One-Pot Synthesis of Uniform Cu_2O and CuS Hollow Spheres and Their Optical Limiting Properties

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Uniform hollow spheres of Cu_2O and CuS were successfully synthesized by chemical transformation of in situ formed sacrificial templates containing Cu(I) in aqueous solutions. The shell thickness of these hollow spheres can be adjusted through the choice of the bromide source used for the formation of intermediate templates. Specifically, thick-shell hollow spheres (about 130−180 nm in shell thickness) were obtained by using CuBr solid spheres as the templates, which were formed by the reduction of $CuBr_2$ with ascorbic acid; on the other hand, thin-shell hollow spheres (about 20−25 nm in shell thickness) were obtained by using spherical aggregates consisting of the Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions as the templates, which were formed by the reduction of $CuCl_2$ with ascorbic acid in the presence of $(C_4H_9)_4NBr$. In both cases, crystalline Cu_2O hollow spheres were directly obtained at room temperature, while amorphous Cu_2S hollow spheres were first obtained at room temperature and transformed into well-crystallized CuS hollow spheres after a hydrothermal treatment at 160 °C. The optical limiting properties of the thin-shell hollow spheres of Cu_2O and CuS were characterized by using nanosecond laser pulses. Strong optical limiting responses were detected for both the Cu_2O and CuS hollow spheres, which make these semiconductor hollow spheres promising materials for applications in the protection of human eyes or optical sensors from high-power laser irradiation.

Introduction

Hollow structures have received considerable attention recently because of their potential applications in catalysis, controlled delivery, lightweight fillers, low-dielectric-constant thin films, photonic crystals, confined-space chemical reactors, and biomedical diagnosis and therapy.[1−6] Various methodologies have been developed to generate micro- and nanostructures with hollow interiors, which involve templates such as polymer and silica spheres,[7] emulsion droplets,[8] polymer/surfactant micelles,[9] and bubbles,[10] as well as chemical processes based on the Kirkendall effect,[11] Ostwald ripening,[12] or chemically induced self-transformation.[13] Among them, the sacrificial template-directed chemical transformation method based on the Kirkendall effect has been demonstrated to be an effective approach. Reactive sacrificial templates, which act as both reactive precursors and templates, are free not only from the template removal problem but also from the limited morphologies of hard templates, because the precursors can be fabricated through all the techniques developed for materials morphosynthesis.[11] In this regard, a variety of inorganic hollow structures have been successfully prepared by employing reactive sacrificial templates.[14−19] Furthermore, it is worth noting that hydrothermal template techniques have been successfully used for the synthesis of a variety of inorganic hollow spheres in the presence of different templates owing to the specific physical properties of the hydrothermal techniques.[20]

Semiconductor transition-metal oxides and chalcogenides have been of much interest because of their excellent properties

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and wide-range potential applications. In particular, as a p-type semiconductor with a band gap of 2.17 eV, cuprous oxide (Cu_2O) is a promising material with potential applications in solar energy conversion, catalysis, and sensing.[21−23] Copper sulfides have the ability to form various stoichiometries, at least five phases of which are stable at room temperature: i.e., covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurlite ($Cu_{1.95}S$), and chalcocite (Cu_2S).[17] Their complex structures and valence states result in some unique properties and promising applications in numerous fields, such as solar cells, optical filters, superconductors, and chemical sensors.[24−27] Many recent efforts have been devoted to the synthesis of cuprous oxide and copper sulfide micro- and nanostructures with modulated morphologies and architectures. Morphology-controlled synthesis of Cu_2O particles has been realized by different methods.[22,23,28−31] In particular, Cu_2O nanocages have been obtained via a Pd-catalyzed solution route, which involves the formation of octahedral Cu_2O nanocrystals and a subsequent spontaneous hollowing process.[29] Hollow Cu_2O spheres were formed by reductive conversion of aggregated CuO nanocrystallites using *N*,*N*-dimethylformamide as a reducing agent.[30] Multishelled Cu_2O hollow spheres with single-crystalline shell walls have also been synthesized with the assistance of multilamellar vesicles.[31] On the other hand, copper sulfide micro- and nanostructures with different compositions and morphologies, including nanoparticles, nanoplates, and complex structures, have been successfully synthesized.[16,17,24,27,32−34] Specifically, copper sulfide mesocages were produced through chemical transformation by employing Cu_2O as a reactive sacrificial template.[16,17] Micrometer-sized CuS hollow spheres were prepared on the basis of a template interface reaction between CuCl and sulfur liquid droplets,[34] while nanosized CuS hollow spheres were synthesized by using surfactant micelles as soft templates.[24] However, it remains a challenge to achieve the facile synthesis of hollow spheres of both Cu_2O and CuS by employing a general sacrificial template.

