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Annual Review of Materials Research Surface Chemistry of Metal Phosphide Nanocrystals

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Abstract

Semiconducting and metallic metal phosphide nanocrystals have gained increased attention in the materials science and engineering community due to their demonstrated and theoretical promise in both emissive and catalytic applications. Central to realizing the full potential of nanoscale metal phosphides is a thorough understanding of their surfaces and how surface chemistry impacts their function. In this review, we document what is known about the surface chemistry of metal phosphide nanocrystals, including both as synthesized and postsynthetically modified species, and draw a connection between surface chemistry and functional properties. This survey is intended to provide a comprehensive view of metal phosphide nanocrystal surface chemistry and how it differs across the families of phosphide materials. A clear distinction emerges between the semiconducting and metallic phosphides from both a synthetic and applied standpoint. We seek to expose key knowledge gaps and targets for further scientific and technological development.

1. INTRODUCTION

The history of metal phosphides dates to the 1700s with the synthesis of Zn_3P_2 by Andreas Marggraf, followed later that century by Bertrand Pelletier's synthesis of 20 more metal phosphides from the pure metals and white phosphorus (1). Applications of these metal phosphides, however, came much later. Among the metal phosphides are both metallic phases like Ni₂P, Cu₃P, and Ir₂P and semiconducting phases like Zn₃P₂, GaP, and InP (2). This electronic structure is, in part, what dictates the ultimate utility of these materials. Since the development of the III-V semiconductors for electronic applications in the 1950s (3), the importance of metal phosphides in materials science and engineering has grown. This development has continued to this day with the new dimension of physical scaling playing a prominent role.

For nanoscale metal phosphides, it is not only the electronic structure of the core that controls function, but also the structure and composition of the nanomaterial surface. The covalency of metal phosphide lattices (arising from the relatively low electronegativity of P) (4) and their ease of oxidation [arising from the ease of accessing the P(V) oxidation state] (2) make the surface even more important for this class of materials relative to others. The facet termination (M versus P) and the degree of nonstoichiometry are the primary factors that establish surface chemistry in binary metal phosphide nanocrystals (**Figure 1**). Nanocrystals can range from stoichiometric, bearing the expected numbers of anions and cations needed to perfectly balance charge (i.e., 1:1 In:P for InP or 3:2 Zn:P for Zn₃P₂), to excessively nonstoichiometric, as can be the case for semiconductor nanocrystals like InP, which may be prepared with nearly a monolayer of excess cations.

The binding of ligands to all types of nanocrystal surfaces can be systematically described using an adapted version of the covalent bond classification method (5–7). Using this formalism, neutral L-type Lewis bases like trioctylphosphine (TOP) and primary amines are the predominant type of surface termination in the case of stoichiometric nanocrystals. In the case of nonstoichiometric, metal-rich nanocrystals, anionic X-type ligands are an important contributor to the surface



Figure 1

Representative surface chemistry of stoichiometric (*left*) and nonstoichiometric (*right*) metal phosphide nanocrystals illustrating neutral L-type ligand coordination, Z-type ion pair coordination, ionic X-type ligand coordination, and covalent surface modification.

chemistry due to the need for charge balance. Interestingly, excess metal cations, together with their X-type ligands, can be displaced from nanocrystal surfaces as Z-type metal-ligand complexes (8, 9). Such metal-ligand complexes can also be added to nanocrystal surfaces and exchanged for preexisting surface complexes (10–12). Surface lability can lead to changes in nanocrystal stoichiometry during purification and manipulation. Variability in nanocrystal composition and its evolution as a function of reaction conditions have been most well studied for II-VI nanocrystals but are becoming a primary focus for metal phosphide nanocrystals as their properties are optimized for technological applications.

In the following sections, we document our collective understanding of the as-synthesized and postsynthetic surface chemistry of metal phosphide nanocrystals and reveal the connection between surface chemistry and nanomaterial function. This survey is intended to provide a holistic view of what is known about metal phosphide nanocrystal surface chemistry and how it differs across the families of phosphide materials. Ultimately, we hope to expose key knowledge gaps and targets for further research and technological development.

2. SEMICONDUCTING MAIN GROUP METAL PHOSPHIDE NANOCRYSTALS

2.1. Background and Rationale

In the field of semiconductor nanocrystals, main group metal phosphides have risen to prominence to stand alongside the traditional metal chalcogenide materials as exemplary candidates for current and next-generation technologies. In this regard, III-Ps, and in particular InP, have been vigorously developed as lower-toxicity alternatives to cadmium-based nanocrystal emitters for both downconversion and electroluminescent applications (13, 14). While light emission has been a dominant focus of semiconducting metal phosphide research, photovoltaic and related applications are also of interest, with II-Ps like Zn₃P₂ being recommended as earth-abundant materials with considerable promise (15, 16). For both light emission, which relies on carrier recombination, and photovoltaic applications, which rely on carrier separation, the nanocrystal surface plays a critical role in determining function. Researchers in the field have struggled to identify the nature of these materials' surfaces with a high level of atomic specificity and to develop strategies to modify and manipulate them postsynthetically to overcome properties arising from surface defects. In this section, we outline what is known about the surface chemistry of semiconducting main group metal phosphide nanocrystals with an initial emphasis on InP, which has been extensively investigated in this regard. We highlight features of surface chemistry on native as-synthesized nanocrystal surfaces as well as the use and study of postsynthetic strategies to alter the structure, stability, function, and processability of these materials.

