Materials Science-Poland, *Vol. 28*, *No. 3*, *2010*

Morphology and characterization of cockloft-like ZnO/morin hybrid

Y. LI*, Y.-L. ZOU

College of Science, Civil Aviation University of China, Tianjin, 300300 P.R. China

Morin modified multilayer ZnO with a cockloft-like morphology was fabricated in alcohol solution, using hydrothermally synthesized ZnO nanodisks and morin as the precursors. The samples were characterized by field emission scanning electron microscopy, X-ray diffractometry, Fourier transform infrared spectroscopy and fluorescence spectroscopy. The results show that the cockloft-like ZnO hybrid, having hexangular morphology with the diameter of 1.5–2 μm and the thickness of ca. 1 μm, is composed of a multilayer flatform stacked by numerous ZnO nanodisks in its middle and a meshlike muffle made up of countless morin nanoparticles with the diameter of ca. 40 nm. The UV emission of the as-fabricated product is obviously attenuated by morin nanoparticles assembling on the surface of the ZnO nanodisks.

Keywords: *zinc oxide; morin; modification; morphology; cockloft; disk*

1. Introduction

ZnO, a n-type II–VI compound semiconductor with a direct band gap energy of 3.37 eV at ambient temperature and strong exciton binding energyof 60 meV, has currently attracted intensive interest in optics, electronics, catalysis, etc. Many papers focused on the synthesis of various ZnO nanostructures with particular morphologies, such as nanowires [1, 2], nanobelts [3], nanorods [4], nanotubes [5–7] and nanodisks [8]. Furthermore, various elements and compounds were doped into ZnO structure to improve its properties, such as Pt [9], titanate [10], CdS [11] and PbS [12]. The fabrication and the toluene sensing properties of TiO_2-doped ZnO nanostructures have been reported. It was found that a TiO_2-doped ZnO sensor exhibits remarkably enhanced responsiveness to 100 ppm toluene [13]. A colloidal Fe-doped ZnO nanocrystal was synthesized and its distinct ferromagnetic resonance signal at room temperature was revealed [14]. On the other hand, organic dyes such as cationic azobenzene dye [15] and rhodamine [16] are increasingly used as dopants and modifiers of inorganic nanomaterials. Among all the organic dyes, morin is usually used as a useful

*Corresponding author, e-mail: Liyan01898@163.com

dopant or modifier, especially as a fluorescent reagent. The photoluminescence of porous anodized aluminum oxide impregnated with morin was investigated [17]. A SiO_2-morin nanocomposite was successfully synthesized and the reactivity of the nano SiO_2, in terms of selective binding and extraction of heavy metal ions was greatly improved by morin modification [18]. The interaction between morin and TiO_2 was investigated by analyzing the UV-vis absorption, UV-vis diffuse reflectance spectrum [19]. Morin was also intercalated into NaY zeolite, as a modified electrode material [20]. The synthesis and the photocatalytic property of the dye-sensitized ZnO have been reported [21]. ZrO_2/morin nanocomposite was fabricated by a simple heat refluxing method and the enhancement of its photoluminescence was disclosed [22]. To our knowledge, there have been no reports on morin modified ZnO. Therefore, it is necessary to research the fabrication and characterization of morin modified ZnO structure. In this paper, we report a cockloft-like structure of morin modified multilayer ZnO, and its properties are characterized via X-ray diffractometry, field emitting scanning electron microscopy, Fourier transform infrared spectrometry and fluorescence spectrometry.

2. Experimental

Materials. All reagents such as zinc chloride ($ZnCl_2$, 98%), ammonia ($NH_3 \cdot H_2O$, 25%), and N,N,N-trimethyl-1-hexadecanaminium bromide (CTABr, $C_{19}H_{42}BrN$, 99%), morin hydrate ($C_{15}H_{10}O_7 \cdot xH_2O$, 99.5%) and absolute ethanol (C_2H_5OH, 99.7%), purchased from Kewei Company of Tianjin University, were analytical grade, and were used without further purification.

