

An Analogous Solution-Liquid-Solid (ASLS) Growth Route to InP Hollow Spheres and a Honeycomb-Like Macroporous Framework

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Hollow spheres and a honeycomb-like macroporous framework structure of InP have been successfully fabricated by employing Au/In core/shell composite colloid droplets formed in situ as the template and catalyst for a simple analogous solution-liquid-solid (ASLS) growth route. SEM images show that the morphology of the obtained InP is mostly micrometer-scale hollow spheres (>80 %) accreted with honeycomb-like structures (<5 %). These hollow spheres have

well-defined voids and homogeneous walls, and the surface of the obtained InP hollow spheres is porous, which indicates that the building blocks are InP nanoparticles formed by solidification on the surface of Au/In core/shell droplets. A possible growth mechanism for the micrometer hollow spheres and honeycomb-like macroporous framework is proposed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Over the past decade, hollow microspheres and highly porous inorganic materials with well-defined pore sizes have become an important area of research.^[1] The main thrust of these intensive investigations stems from their wide application,^[2] such as small containers for microencapsulation, catalysis, controlled delivery, artificial cells, light fillers, acoustic insulation, photonic crystals, optical devices, etc.^[3] Porous spherical beads can also be used to improve the properties of materials by increasing the accessible surface. Macroporous materials with pore sizes > 50 nm and with well-defined and controllable porosity have attracted particular interest because of their unique optical, catalytic, and mechanical properties.^[4] Macroporous supports can be designed to provide optimal flow and improved efficiencies in catalysis and large-molecule separation processes, as well as to permit immobilization and stabilization of large guest molecules.^[5] Due to the importance of these specific morphologies and assemblies, notable progress has been made in structural, compositional, and morphological control, in processing aspects of porous solids, and new applications of these materials. Some important synthetic strategies have also been reported for the control and preparation of these peculiar hollow microspheres and ordered three-dimensional macroporous framework. Among these methods, templating techniques are the most appropriate and versatile method to produce hollow spheres and macroporous

materials. The templates used include polystyrene latex spheres,^[4a, 6] liquid crystals,^[7] surfactant vesicles,^[8] macroporous active carbon,^[9] emulsions,^[4b] etc. So far, various hollow spheres and macroporous materials have been fabricated by this universally applied template-directed synthesis, including oxides,^[4a, 6] graphite and diamond,^[10] semiconductor Si,^[11] CdS,^[11a] and metals.^[11f]

Recently, III–V semiconductor nanoparticles, which are well-known electronic and optoelectronic materials, have received renewed interest due to their technological importance.^[12] InP is an especially intriguing target for research because of its extensive use in the sources and detectors in fiber optic communications and high-speed electronic applications. Several new strategies have been developed to synthesize InP nanocrystals with different morphologies, such as high-quality InP nanocrystals obtained in a noncoordinating solvent^[13] or aqueous solution,^[14] InP nanowires or nanotubes by a laser ablation process by a vapor-liquid-solid (VLS) growth mechanism,^[15] or a solution-phase synthesis by a solution-liquid-solid (SLS) mechanism,^[16] with the goal of lowering the processing temperature and avoiding complex reactions and toxic precursors. In addition, the widespread research into porous III–V semiconductors is fuelled by the exhibition of new properties and a large potential for applications in nonlinear optical materials.^[17] The porosity of a III–V compound induces bandgap widening and further results in blue and ultraviolet luminescence.^[18] For example, two-dimensionally nanostructured porous GaP membranes exhibit a strongly enhanced optical second harmonic generation in comparison with the bulk materials.^[19] Our group has made significant progress towards the synthesis of III–V semiconductors, such as InP,^[20] GaP,^[14] and InAs,^[21] with desired morphologies by simple and effective solvothermal methods. Up to now,