2.2. InP: As Synthesized

One of the earliest examples of a high-quality InP nanocrystal synthesis was reported in 1994 by Nozik and coworkers (17). Using a solvothermal method, InP was synthesized via the reaction of chloroindium oxalate and P(SiMe₃)₃, while using TOP and trioctylphosphine oxide (TOPO) as surface stabilizing ligands, building on previous work in the II-VI family (18). Variations on this theme have been made, including a dehalosilation reaction approach in which InCl₃ and P(SiMe₃)₃ were combined in TOPO (19). The surface chemistry of InP nanocrystals derived from such TOPO-based syntheses was investigated by ³¹P solid-state nuclear magnetic resonance (NMR) spectroscopy (20). A wide distribution of surface species was observed and attributed to a variety of ligand–nanocrystal bonding environments including unidentate and bidentate

coordination and oxidic defects at both In and P. This finding contrasted with earlier studies of TOPO/TOP-capped CdSe nanocrystals in which only one surfactant site was identified (21).

With these early synthetic methods established, InP has dominated the field of III-V nanocrystal research. The turn of the millennium brought about tremendous change in the synthesis of InP nanocrystals arising from the seminal work of Battaglia & Peng (22), in which InP was synthesized using a hot injection method (18). Importantly, this is also the first instance of InP surface ligation by carboxylates (derived from, e.g., lauric, myristic, palmitic, or stearic acid). InP nanocrystals prepared by this method tend to be indium rich, and those excess indium ions are charge balanced by coordinated carboxylate. While the structure of this carboxylate-rich surface is not yet fully understood in the case of larger nanocrystals, Cossairt and coworkers (23, 24) were able to identify, isolate, and structurally characterize an $In_{37}P_{20}(O_2CR)_{51}$ cluster intermediate in this synthesis. The single-crystal X-ray diffraction structure of this cluster shows a dense, interconnected ligand network composed of entirely bidentate and largely bridging carboxylate ligands (Figure 2a,b). Studies in solution or in the presence of added Lewis bases or Brønsted acids suggest ligand rearrangement associated with L-type ligand binding and concomitant shifts to monodentate carboxylate coordination (9, 25, 26). X-type ligand exchange studies at InP cluster surfaces have shown similar behavior to InP nanocrystals in terms of equilibrium constants but have allowed for elucidation of additional L-type binding events prior to exchange (27). Theoretical studies have also informed our understanding of the metal-rich and carboxylate ligated surface of InP nanocrystals. An important conclusion from this work is that the average nearest neighbor In-In distance at the particle surface increases as the surface curvature decreases and the particle size increases (Figure 2c) (28). In the $In_{37}P_{20}$ cluster, the average In–In distance is 4.7 Å, and in a 3-nm nanocrystal, the average distance is 5.7 Å (28). Another important conclusion of this work is the impact of the observed surface structure on reactivity, where the results indicate the presence of both labile and stable sites on cluster and nanocrystal surfaces that are correlated to the average In-In distance.

As might be expected based on the oxidative sensitivity of P(III), oxygen-containing reagents and by-products have been considered species to avoid in InP synthesis. Central to this idea is the observation documented by Delpech, Nayral, and coworkers (29) that the presence of carboxylate ligands in the synthesis of InP quantum dots leads to the in situ formation of water from



Figure 2

(*a*) Single-crystal X-ray diffraction structure of $In_{37}P_{20}(O_2CR)_{51}$ and (*b*) the representative carboxylate binding motifs seen at the cluster surface. Panels *a* and *b* adapted with permission from Reference 24; copyright 2016 American Chemical Society. (*c*) The progression of stability as a function of nearest neighbor In–In distance for analogous In-P complexes, clusters, and quantum dots. Panel *c* adapted with permission from Reference 28; copyright 2018 American Chemical Society. Abbreviations: ESC, earliest stage cluster; MSC, magic-sized cluster; QD, quantum dot.



Differential surface chemistry outcomes when preparing InP nanocrystals from indium amidinate precursors under argon versus H_2 atmosphere (*top*) along with representative ³¹P solid-state nuclear magnetic resistance data showing the presence and absence of surface oxides (*bottom*). Figure adapted with permission from Reference 32; copyright 2017 American Chemical Society.

decarboxylative coupling (ketonization) at elevated temperatures. This decomposition reaction leads to a partially oxidized shell at the surface of InP and was suggested to impact the photoluminescence (PL) of these materials. The effect of an oxide shell on quantum yield (QY) remains inconclusive, at least for moderate QY samples (30, 31). To deliberately avoid the growth of an indium oxide or indium phosphate shell, the indium precursor can be altered to eliminate reactive oxygen groups. One example of indium precursor development in this regard is indium amidinate, which results in the desired non-oxidized InP surface at relatively mild temperatures (e.g., 150° C) and the formation of an oxidic shell at higher temperatures (**Figure 3**) (32). However, repeating the high-temperature synthesis under a reducing atmosphere of H₂ gas instead of Ar leads to an oxide-free surface that facilitates subsequent core or shell growth. Intriguingly, the mechanism of nanocrystal surface protection was concluded to be from the formation of surface (InP)–H bonding interactions, similar to what is seen for surface termination in group IV nanocrystals synthesized under reducing conditions or in a plasma (33–35).

With knowledge of the issues surrounding surface oxidation in carboxylate-based syntheses, researchers have sought alternative chemistries that lead to both size control and high-quality nanocrystals. In 2013, Song et al. (36) introduced the use of indium halides and aminophosphines in an amine solvent for the synthesis of InP nanocrystals. This chemistry was followed up with detailed mechanistic and optimization studies by a number of groups, with that of Hens notable among them (37–40). Based on the conditions of the synthesis, the surface chemistry of these materials is distinct, and in fact, the synthesis results in tetrahedral particles terminated by cation-rich (111) facets, in contrast to the more spherical nanocrystals formed from the indium carboxylate/P(SiMe₃)₃ synthesis. Chemical and spectroscopic analyses indicate that both the amine and halide ligands participate in the stabilization of the metal-rich facets. Based on density functional theory calculations, it has been proposed that fractional dangling bonds of the In-rich (111) surface could be completely passivated by three halide and one primary amine ligand per (2 \times 2) surface unit, satisfying the eight-electron rule (41).

