



Tuning visible emission by choosing excitation wavelength in Mg-doped ZnO/silica composites

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ABSTRACT

Magnesium-doped ZnO/silica composites with tunable photoluminescence (PL) in a wide range were successfully synthesized by a facile solution decomposition method. Moreover, under suitable excitation, the Commission Internationale de l'Eclairage chromaticity coordinates were (0.31, 0.36), indicative of a white emission. Mg-doping plays an important role in the defect control, consequently intensifying sharply the PL emission of the composites. By the Gaussian fitting of the PL excitation spectrum, a possible mechanism was proposed for the wavelength tunability of the Mg-doped ZnO/silica composites.

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1. Introduction

Wavelength tunability is a key aspect for light-emitting materials [1], and is one of the critical properties driving research on semiconductor quantum dots [2,3]. As a direct band semiconductor with wide band-gap (~3.3 eV at room temperature), wurtzite zinc oxide has attracted much attention as a luminescent material for both fundamental research and applications [4,5]. Two emission bands are usually found in ZnO, an UV excitonic emission band and a defect related visible emission band [6,7]. Moreover, visible photoluminescence (PL) from ZnO could be tuned in a wide range from blue to green and orange through chemical doping, particle sizes control or surface control [8,9].

In recent years, ZnO/silica composites have attracted much attention for their unique PL properties [10,11], and the authors have reported a strong blue-violet emission in the ZnO/silica composites prepared by sol-gel technique [12]. It is known that synthesis methods have important effect on the properties of the composites. Here, Mg-doped ZnO/silica composites with tunable PL were fabricated by a solution decomposition method. The visible

emission of the composite can be tuned by changing the excitation wavelength, and white light emission can be obtained under suitable excitation wavelength.

2. Experimental

Mg-doped ZnO/silica composites were prepared by solution decomposition synthesis using zinc nitrate, magnesium nitrate, tetraethoxysilane (TEOS) and dilute nitric acid. For zinc solution, zinc nitrate and magnesium nitrate were dissolved in water, and small amount of dilute nitric acid was dropped into the solution to adjust pH value to 4, which ensures the solution clear. TEOS was mixed with ethanol in equal volume to obtain TEOS solution, which was added to the zinc solution, and after stirring for 1 h, a homogeneous composite solution was obtained. The composite solution was heated at 600 °C in air for 15 min to obtain the Zn_{1-x}Mg_xO:SiO₂ composite. The mole ratio of SiO₂ to Zn_{1-x}Mg_xO in the composite was varied from 0 to 0.45, and MgO content *x* varies from 0 to 0.25.

Room temperature PL spectra were recorded on a JASCO FP-6500 spectrofluorometer. X-ray diffraction (XRD) was carried out on a Philips X'pert-pro X-ray diffractionmeter with Cu K_α radiation. The morphologies of products were observed by an FEI Quanta200 scanning electron microscopy (SEM).

3. Results and discussion

All composites present broad PL excitation from 250 nm to 450 nm. Fig. 1(a) shows the PL excitation spectra of the composites Zn_{1-x}Mg_xO:0.2SiO₂ with different Mg content. It can be seen that Mg-doping at appropriate amount greatly enhances the PL excitation intensity. According to Fig. 1(b), the introduction of silica inhibits the PL excitation between 360 nm and 420 nm, but inten-

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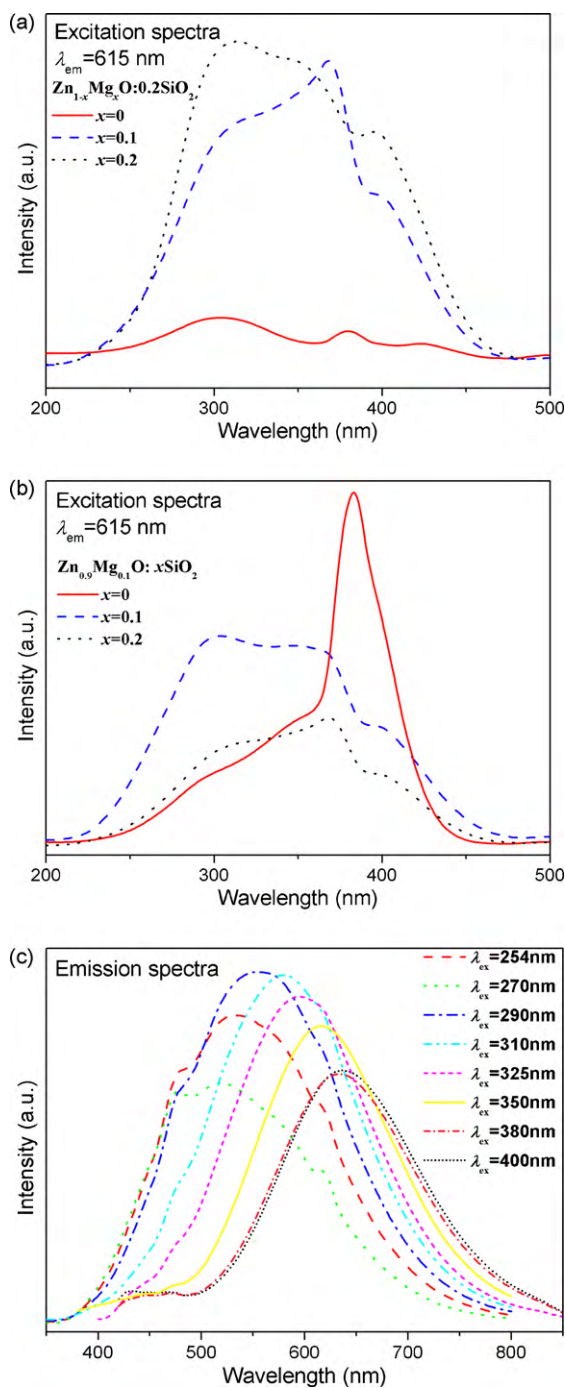


