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Sterically Encumbered Tris(trialkylsilyl) Phosphine Precursors for Quantum Dot Synthesis

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ABSTRACT: The synthesis of nanomaterials with a narrow size distribution is challenging, especially for III–V semiconductor nanoparticles (also known as quantum dots). Concerning phosphides, this issue has been largely attributed the use of overly reactive precursors. The problem is exacerbated due to the narrow range of competent reagents for III–V semiconductor syntheses. We report the use of sterically encumbered tris(triethylsilyl) phosphine and tris(tributylsilyl) phosphine for InP quantum dot (QD) synthesis among others. The hypothesis was that these reagents are less reactive than the near-ubiquitous precursor tris(trimethylsilyl) phosphine and can be used to create more homogeneous materials. It was found that the InP products' quantum yields and emission color saturation (fwhm) were



improved, but not to the levels realized in CdSe QDs. Regardless, these reagents have other positive attributes; they are less pyrophoric and can be applied toward the synthesis of II–V semiconductors and organophosphorus compounds. Concerning safe practices, we demonstrate that ammonium bifluoride is an effective replacement for highly toxic HF for the post-treatment of III–V semiconductor quantum dots.

S emiconductor quantum dots (QDs) have utility in optical,¹ electronic,²⁻⁴ biomedical imaging,^{5,6} and biosensing ⁹ applications due to their many unique properties. Several protocols have been developed for the synthesis of QDs largely based on the rapid injection method for II-VI CdE (E = S, Se, Te) dots reported in 1993.¹⁰ In fact, the amount of effort put forth in synthetic development has resulted in protocols to produce materials with narrow emission profiles and ~100% quantum yields, especially for semiconducting PbSe and CdSe. However, the presence of lead and cadmium¹¹ has instigated significant research into QD toxicity¹² and diminished the prospects for their commercial use. This has spurred the development of the colloidal synthesis of III-V semiconductor nanoparticles, such as InP,¹³ which can span the visible region of the electromagnetic spectrum.¹⁴ Generally, good size distributions are realized by an initial nucleation of nanoparticles followed by focused growth, whereby smaller QDs grow faster than larger ones (and thus "catch up").^{15–17} Unfortunately, synthesis of monodisperse InP QDs is a problem that has been attributed to the difficulty in separating the nucleation and growth phases.¹⁸⁻²⁰ Magic-sized clusters may initially form during preparation, which minimizes synthetic tunability by precursor design and thus creates roadblocks for the preparation of monodisperse materials.^{21,22}

Various phosphorus precursors including elemental P_{red} , P_4 , alkyl phosphines, and aminoalkyl phosphines have been

employed for metal phosphide synthesis.²³ Tris(trimethylsilyl) phosphine, TMS₃P, is a common reagent for InP QDs, although its use results in suboptimal size distributions and emission color saturation (spectral fwhm). Several groups have noted that TMS₃P is overly reactive,^{18,20} resulting in poorly defined nucleation and subsequent focused growth steps necessary for producing high quality materials.¹⁵ Several schemes have been employed to subvert this issue. For example, Peng and co-workers first nucleated InP QDs at a high temperature and then alternatively injected TMS₃P and indium precursors for subsequent growth at a lower temperature.²⁴ The product size distributions were narrowed as a result. Recent publications have reported improved results using similar, albeit somewhat more complex schemes,^{25,26} especially Ramasamy et al., who demonstrated ~120 meV emission line widths that are competitive with what can be realized from CdSe QDs (~80 meV). Other attempts to create monodisperse InP QDs employed modified phosphorus anion precursors. For example, Harris and Bawendi synthesized a

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 $(Me_3Ge)_3P$ precursor due to the reduced lability of the germane ligand compared to TMS.¹⁹ Unfortunately, the improvement in InP QD properties was modest. Gary et al. attempted to tune the reactivity of $(R_3Si)_3P$ -type phosphorus precursors by modulation of the R groups' electronic and steric properties. Specifically, they coordinated the P³⁻ anion with various substituted triarylsilyl ligands; this added bulk and affected the polarization of the P–Si bonds. However, it was found that the QDs synthesized with substituted triarylsilyl-phosphines exhibited final size distributions that were not improved because of the slow rate of nucleation.²⁰ The use of bulky R groups was also reported in other publications,^{27,28} again with modest results on minimizing polydispersity.