2.3. InP: Postsynthetic Modification

To improve the properties of InP nanocrystals, the surface chemistry may be postsynthetically modified. The chemical approach depends on the desired function. Below, we elaborate on three specific areas in this regard: light emission, charge transfer, and stability/processability.

2.3.1. Light emission. Nozik and coworkers (42) developed an early example of a postsynthetic surface treatment method to attempt to address the low QYs of as-synthesized InP nanocrystals. They treated InP nanocrystals with hydrofluoric acid (HF), which resulted in etching of the nanocrystal surface, thereby removing undercoordinated surface atoms believed to act as electronic carrier traps. This was corroborated by a blue shift in the PL maximum, indicating smaller nanocrystals as a result, as well as a QY increase by over an order of magnitude (to 30%). It was proposed that etching with HF removes surface phosphorus vacancies that served as electron traps. However, it was later found that the etching process may in fact be photochemical in nature, suggesting that photogenerated carriers play a role. Based on observations of hole trap states by electron paramagnetic resonance spectroscopy and the implication that they are relevant to etching in bulk InP, Weller and coworkers (43) suggested that surface hole traps are associated with undercoordinated P atoms. They further claimed that elimination of these traps upon etching in combination with the filling of the P vacancies by fluoride results in strong enhancement of the band edge PL. This photochemical HF treatment has been further investigated in InP nanocrystals passivated by amine surface ligands, in which the combination of HF and sulfuric acid under UV illumination led to electrostatically stabilized InP nanocrystals with a significant increase in QY (44). In an interesting development of the HF surface treatment chemistry, Alivisatos and coworkers (45) have recently shown that lower concentrations of HF do not lead to etching (Figure 4a). Instead, fluoride ions coordinate underpassivated indium sites on the surface. This leads to an increased QY of up to 48% as well as a PL redshift and increased PL lifetimes attributed to exciton delocalization over the outermost surface layer of the InP nanocrystals. Interestingly, this work also points to the use of other sources of fluoride anion as being good candidates for trap passivation at InP nanocrystal surfaces (46).

Beyond HF etching and fluoride passivation, other surface treatments have been shown to dramatically impact the luminescence of InP nanocrystals. Cossairt and coworkers (10) explored the treatment of InP nanocrystal surfaces with divalent Lewis acids. Treatment of InP nanocrystals with cadmium carboxylate led to a PL increase of up to 49% along with a red shift in the optical spectra, while treatment with zinc carboxylate led to a more modest increase in PL and a blue shift. NMR and X-ray spectroscopic characterization suggested that the PL enhancement arose from displacement of native indium carboxylate and coordination of the divalent Lewis acids as Z-type ligands. The use of Z-type ligands to passivate trap states at InP nanocrystal surfaces has since been further investigated by others (12). Gamelin, Cossairt, and coworkers (11) have reported on the charge carrier dynamics of Lewis acid-modified InP nanocrystals. Using a combination of transient absorption and transient PL spectroscopy, the authors proposed that divalent Lewis acids increase PL by decreasing the concentration of (or eliminating) surface electron traps associated with undercoordinated surface indium ions, which are removed by the Z-type ligand exchange mechanism (Figure 4b). Similar conclusions were also made for fluoride treatment, in which this small, hard anion can coordinate surface indium sites, leading to effective electron trap passivation. Related work by Schaller and coworkers (47) examined the attachment of S^{2-} and $Sn_2S_6^{4-}$ ligands to the surface of the InP via a room temperature ligand exchange process. After coordination of the inorganic ligand to the nanocrystal surface, not only did samples display improved QYs of up to 35%, they also showed increased stability during thermal cycling. Using



(*a*) The treatment of InP nanocrystals with HF and corresponding changes in absorption and PL upon surface fluoridation. Panel adapted with permission from Reference 45; copyright 2018 American Chemical Society. (*b*) The relative distribution of electron and hole traps in as-synthesized and surface-treated InP nanocrystals. Panel adapted with permission from Reference 11; copyright 2019 American Chemical Society. Abbreviations: DMSO, dimethylsulfoxide; HF, hydrofluoric acid; IL, ionic liquid; PL, photoluminescence; QY, quantum yield.

time-resolved spectroscopy, the increased PL was similarly attributed to reduction of electron trapping at undercoordinated indium sites. Recent work has elaborated on these studies of InP treatment with divalent Lewis acids by investigating the addition of metal halide salts. By treating the surface of InP with more electronegative ions, the luminescent properties of the material improved, leading to the hypothesis that in addition to simple trap passivation models, withdrawal of excess negative charge from the InP core may be important for maximizing PL (48).

The most common way to increase the stability and PL of InP nanocrystals is via the growth of a protective shell layer on the surface of the InP core. An early attempt to shell InP was performed by Nozik and coworkers (49), in which lattice matched ZnCdSe was grown on the surface of the material. Due to the difference in electronic structures of InP and ZnCdSe, a type II heterostructure was formed in which the hole wavefunction was confined to the InP core, but the electron wavefunction was delocalized throughout the entire heterostructure, leading to a PL redshift of up to \sim 300 meV. Shell growth removed unpassivated surface In sites that served as electron traps, resulting in a QY increase to 10%. After the success of the ZnCdSe core/shell system was established, other materials were explored as shell materials on the InP core, with ZnS playing a prominent role. It was demonstrated that the introduction of the ZnS layer created a type I heterostructure that confined both electrons and holes to the InP core, increasing the PL up



The shelling of In(Zn)P with ZnSe versus ZnMgSe and the relative impact on lattice strain, quantum yield, and trap state concentrations. Abbreviation: PLQY, photoluminescence quantum yield. Figure adapted with permission from Reference 54; copyright 2020 American Chemical Society.

