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Luminescence of nanosized ZnO/polyaniline films prepared by self-assembly

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Abstract

ZnO sol was prepared and ZnO monolayer film and nanosized ZnO/polyaniline (PAN) multylayer films were coated on polished Al foil using the layer-by-layer self-assembly method. UV–vis absorbance, reflection and photoluminescence spectroscopy were obtained to investigate the luminescent properties of the samples. The ZnO sol has a single excitation peak in the UV (ultraviolet) region and a single emission peak in the green region. The excitation spectra of ZnO monolayer film and ZnO/PAN multylayer films show a continuous wide band without evident peak, and the emission spectra consist of three parts with peaks in UV, blue and green region, respectively.

Keywords: A. Films; B. Spectroscopy; C. Optical properties; D. ZnO

1. Introduction

As a semiconductor material, ZnO has many useful properties such as excellent transmittance for visible light, very high piezoelectricity and high gas sensitivity. The well known luminescent material ZnO is useful for various applications such as vacuum fluorescent display (VFD) [1], field emission display (FED) [2] and electroluminescent display (ELD) [3]. Due to its wide band gap of 3.37 eV at room temperature, ZnO is attracting considerable attention as one of the important candidates for potential applications such as UV light-emitting diodes and laser diodes [4].

ZnO film has been prepared by dc sputtering, rf magnetron sputtering, molecular beam epitaxial growth, chemical vapor deposition, spin-coating, dip-coating, and so on. The layer-by-layer self-assembly method as a technique to prepare thin film has many advantages: it allows detailed molecular-level control over the films composition and thickness, and is independent on the substrate size and topology [5].

In this paper, ZnO/PAN nanosized films were coated on polished Al foil using the layer-by-layer self-assembly method, and the luminescent properties of the films were investigated.

2. Experimental

$Zn(OAc)_2$ ($Zn(CH_3OO)_2{\cdot}2H_2O$) was placed into a distillation apparatus filled with anhydrous ethanol and boiled at 80 °C until a transparent solution was obtained. Then $LiOH{\cdot}H_2O$ powder was added in the solution and the mixture was sonicated to dissolve the powder to obtain the ZnO sol.

Al foil was heat-treated at 500 °C for 5 h and then etched in 1.0 M NaOH for 2 min to remove the native oxide. After washing thoroughly with distilled water, the Al foil was then electropolished in a mixed solution of $HClO_4$:CH_3CH_2OH = 1:4 for 1 min and promptly rinsed with distilled water.

Al foil was immersed in the ZnO sol for 10 min, rinsed with deionized water and dried at 70 °C. Then the Al foil was immersed in the PAN solution for 10 min, washed with deionized water and dried at 70 °C. By repeating the same adsorption cycles multilayer ZnO/PAN films were grown. Finally, the film was dried in an oven at 70 °C.

The absorbance spectrum of the ZnO sol and the diffuse reflection spectra of the ZnO/PAN films were recorded on a Hitachi 3010 UV–vis spectrophotometer. The excitation and emission spectra of the samples were recorded with a Hitachi

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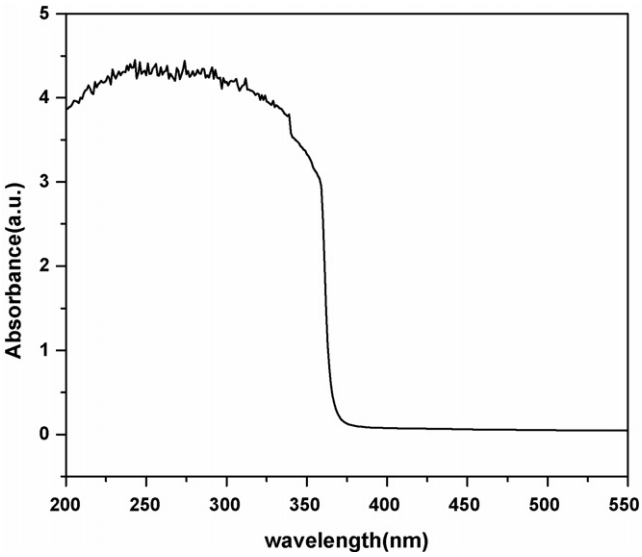

Fig. 1. Absorption spectrum of ZnO sol.

