Eu-doped ZnO films show that for the Eu doping concentration 6 at.%, ZnO film has a stronger red emission at 613 nm with excitation wavelength at 280 nm.

1 Introduction

At present, the dye-sensitied solar cells (DSSC) have attracted wide use in various applications. It has the advantages of low cost, simple preparation procedure, and plenty materials supply, which has become the research focus of the new energy field [1]. However, the efficiency of the DSSC is much lower than that of crystalline silicon cells [2]. Therefore, how to improve the efficiency of the DSSC is an important problem. In DSSC, the photoanode semiconductor film, being the key factor in dominating cell's performance, is not only the carrier of the adsorbed dye but also the route of electron transport and the locality of recombination reaction [3].

Considerable efforts have been devoted to the development of more efficient photoanode materials including varies nanostructure of TiO_2 and ZnO. Compared with the TiO_2, ZnO has higher electronic mobility. It makes ZnO material is a very good alternative to TiO_2 [4]. To improve the efficiency of DSSC, many dyes have been synthesized, however, these only absorb visible light in the wavelength range 300–800 nm, so most of UV light is not utilized [5, 6]. If the UV light can be transferred to visible light and reabsorbed by dye in the DSSC, the efficiency of DSSC will be effectively improved [7–9]. Rare-earth (RE) ions are better luminescent centres than the transition metal elements because their 4f intrashell transitions originate at narrow and intense emission lines [10–12]. In this paper, we report a new and simple method to prepare different concentrations in molarities RE ions Eu-doped ZnO films up-conversion film materials on the ITO glass substrates by USP [13].

We report the different concentrations Eu-doped ZnO films were prepared by USP, and the morphology, structure of the Eu-doped ZnO films were characterized by SEM, XRD. The optical properties of the Eu-doped ZnO films were studied by PL.

2 Experimental

2.1 Fabrication of the Eu-doped ZnO films

The Eu-doped ZnO films were synthesized by USP under atmospheric pressure onto the ITO glass substrate.

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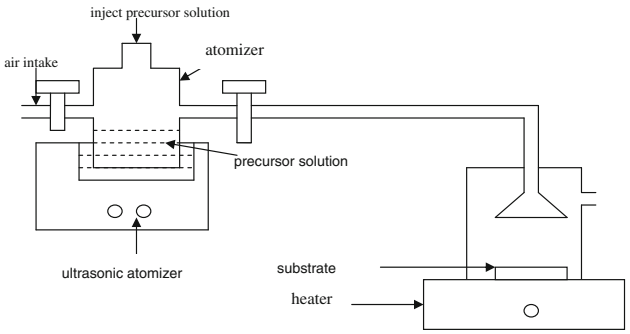

Fig. 1 The diagram of the ultrasonic spray pyrolysis method

The starting solution was 0.4 M of zinc acetate (Zn $(CH_3COO)_2{\cdot}H_2O$) prepared by dissolving the equivalent mass of zinc acetate in aqueous solution. To these solution, $EuCl_3$ was added. Eu doping concentrations were set at 0, 3, 6 and 9 % in molarities. The ITO substrates were cleaned successively with acetone, ethanol and distilled water in an ultrasonic cleaning system. The distance of source-substrate was fixed at 3 cm and the substrates temperatures was fixed at 400 °C. The deposition time was setting for 30 min. The USP experiment device is shown in Fig. 1.

2.2 Sample characterization

The surface morphology of the Eu-doped ZnO films were tested by 1530VP field emission scanning electron microscope. The crystal structure of the Eu-doped ZnO films were characterized by D8 Advance X-ray polcrystalline diffraction. And, the optical properties of the Eu-doped ZnO films were studied by RF-5301PC fluorescence spectrometer.