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most effort has been focused on the formation of one-dimensional III–V semiconductors. One of the most important growth mechanisms for one-dimensional nanostructures is the VLS mechanism in chemical vapor deposition (CVD) or laser ablation using Au as the catalyst.^[15] Recently, the VLS mechanism was extended in solution for the preparation of InAs quantum rods with controlled lengths and diameters by applying a nanocrystalline gold catalyst to the reaction of InCl_3 with tris(trimethylsilyl)arsane $[\text{As}(\text{TMS})_3]$ at 360 °C,^[22] which can also be considered as an improved SLS route.^[16] A detailed investigation of these reported methods helped us find that there is one common factor, namely the existence of alloy liquid droplets that serve as a nucleation catalyst for the formation of one-dimensional nanostructures at the given elevated temperature, such as the In–Au alloy liquid droplets in the formation of InP and InAs nanowires.^[15,22] The essence of the catalytic functions of these liquid droplets is the existence of supersaturation, which supports the whisker growth at the liquid/solid interface. However, a high reaction temperature is a prerequisite for the formation of In–Au alloy liquid droplets in all these reports. We therefore wondered what the results would be if the temperature is too low to form the In–Au alloy in a given reaction system. In order to find the answer to this question we decided to exploit an analogous SLS (ASLS) growth route to synthesize InP spherical assemblies, which can be considered as an extension of the SLS method. The latter has traditionally been applied to grow 1D III–V semiconductors containing low-melting-point metals such as indium by decomposition of indium-containing organometallic complexes as intermediate and catalyst for the directed growth of III–V one-dimensional structures.^[16] In our approach, to obtain a solution-controllable synthesis of InP with the desired hollow sphere morphology we introduced gold nanoparticles (formed by reduction of HAuCl_4 in solution) into the classical SLS system^[16,20,21] and controlled the system temperature at 200 °C. The in-situ formed gold nanoparticles act as a colloidal template for the synthesis of spherical assemblies.

Results and Discussion

The XRD patterns (Figure 1a) of the samples agree well with the bulk InP reflection,^[23] thus indicating the same cubic zinc blende lattice structure. Judging from the XRD pattern, the products have very high crystallinity under the given experimental conditions. No component of the Au catalyst can be detected in Figure 1a, thus indicating that its content is less than the resolution limit of XRD. SEM images, as shown in Figures 2a and b, give a general view of the obtained InP micrometer hollow spheres under low magnification. Many collapsed and hemispherical hollow spheres can also be seen in Figure 2a, thus indicating the hollow structure of the spheres. Figures 2c and d display images of typical, collapsed hemispheres, from which it can be seen that the obtained hollow spheres are about 3–6 μm in diameter with a wall thickness of 1 μm . The opening and

collapse are probably due to decomposition of the templates when washing with dilute HCl. Figure 3 displays the SEM images of the obtained InP hollow spheres at high magnification; the porous nature of the surface can clearly be seen. Figure 3 also confirms that the building blocks of the InP hollow spheres are InP nanoparticles. Interestingly and surprisingly, some ordered honeycomb-like macroporous networks are also found to accrete with the hollow spheres, as shown in Figure 4. The pore diameter of the ordered honeycomb-like macroporous network is approximately 2–5 μm . A key feature of these networks is the interconnectedness of their pores; an SEM image at high magnification (Figure 4b, arrowed) shows that some of the voids

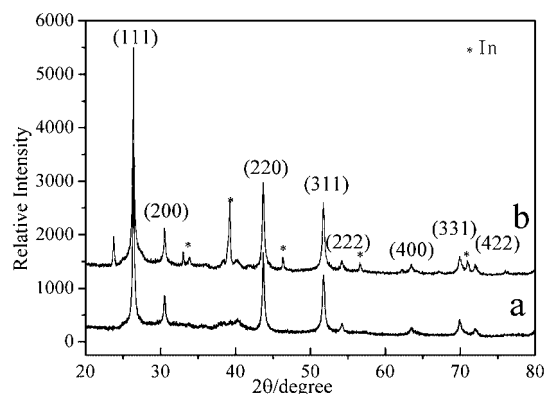


Figure 1. XRD pattern of obtained InP samples (a) after HCl treatment and (b) without HCl treatment, indicating the presence of In.

