

## Novel Fabrication of CdS Hollow Spheres Induced by Self-assembled Process

Kyong-Hoon Choi, Weon-Sik Chae,<sup>†</sup> Jin-Seung Jung,<sup>‡</sup> and Yong-Rok Kim<sup>\*</sup>

*Photon Applied Functional Molecule Research Laboratory, Department of Chemistry, Yonsei University, Seoul 120-749, Korea. \*E-mail: yrkim@yonsei.ac.kr*

<sup>†</sup>*Korea Basic Science Institute, Gangneung Center, Gangnung 210-702, Korea*

<sup>‡</sup>*Department of Chemistry, Kangnung National University, Gangnung 210-702, Korea*

*Received February 5, 2009, Accepted March 30, 2009*

Micro-size CdS spheres of hollow shape were fabricated through the self-assembly of high density arrow-like nanorods. The synthesis of the CdS hollow spheres were accomplished in an aqueous solution of cadmium nitrate and triblock copolymer (Pluronic P123) at low temperature (80 °C) through the slow release of S<sup>2-</sup> ions from thioacetamide. Morphology of the fabricated CdS hollow spheres was characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The results indicate that the arrow-like CdS nanorods are simultaneously grown and attached each other to form the building units that become the spheres with hollow inside as a self-assembled process. The CdS spheres have a diameter of 2~3 μm and consist of the nanorods with a length of ~800 nm. The nanocrystal building blocks have a hexagonal CdS structure.

**Key Words:** Hollow, CdS, Sphere, Arrow-like nanorods, Self-assembly

### Introduction

Over the past decade, the synthesis of inorganic nanocrystals has attracted much interest because of their potential applications in the design of new materials and devices in various fields of catalysis, medicine, electronics, and cosmetics, etc.<sup>1-4</sup> In addition, the morphology and functionality controls of nanostructured materials have attracted much attention in recent years for the generation of specific properties (optical, electrical, mechanical, chemical, etc.).<sup>5,6</sup> Therefore, well-controlled synthetic methods and the understanding of the mechanisms of these various properties which strongly correlates to the sizes and shapes of the nanomaterials have become important issues in nanoscience.<sup>7-11</sup>

Among the distinct geometric structures of inorganic materials, the hollow sphere (with dimensions ranging from nanometer to micrometer) has become an important class of materials that are potentially useful for a wide range of applications such as delivery vesicle systems, photonic crystals, fillers, and catalysts.<sup>12-14</sup> Until now, a variety of hollow nanomaterials comprised of metals, ceramics, polymers, or composites have been fabricated. The majority of reported hollow nanomaterials have been made with template-assisted processes that involve either organized reaction fields, such as emulsion vesicles,<sup>15,16</sup> emulsion droplets, and bicontinuous microemulsions,<sup>17-19</sup> or overlay of colloidal particles, such as silica or latex polymer spheres.<sup>20,21</sup> However, these methods are somewhat labor-intensive that require multiple steps in a sequential manner and, also, the homogeneity of resulting morphology is difficult to maintain due to the soft organic reaction field. Therefore, the strategies involving facile fabrication methods, including the controlled organization of primary building units into curved hollow structures, are new challenges to the synthesis of inorganic hollow materials.

In this study, we report a simple "one-pot" approach to syn-

thesize CdS hollow microspheres using a triblock copolymer (Pluronic P123) as a structure-guiding reagent at low temperature (80 °C). It is suggested that the formation of the arrow-like nanorod simultaneously leads the formation of the hollow CdS sphere as a self-assembled process.

### Experimental

Various nanostructures of star-like and spherical CdS microspheres have recently been introduced using the lyotropic triblock copolymer.<sup>9</sup> In this study, the nonionic surfactant triblock copolymer (Pluronic P123, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was utilized as a structure-guiding reagent for the preparation of the CdS hollow microspheres in aqueous solution. 5.0 g Pluronic P123 (Aldrich) and 1 mL of 15 M nitric acid were dissolved in 80 mL distilled water under vigorous stirring condition at 80 °C. After the mixture was dissolved completely, 10 mL aqueous solution of 0.08 M Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Kanto Chemical) was added to the solution. The mixture was kept at 80 °C for 250 h for the formation of hollow microspheres. After the aging time of 250 h, 5 mL aqueous solution of 0.32 M thioacetamide (TAA, ACROS) was added to the triblock copolymer solution and homogeneously mixed. This mixture was maintained for 10 h at 80 °C without agitation, which gradually yielded a pale yellow solution that changed to deep yellow precipitation in the bottom of the reaction flask. The temperature was maintained at 80 ± 1 °C during all reactions. After cooling to room temperature, the yellow precipitate was washed through centrifugation-redispersion cycles. During the cycles, each successive supernatant was decanted and replaced with deionized water and ethanol.

