Preparation of Size-controllable (Cu-ZnO)@C Core- and Yolk-shell Nanoparticles

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ABSTRACT

The (Cu-ZnO)@C core-shell nanoparticles were prepared by carbonization of Cu2+- and Zn2+-CD (Cu/Zn ratio=1; (Cu+Zn)/CD=3) at 573 K for 2 hrs. By X-ray absorption and diffraction spectroscopies, the major compounds in the Cu-ZnO@C core-shell nanoparticle are metallic copper (Cu) and ZnO. Cu2O is not observed. The TEM images indicate that the (Cu-ZnO)@C core-shell nanoparticle have the average Cu diameter of 20 nm, which are nearly in a spherical shape and isolated individually. After etching of Cu from the (Cu-ZnO)@C, the sizes of Cu encapsulated within the carbon-shell has reduced to 3-14 nm in diameters to form Cu-ZnO@C yolk-shell nanoparticles.

Keywords: *Size-controllable, Cu-ZnO@C, EXAFS, XANES.*

1 INTRODUCTION

ZnO is an important catalyst for catalytic reactions such as hydrogenation and partial oxidation. Zn@ZnO core-shell structures are of increasing interest because of the heterojunctions established at the interface of the composite materials [1] which enhance the optical emission, field emission, solar energy conversion [2]. The potential applications of the Zn@ZnO core-shell materials attribute to its room temperature ferromagnetism [1]. Recently, numerous elements such as Al, Mg, Co, Ni, Ga, In, Sn and Cu have been doped or alloyed into ZnO [3]. Among the elements, Cu can modify the luminescence of ZnO crystals by creating localized impurity levels. In addition, Cu behaves like an acceptor in ZnO crystals which can help to form the p-type ZnO [3].

Porous carbons impregnated with nanosize active metals possess high reactivity for catalytic reactions [4]. Carbon-coated catalysts often lose the catalytic activity over time [5]. Cu/ZnO/carbon catalysts have been used in steam reforming. Catalysts containing both Cu and ZnO have relatively high methanol conversion [5,6]. Hydrogenation of CO2 and CO to CH3OH can be catalyzed by Cu/ZnO-based catalysts. Interactions between Cu and ZnO may be associated with it high catalytic activity [7]. Cu-based catalysts have also been used in catalytic partial oxidation of methanol (POM) for H_2 fuels. The combined Cu and ZnO have a high H_2 generation reactivity for applications in fuel cells. Thus, in the present work, the Cu-ZnO@C core- and yolk-shell nanoreactors have been designed. The nanoreactor catalysts were also characterized by XRD, TEM, and XANES.

2 EXPERMENTAL

The Cu@C and (Cu-ZnO)@C core-shell nanoparticles were prepared by carbonization of Cu^{2+}- and Zn^{2+}-CD complexes having the Cu/Zn and (Cu+Zn)/CD ratios of 1 and 3, respectively at the temperature of 573 K for 2 hrs [8]. The (Cu-ZnO)@C yolk-shell nanoparticles were prepared by etching of partial Cu from the (Cu-ZnO)@C using 1 N HNO_3. The (Cu-ZnO)@ C core- and yolk-shell nanoparticles were dried at 373 K for 24 hrs, calcined in 5%O_2/N_2 (50 mL/min) at 523 K for 15 min, and reduced in 5%H_2/N_2 (50 mL/min) at 523 K for 15 min.

Chemical structures of the (Cu-ZnO)@C core- and yolk-shell nanoparticles were determined by X-ray diffraction (XRD) (D8 advance, Bruker) with a Cu Kα radiation (λ=1.542□Å). Samples were scanned using the Sol-X detector from 10 to 80° (2θ) at a scan rate of 3°/min. The images of the (Cu-ZnO)@C core- and yolk-shell nanoparticles were also determined by high resolution transmission electron microscopy (TEM) (JEOL JEM-3010).

The X-ray absorption spectra of copper in the (Cu-ZnO)@C core- and yolk-shell nanoparticles were collected on the Wiggler BL17C beam line at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The energy storage ring was operated under the energy of 1.5 GeV at top-up ring current model (300 mA). The EXAFS data were analyzed by the UWXAFS 3.0 and FEFF 8.0 simulation programs [9].

