3-D Ordered Mesoporous Cd_{x}Zn_{1-x}S Ternary Compound Semiconductors with Controlled Band Gap Energy

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Ordered mesoporous Cd_{x}Zn_{1-x}S ternary compound semiconductors were prepared with a simple nano-casting method using 3-D cubic la3d meso-structured silica, KIT-6, as a hard-template with the easily available precursors of 3CdSO_{4}, 8H_{2}O and ZnSO_{4}, 7H_{2}O. Thermal reduction of impregnated precursors resulted in the crystalline networks within the mesopore of the silica template, then the ordered mesoporous Cd_{x}Zn_{1-x}S materials were obtained by etching the silica template with NaOH aqueous solution. The synthesized Cd_{x}Zn_{1-x}S materials exhibit high surface area, uniform pore size, single gyroidal tetragonal I_{4}/a meso-structure, crystalline framework, and finely tuned band gap energies by controlled chemical composition.

Keywords: Mesoporous Cd_{x}Zn_{1-x}S, Compound Semiconductor, Nano-Casting, Band Gap.

1. INTRODUCTION

Since the first report of the synthesis of silica-based ordered mesoporous materials by scientists at Mobil, great interest has arisen in this research area.1,2 The ordered mesoporous materials with carbon, inorganic, and organic–inorganic hybrid frameworks have been widely investigated for application in the fields of adsorbent, catalysis and energy devices, due to their high surface area, uniform pore size and long-range ordered meso-structures.3–8 Because the high surface area offers a huge number of reaction sites, the mesoporous materials have gained much attention as adsorbents and catalysts.3,9 Among them, mesoporous materials with silica, carbon or metal oxide frameworks have been the main focus of a large number of papers reported to date. However, due to the lack of suitable precursors, there have only been a few examples of the synthesis and application of ordered mesoporous compound semiconductor.10

The nano-structured II–VI compound semiconductors, such as ZnX, and CdX (X = S, Se, Te), are important semiconductor material due to their outstanding optical and catalytic properties.11–13 Ordered mesoporous semiconductors are especially attractive due to their band gap tenability, achieved through framework size control.14 Due to the fact that semiconducting properties are mainly affected by band gap energy, the band gap engineering of the material is very important, therefore, band gap tunability has a considerable impact on applications such as in solar cells, photodetectors, or light emitting diodes.

In this work, we report the synthesis of 3-D ordered mesoporous Cd_{x}Zn_{1-x}S via a nano-casting method using a KIT-6 silica template with various molar ratios of the metal precursor. The template-free mesoporous Cd_{x}Zn_{1-x}S materials thus obtained exhibited finely controlled band gap energies by the variation of metal molar composition.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Mesoporous Silica Template KIT-6

The mesoporous silica template KIT-6 was synthesized following the published method with simple modifications.15 First, 30 g of Pluronic triblock copolymer P123 (Aldrich, EO_{20}PO_{70}EO_{20}, M_{w} = 5800) was dissolved in a mixed solvent of 30 g of n-butanol (Aldrich, anhydrous, 99%), 59 g of HCl (Samchun Chemical, 35–37%) and 1085 g of distilled water. After the dissolving process, the clear polymer solution was put into a water bath at 35 °C and strongly stirred for 3 h to reach thermal equilibrium. After thermal equilibrium was reached, 64.5 g of tetraethyl orthosilicate (Samchun Chemical, 98%) was added, and the solution was vigorously stirred at 35 °C for
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24 h. Subsequently, this reaction mixture was hydrothermally treated at 100 °C for 24 h, then precipitates were filtered, dried and washed with water and ethanol. Afterwards, the P123 polymer removal process was carried out by calcination at 550 °C for 3 h in air, to obtain the ordered mesoporous silica KIT-6.

2.2. Synthesis of Mesoporous Cd\textsubscript{x}Zn\textsubscript{1−x}S Material

Cadmium sulfate (3CdSO\textsubscript{4}·8H\textsubscript{2}O, Sigma-Aldrich, ACS reagent, ≥99.0%) and zinc sulfate (ZnSO\textsubscript{4}·7H\textsubscript{2}O, Aldrich, 99%) were used as received. For synthesizing the mesoporous CdS and/or ZnS, 2.28 g of 3CdSO\textsubscript{4}·8H\textsubscript{2}O or 3.80 g of ZnSO\textsubscript{4}·7H\textsubscript{2}O were dissolved in 3.0 g of distilled water, respectively, and this solution was impregnated into the mesopore of KIT-6 silica template (3.0 g) by the incipient-wetness method. After the drying process, the composites were reduced at 500 °C for 3 h under H\textsubscript{2} flow (20 cm\textsuperscript{3}·min\textsuperscript{−1}) for crystallization of the material. In the cases of mesoporous CdS and Cd\textsubscript{y}Zn\textsubscript{1−y}S materials, the reduction process was carried out for 2 h due to differences in crystallization. Afterwards, etching the silica template by 2 M NaOH aqueous solution treatment produced the mesoporous CdS and/or ZnS materials. The mesoporous Cd\textsubscript{y}Zn\textsubscript{1−y}S materials were synthesized with same procedures above, with controlled molar ratios of the precursor reagents.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV instrument equipped with Cu K\textsubscript{α} radiation operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) images were taken using a JEOL JEM 3010 instrument at an accelerating voltage of 300 kV. Nitrogen sorption isotherms were measured with a Micromeritics Tristar 3000 at liquid N\textsubscript{2} temperature, and the diffuse reflectance UV-visible spectra were obtained with a Shimadzu UV-3600 spectrometer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Mesoporous Silica Template KIT-6

