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Hydrothermal Route to InAs Semiconductor Nanocrystals

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Spherical InAs nanocrystals of 30–50 nm were hydrothermally synthesized at 120 °C, which showed a 100 meV-blueshift of band gap absorption and phonon confinement of optical vibration mode. The study of hydrothermal formation mechanism indicated that crystalline InAs could be obtained in an extended pH range (∼–0.15 to 14).

The III−V(13−15) group compound semiconductors are well-known electronic and optoelectronic materials.[1−3] Since 1990, considerable effort has been spent on preparation and characterization of the nanocrystals (NCs) or quantum dots (QDs) of III−V semiconductors for their novel electronic structures, optical properties (e.g., quantum confinement effect), and potential application in photovoltaic cells, fluorescent biological labels, light-emitting diodes, and QD lasers.[4] Indium arsenide (InAs) is one of the narrow band-gap III−V group semiconductors ($E_g = 0.35$ eV, 3543 nm) and has a rather great excitonic diameter (62 nm)[5] which is expected to possess pronounced quantum confinement effects due to the relative covalent bonding and direct band gap structure,[6] and depending on the degree of size quantization, its optical band gap is potentially tunable from the near-infrared to the visible range.

Conventional routes to prepare InAs include solid-state metathesis reactions at 600 °C,[6] metallorganic chemical vapor deposition (MOCVD),[7] and molecular beam epitaxy (MBE).[8] In the past decade, organic solution-phase reactions became the most important synthetic approach to III−V group semiconductor NCs. Crystalline InAs can be obtained by organometallic reactions in 1,3-diisopropylbezene (203 °C), which is described as a solution−liquid−solid growth mechanism.[9] Nanocrystalline InAs can be obtained from the reaction of $In(acac)_3$ with $As(SiMe_3)_3$ in refluxing triglyme (216 °C),[10] or by dehalosilylation reaction between anhydrous InX_3 (X = Cl, Br, I) and $As(SiMe_3)_3$ in toluene,[5] or trioctylphosphine,[11] or by thermolysis of a mixture of $InCl_3$ and $As(NMe_2)_3$ in 4-ethylpyridine at 167 °C.[12] InAs NCs can also be obtained by reduction reaction in solvothermal system.[13,14] All of the above methods are carried out in organic solvents and need a nonaqueous and nonoxygen environment.[15] Recently, it has been found that InP and GaP can also be formed under hydrothermal conditions.[16]

Here, we report the hydrothermal synthesis of InAs in aqueous solution at 120 °C. The reaction can be formulated as follows:

$$6Zn + 2In^{3+} + As_2O_3 + 6H^+ \rightarrow 2InAs + 6Zn^{2+} + 3H_2O$$

The as-prepared products are crystalline InAs of ∼30−50 nm with no obvious oxidation or hydrolysis occurring at their surfaces, and they show a 100 meV-blueshift of band gap absorption and phonon confinement of the optical vibration mode. The hydrothermal formation mechanism is discussed.

In a typical hydrothermal procedure, indium trichloride ($InCl_3{\cdot}4H_2O$, 99.99%, 0.506 g), excess arsenous oxide

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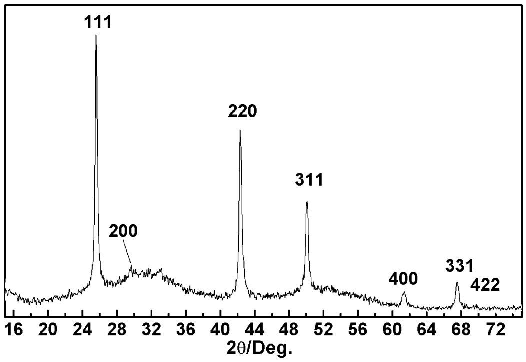

Figure 1. XRD pattern of InAs nanocrystals via hydrothermal reaction at 120 °C for 24 h.

(As_2O_3, 99%, 0.495 g), and metal zinc powder (99.99%, 0.328 g) were mixed into 50 mL of HCl aqueous solution ($[H^+] = \sim 0.7-1.4$ mol·L^{-1}), which was sealed in a stainless Teflon-lined autoclave of 60 mL, heated at 120 °C for ∼18−24 h, and then cooled to room-temperature naturally. The black precipitate was collected and washed with carbon disulfide, anhydrous methanol, and distilled water, and desiccated in a vacuum at 50 °C for 2 h. (***CAUTION!*** Great care should be taken when using the toxic arsenous oxide, As_2O_3.) The black product was dispersed and etched in an *n*-butanolic solution containing 8% HF and 12% H_2O and stirred for 20 h, and then centrifugally separated.

