

# Surface Chemistry and Quantum Dot Luminescence: Shell Growth, Atomistic Modification, and Beyond

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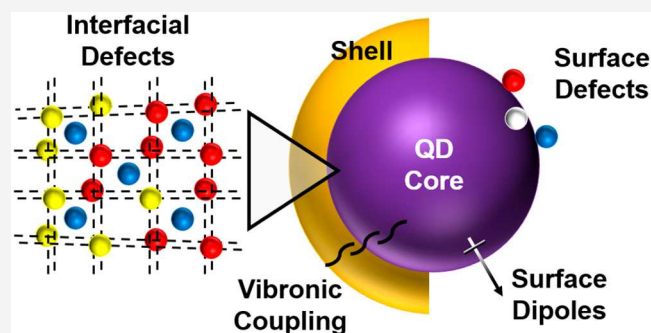


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**ABSTRACT:** Quantum dots are used in the research laboratory and in commercial applications for their bright, size-tunable luminescence. While empirical synthesis and processing optimization have led to many quantum dot systems with photoluminescence quantum yields at or approaching 100%, our understanding of the chemical principles that underlie this performance and our ability to access such materials on demand have lagged. In this Perspective, we present the status of our understanding of the connections between surface chemistry and quantum dot luminescence. We follow the historical arc that began with shell growth, which then led to an atomistic description of surface-derived charge trapping, and finally has brought us to a more nuanced picture of the role of surface concepts like surface dipoles and vibronic coupling.



chemistry in luminescence properties, including emerging

Following more than three decades of constant development, today quantum dots are widely used in displays, solid-state lighting, and biological imaging for their bright, tunable luminescence characteristics and ease of processing.<sup>1,2</sup> For some compositions, including CdSe and InP, photoluminescence quantum yields (PLQYs) in the visible approaching 100% are now achievable, if not routine. While bright emission can sometimes be a coincidental byproduct of synthesis or the result of empirical optimization, a deep understanding of the underlying structural and electronic properties that control luminescence is critical to the design of bright, color-pure quantum dot emitters. Today it is appreciated that many properties of quantum dots are controlled not only by the quantum confined nature of the semiconductor core but also in large part by their surface chemistry. The question we want to address in this Perspective

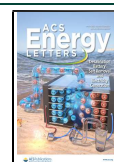
The question we want to address in this Perspective is: How does surface chemistry impact quantum dot luminescence?

under-passivated atoms or defects at the surface that serve as sites for charge carrier trapping.<sup>3–5</sup> An early synthetic strategy developed to eliminate these trap sites was shelling, which aimed to separate the quantum dot core and its charge carriers from the surrounding environment using a wider bandgap semiconductor layer that is structurally well-matched to minimize strain at the core/shell interface.<sup>6–10</sup> Our understanding of the atomistic details that underlie luminescence enhancement in shelled quantum dots has been advanced by detailed spectroscopic and structural investigations, as well as by targeted ionic and molecular chemical treatments of the quantum dot surface. Taken together, these studies are revealing a picture that is more complex and nuanced than previously appreciated. Factors including alloying (or doping), surface dipoles and (more generally) ligand electronegativity, and vibronic coupling are emerging as critical factors in understanding the origins of quantum dot luminescence and consequently our ability to control it. In this Perspective, we

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is: How does surface chemistry impact quantum dot luminescence? A primary answer to this question relates to



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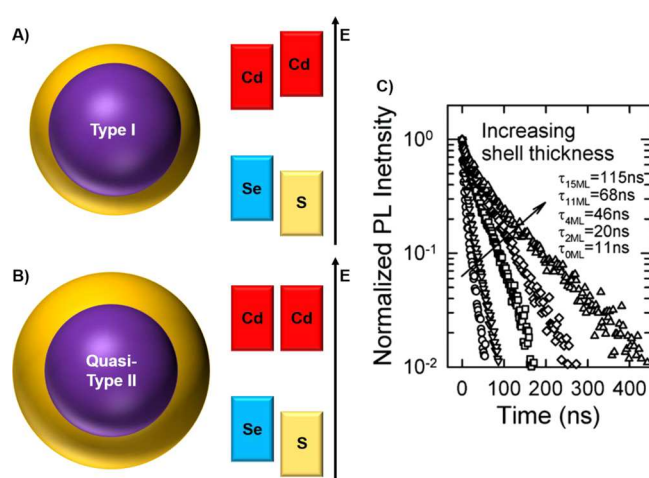
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seek to piece this knowledge together to reveal the current state of how surface chemistry impacts luminescence in quantum dots and how this knowledge can be used to advance the synthesis of perfect luminophores of diverse compositions for next-generation technologies.