Herein, a facile, one-pot, aqueous solution route was reported for the controlled synthesis of uniform hollow spheres of cuprous oxide and copper sulfides by chemical transformation of in situ formed sacrificial templates containing Cu(I). The shell thickness of these hollow spheres can be adjusted through the choice of the bromide source used for the formation of intermediate templates. In particular, monodisperse, well-crystallized, thin-shell Cu_2O and CuS hollow spheres with a shell thickness of about 20−25 nm were produced by using $(C_4H_9)_4NBr$ as the bromide source. It was revealed that these Cu_2O and CuS hollow spheres exhibited remarkable optical limiting effects, which could make them useful for protecting human eyes or optical sensors from high-power laser irradiation.

Experimental Section

Hollow spheres of a variety of copper-based oxide and sulfide materials including Cu_2O, Cu_2S, and CuS were achieved by the formation of intermediate Cu(I)-containing templates followed by their transformation into the final hollow structures in aqueous solutions. Notably, thick-shell and thin-shell hollow spheres were obtained by employing $CuBr_2$ and $(C_4H_9)_4NBr$ as the bromide source, respectively. In a typical procedure for the synthesis of thick-shell oxide and sulfide hollow spheres, an aqueous solution was first prepared by mixing 20 mL of water, 0.4 mL of PVP (poly(vinylpyrrolidone); MW = 30 000, Beijing Chemical Co.) solution (1.0 wt %), and 0.2 mL of $CuBr_2$ solution (0.1 M). Then 1.0 mL of ascorbic acid solution (0.1 M) was added to the solution, and the mixture was stirred for 3 min and became turbid shortly, indicating the formation of CuBr particles. For the synthesis of oxide hollow spheres, 1.0 mL of NaOH solution (0.2 M) was added to the above turbid precursor solution under stirring, and the resulting solution was then kept for 15 min at room temperature without stirring. The resultant Cu_2O products were collected by centrifugation, washed with water several times, and dried in air. For the synthesis of sulfide hollow spheres, 0.4 mL of Na_2S solution (0.1 M) was added to the turbid precursor solution under stirring, which was then kept for 30 min at room temperature without stirring, resulting in the formation of poorly crystallized Cu_2S hollow spheres. This brown reaction mixture was then transferred into 25 mL stainless-steel autoclaves lined with poly(tetrafluoroethylene) (PTFE, Telfon) and maintained at 160 °C for 24 h, leading to the formation of well-crystallized CuS hollow spheres. The resultant Cu_2S and CuS products were also collected by centrifugation, washed with water several times, and dried in air. On the other hand, the synthesis of thin-shell oxide and sulfide hollow spheres was realized under similar conditions except for the use of 2.0 mL of $(C_4H_9)_4NBr$ solution (0.1 M) and 0.2 mL of $CuCl_2$ solution (0.1 M) instead of 0.2 mL of $CuBr_2$ solution (0.1 M). However, it should be noted that loose aggregates containing Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions were formed instead of CuBr solid spheres in the precursor solution before the addition of NaOH or Na_2S.

The solid products were characterized by scanning electron microscopy (SEM; Hitachi S4800, 5.0 kV), transmission electron microscopy (TEM; JEOL JEM-200CX, 160 kV), X-ray diffraction (XRD; Rigaku Dmax-2000), and UV−vis spectroscopy (Perkin-Elmer Lambda 35). Energy-dispersive X-ray (EDX) spectroscopy was performed with a Horiba EMAX-2000 EDX system attached to the SEM microscope. The optical limiting effects of the hollow spheres were investigated by the fluence-dependent transmittance measurement. The hollow spheres were dispersed in ethanol, and the sample cell was 5 mm thick. The laser source is a Q-switched

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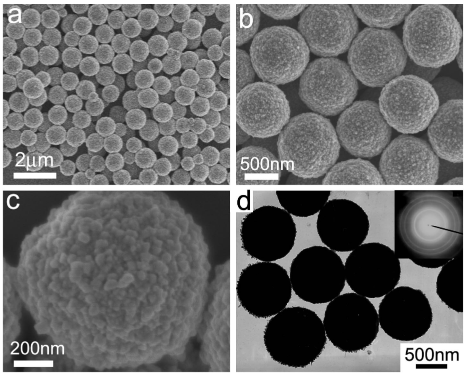

Figure 1. SEM (a−c) and TEM (d) images of CuBr spheres obtained in the presence of 2 g L^{-1} PVP. The inset shows the ED pattern corresponding to a single sphere.

