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Synthesis of ZnO Nanostructures for Photoluminescent Ink Applications

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ABSTRACT

In this study, we have successfully synthesized ZnO nanoparticles (ZnO NPs) using co-precipitation and hydrothermal methods. ZnO NPs were fabricated by co-precipitation for spherical shape, while the hydrothermal method was for rod-shaped morphology. The XRD analysis shows that ZnO NPs possess a hexagonal wurtzite structure for two synthesis methods. The UV-Vis spectra analysis shows that the ZnO NPs have an absorption peak at the wavelength of 355 nm. The PL spectra result reveals that ZnO NPs synthesized by co-precipitation have two peaks at about 570 nm and 650 nm, while ZnO nano-rods synthesized by the hydrothermal method have a PL peak at 650 nm. Luminescent inks based on ZnO nano-rods and nano spherical particles were printed on filter paper using a screen printing method. The logos of the *"Faculty of Graphic Arts and Media"* samples show bright yellow and pink fluorescence under UV irradiation 365 nm and are invisible under normal light.

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1. Introduction

ZnO nanoparticles (ZnO NPs) are nontoxic semiconductors with a wide bandgap (Eg ≈ 3.37 eV). Due to their large exciton binding energy (60 ≈ meV), ZnO NPs are highly stable at room temperature. They are applied in many fields, such as optoelectronics [1], [2], photocatalysis [3], packaging [4], [5], [6], and luminescent inks [7].

Many studied results [1], [2], [7] indicated that ZnO NPs exhibit a strong emission in the visible light region. Thus, they are suitable for security ink applications. Besides, polyvinyl alcohol (PVA) is a biodegradable polymer with some advantages, such as a non-toxic, high-transparency film and being accessible to dissolve in water. As a result, PVA can be applied in many fields, such as paper coating, glue, pharmaceuticals, construction, packaging films, and especially printing ink. In printing ink applications, PVA can be used as a distribution media and a viscosity modifier of the ink. These can be tailored to specific concentrations and levels of viscosity to meet many established printing methodologies.

Investigated results recently show that ZnO NPs can be used in anti-counterfeiting ink applications [2], [7], [11], for printed electronic devices [1], for antibacterial activities in conventional ink [8]-[10], and for enhancing faster-drying ultraviolet (UV) offset printing inks. Few researchers have investigated the different fluorescence emission colors of ZnO NPs applied in anti-counterfeit printing inks, especially in photoluminescent ink applications. Thus, we have focused on the structural and photoluminescent ink properties of ZnO NPs in this study.

2. Experiments

2.1. Materials

Zinc acetate (Zn(CH3COO)2.2H2O, 99%), Sodium hydroxide (NaOH 96%), and Poly(vinyl alcohol) (PVA) used as a distribution media and the viscosity modifier of ink were purchased from Aldrich. Citric acid monohydrate (C6H8O7.H2O) and ethylene glycol (C2H6O2) were purchased from Xilong.

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2.2. Synthesis of ZnO nanoparticles by co-precipitation method

$Zn(CH_3COO)_2.2H_2O$, Sodium hydroxide (NaOH 96%), and poly(vinyl alcohol) (PVA) were used for synthesis. First, 100 ml of 0.4 M $Zn(CH_3COO)_2.2H_2O$ solution was vigorously stirred for 45 min at 80◦C. Then, 100 ml of 0.2 M NaOH was dropped into the Zinc acetate solution. The white colloidal solutions were then continuously stirred for 45 min, and the product was centrifuged at 6,000 rpm and washed with deionized water.

2.3. Synthesis of ZnO nanoparticles by hydrothermal method.

ZnO nanoparticles (ZnO NPs) were synthesized using the hydrothermal method. The first solution concentration of 0.4 M, containing 8.8 g of $Zn(CH_3COO)_2.2H_2O$, was dissolved in 200 ml of deionized water for 30 min at 80 ºC. Then, a concentration of 2.8 M NaOH (5.8 g) was dissolved in 100 ml of deionized water for 30 min at 80 ºC. The second solution was dropped into the first solution and stirred for 30 min at 80 ºC to get the colloidal solution. Then, the solution was placed in the Teflon stainless steel autoclave, which was hydrothermally heated at 100 ºC for 12 h and then cooled to room temperature.

