Synthesis of InP and InAs quantum rods using Indium Acetate and Myristic acid

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ABSTRACT

The development of solution based synthesis approaches for preparing nanocrystals of III-V semiconductor presents a significant & important challenge especially with relation to shape control to achieve rod growth. To this end, a novel approach for synthesis of soluble semiconductor quantum rods using metal nanoparticles to direct and catalyze one-dimensional growth is developed. The synthesis method is useful in particular for III-V semiconductor with cubic lattice, where the utilization of surfactant-controlled rod-growth is not easily realized. The growth takes place *via* the solution–liquid–solid (SLS) mechanism where proper precursors are injected into a coordinating solvent as we reported in earlier work for InAs nanorods. Herein, we report the synthesis of high quality InP nanorods using Indium Acetate and myristic acid with gold nanoparticles as the catalysts in the SLS growth mode. A similar route was successfully developed for the growth of InAs nanorods. We find that the amount of Au catalyst in the reaction is an important parameter to achieving shape control. Transmission electron microscope (TEM) images of InP and InAs nanocrystals revealed that the crystals are mostly rod-shaped. XRD measurements, absorption spectra were preformed for the nanorods characterization.

INTRODUCTION

An important challenge in current nanocrystal research is that of achieving shape control, as the properties the nanostructures can also be modified by the change of shape [1,2,3,4,5]. This has been convincingly demonstrated for semiconductor quantum rods (QRs), that serve as a model system for evolution of properties from zero-dimensional dots to one dimensional quantum wires. In the prototypical CdSe system QRs were found to have linearly polarized emission [6] and lasing unlike spherical dots, and the lasing threshold in rods was significantly reduced [7]. Moreover, photocells with QRs were found to provide improved performance over dots, and QRs are more readily accessible for integration into nanoelectrode structures.

While CdSe (and other II-VI semiconductor) QRs are grown via a surfactant control growth approach, we found that this approach is difficult to realize in the cubic-structured III-V semiconductor nanocrystals. In these higher symmetry nanocrystals, it is deemed to be more difficult to find chemically dissimilar surfaces to allow for the growth kinetics to be modified by preferential binding of ligands as required in the surfactant controlled growth strategy. Instead, we developed the use of small gold nanocrystals to catalyze and direct rod growth via the solution-liquid-solid (SLS) mechanism [2]. While the SLS mechanism [8] has been applied to nanowire growth successfully [9], its use for length controlled rod growth has been more limited [2,10]. In our previous work, InCl$_3$/trioctylphosphine (TOP) was used as the precursor for indium focusing primarily on InAs QRs. The reaction was found to take place on a rapid

timescale and has to be quenched a few second after its initiation. This is believed to be one of the reasons for appearance of kinks in the longer InAs QRs grown using that method.

In the present work, we focus on growth of InP QRs. We specifically targeted strategies to slow down the reaction, which would lead to reduced kinking. To this end we changed the indium precursor to In(Ac)$_3$ in myristic acid following earlier work of Peng on growth of spherical III-V dots [11]. As in our earlier work, we employ the use of Au clusters as the seed particles and this route was applied to both InP and InAs QRs and was specifically found to be well suited for growth of InP QRs.

EXPERIMENTAL DETAILS

InP nanorod synthesis. Triphenylphosphine coated Au clusters with diameter of 1.4 nm and the suggested formula Au$_{101}$(PPh$_3$)$_{21}$Cl$_5$ (denoted as Au$_{101}$) were synthesized by the published procedures [12]. In a typical preparation of InP rods, 1.6 gr TOPO (trioctylphosphine-oxide) 0.24gr (0.80 mmol) of In(III)Acetate, 0.55gr (2.40mmol) of Myristic Acid were put in 4-neck flask as the growth solution. The mixture was heated to 110-20°C to obtain an optically clear solution and pumped for 2 hours. The system was purged with Ar three times, and then further heated to 360°C under Ar flow & vigorously stirring. A stock solution containing 65 mg (0.25 mmol) tris(trimethylsilyl)phosphine and 0.52gr gold nanocrystal/toluene solution (18mg Au$_{101}$ clusters in Toluene 0.5gr) was diluted with 0.5 gr TOP. The stock solution was injected within 0.1 second under vigorous stirring, leading to the decrease of the reaction temperature to about 330°C. 20 sec later 1.5 gr of TOP was injected for further cooling, and the temperature dropped to 270°C and then stabilized on 270±5°C, after 20 min the reaction was cooled to room temperature. A 2-step separation procedure was conducted to obtain InP nanorods. First, the product was diluted with toluene and centrifuged at 6000 rpm for 20 min. Large InP nanorods (100-150x4nm) were precipitate while smaller (20-30x4nm) nanorods were left in the supernatant. Second, the smaller nanorods were precipitated by adding methyl alcohol and then centrifuged at 6000 rpm for 10 min and re-dissolved in toluene.