Fabrication. The fabrication of morin decorated ZnO disks was carried out according to the following procedure. In the first step, 6 g of $ZnCl_2$ and 0.05 g of CTABr were dissolved into 90 cm^3 of distilled water, and then 6.5 cm^3 of ammonia was slowly dropped into the former solution under vigorous stirring to form the reactant mixture. Subsequently, the solution was loaded in a 250 cm^3 beaker placed in a water bath and was hydrothermally treated, first at 95 °C for 3 h and then at 50 °C for 1 h. The resulting white precipitate was washed several times with distilled water and alcohol, and dried at 60 °C for 10 h in an oven to obtain ZnO products. In the second step, the as-synthesized ZnO particle was mixed with 10 cm^3 of morin solution, using alcohol as a solvent, and the mixture was thoroughly mixed until it was dried by natural evaporation in atmosphere to obtain the products.

Characterization. The morphologies of the as-synthesized samples were investigated by 1530VP model field emission scanning electron microscopy (FESEM). The X-ray diffraction (XRD) pattern of the obtained particles was identified on a DX-2000 X-ray diffractometer with CuK_α radiation (λ = 0.1542 nm). Photoluminescence (PL) spectra of these samples were measured with a WGY-10 fluorescence spectrophotometer with a Xe lamp (150 mW). The excitation wavelength was fixed at 230 nm.

The spectrum of these samples at ambient temperature was observed in the wavelength range of 350–600 nm. Fourier transform infrared spectroscopy (FTIR) measurements of the samples were undertaken on a Nicolet 380 spectrometer with the spectral resolution of 1 cm^{-1}. The samples were mixed with KBr, in the weight ratio of sample-to-KBr of 1:100, and were then pressed into pellets for characterization.

3. Results and discussion

FESEM images and XRD spectra. Figure1 shows the images of the as-prepared ZnO disks and the mesh-like morin masked multilayer ZnO. In Figure 1a, a very large number of nanodisks 1.5 μm in diameter and ca. 50–100 nm thick can be observed, which can be easily indexed to a wurtzite ZnO structure (Fig. 2a) and has an unclear hexagon shape.

