Materials Research Bulletin 44 (2009) 216–219

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

Efficient rapid microwave-assisted route to synthesize InP micrometer hollow spheres

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ARTICLE INFO

Article history:
Received 13 January 2008
Received in revised form 4 March 2008
Accepted 30 March 2008
Available online 14 April 2008

Keywords:
A. Inorganic compounds
A. Semiconductors
B. Chemical synthesis
C. X-ray diffraction
D. Microstructure

ABSTRACT

The efficiencies of two methods of synthesizing InP micro-scale hollow spheres are compared via the analogous solution–liquid–solid (ASLS) growth mechanism, either through a traditional solvothermal procedure, or via a microwave-assisted method. Scanning electronic microscopy (SEM) images show that most of the as-grown samples are micrometer hollow spheres, which indicates the efficiency of both methods. For traditional solvothermal route, long time (10 h) is necessary to obtain the desired samples, however, for the microwave-assisted route, 30 min is enough for hollow spherical products. An optimal choice of microwave irradiating time allows reducing the reaction time from hours to minutes. The proposed ASLS growth mechanism has also been discussed in detail.

1. Introduction

The synthesis of III–V semiconductor nanocrystals has been an area of intense research over the past 20 years. Due to its extensive uses in the sources and detectors in fibers optic communication, and high-speed electronic application, notable progress has been made in the fabrication of crystalline III–V semiconductor InP nano- or micro-crystals with desired morphologies and sizes with the goal of green synthesis, namely, lowering processing temperature and reducing time, avoiding complex reactions and toxic precursors. Up to now, a large number of methods have also been successfully applied to synthesize InP nanocrystals, such as, high quality InP nanocrystals obtained in a noncoordinating solvent [1,2] or aqueous solution [3], InP nanowires or nanotubes through the vapor–liquid–solid growth mechanism [4,5] or solution-phase synthesis via a solution–liquid–solid mechanism [6], the single-crystalline InP nanosprings via the simple thermochemical process [7], etc. And recently, a novel sonochemical method has also been developed for the synthesis of InP nanocrystals [8]. To circumvent the tedious and time-consuming process, it is commonly accepted that toward greener nanoscience or nanotechnology is very important [9]. It is well known that microwave synthesis is a relatively new chemical method to facilitate and accelerate chemical reactions and could be another avenue for green synthesis of nanomaterials [10,11]. Several attributes of microwave heating contribute to greener nanosyntheses, including shorter reaction time, reduced energy consumption, and better product yields. Therefore, the microwave irradiation has been widely applied in the field of nanoscience and nanotechnology [10–14].

Hollow spheres are an appealing structural design for many applications ranging from the delivery of encapsulated products for cosmetic and medical purposes to their use as lightweight composite materials and as fillers with low dielectric constant in electronic components [15]. Applications for hollow microspheres also cover areas such as catalysis, piezoelectric transducers, and manufacture of advanced materials [16]. And their preparation in the submicron diameter range has been an active area of materials research [15,17,18].

In this communication, the efficiencies of two methods of synthesizing III–V InP hollow spheres are compared, either through our previously reported solvothermal procedure [19] or via a microwave-assisted method. We introduce gold nanoparticles (reduced from $HAuCl_4$ in solution) into the classical SLS system [6,20] and control the system temperature at *ca.* 200 °C, in which the in situ formed gold nanoparticles were applied as the colloidal template for synthesizing spherical assemblies. As expected, InP hollow spheres assembled by nanoparticles has been successfully synthesized via the analogous solution–liquid–solid (ASLS) growth mechanism [19].