The highly ordered cubic Ia\textit{3d} meso-structures of synthesized KIT-6 silica template could be confirmed by the low angle XRD pattern in Figure 1(A). There are several diffraction peaks of the Ia\textit{3d} space group appearing in the range lower than 2°, corresponding to (211), (220), (420), and (332), respectively. Figure 1(B) shows the nitrogen adsorption−desorption isotherms and the corresponding BJH pore size distribution curve from the adsorption branch. As shown by the sorption isotherms, the KIT-6 material has a type-IV hysteresis loop in the range of \( p/p_0 = 0.65−0.75 \) that is uniquely characteristic to mesoporous material. Also, the KIT-6 material exhibits a very high specific BET surface area of 689 m\textsuperscript{2}·g\textsuperscript{−1}, a large total pore volume of 0.78 cm\textsuperscript{3}·g\textsuperscript{−1}, and a very uniform pore size of 7.3 nm.

3.2. Mesoporous Cd\textsubscript{x}Zn\textsubscript{1−x}S Materials

\( N_2 \) adsorption−desorption isotherms of the mesoporous Cd\textsubscript{x}Zn\textsubscript{1−x}S materials are shown in Figure 2. All of the replicated materials show a type-IV hysteresis loop in the range of \( p/p_0 = 0.8−1.0 \), and BJH pore sizes of about 20 nm achieved from adsorption branches (inset of Fig. 2) are very similar to each other, despite of the differences in composition. The 20 nm pore is much larger than the wall thickness of the silica template (3.9 nm). It is well-known that the large pores are generated when microporous linker channel between two chiral pore systems of KIT-6 silica is broken, resulting in single gyroid structures with meso-phase transformation from the cubic Ia\textit{3d} silica template to a lower symmetry in the replica. Thus, the replicated mesoporous Cd\textsubscript{x}Zn\textsubscript{1−x}S materials have high BET surface areas and large pore volumes (Table I).

As depicted in Figure 3(A), all the low-angle XRD patterns of the mesoporous Cd\textsubscript{x}Zn\textsubscript{1−x}S materials are quite...
different from the diffraction pattern of the KIT-6 silica template. A new (110) peak appears in the lower angle region, which indicates the meso-structure transformation from cubic Ia3d to tetragonal I4/a, or the lower space group of the resulting mesoporous Cd_{x}Zn_{1-x}S materials after the silica template etching process. This is why the Cd_{x}Zn_{1-x}S frameworks are only crystallized in one of the two chiral pore systems of KIT-6 silica. This meso-phase transformation has also been observed in the synthesis of mesoporous carbons and metal oxides from 3-D Ia3d meso-structured silica templates such as KIT-6 or MCM-48,16,18 Thus, meso-phase transformation supports the generation of large pore size after silica removal.

The developed crystalline frameworks of the synthesized mesoporous Cd_{x}Zn_{1-x}S materials could be confirmed from the wide-angle XRD patterns in Figure 3(B). As shown in Figure 3(B) ((a) and (g)), the mesoporous CdS and ZnS have wurtzite hexagonal P6_mmc and zinc blende cubic F-43m crystal structures, respectively. The lattice parameters calculated from wide angle XRD patterns of CdS (a = 4.135 Å, c = 6.713 Å) and ZnS (a = 5.403 Å) totally match with the reference values from the JCPDS card (#77-2306, hexagonal P6_mmc CdS, a = 4.136 Å, c = 6.713 Å; #65-5476, cubic F-43m ZnS, a = 5.404 Å). The mesoporous CdS has sharper diffraction peaks than ZnS, indicating the crystallite size of CdS is larger than ZnS. The crystallite size of CdS calculated by Scherrer’s formula is about 13 nm that is larger than the mesopore size of the KIT-6 silica template (7.3 nm). It is suspected that the crystallization process of CdS occurred outside the silica mesopore, so meso-structures collapsed after the silica template removal process, resulting in no specific diffraction peaks in the low-angle XRD pattern in Figure 3(A) (a).

In contrast, the mesoporous ZnS has a crystallite size of about 5 nm, smaller than mesopore of silica, suggesting that the ZnS species are crystallized in silica pores, forming an ordered meso-structured network. As a result, the replicated ZnS shows several diffraction peaks in the low angle region (Fig. 3(A) (g)). The crystal phase of Cd rich (x = 0.5–0.9) materials are similar to that of wurtzite CdS, and Zn rich (x = 0.3–0.1) materials are similar to the zinc blende ZnS. Thus, the diffraction peaks of mesoporous Cd_{x}Zn_{1-x}S gradually shift with the changes in the molar ratio of Cd and Zn, due to the atomic size difference of the two.