The X-ray powder diffractrion (XRD) pattern was recorded on a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd., Cu Kα radiation, 1.54184 Å). Figure 1 shows the XRD pattern of InAs NCs prepared in the hydrothermal system. All the diffraction peaks can be indexed as the zinc blende phase of InAs with lattice constant $a = 6.037$ Å which is close to the standard data.[17] The broad diffraction intensities at 32° show a small amount of amorphous arsenic existed. No other crystalline impurities including elements (In or As), oxides (arsenic oxides or arsenous oxides), and $In(OH)_3$ can be detected by XRD. According to the half-widths of the major diffraction peaks (111, 220, and 311), the mean crystalline size of the InAs NCs is about 30 nm by using the Debye−Scherrer equation.[18]

The Raman spectrum of the InAs NCs (Figure 2) was recorded in a backscattering geometry at 300 K, with the 514.5 nm line of an Ar^+ ion laser by using a confocal laser micro-Raman spectrometer (France JY Company), and it shows strong phonon confinement,[19] that is, broad and red-shifted transverse-optic (TO) and longitudinal-optic (LO) mode in contrast to bulk InAs ($\omega_{TO} = 217$, and $\omega_{LO} = 237$ cm^{-1}). Also, at the position of the bulk LO phonon line, two lines occurred at 232 and 242 cm^{-1}, respectively, which were previously found in a wetting InAs layer in a superlattice of $(AlAs)_{30}(InAs)_{1.5}$ at 80 K,[20] and needed to be studied in more detail.

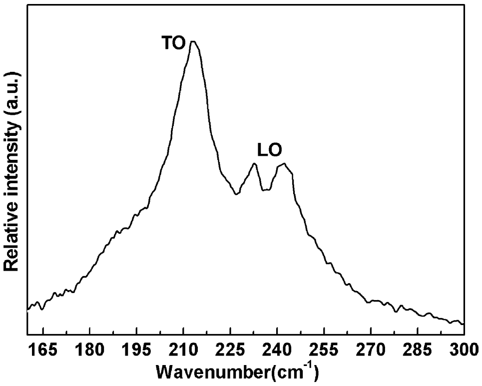

Figure 2. Raman spectrum of the InAs NCs.

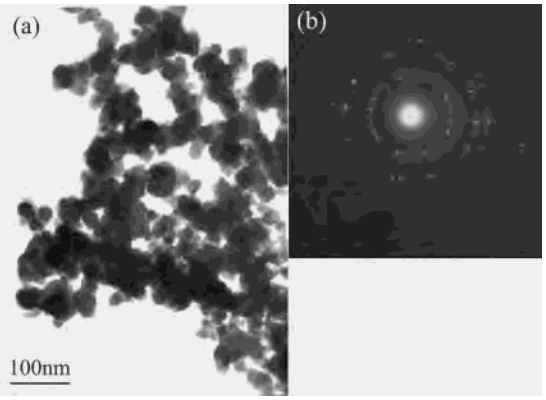

Figure 3. (a) TEM image and (b) SAED pattern of the InAs NCs.

The transmission electron microscope (TEM) images and selected area electron diffraction (SAED) pattern of the InAs NCs were obtained using a Hitachi model H-800 transmission electron microscope operated at 200 kV, and shown in Figure 3a,b, respectively. Conglomerate spherical nanoparticles 30−50 nm in diameter can be found in Figure 3a, and the concentric diffraction rings in Figure 3b can be indexed outward as 111, 220, and 311 diffractions.

The X-ray photoelectron spectra (XPS) were employed to characterize the surface component of the as-prepared InAs NCs, which were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer (Al Kα, 1486.6 eV, C1s, 284.7 eV as internal reference). Neither the peak from metal indium (443 eV) nor those from indium oxides (444.9 eV for In_2O_3, 445.0 eV for $In(OH)_3$) can be observed in In 3d region, and no arsenic oxides are observed (44.9 eV for As_2O_3 and 46.2 eV for As_2O_5) in As 3d region.[21] The molar ratio of In/As is 1.10:1, which is calculated from the peak areas of In $3d_{5/2}$ and As 3d. Other impurities, including chloride ions and zinc ions, are not detected from the XPS. Therefore, it can be concluded that, in acidic hydrothermal conditions, the as-prepared product is pure InAs NCs without obvious oxidation or hydrolysis occurring at the surface.

The infrared absorption spectrum of the InAs nanocrystals was recorded by the Magna 750 FT-IR spectrometer (Nicolet Co. Ltd., U.S.A.) and shown in Figure 4. According to the

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(17) Joint Committee on Powder Diffraction Standards (JCPDS), File 15-869, InAs, $a = 6.058$ Å.