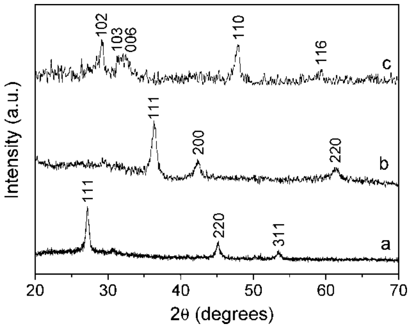

Figure 2. XRD patterns of CuBr spheres (a) and the templated thick-shell hollow spheres of Cu_2O (b) and CuS (c).

YAG laser (Surelite-III, Continuum Corp.), which delivers the fundamental laser pulses with a pulse duration of 5.6 ns and a wavelength of 1064 nm. To avoid thermal effects and make every pulse meet new particles, the lasers irradiated the suspensions every 15 s.

Results and Discussion

Formation of Thick-Shell Hollow Spheres. For the synthesis of thick-shell hollow spheres of cuprous oxide (Cu_2O) and copper sulfides (Cu_xS), CuBr solid spheres were first prepared as sacrificial templates. Figure 1 shows the typical SEM and TEM images of the CuBr product obtained by the reaction between $CuBr_2$ and ascorbic acid in the presence of 2 g L^{-1} PVP. It can be seen that the product consists of uniform spheres with an average diameter of about 900 nm, and these microspheres usually exhibit relatively rough surfaces composed of nanoparticles smaller than 50 nm. The XRD pattern of the obtained microspheres is shown in Figure 2a. All the diffraction peaks can be indexed to the γ-CuBr crystal of the cubic structure (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 06-0292), suggesting the formation of pure crystalline CuBr microspheres. The electron diffraction (ED) pattern of a single CuBr sphere is shown in Figure 1d, which shows clear diffraction rings corresponding to γ-CuBr, indicating the polycrystalline nature of the CuBr spheres.

In the present system, ascorbic acid was selected as the reducing agent and $CuBr_2$ was used as both the copper and bromine sources. Being a weak reducing agent, ascorbic acid can reduce Cu^{2+} to Cu^+ ions in aqueous solution, which would combine with the Br^- ions in the solution to form the CuBr precipitates ($K_{sp} = 6.27 \times 10^{-9}$) at room temperature.[35] It was observed that the CuBr microspheres were not very stable in aqueous solutions and the presence of excess ascorbic acid in the aqueous solution helped to prevent the CuBr microspheres from oxidation. After the excess ascorbic acid is washed off, the CuBr microspheres can be oxidized relatively easily; hence, special care should be taken when these microspheres are separated from the solution.

It was found that PVP played an important role in the formation of spherical CuBr particles. To clearly show the effect of PVP on the morphology of the CuBr particles, the synthesis was carried out at different PVP concentrations (Figure S1, Supporting Information). When there was no PVP in the starting solution, only polyhedral CuBr products with relatively smooth surfaces were obtained. When 0.004 g L^{-1} PVP was added to the solution, aggregated polyhedral particles were obtained, and nearly spherical particles with rough surfaces were produced when the PVP concentration was increased to 0.04 g L^{-1}. Spherical particles were generated only when the PVP concentration was above 0.4 g L^{-1}. As a well-known capping or stabilizing agent, PVP molecules with long chains can be adsorbed to the CuBr particle surfaces via physical and chemical bonding. When a smaller amount of PVP was added to the reaction system, the capping effect of PVP toward CuBr particles was weaker or insufficient, and thus, particles with polyhedral shapes similar to that in the absence of PVP were formed. On increasing the amount of PVP, the CuBr particles were encircled completely by PVP molecules and CuBr nanocrystals with smaller and nearly spherical shapes were formed, which preferred to aggregate into large spheres. This unique role of PVP for the formation of spherical structures was frequently reported; examples include the formation of monodisperse CdS spheres by the aggregation of smaller nanoparticles.[36]

The in situ formed CuBr microspheres can be used as a general sacrificial template for the controlled synthesis of Cu_2O and Cu_xS hollow spheres by directly adding NaOH and Na_2S solutions to the turbid solution containing CuBr microspheres, respectively. Since the thus obtained hollow spheres of Cu_2O and Cu_xS have relatively thicker shells compared with the hollow spheres obtained by using Cu(I)-containing aggregates as the template as described below, hereafter the former hollow spheres are denoted as thick-shell hollow spheres and the latter hollow spheres are denoted as thin-shell hollow spheres. Upon the addition of NaOH aqueous solution at room temperature, the white dispersion of the CuBr spheres became yellow quickly. The XRD pattern of the products (Figure 1b) indicates the formation of pure Cu_2O crystals of cubic structure (JCPDS card no. 05-0667). As shown in Figure 3, after reacting with NaOH, the CuBr solid spheres were almost completely converted into Cu_2O hollow spheres with diameters mainly ranging from 800 to 1200 nm and a shell thickness of about 130−170

