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A Self-Sacrificing Template Route to Spinel $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) Porous Microspheres

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A facile, self-sacrificing template route has been developed to synthesize spinel $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) porous microspheres. The BET surface areas of the products are around 70 m^2g^{-1}. The urchin-like $In_{2.77}S_4$ microspheres precursor acts as both starting material and template to confine the growth of the final products. The phase structures and morphologies of the products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and electron diffraction. Possible formation process and growth mechanism for the porous structure are proposed based on the experimental results.

Introduction

Porous solid materials are of practical significance as useful supports due to their interconnected pore structure, large surface area, and small pore size.[1,2] Recently, the preparation and investigation of nano-/micro-sized porous spheres has attracted considerable attention because of their technical applications in catalysis, drug-delivery systems, separation techniques, photonics, as well as piezoelectric and other dielectric devices.[3,4] Rapid solvent removal,[5] porogen leaching,[6] double-emulsification,[7,8] and solution-induced phase separation[9] have been used to fabricate porous microspheres based on an emulsion–solvent evaporation method. However, these methods are rather complicated for repeatable production and subtle manipulation.

In recent years, multinary chalcogenide compounds have been the subject of intense research,[10,11] and considerable progress has been made in the synthesis and characterization of ternary semiconductor crystallites.[12,13] Various ternary semiconducting compounds with formula $A^{II}B^{III}{}_2X^{VI}{}_4$ have been of special interest due to their unusual properties (e.g. wide transparency intervals, high value of non-linear susceptibility combined with natural birefringence) and potential applications (e.g. electro-photographic films, switches, optical filters, photodetectors, magnetic field control lasers, light modulators, optoelectronics, and Schottky diodes).[14–18] The type I-III-VI ternary semiconductors $CuIn_5S_8$ and $AgIn_5S_8$ are also of great technological and scientific interest because of their possible application in semiconductor devices and optical and quantum electronics.[19]

Both $M^{II}In_2S_4$ and $M^{I}In_5S_8$ show n-type conductivity and crystallize in the spinel-type cubic structure with the space group $Fd\bar{3}m$. There are theoretical and practical reasons to believe that they can all be used as an absorber layer material for a p-n junction solar cell.[18,20,21] Many efforts have been made to study the magnetic, optical, electrical, and semiconducting properties of $M^{II}In_2S_4$[22–26] and the electrical and optical properties of $M^{I}In_5S_8$.[19,27,28]

Conventionally, $M^{II}In_2S_4$ and $M^{I}In_5S_8$ powders are prepared by solid-state reaction methods under high temperature and vacuum conditions for a long time.[19,29,30] Recently, many methods such as metal-organic chemical vapor deposition (MOCVD),[31] chemical vapor transport,[32] precipitation,[33] hydrothermal/solvothermal techniques,[26,34] and a chemical spraying route[18] have been reported for the preparation of $M^{II}In_2S_4$. As for the synthesis of $M^{I}In_5S_8$, spray deposition,[35] pulsed-laser deposition,[36] sequential deposition,[37] and thermal-deposition[38] methods have also been reported. However, the complicated synthesis process and the requirements for special instruments or harsh conditions in these processes are the main disadvantages of these methods. To the best of our knowledge, the extensively applicable self-sacrificing template method has not been reported to be applicable for the fabrication of porous microspheres of a series of $M^{II}In_2S_4$ and $M^{I}In_5S_8$ compounds.

In this paper, we report the successful devolepment of a rational self-sacrificing template route to prepare spinel $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) porous microspheres at low temperature (180 °C). The precursor $In_{2.77}S_4$ was obtained by a convenient mixed-solvent/thermal method at 160 °C in an "aqueous solution/water-immiscible organic solvent" system

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using $InCl_3·4H_2O$ and thiourea (Tu) as the starting materials and a water-immiscible organic solvent (WIOS) plus distilled water as the solvent.

