

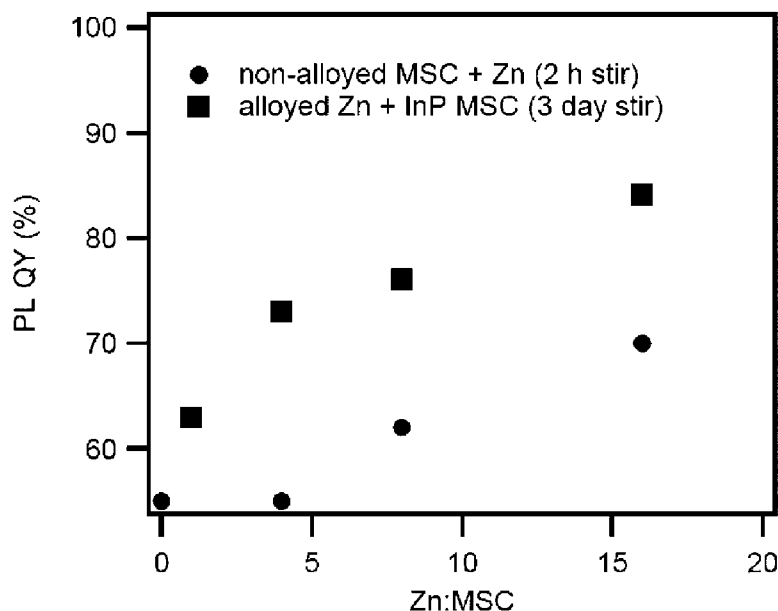
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**FIG. 14**

(57) Abstract: Zinc- and gallium-doped indium phosphide clusters that serve as single-source precursors for quantum dot synthesis, methods for making zinc- and gallium-doped indium phosphide clusters, methods for making zinc- and gallium-doped indium phosphide quantum dots from the zinc- and gallium-doped indium phosphide clusters, and methods for making zinc- and gallium-doped indium phosphide core/shell quantum dots from the zinc- and gallium-doped indium phosphide quantum dots.

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INDIUM PHOSPHORUS QUANTUM DOTS, CLUSTERS, AND RELATED METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of U.S. Application No. 62/927,003, filed October 28, 2019, and U.S. Application No. 62/795,952, filed January 23, 2019, each application expressly incorporated herein by reference in its entirety.

STATEMENT OF GOVERNMENT LICENSE RIGHTS

10 This invention was made with government support under Grant Nos. CHE1552164, DMR1719797 and NNC1542101, awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

15 The release of the Kindle Fire HDX tablet in 2013 marked the introduction to the use of quantum dots (QDs) in commercial displays. Samsung then commercialized the first cadmium-free quantum dot film-based display in 2015. Since then, the display industry has steadily embraced quantum dot technologies, with dozens of products now available from every major display manufacturer. Today, a variety of new implementations of quantum dots are poised to change the way we view the world through screens.

20 Given current metrics for commercial-grade quantum dots, cadmium-free QD materials based on indium phosphide still lag behind the champion CdSe materials in terms of quantum yield and emission linewidth, reducing the practical color gamut coverage provided by these less-toxic materials. One of the principle approaches to further improving the properties of indium phosphide (InP) quantum dots involves increasing the complexity of the material itself through core alloying and the formation of gradient core/shell and core/shell/shell materials. Over the past decade, many different methods to make high photoluminescence quantum yield (PLQY) InP QDs have been developed that rely on optimized shell growth. Thick ZnSe shells have been demonstrated to thermodynamically isolate charge carriers and increase InP PLQY above 40%. InP/ZnSe/ZnS core/shell/shell nanoparticles have recently been reported to facilitate high
30 PLQY (>70%) by lowering lattice strain and improving passivation of the InP core. The

highest reported InP quantum yield relied on this strategy to achieve 95% PLQY with highly designed InP/ZnSe/ZnS QDs.

In numerous reports, including several of the above preparations of core/shell quantum dots, the synthesis of InP cores is performed in the presence of a Zn^{2+} source. The addition of Zn^{2+} has been demonstrated to improve quantum yields and result in narrower size distributions when compared to syntheses that do not incorporate Zn^{2+} . The mechanism and origin of this phenomenon is not well understood, but it is thought that zinc is involved in both the nucleation as a gating precursor to moderate conversion kinetics, and also as an aliovalent Z-type ligand at the InP surface, altering growth and modulating the lattice constant between the core and shell layers of the final heterostructures. Building off of these methodologies, isovalent Ga^{3+} has recently gained traction as a potential ingredient to modulate InP nucleation, growth, and photophysics. For example, InP/GaP/ZnSe systems have been demonstrated to achieve up to 85% PLQY. In another study, using different gallium precursors in the synthesis of Ga-doped InP imparted distinct reactivity and optical properties on the final QD cores. Cation exchange was demonstrated in a Zn-doped InP system, which, when exposed to gallium oleate resulted specifically in Ga-for-Zn cation exchange, resulting in >70% PLQY.

To date, studies on zinc and gallium incorporation into InP QDs have been approached from a purely empirical standpoint with little attention to the creation of new, generalizable principles to move the field forward. Much of this research has focused on the synthesis of zinc and gallium alloyed InP QDs from molecular precursors, which is limited by the inherent reactivity of the precursors themselves and fails to provide control over the extent of alloying. Instead, InP clusters present a stoichiometrically precise platform to introduce dopant ions in a controlled and precise fashion.

Despite the advances in the zinc and gallium incorporation into InP QDs noted above, a need exists for new zinc and gallium-containing InP QDs having effective PLQYs as well as methods for making such with zinc and gallium-containing InP QDs. The present invention seeks to fulfill these needs and provides further related advantages.

SUMMARY OF THE INVENTION

In one aspect, the invention provides an indium phosphide cluster doped with zinc or gallium, wherein the ratio of In: P: Zn in the zinc-doped indium phosphide cluster is represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c$, wherein a is an integer from about 20 to about 40, b is an integer from about 10 to about 25, and c is an integer from 1 to about 20, and wherein the ratio of In: P: Ga in the gallium-doped indium phosphide cluster is represented by the formula $\text{In}_d\text{P}_e\text{Ga}_f$, wherein d is an integer from about 20 to about 40, e is an integer from about 10 to about 25, and f is an integer from 1 to about 20.

In another aspect, the invention provides methods for making an indium phosphide cluster doped with zinc or gallium. In certain embodiments, the method comprises reacting an indium phosphide cluster with a zinc precursor or a gallium precursor effective for incorporating zinc or gallium, respectively, into an indium phosphide cluster to provide a zinc- or gallium-doped indium phosphide quantum dot, respectively.

In a further aspect, the invention provides methods for making an indium phosphide quantum dot. In certain embodiments, the method comprises growing the indium phosphide cluster doped with zinc or gallium described herein by heating the cluster in a solvent at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc or gallium.

In another aspect, the invention provides methods for making an indium phosphide core/shell quantum dot. In certain embodiments, the method comprises:

- (a) growing the indium phosphide cluster doped with zinc or gallium by heating the cluster in a solvent at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc or gallium, as described herein; and
- (b) shelling the indium phosphide quantum dot doped with zinc or gallium with a shell-forming material, to provide an indium phosphide core/shell quantum dot.

DESCRIPTION OF THE DRAWINGS

The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same become better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings.

FIGURES 1A-1F present characterization of cluster doping with zinc and gallium precursors: UV-Vis and PL spectra for Zn-doped InP clusters (1A); UV-Vis spectra for Ga-doped InP clusters (1B); powder XRD patterns of Zn-doped InP clusters (1C); powder XRD patterns of Ga-doped InP clusters (1D); ^{31}P NMR spectra of Zn-doped InP clusters (1E); and ^{31}P NMR spectra of Ga-doped InP clusters (1F).

FIGURE 2 shows the elemental analysis (ICP-OES) of clusters after exposure to cation exchange conditions.

FIGURES 3A and 3B compare UV-Vis spectra of zinc- (3A) and gallium- (3B) doped InP QDs (zinc and gallium equivalents refer to original added concentration during cluster cation exchange).

FIGURES 4A-4C present characterization of zinc-doped InP QDs: UV-Vis and PL spectra of representative zinc-doped InP/ZnSeS sample (4A); PLQY (4B); and FWHM versus the amount of zinc added during cation exchange to InP clusters (4C).

FIGURES 5A-5C present characterization of gallium-doped InP core/shell QDs: UV-Vis and PL spectra for representative gallium-doped InP/ZnSeS core/shell QDs synthesized using initial $[\text{Ga}^{3+}]$:cluster ratio of 4 (5A); PLQY vs initial $[\text{Ga}^{3+}]$:cluster ratios for final core/shell QDs (5B); and FWHM vs initial $[\text{Ga}^{3+}]$:cluster ratios for final core/shell QDs (5C).

FIGURES 6A-6C compare UV-Vis spectrum (left) and PL spectra (right) of InP MSC: with increasing zinc concentrations (6A); normalized comparison of InP MSC PL and a zinc-treated InP PL (6B); and the emission of all zinc species corresponding to traces in the absorbance spectrum (6C).

FIGURE 7 compares ^{31}P NMR (283.5 MHz, C_6D_6) spectra of clusters and increasing zinc equivalents (24, 16, 8, 4) (room temperature).

FIGURES 8A-8C compare MALDI-TOF spectra of InP MSCs ligated with oleate (OA) (8A), myristate (MA) (8B), and phenylacetate (PA) (8C). The largest mass peak in each sample matches with the calculated mass (dashed line) of a $[\text{In}_{31}\text{P}_{20}(\text{O}_2\text{CR})_{32}]^+$ fragment.

FIGURE 9 compares low-mass MALDI-TOF spectra of InP MSC with increasing zinc equivalents (50, 37, 16, 8, 4). The dashed lines correspond to fragment masses of 10,070 g/mol and 8,684 g/mol.

FIGURES 10A-10D compares ICP and pXRD data of zinc treated clusters: measured molar ratios of Zn:P versus the stoichiometric addition of zinc (10A) (data points highlighted in the circle correspond to QD samples) (the dashed line represents the complete 1:1 exchange of zinc for indium based on the added stoichiometry; the zoomed out plot of FIGURE 10A highlights the plateau of zinc incorporated in the clusters (10B); pXRD of InP MSC, 4 Zn, and 16 Zn samples is shown in comparison to bulk InP (10D); the zoom-in of the peaks at 46 and 51 2 θ of FIGURE 10D may have shifted to higher angles (10C) (the dashed line is to guide the eye through the InP MSC peak maxima).

FIGURE 11 shows stacked UV-Vis spectra of hot-injection reactions (0, 1, 4, 8, 16, 37, 50, 100 Zn equivalents) to convert alloyed InP clusters into QDs.

FIGURES 12A and 12B compare pXRD of alloyed QD products and representative TEM images of select samples, respectively.

FIGURES 13A-13D compares UV-Vis and PL spectra of QD products from 0 Zn, 4 Zn, 8 Zn, and 16 Zn and InP precursors, respectively.

FIGURE 14 compares quantum yields (QYs) versus the amount of zinc added to InP clusters.

FIGURE 15 compares ICP data (relative to P) for Zn-doped clusters.

FIGURES 16A and 16B show pXRD of zinc-alloyed QD products (16A) and representative TEM images (16B) of select samples (Zn1, Zn4, Zn16, and Zn 37 refer to the original [Zn²⁺] : cluster ratios during cation exchange).

FIGURES 17A-17D shows UV-Vis, PL, PLQY, and ICP-OES spectra of zinc-alloyed InP QDs synthesized from alloyed clusters.

FIGURE 18 compares powder XRD patterns for gallium doped InP QDs. Legend refers to initial stoichiometry of added Ga(OAc)₃ relative to InP cluster.

FIGURE 19 compares PLQY of final gallium-doped InP/ZnSeS core-shell QDs vs equivalents of added [Ga³⁺] during initial cation exchange.

DETAILED DESCRIPTION OF THE INVENTION

As the commercial display market grows, the demand for low-toxicity, highly emissive, and size-tunable semiconducting nanoparticles has increased. Indium phosphide (InP) quantum dots (QDs) represent a promising solution to these challenges but suffer from low inherent emissivity resulting from charge carrier trapping. Strategies to improve the emissive characteristics of indium phosphide often involve zinc incorporation and the fabrication of core/shell heterostructures. InP clusters are high fidelity platforms for determining processes such as cation exchange and surface doping with exogenous ions because these clusters are used as single-source precursors for quantum dot synthesis.

As described herein, zinc and gallium ions were incorporated into InP clusters to provide doped clusters as single-source precursors to emissive heterostructured nanoparticles. Zinc ions readily reacted with InP clusters, resulting in partial cation exchange, whereas gallium resisted cluster incorporation. Zinc-doped clusters effectively converted to emissive nanoparticles, with quantum yields strongly correlated with zinc content. On the other hand, gallium-doped clusters failed to demonstrate improvements in quantum dot emission. These results indicate stark differences in the mechanisms associated with aliovalent and isovalent doping and provide insight into the use of doped clusters to make emissive quantum dots.

InP clusters have been shown to react with cadmium carboxylate to undergo cation exchange, eventually resulting in the full conversion of the InP cluster to Cd_3P_2 clusters (Stein, J. L.; Steimle, M. I.; Terban, M. W.; Petrone, A.; Billinge, S. J. L.; Li, X.; Cossairt, B. M. Cation Exchange Induced Transformation of InP Magic-Sized Clusters. *Chem. Mater.* 2017, 29 (18), 7984–7992. <https://doi.org/10.1021/acs.chemmater.7b03075>). As described herein, other ions can be incorporated into the InP crystal lattice through cation exchange mechanisms, furnishing doped clusters (i.e., alloyed clusters) that are used as single-source precursors in the synthesis of new InP core/shell QDs. The electronic properties of these InP core/shell QDs is determined by the concentration and/or location of the dopant ions in the treated cluster material.

In one aspect, the present invention provides methods for the incorporation of aliovalent Zn^{2+} and isovalent Ga^{3+} into the InP cluster and demonstrates the advantageous

role these ions have on the photoluminescent properties of core/shell quantum dots derived from those clusters.

The present invention provides zinc- and gallium-doped indium phosphide clusters that serve as single-source precursors for quantum dot synthesis, methods for making zinc- and gallium-doped indium phosphide clusters, methods for making zinc- and gallium-doped indium phosphide quantum dots from the zinc- and gallium-doped indium phosphide clusters, and methods for making zinc- and gallium-doped indium phosphide core/shell quantum dots from the zinc- and gallium-doped indium phosphide quantum dots.

Zn- and Ga-doped InP clusters: Single-source precursors for QD synthesis

In one aspect, the invention provides an indium phosphide cluster doped with zinc or gallium, wherein the ratio of In: P: Zn in the zinc-doped indium phosphide cluster is represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c$, wherein a is an integer from about 20 to about 40, b is an integer from about 10 to about 25, and c is an integer from 1 to about 20, and wherein the ratio of In: P: Ga in the gallium-doped indium phosphide cluster is represented by the formula $\text{In}_d\text{P}_e\text{Ga}_f$, wherein d is an integer from about 20 to about 40, e is an integer from about 10 to about 25, and f is an integer from 1 to about 20.

It will be appreciated that in a related aspect, the indium phosphide cluster of the invention is an indium phosphide cluster doped with zinc and gallium. Indium phosphide quantum clusters doped with zinc and gallium can be prepared by the methods described herein for the preparation of indium phosphide cluster doped with zinc or gallium. Mixed zinc- and gallium-doped indium phosphide clusters can be prepared by the methods described herein, modified to include doping with a combination of zinc and gallium precursors, or sequentially by first doping an indium phosphide cluster with one precursor (i.e., either zinc or gallium precursor), followed by doping the product cluster with the other precursor.

Thus, in a related aspect, the invention provides an indium phosphide cluster doped with zinc and gallium, wherein the ratio of In: P: Zn: Ga in the doped indium phosphide cluster is represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c\text{Ga}_f$, wherein a is an integer from about 20 to about 40, b is an integer from about 10 to about 25, c is an integer from 1 to about 20, and f is an integer from 1 to about 20.

In certain embodiments, for the zinc-doped indium phosphide cluster having the ratio of In: P: Zn as represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c$, c is an integer from about 1 to about 5. In other embodiments, c is an integer from about 5 to about 15. In further embodiments, c is an integer from about 15 to about 20.

5 In certain embodiments, for the gallium-doped indium phosphide cluster having the ratio of In: P: Ga as represented by the formula $\text{In}_d\text{P}_e\text{Ga}_f$, f is an integer from about 1 to about 5. In other embodiments, f is an integer from about 5 to about 15. In further embodiments, f is an integer from about 15 to about 20.

10 In certain embodiments, the zinc-doped indium phosphide cluster has In:Zn molar ratios ranging from about 1:0 to 1:0.4.

In certain embodiments, the gallium-doped has In:Ga molar ratios ranging from about 1:0 to 1:0.2.

In certain embodiments, the indium phosphide cluster doped with zinc and/or gallium has a particle size from about 1 nm to about 3 nm.

15 In certain embodiments, the indium phosphide cluster used as a starting material for preparing the product indium phosphide cluster doped with zinc and/or gallium is $\text{In}_{37}\text{P}_{20}(\text{O}_2\text{C}_{14}\text{H}_{27})_{51}$.

Methods for making Zn- and Ga-doped InP clusters

20 In another aspect, the invention provides methods for making an indium phosphide cluster doped with zinc or gallium. In certain embodiments, the method comprises reacting an indium phosphide cluster with a zinc precursor or a gallium precursor effective for incorporating zinc or gallium, respectively, into an indium phosphide cluster to provide a zinc- or gallium-doped indium phosphide quantum dot, respectively.

25 In a related aspect, the invention provides methods for making an indium phosphide cluster doped with zinc and gallium. In certain of these embodiments, the method comprises reacting an indium phosphide cluster with a zinc precursor and a gallium precursor effective for incorporating zinc and gallium into the indium phosphide cluster to provide a zinc- and gallium-doped indium phosphide quantum dot.

30 Incorporating (or doping) zinc (i.e., Zn^{2+}) and/or gallium (Ga^{3+}) into the indium phosphide cluster is either an additive incorporation, a cationic exchange process in which

In^{3+} ions of the cluster are exchanged for Zn^{2+} or Ga^{3+} ions from the precursors, or a combination of both addition and exchange.

In certain embodiments, the indium phosphide cluster is $\text{In}_{37}\text{P}_{20}\text{X}_{51}$, wherein X is a carboxylate ion. Suitable indium phosphide clusters useful in the doping processes for making Zn/Ga-doped InP quantum dots described herein include indium phosphide InP clusters that are capable of exchanging In^{3+} with Zn^{2+} and/or Ga^{3+} (or incorporating Zn^{2+} and/or Ga^{3+} into the cluster). Such InP clusters are known in the art. Representative InP clusters useful in the methods include $\text{In}_{37}\text{P}_{20}\text{X}_{51}$ (where X is a carboxylate, such as $\text{C}_{13}\text{H}_{27}\text{CO}_2$). Other useful InP clusters include derivatives of the noted cluster that result from treatment with amines (e.g., primary, secondary, and tertiary amines) carboxylic acids, thiols, and related species (see, e.g., B. Cossairt et al., *Chem. Comm.*, 2017, 53, 161-164).

In certain embodiments, the zinc precursor is a mixed alkyl-carboxylate zinc, a zinc carboxylate [$\text{Zn}(\text{RCO}_2)_2$, where R is a C1-C20 alkyl group], a zinc halide [ZnX_2 , where X is a halide or pseudo-halide] or a zinc amide [$\text{Zn}(\text{NR}_2)_2$, where R is a C1-C10 alkyl group]. In one embodiment, the zinc precursor is a mixed alkyl-carboxylate zinc. A representative mixed alkyl-carboxylate zinc is $\text{Zn}_5(\text{Et})_4(\text{OAc})_6$.

In certain embodiments, the gallium precursor is a mixed alkyl-carboxylate gallium (e.g., dimers), a gallium carboxylate [$\text{Ga}(\text{RCO}_2)_3$, where R is a C1-C20 alkyl group], a gallium halide [GaX_3 , where X is a halide or pseudo-halide], or a zinc amide [$\text{Ga}(\text{NR}_2)_3$, where R is a C1-C10 alkyl group] (e.g., dimers). In one embodiment, the gallium precursor is a mixed alkyl-carboxylate gallium. A representative alkyl-carboxylate gallium is [$\text{Ga}(\text{Me})_2(\text{MA})$] $_2$. In another embodiment, the gallium precursor is a gallium carboxylate. A representative alkyl-carboxylate gallium is $\text{Ga}(\text{OAc})_3$.

In the above method, zinc and/or gallium are incorporated into the indium phosphide cluster. In certain embodiments, from 1 to about 20 In^{3+} ions are exchanged for Zn^{2+} ions based on indium phosphide molar basis. In certain embodiments, from 1 to about 20 In^{3+} ions are exchanged for Ga^{2+} ions based on indium phosphide molar basis. In other embodiments, from 1 to about 20 Zn^{2+} ions are added to the indium phosphide cluster

based on indium phosphide molar basis. In other embodiments, from 1 to about 20 Ga^{3+} ions are added to the indium phosphide cluster based on indium phosphide molar basis.

The invention also provides indium phosphide clusters doped with zinc and/or gallium prepared by the methods described herein.

5 Methods for making Zn- and Ga-doped InP QDs from Zn- and Ga-doped InP clusters

In a further aspect, the invention provides methods for making an indium phosphide quantum dot. In certain embodiments, the method comprises growing the indium phosphide cluster doped with zinc and/or gallium described herein by heating the cluster
10 in a solvent (e.g., cluster solution) at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc and/or gallium.

In one embodiment, the indium phosphide cluster is grown by injecting a suspension of the cluster into a solvent at a temperature sufficient to facilitate cluster growth. Cluster growth was monitored by UV-Vis and PL and once the endpoint of cluster
15 growth was reached (e.g., after 15 minutes at 290°C) the reaction was cooled and the quantum dots were isolated.

Suitable predetermined times range from about 5 minutes to about 2 hours and predetermined temperatures range from about 250°C to about 350°C.

The invention also provides indium phosphide quantum dot having an indium phosphide quantum dot core doped with zinc and/or gallium prepared by the methods
20 described herein.

Methods for making Zn- and Ga-doped InP core/shell QDs from Zn- and Ga-doped InP QDs

In another aspect, the invention provides methods for making an indium phosphide core/shell quantum dot. In certain embodiments, the method comprises:
25

(a) growing the indium phosphide cluster doped with zinc and/or gallium by heating the cluster in a solvent at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc and/or gallium, as described herein; and

(b) shelling the indium phosphide quantum dot doped with zinc and/or gallium with a shell-forming material, to provide an indium phosphide core/shell quantum dot.

As used herein, the term "shelling" refers to the process of growing a shell around a quantum dot core by shell growth methods known to those of skill in the field of quantum dot production.

In certain embodiments, shelling comprises injecting the indium phosphide quantum dot doped with zinc and/or gallium into a shell-forming medium comprising a shell-forming material to provide the core/shell quantum dot. In certain of these embodiments, the indium phosphide quantum cluster doped with zinc and/or gallium and the shell-forming medium are contacted for a predetermined time and at a predetermined temperature (e.g., 40 minutes at 300°C) effective to provide the core/shell quantum dot.

Suitable predetermined times range from about 5 minutes to about 2 hours and predetermined temperatures range from about 250°C to about 350°C.

Suitable shell-forming materials include shell-forming cations from Group II (e.g., Zn, Cd) and Group III (e.g., In, Ga), and anions from Group V (e.g., P, As) and Group VI (e.g., O, S, Se, Te).

In certain embodiments, the shell is a shell selected from ZnS, ZnSe, CdS, CdSe, and ZnSeS shells, and shells that are alloys and mixtures thereof.