A recent advancement in InP synthesis concerns the inclusion of zinc carboxylates in the core preparation. In fact, zinc additives may be present in overwhelming abundance. As zinc carboxylates are minimally productive precursors for Zn_3P_2 ,^{29,30} they instead participate in the reaction mechanism to increase the monodispersity and enhance the luminescence of the core InP products. While a variety of roles for zinc in InP QD production have been proposed, recently Koh et al. demonstrated complexation of zinc with TMS₃P to mollify the phosphorus reactivity.³¹ It is notable that Ramasamy et al. used a Zn–P complex for growing as-prepared InP QDs in their report.²⁵

The works of Gary et al. and Koh et al. prompted our investigation into the use of sterically encumbered triakylsilyl phosphine ligands for InP QD synthesis in the presence of zinc additives. In this regard, two alkylsilylphosphines, tris-(triethylsilyl) phosphine and tris(tributylsilyl) phosphine, were synthesized. These reagents are shown to be less reactive than TMS₃P. Combined with zinc carboxylate additives, their use resulted in improved properties; however, the emission color saturation was not as narrow as can be achieved with CdSe QDs. Regardless, it was found that these precursors are significantly less pyrophoric than TMS₃P, for which we recommend their usage. They are competent precursors for preparing II–V nanomaterials as well as molecular organophosphide compounds.

This report also examines the enhancement of InP emission that occurs with surface etching with using fluorides.^{22,23} HF treatment of InP quantum dots is a photochemical reaction that can dramatically enhance brightness.^{32–34} However, the handling of HF acid should be avoided due to the extreme hazards associated with exposure. Several alternatives, such as NH₄F and in situ etchants with salts [BF₄]⁻ and [PF₆]⁻, have also been suggested.^{32,35} In this study, XPS and optical data demonstrate that ammonium bifluoride, NH₄HF₂, is an effective alternative to HF. Ammonium bifluoride etched InP QDs were used as substrates for ZnSeS shell growth to prepare water-soluble core/shell nanoparticles.^{8,36}

EXPERIMENTAL SECTION

Materials. Ammonium hydroxide solution (certified ACS plus), 1,2-dimethoxyethane (DME, certified), and toluene (certified ACS) were obtained from Fisher. DME was dried over molecular sieves prior to use. Ammonium bifluoride (95%), indium acetate (99.99%), potassium metal (98%), red amorphous phosphorus (~100 mesh, 98.9%), and sodium metal (99%) were obtained from Alfa Aesar. Chlorotriethylsilane was purchased from Oakwood Chemical. N,N,N',N'-Tetramethyldiaminomethane (>99%), tributylchlorosilane (>97%), triethylsilyl trifluoromethanesulfonate, and trifluoromethanesulfonic anhydride were purchased from TCI America. Diethyl zinc (95%) and tri-n-octylphosphine (TOP, 97%) was purchased from

Strem Chemical. Chloroform, dichloromethane (ACS reagent, > 99.5%),], *n*-hexane, methanol, 1-octadecene (ODE, 90%), oleic acid (90%, recrystallized before use), 2-propanol, sodium hydroxide (97% reagent grade), and triethylamine (\geq 99%) were from Sigma-Aldrich. Chloroform was dried over molecular sieves before use. Zinc stearate was from Acros Organics. Cadmium oxide (>99%), coumarin-102 (97%, dye standard), and myristic acid (98.5%) were from Fluka. Size-exclusion solid support (Biobeads, S-X1) was purchased from Biorad. The water-solubilizing agent 40% octylamine-modified poly(acrylic acid)³⁷ was prepared as described in ref 38.

Synthesis of Tris(triethylsilyl) Phosphine, TES₃P. Warning! These syntheses involve highly pyrophoric reagents and products. These procedures require expertise with air-free techniques and should not be attempted by a novice.

