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Color Tuning and Ce^{3+} Doping in InP/ZnS Quantum Dots

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Group III-V semiconducting nanocrystals (NCs) have attracted tremendous attention as an eco-friendly alternative to the current workhorse CdSe quantum dot. The lower photoluminescence quantum yield and operational stability of III-V have led to many investigations aimed at improving these systems. The isolation of the active quantum dot as a core-shell structure has been proposed as a way to improve its optical properties and stability. Alternatively doping is also proposed as a means to improve these aspects. Here we attempt to introduce a new chemical synthesis route of InP/ZnS core-shell type quantum dots (QDs). Color control was achieved by tuning the size of the QDs. QDs having photoluminescence (PL) emission under UV irradiation from infrared (IR) to blue were successfully synthesized. This synthesis method is also highly suited for doping. We also present preliminary results regarding Ce^{3+} doping of InP QDs.

Keywords: Semiconducting nanocrystals, Nontoxic quantum dots, Color tuning, Doped quantum dots

1. INTRODUCTION

Semiconductors based on group III-V elements are having tremendous applications in the fabrication of new cutting-edge classes of electronic and optoelectronic devices such as high-electron-mobility and heterostructure bipolar transistors, diode lasers, light-emitting diodes, photodetectors, electro-optic mod-

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ulators, and frequency-mixing components [1]. Although binary, ternary and core-shell structures like InN, GaN, InGaN, InP/ZnS core-shell structure, and InGaAs/GaAs are already reported among these interesting class of materials, InP is getting much more attraction since it is a direct bandgap materials. It is having a bandgap of 1.27 eV which is suitable for getting visible emission in the quantum confinement regime when excited with a suitable UV source. Group III elements are relatively nontoxic [2-4], and this give an aditional advantage of being envaironmentally friendly when they are considered for industrial mass production for biological, display and solar energy harvesting applications.

Advancements in colloidal chemistry have provided methods to prepare high quality nanocrystals of various semiconducting materials with varying surface properties and chemical constitution making them suitable for diverse applications [5-9]. As the InP nanocrystals (NCs) alone showes low quantum yield (QY), there had been a large number of attempts reported so far for the synthesis of InP QDs and their core-shell (CS), core-shell-shell (CSS) and other varients to improve their QY [10-20]. Not only their low QY but also their self-quenching due to reabsorption/energy transfer, thermal stability, and chemical stability are to be addressed in order to improve their industrial acceptability to replace the poisonous current workhorse semiconducting materials such as CdSe and PbSe. Recently a systematic study of precursors and their roles in alloyed core-shell In(Zn)P/ZnS QDs have yielded very high QY of 78% [21]. Of the various methods adopted for the improvement of semiconducting NCs, doping the NC core with transition metals are having wide acceptance since they are reported with capacities to eliminate the self-quenching in semiconductors and greatly enhancing their thermal and chemical stability.

Moreover doped QDs improves the emissive performance of the materials without any highly toxic elements [22-27]. When compared to the II-VI doped QDs, the InP system as III-V semiconducting nanocrystal is still in a very nascent stage. The origin of the dopant emission, reasons for their higher intensity, tunability of emission, the distribution of energy levels, emission spectral width, and several other associated properties are presently hot topics of investigation. One of the main obstacle for providing variety of materials for such study is the lack of synthetic protocol that can be adaptable for a variety of dopants which are having the requrements for getting into the InP crystal lattice. This work elaborates on a novel method of InP/ZnS QDs synthesis which also promotes easy doping of the InP core.

2. EXPERIMENTAL

2.1. Materials

Except for tris(trimethylsilyl)phosphine (10 wt%, Strem Chemicals), all reagents and solvents were purchased from Sigma-Aldrich and used as received (indium acetate (99.99%), myristic acid (>99%), tris(trimethylsilyl) phosphine (95%), sulfur (99.5%), 1-octadecene (90%)). 1-Octadecene (ODE) was distilled from molten sodium and stored over pre-activated molecular sieves in amber colored bottle under nitrogen atmosphere.