In certain embodiments, the shell is a shell selected from InP, GaP, In₂O₃, ZnO, and CdO shells, and shells that are mixtures thereof.

Suitable shell-forming media include solvents in which the shell-forming materials can be dissolved or suspended.

In certain embodiments, the shell has a thickness from 1 to about 6 monolayers. As used herein, the term "monolayer" refers to a single layer of a shell-forming material surrounding the quantum dot core.

In certain embodiments, the core/shell quantum dot has a particle size from about 2 nm to about 6 nm. As used herein, the term "particle size" refers to the particle diameter.

In certain embodiments, the indium phosphide core/shell quantum dot advantageously has a photoluminescent quantum yield from about 40% to about 90%.

The invention also provides an indium phosphide core/shell quantum dot having an indium phosphide core doped with zinc and/or gallium prepared by the methods described herein.

The following is a description of the preparation and characterization of the zinc- and gallium-doped indium phosphide clusters, methods for making zinc- and gallium-doped indium phosphide clusters, methods for making zinc- and gallium-doped indium phosphide quantum dots from the zinc- and gallium-doped indium phosphide clusters, and methods for making zinc- and gallium-doped indium phosphide core/shell quantum dots from the zinc- and gallium-doped indium phosphide quantum dots.

Cluster Cation Exchange with Zn and Ga

In the developments of the present invention, doping InP clusters through a cation exchange process began with treating the cluster with different zinc precursors. Zinc myristate proved to be relatively unreactive toward cation exchange at room temperature, resulting in no zinc incorporation as evidenced by UV-Vis and ^{31}P NMR spectroscopy, whereas treatment with Et_2Zn led to cluster decomposition. Mixed alkyl, carboxylate zinc precursors were examined, including $\text{Zn}_5(\text{Et})_4(\text{OAc})_6$, which has previously been demonstrated to serve as a reactive precursor in the synthesis of zinc phosphide quantum dots (Orchard, K. L.; White, A. J. P.; Shaffer, M. S. P.; Williams, C. K. Pentanuclear Complexes for a Series of Alkylzinc Carboxylates. *Organometallics* 2009, 28 (19), 5828–5832. <https://doi.org/10.1021/om900683z>; Glassy, B. A.; Cossairt, B. M. Resolving the Chemistry of Zn_3P_2 Nanocrystal Growth. *Chem. Mater.* 2016, 28 (17), 6374–6380. <https://doi.org/10.1021/acs.chemmater.6b02782>). Treatment of $\text{In}_{37}\text{P}_{20}(\text{MA})_{51}$ (MA = myristate, $^-\text{O}_2\text{C}(\text{CH}_2)_{12}\text{CH}_3$) with 4–24 molar equivalents of Zn^{2+} using $\text{Zn}_5(\text{Et})_4(\text{OAc})_6$ for 72 hours at room temperature resulted in slight changes in the UV-Vis spectrum and the powder XRD pattern (FIGURES 1A and 1C). The photoluminescence spectra of clusters exposed to these lower $[\text{Zn}^{2+}]$ displayed a broad emissive feature that is distinct from pure InP cluster emission, providing an indication of the extent of zinc doping. The ^{31}P NMR spectrum (FIGURE 1E) of these products shows significant broadening of the primary cluster resonances and slight upfield shifts, suggesting that the structure of the original InP cluster has been altered in a non-site-selective manner while keeping the low-symmetry

phosphide sublattice relatively intact. As determined by ICP-OES, the amount of zinc present in the final material relative to indium increases as the initial $[\text{Zn}^{2+}]$ increases, eventually reaching a maximum of 1.3:1 Zn:In (See FIGURE 2, Table 1, and FIGURE 15). The changes in the core structure upon zinc incorporation are also evident in the MALDI-TOF mass spectra of the doped clusters, where a shift to lower m/z ratios and broadening is observed upon increased zinc incorporation.

Achieving cation exchange with gallium proved more challenging. Precursor development for accessing gallium-based nanomaterials is limited compared to zinc. Common gallium precursors used in quantum dot and vapor-phase deposition synthesis include gallium acetylacetonate, trimethylgallium, and tris(dimethylamido)gallium. No gallium analogue to the mixed alkyl/carboxylate zinc cluster exists, though gallium dimers of the form $[\text{Ga}(\text{R})_2\text{X}]_2$ (R = alkyl, X = carboxylate) have been reported. Brief examination of this gallium reagent as a precursor showed heterogeneous gallium incorporation and was not pursued further. Instead, gallium acetate, $\text{Ga}(\text{OAc})_3$, was chosen as the most suitable gallium precursor due to its synthetic accessibility and ready analogy to the indium acetate precursors common in InP synthesis. Stirring a toluene solution of $\text{In}_{37}\text{P}_{20}(\text{MA})_{51}$ with increasing equivalents of $\text{Ga}(\text{OAc})_3$ at room temperature for 48 hours, followed by cluster purification resulted in UV-Vis absorbance spectra and powder XRD patterns that resemble undoped cluster material (FIGURES 1B and 1D). However, the ^{31}P NMR spectra (FIGURE 1F) show both new resonances attributed to gallium-doped clusters, as well as subtle shifts in the phosphide core resonances of the starting pure-phase cluster, suggesting gallium coordination at the cluster surface. After the cluster has been treated with approximately 16 equivalents of gallium, no further change is observed in the ^{31}P NMR spectra, indicating saturation and no further gallium incorporation. In fact, heating a mixture of InP cluster and 100 eq. $\text{Ga}(\text{OAc})_3$ at 80 °C for 24 hours furnished a ^{31}P NMR spectrum very similar to that of other, more mild doping conditions. This gallium doping saturation is corroborated by the elemental analysis of the treated cluster samples (FIGURE 2), where the Ga:In ratio saturates at approximately 0.07 upon adding 24 equivalents of $\text{Ga}(\text{OAc})_3$ to the cluster (see Table 1), suggesting incorporation of on average 2-3 equivalents of Ga^{3+} into the resultant clusters.

Table 1. Molar ratios of doped cluster species by ICP-OES. The $[\text{Zn}^{2+}]$ source was $\text{Zn}_5(\text{Et})_4(\text{OAc})_6$ and the $[\text{Ga}^{3+}]$ source was $\text{Ga}(\text{OAc})_3$.

Eq. added $[\text{Zn}^{2+}]$ or $[\text{Ga}^{3+}]$ relative to cluster	Zn : In	Ga : In
1 eq.	0.059	0.012
4 eq.	0.105	0.004
8 eq.	0.126	0.051
16 eq.	0.200	0.038
24 eq.	0.246	0.074
37 eq.	0.679	0.076
50 eq.	0.429	0.025
75 eq.	1.061	0.009
100 eq.	1.282	0.011

These results demonstrate how charge and size differences between Zn^{2+} and Ga^{3+} impact the ability of the dopant metals to enter into the InP cluster crystal lattice. While both dopants are smaller than In^{3+} (80 pm), the effective ionic radius of Zn^{2+} (74 pm) matches more closely than Ga^{3+} (62 pm). A similar trend is observed in the chemical hardness, η , where Zn^{2+} (10.88) is more closely matched with In^{3+} (13) compared to Ga^{3+} (17). The mechanism of Zn^{2+} cation exchange likely follows that of Cd^{2+} wherein an initial topotactic surface exchange occurs. In the case of these divalent ions, exchange into the core requires either charge compensation at the surface (i.e., loss of carboxylate) at modest dopant levels or eventual expulsion of phosphorus anions and formation of obligate phosphorus vacancies at high concentrations. This appears to occur in a non-destructive manner in the case of Cd^{2+} because of its similar size (95 pm) and hardness (10.29) when compared with In^{3+} , but in the case of Zn^{2+} , the smaller ionic radius precludes cation exchange into the core without at least partial cluster dissolution. In the case of isovalent Ga^{3+} , the lack of obligate anion loss and vacancy formation eliminates possible mechanisms for relieving strain induced upon incorporation of this smaller cation. Therefore, Ga^{3+} is not readily incorporated beyond the surface. Even exposing the InP cluster to 100 eq. of $\text{Ga}(\text{OAc})_3$ at 80 °C for 24 hours resulted in minimal incorporation or

phosphide lattice dissolution, instead retaining strong interactions between the Ga^{3+} and its associated hard acetate ions. Similar charge-balancing effects have been invoked in gallium for zinc aliovalent cation exchange in InP QDs.

The preparation and characterization of representative Zn-doped InP clusters by cationic exchange are described in Examples 1 and 2. The preparation and characterization of representative Ga-doped InP clusters by cationic exchange are described in Example 2.

Conversion of Doped Clusters to InP and Core/Shell QDs

The modified InP clusters (i.e., Zn- and Ga-doped InP clusters) were utilized as single-source precursors for synthesizing high PLQY InP QDs. First, the cluster conversion to doped InP QD cores was examined to determine if dopant concentrations can be maintained upon QD synthesis. The conversion of InP clusters to larger QDs has previously been studied, identifying high temperatures and short reactions times as optimal for producing monodisperse QD samples. Zinc- and gallium-doped clusters were dissolved in 1 mL 1-octadecene (1-ODE), and rapidly injected into a flask of 1-ODE at 300 °C. The reaction was monitored by UV-Vis and PL spectroscopy and after 15 minutes of core growth, the reaction was cooled, and the resulting material was purified. With increasing zinc content, the final absorbance feature (FIGURE 3) blue-shifted from 580 nm (0 eq added Zn^{2+}) to a less defined feature at 490 nm (100 eq added Zn^{2+}). The absorbance features of the two samples with greater than 50 eq. added Zn continued to blue-shift even at room temperature in the day following QD growth, indicating instability of the resultant doped materials.

The trend observed in the absorbance spectra for zinc doped InP QDs is reflected by the particle sizes measured by transmission electron microscopy (TEM). Representative TEM images of samples treated with initial $[\text{Zn}^{2+}]$:cluster ratios of 1, 4, and 16 indicate particle diameters of 2.6 nm, 2.3 nm, and 2.1 nm (see FIGURE 16B). The moderate size differences across this family of zinc-doped InP QDs is consistent with previous reports of zinc-doped InP QDs prepared from mixtures of indium and zinc carboxylates and $\text{P}(\text{TMS})_3$, wherein the presence of zinc during nucleation serves to moderate the precursor reactivity and results in smaller particles. In a number of the imaged samples and corroborated through powder XRD (FIGURE 16A), the presence of In_2O_3 was observed which is

consistent with other reports of Zn-doped InP prepared from molecular precursors of indium and zinc carboxylates and tris(trimethylsilyl)phosphine. At higher $[\text{Zn}^{2+}]$:cluster ratios, a high level of morphological variation is observed, precluding quantitative size measurement. This variation is also observed in the powder XRD patterns at high $[\text{Zn}^{2+}]$:cluster ratios, which are significantly broadened, indicating a loss of crystallinity (see FIGURE 16A). The powder XRD patterns of samples treated with initial $[\text{Zn}^{2+}]$:cluster ratios of 1, 4, and 16 do not display peak shifts to higher degrees 2θ , which would correspond to lattice contraction consistent with homogeneous zinc alloying throughout the crystalline domain. This suggests that zinc doping is heterogeneous and likely limited to the outer layers of the InP QDs.

The PLQY of the doped clusters correlates with the extent of zinc incorporation, increasing from 0.2% for the undoped samples to 19% PLQY with the QDs synthesized from doped clusters using 16 equivalents of $[\text{Zn}^{2+}]$ (see FIGURE 17). These PLQYs are comparable to the range reported for zinc-doped InP QDs prepared by a one-pot synthesis from molecular precursors and with reports of post-synthetic functionalization of InP surfaces with Zn^{2+} as a Z-type ligand. The measured Zn:In ratios of these QDs are higher compared to that of the measured Zn:In ratios in the doped cluster precursors, indicating that higher concentrations of zinc can be incorporated into the QD crystal lattice. It has been posited by that phosphorus vacancies form to balance charge as zinc is incorporated, which is consistent with our experimental data (Pietra, F.; De Trizio, L.; Hoekstra, A. W.; Renaud, N.; Prato, M.; Grozema, F. C.; Baesjou, P. J.; Koole, R.; Manna, L.; Houtepen, A. J. Tuning the Lattice Parameter of $\text{In}_x\text{Zn}_y\text{P}$ for Highly Luminescent Lattice-Matched Core/Shell Quantum Dots. *ACS Nano* 2016, 10 (4), 4754–4762. <https://doi.org/10.1021/acsnano.6b01266>).

The gallium-doped clusters are also effective precursors for synthesizing doped InP QDs. Unlike the zinc-doped QDs, gallium-doped QDs exhibit a slight redshift in the absorbance feature compared to undoped material (see FIGURE 3). This suggests that the gallium ions are not accumulating at high concentrations in the crystal lattice and are not contributing significantly to the electronic structure of the QDs, because GaP has a larger bandgap than InP. This is corroborated by the powder XRD patterns, which is

predominantly zincblende InP (see FIGURE 18), and the ICP-OES analysis, which indicates similar Ga:In ratios as were found in the doped cluster samples (See Table 2).

Table 2. Molar ratios of gallium-doped InP QD species by ICP-OES.

Eq. added $[Ga^{3+}]$ relative to cluster	Ga:In in QDs
1 eq.	0.016
8 eq.	0.062
16 eq.	0.042
24 eq.	0.113
37 eq.	0.098
50 eq.	0.031
75 eq.	0.007
100 eq.	0.009

5 Further, in contrast to the zinc-doped InP QDs, the gallium-doped species exhibited <1% PLQY across the series, similar in nature to undoped InP QDs.

The Zn- and Ga-doped InP QD materials were used as synthons for high PLQY QD materials. Zinc-doped InP QD cores were expected to interface more epitaxially with ZnSe and ZnS shells (having a 7.7% and 3.4% lattice mismatch, respectively, with InP), as the zinc doping should improve the lattice mismatch. A ZnSeS gradient alloy shell was selected to mitigate direct contact between ZnS and InP and to confine the exciton to the core more effectively (via a type 1 core/shell architecture). Experimental conditions for shell growth were adapted from a report by Lee and co-workers who were able to synthesize InP/ZnSeS via molecular precursors with PLQYs up to 65% with 70 nm FWHM emission linewidths (Lim, J.; Bae, W. K.; Lee, D.; Nam, M. K.; Jung, J.; Lee, C.; Char, K.; Lee, S. InP@ZnSeS, Core@Composition Gradient Shell Quantum Dots with Enhanced Stability. *Chem. Mater.* 2011, 23 (20), 4459–4463. <https://doi.org/10.1021/cm201550w>). Briefly, zinc stearate was added in excess of InP (10:1 Zn:In in the case of undoped cluster samples) at 200 °C, after which a solution of TOPSe followed by TOPS was added. Under these conditions, a ZnSeS shell of approximately 5 monolayers was targeted. After

incubation, the temperature was gradually increased (see experimental section below for complete details).

The PLQYs of InP/ZnSeS particles with initial $[\text{Zn}^{2+}]$:cluster ratios of 0, 4, 8, and 16 are presented in FIGURES 4A-4D, respectively. There is a direct correlation between increased PLQY and increasing $[\text{Zn}^{2+}]$:cluster ratios during the initial cation exchange reaction, where the highest PLQY, 85%, was measured for the sample with initial $[\text{Zn}^{2+}]$:cluster ratio of 16. While the emission linewidths are broad in comparison to other shelling procedures that report linewidths in the range of 40-60 nm, there is a consistent decrease in linewidth from samples with initial $[\text{Zn}^{2+}]$ of 0 equivalents (85 nm) to $[\text{Zn}^{2+}]$ of 16 equivalents (66 nm). This decrease in FWHM is likely a result of increasingly uniform shell deposition.

To investigate whether these results are the effect of increasing zinc doping into clusters or rather just the presence of zinc in the reaction mixtures, experiments were performed in which zinc doping via cation exchange did not occur prior to cluster conversion. In these experiments, InP clusters were briefly (2 hours vs 72 hours) exposed to 4, 8, and 16 equivalents of $[\text{Zn}^{2+}]$. At this short time interval, doping was not observed in the 2 h samples as evidenced by ^{31}P NMR spectroscopy or UV-Vis / PL spectroscopy. These samples were then converted to InP QDs via hot-injection and subjected to shell growth via analogous conditions. The optical properties of QDs prepared from cation-exchanged clusters (72 hours) were significantly different compared to samples that were only briefly exposed to zinc cations (see FIGURE 4, light squares versus dark circles), exhibiting universally higher PLQY and comparable FWHM. These results indicate the importance of fully equilibrating zinc into the InP cluster lattice during cation exchange, and the effects that full cation exchange has on subsequent QD core/shell synthesis.

Gallium-doped clusters were next employed as single-source precursors for core/shell QD synthesis using similar reaction conditions. While the levels of gallium doping are lower compared to that of zinc, it was still expected that the presence of gallium might aid in the formation of a more defect-free core/shell interface. This should arise from the smaller ionic radius of gallium acting to contract the overall InP lattice constant and aligning it more closely with ZnSe and ZnS. Subjecting the gallium-doped cluster samples

to core/shell QD synthesis furnished InP/ZnSeS materials with PLQYs in the range of 45-60% (FIGURES 5 and 19). In contrast to the zinc-treated clusters, the cluster samples exposed to higher initial $[Ga^{3+}]$ during cation exchange exhibited a lower PLQY after the shelling procedure as compared to undoped samples. Furthermore, the FWHM of PL emission for the gallium-doped InP/ZnSeS materials increased significantly as the PLQY decreased, indicating that exposing InP clusters to increasing concentrations of $Ga(OAc)_3$ has a deleterious effect on both the PLQY and the FWHM of excitonic emission. The powder XRD patterns for these core shell materials showed reflections shifted away from pure zincblende InP, indicating that the ZnSeS shell has interfaced with the InP core. ICP results (Table 3) demonstrate that the gallium concentration relative to indium in the final core/shell material is similar to the unshelled InP QDs.

Table 3. ICP ratios of gallium doped InP/ZnSeS core-shell QDs.

Eq. added $[Ga^{3+}]$ relative to cluster	Ga : In	Zn : In	Se : In	S : In	P : In
4 eq.	0.015	4.00	0.60	3.12	0.73
8 eq.	0.035	6.71	0.49	3.58	0.98
16 eq.	0.050	7.78	0.63	--	0.72
24 eq.	0.103	4.81	0.40	0.30	0.61
37 eq.	0.101	3.76	0.45	0.15	0.75
75 eq.	0.002	2.36	0.79	0.59	0.82
100 eq.	0.002	2.69	0.65	0.10	0.78

The distinct reactivity between zinc-doped and gallium-doped clusters raises the concern that the diminished PLQY observed with gallium-doped clusters might be a result of the relatively low concentrations of gallium achievable through cluster cation exchange. Gallium acetate exhibited lower reactivity toward cation exchange than $Zn_5(Et)_4(OAc)_6$, and as a result the concentration of gallium in the clusters (and later, in the core/shell QDs) was much lower compared with zinc-doped clusters. Thus, a method was developed for increasing the extent of gallium incorporation as a means to evaluate the effect of gallium content on the resultant QD PLQY. The reaction of InP clusters with 4, 8, and 16

equivalents of $[\text{Ga}^{3+}]$ using $[\text{Ga}(\text{NMe}_2)_3]_2$ in toluene solvent at room temperature resulted in a red-shifting of the primary absorbance feature. It should be noted that this shift is similar to what has been observed upon treatment of InP clusters with primary amine, and therefore may be an effect of ligand exchange rather than an indication of cation exchange.

- 5 The ^{31}P NMR spectra for this series of cation-doped clusters indicated a loss of the characteristic cluster phosphide resonances, and at 8 and 16 equivalents of $[\text{Ga}^{3+}]$ a broad feature is observed in the phosphide region. ICP results of purified clusters indicate that upon exposure to 8 and 16 equivalents of $[\text{Ga}^{3+}]$, the resultant materials had an In:Ga ratio of 1:0.24 and 1:0.43, respectively (see Table 4), a significant increase in gallium content
10 relative to using $\text{Ga}(\text{OAc})_3$.

Table 4. ICP ratios of gallium doped InP clusters using $[\text{Ga}(\text{NMe}_2)_3]_2$.

Eq. added $[\text{Ga}^{3+}]$ relative to cluster	In : Ga : P in purified cluster material
4 eq.	1 : 0.015 : 0.52
8 eq.	1 : 0.035 : 0.51
16 eq.	1 : 0.050 : 0.51
16 eq. + 16 eq. myristic acid	1 : 0.103 : 0.53

- While it is difficult to determine the extent of cation exchange in this reaction relative to gallium incorporation on the surface, these samples present a useful comparison
15 as gallium-rich precursors for core/shell QDs.

- Using these gallium-rich materials in the synthesis of InP/ZnSeS in an analogous method as before, did not produce material with PLQY greater than that obtained from undoped clusters. Instead, PLQY between 58% and 74% were obtained using these samples. ICP analysis reveals that these materials have higher gallium content, exhibiting
20 In:Ga ratios of up to 1:0.16 (see Table 5).

Table 5. ICP ratios and PLQY of gallium doped InP/ZnSeS core-shell QDs using $[\text{Ga}(\text{NMe}_2)_3]_2$.

Eq. added $[\text{Ga}^{3+}]$ relative to cluster	In : Ga in core-shell QD material	PLQY in core-shell QD material
4 eq.	1 : 0.11	74%
16 eq.	--	15%
16 eq. + 16 eq. myristic acid	1 : 0.16	58%

A further complication with this method arises from the poor stability from these
 5 doped clusters due to the presence of the amide ligands. In fact, when using cluster exposed
 to 16 eq. $[\text{Ga}^{3+}]$ in the absence of stabilizing myristic acid ligands, QD dissolution and
 decomposition was observed during synthesis, resulting in 15% PLQY in the final material.
 The presence of myristic acid is helpful in improving the solubility and stability of the
 clusters without affecting the cluster In:Ga ratios (see Table 4). These results indicate that
 10 even using gallium-rich clusters, no discernable increase in PLQY is obtained upon
 core/shell QD synthesis, and that using $[\text{Ga}(\text{NMe}_2)_3]_2$ to introduce gallium into the cluster
 presents further complications regarding cluster stability and solubility.

A similar trend in PLQY is observed following the post-synthetic surface-treatment
 of native, unshelled InP QDs with metal carboxylates. In previous work, treatment of InP
 15 QDs with either cadmium carboxylate or zinc carboxylate resulted in significant
 enhancement in PLQY (increasing from <1% PLQY to 16% for Zn treatment and 30% for
 Cd treatment) (Stein, J. L.; Mader, E. A.; Cossairt, B. M. Luminescent InP Quantum Dots
 with Tunable Emission by Post-Synthetic Modification with Lewis Acids. *J. Phys. Chem.
 Lett.* 2016, 7 (7), 1315-1320. <https://doi.org/10.1021/acs.jpclett.6b00177>). This PLQY
 20 enhancement was attributed to passivation of the surface trap states by the metal
 carboxylate that was facilitated by the high affinity for Cd^{2+} and Zn^{2+} to bind to the surface
 of the QD. Treating InP QDs with gallium myristate in an analogous manner resulted in a
 slight blueshift in the absorbance peak yet did not produce a PLQY enhancement. This
 lack of surface passivation and PLQY enhancement may arise from low thermodynamic

driving forces for gallium binding or cation exchange, which in turn are a function of the smaller size and higher chemical hardness of gallium ions compared to indium and higher obligate ligand (anion) coordination number compared to zinc.

5 The preparation and characterization of representative Zn-doped InP quantum dots and Zn-doped InP core/shell quantum dots are described in Examples 1 and 2. The preparation and characterization of representative Ga-doped InP quantum dots and Ga-doped InP core/shell quantum dots are described in Example 2.

