Topotactic synthesis of mesoporous ZnS and ZnO nanoplates and their Photocatalytic Activity

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The solvothermal method using ethylenediamine as a liquid medium has been regarded as an economic and convenient route to obtain nanostructured materials [1,2]. Zinc sulfide (ZnS) is a wide-bandgap semiconductor of 3.80 eV for hexagonal wurtzite phase and of 3.66 eV for cubic zinc-blend phase. Similarly ZnO is one of the most important functional oxides for optoelectronics and photocatalysis due to its bandgap energy of 3.20 eV. Its potential applications were demonstrated as nanosized sensors and field-effect transistors based on ZnO nanobelts, and for photocatalytic degradation of organic dyes [3]. A few studies have recently been done to fabricate nanostructured ZnS and ZnO with high surface-to-volume ratios for improved performance. It is interesting to note the result of Hue et al. that nanoporous ZnS nanoparticles prepared via a low-cost and self-assembly route, can have high ratio of surface to volume and aggregation of nanoparticles during photocatalytic reaction of dyes [4]. Nevertheless the fabrication of porous ZnS and ZnO platelets has not been reported yet.

In this contribution we prepared the $ZnS(en)_{0.5}$ complex precursor by solvothermal routes using ethylenediamine as a single solvent and obtained porous ZnS and ZnO nanoplates through thermal treatment of the complex. In particular, the local structures confined in the platelets were elucidated with synchrotron radiation techniques of powder XRD and XAFS. Photocatalytic water splitting and photocatalytic degradation of organic dye were performed in order to measure the catalytic performance of the synthesized ZnS(en)_{0.5} complex and its derivatives.



Fig. 1. Zn K-edge XANES spectra of the ZnS(en)_{0.5}, its calcined derivatives, and reference materials: (A) (a) ZnS(en)_{0.5}, (b) Zn400, (c) Zn500, and (d) bulk ZnS, and (B) (a) Zn550, (b) Zn600, and (c) bulk ZnO. Inset plots are their respective Fourier-transformed RSF spectra.

Fig. 1A displays Zn K-edge XANES of ZnS(en)0.5 (a), Zn400 (b), Zn500 (c), and bulk ZnS (d). We found that the XANES features of Zn400 and Zn500 are closer to those of

ZnS(en)0.5, rather than those of bulk ZnS. On the other hand, Fig. 1B shows that the Zn K-edge XANES spectra of grains produced by calcinations at 550 and 600 $\,^{\circ}$ C are almost the same as that of bulk ZnO.

^[1] J. S. Hu, L. L. Ren, Y. G. Guo, H. P. Liang, A. M. Cao, L. J. Wan and C. L. Bai, Angew. Chem. Int. Ed. 44, 1269 (2005).

^[2] S.H. Yu and M. Yoshimura, Adv. Mater. 14, 296 (2002).