



Recent advances in colloidal indium phosphide quantum dot production

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The narrow, color-tunable luminescence of quantum dots (QDs) brought them to the forefront of commercial lighting and solar cells. Indium phosphide (InP) QDs emerged as the most promising replacement for cadmium selenide-based QDs for luminescence in the visible range (450–700 nm). Here, we consider areas of QD synthesis most relevant for future advances in InP. Advances in precursor chemistry, namely single-source precursors, facilitate synthesis of materials with more homogeneous properties. These isolable intermediates have atomically precise structure that introduces a scheme for the atom economy in InP QD synthesis. Methods for obtaining luminescent InP QDs are presented with emphasis on shorter reaction times, fewer steps, and less hazardous reagents. With these advances in luminescence quantum yield (QY), minimization of sample heterogeneity, and enhanced stability, emphasis on reproducibility, safety, and other green chemistry principles can be prioritized. The methods reviewed here highlight areas conducive to goals related to material properties and greener synthetic methods.

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Current Opinion in Green and Sustainable Chemistry 2018, 12:76–82

This review comes from a themed issue on **Selected papers from the ACS Symposium on Green chemistry synthesis of nanomaterials and manufacturing**

Edited by **Cory Jensen** and **Nastassja Lewinski**

Available online 18 June 2018

<https://doi.org/10.1016/j.cogsc.2018.06.004>

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Introduction

Quantum dots (QDs) are nanometer-sized semiconductors, frequently with sub-10 nm diameters. There are robust colloidal syntheses for a wide range of materials, but the most established materials include cadmium and lead chalcogenides because of their favorable properties [1] for applications ranging from displays [2] and lighting [3] to imaging [4] and security [5]. Indium phosphide (InP) emerged as a good alternative to Cd-based QDs, as they both emit across the visible range (450–700 nm) [6], but full investment in InP remains

limited by the more challenging syntheses available. The phosphorous precursors used are sensitive to oxidation therefore, the types of precursor molecules available are limited. The poorly controlled reactivity of these precursors often results in QDs with a large range of sizes (broad size-distribution, less-specific luminescence colors) and poor luminescence QYs (<1%) [7]. Although the inherent green improvement in removing or not using a toxic heavy metal seems like a natural direction to move in, the true overall benefit of currently available InP based technologies is still debated. For example a full cradle-to-grave analysis of the energy consumption of Cd-based QD displays and InP-based QD displays using established, standard synthetic and processing methods can be found elsewhere [8].

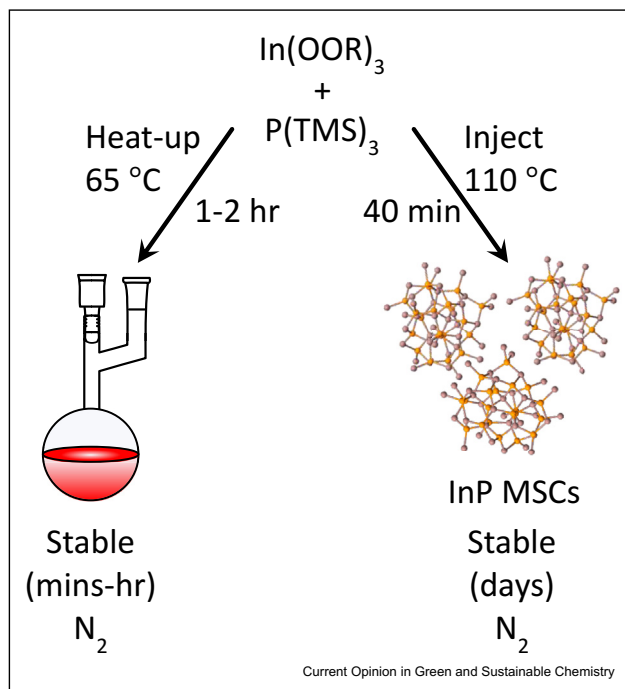
For greener, more sustainable nanomaterials, focus on improvement of synthetic methods has successfully integrated safer, less reactive precursors and improved reproducibility as well as making them more “user friendly” [9]. For QDs, improvements in synthesis can result in reduction of material quality with the most important properties of QDs depending on their final use [10]. For InP QDs, the dominant interest is their color-tunable luminescence, and synthetic advances concern improvements in their optical properties such as brightness (large absorption and high luminescence QY, color purity) and tunability (narrow size-distribution for small full-width-half-max) [7], and stability and chemical yield. The latter two are of increasing interest as the materials advance to applications demanding more efficient and long-term use of resources [11]. QY is also particularly crucial in applications as it describes the ratio of photons emitted to photons absorbed. Decreases, or quenching, of QY often occurs for several reasons such as interactions with the solvent or surface traps that lead to nonradiative decay of photons. High QY is necessary for applications that require light emission, namely displays. So, although simple changes in precursors and reaction conditions can decrease waste, increase energy efficiency, and reduce hazards, for such improvements to catch on, the QD products must have properties comparable to, if not better than, those from standard methods. The broad criteria for assessment of QDs can complicate integration of greener principles and sustainable practices. Here, we present directions for InP QD synthesis established within the past 2–3 years that provide pathways to quality materials with greener practices in mind.