10 In summary, as described herein, InP clusters were doped with Zn^{2+} and Ga^{3+} by cation exchange. The most effective zinc precursor was a mixed alkyl-carboxylate cluster, $\text{Zn}_5(\text{Et})_4(\text{OAc})_6$, whereas both $\text{Ga}(\text{OAc})_3$ and $[\text{Ga}(\text{CH}_3)_2(\text{MA})]_2$ displayed similar activity toward cluster doping. Zinc demonstrated efficient doping of the cluster while gallium proved resistant toward cluster doping. This disparity in reactivity may be due to differences in chemical hardness, ionic radii, and valency of Zn^{2+} and Ga^{3+} compared to In^{3+} . These doped cluster samples were then evaluated as precursors for emissive
15 InP/ZnSeS core shell nanomaterials. The zinc-doped samples exhibited improved emissive performance (PLQY and FWHM) compared to undoped samples, achieving 85% PLQY and 70 nm FWHM in the final material after exposing the InP cluster to 16 eq $[\text{Zn}^{2+}]$. The InP/ZnSeS core shell material using gallium-doped clusters exhibited lower emissive performance even after developing a strategy to obtain higher gallium doping using
20 $[\text{Ga}(\text{NMe}_2)_3]_2$.

As used herein, the term "about" refers to $\pm 5\%$ of the specified value.

The following examples are provided for the purpose of illustrating, not limiting, the invention.

EXAMPLES

25 Materials and Methods

All glassware was dried in a 160 °C oven overnight prior to use. All reactions, unless otherwise noted, were run under an inert atmosphere of nitrogen using a glovebox or using standard Schlenk techniques. Diethyl zinc and $\text{P}(\text{SiMe}_3)_3$ is pyrophoric, extremely reactive, and should be handled with caution. Indium acetate (99.99%), myristic acid
30 (99%), gallium nitrate hydrate (99.9%), zinc acetate (99.99%), zinc stearate, acetic

anhydride, trioctylphosphine (TOP), (97%), sulfur (>99%), selenium (99.99%), and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile DCTB ($\geq 99.0\%$) were purchased from Sigma-Aldrich Chemical Co. and used without further purification. [Ga(NMe₂)₃]₂ (98%) and diethylzinc (>95%) was purchased from Strem Chemicals and used without further purification. Bio-Beads S-X1 were purchased from Bio-Rad Laboratories. All solvents, including 1-ODE, toluene, pentane, ethyl acetate, and acetonitrile, were either purchased from Sigma-Aldrich Chemical Co., or collected from a still and stored over 4 Å molecular sieves in a nitrogen-filled glovebox. 1-Octadecene was dried over CaH₂, distilled, and stored over 4 Å molecular sieves in a nitrogen-filled glove box. C₆D₆ was purchased from Cambridge Isotope Laboratories and were similarly dried and stored. Bio-Beads S-X1 were purchased from Bio-Rad Laboratories. Omni Trace nitric acid was purchased from EMD Millipore and used without further purification. 18.2 MΩ was collected from an EMD Millipore water purification system. P(SiMe₃)₃ was prepared following literature procedures (Gary, D. C.; Cossairt, B. M. Role of Acid in Precursor Conversion During InP Quantum Dot Synthesis. *Chem. Mater.* 2013, 25 (12), 2463–2469. <https://doi.org/10.1021/cm401289j>).

³¹P and ¹H NMR spectra were collected on a 700 MHz Bruker Avance spectrometer. UV–Vis spectra were collected on a Cary 5000 spectrophotometer. TEM images were collected on an FEI Tecnai G2 F20 microscope using ultrathin carbon film on holey carbon grids purchased from Ted Pella Inc. Powder X-ray diffraction patterns were collected with a Bruker D8 Discover with IμS 2-D XRD system. Fluorescence and quantum yield measurements were taken on a Horiba Jobin Yvon FluoroMax-4 fluorescence spectrophotometer with the QuantaPhi integrating sphere accessory. ICP-OES was performed using a Perkin Elmer Optima 8300. MALDI-TOF mass data were collected on a Bruker Autoflex II instrument using DCTB as the matrix. All XPS spectra were collected using a Surface Science Instruments S-probe spectrometer. Cluster samples dispersed in toluene were mixed with toluene solutions of the matrix and spotted on a stainless-steel plate in a glovebox. Desorption and ionization of samples was achieved by irradiation with a pulsed nitrogen laser. Mass spectra were measured with the detector in linear positive mode with a laser intensity between 5-15%. Calibration was performed

using external standards ubiquitin I, myoglobin and cytochrome C. Data was smoothed and fitted in Igor Pro using binomial smoothing algorithms.

Example 1

The Preparation and Characterization of Representative Zn-doped InP Clusters,

Zn-doped InP Quantum Dots, and Zn-Doped InP Core/Shell Quantum Dots

In this example, the preparation and characterization of representative Zn-doped InP clusters, Zn-doped InP quantum dots, Zn-doped InP core/shell quantum dots are described. As described below, the Zn-doped InP quantum dots were prepared from InP clusters by cationic exchange.

Cadmium cation exchange demonstrated that the InP MSC undergoes facile cation exchange and structural rearrangement with full conversion to Cd_3P_2 (Tessier, M. D.; Dupont, D.; De Nolf, K.; De Roo, J.; Hens, Z. Economic and Size-Tunable Synthesis of InP/ZnE (E = S, Se) Colloidal Quantum Dots. *Chem. Mater.* 2015, 27 (13), 4893–4898. <https://doi.org/10.1021/acs.chemmater.5b02138>). Using this model, the analogous reaction with zinc was evaluated, noting the differences in polarizability, ionic radius, and charge of these cations. Whereas Cd^{2+} is a softer acid than In^{3+} , with a chemical hardness η of 10.29, Zn^{2+} (10.88) lies closer to In^{3+} (13) as an intermediately hard acid. In addition to this less favorable replacement in a soft P anionic lattice, the single bond covalent radius difference between In (142 pm) and Zn (122 pm) may induce structural contraction.

The InP cluster was used as a platform for zinc cation exchange to provide Zn-doped InP clusters useful as precursors for InP QDs that would be more susceptible to epitaxial-like shell growth of ZnE (E = S or Se). Selecting an appropriate zinc source for these reactions was paramount. Unlike the immediate reaction we observed between cadmium carboxylate and InP MSCs, zinc carboxylates could be considered fairly inert with additional complications arising from solubility in compatible solvents. Three zinc precursors with a range of reactivities were evaluated: zinc myristate [$\text{Zn}(\text{MA})_2$], a pentanuclear zinc cluster [$\text{Zn}_5(\text{O}_2\text{CH}_3)_6(\text{Et})_4$] denoted Zn5 cluster, and diethyl zinc (ZnEt_2). The predicted range of reactivity is based on previous NMR studies performed between these precursors and $\text{P}(\text{SiMe}_3)_3$ in the synthesis of Zn_3P_2 QDs. Initial experiments evaluated the reactivity of these species with InP MSCs by tracking the UV-Vis absorption

and analyzing the structural composition of the resulting products with pXRD and ^{31}P NMR spectroscopy. From this series of zinc precursors, varying the concentration and reaction temperature led to assessing that the Zn5 cluster, added to the InP MSC at room temperature, resulted in the most robust and isolable products. Proceeding forward, cation exchange reactions were performed by titrating a solution of Zn5 cluster into InP MSCs and stirring at room temperature until the reaction was gauged complete by ^{31}P NMR after 3 days. The modified electronic and physical properties of alloyed clusters were characterized using UV-Vis/NMR spectroscopy and MALDI-TOF/XRD/ICP.

InP Clusters as a Scaffold for Zinc Cation Exchange

The optical transitions of the $\text{In}_{37}\text{P}_{20}$ MSC can be diagnostic of reactions taking place at the surface, including with amines, water, and cadmium carboxylates. Room temperature titration of Zn5 lead to negligible shifts of the absorbance maximum up to 37 equivalents of Zn^{2+} relative to the MSC, shown in FIGURE 6. Above 37 equivalents, the cluster peak starts to blue-shift and broaden, which was assigned as the gradual dissolution of InP through zinc incorporation into the core that leads to cluster destabilization. The surface interaction of exogeneous ligands or Lewis acids strongly impacts the electronic transitions (HOMO-1 to LUMO and HOMO to LUMO) responsible for the lowest energy absorption feature given that much of the electronic density of these orbitals is localized near the surface. The following data and characterization support the hypothesis that zinc does indeed exchange with indium on the surface of the cluster, thus one possibility for the unchanging absorbance feature is that the energetic overlap between zinc and the cluster is minimal or otherwise closely aligned with indium.

While the absorbance maximum is persistent at 386 nm, the PL of the cluster is not. At 298 K, the InP MSC consistently exhibits weak emission, shown in FIGURE 6B, that is associated with structural distortions of the cluster upon excitation. In larger as-synthesized InP quantum dots, the photoluminescence quantum yields (PLQYs) are <1% due to non-radiative pathways arising from under-coordinated or oxidized surface sites. In the case of InP QDs, the replacement of zinc for indium and concurrent passivation of phosphorus improved the PLQYs. After several days, all samples stirring with Zn5 cluster exhibited growth of a distinct broad emission feature centered at 526 nm (90 nm FWHM),

shown in FIGURE 6. The weak intensity did not significantly change by increased relative zinc equivalents between 4-37, while at concentrations above 37 equiv., the PL decreased, corresponding to the diminishing absorbance feature and gradual dissolution of the cluster. Growth of this proposed PL band edge feature is believed to be related to the Z-type ligand exchange of zinc for indium exclusively between the 16 indium ions on the surface of the cluster, comparable to observations with InP QDs. This effect is likely satisfied with the replacement of just a few surface indium ions while further zinc addition up to 37 equivalents suggests that the energy loss pathways still originate from the core lattice vibrations. The broadness of the emission feature is also related to the non-selective nature of cation exchange and what is likely an average population of clusters with similar but variable structures and compositions.

Discerning the structural impact of indium-to-zinc exchange is aided by ^{31}P NMR spectroscopy. The pseudo- C_{2v} -symmetric InP cluster has 11 unique phosphorus environments (two P atoms reside on the molecular C2 axis, and the remaining 18 P atoms are related by the C2 axis resulting in nine additional resonances), shown in FIGURE 7, which can be assigned to different sites based on their proximity to In-O neighbors and shielding arguments. The addition of 4 equiv. Zn slightly broadens the distinct resonances as expected with a difference in shielding tensors and this effect is observed with further equivalents of zinc due to the non-site selective nature of the exchange. Zinc phosphide nanocrystals have a phosphorus resonance at -200 ppm which would be consistent with the lack of significant shifts in this series of alloyed clusters. In comparison, a progressive upfield shift was observed with cadmium cation exchange as the alloyed cluster took on increasing cadmium-phosphide character, where Cd_3P_2 clusters have a phosphorus resonance at -364 ppm.

Mass spectrometry has proven to be a valuable technique for the identification of semiconductor nanoclusters and their alloyed derivatives. Previously, the mass spectrum of phenylacetate-capped $\text{In}_{37}\text{P}_{20}$ MSCs obtained using MALDI-TOF showed that the largest mass peak was centered at $8,500$ m/z, indicating that a portion of the intact cluster (mass $11,759$ g/mol) must be displaced during ionization. Since then, a series of carboxylate-ligated $\text{In}_{37}\text{P}_{20}$ MSCS were characterized to identify a consistent fragmentation

pattern that can aid in the identification of alloyed intermediates. Shown in FIGURES 8A-8C are the mass spectra of phenylacetate, oleate, and myristate-capped InP MSCs with the zoom inset highlighting the largest and most apparent mass peak. The masses of these fragments correspond closely to a parent fragment ion that retains an
5 $[\text{In}_{21}\text{P}_{20}]^{3+}$ core, 10 surface-coordinated $\text{In}(\text{O}_2\text{CR})_3$, and 2 $^-\text{O}_2\text{CR}$, with the respective carboxylate ligands.

A mass profile was determined through the exchange of zinc and indium, as shown in FIGURE 9. Following addition of any amount of zinc to cluster, the largest mass peak broadens significantly. This may be attributable to the non-selectivity of exchange in
10 which zinc does not preferentially replace the 10 $\text{In}(\text{O}_2\text{CR})_3$ remaining on the parent fragment, in addition to the strong probability that there is a distribution of clusters with less or more zinc exchanged for indium. Also, it cannot be disregarded that any potential zinc intercalating into the core would need to account for charge balance. Noticeably, the 4 Zn sample has a broad peak that is not shifted beyond that of the pure InP MSC which may be
15 telling of more preferential exchange with the indium carboxylates that are lost during irradiation and ionization. Conversely, samples with 8 Zn and higher were shifted to smaller masses. Envisioning a cluster with partial surface exchange of zinc for indium and replacing half of the ten $\text{In}(\text{O}_2\text{CR})_3$ with $\text{Zn}(\text{O}_2\text{CR})_2$ corresponds to a fragment mass of 10,070 m/z, as indicated by the dashed black line that crosses through the broad peak of
20 8 Zn. Furthermore, in the case of hypothetical complete surface exchange with zinc, the fragment mass would be 8,684 g/mol, shown by the second dashed line, intersecting with the 16 Zn and 37 Zn sample peaks. These mass fragment distributions strongly support our assignment of primarily surface exchange with zinc, i.e., topotactic exchange. At higher concentrations of added zinc, interpretation of cluster fragmentation becomes more
25 challenging as the cluster dissociates in a less predictable manner, consistent with cluster dissolution.

To complement these findings, compositional analysis of purified samples was performed. To verify removal of free Zn^{2+} , alloyed cluster samples were purified by gel permeation chromatography (GPC) in which two consecutive columns were completed
30 with aliquots taken after each column fraction for ICP analysis. The molar ratios of each

aliquot verified that free Zn5 was removed following a single GPC purification. The plots in FIGURES 10A and 10B show the Zn:P molar ratio of purified samples measured by ICP versus the initial reaction stoichiometry. The dashed line is representative of 1:1 cation exchange, at least to 37 equivalents, beyond which an excess of zinc was useful to evaluate the role of zinc concentration and verify if conversion to Zn₃P₂ nanomaterials was accessible. At lower equivalents, exchange appears to occur nearly stoichiometrically while above 4 equivalents, the composition deviates from stoichiometric exchange and seemingly plateaus at 37 equivalents (see FIGURE 10B, zoomed out plot).

Based on the gradual disappearance of the cluster absorbance feature and significant broadening of the ³¹P NMR cluster resonances, the measured molar ratios of samples with 50, 75, and 100 zinc equivalents represent an amorphous mixed metal phosphide series of compounds. This data indicates that beyond the exchange of surface indium carboxylate, it is likely that only a few zinc atoms diffuse into the In₂₁P₂₀³⁺ core before destabilization. The powder X-ray diffraction pattern hints at this eventual dissolution as well. The distinct cluster crystal twist-boat phase is primarily conserved at 4 and 16 zinc equivalents but there is a minor shift to higher diffraction angles in the 16 Zn sample which would correspond to lattice contraction (FIGURE 10).

Together, these data support a mechanism of exchange between the 16 surface indium and zinc from the Zn5 cluster, after which several zinc atoms may exchange within the In₂₁P₂₀⁺ core but a threshold is reached leading to destabilization of the cluster. The formation of a zinc phosphide cluster was not observed under these conditions. A similar initial progression of cation exchange was observed between cadmium and InP MSCs as well, but differences between the HSAB profile and ionic radius of cadmium and zinc, and the lattice energy of the resulting II-V cluster limit further stable intercalation of zinc atoms into the strained InP cluster core.

Alloyed Cluster Single-Source Precursors for Quantum Dots

InP QDs were grown via a hot injection of InP alloyed clusters (40 mg dissolved in 1 mL 1-octadecene [ODE]) into a bath of ODE (5 mL) at 290 °C under a nitrogen atmosphere. Unlike other MSC materials that progress towards larger nanomaterials via Ostwald staging, i.e., quantized monomer addition, or oriented attachment, InP particle

evolution occurs by cluster dissolution and re-nucleation by monomer species distinct from those derived from molecular precursors involving $\text{P}(\text{SiMe}_3)_3$. Growth reactions were monitored by UV-Vis and PL spectroscopy (FIGURE 11) and growth was complete within 5-10 minutes over all concentrations of zinc (0-100 equivalents). Based on the absorbance values at high energy wavelengths, the concentration of InP particles was consistent across reactions performed under these conditions. With increasing zinc content, the final LEET blue-shifted from 580 nm (0 Zn) to a less defined feature at 490 nm (100 Zn). Furthermore, the samples with 50+ equivalents of zinc continued to blue-shift at room temperature in the day following QD growth, indicating that the product obtained at elevated temperatures could not maintain a stable crystal phase.

The trend observed in the absorbance spectrum is reflected by the particle sizes measured by transmission electron microscopy (TEM). A representative TEM image of 1 Zn, 4 Zn, and 16 Zn is shown in FIGURE 12B where measured particle diameters are 2.6 nm, 2.3 nm, and 2.1 nm, respectively. Particle diameters were not measured for the 37 Zn sample due to the observed morphology variation and it is possible that amorphous Zn_3P_2 exists among the diverse population of particles present. Additionally, the pXRD pattern of the 37 Zn sample was significantly broadened, indicating a loss of crystallinity (FIGURE 12A). InP QDs with a ratio of 0, 4, 8, and 16 Zn:MSC were evaluated.

Notably, only QD reactions that included some amount of zinc were accompanied by the formation of ca. 11 nm diameter In_2O_3 nanocrystals (shown in FIGURE 12B, TEM images), as confirmed by lattice fringe analysis and pXRD. In_2O_3 by-products have been previously observed as a thermolysis product of indium carboxylates that were displaced from InP QD surfaces by zinc and cadmium carboxylates. It is believed that zinc substitutes into indium sites and the ejected indium carboxylates decompose as In_2O_3 , and this process is initiated during cluster dissolution and growth because In_2O_3 was observed regardless of the extent of alloyed cluster precursor purification.

In_2O_3 diffraction peaks overlap with two of the major InP diffraction peaks at 43 and 53 2θ . While most of the In_2O_3 can be removed through careful size selective precipitation, a thorough analysis of the InP diffraction patterns has been limited. A cursory examination of the InP pXRD data does reveal that no other crystalline phosphide phases

are present. Homogeneous zinc alloying, or lattice contraction, would be distinguishable by shifts to higher angles which is not apparent in the strongest peak at 26 2 θ . Thus, it is believed that the extent of zinc alloying that occurs is limited to the outer layer of the InP QD.

5 In agreement with surface zinc passivation, the measured InP PL QYs increase from 0.15% up to 19% in 0 Zn and 16 Zn, respectively (FIGURES 13A-13D), although this quantification includes both InP band edge emission and the non-suppressed trap emission. These QYs are also comparable to the range reported for zinc-alloyed InP QDs prepared by a one-pot molecular precursor synthesis. The compositional analysis of our particles (4,
10 8, and 16 Zn equivalents) shows that zinc, indium, and phosphorus are all present. The measured Zn:P ratio nearly doubles from that of the measured Zn:P in the alloyed clusters (FIGURES 10A-10D).

 Although there is no discernable lattice contraction suggested by the X-ray diffraction patterns, the impact of zinc alloying on the lattice parameter of these InP QDs
15 was studied. ZnS and ZnSe have a 7.6% and 3.4% lattice mismatch with InP, respectively, but the detrimental impact of lattice strain can be alleviated through the formation of a gradient alloy at the interface and consequently, improve core-shell optical properties. ZnSeS gradient alloy shell was selected to mitigate direct contact between ZnS and InP and to confine the exciton in the core more effectively than ZnSe with ZnS. Experimental
20 conditions were optimized to afford PLQYs up to 65% and 70 nm FWHM emission linewidths (Gary, D. C.; Petrone, A.; Li, X.; Cossairt, B. M. Investigating the Role of Amine in InP Nanocrystal Synthesis: Destabilizing Cluster Intermediates by Z-Type Ligand Displacement. *Chem Commun* 2017, 53 (1), 161–164. <https://doi.org/10.1039/C6CC07952K>). Briefly, zinc stearate was added in excess of InP
25 (10:1 Zn:In) at elevated temperatures after which a solution of TOPSe and TOPS was added over a gradual heat-up. Further details regarding shell growth are described below.

 The plot in FIGURE 14 summarizes the measured PL QYs of InP/ZnSeS particles with an initial Zn:MSC ratio of 0, 4, 8, and 16. There is a direct correlation between improved PL QYs and increasing Zn:MSC ratios where the highest QY, 85%, was
30 measured for the 16 Zn sample. In contrast, a 55% PL QY was measured for the

non-alloyed InP QD control sample. While the emission linewidths are broad in comparison to other shelling procedures that report linewidths in the range of 40-60 nm, there is a consistent decrease from 0Zn, 85 nm FWHM at 586 nm, to 16Zn, 66 nm FWHM at 556 nm, which likely corresponds to more uniform shell deposition.

5 InP QD growth reactions were performed in a fashion analogous to the molecular precursor approach. InP MSCs were stirred with Zn5 for only 2 hours, over which evidence of alloying was not observed by PL or ^{31}P NMR spectroscopy, then these compounds were converted to InP QDs via hot-injection at 290 °C. The QD optical properties of the 2 hour cation exchange reaction were comparable to that of the 3 day cation exchange but
10 following shell growth, a stark difference can be seen between the two experiments (FIGURE 14). Clusters that were only given 2 hours to react with Zn5 before QD growth had consistently lower PL QYs with a maximum of 70%, considered to be direct evidence identifying the importance of equilibrating to an alloyed cluster end-product before utilizing these materials as single-source precursors.

15 As described herein, in one aspect of the invention, a topotactic exchange of zinc for the 16 surface indium of the $\text{In}_{37}\text{P}_{20}$ MSC along with gradual cluster dissolution was observed as zinc initially diffuses into the core. The replacement of indium with this divalent cation with a shortened M-P bond length contributes to structural instability. The formation of robust InP clusters with pre-formed Zn-P bonds can be utilized as a single-
20 source precursor for alloyed InP QDs. Because nanocrystal growth proceeds via dissolution of the cluster, rather than oriented attachment or Ostwald staging, this synthetic route benefits from monomer species unique from those in the molecular nucleation pathways. Upon shelling, a clear trend was observed in which the QYs of InP/ZnSeS increased from 55% to 85% on the basis of Zn:MSC concentration. The improved InP QD
25 optical properties is attributable to zinc alloying at the surface considering the absence of significant lattice contraction. Notably, the optical properties of InP/ZnSeS core/shell nanocrystals are greatly improved, indicated by an increase in PL QY of approximately 10%, following equilibration of the alloyed cluster precursors prior to QD growth. Atomically precise InP MSCs provide a robust model for cation exchange studies and have

now been applied as viable precursors towards larger alloyed nanocrystals, expanding upon the valuable chemistry of composition tailoring in covalent III-V materials.

Experimental

Synthesis of InP MSCs

5 InP magic-sized clusters (MSCs) were synthesized following a modified preparation (Xi, L.; Cho, D.-Y.; Besmehn, A.; Duchamp, M.; Grützmacher, D.; Lam, Y. M.; Kardynal, B.E. Effect of Zinc Incorporation on the Performance of Red Light Emitting InP Core Nanocrystals. *Inorg. Chem.* 2016, 55 (17), 8381–8386). Indium acetate (1.40 g, 4.8 mmol) and myristic acid (3.98 g, 17.4 mmol) were heated neat at 100 °C under
10 reduced pressure overnight. Dry toluene (40 mL) was added to the reaction flask at room temperature under N₂ the following day, after which P(SiMe₃)₃ (698 µL, 2.4 mmol) was measured into 5 mL of toluene and injected into the indium myristate solution at 100 °C. Cluster growth was complete within 1 hour as indicated by the characteristic absorbance peak at 386 nm. The particles were concentrated down to a minimal volume of toluene,
15 centrifuged to remove insoluble products, and purified by GPC.

