Open Journal of Synthesis Theory and Applications, **2012, 1, 18-22**
http://dx.doi.org/10.4236/ojsta.2012.12004 Published Online July 2012 (http://www.SciRP.org/journal/ojsta)

Preparation and Characterization of Silver Doped ZnO Nanostructures

Nguyen Van Nghia*, Tran Nam Trung, Nguyen Ngoc Khoa Truong, Doan Minh Thuy
Department of Physics, Quy Nhon University, Quy Nhon, Vietnam
Email: *nguyenvannghia@qnu.edu.vn

Received April 25, 2012; revised June 7, 2012; accepted July 3, 2012

ABSTRACT

ZnO was prepared by hydrothermal method. The result of scanning electron microscopy showed that the materials had nano rod structures. Ag-doped ZnO was prepared by UV-photoreduction. Crystalline phases and optical absorption of the prepared Ag-doped ZnO samples were determined by X-ray diffraction, Raman spectrum, UV-visible, and UV-photoreduction spectrophotometer. X-ray analyses revealed that Ag was doped ZnO crystallizes in hexagonal wurtzite structure. The incorporation of Ag^+ in the site of Zn^{2+} provoked an increase in the size of nanocrystals as compared to pure ZnO. The photocatalytic and photoluminescence properties of materials were considered.

Keywords: Nanostructures; Photocatalysis; Hydrothermal; ZnO; Silver Doping

1. Introduction

Nanostructured ZnO materials have received considerable interest from scientists due to their remarkable performance in electronics, optics and photonics. ZnO is a wide band gap (3.37 eV at room temperature) compound semiconductor that is appropriate for short wavelength optoelectronics applications. The large exciton binding energy (60 meV) in ZnO crystal allows efficient excitonic emission at room temperature. Therefore, ZnO nanostructures have had a wide range of high technology applications like surface acoustic wave filters, photonic crystals, gas sensors, photocatalysis [1-3]. Because of having a wide bandgap, ZnO can only be activated by ultraviolet light of wavelength below 385 nm. The ultraviolet light reaching the earth's surface is less than 5% of the solar energy, which is too low to attain significant photodegradation in commercial application. Some interesting approaches have been adopted to extend the photoresponse of ZnO toward the visible spectral region, such as implanting transitional metal ions [4,5].

Metal silver is also a significant visible light photosensitizer, which is stable and nontoxic. Ag is also relatively cheap; thus Ag modification is of great significance for industrial practice. The improvement in efficiency of photocatalytic reactions under visible light is explained as the result of a vectorial transfer of photogenerated electrons and holes from metal to semiconductor. Moreover, ZnO modified by Ag can improve the distribution of surface charges, accept a conduction band generated by solar light irradiation during photoreaction, prevent the recombination of the photogenerated electron-hole. Many researchers reported that ZnO thin film with Ag doping, which enhances ultraviolet emission and improves electrical and optical properties, was prepared by wet chemical [6], DC magnetron sputtering [7] and pulsed laser deposition [8].

In this work, silver nanoparticles were deposited on the surface of ZnO nanorods (prepared by hydrothermal method) by using a photochemical reduction under UV irradiation. We also have compared the photocatalytic properties of Ag-doped ZnO and ZnO nanorods (ZnO-NRs).

2. Experimental

2.1. ZnO-NRs Preparation

4,6 g of zinc acetate $(Zn(OAc)_2$ powders were dissolved in 40 ml a solvent etanol under stirring for 1 h (called M1 solution). The M2 solution was prepared by adding 2,5 g oxalic acid $(H_2C_2O_4)$ into 40 ml etanol under stirring. M2 was slowly poured in the M1 solution under ultrasonic wave (35 kHz, 100 W) for 30 minutes. The sonicated solution was then moved to a teflon vessel and put in a stainless steel autoclave for carrying out the hydrothermal treatment at 140˚C for 20 hours. The stainless steel was then opened at room temperature and the precipitates were separated and washed repeatedly by deionized water until the pH value of the washing solution became lower than 7. The final as-prepared product was dried under vacuum at temperature of 80˚C for 12 hours. Then

---

*Corresponding author.

the product was calcined at temperature of 450˚C for 1 hour in air.

