Chemical Conversion Synthesis and Optical Properties of Metal Sulfide Hollow Microspheres

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A facile chemical conversion method has been demonstrated to prepare various metal sulfide hollow microspheres. The present strategy utilizes the large difference in solubility between ZnS and other metal sulfides (Ag_2S , PbS, CuS, Cu₂S, Bi₂S₃, and Sb₂S₃) for the effective transformation and shows mild growth conditions and good reproducibility. The morphology, structure, and composition of the yielded hollow nanostructures have been confirmed by transmission electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction measurements. The optical properties of the metal sulfide hollow microspheres have been systematically investigated by absorption, micro-Raman, and photoluminescence spectroscopy. The results demonstrate that these metal sulfide hollow microspheres possess good optical quality with tunable band gaps and luminescence properties, which indicate their broad potential applications. This simple chemical conversion technique can be further extended to the synthesis of other semiconductors with various morphologies.

I. Introduction

Well-defined hollow micro- and nanospheres have recently attracted much attention in physics, chemistry, and material science communities because of their unique properties including low density, high specific surface area, and distinct optical properties.^{1–8} Until now, hollow spheres made of various materials such as metals, semiconductors, and organic materials have been extensively investigated.^{1–19} Among the above-mentioned hollow spheres, the study of semiconductor metal sulfide hollow spheres is of particular interest for the potential applications of such materials in the fields of optics, electronics, and optoelectronics.^{9–13} Templates, including bacteria, polystyrene, block copolymers, silicon spheres, polymer latex spheres, and emulsion droplets/micelles, have been successfully employed to synthesize metal sulfide hollow spheres.^{14–19}

However, the reported template methods always require extremely complicated synthetic procedures and are usually

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suitable only for a certain specific material.²⁰ The development of a facile, versatile synthetic pathway to prepare various metal sulfide hollow microspheres is very important and quite necessary. In particular, it is highly desirable for such a method that can convert the chemical compositions of hollow microspheres without destroying the original morphology. Recently, cation exchange has been demonstrated as an effective way to convert the chemical compositions of nanostructures without destroying the original morphology.²¹ Nevertheless, little has been devoted to the conversion of one kind of metal sulfide hollow microspheres to others to realize diversification of the yielded hollow microsphere compositions to broaden their potential applications. Moreover, in spite of earlier efforts on the synthesis of metal sulfide hollow micro- and nanospheres, the optical properties of the yielded products are rarely systematically reported.^{14–19} A detailed exploratory study of their room-temperature optical properties can be much interesting as a result of their technological importance and fundamental interests.

In this article, we present the successful realization of various metal sulfide hollow microspheres (Ag₂S, PbS, CuS, Cu₂S, Bi₂S₃, and Sb₂S₃) transformed from the ZnS hollow microspheres. The key point of the method is to utilize the large difference in solubility between ZnS and the other metal sulfides for the effective transformation. Systematic optical investigation demonstrates that the yielded hollow microspheres possess good optical quality with tunable band gaps and luminescence properties. The prepared metal sulfide hollow microspheres may find potential applications in photocatalysts, photovoltaic cells, nanoscale chemical reactors, energy-storage media, drug-delivery carriers, and artificial cells because of their unique hollow geometrical shapes and optical properties.^{9–14,22} Although the current work focuses on the synthesis and optical properties of metal sulfide hollow spherical structures, other semiconductors

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with various shapes and different properties are expected to be synthesized under similar chemical conversion approaches.

II. Experimental Details

Synthesis of ZnS Hollow Microspheres. The preparation details for ZnO spherical structures can be found in our recently published papers.²³ As a typical synthesis process, silicon or quartz substrates were put into a glass bottle containing 40 mL of a mixed solution of 25 mM Zn(NO₃)₂·6H₂O, 25 mM C₆H₁₂N₄, and 6.8 mM $C_6H_5Na_3O_7 \cdot 2H_2O$. The sealed bottle was then heated to 90 °C for about 50 min in a conventional laboratory oven. After the product is washed, dried, and annealed at 400 °C under an air atmosphere for 120 min, the synthesis of ZnO microspheres can be realized. The obtained ZnO microspheres on substrates (silicon or quartz slides) were transferred to a glass bottle containing 40 mL 0.2 M thioacetamide (TAA). The sealed bottle was then heated to 90 °C for 2-9 h in a conventional laboratory oven to synthesize ZnO/ZnS core/shell structures. Subsequently, the as-prepared ZnO/ZnS microspheres were transferred into a bottle containing a dilute sulfuric acid solution (0.05 M) for 90 min. This dilute acid solution can react with ZnO to dissolve it gradually without destroying ZnS. The final products on the substrates were washed repeatedly with deionized water several times and then dried at 60 °C before being used for the next step in the reaction and further characterization.

