JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Communication

Scalable Synthesis of InAs Quantum Dots Mediated through Indium Redox Chemistry

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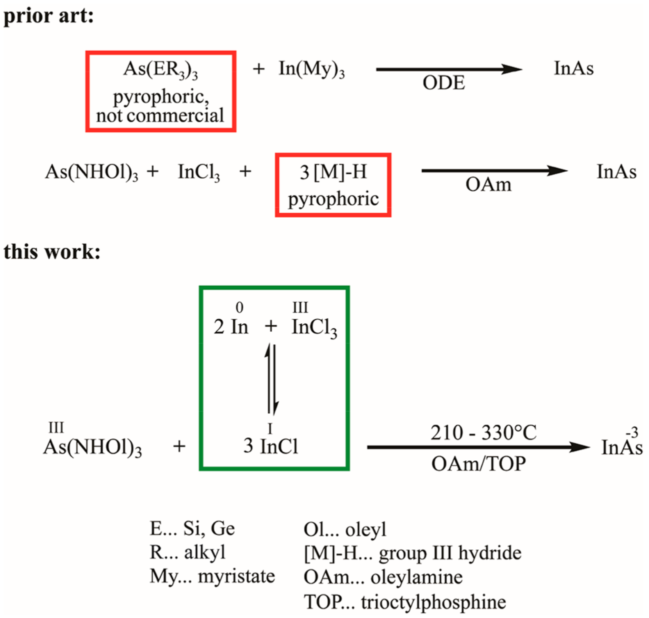
Cite This: *J. Am. Chem. Soc.* 2020, 142, 4088−4092

ABSTRACT: Next-generation optoelectronic applications centered in the near-infrared (NIR) and short-wave infrared (SWIR) wavelength regimes require high-quality materials. Among these materials, colloidal InAs quantum dots (QDs) stand out as an infrared-active candidate material for biological imaging, lighting, and sensing applications. Despite significant development of their optical properties, the synthesis of InAs QDs still routinely relies on hazardous, commercially unavailable precursors. Herein, we describe a straightforward single hot injection procedure revolving around In(I)Cl as the key precursor. Acting as a simultaneous reducing agent and In source, In(I)Cl smoothly reacts with a tris(amino)arsenic precursor to yield colloidal InAs quantitatively and at gram scale. Tuning the reaction temperature produces InAs cores with a first excitonic absorption feature in the range of 700−1400 nm. A dynamic disproportionation equilibrium between In(I), In metal, and In(III) opens up additional flexibility in precursor selection. CdSe shell growth on the produced cores enhances their optical properties, furnishing particles with center emission wavelengths between 1000 and 1500 nm and narrow photoluminescence full-width at half-maximum (FWHM) of about 120 meV throughout. The simplicity, scalability, and tunability of the disclosed precursor platform are anticipated to inspire further research on In-based colloidal QDs.

Colloidal quantum dots (QDs) form a class of nanomaterials with exceptional optoelectronic properties.[1] Specifically, the infrared part of the electromagnetic spectrum is seeing heavy exploration in applications including sensing,[2,3] lighting,[4−6] biological imaging,[7−9] and photovoltaics.[10,11] While III−V semiconductor QDs are strong contenders for these areas, their synthetic development has long lagged behind other established systems such as II−VI and IV−VI semiconductor QDs.[12,13] Here, we report a new approach to the synthesis of InAs QDs employing a redox-active In precursor acting as both reducing agent and In source. Traditionally, colloidal III−V semiconductor QDs are synthesized employing In(III) carboxylates and pyrophoric pnictide precursors, as depicted in Scheme 1.[7,10,14,15] Some of these precursors are not available commercially, hindering adoption by the scientific community and private industry alike. In recent years, an alternative set of synthesis routes has emerged harnessing tris(amino)arsine species as the As precursor, together with In(III) halides, in oleylamine as a coordinating solvent.[16−19] These As species exhibit markedly lower reactivity, rendering them attractive as a synthetic platform in the exploration of synthetic conditions toward quality nanomaterials with high tunability. However, the highly oxidized nature of the central As(III) in these compounds necessitates the introduction of an external reducing agent, commonly in the form of group III metal hydrides. The high reactivity and concomitant pyrophoric nature of these agents has proven a consistent issue, in particular for large-scale synthesis. Drawing from a vast body of literature on the rich redox chemistry of group III metals, In(I) halides have been identified as a new alternative.

