

Colloidal quantum dots for optoelectronics

A.J. Houtepen¹, E.H. Sargent^{2,3}, I. Infante^{4,5}, J.S. Owen⁶, P.B. Green^{7,8}, R.D. Schaller^{9,10}, S. Bals^{11,12}, S. Zeiske², T. Stöferle¹³, Z. Hens^{7,8*}

- 1 Optoelectronic Materials Section, Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands
- 2 Department of Chemistry, Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois, USA
- 3 Department of Electrical and Computer Engineering, University of Toronto, Toronto, Canada
- 4 BCMaterials, Basque Center for Materials, Applications, and Nanostructures, Leioa, Spain
- 5 Ikerbasque Basque Foundation for Science, Bilbao, Spain
- 6 Department of Chemistry, Columbia University, New York, New York, United States
- 7 Physics and Chemistry of Nanostructures, Department of Chemistry, Ghent University, Gent, Belgium
- 8 Center of Nano and Biophotonics, Ghent University, Gent, Belgium
- 9 Department of Chemistry, Northwestern University, Evanston, Illinois, USA
- 10 Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois, USA
- 11 EMAT, University of Antwerp, Antwerp, Belgium
- 12 NANOLab Center of Excellence, University of Antwerp, Antwerp, Belgium
- 13 IBM Research Europe — Zurich, Rüschlikon, Switzerland

* Corresponding author: zeger.hens@ugent.be

Abstract

Colloidal quantum dots (QDs) are semiconductor nanocrystals that have unique size-tunable optoelectronic properties and are suitable for wet processing. QD research aims to answer fundamental questions about the chemical and physical properties of nanoscale materials and use these tools for technological applications ranging from bio-imaging to quantum optics. At the core of this field is a set of synthetic, processing, and analytical methods designed to produce QDs in uniform ensembles that meet the highest performance standards. This Primer reviews QD fabrication methods with a focus on the applications of QDs in printed optoelectronics and quantum optics. After outlining the current state-of-the-art QD syntheses the experimental and computational analysis of QDs is discussed. These topics are then connected to the methodologies, processes and concepts required for developing QD-based photodetectors, light-emitting devices, and quantum optics applications. Special attention is given to challenges in reproducibility and current limitations of the field, such as the need to balance non-restricted material composition with high performing technology while achieving long-term stability in QD devices under operating conditions. Finally, the ongoing advancement in QD synthesis, precise atomic-level analysis and computational methodologies are highlighted as key drivers toward rational QD design, particularly in understanding how structural changes under loading impact QD properties.

[H1] Introduction

Quantum dots (QDs) are nanometer-sized semiconductor crystallites where the energies of electrons and **excitons [G]** are governed by nanocrystal size and shape, a phenomenon known as **quantum confinement [G]**.¹⁻³ Wet chemical methods enable QDs to be synthesized by precipitation reactions yielding colloidal dispersions of QDs. QD research advanced significantly after the discovery that adjusting the balance between **nucleation [G]** and growth in a colloidal synthesis allows for the production of large batches of QDs with precisely controlled size and shape.⁴ Access to semiconductor **nanocolloids [G]** with tunable optoelectronic properties sparked an extensive research effort into the fundamental aspects of size quantization,⁵ and inspired the formation of QD devices by wet-processing methods, such as spin coating, bar coating or inkjet printing (**Supplementary Information S1**).⁶ **Figure 1** illustrates how various technologies resulted from QD solution processibility, including solar cells and photodetectors,⁷ color-converted and electroluminescent light emitting diodes (LEDs),^{8,9} **luminescent solar concentrators (LSCs) [G]**,¹⁰ optically pumped lasers,¹¹ electrically pumped superluminescent LEDs,¹² and initial milestones in quantum technology.¹³ Notably, QD-based devices derived from this research often address gaps in contemporary technology, such as QD-enhanced displays providing unmatched color rendering,¹⁴ and infrared imagers offering a low-cost alternative to existing systems and new capabilities for multispectral imaging.¹⁵

QD technology requires QDs of the highest quality. Initially, the most-used QDs involved Cd-based II-VI and Pb-based IV-VI chalcogenides for applications involving visible and infrared light, respectively. Later, research was extended to Pb-based perovskites for their excellent optical properties,¹⁶ In-based III-V pnictides and Cu-based I-III-VI₂ chalcopyrites, which fully comply with regulations on hazardous substances,¹⁷ and Zn- and Hg-based II-VI chalcogenides to cover ultraviolet and mid infrared wavelengths.¹⁸ The potential of these different QDs can be evaluated using various figures of merit. As listed in **Table 1**, these include typical linear characteristics of optical materials, such as the **photoluminescence quantum yield [G]** (PLQY) and the emission linewidth. Applications in lasing and quantum optics, on the other hand, require more specific properties, such as the **biexciton [G]** lifetime and the exciton **dephasing [G]** time, which are summarized in **Table 2**. Achieving the most desirable properties for a given application relies on a high level of control over QD synthesis and careful modifications of the QD surface. For instance, forming **core/shell [G]** heterostructures can suppress non-radiative recombination of electron-hole pairs through passivation of surface-localized **trap states [G]**.¹⁹ Replacing long organic ligands — typical as-synthesized surface terminations — with shorter moieties enhances charge-carrier mobility in QD assemblies,²⁰ while a graded core/shell interface reduces non-radiative recombination of biexcitons by impeding **Auger recombination [G]**.²¹

This Primer surveys the key methods required for producing high-quality QDs, with an emphasis on essential concepts and insights. Starting from the latest progress in QD synthesis, experimental and computational methods to determine the atomistic structure, surface composition, and optoelectronic properties of QDs are discussed. While examples will be taken from literature on CdSe, InP, CsPbBr₃ and PbS QDs, which have been most extensively researched, many results can be generalized to a broader range of QDs. Material synthesis and analysis are then connected to advancements in QD processing and the development of color-conversion, printed optoelectronics and quantum applications. This Primer addresses the reproducibility and limitations of current methods, emphasizing the need for QDs composed of high-performance materials that are stable under operational conditions and not subject to toxicity restrictions. With continued progress in

QD synthesis, precise atomic-scale analysis, and computational methodology, there is a promising outlook for rational QD design.

[H1] Experimentation

As outlined in **Figure 1**, the discovery of the hot injection synthesis of cadmium chalcogenides gave rise to a range of synthetic protocols for the formation of QDs with different composition, heterostructure, or shape. In parallel, studies addressed the chemical mechanisms of the underlying reactions, proposing strategies for size control and addressing the problem of polydispersity. This section will cover these general, mechanistic insights. A more exhaustive overview of synthesis protocols is provided in **Supplementary Information S2**.

[H2] Quantum dot synthesis methods

A QD synthesis typically starts from (I) precursors that react to form solutes, followed by the precipitation of these soluble building blocks into crystals by (II) nucleation and (III) growth (**Figure 2a**). Typically, this synthesis is implemented through the swift injection of one or more precursors into the hot surfactant mixture, a process known as hot injection. Reaction conditions, including the composition of the reaction mixture as well as the injection and reaction temperature, are designed to produce an ensemble of QDs with a narrow size distribution. In this respect, hot injection was seen as implementing La Mer's canonical model of particle formation,²² in which **monodisperse [G]** colloids are obtained through a burst of nucleation that is initiated by the **supersaturation [G]** of solutes formed by the precursor conversion (**Figure 2b**). In line with **Figure 2a**, the (I) buildup of supersaturation is caused by the formation of solutes from the precursor conversion reaction and leads to crystallization through (II) nucleation and (III) growth. Furthermore, the average size of the QD ensemble can (IV) further evolve after completion of the precursor conversion through ripening, which can induce unwanted broadening of the size-distribution. Many successful examples exist, however, of QD syntheses that slowly heat the precursors and surfactants to the synthesis temperature or gradually add precursors using a syringe pump. Such methods are inherently more scalable, and produce size distributions that rival those of hot injection techniques.²³

As outlined in **Supplementary Information S2**, a range of synthetic procedures has been developed, leading to monodisperse QD batches that are optically active across a broad range of wavelengths (**Table 1**). Even so, reproducing these results can be difficult as the purity of synthetic precursors and specificity of reaction conditions can strongly affect QD formation. Thus, improving QD syntheses typically relies on empirical optimization, where synthetic design is only weakly linked to the accepted mechanism of QD formation. Better mechanistic insight can, however, support the development of even higher performing materials at larger scale and improve the understanding of the relation between QD structure and function.

[H3] Size control by balancing nucleation and growth kinetics

The reaction between precursors is an essential component of QD synthesis. Its reliability affects synthetic reproducibility as it governs the balance between nucleation and growth stages by controlling the supply rate, Q , of soluble building blocks. Sugimoto argued that at the moment nucleation stops, the solute supply rate matches the QD growth rate (the rate at which building blocks are incorporated in existing QDs).²⁴ The supply rate is given by the product of the growth rate G per QD and the number of crystals n :

$$Q = G \times n \quad (1)$$

Eq. 1 explains how the interplay between solute supply, nucleation and growth can be leveraged to adjust the QD size. An inverse relation exists between the final number of QDs produced during nucleation and the growth rate, meaning that faster growth kinetics lead to fewer nuclei and larger final sizes. Similarly, the solute supply kinetics can tune the extent of nucleation. Reactive precursors that supply solutes more rapidly will promote nucleation — producing a higher n at fixed G — and thus decrease the QD size.²⁵

Several classes of reagents derived from phosphine chalcogenides,^{25,26} chalcogenoureas,^{27,28} dichalcogenides,²⁹ and aminophosphines³⁰ have been used to provide orders of magnitude differences in the conversion reactivity and study its impact on size control. Moreover, independent control over the conversion reactivity allows the temperature of the synthesis and the solute supply to be decoupled, and the influence of temperature on the nucleation and growth stages to be isolated from the precursor reaction.^{30,31 30,31}

[H3] Formation of monodisperse quantum dot batches

While size control determines the range of wavelengths accessible to QDs of a single material (λ_x in **Table 1**), monodisperse QD batches show a minimal spread around a single wavelength ($\Delta\lambda_x$ in **Table 1**), thereby emitting more monochromatic colors or enhancing charge-carrier mobility. According to La Mer's model, solute supply creates a supersaturated mixture in which a burst of nucleation quickly establishes an ensemble of crystals that then grow slowly in unison (**Figure 2b**).²² The monodispersity of the ensemble results from the short nucleation period that separates the nucleation and growth stages in time. Alternatively, monodisperse distributions can result from size dependent growth kinetics that narrow the polydispersity during growth, a process commonly called size focusing.

Size-dependent growth kinetics are a natural consequence of mass transport limitations when growth is limited by the kinetics of solute diffusion to the crystal rather than the kinetics of solute attachment to its surface. Solutes become depleted near the QD surface, which induces an inverse dependence of G on the QD radius as outlined in **Figure 2c**. Under such conditions, the faster growth of smaller QDs will focus the size distribution as the ensemble of sizes grows.³² The broad acceptance of this mechanism, and the assumption of size-independent attachment kinetics, led numerous groups to explain the narrowing of the QD optical spectrum by diffusion-limited growth mechanisms.³³ However, direct evidence of diffusion-limited growth of QDs is lacking, and estimates of the growth rate constant are orders of magnitude smaller than diffusion in studies of CdSe and PbS.^{34,35} Similarly, while explaining QD synthesis through burst nucleation is common practice, this mechanism is not well supported by experiments.³⁶

The size and size dispersion of a growing QD ensemble can be measured using *in situ* small angle x-ray scattering, or *ex situ* optical measurements (**Supplementary Information S2**). Combining both methods, recent studies found a long nucleation stage that substantially overlaps with the growth process.^{30,35,37,38} These findings clearly contrast with the argument that La Mer's burst nucleation drives the narrow polydispersity typical of QDs. The narrow size distribution observed under those conditions therefore must arise from size distribution focusing during growth.

Interestingly, those studies also argue that the size distribution focusing is not caused by diffusion limited growth, but by the reactivity of the surface toward the attachment of solutes. In order to size focus, the reactivity of the QD surface toward solute attachment must decrease as the size grows. A variety of mechanisms could explain the size dependence of the growth kinetics of

nanocrystals, such as size-dependent facet nucleation,^{39,40} ligand penetration,⁴¹ and size-dependent ligand binding (**Figure 2d**).^{42,43} These are new explanations of size focusing with little precedent, as surface reaction limited growth is typically argued to be size independent. Importantly, the reduced surface reactivity of larger QDs toward growth causes the extended nucleation, which counteracts monodispersity.³⁸ Translating these mechanistic insights in practical synthesis protocols should therefore address a better separation of nucleation from growth, and optimize the size dependence of the reactivity toward growth.