2.2. Ag-Doped ZnO Preparation

0,5 g of ZnO-NRs were dispersed into deionized water under stirring. The suspension was sonicated for 30 min by ultrasonic wave. After ultrasonically treated the suspension was further magnetically stirred for 30 min under UV irradiation. Then 0.007 g $AgNO_3$ were added into the suspension ($m_{Ag}:m_{Zn}$ = 1%) and followed by UV illumination for 4 h under stirring. The black powder was centrifuged, rinsed with deionized water repeatedly to purify the product, and finally dried at 70˚C under air for 5 h. The product was denoted Zn-Ag_1.

Using the same method, we prepared products Zn-Ag_2, Zn-Ag_3, Zn-Ag_4, Zn-Ag_5. The more silver ion was doped, the darker in colour of the product was.

2.3. Characterization and Measurement

The morphology dimensions and microstructure measurements of the samples were performed using a Hitachi S4800 scanning electron microscope (SEM). The crystalline phases of the obtained samples were characterized by using a Siemens D-5005 X-ray powder diffractometer (XRD) with a monochromatized Cu-Kα irradiation (λ = 1.54056 Å). The Raman spectra were recorded on a Nicolet spectrometer equipped with an optical microscope at room temperature. UV-Vis spectra were measured by a Scan UV-Vis spectrophotometer (Varian, Cary 500).

The photocatalytic activity was evaluated by measuring the decomposition of the aqueous solution of methylene blue (with a concentration of 10 mg/L) under sunlight irradiation for 30 min of pure ZnO-NRs and Ag-doped ZnO. The reactor was equipped with water circulation in the outer jacket in order to maintain a constant temperature. Prior to irradiation, the suspensions were magnetically stirred in dark for 1 h to ensure an establishment of adsorption/desorption equilibrium. Then the solution was filtered to remove "particles". The resulted solution was analyzed by recording variations in the absorption in UV-visible spectra of methylene orange using a Shimadzu 1601-PC Ultraviolet-visible spectrometer.

3. Results and Discussion

The XRD patterns of ZnO-NRs and Zn-Ag_5 are exhibited in **Figure 1**.

As can be seen from **Figure 1**, all the samples were well crystalline, and of hexagonal wurtzite phase (JCPDS file No. 36-1451). However, the Ag-doped samples revealed some additional diffraction peaks marked with "*" associated with the face-centered-cubic phase of metallic Ag (JCPDS file No. 04-0783). The appearance of Ag peaks in the diffraction patterns indicates clearly the formation of crystalline silver clusters in the nanoparticles. This can be demonstrated by SEM image of Zn-Ag_5.

Figure 2(a) shows the image of ZnO nanorods calcined at 450˚C, a large number of open-ended ZnO-NRs with uniform diameters around 300 nm and lengths about several micrometer can be clearly seen in the picture. No obvious damage is found and the materials remain in good shape. **Figure 2(b)** shows that Ag-sensitized ZnO prepared by photoreduction does not cause any change in the morphology compared with pure ZnO. But some newly formed small Ag particles with diameter a few nanometer on the surface of ZnO can be observed clearly.

The EDS spectrum (**Figure 3**) showed that the Zn-Ag_5 material include elements such as Zn, O and Ag. The quality of Ag content deduced from the EDS spectrum about 3% indicate that Ag particles are losed in the reaction process.

The room temperature UV-Vis spectrum of undoped ZnO and Zn-Ag_5 are presented in **Figure 3**. As can be seen from curve A in **Figure 4**, ZnO-NRs have a broad intense absorption below wavelength 400 nm. It is the characteristic absorption of ZnO corresponding to the charge transfer process from the valence band to conduction band in ZnO. In the UV-Vis spectra of the Zn-Ag_5 (curve B), it can be seen that there is a absorption peak

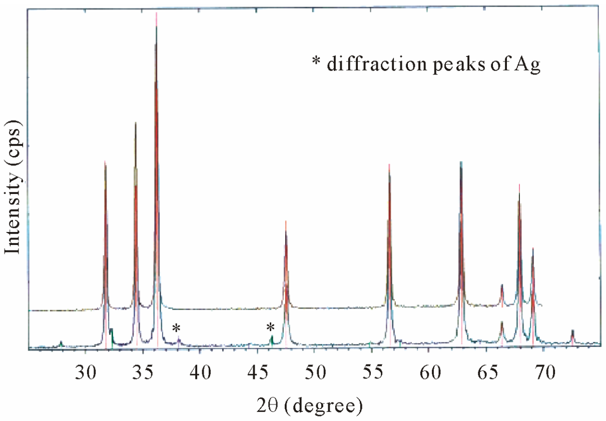

Figure 1. XRD patterns of ZnO and Zn-Ag_5.