Zn₅ Cluster Synthesis

Zn₅(O₂CCH₃)₆(CH₂CH₃)₄ was synthesized following a literature procedure where zinc acetate (1.107 g, 6.03 mmol) was dissolved in toluene (5 mL) and then diethyl zinc (413 µL, 4.02 mmol) was added drop-wise to the stirring solution (Orchard, K. L.; White,
20 A. J. P.; Shaffer, M. S. P.; Williams, C. K. Pentanuclear Complexes for a Series of Alkylzinc Carboxylates. *Organometallics* 2009, 28 (19), 5828–5832). The reaction was allowed to complete at room temperature overnight. The toluene was concentrated under vacuum and then the Zn₅ cluster was precipitated with the addition of heptane. The white solid was dried down and confirmed pure by ¹H NMR.

Zn²⁺ Titrations

25 Typical titration experiments were conducted by dissolving 40 mg of In₃₇P₂₀(O₂C₁₄H₂₇) in toluene (2 mL) and adding varying equivalents (1, 4, 8, 16, 24, 37, 50, 75, and 100) of Zn²⁺ from a stock solution of Zn₅ to stir at room temperature. The Zn₅ stock solution was prepared by dissolving 54 mg (7 × 10⁻³ mol) of Zn₅ in 2 mL of toluene
30 to make a 0.034 M solution. The reaction was monitored by UV-Vis aliquots taken over

2, 20, 48, and 84 h intervals. Reactions to examine the products of InP MSCs and diethyl zinc or zinc myristate were conducted in a similar fashion either at room temperature or heated to 50 °C under N₂ on a Schlenk line. Samples were purified by GPC by loading the reaction solution directly into a toluene-based column. For the 2 h reaction time samples, clusters were dissolved in 1 mL of ODE rather than toluene to prepare for hot-injection.

Alloyed InP QD Growth

In a typical QD growth reaction, the alloyed clusters were resuspended in 1 mL of 1-ODE and rapidly injected into a flask containing 5 mL of ODE at 290 °C under active N₂ on a Schlenk line. The reaction was monitored by UV-Vis and PL aliquots to determine the endpoint of growth, at which point the heating mantle was removed and the flask was placed into a silicone oil bath to rapidly cool down. For sample characterization, ODE was removed under vacuum distillation and the remaining QD paste was resuspended in a minimal amount of toluene inside a glovebox. Acetonitrile was added to precipitate the particles and centrifuged at 7500 rpm for 10 minutes. After removing the clear supernatant, the film of QDs was resuspended in toluene and purified by GPC. For ZnSeS growth, InP QDs were kept in the same flask following the hot-injection reaction in order to keep stoichiometry and volumes consistent.

ZnSeS Shell Growth

Shell growth was performed using a modified literature procedure (Lim, J.; Bae, W. K.; Lee, D.; Nam, M. K.; Jung, J.; Lee, C.; Char, K.; Lee, S. InP@ZnSeS, Core@Composition Gradient Shell Quantum Dots with Enhanced Stability. *Chem. Mater.* 2011, 23 (20), 4459–4463). TOPSe and TOPS stock solutions (1 M) were prepared by dissolving either 128 mg of sulfur powder (4 mmol) or 316 mg of selenium (4 mmol) in 4 mL of TOP. InP QDs that had previously been formed from clusters solutions were estimated to have 0.09 mmol of In³⁺, assuming a 100% conversion of cluster to QD. The InP QD solutions, in approximately 6 mL of ODE, were heated to 220 °C. A suspension of zinc stearate, Zn(st)₂, was prepared by placing 570 mg (0.9 mmol) in 2 mL of ODE and then injected into the QDs. A blue-shift was observed, corresponding to zinc surface passivation, which appeared to stop changing after 15 minutes. At this point, TOPS (810 µL, 0.81 mmol) and TOPSe (90 µL, 0.09 mmol) were measured out into 1 mL of ODE

and then injected into the InP/Zn solution. The temperature was set to 300 °C and the PL was monitored until no further increases were measured (40 minutes following TOPS/Se injection). The reaction was cooled down by placing the flask in an oil bath. For characterization, ODE was removed under vacuum distillation, resuspended in toluene, filtered through a syringe filter (PTFE), and purified by precipitation cycles with toluene/EtOH as the solvent/non-solvent.

Example 2

The Preparation and Characterization of Representative Zn- and Ga-doped InP Quantum Dots and Core/Shell Quantum Dots

In this example, the preparation and characterization of representative Zn- and Ga-doped InP quantum dots and Zn- and Ga-doped InP core/shell quantum dots are described. As described below, the representative Zn- and Ga-doped InP quantum dots were prepared from InP clusters by cationic exchange.

Material Preparations

Zn₅(O₂CCH₃)₆(CH₂CH₃)₄ (Zn5) cluster synthesis

Zn₅(O₂CCH₃)₆(CH₂CH₃)₄ was synthesized following a literature procedure (Orchard, K. L.; White, A. J. P.; Shaffer, M. S. P.; Williams, C. K. Pentanuclear Complexes for a Series of Alkylzinc Carboxylates. *Organometallics* 2009, 28 (19), 5828–5832. <https://doi.org/10.1021/om900683z>) where zinc acetate (1.107 g, 6.03 mmol) was dissolved in toluene (5 mL) and then diethyl zinc (413 uL, 4.02 mmol) was added dropwise to the stirring solution. The reaction was allowed to complete at room temperature overnight. The toluene was concentrated under vacuum and then the Zn₅ cluster was precipitated with the addition of heptane. The white solid was dried in vacuo and confirmed pure by ¹H NMR.

Ga(OAc)₃ synthesis

Following a literature procedure (Stolarov, I. P.; Yakushev, I. A.; Churakov, A. V.; Cherkashina, N. V.; Smirnova, N. S.; Khramov, E. V.; Zubavichus, Y. V.; Khrustalev, V. N.; Markov, A. A.; Klyagina, A. P.; et al. Heterometallic Palladium(II)–Indium(III) and –Gallium(III) Acetate-Bridged Complexes: Synthesis, Structure, and Catalytic Performance in Homogeneous Alkyne and Alkene Hydrogenation. *Inorg. Chem.* 2018, 57

(18), 11482–11491), gallium nitrate hydrate (5 g) was dissolved in 50 ml acetic anhydride in a 3-neck round bottom flask equipped with a stirbar. The flask was equipped with a distillation apparatus and a mineral oil bubbler. The flask was heated to reflux for 2 hours, upon which time orange vapor ceased evolution and a white precipitate had formed (this reaction evolves acetic acid and NO_x gases and care should be taken for proper ventilation and pressure regulation). The remaining solvent was distilled, and the residual white solid was washed with toluene (10 ml) and ethyl acetate (2 x 10 ml) and dried *en vacuo* to afford a white free-flowing powder. The ATR spectrum matched the literature report. The hydroscopic white solid was stored in a N₂-filled glovebox.

10 Zn²⁺ doping of InP cluster

Typical titration experiments were conducted by dissolving 40 mg of In₃₇P₂₀(O₂C₁₄H₂₇)₅₁ in toluene (2 mL) and adding varying equivalents (1, 4, 8, 16, 24, 37, 50, 75, and 100) of [Zn²⁺] from a stock solution of Zn5 to stir at room temperature. The Zn5 stock solution was prepared by dissolving 54 mg (7 x 10⁻³ mol) of Zn5 in 2 mL of toluene to make a 0.034 M solution. The reaction was monitored by UV-Vis aliquots taken over 2, 20, 48, and 84 h intervals. Reactions to examine the products of InP MSCs and diethyl zinc or zinc myristate were conducted in a similar fashion either at room temperature or heated to 50 °C under N₂ on a Schlenk line. Samples were purified by GPC by loading the reaction solution directly into a toluene-based column. For the 2 h reaction time samples, clusters were dissolved in 1 mL of ODE rather than toluene to prepare for hot injection.

20 Ga³⁺ doping of InP cluster

Typical titration experiments were conducted by dissolving 200 mg of In₃₇P₂₀(O₂C₁₄H₂₇)₅₁ in toluene (2 mL) and adding varying equivalents (1, 4, 8, 16, 24, 37, 50, 75, 100 equivalents relative to cluster) of Ga(OAc)₃. The reaction was stirred for 48 hours with UV-Vis monitoring. The solutions were centrifuged to remove insoluble material and the supernatant was purified by GPC by loading into a toluene-based column.

25 Doped InP QD growth

In a typical QD growth reaction, the doped clusters were resuspended in 1 mL of 1-ODE and rapidly injected into a flask containing 5 mL of ODE at 290 °C under N₂ on a

30

Schlenk line. The reaction was monitored by UV-Vis and PL aliquots to determine the endpoint of growth, at which point the heating mantle was removed and the flask was placed into a silicone oil bath to rapidly cool down. For sample characterization, ODE was removed under vacuum distillation and the remaining QD solid was resuspended in a minimal amount of toluene inside a glovebox. Acetonitrile was added to precipitate the particles and centrifuged at 7500 rpm for 10 minutes. After removing the clear supernatant, the film of QDs was resuspended in toluene and purified by GPC. For ZnSeS growth, InP QDs were kept in the same flask following the hot-injection reaction in order to keep stoichiometry and volumes consistent.

Doped InP/ZnSeS core/shell synthesis

Shell growth was performed using a modified literature procedure from Lee et al. (Lim, J.; Bae, W. K.; Lee, D.; Nam, M. K.; Jung, J.; Lee, C.; Char, K.; Lee, S. InP@ZnSeS, Core@Composition Gradient Shell Quantum Dots with Enhanced Stability. *Chem. Mater.* 2011, 23 (20), 4459–4463. <https://doi.org/10.1021/cm201550w>). TOPSe and TOPS stock solutions (1 M) were prepared by dissolving either 128 mg of sulfur powder (4 mmol) or 316 mg of selenium (4 mmol) in 4 mL of TOP. InP QDs that had previously been formed from clusters solutions were estimated to have 0.09 mmol of In^{3+} , assuming a 100% conversion of cluster to QD. The InP QD solution from before was heated to 220 °C. A solution of zinc stearate was prepared by dissolving 570 mg (0.9 mmol) in 2 mL of ODE and then injected into the QDs. A blue shift was observed, corresponding to zinc surface passivation, which appeared to stop changing after 15 minutes. At this point TOPSe (90 μL , 0.09 mmol) was added slowly over the course of one minute and the reaction was allowed to equilibrate for 20 minutes. Next, TOPS (810 μL , 0.81 mmol) was added slowly over the course of 5 minutes and the reaction was allowed to equilibrate for 15 minutes. The temperature was then set to 300 °C and the PL was monitored until no further increases were measured (40 minutes following TOPS injection). The reaction was cooled to room temperature and the 1-ODE was removed under vacuum distillation. The solid was resuspended in toluene and centrifuged to isolate the supernatant, which was then precipitated with acetonitrile. The precipitate was then resuspended in minimal toluene and purified by GPC.

While illustrative embodiments have been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An indium phosphide cluster doped with zinc or gallium,
wherein the ratio of In: P: Zn in the zinc-doped indium phosphide cluster is represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c$, wherein a is an integer from about 20 to about 40, b is an integer from about 10 to about 25, and c is an integer from 1 to about 20, and
wherein the ratio of In: P: Ga in the gallium-doped indium phosphide cluster is represented by the formula $\text{In}_d\text{P}_e\text{Ga}_f$, wherein d is an integer from about 20 to about 40, e is an integer from about 10 to about 25, and f is an integer from 1 to about 20.
2. The indium phosphide cluster of Claim 1, wherein the zinc-doped indium phosphide cluster has In:Zn molar ratios ranging from about 1:0 to 1:0.4.
3. The indium phosphide cluster of Claim 1, wherein the gallium-doped has In:Ga molar ratios ranging from about 1:0 to 1:0.2.
4. The indium phosphide cluster of any one of Claims 1-3, having a particle size from about 1 nm to about 3 nm.
5. A method for making an indium phosphide cluster doped with zinc or gallium, comprising
reacting an indium phosphide cluster with a zinc precursor or a gallium precursor effective for incorporating zinc or gallium, respectively, into an indium phosphide cluster to provide a zinc- or gallium-doped indium phosphide cluster, respectively.
6. The method of Claim 5, wherein the indium phosphide cluster is $\text{In}_{37}\text{P}_{20}\text{X}_{51}$, wherein X is a carboxylate ion.
7. The method of Claim 5, wherein the zinc precursor is a mixed alkyl-carboxylate zinc, a zinc carboxylate, a zinc halide, or a zinc amide.

8. The method of Claim 5, wherein the zinc precursor is a mixed alkyl-carboxylate zinc.

9. The method of Claim 5, wherein the gallium precursor is a mixed alkyl-carboxylate gallium, a gallium carboxylate, a gallium halide, or a zinc amide.

10. The method of Claim 5, wherein the gallium precursor is a mixed alkyl-carboxylate gallium.

11. The method of Claim 5, wherein the gallium precursor is a gallium carboxylate.

12. The method of any one of Claims 5-11, wherein from 1 to about 20 In^{3+} ions are exchanged for Zn^{2+} ions based on indium phosphide molar basis.

13. The method of any one of Claims 5-11, wherein from 1 to about 20 In^{3+} ions are exchanged for Ga^{2+} ions based on indium phosphide molar basis.

14. The method of any one of Claims 5-11, wherein from 1 to about 20 Zn^{2+} ions are added to the indium phosphide cluster based on indium phosphide molar basis.

15. The method of any one of Claims 5-11, wherein from 1 to about 20 Ga^{3+} ions are added to the indium phosphide cluster based on indium phosphide molar basis.

16. An indium phosphide cluster doped with zinc or gallium prepared by the method of any one of Claims 5-15.

17. A method for making an indium phosphide quantum dot, comprising growing the indium phosphide cluster of Claim 1 by heating the cluster in a solvent at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc or gallium.

18. An indium phosphide quantum dot having an indium phosphide core doped with zinc or gallium prepared by the method of Claim 17.

19. A method for making an indium phosphide core/shell quantum dot, comprising

(a) growing the indium phosphide cluster of Claim 1 by heating the cluster in a solvent at a predetermined temperature for a predetermined time to provide an indium phosphide quantum dot doped with zinc or gallium; and

(b) shelling the indium phosphide quantum dot doped with zinc or gallium with a shell-forming material, to provide an indium phosphide core/shell quantum dot.

20. The method of Claim 19, wherein shelling comprises injecting the indium phosphide quantum dot doped with zinc or gallium into a shell-forming medium comprising a shell-forming material to provide the core/shell quantum dot.

21. The method of Claim 19, wherein the indium phosphide quantum cluster doped with zinc or gallium and the shell-forming medium are contacted for a predetermined time and at a pre-determined temperature effective to provide the core/shell quantum dot.

22. The method of any one of Claims 19-21, wherein the shell is a shell selected from the group consisting of ZnS, ZnSe, CdS, CdSe, ZnSeS, and alloys and mixtures thereof.

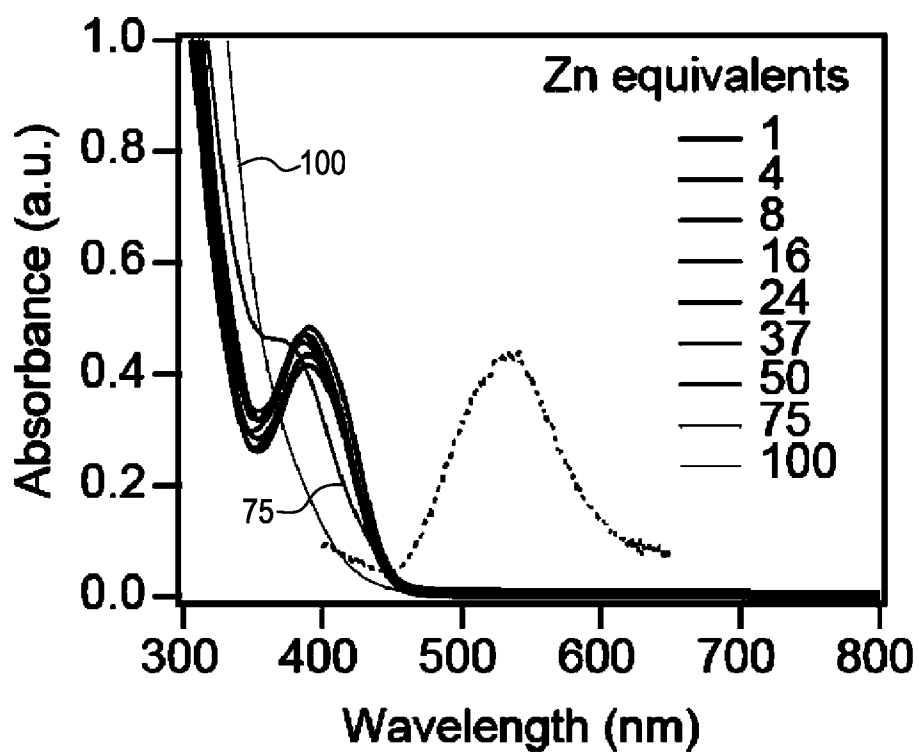
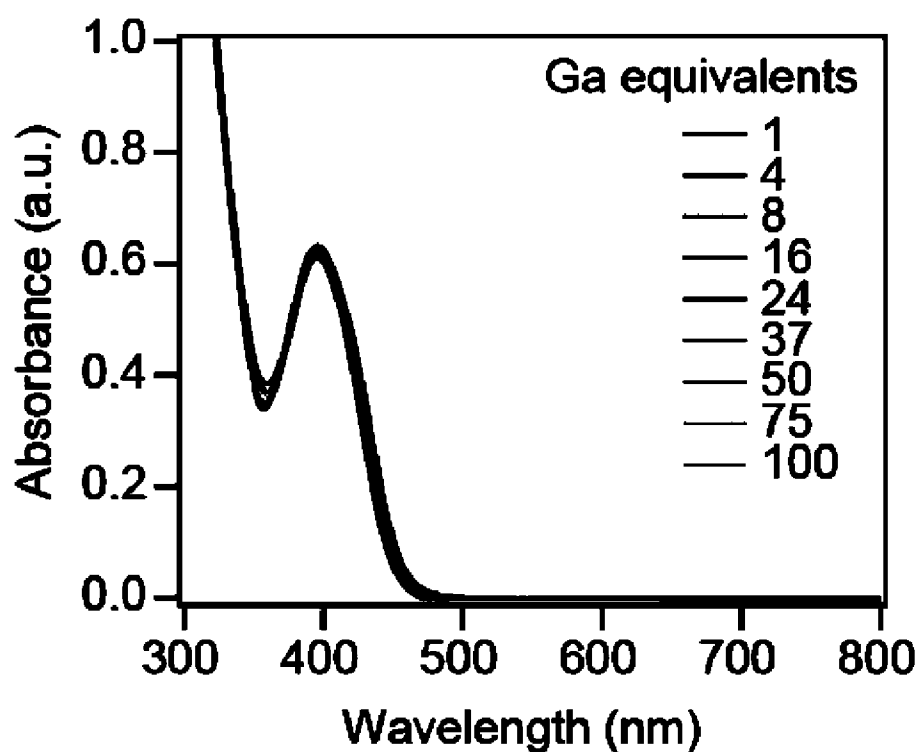
23. The method of any one of Claims 19-21, wherein the shell is a shell selected from the group consisting of InP, GaP, In_2O_3 , ZnO, CdO, and mixtures thereof.

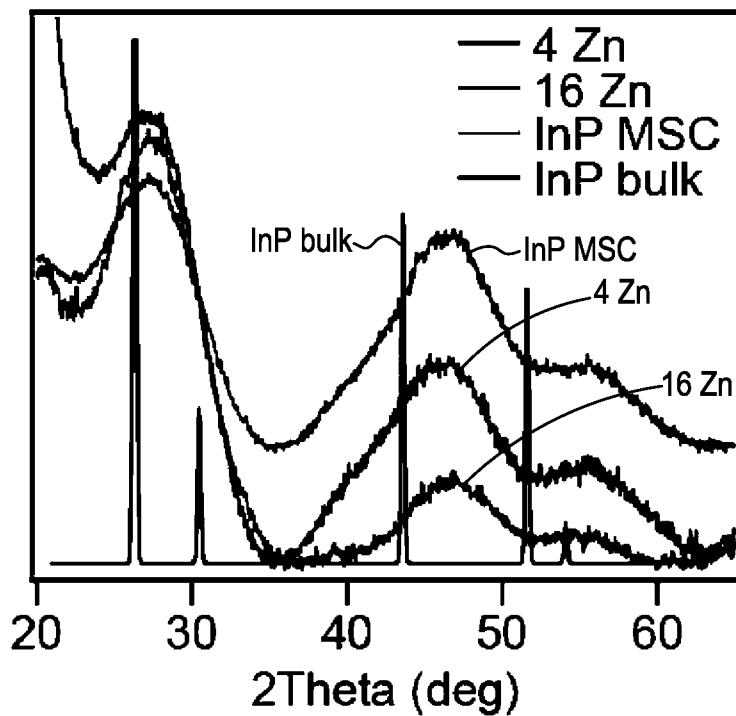
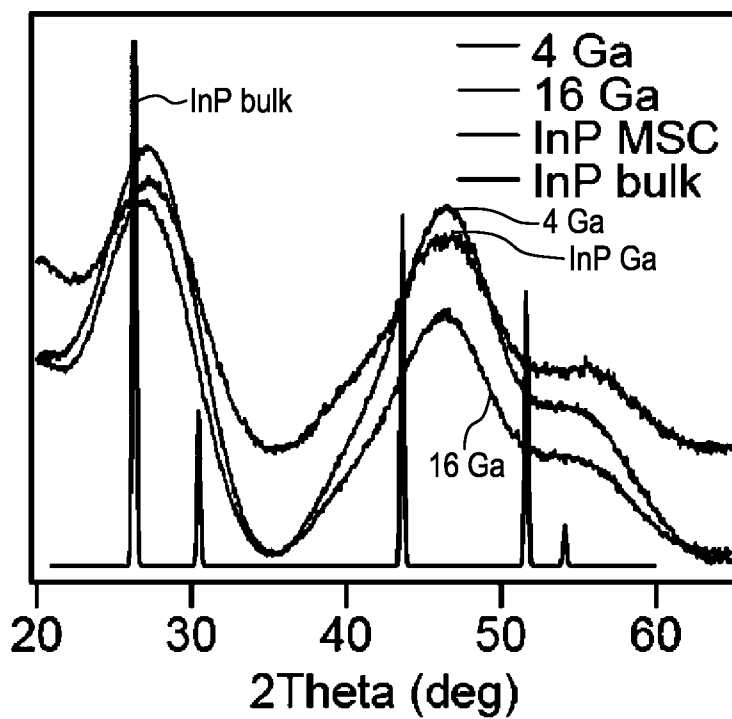
24. The method of any one of Claims 19-21, wherein the shell has a thickness from 1 to about 6 monolayers.