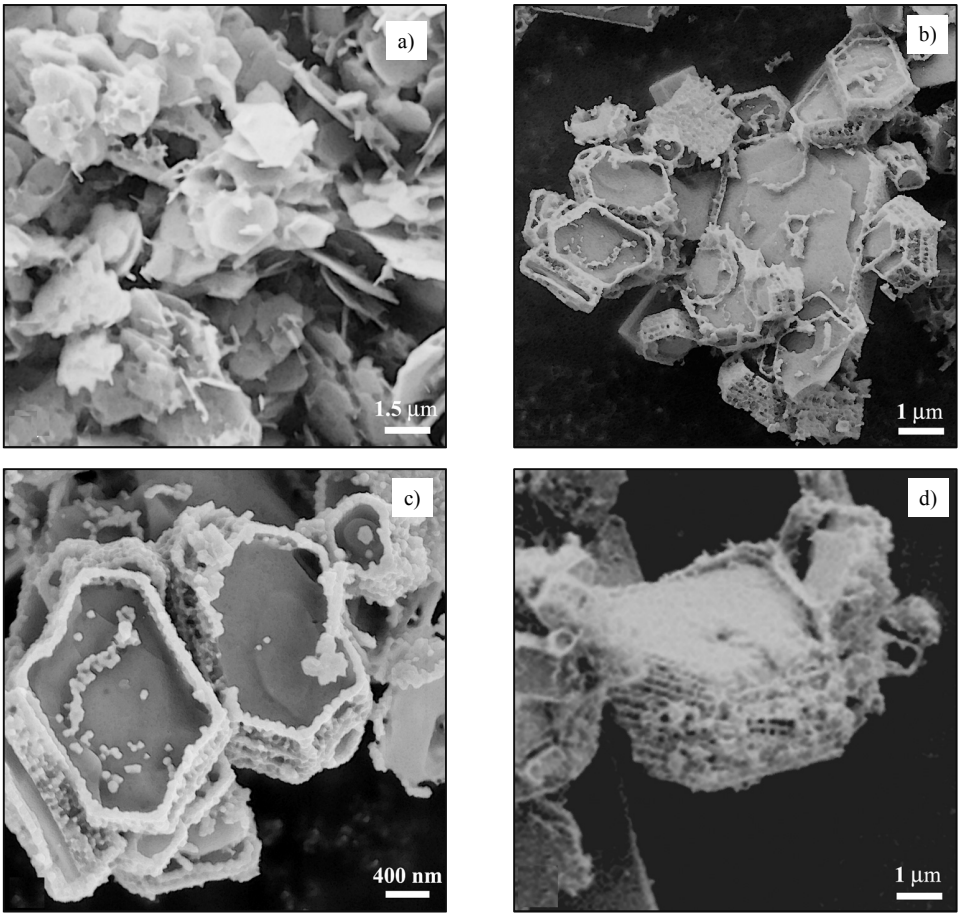

Fig. 1. FESEM images of the fabricated ZnO nanodisks (a) and the cockloft-like ZnO -- formed in morin solution with a concentration of 0.005 mol/dm^3 (b, c, and d)

Here, the synthesis of the as-prepared product was carried out hydrothermally at a relatively low temperature (95 °C) and under magnetic stirring, using zinc chloride and ammonia as the starting materials. But it was reported that the morphologies of ZnO synthesized materials produced under the same conditions usually appear as rods, tubes and particles etc., not disk like shapes. Compared with other synthesis conditions of nano ZnO, the main difference is that continuous stirring was undertaken during the hydrothermal synthesis in this paper. This implies that the dynamic growth mechanism is possibly changed by stirring. In Figure 1b, a particular structure can be clearly observed, which looks like some very regular cockloft type structure. This special structure has hexagular morphology with the diameter of 1.5–2 μm and the thickness of about 1 μm. Further details can be observed in Figure 1c, the cockloft is composed of two components: the middle part of the cockloft is a multilayer flatform made up of ZnO nanodisks and a meshlike muffle composed of morin nano particles with the diameter of about 40 nm. In every single layer of this structure, numerous morin nanoparticles, adsorbing to the fringes of the hexangular ZnO disks, quite orderly form a necklace around the multilayer ZnO flatform. Observing the profile of the outboard surface of the cockloft in Fig. 1d, there are numerous morin particles self-assembled into a nanomesh with pores of ca. 40–100 nm in diameter in a good order.

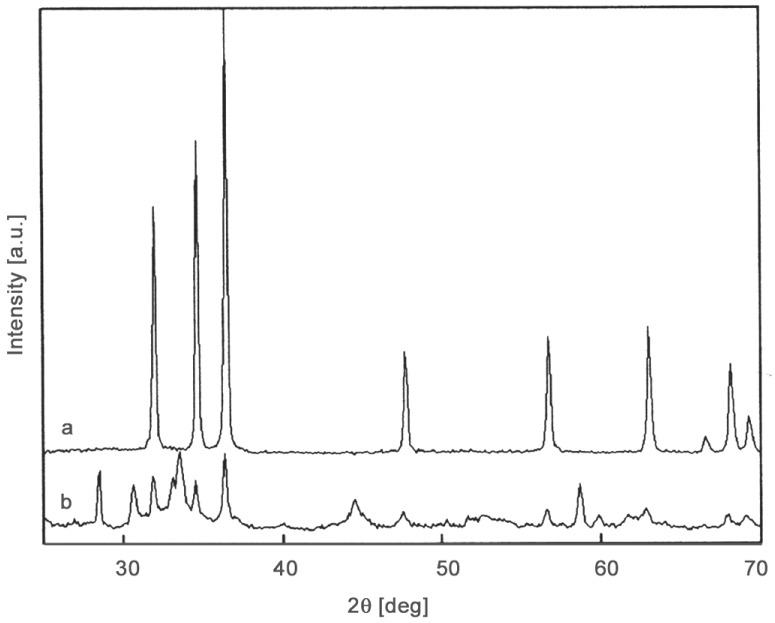

Fig. 2. XRD spectra of the fabricated ZnO nanodisks (a) and the cockloft-like ZnO formed in morin solution with a concentration of 0.005 mol/dm^3 (b)