3 RESULTS AND DISCUSSION

By controlled etching of Cu from the (Cu-ZnO)@C core-shell nanoparticles, the yolk-shell nanoparticles were formed. Figure 1 shows the XRD patterns of the (Cu-ZnO)@C core- and yolk-shell nanoparticles. The broadened X-ray diffraction peaks indicates that the major compounds in the (Cu-ZnO)@C core- and yolk-shell nanoparticles are metallic copper (Cu) and ZnO. Copper oxides are not

observed. The sizes of Cu in the (Cu-ZnO)@C core- and yolk-shell nanoparticles calculated by the Scherrer equation are 20 and 7 nm in diameters respectively.

The TEM images of the (Cu-ZnO)@C core- and yolk-shell nanoparticles are shown in Figure 2. The (Cu-ZnO)@C core-shell nanoparticles having the Cu diameter of 20 nm are nearly in a spherical shape and isolated individually. After partially etching of Cu from Cu-ZnO@C, the Cu in the carbon shells having diameters of 3-14 nm is observed.

To understand oxidation states of Cu in the (Cu-ZnO)@C core- and yolk-shell nanoparticles, their XANES spectra are determined and analyzed by component fitting. The absorption edges of copper and zinc species are observed at 8979 and 9659 eV, respectively. Figure 3 shows that Cu and ZnO are the main species in the (Cu-ZnO)@C core-shell nanoparticles. After partial etching of Cu from the (Cu-ZnO)@C core-shell nanoparticles, (Cu-ZnO)@C yolk-shell nanoparticles are formed. Cu is the main copper compound in the (Cu-ZnO)@C yolk-shell nanoparticles. Copper oxides are not observed.

The EXAFS spectra of the (Cu-ZnO)@C core- and yolk-shell nanoparticles are analyzed in the k ranges of 3.5-12 Å-1. The reliability of the EXAFS data fitting for Cu in (Cu-ZnO)@C core- and yolk-shell nanoparticles is over 99%. Table 1 shows that the bond distances of the first-shell Cu-Cu in (Cu-ZnO)@C core-shell naoparticles are 2.536 Å with CNs of 3-4. After etching of Cu from the (Cu-ZnO)@C naoparticles, their Cu-Cu bond distances are reduced to 2.509-2.513 Å, and their CNs increase (Table 2).

4 CONCLUSION

The major compounds in the (Cu-ZnO)@C core-shell nanoparticles are Cu and ZnO. After controlled etching of Cu from (Cu-ZnO)@C, the sizes of Cu encapsulated in the carbon-shells can be reduced in diameter. The XANES spectra of Cu in the (Cu-ZnO)@C core- and yolk-shell nanoparticles indicate the existence of Cu and ZnO encapsulated in carbon-shell.

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REFERENCES

[1] Khan WS, Cao C, Nabi G, Yao R, Bhatti SH., " Catalyst-free combined synthesis of Zn/ZnO core/shell hollow microspheres and metallic Zn microparticles by thermal evaporation and condensation route," Journal of Alloys and Compounds, 506, 666-72, 2010.

[2] Zeng HB, Liu PS, Cai WP, Cao XL, Yang SK., "Aging-induced self-assembly of Zn/ZnO treelike nanostructures from nanoparticles and enhanced visible emission", Crystal Growth & Design, 7, 1092-1097, 2007.

[3] Wang XB, Song C, Geng KW, Zeng F, Pan F., " Photoluminescence and Raman scattering of Cu-doped ZnO films prepared by magnetron sputtering", Applied Surface Science, 253, 6905-6909, 2007.

[4] Tsoncheva T, Vankova S, Bozhkov O, Mehandjiev D., "Effect of rhenium on copper supported on activated carbon catalysts for methanol decomposition", Journal of Molecular Catalysis A: Chemical, 225, 245-51, 2005.

[5] Kudo S, Maki T, Miura K, Mae K., "High porous carbon with Cu/ZnO nanoparticles made by the pyrolysis of carbon material as a catalyst for steam reforming of methanol and dimethyl ether", Carbon, 48, 1186-1195, 2010.