This preparation is a derivative of that reported by Holz et al.³⁹ as summarized in Scheme 1. We have found that the best results were

Scheme 1. A Summary of the Methods Used to Prepare Sterically Encumbered Phosphorus Reagents



obtained when performing the initial steps in an inert-atmosphere glovebox. To a dried three-neck 500 mL round-bottom flask was added 6.25 g of potassium (156 mmol) and 4.78 g of sodium metal (208 mmol) that were cut and washed with hexanes prior to use. Stirring for a few minutes allowed the Na/K alloy to form. Next, 250 mL dry DME was added followed by 3.8 g of red phosphorus (123 mmol) to produce a red suspension. The round-bottom was fitted with a reflux condenser, an addition funnel, and a filtration column attached to a Schlenk flask as shown in the SI, Scheme S1. The system was sealed, brought into a fume hood, attached to a dry N2 source, and then heated to reflux in an oil bath. After stirring overnight, the suspension became black due to activation of the phosphorus. It was allowed to return to room temperature. Next, a solution of 61 g of chlorotriethylsilane (405 mmol) in 65 mL of dry DME was prepared in a glovebox and was injected into the addition funnel through a septum. The solution was then brought back to reflux for ~48 h. At this time, a gray precipitate formed, and the solution became visibly viscous. After cooling to room temperature, the material was passed through a fritted glass filter while under N2, and the solid material was washed two to three times with either dry hexane, pentane, or DME to capture more product. The resultant solution was sequestered in a Schlenk flask that was dried in vacuuo to remove volatiles including solvents before being sealed to store the crude product in a glovebox. (Warning! The solid byproduct isolated in filtration contains unreacted sodium, potassium, and activated phosphorus. It should be diluted with hexane and slowly deactivated with butanol. The solid will ignite if quenched too quickly or if mishandled.)

The crude product was distilled. A distillation system was assembled in a glovebox and loaded with the crude product. It was taken out and attached to a dry N_2 /vacuum (Schlenk line) source in a fume hood, and the solution was heated incrementally under a

vacuum. Generally, the receiving vessel was cooled in a liquid nitrogen bath to lower the pressure, generally ~100 mTorr. An unidentified byproduct was observed distilling at ~40 °C (the temperature was measured at the distillation head, while the Corning PC-420D hot plate reading was typically 2× higher). This was discarded. The tristriethylsilyl phosphine product distilled over at $110 \rightarrow 120$ °C when the oil bath was set to $270 \rightarrow 290$ °C. In this example, 28 g of product was recovered (60% yield) with ~80% purity. Several preparations were performed throughout this study, and it was found that the product purity was variable over a range of 50% \rightarrow 80%. We also found that the purities increased as we gained experience performing the reaction. The byproducts were bis(triethylsilyl) phosphine hydride, TES₂PH, and triethylsilyl phosphine dihydride, TESPH₂ (see examples of ³¹P NMR in the SI, Figure S1). All attempts to modify the reaction to prevent the formation of these byproducts were thwarted. High purity was realized via the reaction of the distilled products with silvl triflates as discussed below.

Ligation of TES₂PH and TESPH₂ with Triethylsilyl Triflate for High Purity TES₃P. The hydride byproducts can be converted to the ligand-saturated product via ligation with the silyl triflate as shown in Scheme 1.⁴⁰ All reactions were performed in an inert atmosphere glovebox. Crude tris(triethylsilyl) phosphine was characterized with ³¹P NMR to determine the initial purity and the subsequent reaction stoichiometry. In this example, 1.2 g of an 80% pure tris(triethylsilyl) phosphine product was added to 5 mL of dry dichloromethane with additional 0.30 g of triethylsilyl trifluoromethanesulfonate (~0.26 mL, 1.13 mmol) and 0.171 g of excess triethylamine (0.235 mL, 1.69 mmol). After stirring overnight, pure tris-triethylsilyl phosphine was isolated by vacuum distillation as revealed by NMR characterizations in the SI (Figure S2). ¹H NMR (400 MHz, CDCl₃): δ 1.01 (t, H₃C-), 0.80 \leftarrow 0.70 (b, -CH₂-Si). ¹³C (400 MHz, CDCl₃): δ 8.30 (d, J = 5.5 Hz), 8.23. ³¹P (400 MHz, CDCl₃): δ -288.0.

Synthesis of Tris-tributylsilyl Phosphine, TBS₃P. Tris-(tributylsilyl) phosphine was prepared as for the ethyl derivative using tributylchlorosilane. However, the distillation process simply removed low molecular weight byproducts and solvents as the product(s) did not vaporize under any condition. The yields were typically ~50% as characterized with ³¹P NMR, see Figure S3 for a typical example. The major byproducts are bis(tributylsilyl) phosphine hydride, TBS₂PH, and to a lesser extent tributylsilyl phosphine dihydride, TBSPH₂. The low yield necessitated additional ligation with the silyl triflate as outlined below.