## ■ SHELLING

To reliably increase the quantum yield of colloidal quantum dots, a shell of a wider bandgap semiconducting material is grown on the surface (Figure 1).<sup>6–9</sup> This serves a two-fold



**Figure 1.** Quantum dot shelling and classification by relative band edge alignment into type I (A) and quasi-type II systems (B). (C) Representative TRPL data for CdSe/CdS QDs as a function of shell thickness showing increasing lifetimes. Reprinted in part from ref 16. Copyright 2011 American Chemical Society.

purpose: to localize the photoexcited electron/hole pair to the core of the material and to help passivate surface defects that are largely responsible for the loss of luminescence in these materials. The traditional type I architecture has been explored in depth, with quantum yields exceeding 75% for materials such as CdSe/ZnS.<sup>11,12</sup> Alloying at the CdSe/ZnS interface can allow for a better lattice match and result in even higher quantum yields, especially with the addition of a ZnS outer shell layer.<sup>13</sup> Additionally, there have been many reports of remarkable increases in PLQY when CdSe was shelled with CdS.<sup>6–10</sup> When thicker CdS shells are applied, further redshifts with increasing shell thickness are observed along with lengthened exciton lifetimes, features indicative of a shift to a quasi-type II electronic structure (Figure 1). In quasi-type II systems, the conduction band edge energies of the core and shell materials are aligned, allowing the electron to be delocalized to the shell where it could encounter an electron trap. However, the confinement of the photogenerated hole to the core of the material leads to the suppression of nonradiative recombination as the carriers are spatially separated. In such cases, interaction of the trapped electron with a thermal vibration can allow the electron to repopulate the internal excitonic energy level and radiatively recombine. One such thick-shelled, quasi-type II CdSe/CdS system was described by Bawendi *et al.* with reported PLQY reaching up to 98%.<sup>8</sup> This was accomplished by an alternating deposition of cadmium and sulfur onto the surface of the CdSe nanocrystal using a successive ionic layer adsorption and reaction (SILAR) approach.<sup>8</sup> Further development of these thick-shelled CdSe/

CdS heterostructures was achieved through altering the shell precursor composition, with octanethiol replacing S(SiMe<sub>3</sub>)<sub>2</sub> as the chalcogen precursor. This change in chemistry allowed quantum yields to be maintained at or above 97% and reduced the fluorescence intermittency (*i.e.*, blinking) of the material, resulting in average on-times increasing from 60% to 90%, creating more reliably emissive ensembles.<sup>14</sup> Alivisatos *et al.* reported that omitting oleylamine results in reduced desorption of Cd(oleate)<sub>2</sub> surface ligands and thus higher ligand coverage, along with reduced charge trapping.<sup>15</sup> By first controlling the surface stoichiometry of the core and inner shells, then performing additional shelling reactions, the quantum yield can reach 100% for thick-shelled CdSe/CdS.