to 23% while also improving the overall heterostructure stability (50, 51). While the ZnS shell on the InP core greatly increased the QY of the material, the variation in lattice constants led to a highly strained interface (7.8% lattice mismatch). In an attempt to reduce this strain and further increase the QY, a gradient shell approach was developed in which the InP cores were first shelled with a ZnSe shell, then a ZnS shell (52). By utilizing the initial ZnSe shell, lattice mismatch was reduced to 3.4% and 4.6% between the ZnSe and ZnS shell layers, respectively, allowing for thicker shells to be grown on the InP core. Not only did this increase the material's QY to over 40%, it also improved photostability, as demonstrated by stable QYs of over 20% after 25 h of UV irradiation. Gradient and multishell heterostructures have continued to be investigated, with the core/shell/shell method applied to furnish InP/GaP/ZnS (53). While the lattice mismatch of this interface is higher (6.8%) than that of ZnSe, the GaP layer is proposed to improve the interface between InP and the strongly confining ZnS outer shell, leading to higher localization of the photoexcited carriers in the InP core and a QY of up to 85%. Additionally, it was demonstrated that the InP/GaP/ZnSe material retained its high emissivity at elevated temperatures for extended periods of time when compared to InP/ZnS. Attempts to create core/shell/shell materials with even lower strain at the interface have continued, leading to the utilization of highly reactive Mg and Zn precursors to grow a zinc blende Mg(Zn)Se shell around an In(Zn)P core (Figure 5) (54). Not only did this core/shell/shell system effectively localize charge carriers in the In(Zn)P core, but carrier trapping at interfacial trap states was also reduced, as shown by a narrowing of the emission spectra, especially the asymmetric low-energy feature correlating to hole trapping (55).

While a vast majority of InP core/shell materials are based on a type I architecture, a variety of type II heterostructures have also emerged. For example, a purely type II InP emitter was developed by introducing a CdS shell, which enhanced the emission of InP to a QY of 36% while also red shifting the PL maximum by 68 nm (56). Variations of shell thickness in InP/CdS core/shell nanocrystals in fact show a transition from type I to type II band alignment at around three to four monolayers (57). The same study showed that blinking suppression was not strongly correlated with shell thickness, whereas biexciton lifetimes were (57). Hens and coworkers (58) further developed the InP/CdX (X = S, Se) shelling studies. Not only did these materials show enhanced PL and the characteristic bathochromic shift of a type II material, they also absorbed

more strongly at 450 nm, making them ideal candidates for light-emitting diode downconverters. Additionally, by further tuning the concentration of cadmium in alloyed II-VI shells, strain-free core-shell nanoparticles can be obtained (58).

While the use of a cadmium chalcogenide shell allows access to redder emission than that of native InP, due to the inherent toxicity of cadmium, efforts have been made to find suitable alternative near-infrared (NIR) InP emitters. One solution developed by Nizamoglu and coworkers (59, 60) used a shell of ZnO grown via thermal decomposition of zinc acetylacetonate at 230°C on the surface of InP cores. The resulting material showed the red emission shifted by 46 nm and fabrication of luminescent solar concentrators with efficiencies of up to 17%. Pushing even further into the NIR, Alivisatos and coworkers (61) demonstrated the growth of a $Y_{1-x}Ln_xF_3$ shell on an InP core followed by the growth of a LnF_3 shell. Due to the intrinsic doped nature of the primary shell, these materials showed multiemissive properties with three main regimes arising from InP band edge recombination, InP trap state recombination, and emission from the Yb³⁺ F^{7/2}-to-F^{5/2} transition. Unfortunately, the QY of these samples was only 0.1%, leaving room for further development. Improvement in NIR emissive InP has also been pursued through copper doping (62). By introducing a copper ion into the lattice, a mid-gap hole trap was introduced, allowing for lower-energy emission upon recombination of the conduction band electron with the copper-localized hole (63). This emission can be further enhanced via surface treatment of the nanocrystal either prior to copper incorporation or postsynthetically, leading to QYs exceeding 60% (64).

2.3.2. Charge transfer. A large body of work has focused on replacing the native ligand shell from as-synthesized InP with less insulating or otherwise functionally distinct species. Interparticle electronic communication or the charge transfer ability of the nanocrystals can be enhanced using this method (65). One of the early examples in this regard was replacing the TOP/TOPO ligand shell in as-synthesized InP with 4-tertbutylpyridine to improve charge transfer with TiO₂ for photosensitization applications (66). Further studies by Soci and coworkers (67) showed that polaron generation yield in InP/poly(3-hexylthiophene) donor-acceptor pairs is enhanced by efficient exciton dissociation and charge transfer when pyridine ligands are used in place of oley-lamine. Further examination of ligand exchange for charge transfer purposes was carried out by Jeong and coworkers (68), in which exchanging myristic acid for thioacetic acid led to films of individual yet proximally packed nanocrystals. These condensable nanocrystal films produced currents two to five orders of magnitude higher than as-synthesized myristate-capped InP.

More recent studies have focused on exchanging organic capping ligands for a variety of fully inorganic ligands to further increase charge transfer and transport properties. Talapin and coworkers (69) developed azide-capped InP, a possible starting point for entirely III-V heterostructures. Additionally, Talapin and coworkers have demonstrated the ligation of InP with a series of polyoxo anions, including PO_4^{3-} , VO_4^{3-} , WO_4^{2-} , MOO_4^{2-} , and HPO_3^{2-} , once again creating a library of entirely inorganic InP nanocrystals (**Figure 6a**). Such oxo-based ligands were designed to be more oxidatively stable by virtue of their larger HOMO-LUMO (highest-energy occupied molecular orbital–lowest-energy unoccupied molecular orbital) gaps compared with chalcogenide-based inorganic ligands and to facilitate integration of the nanocrystal using techniques like sol-gel chemistry. Further expanding the library of inorganic ligands, Kovalenko and coworkers (70) successfully demonstrated the application of InCl₃ ligands onto the surface of InP nanocrystals (**Figure 6b**), creating cation-pure inorganic solids ideal for integration into optoelectronic devices.