2.4. Synthesis of luminescent ZnO nano ink

In this study, ZnO nanoparticles synthesized by the co-precipitation and hydrothermal methods were used as pigments for ink formulation, and poly(vinyl alcohol) (PVA) was used as a distribution media and the viscosity modifier of the ink. First, 20 g of PVA was dissolved in 200 ml of deionized water using a magnetic stirrer. The mixture was continuously stirred overnight at 80 ºC to get a transparent solution. Second, the mixture of PVA solution, ethylene glycol (EG), and deionized water with the ratio (w/w) of 1:4:10 was stirred together at 80 ºC for 30 min. The mixture was used as the vehicle in an ink formulation. Lately, ZnO nanoparticles 15% (w/w) were dispersed in the vehicle. The ink was vigorously stirred for 1 h and homogenized using the ultrasonic method for 30 min. Citric acid was used to adjust the pH of the ink. The ZnO nanoparticle ink (pH = 7) was printed on filter papers using the screen printing technique (Fig. 1).

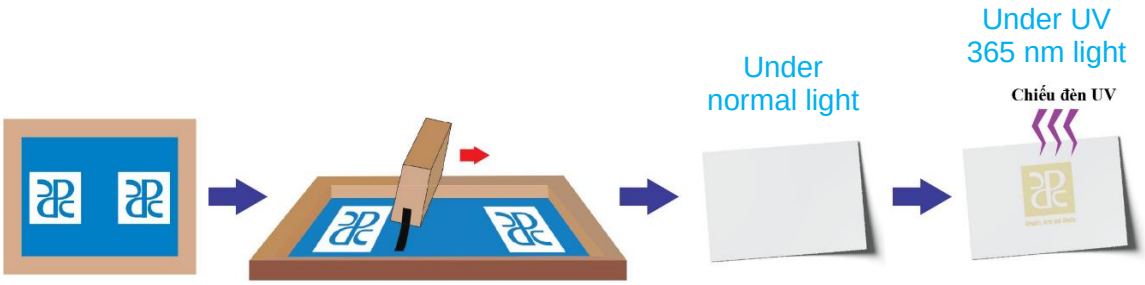

Fig. 1. *ZnO luminescent ink printed on filter paper using the screen printing method*

3. Results and discussions

3.1. Structural and morphological analysis

Fig. 2(a) displays the XRD pattern of ZnO nanoparticles (ZnO NPs) synthesized by the co-precipitation method. The result shows that ZnO NPs have the hexagonal wurtzite structure (JCPDS 04-020-0364) with the planes of (100), (002), (101), (102), (110), (103), (200), (112), (201). The average crystallite size (D) calculated from formula (1) is about 17.5 nm.

$$D = \frac{0.9\lambda}{\beta_{hkl}\cos\theta} \quad (1)$$

Where D, λ = 1.5406 Å, θ, and β_{hkl} are the mean crystallite size, the X-ray wavelength, the Bragg angle, and the full-width at half maximum (FWHM) of the diffraction peaks for the ZnO NPs, respectively.

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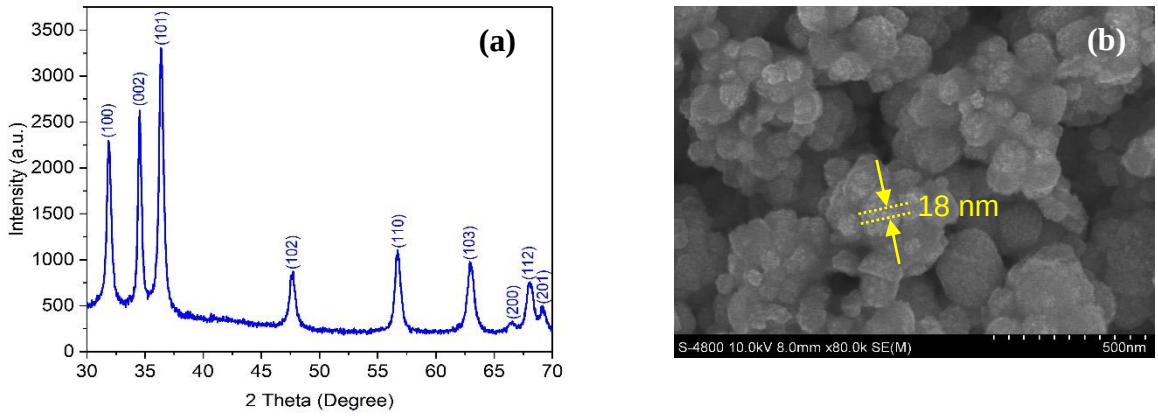