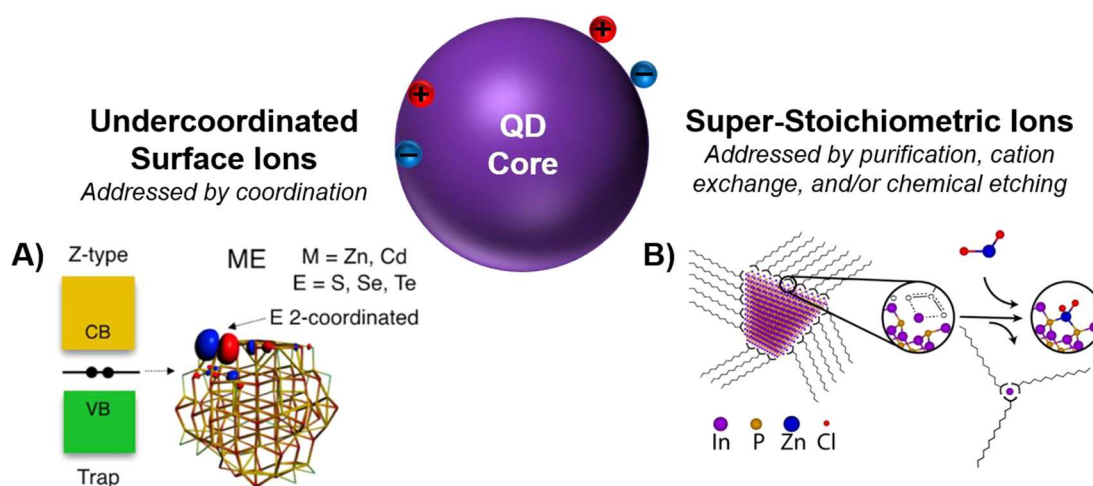
While it is not expected that the nature of trap states in II–VI and III–V QDs would be fundamentally distinct, II–VI QDs have relied on the aforementioned quasi-type II architectures to achieve the highest PLQY while III–V QDs have predominantly relied on the type I architecture to achieve high PLQY.<sup>17</sup> This focus on type I zinc chalcogenide shells in the III–V family may be a byproduct of considering InP as a replacement for Cd-containing materials,<sup>18,19</sup> as well as the ease of Cd alloying in InP lattices.<sup>20–22</sup> However, because of lattice strain between the InP core and the typical ZnS shell layer, new approaches using gradient shells have risen in popularity as a way to manage lattice mismatch and improve quantum yield further.<sup>23,24</sup> Although gradient shells have dominated research for the past decade, a recent shift in synthesis approach has occurred, with treatment/tuning of the native core's surface before shelling emerging as a highly important factor. For example, Peng *et al.* demonstrated that control over the surface stoichiometry of the native nanocrystals resulted in PLQYs as high as 93% for III–V-based emitters.<sup>25</sup> By removing excess indium at the surface of the core, indium atoms were prevented from incorporating into the shell, allowing the pristine shell layer to effectively serve as an energetic barrier to confine the photogenerated carriers to the core. This fine surface control has been further developed by surface etching using HF prior to shelling InP QDs. This process removes both excess indium on the surface and phosphates that result from surface oxidation. The removal of these species, followed by the growth of gradient ZnSeS shell, led to near unity PLQY, with high stability maintained for ~4300 h.<sup>18</sup>

## ■ ATOMISTIC CHEMICAL MODIFICATION

Taken together, the historical development of shelling chemistry and the assessment of its impact on PLQY have revealed the importance of control of the core/shell interface in achieving unity quantum yields. Pushing our understanding

Pushing our understanding beyond these empirically determined design principles, however, necessitates an atomistic description of QD surface chemistry.

beyond these empirically determined design principles, however, necessitates an atomistic description of QD surface chemistry. A wide variety of chemical treatments have led to enhancement of PLQYs without the growth of a full shell, prompting more in-depth investigations to interrogate the



**Figure 2.** Electronic trap sites in binary QDs arising from undercoordinated surface ions and superstoichiometric ions. (A) A 2-coordinate chalcogenide ion resulting from Z-type ligand displacement at the surface of a II–VI QD acting as a site for hole trapping. Reprinted from ref 4. Copyright 2017 American Chemical Society. (B) Exchange of indium carboxylate for zinc chloride results in an enhanced quantum yield in InP QDs. Reprinted from ref 33. Copyright 2020 American Chemical Society.

