Inorg. Chem. **2008**, *47*, 699–704

Lithography inside $Cu(OH)_2$ Nanorods: A General Route to Controllable Synthesis of the Arrays of Copper Chalcogenide Nanotubes with Double Walls

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Received July 21, 2007

A series of well-aligned arrays of copper chalcogenide nanostructures, including Cu_7S_4 and $Cu_{2-x}Se$ nanotubes with double walls have been successfully prepared by using $Cu(OH)_2$ nanorods as sacrificial templates. This new method is based on layer-by-layer chemical conversion and inward etching of the sacrificial templates, which is essentially a kind of lithography inside the $Cu(OH)_2$ nanorods. The key step of the process involves repeated formation of the copper chalcogenide wall and the dissolution of the $Cu(OH)_2$ core for two consecutive cycles. A large difference of the solubility product (K_{sp}) between the copper chalcogenide wall and the $Cu(OH)_2$ core materials is crucial for the direct replacement of one type of anions by the other. Our work provides a novel and general approach to the controllable synthesis of the arrays of copper chalcogenide nanotubes with double walls and complex hierarchies.

Introduction

Over the past several years, considerable attention has been paid to fabricate nanostructures with hollow interiors including tubular nanostructures, owing to their superior performance in applications such as energy conversion,[1,2] drug release,[3] gas storage,[4,5] rechargeable battery,[6] catalysis,[7,8] and sensing.[9]

Recently, hollow structures, in particular those with complex double-wall/shell structures have increasingly attracted lots of attention as a result of their interesting properties.[10−15] For example, Prodan and co-workers reported a unique plasmon hybridization on hollow spheres with two concentric gold nanoshells, thus providing a novel method of tuning resonance frequency by nanostructure engineering.[10] Dähne and co-workers demonstrated that polyelectrolyte capsules with a shell-in-shell structure exhibit an enhanced mechanical strength and preserved permeability.[11,12] Xia's group reported that the Au/Ag alloy multiwalled nanotubes exhibit red-shift of the surface plasmon resonance (SPR) peak and might serve as excellent substrates for the

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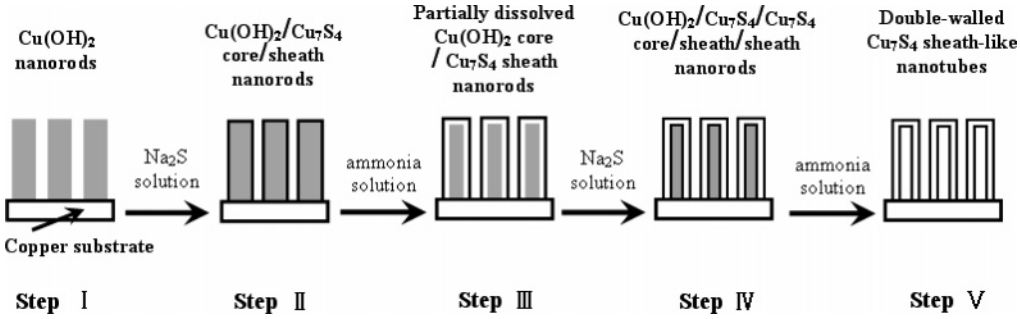
10.1021/ic701448k CCC: $40.75 © 2008 American Chemical Society
Published on Web 12/14/2007

Scheme 1 Schematic Illustration for the Formation of Double-Walled Cu_7S_4 Sheath-like Nanotube Arrays



surface-enhanced Raman spectroscopic detection of molecular species with ultrasensitivity in the spectral region from red to near-infrared.[13] Similar structures can also be found in nature, for example, Gram-negative bacteria possess two cell walls which are separated by an aqueous phase.[16,17] Due to their complex structural characteristics, the rational preparation of double-walled hollow nanostructures is relatively difficult, and it can be extremely technically demanding. Nearly all the methods for fabricating multiwalled hollow nanostructures are so far based on outward growth from the surface of the template or the assistance of some special organic materials,[10−15,18−20] so the diameter of the as-prepared tubes (or hollow spheres) can only become bigger than that of the templates. Therefore, an alternative approach to fabricate well-aligned arrays of nanotubes and other related hollow nanostructures with double-walls is currently of intense interest.