Scheme 1. Routes Yielding High-Quality InAs QDs

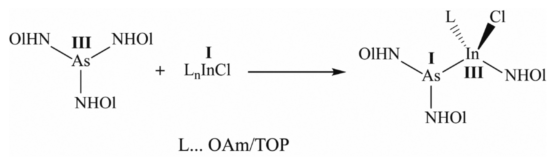


Received: November 15, 2019
Published: February 19, 2020

https://dx.doi.org/10.1021/jacs.9b12350

In(I) has long been utilized as a mild reducing agent in synthetic organic chemistry,[20−22] potentially eliminating the need for a highly reactive, external hydride source. In(I)Cl is commonly synthesized from In metal and In(III)Cl at high temperatures; however, in solution it is often found to be prone to disproportionation.[23] This additional equilibrium is hypothesized to provide the active reductant in a controlled manner. Consequently, a concise synthetic approach to colloidal InAs QDs is proposed in Scheme 1. Combining both In source and reducing agent in one species leads to a considerably more straightforward synthetic procedure compared to the best-performing literature methods. Sequential reduction of As(III) through insertion of In(I) into the As−N bonds of the As precursor is thought to give rise to the observed reactivity (Scheme 2).

Scheme 2. First Step in the Reduction of As(III) by In(I)



Shortly before synthesis, tris(dimethylamino)arsenic is subjected to a transamination with oleylamine as described previously.[19] Oleylamine serves as the main solvent. Addition of trioctylphosphine has been found necessary to keep quality and yield of InAs QDs high throughout the reaction. A typical progression of a synthesis conducted at 240 °C is shown in Figure 1.

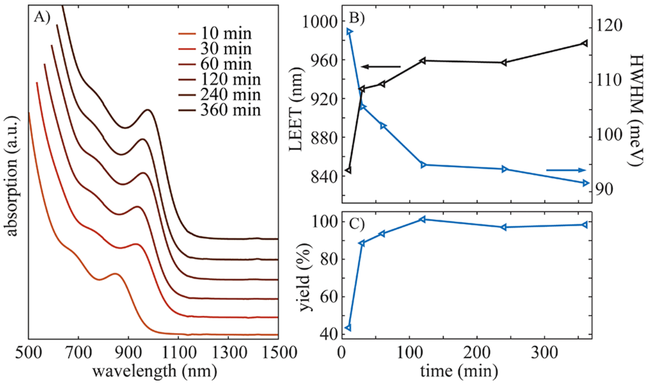


Figure 1. (A) Absorption spectra, (B) maxima and half-width at half-maximum of lowest-energy electronic transition, and (C) yield of InAs over the course of a core synthesis conducted at 240 °C. Absorption curves are offset for clarity.

The lowest energy electronic transition (LEET), as tracked by the first absorption maximum and its half-width at half-maximum (HWHM), appears well developed over the entire course of the reaction. The feature approaches a final maximum of 977 nm and a narrow HWHM of 92 meV. Furthermore, the chemical yield of the reaction was analyzed. This is made feasible by the fact that InAs shows a linear relationship between absorption at 450 nm and number of formula units of InAs present.[24] To this end, aliquots were purified through a single precipitation, redispersed in CCl_4, and pushed through a 200 nm syringe filter. Essentially complete conversion of the As precursor to InAs within a reaction time of 90 min at this temperature is observed. Figure 2A shows a representative transmission electron microscopy (TEM) image of an InAs core sample synthesized at 320 °C. Powder X-ray diffraction patterns (Figure 2B) confirm the zinc blende crystal structure of the InAs QD cores. The absence of additional peaks corresponding to elemental In or As further supports a good match in reactivity within the precursor redox couple. While emission from InAs cores drawn directly from the reaction mixture is fully quenched, a standard workup procedure consisting of two precipitation-redispersion cycles recovers emission properties typical of colloidal InAs QD samples with photoluminescence quantum yields (PLQYs) around 1% or less. The particles synthesized by the reported method can be worked up with benchtop solvents in air without compromising their optical properties, again emphasizing the method's robustness. Further, the protocol can be scaled up to yield more than 1 g of inorganic InAs cores, producing InAs QDs with essentially the same properties compared to small-scale batches, as exemplified by the absorption spectrum in Figure 2C.

