Nonthermal plasma synthesis of size-tunable, photoluminescent InP nanocrystals and incorporation into hybrid solar cells with P3HT

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Abstract: Indium phosphide nanocrystals are of interest for photovoltaic applications due to the ability to tune the bandgap over a wide range. This work demonstrates the ability to synthesize size-tunable, photoluminescent indium phosphide nanocrystals using a nonthermal flow-through plasma. In addition, we demonstrate the use of indium phosphide nanocrystals in a polymer based hybrid solar cell with P3HT.

Keywords: Nanocrystal, Photoluminescent, Hybrid Solar Cell, Photovoltaics

1. Introduction

Semiconductor nanocrystals (NCs) have attracted much attention during the past 20–30 years. The ability to adjust the optical properties, surface-to-volume ratio, and tailor the surface of the NCs allows for the development of a new generation of materials and devices. Tunable absorption is of particular interest for photovoltaic applications since there are few bulk materials with the optimal bandgap for absorbing the broad solar spectrum. In contrast, NCs’ bandgap can be adjusted as function of their size [1]. Early work on NCs focused on compound II-VI semiconductor NCs, such as CdSe and CdTe, or the Pb-based IV-VI compounds, PbS, PbSe, and PbTe [2]. These materials are relatively easy to synthesize using colloidal techniques. However, continuous synthesis processes have not been widely developed. In addition, these materials contain toxic heavy metals, limiting their potential for large-scale applications such as photovoltaics due to environmental concerns. More recently NC materials which are less toxic have been synthesized with colloidal techniques including Si, Ge, and InP [3,4,5]. Major drawbacks to these methods are the long reaction times, poor yields, and organic ligands attached to the NCs.

Indium phosphide NCs are of particular interest due to the ability to adjust the bandgap over the entire visible and near infrared range of the spectrum, and the relative ease of further adjusting the material’s properties by including dopants such as Ga and As. Early work on the synthesis and fundamental properties of InP NCs was performed by Nozik’s group using a colloid-based synthesis method [5,6]. However colloidal synthesis of InP NCs requires high temperatures and long reaction times, up to days per batch. In addition, this synthesis process yields NCs that are surrounded by organic molecules.

We have previously reported a nonthermal plasma based process which yields high quality, free-standing, size-controlled Si and Ge NCs [7,8]. This process relies on the ability of the plasma environment to dissociate the precursors and allow for rapid nucleation and formation of NCs. We have shown that formation of nanocrystals occurs on the order of milliseconds and the NC size can be controlled by adjusting the residence time of the NCs in the plasma.

This work focuses on the development and characterization of a nonthermal plasma process used to synthesis InP NCs. In addition, we demonstrate their incorporation into a NC-polymer film to form a hybrid solar cell.

2. Synthesis and Functionalization Methods

Indium phosphide NCs were synthesized using a nonthermal, radio-frequency (13.56 MHz) plasma operated between 1.6 and 3 Torr with 50-80 Watts of input power. A system schematic can be seen in Fig. 1. This reactor design is described in detail in ref [7].

Phosphine (PH$_3$) diluted in hydrogen (H$_2$) and trimethylindium (TMin) (In(CH$_3$)$_3$) were used as the phosphorous and indium sources, respectively. Trimethylindium sublimes at room temperature allowing for its vapor to be entrained in Ar carrier gas. Additional Ar is used to sustain the plasma and dilute the precursors.

Indium phosphide NCs are collected on a filter as a dry powder. As produce InP NCs are highly susceptible to oxidation, therefore all handling and transfer must be done in an oxygen and water free environment. A glove box and standard Schlenk line techniques are used for

Figure 1: Photograph and schematic of flow-through non-thermal plasma.
non-functionalized samples. As-produced InP NCs can be functionalized using organic ligands to form a colloid or to be incorporated into devices.

Plasma synthesized InP NCs can be functionalized with a variety of ligands including hexylamine, oleic acid, trioctylphosphine oxide (TOPO), and myristic acid. Attachment of ligands happens over a period of less than one hour at temperatures below 200 °C. Absorption measurements were carried out using InP NCs that were heated to 170 °C in a solution of myristic acid and mesitylene for 1 hour.

As produced InP NCs show negligible photoluminescence (PL). In order to enhance the (PL), a wide bandgap material, ZnS, is grown around the InP NCs to form a shell structure. To grow the ZnS shell, the InP NCs were transferred into a solution of 50 ml 1.0 mM myristic acid (coordinating ligand) in octadecene and heated to 200 °C for 30 min to form a colloid. The colloid was then heated to 220 °C for an injection of 0.5 ml preheated 50 mM zinc stearate in octadecene for 15 minutes, followed by an injection of 0.5 ml preheated 50 mM sulfur in octadecene for 15 min. The injections of the zinc and sulfur precursors were performed three times to form an InP-ZnS core-shell structure with three monolayers of ZnS. The colloid was then cooled and washed to form an air-stable colloid which exhibited strong PL.