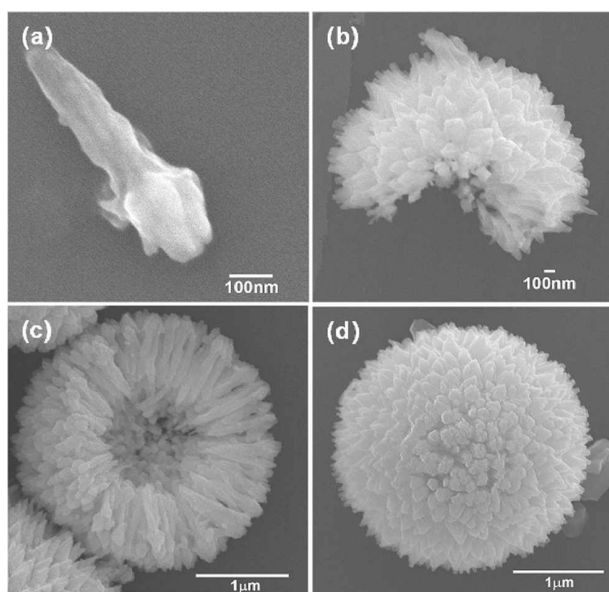
The powder that precipitated from the reactions was subjected to the measurements of field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), transmission electron microscopy (TEM, JEOL JEM-2000EXII),

and powder X-ray diffraction (XRD, BRUKER D8 Advance). Absorption and emission spectra were obtained from a diffuse reflectance UV-Vis spectrophotometer (Jasco V-550) equipped with an integrating sphere (Jasco ISV-469) and spectrofluorometer (Hitachi, F-4500), respectively.

### Results and Discussion

Figure 1 illustrates the formation of the hollow CdS microspheres. The uniform arrow-like CdS nanorods were grown in an aqueous solution using the amphiphilic triblock copolymer as a structure-directing reagent as similarly with the previous reports.<sup>9,22</sup> The grown CdS nanorods, as a building unit, were spontaneously self-assembled to form the hollow spheres. As indicated, the CdS spheres have a hollow, dandelion-like morphology that consists of numerous one-dimensional nanorods. The diameter of these nanorods is approximately 110 nm with caps of 170 nm in diameter. The length of a single nanorod is in the range of 600 - 800 nm, depending on the synthesis conditions. These CdS nanorods are aligned perpendicular to the spherical surface and point toward a common center around a hollow cavity (Fig. 1c). The thickness of the shell wall is equal to the nanorod length.

The XRD pattern of the prepared hollow CdS spheres is shown in Figure 2a. All the diffraction peaks can be indexed as pure hexagonal wurtzite CdS with cell parameters  $a = 4.136$  Å and  $b = 6.713$  Å, which are consistent with the values in the standard card (JCPDS card number 41-1049). No impurities can be detected in this pattern, indicating that high purity CdS spheres are obtained under these experimental conditions. The strong intensity of the (002) peak likely implies the orientational growth of [001] direction in the CdS crystals. Energy-dispersive spectrum (EDS) analysis of the CdS microspheres indicates that the molar ratio of Cd:S is 1.02:1.00 similar to that of the stoichiometric composition (Fig. 2b). The Cu and C

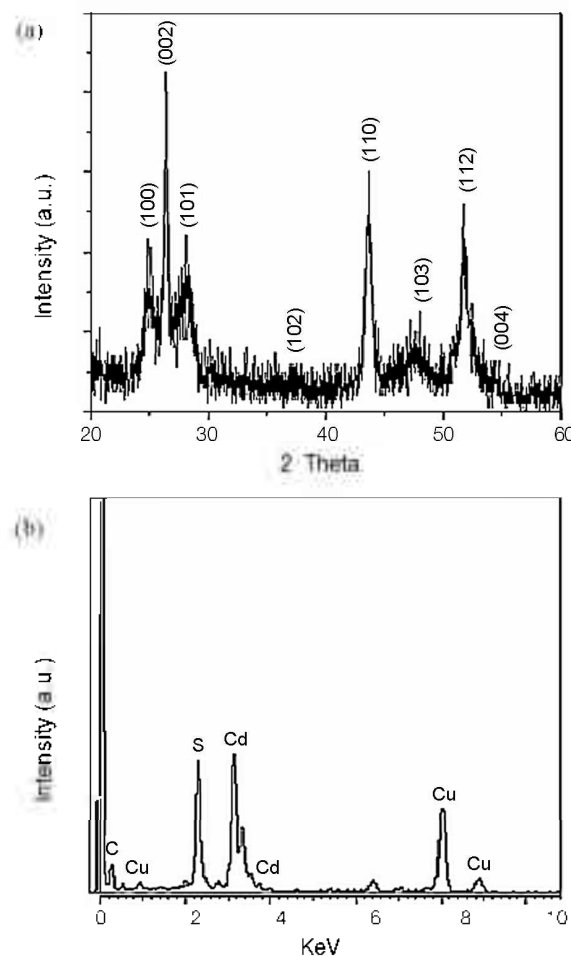


**Figure 1.** SEM images of hollow CdS microspheres: (a) A single component of the arrow-like CdS nanorod, (b-e) the partially broken shapes of the hollow CdS microspheres, and (d) a completed shape of the hollow CdS microspheres.