The highly ordered meso-structure and very uniform pore sizes with amorphous framework were represented in Figure 4(A). In contrast with the KIT-6 silica template, mesoporous CdS exhibits disordered meso-structures with developed crystalline framework, as shown in Figure 4(B). The disordered meso-structures are in good agreement

**Table I.** Physical properties of the materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m^{2} g^{-1})</th>
<th>V_{m} (cm^{3} g^{-1})</th>
<th>D_{p} (nm)</th>
<th>E_{g} (eV)</th>
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<tbody>
<tr>
<td>KIT-6</td>
<td>689.0</td>
<td>0.78</td>
<td>7.3</td>
<td>–</td>
</tr>
<tr>
<td>CdS</td>
<td>81.2</td>
<td>0.38</td>
<td>18.3</td>
<td>2.43</td>
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<tr>
<td>Cd_{x}Zn_{1-x}S</td>
<td>85.1</td>
<td>0.38</td>
<td>21.7</td>
<td>2.47</td>
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<tr>
<td>Cd_{x}Zn_{1-x}S</td>
<td>79.8</td>
<td>0.32</td>
<td>18.0</td>
<td>2.61</td>
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<tr>
<td>Cd_{x}Zn_{1-x}S</td>
<td>102.9</td>
<td>0.67</td>
<td>19.7</td>
<td>2.78</td>
</tr>
<tr>
<td>Cd_{x}Zn_{1-x}S</td>
<td>131.8</td>
<td>0.65</td>
<td>20.1</td>
<td>3.10</td>
</tr>
<tr>
<td>Cd_{x}Zn_{1-x}S</td>
<td>119.8</td>
<td>0.93</td>
<td>19.7</td>
<td>3.47</td>
</tr>
<tr>
<td>ZnS</td>
<td>123.7</td>
<td>0.82</td>
<td>19.6</td>
<td>3.64</td>
</tr>
</tbody>
</table>

**Notes:** aSurface areas were calculated by BET method; bTotal pore volumes were estimated at p/p_{0} = 0.99; cPore sizes were calculated by using the BJH method; dBand gap energies were estimated from the Kubelka-Munk plots.

**Figure 3.** (A) Low and (B) wide angle XRD patterns of mesoporous Cd_{x}Zn_{1-x}S materials, where x is equal to (a) 1.0 (CdS), (b) 0.9, (c) 0.7, (d) 0.5, (e) 0.3, (f) 0.1, and (g) 0.0 (ZnS), respectively. The symbols (■) and * indicate hexagonal CdS (#77-2306) and cubic ZnS (#65-5476).

**Figure 4.** TEM (a) and HR-TEM (b), (c) images of the mesoporous materials. (A) KIT-6 silica template, mesoporous (B) CdS, (C) Cd_{x}Zn_{1-x}S and (D) ZnS.
with the low-angle XRD pattern of CdS in Figure 3(A) (a). Thus, the HR-TEM image of CdS in Figure 4(B) (c) indicates the (101) plane of the crystallite, supporting the developed crystal structure which was expected from the wide angle pattern (Fig. 3(B) (a)). In contrast to the CdS, the Cd$_x$Zn$_{1-x}$S and ZnS show highly ordered meso-structures and uniform pore sizes as depicted in Figures 4(C) (c) and (D) ((a), (b)), respectively. As shown in Figures 4(C) (c) and (D) ((a), (b)), the mesoporous Cd$_x$Zn$_{1-x}$S and ZnS materials also have crystalline framework.

The optical properties of mesoporous Cd$_x$Zn$_{1-x}$S replicas are studied by diffuse reflectance UV-visible spectroscopy. As shown in Figure 5(A), the light absorption edge of the materials gradually blue shifts with a decrease in the cadmium composition (x) (a. 100% CdS $\rightarrow$ g. 100% ZnS). The band gap energies ($E_g$) of mesoporous Cd$_x$Zn$_{1-x}$S were estimated by the Kubelka-Munk equation. The band gap energy of mesoporous Cd$_x$S (2.43 eV) and ZnS (3.64 eV) are slightly larger than those of bulk CdS (wurtzite, 2.42 eV) and ZnS (zinc blende, 3.50 eV). This band gap widening phenomenon of the mesoporous materials seems to show a quantum confinement effect. The band gap energies of the ternary compound semiconductors linearly increase from 2.47 eV to 3.47 eV with a decrease in the cadmium composition (x) from 0.9 to 0.1. Detailed values of band gap energy of mesoporous Cd$_x$Zn$_{1-x}$S materials are presented in Table I.

4. CONCLUSION

We demonstrated that the ordered mesoporous multi-component metal sulfides could be easily obtained via a nano-replication approach with a controlled molar ratio of the precursors. The semiconductor replicas exhibit high surface area, large pore volume, uniform pore size, crystalline framework and tunable band gap energy by the control of their composition. This facile synthesis approach is expected to be very useful for the preparation of highly ordered mesoporous compound semiconductors for applications in photovoltaics, light emitting diodes, sensors and catalysis.

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References and Notes


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