InAs nanorod synthesis. In a typical preparation of InAs rods, 2.0 gr TOPO (trioctylphosphine-oxide) 0.54gr (1.9 mmol) of In(III)Acetate, 1.27gr (5.6mmol) of Myristic Acid were put in 4-neck flask as the growth solution. The mixture was heated to 110-20°C to obtain an optically clear solution and pumped for 2 hours. The system was purged with Ar three times, and then further heated to 360°C under Ar flow & vigorously stirring. A stock solution containing 68 mg (0.23 mmol) (TMS)$_3$As and 0.52gr gold nanocrystal/toluene solution (18mg Au$_{101}$ clusters in Toluene 0.5gr) was diluted with 0.5 gr TOP. The stock solution was injected within 0.1 second under vigorous stirring. 20sec later 1.5 gr of TOP was injected for further cooling, after 10min of heating at 270±5°C the reaction was cooled to room temperature. The rods were purified and size- selected by centrifugation. The raw product was diluted with toluene, removed to 5 ml vials, stopped with septum under nitrogen and centrifuged stepwise to obtain rods of different sizes.

InP and InAs nanorods were characterized using UV-VIS absorption, photoluminescence (PL), transmission electron microscopy (TEM), X-ray diffraction (XRD).

RESULTS AND DISCUSSION

The synthesis approach to achieve shape control for InP and InAs rod growth combines the principles of colloidal growth of high quality semiconductor nanocrystals, with one-dimensional growth achieved *via* the SLS mechanism. We use Au clusters as the seed particles for rod growth as reported in our earlier work but here we focus our attention to InP nanorods and also use a different indium pre-cursor, namely $In(Ac)_3$ with Myristic acid. We found that replacing the $InCl_3$ by $In(Ac)_3$ and the addition of Myristic acid as fatty acid ligand, improved the shape of InP nanorods compared to what could be achieved with $InCl_3$.

A demonstration of the results obtained for the InP & InAs rods, using Au_{101} clusters as the catalyst particles, are shown in Figure 1 and Figure 2. The TEM images present the InP nanorods and nanowires & InAs nanorods which clearly reveal the one dimensional growth mode. Moreover, the darker contrast apparent on one end of the rods suggests clearly that Au is indeed present in one end. This is most obvious in the InP rods shown for example in Fig. 1a, as the difference in contrast between InP and Au is most pronounced. Most of the InP rods are not kinked. We note that while the bulk Au melting point (1064 °C) is significantly higher than the reaction temperature used in the colloidal nanocrystal growth (300-360°C), the reaction still works via the SLS mode since the melting point is significantly reduced for the small diameter Au clusters used as seeds [13,14]. Compared to our earlier work with $InCl_3$, the reaction rate is indeed slower which, at least for the InP nanorods, allowed for improved control of the growth.