Herein, we propose a new method that can fabricate arrays of double-walled nanotubes without any organic material assistance based on layer-by-layer chemical conversion and etching of the sacrificial template of $Cu(OH)_2$ nanorods from the outside to the inside. In effect, this approach is a kind of lithography inside the $Cu(OH)_2$ nanorods.

Recently, we successfully synthesized well-aligned arrays of Cu_7S_4 sheath-like nanotubes with single walls.[21] In this paper, the arrays of the sheath-like Cu_7S_4 and $Cu_{2-x}Se$ nanotubes with double walls have been successfully fabricated by templating with the $Cu(OH)_2$ nanorods without any organic material assistance. To the best of our knowledge, there has been no report on the controllable synthesis of these double-walled copper sulfide and copper selenide nanostructures. The advantageous features of our nanorod lithography method are its inner replacement/etching fashion without materials accumulation as well as its simplicity, generality, convenience, and effectiveness.

Experimental Section

Synthesis of $Cu(OH)_2$ Nanorod Array Precursors. The synthesis of $Cu(OH)_2$ nanorod array precursors have been described in detail elsewhere.[21,22]

Synthesis of the Array of Cu_7S_4 Nanotubes with Double Walls on Copper Foil. A typical procedure to synthesize the double-walled Cu_7S_4 nanotubes was performed as follows. $Cu(OH)_2/Cu_7S_4$ core/sheath nanorod array was prepared by first immersing the $Cu(OH)_2$ nanorod array grown on copper foil in Na_2S solution (0.01 M) for 3−10 min to get $Cu(OH)_2/Cu_7S_4$ core/sheath nanorod array. Then it was immersed in an ammonia solution (6 wt %) and kept for only several minutes to remove the inner $Cu(OH)_2$ core partially. After the array was taken out from the ammonia solution and washed with distilled water, it was immersed in the Na_2S solution again for 10−30 min and then in the ammonia solution (12 wt %) for 8 h to remove the inner $Cu(OH)_2$ core completely. The resultant product was then washed with distilled water and ethanol and dried in air.

Synthesis of the Array of $Cu_{2-x}Se$ Nanotubes with Double Walls on Copper Foil. A typical procedure to synthesize the double-walled $Cu_{2-x}Se$ nanotubes was performed as follows. The Se^{2-} source solution was prepared by putting 0.015 g of Se and 0.03 g of $NaBH_4$ in 40 mL of NaOH solution (0.005 M), with reference to the reported literture.[23] The $Cu(OH)_2$ nanorod array on copper foil was immersed in it and kept for 10−30 min to prepare the $Cu(OH)_2/Cu_{2-x}Se$ core/sheath nanostructures. The obtained $Cu(OH)_2/Cu_{2-x}Se$ core/sheath nanorod array was immersed in an ammonia solution (6 wt %) and kept for only several minutes to remove the inner $Cu(OH)_2$ core partially. After the foil was taken out from the ammonia solution and washed with distilled water, it was immersed in the Se^{2-} source solution again for 30−60 min and then into the ammonia solution (12 wt %) for 8 h to remove the inner $Cu(OH)_2$ core completely. The resultant product was then washed with distilled water and ethanol and dried in air.

Characterization of the Samples. The as-prepared samples were characterized by X-ray powder diffraction in a Rigaku D/max-γB X-ray diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) operated at 40 kV and 80 mA. Field-emission scanning electron microscopy measurement was taken by a JEOL-7500B scanning electron microscope. Transmission electron microscopic images were taken with Hitachi H-800 and JEOL-2010 transmission electron microscope performed at an accelerating voltage of 200 kV, respectively.