2.2. Synthesis of InP/ZnS core-shell quantum dots

In a typical protocol for synthesis, a custom made autoclave with a Pyrex glass inner vessel along with a Schlenk reactor was taken into a glove box. The Pyrex glass inner vessel was charged with 0.8 mmol of tris(trimethylsilyl) phosphine ($P(TMS)_3$) and applied vacuum for an hour to remove n-hexane. Subsequently 0.8 mmol of indium acetate ($InAc_3$), 2.90-3.68 mmol myristic acid (MyA) and 7.00 mL 1-octadecene was charged into the Schlenk reactor and heated to 180 °C for 10 min. This clear mixture was injected into the autoclave inner vessel. After sealing the autoclave, reaction mixture inside the autoclave was heated up to a temperature of ~300°C (using a rate of 2°C/s). Along with heating it was stirred perfectly using a magnetic stir bar. The reaction mixture was kept at this temperature for a certain period of time (2 min-2 hrs) to grow the InP QDs. The mixture was then brought down to 150°C and released the pressure. Zinc stearate and sulfur (0.4 mmol each) was added and the autoclave was again sealed and heated up to a temperature of ~230°C keeping the stirring on. After keeping at this temperature for 30 minutes the mixture was brought down to room temperature by immersing in cold water. To isolate the QDs, acetone was added for precipitation followed by centrifugation. The resulting precipitate was dispersed in chloroform. No size sorting procedures were performed for any of the samples.

2.3. Synthesis of Ce^{3+} ion-doped InP/ZnS core-shell QDs in one-pot protocol

InP core was synthesized following the InP synthetic procedure reported before. After the desired growth time, the reaction mixture was cooled to 130°C. A slurry of cerium acetate ($Ce(OAc)_3$) in ODE was made by heating 5 and 10 mol % $Ce(OAc)_3$ in 2 mL ODE at 200°C. This slurry was added to the reaction mixture at 130°C in one-shot. The reaction mixture was further heated to 210°C for the diffusion of Ce^{3+} ions into the InP nanocrystals. For the growth of ZnS shell, the reaction solution was cooled down to 150 °C. Zinc stearate (0.1 M in ODE) and sulfur (0.1 M in ODE) precursors (1.2 ml each) were added consequently to the reaction flask with the InP/ZnSe nanocrystals, waiting for 10 min between each injection at 150°C. After that, the temperature was increased to 220°C for 30 min to allow the growth of ZnS shell.

2.4. Measurements

Room temperature UV–vis absorption spectra of the QDs were measured with a Shimadzu UV 3600, UV-vis-NIR spectrometer in chloroform. Photoluminescence (PL) spectra were collected on Horiba/ Jobin-Yvon spectrofluorometer (SPEX 270 M) in chloroform. The fluorescent quantum yield (QY) of the QDs prepared was measured and estimated by comparing their fluorescence intensities with those of primary standard dye solutions (with emission close to the QDs) at the same optical density (0.05) at the same excitation wavelength. The transmission electron microscopy (TEM) images of the QDs were obtained using a JEOL JSM-890 at 200 KV to analyze their average size and size distribution. Low-coverage samples were prepared by placing a drop of a dilute $CHCl_3$ dispersion of QDs on a copper grid (300 mesh) coated with an amorphous carbon film.

3. RESULTS AND DISCUSSION

Recent reports have shown that high temperature processes are advantageous for the synthesis of doped QDs since the thermal diffusion of dopants into the hosts is high at elevated temperatures [26]. High pressure reactions were also reported with high efficiency to produce doped nanocrystals [28]. In this work we report on a combination of these conditions to prepare core-shell type InP QDs. The procedure for synthesizing InP/ZnS QDs can be divided into three steps as follows.

Synthesis of indium myristate (InMy): Indium for the InP core is supplied from a pre-prepared indium myristate solution in 1-octadecene. This is prepared by the treatment of indium acetate (IA) with myristic acid (MA) in 1-octadence at 180ºC. InMy was formed as a clear solution at this temperature.

Synthesis of InP core: $P(TMS)_3$ (PTMS) is the P donor in this reaction and was used as an n-hexane solution. The n-hexane was removed before the reaction started. Pre-prepared InMy reacts with $P(TMS)_3$ at 300ºC to produce InP QDs of varying size based on the reaction time and excess myristic acid amount in InMy solution.

Overgrowth of the ZnS shell: The overgrowth of ZnS shell was achieved by the reaction of zinc stearate and sulfur at relatively lower temperature for a period of 30 minutes. The amount of Zn and the way it added to the reaction mixture is important as it can influence the way the core QDs are formed [20, 29].