Precursors and intermediates with established structure

Colloidal QD syntheses are characterized by nucleation of reactants and subsequent growth into QDs. The main methods for precursor conversion include hot-injection and heat-up synthesis [12,13]. Heat-up methods are notorious for producing QDs with broad size-distributions [13]. This will be addressed in the *Fluoride Etching* subsection of the [Methods in luminescence section](#). Synthesis by hot-injection is widely used because there is good separation between nucleation and growth forming particles with narrow-size distribution [12]. The hot-injection method can also lead to unwanted and unknown intermediates. For InP, typically a phosphine precursor is injected into a flask with an indium precursor, usually a carboxylic acid or halide complex [14]. Phosphines are very reactive, and the phosphine precursor commonly used in indium phosphide syntheses, *tris*(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$), can be protonated in the presence of carboxylic acid [15]. Rapid nucleation induced by hot-injection can lead to quick depletion of the phosphorous precursor and monomer reserves, yielding non-uniform and poorly luminescent QDs [14]. When the InP nuclei become QDs via Ostwald ripening, small particles dissolve and large particles become larger, which results in a broad size distribution. There are many variations in terms of precursors [16–18] or even the addition of other cations [19,20] to improve the properties of the final materials.

An attractive alternative to the separate-source In^{3+} and P^{3-} precursors are single-source precursors, which are stable molecules and clusters containing both the cation and anion of the desired material [18]. A range of molecules are available, but larger clusters are advantageous as they are often readily isolated by crystallization as intermediates (magic-sized clusters) with known structure and composition and can retain solubility in organic solvents [21]. By knowing the surface and core structure of the cluster precursor, these advantages provide better control over reaction reproducibility, QD size, and sample homogeneity. Chalcogenide-based clusters are well established [22] but intermediates for InP QD synthesis are rarely isolated. [Figure 1](#) shows two methods used to form InP precursors. Simple combination of the In^{3+} and P^{3-} precursors and heating at 65 °C for 1–2 h forms a red solution ([Figure 1](#), left). This InP precursor continues to react at room temperature and must be used to make QDs immediately to minimize variation in final sample properties. Other work on more stable III-V precursors isolated InP dimers [18,23] and recently, Cossairt and co-workers isolated and characterized an InP magic-sized cluster [24] and demonstrated reproducible synthetic control over InP QDs with clusters formed from several alkyl carboxylic acids [25]. The straightforward synthesis at a lower temperature of 110 °C forms cluster after injection of