2.3.3. Dispersibility, processability, and stability. While highly dispersible in common organic solvents, InP suffers from a lack of colloidal stability in aqueous media. To mitigate this,



Semiconductor nanocrystals (NCs) capped by (*a*) oxyanion-based ligands or (*b*) halometallate ligands. Panel *a* adapted with permission from Reference 69; copyright 2014 American Chemical Society. Panel *b* adapted with permission from Reference 70; copyright 2014 American Chemical Society.

a variety of hydrophilic capping ligands have been investigated, including mercaptosuccinic acid and polyethylene glycol-functionalized carboxylic acids and amines (71, 72). To not only increase the biocompatibility of shelled InP nanocrystals but also increase the efficacy of the material as a biological probe, penicillamine has been attached as the capping ligand (73). Not only does penicillamine allow for the suspension of the nanocrystals in aqueous media, but it is also robust to detrimental disulfide formation that is commonly seen in other biologically compatible thiol ligands like cysteine. Additionally, penicillamine induces a chiral response to light and can be partially exchanged with other ligands while maintaining colloidal stability. This has allowed for the attachment of more exotic ligands to the surface, such as 1-(carboxymethyl)-4,7-bis[(6carboxypyridin-2-yl)methyl]-1,4,7-triazacyclononane [otherwise known as H(3)bpatcn], which can chelate lanthanide ions, leading to dual optical/magnetic biological probes.

The use of silica and related outer shells in InP-based nanocrystals has also proved useful for improving processing and stability. This trend started gaining traction when Palomares and coworkers (74) succeeded in growing a silica shell around an InP/ZnSe core, demonstrating that the silica shell greatly increased the biocompatibility of the material and preserved luminescence in vitro. Liu and coworkers (75) expanded on the core/shell/SiO₂ motif; following attachment of a suitable polypeptide, the core/shell/shell material was conjugated with various upconverting nanoparticles, leading to biocompatible dual-emission fluorescence probes. By contrast, Reiss and coworkers (76) encapsulated InP/ZnSeS/ZnS in alumina. This material retained a QY of over 30% after 32 h of irradiation and experienced reduced drift in the emission maximum.

Although much work has been done on encapsulating core/shell materials in chemically resistant outer shells, ligand exchange on the core/shell surface has also been shown to positively impact stability. Perhaps the most apparent example of this is the exchange of oleate and TOP with 1,2-hexadecanedithiol. Using this bidentate surface ligand, Kim and coworkers (77) were able to stabilize InP/ZnS nanocrystals to such an extent that after 400 h of air exposure, the change in QY was negligible. While not focused on the stabilization of the core/shell materials, Chin and coworkers (78) exchanged the surface ligands on InP/ZnS quantum dots with a series of dithiocarbamate ligands, demonstrating exciton delocalization to the surface and significant red shifts in the PL spectra.

2.4. II-Ps

Beyond the III-Ps discussed above, researchers have also been interested in phosphides prepared from group II metals, including zinc and cadmium. This area of synthesis and surface chemistry is in its infancy by comparison with InP, but some important insights have been made regarding the growth, stabilization, and postsynthetic modification of these nanocrystals.

An early entry point to this field came in the early 1990s when Buhro and coworkers (79, 80) explored the methanolysis of metal disilylphosphido precursors {namely, $[CdP(SiPh_3)_2]_2$ }. Intriguingly, thermal decomposition of nanocrystalline Cd_3P_2 prepared by this route indicated the presence of silylether coproducts [both O(SiPh_3)_2 and MeOSiPh_3] in addition to bulk Cd_3P_2 and P_4 . This strongly suggested that both surface P and Cd were ligated, with P being coordinated by silyl cations and surface Cd ligated by methoxide. This methanolysis method offered an early example of the ability to vary the covalent surface substituents in these systems. Prior to this report, Henglein and coworkers (81) prepared Cd_3P_2 nanocrystals from the reaction of aqueous solutions of cadmium ions and PH_3; particle growth was arrested with the addition of polymeric polyphosphate stabilizers, which presumably stabilize the particles by adhering to their surfaces. These early studies indicated that the coordination chemistry of II-P nanocrystal surfaces is a critical issue in nanoparticle stabilization.

The next significant development in II-P chemistry was introduced by Buriak and coworkers (16) with their synthesis of Zn_3P_2 nanocrystals using $ZnMe_2$ and $P(SiMe_3)_3$ in a mixture of TOP and octadecene. The resulting nanocrystals were very reactive and prone to agglomeration. It was later demonstrated using a combination of ¹H NMR and IR spectroscopy that the Zn-rich surfaces were terminated by CH₃ groups, with additional evidence for surface PH_x(SiMe₃)_{3-x} (82). The surface methyl groups could be readily exchanged by addition of protic species like carboxylic acids, phosphonic acids, or thiols, releasing methane and leading to colloidally stable nanocrystals ligated by the corresponding conjugate bases (**Figure 7**). Modifications of this synthetic approach by Glassy & Cossairt (83, 84) included zinc carboxylates in the synthesis in addition to ZnMe₂. The speciation of zinc, and hence the nucleation, growth, and final surface chemistry of the nanocrystals, was tunable depending on the relative concentration of zinc carboxylate and ZnMe₂. Similarly, syntheses of Cd₃P₂ based on reactions between P(SiMe₃)₃



Figure 7

A Zn₃P₂ nanocrystal surface ligated by CH₃ groups undergoes ligand exchange with Brønsted acids to release methane and form nanocrystals ligated by the corresponding conjugate base. This change in surface chemistry impacts colloidal stability. Figure adapted with permission from Reference 82; copyright 2014 American Chemical Society.