Results and Discussion

Figure 1 shows the XRD patterns of the as-obtained samples. The XRD pattern of the precursor is shown in Figure 1a; it can be indexed to the cubic spinel structure $In_{2.77}S_4$ with lattice constant a = 10.74 Å, consistent with reported values (JCPDS card file No. 88-2495: a = 10.72 Å). The XRD patterns shown in Figure 1b–i can be indexed to cubic spinel structure $MnIn_2S_4$ (JCPDS card file No. 85-1229), $ZnIn_2S_4$ (48-1778), $CdIn_2S_4$ (27-0060), $FeIn_2S_4$ (80-0608), $CoIn_2S_4$ (79-1015), $NiIn_2S_4$ (79-1016), $CuIn_5S_8$ (24-0361), and $AgIn_5S_8$ (24-1477). All nine XRD patterns are very similar as they have the same crystal structure. No characteristic peaks for other impurities, such as metal sulfides (In_2S_3) are observed. The composition of the samples was further analyzed by ICP. The results reveal that the molar ratio of M^{II} (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) to In and S, and M^{I} (M^{I} = Cu, Ag) to In and S is 1:2.03:4.08, 1:1.95:4.03, 1:1.99:4.05, 1:2.02:4.08, 1:2.02:4.07, 1:1.96:3.99, 1:4.91:7.96, and 1:4.96:8.03, respectively.

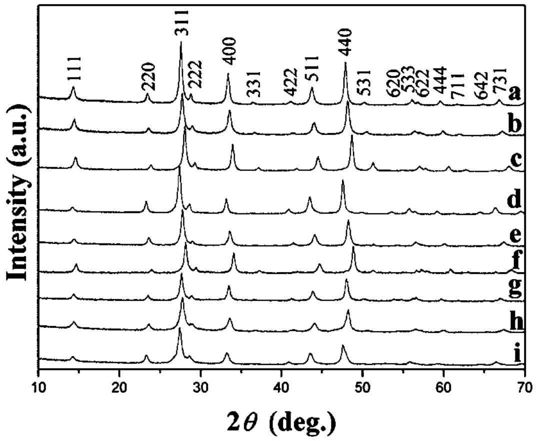

Figure 1. XRD patterns of the as-prepared $In_{2.77}S_4$ precursor (a), $MnIn_2S_4$ (b), $ZnIn_2S_4$ (c), $CdIn_2S_4$ (d), $FeIn_2S_4$ (e), $CoIn_2S_4$ (f), $NiIn_2S_4$ (g), $CuIn_5S_8$ (h), and $AgIn_5S_8$ (i).

Figures 2a and b show SEM images of the as-synthesized precursor $In_{2.77}S_4$ sample, and reveal that the product consists of large-scale porous spheres with a large size distribution (1–6 µm in diameter). It is obvious that the sphere is built up by many interconnected slightly bending flakes with a thickness of about 60 nm, which entangle together to form a network on the surface of the sphere (Figure 2b). Figure 2c is the TEM image of this sample and the inset is the high-magnification TEM image of the surface of the porous microspheres. These images further confirm the spherical urchin-like architecture of the product and the flakes on the surface can also be clearly observed. The corresponding ED patterns in Figure 2d show several diffraction rings, which can be characterized as the (111), (220), (311), (400), (511), and (440) planes (from inner to outer) and further reveal the cubic spinel structure of the product.

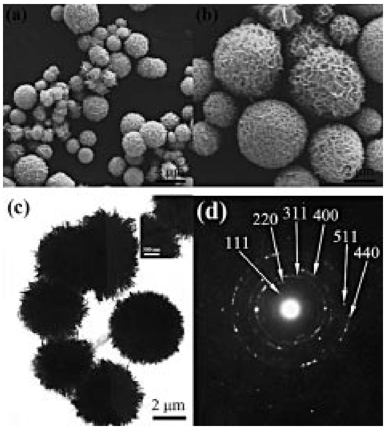

Figure 2. (a), (b) SEM images of the as-prepared $In_{2.77}S_4$ precursor. (c) TEM image of the as-prepared $In_{2.77}S_4$ precursor (inset: TEM image at high magnification). (d) Corresponding ED patterns.

Figure 3 shows an SEM image of the as-synthesized $MnIn_2S_4$ sample using the $In_{2.77}S_4$ precursor as the reactant. It can be seen that the product also consists of porous microspheres, on the surface of which a network of interconnected bending flakes has formed (the SEM image at high magnification is shown in the inset). The TEM images shown in Figures 3b and c also show evidence for the morphological structure, and the corresponding ED patterns (inset of Figure 3b) also reveal that the $MnIn_2S_4$ product has a cubic spinel structure.