[H3] Growth by ripening

In the absence of solute generation from precursor conversion, the QD size can still evolve through ripening. As depicted in **Figure 2e**, the ensemble can cannibalize itself by the exchange of monomers, shrinking some crystals to grow others, a process known as Ostwald ripening. Typically, Ostwald ripening is associated with the slow and steady increase in size and polydispersity of a QD ensemble. Interestingly, the inverse process has also been observed, which *narrows* the size distribution and increases the surface area of the ensemble, as first reported by Klabunde in studies of gold.⁴⁴ This so-called digestive ripening can be triggered by exposure to a surfactant ligand and heat, after which a broad distribution of large sizes narrows down and shrinks to smaller average size. While digestive ripening of gold in thiol solution is well established, recent reports indicate that digestive ripening can also be used to improve the polydispersity and reduce the size of metal chalcogenide and perovskite QDs.⁴⁵⁻⁴⁷

The simultaneous reduction in diameter and narrowing is an apparent violation of the Gibbs-Thompson relationship, which argues that the surface tension is reduced as the average size increases and the total surface area drops. That discrepancy is an indication that strong ligand-surface bonding in QDs can lead to enthalpically favorable surface energies. Similar arguments can explain the stability so called “magic size clusters”, as shown in **Figure 2f**. Both examples indicate that ligand stabilization of the QD surface is an important component of polydispersity control and presents a new angle to achieve QDs with molecule-like homogeneity.

[H1] Results

QDs are hybrid objects, combining a crystalline inorganic core with a surface often terminated by organic ligands. The interplay between core and surface determines the optoelectronic properties of QDs, and establishing this relationship between structure and property requires a broad range of analytical techniques, from determining the QD geometry to understanding the relaxation of photo-excited QDs. This section provides an overview of the most important methods for experimental and computational QD analysis, with additional background contained in **Supplementary Information S3-S8**.

[H2] Quantum dot characterization

Advances in colloidal synthesis have yielded semiconductor nanocrystals with a broad range of geometries. Zero-dimensional (0D) QDs, featuring **strong confinement [G]** in 3 directions, can be made as quasi-spheres, cubes or tetrahedrons. 1D quantum rods with confinement in 2 directions or 2D quantum wells confined in one direction can be obtained with narrow size dispersion (**Supplementary information S2**).^{48,49} In addition, multi-step reactions have been developed to form epitaxial heterostructures, such as 0D core/shells,¹⁹ 1D dot-in-rod,⁵⁰ or a 2D core/crown structures.⁵¹ Standard QD characterization therefore involves data on elemental composition, size and shape, and crystal structure. Moreover, given the strong relation between QD geometry and optoelectronic properties, such studies are always combined with optical spectroscopy. Absorption spectroscopy, for example, provided the first evidence of quantum confinement in semiconductor nanocrystals as manifested by a blue-shifted **band-edge transition [G]** with a reduction in QD size,^{1,52-54} and now **sizing curves [G]** provide a rapid way of converting band-edge energy into a QD size.⁵⁵

Figure 3 displays an example of various characterization methods for InP/ZnSe core/shell QDs.⁵⁶ Lower magnification transmission electron microscopy (TEM) images provide an overview of the distribution of sizes and shapes within the QD ensemble, while high resolution TEM (HR-TEM) yields more detailed insight in crystallinity. Crystallinity can be further confirmed through powder X-ray diffraction (XRD), which shows diffraction mostly in line with bulk ZnSe, which dominates the QD volume. Small-angle X-ray scattering and total scattering can provide further insight in the QD size and atomic structure (**Supplementary Information S3**).^{31,57} Opposite from the XRD pattern, the Raman spectrum features separate modes of the InP core and the ZnSe shell. Shifts with respect to InP- or ZnSe-only modes can be related to compressive and tensile strain.⁵⁸ The average elemental composition can be obtained through Rutherford backscattering spectrometry (RBS) on QD films, but also through inductively coupled plasma optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS) on dissolved QDs. More extensive chemical information can be obtained from X-ray photoelectron spectroscopy (XPS) or X-ray absorption spectroscopy (XAS) (**Supplementary Information S3**). These structural and elemental data are complemented by optical spectroscopy, where UV-Vis absorbance yields the QD band-edge transition and photoluminescence (PL) spectroscopy yields the emission wavelength, linewidth and the PLQY; three of the figures of merits listed in **Table 1**.

[H2] Analysis of quantum dot core and surface

[H3] The quantum dot core

The characterization methods illustrated in Figure 3 provide insight into QD quality needed for optimizing synthetic methods or application development but lack the precision required to

construct realistic QD models. To obtain more detailed information on the geometry of the inorganic QD core, TEM is a preferred technique. Among the many TEM imaging modes (discussed in **Supplementary Information S4**) high-angle annular dark field scanning TEM (HAADF-STEM) yields images in which intensity scales with the atomic number Z^n (**Figure 4a-b**). In that way, the core and shell in heterostructures can be distinguished.⁵⁹ Moreover, in combination with spectroscopic techniques such as energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS), spatial composition maps of QDs can be obtained (**Figure 4c**).

While TEM can image QDs with atomic resolution, deriving the 3D structure of QDs from TEM images is not straightforward. Conventional TEM provides a 2D projection of a 3D object, which can be a poor representation of the actual geometry. Using TEM for 3D characterization is possible through electron tomography, a technique where a series of projection images is acquired while tilting the sample over a range of angles that is as wide as possible.⁶⁰ However, QDs can suffer from considerable beam damage caused by exposure to high energy electrons during such time consuming studies.⁶¹ A less demanding alternative is using advanced algorithms for 3D reconstruction to extract a 3D model of a QD from a single 2D projection.⁵⁹ This can be done through a quantification of the image intensities in a STEM image, followed by molecular dynamics simulations (**Figure 4d-g**).⁶² The latter approach may be a route towards high throughput characterization of QDs, eventually leading to an average structure, based on the characterization of many individual crystals.

A recent development to overcome electron beam damage is 4D STEM, a technique where a full diffraction pattern is collected at each scan position.⁶³ Deviations of the center of mass in these diffraction patterns are directly related to the electrostatic potential field, which results in an image intensity that depends linearly on the atomic number. Moreover, in 4D STEM, all electrons are collected by a hybrid pixelated direct electron detector, whereas in HAADF-STEM only electrons scattered to relatively high angles are detected. 4D STEM can therefore be considered a very promising technique to resolve the atomic structure of QDs with limited electron beam damage. Alternatively, coherent diffractive imaging (CDI) is increasingly being used as a means to reconstruct atomistic structures of an object from the electron- or x-ray diffraction pattern.^{64,65} CDI and time-dependent CDI might permit tomography and even movies of atomic motion as excitations displace atoms from equilibrium. Finally, an exciting outlook in the field of TEM is the possibility to perform experiments under the influence of specific triggers such as heat or light,⁶⁶⁻⁶⁸ where dedicated sample holders enable investigation of QDs in a liquid environment. In this manner, the behavior of QDs during application can be studied directly, which can lead to improved structure property connections.

[H3] The quantum dot surface

The initial methods for synthesizing colloidal QDs from metalorganic precursors employed coordinating solvents, such as trioctylphosphine oxide, under the assumption that these moieties would impart colloidal stability by binding to the QD surface.⁴ However, a detailed understanding of QD surface chemistry only emerged after years of in-depth chemical analysis. In particular, studies on CdSe QDs synthesized using cadmium carboxylates as the metal precursor showed that these QDs mostly carry no electric charge when dispersed in apolar media,^{69,70} have an excess of cations as compared to bulk CdSe,^{71,72} and bind two carboxylate ligands for each excess Cd^{2+} metal cation.⁷³ These observations demonstrated that QDs can be effectively seen as inorganic/organic hybrids, where the properties of the inorganic core and the organic ligand shell are tightly interconnected. As outlined in **Box 1**, this insight inspired a classification of QDs based on the ligand binding motif, as described by the covalent-bond classification scheme.⁷⁴ For each of the resulting

QD classes, charge neutrality is a guiding principle that relates the core and surface composition. In the case of CdSe QDs, for example, neutral L-type ligands — Lewis bases like primary amines — will cap stoichiometric QDs, whereas X-type oleates will terminate non-stoichiometric, Cd-rich QDs. Here, the net charge is to be calculated as the sum of the most stable oxidation states of all components.

Nuclear magnetic resonance (NMR) spectroscopy has been used to analyze QD surface chemistry. In ^1H solution NMR, ligands bound to QDs can be identified by their broadened resonances, small diffusion coefficients, and negative cross peaks in a 2D **nuclear Overhauser effect [G]** (nOe) spectrum (**Figure 5a-c**).⁷⁵ While the latter two are a result from the QD dictating the diffusion and tumbling behavior of bound ligands, the ^1H NMR line broadening is more complex. Faster T_2 relaxation and heterogeneous broadening — demonstrated through **spectral hole burning [G]** — indicate that both restricted motion and a variety of local environments within the ligand shell contribute to the linewidth.⁷⁶ As a result, resonance linewidth is a sensitive probe of the ligand-solvent interaction, where better solvation results in more narrow resonances.⁷⁷ Opposite from bound ligands, ligands in rapid exchange between a bound and free state will show narrow resonances with high diffusion coefficients, often indiscernible from the free ligand. However, such dynamic ligand binding can still lead to negative nOe cross peaks, which makes the combination of 1D, diffusion-ordered spectroscopy (DOSY) and nuclear Overhauser effect spectroscopy (NOESY) NMR a powerful toolbox to analyze the QD ligand interaction (**Supplementary Information S5**).⁷⁸

A limitation of ^1H solution NMR is the excessive line broadening of protons close to the QD surface due to increasingly fast **T_2 relaxation [G]**. Binding motifs should therefore be identified indirectly, through ligand exchange reactions, or by combining solution NMR with infrared or solid-state NMR spectroscopy. Opposite from solution NMR, infrared spectroscopy can probe the functional group by which ligands bind to the QD surface, a characteristic that is regularly used to distinguish, for example, carboxylic acids from carboxylates, and identify specific binding modes.⁷⁹ Solid-state NMR, on the other hand, can address a broad range of nuclei, including spin $\frac{1}{2}$ nuclei such as ^{31}P , ^{77}Se , or ^{113}Cd . Apart from identifying different chemical environments, cross polarization NMR spectroscopy provides insight into the coupling between the organic ligand shell and the inorganic QD core. In the future, such studies might benefit from the introduction of dynamic nuclear polarization enhancement, which cuts acquisition time and enables spectral features of different nuclei to be correlated.⁸⁰

[H3] Quantitative analysis of ligand binding

QDs in apolar media must remain charge neutral; therefore, X-for-X and L-for-L exchanges are possible, whereas X-for-L or L-for-X are not (**Box 1**). Solution NMR can be used to monitor the titration of a QD dispersion with a new ligand, where the resulting shift of the exchange equilibrium provides insight into the binding and packing of ligands. First developed for CdSe QDs, X-for-X titrations indicated that ligands do not form a homogenous shell, but rather bind to specific facets.⁸¹ An even more fruitful understanding was that, in the case of QDs classified as $\text{ME}(\text{MX}_n)$, the entire MX_n metal salt acts as a Z-type ligand — a Lewis acid — that can be displaced by the addition of L-type ligands, such as primary amines.⁸² This L-type driven Z-type displacement was linked to a dramatic loss of PL efficiency, while displacement isotherms, representing ligand coverage as a function of L-type ligand concentration, were used to survey the binding strength of, for example, cadmium oleate to CdSe and CdS.⁸²⁻⁸⁴ Such studies showed a pronounced heterogeneity of binding sites at the QD surface, featuring stronger binding on specific facets and weaker binding on edges and corners; a conclusion confirmed by ab-initio calculations of the site-dependent desorption energy (**Figure 5d-e**).^{81 81}

[H2] Computational analysis

[H3] Density functional theory

Determining the geometry, electronic energy levels, and optoelectronic properties of a QD has been a central aim of the theoretical and computational analysis of QDs, and several methods are available for this purpose (**Figure 6a** and **Supplementary Information S6**). Initial studies involved macroscopic models based on the **effective-mass approximation** [G],⁵ which provided analytical expressions for electronic energies, but reduced QDs to geometric shapes, such as spheres or ellipsoids.⁸⁵ Later, atomistic approaches, such as tight-binding and pseudopotential methods,^{86,87} led to more detailed insights into the relationship between the properties and the geometry of QDs. However, to recover bulk coordination and maintain overall charge neutrality, early atomistic methods were typically applied to unrelaxed QD models with surfaces terminated by pseudo-ligands; dummy atoms with scaled partial charges that passivate dangling bonds and preserve overall neutrality.⁸⁵ This approach inevitably neglected the impact of the QD surface on QD properties, a limitation that more recent computational studies overcome by applying first-principles methods like density functional theory (DFT) to QDs. In DFT, QD surfaces need no passivation by pseudo-ligands and geometry optimization is possible without ad-hoc parametrization. The result is a more comprehensive description, where electron orbitals are obtained by considering both the QD core and the surface, eventually using a QD geometry that incorporates the actual surface ligands.