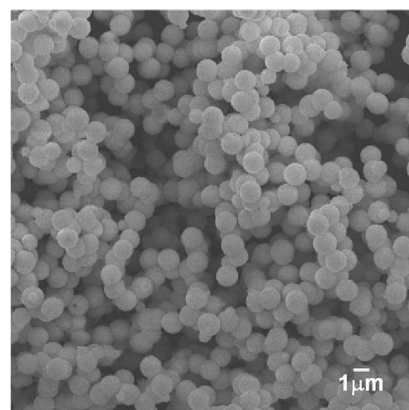
peaks in the EDS spectrum are expected to result from a carbon-coated copper TEM grid.

A typical SEM image (Fig. 3) of the hollow CdS spheres shows that the product consists of a large quantity of spheres. Under the given experimental conditions, most of the CdS spheres have the same morphology with a diameter ranging from 2 to 3 μm.

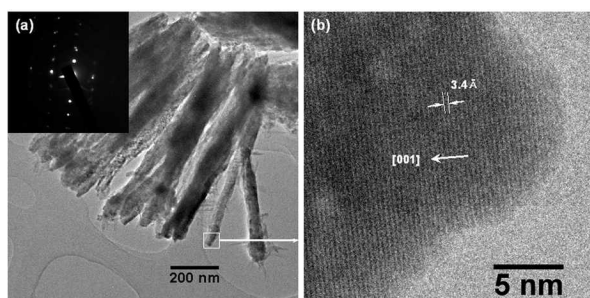
CdS nanorods disassembled from the CdS microspheres under ultrasonic condition are shown in the TEM image of



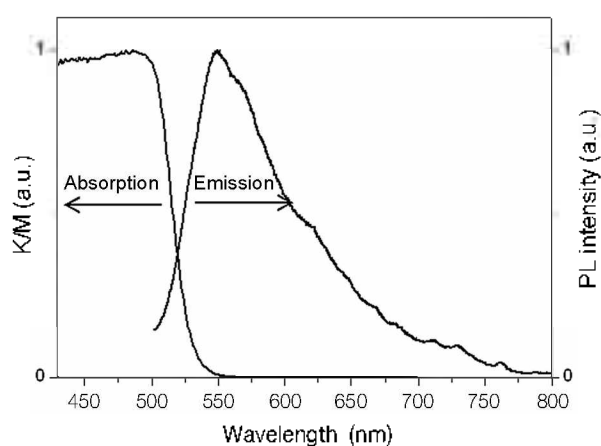
**Figure 2.** (a) XRD pattern and (b) EDS spectrum of hollow CdS spheres prepared by self-assembly.



**Figure 3.** Large scale SEM image of hollow CdS microspheres.



**Figure 4.** (a) TEM image and (b) HRTEM image of disassembled CdS nanorods after ultrasonication with hollow CdS spheres. The upper left inset in (a) corresponds to the SAED pattern of an arrow-like CdS nanorod.



**Figure 5.** Absorption and emission spectra of hollow CdS spheres at room temperature. The absorption spectrum is obtained by applying the Kubelka-Munk function to the diffuse reflectance spectrum. The excitation wavelength is 320 nm for the emission spectrum.

Figure 4a, which also have the arrow-like end points. The selected area electron diffraction (SAED) pattern inserted into Figure 4a shows that the nanorods can be indexed as a single crystalline hexagonal CdS that is in agreement with the XRD result. Figure 4b shows a typical high-resolution transmission electron microscopy (HRTEM) image of the nanorod shown in Figure 4a. The image clearly reveals that only the fringes of the (002) lattice planes with a lattice spacing of approximately 0.34 nm can be observed, indicating that the constitutional CdS nanorod is a single crystal with a growth direction of [001] along the c axis of the nanorods.