In our efforts to optimize the synthesis we varied different reaction parameters. We find that the In:P ratio determines the yield of two different main rod size: shorter nanorods and longer ones. For larger ratio of In:P of 3.5:1 the yield of longer rods increases, as can be seen in figure 2. For a smaller ratio of 2:1 the yield of shorter nanorods increases with little production longer rods (figure 1a). In this case, the main fraction of nanorods is of dimensions $25\pm6 \times 3.8\pm0.8$ nm. The increased length in the case of higher ratio of In:P is likely due to the increased indium reaction rate leading to more rapid growth and to longer rods.
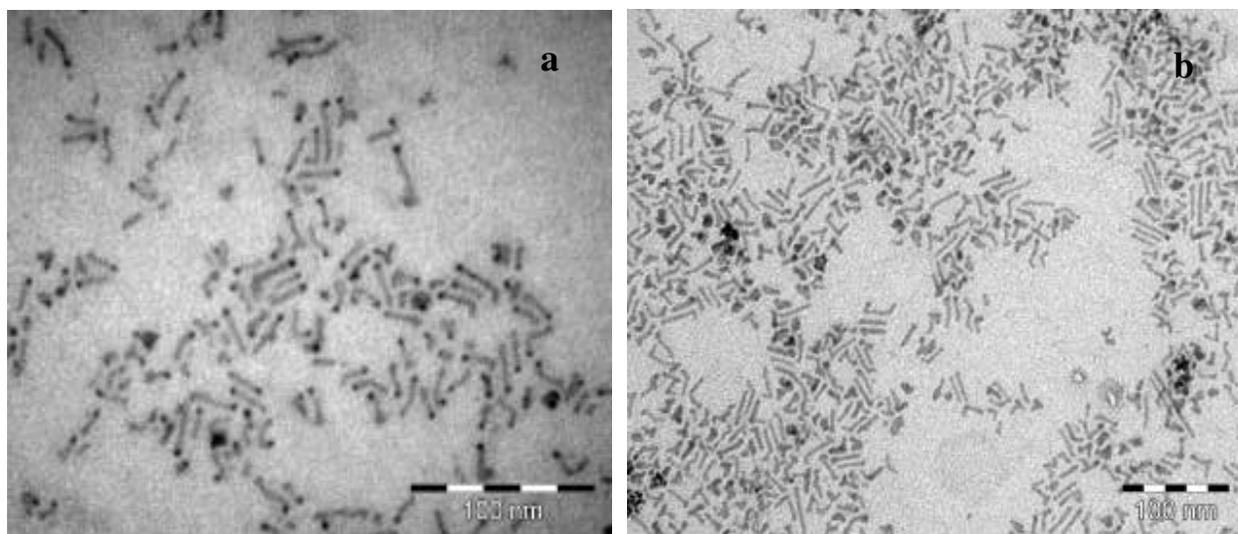

Figure 1: TEM images of InP (a) and InAs (b) rods synthesized using Au101 clusters as catalyst. On some of the particles the Au seed is seen on the edge as a black dot.
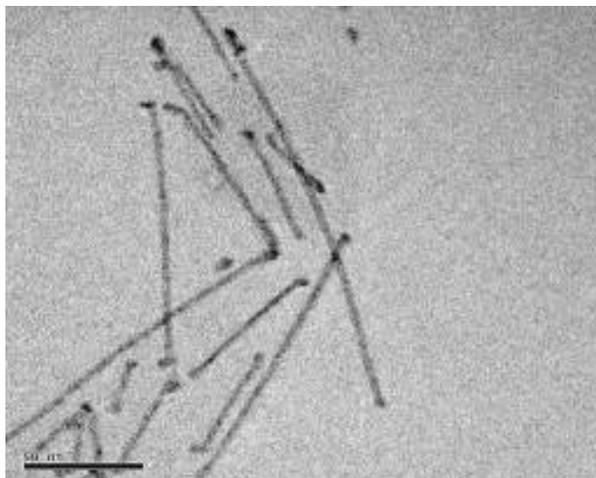
Figure 2: TEM image of InP wires synthesized using Au101 clusters as catalyst. On some of the particles the Au seed is seen on the edge as a black dot (scale marker bar is 50nm).

The synthesis yields InP quantum rods with a uniform diameter but distributed in length, along with byproducts including a small fraction of InP quantum dots and In particles and centrifugation was used to separate these products. In the first step of separation, the product dispersed in toluene was centrifuged at 6000 rpm (rcf-relative centrifugal force ~4000 g) for 20 min. In this step, nanorods and dots remained in the supernatant while the fraction of longer rods as shown in figure 2, remains in the precipitate. In the second step, nanorods were obtained.