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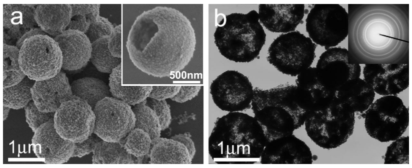

Figure 3. SEM (a) and TEM (b) images of thick-shell Cu_2O hollow spheres. The inset in (a) shows a broken hollow sphere. The inset in (b) shows the ED pattern corresponding to a single hollow sphere.

nm. The ED pattern of a single hollow sphere exhibits clear rings ascribed to the Cu_2O crystal, indicating the polycrystalline nature of the hollow Cu_2O spheres. The diameter of these hollow spheres is basically comparable to that of the original CuBr spheres, suggesting that the in situ formed CuBr spheres actually acted as a reactive sacrificial template for the formation of the thick-shell hollow Cu_2O spheres.

Similarly, thick-shell hollow Cu_xS spheres can also be obtained by adding Na_2S solution to the reaction solution containing the CuBr spheres. When the reaction between Na_2S and the CuBr spheres was carried out at room temperature, well-defined hollow spheres of copper sulfide with rough surfaces were obtained (Figure S2, Supporting Information). The obtained hollow spheres were rather uniform with a diameter of about 1.0−1.2 μm and a shell thickness of about 150−180 nm. However, the XRD pattern of the as-prepared hollow spheres suggests that they are poorly crystallized or basically amorphous. The EDX result indicates that the molar ratio of Cu to S in these hollow spheres is nearly 2:1, indicating that they predominantly consist of amorphous Cu_2S (Figure S3, Supporting Information).

It has been documented that the copper−sulfur system can exist in the amorphous Cu_2S and crystalline covellite (CuS) phases with several phases of varying stoichiometries between these two ideal compositions and the transformation from amorphous Cu_2S to crystalline CuS can occur due to the spontaneous disproportion from the Cu(I) phase to the Cu(II) phase.[37] Accordingly, a hydrothermal treatment of the reaction solution containing the amorphous Cu_2S product was carried out to produce crystalline copper sulfide products. After being hydrothermally treated at 160 °C for 24 h, the amorphous Cu_2S transformed into crystalline CuS of the covellite phase (JCPDS card no. 06-0464), as indicated by the XRD pattern shown in Figure 1c. Moreover, the EDX analysis of the product indicates that it has a Cu:S ratio of 52.9:47.1, which is near the stoichiometric ratio of CuS with a slight Cu excess (Figure S3, Supporting Information), indicating the formation of the crystalline CuS phase with the possible coexistence of a small amount of Cu_2S or other intermediate sulfide species as amorphous impurities. Figure 4 shows typical SEM and TEM images of the hydrothermally treated copper sulfide hollow spheres. It can be seen that the obtained CuS product exclusively consists of uniform hollow spheres with rough surfaces, which look like the Cu_2S hollow spheres obtained without hydrothermal treatment. The hollow CuS spheres show a shell thickness of about 150−180 nm, which is similar to that of the original Cu_2S hollow spheres, but have a diameter of about 1.0−1.1 μm, which is a little smaller than the diameter of the original Cu_2S hollow spheres, indicating a slight condensation for the hollow spheres after the crystallization from the amorphous phase. The ED pattern of a single CuS hollow sphere exhibits clear rings ascribed to the covellite-phase CuS, suggesting that the hollow spheres are actually polycrystalline and consist of primary CuS nanocrystals. It may be noted that the diameter of both the Cu_2S and CuS hollow spheres is basically comparable to that of the original CuBr solid spheres (~0.9 μm in diameter), suggesting that the CuBr microspheres still played the role of sacrificial templates for the formation of the Cu_xS hollow spheres. Therefore, it may be concluded that the in situ formed CuBr microspheres can be employed as a general sacrificial template for the fabrication of hollow microspheres of both cuprous oxide and copper sulfides.