By employing DFT from the outset, the challenge in describing QDs shifts to constructing QD models that accurately reflect their geometrical and chemical properties. QD models are therefore built according to the experimental QD composition and ligand binding motif (**Figure 6b**). Model building is further supported by TEM imaging, which helps identify the exposed crystal facets and may, eventually, provide an atomically precise QD structure. In absence of such detailed information, QD models can be set up using the **Wulff construction** [G], where a given shape can be imposed by adjusting the surface energy of specific facets.⁸⁸ Since QD facets can be abruptly terminated, it is essential to maintain charge balance by removing or adding atoms, while preserving the ligand binding motif and the correct QD stoichiometry. Neglecting this aspect can lead to unintended artificial n- or p-doping, resulting in QD models that significantly deviate from real QDs. Once the QD model is established, the structure, including the surface, is allowed to relax, and the electronic structure is computed (**Figure 6b-c**).

[H3] Relating geometry and electronic structure

A breakthrough in the study of QDs by DFT was the introduction of non-stoichiometric QD models, where carboxylate ligands balanced the excess cadmium.⁸⁹ Building on this result, the impact of different ligand types on the QD electronic properties could be investigated.⁹⁰ In particular, the displacement of Z-type ligands was found to profoundly alter the electronic structure by creating two-coordinated Se atoms that give rise to mid-gap states formed by localized, non-bonding Se 4p orbitals (**Figure 6c**). The presence of these states, which act as surface traps, aligned with the experimental observation that Z-type displacement quenches the PL.⁸² This discovery highlights that the interplay between a geometrical and an electronic feature — an undercoordinated surface atom yielding a trap state — impacts the competition between radiative and non-radiative processes and therefore the PLQY. These findings are broadly applicable, extending to larger QDs, other Z-type ligands, and different II-VI and III-V QDs of various shapes.⁹¹⁻⁹³

The continuous improvement of computational architectures allows DFT computations on QDs 3 to 4 nm in size. Interestingly, DFT studies on such QDs yielded an energy separation between the highest occupied (HOMO) and lowest unoccupied orbital (LUMO) smaller than the band gap of the same material in bulk, computed at the same level of theory.⁹⁴ Contradicting a basic characteristic of quantum confinement, this finding points towards an intrinsic issue in the construction of QD models. Typically, such models feature surface facets with the same geometry as bulk lattice planes. For bulk semiconductor surfaces, such facets are known to create surface states that can be eliminated by **surface reconstructions** [G]. Such reconstructions follow specific patterns where atoms can be expelled to form vacancies so as to suppress charge accumulation on the facet, and the related surface states (**Figure 6d**).⁹⁵ Interestingly, introducing such reconstructed facets in QD models yielded bandgaps consistent with expected values based on nanocrystal sizes (**Figure 6e**). Importantly, this result enabled simulations of core-shell structures at the atomistic level, providing valuable insights into the energy level alignment of core and shell components in systems that closely mirror experimental structures.⁹⁶

[H2] Time-resolved analysis

[H3] Time-resolved spectroscopy

As outlined in **Supplementary Information S7**, photo-excited QDs exhibit a range of competing relaxation pathways. Among these, radiative recombination and stimulated emission are widely used in light emission applications, while others are mostly seen as unwanted loss pathways. Preferred methods to analyze and quantify the relaxation of the photo-excited state are time-resolved PL (TRPL) and femtosecond pump-probe methods, such as transient absorption (TA). In TA, the change of the absorbance spectrum is probed with varying delay relative to an optical pulse with a typical time resolution of ~ 100 fs. In transient PL, the decaying emission intensity is recorded after pulsed excitation, with the most advanced setups offering ps or fs time resolution.

Figure 7a-c summarizes a time-resolved spectroscopy study on CsPbBr₃ QDs.⁹⁷ TRPL at low-power excitation with ns resolution gives access to the radiative recombination rate of single excitons, a QD figure-of-merit listed as the radiative lifetime $\tau_{X,rad}$ in **Table 2**. At higher pump power, a short-lived, red-shifted emission band appears that is assigned to a biexciton population that quickly decays through Auger recombination. A complementary picture emerges from the TA map, which details the change in absorbance as a function of photon energy and delay time. Here, excitons occupying the band-edge states reduce or bleach the band-edge absorption, while biexcitons give rise to a short-lived band of stimulated emission, see **Supplementary Information S6** for details. From the TA map, both energetic shifts and relaxation time constants of different photo-excited states can be deduced. Interestingly, the size-dependent electronic structure and interfacial or surface features of QDs fundamentally influence the energy and recombination rate of excited states, which offers inroads to design material responses to advance applications.⁹⁸⁻¹⁰³ Here, a key result has been the increase of the biexciton Auger lifetime $\tau_{BX,Auger}$ in CdSe/CdS QDs through the design of the core/shell structure (**Table 2**).^{21,104}

Additional processes that can be tracked using time-resolved spectroscopy include intraband **carrier cooling** [G], **carrier trapping** [G], charge and **energy transfer** [G], and **exciton spin relaxation** [G].⁹⁸⁻¹⁰³ Means to understand thermalization of QDs and their surroundings can be important as heat dissipation processes may affect the long-term performance of QDs. Some studies have begun to investigate such questions with a focus on spectroscopies that target ligand thermalization after photo-excitation of QDs,^{105,106} or probe energy transfer across the semiconductor-organic interface by excitation of ligand vibrations.¹⁰⁷

[H3] Time-resolved diffraction for structural dynamics

Powder XRD is a widely used diffraction-based method to identify QD synthesis products. In addition, Scherrer broadening of diffraction peaks provides insight in average particle size (**Figure 7d**) and single crystal diffraction and x-ray atomic pair distribution function analysis led to atomically precise structure models for magic size clusters.^{108,109} Combining static diffraction with in-situ heating, early studies already revealed size-dependent melting temperatures that are reduced substantially from bulk owing to high surface energy,¹¹⁰ and related reports pointed towards ligand- and shell-induced surface strain.¹¹¹ On the other hand, relaxation processes in excited QDs, such as charge-carrier cooling, non-radiative recombination, and three-particle Auger recombination, impart energy to the lattice through phonons. As a result, QDs may sinter or even ripen; the QD lattice can distort, melt or undergo solid-solid transformations; the QD surface may reconstruct; and ligands may rearrange or detach.^{112,113} In addition, the Coulomb field of photogenerated charges can locally distort the lattice. The resulting polarons lower the overall system energy, and feature prominently in metal halide perovskite QDs.¹¹⁴

Pulsed diffraction probes derived from synchrotrons and free electron laser x-ray sources,¹¹⁵⁻¹¹⁷ as well as keV and MeV pulsed electron sources,^{68,118-120} now offer means to monitor transient structural changes of the QD lattice. Similar to pump-probe spectroscopy, such experiments involve diffractive probing with a repetitious generation of non-equilibrium charge carriers, most commonly by pulsed photon absorption or electrical charge injection. **Figure 7e** illustrates how pump-induced changes in XRD signals relative to the un-excited sample give insights into structural changes. Lattice expansion, for example, leads to derivative-like difference signal, while phase changes and disordering result in a net loss of diffraction.¹²¹ **Figure 7f** shows a graphical interpretation of data from **Figure 7e** in terms of a solid-solid phase transition from orthorhombic to cubic symmetry.

[H2] From sub-ensembles to single quantum dots

The size and shape dispersion of QD ensembles can obscure detailed information regarding electronic density of states. Fluorescence line narrowing experiments (FLN), such as those shown in **Figure 8a**, circumvent this issue by employing narrow-bandwidth, resonant excitation [G] to selectively excite a lower-energy-absorbing sub-ensemble of QDs. This approach provided insight regarding the fine-structure of the lowest-energy exciton states (**Supplementary Information S7**). FLN studies established the order and spacing of the bright and dark levels, phonon-assisted emissions (shifted by a phonon energy from a state), and emission from charged exciton states.¹²²⁻¹²⁴ CdSe and InP QDs, for example, feature a lower-energy dark state and a higher energy optically active bright state; an ordering that strongly increases the excited-state lifetime at low temperature, owing to reduced thermal access to the photon-coupled state.^{122,125,126} Quantum confinement was found to strongly affect fine structure spacings, with dark-bright splitting up to tens of meV for small QDs relative to a sub-meV bulk value.¹²⁷

Unhampered by ensemble averaging, microPL (μ PL) studies on single QDs showed crucial characteristics including spectral diffusion [G] and fluorescence intermittency or blinking [G]. As shown in **Figure 8b**, periods of weak QD emission correlate with short excited state lifetimes, which indicates that the low PLQY state may result from charged QDs that facilitate non-radiative Auger recombination. When Auger recombination can be suppressed, the PL intermittency is indeed greatly reduced, and lifetimes change less substantially even upon charging. Hence, unabated QD charging can deteriorate PLQY and, therefore, the efficiency of quantum light emitting diodes (QLEDs); a finding highlighting the importance of rare ionization processes for fast, non-

radiative relaxation, regardless of surface trap passivation.¹²⁸⁻¹³¹ The 2D maps of PL intensity versus excited state lifetime (**Figure 8b**, right hand side) help to evaluate quenching mechanisms. For instance, neutral excitons emit slow with high intensity whereas 3-particle Auger recombination active in charged dots reduces PL intensity and excited state lifetime, while Auger suppressed particles show higher brightness and longer lifetime than usual charged QDs. In addition, PL excitation spectroscopy on single QDs has been demonstrated, which helped to confirm electronic structure theory especially of hole states that can be challenging to characterize in QDs with a large hole effective mass and, consequently, a narrow energy spacing in the valence band.¹³² Furthermore, fluorescence correlation spectroscopy (FCS) has enabled analysis of single QDs in colloidal dispersion that offer insight into homogeneous PL linewidths.¹³³ Both FLN and μ PL spectroscopies, including FCS, have the potential to become especially insightful if eventually possible to combine with atomic-resolution methods such as STEM or x-ray tomography.

[H2] Charge transport in quantum dot films

[H3] Mobility

Many applications of QDs require the transport of electrons and holes between QDs in solid films, which take place via **drift [G]** or **diffusion [G]** of charge carriers. These processes are governed by the density (n), lifetime (τ), and mobility (μ) of the charge carriers, which is defined as the ratio between the speed of charge carriers and the applied electric field. The requirements on these parameters strongly depend on the application. QD LEDs contain a few layers of QDs at the most, wherein electrons and holes are injected directly from contacts. Here, a high mobility is not required. Photodiodes operate at reverse bias (V_R) where most transport occurs via drift. The minimum mobility (μ_{min}) is set by the requirement to extract charge carriers from the absorber layer with thickness (x) faster than the carrier lifetime, such that $\mu > x^2/\tau V_R$. For a 200 nm thick QD film at 2 V reverse bias and a carrier lifetime of 2 ns,^{134,135} one thus obtains $\mu_{min} = 0.02 \text{ cm}^2/\text{V} \cdot \text{s}$. Solar cells usually rely on the extraction of carriers via diffusion. In that case, the minimum mobility is determined by the requirement that the carrier diffusion length L_D exceeds the film thickness, such that $L_D = \sqrt{D\tau} > x$ and thus $\mu > x^2 e/\tau k_B T$. Using the same numbers as before, one finds $\mu_{min} = 1.6 \text{ cm}^2/\text{V} \cdot \text{s}$. High-speed photodetectors and transistors would require even higher mobilities.

[H3] The hopping limit

In QD films, long-range charge transport is limited by the rate at which carriers hop from QD to QD. Hopping involves a transfer of charge from an initial and to a final orbital on adjacent QDs whose energy is temporarily aligned through thermal activation (**Figure 9a**). The rate constant k_{ET} for hopping can then be described with the Marcus equation:

$$k_{ET} = \frac{2\pi}{\hbar} J^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\pi\lambda k_B T}\right) \quad (2)$$

Here λ is the **reorganization energy [G]**, ΔG° is the free energy difference, and J is the electronic coupling between the adjacent QD orbitals. For weak coupling, J can be approximated by a tunneling term, where lower and shorter barriers lead to larger coupling. For identical QDs, ΔG° is 0, and the activation energy amounts to $\lambda/4$. Size dispersion results in a distribution of the HOMO and LUMO energies, and differences in ligand packing or the surrounding electrostatic environment further shift the energy levels, increasing ΔG° . The reorganization energy λ is usually dominated by polarization of the environment due to charge transfer and is, in that case, equivalent to the

solvent reorganization term λ_0 in the Marcus theory.¹³⁶ In the hopping or weak coupling limit, the mobility is proportional to k_{ET} :

$$\mu = \frac{(2r + d)^2}{6k_B T} k_{ET} \quad (3)$$

Here, r is the QD radius and d the QD interdistance. Hence, a lower reorganization energy, a smaller spread in site energies, or increased electronic coupling will enhance mobility.