Synthesis of Other Metal Sulfide Hollow Microspheres. The synthesis of other metal sulfide hollow microspheres was realized by transferring the silicon or quartz substrates with ZnS hollow microspheres on them to a glass bottle containing 40 mL of an aqueous solution. As for Ag₂S, PbS, CuS, Cu₂S, Bi₂S₃, and Sb₂S₃, the aqueous solutions used are 50 mM AgNO₃, 50 mM Pb(NO₃)₂, 100 mM Cu(NO₃)₂, 20 mM CuCl, 100 mM Bi(NO₃)₃, and 150 mM $C_8H_4K_2O_{12}Sb_2$, respectively. Because Cu^+ , Bi^{3+} , and Sb^{3+} are apt to hydrolyze in water, a small amount of tartaric acid (70 mM) was added to the latter three solutions. In the case of an aqueous Bi(NO₃)₃ solution, 2 mL of triethanolamine was also added. During the reaction process, the solution temperature was kept at 90 °C. The final products on the substrates were washed with deionized water repeatedly and then dried at 60 °C. For better crystal quality, some of the as-prepared metal sulfide hollow microspheres were annealed in an argon atmosphere.

Characterization of the Samples. The morphology and structure of the samples were characterized using a field-emission scanning electron microscope (FE-SEM, Philips XL30FEG) with an accelerating voltage of 5 kV and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). Selected-area electron diffraction (SAED) and energy-dispersive X-ray (EDX) microanalysis were also performed during the TEM and SEM observations. X-ray diffraction (XRD) was carried out on a diffractometer (Bruker/D8 Discover with GADDS) equipped with a Cu K α source ($\lambda = 1.5406$ Å). The UV-visible absorption spectra of the obtained metal sulfides were recorded using a Nicolet Evolution 300 spectrophotometer (Thermo Electron Corporation) with a bare quartz slide substrate as a background reference. Raman and photoluminescence (PL) spectra were measured at room temperature on a Jobin Yvon LabRAM HR 800UV micro-Raman/PL system. Raman spectra were recorded at the backscattering configuration under the excitation of a HeCd laser (325.0 nm) for ZnS and Ag₂S hollow microspheres and an Ar⁺ laser (514.5 nm) for the other metal sulfides. PL spectra of ZnS- and PbS-modified ZnS hollow microspheres were taken under HeCd laser excitation.

III. Results and Discussion

Structural and Compositional Characterization of ZnS Hollow Microspheres. To convert ZnO microspheres to ZnO/ ZnS core/shell microspheres, we transfer the ZnO microspheres into a solution containing 0.2 M TAA. The TAA solution provides sulfide ions to react with zinc ions dissolved from the ZnO



Figure 1. FE-SEM images of the ZnS hollow microspheres obtained at different sulfidation times: (a) 2, (b) 6, and (c) 9 h. (d, e) TEM images of the obtained ZnS hollow microspheres corresponding to SEM images in panels b and c, respectively. (f) HRTEM image of a ZnS hollow microsphere shell.

microspheres to form ZnO/ZnS core/shell structures. After the ZnO cores dissolve in dilute sulfuric acid solution, the synthesis of ZnS hollow microspheres can be realized. Figure 1a-c presents the FE-SEM images of three samples obtained at different sulfidation times (2, 6, and 9 h). If the sulfidation time is very short (2 h), then the obtained ZnS hollow spheres are seriously deformed as shown in Figure 1a, probably because the shells of the hollow microsphere are too thin to support themselves. As the sulfidation time is increased to 6 h, the shells are robust enough, and as depicted in Figure 1b, the yielded hollow spheres are whole with smooth surfaces. With the further increase in the sulfidation time to 9 h, the thickness of microsphere shells is obviously increased, and the surface becomes rough with nanodots grown on the shells (Figure 1c). The formation of nanodots on the hollow microsphere shells is probably due to the fact that the zinc ions dissolved from ZnO react with sulfide ions and then grow on the shells. In the following text, we will employ the ZnS microspheres with thicker shells (as demonstrated in Figure 1c) to synthesize various other metal sulfide hollow microspheres (i.e., all of the samples that were used to make other metal sulfide microspheres were left in the TAA solution for 9 h).