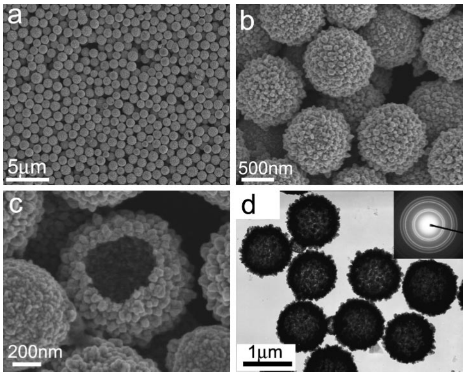

Figure 4. SEM (a−c) and TEM (d) images of thick-shell CuS hollow spheres. The inset shows the ED pattern corresponding to a single hollow sphere.

Formation of Thin-Shell Hollow Spheres. It is interesting to find that uniform thin-shell hollow spheres of Cu_2O and Cu_xS with a shell thickness of about 20−25 nm can be readily obtained if Cu(I)-containing aggregates instead of CuBr solid spheres are employed as the template. In this case, $(C_4H_9)_4NBr$ and $CuCl_2$ were used as the bromide and copper sources, respectively, rather than the use of $CuBr_2$ as both the bromide and copper sources. After the reductant ascorbic acid was added to the solution, the solution became turbid, but no solid precipitates could be separated from the solution by simple centrifugation, indicating the formation of Cu(I)-containing aggregates rather than CuBr solids. Then thin-shell Cu_2O and Cu_xS hollow spheres can be produced upon the addition of NaOH and Na_2S to the solution, respectively. As shown in Figure 5a,b, uniform Cu_2O hollow spheres with a diameter of about 570 nm and a shell thickness of about 20 nm were obtained in a large yield when NaOH was added to the reaction solution at room temperature. The corresponding XRD pattern suggests that the hollow spheres are pure crystalline Cu_2O hollow spheres (Figure 6a).

On the other hand, poorly crystallized Cu_2S hollow spheres with a shell thickness of about 25 nm were obtained when Na_2S was added to the reaction solution at room temperature (Figure S4, Supporting Information). After being hydrothermally treated at 160 °C for 24 h, these Cu_2S hollow spheres transformed into well-crystallized CuS, which was demon-

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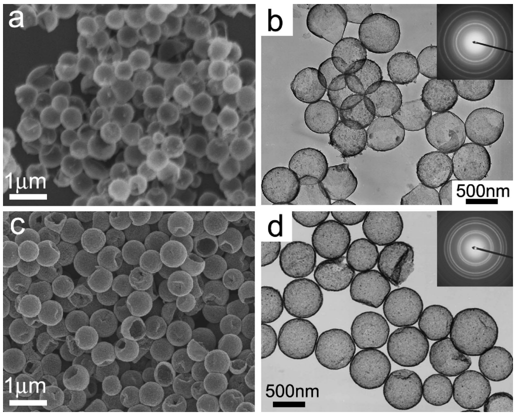

Figure 5. SEM (a, c) and TEM (b, d) images of thin-shell hollow spheres of Cu_2O (a, b) and CuS (c, d). The insets show the related ED patterns.

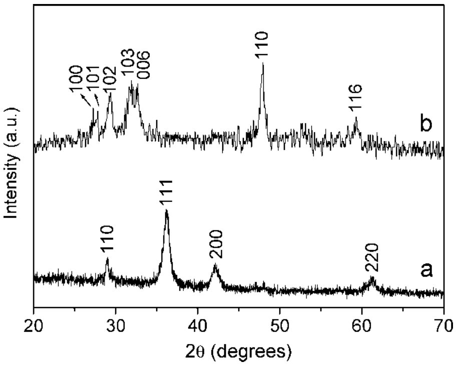

Figure 6. XRD patterns of thin-shell hollow spheres of Cu_2O (a) and CuS (b).

strated by the XRD pattern shown in Figure 6b. However, the apparent amorphous background in the XRD pattern suggests that there also possibly coexists a small amount of Cu_2S or other intermediate sulfide species as amorphous impurities in the product. As shown in Figure 5c,d, uniform CuS hollow spheres with a diameter of about 570 nm and a shell thickness of about 25 nm were obtained in a large yield. The polycrystalline nature of the hollow spheres was indicated by the related ED pattern. Furthermore, the EDX analysis of the Cu_xS hollow spheres before and after the hydrothermal treatment suggests that the molar ratio of Cu to S is nearly 2:1 and 1:1 for the products before and after the hydrothermal treatment, respectively (Figure S5, Supporting Information), confirming the transformation from amorphous Cu_2S to crystalline CuS upon the hydrothermal treatment.