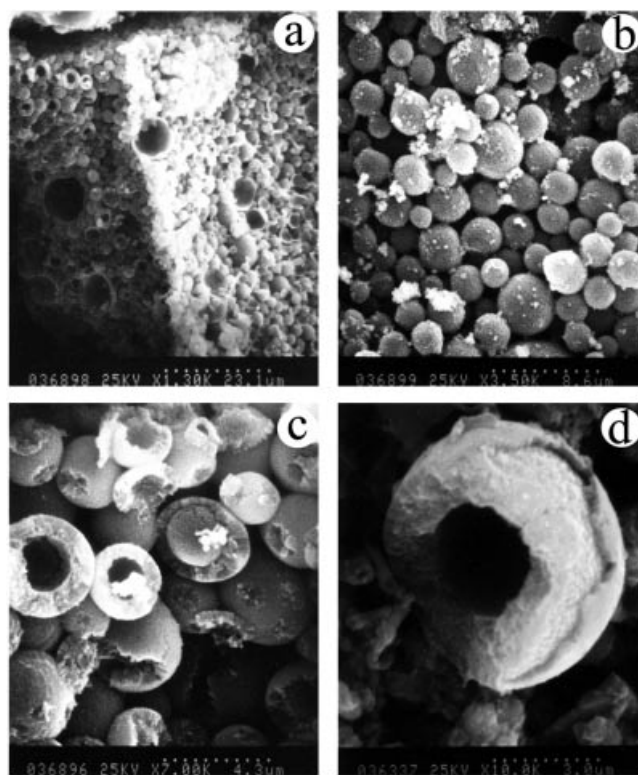


Figure 2. SEM images of obtained InP micrometer hollow spheres: (a) and (b) show the obtained InP micrometer hollow spheres at low magnification and (c) and (d) show the collapsed and broken InP spheres at high magnification, indicating their hollow nature.

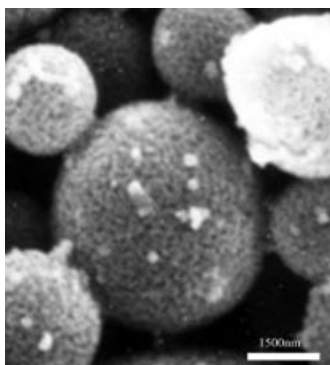


Figure 3. SEM images of obtained InP hollow spheres at high magnification, showing the porous surface structure.

are connected to their neighbors by smaller windows. Such microstructures allow these macroporous networks to be filled with different liquid precursor solutions in the second templating process. These small windows play important roles in the fabrication of the desired morphologies as they provide the necessary channels to allow the precursor solution to flow through and form a shell throughout the entire void. The arrow in Figure 4c shows some InP spheres inlaid in the macroporous network, which further prove the proposed formation mechanism.

XPS spectra were recorded to identify the surface composition of the as-prepared products. The bonding energies obtained from the XPS analysis were corrected for specimen charging by referencing the C 1s line to 287.60 eV. Figure 5a shows the XPS survey spectra of InP. No obvious impurities (besides the Au catalyst and trace amounts of adsorbed O₂) can be detected in the samples, thus indicating that the products have high purity and the level of impurities is lower than the resolution limit of XPS (1 at%). The typical high-resolution spectra of In 3d and P 2p are shown in Figure 5b. The binding energy values are 443.74 eV for In 3d_{5/2} and 451.38 eV for In 3d_{3/2}. The P 2p core shows two peaks, one at 128.88 eV corresponding to P from InP and the other at 132.95 eV (arrowed) corresponding to oxidized P species due to exposure to the air. The peak areas of these high-resolution scans were measured and used to calculate the In/P ratio for the product. The

quantification of the peaks gives an atomic ratio of In/P of 0.43:0.53. The excess P perhaps comes from the added P raw materials. All of the observed binding energy values for In 3d and P 2p coincide with the reported data within the experimental errors.^[24]