Fig. 2.*(a) XRD patterns of ZnO NPs synthesized by the co-precipitation method, (b) SEM images of ZnO nanoparticles*

Fig. 2(b) illustrates the SEM image of ZnO NPs. The result indicates that ZnO NPs are spherical, with average particle sizes of about 18 nm. This result is in good agreement with the XRD analysis.

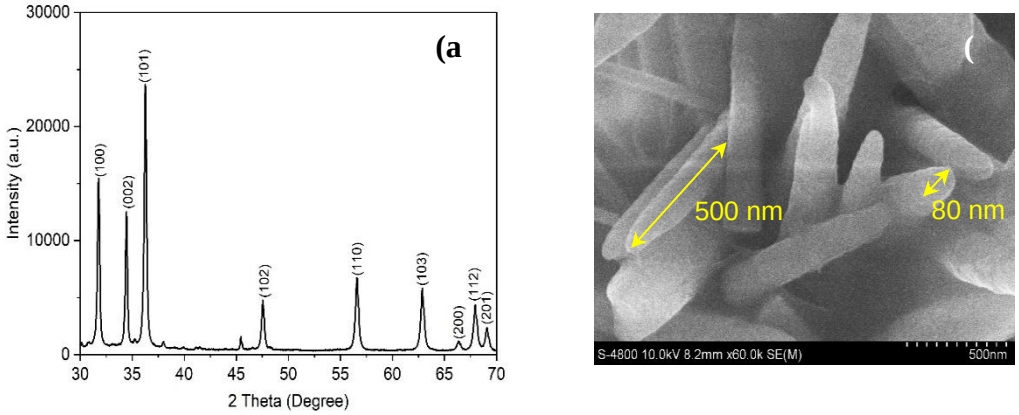

Fig. 3.*(a) XRD patterns of ZnO NPs synthesized by the hydrothermal method, (b) SEM images of ZnO nanorods*

Fig. 3(a) shows the result of ZnO NPs synthesized by the hydrothermal method. ZnO NPs also possess a hexagonal wurtzite structure (JCPDS 04-009-7657) similar to the co-precipitation method. The average crystallite size is about 28 nm. Fig. 3(b) reveals SEM images of ZnO NPs synthesized in an autoclave at temperatures of 100°C. The result shows the rod-shaped morphology of ZnO NPs. The average length and width of ZnO Ns are about 500 nm and 80 nm, respectively.

3.2. Optical properties of ZnO nanoparticles (ZnO NPs)

Fig. 4 displays UV-vis spectra of ZnO NPs synthesized by hydrothermal and co-precipitation methods. The UV-vis spectra shows the ZnO NPs' absorption peak at about 355 nm. The result indicates that the ZnO NPs are suitable for security ink applications. A UV light source with a wavelength of 365 nm may be used for excitation.

Fig. 5(a) shows the PL spectra of ZnO NPs fabricated by the hydrothermal and co-precipitation methods. The result indicates that ZnO NPs synthesized by co-precipitation methods have a broad emission at about 570 nm and 650 nm. The photoluminescence (PL) emission at 570 nm is attributed to the transition from oxygen vacancies (V_O) states to zinc vacancy (V_{Zn}) defects [12]. The PL emission at 650 nm is due to the transition between Zn_i and oxygen interstitials (O_i) states [12]. However, ZnO NPs

synthesized by the hydrothermal method show an emission peak at 650 nm. The PL peak related to oxygen vacancies states was reduced, and the emission peak at 650 nm indicates the transition between Zn_i and O_i states. Fig. 5(b) shows the CIE (x, y) color coordinates of ZnO nanoparticles with two synthesized methods, respectively. The values of the CIE (x, y) change from yellow to near pink. The PL analysis indicates that ZnO NPs synthesized by the two methods have the potential for luminescent ink applications.