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0025-5408/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.materresbull.2008.03.034

2. Experimental

The detailed efficient solvothermal procedure to InP hollow spheres has been reported elsewhere [19]. Here, it is a simple description for microwave-assisted process. The microwave synthesis of InP microspheres was carried out in microwave synthesis system (WX-4000, maximal temperature $\sim$240 °C and maximal pressure $\sim$40 atm). Typical process is as follows: $InCl_3{\cdot}4H_2O$ (1.00 g), $HAuCl_4$ ethanol solution (2 ml, 70.2 mM), P_4 (0.32 g) and KBH_4 (1.60 g) were placed in the microwave reaction kettle, with ethylenediamine as solvent. Then the autoclave was closed and put into the microwave synthesis system for *ca.* 30 min under 180–220 °C and the microwave power was 600 W. When the reactions were finished, the products were cooled to room temperature naturally. Then the products were filtrated and first washed with dilute hydrochloric acid (0.1 M) to remove residual In and absolute ethanol three times. Finally the products were dried in the vacuum oven at 50 °C. The InP products synthesized through traditional solvothermal procedures are designated as T-InP, and the samples synthesized by the microwave-assisted reaction are designated as M-InP.

The final products were characterized by various techniques. X-ray powder diffraction (XRD) was carried out on a Rigaku D/max rA X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The scan rate of 0.05°/s was applied to record the pattern in the 2θ range of 20–80°. The morphology and size of as-prepared products were observed by scanning electronic microscopy (SEM) images, which were performed on an X-650 scanning electronic micro-analyzer.

3. Results and discussions

Fig. 1a is the X-ray powder diffraction (XRD) pattern of the samples T-InP after HCl treatment, which is consistent with the bulk InP reflection (JCPDS file No. 32-452) indicating the same cubic zinc blende lattice structure. Fig. 1c is the corresponding XRD pattern of M-InP, which is not obviously different from Fig. 1a. Contrasts with the XRD pattern Fig. 1a and c, the products have higher crystallinity under solvothermal condition than that under microwave-assisted route. Here, Au catalyst component cannot be detected in the XRD patterns, indicating its content is less than the resolution limit of XRD. The presence of In before the HCl treatment has been testified by XRD as shown in Fig. 1b for T-InP samples and Fig. 1d for M-InP samples.

SEM images of the obtained samples after HCl treatment are displayed in Fig. 2. Fig. 2a and b give the panorama of T-InP micrometer hollow spheres under different magnifications. Plentiful collapsed and hemispherical hollow spheres are also found in close-up of Fig. 2b, indicating the hollow structure of the spheres. Fig. 2c,d display the images of M-InP micrometer spheres. Inserted in Fig. 2c is the typical collapsed hollow spheres for M-InP samples. From the given SEM images, it can be seen that the obtained hollow spheres from the two methods have nearly similar size, namely, *ca.* 3–6 μm in diameter and *ca.* 1 μm in wall thickness. The openings and collapse are probably due to the decomposition of templates by the washing-up of diluted HCl. In addition, Fig. 2b and d gives further fine information that the building blocks of InP hollow spheres are InP nanoparticles and the porous surface nature. Carefully compared the samples, one can find that there are obviously porous surface natures for T-InP relative to the compact surface of M-InP samples.

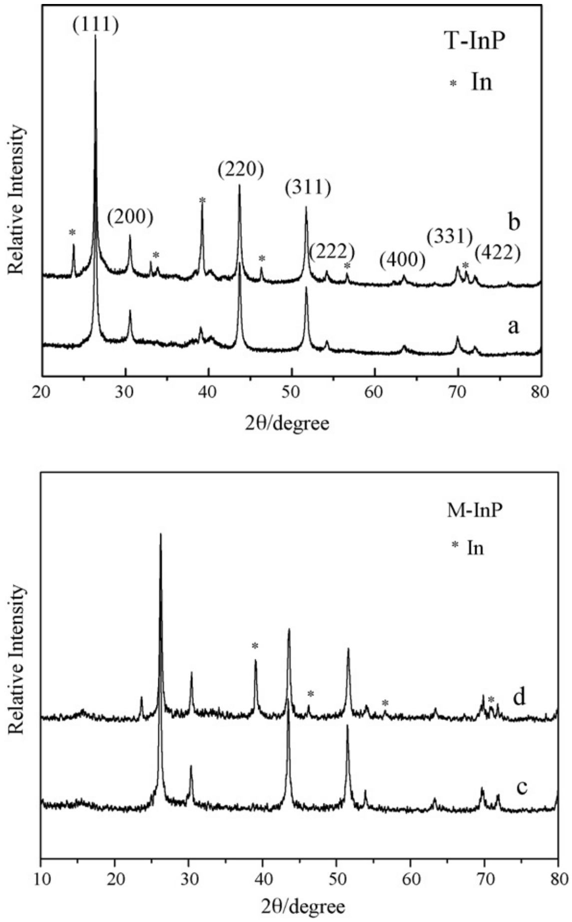


Fig. 1. The XRD patterns (a) for T-InP samples and (c) for M-InP samples after HCl treatment; the XRD patterns (b) for T-InP samples and (d) for M-InP samples without HCl treatment.