Preparation of Tributylsilyl Triflate. This procedure is based on ref 41. First, tributylsilanol was prepared by the reaction of tributylchlorosilane with aqueous ammonium hydroxide exactly as outlined in ref 42. ¹³C NMR (400 MHz, CDCl₃ ppm): δ 26.64, 25.52, 15.48, 13.77. Next, 1 g of tributylsilanol (4.62 mmol) and 1.34 g of trifluoromethanesulfonic anhydride (4.75 mmol) were mixed for 4 h at 45 °C in an oil bath. The temperature was lowered to ambient, and 1.086 g of tributylchlorosilane (1.2 mL, 4.62 mmol) was added. A vacuum was applied to remove any high vapor pressure byproducts, and ¹³C NMR analysis demonstrated high purity of the resulting tributylsilyl triflate product as shown in Figure S4 of the SI. ¹³C NMR (400 MHz CDCl₃): δ 123.19, 120.03, 116.88, 113.72, 26.05, 24.23, 13.46, 13.38.

Ligation of TBS₂PH and TBSPH₂ with Tributylsilyl Triflate for High Purity TBS₃P. ³¹P NMR was used to ascertain the molar ratios of the singly and doubly ligated phosphine hydride byproducts to the target tris(tributylsilyl) phosphine. The resulting stoichiometry was used to determine the mass of triflate needed to fully ligate the byproducts. In this example, the starting material was 50% pure, which was typical. First, 0.934 g of tributylsilyl triflate (2.68 mmol), 2.84 g of the tributylsilyl phosphine(s) mixture, and 0.403 g of triethylamine (~0.56 mL, 3.98 mmol) were mixed in 5 mL of dry dichloromethane. After stirring overnight, all byproducts were removed under a vacuum, and the resulting products were characterized by ¹H, ¹³C, and ³¹P NMR. The presence of byproducts was significantly minimized; however, we endeavored to enhance the purity tris(tributylsilyl) phosphine further. As the product could not be distilled under a vacuum and was found to be unstable in alumina (exposure resulted in some P–H bond formation) and silica (extreme degradation), the product was isolated by size exclusion gel chromatography using a polystyrene solid phase with a dry toluene eluant. The first eluted fraction (0.2 g) achieved the best level of purity according to NMR characterizations (Figure S5 of the SI). ¹H NMR (400 MHz, CDCl₃): δ 1.45 \leftarrow 1.25 (b, $-CH_2CH_2-$), 0.95 \leftarrow 0.85 (b, H_3C-), 0.80 \leftarrow 0.70 (b, $-CH_2-Si$). ¹³C NMR (400 MHz, CDCl₃): δ 26.8, 17.2, 17.1, 13.7. ³¹P (400 MHz, CDCl₃): δ –279.4 ppm.

Synthesis of InP QDs. The procedure of Koh et al.³¹ was modified for InP core QD synthesis. In a typical preparation, 58 mg of indium acetate (0.2 mmol), 144 mg of myristic acid (0.63 mmol), and 400 mg of zinc stearate (0.63 mmol) were added into a 50 mL three-necked round-bottom flask with 10 mL of ODE. The mixture was degassed at 110 °C for 1 h. Afterward, the solution was backfilled with N₂, and the heating mantle was removed. During this time, 0.2 mmol of a phosphorus precursor solution (TMS₃P, TES₃P or TBS₃P) in 1.5 mL of TOP was prepared in a glovebox. This was injected at ~80 °C into the reaction solution, which was immediately heated to 300 °C within 4 min. A growth time of 15 min continued after the solution reached 300 °C, during which time the QDs experienced some increase in size as shown in Figure S6. Many of these parameters were varied in the course of this investigation, see the Discussion section.

Ammonium Bifluoride Treatment. InP core QDs were precipitated by adding 2-propanol followed with methanol. Centrifugation resulted in a pellet that was dissolved in hexane, and subsequently added to a solution of 177 mg of myristic acid in 10 mL of ODE in a three-neck round-bottom flask. The hexane was removed at 50 °C under a vacuum until the pressure reached equilibrium. Afterward, a small chip (~10 mg) of NH_4HF_2 was added to the solution that was stirred overnight (generally ~14 h) at 50 °C under a N₂ atmosphere.