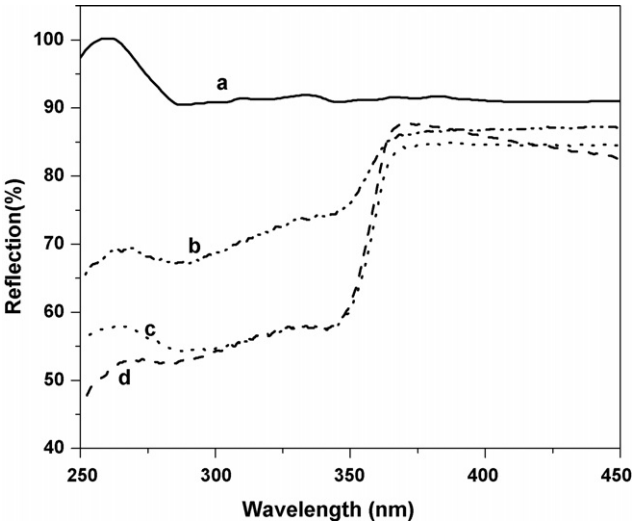

Fig. 3. Diffuse reflection spectra of Al foil and multilayer ZnO/PAN film on Al foil: (a) Al foil; (b) Al-$(ZnO/PAN)_5$ film; (c) Al-$(ZnO/PAN)_{15}$ film; and (d) Al-$(ZnO/PAN)_{20}$ film.

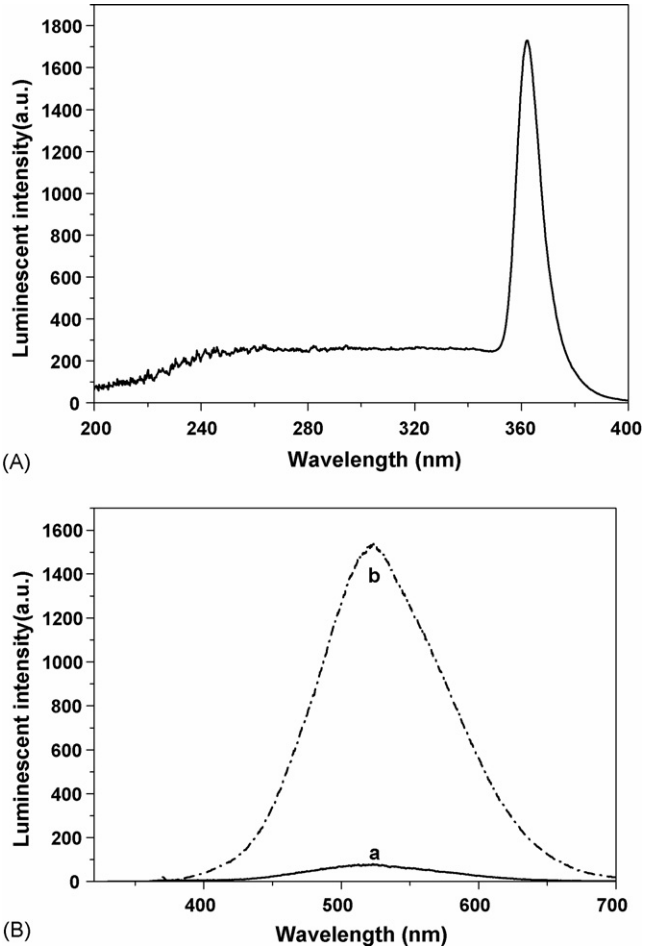

Fig. 2. Excitation and emission spectra of ZnO sol: (A) excitation spectrum by monitoring emission at 523 nm; (B) emission spectra by exciting at: 320 nm (a) and 362 nm (b).