The outstanding change of the XRD patterns of the prepared samples can be caused by the self-assembled structure of morin particle to multilayer ZnO. Except

XRD peaks at 31.84°, 34.81° and 36.33°, all XRD diffraction peaks of the multilayer ZnO in Fig. 2, spectrum a almost disappear and several peaks related to morin appear in spectrum b, due to the dispersion and the absorption of X-ray by morin particles. The XRD measurement results reflect the morphology of the ZnO multilayer masked by morin mesh in a visible manner.

Based on the results above, the assembly mechanism of morin-modified ZnO can be proposed as follows. ZnO nanodisks come out under stirring in hydrothermal system during the first step of the synthesis. In the second step, morin nanoparticles crystallized from the alcohol solution preferentially adsorb on the fringe of these nanodisks to form a laciness round ZnO nanodisks. Then, the nanodisks stack together along plane (0001) by the dipolar force of ZnO, and meanwhile morin nanoparticles belonging to the neighbouring laciness combine with each other to form a meshlike muffle. In this way, the cockloft-like ZnO/morin composite structure is achieved.

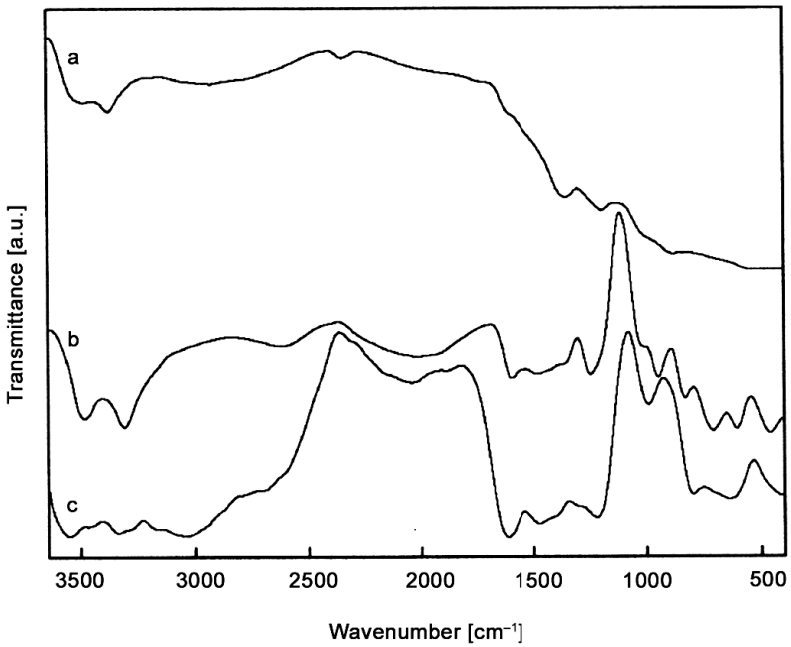

Fig. 3. FTIR transmittance spectra of the fabricated ZnO nanodisks (a), the cockloft-like ZnO formed in morin solution with a concentration of 0.005 mol/dm^3 (b) and pure morin (c)

FTIR spectra. Figure 3 shows the FTIR spectra of ZnO disks (spectrum a), morin-modified ZnO (spectrum b) and morin (spectrum c). In spectrum a, the absorption peaks of ZnO nanodisks located at 560 and 902 cm^{-1} can be attributed to the bend vibration and the stretching vibration of Zn–O, respectively. The peaks at 1196 cm^{-1} and 1340 cm^{-1} are assigned to the C–O bond of CTABr remains. The peaks at 1613 cm^{-1} and 2359 cm^{-1} are assigned to OH^- and CO_3^{2-}. The peaks at 1620, 1460 and 1216 cm^{-1} in the spectra of morin (Fig. 3, curve c) can be assigned to the C=C vibration in benzene rings and

asymmetric stretching vibration of C–O–C, respectively. The bands between 993 and 630 cm^{-1} are assigned to the stretching vibration of –C–OH [19]. Comparing the IR spectrum of ZnO nanodisks and morin with that of the as-fabricated morin modified ZnO, the bands at 993, 797 and 630 cm^{-1} disappeared with the appearance of new bonds at 951, 832, 714, 609 and 463 cm^{-1}. Weak bands at 902 and 560 cm^{-1} corresponding to Zn–O were concealed by strong ones. It implies that some new chemical bonds were formed between ZnO disks and morin particles.

