

A Novel Approach for the Preparation of InP Nanocrystals

ZHAOYONG SUN, JUN ZHANG, MING ZHANG, and JIYE FANG
UNIVERSITY OF NEW ORLEANS, NEW ORLEANS, LA, 70148

ABSTRACT

III-V semiconductor nanocrystals are of considerable interest due to their extensive applications in the optoelectronic and biomedical fields. In order to meet the practical use, the convenient and scalable production of III-V narrow-disperse nanocrystals is inspiring. We report an efficient and rapid method of preparing InP nanocrystals using a wet-chemical redox synthetic approach with a noncoordinating solvent, employing organic reducing agent $\text{LiBH}(\text{CH}_2\text{CH}_3)_3$ and yellow phosphor. As advantages of this approach, reaction temperature is relatively low (80°C - 120°C) and reaction time is less than 2 hours. Our characterization shows that the photoluminescence properties of InP nanocrystals are highly dependent on the particle size.

INTRODUCTION

The syntheses and properties of semiconductor nanocrystals (NCs) have been extensively studied over many years due to the fact that their optical behaviors vary as a function of crystalline size. II-VI and III-V thin film semiconductors are the hot materials which have therefore been investigated by many research groups. Recently, II-VI and IV-VI semiconductor NCs have also attracted great interests because they are readily prepared and easily available in commercial quantities [1-6]. However, the traditional preparation method for producing III-V semiconductor NCs requires strict experimental conditions (e.g. high temperature up to 300°C) and is a time-consuming process, usually several (2-5) days [7-9]. In order to prepare InP NCs, the source of P is normally tris(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$) and a thermal decomposition of this precursor is often employed. Although Battaglia et al. recently progressively improved the formation of InP NCs [10] by eliminating TOPO or DDA from the reaction system and shortened the reaction time from a few days to a few hours, $\text{P}(\text{TMS})_3$ as a very expensive precursor of P still has had to use. Later improvement by Madalina Furis et al. [11] didn't further reduce the high-reaction temperature ($\sim 300^\circ\text{C}$) and relatively long-reaction time (2-3 hours).

In this paper, we describe a new preparation method to fabricate InP NCs at relatively low reaction temperature without $\text{P}(\text{TMS})_3$ precursor.

EXPERIMENT

Synthesis of InP NCs

Dehydrated InCl_3 , trioctylphosphine (TOP), oleic acid (90%), hexadecane, red phosphorus and superhydride [$\text{LiBH}(\text{CH}_2\text{CH}_3)_3$] solution (1M) in THF were purchased from Aldrich without further purification. TOP and yellow phosphorus solution in toluene which was prepared from red phosphorus were house-made and stored under argon. Superhydride in dioctylether solution (1 M) was prepared following a method reported by Sun [12].

In a typical experiment, 0.1mmol of InCl_3 , 0.05ml of oleic acid and 0.15ml of TOP were mixed with 7ml of hexadecane in a three-neck round-bottom flask equipped with a condenser. The system was vacuumed at room temperature and at 110°C for a while, respectively. At 100°C , 0.2ml toluene solution of yellow phosphorus ($\sim 0.8\text{M}$) was rapidly injected into the vigorously stirred mixture under argon and the system was refluxed for $\sim 30\text{min}$. Subsequently, 0.6ml dioctylether solution of superhydride (1M) was injected into the system under agitation and argon protection. The color of the solution quickly turned dark grey and black shortly. After several minutes, the colloid system was cooled down to room temperature by quickly removing the heating source. InP NCs were washed for 2 times and then stabilized by adding a little bit of capping ligand (such as a small amount of oleic acid). These NCs could be isolated by adding a sufficient amount of ethanol and separating with centrifugation. Particle size of InP NCs could be varied by synthesizing samples under different reaction conditions with tuning several parameters, including different refluxing time after injection of the P solution (e.g. 1 hour or 30min), different solvent systems (hexadecane or octyl ether) and with or without oleyamine.

Characterization of InP NCs

The resulting InP NCs were characterized by using transmission electron microscope (TEM) (JEOL 2010) and X-ray diffractometer (XRD) (Philips X-pert system). The absorption and photoluminescence (PL) spectra were recorded by Agilent 8453 spectrometer and PerkinElmer LS-45 luminescence spectrometer, respectively.

