

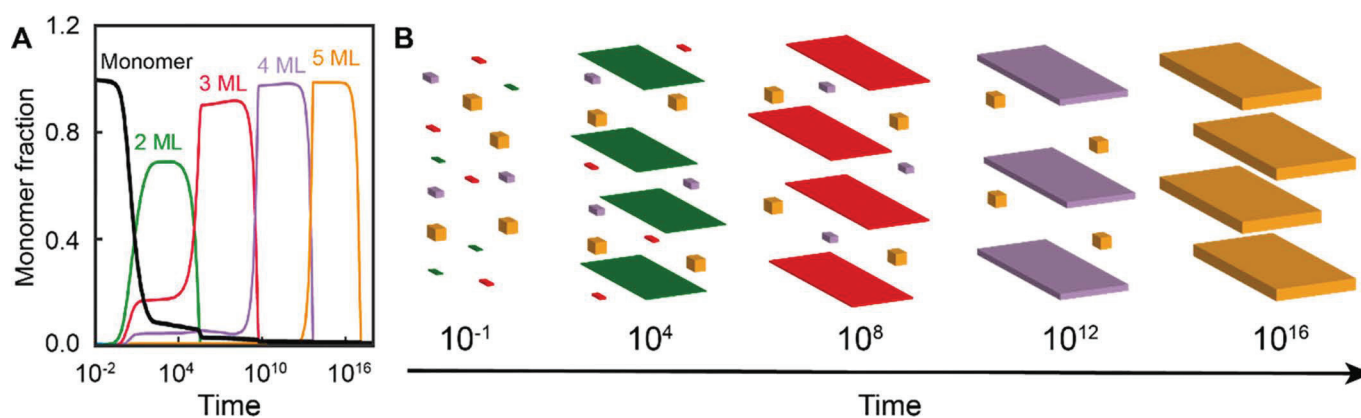
Klaus Boldt

# The Advances of Quantum Dot Research since 1993

The paper on the hot-injection synthesis of colloidal nanocrystals by Murray, Norris and Bawendi [1] from 1993 is without a doubt the pivotal publication that earned the three Nobel laureates in chemistry their recognition. It changed the field from the discovery and confirmation of the new quantum size effect into a hotbed of new developments, simply because nanoparticles were now accessible with a size purity that allowed to study the physical effects of size in unprecedented detail, ranging from fundamental spectroscopy to the kinetics of nucleation and the fabrication of new metamaterials. This article discusses the most seminal discoveries, in the subjective view of the author, that have resulted from the achievements that were recognized by the Nobel committee. Unsurprisingly, these involve many of the main protagonists, since the research of Ekimov, Brus, and Bawendi has spawned a very active and engaging community.

A direct result from the availability of high-quality nanocrystals was the ability to observe the photoluminescence of single quantum dots. In these experiments, Nirmal et al. observed that instead of emitting photons continuously, these particles switch abruptly between a luminescent, bright state and a non-emissive dark state [2]. The phenomenon was quickly explained by Alexander L. Efros, who, having already provided the physical explanation for the quantum size effect [3, 4], is the person who, most of all, deserves to be recognised as one of the fathers of the field. In his 1997 paper in *Physical Review Letters*, he explained the fluorescence intermittency or “blink-

ing” as switching of the nanocrystals between a charged and a charge-neutral state [5]. The charged state does not emit due to an Auger-like mechanism, in which the energy resulting from the recombination of an excited electron/hole pair (exciton) is transferred to the extraneous charge carrier, which undergoes intra-band excitation. Its energy is subsequently dissipated as heat. This mechanism is absent in bulk semiconductors, because the intra-band excitation violates conservation of the crystal momentum. This selection rule is increasingly lifted with decreasing volume of the particles, making the Auger recombination a true effect of the nanoscale [6]. Being about two orders of magnitude faster than radiative recombination, the Auger mechanism effectively suppresses the radiative recombination channel of the quantum dots. The same process is not only responsible for the off-times, it also provides one possible mechanism for charging the particles in the first place: by exciting two excitons at the same time, the recombination of one of them is able to promote one of the charge carriers of the second exciton out of the potential well of the nanocrystal. This mechanism can be highly detrimental: it interferes with the reliable emission for applications ranging from single photon sources for quantum computers to fluorescent markers in live cells. At the same time, the reverse process – fission of a single, hot exciton into two pairs of charge carriers in a lower energy state – provides the basis for multi-exciton generation and devices with an external quantum efficiency of >100 %. As such, the discovery of quantum dot blinking and the Auger effect in these systems has kept the field busy for 30 years.