3 Results and discussion

Figure 2 shows the surface morphology of undoped ZnO thin films. Figure 2a, b is SEM images with different magnification. It can be seen that ZnO thin film is smooth and crackless, the crystalline grains were growing irregularly. Figure 3 shows SEM images of ZnO films with different Eu doping concentrations in molarities. From the Fig. 3 (a) 3 at.%, (b) 6 at.% and (c) 9 at.%, it can be seen that with Eu concentrations increased, the size of grain is growing gradually. When Eu doping concentration is 3 at.%, the grains grew in different sizes and its shape transformed from graininess to lamellae. When Eu doping concentration is 6 at.%, the surface morphology of film is smooth and dense, its shape is graininess in different sizes. Particle diameter is about 200–250 nm. When Eu doping concentration is 9 at.%, the surface morphology is smooth, particle size is uniform and petal shape. From Figs. 2 and 3, it can be seen that there is something in common. Figure 3a, c is petal shape, but Fig. 2 is granular. From the above observations can be found that Eu doping concentration can change surface morphology of ZnO. Because the effective radius of Eu^{3+}(96 pm) is larger than that of Zn^{2+}(74 pm), Eu^{3+} occupies part of lattice position of Zn^{2+}, ZnO normal lattice arrangement is changed, Lattice parameter increases. The impact of ZnO lattice is dependent on the Eu doping concentration.

Figure 4 shows XRD pattern ZnO film and the Eu-doped ZnO films. It can be seen that all the samples have a wider broadband diffraction in the angle of 10°–30°. It is caused by the amorphous diffraction of ITO glass. Observing the diffraction pattern can see that with Eu doping concentrations in molarities changed, the characteristic peaks of the Eu-doped ZnO films are different. For Eu doping concentration 3 at.% ZnO sample, major diffraction peaks appear at (100) and (101), however, the diffraction peak at (002) is disappeared. For Eu doping concentration 6 at.% ZnO sample, three major and other characteristic peaks arise at the angle of $2\theta = 31.5°$, 34.3°, 36.1°, 47.6°, 56.7°, 62.9°, these correspond to (100) (002) (101) (102) (110) (103) orientation of ZnO crystal. Lattice parameter of Eu-doped ZnO is $a = 0.32539$ nm, $c = 0.52107$ nm. It illustrated that the Eu-doped ZnO films are hexagonal polycrystalline structure.