Results and Discussion

The K_{sp} values of copper sulfide (10^{-48}) and copper selenide (10^{-61}) are much smaller than that of $Cu(OH)_2$

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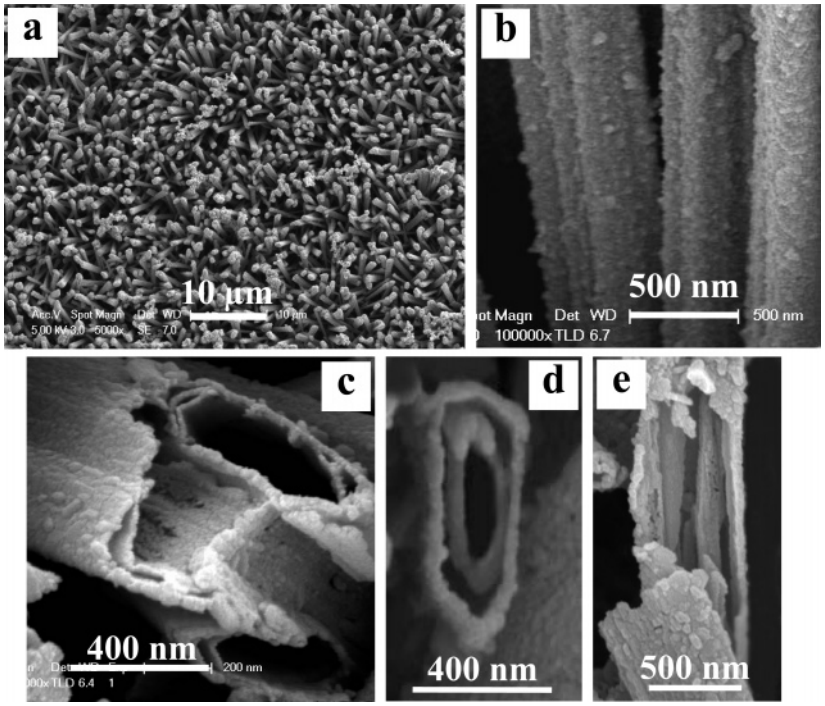

Figure 1. FESEM images of (a) the top view of the array of double-walled Cu_7S_4 nanotubes, (b) a side view of the array of double-walled Cu_7S_4 nanotubes, (c) some broken double-walled Cu_7S_4 nanotubes, (d) a section view of a broken double-walled Cu_7S_4 nanotube, and (e) a side view of a broken double-walled Cu_7S_4 nanotube.

(10^{-20}). This implies that the $Cu(OH)_2$ nanorods can act as both precursors to synthesize more stable chalcogenides and templates to obtain structures with hollow interiors. Our strategy for the synthesis of the highly ordered array of Cu_7S_4 nanotubes with double walls is illustrated in Scheme 1. The first step requires the synthesis of the $Cu(OH)_2$ nanorod array grown on a copper substrate (step I). When the as-prepared $Cu(OH)_2$ nanorod array is immersed into Na_2S solution, S^{2-} will replace OH^- immediately on the surface of each $Cu(OH)_2$ nanorod to produce $Cu(OH)_2/Cu_7S_4$ core/sheath nanostructures (step II). As reported in our previous study,[21] single-walled Cu_7S_4 sheath-like nanotubes have been prepared by dissolving the inner $Cu(OH)_2$ core completely in ammonia solution. However, in order to obtain nanostructures with double walls, the unreacted $Cu(OH)_2$ core should be controlled to be dissolved partially in an ammonia solution with a lower concentration (step III). An interlayer would exist between the inner $Cu(OH)_2$ core and the outer Cu_7S_4 sheath. On the basis of the fact that small molecules or ions can penetrate through the Cu_7S_4 sheath, proper molecules or ions can be chosen to introduce into the interlayer and react with the inner $Cu(OH)_2$ core used as a sacrificial template. In our experiment, the film is immersed in Na_2S solution again and $Cu(OH)_2$ core/Cu_7S_4 sheath/Cu_7S_4 sheath nanostructures will be obtained when S^{2-} ions penetrate the outer Cu_7S_4 sheath and react with the inner undissolved $Cu(OH)_2$ nanorods to form another Cu_7S_4 sheath (step IV). At last, after the inner remnant $Cu(OH)_2$ core is removed completely in the ammonia solution, Cu_7S_4 nanotubes with double walls will be obtained (step V).