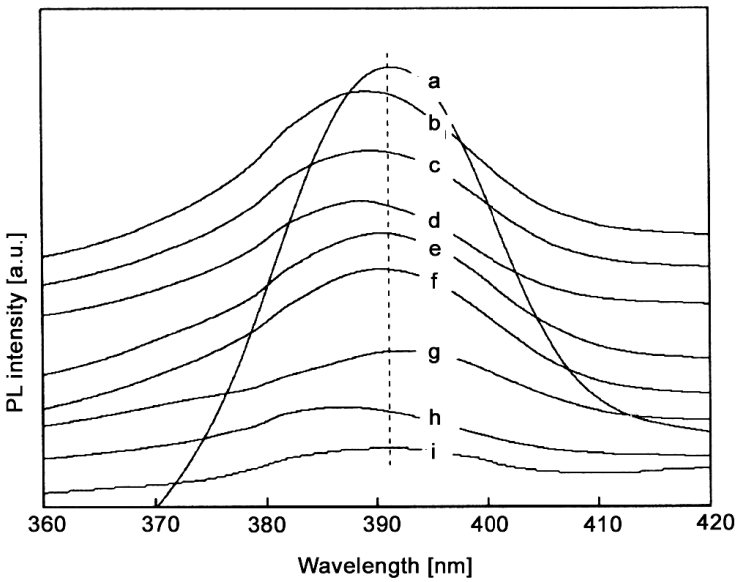

Fig. 4. Room temperature PL spectra of the fabricated ZnO nanodisks (a), the cockloft-like ZnO formed in morin solution using alcohol as the solvent with the concentration of: b) 0.003 mol/dm^3, c) 0.005 mol/dm^3, d) 0.007 mol/dm^3, e) 0.009 mol/dm^3, f) 0.011 mol/dm^3, g) 0.013 mol/dm^3, h) 0.015 mol/dm^3 and i) 0.017 mol/dm^3

PL spectra. Figure 4 shows the room temperature PL spectra of ZnO nanodisks and morin modified ZnO nanodisks. It is clearly observed that the intensity of the UV emission at about 396 nm [23, 24] evidently decreases as the dosage of morin increases in the fabrication process of the morin modified ZnO nanodisks. In general, the intensity of the UV emission of the reported morin doped inorganic oxide is usually strongly enhanced by introducing an appropriate dosage of morin into oxide [19]. Here, the attenuation of the UV emission is caused by absorption of the exciting light by morin and the emittion from nano ZnO. The fact is that ZnO particles are muffled by numerous morin particles, which reduces the intensity of the excitation light arriving at the surface of ZnO and the emission emitted from the ZnO surface. The radical of morin does not integrate into ZnO structure and does not change the energy band structure, and therefore the emission mechanism of ZnO nanodisks cannot be changed.

4. Conclusion

A well ordered structure of morin modified multilayer ZnO with a cockloft-like morphology can be successfully fabricated via a simple adsorption process in alcohol solution, using ZnO nanodisks synthesized in a hydrothermal system and morin as the precursor. The cockloft-like ZnO composite, having a wurtzite structure and a hexangular morphology with the diameter of 1.5–2 μm and the thickness of about 1 μm, is composed of two parts: a multilayer flatform stacked by numerous ZnO nanodisks in its middle and a meshlike muffle made up of a very large number of morin nanoparticles with diameters of ca. 40 nm. Comparing the IR spectrum of the ZnO nanodisks and morin with that of the as-fabricated cockloft type composite, it can be observed that the bands at 993, 797 and 630 cm^{-1} disappear with the occurrence of the new bands at 951, 832, 714, 609 and 463 cm^{-1}, which implies that some new chemical bonds are formed between ZnO disks and morin particles. The UV emission of the as-fabricated product is obviously attenuated by morin nanoparticles assembling on the surface of ZnO nanodisks.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51002183), and jointly supported by the National Natural Science Foundation of China and the Civil Aviation Administration of China (Grant No. 61079010).