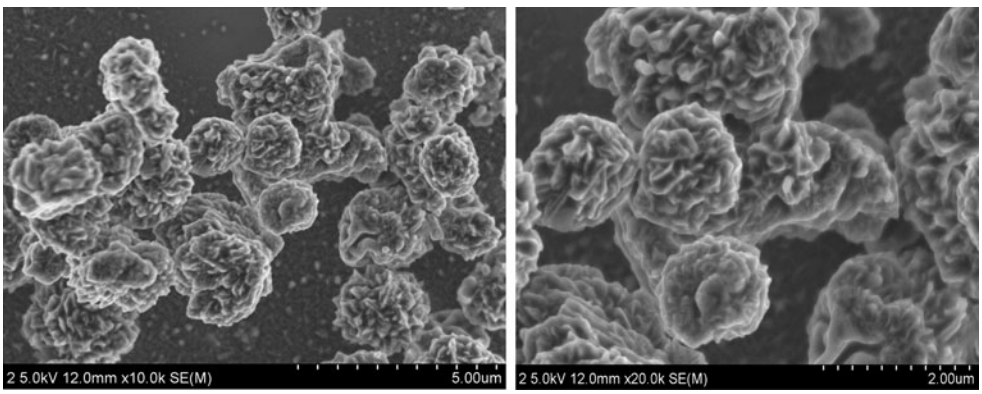

Fig. 2 SEM images of ZnO thin films

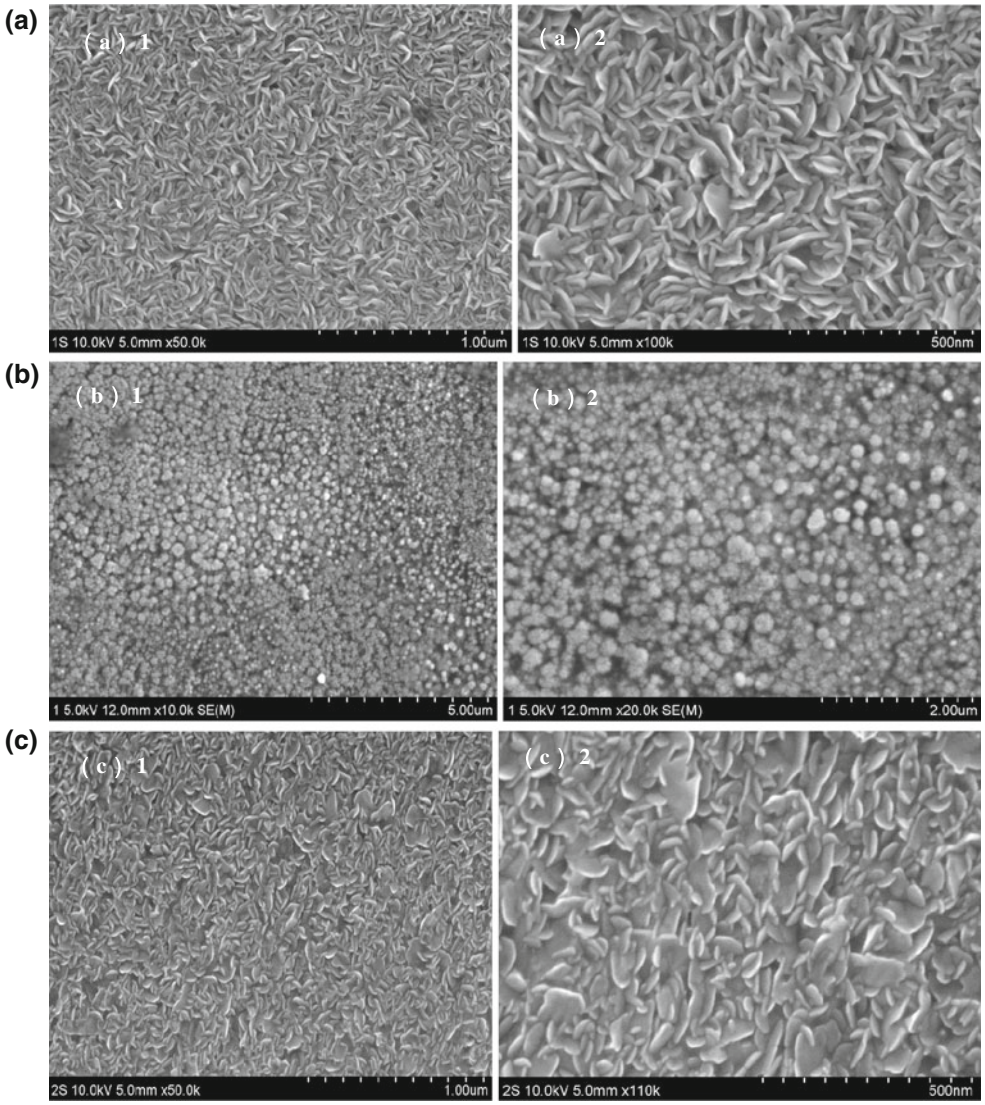

Fig. 3 SEM images of different concentrations Eu-doped ZnO thin films: Eu doping concentrations were 3 % (**a**), 6 % (**b**) and 9 % (**c**), respectively

Lattice parameter of the same method preparing ZnO is a = 0.32500 nm [14], Eu changed the ZnO lattice parameter. For Eu doping concentration 9 at.% ZnO sample, diffraction peaks appear at (100), but the diffraction peaks at (002) and (101) are disappeared. We can summarize that Eu doping concentration changes lattice orientation of ZnO. This is because Eu^{3+} changed the diameter of the precursor. Moreover, a new diffraction peak was observed in all samples at angle of $2\theta = 50.5°$ and with the Eu doping concentration increased, diffraction peak intensity is stronger. Compared with the standard card of JCPDS. This peak is the characteristic peak of Eu_2O_3. That is to say that rare earth element existed in the form of Eu^{3+} in the ZnO crystal.