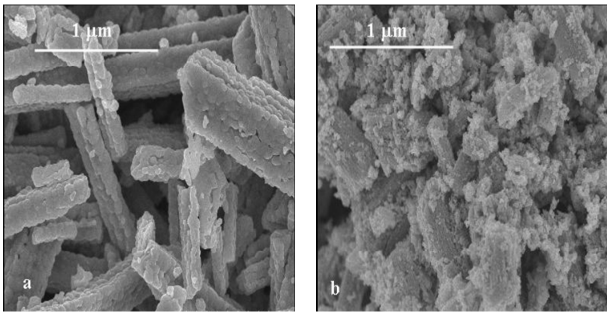

Figure 2. SEM images of ZnO nanorods (a) and Zn-Ag_5 (b).

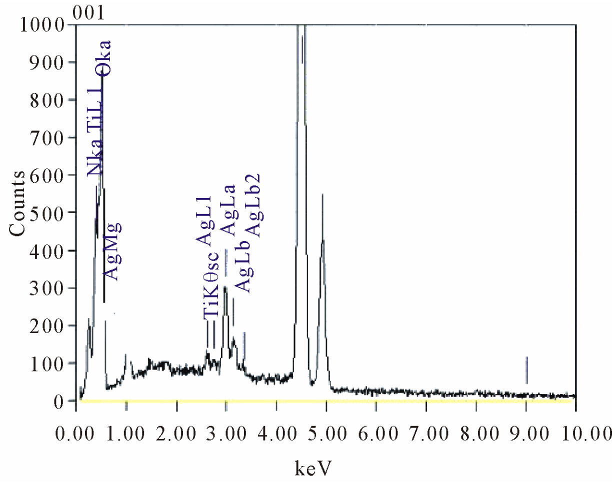

Figure 3. EDS spectrum of Zn-Ag$_5$.

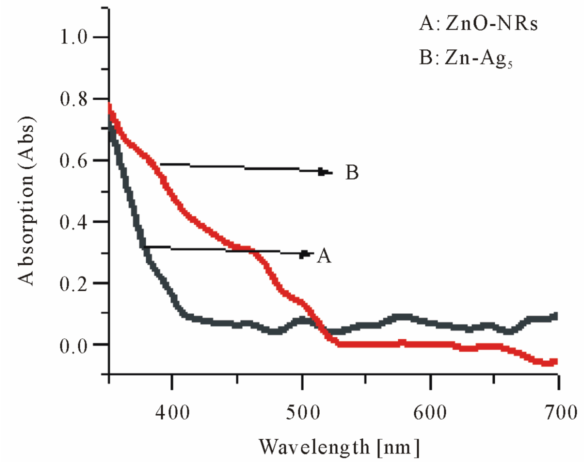

Figure 4. UV-Vis spectrums of ZnO and Zn-Ag$_5$.

around 460 nm in the visible range. This is the characteristic of surface plasmon absorption corresponding to Ag^0 particles [9]. So the modification decrease in bandgap energy of ZnO.

Figure 5 presents the room temperature Raman spectrum of ZnO-NRs and Zn-Ag$_5$. It can be seen that the spectrum of ZnO (curve A) consists of five peaks located at about 100, 140, 380, 437, and 580 cm^{-1} which correspond to the fundamental phonon modes of hexagonal ZnO, respectively. The curve B which is the spectrum of Zn-Ag$_5$ has four peaks located at about 100, 140, 241, and 580 cm^{-1}. There appeared a broad Raman peak at about 241 cm^{-1} exclusively for the Ag-doped samples. The intensity of this peak decreased drastically on doping the silver in the samples. We can recall that the incorporation of Ag in our ZnO nanoparticles reduces their crystallinity [8].

Figure 6 shows room-temperature PL spectrums of ZnO and Zn-Ag$_5$ at the excitation wavelength of 325 nm. We can see that a blue-green emissions at about 520 nm