As already shown in Figure 1b,c, one can see that some of the shells have a partially opened mouth on them, clearly demonstrating the hollow nature of the prepared microspheres. The opened mouths on the shells of the hollow spheres can be attributed to the fact that ZnS is eroded by dilute sulfuric acids during the process of dissolving ZnO from the ZnO/ZnS core/shell structures. Although some of the microspheres are "closed", further evidence for the hollow structure can be found from the TEM observation. Figure 1d,e presents TEM images of the obtained ZnS hollow microspheres corresponding to the SEM images in Figure 1b,c, respectively. The strong contrast difference in the microspheres with a light inner center and a relative dark edge further confirms that the yielded ZnS microspheres are all hollow. From these two TEM images, one can also conclude that the thicknesses of microsphere shells obviously increase with sulfidation time. HRTEM observation can give further insight into the structural features of these obtained hollow microspheres. Figure 1f shows

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Figure 2. (a) EDX spectra and (b) XRD patterns of the obtained ZnS hollow microspheres (curve a) and Ag₂S hollow microspheres (curve b).

a HRTEM image of a typical hollow microsphere shell, which clearly exhibits that the shell is composed of ZnS nanocrystalline grains with a polycrystalline nature. The composition of the ZnS hollow microspheres can be easily identified by the EDX and XRD spectra in Figure 2.

Compositional and Structural Characterization of Ag₂S Hollow Microspheres. The main attempt in the present work is to synthesize various metal sulfide hollow microspheres and to investigate the optical properties. Here, we describe the transformation from ZnS hollow microspheres to Ag₂S ones in detail and then extend this method to the synthesis of other metal sulfide hollow microspheres in the next section. To make the conversion of ZnS hollow microspheres to Ag₂S ones, we transfer the substrates with ZnS hollow microspheres on them into 40 mL of a 50 mM aqueous silver nitrate solution for 7 h. A rapid color change (from white to black) is observed right after immersing the ZnS hollow microspheres into the above-mentioned solution, indicating the formation of new products.

To confirm the chemical composition of the newly formed materials, we have employed EDX spectroscopy to analyze the yielded products. Curves a and b in Figure 2a are the EDX spectra of the hollow microspheres before and after the chemical reaction, respectively. Curve a indicates that the hollow microspheres before the chemical reaction are composed of Zn and S elements. The signal of Cu originates from the copper grid, whereas the C peak comes from the carbon film on the Cu grid. After the chemical reaction is finished, the absence of Zn and the appearance of Ag peaks clearly confirm the total transformation from ZnS to Ag₂S. XRD measurements have also been performed to identify the microstructural transformation. The results are shown in Figure 2b, from which it can be clearly observed that only diffraction peaks originating from monoclinic Ag₂S (Joint Committee for Powder Diffraction Standards (JCPDS) no. 14-0072) are detected after the chemical reaction, further confirming that the ZnS (JCPDS no. 05-0566) hollow microspheres have been completely converted into Ag₂S ones.

FE-SEM and TEM measurements have also been carried out to demonstrate the fact that the yielded products are morphologically retained after the chemical reaction. Figure 3a,b shows the FE-SEM and TEM images of the prepared Ag₂S hollow microspheres. Compared with morphology of the ZnS microspheres in Figure 1c, no significant changes were observed, confirming the successful realization of morphology transfer from one material to another. The HRTEM image shown in Figure 3c indicates that the hollow microsphere shells are polycrystalline with a single-crystalline local area. The enlarged HRTEM image of Figure 3d further confirms that the local area of the hollow microsphere shell is single-crystalline. The lattice fringe spacing is measured to be 0.27 nm, which is consistent with the unique 0.2664 nm separation between two (120) planes in bulk Ag₂S



Figure 3. (a) FE-SEM and (b) TEM images of the prepared Ag_2S hollow microspheres. (c, d) HRTEM images of a Ag_2S hollow microsphere shell. The inset in panel d shows the SAED pattern corresponding to the local single-crystalline area.

crystallites.²⁴ The corresponding SAED pattern displayed in the inset of Figure 3d suggests the crystallinity of the local area. There are some additional diffraction spots, which may be due to the large diameter of the electron beam and the small diameter of the local single-crystalline area.