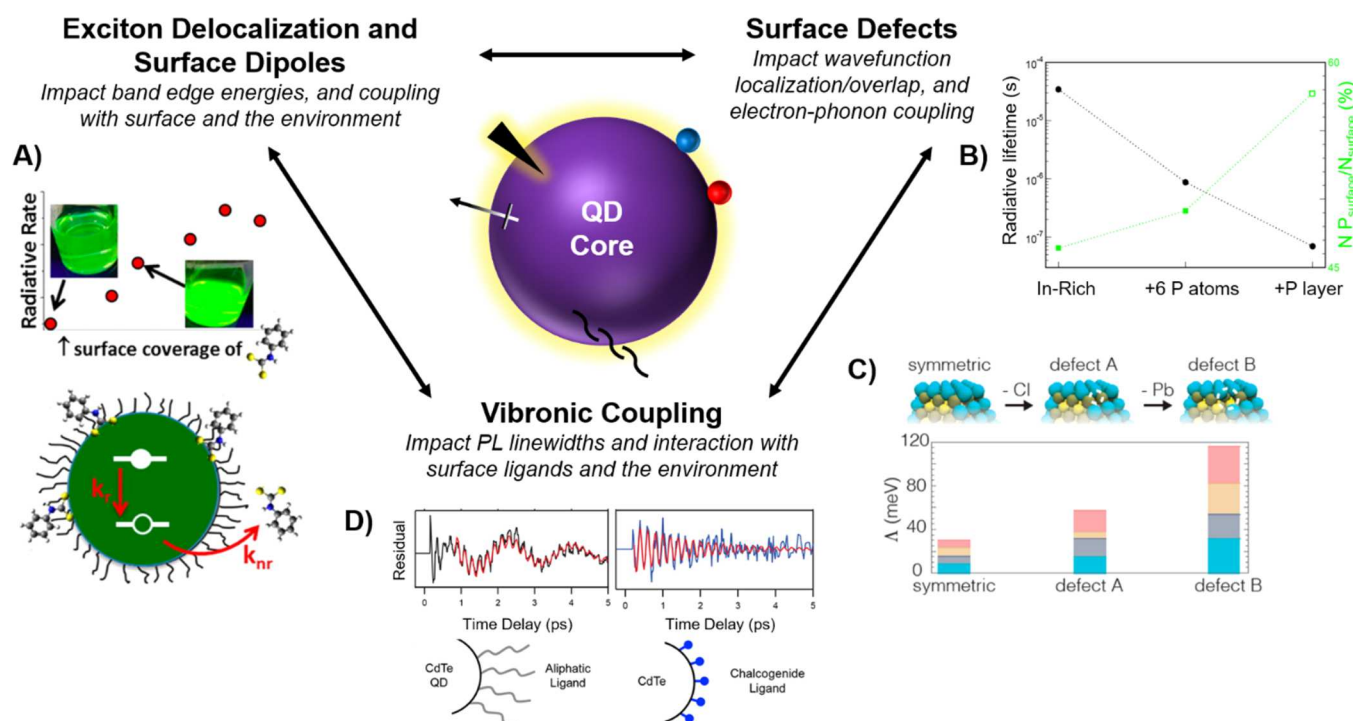
origin of these effects. This atomistic approach, in contrast with shelling, has allowed for examining cationic or anionic surface sites separately, revealing the critical role of stoichiometry and the presence of undercoordinated surface sites in QD luminescence (Figure 2). A variety of both shallow and deep trap states have been identified and implicated spectroscopically for II–VI and III–V quantum dots.<sup>3,26–29</sup> Eliminating these surface traps is a crucial step in obtaining bright QDs, because these traps act as local energy minima that can prevent or delay electron–hole recombination.<sup>30</sup>

Theoretical models have provided guiding principles for the chemical identity of surface traps that can be experimentally verified. For example, for II–VI QDs with a zinc blende structure, it has been concluded that a primary source of surface hole traps are stable two-coordinate chalcogenide ions at the QD surface that arise from the displacement of, or a synthesis-specific lack of termination by metal complexes, or so-called “Z-type” ligands (Figure 2A).<sup>3,4</sup> Adapting Green’s formulation, ligands that coordinate the nanocrystal surface are commonly classified as L, X, and Z-type for datively bound neutral donors (Lewis bases), anionic one-electron donors, and neutral acceptors (Lewis acids), respectively.<sup>31,32</sup> Intriguingly, two- and three-coordinate metal ions at the QD surface did not show a propensity to form midgap trap states. Because of this, the addition of neutral L-type ligands to the undercoordinated cation sites was expected to not dramatically impact the luminescence properties in these systems.<sup>4</sup> Furthermore, it has been shown that depending on the relative positions of the valence and conduction band edges of a QD material, chemical oxidation (*i.e.*, by air) or n-type doping during synthesis can result in surface speciation that also introduces midgap traps.<sup>3</sup>