In order to study the optical properties of different concentrations Eu-doped ZnO thin films, the excitation and PL measurements were performed at room temperature.

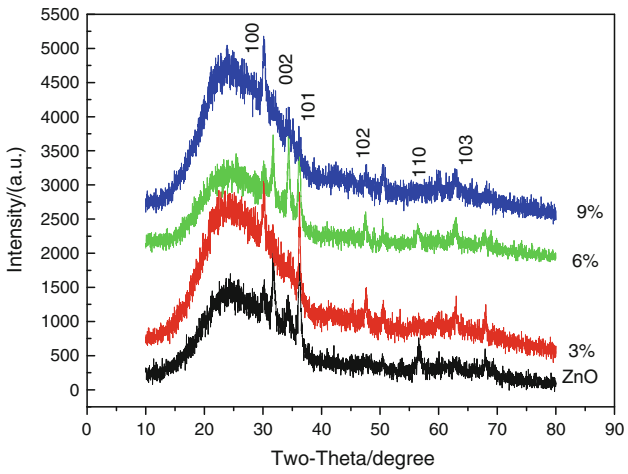

Fig. 4 XRD pattern of different concentrations Eu-doped ZnO thin films

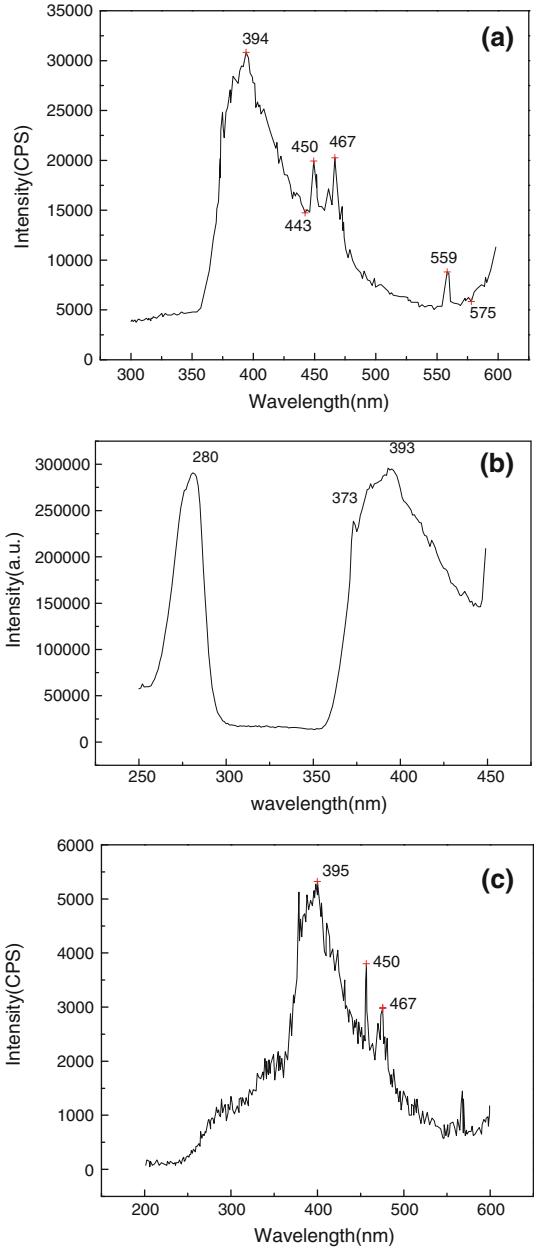

Fig. 5 Excitation spectrum of different concentrations Eu-doped ZnO thin films (λem = 613 nm): Eu doping concentrations were 3 % (**a**), 6 % (**b**) and 9 % (**c**), respectively