UV-Vis absorption and PL spectra of the hollow CdS spheres are presented in Figure 5. The absorption spectrum indicates that the band-gap transition occurs at  $\sim 530$  nm. The hollow CdS spheres yield a slightly blue-shifted absorption spectrum compared with that of the bulk spherical CdS band-gap transition at  $\sim 550$  nm.<sup>9</sup> Such a spectral shift is expected to be due to the quantum effect although it is not as significant as those of other small CdS nanoparticles since the domain of the nanorods in the synthesized CdS sphere is much larger than the exciton Bohr diameter (48 Å) of CdS.<sup>23,24</sup> Room-temperature PL spectrum of the hollow CdS spheres exhibits a broad emission peak centered around 554 nm. The observed emission spectrum is located near the absorption edge, which

originates from the direct exciton recombination and/or shallow and deep trapped exciton recombination as expected.<sup>25,26</sup>

## Conclusions

Conclusively, micrometer-sized hollow CdS spheres of uniform size, which consist of arrow-like CdS nanorods, were successfully prepared using the triblock copolymer as a structure-guiding reagent at low temperature (80 °C). The hollow CdS microspheres consist of arrow-like CdS nanorods with single-crystalline hexagonal phase. The experimental observation suggests that the formation of the arrow-like CdS nanorod simultaneously leads to form the hollow CdS sphere as a self-assembled process. It is believed that such self-assembling phenomena could be applied for other chalcogenide semiconductors to induce the different morphologies.

**Acknowledgments.** This work was supported by the KOSEF through the Pioneer Converging Technology Program (No. M1071160001-08M1116-00110) and Korea Health 21 R&D Project, Ministry of Health & Welfare, Republic of Korea (No. A085136). K.-H.C. thanks the fellowship of the BK 21 program from the Ministry of Education and Human Resources Development. Prof. J.-S. Jung thanks a grant from the Information Technology Research Center (IITA-2009-C1090-0902-0044).

## References

- Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393.
- Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
- Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; Elsayed, M. A. *Science* **1996**, *272*, 1924.
- Cho, Y.-G.; Choi, K.-H.; Kim, Y.-R.; Jung, J.-S.; Lee, S.-H. *Bull. Kor. Chem. Soc.* **2009**, in press.
- Caruso, F. *Adv. Mater.* **2001**, *13*, 11.
- Burda, C.; Chen, X.; Narayanan, R.; Elsayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
- Liu, B.; Zeng, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 8124.
- An, B.-I.; Ryu, K.-H.; Kim, Y.-R.; Lee, S.-H. *Bull. Kor. Chem. Soc.* **2007**, *28*, 1049.
- Chae, W.-S.; Shim, H.-W.; Lee, E.-S.; Shin, E.-J.; Jung, J.-S.; Kim, Y.-R. *J. Phys. Chem. B* **2005**, *109*, 6204.
- Chae, W.-S.; Lee, S.-W.; Kim, Y.-R. *Chem. Mater.* **2005**, *17*, 3072.
- Chae, W.-S.; Lee, S.-W.; An, M.-J.; Choi, K.-H.; Moon, S.-W.; Zin, W.-C.; Jung, J.-S.; Kim, Y.-R. *Chem. Mater.* **2005**, *17*, 5651.
- Ma, Y.; Qi, L.; Ma, J.; Cheng, H. *Langmuir* **2003**, *19*, 4040.
- Zhong, Z.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, *12*, 206.
- Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642.
- McKelvey, C. A.; Kaler, E. W.; Zasadzinski, J. A.; Coldren, B.; Jung, H. T. *Langmuir* **2000**, *16*, 8285.
- Hotz, J.; Meier, W. *Adv. Mater.* **1998**, *10*, 1387.
- Walsh, D.; Hopwood, J. D.; Mann, S. *Science* **1994**, *264*, 1576.
- Ohmori, M.; Matijevic, F. *J. Colloid Interface Sci.* **1992**, *150*, 594.
- Sims, S. D.; Walsh, D.; Mann, S. *Adv. Mater.* **1998**, *10*, 151.
- Mandal, T. K.; Fleming, M. S.; Walt, D. R. *Chem. Mater.* **2000**, *12*, 3481.
- Caruso, F.; Spasova, M.; Susha, A.; Giersig, M.; Caruso, R. A. *Chem. Mater.* **2001**, *13*, 109.
- Yang, C. S.; Awschalom, D. D.; Stucky, G. D. *Chem. Mater.* **2002**, *14*, 1277.
- Zhang, J. Z. *Acc. Chem. Res.* **1997**, *30*, 423.
- Kavanuma, Y. *Phys. Rev. B* **1988**, *38*, 9797.
- O'Neil, M.; Marohn, J.; McLendon, G. *J. Phys. Chem.* **1990**, *94*, 4356.
- Chae, W.-S.; Ko, J.-H.; Hwang, I.-W.; Kim, Y.-R. *Chem. Phys. Lett.* **2002**, *365*, 49.