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Aqueous synthesis of III–V semiconductor GaP and InP exhibiting pronounced quantum confinement†

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A mild aqueous synthesis route was successfully established to synthesize well crystallized and monodisperse GaP and InP nanocrystals, which were proved to exhibit pronounced quantum confinement by room-temperature UV/Vis adsorption and photoluminescence (PL) spectra.

Group III–V nanocrystalline semiconductors have received much attention due to their usefulness in high-speed digital circuits, microwave devices, and optoelectronics. Compared to I–VII and II–VI semiconductors, III–V materials have a greater degree of covalent bonding, a less ionic lattice, and larger exciton diameters. For this reason, quantum size effects on the optical spectra have been predicted to be more pronounced in the III–V class of materials than in II–VI materials.[1]

Several routes to III–V compound semiconductors have emerged in the last decade,[2] including dehalosilylation and related reactions,[3,4] a metathesis reaction,[5,6] pyrolysis of single-source precursors that incorporate the elements of a compound in a single molecule,[7] and chemical vapor deposition.[8,9] These methods are very mild in comparison with conventional solid-state reaction (usually above 1000 °C),[10,11] but they still require a relatively high processing temperature or post-treatment temperature (200–500 °C) to obtain well-crystallized products. Recently, there have been considerable efforts to explore new solution routes to III–V semiconductors, with the goals of searching for mild preparation conditions,[12] for instance, decreasing processing temperature, avoiding complex reactions and toxic precursors. However, up to now, it has been very challenging to prepare III–V semiconductors in aqueous solutions, mainly due to the strong hydrolysis of GaX_3, InX_3 (X = Cl, Br, I) and their corresponding organometallic compounds. More important, from the green chemistry point of view, water is the ideal media for the solution route to III–V semiconductors, which has been driving us to explore the possibility of preparing III–V semiconductors in aqueous solution under mild conditions.

Herein, we present the first aqueous preparation of high-yield, relatively monodisperse, well crystallized GaP and InP nanocrystallites, exhibiting pronounced quantum confinement. The reaction is carried out in an aqueous solution at 120–160 °C and involves the transportation of phosphorus by I_2 and a circulation between H_3PO_4 and H_3PO_3.[13] The whole process can be formulated as Scheme 1, taking GaP as the example.

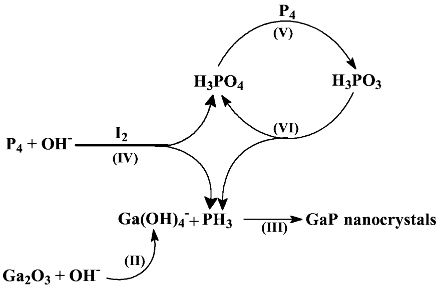
Initially, our research revealed that in fact little GaP and InP could be obtained in an alkali solution, taking advantage of the reaction of $Ga(OH)_4^-$ with PH_3 which was produced from white phosphorus dismutation in alkali solutions.

$$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^- \qquad (I)$$

$$Ga_2O_3 + 2OH^- + 3H_2O \rightarrow 2Ga(OH)_4^- \qquad (II)$$

$$Ga(OH)_4^- + PH_3 \rightarrow GaP + 3H_2O + OH^- \qquad (III)$$

However, the rate of white phosphorus dismutation in alkali solutions is very slow, and thus, the amount of PH_3 is too small. Our experiment shows the yield of GaP in alkali solution is only about 12%. In order to improve the yield of GaP, we added iodine to induce the dismutation of white phosphorus, based on reaction (IV).



Scheme 1 Schematic growth path of nanocrystalline GaP; (II)–(VI) represent the corresponding reactions in the text.

$$P_4 + 2I_2 + 4OH^- + 4H_2O \rightarrow 2PH_3 + 2H_3PO_4 + 4I^- \qquad (IV)$$

The addition of iodine, on one hand, accelerated the rate of white phosphorus dismutation, and on the other, induced another circular reaction between H_3PO_4 and H_3PO_3. It is well known that H_3PO_4 can be immediately reduced to H_3PO_3 by white phosphorus based on reaction (V), while H_3PO_3 is unstable and decomposes to PH_3 and H_3PO_4, with the regenerated H_3PO_4 reacting with white phosphorus again, so that reactions (V) and (VI) occur in a cycle:

$$P_4 + 6H_3PO_4 + 6H_2O \rightarrow 10H_3PO_3 \qquad (V)$$

$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4 \qquad (VI)$$

Thus, the amount of PH_3 is significantly improved. Reaction (III) progresses continually until one of the raw materials runs out. As a result, the yield of GaP reached above 90% after the addition of iodine to the system. For circulation to be most efficient white phosphorus should be present in excess in the experiment.

XRD patterns as shown in Fig. 1 can be indexed to the zinc blende structure of GaP (Fig. 1A) with a = 5.48 Å and InP (Fig. 1B) with a = 5.89 Å. Average crystallite sizes estimated by the Scherrer equation are about 5 nm for GaP and 8 nm for InP.