When the bandgap of the shell material is larger than that of the core, both electrons and holes are confined in the core and such type of CS systems are classified as type-I. In such CS QDs, the shell is used to passivate the surface of the core in order to improve its optical properties. Bulk bandgap of ZnS is higher than that of InP. Hence InP/ZnS system act as a type-I quantum dot. Apart from electron confinement, ZnS shell

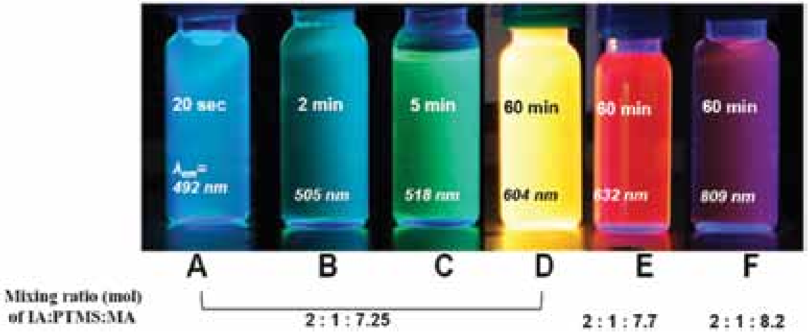

FIGURE 1
Different colored InP/ZnS QD samples prepared under UV illumination. (A-D) PL emission depending on the reaction time of 20 sec to 60 min at the fixed mixing ratio (2:1:7.25 of IA:PTMS:MA), (E,F) PL emission depending on mixing ratio (from 2:1:7.7 to 2:1:8.2 of IA:PTMS:MA) at the reaction time of 60min.

physically separates the surface of the optically active core from its surrounding medium. Consequently, the sensitivity of the QD towards the local environment like oxygen or water molecule is reduced. With respect to core QDs, CS systems exhibit generally enhanced stability against photodegradation. At the same time, shell growth reduces the number of surface dangling bonds, which can act as trap states for charge carriers and thereby reduce the fluorescence QY. At the same time it significantly improves the fluorescence QY and stability against photobleaching, the shell growth is accompanied by a small red shift of the excitonic peak in the UV/Vis absorption spectrum and the photoluminescence (PL) wavelength. This observation is attributed to a partial leakage of the exciton into the shell material.

3.1. Color Tuning

The size and hence the emission color of the core was tuned by controlling the MyA concentration and the reaction time. Emission color tuning was achieved from λ_{em} = 490 to 810 nm. Various QDs synthesized by color tuning of InP/ZnS core-shell QDs under UV illumination can be seen in Figure 1. Absorption spectra of these samples are shown in Figure 2(a) and the emission spectra is depicted in Figure 2(b). The characteristic absorption and emission spectra shows the formation of core-shell type InP nanocrystals. Relatively high photoluminescence (PL) intensities shows the formation of core-shell type QDs. From the relatively narrow emission peaks the QDs could be assessed to be monodisperse.

Monodispersity of these samples was confirmed from their TEM images. Figure 3 shows the TEM image of the InP/ZnS QDs showing red PL. This red

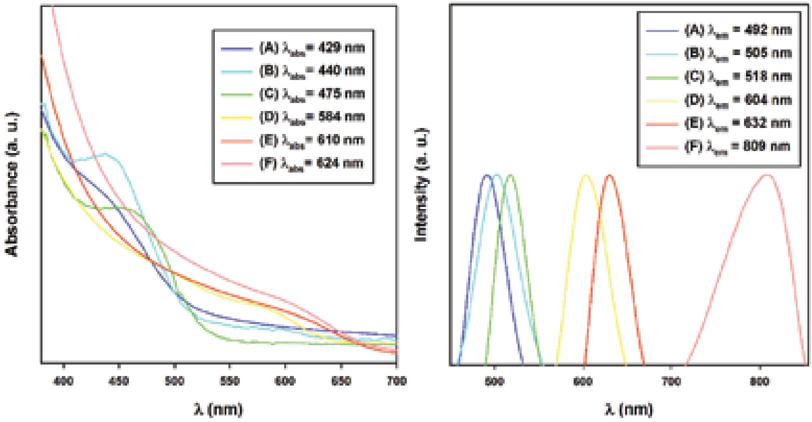

FIGURE 2
Optical characteristics of InP/ZnS QDs (a) UV-vis spectra of InP/ZnS NCs synthesized (b) PL spectra of InP/ZnS NCs synthesized

