In situ Synthesis of Ag_2S Nanosized Particles in Porous Materials Using Single-source Precursor

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Ag_2S nanoparticles were synthesized in situ by thermal decomposition of a single-source precursor (SSP, silver diethyldithiocarbamate) in the pores of porous Vycor glass (PVG). The precursor was incorporated into PVG by sublimation or impregnation of a solution of the precursor. The band gaps of Ag_2S in PVGs were estimated to be 1.63 and 1.43 eV for the samples prepared by the decomposition of the precursor incorporated by these two methods, indicating occurrence of quantum size effect in the nanoparticles.

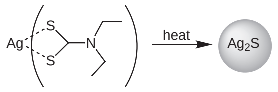
Recently, interests in nanohybrid chemistry has been growing because organic–inorganic nanohybrids have potentials giving properties which are much superior to those of the individual components.[1–4] Ag_2S semiconductor has been an attractive target of research because of its applicability to optical and electronic devices such as photovoltaic cells, IR detectors, and superionic conductors.[5–7] However, size control of Ag_2S nanoparticles is difficult because Ag_2S nanoparticles readily aggregate into bulk.[8]

We have selected porous Vycor glass (PVG, Corning 7930) as a transparent host having nm-order pores. PVG is an inorganic host that can be used to encapsulate some nanocomposites with a variety of materials, such as semiconductor, oxides, and polymers. PVG possesses a porous structure of essentially pure silica with interconnecting pore diameter 4 nm, and pore volume of about 28%.[9,10] Here, we demonstrate two methods for incorporating Ag_2S nanosized particles into the pores of PVG suppressing the aggregation of Ag_2S nanoparticles into bulk.

In this paper, we have employed a single-source precursor (SSP),[11] silver diethyldithiocarbamate [$Ag(S_2CNEt_2)$], and introduced it into the pores by the following two techniques, vapor phase introduction by sublimation (-VPI) and liquid-phase introduction by impregnation in the solution (-LPI).[12–14]

[$Ag(S_2CNEt_2)$] was purchased from Aldrich. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer Multiflex using monochrometer Cu Kα radiation. The measurements were carried out in air at room temperature at the conditions; accelerating voltage and filament current for X-ray source 40 kW/40 mA, scan speed 3°/min, and sampling width 0.1°. Thermogravimetry (TG) was carried out with a TGA-50 (Shimadzu). UV–visible spectra were recorded with V-570 (JASCO) in the range 200–1400 nm with a resolution of 2 nm. The amounts of Ag incorporated in PVG were determined by ICP analysis (inductively coupled plasma) (JOBIN YVON, ULTIMA2).

[$Ag(S_2CNEt_2)$] was sealed in a glass tube under vacuum. Then the tube containing the precursor was heated at 400 °C for 1 h to produce Ag_2S nanoparticles (Scheme 1). The inner pressure of the tube should be less than 1 atm in the process of decomposition of the precursor by limiting the feeding amount of the precursor. The resulting product was characterized by XRD. The XRD spectrum of the sample is shown in Figure 1. The diffraction peaks observed at $2\theta = 26.3$, 29.0, 31.5, 34.4, 36.6, 37.7, 40.7, 43.4, and 53.3° were assigned to the diffraction peaks of Ag_2S: the (012), (111), $(\bar{1}12)$, $(\bar{1}21)$, (112), $(\bar{1}03)$, (031), (200), and $(\bar{2}13)$ planes.[15,16] The average particle size of the sample was calculated by the Scherer equation from the XRD spectrum, and was found to be 60 nm. TG spectrum of [$Ag(S_2CNEt_2)$] is shown in Figure S1 (See: Supporting Information). The TG curve exhibited weight loss of 50% at 220–300 °C. These results indicated that [$Ag(S_2CNEt_2)$] can be converted to Ag_2S nanoparticles by thermal decomposition under vaccum.[17]



Scheme 1. Synthesis of Ag_2S nanoparticles from a precursor of silver diethyldithiocarbamate [$Ag(S_2CNEt_2)$].

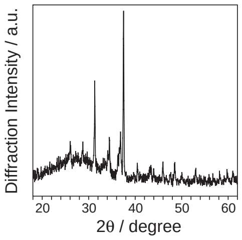


Figure 1. XRD pattern of Ag_2S nanoparticles synthesized by thermal decomposition of [$Ag(S_2CNEt_2)$] in a glass tube under vacuum.