[H3] Band-like transport

Stronger coupling gives rise to mini-bands with a width $W = 4J$, which results in a broadening of optical features and a decrease in the bandgap (**Figure 9b**).¹³⁷ The limit of strong coupling is formed by bulk semiconductors, where W equals the width of the conduction or valence band (**Figure 9c**). When W exceeds the spread in site energies and the activation energy, electrons can delocalize across multiple QDs. In this case, scattering with lattice phonons, ionized impurities or other charge carriers results in a mobility $\mu = e\tau/m^*$, proportional to the scattering time τ and inversely proportional to the **effective mass** (m^*) **[G]**. Opposite from hopping transport, the mobility in the band-like transport regime reduces with increasing temperature due to more effective phonon scattering. Temperature deactivation of the mobility is therefore often seen as evidence for band-like transport.¹³⁸⁻¹⁴⁰

[H3] The mobility spectrum

The exchange of the as-synthesized long ligands by short organic or inorganic moieties has been used to enhance the mobility in QD films by orders of magnitude, reaching the required limits for device applications (**Supplementary Information S8**). Such films are not characterized by a single mobility; rather mobility depends on the charge carrier density and frequency at which carrier motion is probed. In QD films, disorder in size, electronic coupling, electrostatic environment and the presence of shallow defects create a spread in energy levels, which increases the activation energy for hopping (**Figure 9a**). A higher orbital occupation, for example related to doping, photoexcitation or gating, decreases the average activation energy and thus increases the measured mobility. The highest charge densities are achieved in electrochemically-gated transistors,^{141,142} followed by field-effect transistors.¹⁴³ Photoconductivity and Hall measurements usually operate at low occupation.^{141,142} Furthermore, domains of strongly coupled QDs are often separated by regions with weaker coupling (grain boundaries). The mobility within a single domain can be high, while the long-range mobility is limited by the grain boundaries. Therefore, mobility measured in a transistor geometry will depend on the distance between the source and drain electrodes. Contactless measurements like time-resolved microwave conductivity (TRMC) or THz conductivity probe charge transport by measuring the absorption of GHz or THz radiation by free carriers.¹³⁸ Within half a period of the ac field the carriers only probe a small volume of the sample and are much less sensitive to long-range disorder. The fact that the measured THz or GHz mobility is often higher than reported dc mobilities reflects the fact that mobility is a spectrum, not a number.

[H1] Applications

QDs offer significant potential for integration in diverse technologies due to their widely tunable optoelectronic and chemical properties. Examples include thermoelectrics;¹⁴⁴ non-volatile memories;¹⁴⁵ solar energy harvesting;^{13,146-148} optoelectronics, ranging from color-conversion in

displays and lighting to electroluminescent diodes and image sensors;^{149,150} and quantum photonics.¹⁵¹ However, as-synthesized QDs are often ill-suited for these applications. The capping of insulating organic ligands prevents charge transfer to and from QDs and can be incompatible with preferred solvents or an envisaged polymer matrix. QD applications therefore typically start with ligand exchange, which is nowadays mostly part of an initial QD ink formulation process (**Supplementary Information S8**). By means of such inks, QDs are processed into densely packed thin films using versatile wet-deposition techniques like spin-, spray-, and dip-coating, and scalable methods such as inkjet, roll-to-roll, and transfer printing.^{21–24}

Luminescent color-convertors are typically made by dispersing QDs in a polymer encapsulant,¹⁵² whereas optoelectronic devices are formed by integrating QD films in multilayer stacks. Fabrication methods include metal thermal evaporation, atomic layer deposition (ALD), and sputtering techniques. By adjusting the device architecture, such stacks can function as LEDs and photodetectors (PDs),² but also as QD solar cells, lasers, or transistors. Interestingly, several studies showed that these fabrication steps can be replaced by a printed equivalent, leading to fully printed QD optoelectronics.¹⁵³ Opposite from such dense QD films, which easily contain trillions of QDs per cm², applications in quantum technology require single QDs. While proof-of-principle studies can make use of random deposition, even within the gap separating two gold electrodes, deterministic deposition of single QDs on substrates remains an outstanding challenge.

[H2] Quantum-dot-based color-converters

With a narrow emission and a broad excitation spectrum, QDs are nearly ideal fluorophores for spectrum-on-demand light sources based on **luminescent color-conversion [G]**. As shown in Figure 10, the partial conversion of the blue light of an InGaN LED into nearly monochromatic red and green emission lines by QDs has been used to create a backlight for liquid crystal displays (LCD) that gives access to a much broader color gamut than the spectral filtering of white light (**Figure 10a**),^{154,155} realize white LEDs where the addition of a narrow red QD emission to prevailing powder phosphors, such as YAG:Ce, improves **color rendering [G]** and reduces the **color temperature [G]** without wasted infrared emission,¹⁵⁶ (**Figure 10b**) and form microLED displays, in which red and green primary colors are formed through QD-on-chip color-conversion starting from a single blue microLED pixel array (**Figure 10c**).¹⁵⁷ Furthermore, the same principle of color-conversion by QDs has been implemented in LSCs, in which QDs embedded within a window pane re-emit absorbed sunlight towards solar cells mounted at the pane edges.¹⁰

In LCDs, a QD-in-polymer film is typically inserted within the optical stack that diffuses and filters the backlight.¹⁵⁸ Through this remote phosphor approach, QD are exposed to relatively low optical power – typically 0.1 W/cm² – and encapsulation methods can mitigate possible photodegradation issues. QD-on-chip color-conversion – preferred for lighting and mini/microLED displays – involves significantly higher optical power levels – 10-100 W/cm² – and operation temperatures of 100 °C or more. While QDs deteriorate more quickly under such conditions, warm white LEDs with excellent color rendering and a luminous efficacy as high as 170 lm/W were demonstrated using Cd- and InP-based QDs.^{159,160} Furthermore, turning a blue pump light into a single, monochromatic light source was achieved using InP/ZnSe/ZnS QDs with near unity PLQY on-chip.⁸

Ideally, QDs for color-conversion feature a high absorption coefficient at the pump wavelength, a narrow, broadly tunable, and fast PL with a near unity PLQY, irrespective of temperature, and minimal spectral overlap between absorption and emission. Strong light absorption minimizes the amount of QDs needed and is key to fully absorb blue light across films a few μm thick in QD-on-

chip microLEDs. Narrow and broadly tunable emitters offer the widest color gamut for displays, as shown in the **chromaticity diagram [G]** in **Figure 10d**, and enable a desired emission spectrum to be precisely reproduced. A near unity PLQY maximizes conversion efficiency, and a short radiative lifetime avoids saturation at high pump powers. Minimal spectral overlap is essential to avoid self-absorption, which exacerbates conversion losses unless the PLQY is 100%. According to Table 1, CdSe/CdS QDs stand out for blue-to-red color-conversion. In particular since the CdS shell strongly absorbs blue light, self-absorption can be suppressed by increasing the shell volume. CsPbBr₃ QDs are even more narrow emitters, feature a similar absorption coefficient for blue light, but offer little tunability of the absorption coefficient at the emission wavelength. The most widely used color-converters, however, are InP/ZnSe or InP/ZnS QDs, which are free of restricted elements such as Pb or Cd. Even so, since only the InP core effectively absorbs blue pump light, using these to make QD-on-chip microLEDs remains challenging.

[H2] Quantum-dot-based printed optoelectronics

[H3] Quantum dot photodetectors

QD films have been integrated as the photosensitive layer in photoconductors, phototransistors, and photodiodes, see **Supplementary Information S9** for details on fabrication methods. QD photodetectors (QDPDs) stand out by their capability of detecting short-wave (SWIR) and mid-wave infrared light. However, to fully lever the distinctive potential of QDs in this field, it is critical to link the QD electronic properties, the inner physics of the device comprising the QD film and other layers, and the consequent device characteristics.^{13,148}

For QDPDs in a photodiode architecture, photon absorption is accompanied by generation of excitons within the QD layer. These bound electron-hole pairs dissociate into free carriers, which are transported through the charge transport layers (CTLs) to the metal electrodes, where they are collected as photocurrent (**Figure 11A**). In terms of characterization, the initial steps of photon absorption and exciton generation are analyzed using optical techniques such as absorption spectroscopy, PL, TRPL, **external quantum efficiency (EQE)**, **[G]** and TA (**Figure 3** and **Figure 7**). Band-alignment can be derived through UV photo-electron spectroscopy (**Supporting Information S3**). Charge carrier dynamics, encompassing both transport and recombination processes, are evaluated through methods such as electroluminescence (EL), transient photocurrent (TPC) and photovoltage, intensity-dependent photocurrent, and voltage bias-dependent EQE measurements. Charge extraction at the interfaces with CTLs and electrodes, in turn, is critically assessed using techniques such as space-charge-limited current (SCLC), impedance spectroscopy, charge extraction by linearly increasing voltage (CELIV), and transient electroluminescence (TEL). Collectively, these techniques provide a framework for elucidating the interplay between single photophysical processes and overall device performance.

Different electro-optical probing techniques, complemented by spectral analysis, are employed to characterize the performance parameters of QDPDs. Wavelength-dependent **responsivity [G]**, EQE, and **detectivity [G]** quantify the light absorption capabilities and light response of QDPDs. As a function of the QD bandgap, QDPDs can be classified into three categories: wide-bandgap ultraviolet (UV, such as graphene, ZnO, and ZnSe QDs), visible (VIS, such as CdS, CdSe, and perovskite colloidal QDs), and narrow-bandgap infrared (IR) photodetectors (such as InAs, PbS, and HgTe colloidal QDs). Depending on the device geometry and operating mode, responsivities ranging from 10⁶-10⁹ A/W across the UV-to-IR spectral window have been reported, with phototransistors currently exhibiting superior performance compared to their photodiode (10-10⁵ A/W) and photoconductor (10⁻⁴-10³ A/W) counterparts.^{135,149} Furthermore, detectivities of 10¹⁸

Jones in the UV range and roughly 10^{12} Jones for wavelengths greater than $1.8\ \mu\text{m}$ have been achieved across various device geometries.^{135,149}

Characterizing the response speed of a photodetector, the 3dB cut-off frequency depends on the carrier lifetime and the RC circuit time of the photodetector circuit. It quantifies the QD-PD's ability to respond to modulated light across different frequencies. TPC and TA are commonly employed to assess the temporal response, including fall and rise times. These measurements provide valuable insight into charge carrier dynamics, encompassing parameters such as carrier mobility, lifetime, and trapping/de-trapping processes. Response times as fast as a few nanosecond, if not even lower, are reported for CQDs targeting the SWIR and VIS-NIR spectral regime.^{135,161}

[H3] Quantum dot-sensitized solar cells (QDSSCs).

Colloidal QDs have been incorporated into photovoltaic solar cells primarily as light-absorbing sensitizers in QD-sensitized solar cells (QDSSC) and as the light-absorbing layer in QD solar cells (QDSC) and QD-heterojunctions. The tunability of the bandgap and light absorption properties, coupled with the potential for flexible and low-cost fabrication, positions QD-based solar cells as a promising area for innovation and the advancement of future solar energy technologies.

A QDSSC consists of three primary components: a QD-sensitized photoanode, a counter electrode, and an electrolyte containing a redox couple. The photoanode is typically composed of nanostructured metal oxides, such as ZnO, SnO₂, or TiO₂, coated with fluorine-doped tin oxide or indium tin oxide. The selection of QDs for sensitization depends on the desired optical and electronic properties, with widely used materials including CdS, CdSe, CdTe, InAs, Ag₂S, PbS, and CuInS₂.^{162,163} Various synthesis and sensitization techniques are employed for QDs, including chemical bath deposition, successive ionic layer adsorption and reaction, solution-based hydrothermal synthesis, hot-injection colloidal synthesis, and direct adsorption. The key differences among these methods are primarily associated with their effectiveness in controlling nanoparticle agglomeration, spatial distribution, precursor utilization efficiency, processing time and resource requirement, and overall scalability. The electrolyte, generally based on sulfide-polysulfide or iodide-triiodide redox couples in a liquid or quasi-solid-state, is positioned between the photoanode and the counter electrode, which is often composed of Pt or Cu₂S.

The operation of a QDSSC can be sequenced into four processes as shown in **Figure 11B**. First, photon absorption and subsequent exciton generation occurs within the QDs. Then, electrons are transferred from the QDs to the metal oxide and the oxidized QDs are regenerated via electron donation from the redox electrolyte. Lastly, redox regeneration occurs at the counter electrode. Similar to colloidal quantum dot photovoltaics, the initial light absorption and exciton generation can be analyzed using optical techniques such as absorption spectroscopy, PL, and TRPL. For charge transport characterization and carrier lifetime measurements, transient techniques such as TRPL, photoconductance decay, short-circuit current decay, and open-circuit voltage decay (OCVD) are commonly employed.¹⁶⁴ The regeneration of oxidized QDs is typically investigated using a combination of electrochemical impedance spectroscopy (EIS), surface photovoltage spectroscopy, OCVD, and TA. The redox regeneration process at the counter electrode, which plays a crucial role in sustaining continuous charge flow, is studied using techniques that focus on catalytic activity, charge transfer dynamics, and interfacial electrochemistry. The most relevant methods for this purpose include EIS, chronoamperometry, Raman spectroscopy, and Fourier-transform infrared spectroscopy.