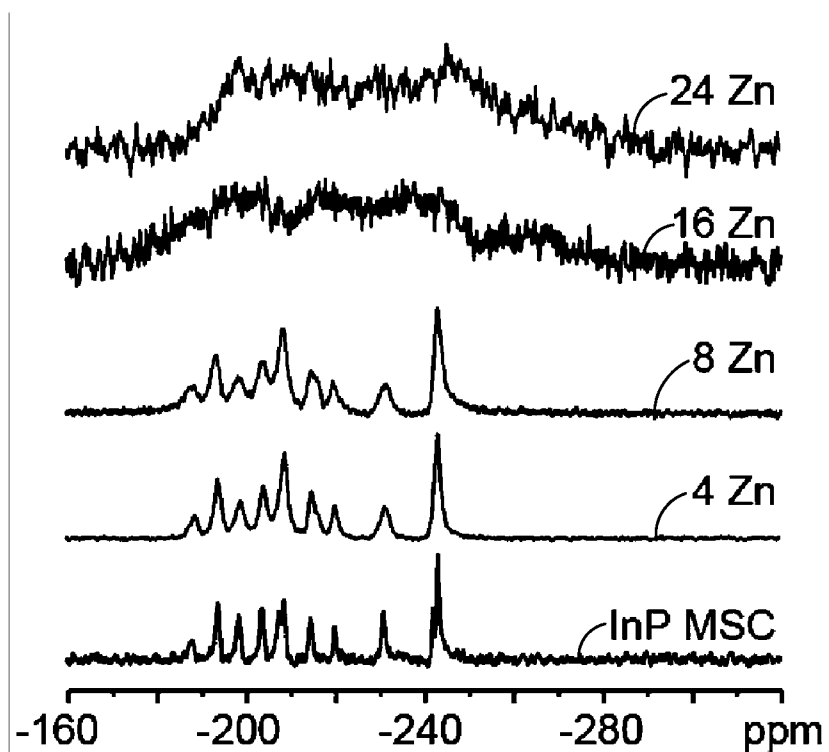
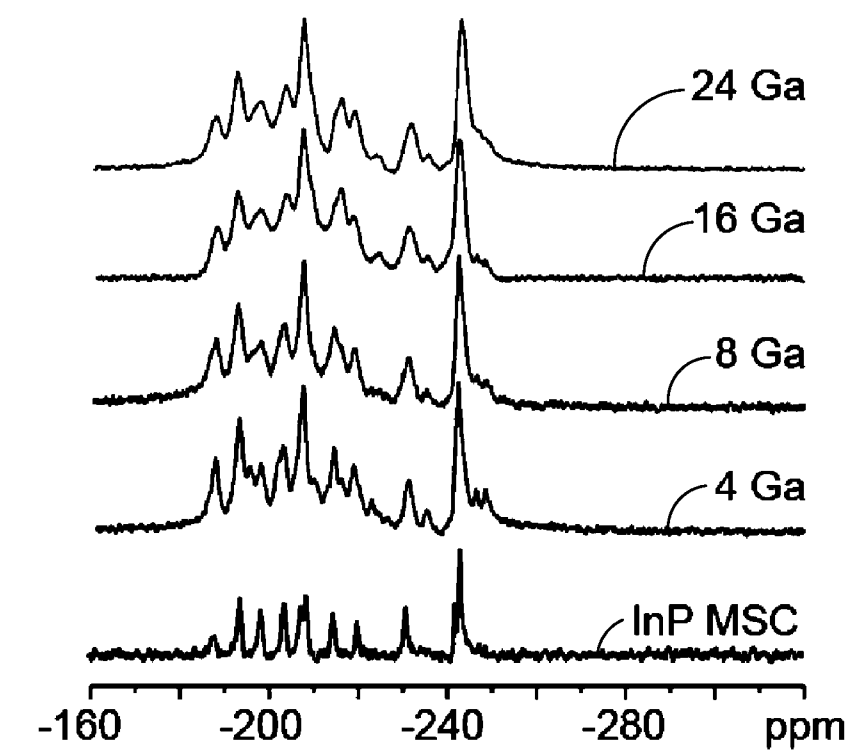
25. The method of any one of Claims 19-21, wherein the core/shell quantum dot has a particle size from about 2 nm to about 6 nm.

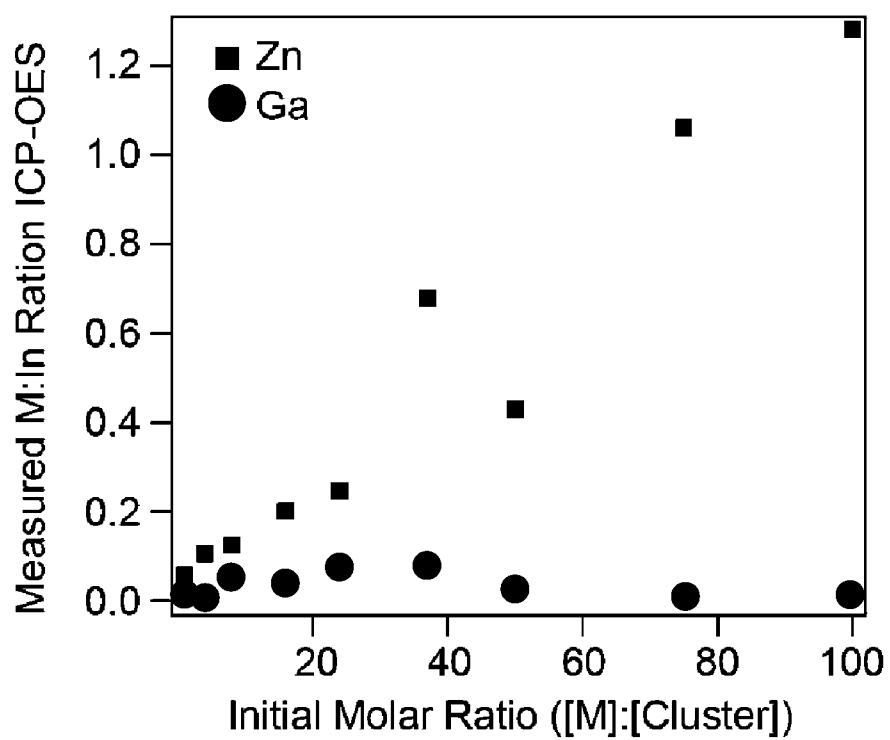
26. The method of any one of Claims 19-21, wherein the indium phosphide core/shell quantum dot has a photoluminescent quantum yield from about 40% to about 90%.

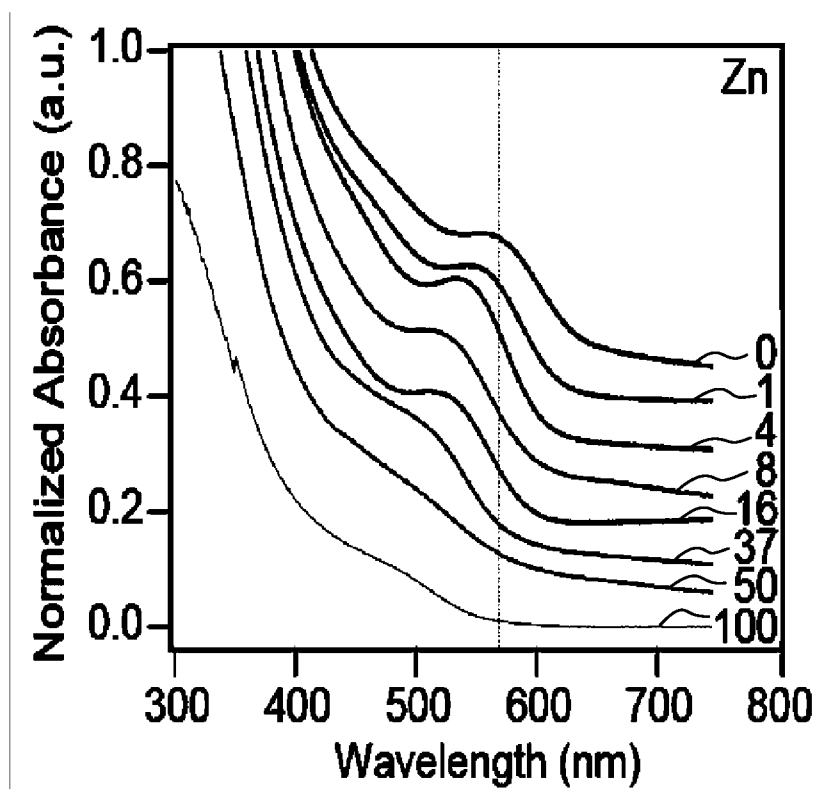
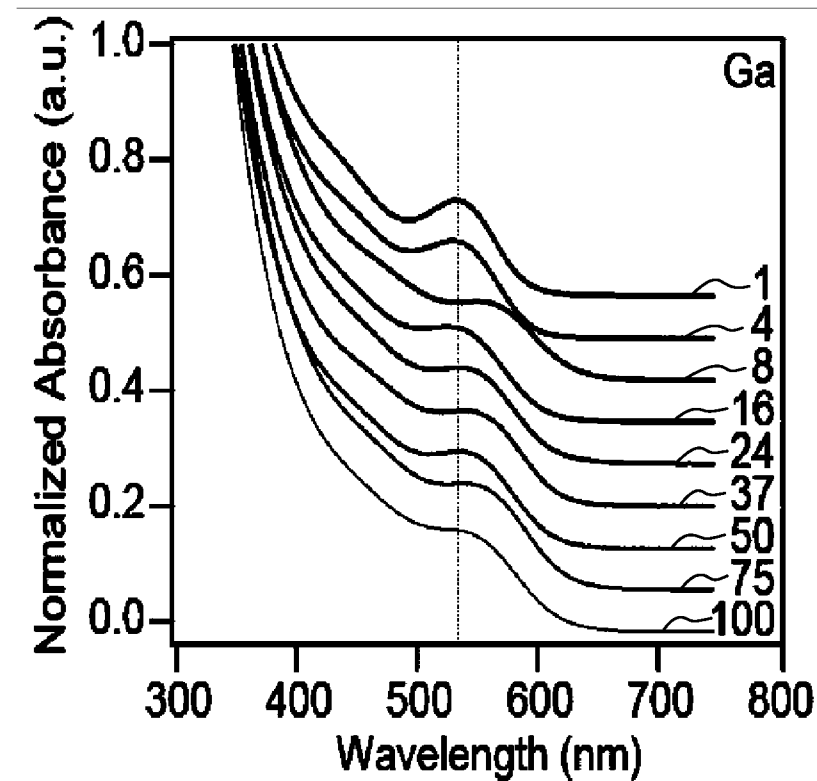
27. An indium phosphide core/shell quantum dot having an indium phosphide core doped with zinc or gallium prepared by the method of any one of Claims 19-21.

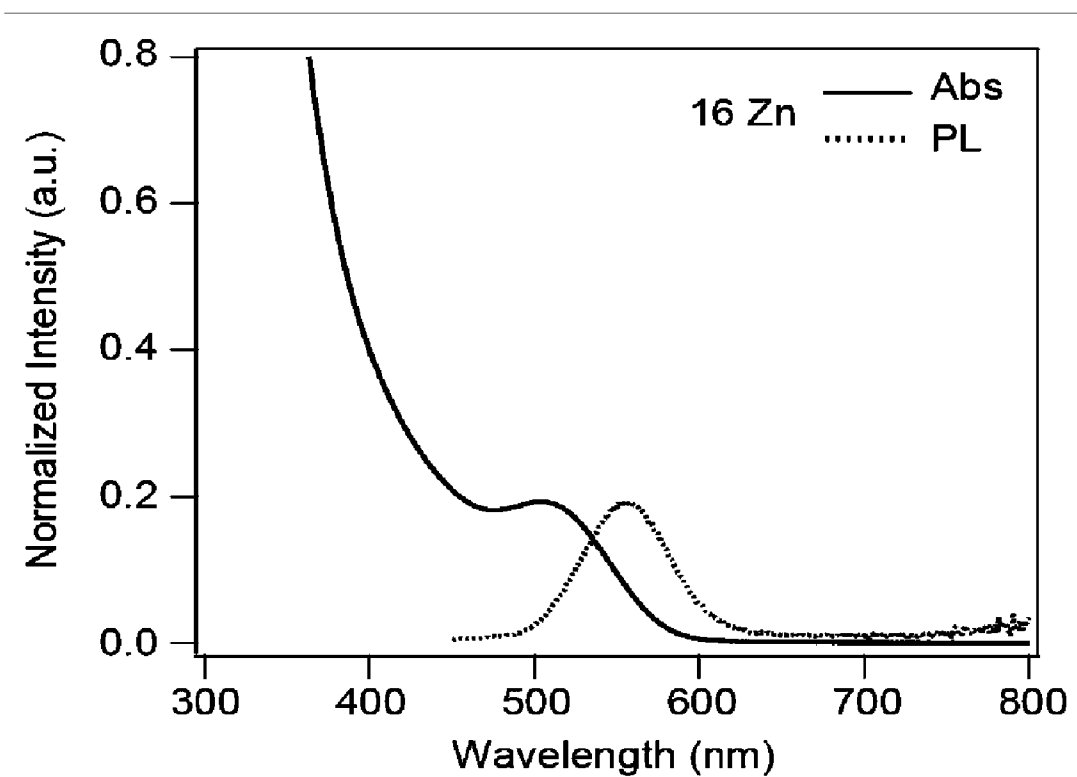
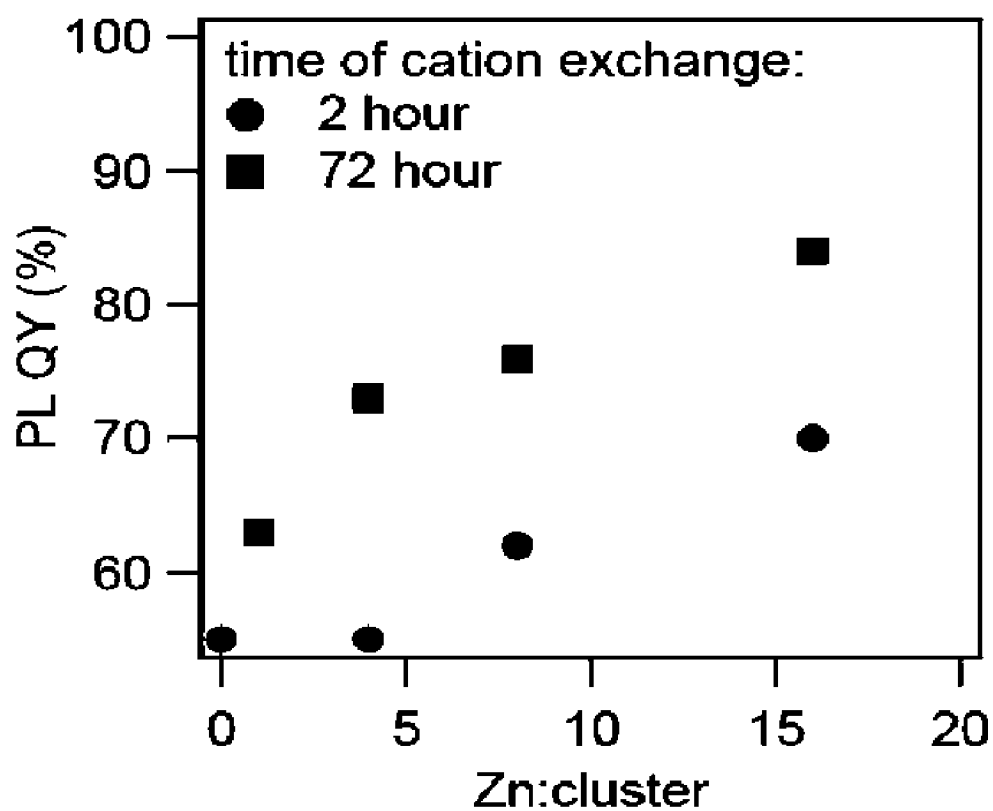
**FIG. 1A****FIG. 1B**

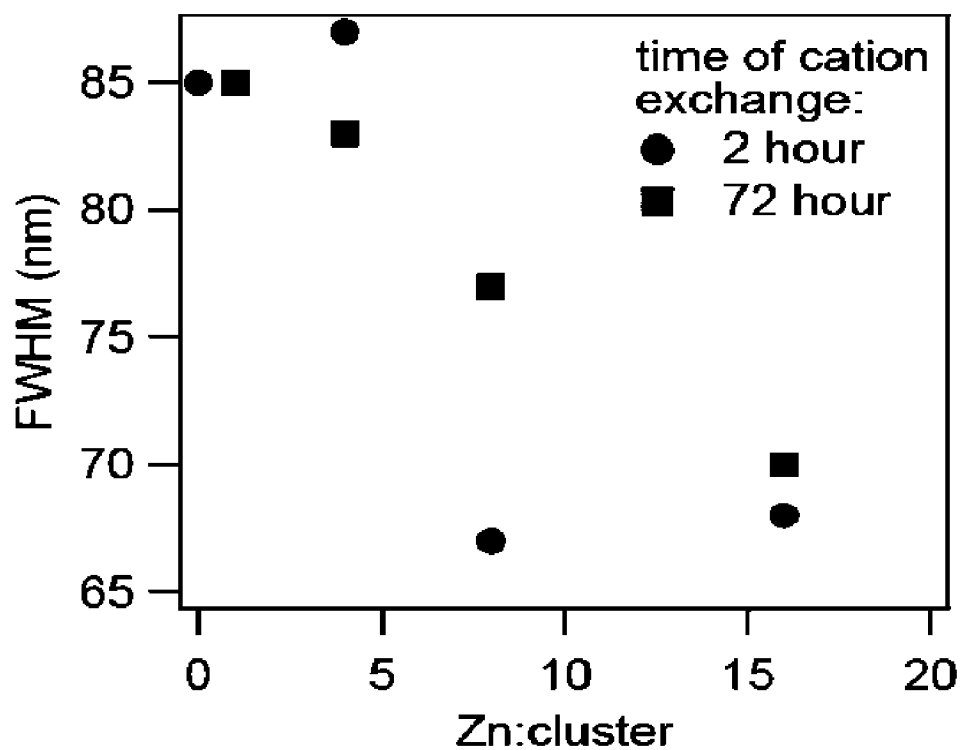
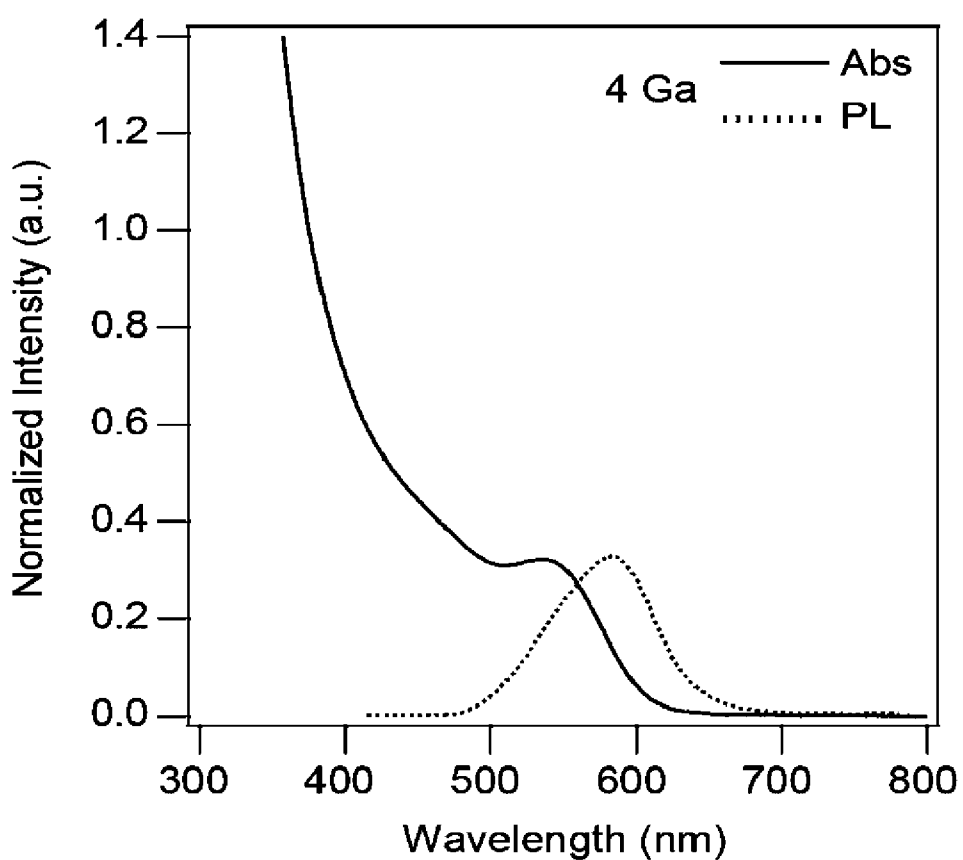
**FIG. 1C****FIG. 1D**

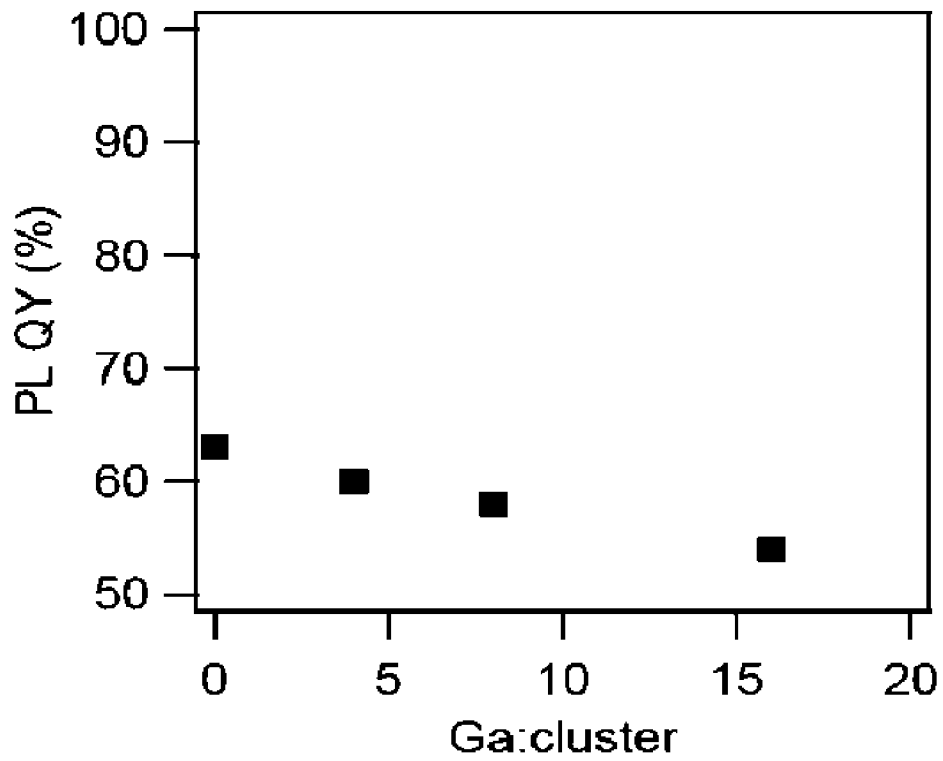
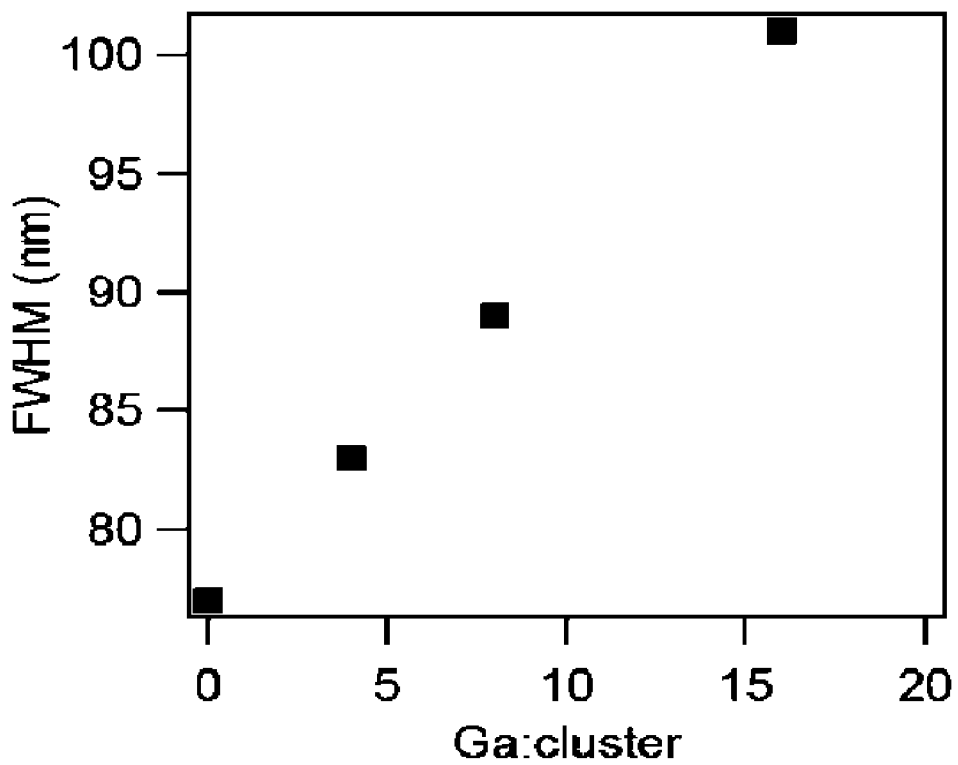
**FIG. 1E****FIG. 1F**