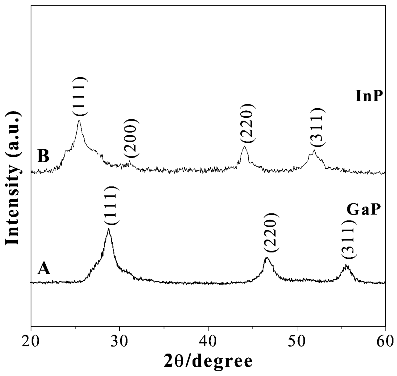


Fig. 1 The X-ray powder diffraction (XRD) patterns of the as-prepared products, (A) for GaP nanocrystals and (B) for InP nanocrystals.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b210164e/

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Transmission electron microscopy (TEM) images for the samples as shown in Fig. 2 reveal relatively monodisperse particles with an average size of about 5 nm for GaP (Fig. 2A) and 8 nm for InP (Fig. 2D) in good agreement with the XRD results. Fig. 2B and E show HRTEM images of the obtained GaP and InP nanoparticles, respectively, in which lattice planes can clearly be seen. Selected area electron diffraction clearly confirm the (111), (220) and (311) planes for GaP and InP with zinc blende structure.

Further evidence for the formation of GaP and InP also can be confirmed by the X-ray photoelectron spectra (XPS), no obvious peak for gallium oxide, indium oxide and phosphorus oxide is observed in their XPS spectra. The quantification of peaks gives the ratio of Ga : P as 1.00 : 1.03 in GaP and In : P of 1.00 : 1.02 in InP, in good agreement with the energy-dispersive X-ray (EDX) analysis results, which gives the ratio of Ga : P as 1.00 : 1.02 in GaP and In : P of 1.00 : 1.01 in InP.

The onset of optical absorption would be shifted to higher energy when the particles are significantly smaller than the bulk exciton diameter. For 8 nm as-prepared InP particles, this predicts a blueshift in the absorption spectrum of 0.2 eV, and indeed the particles show a pronounced quantum confinement effect (1.55 eV, curve a in Fig. 3B). The PL spectrum (excitation at 600 nm) was taken in reflection geometry and showed an emission band at 850 nm for the InP particles (curve b in Fig. 3B). The blueshift in GaP particles was also observed in the absorption spectrum, exhibiting a pronounced quantum confinement effect (Fig. 3A).

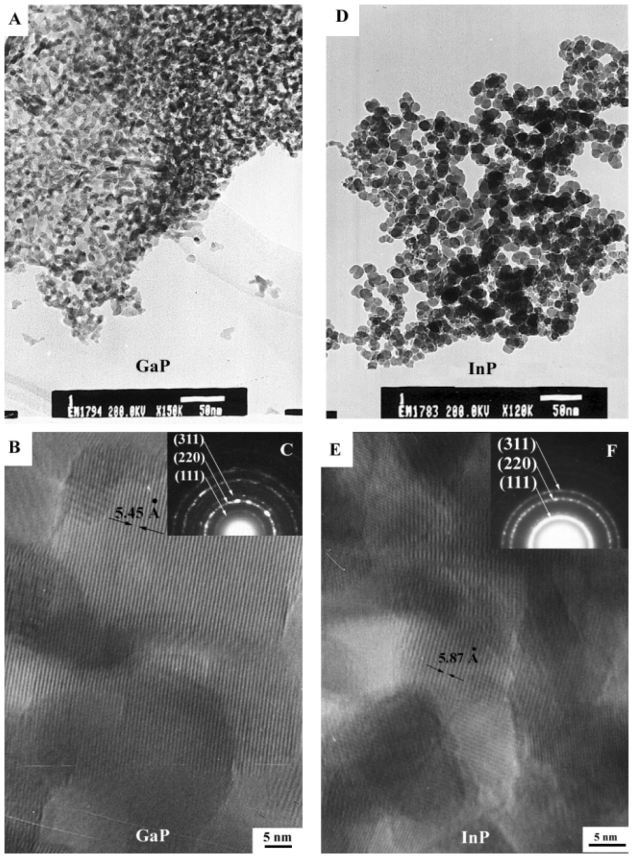

Fig. 2 TEM images of the as-prepared products, (A) for GaP nanocrystals and (D) for InP nanocrystals. HRTEM images of the as-prepared products, (B) for GaP nanocrystals and (E) for InP nanocrystals. ED patterns of as-prepared products, (C) for GaP nanocrystals and (F) InP particles.

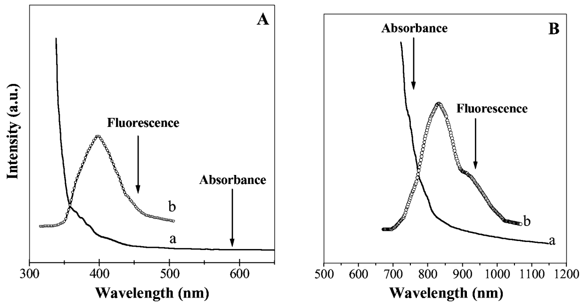

Fig. 3 Absorption and photoluminescence (PL) spectra of as-prepared products, (A) for GaP nanocrystals and (B) for InP nanocrystals.

The preparation of III–V semiconductor GaP and InP in aqueous solution under mild conditions is established for the first time. The obtained GaP and InP nanocrystals were relatively monodisperse and well crystallized, exhibiting pronounced quantum confinement effects. This is the first time that nearly all goals (lower temperature, no organmetallic reaction, no extreme conditions, using water as media and relatively high yield) have been realized, despite considerable efforts on the synthesis of III–V semiconductors in the recent years. This work opens a new aqueous route to synthesize highly covalent nonmolecular solid materials. Moreover, because of the simplicity and cleanness of this route, it may potentially be applied on the scale of industrial production.

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