

Synthesis and characterization of copper oxide decorated zinc oxide nanorods

S. K. Lim^{*}, S. H. Hong^{*}, S. H. Hwang^{*}, S. Kim^{*}, D. J. Lee^{**} and H. S. Kim^{***}

^{*}Division of Nano & Bio Technology, DGIST, 711-873, Daegu, Republic of Korea, limsk@dgist.ac.kr

^{**}Eco-Composite Material Center, KICET, Seoul 153-801, Republic of Korea, domgjee@kicet.re.kr

^{***}Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea, hanseongkim@pusan.ac.kr

ABSTRACT

One-dimensional nanostructures in the form of nanorods, nanowires, nanofibers or nanotubes, appear as an exciting research area for their great potential of applications. Zinc oxide is an n-type semiconductor that has been well known for its applications in pigments, rubber additives, gas sensors, solar cells, varistors, and optical devices. In this aspect, many of the previous investigations on pure and doped zinc oxide prepared by different methods like precipitation, hydrothermal, microemulsion, ultrasonic, sol-gel, solid-state reaction. In this study, we report the synthesis of copper oxide decorated zinc oxide nanorods by microemulsion and solvothermal method. The results showed that the copper oxide were successfully grown on the zinc oxide nanorods substrates

Keywords: copper oxide, zinc oxide, microemulsion, nanorod, solvothermal

1 INTRODUCTION

The synthesis of nanometer-sized one-dimensional Zinc oxide materials has attracted considerable attention because of their great potential for fundamental studies of the role of dimensionality and size in the physical properties as well as for many applications such as transparent electrode in solar cells, gas sensors and optical switch [1, 2]. Therefore, research of a morphologically controllable synthesis of ZnO is very important. Recently, strong efforts have been made to fabricate one-dimensional ZnO synthesized for example, by the high-temperature physical evaporation, the micro emulsion process and the template induced method [3, 4]. Among all these methods, the solution based synthesis, by thermal treatment of the reactant in different solvents, maybe the most simple and effective way to prepare sufficiently crystallized materials at relatively low temperatures. The benefits of a utilizing solution-based method have involved the considerable influence of reaction species on the size and morphology. However, pure zinc oxide is not stable in air and its electrical properties are significantly affected by adsorption of O₂, CO₂, hydrocarbons, S-containing compounds, and water. Therefore, single crystals and polycrystalline of zinc oxide have been modified to enhance their mechanical, electrical,

and optical properties. Apart from the design of specific nanostructure, another method to improve the performance is to introduce other species as sensitizers or promoters through either loading noble metal nanoparticles such as Au, Ru, Pt, Ag, Pd or doping with cheap transition metal ions [5, 6]. In this study, we report the synthesis of copper oxide decorated zinc oxide nanorods by microemulsion and solvothermal method.

2 EXPERIMENTAL

2.1 Synthesis of Zinc Oxide Nanorods

The synthesis of ZnO nanorods was carried out in microemulsion, which was consisting of 5 g of surfactant sodium lauryl sulfate (SLS) and 2 mmol of ZnAc₂·2H₂O both dispersed in 60 ml xylene by stirring until a homogenous slightly-turbid appearance of mixture was obtained. Then hydrazine monohydrate 2 ml and ethanol 8 ml mixture solution was added drop-wisely to the well-stirred mixture at room temperature by simultaneous agitation. The resulting precursor-containing mixture was subsequently heated to the 140°C for refluxing. After refluxing for 5 hours, a milky-white suspension was obtained and centrifuged to separate the precipitate which was rinsed with absolute ethanol and distilled water for several times and dried in vacuum oven at 70°C for 24hours.