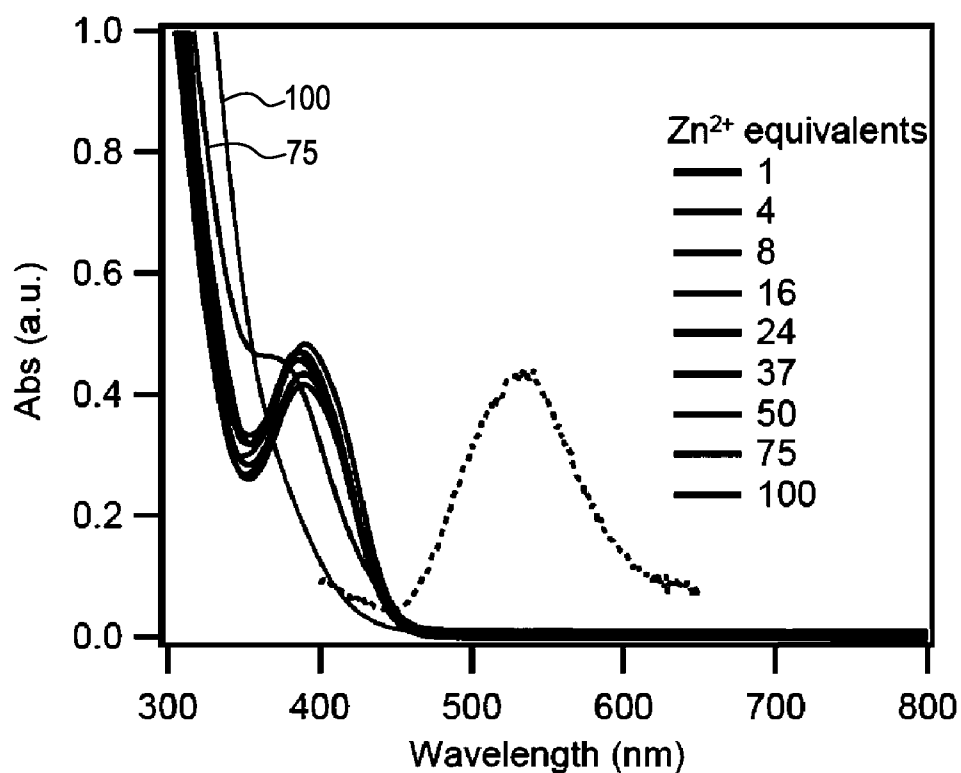
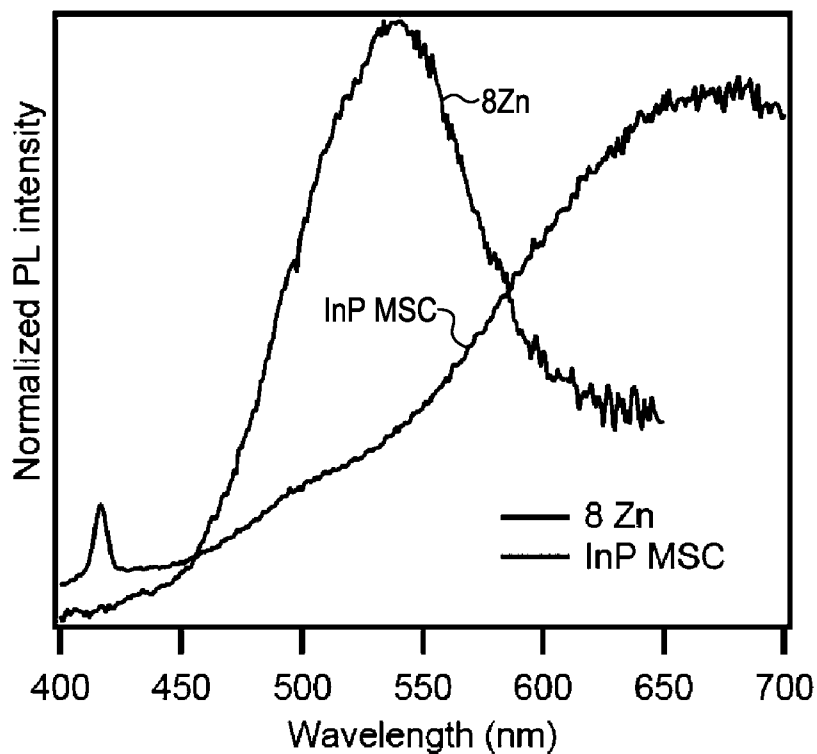
***FIG. 2***

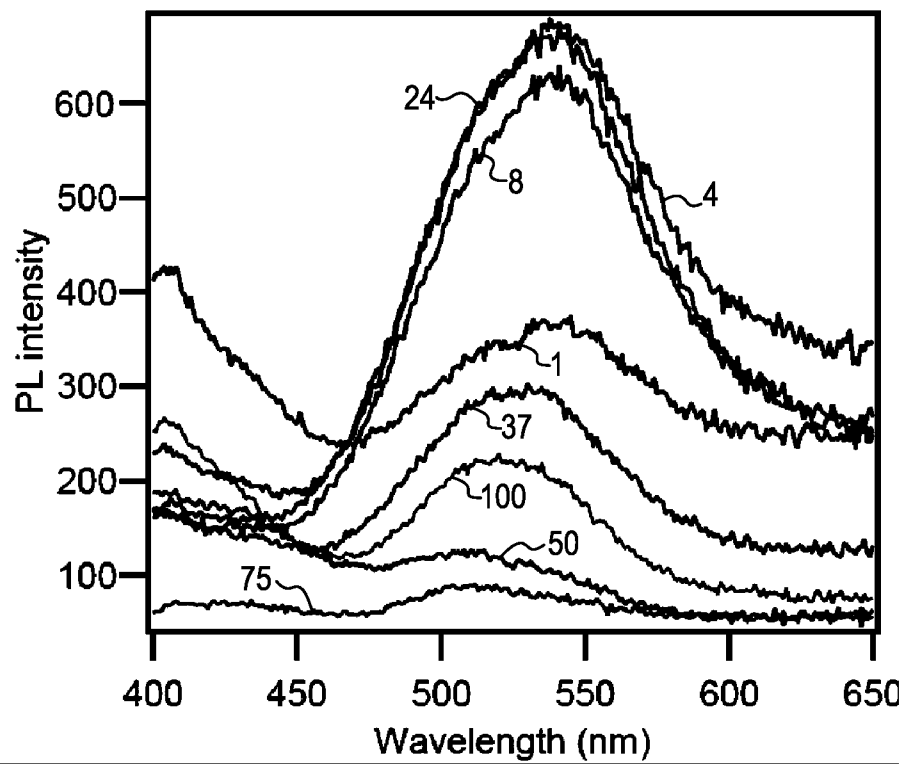
**FIG. 3A****FIG. 3B**

**FIG. 4A****FIG. 4B**

**FIG. 4C****FIG. 5A**

***FIG. 5B******FIG. 5C***

**FIG. 6A****FIG. 6B**

***FIG. 6C***

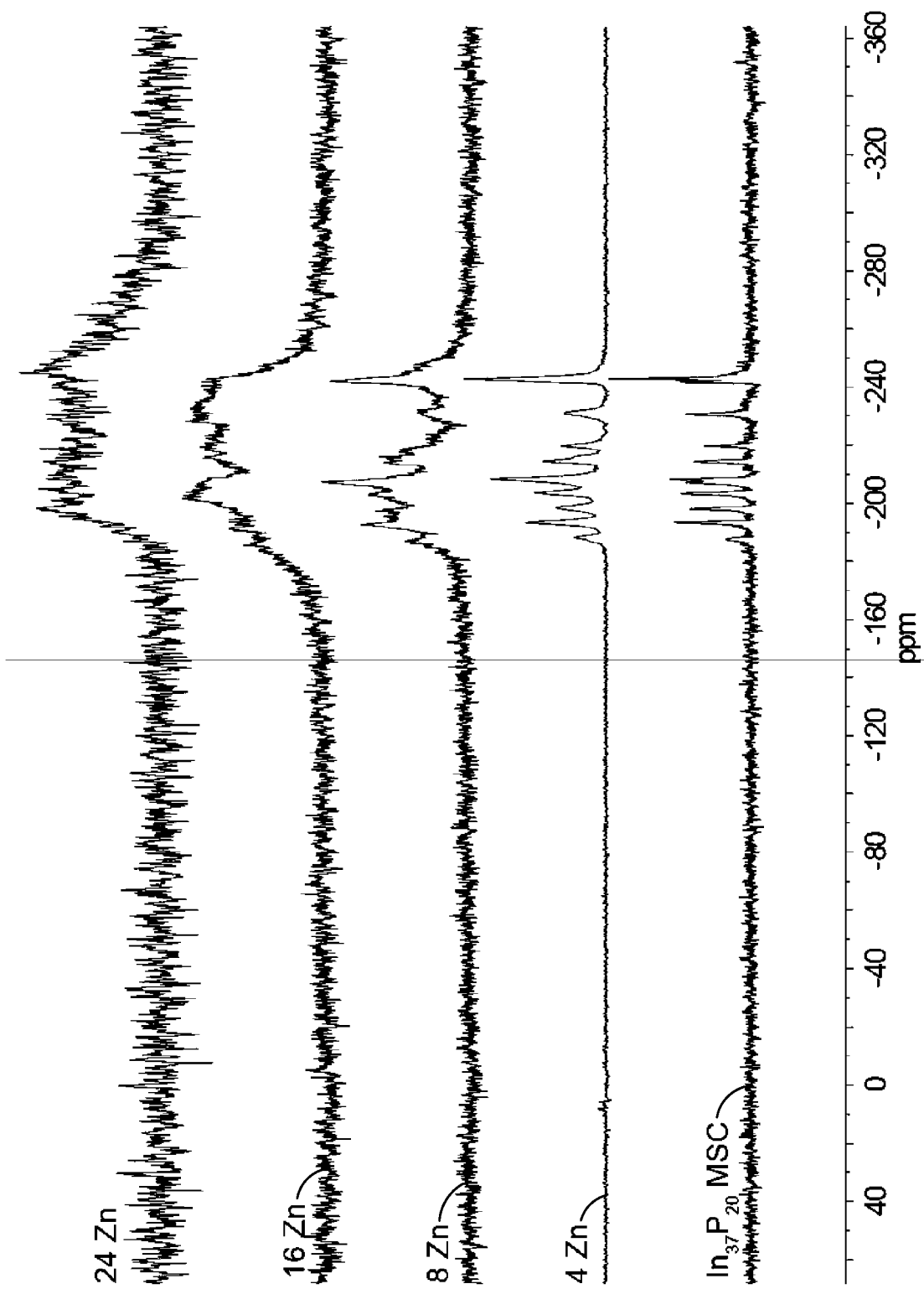
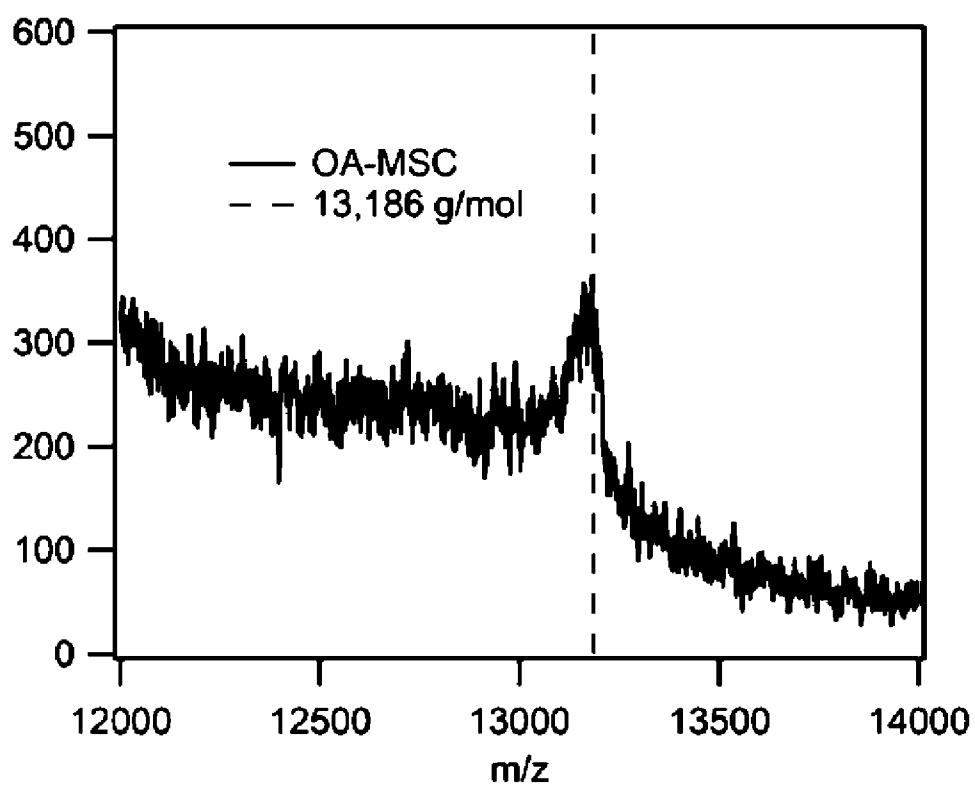
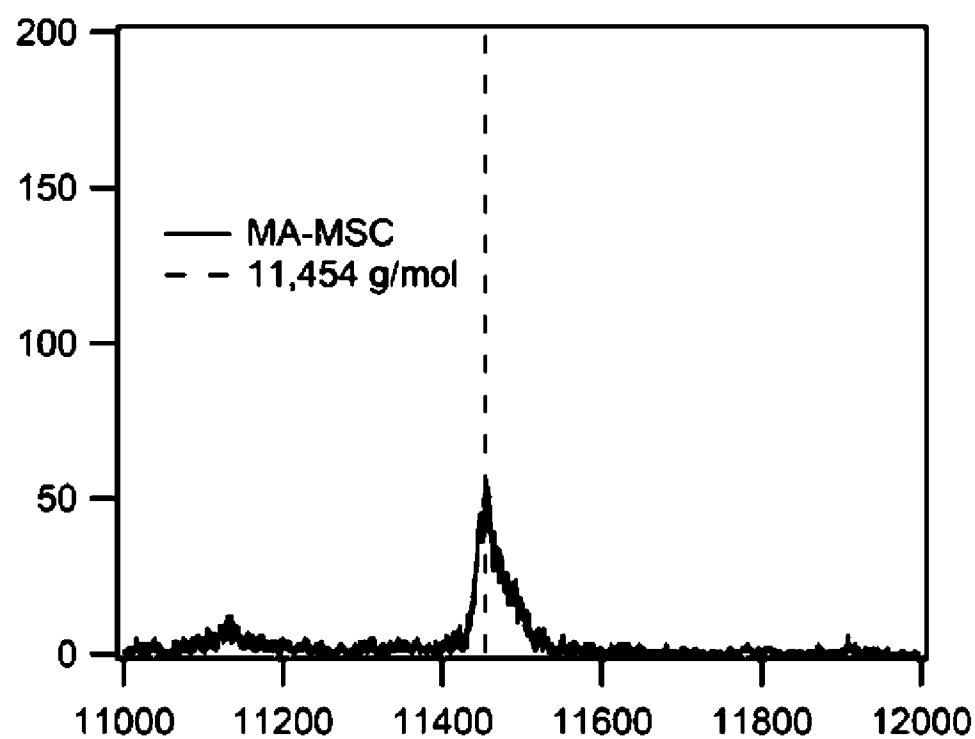
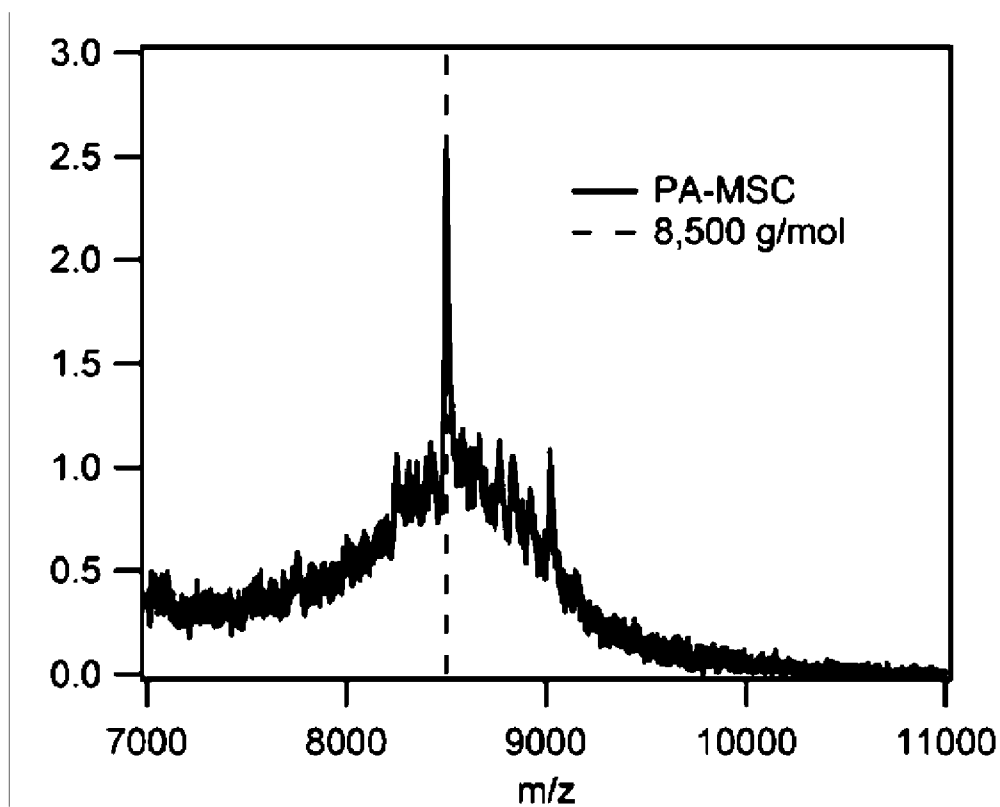
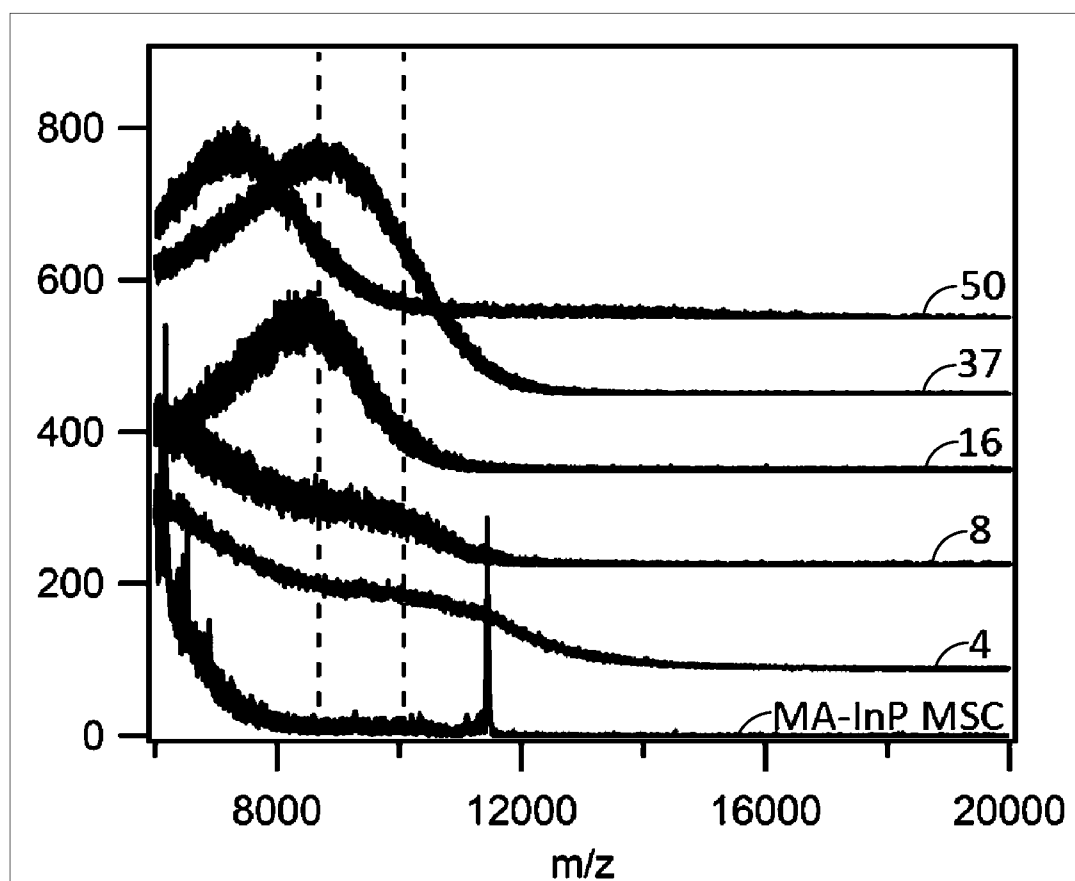
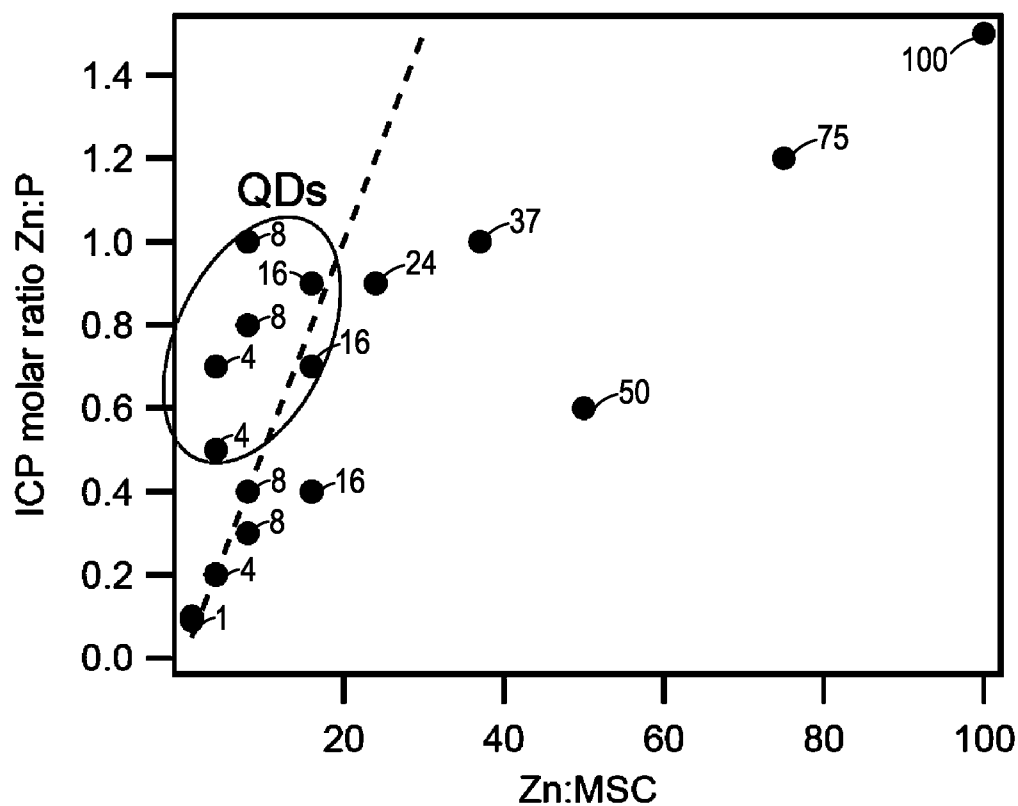
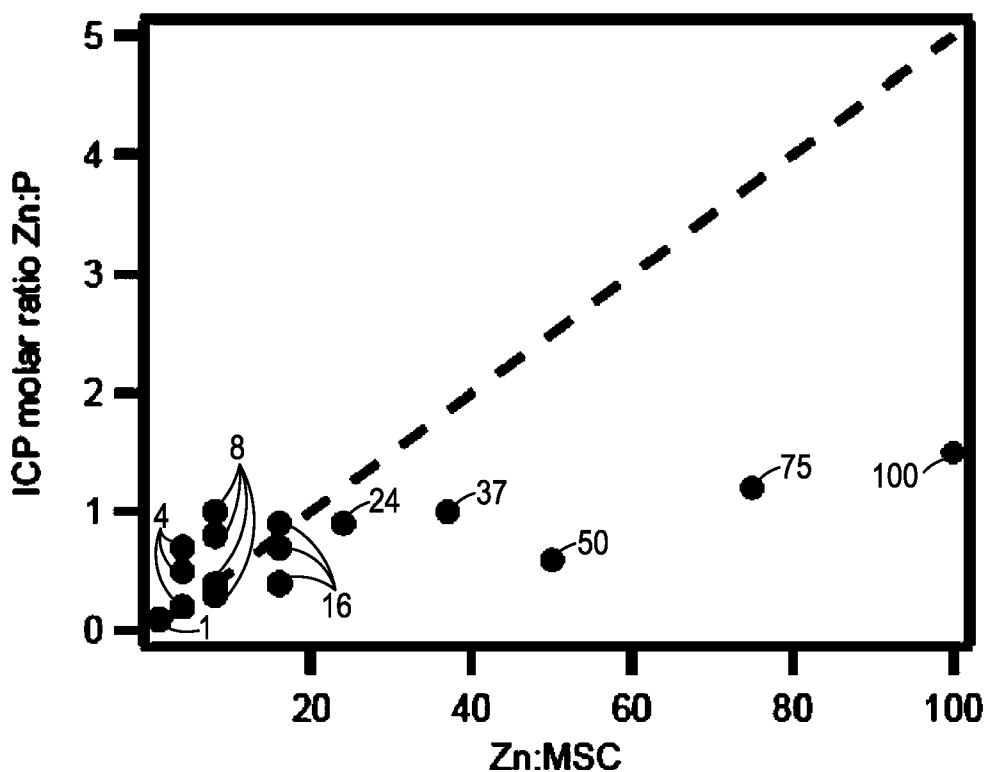
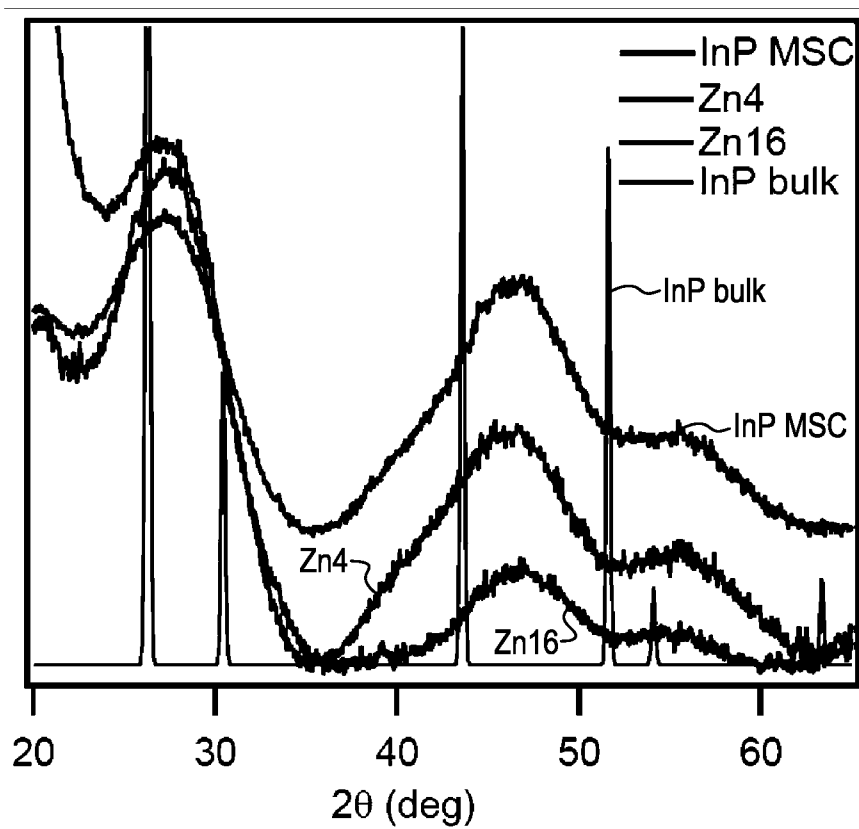
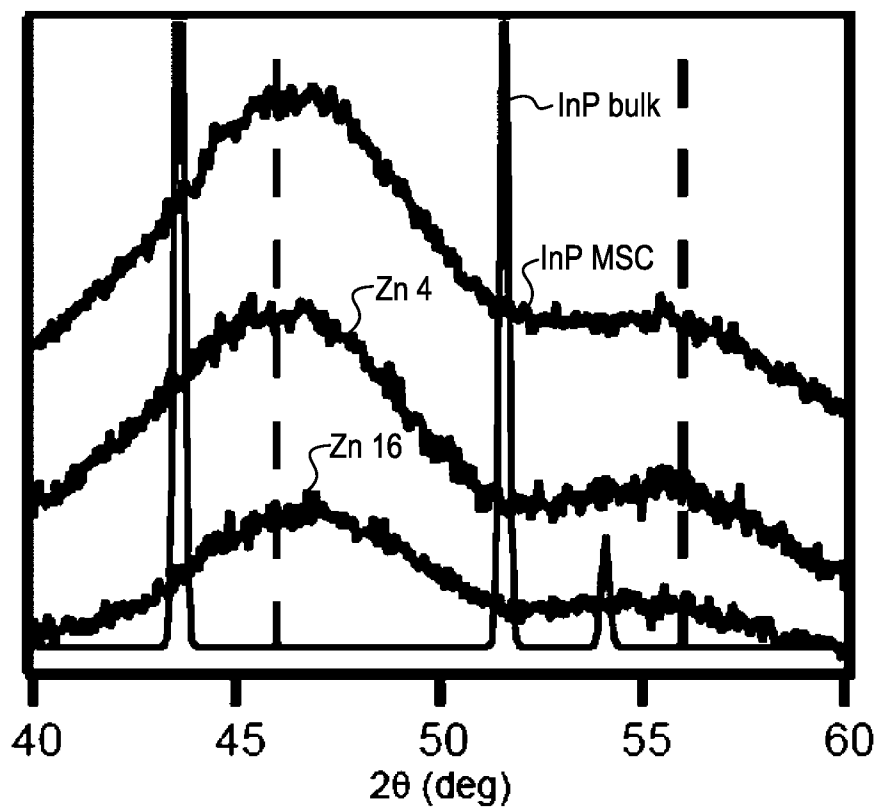


