Charge transfer studies of indium phosphide-polymer nanocomposites

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Abstract

Indium Phosphide quantum dots (InP QDs) having various applications can be used for both LEDs and photovoltaics owing to its highly luminescent properties and energy harvesting potential respectively. In our work we have synthesized InP QDs using hot injection technique. Further post synthesis treatment was given and InP/ZnS core shell nanocrystals were grown on InP core. Composites with P3HT conducting polymer were made in order to study the charge transfer/energy transfer phenomenon. InP and InP/ZnS QDs show an effective phenomenon of energy transfer and PL increment is observed in the case of composites. Whereas in the case of treated InP QDs a decrement in the PL was observed. Treatment results in removal of the surface defects and traps which help in effective charge transfer rather than energy transfer. Post synthesis treatment increases the monodispersity of the QDs which results in high quality QDs without any defects. With a simple post synthesis treatment,InP QDs can be used for both LEDs as well as photovoltaic applications. The future work involves the device fabrication of InP QDs and treated InP QDs for LED and solar cells respectively. Various characterization such photoluminescence, transmission electron microscopy, selected area diffraction was done in order to confirm the charge/energy transfer phenomenon. Copyright © 2016 VBRI Press.

Keywords: Quantum Dots, indium phosphide, hybrid, P3HT, energy transfer, post synthesis treatment.

Introduction

A new era of hybrid organic/inorganic solar cells have emerged over the pure organic solar cells [1]. The hybrid solar cells offer various advantages over other solar cells such as increased carrier mobility due to the incorporation of inorganic nanoparticles. nanoparticles have tunable These inorganic absorption and emission spectra as their band gap can be tuned by varying their particle size; better thermal and optical stability; and high carrier mobility [2,3]. Researchers have explored various inorganic nanoparticles such as TiO₂, PbS, CdSe etc. Various simple synthesis methods, charge transfer studies, devices have already been established by the researchers. But a very less explored inorganic nanoparticle is Indium Phophide (InP) and hence it offers a wide scope of research to explore its various properties. Indium Phosphide belongs to III-V semiconductor group and hence provides various advantages over CdSe system. Firstly, being Cadmium free, it is non- toxic as compared to CdSe; secondly they are more robust due to the presence of covalent bonds [4]. Moreover, InP is a potential energy harvester as well as an ideal material for LED applications [5,6]. But, synthesis of InP is quite

difficult due to long reaction hours and use of tris(trimethylsilyl)phosphine (TMS₃P) which is highly toxic and flammable [7-9]. Due to this only few work on charge transfer studies of Indium phosphide and conducting polymer have been reported. In this work we have synthesized InP using Trioctylphosphine as a source of phosphorus rather than the toxic TMS_3P [10]. A post synthesis treatment was given to as synthesized InP QDs in order to remove surface defects, increase monodispersity and increase photoluminescence intensity. Till now researchers have done HF etching after synthesis in order to increase photoluminescence and quantum yield. In this work a novel post synthesis treatment is done rather than the HF etching [11, 12]. A shell of wide band gap material i.e. ZnS was grown over the InP to make the QDs more robust against oxidation. InP/ZnS QDs were grown by single pot route avoiding the oxidation risk which is generally involved in double pot synthesis. Double pot synthesis leads to inferior properties of the QDs due to the oxidation of the core before growth of the shell [13]. Moreover growing a shell also removes surface defects and increases band to band recombination which in turns increases the photoluminescence intensity. The synthesized InP,

treated InP and InP/ZnS core shell was used to form hybrid with Poly(3-hexylthiophene-2,5-diyl) (P3HT)polymer.

An increase in photoluminescence on adding InP to P3HT solution suggest that Förster resonance energy transfer (FRET)is taking place between P3HT and InP QDs composite. When an excited donor particle is bought in the close proximity (~10-100Å) of a ground state acceptor then resonant energy transfer occurs from donor to acceptor [14]. The energy transfer takes place by means of intermolecular longrange dipole-dipole coupling. A spectral overlap between the emission spectra of donor and absorbance spectra of acceptor is one of the necessary conditions for FRET [15]. The other important necessary condition is the distance between the acceptor and donor. The efficiency of FRET is inversely proportional to the sixth power of intermolecular separation [16]. So as the separation increases, the efficiency of FRET decreases.

Till now researchers have observed the FRET phenomenon with InP/ZnS and various dyes such as lissaminerhodamine B ethylene diamine (LiRh), Texas red cadavarine C5 (TxRed), and rhodamine 101 (Rh101). They confirmed that InP is an excellent energy harvester with potential use in biomedical and photovoltaic applications because of the efficient energy transfer [17].

In this work an effort has been made to study the energy/charge transfer mechanism between InP and P3HT and underlying phenomenon which occurs after the treatment of the as synthesized InP QDs and after coating a shell of ZnS i.e. InP/ZnS core shell QDs. This work has been done for the first time where a simple and efficient post synthesis treatment can change the phenomenon from efficient energy transfer to charge transfer. With this InP QDs can be used for LEDs as well as solar cells.

