XAFS Study on Ag$_2$S Semiconductor Clusters Designed in Nanopores and Their Photoluminescence Properties

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Abstract. Ag$_2$S clusters were prepared in microporous ZSM-5 and mesoporous AlMCM-41. The state of Ag was analyzed by EXAFS. The pore size of the host has great effects on the photoluminescence property of Ag$_2$S. Compared with Ag$_2$S/ ZSM-5, the emission of Ag$_2$S/ AlMCM-41 shifts to the longer wavelength region.

Keywords: Ag$_2$S cluster, micropore, mesopore, EXAFS, photoluminescence.

PACS: 78.55.Mb

INTRODUCTION

Silver sulfide (Ag$_2$S) possesses sensitivity in a broad range of wavelengths and wide applications as photoelectric materials [1-3]. As the sizes decrease to nano-scale, semiconductor particles will demonstrate new photophysical and photochemical properties different from bulk [4]. However, the quantum-sized clusters or particles are not stable. Using the well-defined micro cavities of zeolite, Ag$_2$S could be highly dispersed in zeolite and show unique photoluminescence properties [5-8]. The structures of the hosts may have different effects on the photoluminescence properties of semiconductor clusters. In this study, Ag$_2$S clusters were synthesized in zeolites with microporous structure and AlMCM-41 with mesopores larger than zeolite micropores.

EXPERIMENTAL SECTION

A typical procedure is as follows. AgNO$_3$, NH$_4$NO$_3$ and NH$_4$OH (28 wt%) were dissolved in deionized water. Then NH$_4$ZSM-5 (Si: Al=35.5: 1) was added to the solution. After stirred in the dark for 24 h, the ion-exchanged product was obtained by centrifugal separation. The product was washed by deionized water and dried at 383 K for 24 h. The obtained grayish powder was noted as Ag$_2$S/ZSM-5(Si/Al=72). For the synthesis of AlMCM-41, at first, C$_{16}$H$_{33}$(CH$_3$)$_3$NBr (CTAB) was solved in the NH$_3$·H$_2$O solution, then Ti(OEt)$_4$ and Al(NO$_3$)$_3$ were added in sequence under stirring. The mole ratio was Si:Al:CTAB: NH$_3$:H$_2$O=1:0.02:0.12:8.6:82. After 3 h, the gel was transferred into an autoclave and kept at 393 K for 48 h. After filtering, washing, drying and calcination, AlMCM-41 was obtained. Ag$_2$S/AlMCM-41(Si/Al=50) was prepared by the same procedure.

Photoluminescence measurements were carried out using an F-4500 fluorescence spectrophotometer (Hitachi) at 77 K. XAFS spectra for Ag K-edge absorption were measured in the transmission mode at BL01B1 line of Spring-8 [9-10]. Fourier transformations were performed on $k^2$-weighted EXAFS oscillations $k^2\chi(k)$, in the range of 0.3-1.4 nm$^{-1}$ for the Ag$_2$S/zeolite samples.

RESULTS AND DISCUSSION

Ag$_2$S Clusters in Micropores

The Ag$_2$S clusters were prepared in zeolite ZSM-5 by the reaction of Ag$^+$ ion exchanged ZSM-5 and Na$_2$S aqueous solution. The maximum diameter of a sphere
that can be included in the framework of ZSM-5 is about 0.63 nm. The growth of Ag$_2$S clusters was restricted by the framework of ZSM-5.

**FT-EXAFS SPECTRA OF Ag$_2$S IN ZEOLITE**

Figure 1 shows the FT-EXAFS for Ag$_2$S fine particles and Ag$_2$S/ZSM-5. From comparison with the Ag K-edge EXAFS spectrum of reference Ag$_2$S semiconductor particles, the peaks at around 2.0 and 2.8 Å can be assigned to the neighboring S and Ag atoms, respectively. All zeolite samples having the different Ag content exhibited almost similar spectra. These results indicate that the Ag$^+$ ions in zeolite cavities transformed into Ag$_2$S nanoparticles after the sulfurization.

**FIGURE 1.** Fourier transform of Ag K-edge EXAFS for the reference Ag$_2$S fine particles (Top) and the Ag$_2$S/ZSM-5 (Bottom).

**PHOTOLUMINESCENCE SPECTRA OF Ag$_2$S IN ZEOLITE**

The photoluminescence spectra of Ag$_2$S/ZSM-5 are shown in Figure 2. The photoluminescence peaks of Ag$_2$S/ZSM-5 were observed at the shorter wavelength regions than that of Ag$_2$S without support. The photoluminescence peaks of Ag$_2$S/ZSM-5 prepared with the higher Ag$^+$ concentration shifts to the longer wavelength regions and becomes broader, which may be caused by the formation of larger Ag$_2$S clusters with various sizes.

**FIGURE 2.** Photoluminescence spectra of Ag$_2$S/ZSM-5-0.2 (Ag$^+$ concentration 0.2 mol·l$^{-1}$), Ag$_2$S/ZSM-5-0.5 (Ag$^+$ concentration 0.5 mol·l$^{-1}$) at 77 K by excitation at 460 nm.

**Ag$_2$S Clusters in Mesopores**

Mesoporous silica AlMCM-41 has 1-dimension pores with diameter about 3 nm. Ag$_2$S cluster can grow larger in mesopores than in micropores, which may result in different photoluminescence properties.

**FT-EXAFS SPECTRA OF Ag$_2$S IN AlMCM-41**

Figure 3 shows the FT-EXAFS for Ag$^{+}$/AlMCM-41 and Ag$_2$S/AlMCM-41. After ion exchange, the peak at about 1.7 Å observed with Ag$^{+}$/AlMCM-41 can be assigned to the neighboring O atoms. On the other hand, the presence of reduced Ag species is not observed. After reaction with Na$_2$S the main peak is shift to 2.0 Å, which means Ag$_2$S cluster is formed.
It is known that semiconductor quantum dots exhibit size-dependent photoluminescence. The broad distribution of emission indicates that the Ag$_2$S particle size varies in a wide range in AlMCM-41.

CONCLUSION

FT-EXAFS data reveal that Ag$_2$S clusters or nanoparticles can be synthesized by the reaction of Ag$^+$ ion exchanged porous materials with Na$_2$S solution. Micropores and mesopores control the size of Ag$_2$S, which results in different photoluminescence properties. The photoluminescence properties of Ag$_2$S in porous materials can be controlled by changing the pore sizes of hosts.

ACKNOWLEDGEMENTS

The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area “Molecular Nan Dynamics” from Ministry of Education, Culture, Sports, Science and Technology (No. 17360388), (No.1734036) & (No. 18656238). The X-ray adsorption experiments were performed at the Spring-8 (2006A1278-NXa-np). This work is partly performed under the project of collaborative research at the Joining and Welding Research Institute (JWRI) of Osaka University.

REFERENCES