References

[1] AHSANULHAQ Q., KIM S.H., HAHN Y.B., J. Phys. Chem. Solids, 70 (2009), 627.
[2] GAO H., ZHOU M.Y., JI H., WANG X.Z., ZHANG Z.G., J. Alloy Compd., 464 (2008), 234.
[3] LIN C.F., LIN H., ZHUANG D.T., LI J.B., J. Nanosci. Nanotechn., 9 (2009), 1976.
[4] ZHU H.L., YANG D.R., ZHANG H., Inorg. Mater., 42 (2006), 1210.
[5] LIU J.P., HUANG X.T., J. Solid State Chem., 179 (2006), 843.
[6] LI Y., FENG H., ZHANG N., LIU C., Mater. Sci.-Poland, 27 (2009), 551.
[7] LI Y., LIU C., ZOU Y., Chem. Pap., 63 (2009), 698.
[8] GAO P., YING C., WANG S.Q., YE L.N., GUO Q.X., XIE Y., J. Nanopart. Res., 8 (2006), 131.
[9] DJINOVIC V.M., MANCIC L.T., BOGDANOVIC G.A., VULIC P.J., ROSARIO G., SABO T.J., MILOSEVIC O.B., J. Mater. Res., 20 (2005), 102.
[10] LIU G., LI G.S., QIU X.Q., LI L.P., J. Alloy Compd., 481 (2009), 492.
[11] LUO Y.L., Colloid J., 71 (2009), 370.
[12] NTWAEABORWA O.M., KROON R.E., KUMAR V., DUBROCA T., AHN J.P., PARK J.K., SWART H.C., J. Phys. Chem. Solids, 70 (2009), 1438.
[13] ZENG Y., ZHANG T., WANG L.J., KANG M.H., FAN H.T., WANG R., HE Y., Sensor Actuat B. Chem., 140 (2009), 73.
[14] SINGHAL A., ACHARY S.N., TYAGI A.K., MANNA P.K., YUSUF S.M., Mater. Sci. Eng. B. Adv. Funct. Solid State Mater., 153 (2008), 47.
[15] WAN T., XU H., YUAN Y., HE W., J. Wuhan Univ., Tech.-Mater. Sci. Ed., 22 (2007), 466.
[16] COSTELA A., GARCÍA-MORENO I., GÓMEZ C., GARCÍA O., SASTRE R., Appl. Phys. B., Lasers Opt., 75 (2002), 827.

[17] SHEN Y., JIA R.P., LUO H.Q., CHEN X.G., XUE D.S., HU Z.D., Spectrochim Acta. A. Mol. Biomol. Spectr., 60 (2004), 1007.
[18] ZOU X.J., CUI Y.M., ZHU X.B., HU Z., CHANG X.J., J. Sol-Gel Sci. Techn., 50 (2009), 35.
[19] ZHOU Q.H., ZHANG H.M., WANG Y.Q., ZHOU X.D., Spectrochim Acta. A, 72 (2009), 110.
[20] ZENDEHDEL M., BABAEI A., ALAMI S., J. Incl. Phenom Macr., 59 (2007), 345.
[21] YANG G., CHAN S., J. Nanopart. Res., 11 (2009), 221.
[22] LIU X.L., LI Y., WANG X.Y., Mater. Lett., 60 (2006), 1943.
[23] WANG L.J., GILES N.C., J. Appl. Phys., 94 (2003), 973.
[24] WANG H.Q., WANG G.Z., JIA L.C., TANG C.J., LI G.H., J. Phys. D.Appl. Phys., 40 (2007), 6549.

Received 12 February 2010