The overall photovoltaic performance of a QDSSC is ultimately evaluated through standard current-voltage (J-V) measurements, which yield key performance parameters, including the fill factor, open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and power conversion efficiency (PCE). In state-of-the-art QDSSCs, the PCE has surpassed 15%, with recent advancements achieving values exceeding 17%.¹⁶⁵⁻¹⁶⁷ In the coming years, research on QDSSCs should focus on minimizing charge recombination losses, enhancing QD material stability, and improving the efficiency of charge transfer processes. This includes advancing interface engineering and optimizing counter electrode materials. Further development of synthesis techniques, doping processes, and substrate treatments will also be essential for improving device performance and achieving commercial viability.

[H3] Quantum dot light-emitting diodes.

QD light-emitting diodes (QLEDs) make use of a diode architecture optimized to inject charge carriers into a QD film. QLEDs constitute monochromatic light sources that can seamlessly cover the full visible spectrum. QLEDs rely upon the injection of charge carriers from the metal electrodes into the adjacent CTLs. These carriers are transported through the CTLs and the QD emissive layer recombining radiatively and thus, emitting light at a wavelength determined by the QD size (**Figure 11C**). Notably, each of these steps—charge injection, transport, and recombination—occurs at distinct spatial locations within the QLED device and on different time scales. Charge injection is analyzed using techniques such as current-voltage (I-V) measurements, impedance spectroscopy, and EL; charge transport dynamics are often probed through SCLC measurements and CELIV. The radiative recombination processes in the QD film can be investigated via EL, EQE, TEL, and thermally stimulated luminescence measurements.

QLEDs emitting visible light are broadly categorized based on the primary emission color as blue, green, and red. For each of these categories, QDs with PLQYs above 95% and, in some cases, reaching unity are available (**Table 1**). The electrical device characteristics and temporal response are assessed using turn-on voltage and fall/rise time,^{168,169} reporting on charge transport dynamics, carrier recombination, and device efficiency. Full assessment of optical performance relies on spectral analysis, luminance, and radiant flux measurements in combination with electrical characterization, as well as imaging and spatial analysis. Key parameters include the luminous efficacy, EQE, and color rendering index, which collectively provide a comprehensive picture of light output and color quality. The EQE is critical for understanding the efficiency with which electrical energy is converted into light, while luminous efficacy measures the LED's effectiveness in producing visible light as perceived by the human eye. To-date, EQEs of QLEDs have reached 20%,^{14,168} with some devices even exceeding 25% and approaching, if not even surpassing, 30%.^{170,171} Notably, there is a significant discrepancy in stability among different colors of QLEDs. Red QLEDs exhibit superior longevity, with a $T_{50} > 10^6$ h at 100 nits, currently outperforming their blue and green counterparts.¹⁴ Enhanced understanding of these parameters is essential for advancing QLED technologies, particularly in applications requiring high color accuracy and luminous output, such as display technologies, general illumination, and automotive lighting systems.

QDPDs and QLEDs thus share a set of common performance constraints, including poor charge transport and electric field distribution, losses due to inadvertent recombination, incomplete surface passivation, insufficient light absorption, and inefficient charge collection or injection. These limitations are intrinsically linked to the physical and structural properties of the QD-based optoelectronic device, as well as the material characteristics of the quantum dots. Examples of these

properties include charge carrier mobility, QD size and shape, QD surface defect density, and interface quality.

[H2] Quantum optics

Whereas atoms have been traditionally at the heart of quantum optics,¹⁷² QDs are emerging as a viable, solid-state alternative. This evolution is spear-headed by the technological developments with epitaxially-grown III-V QDs.¹⁷³ Even so, colloidal QDs have been penetrating more and more into these domains recently, even if QD-based quantum optics faces considerable challenges (**Supplementary Information S10**).^{174,175} Most mature are single photon sources, which are a central component for quantum communication,¹⁷⁶ photonic quantum computing schemes,¹⁷⁷ and quantum sensing.¹⁷⁶ Existing commercial products are based on epitaxial QDs. While limited to narrow wavelength range and in need of deep cryogenic cooling, epitaxial QDs offer a benchmark for colloidal QDs, which promise a wide tunability and easier fabrication but need better stability, photon quality (indistinguishability and purity), and efficiency before commercial applications become viable. An important advance, that up to now is only fully exploited with epitaxial QDs, is integration into optical microcavities that allows to boost the performance of single photon sources,¹⁷⁸ and enables effective photon-photon interactions that can be realized in the strong light-matter coupling regime.¹⁷⁹ Beyond single QD devices, collective effects may be used to generate multi-partite entangled states that could become a useful resource for both quantum computing and sensing applications. Cooperative emission from several emitters currently appears challenging with epitaxial QDs, whereas there has been promising, initial demonstrations with colloidal QDs. On the other hand, entanglement and efficient extraction of the correlated photons still need to be established.

[H3] Single photon sources

Stable emission, both spectrally and by intensity, is essential to even consider a QD as a source of single photons.^{180,181} This can be determined for individual QDs using μ PL.¹⁸² Resonant excitation with detection of the phonon replica,¹⁸³ and photon-correlation Fourier-spectroscopy¹⁸⁴ can give access to fluctuation time scales below the millisecond regime, and some techniques can even extract such information from ensembles.¹⁸⁵ Refining synthesis, structure and composition can help to reduce detrimental effects like charge fluctuations and traps. With colloidal II-VI QDs, the growth of thick or graded multi-shells tremendously improved the emission stability.^{186,187} Lead halide perovskite QDs, on the other hand, exhibit low spectral diffusion and blinking at cryogenic temperature,¹⁸⁸ but at room temperature there is fluorescence intermittency,¹⁸⁹ where shells are beneficial, too.¹⁹⁰ Furthermore, research on epitaxial QDs and 2D materials has created a manifold of techniques like resonant excitation and encapsulation in crystalline matrices that could be adapted for colloidal QDs to further improve their performance.^{191,192 191,192}

Common metrics for characterizing single photon sources are:¹⁹³ efficiency, measuring the fraction of the generated photons extracted into a usable mode; purity, expressing how multi-photon emission events disturb the single-photon emission; indistinguishability, quantifying the extend at which the created photons show genuine quantum interference on a beam splitter; and repetition rate, providing the rate at which individual photons can be generated. Associated with these metrics are distinct characterization methods and optimization routes.¹⁷³ The tell-tale signature of single-photon sources is photon anti-bunching,^{194,195} as can be observed in a Hanbury-Brown Twiss setup where the light from the QD is split with a 50:50 beam splitter and then detected on two single-photon counters (**Figure 12a, top**). As shown in Figure 12a, bottom, the impurity is characterized by the deviation of the zero-time second-order autocorrelation $g^{(2)}(t=0)$ from

zero. QDs can achieve $g^{(2)}(t = 0) < 0.02$ ¹⁹⁶ (**Table 2**), but the presence of multiple emissive states like biexcitons,¹⁹⁷ trions, and fine-structure states¹⁹⁸ can increase impurity. While near or far resonant optical excitation is the easiest and most often employed method to drive QDs, electrical excitation — which has practical advantages for applications — is feasible.¹⁹⁹ A key property for many quantum optical applications is that indistinguishable photons are produced. Here, only very recently, it was possible to demonstrate this with lead halide colloidal quantum dots at cryogenic temperatures by observing Hong-Ou-Mandel interference on a beam splitter (**Figure 12b**).¹⁹⁸

[H3] Quantum dots in microcavities

An established way to improve the efficiency and purity of single-photon sources is the incorporation of QDs in optical microcavities,²⁰⁰ where the Purcell effect fosters photon emission into the well-defined cavity mode. The Purcell effect occurs in the weak light-matter interaction regime where the loss rate from the cavity and spontaneous decay exceed the coupling rate between the light field and the excitons in the material. Single QDs have been embedded into microspheres,²⁰¹ plasmonic nanocavities,²⁰² and tunable, open microcavities,²⁰³ by which Purcell-enhanced emission with improved purity and emission rate was demonstrated.

In the strong-light matter interaction regime, the light-matter coupling rate dominates over the photonic and excitonic losses, and exciton-polariton quasi-particles form whose wavefunction consists of part photon and part exciton. The energy spectrum acquires the characteristic anti-crossing between the photonic and the excitonic state (**Figure 12c**), and eventually at high excitation fluence, the polaritons spontaneously coalesce into a non-equilibrium Bose-Einstein condensate with macroscopical coherence.²⁰⁴ Since the exciton-polaritons are a kind of interacting photons, the approach is attractive for quantum optical applications that require effective photon-photon interactions.²⁰⁵

Exciton-polaritons have been realized with colloidal II-VI QDs in tunable, open microcavities,²⁰⁶ even in solution,²⁰⁷ and more exotic realizations like plasmonic hole arrays²⁰⁸ as well as in structures that support bound-states-in-the-continuum.²⁰⁹ Due to their small inhomogeneous broadening and therefore lower excitonic disorder, colloidal II-VI nanoplatelets are an attractive material that has shown strong light-matter coupling and low-threshold room-temperature polariton condensation.^{210,211} More recently, lead halide perovskite quantum dots have joined the family of polaritonic materials,²¹² where polariton condensation has been observed in waveguides at cryogenic temperatures,²¹³ and in a tunable, textured microcavity at room-temperature.^{206,214}

[H3] Coherence and collective quantum effects

A key property for quantum optical applications is the dephasing or decoherence of the electronic states.¹⁷⁵ The need for coherence is obvious in the context of qubits, where a superposed or entangled quantum state should be preserved over a long time. However, decoherence also impacts single photon emitters by reducing the indistinguishability of the generated photons and the coupling to microcavities by spectral broadening. Various physical effects lead to decoherence in colloidal QDs (**Supplementary Information S10**), of which some can be alleviated by using cryogenic cooling, while others are intrinsic to the material. Experimentally, four-wave mixing experiments allow to obtain the dephasing time T_2 on the ensemble level, yielding ~ 100 ps for II-VI,²¹⁵ and tens of picoseconds for lead halide perovskite QDs at cryogenic temperatures (**Table 2**).²¹⁶ Furthermore, dephasing close to the fundamental limit of $T_2 = 2T_1$, with T_1 being the exciton decay time was observed for some QDs.^{217,218}

With long-lasting coherence of the emitters, cooperative quantum effects like superfluorescence can occur, where an ensemble of emitters spontaneously synchronizes the phase of their quantum state and collectively emit like an effective macroscopic emitter. Due to the stringent requirements on homogeneous and inhomogeneous broadening as well as high oscillator strength, lead halide perovskite quantum dots stand out from both epitaxial and colloidal QDs. Supercrystal assemblies of CsPbBr₃,²¹⁹ also in the form of self-assembled whispering-gallery mode resonators,²²⁰ showed the key characteristics of superfluorescence (**Figure 12d**): a delayed emission pulse with radiative decay acceleration and nonlinear peak intensity. Using binary superlattice assemblies allowed to control the lattice geometry and thereby the occurrence of superfluorescence.²²¹ These cooperative effects could be exploited to generate more complex multi-photon quantum states of light.

[H1] Reproducibility and data deposition

QDs are complex and sensitive materials, for which slight variations in synthesis, storage, measurement and processing conditions can have a significant impact on QD properties and device performance. Controlling the composition and structure of precursors and solvents used is an essential first step for reproducible QD research. Impure surfactants in a QD synthesis, such as tri-*n*-octylphosphine oxide (TOPO), oleylamine, and *n*-alkylphosphonic acids can induce batch-to-batch variations in QD size, crystal structure or composition.²²²⁻²²⁴ Although synthetically convenient, procedures that generate metal surfactant complexes *in situ* by liberating water have proven especially problematic. Despite extensive degassing, the Lewis acidity of these complexes retains water coproduct, which greatly influences the kinetics of precursor conversion.²²⁵ Similarly, the combination of elemental chalcogens with octadecene and oleylamine produces complex mixtures that slowly change as volatile components are liberated, thereby influencing the precursor reactivity.²²⁶

Eliminating sources of synthetic variability is essential to understanding precursor reactivity from a mechanistic perspective and making an informed choice about reagents and synthetic conditions. Abiding to such synthetic standards is also key to isolating QDs post synthesis with a well-defined surface termination. Contaminated surfactants can complicate the assignment of the surface structure, modify the ligand exchange reactivity,²²⁷ and cause beam damage during TEM imaging.²²⁸ Moreover, work-up procedures can affect the ligand surface concentration, or change the surface chemistry altogether, as shown for QD purification methods using alcohols as the non-solvent.²²⁹ Given the importance of surface structure and ligand exchange reactions for QD processing, synthesis, purification and isolation methods can have a direct impact on device performance. Scientists in QD research should therefore heed reproducibility, by eliminating known sources of variability, drawing conclusions after duplicating experiments, and duly reporting experimental procedures.

