

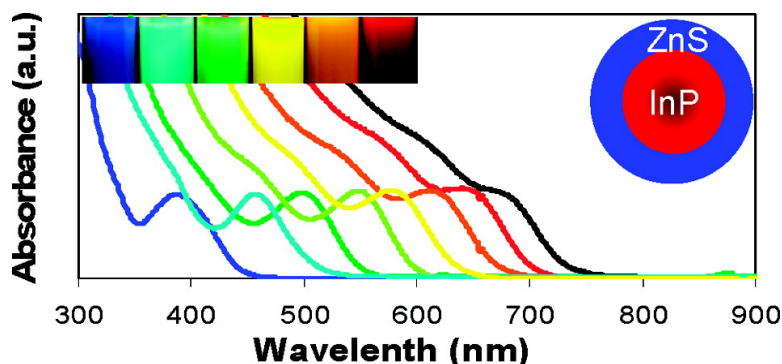
Communication

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Colloidal InP Nanocrystals as Efficient Emitters Covering Blue to Near-Infrared

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The most promising application of colloidal semiconductor nanocrystals (quantum dots or q-dots) is probably as emitters in biomedical labeling,^{1–3} LEDs,⁴ lasers,⁵ etc. CdSe q-dots as the current workhorse have been well developed for such uses. However, CdSe is environmentally restricted and has little future in industry. Among all II–VI and III–V semiconductors, InP is probably the only one which could offer a compatible, or even broader, emission color range similar to that of CdSe q-dots but without intrinsic toxicity since InP has neither Class A elements (Cd and Hg), nor Class B elements (As and Se). Synthesis of high quality InP and other III–V q-dots,^{6–14} unfortunately, is challenging. Existing problems surrounding InP q-dot emitters include poor emission efficiency, poor control of size distribution, poor size tenability, and/or poor stability. Furthermore, the synthetic procedure of InP q-dots is more complicated than that for CdSe nanocrystals. This report intends to explore solutions for these problems.

A typical synthesis for InP core and InP/ZnS core/shell nanocrystals is provided as Supporting Information. The growth of InP q-dots was performed typically below 190 °C, and no pumping of the reaction system was performed at any stage although Ar flow was in place. No size sorting was applied to any sample used for obtaining data in this report. Water-soluble InP/ZnS core/shell q-dots were made by the ligand exchange reaction with mercaptopropionic acid (MPA) with pH = 10–11.

The existing synthetic schemes of InP and other III–V q-dots are generally complex and not flexible.^{6–14} This complexity likely plays a key role in determining the poor properties of the resulting InP q-dots. In a typical InP q-dots synthetic scheme, the reaction mixture must be pumped under vacuum for several hours. The reaction would also need several days,^{6,8,9,11,13} or the resulting q-dots would have a much limited size range.^{10,12–14} When fatty acids were used as the ligands, the chain length and concentration of the fatty acid ligands were both limited in a narrow range for choice, and reaction temperature typically needed to be over 250 °C in a noncoordinating solvent.¹⁰ Unlike CdSe q-dots, fatty amines could not be used for the synthesis of InP q-dots in the original report carried out in a noncoordinating solvent.¹⁰ Careful analysis based on the knowledge learned recently motivated us to hypothesize that the thorough degassing needed in InP synthesis was due to the high activity of hydrolysis of In carboxylates under elevated temperatures to form In₂O₃ nanocrystals.¹⁶ If the synthesis could be carried out at a lower temperature, one may be able to perform the synthesis without this tedious degassing process. Synthesis using lower reaction temperatures is quite favorable from an operational standpoint and is also more energy efficient. To make the In carboxylate reactive enough for the formation of InP, activation reagents would be needed. Fatty amines have been known as common activation reagents and good ligands for improving emission properties of II–VI q-dots. Furthermore, amines would

be needed for the efficient growth of ZnS shell on the surface of the InP through our one-pot approach (see below). As described above in the typical synthesis, only fatty amines with a short hydrocarbon chain were used because of the low temperature requirement.¹⁷ The fatty amines were introduced along with P(TMS)₃ to further suppress the formation of In₂O₃.