The composition and phase purity of the double-walled nanotubes scraped from the copper substrates are examined by X-ray diffraction (XRD). Figure S1 (see Supporting Information) shows the XRD pattern of the copper sulfide nanotubes with double walls which are prepared after the arrays of $Cu(OH)_2$ nanorods react with Na_2S solution for two cycles. The reflection peaks of the product can be well indexed to the monoclinic Cu_7S_4 (JCPDF 23-0958) with lattice constants $a = 53.808$ Å, $b = 30.956$ Å, and $c = 13.392$ Å.

Field-emission scanning electron microscopy (FESEM) is used to observe the morphologies and structures of the double-walled Cu_7S_4 nanotube arrays. The FESEM images in Figure 1a (top view) and 1b (side view) show the array of the well-aligned Cu_7S_4 nanotubes with close tips and diameters of 250−700 nm, which has a morphology similar to that of the array of the $Cu(OH)_2$ nanorod precursors (Supporting Information Figure S2). The walls of these nanotubes are not smooth, and they are factually built from many smaller nanoparticles instead of nanowires in the single-walled Cu_7S_4 nanotubes described in our previous report.[21] The difference in the building blocks of the two kinds of nanotubes may result from the different reaction time between $Cu(OH)_2$ nanorod arrays and Na_2S solution. Longer reaction time is favorable to the formation of nanoparticles on the nanotube walls. For the synthesis of single-walled Cu_7S_4 nanotubes, a longer reaction time such as 20 min also resulted in nanotubes with walls made up of many small nanoparticles. The as-prepared Cu_7S_4 nanotube arrays exhibit good mechanical stability. For example, during the post-treatment, although the arrays had been immersed in ammonia solution for a long time and washed with distilled water and ethanol many times, the structure of the nanotubes was still intact without sign of breakage. To determine

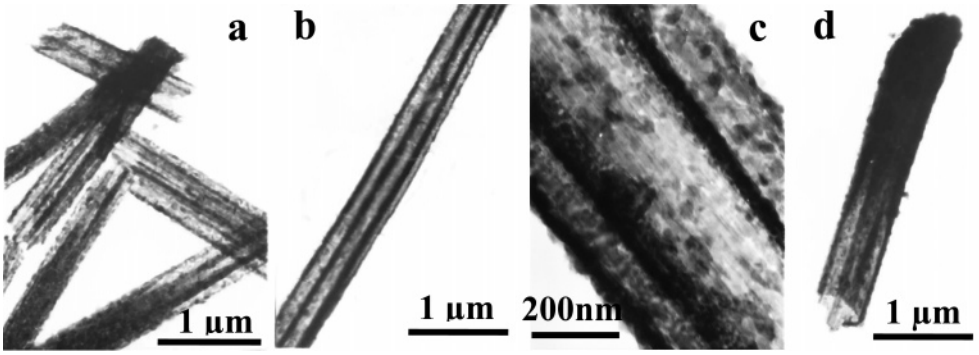

Figure 2. TEM images of (a) some broken double-walled Cu_7S_4 nanotubes, (b and c) the body of a typical double-walled Cu_7S_4 nanotube, and (d) the tip of the double-walled Cu_7S_4 nanotube.

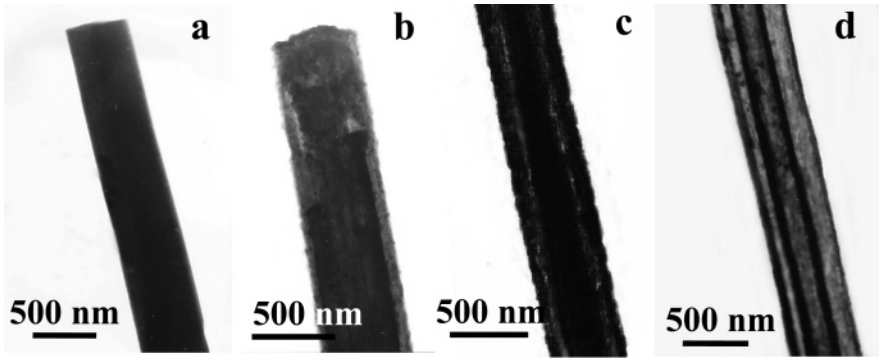

Figure 3. TEM images for the evolution process of double-walled Cu_7S_4 nanotubes: (a) $Cu(OH)_2$ nanorod, (b) $Cu(OH)_2/Cu_7S_4$ core/sheath nanorod, (c) partially dissolved $Cu(OH)_2$ core/Cu_7S_4 sheath nanorod, and (d) double-walled Cu_7S_4 nanotube.