Figure 1

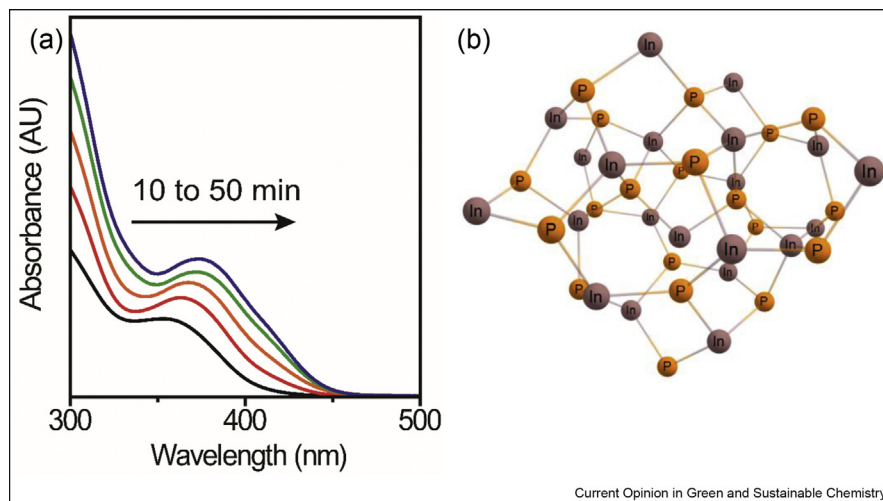


InP precursor synthesis. Left: Simple heating of the indium and phosphorous precursors forms a red solution stable for short times in inert atmosphere. Right: Injection of the phosphorous precursor into the indium precursor solution forms clusters stable for long times in inert atmosphere.

$\text{P}(\text{TMS})_3$ into a solution of indium(III) myristate ([Figure 1](#), right). The reaction can be monitored using UV–vis absorption as the cluster absorption feature near 360 nm red-shifts over the course of the synthesis, as shown in [Figure 2a](#). Heating for 40 min reproducibly forms these stable, isolable cluster intermediates. [Figure 2b](#) shows one illustration of the $\text{In}_{21}\text{P}_{20}$ cluster core. The complete structure is depicted in Ref. [24]. This structure confirms pre-formation of In–P bonds and pseudo-tetrahedral coordination geometry around the In and P atoms, as expected for the zinc blende structure of bulk InP. The cluster, including all surface indiums, is passivated by anionic (X-type) phenylacetate ligands with varying coordination modes.

This cluster provides unprecedented control over InP QD size and size-distribution in a highly reproducible fashion. By isolating magic-sized clusters, QD growth can progress via a lower energy second step, rather than through aggregative growth, consuming less energy. Further advances in precursor development can improve chemical yield and facilitate product isolation and purity. The use of a precursor with known structure is unusual in InP QD synthesis, but is key to assessment of greenness through the atom economy. But, additional considerations related to InP QD quality beyond color tunability and size-distribution, namely luminescence

Figure 2



Spectra and partial structure of the indium phosphide cluster. (a) UV-Vis absorption spectra of aliquots taken during cluster growth using the procedure in Ref. [25] As the reaction proceeds, the feature near 360 nm red-shifts to 390 nm due to the presence of the stable cluster intermediate. (b) Modified structure of $\text{In}_{21}\text{P}_{20}$ cluster core. The full structure can be found in Ref. [25] The structure shows pseudo-tetrahedral bonding and formation of In-P bonds presenting a lower energy pathway to InP QD formation.

QY are still a driving factor in the choice of synthetic method. The following section, [Methods for luminescence](#), describes two ways to obtain luminescent InP QDs: fluoride etching and shell growth.

Methods for luminescence

The main applications for InP QDs described in the Introduction are highly dependent on QD luminescence. The best QDs have high luminescence QYs (80%) and narrow full-width-half-max (fwhm, <40 nm) to obtain color-specific emitted light efficiently. The two most popular methods used to achieve significant luminescence are hydrofluoric acid (HF) etching and shell growth. To-date, these are most often post-synthetic methods employed for improving already-synthesized InP QDs. Fluoride etching and shell growth are discussed in the next sections with emphasis on a microwave-assisted ionic liquid (MAIL) method for obtaining luminescent InP QDs.

Fluoride etching

The first method used to obtain InP with significant luminescence was HF etching [26]. Etching the QD surface with HF improves QYs [17,27] and is attributed to the removal of surface defects such as surface phosphorous vacancies [28]. HF, however, is highly corrosive and detrimental to our health [29,30] and is not a practical solution for improving the quality of QDs.