In both the reported VLS route and its extension in solution, the noble metal Au and the in-situ formed alloy species function as catalysts for the nucleation and further direct the growth of 1D nanostructures. Thus, the reaction temperature must be higher than the eutectic temperature of the alloy. Once formed, the In–Au alloy liquid droplets dissolve the reactants and the subsequent supersaturation supports one-dimensional structure growth at the liquid/solid interface.^[15,22] In our approach, however, the obtained product is spherical rather than the usual one-dimensional nanostructure. Our reaction temperature (200 °C) is lower than that of the melting point of bulk gold and higher than that of the melting point of In and P₄ (157 and 44.1 °C, respectively), therefore the Au–In alloy cannot form. Banin has reported that InAs nanorods do not yield one-dimensional growth at a lower reaction temperature of 300 °C, which indicates that reaction temperatures of at least 360 °C are required for the onset of Au melting.^[22] This value is consistent with theoretical studies that predict a melting temperature for Au₁₄₆ (diameter ca. 1.6 nm) of ca. 350 °C, increasing to ca. 480 °C for Au₄₅₉ (diameter ca. 2.5 nm).^[25] The current low temperature (200 °C) may not suffice to activate the gold particles as catalysts to direct the growth of the one-dimensional nanoscale material. However, the reduced liquid In becomes coated on the newly formed Au nanoparticles due to the physical tendency to reach the lowest energy level and forms Au/In core/shell droplets. These droplets further serve as a second template for the nucleation of InP nanoparticles, therefore the function of the Au/In core/shell droplets is as a template for a spherical structure^[16] rather than a nucleation catalyst for the formation of a one-dimensional structure.^[15,22] In the region of scattered Au/In core/shell beads, however, the P₄ molecules in solution will react with the In on the surface of Au/In beads (Path 1 in Scheme 1). Thereafter, the formed InP nanoparticles solidify to form a compact InP layer on the surface of the Au/In core/shell droplets, which blocks the further

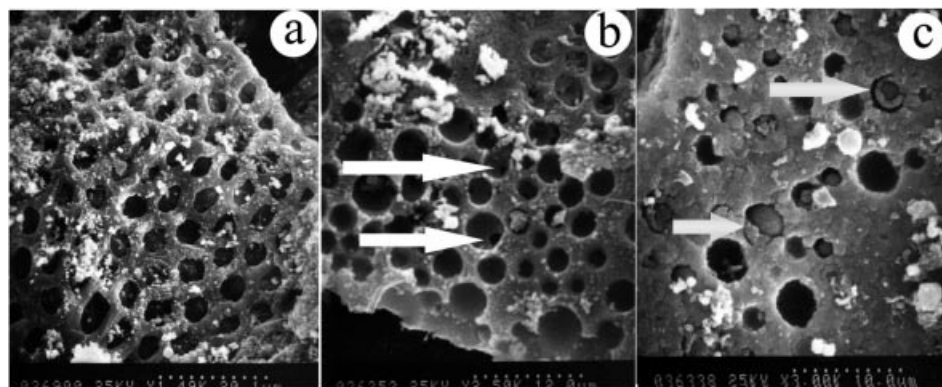


Figure 4. (a)–(c) SEM images of obtained InP honeycomb-like macroporous network (<5%). The arrow in (c) shows some InP spheres inlaid in the macroporous network.