whether these close-tip nanostructures have hollow interiors with double walls, the Cu_7S_4 array film is scraped slightly to break the structure of the close tips. Figure 1c shows the FESEM image of some broken structures of the Cu_7S_4 nanotube array. It reveals that these rod-like nanostructures have hollow interiors with double walls and actually exist in sheath-like nanotube array. Figure 1d and 1e show typical FESEM images of the Cu_7S_4 nanotubes with section and side views, respectively, which demonstrate that the nanotube has double walls. It is noted that the wall thickness of the nanotubes can be controlled by varying the reaction time between $Cu(OH)_2$ nanorod arrays and Na_2S solution while the interlayer between the inner and outer tubes can be adjusted by varying the reaction time between $Cu(OH)_2$ nanorod and ammonia solution.

The morphology and structures of the double-walled nanotubes are further investigated by transmission electron microscopy (TEM). The TEM images of the Cu_7S_4 product in Figure 2a,b show that all of the one-dimensional nanostructures have a strong contrast difference among the walls (dark), the interlayer (light), and center (light), suggesting the hollow structures with double walls, which is consistent with the results of FESEM images in Figure 1. The magnified TEM image shown in Figure 2c further confirms that the wall of the nanotube is constructed from small Cu_7S_4 nanoparticles. A typical TEM image of the double-walled nanotube with a close tip is shown in Figure 2d, which reveals that the inner and outer sheaths are connected at the tip. According to our strategy, there should be an interlayer between the inner and outer sheaths at the tip. The formation of this connection may be caused by the unsymmetrical reaction.

Figure 3 presents the TEM images for the formation process of Cu_7S_4 nanotubes. The TEM image of the $Cu(OH)_2$ nanorod prepared on the copper substrate is shown in Figure 3a, revealing that the nanorod is smooth on the surface with a diameter of about 500 nm. When the $Cu(OH)_2$ nanorod precursor reacts with Na_2S solution for 3−5 min, a layer of Cu_7S_4 is produced on the surface of the nanorod. The TEM image of the $Cu(OH)_2$ nanorod coated with Cu_7S_4 is shown in Figure 3b. Across the rod, the intensity profile shows a clear variation, and the edge surfaces shows lighter contrast, suggesting that Cu_7S_4 is covered on the surface of $Cu(OH)_2$ nanorod to form a continuous coating layer. After the $Cu(OH)_2/Cu_7S_4$ core/sheath nanorod array is immersed in the ammonia solution (6 wt %) for about 3 min to dissolve the $Cu(OH)_2$ core partially, an interlayer between the outer Cu_7S_4 sheath and the inner $Cu(OH)_2$ core is formed (Figure 3c). When the film is immersed in Na_2S solution again, the S^{2-} ions penetrate the outer Cu_7S_4 sheath wall and react with the remnant $Cu(OH)_2$ nanorod core to form another Cu_7S_4 sheath. Therefore, the $Cu(OH)_2$ core/Cu_7S_4 sheath/Cu_7S_4 sheath nanostructures are obtained. Finally, to obtain hollow structures, the unreacted $Cu(OH)_2$ core should be removed. As shown in Figure 3d, the Cu_7S_4