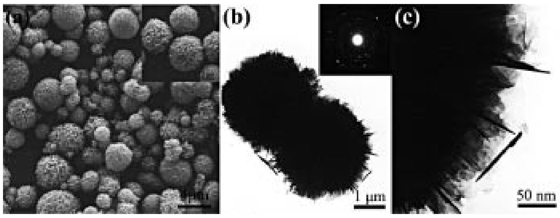

Figure 3. (a) SEM and (b), (c) TEM images of the as-synthesized $MnIn_2S_4$ sample [inset of (a): SEM image at high magnification; inset of (b): corresponding ED patterns].

The SEM images of the other samples, viz. $ZnIn_2S_4$, $CdIn_2S_4$, $FeIn_2S_4$, $CoIn_2S_4$, $NiIn_2S_4$, $CuIn_5S_8$, and $AgIn_5S_8$, are displayed in Figures 4a–h. They all have the same morphology (porous microspheres) as those in Figure 2, which implies that these $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) products still keep the morphology of the $In_{2.77}S_4$ precursor. It is therefore reasonable to deduce that the precursor $In_{2.77}S_4$ porous microspheres play a critical role in the formation of the morphology of the final products.

The surface areas of the as-prepared representative products were determined by the BET method. The BET surface areas of the $In_{2.77}S_4$ precursor and $MnIn_2S_4$, $ZnIn_2S_4$, $FeIn_2S_4$, and $CuIn_5S_8$ are 73.6906, 63.6089, 73.4746, 66.9709, and 62.4300 $m^2 g^{-1}$.

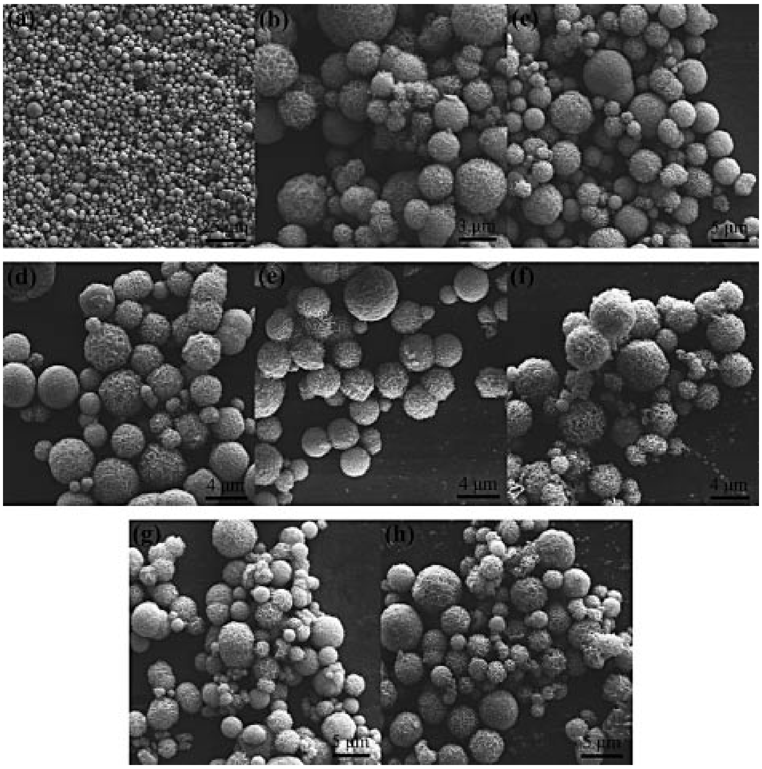

Figure 4. SEM images of as-synthesized (a), (b) $ZnIn_2S_4$, (c) $CdIn_2S_4$, (d) $FeIn_2S_4$, (e) $CoIn_2S_4$, (f) $NiIn_2S_4$, (g) $CuIn_5S_8$, and (h) $AgIn_5S_8$.

Based on the experiments, a possible formation process of $M^{II}In_2S_4$ and $M^{I}In_5S_8$ in this reaction system can be proposed. The reaction of Tu with H_2O can release S^{2-} ions,[39,40] which react with metal ions (Mn^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{+}, Ag^{+}) to produce $M^{II}S$ or $M_2^{I}S$. The subsequent reaction of $In_{2.77}S_4$ with $M^{II}S$ or $M_2^{I}S$ results in the formation of $M^{II}In_2S_4$ or $M^{I}In_5S_8$. These processes can be summarized as follows:

NH_2CSNH_2 (Tu) + 2 $H_2O \rightarrow H_2S + 2\ NH_3 + CO_2$

$M^{2+} + S^{2-} \rightarrow M^{II}S$ or $M^{+} + S^{2-} \rightarrow M^{I}_2S$

In_2S_3 ($In_{2.77}S_4$) + $M^{II}S \rightarrow M^{II}In_2S_4$ or 5 In_2S_3 ($In_{2.77}S_4$) + $M^{I}_2S \rightarrow$ $2\,M^{I}In_5S_8$

Actually, the spinel structure $In_{2.77}S_4$ can be represented by $(In_{1-x})(In_2)S_4$. When it reacts with metal sulfides, some metal atoms (Mn, Zn, Cd, Fe, Co, Ni, Cu, Ag) occupy part of the tetrahedral sites and the rest of the metal atoms occupy part of the octahedral sites to form the $(M^{II}_xIn_{1-x})(M^{II}_{1-x}In_{1+x})S_4$ or $(M^{I}_{1/2-x}In_{1/2+x})(M^{I}_xIn_{2-x})S_4$ spinel structure.

Interestingly, if the $In_{2.77}S_4$ precursor is replaced by the appropriate amount of $InCl_3{\cdot}4H_2O$ and Tu, directly mixed with the metal (M^{II} or M^{I}) salt, and loaded into an autoclave, then the product was not pure $M^{II}In_2S_4$ or $M^{I}In_5S_8$. For the synthesis of $MnIn_2S_4$ only $In_{2.77}S_4$ is obtained here, whereas in other procedures unreacted $M^{II}S$ and M^{I}_2S impurities still exist, which increases the reaction time and the amount of Tu needed.

The amount of distilled water is also a crucial factor for the formation of pure $M^{II}In_2S_4$ or $M^{I}In_5S_8$. When the volume of distilled water in the reaction system reached 1 mL, $In(OH)_3$ impurities could be observed, which may result from the hydrolysis of the $In_{2.77}S_4$ precursor.

From the above analyses, it can be seen that the $In_{2.77}S_4$ precursor may serve as a "self-sacrificing template" to confine the formation of the $M^{II}In_2S_4$ and $M^{I}In_5S_8$ porous microspheres. To investigate the template effect of the $In_{2.77}S_4$ precursor, some contrast experiments were performed. During the preparation of the $In_{2.77}S_4$ precursor, increasing of the volume of distilled water to 10–40 mL caused the formation of $In_{2.77}S_4$ porous microspheres (marked with arrow I) and smooth microspheres (marked with arrow II) simultaneously, as shown in Figure 5a. When this $In_{2.77}S_4$ precursor was used as the reactant, the obtained $M^{II}In_2S_4$ and $M^{I}In_5S_8$ samples also consisted of porous microspheres (marked with arrow I) and smooth microspheres (marked with arrow II), as shown in Figures 5b and c. The final products still kept the morphology of the precursor, which confirmed the self-sacrificing template effect of the $In_{2.77}S_4$ precursor.

A possible growth mechanism for the porous architecture of the $In_{2.77}S_4$ precursor and obtained $M^{II}In_2S_4$ and $M^{I}In_5S_8$ can also be tentatively proposed. During the synthesis of the $In_{2.77}S_4$ precursor, small $In_{2.77}S_4$ spheres are formed first in the "aqueous solution/water-immiscible organic solvent" system because of the interfacial tension. Subsequently, the $[In(Tu)_n]Cl_3$ complex solution[41] reacts on the surface of the spheres to form $In_{2.77}S_4$ flakes in different directions. These flakes then collide with each other and yield an entangled network morphology. Upon interleaving,

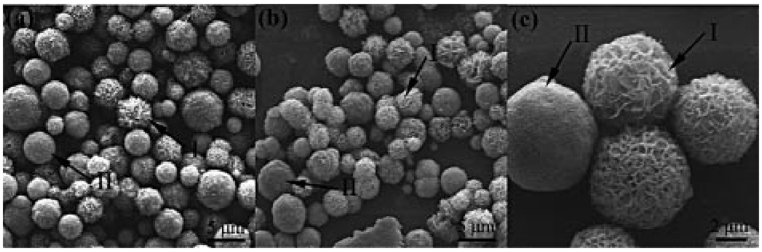

Figure 5. SEM images of (a) as-prepared $In_{2.77}S_4$ precursor with the amount of distilled water increased to 10–40 mL and (b), (c) the $MnIn_2S_4$ sample produced using a mixture of porous and smooth microspheres of $In_{2.77}S_4$ as the reactant.