Synthesis of InP/ZnSeS QDs. The quantity of InP QDs was determined using the regression of Xie et al.⁴³ In this example, we attempted to grow a five monolayer ZnS shell on 5.4×10^{-7} moles of ~2 nm diameter QDs. First, 0.327 g (0.52 mmol) of zinc stearate was added into the ammonium bifluoride treated core dots (prepared with TBS₃P) under a high N₂ flow. The temperature was raised to 200 °C and degassed for 1 h. Next, the temperature was raised to 200 °C under N₂, upon which 0.1 mL of 1.0 M TOPSe in 0.9 mL of TOP was added into the vessel by manual injection. Afterward, 17 mg (0.53 mmol) of elemental sulfur in 5 mL of ODE was injected through a septum using a syringe injector over the course of ~1.5 h.

Water Solubilization of InP/ZnSeS QDs. As-prepared InP/ZnSeS QDs were processed via precipitation and weighed after drying. Next, ~5 times the QDs' weight of 40% octylamine-modified poly(acrylic acid) was added, and the QD/polymer mixture was dissolved with ~2 mL of chloroform and was shaken until clear (sometimes a drop of methanol assisted in realizing optical clarity). The solvent was removed under a vacuum, and the resultant film of polymer encapsulated QDs was solubilized in 0.1 M aqueous NaOH. Some samples require sonication and filtration using a 0.2 μ m filter; all samples were purified with dialysis using Millipore Amicon Ultra 100 K MWCO centrifugal filters against deionized water.

Synthesis of Cd₃P₂, Zn₃P₂, and Tris(dimethylaminomethyl)phosphine. The procedures of Xie et al.,⁴⁴ Mobarok et al.,⁴⁵ and Prishchenko et al.⁴⁶ were used to prepare Cd₃P₂ and Zn₃P₂ materials as well as tris(dimethylaminomethyl)phosphine, respectively, as described in the SI.

Characterization. X-ray photoelectron spectroscopy (XPS) was performed on samples that were precipitated and drop cast onto clean Si wafers. XPS spectra were obtained with a KRATOS AXIS-165 surface analysis system. The energy spectra were adjusted using the C 1s 284.6 eV peak as a reference. Transmission electron microscopy (TEM) analyses were performed using a JEOL JEM-3010 microscope operating at 300 keV. TEM grids were prepared by drop casting processed nanoparticle solutions onto 300-mesh carbon-coated Cu grids from Ted Pella. ¹H, ¹³C, and ³¹P NMR spectra were measured with a Bruker Avance DPX400 spectrometer. Air-sensitive TES₃P and TBS₃P were loaded into airtight NMR tubes in a glovebox and diluted with dry NMR solvents. For X-ray powder diffraction (XRD) analysis,

QD samples were precipitated, resuspended in hexane, and dropcasted on Si wafers. X-ray diffraction measurements were performed using a D8 Advance ECO Bruker XRD diffractometer with Cu K α (λ = 1.54056 Å) radiation. Absorption spectra were obtained with a Varian Cary 300 Bio UV/vis. PL emission measurements were taken on a HORIBA Fluoromax-400 or a customized Fluorolog (HORIBA Jobin Yvon) modular spectrometer for NIR measurements. Coumarin 102, rhodamine 101, and fluorescein were used as reference dyes. Absolute quantum yield measurements were also performed using a HORIBA Quanta- ϕ F-3029 integrated sphere at the Center for Nanoscale Materials at Argonne National Laboratory. It was found that the integrating sphere QYs are generally higher than those obtained with dye standards. We nonetheless include the dye standard's data, which likely represent a lower limit.

Pyrophoricity Assessment of Tris(trialkylsilyl) Phosphines. To assess the pyrophoricity of phosphorus reagents, TMS₃P, TES₃P, and TBS₃P were exposed to increasing oxygen levels until ignition using the system shown in Scheme S2.