Therefore, it can be rationally considered that Ag_2S nanoparticles can be synthesized in the pores of PVG by decomposing the precursor after being incorporated in the pores of PVG. For VPI, PVG, and [$Ag(S_2CNEt_2)$] (0.05 g) were placed in a glass tube as shown in Figure 2. Here, the amount of the precursor was low enough to ensure that the inner pressure of the tube

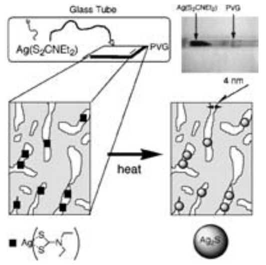


Figure 2. Schematic procedure for in situ synthesis of Ag_2S nanoparticles in a PVG for the case of VPI.

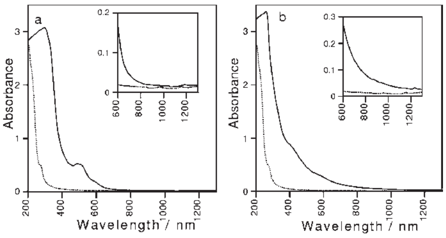


Figure 3. Absorption spectra of Ag_2S/PVG-VPI (solid line), PVG (dotted line) (a), and Ag_2S/PVG-LPI (solid line), PVG (dotted line) (b) measured at room temperature. Inset: enlarged absorption spectra of the two samples.

does not exceed 1 atm in the process of the decomposition. After degassing the tube at 100 °C for 1 h, the tube was sealed under vacuum and then heated at 400 °C for 1 h. For LPI, a piece of PVG ($5 \times 30 \times 1.1\,mm^3$) was immersed in a CH_3Cl solution of 0.0007 g/L of [$Ag(S_2CNEt_2)$] for 0.5 h. After drying the PVG, the piece of PVG sample was sealed in a glass tube under vacuum and then the glass tube was heated at 400 °C for 1 h under vacuum.

The absorption spectra of the PVGs incorporating Ag_2S prepared by VPI method (Ag_2S/PVG-VPI) and by LPI method (Ag_2S/PVG-LPI) are shown in Figures 3a and 3b, respectively. Considering no peaks of PVG in the visible region, the broad peak (600–900 nm) observed for the Ag_2S/PVG should be attributed to Ag_2S nanoparticles incorporated in the pores. The absorption spectrum of [$Ag(S_2CNEt_2)$] incorporated in PVG by the LPI method before the thermal decomposition is shown in Figure 4. The absorption spectra of Ag_2S/PVG-VPI and Ag_2S/PVG-LPI (Figure 3) were different from that of [$Ag(S_2CNEt_2)$] in PVG shown in Figure 4, indicating the conversion of the precursor to Ag_2S nanoparticles. The approximate absorption edges of the Ag_2S/PVG-VPI and Ag_2S/PVG-LPI were 760 and 840 nm, respectively, indicating occurrence of quantum size effect in the Ag_2S nanoparticles. The band gap can be estimated by Tauc's expression, which is written as

$$(\alpha h\nu)^2 = C(h\nu - E), \tag{1}$$

where α is the absorption coefficient of the materials, ν is the frequency of the light, and E is the bandgap. Then the absorption edges of the present samples gave the band gaps estimated to be 1.63 eV (Ag_2S/PVG-VPI) and 1.47 eV (Ag_2S/PVG-LPI). A large bandgap in comparison to bulk Ag_2S (0.92 eV) observed here demonstrated that the particle sizes of the Ag_2S/PVG-VPI and the Ag_2S/PVG-LPI were smaller than that of bulk Ag_2S, and furthermore the size of the nanoparticles in the Ag_2S/PVG-VPI was smaller than that of Ag_2S/PVG-LPI.[18,19] The large particle size of the Ag_2S/PVG-LPI compared with that of the Ag_2S/PVG-VPI should be caused by the aggregation of the precursor, [$Ag(S_2CNEt_2)$], at the time of evaporation of the solvent after being immersed in [$Ag(S_2CNEt_2)$]/CH_3Cl.