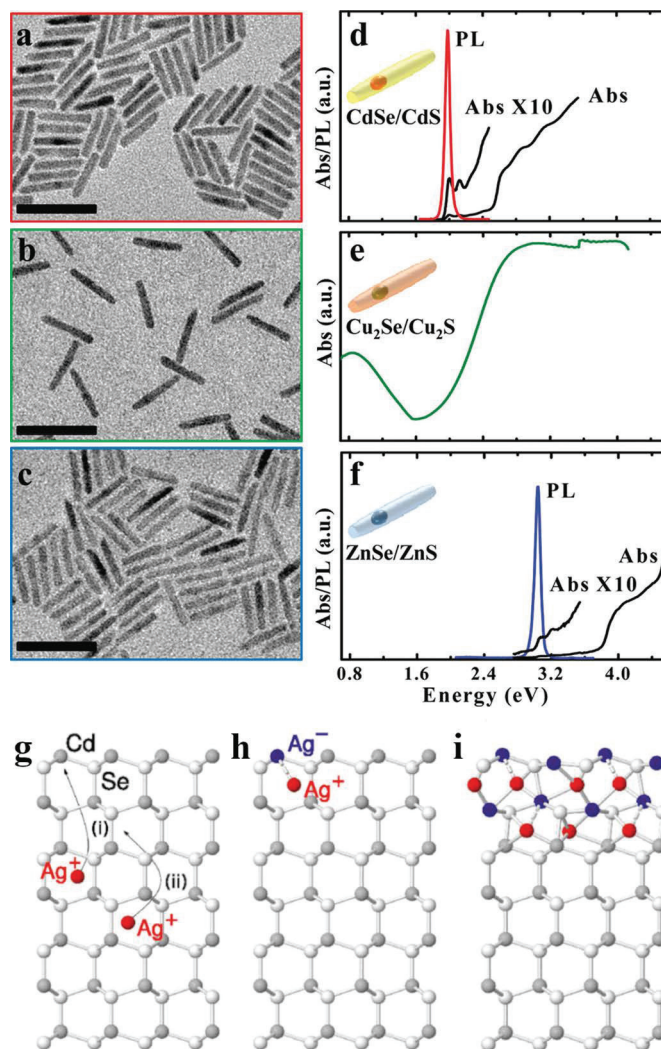
**Fig. 1:** Schematic of the evolution of atomically flat nanoplatelets with increasing thickness in monolayers (ML). Thin platelets grow faster and then ripen to provide material for the more slowly growing, thicker species. © 2021 Pun et al., *Acc. Chem. Res.* **2021**, *54* (7), 1545–1554, licensed under CC-BY-NC-ND 4.0.

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With the hot-injection synthesis firmly established for the preparation of near-spherical, 0-dimensional particles, preparative methods were soon expanded to shape-anisotropic nanocrystals. The first 1-dimensional CdSe nanorods were published by the Alivisatos group in 2000 [7], followed by more complex dot-in-rod structures with a CdSe seed embedded in a CdS rod in 2007 [8, 9]. These structures show very high photoluminescence, emit polarised light, and possess, at the same time, strong quantum confinement and a large, effective volume for the exciton. Therefore, the rate of the Auger mechanism in nanorods is slow enough to make radiative recombination competitive and overcome some of the adverse effects discussed above. The concept of anisotropic growth was extended to two dimensions by Sandrine Ithurria, who in 2008 produced 2-dimensional nanoplatelets in highly concentrated precursor melts [10]. These nanoplatelets are remarkable in that they possess the cubic zincblende structure, yet only grow along two of the possible three dimensions. The preference for in-plane growth is extremely strong, leading to platelets that are atomically flat. This stands in contrast to the quantum dots and rods, which can only be synthesised with an, albeit narrow, size distribution. An elegant mechanism that explains this symmetry breaking was published in 2017 by the Norris group [11]. They showed that growth along the narrow edges of a nanoplatelet is strongly favoured kinetically over island formation on the wide facet, because on the narrow facet the growth does not increase the number of atoms that occupy edge or corner sites. Hence, small, random variations in the shape of small nuclei break the symmetry and push the reaction into a population of platelets with a single thickness. Thicker platelets are formed over time when the feedstock of the nucleating species is used up and larger nuclei can form due to Ostwald ripening (see Fig. 1). This way, successive growth of increasingly thicker nanoplatelets form, until the narrow facet becomes large enough that the kinetic differentiation no longer holds.