Fig. 1. (a) PL excitation spectra of $Zn_{1-x}Mg_xO:0.2SiO_2$ with different Mg content, (b) PL excitation spectra of $Zn_{0.9}Mg_{0.1}O:xSiO_2$ with different Si content, and (c) PL emission spectra of $Zn_{0.8}Mg_{0.2}O:0.2SiO_2$ at different excitation wavelengths.

sifies the excitation below 360 nm. Fig. 1(c) shows that the emission covers nearly the whole visible spectral region. It is seen that the emission wavelength can be tuned in a large range (from 635 nm to 475 nm) only by changing the excitation wavelength. The calculated CIE coordinates for the emission spectrum with an excitation wavelength at 270 nm (0.31, 0.38), which is near the white region (the 1931 CIE diagram) [13]. Moreover, the calculated CIE coordinates for the emission spectrum of $Zn_{0.9}Mg_{0.1}O:0.1SiO_2$ excited at 254 nm are (0.31, 0.36), which just fall within the white region, very close to the standard white light.

It is well known that ZnO usually exhibits a UV emission, and a visible deep-level one. In the visible spectral region, a number

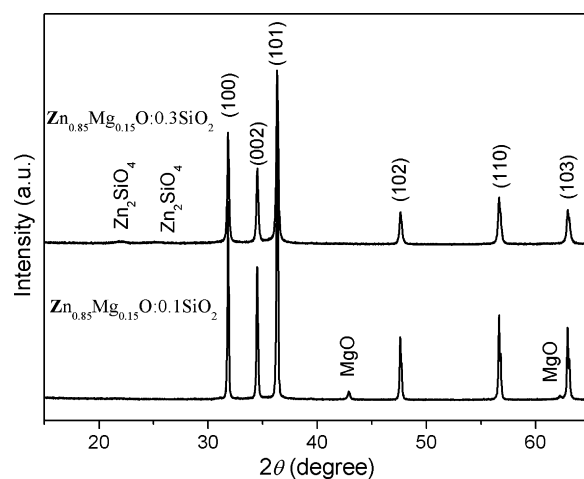


Fig. 2. XRD patterns of $Zn_{0.85}Mg_{0.15}O:xSiO_2$ composites.

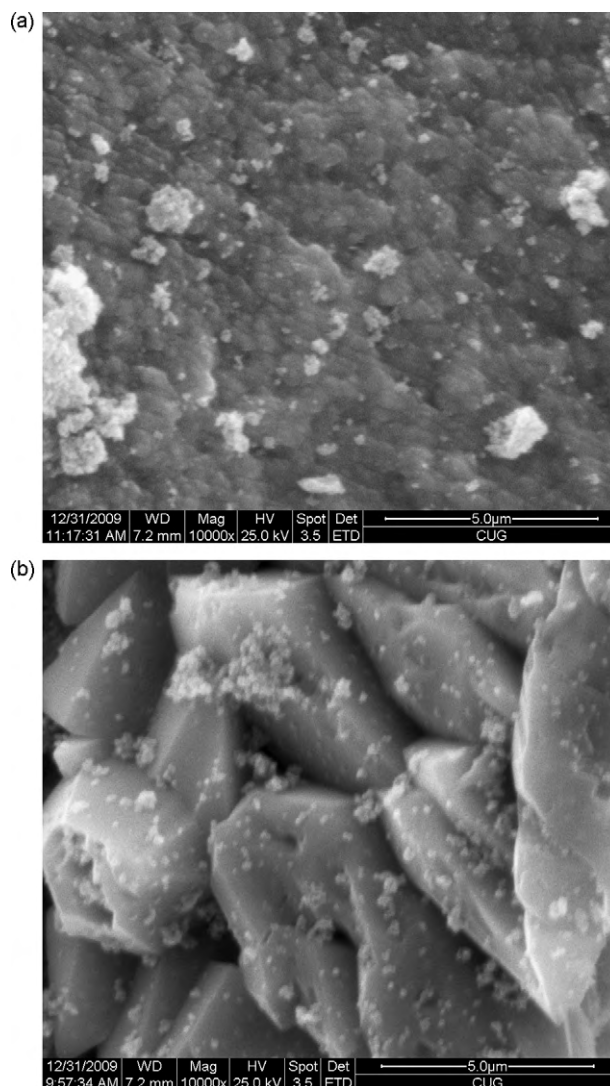


Fig. 3. SEM of (a) $ZnO:0.3SiO_2$ and (b) $Zn_{0.85}Mg_{0.15}O:0.3SiO_2$.