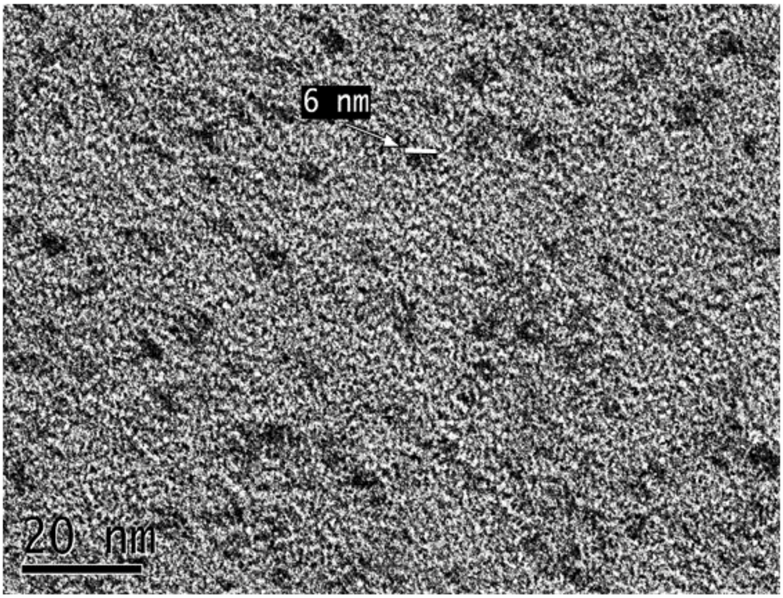

FIGURE 3
TEM images of red emitting QDs (E) from Figure 1

PL (excitonic) peak is located at 632 nm (614 nm) and its average size determined from TEM is 6 nm. The PL spectrum The full width at half maximum of InP/ZnS QDs are greater than in the case of typical CdSe/ZnS QDs because of the polydispersity in the sizes of the former [30]. From the TEM image in Figure 3 it is clear that the samples are quite polydisperse.

3.2. One Pot Synthesis

Having attempted the stepwise addition of precursors in the above procedure, we also tried a one pot protocol for the synthesis of InP/ZnS QDs. For this $P(NMe_2)_3$ was employed as the phosphorus precursor in a protocol which was a modification of a previous report [16]. Indium myristate was prepared *in situ* by treating indium acetate and myristic acid in ODE at 188°C. $P(NMe_2)_3$ was used as the phosphorous donor. The reaction with different combinations of reaction time, reactant amounts and temperatures below 200°C produced InP QDs. The reaction mixture was cooled to 150°C and a 0.1 M solution of Zn and S precursors (both 1.2 mL each) were added to grow a single layer of shell. For the shell growth the reaction temperature was raised to 220°C over a period of 30 minutes. All the samples resulted with PL emission only in blue region. This may be due to the difficulty in stabilization of the free phosphide during the reaction inhibiting the growth of QDs to a larger size. We currenly looking at the possibility of using alkylamines like decyl amine (DA) and dodecyl amine (DDA) to solve this issue.

3.3. Synthesis of Ce^{3+} doped InP/ZnS QDs

Triply ionized rare earth elements have magnetic properties due to their partially filled $4f$ shells, which are well screened by outer closed $5s^2$ and $5p^6$ orbitals. For this reason, the intracenter transitions of $4f$ electrons give rise to sharp emission spectra in various host materials. Luminescent lanthanide doped nanocrystals are unique in that they can convert low energy radiation (typically near infrared) to higher energies such as visible or UV via a process known as upconversion [31]. Up conversion ability of QDs helps them to act like IR antennas in hybrid photovoltaic devices. Rare earth (RE) ions doped III-V compound semiconductors were reported before either by diffusion of RE ions to III-V semiconductor thin films or by molecular beam epitaxy (MBE), to find potential applications in silica fiber based optical communication systems. Transition metal doped InP/ZnS QDs exhibit PL peaks at lower energies than their bandgaps would suggest. Depending on the amount of dopant the bandgap emission of InP disappear and the dopant PL become the dominant. If this trend was replicated in the case of rare earths it would provide an easy method to tune emissions in rare earth doped InP/ZnS QDs.