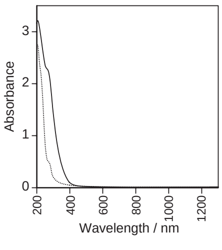


Figure 4. Absorption spectra of [$Ag(S_2CNEt_2)$] introduced into the pores of PVG by liquid phase introduction (solid line) and PVG (dotted line).

The absorption bands around 500 nm would be attributed to organic residues produced by thermal decomposition of the precursor.

The amounts of the Ag_2S nanoparticles in PVG were estimated to be 0.0015 g per g of PVG for Ag_2S/PVG-VPI, and to be 0.021 g per g of PVG for Ag_2S/PVG-LPI.

In conclusion, Ag_2S nanoparticles were synthesized in situ by thermal decomposition of a single-source precursor in the pores of PVG. The precursor of silver diethyldithiocarbamate ([$Ag(S_2CNEt_2)$]) was deposited on PVG using the vapor-phase introduction (-VPI) and liquid-phase introduction (-LPI). Both methods have different advantages: VPI method enables ones to prepare smaller size of Ag_2S nanoparticles compared with LPI method. On the other hand, LPI method leads to introduction of much amount of Ag_2S nanoparticles in PVG compared with VPI method. The methods using single-source precursor described in this paper would open a new methodology for nanohybrid chemistry.

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References

1 M. Behboudnia and P. Sen, *Phys. Rev. B*, **63**, 35316 (2001).
2 H. Tang, G. Xu, L. Weng, L. Pan, and L. Wang, *Acta Mater.*, **52**, 1489 (2004).
3 H.-Y. Lu, S.-Y. Chu, and S.-S. Tan, *J. Cryst. Growth*, **269**, 385 (2004).
4 F. J. Manjon, M. Mollar, B. Mani, N. Garro, A. Cantarero, R. Lauck, and M. Cardona, *Solid State Commun.*, **133**, 253 (2005).
5 K. Akamatsu, S. Takei, M. Mizuhata, A. Kajinami, S. Deki, S. Takeoka, M. Fujii, S. Hayashida, and K. Yamamoto, *Thin Solid Films*, **359**, 55 (2000).
6 K. Rajeshwar, N. R. de Tacconi, and C. R. Chenthamarakshan, *Chem. Mater.*, **13**, 2765 (2001).
7 J. Z. Zhang, *J. Phys. Chem. B*, **104**, 7239 (2000).
8 F. Gao, Q. Lu, and D. Zhao, *Nano Lett.*, **3**, 85 (2003).
9 O. C. Monteiro, A. Catarina, C. Esteves, and T. Trindade, *Chem. Mater.*, **14**, 2900 (2002).
10 L. Armelao, P. Colombo, M. Fabrizio, S. Grossd, and E. Tondello, *J. Mater. Chem.*, **9**, 2893 (1999).
11 P. O'Brien and R. Nomura, *J. Mater. Chem.*, **5**, 1761 (1995).
12 N. H. Tran, R. N. Lamb, and G. L. Mar, *Colloids Surf., A*, **155**, 93 (1999).
13 M. A. Malik, N. Revaprasadu, and P. O'Brien, *Chem. Mater.*, **13**, 913 (2001).
14 N. Revaprasadu, M. A. Malik, P. O'Brien, and G. Wakefield, *J. Mater. Res.*, **14**, 3237 (1999).
15 X. Changqi, Z. Zhicheng, and Y. Qiang, *Mater. Lett.*, **58**, 1671 (2004).
16 M. C. D. Silva, M. M. Conceição, M. F. S. Trindade, A. G. Souza, C. D. Pinheiro, J. C. Machado, and P. F. A. Filho, *J. Therm. Anal. Calorim.*, **75**, 583 (2004).
17 S. H. Liu, X. F. Qian, J. Yin, L. Hong, X. L. Wang, and Z. K. Zhu, *J. Solid State Chem.*, **168**, 259 (2002).
18 Y. Xu and M. A. A. Schoonen, *Am. Mineral.*, **85**, 543 (2000).
19 A. I. Kryukov, N. N. Zinı́chuk, A. V. Korzhak, and S. Y. Kuchmii, *Theor. Exp. Chem.*, **37**, 296 (2001).

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