According to the experimental observation described above, the whole process can be described as follows. After the ZnS hollow microspheres were transferred into silver nitrate solution, cation exchange began at the interfaces between the hollow microspheres and solution. With the increase in the reaction time, the ZnS hollow microspheres completely changed into Ag₂S ones. The driving force for the cation exchange is provided by the large difference in solubility between ZnS and Ag₂S (solubility product constant (K_{sp}) of ZnS is 2.93 × 10⁻²⁵, whereas K_{sp} of Ag₂S is 6.69 × 10⁻⁵⁰).²⁵ The above conversion mechanism suggests that the ZnS hollow microspheres can act as both reactants and templates during the cation-exchange process (i.e., we can extend this chemical conversion approach to the synthesis of other metal sulfide hollow microspheres under the condition that those yielded metal sulfides have lower K_{sp} values than do those of ZnS. In fact, it is because of the large K_{sp} in ZnS that we choose ZnS hollow microspheres as the reactants and templates to synthesize various metal sulfide hollow microspheres.

Extension to the Synthesis of Other Metal Sulfide Hollow Microspheres. To confirm the validity of the above proposal, we have extended this easy and effective method to prepare other metal sulfide hollow microspheres. Several other metal sulfide hollow microspheres (PbS, Cu₂S, CuS, Bi₂S₃, and Sb₂S₃) have been successfully synthesized by transferring the ZnS hollow microspheres into solutions containing the corresponding metal cations. Figure 4a-e presents the FE-SEM images of these yielded metal sulfide hollow microspheres. It is obvious that the morphologies of the ZnS hollow microspheres are all preserved during the cation exchange process. The hollow nature of the microspheres is clearly evidenced by the holes in the surfaces of the obtained microspheres. XRD measurements have been carried out to identify the composition of the products and to analyze the crystalline properties of the prepared samples. It is found that all diffraction peaks are consistent with the corresponding metal sulfides (Figure 4f). EDX measurements have also been performed to check the compositions of the yielded

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Figure 4. FE-SEM images of (a) PbS, (b) Cu_2S , (c) CuS, (d) Bi_2S_3 , and (e) Sb_2S_3 hollow microspheres. (f) XRD patterns of (a) PbS, (b) Cu_2S , (c) CuS, (d) Bi_2S_3 , and (e) Sb_2S_3 hollow microspheres. (g) EDX spectra of (a) PbS, (b) Cu_2S , (c) CuS, (d) Bi_2S_3 , and (e) Sb_2S_3 hollow microspheres.



Figure 5. (a) FE-SEM image of PbS modified ZnS hollow microspheres. (b) EDX spectrum of the corresponding hollow microspheres.

metal sulfide hollow microspheres (Figure 4g). No impurities are detected in any of these samples, indicating the successful transformations from ZnS hollow microspheres to the other metal sulfide hollow structures. Therefore, a facile, versatile method has been demonstrated to synthesize metal sulfide hollow microspheres.

Furthermore, because ZnS hollow microspheres are solid and insoluble in the solutions we used, cation exchange takes place first at the interfaces between the hollow microspheres and solutions. As a result, the synthesis of surface-modified ZnS hollow microspheres can be possible if one stops the chemical reaction before the entire cation exchange. PbS modified ZnS hollow microspheres have been successfully realized along with this proposal by transferring the ZnS hollow microspheres into aqueous solutions containing $Pb(NO_3)_2$ (50 mM, 40 mL) for 60 s. Figure 5a presents the FE-SEM image of the PbS/ZnS hybrid hollow microspheres whereas the corresponding EDX spectrum shown in Figure 5b clearly demonstrates the obtained hollow microspheres composed of Zn, Pb, and S (with the molecular proportion between PbS and ZnS being about 1:3). The Si signal originates from the silicon substrate, whereas the Au peaks should come from the thin gold film sputtered on the surface for the SEM observation. As we know, surface modification is also a current research interest because of the fact that surface-modified nanostructures usually exhibit attractive physical and chemical properties that are different from the those of the constituent components.^{26–29} We will show below the interesting luminescence property from the yielded PbS-modified ZnS hollow microspheres.