These results suggest that $(C_4H_9)_4NBr$ played a key role in the formation of the thin-shell hollow spheres of copper oxide and sulfides. Our preliminary experiment showed that, in the absence of $(C_4H_9)_4NBr$, the reaction between ascorbic acid and $CuCl_2$ was not visible and no precipitates were obtained, which could be attributed to the relatively large solubility of CuCl ($K_{sp} = 1.72 \times 10^{-7}$).[35] If KBr was added to the $CuCl_2$ solution as the bromide source, CuBr spheres could be obtained upon the addition of ascorbic acid, similar to the case of the direct use of $CuBr_2$ as both the copper and bromide sources. Moreover, if $(CH_3)_4NBr$ or $(C_2H_5)_4NBr$ was used as the bromide source, CuBr spheres could still be obtained upon the addition of ascorbic acid. In contrast, if $(C_4H_9)_4NBr$ was used as the bromide source, CuBr spheres could not be obtained although the reaction solution also became turbid, indicating the formation of Cu(I)-containing aggregates. These results suggest that, compared with the $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ ions, the $(C_4H_9)_4N^+$ ions with relatively longer and more hydrophobic alkyl groups could lead to the formation of spherical aggregates consisting of Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions. It has been reported that $(C_4H_9)_4NBr$ can assemble rapidly into aggregates like vesicles in water when mixed with some metal compounds such as $PdCl_2$, $KAuCl_4$, $AgNO_3$, and K_2PtCl_4.[38] Similarly, in the current situation, spherical aggregates consisting of Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions could form upon mixing $(C_4H_9)_4NBr$, Cu^{2+} ions, and ascorbic acid, which subsequently acted as both sacrificial templates and the copper source for the formation of thin-shell hollow spheres of Cu_2O and Cu_xS. Our preliminary experiments showed that both bromide ions and copper(I) were essential for the formation of the aggregate templates. For example, the mixed solutions containing the Cu^{2+} ions did not become turbid when $(C_4H_9)_4NCl$ instead of $(C_4H_9)_4NBr$ was used, and the mixed solution also remained clear when ascorbic acid was not added in the presence of $(C_4H_9)_4NBr$. As expected, no hollow spheres were obtained from these clear solutions after the addition of either NaOH or Na_2S. To summarize, a possible formation process of the copper-based hollow spheres with different shell thicknesses via sacrificial templates is schematically illustrated in Figure 7. In brief, when $CuBr_2$ was used as both the copper and bromide sources, CuBr solid spheres formed, which subsequently acted as sacrificial templates for the formation of thick-shell hollow spheres of Cu_2O and Cu_xS; on the other hand, when $CuCl_2$ was used as the copper source and $(C_4H_9)_4NBr$ was used as the bromide source, spherical aggregates consisting of Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions formed, which subsequently acted as sacrificial templates for the formation of thin-shell hollow spheres of Cu_2O and Cu_xS. The shell thickness of the hollow spheres could be related to the content of Cu(I) ions in the spherical templates. Namely, a relatively smaller content of Cu(I) ions in the loose aggregates would result in a much thinner shell for the final hollow spheres.

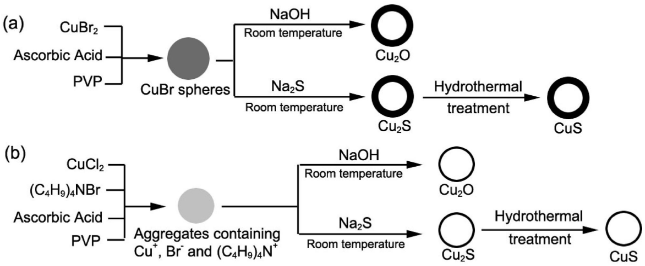

Figure 7. Schematic illustration of the formation of thick-shell (a) and thin-shell (b) copper-based hollow spheres via sacrificial templates.

Optical Properties of the Thin-Shell Hollow Spheres. The optical properties of both Cu_2O and CuS are of interest because of their semiconductor characteristics. Considering that the obtained thin-shell hollow spheres can be readily dispersed in water and ethanol with a good stability, which

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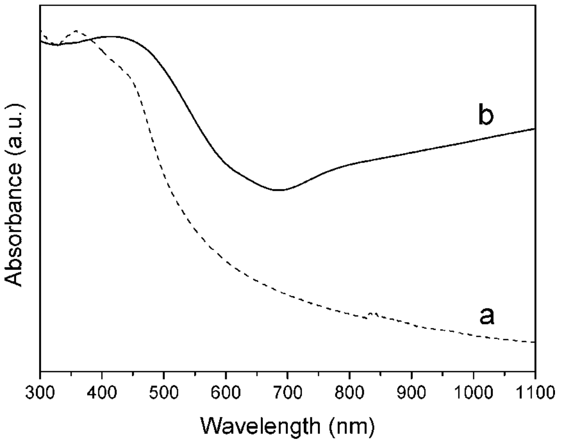