The heterogeneity of most QD ensembles leads to specific problems of misrepresentation when using methods that address QDs one-by-one. TEM, for example, provides unique information on single QDs, but deriving ensemble averaged quantities from TEM images is far from straightforward. High resolution studies should therefore always be complemented with lower magnification images to provide a reliable overview of the sample under investigation, and sample sizes for histograms analysis should be reported, containing at least 300 QDs.^{230,231} Similar challenges arise in computational studies, where relying on a single model structure can lead to biased conclusions. Multiple QD models, including possible conformers, should therefore be tested and compared by total energy, selecting the lowest-energy structure. This remains challenging for relatively large QDs, especially as ligands and solvent need to be included for the total energy

calculations. Additionally, QD coordinates should be made publicly available in repositories like GitHub or Zenodo, allowing testing and validation by computational scientists.

Finally, many of the metrics used to evaluate QD performance, as listed in Table 1, are derived from experimental studies with data that can be readily deposited, assessed for quality and reanalyzed. This, however, is not the case for the PLQY, which is typically reported as a percentage without any reference to the underlying data or calibration procedures. Reliable PLQY measurements are much harder than is typically assumed, and large errors are easily made. Given the central role of this metric in QD research, PLQY certification, similar to the certification that is typical for solar cells,²³² would be a desirable, in particular for studies reporting near unity values. The emerging photothermal threshold quantum yield method seems well-suited for such a purpose.²³³

[H1] Limitations and optimizations

Research on QDs has rapidly evolved from curiosity-inspired to technology-driven. While synthetic methods proved scalable,²³⁴ the requirements imposed by various applications keep challenging QD research. This Primer highlights that QD-based devices can indeed be competitive in terms of performance but must be paired with operational stability and the use of non-restricted materials. Regulations, such as Europe's Restriction of Hazardous Substances (RoHS) directive, cap the amount of toxic elements, including Hg, Cd, and Pb, electronic equipment can contain, and even when QD-based technologies can comply with maximum limits, concerns about public acceptance often translate into zero-Cd or zero-Pb policies. However, as indicated in the metrics listed in **Table 1** and **2**, QDs based on CdSe, CsPbBr₃, or PbS generally perform better than non-restricted alternatives, such as InP and InAs-based QDs. For example, while InP/ZnSe/Zn QDs can attain near-unity PL efficiency in the visible, similar to CdSe and CsPbBr₃, their emission linewidth is relatively broad, biexciton lifetimes are short, and exciton dephasing is fast. InAs QDs, active at wavelengths longer than 1000 nm, exhibit a narrower spectral range, lower PL efficiency, and reduced photodetection sensitivity than PbS QDs. Furthermore, while high-performance III-V/III-V core/shell QDs remain to be demonstrated, the III-V/II-VI hetero-interface is poorly understood,²³⁵ and operational stability of III-V QDs is not yet comparable to that of Cd- and Pb-based QDs. Hence, the need for further research into new synthetic protocols for non-restricted QDs, and the factors limiting performance and operational stability of QD devices.

Continued synthesis optimization could yield more monodisperse InP or InAs QDs, potentially addressing some of these differences. However, the current literature does not offer a general strategy to reduce size-dispersion for a given synthesis. Other challenges appear to be more material specific. For example, the concept of slowing down Auger recombination through graded interfaces has only been demonstrated in CdSe/CdS core/shell QDs, which therefore remain the most widely used for lasing applications. That said, the recent introduction of bulk-like nanocrystals, whose sizes are larger than the limit for strong quantization, may offer a possible alternative.²³⁶ Furthermore, the formation of QD films with *n*- or *p*-type character has been established for PbS QDs, but replicating these results with other QDs has proven difficult. One possible reason is that the facets of III-V semiconductors tend to form surface states.^{96,237} Finally, the recent demonstration of indistinguishable photon emission appears to be specific to CsPbBr₃ nanocrystals, where radiative recombination and exciton decoherence occur at similar rates under cryogenic conditions.¹⁹⁸ Reproducing this achievement with QDs emitting at other wavelengths remains an outstanding challenge.

While performance is essential for QD technology, relatively few studies go beyond demonstrating performance to address stability under operational conditions of QDs and QD devices. Moreover,

the few reported studies show that operational performance loss is a complex problem,²³⁸⁻²⁴⁰ involving issues intrinsic to QDs, to the interaction between QDs and ambient, or the impact of QDs on other layers in a device stack. Moreover, results can be counterintuitive. Monitoring different LSCs in outdoor settings, for example, revealed a gradual degradation for CdSe-based LSCs, but an improvement in performance for InP-based LSCs.²⁴⁰ In many cases, the underlying failure processes remain poorly understood. As a result, synthesis optimizations aimed at improving stability lack a clear direction, which could limit the further development of QD technology.

[H1] Outlook

The field of colloidal QDs has shown a remarkable sequence of breakthrough results. Central to this development is the remarkable versatility of QDs as a material platform, in terms of materials addressed, tuning properties through structure, and compatibility with analysis methods. Lead halide perovskites are only one example of many where new semiconductors were readily formed as nanocolloids. Core/shell geometries, alloyed interfaces, and surface termination are just three cases of structural adaptations that shifted the paradigm of QD technology. With little or no sample preparation, the same QDs can be analyzed by techniques as diverse as solution NMR, STEM, and femtosecond optical spectroscopy. Moreover, computational methods have been established that are increasingly capable of dealing with the complexity of QDs. We expect that the field will continue to use these unique capabilities to make headway and establish QDs as a competitive printable semiconductor in semiconductor and quantum technologies.

In the development of precisely controlled QDs, we foresee a major role for automated synthesis in combination with machine learning (ML) approaches. QDs are a perfect model systems for such approaches since synthesis and processing is possible in solution-based continuous flow or automated batch reactors,²⁴¹⁻²⁴⁶ critical properties and performance (particle size, particle size distribution, optical performance) can be easily and rapidly assessed via in-situ optical spectroscopy, providing a reliable dataset with direct feedback to the synthesis conditions, and reaction parameters can be controlled by tuning flow rates, concentrations and temperatures, providing a programmable feedback-loop based on ML predictions of the measured parameters.^{245,247} The combination of high-throughput screening and ML modeling can enable the discovery and optimization of QDs with unprecedented speed and accuracy. Such methods are expected to deliver rapid progress in the atomistic control of QD size, shape and surface composition. It will also allow screening of new core and shell materials as well as new surface ligands used in QDs.

The structure and properties of QDs are closely related and the atomic precision of QD synthesis and analysis is therefore essential.²⁴⁸ As showcased by the atomically precise thickness of colloidal nanoplatelets, atomic precision suppresses the heterogeneous broadening of properties such as the emission linewidth. Efforts to extend this atomic precision to different QD geometries, such as tetrahedrons, are ongoing.²⁴⁰ This step is closely related to mechanistic understanding of QD growth during synthesis. A promising development is that the atomically precise analysis of the geometry of single QDs is increasingly realistic through real space imaging with STEM and diffractive imaging with pulsed coherent X-rays. Even in the absence of atomically precise ensembles, such methods will provide a new and detailed view on QD ensembles. Moreover, data on the atomistic structure of QDs will greatly help computational studies aimed at understanding structure-property relations.

Operational stability is a part of QD research where more atomistic insight is needed., It is largely unknown how continuous loading — illumination, electric bias, and ambient exposure —

influences the QD properties by modifying the QD structure. Understanding and avoiding the underlying failure processes is essential for QD technology in the long run. For example, a recent study combining NMR with laser excitation showed that illumination induces desorption of oleate from CdSe QDs, a clear example of a failure process that offers insight in how to improve the stability.¹¹² A far more detailed picture on the relation between load, structural changes, and failure can emerge if external stimuli are combined with in-situ analysis methods that offer atomic precision, such as illumination in STEM.²⁴⁹ Similarly, novel time-resolved electron and x-ray probes, derived from free electron lasers, x-ray synchrotron sources, or pulsed electron accelerators, can provide insight into structural or chemical changes after optical or electrical pulses.

Ideally such studies are supported by a computational framework that extends to QDs under load, and that can also capture rare processes that lead to failure. For this purpose, one can leverage machine-learning force fields to perform long time-scale molecular dynamics (MD) simulations. ML-based force fields, trained on accurate quantum mechanical data based on DFT, offer the ability to capture complex interatomic interactions with high accuracy while maintaining computational efficiency.²⁵⁰ This capability is crucial for exploring the dynamics of QDs over extended periods, revealing how vacancy patterns, surface reconstructions, and ligand arrangements evolve under various conditions. This approach can bridge the gap between current static DFT calculations and dynamic real-world conditions, while opening a path to complement real QDs by digital twins, whose development can be tracked as a function of time to map load/structural changes/failure relations. The result would be a more rational framework to direct QD synthesis, design QDs with tailored properties, and enhance reproducibility and reliability in QD technology.

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Author contributions

Introduction (ZH); Experimentation (JSO, PBG, ZH); Results (II, PBG, RDS, SB, ZH); Applications (AJH, EHS, SZ, ZH); Reproducibility and data deposition (AH, JO, SB, ZH); Limitations and optimizations (AH, JO, ZH); Outlook (all authors); Overview of the Primer (all authors).

Competing interests

The authors declare no competing interests.

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Supplementary information

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Display Items:

Table 1. Figures of merit related to absorption or emission of light for different classes of quantum dots (QDs).

Material	λ_x (nm)	$\Delta\lambda_x$ (nm)	PLQY (%)	$\mu_{i,450}$ (10^5 cm^{-1})	Applications
CdSe-based structures ($\lambda_{gap} \sim 715 \text{ nm}$, $d_{conf} \sim 6 \text{ nm}$)					
CdSe QD ^a	430-650	20-30	$\sim 100^{252,253}$	0.81	QD color-conversion (LCDs, on-chip LEDs, microLED), QLEDs, QD lasers, QD-LSCs
CdSe/ZnS QD ^b	450-650	21 (515 nm)	88 (515 nm) ²⁵⁴	0.093	
CdSe/CdS QD ^c	560-650	20-25	95 ²⁵²	0.75	
CdSe NPL ^d	393-643	~ 10	50 (core) 90 (core/crown)	N/A	
InP-based structures ($\lambda_{gap} \sim 915 \text{ nm}$, $d_{conf} \sim 14 \text{ nm}$)					
InP/ZnSe/ZnS QDs ^e	500-700	35-40	100 (630 nm) ⁹	0.48 ^f	QD color-conversion (LCDs, on-chip LEDs, microLED), QLEDs
InP/ZnSe/ZnS QDs ^g	480-650	45-50	90-95 ⁵⁶	0.48 ^f	
CsPbBr₃ structures ($\lambda_{gap} \sim 525 \text{ nm}$, $d_{conf} \sim 6 \text{ nm}$)					
CsPbBr ₃ QDs	440-520 ²⁵⁵	15-25	$\sim 100^{256}$	0.87 ²⁵⁷	QD color-conversion (LCDs, on-chip LEDs, microLED), QLEDs
ZnSe-based structures ($\lambda_{gap} \sim 470 \text{ nm}$)					
ZnSe/ZnS QDs	350-440	$< 10^{258}$	95 ²⁵⁸	0.052	QLEDs
CuInS₂-based structures ($\lambda_{gap} \sim 830 \text{ nm}$)					
CuInS ₂ /ZnS QDs	500-1000 ²⁵⁹	100 (650 nm)	85 ²⁶⁰	Unknown	QD-LSCs
PbS-based structures ($\lambda_{gap} \sim 3000 \text{ nm}$, $d_{conf} \sim 45 \text{ nm}$)					
PbS QDs	600-3000 ^{261,262}	150 (1500 nm)	40-80 (1500 nm) ²⁶³	1.15	QD solar cells, IR imagers, QD-LEDs
InAs-based structures ($\lambda_{gap} \sim 3400 \text{ nm}$)					
InAs QDs ^h	900-1600 ²⁶⁴	100 ²⁶⁴	$< 1^{264}$	1.50	IR imagers, QD-LEDs
InAs/InP/ZnSe QDs ⁱ	750-1100 ²⁶⁵	60-75 ²⁶⁵	40-80 ²⁶⁵	0.67 ^j	
InAs/ZnSe QDs ^h	900 ²⁶⁶	135 ²⁶⁶	70 ²⁶⁶	0.65 ^j	
HgTe structures (zero-gap bulk compound, $d_{conf} \sim 73 \text{ nm}$)					
HgTe QDs	700-100000 ¹⁸	130 ²⁶⁷ (1200 nm)	75 ²⁶⁷ (1200 nm)	2.14	IR imagers, QD-LEDs

Semiconductors are characterized by the wavelength, λ_{gap} , corresponding to the bulk band-edge absorption wavelength and the upper diameter, d_{conf} , that characterized the strong confinement regime.⁵⁵ The intrinsic absorption coefficient, $\mu_{i,450}$, at 450 nm is calculated using bulk optical constants, a core volume fraction of 10% and toluene as the solvent.²⁵¹ For CsPbBr₃, experimental values at 450 nm are given. PLQY: photoluminescence quantum yield; NPL: Nanoplatelet; LCD: Liquid crystal display; LED: light emitting diode; LSC: Luminescent solar concentrator. (a) PLQY strongly depends on surface chemistry; (b) Mostly for green emission; (c) Mostly for red emission; (d) Wavelength range for 2.5 to 9.5 monolayers; (e) Synthesis by tris-trimethyl-silylphosphine; (f) Without ZnS outer shell; (g) Synthesis by tris-diethyl-aminophosphine; (h) Synthesis by tris-trimethyl-silylarsine (i) Synthesis by tris-dimethyl-aminoarsine; (j) without ZnSe outer shell

Table 2. Figures of merit relevant for QD lasing and quantum optics applications for different classes of QDs.