These theoretical studies suggest that the stoichiometry of QD surfaces should play a dominant role in QD PLQY and our ability to tune it. While as-synthesized QDs are typically cation-rich, the surface can be post synthetically modified to tune the cation-to-anion ratio.<sup>34</sup> Sfeir *et al.* reported on the carrier dynamics of CdSe QDs whose surface composition was controlled from cation-rich ( $\sim 80\%$  surface cadmium) to stoichiometric ( $\sim 50\%$  surface cadmium) using *N,N,N',N'*-tetramethylethylenediamine (TMEDA).<sup>35</sup> Tuning the QD stoichiometry in this way requires consideration of the number

and type of ligands to maintain charge neutrality, which was achieved through the displacement of the metal–ligand complex, *i.e.*, cadmium carboxylate. It was observed that the reduced surface cadmium fraction led to a nonlinear decrease in the PLQY and an increase in the PL decay rate due to hole trapping at the newly exposed surface selenium atoms. From these results, surface coverage by cadmium carboxylate and the rate of hole trapping were correlated, noting the heterogeneity in the chemical and electronic structure of the surface selenium sites, which was corroborated by an independent study examining cadmium carboxylate displacement isotherms consistent with considerable surface heterogeneity.<sup>36</sup> In terms of the surface structure, it was hypothesized that this heterogeneity may arise from the facet-dependent orbital interactions of adjacent undercoordinated Se atoms.<sup>35</sup> Specifically, interactions between adjacent selenide ions, which are dominated by  $\sigma$ -type bonding in the (100) plane and  $\pi$ -type bonding in the (111) plane, can translate into different hole-trapping efficiencies.<sup>35</sup>

This effect of stoichiometry modulation has been extended to other surface treatments, with a focus on Lewis acids to passivate undercoordinated anion sites and thereby eliminate hole traps as discussed above. For example, it was demonstrated that QD surface treatment with Z-type ligands (*i.e.*, metal halides and carboxylates) leads to an increase in the PLQY to varying degrees depending on the identity of the Z-type ligand.<sup>5</sup> While the highest PLQYs ( $>70\%$ ) were achieved with  $\text{InCl}_3$  and  $\text{CdCl}_2$  on phosphonate-capped CdTe QDs, the effects were also generalized to CdSe, CdS, InP, and Zn-doped InP QDs. Moderate increases in PLQY were attributed to weaker binding and steric repulsion based on the observation that smaller halide ions and shorter carboxylate chain lengths trend toward higher PLQY. It was also noted that ligands such as amines and alkylammonium chloride that are not Z-type ligands give rise to a smaller increase in PLQY, consistent with previous suggestions of cation vacancies as sites of nonradiative recombination.<sup>37,38</sup> While theoretical models predicted only anion-related trap states upon removal of Z-type ligands, these experimental results drew attention to cation-related trap states, adding to the complexity of addressable QD surface states, especially outside the II–VI family of compounds where



**Figure 3.** Exciton delocalization, surface dipoles, surface defects, and vibronic coupling impact quantum dot optical properties and are often coupled phenomena. (A) Phenylthiocarbamate ligands increase the apparent excitonic radius and enhance the probability of band-edge recombination in CdSe QDs. Reprinted from ref 44. Copyright 2014 American Chemical Society. (B) The radiative lifetime of InP QDs is tuned by surface stoichiometry. Reprinted from ref 46. Copyright 2020 American Chemical Society. (C) Reorganization energy computed for three distinct QDs demonstrating increased electron–phonon coupling strengths, without any noticeable change in ground state electronic structure, for defect-containing QDs. Reprinted from ref 47. Copyright 2020 American Chemical Society. (D) Oscillatory components of transient absorption kinetics show that inorganic surface ligands enhance vibrational coupling of QDs with their environment. Reprinted from ref 48. Copyright 2018 American Chemical Society.

increased covalency could render superstoichiometric cations sites for electron trapping.

Phenomenologically similar effects of Lewis acids on the PLQY of carboxylate-capped InP QDs have been previously reported by our group. We observed that the surface treatment of InP QDs with zinc or cadmium carboxylate leads to increases in the PLQY of up to ~50% and confirmed that zinc and cadmium carboxylate displaces the native surface indium carboxylate (Figure 2B) based on elemental analysis and the eventual formation of independent In<sub>2</sub>O<sub>3</sub> particles from decomposition of the displaced indium carboxylate.<sup>21</sup> Further, extended X-ray absorption fine structure (EXAFS) analysis corroborated that the divalent metal cations were mostly on the surface rather than incorporated into the InP core. This surface treatment is reversible with the use of TMEDA, which cleaves the metal carboxylate from the surface and results in a consistent decrease in PLQY upon titration.