DISCUSSION

Structure and size distribution of InP nanocrystals

A bright field TEM image and an electron diffraction pattern of a typical reaction product are shown as Figures 1 and 2, respectively. According to Figure 1, the average particle size of this sample was estimated as $\sim 5.5\text{ nm}$ with a standard deviation of $\delta < \sim 8.9\%$. The electron diffraction pattern revealed in Figure 2 consists of discrete rings depicting the crystalline nature of the NCs. Several rings were assigned from 111, 200, 220, and 311 diffraction planes. Based on this diffraction pattern, the as-synthesized InP NCs were determined as zinc blende structure. This characterization is supported by an X-ray diffraction pattern (XRD) which is shown in Figure 3. In Figure 3, the diffraction peaks for crystal lattice planes $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ were found at 2θ of 26.3° , 30.3° , 43.7° , and 51.6° , respectively. We also measured the average particle size and size distribution of InP NCs in hexane using a light scattering technique on a Protein Solution DynaPro 99 Molecular Sizing Instrument. The measured

average size is consistent with the size range from TEM observation, although it is realized that the latter might be a more useful tool to identify the size and morphology of nanoparticles.

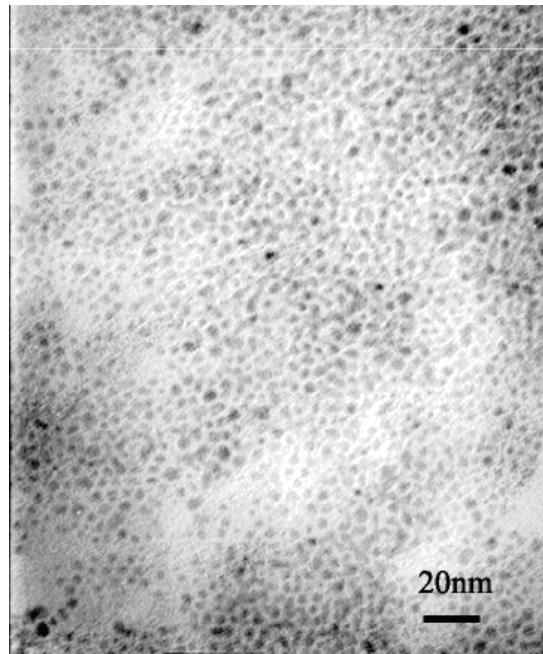


Figure 1. Bright field TEM image of InP NCs

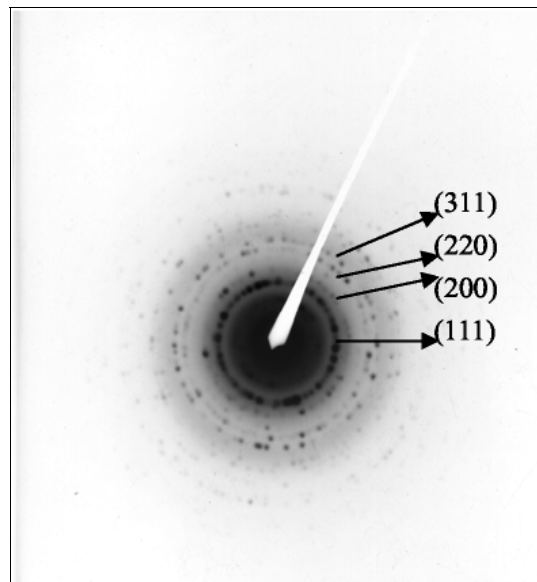


Figure 2. Selected area electron diffraction pattern for InP NCs (reversed image)