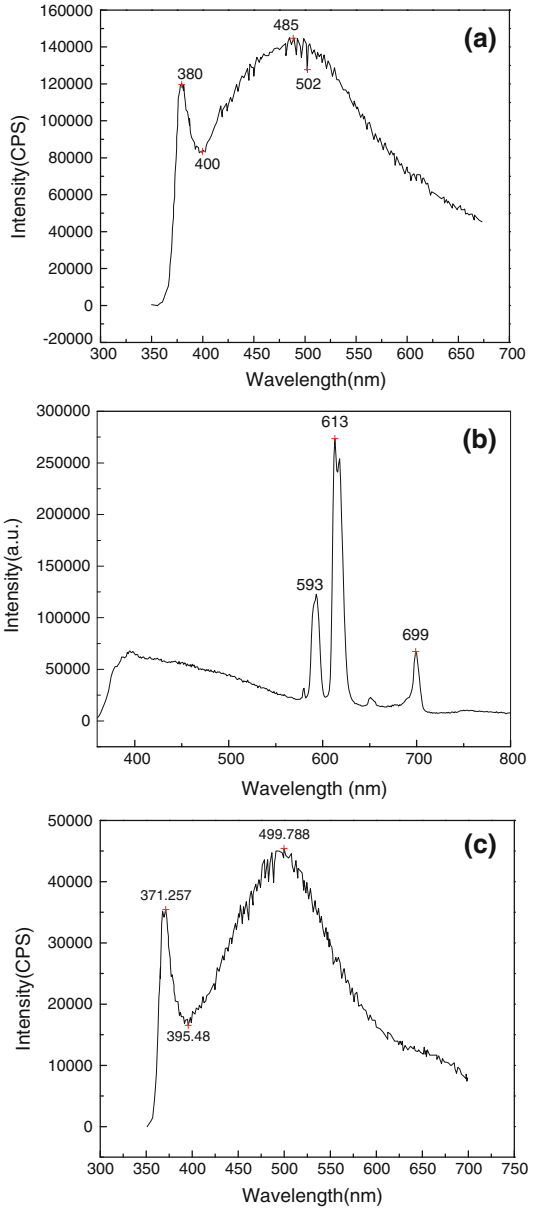

Fig. 6 Emission spectra of different concentrations Eu-doped ZnO thin films (λexc = 280 nm): Eu doping concentrations were 3 % (**a**), 6 % (**b**) and 9 % (**c**), respectively

Figure 5 shows excitation spectra of different concentrations Eu-doped ZnO thin films. The monitoring wavelength was fixed at 613 nm. From Fig. 5a, c, we can see that for the samples with Eu doping concentrations are 3 and 9 at.%, the effective excitation wavelength appeared near 395 nm. For the samples that Eu doping concentration is 6 at.%, the excitation wavelengths appear at 280 and 393 nm. These excitation wavelengths are caused by the electrons transport from the 4f of Eu^{3+} to O^{2-}.

According to excitation spectra, the emission spectra of different concentrations Eu-doped ZnO thin films were carried out in the excitation wavelengths at 280 and 325 nm, as shown in Figs. 6 and 7. The emission spectra in the excitation wavelength at 395 nm can't be observed. From the Fig. 6, we can see that for the samples that Eu doping concentrations are 3 and 9 at.%, the emission spectra is consisted of narrow ultraviolet and broad visible band. The peaks are located at about 390 and 500 nm, but characteristic emission peak of Eu^{3+} can't be observed. For Eu doping concentration 6 at.% ZnO film, there are three emission peaks. Corresponds to $^5D_0 \rightarrow {}^7F_1$ transitions (at 593 nm), $^5D_0 \rightarrow {}^7F_2$ transitions (at 613 nm) and $^5D_0 \rightarrow {}^7F_4$ transitions (at 699 nm) of Eu^{3+} [15].