Figure 8. UV−vis absorption spectra of thin-shell hollow spheres of Cu_2O (a) and CuS (b).

makes them relatively ideal systems for optical investigation, the thin-shell hollow spheres of crystalline Cu_2O and CuS were selected for the measurements of the UV−vis absorption and optical limiting properties. Figure 8 displays the UV−vis absorption spectra of the thin-shell Cu_2O and CuS hollow spheres suspended in water. As shown in Figure 8a, the Cu_2O hollow spheres show two humplike absorptions around 355 and 445 nm, which considerably blue-shifted from the absorption of bulk Cu_2O (~570 nm) possibly as a result of quantum size effects.[29,39−41] In a previous paper a quantum-confinement threshold was deduced to be 14 nm for Cu_2O nanocrystallites,[30] which is slightly less than the shell thickness of the present thin-shell hollow spheres (~20 nm). This can be rationalized by considering that the polycrystalline shell of the hollow spheres actually consists of primary nanocrystallites considerably smaller than 14 nm. Figure 8b presents the absorption spectrum of the CuS hollow spheres, which shows an absorption peak at ~415 nm, which is reminiscent of the absorption for CuS nanowires (~400 nm)[42] and for CuS hollow nanospheres (~470 nm).[24] Moreover, the thin-shell CuS hollow spheres show an increased absorption in the near-IR region, which is characteristic of covellite (CuS).[37] It is noted that the long absorption tail could also be attributed to the scattering effects of the hollow particles;[24] however, since such an absorption tail in the near-IR region was not observed for the thin-shell Cu_2O hollow spheres with a similar sphere size and shell thickness, it might be more appropriate to ascribe the absorption tail to the inherent property of CuS rather than to the scattering effects.

In recent years, there has been increasing interest in materials that exhibit strong optical limiting properties for their potential applications in the protection of sensors and human eyes from intense laser radiations. An ideal optical limiter exhibits a high, linear transmission at low fluence, but its output fluence is greatly attenuated at high fluence. The optical limiting properties of carbon nanotubes have been investigated extensively, and they have been shown to be good candidates for optical limiting applications.[43] The suspensions of thin-shell Cu_2O and CuS hollow spheres in ethanol were found to exhibit remarkable optical limiting properties with nanosecond laser pulses at 1064 nm using carbon nanotubes as the reference. As shown in Figure 9, the suspensions of the Cu_2O hollow spheres exhibit linear absorption with approximately flat transmittances when the incident fluence is below 0.29 J/cm^2, above which the transmittances are significantly attenuated with increasing incident fluence, exhibiting obvious nonlinear optical responses or optical limiting effects. The transmittances of the suspensions formed by the CuS hollow spheres are continuously attenuated with increasing incident fluence from very low fluence, suggesting that the dramatic optical limiting effects occur at an incident fluence much lower than that for the Cu_2O hollow spheres. The limiting threshold, known as the input fluence at which the transmittance decreases to half of the linear transmittance, can be used to compare the optical limiting properties of different materials. Here the linear transmittances for both Cu_2O and CuS hollow spheres were determined by the linear transmittance spectra obtained from the normal optical absorption. The thresholds of Cu_2O and CuS are measured to be 1.78 and 0.51 J/cm^2, respectively. At 1064 nm the carbon nanotubes have exhibited good optical limiting effects, whose thresholds were reported to be about 1.5 and 2.5 J/cm^2 for single-wall carbon nanotubes (SWNTs)[43] and multiwall carbon nanotubes (MWNTs),[44] respectively. It is obvious that the threshold of the Cu_2O suspension lies between those for SWNT and MWNT suspensions while the threshold of the CuS suspension is considerably smaller than those for SWNT and MWNT suspensions. Therefore, both the Cu_2O and CuS suspensions exhibit good optical limiting effects, with the CuS suspension showing relatively stronger optical limiting effects. To the best of our knowledge, this is the first time that the optical limiting effects of the Cu_2O suspension have been reported. It may be noted that, in our previous study, strong optical limiting properties have been observed for the CuS hollow

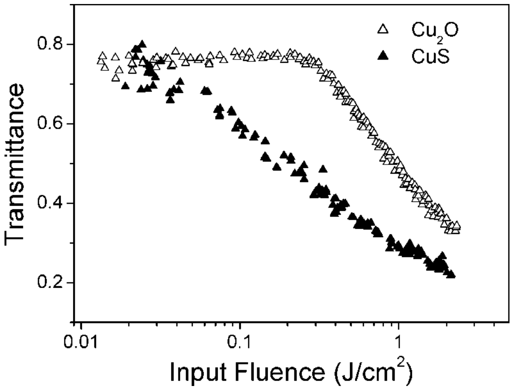

Figure 9. Fluence-dependent transmittance of thin-shell hollow spheres of Cu_2O (△) and CuS (▲) at a wavelength of 1064 nm.