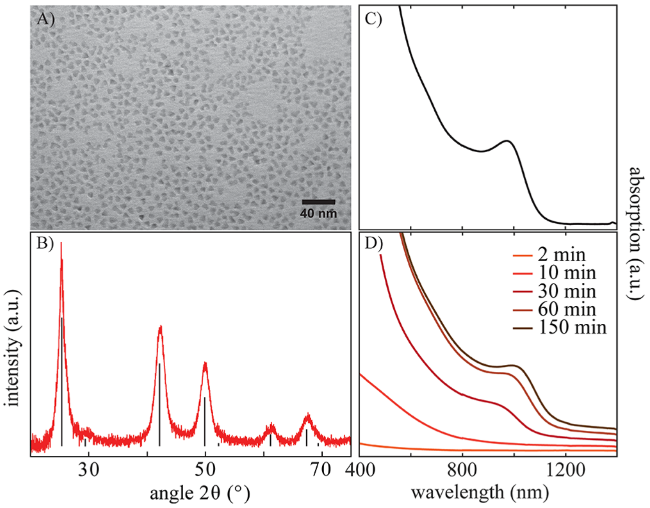


Figure 2. (A) Exemplary TEM and (B) powder X-ray diffraction pattern of InAs QDs synthesized at 320 °C. (C) Final absorption spectrum of a gram-scale batch of InAs QDs. (D) Absorption curve progression of a synthesis conducted at 240 °C employing In(0) and In(III)Cl_3. Absorption curves are offset for clarity.

Investigating the nature of the In equilibrium further, key insights can be confirmed. When conducting the synthesis under standard conditions, disproportionation of In(I)Cl is indicated by the appearance of metallic In at the bottom of the reaction vessel. Nevertheless, control experiments with only In metal or In(III)Cl as In source proved unsuitable for the synthesis of InAs QDs. Conversely, providing both species instead of In(I)Cl should enable the formation of InAs QDs in the case of an accessible equilibrium. Figure 2D shows the progression of an experiment conducted employing an appropriate mixture of In metal and In(III)Cl together, furnishing final particles in a manner comparable to the standard procedure. The appearance of In metal during synthesis might cause concern over the formation of metal nanoparticles. The existence of metal nanoparticles, however, could only be observed in TEM images of samples annealed for multiples of the time required for the completion of QD growth (e.g., 4 h at 240 °C). Reversibility of the equilibrium, as

https://dx.doi.org/10.1021/jacs.9b12350
J. Am. Chem. Soc. 2020, 142, 4088−4092

well as inability of relevant In species besides In(I) to drive the conversion of tris(amino)arsenic toward InAs, are therefore evident. The possibility of employing In(III) salts and In metal over In(I) opens up a more diverse and more widely available range of reagents to be explored in future optimizations of synthesis protocols of In-based colloidal QDs.

Temperature is the main tunability parameter, and it can ranging from 210 to 330 °C, furnishing InAs QDs with LEETs from 700 to 1400 nm through a single hot injection, demonstrating the versatility of this method (Figure 3).

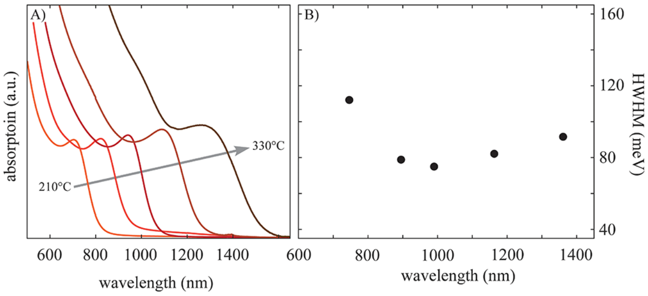


Figure 3. (A) Series of absorption curves showing variation in particle size as a function of reaction temperature. (B) HWHM of LEETs, exhibiting well-defined absorption features throughout.

Particles with absorption features below 800 nm are accessed by adding dodecylphosphonic acid as an additional ligand before hot injection. The findings are summarized in Table S1 in the Supporting Information (SI). Early aliquots and samples synthesized at lower temperatures can appear tetrapodal in shape; temperatures above 300 °C as well as annealing lead to more tetrahedral particles (see SI). Following previous reports, large InAs cores with absorption features beyond 1000 nm can also be produced employing a continuous injection of at least parts of the As precursor (Figure S4 in the SI).[7,10] Producing seeds through a hot injection followed by continuous injection of additional precursor yields larger particles than a simple hot injection at a given temperature, with good optical properties. Employing solely continuous injection was found to produce InAs QDs closer to a single hot injection approach. InAs QDs are known to be prone to oxidation under ambient conditions. Most commonly, this predicament is remedied via epitaxial growth of other semiconductors with wider bandgaps and low lattice mismatch around the InAs cores.[7,25−28] In this work, we demonstrate CdSe shell growth motivated by the common zinc blende crystal structure and almost identical lattice parameters shared by the two materials. Following previously established procedures, CdSe shells were grown on purified InAs QD cores to enhance and stabilize their optical properties, specifically their PLQY and emission profile (Figure 4). Based on calculations for spherical InAs cores,[26] a shell of 0.5 monolayers of CdSe was found to be optimal for all particle sizes and consistently led to narrower emission lineshapes, with a FWHM of approximately 120 meV. The proposed quasi-type II band alignment between InAs and CdSe is thought to lead to a delocalization of electrons into the shell. The concomitant red shift in optical properties red shifts the core-shell particles into the short-wave infrared (SWIR). Emissive in a range of 1000−1500 nm, these particles promise to be relevant for a wide selection of potential optoelectronic applications.