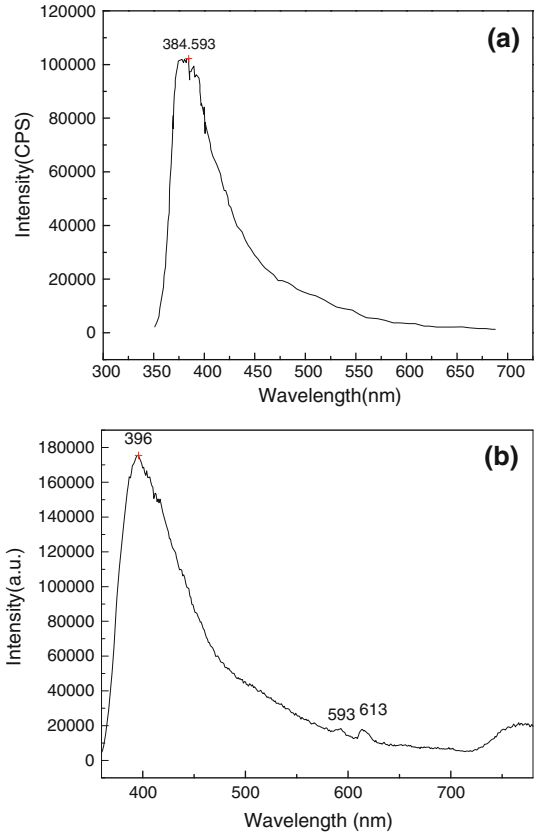

Fig. 7 Emission spectra of different concentrations Eu-doped ZnO thin films (λexc = 325 nm): Eu doping concentrations were 3 % (**a**) and 6 % (**b**)

According to the general rule of Eu^{3+} transitions in crystalline field, as Eu^{3+} is at the case of strictly inversion center, the main emission is orange light at 593 nm. It is caused by the emission of electric dipole transitions ($^5D_0 \rightarrow {}^7F_1$). When Eu^{3+} is out of strict inverted center, the emission of electric dipole transitions ($^5D_0 \rightarrow {}^7F_2$) is emerged at 613 nm. In Fig. 6b we can observe the strongest red light peak at 613 nm. It is very sharp, belongs to typical 4f electron transport of Eu^{3+} and correspond to emission of electric dipole transitions ($^5D_0 \rightarrow {}^7F_2$).

Emission spectra of different concentrations Eu-doped ZnO thin films in the excitation 325 nm, as shown in Fig. 7. From the Fig. 7 we can see that for the samples Eu doping concentrations 3 at.%, the peak wavelength is 396 nm, it caused by near-band-edge emission (NBE) of ZnO. For Eu doping concentration 6 at.%, emission spectra is the similar to the Eu doping concentration 3 at.%. The difference is that besides that 396 nm is observed, there are two weak characteristic emission peaks of Eu^{3+} observed at 593 and 613 nm. That is to say Eu^{3+} was doped in the ZnO film. For Eu doping concentration 9 at.%, there is no emission peak observed.

4 Conclusion

Zn $(CH_3COO)_2{\cdot}H_2O$ and $EuCl_3$ mixing solution, as the precursor solution, prepared the different Eu doping concentrations 0, 3, 6 and 9 at.% ZnO films on the ITO glass substrates by USP. The morphologies, crystal structures and optical properties were investigated by using SEM, XRD and PL. The SEM image shows that the morphology of Eu doping concentrations 3at. and 9at of ZnO films are lamellae. When the Eu doping concentration in molarities is 6 at.%, the morphology of films are graininess and dense, particle diameter is about 200–250 nm. The XRD results indicate that when the Eu doping concentration is 6 at.%, the structure of Eu-doped ZnO films have better hexagonal polycrystalline structure. The PL spectra of different Eu-doped ZnO films show that for the Eu doping concentration 6 at.%, ZnO film has a stronger red emission at 613 nm with excitation wavelength at 280 nm. This wavelength can be reabsorbed and recycled by dye. So it is suggestion that Eu doping concentration 6 at.% ZnO films are expected to be applied as the photoanode of DSSC to improve the efficiency of DSSC.

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