2.2 Synthesis of Copper Oxide Decorated Zinc Oxide Nanorods

The synthesis of 2, 9, 16, 23-tert-nitrothalocyanine copper (II) (TNCuPc)/ZnO nanorods was carried out in solvothermal method, which were consisting of 4-nitrothalonitrile (0.200 mmol), Cu(OAc)₂·H₂O (0.050 mmol), ammonium molybdate (30 mg), and ZnO nanorods (0.450g) were put into a autoclave of 900mL capacity that contained 600mL of ethylene glycol solution. The mixture was then stirred to form a suspension, sealed, and solvothermally treated at 160°C for 72 hours. The obtained composite nanorods was washed with distilled water and ethanol for several times and dried in vacuum oven at 70°C for 4 hours. After TNCuPc/ZnO nanorod structures were calcined in a furnace at 400°C for 2 hours.

2.3 Characterization

Field-emission scanning electron microscopy (FE-SEM) (Hitachi, S-4800) was applied to investigate the morphology of the powders. Fourier transform infrared spectra were obtained from an IRPrestige-21 FT-IR Spectrometer with a resolution of 1 cm^{-1} . The X-ray powder diffraction patterns (XRD) of the products were recorded on a Rigaku D/max 2500 X-ray diffractometer with Cu $K\alpha$ radiation. Optical properties were obtained by the photoluminescence (PL) measurements using SPEX 1403 Spectrophotometer excited by a continuous He-Cd laser with a wavelength of 325 nm. Surface atomic composition analyses were performed by X-ray photoelectron spectroscopy (XPS) (Kratos XSAM 800pci) using the Mg- $K\alpha$ line (1253.6 eV) as the excitation source.

3 RESULTS AND DISCUSSION

The XRD spectra of various samples are shown in Figure 1. Different diffraction patterns were compared with the JPCDS database. The XRD spectra (Fig. 3(a) and (c)) revealed the peaks from ZnO and CuO. Similar results were obtained from previous studies of zinc oxide and copper oxide samples [7, 8]. The pure CuO peaks matched those of monoclinic CuO (JCPDS no. 45-0937, $a=4.6853\text{Å}$, $b=3.4257\text{Å}$, $c=5.1303\text{Å}$) and pure ZnO (JCPDS no. 80-0075: Zincite hexagonal structure, $a=b=3.25\text{Å}$, $c=5.21\text{Å}$).

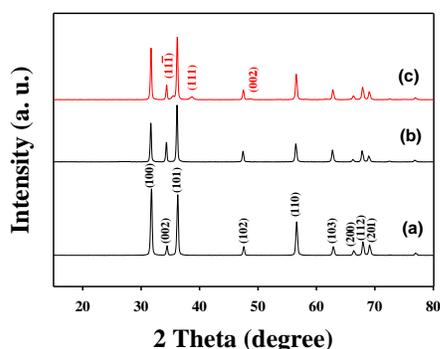
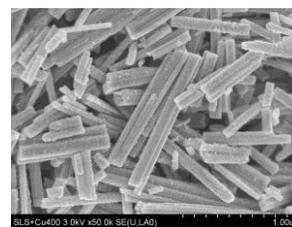
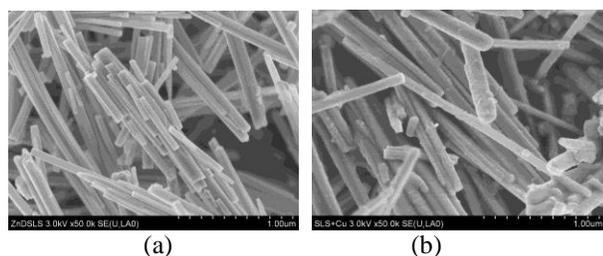


Figure 1. XRD patterns of synthesized (a) ZnO nanorods, (b) TNCuPc/ZnO nanorods and (c) copper oxide decorated ZnO nanorods .

Figure 2 showed the typical SEM images of the pure ZnO nanorods, TNCuPc/ZnO nanorods and CuO decorated ZnO nanorods.



(c)

Figure 2. FE-SEM images of synthesized (a) ZnO nanorods, (b) TNCuPc/ZnO nanorods and (c) copper oxide decorated ZnO nanorods.