Solid-state MAS and cross-polarization ¹H nuclear magnetic resonance data showing the presence of acetate, amine, and oxidic species on the surface of Cd₃P₂ nanocrystals. Abbreviations: FBCP, forth and back cross-polarization; MAS, magic-angle spinning. Figure adapted with permission from Reference 85; copyright 2016 Royal Society of Chemistry.

and cadmium carboxylates in the presence of primary amines led to metal-rich materials bearing metal carboxylate and amine surface termination (85). These II-P (and likewise III-P) surfaces are quite sensitive to water. The introduction of aliquots of water was shown by solid-state ${}^{1}\text{H}/{}^{31}\text{P}$ NMR techniques to lead to formation of surface Cd–OH in addition to P–OH groups derived from HPO₄^{2–} or H₂PO₄[–] moieties, as have been previously characterized on calcium phosphates (**Figure 8**). Similar conclusions have been made using ${}^{113}\text{Cd}$ dynamic nuclear polarization experiments (86). Promiscuous oxide species have also been demonstrated to arise in II-Ps and III-Ps from oxygen-containing ligands themselves, as seen above in InP. As a result, oxygen-free precursor chemistries have been developed to generate clean, oxide-free surfaces. For example, zinc amidinate, P(SiMe_3)_3, and hexadecylamine have been combined in mesitylene at elevated temperatures to give high-quality, nearly stoichiometric Zn₃P₂ nanocrystals terminated by primary amines (87).

While there has been little research on the postsynthetic surface modification of II-P nanocrystals to tune structure and optoelectronic properties, there are hints from theory that such pursuits could be fruitful. Dzade (88) has shown through theoretical calculation that the functionalization of Zn_3P_2 nanoparticle surfaces with 4-aminothiophenol leads to several low-energy adsorption geometries, including a monodentate Zn–S-slant configuration on the (001) surface, a monodentate Zn–S-flat configuration on the (101) surface, and a bidentate Zn–NS–Zn configuration on the (110) surfaces (**Figure 9**). The coordination of 4-aminothiophenol is shown to be driven by strong hybridization between the S and N p-orbitals and the d-orbitals of the interacting surface Zn ions, which resulted in the formation of strong Zn–S and Zn–N chemical bonds. Interestingly, the final equilibrium morphology of Zn_3P_2 is modulated by 4-aminothiophenol coordination, with the reactive (001) and (110) surfaces becoming more pronounced in the equilibrium morphology relative to the (101) facet. This work provides motivation for ligand control of II-P structures and suggests new surface chemistries to explore.



The preferred facet presentation for bare versus 4-aminothiophenol (4ATP)-ligated Zn_3P_2 nanocrystals. Figure adapted with permission from Reference 88; copyright 2020 American Chemical Society.

3. METALLIC TRANSITION METAL PHOSPHIDE NANOCRYSTALS

3.1. Background and Rationale

Transition metal phosphide (TMP) nanocrystals, though not as thoroughly studied as semiconducting metal phosphides, have been widely explored as catalysts for various reactions, including hydrodesulfurization (HDS) (89, 90), the hydrogen evolution reaction (HER) (38, 91-96), the oxygen evolution reaction (OER) (97-99), and hydrogenation (100). Additionally, they are interesting for their magnetic properties (101–103), their ability to serve as cocatalysts in photocatalytic hydrogen evolution (104-106), and their applications in battery technologies (107, 108). While transition metal oxides and chalcogenides have been well known as catalysts in industry for over a century, phosphides have by comparison received less attention until more recently. Part of the reason for this recent attention is the unique way in which phosphorus modulates the activity of the transition metals themselves. In 2005, Liu & Rodriguez (109) predicted that the (001) plane of Ni₂P should be a suitable HER and HDS catalyst based on binding energetics because of a synergistic ensemble effect between Ni and P. Phosphorus moderates binding of H-atoms to the Ni₂P surface so that they neither bind too strongly nor too weakly. Since then, others have explored surfaces on TMPs that are ideal for various forms of catalysis, such as deoxygenation reactions and the OER (110–112), and additional surfaces that are HER active, such as the $(\bar{1}\bar{1}20)$ and $(11\bar{2}1)$ facets on Ni₂P (92, 112, 113). Taking TMPs to the nanometer length scale, as with most catalytic materials, allows for increased surface area, access to nonthermodynamic phases with distinct reactivity, and the ability to chemically design and tailor active sites and nanocrystal morphologies through surface chemistry. In this section, we outline what is known about the surface chemistry of this unique class of materials, both in as-synthesized samples and through postsynthetic modification, with the aim of altering activity and stability.

3.2. Transition Metal Phosphides: As Synthesized

Some of the earliest colloidal syntheses of TMP nanocrystals were demonstrated by Brock and coworkers (101, 114, 115) modeling reactions after the more well-developed syntheses of semiconducting main group metal phosphides like InP. In this approach, P(SiMe₃)₃ was used as the primary phosphorus source, with TOPO acting as both a weakly coordinating solvent and a secondary phosphorus source. Dodecylamine, myristic acid, and hexylphosphonic acid served as ligands to stabilize and solubilize the resulting FeP, MnP, and CoP nanocrystals. They concluded that ligands must bind neither too strongly nor too weakly to get the desired nanoparticle size and structure. TOPO does not bind strongly enough and leads to aggregation, whereas hexylphosphonic acid binds too strongly and leads to small, amorphous particles when used in high concentrations; dodecylamine and myristic acid successfully acted to moderate nucleation and growth.

In the years following, the use of TOPO as a P source and/or a coordinating solvent continued; however, many researchers saw advantages when moving to its reduced form, TOP, due to its more favorable release of PH₃ at elevated temperatures, improving reactivity toward phosphidation (89, 102, 116–118). TOP has been demonstrated to decompose on metal surfaces at quite mild temperatures (~150°C) and has been implicated in carbon contamination of metal and metal phosphide materials (119). Similar to hexylphosphonic acid, TOP can bind metal phosphide nanocrystals strongly and inhibit growth despite its dual function as a source of phosphide. Interestingly, oley-lamine has been shown to give rise to metal-rich metal phosphides in syntheses that use TOP as a P source by acting as a reducing agent and by competing with TOP at the nanocrystal surface, reducing the effective P concentration at the nanocrystal growth front (120). Long-chain amines have continued to be ubiquitous capping ligands for TMP nanocrystals, with oleylamine being a dominant synthetic choice (38, 90, 91, 93, 98, 103, 106, 117, 118, 121–124). Other common capping ligands include alkylphosphonic acids (which can also serve as the P source) (114, 125) and carboxylates, as mentioned above (89, 91, 99, 114, 118, 122, 126, 127).