RESULTS AND DISCUSSION

This effort was initiated to expand the toolkit of phosphorus precursors in the hope of finding a "magic reagent" to create monodisperse InP QDs. In this regard, we examined sterically encumbered phosphorus reagents and the use of zinc additives to prepare the nanomaterials. Two alkylsilyl phosphines, tris(triethylsilyl) phosphine (TES₃P) and tris(tributylsilyl) phosphine (TBS₃P), were synthesized according to Scheme 1 following the methods reported in ref 39. The modified procedure also produced $(SiR_3)_n PH_{3-n}$ byproducts in abundance despite our best efforts to prevent protonolysis.⁴⁷ The ethyl derivative could be purified via distillation, although this is impossible for the butyl species due to its high molecular weight. Fortunately, all the byproducts were converted into the fully ligated targeted compounds via a simple reaction with the corresponding alkylsilyl triflate. The purity of tris(tributylsilyl) phosphine was further enhanced with size exclusion chromatography. And although we demonstrate that these precursors are not "magic reagents" for monodisperse InP QD synthesis, they have numerous positive attributes including less pyrophoricity than the ubiquitous TMS₃P as discussed in the Supporting Information. Furthermore, they are competent precursors for a variety of nanomaterials as well as for organophosphorus compounds.

InP core and InP/ZnSeS core/shell QDs were synthesized using TBS₃P and TES₃P in the presence of zinc additives and were compared to those realized by TMS₃P. The hypothesis was that the enhanced steric properties and potential coordination to zinc would render the phosphorus less reactive such that well-defined nucleation and growth processes would create monodisperse products. A typical procedure was derived from that reported by Koh et al., in which indium acetate, myristic acid, and zinc stearate were degassed in ODE.³¹ Excessive myristic acid was avoided to minimize direct conversion of the ligated phosphorus into a hydride.⁴⁷ According to the "atomic valve" approach of Koh et al., the addition of high quantities of zinc stearate has the dual effect of suppressing InP magic clusters and slowing the reaction of the phosphorus precursor. After the injection of phosphorus precursor at 80 °C, the reaction solution was rapidly heated to 300 °C. During this time, the solution became slightly yellow at 100 °C, the intensity of which increased as the temperature was raised to 300 °C. InP QDs were allowed to grow for 15 min.

Results using the highest purity reagents are shown in Figure 1, where it can be seen that the InP absorption spectra of QDs



Figure 1. Absorption and emission spectra of InP QDs prepared using a variety of phosphorus sources. The emission fwhm in each spectrum is indicated in meV.

created using TBS₃P, TES₃P, and TMS₃P are rather featureless. Furthermore, the emission spectra fwhm vary between ~70– 90 nm (260–295 meV). The highest molecular weight reagent TBS₃P generated the narrowest emission (260 meV); however, it also had the lowest quantum yield (2%) with a best result of 8%. Despite these low values, the brightness of these samples was enhanced upon etching with NH₄HF₂ and the addition of a shell as discussed below. Although the range of quantum yields realized with pure TES₃P straddles that from TMS₃P, we generally found better quantum yields with TES₃P. For example, when increasing the Zn/(In,P) > 3, longer growth times or higher injection temperatures resulted in QYs on the order of 25–29% as discussed below.

The effect of reagent purity was investigated. Given the difficulty of preparing ~100% pure reagents, we performed InP QD syntheses as a function of the TES₃P purity after preparation. As shown in Figure 2A (top), although the InP QDs prepared with 90% pure TES₃P have a respectably narrow emission, this spectrum also noticeably red tails. This sample also had the lowest emission efficiency. Higher purity reagents resulted in better QYs, yet the color saturation suffered. This was a trend seen in many investigations, such as when evaluating the effect of increasing the growth time with 90% pure TES₃P as shown in Figure 2B. Growing the InP QDs for a longer period red-shifted the spectra and resulted in higher emission efficiency (QY \sim 29%), yet the spectral fwhm increased at the same time. Similar behavior was seen in InP QDs made by Möller and co-workers.³⁴ This same trend was again observed when increasing the phosphorus precursor injection temperature as shown in Figure 2C. Higher temperatures promoted red-shifted absorption and emission spectra, and higher quantum yields were observed. It is interesting that a similar observation was made by Lucey et al. despite the fact that they did not use zinc additives in their InP QD preparations.⁴⁸ Regardless, the higher QY samples also suffered a loss of color saturation.