Material	λ_x (nm)	$\tau_{x,rad}$ (293 K, ns)	$\tau_{x,rad}$ (5 K, ns)	$\tau_{BX,Auger}$ (ns)	$T_{2,x}$ (ns)	Single photon purity (293 K)
CdSe-based structures ($\lambda_{gap} \sim 715$ nm, $d_{conf} \sim 6$ nm)						
CdSe QD ^a	430-650	20-25 ²⁶⁸	Unknown	0.006-0.3 ²⁶⁹	Unknown	Unknown
CdSe/ZnS QD ^b	450-650	25 ²⁷⁰	6 ²⁷¹	0.006-0.3	0.109 (FWM) ²⁷²	0.004 ²⁷³
CdSe/CdS QD ^c	560-650	>25 ²⁷⁴	3.6-7.1 ²⁷⁵ (dot-in-rod)	0.3-1.6 ²⁷⁶ 1-100 ²¹	0.110 (FWM) ²¹⁵	0.07 ²⁷⁷
CdSe NPL	393-643	4 ⁴⁸	0.1 ¹²³	~NA	0.001 (FWM) ²¹⁷	Unknown
InP-based structures ($\lambda_{gap} \sim 915$ nm, $d_{conf} \sim 14$ nm)						
InP/ZnSe/ZnS QDs ^d	500-700	Unknown	Unknown	Unknown	0.25 (PCFS) ¹⁵¹	0.077-0.086 ¹⁵¹
InP/ZnSe/ZnS QDs ^e	480-650	30-40 ²⁷⁸	21-38 ¹²⁶	0.06 ²⁷⁸	0.023 (FWM) ²⁷⁹	0.03-0.4 ²⁸⁰
CsPbBr₃-based structures ($\lambda_{gap} \sim 525$ nm, $d_{conf} \sim 6$ nm)						
CsPbBr ₃ QDs ^f	440-520	4-5 ^{97,281}	0.1-0.3 ²⁸² (>10 nm NCs)	0.012 ⁹⁷ (~5 nm QDs)	0.08 (PCFS) ²¹⁸ 0.0245 (FWM) ²¹⁶	0.085-0.4 ¹⁹⁶
PbS-based structures ($\lambda_{gap} \sim 3000$ nm, $d_{conf} \sim 45$ nm)						
PbS QDs	850-3000	1000-2000 ²⁶³	Unknown	0.035 ²⁸³	<0.001 (FWM) ²⁸⁴	0.4 ²⁸⁵
InAs-based structures ($\lambda_{gap} \sim 3400$ nm)						
InAs/ZnSe QDs ^h	900 ²⁶⁶	50-55 ²⁶⁶	Unknown	Unknown	Unknown	Unknown

Semiconductors are characterized by the wavelength λ_{gap} corresponding to the bulk band-edge absorption wavelength and the upper diameter d_{conf} that characterized the strong confinement regime.⁵⁵ NPL: Nanoplatelet; FWM: four-wave mixing; PCFS: Photon-correlation Fourier spectroscopy (a) $\tau_{BX,Auger}$ scales with QD volume; (b) $\tau_{BX,Auger}$ presumed equal to CdSe QDs; (c) $\tau_{x,rad}$ scales with core and shell size; (d) Synthesis by tris-trimethyl-silylphosphine; (e) Synthesis by tris-diethyl-aminophosphine; (f) Radiative rate at 5 K scales with NC volume

Figure Captions:

Figure 1. Timeline highlighting the development of quantum dot (QD) synthesis and technology.

This timeline follows the evolution of QD synthesis and technology from the initial discovery of quantum confinement to precision methods for colloidal QD synthesis (green track) and QD-based optoelectronics (blue track).

Figure 2. Quantum dot (QD) synthesis steps. (a) Breakdown of QD formation with (I) precursor decomposition, (II) nucleation, and (III) growth (n : number of QDs; Q : precursor decomposition rate; G : growth rate per QD). (b) Representation of the La Mer model as a sequence of the (I-III) reaction steps, followed by (IV) ripening (C : solute concentration). (c-d) Illustration of diffusion-limited and reaction-limited growth as two mechanisms for size focusing. (ESC: early-stage cluster; MSC: magic-size cluster). (e) Ostwald and digestive ripening as surface energy-minimization processes leading to a broadening or a narrowing of the size distribution. (f) A magic-sized cluster as a unique atomic arrangement that minimizes surface energy. Panel d is adapted with permission from ref. ⁴³. Copyright 2018 American Chemical Society. Panel f is adapted with permission from ref. ¹⁰⁹. Copyright 2016 American Chemical Society.

Figure 3. Typical characterization methods and results for InP/ZnSe quantum dots (QDs). (a) Bright-field and high-resolution transmission electron microscopy (TEM) images provide an overview of the QD size and crystallinity. Size analysis based on the overview image leads to the size histogram shown on the right. (b) Powder X-ray diffraction (XRD) provides an indication of crystallinity at ensemble level; in this case the pattern is dominated by diffraction from the ZnSe shell. (c) The Raman spectrum provides separate phonons of the InP core and the ZnSe shell, shifts with respect to reference wavenumbers are indicative of strain. (d) Elemental composition can be derived from the Rutherford backscattering spectrum (RBS), where the additional contribution from Cl is related to the QD surface. (e) The UV-Vis and photoluminescence (PL) spectra provide an estimate of the band-edge transition – and therefore the QD size – as well as key figures of merit, such as emission wavelength, linewidth and photoluminescent quantum yields. Adapted with permission from ref. ⁵⁶. Copyright 2022 American Chemical Society.

Figure 4. Chemical and structural characterization of quantum dots (QDs) by electron microscopy and X-ray diffraction. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of a InP/ZnSe core/shell QDs at (a) low and (b) high magnification. The high magnification depicts the ZnSe crystal along the [110] direction. (c) Energy dispersive X-ray spectroscopy (EDS) maps providing evidence for an InP core and a ZnSe shell. (d-g) Illustration on how a 3D model can be extracted by quantifying a 2D HAADF-STEM image (d). Counts of the number of atoms are indicated in (e) and after structural relaxation a 3D model is obtained (f,g). Panels a-c are adapted from ref ²⁸⁶ <https://doi.org/10.1021/acsphotonics.8b00615>. Panels d-g, images courtesy of Kim Dömbgen (ref ²⁸⁷).

Figure 5. Quantum dot (QD) surface chemistry analysis. (a-c) Illustration of the solution ¹H nuclear magnetic resonance (NMR) toolbox applied to oleate-capped CdSe QDs, showing (a) the 1-dimensional ¹H NMR spectrum with an identification of the resonances as indicated, (b) the intensity decay recorded through pulse field gradient spectroscopy, where the slope of the intensity trace yields the diffusion coefficient and, (c) the nuclear Overhauser effect spectroscopy (NOESY) spectrum where cross peaks with the same sign as the diagonal are indicative of species binding to the QD surface. (d-e) Insight obtained from quantitative solution NMR studies, in this case, the (d) surface coverage of CdSe QDs by cadmium oleate as a function of BuNH₂ concentration, where the agreement with an isotherm using two binding sites suggests a heterogeneity of binding sites confirmed by (e) density functional theory calculations of the cadmium oleate displacement energy. Parts a-c are adapted from ref. ⁸⁴, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Parts d-e are adapted with permission from ref. ⁸³. Copyright 2018 American Chemical Society.

Figure 6. Computational analysis of quantum dots (QDs). (a) Illustration of QD modeling approaches and resulting information, comparing effective mass (analytical, ideal geometry), tight binding (MO picture, limited surface, needing parameterization), and density functional theory (DFT, atomistic, detailed surface, no parameterization), with an increasing computational cost from left to right. (B) Schematic representation of an "original" non-stoichiometric CdSe QD with a diameter of 3.5 nm, as synthesized, with

its surface capped by oleate ligands. The QD models are atomistic representations of the original structure used in DFT calculations, where the ligands are replaced with smaller moieties, such as acetate or halides. The excess charge of Cd in the inorganic core is compensated by the anionic ligands, resulting in a charge-balanced, neutral system. (c) A view of a localized trap state, along with its density of states, arising from an undercoordinated Se atom in a CdSe QD model, following the detachment of a Z-type CdCl₂ ligand. (d) Views from different zone axes of CdSe QDs, including a pure model with all facets fully passivated by Cd and Se ions, and a reconstructed CdSe QD model where surface reconstruction patterns mitigate charge accumulation on ion-rich facets, specifically the 111 and $\bar{1}\bar{1}\bar{1}$ planes. (e) (*left*) Electronic structure of the unreconstructed CdSe QD model (3 nm in size), exhibiting a non-existent highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) gap due to the presence of facet-specific trap states. (*center*) The reconstructed CdSe QD model, built upon a vacancy pattern, showing the elimination of trap states and highlighting a clean HOMO-LUMO gap. (*right*) Electronic structure of the surface-reconstructed core-shell CdSe@ZnS system, demonstrating a clean bandgap. Panel c is adapted with permission from ref.⁹⁰. Copyright 2017 American Chemical Society. Panel e is adapted from ref.⁹⁴, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

Figure 7. Time-resolved analysis of quantum dot (QD) properties. (a-c) Transient optical spectroscopy analysis of 4.7 nm CsPbBr₃ QDs, including time-resolved photoluminescence spectroscopy with (a) nanosecond and (b) picosecond time resolution, and (c) femtosecond transient absorption spectroscopy. The different decay components can be assigned to relaxation pathways of photo-excited QDs as indicated. (d) Static X-ray diffraction conveys lattice spacings and crystal symmetry. Full width half maximum (FWHM) diffraction linewidths relate to average particle size. (e) Transient X-ray diffraction static pattern (above) and pump-induced changes in the static pattern (below) for CsPbBr₃ QDs can relate expansion, disordering, or phase transitions. Expansion appears as derivative line shapes with increased diffraction at low Q and reduced diffraction at higher Q, whereas loss of peaks can relate disordering, or in this case, where diffraction is still observed for a cubic phase, convey a solid-solid phase transition (loss of peaks at gray vertical lines denoting orthorhombic peaks). (f) Ambient temperature orthorhombic crystal phase with tilted octahedra convert to a cubic structure upon optical excitation that recovers to the initial state over time. Panels a-c are adapted with permission from ref.⁹⁷. Copyright 2024 American Chemical Society. Panel d is adapted with permission from ref.²⁸⁸. Copyright 1996 American Chemical Society. Panels e-f are adapted with permission from ref.¹²¹, American Chemical Society.

Figure 8. Spectroscopic study spanning sub-ensembles to single quantum dots (QDs). (a) Using narrow linewidth optical excitation set to a wavelength close to the ensemble absorption onset (here for CdSe QDs), light is absorbed only by a sub-ensemble of largest QDs in the ensemble with coupling into the optically active ± 1 state that emits nearly at the same energy (green arrow). Spin relaxation to the optically passive dark state yields a Stokes shifted emission (orange dashed arrow and orange-shaded region). A still redder emission arises from local oscillator (LO) phonon assistance from the optically passive state (red dashed arrow and red-shaded region). Such fluorescence line narrowing spectra (inset) results for indicated QD sizes and reveals a size-dependent spectral shift from optically active to passive, revealing dark-bright splitting size-dependence. (b) For spatially isolated single QD investigations, photoluminescence (PL) intermittency or blinking is shown in the upper row where measured lifetime decreases markedly when PL count rates drop (evaluated by time-tagging each photon arrival time). The lower row shows a particle with suppressed blinking and a reduced distribution of emission lifetimes. Excited state lifetimes show rapid emission for typical QDs that undergo non-radiative Auger recombination, whereas certain core-shell particles, although they occasionally still charge, can still radiate as the Auger process is suppressed, and indeed emit with a shorter lifetime owing to the additional charge. Panel a is adapted with permission from ref.¹²², American Physical Society. Panel b is adapted with permission from ref.²⁸⁹. Copyright 2022 American Chemical Society.

Figure 9. Charge transport limits in quantum dot (QD) films. (a) Weak coupling leads to hopping transport while (b) strong coupling results in mini-band formation and may result in band-like transport, like in bulk semiconductors (c), where the mobility is limited by charge carrier scattering.