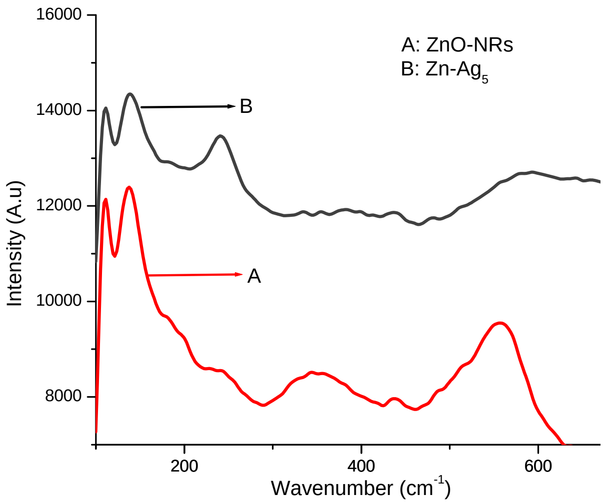

Figure 5. Raman spectrums of ZnO and Zn-Ag$_5$.

were observed in them. The emission centered at 520 nm of Zn-Ag$_5$, which can be fitted to two peaks centered at 516 nm and 630 nm, respectively, as shown in the inset of **Figure 5**. The peak 516 might be attributed to the intrinsic defects (O and Zn vacancies or interstitials and their complexes) in ZnO. The other hand, the Ag-doped ZnO, which prepared, exhibits a new and unusual PL phenomenon at 615 nm; there is the possibility of the formation of a new surface state. The dopant Ag has a great effect on the separation and recombination process of photo-induced charge carriers of ZnO, which can further effect on PL performance. It indicates that the photoluminescence mechanism of Ag/ZnO is very complex and further research is needed.

Figure 7 shows the effect of the Ag content on the photocatalytic activity of Ag-doped ZnO. The photocatalytic degradation ratio of methyl blue (MB) increases rather rapidly initially with the increase of the Ag content and reaches a plateau at the Ag content of 4%. It is worth that the amount of doped silver ion is very important to photoactivity. But an increase in dopant ion can make increasable rate recombination of electron-hole pairs, because silver ions play a central role of recombination, that can make decreasing the photocatalytic activity of material. The photocatalytic mechanism of Ag/ZnO is also complex and it's studied deeply.

We considered the UV-photoreduction mechanisms from the view point of photolysis at ZnO catalyst. Oxidation and reduction occur at the same time in Ag ion photoreduction. In the reduction, the conduction band electrons generated in the ZnO (e$^-$(CB)) by UV irradition can reduce adsorbed Ag$^+$ ions, giving rise to Ag atoms (Ag^0). The reduced Ag is deposited on the ZnO surface. Photochemical reactions induced by ZnO-light are summarized as:

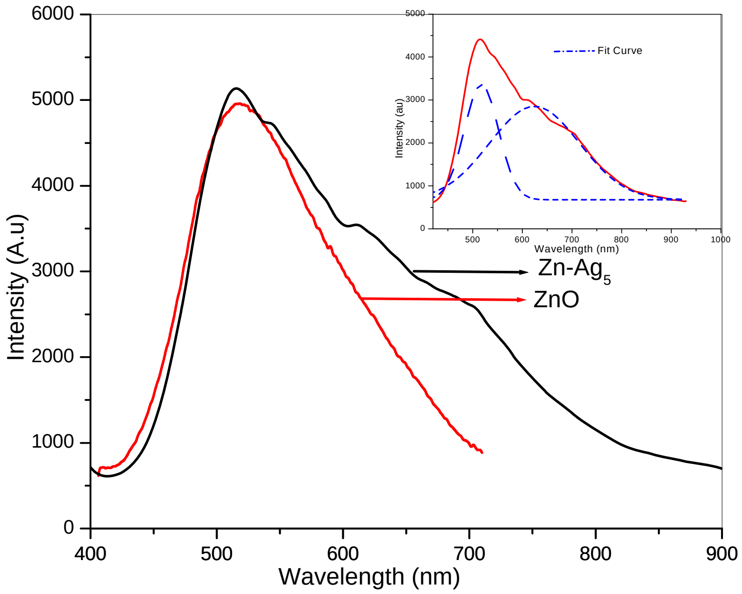

Figure 6. Room-temperature PL spectrum of Zn-Ag$_5$. In the inset, the curves "…"show Gaussian curve fitting.