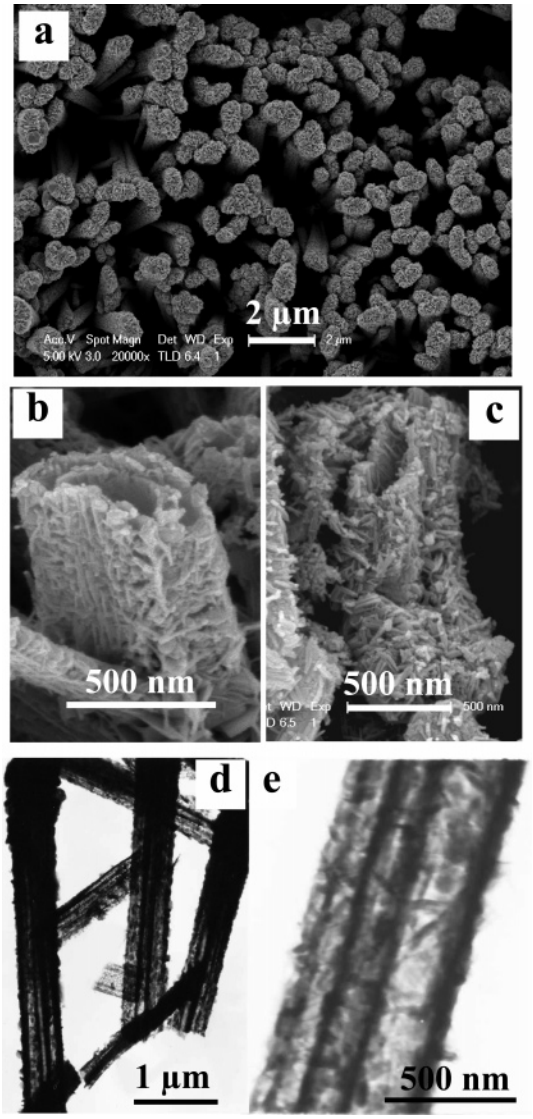

Figure 4. FESEM images of (a) the array of $Cu_{2-x}Se$ nanotubes and (b and c) typical broken double-walled $Cu_{2-x}Se$ nanotubes; TEM images of (d) some double-walled $Cu_{2-x}Se$ nanotubes and (e) the body of a typical $Cu_{2-x}Se$ nanotube.

nanotube with double walls is obtained by removing the inner $Cu(OH)_2$ core in ammonia solution (12 wt %) for 8 h.

In our route, the reaction to form the double-walled Cu_7S_4 nanotube array based on $Cu(OH)_2$ nanorods may take place as the following reaction eqs 1 and 2:

Formation of Cu_7S_4 sheaths

$$7Cu(OH)_2 + 5Na_2S \rightarrow Cu_7S_4 + Na_2SO_3 + 8NaOH + 3H_2O \quad (1)$$

Dissolution of $Cu(OH)_2$ cores

$$Cu(OH)_2 + 4NH_3{\cdot}H_2O \rightarrow [Cu(NH_3)_4](OH)_2 + 4H_2O \quad (2)$$

This method has also been extended to fabricate the array of copper selenide nanotubes with double walls at room temperature. Since copper selenide has much lower solubility ($K_{sp} = 10^{-61}$) than $Cu(OH)_2$ in aqueous alkaline solution, it could be formed when the $Cu(OH)_2$ nanorod array film is immersed in the Se^{2-} source solution. Figure S3 (see Supporting Information) shows the XRD pattern of copper selenide nanotubes with double walls scraped from the copper substrates. All the diffraction peaks can be perfectly indexed to cubic $Cu_{2-x}Se$ (JCPDS 06-0680) with lattice constant $a = 5.73$ Å. Figure 4a shows the FESEM images of the obtained array of $Cu_{2-x}Se$ rod-like nanostructures with close tips. The array of $Cu_{2-x}Se$ nanostructures has a high order and uniformity similar to those of the $Cu(OH)_2$ nanorod templates. We also notice that these rod-like nanostructures have good mechanical stability. Therefore, we had to break them apart to reveal the interior nanostructures. Figure 4b shows the FESEM image of this one-dimensional rod-like nanostructure scraped from copper substrate. The close tip is cut off, indicating that this one-dimensional rod-like nanostructure has hollow interiors with double walls and in fact exists in a double-walled nanotube. A typical FESEM image of a broken $Cu_{2-x}Se$ nanotube with double walls shown in Figure 4c clearly reveals the existence of a hollow interior and the interlayer between the two walls. Both of the outer and inner walls are constructed from many small one-dimensional nanoplate assemblies. Such observations are consistent with the TEM results. Figure 4d shows a low-magnification TEM image of the $Cu_{2-x}Se$ nanotubes. The contrast difference among their walls (dark), interlayer (light), and center (light) further confirms that the $Cu_{2-x}Se$ nanotubes have double walls and close tips. The high-magnification TEM image of a single $Cu_{2-x}Se$ nanotube presented in Figure 4e also reveals that the walls of the nanotubes are built from many small nanoplates. The wall thickness of the $Cu_{2-x}Se$ nanotubes depends on the time of immersing the film in the Se^{2-} source solution. This unique $Cu_{2-x}Se$ product shows a multilevel structure: nanoplates → sheath-like nanotube → double-walled sheath-like nanotube → array of the double-walled sheath-like nanotubes. This organic-free method based on self-assembly coupled with templating of the precursor crystals may form the basis of a new route to hierarchical inorganic hollow structures.