It could be seen that the lengths of these randomly oriented ZnO nanorods could reach several micrometers, and the diameters of those nanorods ranged from 70 to 150 nm. Furthermore, the surface of pure ZnO nanorods was smooth. However, as observed in images (b) in Figure 1, it was found that TNCuPc nanostructure coated on the surface of ZnO nanorods after solvothermal reaction for 72 h. From Figure 1(c), it was found that a lot of CuO nanoparticles uniformly grew on the surface of ZnO nanorods.

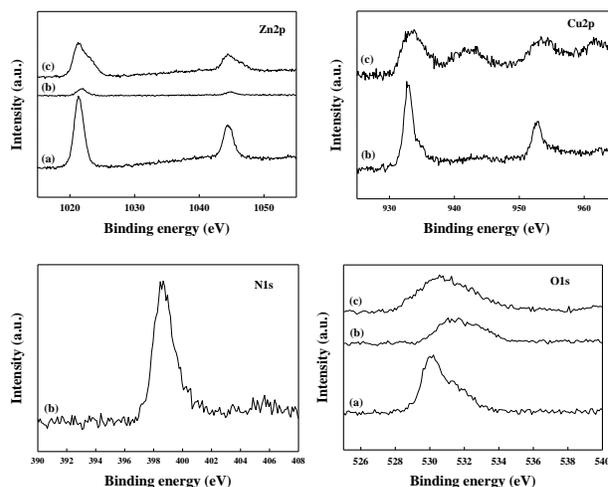


Figure 3. XPS spectra of synthesized (a) ZnO nanorods, (b) TNCuPc/ZnO nanorods and (c) copper oxide decorated ZnO nanorods.

The chemical composition and purity of TNCuPc/ZnO nanorods and CuO decorated ZnO nanorods were studied and compared with that of the ZnO nanorods by XPS analysis. Zn and O elements existed in pure ZnO nanorods, while Zn, Cu, O and N existed in TNCuPc/ZnO nanorods, respectively. Zn, Cu and O existed in CuO decorated ZnO nanorods. The binding energies for the Zn 2p region around 1021 and 1044 eV, the Cu 2p region around 940 eV, and the O1s region around 530 eV.

4 CONCLUSIONS

In summary, by using microemulsion and solvothermal synthesis, TNCuPc/ZnO nanorods and copper decorated

ZnO nanostructures were successfully fabricated. XRD results confirmed the hexagonal wurtzite crystal structure of ZnO and monoclinic CuO. The proposed synthesis method can also be useful for synthesis of copper decorated nanostructures.

5 ACKNOWLEDGMENT

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, also supported by the DGIST R&D Program of the Ministry of Education, Science and Technology of Korea (11-NB-03).

REFERENCES

- [1] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C.L. Lin, *Appl. Phys. Lett.*, 84, 3654, 2004.
- [2] H. Kind, H. Q. Yan, B. Messer, M. Law, and P. D. Yang, *Adv. Mater.*, 14, 158, 2002.
- [3] S. K. Lim, S. H. H. S. Kim, and H. Park, *Sensors and Actuators B*, 160, 94, 2011.
- [4] B. Cheng, W. Shi, J. M. Russel-Tanner, L. Zhang, and E. T. Samulski, *Inorg. Chem.*, 45, 1208, 2006.
- [5] M. Zhang, C. Shao, Z. Guo, Z. Zhang, J. Mu, T. Cao and Y. Liu, *ACS Appl. Mater. Interfaces*, 3, 369, 2011.
- [6] A. F. Lotus, Y. C. Kang, J. I. Walkerc, R. D. Ramsierc, and G.G. Chase, *Materials Science and Engineering: B*, 166, 1, 61, 2010.
- [7] S. K. Lim, S. H. Hwang, and S. Kim, *Cryst. Res. Technol.* 45, 771, 2010.
- [8] M. Yua, R. Wua, and M. Chavalialia, *Sensors and Actuators B*, 153, 321, 2011.