The effects of increasing zinc additives on the properties of InP QDs prepared with 90% pure TES₃P were ascertained. With no or low levels of zinc (<0.2 mmol), the InP QDs were nonemissive. Higher zinc amounts allowed for the observation of emission, although there were minimal-to-no effects on the optical bandgap to a certain point. However, at a Zn/(In,P) ratio of \geq 3, the bandgap of the QDs decreased ~225 meV, and the resultant materials had fairly high quantum yields (~25%). These observations of higher quantum yields and lower fwhm

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Figure 2. (A) The effect of increasing TES_3P reagent purity affords higher quantum yields yet broader emission spectra. The emission fwhm in each spectrum is indicated in meV. (B) The effects of increasing growth time and (C) increasing injection temperature were to enhance quantum yields at the expense of color purity. The best QY of 29% for core InP was realized with a 30 min growth time, 90% pure TES_3P , and an Zn/(In,P) ratio of 3.

due to passivation of surface defects are similar to those of Koh et al.;³¹ however, they did not observe a substantial Zn/(In,P) ratio dependence on the optical properties as demonstrated in Figure 3.

Figure 3. Effect of the addition of increasing levels of zinc first afford an increase in quantum yield and at higher levels result in smaller QDs with sharper excitonic features.

It is interesting to note that a ratio of 3 is the coordination valency of the phosphorus anion and suggests that zinc may be sequestered by phosphorus until the Zn/P ratio is raised to allow free zinc cations to enhance the size distribution and brighten the growing InP QDs. Alternatively, the presence of unbound phosphorus could be detrimental. Overall, these observations demonstrate that the zinc to phosphorus ratio is more important than zinc to indium that has generally been the focus of most research reports.

When exploring the utility of TES_3P for the preparation of other III–V QDs, it was found that GaP quantum dots could not be prepared using a previously published method.⁴⁹ We interpret this result as testimony to the lowered reactivity of the reagent, which prompted further study on other materials and compounds.

II - V Semiconductors and Tris-(dimethylaminomethyl)phosphine. The competency of TES₃P for the synthesis of II–V metal phosphides, specifically Cd₃P₂ and Zn₃P₂, was investigated using previously published protocols. Success was demonstrated in both cases as shown in the powder XRD patterns of the products, see Figures S7 and S8. To venture outside the arena of materials, the synthesis of tris(dimethylaminomethyl)phosphine was investigated using TES₃P and zinc chloride as a catalyst. The NMR spectra shown in Figure S9 confirmed the formation of the product. Most interesting, according to Prishenko et al.,⁴⁶ the reaction proceed via a Zn-P molecular intermediate, similar to Koh et al.'s "atomic-valve" hypothesis.³¹

Etching and Core/Shell QDs. The surface treatment of semiconductor materials with etchants is common and is in fact necessary for observing emission from InP QDs prepared without the use of zinc additives. HF is frequently used for this purpose (see ref 50), which is unfortunate as the use of HF should be strenuously avoided due to its many hazards. This prompted the study of an alternative, ammonium bifluoride (NH₄HF₂), which is used as a wheel cleaner in automatic car washes. In a typical experiment, core InP QDs were treated with ammonium bifluoride under an oxygen-free atmosphere overnight. During the etching process, it was found that excess ligands must be present to maintain colloidal stability. Afterward, the samples must be handled air-free, and as such the samples were processed for optical characterization in a glovebox. It was found that the absorption spectra are blueshifted as shown in Figure 4, and the quantum yields increased

Figure 4. Absorption and emission spectra as a function of NH_4HF_2 etching and shell growth on InP QDs as prepared with TBS₃P.

2 to 4 times; see Table S1 of the Supporting Information. XPS spectroscopy was used to evaluate the effect of ammonium bifluoride exposure to compare against HF treatment as reported by others. As shown in Figure 5A, InP QDs incubated with ammonium bifluoride have an XPS F 1s peak at 684.3 eV and, coupled with blue-shifted In 3d transitions (Figure 5B), demonstrate that fluoride is chemically bound to indium.⁵¹ Zinc's XPS features are unperturbed by ammonium bifluoride treatment (Figure S10), which is interesting as the zinc is likely surface-bound.⁵² The growth of an oxidized P 2p 133.3 eV peak (Figure SC) indicates oxygen sensitivity, which is a result