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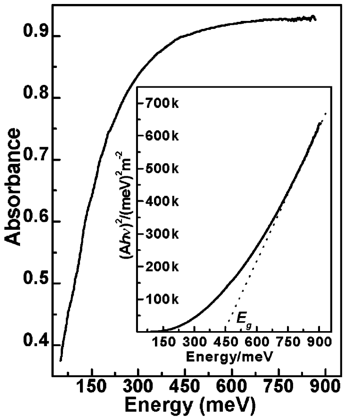

Figure 4. FT-IR absorption spectrum of the InAs nanocrystals and the plot of $(Ah\nu)^2-h\nu$ to get the direct band gap (inset).

formulas for a direct band gap,[22,23] the extrapolating of the curve $(Ah\nu)^2 - h\nu$ (inset) shows they have a direct band gap of 0.45 eV (2756 nm) at room temperature, a blueshift of 100 meV compared to the bulk value (0.35 eV), which is smaller than that of colloidal nanocrystals (8 nm, a blueshift of 650 meV).[11] In the view of the 30−50 nm size of the InAs NCs, it can be concluded that despite the size being less than the exciton Bohr diameter (62 nm), it does not show a profound quantum size effect.

As one typical method of determining arsenic, the Marsh reaction (eq 1) is suitable for reducing most arsenites or arsenates:

$$3\text{Zn} + 9\text{H}^+ + \text{AsO}_3^{3-} \rightarrow 3\text{Zn}^{2+} + \text{AsH}_3 + 3\text{H}_2\text{O} \qquad (1)$$

In our hydrothermal route, this reaction was employed to the in-situ formation of AsH_3, which reacted with In^{3+} ions to form InAs NCs as described in eq 2.

$$\text{In}^{3+}(\text{aq}) + \text{AsH}_3 \rightarrow \text{InAs} + 3\text{H}^+ \qquad (2)$$

Furthermore, the autogenous pressure of arsine in the sealed hydrothermal systems will favor the formation and crystallization of a dense solid, which results in the InAs NCs with zinc blende type at milder temperature (crystalline InAs can be found in the product when the reaction temperature was 80 °C[25]).

In a neutral or alkaline hydrothermal system with the same reactants, InAs NCs can also be obtained, coexisting with other crystalline impurities. The reaction results are collected in Table 1, from which it can be concluded that metallic Zn can also reduce As_2O_3 in neutral or alkaline aqueous solution, and InAs can stably exist in a hydrothermal system in an extended pH range (∼−0.15 to 14). A similar reaction has been employed to prepare InAs in xylene;[13] therein, excess water (more than 3%) should be avoided. Otherwise, it will result in the formation of $In(OH)_3$ in the product, which is similar to the second case in Table 1.

Table 1. Reaction Products of the Hydrothermal Route to InAs NCs

solvent	initial pH	*T*/°C	product
HCl solution	∼0.15 to −0.15	80−180	InAs
H_2O	∼7	180	$In(OH)_3$,[a] ZnO,[b] InAs
$NH_3 \cdot H_2O$	∼14	140−160	ZnO, $In(OH)_3$, InAs

[a] JCPDS PDF 16-161. [b] JCPDS PDF 36-1451.

Therefore, the exclusive product of InAs can only be obtained in acidic conditions. On the other hand, as shown in eqs 1 and 2, acidity will fall along with the formation of AsH_3, and study shows that the initial acidity of the hydrothermal system is a key factor for obtaining pure and crystalline InAs nanocrystals. Too low an acidity (<0.7 mol·L^{-1}) cannot suppress the formation of $In(OH)_3$ from solution. Too high an acidity (2 mol·L^{-1}), however, will promote the decomposition of InAs NCs. Therefore, appropriate acidity (∼0.7−1.4 mol·L^{-1}) is a requisite condition for hydrothermal preparation of InAs NCs and can suppress the surface oxidation of nanocrystals.

In summary, spherical InAs NCs of 30−50 nm have been synthesized via hydrothermal reaction, showing 100 meV blue-shift of the band gap absorption and phonon confinement of optical vibration mode. A certain level of acidity ($[H^+] = \sim 0.7-1.4$ mol·L^{-1}) not only suppressed the hydrolysis of In^{3+}(aq) but avoided decomposition of InAs NCs, which results in pure InAs NCs without surface hydrolysis or oxidation.

Since most of the preparation methods for InAs NCs and QDs were carried out in organic solvents systems, our results indicate that, as one of covalent nonmolecular solids of III−V group semiconductors, crystalline InAs NCs can also be obtained in aqueous solution, which overcomes the hydrolysis and oxidation usually expected. Also, it is possible to obtain other arsenide nanocrystals in hydrothermal systems. Further research on the preparation (monodispersed morphology and effective surface passivation) and optical and electronic properties are underway.

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Supporting Information Available: Additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) For $h\nu > E_g$, the formula is $Ah\nu = B(h\nu - E_g)^{1/2}$, where A is the absorpbance, $h\nu$ is the absorption energy, E_g is the direct band gap, and B is a constant relative to the material. Therefore, E_g of InAs can be determined by extrapolating the curve of $(Ah\nu)^2-h\nu$.

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