Extending the properties of nanoscale objects beyond the confinements of a single quantum dot is not limited to anisotropic shapes. Very early on, quantum dots have been described as ‘artificial atoms’, i.e., objects that possess hydrogen-like states from size-quantisation of the excitons and can be regarded, in first approximation, as hard spheres. It was therefore obvious to make use of the availability of nanocrystal samples with narrow size dispersity and assemble these particles in ordered lattices and supercrystals and mesocrystals. This was first done by the group of Chris Murray, the first author of the hot-injection paper. For binary mixtures, the combination of particle size, shape, material and surface capping offers a practically infinite number of possible combinations, and the work has produced a wealth of different structures, including lattices predicted by the radius ratio rules, ones that do not [12], and even quasicrystalline lattices [13]. The results show very convincingly that the approximation as hard spheres is not valid and that the surface chemistry of the nanocrystals plays a decisive role in their interaction. It also showed that neighbouring particles do not readily interact electronically to form ‘artificial molecules’ or even minibands [14]. However, nanoparticles in highly ordered superlattices exhibit cooperative effects and coherence of the excitons in superlattices with a high long-range order. This leads to superfluorescence, in which the individual emit-

ters couple to form a single giant dipole with long coherence times [15], a phenomenon that is highly attractive for quantum dot-based lasers with size-dependent emission wavelengths.



**Fig. 2:** Transition electron micrographs and optical spectra of dot-in-rod particles during cation exchange, from CdSe/CdS (a, d) via Cu<sub>2</sub>Se/Cu<sub>2</sub>S (b, e) to ZnSe/ZnS (c, f). Reprinted with kind permission © 2012 The American Chemical Society [18]. (g–h) Mechanism of the autocatalytic cation exchange reaction of Cd<sup>2+</sup> against Ag<sup>+</sup>. Reprinted with kind permission © 2014 American Physical Society [20].

The inorganic core of quantum dots is not chemically inert either. In 2007 the Alivisatos group showed that in the moderately ionic II-VI and IV-VI semiconductors the cations can be rapidly and quantitatively exchanged against monovalent silver [16] and copper [17] ions under conservation of the anion sublattice. The reaction occurs at room temperature in a matter of seconds. Prerequisites are the availability of ‘naked’ cations and a complexing agent that is able to bind the released cations from the original quantum dots. While this is in principle also possible in bulk materials, the nanostructure provides the large surface area required for an efficient exchange. Cation exchange can be reversed if enough divalent ions are provided as a thermodynamic driving force. This has led to complex nanomaterials that are either difficult or impossible to synthesise directly. For example, ZnSe/ZnS dot-in-rod structures have been made, starting from CdSe/CdS, by sequential cation ex-

change using  $\text{Cu}^+$  [18] (see Figure 2 a–f).  $\text{Cu}_2\text{Se}$ , having octahedral rather than tetrahedral symmetry, was employed to produce eight-armed octapods by exchanging the cations to  $\text{Cd}^{2+}$  under conservation of the original crystal shape [19]. Such a shape would otherwise be unattainable by direct synthesis of  $\text{CdSe}$ , which, due to its  $F\bar{4}3m$  space group, only forms tetrapods. The cation exchange mechanism was explained by the Norris group in 2014 as a swap between  $\text{Ag}^+$  or  $\text{Cu}^+$  moving on interstitial sites with  $\text{Cd}^{2+}$  or  $\text{Zn}^{2+}$  on lattice sites. The exchange is catalysed by an already exchanged, neighbouring ion. Hence, the cation exchange rapidly proceeds as a continuous front through the nanocrystal [20] (see Figure 2 g–h).

$\text{CdSe}$  has undoubtedly been the work horse of the community, thanks to the ease with which it can be synthesised with precise control over size and shape. Nevertheless, it has its disadvantages, the most pressing being the reliance on toxic cadmium, which is prohibitive for broad, commercial application. The hunt for new materials is as old as the field itself. One of the most exciting advances, though ironically one that does not do away with the issue of heavy metals, was the discovery of methylammonium lead halide perovskites as fluorescent semiconductors in 2009 by Kojima et al. [21]. Compared to the binary semiconductors, the perovskite materials are remarkably defect-tolerant. This is caused by the strong spin-orbit splitting induced by the heavy lead atoms that leads to a very simple band structure without deep intra-band states. Being based on organic cations like methylammonium or formamidinium, the original lead halide perovskites are rather soft materials and not stable against elevated temperatures. In 2015, Kovalenko and co-workers solved that issue by introducing  $\text{Cs}^+$  as the central cation. It raised the temperature range up to 200 °C, making it possible to obtain  $\text{CsPbX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) perovskite nanocrystals from a hot-injection reaction. The reaction produces cubic nanocrystals with remarkable size control and colour purity. Compared to  $\text{CdSe}$ , perovskites are more ionic and are more easily dissolved in a suitable solvent. Also, they easily undergo anion exchange upon introduction of a new halide or even by mixing two samples with different halides [23]. That effect prevents the formation of heterostructures like core/shell or dot-in-rod particles, which is the major approach to increase chemical and optical stability and fabricate nanomaterials with new, emergent properties using binary semiconductor nanocrystals. Hence, tuning the emission colour of perovskites is often done by composition rather than size control. The impact and opportunities from the development of the perovskite quantum dots can be seen in two research articles in this issue of the Bunsen-Magazin.