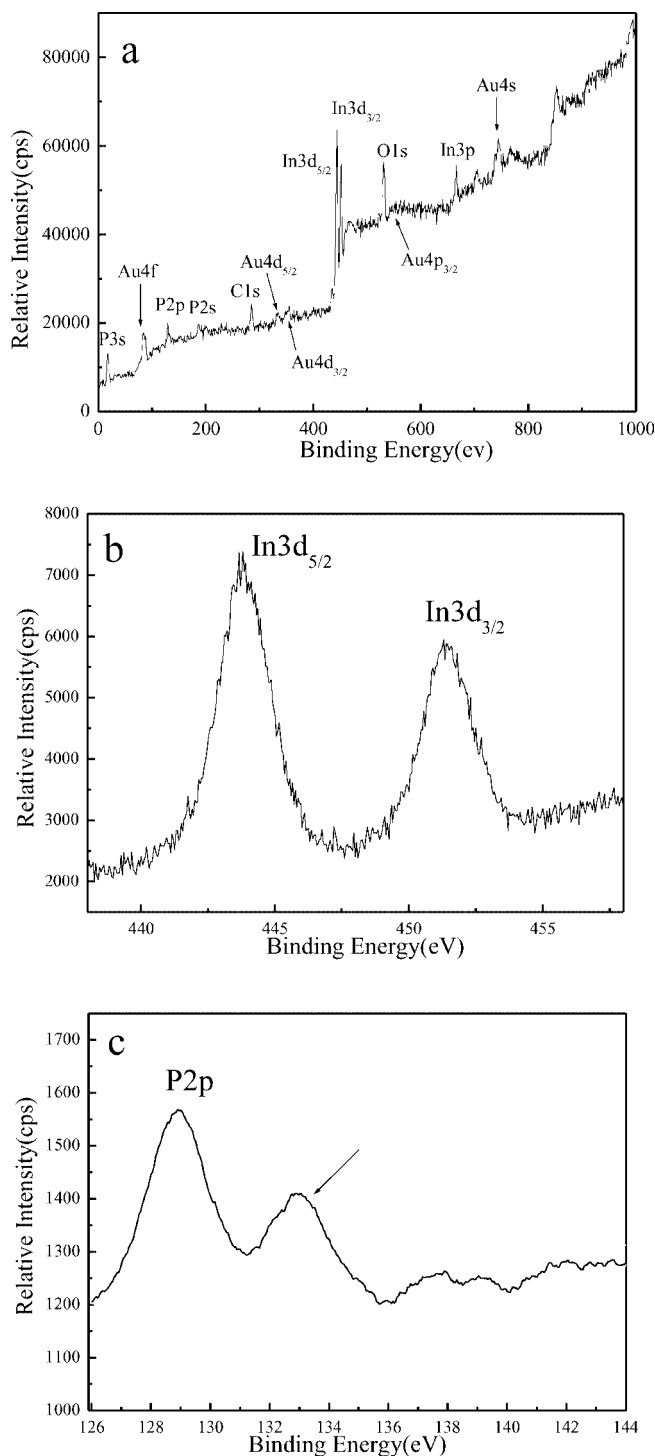
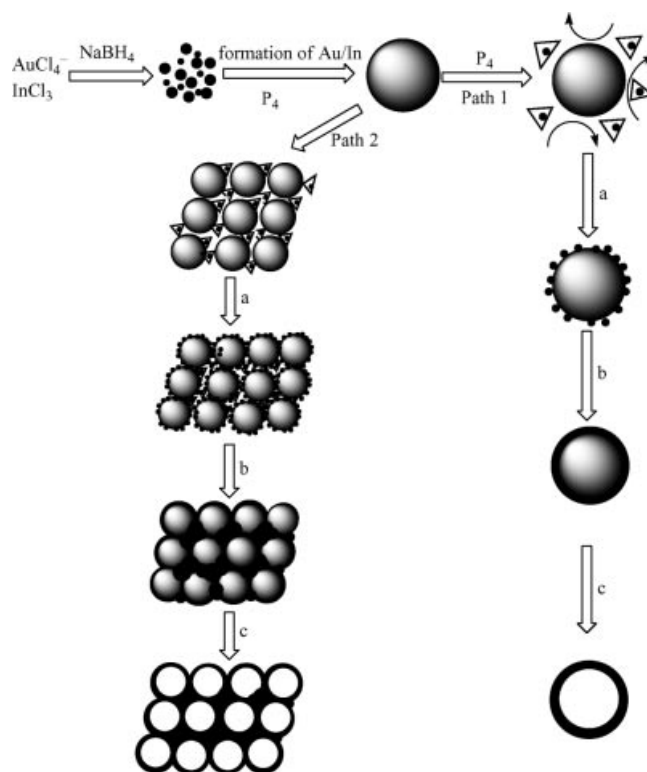


Figure 5. XPS spectra: (a) InP survey spectra, showing the presence of Au catalyst; (b) In 3d; (c) P 2p, with an arrow indicating the oxidized P species.