A less hazardous alternative are ILs with fluoride-containing anions, such as BF_4^- and PF_6^- , which release fluoride upon heating [31]. Although HF may be produced *in situ*, the simple change in fluoride source dramatically reduces the chance of accidents related to

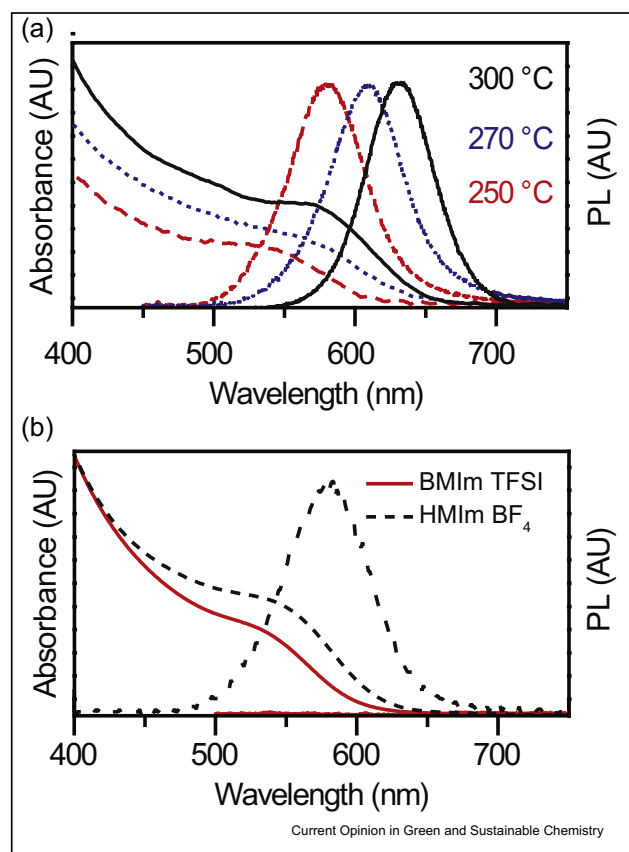
the presence of such a corrosive acid. The IL also aids in rapid reaction heating with heating rates of tens of degrees per second using microwave irradiation. As mentioned in the Introduction, heat-up methods are notorious for producing QDs with broad size-distributions [13]. This is due to thermal gradients in solution as most methods heat by convection causing non-uniform heating. More uniform particles are favored by single-source precursors or rapid heating methods such as induction heating and microwave-assisted synthesis [32].

Microwave-assisted syntheses are frequently used to make oxide nanomaterials. These reactions often occur in polar solvents and aqueous solutions known to induce heating from microwaves through dipolar polarization [33]. This direct heating of solvent often increases heating rates, reducing reaction times and decreasing the amount of side-products. Improved purity and faster reactions are also aided by heating solvents beyond their boiling points, which is possible because microwave vessels are designed to withstand high pressures (up to 30 bar). These advantages can apply to reactions for non-oxide nanomaterials as well, but different solvents are used as the absence of oxygen is often a requirement. Microwave syntheses are usually simple adaptations of conductive heat-up and hot-injection methods, which often use high-boiling, nonpolar solvents such as octadecene. The nonpolar solvents are transparent to microwaves, presenting opportunities for direct heating of precursors in solution, possibly resulting in unique reaction conditions [34]. In the absence of a good microwave absorber, heating will be dominated by the glass vessel and

reactions fail to reach relatively low target temperatures (150 °C). Our group uses ILs in conjunction with microwaves to heat solutions to hundreds of degrees within minutes by ionic conduction regardless of their composition [33,35].

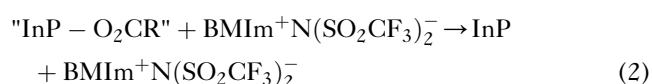
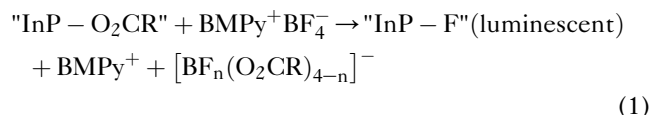
ILs are stable, polar solvents with low volatility and low melting points [36]. If isolated after use, they can be recycled, resulting in reduction of solvent usage and waste. Their ionic and heat dissipating nature can be used in conjunction with microwave reactors. Recently, using a procedure adapted from Lovingood and Strouse [31], we synthesized InP QDs with tunable size and QYs as high as 30% [35]. By using ILs that release fluoride, QDs that are both luminescent and size-tunable, are readily produced. Figure 3a shows the UV–Vis absorption and PL spectra of the resulting InP QDs prepared at different temperatures. As the temperature increases, the absorption and PL peaks red-shift showing that in conjunction with ILs, the size of the QDs can be tuned by changing the temperature.