The last 30 years have seen an explosion of activity in the field of colloidal nanocrystals and quantum dots, which was started by the seminal discoveries of Ekimov, Efros, and Brus, and made possible by the synthetic approach first published by Murray, Norris and Bawendi. The main advances include an in-depth understanding of the photo-physics of individual particles as well as collective behaviour, and precise control over their size, shape, and composition. Many of these principles can be transferred and applied to other material classes like metals, metal oxides, ternary or even quaternary semiconductors. Quantum dots, specifically, have proven to be excellent light converters

that can absorb a broad range of wavelength above their band gap and convert the energy down to a single, narrow emission line. In addition, colloidal nanocrystals are solution-processable and can be easily applied in the form of inks by methods as simple and flexible as ink-jet printing. The first, serious commercial applications have entered the market at the end of the last decade in quantum dot (QLED) displays, in which they produce excellent colour purity. In the next decade, more exciting discoveries can be expected that build on this work.

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### ZITATE

“This means that we are really studying the physics of the material, and not the physics [...] of defects. Because when you start in this field, you are always worried, am I really studying the real thing or just defects. And nobody really wants to study defects.” — Mounji Bawendi on the impact of the Hot Injection synthesis, Nobel Lecture 2023

„Die Energie ist tatsächlich der Stoff, aus dem alle Elementarteilchen, alle Atome und daher überhaupt alle Dinge gemacht sind, und gleichzeitig ist die Energie auch das Bewegende.“ — Werner Heisenberg, <https://gutezitate.com/zitat/167455>

„50 Jahre intensiven Nachdenkens haben mich der Antwort auf die Frage Was sind Lichtquanten? nicht nähergebracht. Natürlich bildet sich heute jeder Wicht ein, er wisse die Antwort. Doch da täuscht er sich.“ — Albert Einstein, <https://gutezitate.com/zitat/177132>

„Wohl keine Entwicklung der modernen Wissenschaft hat das menschliche Denken nachhaltiger beeinflusst als die Geburt der Quantentheorie. Jäh wurden die Physiker eine Generation vor uns aus jahrhundertealten Denkmustern herausgerissen und fühlten sich zur Auseinandersetzung mit einer neuen Metaphysik aufgerufen. Bis zum heutigen Tag wahren die Qualen, die dieser Prozess der Neuorientierung bedeutete. Im Grunde haben die Physiker einen schweren Verlust erlitten: sie verloren ihren Halt in der Realität.“ — Bryce DeWitt, <https://gutezitate.com/zitat/125972>

„Es gibt kein geistiges Eigentum. Sobald eine Idee ausgesprochen ist, ist sie frei, denn: Wer eine Idee von mir empfängt, mehrt dadurch sein Wissen, ohne meines zu mindern, ebenso wie derjenige, der seine Kerze an meiner entzündet, dadurch Licht empfängt, ohne mich der Dunkelheit auszusetzen.“ — Thomas Jefferson, <https://gutezitate.com/zitat/108930>

„Es ist nicht genug zu wissen - man muss auch anwenden. Es ist nicht genug zu wollen - man muss auch tun.“ — Johann Wolfgang von Goethe, <https://gutezitate.com/zitat/279270>

„Das tiefste und erhabenste Gefühl, dessen wir fähig sind, ist das Erlebnis des Mystischen. Aus ihm allein keimt wahre Wissenschaft. Wem dieses Gefühl fremd ist, wer sich nicht mehr wundern und in Ehrfurcht verlieren kann, der ist seelisch bereits tot.“ — Albert Einstein, <https://gutezitate.com/zitat/134577>

„Man kann ein Problem nicht mit den gleichen Denkstrukturen lösen, die zu seiner Entstehung beigetragen haben.“ — Albert Einstein, <https://gutezitate.com/zitat/114919>