Optical Properties of the Yielded Metal Sulfide Hollow Microspheres. To examine the optical properties of these yielded metal sulfide hollow microspheres, we first perform room-temperature UV-visible absorption measurements. From the absorption spectra of the ZnS and Ag₂S hollow microspheres in Figure 6a, it is clear that the absorption edge of the Ag₂S hollow microspheres shows an obvious red shift compared to that of ZnS ones. As we know, the optical band gap E_g of ZnS (Ag₂S) and the corresponding absorption coefficient α near the absorption edge obey the relationship

$$\alpha h \nu = C \sqrt{(h \nu - E_{\rm g})}$$

where *C* is a constant and hv is the photon energy. Hence, the optical band gaps of the yielded products can be obtained by

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Figure 6. (a) UV-visible absorption spectra of metal sulfide hollow microspheres. The inset shows the plots of $(\alpha h\nu)^2 \sim h\nu$ for ZnS and Ag₂S hollow microspheres. (b) Raman spectra of metal sulfide hollow microspheres.

extrapolating the linear portion of the plots of $(\alpha h\nu)^2 \sim h\nu$, as shown in the inset of Figure 6a. The estimated values for the band gap energy of these ZnS and Ag₂S hollow microspheres are 3.9 and 1.1 eV, respectively. Those results are very similar to the reported data of other ZnS and Ag₂S nanostructures,^{30,31} indicating that we have successfully realized the synthesis of hollow microspheres with the same morphology but different optical properties.

Figure 6a has also presented the typical absorption spectra taken from the other metal sulfide hollow microspheres. It is obvious that the absorption edges of the obtained hollow microspheres are different from each other and are all red-shifted compared with those of ZnS, providing the possibility to broaden the potential applications of metal sulfide hollow microspheres. Because ZnS is abundant, stable, and environmentally benign, many kinds of ZnS nanostructures, such as nanowires, nanorods, nanotubes, and hierarchical nanostructures, have been successfully fabricated by a variety of methods for potential optoelectronic device application.³² Unfortunately, the ZnS band gap (3.72 eV) is too large to use in efficient photovoltaic devices.³³ The above experiments demonstrate that the absorption edges of the hollow microspheres can be effectively modulated without destroying the original morphology of ZnS and some of the obtained metal sulfide hollow microsphere band gaps are near the optimal value of photovoltaic conversion, indicating that they may be used in solar energy and photoelectronic applications.²²

Raman spectroscopy can provide valuable structural information on semiconductor nanostructures. However, until now, there has been little work reported on the Raman characterization of metal sulfide hollow microspheres. Figure 6b shows the roomtemperature Raman spectra of the yielded metal sulfide hollow microspheres. The Raman frequencies of the main bands due to

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Figure 7. Room-temperature PL spectra of (a) pure ZnS hollow microspheres and (b) PbS-modified ZnS hollow microspheres with two Gaussian peak fits for the spectrum.

the lattice modes in all of the studied metal sulfide hollow microspheres are similar to the previously reported results for metal sulfide nanostructures with other shaps.^{34–37} It should be noted that strong resonant Raman scattering with high-order longitudinal optical (LO) modes can be obtained in the case of ZnS hollow microspheres. The Raman peaks located at 350, 699, and 1045 cm⁻¹ correspond well to the first-, second-, and third-order LO phonon modes in ZnS, respectively.³⁸ The observation of multiple resonant Raman peaks indicates that the yielded ZnS hollow microspheres possess good optical quality.³⁹ In addition, there is no peak corresponding to the surface optical phonon mode in the Raman spectrum, indicating few defects on the surface of the ZnS hollow microspheres.³⁵

Finally, we present the luminescence characteristics of the yielded hollow microspheres. Figure 7 shows the room-temperature PL spectrum of the ZnS hollow microspheres (curve a). In most cases, the PL spectra of ZnS nanostructures synthesized by wet chemical routes usually display two emission bands.^{40,41} One broad peak at around 400 nm originates from the recombination of free charge carriers at the surface defect sites.⁴⁰ Another peak at around 510 nm is usually attributed to the self-activated defect centers formed by the zinc vacancies inside the lattice.⁴¹ It is clear that the PL spectrum has only a strong broad PL peak at around 510 nm. The absence of a blue emission band at around 400 nm indicates that the yielded ZnS hollow microspheres have small number of defects on their surfaces, which is in good agreement with the observation from Raman spectroscopy.