reaction of P_4 with In molecules in the beads. As a result, when removing the unreacted In by treatment with dilute HCl solution, the inner Au cores separate from the outermost InP shells and finally produce InP hollow spheres (>80%). Upon removal of the support, some collapsed hollow spheres are formed. The presence of In before the HCl

treatment was observed by XRD, as shown in Figure 1b. However, it is reasonable to propose that in the dense and thick regime of Au/In beads, which array in order, P_4 molecules in solution filter into and fill the void spaces among the beads of the crystalline array. The reaction of P_4 with In molecules and subsequent solidification form a compact InP layer on the surface of the Au/In core/shell beads. This process is similar to the formation of InP hollow spheres. However, due to the highly aggregated nature of the array of Au/In beads, the solidification of the InP spheres connects each other into a compact whole containing unreacted In. After the removal of residual In, an ordered three-dimensional porous structure with an array of interconnected spherical pores is formed (Path 2 in Scheme 1, <5%). In addition, some InP spheres inlaid in the macropores are also found (Figure 4c, arrowed), which further demonstrates the template effect of the Au/In core/shell droplets. This large surface area endows InP with many promising applications in separation and adsorption. Moreover, the periodical pores can also serve as cavities to accommodate diverse guest molecules. Scheme 1 outlines the schematic process of the formation of the desired morphology.



Scheme 1. Schematic illustration of the formation of InP micrometer hollow spheres and the honeycomb-like macroporous network: (a) reaction of P_4 with In on the surface of Au/In beads; (b) solidification of InP nanoparticles on the surface of Au/In beads, which leads to the formation of a core/shell structure. (c) removal of In by HCl, leading to the formation of InP hollow spheres or a macroporous network (a triangle represents P_4 molecules). The predominant Path 1 gives the hollow spheres and Path 2 leads to the honeycomb-like macroporous network.

A series of comparison experiments were performed to determine the effect of synthetic conditions on the formation of InP hollow spheres and macroporous networks. Detailed investigation helped us determine that the ratio of In/Au is important for controlling the synthesis of InP nanocrystals with different assemblies, and that the optimal molar ratio of In/Au for the formation of these InP hollow spheres and network is 25:1. At this molar ratio the product is mainly microporous hollow spheres (>80%) with a small amount of a three-dimensional ordered macroporous network. We also found that it is difficult to obtain the desired hollow spheres morphology if the molar ratio of In/Au is too far above or below this ratio. For example, the obtained products are mainly irregular particles with a small quantity of rough spherical products at a ratio of 50:1. These particles resemble an irregular stack that shows some morphological similarity to that of Figure 2b. However, the amount of obtained microscale spherical structures is less than 10%. With a reduction of the ratio, for example to 10:1, the obtained products are poorly crystalline particles.

In order to understand the formation mechanism of InP hollow spheres, the reaction was carried out without the addition of P; all other experimental conditions and parameters were kept constant. The obtained In/Au composite beads are spherical, as shown in Figures 6a and b, and gold nanoparticles exhibiting high contrast can be discerned in the cores of many of them (Figure 6b), which provides firm evidence for our proposed mechanism.

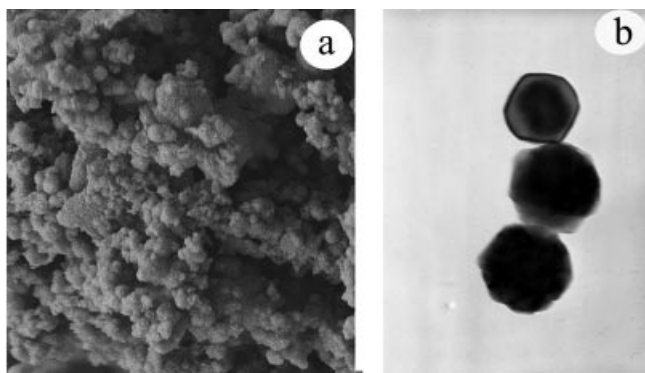


Figure 6. Obtained Au/In spherical composite particles: (a) SEM image, (b) TEM images; gold nanoparticles exhibiting high contrast can be discerned in the cores.