FIG. 7

**FIG. 8A****FIG. 8B**

**FIG. 8C****FIG. 9**

**FIG. 10A****FIG. 10B**

**FIG. 10C****FIG. 10D**

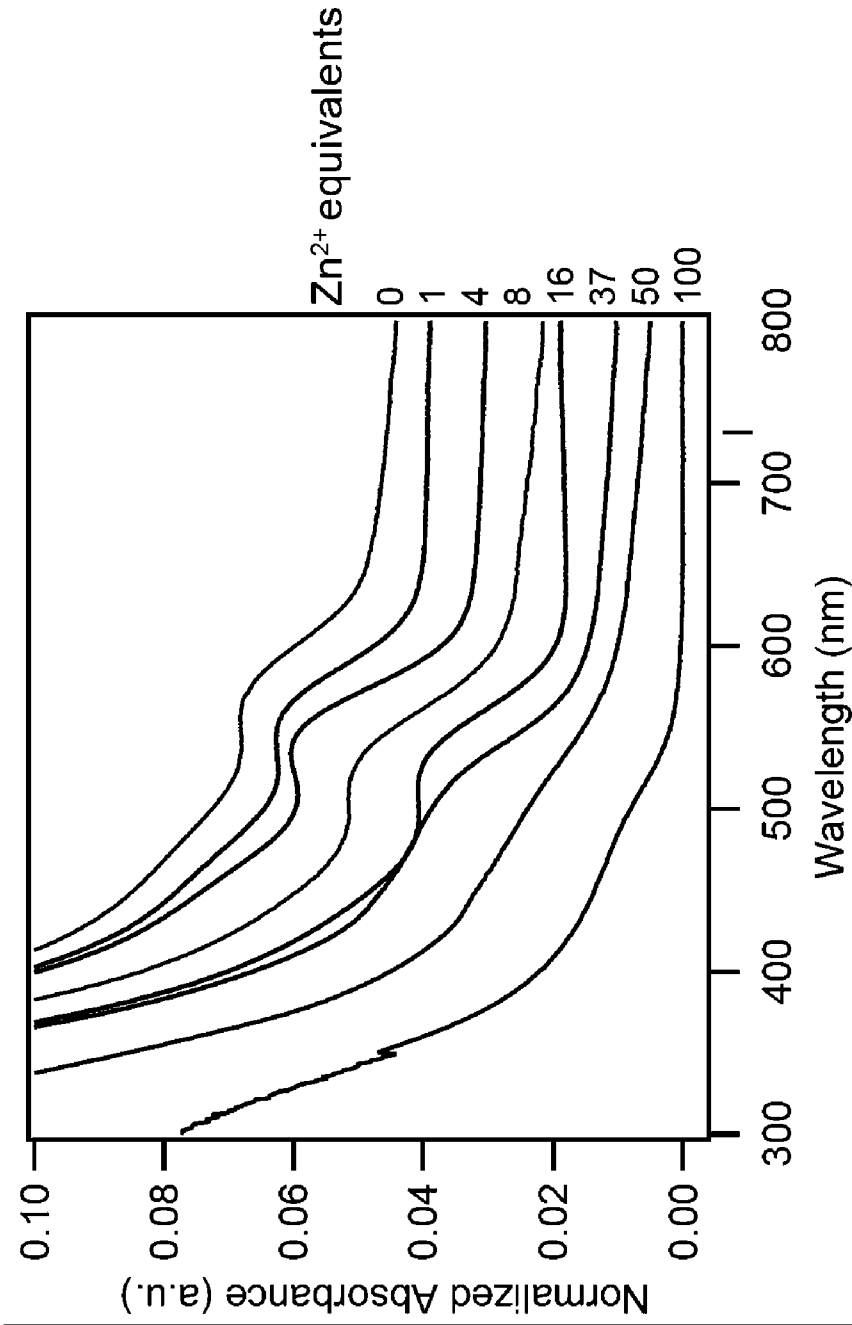


FIG. 11

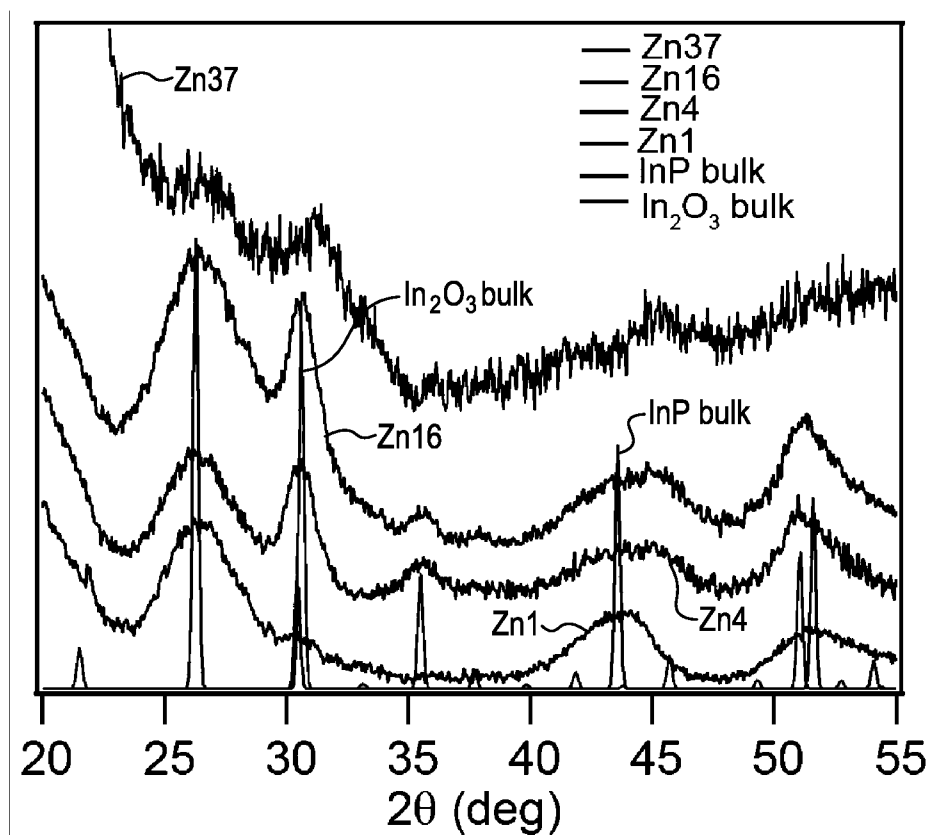
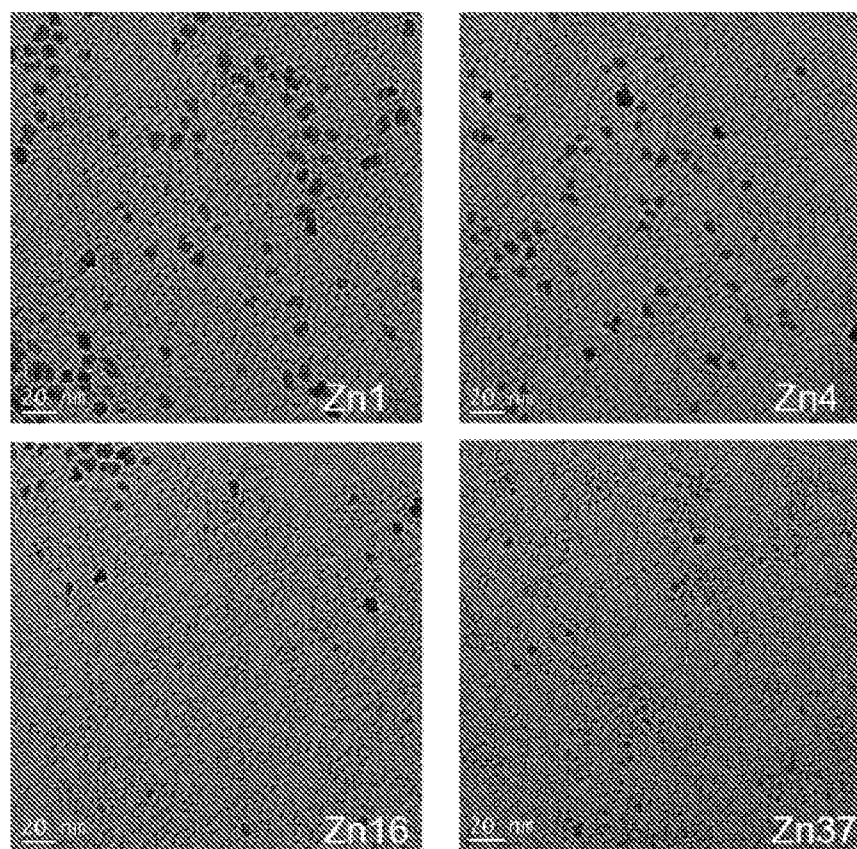
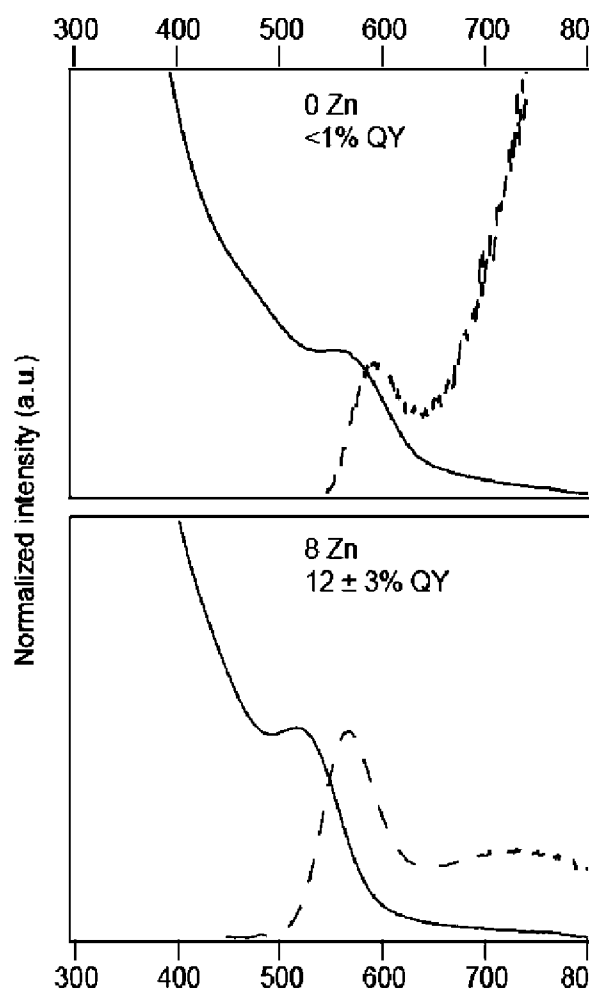
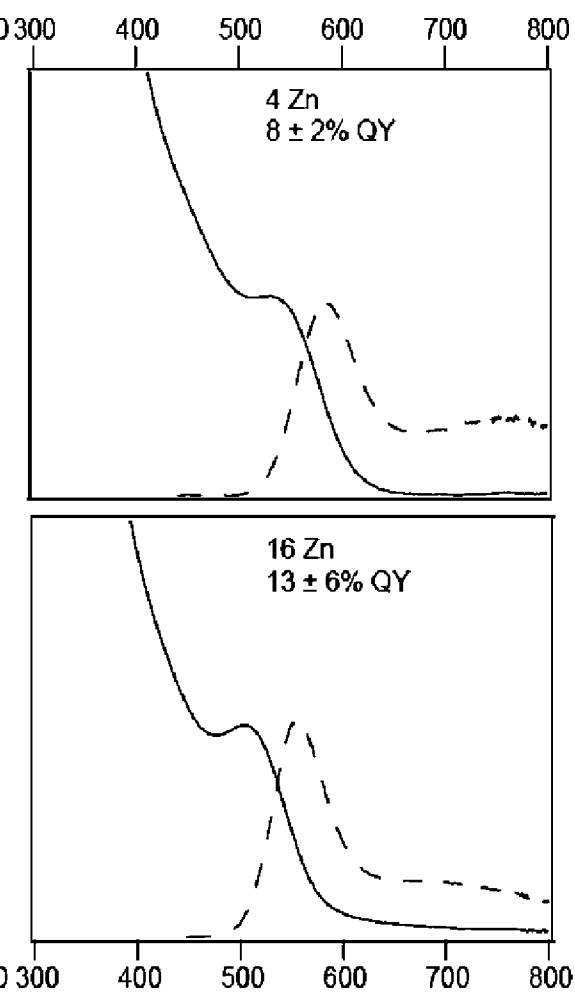
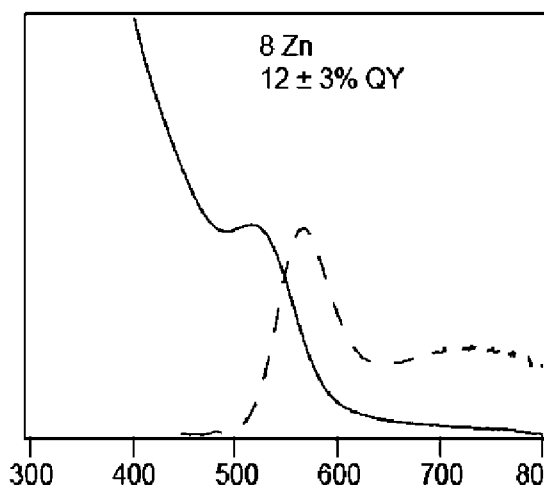
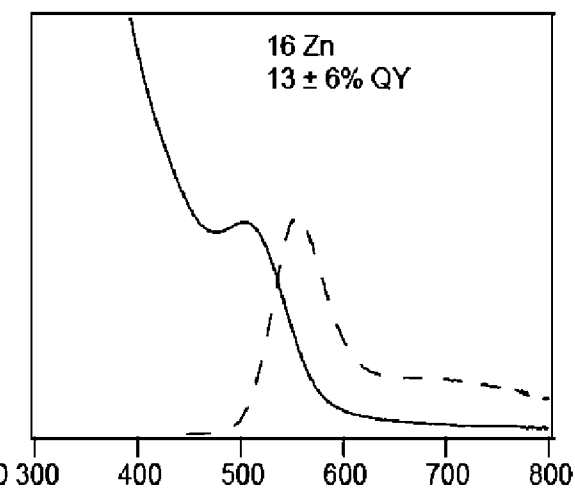
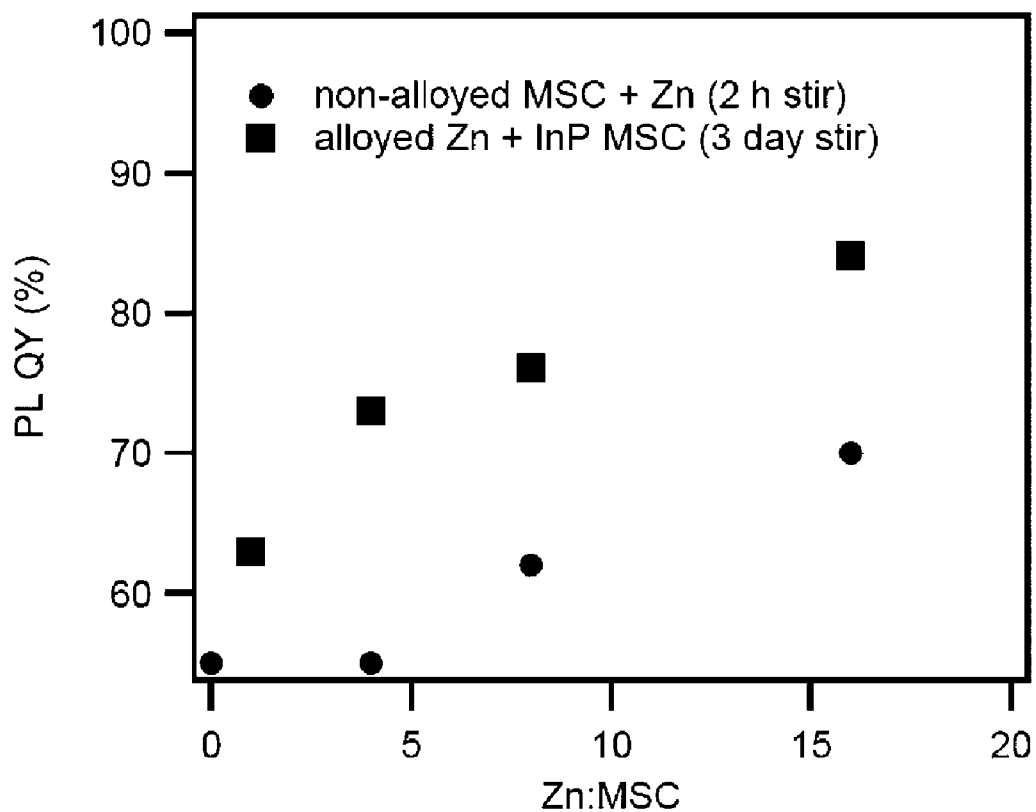
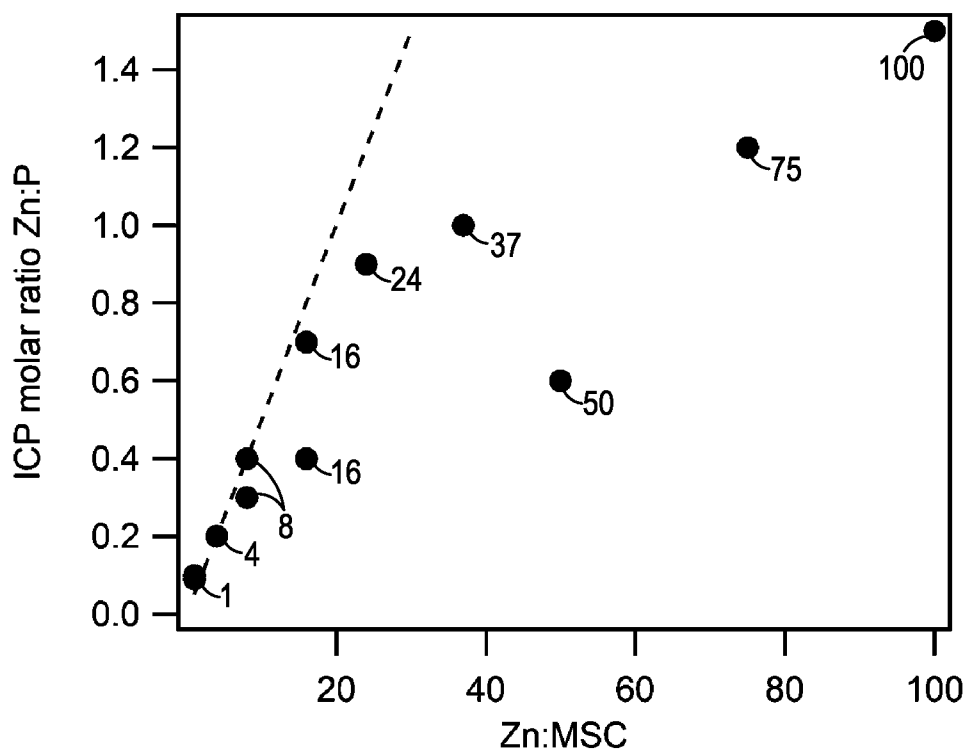
**FIG. 12A****FIG. 12B**