Experimental

Materials

Indium Chloride (98% pure), 1-Octadecene (90% pure), Tri Octyl Phosphine (97% pure), Zinc chloride (95% pure), Sulphur (99.99% pure) of analytical grade were used without further purification.

Above mentioned chemicals were procured from Sigma Aldrich

Method

Indium Phosphide Quantum Dots

0.08 g of Indium Chloride (along with 3 ml of 1-Octadecene was taken in 500ml two neck round bottom flask. Inert gas atmosphere was provided with argon gas. The mixture was heated to $290-310^{\circ}$ C. Then the heater was switched off. When the temperature reached in the range of 290° C, 2 ml of Tri Octyl Phosphine was rapidly injected into the flask. On injection temperature dropped to 275° C.

The solution was allowed to cool down to room temperature. After cooling to room temperature the reaction mixture was stirred overnight under an argon atmosphere. The nanocrystals were finally dispersed in toluene for further characterizations.All chemicals were purchased from Sigma Aldrich.

Shell Formation for Indium Phosphide Quantum Dots (InP/ZnS)

For the formation of shell, 0.01 g of Zinc chloride was taken along with Indium chloride and 1-Octadecene. The same procedure was followed as for the formation of indium phosphide. The solution was allowed to cool down to room temperature. Then again heating was done and at around 180- 190⁰C, solution of Tri Octyl Phosphine and Sulphur was injected drop wise at a very slow rate. The reaction mixture was allowed to cool down to room temperature the reaction mixture was stirred overnight under an argon atmosphere.

For the composites, same concentration of InP, treated InP, InP/ZnS were taken with P3HT. The absorbance of all the solutions was maintained constant.

All chemicals were purchased from Sigma Aldrich. Details of various characterization instruments and the post synthesis treatment are given in the supplementary information.

Results and discussion

Indium Phosphide quantum dots was synthesized using previously reported method by Khanna et al. with slight modifications to reduce long reaction time [10,18]. The current method approach does not involve TMS₃P(Tristrimethylsilylphosphine) which is highly flammable and toxic source of phosphorus. This method is quite fast (~90 minutes) and the synthesized quantum dots are highly monodispersed.



Fig. 1. Apparatus for synthesis of colloidal InP QDs.

Fig. 1 shows the apparatus used for the synthesisInP QDs. A double neck round bottom flask was used for the synthesis. In order to separate the growth and nucleation phase hot injection technique was used. This technique gives a control over the size of the nanoparticle by separating nucleation and growth phases [6]. The synthesis procedure and conditions are already discussed in the experimental section.

The as synthesized InP QDs shows a photoluminescence peak at 490 nm (**Fig. 1** supporting information). It is evident from the figure that there are no surface states present. Surface states are generally present in the form of broad peaks at higher wavelength(λ >600 nm) [**19**].



Fig. 2. PL increment due to FRET in (a) InP, (b) treated InP, (c) InP/ZnS respectively.

Thomas Nann et al added zinc in order to remove the surface states ¹⁹which were present in the as synthesized quantum dots. It is well established fact that growing a shell of wide band gap semiconductor passivates the dangling bond present at the surface. Hence the traps which are present are removed and band to band recombination takes place which contributes towards the increment of PL intensity. So after coating of ZnS on InP core, there was an increment in the PL intensity.

The post synthesis treatment given to InP quantum dots also showed an increment in the PL intensity comparable to InP/ZnS quantum dots. The post synthesis treatment also served the same purpose by removing the defects present in the form of traps between the energy bands. Removal of those traps after treatment leads to increment in the PL intensity. A structural reformation is observed after treatment which is confirmed by the TEM micrographs discussed later.

Further the charge/energy transfer capabilities of the composites of nanoparticles and polymer were studied. When the aliquots of InP QDs were added to P3HT solution, a significantincrement in PL spectra was observed. The PL intensity kept on increasing with further addition of InP nanoparticles which can be seen from **Fig. 2(a)**. The increase in PL suggests that charge transfer is inefficient in case of InP and FRET phenomenon is dominated. The energy from P3HT is transferred to InP which also gets excited and hence contributes towards the increment of PL intensity. The FRET phenomenon has previously been observed in the case of InP and P3HT and various other dyes **[17, 20]**.

In case of InP/ZnS the same pattern was observed as shown in **Fig. 2(b)**. It is apparent from the figure that the increment in PL intensity for InP/ZnS is not as high as that forInP. This is because shell acts as barrier between the donor and acceptor. The distance between donor and acceptor is increased due to which FRET efficiency is decreased.

The behavior of the composites changed when treated InP was added to the P3HT solution.The P3HT solution showed almost no increment on addition of treated InP QDs shown in **Fig. 2(c)**. Moreover, some quenching was observed after the addition of treated InP QDs. This suggests that treated InP has the tendency for efficient charge transfer rather than energy transfer.