As mentioned above, the surface-modified nanostructures usually exhibit physical and chemical properties that are different

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from those of the constituent components. The PL spectrum of the PbS-modified ZnS hollow microspheres is also shown in Figure 7 (curve b), which is different from that of the pure ZnS hollow microspheres (curve a). The spectrum of the PbS-modified ZnS hollow microspheres displays a broad visible emission with a slightly redshift compared with that of pure ZnS hollow microspheres. To our knowledge, this is the first report on the luminescence investigation of the PbS-modified ZnS nanostructures. To identify the origin of the PL changes, we have employed the Gaussian fit for the spectrum of PbS-modified ZnS hollow microspheres. As demonstrated in Figure 7, the luminescence spectrum can be well fitted by two Gaussian peaks centered at about 510 and 600 nm. In comparison with the pure ZnS hollow microsphere case, the spectrum of PbS-modified ZnS hollow microspheres shows quenched green emission (around 510 nm) and a new broad visible emission (around 600 nm). This new broad visible band is similar to that of previously reported Pbdoped ZnS nanostructures.^{42,43} Therefore, we believe that the present observation can be explained as follows. After immersing the pure ZnS hollow microspheres into a Pb(NO₃)₂ aqueous solution for a very short time (tens of seconds), the Pb atoms will fill up the zinc vacancies on and near the surface of the ZnS hollow microspheres. Because the Pb atoms have occupied some of the zinc vacancies, the green emission (around 510 nm) due to the self-activated defect centers formed by the zinc vacancies will be quenched. At the same time, a broad visible emission corresponding to the Pb-doped ZnS appears.^{42,43} Although the detailed luminescence mechanism for the PbS modified ZnS hollow microspheres is worthy of further study, the above experimental results indicate that the surface-modification process has a great impact on the luminescence properties of ZnS hollow microspheres. As a result, the PL properties of the ZnS hollow microspheres can be tuned by controlling the chemical reaction for further broadening their potential optoelectronic applications.

Perspective. Although the current work focuses on the synthesis of metal sulfide hollow microspheres, other pure and hybrid metal sulfide nanostructures are expected to be realized by using ZnS nanostructures with other shapes (e.g., previously reported nanowires, nanorods, nanotubes, hierarchical nano-

structures, etc.³²) as reactants and templates during the chemical conversion process. Furthermore, in addition to ZnS, other semiconductor micro- and nanostructures with large K_{sp} values can also be employed as reactants and templates. Because the properties of materials are related to their compositions, sizes, and morphologies, the yielded micro- and nanostructures may find broad applications in optoelectronics, photocatalyts, photovoltaics, and so on. Hence, the present chemical conversion process is a facile, economic, and versatile way to synthesize semiconductor micro- and nanostructures with different compositions and geometries and novel and unique properties.

IV. Conclusions

In summary, the successful chemical conversion of ZnS hollow microspheres into various metal sulfide hollow microspheres, such as Ag₂S, PbS, CuS, Cu₂S, Bi₂S₃, and Sb₂S₃, was achieved. The morphological and structural characterization showed that the morphology of ZnS hollow microspheres is perfectly maintained after the conversion, whereas the compositional conversion was verified by EDX and XRD. The optical properties of the obtained metal sulfide hollow microspheres were systematically investigated by absorption, micro-Raman, and PL spectroscopy. The absorption spectra revealed that some of the band gaps of these hollow microspheres are near the optimal value of photovoltaic conversion, indicating that the products may be applicable in solar cells and photoelectronics. The micro-Raman results demonstrated that the yielded hollow microspheres possess good optical quality. The PL studies found that the luminescence properties of the ZnS hollow microspheres can be tuned by modifying them with PbS, further broadening their potential applications. We have further expected that the facile method of material synthesis described in this article can be used in a broad range of applications to fabricate innovative semiconductor micro- and nanostructures with different compositions and shapes having unique properties.

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