FIG. 13A**FIG. 13B****FIG. 13C****FIG. 13D**

**FIG. 14****FIG. 15**

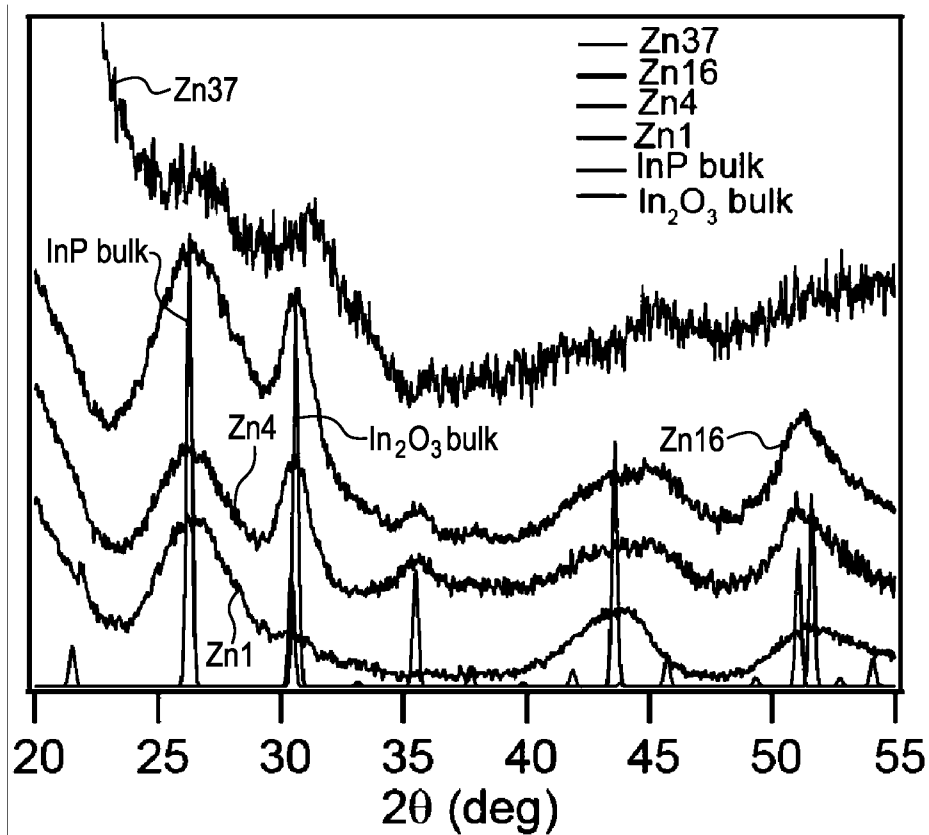
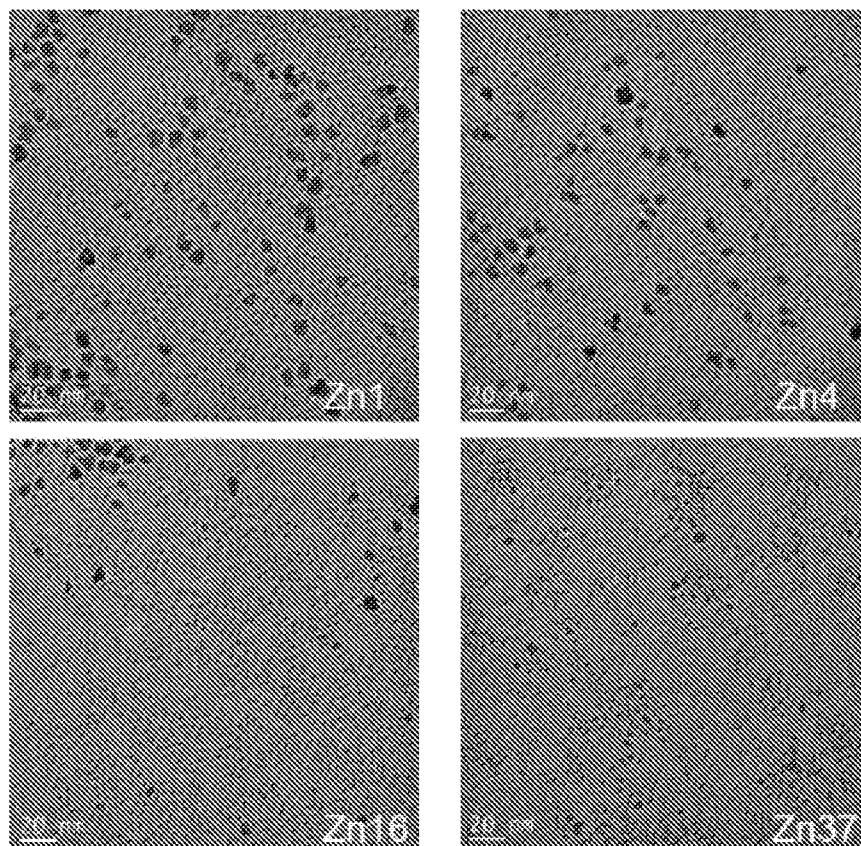
**FIG. 16A****FIG. 16B**

FIG. 17A

FIG. 17B

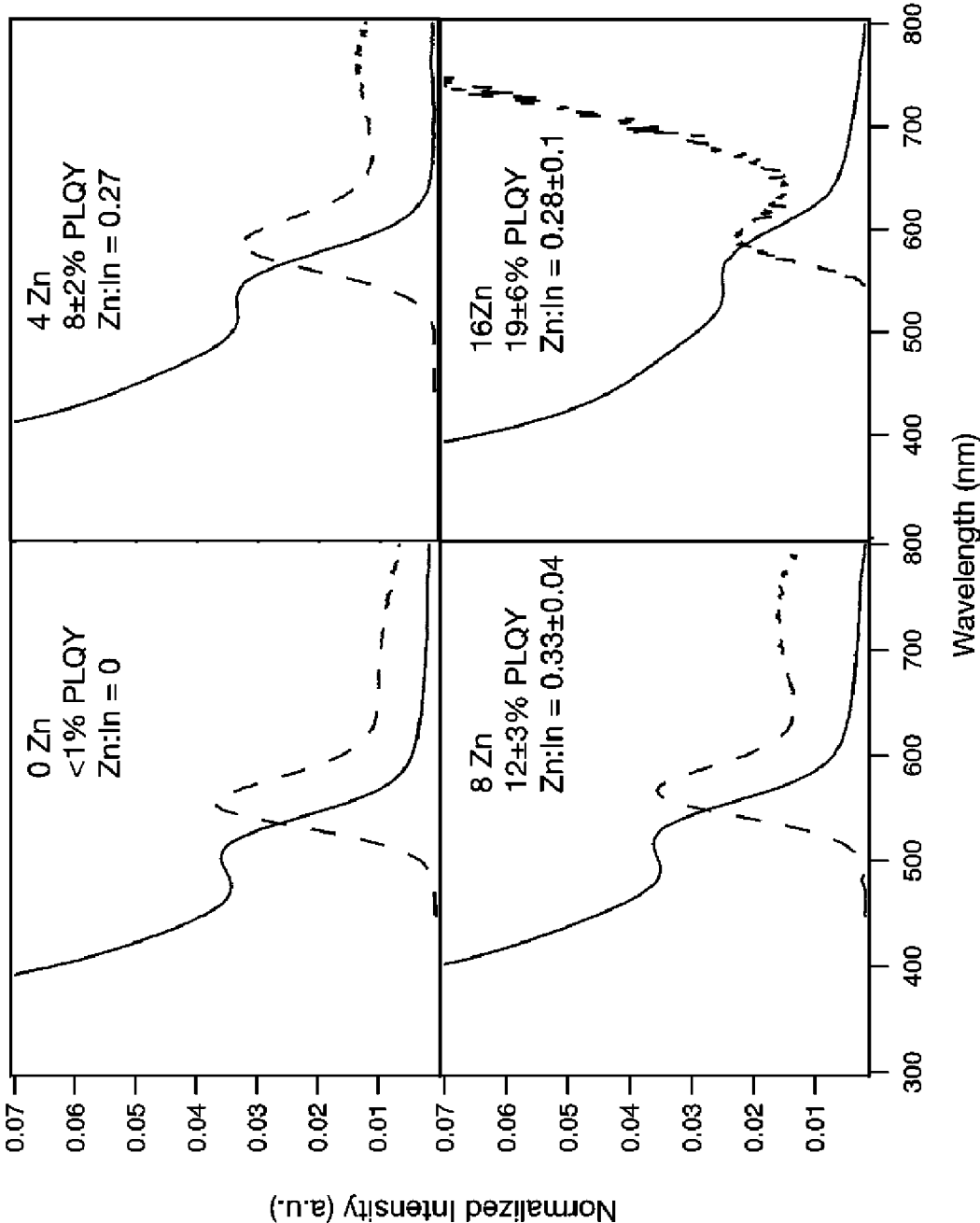


FIG. 17C

FIG. 17D

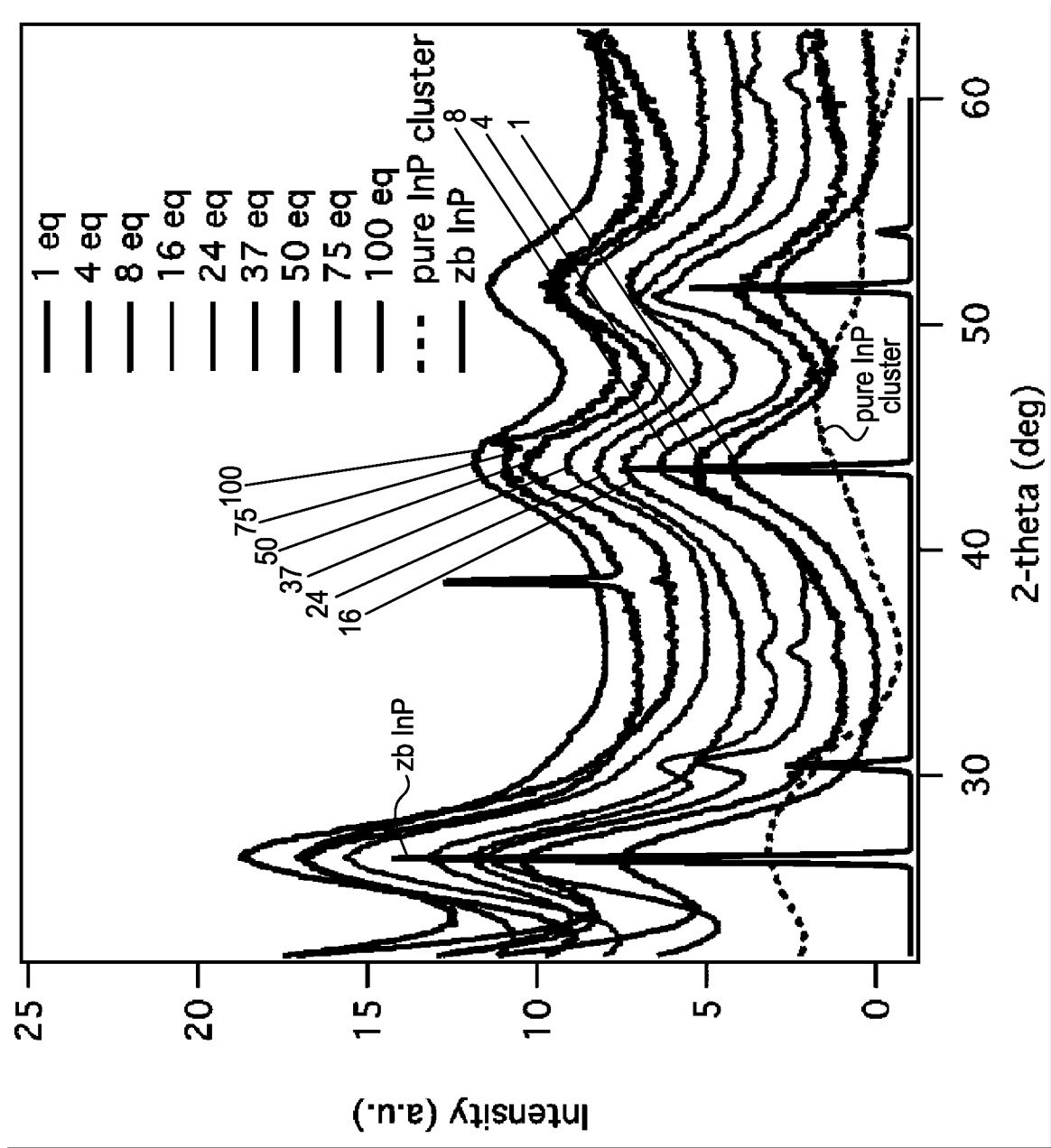
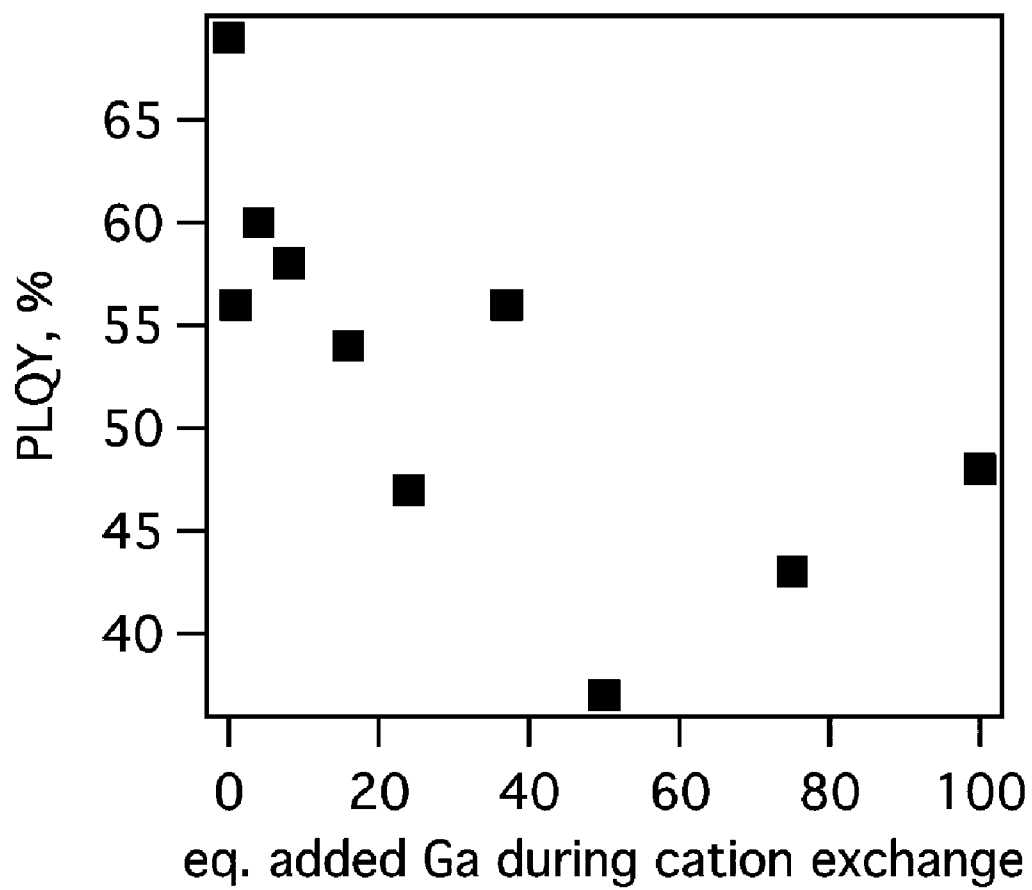


FIG. 18

***FIG. 19***

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/14807

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-4 and 17-27, directed to an indium phosphide cluster doped with zinc or gallium.

Group II: Claims 5-15, directed to a method for making an indium phosphide cluster doped with zinc or gallium.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

****please see the continuation at the end of this form****

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-4 and 17-27

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/14807

A. CLASSIFICATION OF SUBJECT MATTER

IPC - H01L 21/00 (2020.01)

CPC - H01L 51/502, H01L 21/02601, B82Y 30/00, C01G 9/00, H01L 21/02392, B82Y 20/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	↖ BROWN et al., "Synthesis and Degradation of Cadmium-Free InP and InPZn/ZnS Quantum Dots in Solution"; Langmuir, Volume 34, Issue 46 (November 2018); pg 13924-13934 (pg 1-26 in the attached document) (the entire attached document, and more specifically: pg 2, para 1; pg 3, para 2; pg 5, para 2-3; pg 6, para 1-2; pg 7, para 2; pg 10, para 3; pg 11, para 2; pg 15, para 1; pg 26; figure 1; abstract; table 2)	1-2, 4, 17-22 and 24-27
----		-----
Y		23
----		-----
A		3
Y	WO 2015/036762 AI (NANOCO TECHNOLOGIES LTD) 19 March 2015 (19.03.2015); the entire document, and more specifically: para [0005], [0033], [0042]-[0051], [0081]	23
A	↖ PIETRA et al., "Ga for Zn Cation Exchange Allows for Highly Luminescent and Photostable InZnP-Based Quantum Dots"; Chemistry of Materials, Volume 29, Issue 12 (June 2017); pg 5192-5199 (the entire document, and more specifically: pg 5192, col 2, para 2; abstract).	3
A	US 2007/0026645 A1 (LIEBER et al.) 1 February 2007 (01.02.2007); para [0208]	3
A, P	↖ FRIEDFELD et al., "Effects of Zn ²⁺ and Ga ³⁺ doping on the quantum yield of cluster-derived InP quantum dots"; The Journal of Chemical Physics, Volume 151, Issue 19 (November 2019); pg 194702-2 to 194702-9 (the entire document)	1-4 and 17-27
A	↖ WEGNER et al. "Gallium - a versatile element for tuning the photoluminescence properties of InP quantum dots"; Chemical Communication, Volume 55, Issue 11 (First published: 11 January 2019); pg 1663-1666 (the entire document)	1-4 and 17-27

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

11 May 2020

Date of mailing of the international search report

08 JUN 2020

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Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

**continuation of Box III (Lack of Unity) **

Special Technical Features:

Group I requires the ratio of In: P: Zn in the zinc-doped indium phosphide cluster is represented by the formula $\text{In}_a\text{P}_b\text{Zn}_c$, wherein a is an integer from about 20 to about 40, b is an integer from about 1 to about 25, and c is an integer from 1 to about 20, and wherein the ratio of In: P: Ga in the gallium-doped indium phosphide cluster is represented by the formula $\text{In}_d\text{P}_e\text{Ga}_f$, wherein d is an integer from about 20 to about 40, e is an integer from about 10 to about 25, and f is an integer from 1 to about 20, not required by group II.

Group II requires reacting an indium phosphide cluster with a zinc precursor or a gallium precursor effective for incorporating zinc or gallium, respectively, into an indium phosphide cluster to provide a zinc- or gallium-doped indium phosphide cluster, respectively, not required by group I.

Common Technical Features:

Groups I and II share the technical feature of an indium phosphide cluster doped with zinc or gallium.

However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by the article " Synthesis and Degradation of Cadmium-Free InP and InPZn/ZnS Quantum Dots in Solution" to Brown et al. (hereinafter Brown). Brown teaches an indium phosphide cluster doped with zinc (abstract; pg 5, para 2; The InP QD (indium phosphide quantum dot) synthesis uniquely combines the previously reported use of InP magic-sized clusters (MSCs) as a single-source precursor for indium and phosphorus to form InP QDs, with zinc incorporation and subsequent ZnS shelling, to form InPZn/ZnS QDs. In synthesis of InPZn alloyed core quantum dots, a InP MSC solution was injected into hot zinc stearate solution. Please also see instant specification, instant pg 8, ln 21-23: "In certain embodiments, the method comprises reacting an indium phosphide cluster with a zinc precursor or a gallium precursor effective for incorporating zinc or gallium, respectively, into an indium phosphide cluster to provide a zinc- or gallium-doped indium phosphide quantum dot, respectively.")

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

Note: Claim 16 is unsearchable because it is a dependent claim and is not drafted in accordance with the second and third sentences of Rule 6.4(a).