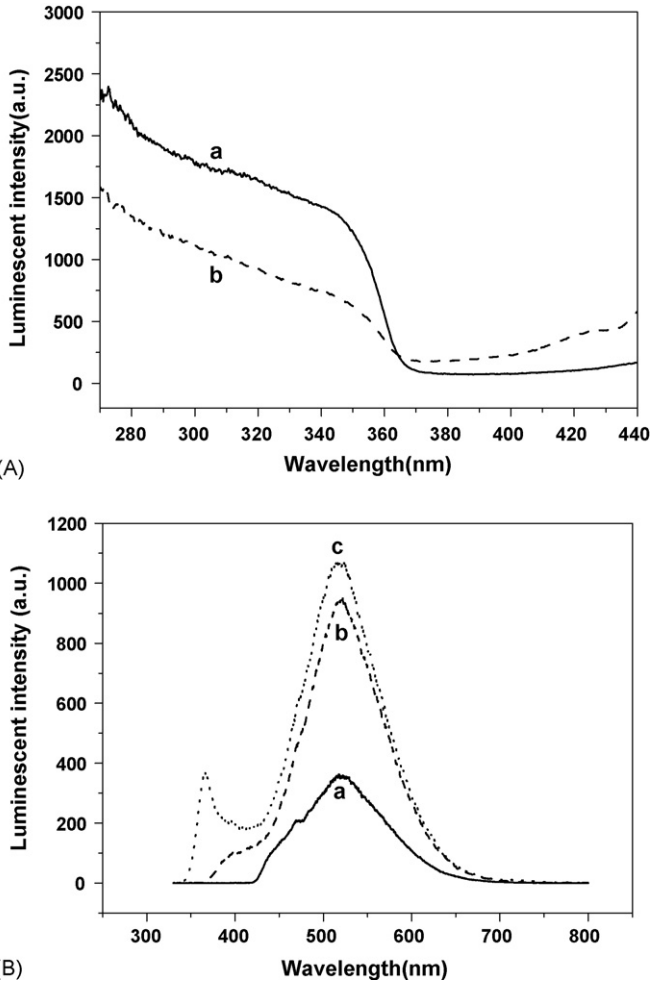

Fig. 4. Excitation and emission spectra of Al-ZnO monolayer film: (A) excitation spectra by monitoring emission at: 520 nm (a) and 469 nm (b); (B) emission spectra by exciting at: 360 nm (a); 345 nm (b); and 320 nm (c).

F-4500 spectrofluorometer. The morphology of the film was observed by S4200 scanning electronic microsope (SEM).

3. Results and discussion

Fig. 1 gives the absorption spectrum of the ZnO sol indicating that the onset of the absorption edge is about 367 nm corresponding to the band gap of about 3.38 eV. If the ZnO sol is excited with UV light, the emission is a wide band spectrum with a peak at about 523 nm as shown in Fig. 2. The excitation spectrum by monitoring the green emission consists of a sharp band with a peak at about 362 nm. ZnO is a semiconductor, and the excitation peak at about 362 nm corresponds to the energy for electron to jump from the valence band to the conduction band. It has been suggested in the literature that the origin of the green luminescence of ZnO at about 523 nm in Fig. 2 is associated with defect-related states, located within the band gap of ZnO. Some authors attribute it to $Zn_i^+ \rightarrow V_{Zn}^-$ transition [6,7], some to CB $\rightarrow V_O^{\bullet\bullet}$ [8,9] transition, and others to CB $\rightarrow O_{Zn}$ [10,11] transition. But none of the opinions has been verified directly yet.

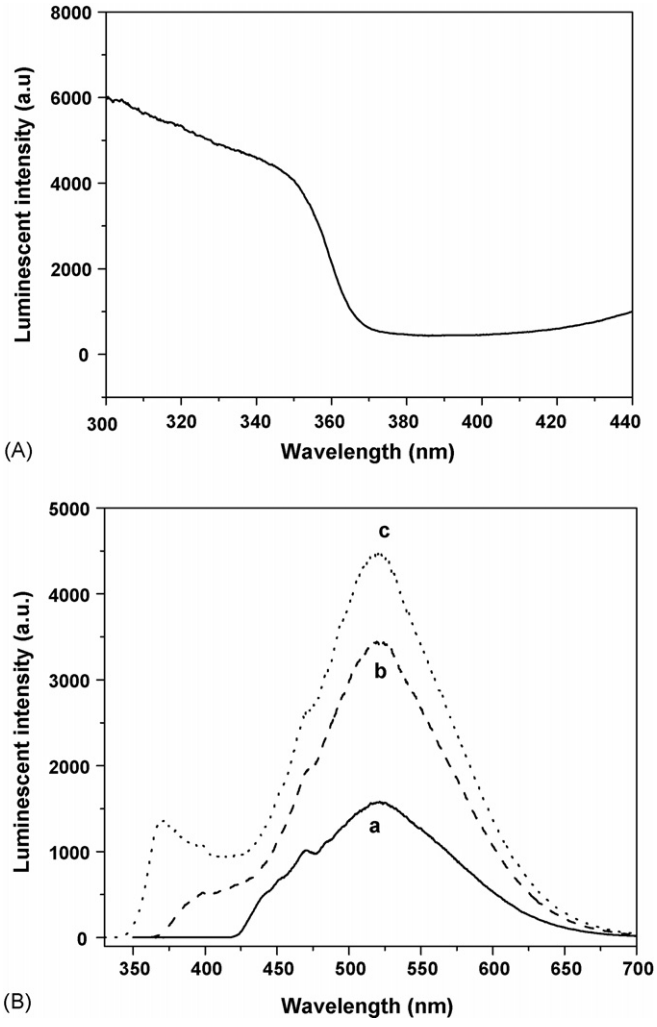

Fig. 5. Excitation and emission spectra of Al-(ZnO/PAN)$_{20}$ film: (A) excitation spectrum by monitoring emission at 520 nm; (B) emission spectra by exciting at: 360 nm (a); 345 nm (b); and 320 nm (c).