It is reported that the noble metal Au with the in situ formed alloy species functions as catalysts for the nucleation and further directs the growth of 1D nanostructure via the VLS [4,5] or SLS mechanism [21]. However, the reaction temperature must be elevated higher than the eutectic temperature. As reported, it is impossible to produce 1D III–V structure at a lower reaction temperature of 300 °C via the In–Au alloy catalysis route in solution [21]. In the process of our experiment, the Au nanoparticles are first reduced by the KBH_4 from the $HAuCl_4$ colloid. The indium is also reduced by the KBH_4. The reaction temperature (180–220 °C) is surprisingly lower than that of the melting point of bulk gold and higher than that of the melting point of In and P_4 (In: 157 °C; P_4: 44.1 °C). Such a low temperature is not enough to activate the gold particles to catalyze the growth of one-dimensional InP [4,5]. Due to the physical tendency to reach the lowest energy level, the newly In liquid coat on Au nanoparticles to form In/Au core/shell droplets which are used as the templates of building the InP nanoparticles [19] rather than the formation of Au–In alloy to direct the growth 1D structure [4,5,21]. Under the thermal or microwave irradiation conditions, the reaction between P_4 molecules and In is on the surface of the In/Au droplets. Thereafter, the formed InP nanoparticles undergo the solidification to form compact InP layer on the surface of the Au/In core/shell droplets, which block the further reaction of P_4 with In molecules in the beads. As a result, when removing the unreacted In by diluted HCl solution, the inner Au cores separate from the outermost InP shells, and finally produce InP hollow spheres. Due to the loss of the support, some collapsed hollow spheres are formed. In addition, the possible density gradient in the sealed autoclave could lead to the ununiformity for the diameter of as-grown InP hollow spheres. Further experiments are going on to