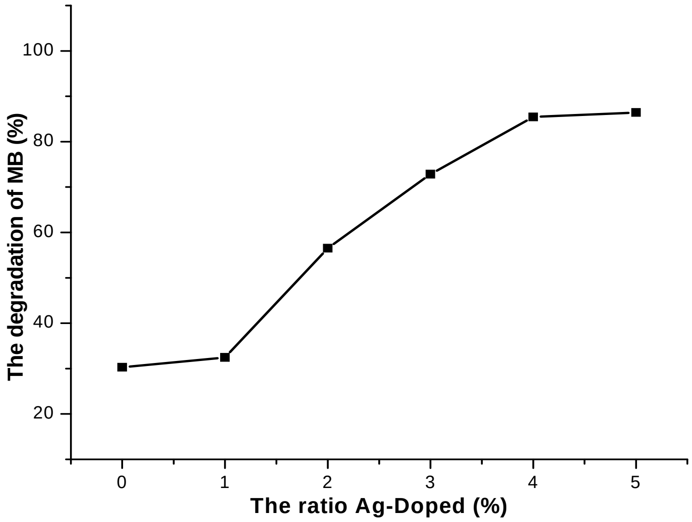

Figure 7. The degradation of MB on the Ag-doped ZnO.

$$ZnO + h\nu \rightarrow e^{-}(CB) + h^{+}(VB) \quad (1)$$

$$Ag^{+} + e^{-}(CB) \rightarrow Ag^{0} \quad (2)$$

$$2H_2O + h^{+}(VB) \rightarrow O_2 + 4H^{+} \quad (3)$$

4. Conclusion

Nanorod ZnO was successfully synthesized by a simple hydrothermal method. Ag-doped ZnO composites were prepared by method of UV-photoreduction with as-synthesized ZnO-NRs. Photocatalytic reactions show that doping Ag into ZnO hole remarkably improves the photocatalytic activity of ZnO under simulated solar light. The PL spectrum result shows that Ag-sensitized ZnO composite not only has the emission intensities at about 318 nm and 520 nm, but also exhibits a new and unusual PL phenomenon at 615 nm, indicating that the dopant Ag has great effects on separation and recombination processes of photo-induced charge carriers of ZnO.

REFERENCES

[1] N. W. Emanetoglu, C. Gorla, Y. Liu, S. Liang and Y. Lu, "Epitaxial ZnO Piezoelectric Thin Films for Saw Filters," *Materials Science in Semiconductor Processing*, Vol. 2, No. 3, 1999, pp. 247-252. doi:10.1016/S1369-8001(99)00022-0

[2] Y. Chen, D. Bagnall and T. Yao, "ZnO as a Novel

Photonic Material for the UV Region," *Materials Science and Engineering*: *B*, Vol. 75, No. 2-3, 2000, pp. 190-198. doi:10.1016/S0921-5107(00)00372-X

[3] P. Mitra, A. P. Chatterjee and H. S. Maiti, "ZnO Thin Film Sensor," *Materials Letters*, Vol. 35, No. 1-2, 1998, pp. 33-38. doi:10.1016/S0167-577X(97)00215-2

[4] G. Skanadan, Y. J. Chen, N. Glumac and B. H. Kear, "Synthesis of Oxide Nanoparticles in Low Pressure Flames," *Nanostructured Materials*, Vol. 11, No. 2, 1999, pp. 149-153. doi:10.1016/S0965-9773(99)00028-8

[5] T. Shinagawa, M. Izaki, H. Inui, K. Murase and Y. Awakura, "Characterization of Transparent Ferromagnetic Fe: ZnO Semiconductor Films Chemically Prepared from Aqueous Solutions," Journal of The Electrochemical Society, Vol. 152, No. 10, 2005, pp. 736-741. doi:10.1149/1.2001247

[6] R. Chen, C. Zou, J. Bian, A. Sandhu and W. Gao, "Microstructure and Optical Properties Ag-Doped ZnO Nanostructures Prepare by a Wet Oxidation Doping Process," *Nanotechnology*, Vol. 22, No. 10, 2011, p. 1

[7] S. H. Jeong, B. N. Park, S. B. Lee and J.-H. Boo, "Structural and Optical Properties of Silver-Doped Zinc Oxide Sputtered Films," *Surface & Coatings Technology*, Vol. 193, No. 1-3, 2005, pp. 340-344. doi:10.1016/j.surfcoat.2004.08.112

[8] B. D. Ahn, H. S. Kang, J. H. Kim, G. H. Kim, H. W. Chang and S. Y. Lee, "Synthesis and Analysis of Ag-Doped ZnO," *Journal of Applied Physics*, Vol. 100, 2006, Article ID: 093701. doi:10.1063/1.2364041

[9] K. Patel, S. Kapoor, D. P. Dave and T. Mukherjee, "Synthesis of Nanosized Silver Colloids by Microwave Dielectric Heating," *Journal of Chemical Sciences*, Vol. 117, No. 1, 2005, pp. 53-60.