Chemistry Nobel Prize Celebrates Colloidal Quantum Dots: Highly-Engineered, Spectrally Pure Light

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The Chemistry Nobel Prize of this year has been awarded to Alexei Ekimov, Luis Brus, and Moungi Bawendi for their significant contributions to the discovery and synthesis of colloidal quantum dots. What initially started as a strategy to explore the physics of reduced dimensionality in matter has transitioned over the past 40 years into a commercially available technology platform, the largest of which provides red and green color sources for displays. In this overview, we will delve into this transition process and the pivotal roles played by the laureates.

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Early in the development of quantum physics, the concept of confinement emerged when materials reached the nanometer scale. At such scales, the optical absorption and emission spectra of nanoparticles was expected to differ from that of bulk materials. However, for a long time (until the 1970s), low dimensionality remained a theoretical concept.

The first breakthrough came with the development of molecular beam epitaxy, which enabled the growth of high-quality semiconductor thin films. Under specific conditions, it is possible to achieve lattice matching between two materials with different band gaps, allowing them to be grown on top of each other. This energy offset was utilized to create structures confined in a single dimension coined *quantum wells* and, later, three-dimensionally confined systems as *quantum dots*. This innovation was a game-changer for light control. Prior to this, controlling the band gap and emission spectrum of a semiconductor was a metallurgical challenge involving the creation of alloys. Two semiconductors could be melted to form an alloy with an optical band gap generally intermediate to those of the initial components. Instead, quantum confinement allowed tuning the band gap using geometric factors while keeping the composition unchanged. This

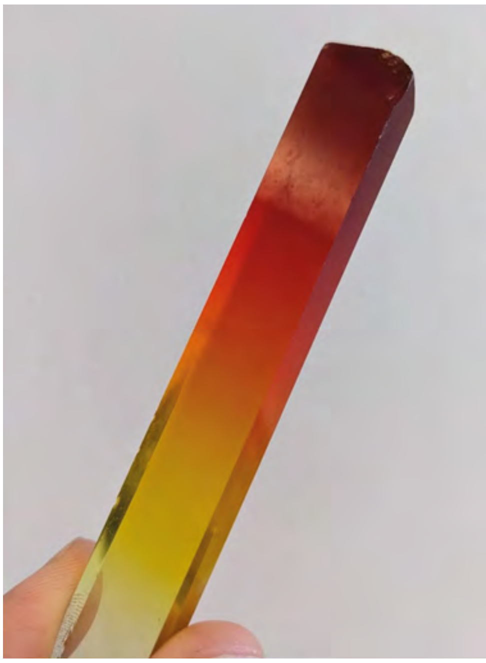

Figure 1. Image of a glass slab grown by Ekimov containing CdSe centers. The thermal treatment conducted on the glass leads to the formation of CdSe quantum dots with various sizes due to the temperature gradient, resulting in a gradient of sizes. Quantum dots at the top are large, resulting in a narrow bandgap and in absorption of almost all visible light. Quantum dots at the bottom are small, pushing their absorption spectrum to the blue resulting in enhanced optical transparency of the glass. Picture Los Alamos National Laboratory, LA-UR-23-31622.

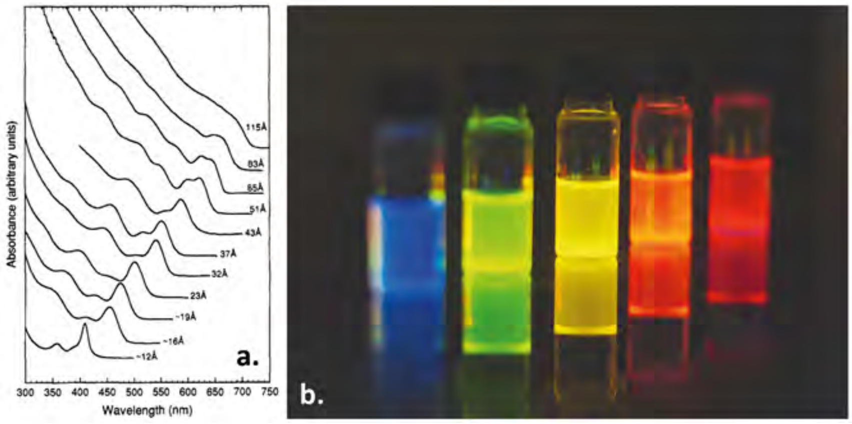

Figure 2. Absorption Spectra of CdSe quantum dots obtained by the hot-injection method as proposed by Bawendi's group in 1993. Figure a is adapted with permission from ref [3]. Copyright {1993} American Chemical Society. b. Image of nanocrystal solutions with various sizes. Nanocrystals are excited with UV light, and what is seen here is their characteristic photoluminescence, peaking at different colors for different sizes.

involved obtaining semiconductors smaller than the exciton Bohr radius, typically a few nanometers for most semiconductors. Epitaxially grown structures utilizing quantum confinement found applications in designing quantum well-based lasers, especially to cover the near-infrared region and its associated telecom applications. It was also employed in the design of quantum well infrared detectors. With the rise of quantum cascade lasers, quantum engineering reached its most complex realization to date.