Since there are no previous reports of colloidal synthesis of rare earth doped InP/ZnS QDs we carried out some preliminary reactions for accomplishing the same. To produce doped III-V system Ce^{3+} ions were selected due to their easy availability. Cerium acetate is insoluble in 1-octadecene. A turbid dispersion of cerium acetate was prepared (5, 7, 10 and 12 % with respect to indium) in 1-octadecene by heating a mixture to 250°C under vigorous stirring and the heating and vigorous stirring was continued until the time of addition. InP core was prepared following the procedure described in previous sections. After the desired core growth time the reaction mixture was cooled to 150ºC and the turbid cerium acetate dispersion was added to the reaction mixture. The core growth was restricted to green emitting QDs since a further low energy PL was expected for that originating from dopant ions. After the addition the reaction mixture was heated to 220ºC for 30 minutes for the diffusion of Ce^{3+} into the InP crystal lattice. After the reaction time the reaction mixture again cooled to 150ºC for the shell growth. Precursors for shell growth were added and the temperature was again raised to 220ºC for shell growth. Multiple shell growth were attempted for preventing the doped Ce^{3+} ions escape from the core by diffusion. The reaction resulted in formation of green InP/ZnS QDs.

The absorption and PL spectra of Ce^{3+} doped QDs can be seen in Figure 4. Detailed analysis of the doped structures revealed the presence of large lumps of possibly undissolved and unreacted cerium acetate in the samples indicating the inefficiency of this method to produce doped QDs. It was reported before that the reaction temperature has influence on the diffusion of dopants in the QD cores [26]. Xie and coworkers has showed that temperature to be a key factor in successful doping of InP nanocrystals. They have found that with the increase of temperature lattice diffusion of dopants increases into the core. Based on this result, we have carried out high temperature reaction to induce diffusion of rare earth elements into the InP core. To have a 300ºC reaction temperature, it is necessary to increase the amine alkyl chain length. Hexadecyl amine was chosen due to its high boiling point (330 ºC) and low melting point (43ºC). When using the hexadecyl amine, the reaction mixture was found difficult to disperse in solvents after the reaction.

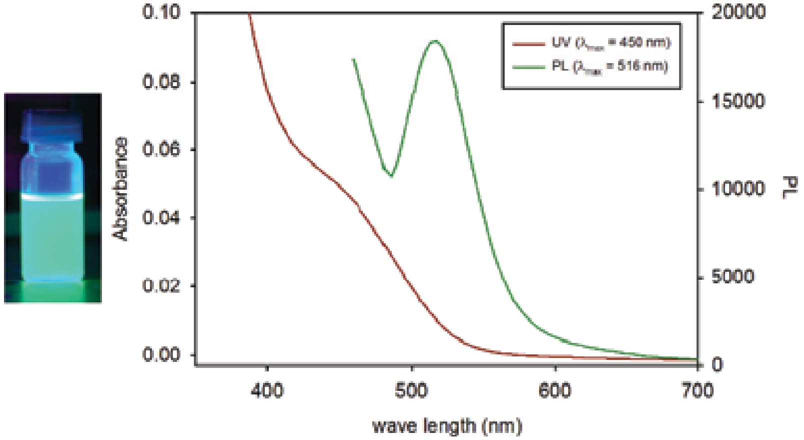

FIGURE 4
UV-vis and PL spectra of Ce^{3+}(5 %):InP/ZnS green emitting doped QDs

4. CONCLUSION

A crucial point for the application of fluorescent InP QDs is their relative nontoxic nature. Enhanced relevancy can be achieved by improving chemical and thermal stability for InP QDs and their PL. A convenient method for preparing InP/ZnS core-shell type QDs at elevated temperature and pressure has been introduced. Formation of QDs was successfully confirmed by following their optical spectra and TEM. The presented synthetic protocol allows easy doping of InP QDs. The attempts to develop a one-pot synthesis of InP/ZnS QDs was hampered due to uncertainty surrounding the fate of phosphorus in the reaction mixture. All the one-pot syntheses yielded blue QD showing significant impediments to the formation of larger particles in such a reaction. Doping the InP core with Ce^{3+} was attempted at 180°C, this reaction yielded green QDs but was hampered by the insolubility of the cerium precursor. We are currently pursuing doping at higher temperatures.

5. ACKNOWLEDGMENT

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