Fig. 3 Rate of increment of PL intensity on adding aliquots of (a) InP (b) Treated InP (c) InP/ZnS QDs respectively to P3HT solution.

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Fig. 3 shows the rate of increment of PL intensity on addition of aliquots of InP, treated InP, InP/ZnS marked as a,b,c respectively. It can be seen from Fig. 3 that rate of increment of PL intensity is maximum for InP and least for treated InP. As discussed earlier, InP QDs has certain defects which are present in the form of traps between the valence and conduction band. So charge carriers are trapped in these traps and hinders in an efficient charge transfer and hence FRET mechanism is dominated over charge transfer. Whereas in treated InP QDs, the absence of traps and defects results in efficient charge transfer and hence enhancement in the PL intensity is minimum. The rate of increment in the case of InP/ZnS is less as compared to InP because of the shell as discussed above. The shell acts as a barrier for the charge carriers and moreover the distance between the donor and acceptor has increased which reduces FRET efficiency.



Fig. 4. Model Explaining the increment of PL in (a) InP QDs and (b) charge transfer in treated InP

Fig. 4 shows a model describing the exact phenomenon occurring when InP QDs are mixed with P3HT polymer to form composites. Fig. 4(a) shows the case of untreated InP QDs which are as synthesized and have surface defects in the form of traps. These traps hinder the direct band to band recombination of the charge carriers. When the InP-P3HT composite is excited during the PL experiment, the electrons of P3HT are excited and move to conduction band. In this process InP also gets excited and someof the ground electrons of InP gets trapped in between the conduction and valence band. When the electrons of P3HT relax to the ground state, the energy released in turns excites the electrons of InP QDs, both the ground level electrons and trapped electrons. All the electrons including the trapped electrons are excited and relax back to the ground level. The energy released during this process contributes towards the enhancement of PL intensity.

The time taken by the electrons in the trapped state to recombine is less as compared to the electron present in the ground state. All these factors contributes for the enhancement in the PL spectra after adding InP QDs to P3HT solution. This aids in the detrapping of electrons and PL enhancement.

Fig. 4(b) explains the mechanism for the treated InP QDs. Due to the absence of any defects; there are no trapped electrons between conduction band and valence band. Hence on excitation by the energy released by P3HT, only ground level electrons are excited. After treatment, removal of defects leads to efficient charge transfer. The FRET phenomenon is suppressed by the charge transfer phenomenon. This results in quenching of the PL intensity rather than increment of the PL.



Fig. 5. TEM micrographs composites of P3HT with (a) InP (b) Treated InP (c) InP/ZnS QDs $\,$

An investigation of the morphologies of the synthesized QDs was carried out by transmission electron microscopic (TEM) studies. **Fig. 5** shows the TEM images of composites of untreated InP, treated InP, InP/ZnS core shell with P3HT respectively.

Fig. 5(a) shows InP QDs dispersed the P3HT polymer matrix. Spherical nanoparticles are synthesized. High agglomeration among particles can be seen from the TEM micrograph. The diffused rings of the SAED pattern showed in the inset of figure 5(a) shows the amorphous nature of InP QDs. The amorphous nature is due to the extreme small size of the QDs. The treated InP QDs are shown in figure 5(b). Treated InP shows perfect spherical cluster of smaller InP ODs The treatment resulted in the enhancement in crystallinityas indicated by its SAED pattern (inset of Fig. 5(b)) and monodispersity of the nanoparticles due to the structural reformation of the InP QDs which subsequently leads to PL increment. Structural reformation leads to long range ordering as compared to the untreated InP QDs where short range ordering is present.

In his work we observed the FRET phenomenon which is known for years but limited application seen in the case of InP QDs. A simple post synthesis treatment changes the energy transfer to charge transfer mechanism which makes InP QDs suitable for various optoelectronic devices.

Conclusion

InP QDs were synthesized using trioctylphosphine rather than the conventional toxic & hazardous TMS₃P. Further InP/ZnS core shell QDs were grown using single pot hot injection technique to protect the InP-core against oxidation & to make the resulting structure robust. A simple post synthesis treatment was given to InP QDs which lead to the increment of PL intensity and crystallinity of QDs. An enhancement in properties is observed due to structural reformation taking place during the treatment. Composites of InP, treated InP and InP/ZnS core shell QDs were made with P3HT polymer. FRET phenomenon was observed in the case of InP and InP/ZnS QDs. The charge transfer phenomenon was not efficient in these two cases. Whereas in the case of treated InP, due to removal of defects, the charge transfer phenomenon is dominated over FRET process. With two different phenomena occurring with InP QDs by just a simple post synthesis treatment, we can explore its potential in two different applications. The untreated InP showed an enhancement in PL due FRET and hence can be used in organic LEDs whereas the treated one showed PL quenching due to charge transfer and can be used for photovoltaic applications respectively.

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Author's contributions

Conceived the plan: SNS; Performed the experiments: AP; Data analysis: SNS,AP; Wrote the paper:SNS AP. Authors have no competing financial interests.

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