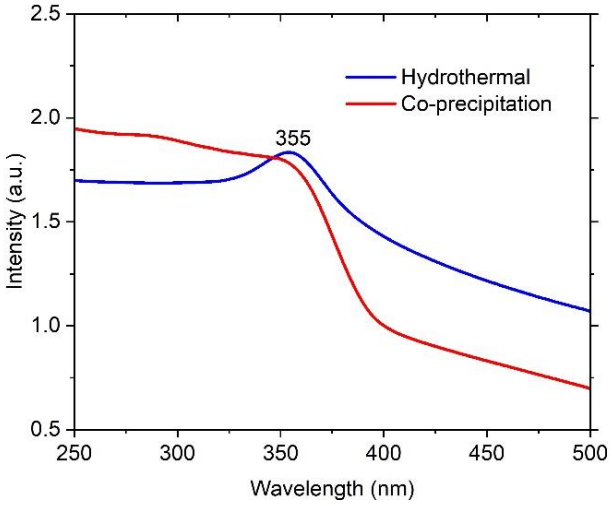

Fig. 4. *UV-Vis spectra of ZnO nanoparticles synthesized by hydrothermal and co-precipitation methods*

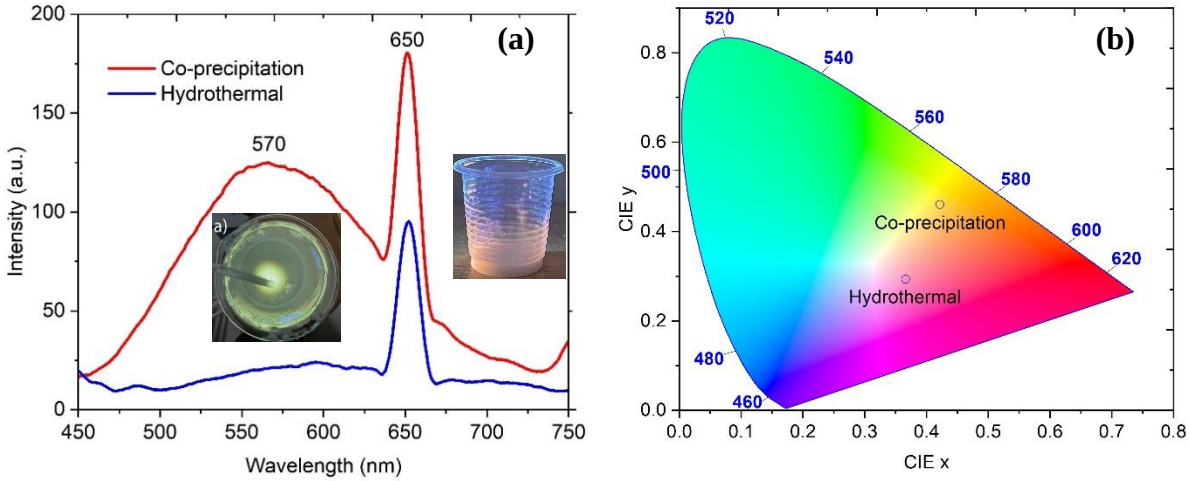

Fig. 5. *(a) PL spectra of ZnO nanoparticles synthesized by hydrothermal and co-precipitation methods, (b) CIE (x, y) diagram of ZnO nanoparticles with two synthesized methods*

Fig. 6(a) and (b) show luminescent inks based on ZnO nano-rod pigments under normal light and UV 365 nm light excitation, respectively. Fig. 6(c) and (d) display a logo sample of the Faculty of Graphic Arts and Media printed on filter paper using the screen printing method under normal light and UV 365 nm light. The result shows that the logo sample is invisible under normal light and emits pink light under UV 365 nm excitation. Similarly, Fig. 6 (e) and (f) reveal the luminescent ink based on ZnO nanoparticle pigments under normal light and UV light. The result indicates that the sample is invisible

under normal light and emits bright yellow light under UV irradiation 365 nm. Therefore, ZnO nanomaterials have potential applications in information encryption and anti-counterfeiting packaging.