Ligands have been shown to control the shape and size of TMP nanocrystals, consistent with what is seen for the more widely explored metal (e.g., Au, Ag, Cu, etc.) nanocrystal family. For example, nanorods of various TMPs were formed by Hyeon and coworkers (117) using a syringe pump to controllably deliver metal-TOP complexes into different solvent mixtures. Delivering a Mn-TOP complex solution into TOPO resulted in MnP nanorods; however, switching TOPO for octyl ether and oleylamine led to spherical MnO nanoparticles. Mixtures of Co₂P nanorods and spherical particles resulted from the use of Co-TOP and Co-oleylamine complexes in octyl ether and oleylamine but switching to hexadecylamine resulted in purely nanorod-shaped particles with a higher aspect ratio (117). An Fe-TOP complex solution added to octyl ether and oleylamine made Fe_2P nanorods (103), while adding the complex to TOPO resulted in FeP nanorods, indicating that the more reducing conditions created by the amine solvent were able to promote the formation of iron in reduced oxidation states [e.g., Fe(II) and Fe(I)] (117). The authors hypothesized that more strongly binding ligands (e.g., TOP) were bound to the particles perpendicular to the growth plane, while more weakly binding ligands (e.g., oleylamine) were on the growth plane, allowing the anisotropic growth of the nanorods with the continuous injection of precursors (Figure 10a). These syntheses show the importance of the choice of surfactants for the phase, shape, and size of TMP colloidal nanoparticles among other factors, such as temperature and speed of injection.

Research groups led by Chiang and Schaak (122, 128) independently found that varying the surfactants could lead to hollow TMP nanoparticles, especially when metal nanoparticle intermediates were implicated. Oleylamine-capped Ni nanoparticles were treated with TOP to form hollow Ni₂P nanoparticles; oleylamine acted as a barrier for P diffusion into the particles, and Ni diffused out of the nanocrystal core via the Kirkendall mechanism (126, 129). Replacing oleylamine for hexadecylamine also resulted in hollow nanoparticles; however, using oleic acid led to Ni₂P nanorods, and the addition of TOPO resulted in solid spherical nanoparticles (122).

Henkes & Schaak (118) also showed the importance of ligand coordination in the conversion of metal nanoparticles to metal phosphides while maintaining the original shape of the metal nanoparticle. Following literature procedures, they were able to make Rh nanoparticles of various shapes (cube, triangle, multipod with thin arms, and multipod with thick arms) (Figure 10b),



(*a*) The growth of transition metal phosphide nanorods based on the relative positions of strongly and weakly binding surfactants. Panel adapted with permission from Reference 117; copyright 2005 American Chemical Society. (*b*) Transmission electron microscopy images showing retention of the morphology of Rh nanoparticles upon thermally driven phosphidation using trioctylphosphine (TOP) to give Rh₂P. Panel adapted with permission from Reference 118; copyright 2008 American Chemical Society.

followed by conversion to Rh₂P while maintaining the original morphology. The Rh nanoparticles were stabilized with poly(vinylpyrrolidone); however, they then did not dissolve in the TOP solution. Therefore, cosolvents were added to promote solubility in TOP. The choice of cosolvent was important for maintaining shape purity as some cosolvents resulted in differently shaped particles; e.g., oleic acid resulted in spherical Rh₂P nanoparticles. A mixture of oleylamine and TOP usually resulted in the best shape purity. The cosolvents and other stabilizing ligands made it so that the Rh and Rh₂P nanoparticles could kinetically stabilize different facets, promoting shape control relative to the thermodynamically preferred octahedron morphology.

3.3. Transition Metal Phosphides: Postsynthetic Modification

For catalytic applications, the conventional wisdom is that activity can be improved by increasing the number of active sites at the surface. For colloidal nanoparticles, that is usually accomplished by



The removal of carboxylate and amine ligands from CoP nanocrystal surfaces following treatment with [Et₃O][BF₄]. Subsequent ligation studies demonstrate decreasing overpotentials for hydrogen evolution reaction in the order of $O_2CR \gg H_2NR >$ unligated. Abbreviations: Et, ethyl; Me, methyl. Figure adapted with permission from Reference 91; copyright 2019 American Chemical Society.

thermal annealing to remove the stabilizing ligands, thereby exposing active sites and preventing active site poisoning through competitive coordination (91, 93, 99, 121, 130). A more systematic investigation of ligand effects on CoP nanoparticles for electrocatalytic hydrogen evolution in aqueous media was conducted by Ung & Cossairt (91) (Figure 11). They found that common carboxylate and amine ligands did indeed impede catalysis; however, the effect was one of limiting access to surface active sites and not poisoning. Carboxylates tended to bind more strongly to the nanoparticle surface, vielding high ligand densities. This led to a strong dependence of electrocatalytic activity on carboxylate chain length due to increased hydrophobicity. Additional evidence of the importance of the ligand environment is provided by Brutchey and coworkers (124), who showed that carbene-ligated copper phosphide nanocrystals were more active for HER than assynthesized oleylamine-ligated particles, because the carbene surface ligands reduced unfavorable electrostatic interactions between the catalyst surface and the substrate. Ligand exchange and removal is also effective in other catalytic processes. For example, Fu and coworkers (106) exchanged the native TOP/oleylamine ligands for poly(vinylpyrrolidone) ligands to make Ni₂P nanoparticles soluble in aqueous media for the photocatalytic evolution of hydrogen. Similarly, Brock and coworkers (89) exchanged TOP/TOPO ligands with mercaptoundecanoic acid to improve HDS activity on Ni2P nanocrystals. Both ligand-exchanged nanocrystals and those washed with CHCl3 remained stable under reducing conditions and had improved HDS activity compared with assynthesized Ni_2P . The wash with CHCl₃ doubled the surface area of the nanoparticles, while the ligand-exchanged particles had similar surface areas as the as-synthesized particles. Of special note is that the as-synthesized nanoparticles outperformed bulk Ni₂P and had six times the surface area even with ligands still fully attached (89). A later report by Brock and coworkers (90) removed ligands entirely through calcination to improve HDS catalytic activity and incorporated the nanoparticles into a silica network to prevent sintering.