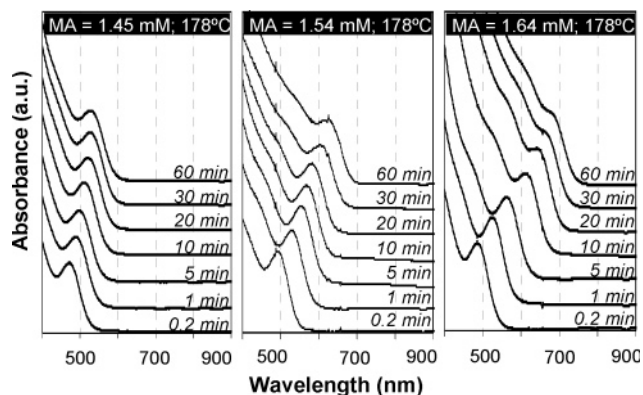


Figure 1. Temporal evolution of UV–vis spectrum of InP nanocrystals grown with different MA concentration.

The new synthetic scheme developed for InP q-dots at relatively low temperatures is quite similar to those developed for CdSe nanocrystals including the solvent, ligands, precursors, and no necessary thorough degassing. The absorption peak (shoulder) position of the InP could be continuously tuned between 390 and 720 nm through this new synthetic scheme. The size range reachable for one reaction was readily tuned by the concentration of the amines, the concentration and chain length of the fatty acids used for dissolving In(AC)₃, and the reaction temperatures (below 200 °C). The most convenient method in tuning the size was by varying the concentration of the fatty acid. In Figure 1, when myristic acid (MA) was changed from 1.45, to 1.54, and then to 1.64 mM under the typical synthetic conditions and reacted for 60 min, the absorption peak (shoulder) of the nanocrystals were around 500, 600, and 700 nm, respectively. Conversely, the absorption peak of the InP nanocrystals in our previous high temperature approach, even with five times the secondary injections, could only be between the 520 and 590 nm range.¹⁰

The absorption peaks and shoulders shown in Figure 1 indicate that the size distribution of the InP nanocrystals should be decent. It is well-known that the absorption spectrum shifts to red as the size of the nanocrystals increases and the sharp excitonic peaks become shoulders. The photoluminescence (PL) and PL excitation (PLE) spectra of one sample with a relatively large size of InP nanocrystals are shown in Figure 2a. Evidently, the PLE and UV–vis overlap reasonably well. The confirmation of a narrow size distribution can be directly found by using a transmission electron microscope (TEM) (Figure 2, panels c and d), which reveals that the size distribution is more or less the same as high quality CdSe

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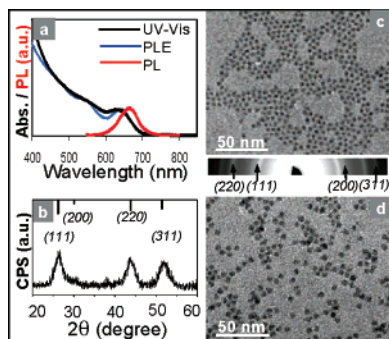


Figure 2. (a) UV-vis, PL, and PLE of one InP q-dot sample; (b) XRD of an InP q-dots sample; (c and d) TEM images of InP q-dots with two different sizes. The inset between panels c and d shows the electron diffraction.