Despite this success, epitaxy remains a complex method, characterized by its low throughput and high cost. Additionally, the presence of a lattice-matched substrate constrains the library of available materials and renders them incompatible with certain applications, such as trackers in biological media. Therefore, alternative methods have been explored to obtain quantum-confined luminescent materials [1].

In the 1980s, Alexei Ekimov, working at the Vavilov State Optical Institute, investigated the emission properties of metal halide materials while growing them within a silicate matrix [2]. He observed optical features similar to those of bulk materials but shifted towards higher energy. Ekimov, aware of developments in epitaxially grown heterostructures, attributed this effect to quantum confinement. This attribution was confirmed by measuring the particle size using small-angle X-ray scattering [3]. Using the same strategy, he was able to obtain CdSe (see fig. 1), CdS, as well as GaP nanocrystals in glass matrix [4]. However, those materials only displayed weak light emission at room temperature due to a large number of defects in their structure.

Around the same time, and under the suggestion of Alexei Ekimov, the formalism for calculating optical transitions in isolated, nanoscale, quasi-perfect spheres of semiconductors, was developed by Alexander Efros working at Ioffe Institute [5]. This seminal paper would lay the foundation of the theory to be used in the 40 years to come.

Two years later, the team led by Brus at Bell Labs explored a completely different approach, attempting to grow nanoparticles in a liquid medium. Their initial focus was on CdS [6], and the early concept of colloidal synthesis relied on water-based methods. They successfully described the spectrum using an effective mass approximation while also taking into account the electron-hole interaction [7]. They also observed a shift in the optical features toward higher energy, but these features were not immediately attributed to quantum confinement. During this time, Moungi •••

Figure 1. Group photo from the Conference "30 Years of Colloidal Quantum Dots" taken during the 2014 conference held at ESPCI to celebrate the 30th anniversary of quantum dots. The three 2023 Nobel Prize laureates' are highlighted with medals.

Bawendi, a postdoctoral scholar working in Brus' team, obtained a position at MIT. There, along with two graduate students, Christopher Murray and David Norris, they developed a new chemical method for colloidal particle growth, known as the hot-injection method [8].

There were two main changes compared to the previous synthesis developed at Bell Labs. Firstly, the team of Bawendi switched to organic solvents, and secondly, they introduced ligands. These surfactant molecules played a critical role in particle growth. By making the surface less available, the growth kinetics could be adjusted, giving a precise control of the nanoparticle size. Furthermore, ligands facilitated interactions with the solvent, maintaining particle colloidal stability. They also participated in the electronic passivation of the surface, addressing a major issue in such materials. For illustration, a 2.5 nm-sized particle has 80% of its atoms on the surface. This new growth method resulted in reduced polydispersity, allowing the distinction of multiple transitions in ensemble spectra, akin to atomic transitions (see Figure 2).

Although synthetic methods have expanded, including the heat-up approach where all ingredients are mixed at room temperature and then heated [9] as well as the demonstration of core-shell structures [10], the hot-injection method remains the core technique for growing nanocrystals today. The benefits of these quantum dots as light sources quickly found applications in areas such as biolabeling, single-photon sources and displays.

The latter application has been a game changer for colloidal quantum dots, marking a transition from academic laboratories to the industrial world. QD Vision, a spin-off from Bawendi's group, has been a pioneer in this field, enabling the design of robust quantum dots capable of sustaining out-of-equilibrium conditions, high temperatures, and long-term operation (up to 30,000 hours), essential requirements for displays. The advantage of nanocrystals over previous generations of emitters used in displays mainly stems from their narrow photoluminescence linewidth. This results in a broader color palette, particularly in a better green, which is crucial for a market where sports events drive a significant portion of TV purchases.

Thanks to nearly 40 years of development, the synthesis of quantum dots has reached an unparalleled level of precision, in a few examples with an accuracy down to the atomic scale and the capacity to grow a wide range of materials. In 2014, a conference celebrating the 30th anniversary of quantum dots was organized at ESPCI Paris. Among the attendees, the three chemistry Nobel laureates from 2023 were prominently featured in the first line, see Figure 3.

As stated by Prof. Heiner Linke, Member of the Nobel Committee for Chemistry, "we believe that many new applications are still coming". In 2022 QD color conversion on the front face of OLED displays was first commercialized and likely we will see QDs used in color conversion for MicroLED displays in the near future. Bright, color-pure, and energy-efficient quantum dot LEDs are a new light-emitting display technology which is expected to reach the market in the coming years. In 2018, quantum dot infrared image sensors able to achieve military-grade performance at a fraction of the cost of historical technologies were first commercialized and likely will grow into a significant product space in the future. Other prospects include their use as high efficiency color optimizers for agriculture by matching the lighting spectrum with the absorption of plants, where they already have met success in the form of large-scale polymer films encapsulating non-toxic QDs. QDs continue to be made and sold for use in biological imaging and solid-state lighting and it can be anticipated that their use in security inks and spectrometers will emerge. Further fields of potential commercial use of these materials in optoelectronic devices comprise QD solar cells and electrically pumped QD lasers. ●

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