The InP rods were characterized structurally with both XRD and HRTEM (high resolution TEM). The XRD pattern is shown in figure 3. The peaks correspond to the zincblende lattice of bulk InP indicating the crystalline growth of the nanorods. In HRTEM (not shown), we could identify that most of the rods grow along the (111) direction, in agreement with what we observed in our earlier work for InAs rods.
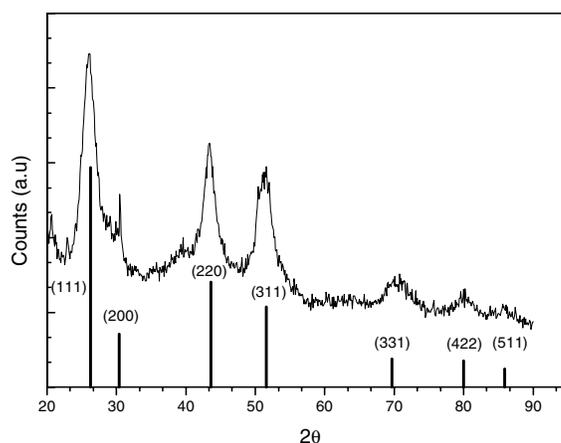

Figure 3: Powder X-ray diffraction patterns of the first fraction of InP rods. The powder was washed with water before measurements to remove excess surfactants.
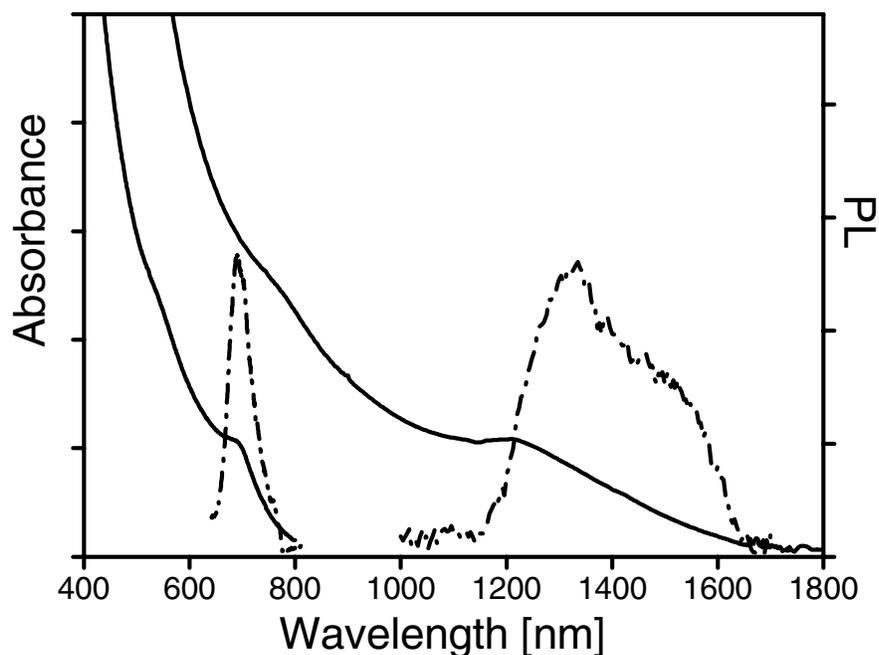
Figure 4: absorption (solid lines), and PL of InP and InAs nanorods. The PL was measured using 532 nm excitation for InP rods and 632 nm for InAs rods.

The basic optical properties of InP and InAs nanorods synthesized by this method were characterized using absorption and PL measurements. Figure 4 shows the spectra for both InAs and InP. In the case of InP rods, the position of the shoulder in the absorption spectrum is at ~700 nm, while for the InAs rods at 1250 nm. This reflects the quantum confinement in each of the systems. The PL in both InP and InAs rods is weak but still shows a signature of band gap emission. The very broad emission in the case of InAs is assigned to the relatively broad size distribution in these rods.

CONCLUSIONS

We have shown that the solution–liquid–solid (SLS) mechanism can be used for the synthesis of III-V semiconductor nanorods with cubic lattice. Using In(Ac)3 and myristic acid yielded well-controlled InP rods, that are not kinked. We attribute this improved control to the slower growth achieved through the use of the less reactive indium precursor compared with $InCl_3$ used in our earlier work. The length of the InP rods could be controlled by changing the ratio of the In/P precursors. InP rods will be interesting for the study of the evolution of properties from 0D dots to 1D wires. Furthermore, it will be interesting to examine the possibility of integrating them in solar cells.

ACKNOWLEDGMENTS

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