Figure 3



Absorption and photoluminescence spectra of InP QDs prepared using microwave-assisted IL methods. (a) Increasing the reaction temperature from 250 to 300 °C increases the size of the QDs, red-shifting their absorption and luminescence spectra. (b) For samples prepared at 800 W set-power and 280 °C, only the sample prepared with the BF₄-containing IL exhibits PL. The BMIm TFSI IL rapidly heats the reaction mixture, but no fluoride is produced and no luminescence is observed.

Equation (1) shows a general proposed form of this reaction in which “InP–O₂CR” can be either InP precursor discussed in the Precursors and Intermediates Section and R is CH₃(CH₂)₁₃ or CH₃(CH₂)₁₅. The 1-butyl-4-methyl pyridinium tetrafluoroborate (BMPy BF₄) IL acts as a fluoride reservoir for surface cleaning, likely forming [BF_n(O₂CR)_{4-n}][–] species and InP QDs with modified surfaces (InP–F) that luminesce. This eliminates extra steps for obtaining luminescent QDs through post-synthetic methods.

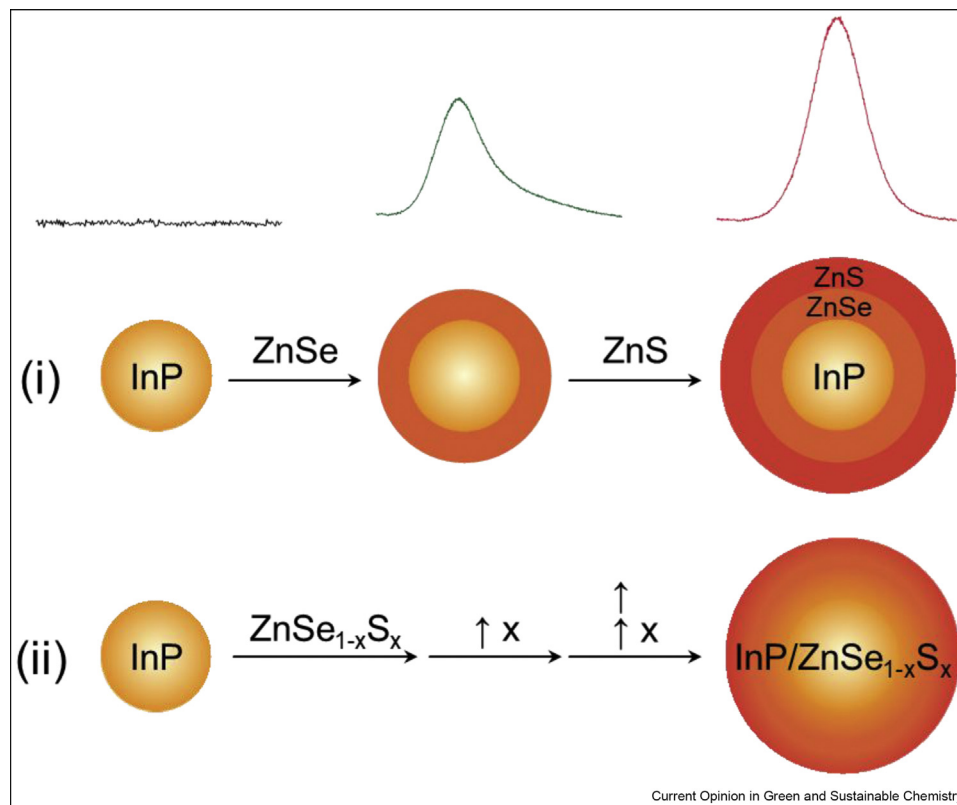


QDs can form with the addition of ILs without fluorine, such as 1-butyl-3-methyl imidazolium *bis*(trifluoromethane)sulfonimide (BMIm TFSI). Equation (2) shows the reaction of an InP precursor with this IL in which the IL absorbs microwaves releasing the energy as heat and rapidly heating the reaction forming non-luminescent QDs. The rapid heating induced by the IL reduces reaction times from hours to minutes and because the sealed microwave vessel can withstand high pressures, solvents with lower boiling points can be used. Using decane instead of the higher boiling octadecene as solvent aids in the purification of the product InP QDs and separation of the IL. But, as the TFSI anion doesn't release fluoride, the resulting QDs don't luminesce. Figure 3b illustrates how QD PL is improved in the presence of 1-hexyl-3-methyl imidazolium tetrafluoroborate (HMIm BF₄) IL but not BMIm TFSI. Using the dual-purpose BF₄-containing ILs as the microwave absorber and surface modifier, we can produce luminescent QDs without the hazardous acid, HF.