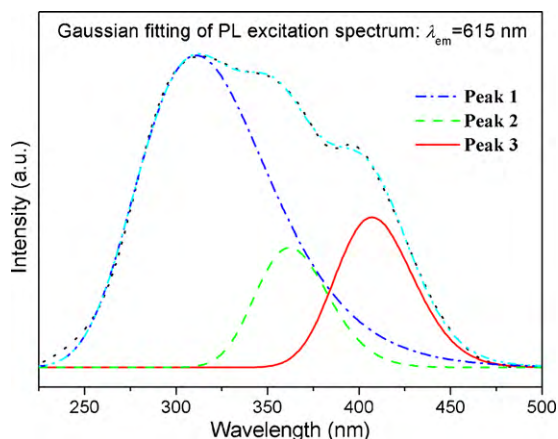


Fig. 4. Gaussian fitting of PL excitation spectrum of $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}:0.2\text{SiO}_2$.

of different PL peaks from ZnO have been reported. The UV band has an excitonic nature, and visible emissions are attributed to the defect emission, although the origin of them still represents a matter of debate. No significant ZnO excitonic emission is observed along with the strong visible emission, indicating that most of the excited carriers recombine at deeply trapped defects in ZnO [14]. Green emission is often attributed to singly ionized oxygen vacancies [15,16], and also to oxygen vacancies and zinc interstitials [17]. Yellow emission is typically attributed to oxygen interstitials [18]. Orange-red emissions are often observed in oxygen-rich samples [14], and attributed to oxygen interstitials [17]. In this method, nitrate is need for efficient PL, but the introduction of urea leads to lower PL intensity. Therefore, there are several optically active defect centres in the composites prepared by solution decomposition method.

The XRD patterns of $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}:0.1\text{SiO}_2$ and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}:0.3\text{SiO}_2$ are presented in Fig. 2. It is seen that wurtzite-type ZnO (JCPDS No. 80-0075) is the major phase of both composites. MgO phase (JCPDS No. 45-0946) has been identified in the composite with less silica, but weak and broad diffraction peaks of Zn_2SiO_4 phase (JCPDS No. 14-0653) presents in the composite with more silica. Considering that the ionic radii of Zn^{2+} and Mg^{2+} ions are very close, both ZnO and MgO phases are solid solutions. With the increase of silica content, the peaks of the MgO crystalline disappear, but those of Zn_2SiO_4 crystalline are observed. The introduction of silica decreases the content of ZnO by forming Zn_2SiO_4 phase, and modifies the surface and defects of ZnO particles, consequently lower the PL emission intensity. Therefore, the silica inhibits the PL excitation, especially the excitation between 360 nm and 420 nm.

Fig. 3 shows the scanning electron microscopy (SEM) of $\text{ZnO}:0.3\text{SiO}_2$ and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}:0.3\text{SiO}_2$ composites. It is seen that the former is denser, but the latter presents more interfaces. The energy-dispersive X-ray (EDX) analysis shows the presence of Zn, O, indicating that the crystalline in Fig. 3 is ZnO. ZnO crystallines show much clearer interfaces in the $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}:0.3\text{SiO}_2$ sample than in the $\text{ZnO}:0.3\text{SiO}_2$ sample, indicating that Mg-doping inhibits the reaction between ZnO and silica, which may be the reason why

Mg-doping at appropriate amount greatly enhances the PL intensity.

Fig. 4 shows the Gaussian fitting of the PL excitation spectrum of $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}:0.2\text{SiO}_2$. The broad excitation band can be well fitted by 3 Gaussian peaks: Peak 1 centered at 310 nm, Peak 2 at 362 nm, and Peak 3 at 407 nm. Peak 2 corresponds to the excitation from valence band to conduction band of ZnO semiconductor [19], and Peak 3 most probably results from defect excitation [11]. The low energy excitation ($\lambda \geq 380$ nm) results in orange-red emission. Under the excitation of higher energy, excitons form and more electrons are excited into the conduction band, leading to stronger PL emission at yellow, green and blue bands. Therefore, the emission wavelength of the Mg-doped ZnO/silica composite can be tuned easily by changing the excitation wavelength.

4. Conclusions

We have synthesized Mg-doped ZnO/silica composites by a simple solution decomposition method, and Mg-doping greatly enhances PL emission intensity. The emission spectra cover nearly the whole visible spectral region, and the emission wavelength can be tuned in a large range (from 635 nm to 475 nm) only by changing the excitation wavelength. Moreover, white light can be obtained under appropriate excitation. Because of their tunable PL, the Mg-doped ZnO/silica composites have potential applications in luminescence devices and electronic apparatuses.

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