As is well known, it is very important to select appropriate solvents for the design of solid-state compounds by a solvothermal route.^[20,26] Based on our control experiments, we found that ethylenediamine plays an important role in the formation of InP particles under our conditions as it can disperse yellow phosphorus to form a brown dispersion and readily dissolve KBH_4 , which means that it increases the surface area of the reactants and promotes the reaction at given temperatures.^[20] When other solvents were used, such as ethanol, benzene, DMF, or pyridine, the reaction either did not take place or the products could not be identified. Strongly polarizing solvents such as ethylenediamine

at the appropriate temperature provide conditions that are adequate to greatly enhance solubility, diffusion, and crystallization.

The same route has also been applied to the synthesis of GaP, using GaCl_3 instead of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ as the source. The obtained GaP micrometer spheres, with a diameter of ca. 3–4 μm , are shown in Figure 7. Some spheres with small openings in the surface can also be observed (inset in Figure 7), thus indicating that the obtained GaP spheres have a hollow structure. However, at the given temperature (200 °C) the obtained GaP hollow spheres are very poorly crystalline.

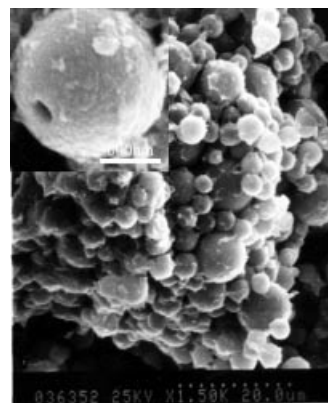


Figure 7. GaP micrometer-sized hollow spheres obtained in the same approach; the inset shows the small openings in the surface of GaP spheres, which indicate the hollow structure of the obtained GaP spheres.

Conclusions

In summary, we have demonstrated an effective analogous solution-liquid-solid (ASLS) growth route to meso-scale InP hollow spheres accreted with honeycomb-like structures, in which the Au/In core/shell droplets formed in situ serve as the template and catalyst. These hollow spheres have well-defined voids and homogeneous walls. The surface of the InP hollow spheres obtained is porous, which further indicates that the building blocks are InP nanoparticles formed by solidification on the surface of Au/In core/shell droplets. A systematic investigation has shown that the correct ratio of indium/noble metal is a prerequisite for the synthesis of InP novel structures, and that the optimal ratio is 25:1. The same experimental process has been applied to GaP hollow spheres and will be extended to other important metal phosphides with desired morphologies.

Experimental Section

Analytical-grade reagents and solvents were purchased from Shanghai Chemistry Co. Ltd and used without further treatment. Typical procedure: 40 mL of ethylenediamine, 1.11 g of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, 0.5 g of yellow phosphorus, 2 mL of an ethanol solution of HAuCl_4 (0.0758 M) and 1.6 g of KBH_4 were placed in a 50-mL Teflon-lined autoclave. The autoclave was maintained at 200 °C

for 10 h, and then cooled to room temperature naturally. The black products were filtered off and washed with absolute alcohol and dilute aqueous HCl (1 M). Finally, the products were dried in vacuo at 50 °C for 1 h. The key to the fabrication of InP hollow spheres and macroporous network is the control of the In/Au ratio. During the formation of the desired InP hollow spheres, the influence of this ratio was investigated in detail and control experiments were performed with different molar ratios of In/Au, such as 120:1, 100:1, 80:1, 50:1, 25:1, and 10:1. In addition, in order to understand the formation mechanism, different solvents, such as ethanol, benzene, DMF, and pyridine were selected to investigate the optimal experimental conditions.

The final products were characterized by various techniques. X-ray powder diffraction (XRD) was carried out with a Rigaku D/max rA X-ray diffractometer with Cu- K_{α} radiation ($\lambda = 1.54178 \text{ \AA}$). A scan rate of 0.05° per second was applied to record the pattern in the 2θ range of $20\text{--}85^{\circ}$. The morphology and size of as-prepared products were determined from SEM images, which were recorded with an X-650 scanning electronic microanalyzer. To obtain further evidence for the purities and compositions of the as-prepared products, the X-ray photoelectron spectra were recorded with an ESCA-Lab MKII X-ray photoelectron spectrometer, using Mg- K_{α} radiation as the exciting source.

Acknowledgments

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