In a study that followed, ultrafast TA and TRPL spectroscopy were used in tandem to probe the charge carrier dynamics of the surface-treated InP QDs.<sup>39,40</sup> Interestingly, it was revealed that of both electron and hole traps that exist in InP QDs, it is the electron traps that are eliminated as a result of the surface treatment by the divalent Lewis acids. A similar effect was also observed for treatments with fluoride. Taken together, this elimination of electron traps points to indium dangling bonds as a possible culprit in the low PLQY. Coordination by small, hard anions like fluoride, or replacing undercoordinated indium with cadmium or zinc carboxylate eliminates these sources of electron trapping. This mechanism

of trivalent indium carboxylate displacement by divalent Lewis acids was recently given further support from thermodynamic measurements by Alivisatos *et al.* (Figure 2B). In these studies, isothermal titration calorimetry was used to show that metal halides displace indium carboxylates, enhancing the luminescence, and revealing the importance of interligand interactions at QD surfaces.<sup>33</sup>

## ■ THINKING BEYOND TRAP STATES

Atomistic surface modifications can do more than simply passivate or introduce electronic trap states (Figure 3). Fluorination of an InP QD surface is a facile method for PLQY enhancement that has been known for as long as the synthesis of colloidal InP QDs has existed.<sup>41</sup> Recently, Alivisatos *et al.* revisited the surface passivation of InP with fluoride and offered new hypotheses regarding the structural and electronic modifications that influence the PL properties.<sup>42</sup> The observation that surface fluoride ions, when used at low concentrations before etching effects dominate, cause a redshift in both absorption and emission was attributed to greater delocalization of electrons in the conduction band, along with the decrease of the optical oscillator strength due to the highly electronegative fluoride layer. The oscillator strength of QDs, which is dependent on the QD ligand environment and is influenced by the shape and symmetry of the charge carrier wave functions, was calculated to show a decrease with fluoride passivation of surface indium sites.<sup>42</sup> This agrees with the longer radiative PL decay time (*i.e.*, lower radiative recombination rate) that was measured, as oscillator strength

is proportional to the radiative recombination rate. The strong electron-withdrawing property of fluorides, combined with their small size and high binding affinity, makes the optical properties of InP/F distinct from as-synthesized or shelled InP QDs. Upon further investigation of metal halide passivation on InP QD surfaces, it was proposed that PLQY enhancement is influenced by the electron-withdrawing effects of the surface ligands that withdraw the negative charge from the surface and reduce hole trapping.<sup>33</sup>

The above study of fluoride on InP QDs highlights the ability of surface ligands to independently modulate electron and hole wave functions.<sup>42</sup> The effects of surface ligands that are “exciton-delocalizing” have also been reported by Weiss *et al.* in the case of CdSe QDs capped with phenyldithiocarbamate (PTC) by ligand exchange (Figure 3A).<sup>43,44</sup> To achieve mixing with the exciton wave function, the ligand orbitals must have a suitable match in both energy and symmetry. Successful electronic coupling of QD exciton and ligand orbitals in the case of PTC was demonstrated by a characteristic redshift, along with an increase in the PLQY and the oscillator strength of emissive transitions, due to the delocalization of the charge carrier wave functions. Similarly, Dukovic *et al.* showed that inorganic chalcogenide ligands, such as Se<sup>2-</sup>, on CdTe QDs behave as if they are a passivating shell layer.<sup>45</sup> Significant delocalization of the carrier wave functions beyond the QD surface itself was observed.

If chalcogenide ligands can couple strongly to exciton wave functions in II–VI QDs, this naturally leads to a question about the role of pnictides on III–V QDs. As discussed previously, Peng *et al.* have recently demonstrated experimentally that stoichiometry control of InP cores to increase the relative ratio of P:In is a viable strategy to enhance QY in these materials.<sup>25</sup> Their hypothesis focused on reducing indium alloying in the shell as the mechanism for PLQY enhancement, but recent computational work may suggest an additional factor. Califano *et al.* modeled atomistically ideal and fully passivated InP QDs and found that these structures may still exhibit undesirable PL properties. The long radiative lifetimes, broad line widths, and low PLQY were attributed to a relative displacement between the electron and hole wave functions and therefore reduced coupling between them.<sup>46</sup> The addition of a few P atoms on the In-rich surface, however, was shown to reduce the radiative lifetime (Figure 3B) and the Stokes shift, suggesting a path forward to increasing QY by controlling the core stoichiometry.