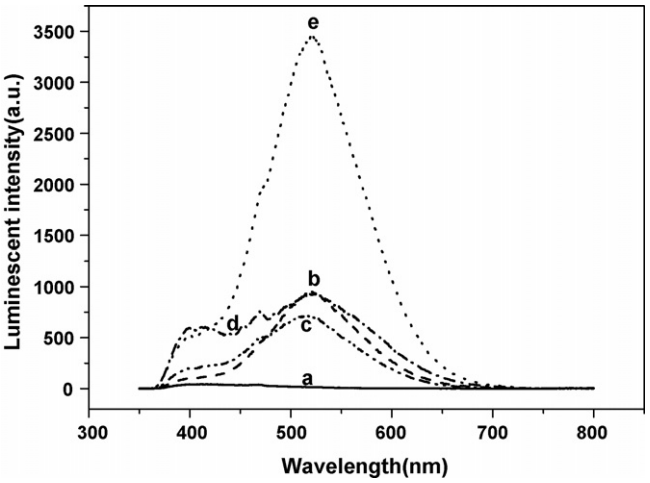

Fig. 6. Emission spectra of various films excited by 345 nm UV light: (a) Al foil; (b) Al-ZnO monolayer film; (c) Al-(ZnO/PAN)$_5$ film; (d) Al-(ZnO/PAN)$_{15}$ film; and (e) Al-(ZnO/PAN)$_{20}$ film.

The diffuse reflectivity of polished Al foil approximates to 100% and does not show any luminescence. If ZnO or ZnO/PAN film was coated on the Al foil, the diffuse reflectivity drops and the onset of the absorption is approximately equal to that of the ZnO sol as shown in Fig. 3. The excitation spectrum of ZnO monolayer or ZnO/PAN multilayer films is continuous without evident bands or lines, which differs greatly from the excitation spectrum of ZnO sol. If ZnO or ZnO/PAN film was excited with UV light such as 320 or 345 nm, the emission spectra consist of three parts: one wide band in the visible region with peak at about 520 nm, one wide band in the UV region with a peak at about 398 nm, and one weak peak at about 470 nm. When the films are excited with longer UV light such as 360 nm, the UV emission disappears while that at 470 nm intensifies as shown in Figs. 4 and 5. Unlike the results by Kovtyukhova et al. [12], the excitation and emission spectra of monolayer ZnO film and ZnO/PAN multilayer film show no difference. In comparison with the 523 nm green emission of ZnO sol, the green emission of monolayer ZnO film and ZnO/PAN multilayer film shows blue shift. The UV emission at about 398 nm may be attributed

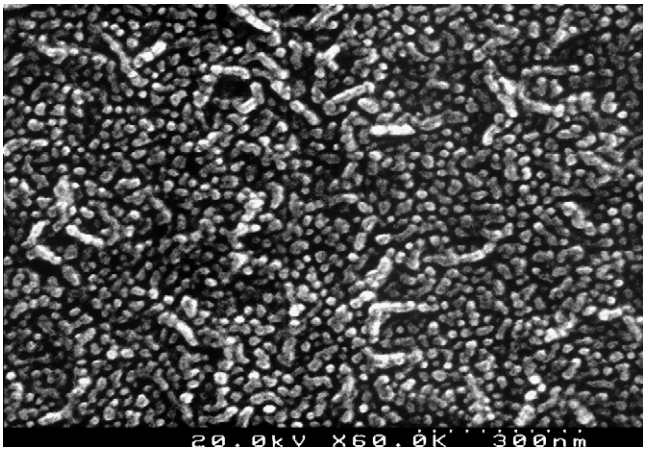

Fig. 7. SEM micrograph of the Al-(ZnO/PAN)$_{20}$ film.

to exciton emission [13], but the emission at about 469 nm has not been reported yet.

If the thickness of the ZnO/PAN film increases by increasing the layer number of the film, it can be seen that the luminescent intensity will increase, but the shape of the spectra and the peak position show no change as indicated in Fig. 6. SEM micrograph of the Al-$(ZnO/PAN)_{20}$ film is shown in Fig. 7, and it can be seen that the film is composed of granular particles of about 30 nm size.

4. Conclusion

ZnO monolayer film and ZnO/PAN multylayer nanosized films coated on Al foil show similar luminescent peoperties. The excitation appears as a continuous wide band without evident peak, and the emission spectra consist of three parts with peaks in UV, blue and green region, respectively, which differs greatly from the excitation and emission spectra of ZnO sol.

Acknowledgement

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