these newly formed thin flake interfaces become strongly undulated, which results in a slight bending of the flakes in order to relax the strain due to the elongation of the flakes.[42] This process continues until the spheres become completely covered, thereby minimizing the interfacial free energy, to finally give the $In_{2.77}S_4$ porous spheres.[43] Subsequent reaction of the metal salts and Tu on the interface of the $In_{2.77}S_4$ porous spheres gives the final $M^{II}In_2S_4$ and $M^{I}In_5S_8$ porous microspheres. When the amount of distilled water is increased in the preparation of the $In_{2.77}S_4$ precursor, the volume of the aqueous solution increases and many of the initial $In_{2.77}S_4$ spheres are unable to form an interface with the water-immiscible organic solvent, which results in the coexistence of smooth and porous $In_{2.77}S_4$ spheres (Figure 5a). Actually, our experiments showed that the smooth $In_{2.77}S_4$ microspheres occur in the product when the volume of distilled water is above 10 mL. All the obtained $In_{2.77}S_4$ samples consist of porous microspheres and smooth microspheres when the volume of distilled water is in the range 10–40 mL.

Conclusions

In summary, porous microspheres of the ternary semiconductors $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) have been successfully synthesized by a simple self-sacrificing template method using $In_{2.77}S_4$ porous microspheres as the starting material. The possible formation process for the product and a growth mechanism for the porous architecture have been tentatively proposed and discussed in detail. This novel synthesis is performed under ambient conditions and can be easily operated. It is expected to be extendable to the synthesis of other ternary inorganic compounds.

Experimental Section

General: All chemical reagents were of analytical grade, purchased from Shanghai Chemical Reagent Company and used without further purification.

Preparation of the Precursor $In_{2.77}S_4$ Porous Microspheres: In a typical procedure, 2 mmol of $InCl_3\cdot 4H_2O$ (0.586 g) and a slight excess of Tu (0.25 g) were put into a Teflon-lined autoclave of 60 mL capacity and dissolved in 2–3 mL of distilled water to form a solution. The autoclave was then filled with a water-immiscible organic solvent (WIOS, e.g. benzene, toluene, hexane, cyclohexane) up to 90% of the total volume, sealed, and maintained at 160 °C for 12 h. After cooling to room temperature naturally, the final products were filtered off, washed with absolute ethanol and distilled water several times, and then dried under vacuum at 60 °C for 4 h. An orange-red powder was obtained.

Preparation of $M^{II}In_2S_4$ (M^{II} = Mn, Zn, Cd, Fe, Co, Ni) and $M^{I}In_5S_8$ (M^{I} = Cu, Ag) Porous Microspheres: A given amount of divalent metal salt [$MnCl_2\cdot 4H_2O$, $Zn(CH_3COO)_2\cdot 2H_2O$, $CdCl_2\cdot 2.5H_2O$, $FeSO_4\cdot 7H_2O$, $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$] or univalent metal salt (CuCl or $AgNO_3$), the $In_{2.77}S_4$ precursor, Tu, and 2–3 drops of distilled water were loaded into the Teflon-lined autoclave, which was then filled with WIOS up to 90% of the total volume, sealed, and maintained at 180 °C for 20 h. After cooling to room temperature naturally, the products were filtered off, washed with absolute ethanol and distilled water several times to remove impurities, and dried in vacuo at 60 °C for 4 h.

Sample Characterization: The X-ray powder diffraction (XRD) patterns were recorded with a Philips X'pert PRO SUPER diffractometer with Cu-K_α radiation (λ = 1.541874 Å). Direct elemental analysis was performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an Atomscan Advantage (Thermo Jarrell Ash Corporation) instrument. The SEM images were taken with an X-650 scanning electronic microanalyzer. The TEM images and electron diffraction (ED) patterns were obtained with a Hitachi H-800 transmission electron microscope, at an accelerating voltage of 200 kV. For TEM investigation, one or two drops of the solution containing the as-prepared composites were deposited onto an amorphous carbon film supported on a copper grid and allowed to dry at room temperature in air. The surface areas of the samples were evaluated from nitrogen adsorption data by the Brunauer–Emmett–Teller (BET) technique at 77 K with a Micromeritics ASAP 2000 analyzer.

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