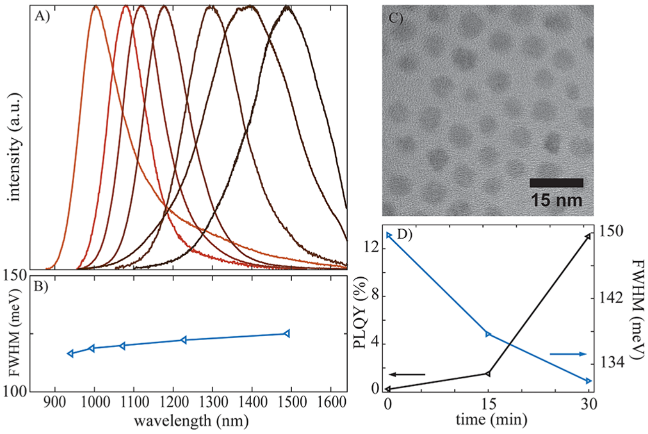


Figure 4. (A) Tunability of emission properties of InAs/CdSe core-shell QDs with different core sizes. (B) Narrow PL FWHM values of approximately 120 meV are maintained throughout the whole tunability range. (C) HR-TEM of core−shell particles. (D) Typical evolution of PLQY and PL FWHM during shell growth.

Figure 4D shows a typical progression of PLQY and FWHM during shell growth for a sample with final emission centered at 1250 nm. Shape and size uniformity of the synthesized core−shell particles is consistently improved compared to core-only particles. To further demonstrate the compatibility of InAs-based QDs synthesized by this method with established passivation strategies, subsequent shell growth of CdS and ZnS (see SI) was conducted. Both materials form a type I band alignment with the underlying particle to furnish core−shell−shell constructs with superior ambient and long-term stability. While in the case of CdS a modest red shift is observed, ZnS shells tend to blue shift the emission, pointing toward alloying of the two shells. Both shells promote high PLQY and stability, imparting this passivation strategy with a degree of flexibility.

In conclusion, the translation of the rich redox chemistry of In compounds into the field of colloidal nanomaterial synthesis was demonstrated. The use of In(I) as the active species opens up a new platform for the development and optimization of In-based QD synthesis. Comparably slow reaction kinetics and a dynamic equilibrium between In species allows for at-scale synthesis of InAs-based QDs spanning an optical window starting in the near-infrared (NIR) and reaching far into the SWIR. The scheme developed here combines a synthesis of colloidal InAs QDs without the need for pyrophoric precursors, along with an internal reducing agent to convert tris(amino)arsenic precursors. Taken together, the simplicity, scalability, and tunability of the reported approach should inspire research into a new direction for In-based colloidal QD preparations and their industry-relevant applications in the NIR and SWIR.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b12350.

Chemicals, instrumentation, synthetic procedures and conditions, and further absorption and TEM data (PDF)

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https://pubs.acs.org/10.1021/jacs.9b12350

Notes

The authors declare the following competing financial interest(s): M.G., D.F., and M.G.B. have filed a provisional patent application relating to this work.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under grants no. DMR-1905164 (M.G.) and ECCS-1449291 (D.F.). D.F. was supported by a Boehringer Ingelheim Fonds fellowship. C.F.P. was supported by the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under award no. DE-SC0001088 (assisted with quantum yield data). C.F.P. also acknowledges a National Science Foundation Graduate Research Fellowship under grant no. 1122374. L.W. was funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under award no. DE-FG02-07ER46454 (assisted with emission spectra). E.C.H. acknowledges support by the U.S. Department of Defense, Air Force Office of Scientific Research, National Defense Science and Engineering Graduate (NDSEG) Fellowship, 32 CFR 168a. This work made use of the MRSEC Shared Experimental Facilities at MIT, supported by the National Science Foundation under award no. DMR-1419807.

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