**The role of ligand coupling through orbital mixing, phonon interactions, and surface dipole modulation has created a vast new parameter space for system design.**

A complex relationship between photoluminescence and vibrational lattice modes (phonons) is also emerging. Electron–phonon coupling has been shown to be large in colloidal QDs and can promote high rates of nonradiative recombination and dramatically impact luminescence line widths, especially in single-particle spectra.<sup>49–51</sup> Recent work from Wood *et al.* posits, in fact, that the primary impact of surface passivation is not the elimination of electronic defect states, but rather mechanical stabilization of the QD surface. In

contrast to the approaches discussed above, which aim to remove electronic trap states at QD surfaces, this work suggests that nonradiative rates might be better controlled by engineering mechanical stability and electron–phonon coupling at the NC surface.<sup>52</sup> Bawendi *et al.* have also demonstrated the interplay between luminescence broadening and the shell composition of CdSe/CdS QDs.<sup>51</sup> They found that the most drastic broadening occurs when the photoexcited electron wave function spreads into the shell, while the hole stays localized in the core. An interesting consequence of this decreased wave function overlap is polarization of the nanocrystal excited state, which enhances electron coupling to longitudinal optical phonons. Alternatively, through increased Fröhlich coupling in the CdS shell compared to the CdSe core, the photoexcited electron can also interact with shell phonons more than it does with the core. These findings were reinforced by studies from Wood *et al.* which showed that exciton coupling to localized vibrations arising from under-coordinated surface atoms broaden PL line widths, consistent with the observations that homogeneous PL line widths decrease with increasing QD size.<sup>47</sup>

Phonons have also been noted to play a critical role in the emission of InP core/shell structures, with recombination processes involving both optical and acoustic phonons of the core and shell materials.<sup>53</sup> As the shell composition changes and allows for more electron wave function delocalization, slight polarization of the exciton occurs and the electron–phonon coupling is increased, resulting in decreased lifetimes observed *via* low-temperature TRPL spectroscopy. Notably, at low temperatures, the dark state of InP is dominant, requiring electron–phonon coupling to become emissive. Phonons also broaden the dark state emission spectrum of InP, suggesting another potential avenue for tuning the emission line width, although the impacts for room-temperature applications in ensemble samples remain unknown.

Beyond shelling, phonon interactions can also be tuned by altering the capping ligands of the material.<sup>48</sup> By tuning the capping groups from aliphatic ligands to inorganic chalcogenides, for example, it is possible to critically damp the acoustic phonons present in the material, ascribed to energy dissipation once phonons reach the surface and dissipate into the surroundings (Figure 3D). In other studies, an exciton-induced electron density shift in InP clusters has been demonstrated to directly affect the vibrational motion of the carboxylate ligands on the surface using transient IR spectroscopy.<sup>54</sup> These results raise many questions regarding the extent of vibronic coupling to surface ligands and how to use this property to direct exciton relaxation pathways, a topic we expect will become highly relevant to future quantum dot design as the application space continues to broaden beyond the realm of displays, lighting, and biological imaging.

In conclusion, chemists, materials scientists, and engineers have contributed to significant advances in our understanding of how surface chemistry impacts QD luminescence by combining synthesis, spectroscopy, and experimentally verifiable theoretical models. This work has moved us from empirical optimization of shelling chemistry, to the ability to atomistically tailor the surface chemistry and specifically address relevant defect or trap sites, ultimately resulting in improved optical properties through rational design. In addition, the role of ligand coupling through orbital mixing, phonon interactions, and surface dipole modulation has created a vast new parameter space for system design. Whereas

early high-performing QD emitters relied on thick, insulating shell layers, thereby restricting applications to passive down-conversion, more modern approaches that focus on atomistic interfacial tuning generate core/shell QDs with high quantum yields that can still be modulated through electrical injection, paving the way for electroluminescent systems on the horizon.

As our sophistication to take advantage of trap passivation and ligand coupling advances, future generations of QDs with perfect quantum yields without shell layers may be possible, opening new opportunities in areas like catalysis and quantum information.

As our sophistication to take advantage of trap passivation and ligand coupling advances, future generations of QDs with perfect quantum yields without shell layers may be possible, opening new opportunities in areas like catalysis and quantum information. All in all, the future of QDs is bright!

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### Notes

The authors declare no competing financial interest.

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