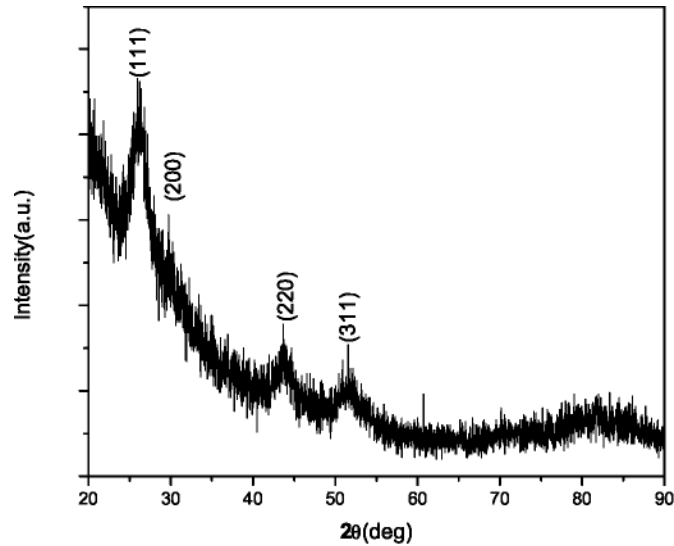


Figure 3. XRD pattern of InP NCs

Spectral properties of InP NCs

The spectral properties of InP NCs have been extensively investigated by many groups [9, 11, 13-15]. Commonly it was accepted that the absorption and PL peaks would have a red-shift when the size of NCs is increased, due to the quantum confinement effects [11]. The PL spectra consist of a sharp peak associated with the band-edge emission and a broad infrared feature associated with deep level surface trap emission [11]. After HF etching, the emission efficiency associated with the band-edge emission increases greatly and the emission associated with surface states is eliminated from the PL spectrum [13, 15]. Our results indicate that the absorption peaks of InP NCs can be observed within UV-Visible region but only a very weak shoulder [Figure 4 (a)]. The PL spectra exhibit a strong dependency on the InP nanocrystalline size (see Figure 4(b)) which is consistent with the results from other research teams. The sizes of different InP NCs we used here were determined using a light scattering technique. The excitation wavelengths for each corresponding emission spectrum are set to their peak wavelengths, respectively. Based on Fu's work [16], the PL spectroscopy we measured is most likely similar to "global excitation spectroscopy", that means that the excitation energy is above the absorption peak (so all sizes present in the sample are excited and the spectra are a little bit of broad). In this case, however, the spectral features are a little different in comparison with the results from samples prepared using the typical synthetic methods. Firstly, only the sharp feature corresponded to the radiative recombination inside the NCs shows up. We didn't observe the broad feature in the PL spectra for all samples even without HF etching process, indicating that the surfaces of InP NCs may have been passivated by organic molecules during the preparation. Secondly, the sharp emission peaks from smaller NCs can locate in the near UV regions (~430nm) which are shorter than those observed before (usually between 500nm and 700nm).

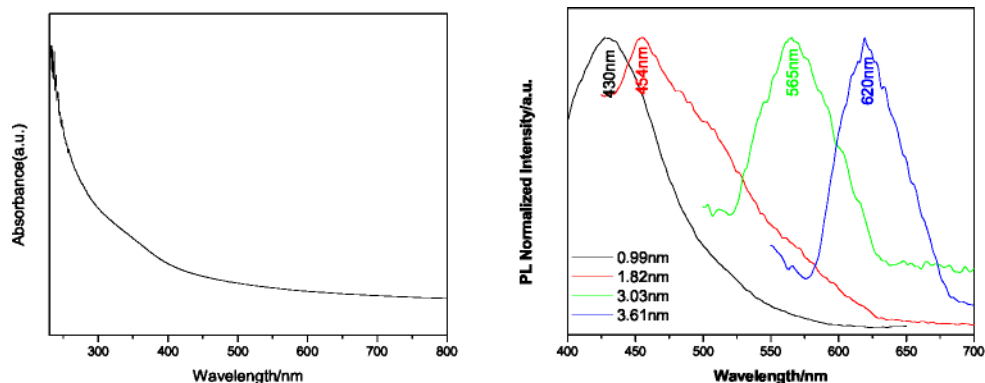


Figure 4. (a) absorption spectrum of InP NCs (~0.99nm), and (b) PL spectra of InP nanocrystals (~ 0.99 nm, ~1.82nm, ~3.03nm, ~3.61nm). Sizes were determined using light-scattering technique.

CONCLUSIONS

The synthesis of InP nanocrystals has been carried out by using a wet-chemical approach at a relatively low temperature. Using this fast and convenient synthesis, InP nanocrystals with various sizes can be achieved. The luminescence ranged from near UV throughout most of the visible spectrum. This luminescent property of InP nanocrystals provides a great benefit to development of optoelectronic devices and application in life science.

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