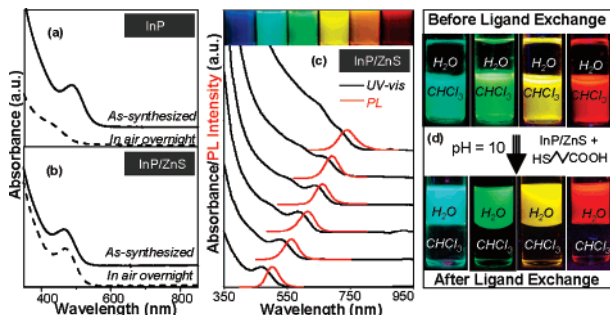


Figure 3. Air stability of (a) InP and (b) InP/ZnS core/shell q-dots; (c) UV-vis and PL spectra of different sized InP/ZnS core/shell q-dots; (d) pictures of InP/ZnS core/shell q-dots before/after ligand exchange.

nanocrystals grown through similar approaches.¹⁷ The crystal structure of the nanocrystals revealed by electron diffraction (inset between Figure 2c and 2d) is zinc-blende. The X-ray diffraction pattern (XRD) further confirmed this structure (Figure 2 (b)). The crystal domain size estimated from the peak width using the Sherrer equation matched reasonably well with the size determined by TEM (Supporting Information).

One critical problem of InP nanocrystals as emitters is their chemical instability, which is substantially worse than that of CdSe nanocrystals at least in terms of oxidation. Figure 3a shows that, after 12 h in air, the absorption spectrum of an InP q-dot sample shifted to blue drastically, indicating the fast shrinkage of the inorganic core by air oxidation. To solve this problem and also enhance the PL brightness, methods were developed to grow a ZnS shell around the InP nanocrystals in a one-pot fashion (see procedure above). Figure 3b shows the air stability of the resulting InP/ZnS core/shell q-dots. Different from the plain core ones, the exposure to air of this core/shell sample did not change the absorption properties of the nanocrystals, indicating a much improved stability.

The PL quantum yield (QY) of the InP plain core q-dots was low (<1%), but it reached as high as above 40% for the core/shell ones. The band gap PL color of the InP/ZnS core/shell q-dots span from blue to near-infrared (NIR) (450 to 750 nm, Figure 3c). A photograph of several core/shell samples emitting from blue to red are shown in the inset of Figure 3c. It should be pointed out that the much improved air-stability, substantially enhanced PL QY, and tolerance to thiol-coating (see below) strongly suggest the formation of core/shell nanocrystals. TEM also revealed the size increase by the shell growth. However, it is unclear whether the external shell was pure ZnS or an alloy shell because of the one-pot nature of the core/shell growth. This could only be clarified by future work.

For the current workhorse of q-dot emitters, CdSe ones, the PL peak at 650 nm is approximately the longest wavelength. The

extension from the 650 to 750 nm window by the InP q-dots is particularly interesting for biomedical labeling because of the transparency of body tissues in this window.² For biological applications, q-dots should somehow vendor water solubility and stability.³ The InP/ZnS core/shell nanocrystals synthesized here could be readily transferred into water without losing its PL brightness by using hydrophilic thiol ligands (Figure 3d). The preliminary results indicate that, after storing these water-soluble core/shell q-dots under ambient conditions for at least 3-months, their emission properties were retained.

In summary, InP nanocrystals with controlled size and size distribution were successfully synthesized in a much extended size range without prolonged heating. The new synthetic scheme allows such synthesis to be performed under much reduced reaction temperatures (<190 °C). Overall, the synthetic schemes described here are as simple as those developed for the standard CdSe q-dots. This judiciously designed reaction system not only allowed simplification of the reaction conditions and operation procedure for InP nanocrystals, but also enabled the direct growth of InP/ZnS core/shell nanocrystals in a one-pot fashion, which yielded efficient, stable, and water-soluble (after ligand exchange) q-dot emitters from blue to NIR. These results further indicate that other III–V q-dots with high quality may be made in the same fashion as it has been done for the II–VI ones. In addition to their fundamental implications, the high performance of the InP/ZnS core/shell q-dots coupled with their low intrinsic toxicity may further promote industrial applications of q-dot emitters.

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Supporting Information Available: Experimental and supporting results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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