Modifying the surface to change what the substrate is exposed to can have a direct impact on catalytic and electrochemical activity and is the main reason that researchers remove or exchange surface ligands (131). Other approaches to tune the environment in which the substrate interacts with the catalyst are creating three-dimensional structures of metal phosphide nanoparticles through gelation (127) and generating purposeful inorganic coatings (107). Using the former,



The programmable synthesis of multimetallic phosphide 1D nanorods (NRs) mediated by core/shell nanostructure formation. Figure adapted with permission from Reference 132; copyright 2020 American Chemical Society.

Brock and coworkers (127) exchanged TOP/oleylamine ligands for 11-mercaptoundecanoic acid, 4-fluorothiophenol, or 1-dodecanethiol. In the sol-gel route, particles were oxidized so that P–O–P bonds linked Ni₂P nanoparticles; in a second method, Ni²⁺ was added to the colloidal suspension of mercaptoundecanoic acid–capped Ni₂P nanoparticles and bound to the pendant carboxylate tails. The preparation of gels generated a more easily usable material with the same surface area advantages found through nanoscaling. In another example, Sanchez and coworkers (107) decomposed surface ligands on 25-nm Ni₂P nanoparticles at 400°C to create a C-coating to make negative electrodes for lithium-ion batteries. This coating enabled diffusion of Li⁺ and good conductivity while preventing oxidation of the nanoparticle surface.

To better understand the thermodynamics and stoichiometry of hydrogen binding on metal phosphide surfaces, Mayer and coworkers (123) soaked CoP in an H₂ atmosphere and used this H₂-treated CoP to hydrogenate alkynes and phenoxy radicals. They were able to determine the quantity of hydrogen on the CoP surface by quantifying the yields of the hydrogenated products. Furthermore, an approximate range of bond dissociation free energies for the CoP–H intermediate could be determined by studying a series of well-defined H-atom donors and acceptors. Another attempt to better understand catalysis at metal phosphide surfaces was made by Zhang et al. (132), who formed nanocrystalline Co₂P rods as seeds for the growth of a metal phosphide shell (**Figure 12**). This core-shell approach to metal phosphide synthesis enabled the formation of controlled multimetal phosphide nanorods with a consistent shape and size. Moreover, the Co₂P orthorhombic crystal structure could be retained upon annealing. Therefore, they were able to determine the impact of composition on the OER without the interference of many other factors. They saw that bimetallic phosphides outperformed Co₂P alone, with cobalt iron phosphide leading the pack in terms of OER activity.

4. CONCLUSIONS AND OUTLOOK

Surface chemistry is both the current and future frontier of metal phosphide nanomaterial design. Surface ligands not only control structure and morphology, but also are essential in controlling nanocrystal function by passivating defects and maximizing optoelectronic performance, altering activity for inner-sphere chemical transformations, and controlling extra-particle solvent and substrate interactions important in charge transfer and catalysis. The surface chemistry of metal phosphide nanocrystals is initially dictated by the synthesis conditions, with surfactants and coordinating ions present that serve to both kinetically trap the growing particles and passivate undercoordinated surface atoms that introduce electronic defect states. The as-prepared surface chemistry of metal phosphide nanocrystals has been predominantly explored using a combination of IR, NMR, and various X-ray spectroscopic methods in addition to theory. However, the complexity of the as-prepared surface is often difficult to fully capture using these methods. Postsynthetic modification of the native metal phosphide surface can be used not only as a strategy to probe the native surface, but also to augment the function of the nanocrystals.

Of all the metal phosphide nanomaterials, InP surface chemistry has been the most extensively investigated. In the case of InP, research has been dominated by trying to find and eliminate electronic trap states arising from undercoordinated surface ions. InP surfaces tend to be cation rich; hence, a combination of both X-type and L-type surface ligands are needed for charge balance and kinetic stabilization. In addition, discussion of surface oxidation has been widespread, and methods to eliminate oxidic contaminants and by-products during synthesis have played a central role in methods development. The surface chemistry of II-P materials has been demonstrated to be quite similar. Interestingly, the surface chemistry of TMP surfaces, in which catalytic activity is dominated by inner-sphere reactivity, has been explored far less. Surfaces are most commonly described as nearly stoichiometric, with passivation and stabilization being largely met by L-type ligand coordination. X-ray photoelectron spectroscopy analysis and density functional theory calculations show metal-phosphorus bonding that is quite covalent in nature with electron density equally distributed across the metal and phosphorus atoms. As such, strategies to covalently modify these surfaces to tune their catalytic reactivity by changing their electronic structure and/or interfacial properties by using radical or related atom transfer chemistries are likely to be a productive line of inquiry. While oxidation must be an issue for these materials, systematic studies to control and understand its impacts are lacking.

Much remains to be discovered when it comes to nanocrystal surfaces, and this is true for metal phosphides as much as for any other material. The interplay of bond covalency and elevated reactivity observed at metal phosphide surfaces creates a challenge but also a unique opportunity to build new functionality. Only when we can make and manipulate metal phosphide surfaces with atom-level specificity will we be able to take full advantage of this exciting class of materials.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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