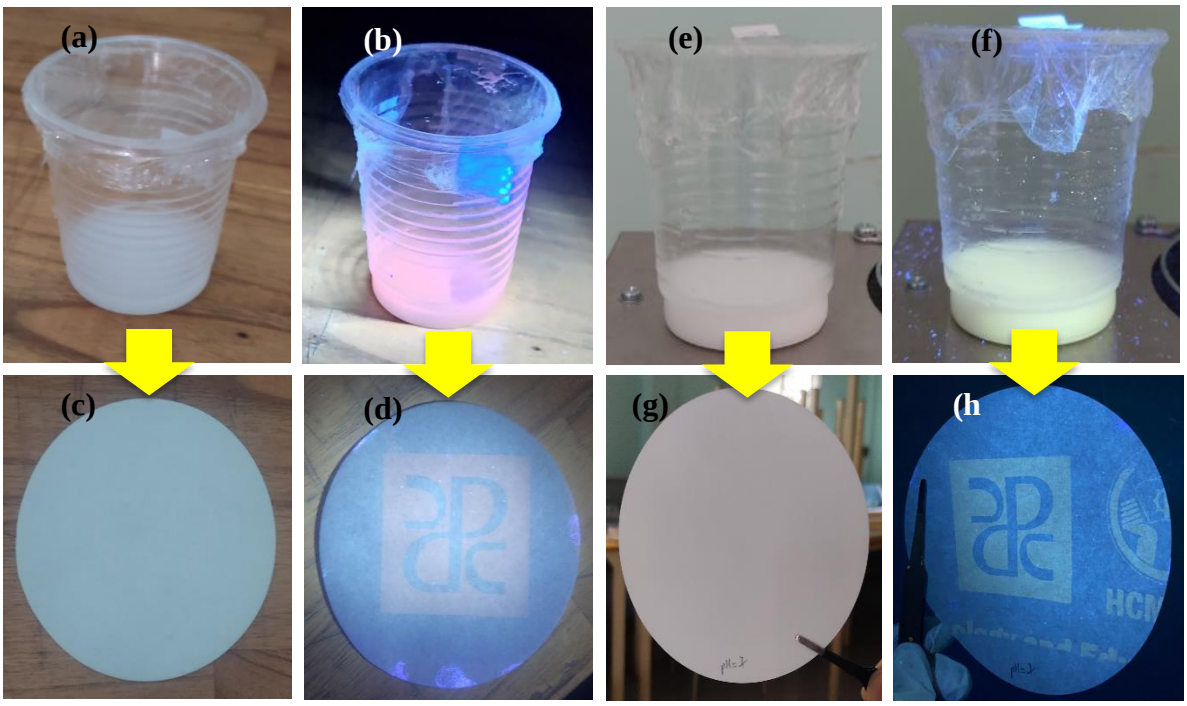

Fig. 6. *(a) Luminescent inks with ZnO nanoparticles synthesized by hydrothermal and co-precipitation methods under normal light and UV 365 nm light, (b) Logos of Faculty of Graphic Arts and Media ZnO were printed on filter paper by nano inks under normal light and UV 365 nm light.*

4. Conclusion

In summary, ZnO nanomaterials were successfully synthesized by the co-precipitation and hydrothermal methods. ZnO nanomaterials were used as luminescent pigments in an ink formulation. ZnO nanopigments were dispersed in the vehicle, including PVA, water, and ethylene glycol, to obtain an ink formulation. The fluorescent ink has a bright yellow and pink emission under UV irradiation 365 nm. The ZnO nano pigments-based fluorescent ink is environmentally friendly and can be used in the fields of information encryption and anti-counterfeiting packaging.

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Conflict of Interest

The authors declare no conflict of interest.

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