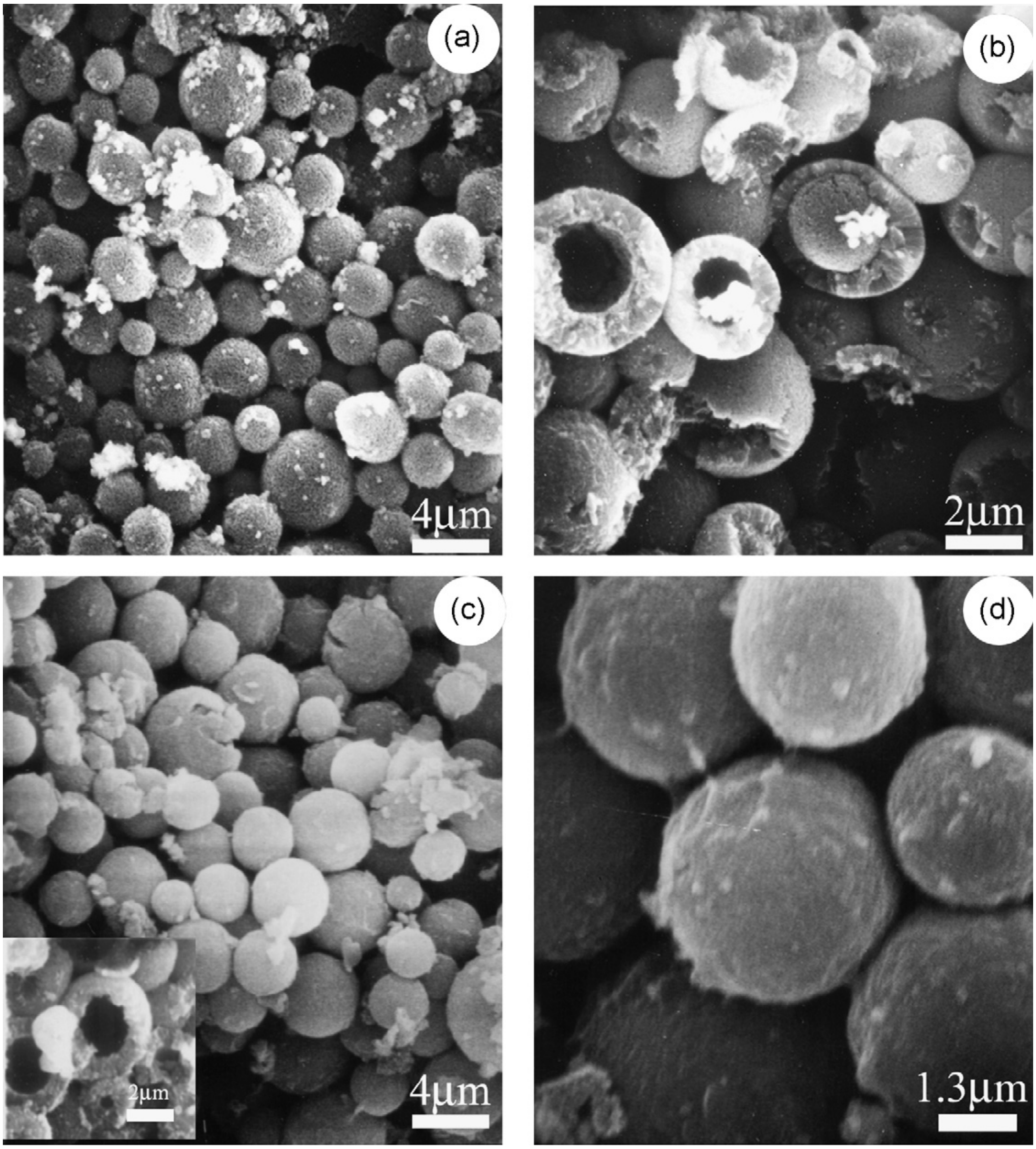
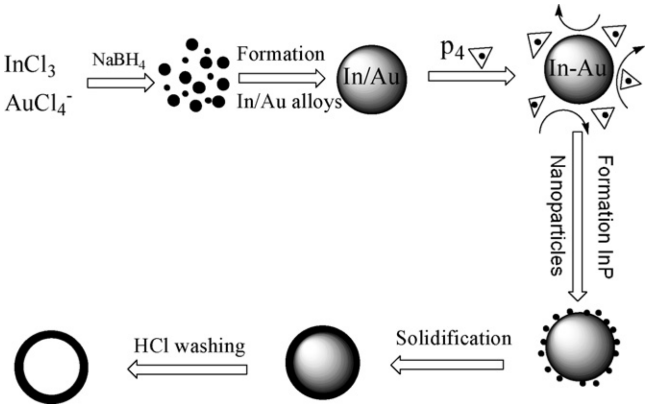


Fig. 2. The SEM images (a and b) for T-InP samples and (c and d) for M-InP samples after HCl treatment. Inserted in (c) is the close-up of hollow nature for M-InP samples.



Scheme 1. The proposed formation mechanism for InP hollow spheres.

adjust the experimental conditions in order to obtain the desired hollow spheres with uniform diameter. Scheme 1 describes the formation mechanism of InP micro-scale hollow spheres.

4. Conclusions

In summary, two efficient methods, namely solvothermal and microwave procedures have been successfully applied to synthesize InP micron hollow spheres. Through the contrast between the XRD patterns and SEM images, it is found that the samples obtained under solvothermal procedure have higher quality than those obtained under microwave irradiation condition. However, the microwave-assisted route is the more efficient method to overcome tedious and time-consuming process and reduces the reaction time from several hours to several minutes.

Acknowledgments

Financial supports from the Shandong Province Doctoral Foundation (No. 2006BS04039) and Shandong Province Natural Science Foundation (No. Y2005B02) are gratefully acknowledged.

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