Figure 10. Colloidal quantum dot (QD) color-conversion. Working principle of QD color-conversion for (a) Liquid crystal displays (LCD) backlights, (b) warm white light emitting diodes (LEDs), and (c) blue microLED arrays, showing schematically the integration of QDs in the device (bottom) and the resulting emission spectrum (top). (d) Chromaticity diagram showing a locus of color points accessible to QDs with an emission linewidth of 20 nm. The light grey line represents the REC 2020 standard for RGB displays (International Telecommunications Union (ITU) Recommendation BT. 2020). The while line represents the Planckian locus used to assign a color temperature to white light emitters.

Figure 11. Colloidal quantum dot-based photodetectors (QDPDs), sensitized solar cells (QDSSCs), and light emitting diodes (QLEDs) working principles and performance limiters explored via electro-optical characterization techniques. Key processes in (a) QDPDs, (b) QDSSCs, and (c) QLEDs occurring across different time scales, along with selected experimental techniques for probing each process.

Figure 12. Quantum optics with colloidal QDs. (a) Using a Hanbury-Brown Twiss setup, the second order correlation function of the emitted photon stream can be measured. Non-classical light emission from a single quantum emitter (here: CdSe/ZnS CQDs at room temperature) exhibits characteristic anti-bunching with a deviation of the zero-time second-order autocorrelation, $g^{(2)}(t = 0) < 0.5$ whereas an ensemble shows a flat correlation curve, because thermal bunching occurs typically on time scales faster than the avalanche photo detector (APD) time resolution. (b). Hong-Ou-Mandel indistinguishability is measured by interfering subsequently generated photons with the same energy, polarization and spatial mode. With metal halide perovskite CQDs at cryogenic temperature, the signal shows a dip at zero delay compared to distinguishable photons as both photons will coalesce on the beam splitter and propagate into the same APD. (c). Integrating CQD in a tunable open microcavity enables the creation of exciton-polaritons in the strong light-matter interaction regime as evidenced by the characteristic anti-crossings between the excitonic and photonic states (here: CdSe nanoplatelets at room temperature). (d). Ordered CQD superlattices can be formed through drying-mediated self-assembly. With metal halide perovskite CQD at sufficiently low temperature, the emitting dipoles can spontaneously synchronize their phases, giving rise to superfluorescent emission bursts, which can be observed by decay acceleration, superlinear peak intensity, delay shortening and Burnham-Chiao ringing. Panel a is adapted from ref.²⁹⁰, Springer Nature Limited. Panel b is adapted from ref.¹⁹⁸, Springer Nature Limited. Panel c is adapted with permission from ref.²⁰⁶, American Chemical Society. Panel d is adapted from ref.²¹⁹, Springer Nature Limited.

Box

Box 1 – Describing QDs as chemical compounds

[NRMP-24-033-Hens-b1.ai]

[bH1] Ligand classification. Given the boundary condition of charge neutrality, the QD-ligand interaction can be conveniently described through binding motifs based on the covalent bond classification. As shown in the figure (adapted with permission from ref²⁹⁸ Royal Society of Chemistry), this scheme discerns three types of ligands:

- L-type ligands: Lewis bases in their neutral form, contributing two electrons to the QD-ligand bond.
- X-type ligands: Compounds in their neutral form, contributing one electron to the QD-ligand bond.
- Z-type ligands: Lewis acids in their neutral form, contributing no electrons to the QD-ligand bond

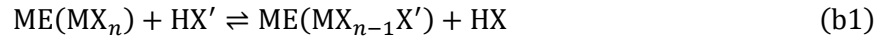
Often, X-type ligands will end up at the QD surface as anions that balance the charge of excess metal cations. Such ligands can also exhibit mixed character or even act in consort with another X-type ligand, forming a bound ion pair. For example, bound carboxylates could be classified as LX ligands, the additional L-type character arising from the carbonyl. Ion pairs often occur in reactions involving a mixture of amines and halide or carboxylic acids, forming ammonium halides or ammonium carboxylates. Such species can be labeled as XX' or X₂.²⁹¹ The distinction between X or XX' is important as it dictates how post processing ligand exchanges need to be optimized.

[bH1] Binding motifs. Using the ligand classification, a QD can be written down as a chemical compound by combining the stoichiometric QD core with the ligand-QD binding motif. Writing a compound semiconductor as ME, where the metal M has an oxidation state +*n*, examples include:

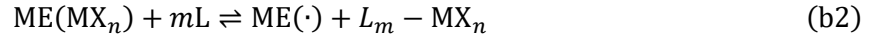
Binding motif	Description	Pictogram	Examples
ME(MX _n)	Cation-rich QD passivated by X-type ligands	[NRMP-24-033-Hens-b1.2.ai]	CdSe(Cd(RCOO) ₂) ₂ , ⁷³ PbS(Pb(RCOO ₂)) ₂ , ²⁸ InP(In(RCOO) ₃) ₃ ⁷⁹
ME(L)	Stoichiometric QD passivated by L-type ligands	[NRMP-24-033-Hens-b1.3.ai]	CdSe(RNH ₂) ₂ ²⁹²
ME(MX _n)(L)	Cation-rich QD with a mixed shell of X and L ligands. No definite X:L stoichiometry.	[NRMP-24-033-Hens-b1.4.ai]	InP(InCl ₃)(RNH ₂) ₂ ²⁹³ InAs(InCl ₃)(RNH ₂) ₂ ²⁹⁴
ME(X ₂)	Stoichiometric QD with a mixed shell of positive and negative X-type ligands in a 1:1 stoichiometry.	[NRMP-24-033-Hens-b1.5.ai]	CsPbBr ₃ (RCOO)(RNH ₃) ₂ ²⁹⁵ CsPbBr ₃ (RCOO)(RNH ₃) ₂ ²⁹⁵ HgSe(Cl)(RNH ₃) ₂ ²⁹⁶ PbS(Cl)(RNH ₃) ₂ ²⁹⁷

[bH1] Ligand exchange reactions. Writing the QD-ligand construct as a chemical compound, ligand exchange processes can be expressed as chemical reactions that highlight the underlying

breaking and formation of bonds. For example, exposing an $\text{ME}(\text{MX}_n)$ QD to an organic acid MX' can lead to an $\text{X} - \text{X}'$ exchange according to:



Similarly, the displacement of an MX_n moiety by addition of L-type ligands can be expressed as:



Here, $L_m - \text{MX}_n$ is the resulting acid-base adduct.

Glossary

Auger recombination. Mechanism of non-radiative recombination of biexcitons, where a first electron hole pair recombines by transferring energy to a second electron hole pair. The process becomes faster for electron-hole pairs confined in smaller volumes.

Band-edge transition. Electronic transition between the HOMO and LUMO of a QD. Terminology is derived from bulk semiconductor physics, where the HOMO and LUMO are the states at the top of the valence and conduction band, respectively.

Biexciton. Excited state of a QD consisting of two electron-hole pairs.

Blinking. Emission characteristic of single QDs, involving sudden transitions between different levels of brightness.

Carrier cooling. Relaxation of a charge carrier to the band edges, the CB in the case of electrons and the VB in the case of holes. Carrier cooling follows, for example, non-resonant photoexcitation.

Carrier trapping. Transfer of a charge carrier to a localized, lower-energy state.

Chromaticity diagram. A 2D representation that shows all the perceivable hues by the standard observer as (x, y) pairs, where x and y measure the relative stimulation of standardized red and green light receptors, yielding the stimulation of the blue receptor as $1-x-y$.

Color rendering. Describes how an illuminant impacts the perceived color, either consciously or subconsciously, by comparing the appearance of the color with a standard illuminant. Quantified through the color rendering index (CRI), where a CRI of 90 is typically used as a benchmark for white LEDs.

Color temperature. A parameter describing the color of a visible light source by comparing it to the color of light emitted by a black body radiator. Warm white light corresponds to color temperature in the range 2700-3000 K.

Core/shell. Quantum dot geometry in which a core consisting of a first semiconductor is embedded within a shell of a second semiconductor.

Dephasing. Loss of quantum-mechanical coherence after optical excitation, resulting in the collapse of the state from a superposition into either the unexcited or the excited state. See also T_2 relaxation.

Detectivity. Figure of merit for a photodetector used to characterize performance, equal to the reciprocal of noise-equivalent power, normalized per square root of the sensor's area and frequency bandwidth.

Diffusion. Transport of charge carriers caused by a gradient in the carrier concentration.

Drift. Transport of charge carriers caused by a force, typically an electric field.

Effective mass approximation (EMA). A computational approach treating charge carriers as quasi particles characterized by an effective mass that accounts for the crystal potential. The EMA, and the related $k\cdot p$ theory, describes quantized energy levels in quantum dots.

Effective mass. Mass assigned to conduction-band electrons or valence-band holes to account for the impact of the crystal potential on the dynamics of motion.

Energy transfer. Process by which an excited quantum system relaxes by the simultaneous excitation of a neighboring quantum system. Energy transfer is induced by dipolar coupling and involves for two adjacent QDs the simultaneous recombination and formation of a band-edge exciton.

Exciton spin relaxation. Relaxation process that involves a change of spin or total angular momentum of the band-edge exciton. For example, cooling from the bright to the dark exciton state.

Exciton. The excited state of a quantum dot consisting of one electron-hole pair. The term is derived from solid-state physics, where exciton describes a quasi-particle in a semiconductor that consists of an electron/hole pair bound through Coulomb interaction.

External quantum efficiency (EQE). Figure of merit for a photodetector, defined as the ratio between the flux of photons incident on the photodiode, and the resulting current of photo-generated charge carriers. An EQE of 100% means that for each absorbed photon, one charge carrier passes through the external circuit.

Luminescent color-conversion. Interpretation of photoluminescence as a method to convert the color related to the higher energy absorbed by photons to the color of the lower energy emitted by photons. QDs have the advantage of converting light across a broad spectral range into a spectrally narrow emission, which corresponds to a saturated color.

Luminescent solar concentrator (LSC). Device for concentrating sunlight for better solar energy conversion based on the re-emission by photoluminescence of absorbed sunlight under conditions of total internal reflection in a thin, transparent slab. Typically, solar cells are placed at the edges of the slab.

Monodisperse. Refers, in principle, to an ensemble of QDs with all the same size. In practice, a size dispersion below 5% is considered monodisperse.

Nanocolloid. Colloidal dispersion or suspension consisting of nanometer-sized solid particles in a liquid matrix.

Nuclear Overhauser effect. Transfer of spin polarization between adjacent protons, where the spin flip of a first proton is accompanied by the reverse spin flip of a neighboring proton. The process is effective in molecules that tumble slowly in solution, such as ligands bound to QDs.

Nucleation. Part of the precipitation process that involves the formation of new nanocrystals out of the growth species or monomers. According to classical nucleation theory, nucleation forms the smallest possible nanocrystals that are stable against redissolution.

Photoluminescence quantum yield (PLQY). Ratio between the number of photons absorb and emitted by a luminescent material. Typically expressed as a percentage and used as a measure of

the internal efficiency of the photoluminescence, where a PLQY of 100% implies that for each absorbed photon, one photon is re-emitted.

Quantum confinement. A quantum mechanical effect by which the kinetic energy of a particle, such as an electron, increases when confined in a smaller volume.

Reorganization energy. Energy reduction related to the relaxation of a structure after charge transfer, for example related to changes in local coordination.

Resonant excitation. Optical excitation of charge carriers across the band gap where the photon energy matches the band-gap energy.

Responsivity. Figure of merit for a photodetector, defined as the ratio between the photocurrent and the incident optical power.

Sizing curve. A calibration curve that relates the energy gap of a QD measured through absorption spectroscopy with the QD size. TEM or SAXS are typically used to determine the size of the QDs.

Spectral diffusion. Uninterrupted variation of the emission spectrum of single QDs, fluctuating back and forth around an average photon energy.

Spectral hole burning. The selective saturation of spin population with a narrow chemical shift range. In a heterogeneous resonance, this saturation creates a dent or spectral hole in the resonance.

Strong confinement. A regime of size quantization in which the quantization energy is the dominant contribution to the energy of electron-hole pairs.

Supersaturation. A state of a solution where the solute concentration exceeds the solubility. Typically defined as the ratio between the solute concentration and the solubility.

Surface reconstruction. Reorganization of the atoms in a surface facet, forming a 2D lattice that is different from the corresponding bulk lattice plane.

T_2 relaxation. Loss of phase coherence between spins in the transversal plane.

Trap state. An electronic level within the energy gap separating the band of occupied and the band of unoccupied states. Such levels can provide a recombination pathway for an electron-hole pair, whereby these charge carriers are successively trapped in this state.

Wulff construction. A geometric method for predicting the equilibrium shape of a crystal by minimizing the total surface free energy. The distance between each surface facet and the crystal center is taken proportional to the surface energy of the facet, so low-energy facets become dominant.

TOC Blurb

Colloidal quantum dots (QDs) are nanometer-sized semiconductors with unique, size-dependent, optoelectronic properties due to quantum confinement. This Primer discusses various synthetic methods and chemical compositions of QDs, emphasizing their applications in optical devices such as solar cells, color-converters, light-emitting diodes, and quantum optics.

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