Shell growth

The most common method for obtaining luminescent InP QDs is the addition of material to the initial, core QDs (Figure 4). Typically, a cation and anion are added to the QDs forming a shell in this well-established process [37]. Other processes such as alloying, cation exchange, and diffusion doping can yield similar results and because it is not trivial to structurally characterize the final QDs as core/shell or alloys, shell growth usually refers to the method used to make the QDs as opposed to the final structure. For bright luminescence, it is preferable to have a shell of a wider band gap semiconductor. This Type I band offset increases the QY of the QDs by preventing escape of the electrons and holes from the core QD and passivated defects on the QD surface, also increasing luminescence [38]. Although not a new method, recent modifications for InP QDs have

Figure 4



Shell growth on InP cores. Top: During shell growth, the luminescence intensity increases and becomes more symmetric. (i) Step-wise addition of ZnSe and ZnS forms InP/ZnSe/ZnS core-multishell structures, although some alloying is likely to occur. (ii) InP gradient alloys form when zinc, selenium, and sulfur precursors are added to the InP cores with increasing amounts of sulfur precursor (InP/ZnSe_{1-x}S_x).

dramatically increased QD brightness and stability [39–45].

For InP, ZnSe and ZnS shells are most often used. This is for two main reasons: ZnSe and ZnS have wider band gaps and small lattice mismatches with InP. The latter is important for minimization of defects that form at the interface between the core and shell layers. These defects are known to reduce QYs, and the highest QYs are from materials with mixtures of ZnSe and ZnS. QDs with InP/GaP/ZnS core/shell structure have very high QYs of 85% [40,46]. InP/ZnS core/shell QDs with QYs of 87% for green luminescence were recently reported [47] and 80% QY was achieved with a InP/ZnSeS combination [48,49]. These also incorporated zinc cations in the initial stages of the synthesis, a technique of interest for synthesizing higher quality InP [19,50]. The role of the zinc is not well established [51], but one recent explanation is that formation of zinc phosphorous complexes results in the slow release of phosphorous (from breaking Zn-P bonds) leading to more controlled QD growth [52]. Despite these high QYs, the reaction times for these core/shell syntheses range from hours to days. Never-the-less, they provide a pathway to stable, bright Cd-free QDs.

Conclusions and future directions

There are many syntheses for quality InP QDs, obtaining narrow size-distribution and fwhm and good PLQYs. Within these, magic-sized clusters provide a pathway for better size tunability and final QD size-distribution. The clusters are stable intermediates with atomically precise structures aiding in synthesis reproducibility. Luminescence of InP QDs is not trivial to achieve, but post-synthetic modifications including HF etching and shell growth are well established. Ionic liquid decomposition to release fluoride provides an alternative to using HF, and microwave-assisted methods can be designed to produce InP QDs with tunable size and bright luminescence without post-synthetic modification. Addition of cations such as zinc and gallium form some of the brightest materials, and the current state-of-the-art procedures add ZnSeS shells to InP QDs formed with zinc.

Future work requires increased interest in reproducible synthesis by isolating stable intermediates with known structures, using less reactive precursors, and reducing the number of reaction steps. Applications will define the properties needed in QD samples, and balancing the interdependent requirements for high-quality materials

is not trivial. Integrating small changes in synthetic methods while moving in greener directions, especially reducing hazards, using less solvent, and fewer reaction steps, can align with improving product quality and is essential to justify the pursuit of Cd-free materials.

Conflict of interest statement

Nothing declared.

Acknowledgements

This work was supported by Kansas State University. This material is based upon work supported by the National Science Foundation under Grant No. CHE-1654793.

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