Figure 5. XPS spectra of core and NH_4HF_2 treated InP QDs. (A) Fluorine is present on the ammonium bifluoride treated InP QD surface. (B) The blue shift of the In 3d peaks is likely due to In–F bond formation as per ref 51. (C) Inadvertent air exposure when loading the processed sample into the XPS resulted in oxidation of the phosphorus as evident from the growth of the P 2p 133.3 eV peak.

of this sample's air exposure when loading it into the XPS spectrometer. This is consistent with our observations on emission quenching when the etched InP QDs were processed outside of a glovebox, see Table S1. Other XPS characterizations are found in the SI. To summarize, the treatment of InP core QDs with ammonium bifluoride appears identical to that realized with HF etching.

InP QDs prepared with TES₃P and TBS₃P were shelled with a higher bandgap semiconductor to verify that the materials are good substrates for overcoating. This is important because core materials are not generally efficacious in most applications due to a lack of stability and suboptimal optical properties. To this end, core dots were etched with ammonium bifluoride and then were heated to 200 °C with additional zinc stearate, whereupon a small quantity of trioctylphosphine selenide was added. Next, a ZnS shell was grown at the same temperature by the addition of elemental sulfur dissolved in ODE using a syringe injector. In general, we have found that the slow introduction of shell precursors produces better results, likely due to suppression of nucleation of nanoparticles composed of the shell materials. Optical spectra for core, post NH₄HF₂ treated cores, and core/shell QDs for one set of InP dots prepared with TBS₃P are shown in Figure 4. The ammonium bifluoride etching obviously blue shifts and broadens both absorption and emission, while the shelling appears to red shift the absorption beyond the original core. This is sensible as the 2 nm core diameter (based on the regression by Xie^{43}) increased to 3.2 \pm 0.4 nm for the core/shell species as measured by TEM, see Figure S11. However, the emission of the core/shell did not energetically track the absorption, resulting in a smaller Stokes' shift. This is likely due to suppression of hole trap sites that have been proposed to be responsible for the wide energy gap between absorbing and emitting states.^{53,54} These results also suggest that the shell alloys into the core, which was further corroborated with XRD data that demonstrate a crystal structure for InP/ZnSeS that conforms to neither InP, ZnSe, nor ZnS, see Figure S12.

It was found that core/shell QDs prepared using our procedure have emission efficiencies in the 30% \rightarrow 40% range, which represents an increase from the core dots that have QYs typically between 2% and 15%. The emissions were typically blue-shifted (Table S1). Core/shell InP/ZnSeS dots were water-solubilized using 40% octylamine-modified poly(acrylic acid)³⁷ to demonstrate potential bioimaging and sensing applications. Encapsulating the core/shell QDs in the polymer resulted in a ~50% reduction of quantum yield, and the resultant dispersion was stable on a several-month-long time scale.

CONCLUSION

Methods to prepare pure high molecular weight phosphorus precursors for InP, Cd_3P_2 , and Zn_3P_2 quantum dots and organophosphorus compounds are reported. These reagents are less pyrophoric than TMS_3P , which is commonly employed for metal phosphide syntheses. With regard to safe chemistry, the use of ammonium bifluoride as an alternative to HF treatment for semiconductor processing is also presented.

The combination of sterically encumbered phosphorus reagents with zinc additives did not result in monodisperse size distributions for InP quantum dots. Although disappointing, this information contributes to our general knowledge of the factors that govern controlled monomer delivery rates in the quest to optimize the size distributions of InP and other III–V quantum dots. Regardless, the nanomaterial products created with these reagents had better optical properties compared to those generated with commercially available TMS₃P. Core/shell InP/ZnSeS QDs are robust such that they can be water solubilized, making them candidates for fluorescent labels in biological applications.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02440.

Details on the synthesis of pyrophoric chemicals and characterization; NMR, optical, XPS, and XRD spectra; and tabulated optical data (PDF)

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ABBREVIATIONS

ODE, 1-octadecene; QD, quantum dot; QY, quantum yield; PL, photoluminescence; TES₃P, tris(triethylsilyl) phosphine; TBS₃P, tris(tributylsilyl) phosphine; TMS, tri(methylsilyl); TMS₃P, tris(trimethylsilyl) phosphine

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