The formation of the array of $Cu_{2-x}Se$ nanotubes with double walls based on $Cu(OH)_2$ templates can be formulated as the following reaction equations:

Preparation of the Se^{2-} source solution[23]

$$Se + NaBH_4 + 4NaOH \rightarrow Na_2Se + Na_3BO_3 + 3H_2\uparrow + H_2O \quad (3)$$

Formation of $Cu_{2-x}Se$ sheaths[24]

$$(2-x)Cu(OH)_2 + (2-x)Na_2Se \rightarrow Cu_{2-x}Se + (1-x)Se + 2(2-x)NaOH \quad (4)$$

In addition to preparing double-walled copper chalcogenide nanotubes, double-walled Cu_7S_4 and $Cu_{2-x}Se$ nanocages have also been prepared by using Cu_2O nanocubes as the sacrificial template based on the same principle. The details are described in Supporting Information (Figures S4−S6).

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Conclusions

In summary, the synthesis of well-aligned arrays of Cu_7S_4 and $Cu_{2-x}Se$ nanotubes with double walls has been demonstrated by using $Cu(OH)_2$ nanorods as sacrificial templates. This inward replacement/etching method has also been successfully extended to the fabrication of Cu_7S_4 and $Cu_{2-x}Se$ nanocages with double walls by using Cu_2O nanocubes as precursors. The key step of the process involves repeated formation of the copper chalcogenide wall and the dissolution of the $Cu(OH)_2$ or Cu_2O core for two cycles. Great difference in solubility product (K_{sp}) is a linchpin for the direct exchange between the two kinds of anions involved. This work opens up a novel and general approach to the controllable synthesis of copper chalcogenide hollow nanostructures with double walls and complex hierarchies. Theoretically, the method can be used to prepare many multiwalled hollow nanostructures with homojunction or heterojunction. Furthermore, we envisage that this synthesis strategy can be applied to many other metal-based systems such as Ag, Zn, Al, Fe, and to even inorganic/organic complex materials systems. The synthesis of Ag_2S and ZnS hollow nanostructures with double walls is ongoing. A host of potential applications of these nanostructures is anticipated in areas such as delivery systems, storage systems, catalysis, surface-enhanced Raman scattering detection, and chemical sensing and separation. Above all, the facile yet controlled formation of well-aligned arrays of these nanostructures that accentuate the hierarchy, porosity, and anisotropy will facilitate nanostructured materials processing and help to meet design criterions of future devices.

Acknowledgment. This project was financially supported by the National Natural Science Foundation of China (NSFC Grants 20301005 and 20576024), the Excellent Young Teachers Program of the Ministry of Education of China, and the Scientific Research Foundation for the Returned Overseas Chinese Scholars supported by the State Education Ministry. S.Y. acknowledges support from the Research Grant Council of Hong Kong (Grant 604206).

Supporting Information Available: FESEM images of the $Cu(OH)_2$ nanorod array, XRD patterns of double-walled Cu_7S_4 and $Cu_{2-x}Se$ nanotubes, and experimental procedures, XRD patterns, FESEM and TEM images, and their descriptions of the Cu_2O nanocubes and double-walled Cu_7S_4 and $Cu_{2-x}Se$ nanocages. This material is available free of charge via the Internet at http://pubs.acs.org.

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