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spheres with a diameter of about 200 nm and a shell thickness of about 30 nm.[24] Compared with those CuS hollow spheres, the current thin-shell CuS hollow spheres with a diameter of about 570 nm and a shell thickness of about 20−25 nm showed somewhat weaker optical limiting properties, which could be partly attributed to the differences in the diameter and shell thickness of the CuS hollow spheres. However, the relationship between the optical limiting property and the diameter and shell thickness of the CuS hollow spheres remains to be invesitigated in more detail.

In general, the origins of optical limiting effects can be attributed to two-photon absorption, free carrier absorption, and nonlinear scattering. As Cu_2O is a direct band gap semiconductor with a band gap of ~2.17 eV and the incident photon energy is 1.17 eV (1064 nm), which is smaller than the band gap but larger than half of the band gap, two-photon absorption is generally a nonlinear optical process and could be the main mechanism of the optical limiting effects. The incident photon energy is also smaller than the band gap of CuS, so two-photon absorption could also occur; however, since CuS is an indirect band gap semiconductor, there is certain linear absorption at 1064 nm, so the free carrier absorption induced by the linear absorption would also play an important role in the optical limiting effects. It is known that, for the objects with sizes comparable to the wavelength, the nonlinear scattering due to the bubbles and microplasma is significant.[45] The bubbles are formed by heat transfer from particles to the surrounding solvent, and their contribution to the nonlinear scattering is obvious within several nanoseconds.[46] The microplasma are generated by the ionization with the intensive laser, and the rapid expansion of the microplasma will strongly scatter the incident laser pulse.[47] In the current situation, the thin-shell Cu_2O and CuS hollow spheres could provide rather dense initiation sites in the polycrystalline shell for the formation of bubbles and microplasma during nanosecond-pulse irradiation, thus enhancing the nonlinear scattering and the optical limiting effects. Moreover, the field enhancement along the interfaces between the inner vacuum and the Cu_2O or CuS shell with some properties of an electric conductor could also contribute to the enhanced optical limiting properties of the hollow spheres. As for the different optical limiting effects exhibited by the Cu_2O and CuS hollow spheres, the stronger free-carrier absorption in the CuS hollow spheres, which is more effective than two-photon absorption, could be responsible for their stronger optical limiting effects. Nevertheless, a more detailed investigation on the optical limiting properties of the obtained semiconductor hollow spheres is required for elucidating the exact origination of the remarkable optical limiting effects, which is currently under way.

Conclusions

A facile one-pot synthesis of uniform hollow spheres of Cu_2O and Cu_xS (e.g., Cu_2S and CuS) has been realized by chemical transformation of in situ formed sacrificial templates containing Cu(I) in aqueous solutions. The shell thickness of these hollow spheres can be adjusted through the choice of the bromide source used for the formation of intermediate templates. When $CuBr_2$ was used as both the copper and bromide sources, CuBr solid spheres formed by the reduction of $CuBr_2$ with ascorbic acid in the presence of PVP, which subsequently acted as sacrificial templates for the formation of thick-shell hollow spheres of Cu_2O and Cu_xS (about 130−180 nm in shell thickness). On the other hand, when $CuCl_2$ was used as the copper source and $(C_4H_9)_4NBr$ was used as the bromide source, spherical aggregates consisting of Cu^+, Br^-, and $(C_4H_9)_4N^+$ ions formed, which subsequently acted as sacrificial templates for the formation of thin-shell hollow spheres of Cu_2O and Cu_xS (about 20−25 nm in shell thickness). In both cases, crystalline Cu_2O hollow spheres were directly obtained at room temperature, while poorly crystallized Cu_2S hollow spheres were first obtained at room temperature and transformed into well-crystallized CuS hollow spheres after a hydrothermal treatment at 160 °C. A strong optical limiting response has been detected for the thin-shell hollow spheres of both Cu_2O and CuS, which could open up new applications for semiconductor hollow spheres in the field of optical limiting, such as the protection of human eyes or optical sensors from high-power laser irradiation.

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Supporting Information Available: SEM images of CuBr products obtained at different PVP concentrations and thin-shell Cu_2S hollow spheres, SEM and TEM images and XRD pattern of thick-shell Cu_2S hollow spheres, and EDX spectra of thick- and thin-shell Cu_xS hollow spheres (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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