3. Nanocrystal Characterization

Indium phosphide NCs rapidly oxidize making it difficult to characterize the material without surface passivation. Figure 2 shows a TEM bright field image of myristic acid capped InP NCs drop casted onto a carbon coated TEM grid with an insert of the selected area electron diffraction pattern showing rings from the (111), (220), and (311) InP planes. The size distribution is generally between a standard deviation of 15 – 25% of the mean diameter, indicating that our process yields fairly monodisperse NCs.

Particular interest is focused on the quantum confinement behavior of the NCs. In order to adjust the size, the NC’s residence time is adjusted from ~2-6 ms. The residence time is adjusted by scaling the total flow rate of the precursors while keeping the ratio between them and pressure constant. This work uses a ratio of 90 Ar : 17 H₂ : 3 PH₃ : 1 TMIn with total mass flow rates of 56-172 standard cubic centimeters per minute (scfm), which translates to residence times between ~2-6 ms. No significant difference in NC size is observed when adjusting the concentration of PH₃ and TMIn with respect to Ar.

The first excitonic peak of the optical absorption in the NCs corresponds to the bandgap. Due to quantum confinement, the bandgap should increase as the nanocrystals become smaller. Figure 3 shows that as the NCs become smaller the first exciton peak blue-shifts.

Figure 2: Bright field TEM image and insert of selected area diffraction.

Figure 3: UV-Visible absorption of myristic acid capped InP NCs in mesitylene, inset of size distribution measured by TEM images for residence times of 4 and 6 ms.

Figure 4: Photoluminescence spectra of oxidized InP and InP-ZnS core-shell NCs with corresponding UV-Vis absorption spectra. Inserts of photographs of InP-ZnS core-shell NCs excited with 365 nm source.
These absorption measurements were performed on myristic-acid-capped NCs in mesitylene. The shoulder in the absorption, from the first exciton peak and the broadening of this peak is due to the size distribution of the samples.

As produced InP NCs show negligible PL, however other synthesis methods see similar behavior. It is believed that the lack of radiative recombination is due to dangling bonds on surface P atoms [10]. We have observed that as the NCs oxidize the PL efficiency increases. This is believed to happen due to passivation of these P dangling bonds, or the removal of the surface P atoms due to volatile oxide formation which would leave a layer of indium oxide at the surface of the NC. However quantum yields of oxidized NCs are still on the order of one percent, indicating there are still a large number of non-radiative recombination sites.

In order to increase the quantum yield two methods are commonly used: etching using hydrofluoric acid, and the formation of an inorganic ZnS shell around the InP core [9,10]. We have studied the use of growing a ZnS shell on the NCs. When 3 layers of ZnS are grown on the InP core the quantum yield is observed to be as high as 15%. Using this technique we have been able to produce samples with green to red PL by altering the NC size. Figure 4 shows PL spectra of an oxidized sample and two ZnS capped samples. The absorption spectra correspond to the samples before oxidation and ZnS capping. The photograph inserts show the samples excited by a 365 nm source.

4. Hybrid InP/P3HT Photovoltaic Devices

InP NCs were taken from the plasma process as a dry powder. The powder was then mixed with poly(3-hexylthiophene) (P3HT) in 1,2-dichlorobenzene and spun onto a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PDOT:PSS) coated indium tin oxide (ITO) on glass substrate. Aluminum top contacts were then thermally evaporated on top of the dried film of blended InP NCs and P3HT. Figure 5 shows the device structure. This process is described in detail in ref. [11] with the exception of using Si NCs instead of InP NCs.

Figure 6 shows the current-voltage characteristic of a solar cell made with non-functionalized InP NCs with a mean diameter of approximately 4-5 nm that are mixed with P3HT in 1,2-dichlorobenzene with a weight ratio of 28% InP/P3HT. The mixture is sonicated to break apart the NC agglomerates just prior to film formation. The solution is spin cast onto the substrate. This process yields films on the order of 100’s of nm thick. Under A.M. 1.5 solar simulating light we observe the devices to have an open-circuit voltage of 0.45 V and the short-circuit current density of ~0.05 mA/cm². As is to be expected, if InP NCs are not incorporated into the devices little photocurrent is observed as there is no electron accepting material. We believe that the electrons are transported to the aluminum contact through a network of InP NCs.

5. Conclusion

Size-controlled, photoluminescent InP NCs have been synthesized using a nonthermal radio frequency plasma. By adjusting the residence time of the NCs in the plasma from 2-6 ms, NCs of ~2 - 4 nm in diameter are synthesized. As-produced InP NCs show negligible PL. However, PL can be increased with quantum yields of up to 15% by forming an InP-ZnS core shell structure. A hybrid device using InP NCs/P3HT has been demonstrated. Under A.M. 1.5 light, InP NCs/P3HT devices show open circuit voltages of 0.45 V and short circuit currents density of ~0.05 mA/cm². Our initial results of being able to produce devices from NCs without organic ligands and their incorporation into a working device are promising for applications in photovoltaics and other optoelectronics.
Acknowledgments
This work was supported primarily by the NSF MRSEC Program under Award Number DMR-0819885 and by the University of Minnesota Center for Nanostructure Applications.

References