[6] S. Sa, H. Silva, L. Brandão, J.M. Sousa, A. Mendes, "Catalysts for methanol steam reforming-A review", Applied Catalysis B: Environmental, 99, 43-57, 2010.

[7] Kiss J, Witt A, Meyer B, Marx D., "Methanol synthesis on ZnO(0001). I. Hydrogen coverage, charge state of oxygen vacancies, and chemical reactivity", Journal of Chemical Physics, 130, 2009.

[8] Y.M. Chiu, C.H. Huang, F.C. Chang, H.Y. Kang, H.P. Wang, "Recovery of copper from a wastewater for preparation of Cu@C nanoparticles", Sustain. Environ. Res., 21, 279-281, 2011.

[9] Stern EA, Newville M, Ravel B, Yacoby Y, Haskel D., "The UWXAFS analysis package: philosophy and details", Physica B: Condensed Matter, 208-209, 117-120, 1995.

Table 1: Speciation parameters of copper (the 1st shell of Cu-Cu) in the (Cu-ZnO)@C core- and yolk-shell nanopartcles.

Cu diameter (nm)	Core metal structure	R (Å)	CN	σ^2
20	Core-shell	2.536	3.41	0.011
14	Yolk-shell	2.509	5.6	0.013
7	Yolk-shell	2.522	5.2	0.010
3	Yolk-shell	2.513	5.2	0.020

Note: CN: Coordination Number, R: Bond distance, σ^2: Debye-Waller factor.

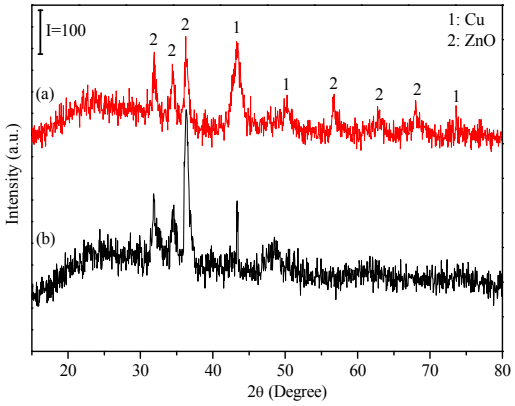

Figure 1: XRD patterns of (Cu-ZnO)@C (a) core- and (b) yolk-shell nanoparticles having the Cu sizes of 20 and 7 nm, respectively.

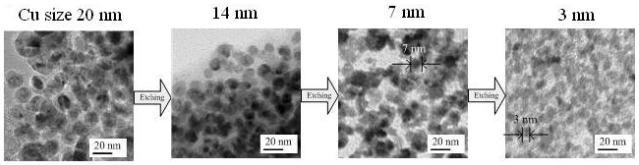

Figure 2: TEM images of the (Cu-ZnO)@C core-shell nanoparticle. The Cu size is 20 nm, and the controlled etching the Cu sizes can be reduced to 14, 7, and 3 nm, in diameter.

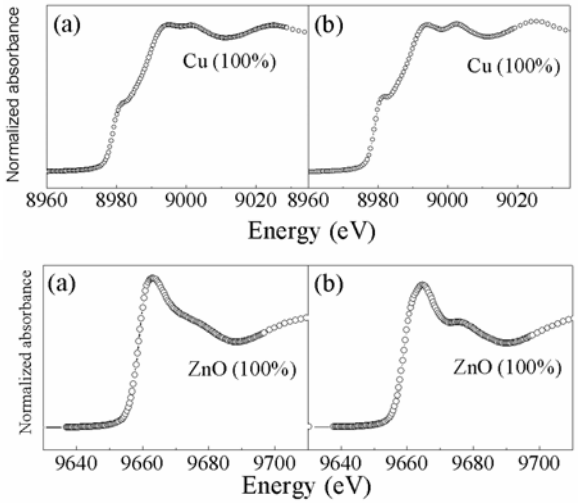

Figure 3: Component-fitted XANES spectra of (A) Cu and (B) Zn in the (Cu-ZnO)@C (a) core- and (b) yolk-shell having the Cu sizes of 20 and 7 nm, respectively.