



Scientific Background to the Nobel Prize in Chemistry 2023

## QUANTUM DOTS – SEEDS OF NANOSCIENCE

The Nobel Committee for Chemistry



## Quantum dots — seeds of nanoscience

The Royal Swedish Academy of Sciences has decided to award **Moungi G. Bawendi, Louis E. Brus, and Aleksey I. Yekimov** the Nobel Prize in Chemistry 2023, for the discovery and synthesis of quantum dots.

### Introduction

This year's Nobel Prize in Chemistry recognizes the discovery and synthesis of nanometre-sized semiconductor crystals, the properties of which are determined by quantum size effects. Referred to as quantum dots, such nanoparticles are so small that their physical size determines the quantum mechanical states of the material's charge carriers.

Quantum dots constitute a new class of materials that is neither molecular nor bulk. They have the same structure and atomic composition as bulk materials, but their properties can be tuned using a single parameter, the particle's size. For example, the optical absorption and emission of CdSe quantum dots can be tuned across nearly the entire visible range of the optical spectrum. This is possible because the energy bandgap of CdSe quantum dots varies between 1.8 eV (its bulk value) to 3 eV (in the smallest quantum dots, see Fig. 1). Other material properties that are tuneable by quantum dot size include redox potentials<sup>1</sup>, melting temperature<sup>2</sup>, and solid-solid phase transitions,<sup>3</sup> to name just a few.

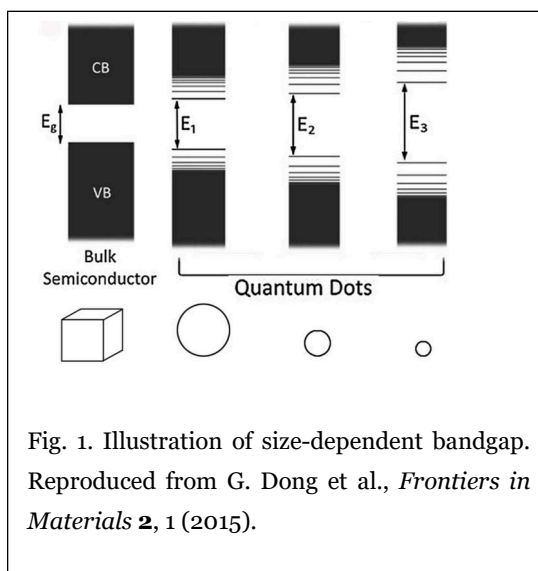


Fig. 1. Illustration of size-dependent bandgap. Reproduced from G. Dong et al., *Frontiers in Materials* **2**, 1 (2015).

The discovery of quantum dots, and the ability to synthesize such materials with high accuracy but relatively simple chemical methods, was an important step in the development of nanoscience and nanotechnology. The core principle of nanoscience is that, at the scale of nanometres, materials and particles attain new, size-dependent properties that can be harnessed and controlled for novel applications. The tools of chemistry are an indispensable enabler of nanotechnology, with applications in areas as diverse as biotechnology, catalysis, sensing, medical diagnostics, electronics, photonics, and quantum technology.



Today it is possible to produce quantum dots with highly controlled, size-dependent properties using relatively low-cost, solution-phase batch chemistries that make these revolutionary materials widely available. With an estimated total market size of USD 4 billion in 2021, quantum dots are used as high-quality light emitters in illumination and in display technology,<sup>4</sup> as well as for biomedical imaging.<sup>5</sup> Ongoing nanotechnology research also explores applications of quantum dots in infrared photodetection, solar energy conversion, light-emitting diodes, diagnostics and photocatalysis.

### **Theory and early observations of quantum size effects**

The basic theoretical concept underlying quantum dots is referred to as the ‘particle-in-a-box’ problem. When a quantum mechanical particle, such as an electron, is confined inside a ‘box’ with a size  $L$  comparable to the particle’s de Broglie wavelength, the energies of the wave function’s allowed eigenstates depend critically on  $L$ , and the energy spacing  $\Delta E$  scales as  $1/L^2$ . This concept has been textbook material since the very early days of quantum mechanics.<sup>6</sup>

Related wave function concepts are foundational to our understanding of the electronic structure of molecules and crystalline materials, the dispersion of energy bands, the formation of bandgaps, and the origin of metallic, semiconducting or isolating properties in bulk materials.<sup>7,8,9</sup>

The concept that material properties can depend on the macroscopic dimensions of a small particle was pioneered in 1937 by Herbert Fröhlich. He pointed out that the free-electron gas model for metals<sup>8,10</sup> gives very different results for small particles compared to bulk metals, and that these differences should manifest themselves in a measurable material property, namely the electrons’ specific heat.<sup>11</sup> He estimated that the observation of this effect would require metal particles smaller than 10 nm and temperatures on the order of a few degrees Kelvin.<sup>11</sup>

In the following decades, various researchers presented further theoretical studies of such quantum size effects. For example, building on earlier work by Landau,<sup>12</sup> and following experimental observations of oscillations of material properties as a function of magnetic field,<sup>13</sup> Lifshitz and Kosevich predicted a periodicity of the thermodynamic potential due to quantum size effects.<sup>14</sup> Kubo predicted a quantum size effect on the electronic heat capacity as well as on spin-flip processes in metals, and proposed to observe such effects using spin-resonance experiments at low temperatures.<sup>15</sup> Sandomirskii pointed out that quantum size effects should be observable more easily in semiconductors compared to metals, owing to the smaller effective electron mass and thus the larger de Broglie wavelength in semiconductors.<sup>16</sup> Quantum size effects should manifest themselves as an effective increase of the semiconductor’s bandgap as particle size is reduced, observable as a shift of the optical absorption edge.<sup>16</sup> They were also predicted to cause a shift of the conduction band edge and valence band edge in semimetals, inducing a transition from metallic to semiconducting properties that should be observable in optical characteristics.<sup>17</sup>



During the 1960s, the development of microelectronics stimulated a strong interest in the electronic properties of thin films. In experiments conducted in thin bismuth layers,<sup>18</sup> as well as in two-dimensional electron gas formed at silicon surfaces,<sup>19</sup> quantum effects manifested themselves as oscillations of resistivity, Hall resistance and magnetoresistance as a function of film thickness.<sup>20</sup> The periodicity of the observed oscillations matched the electron wavelength at the expected effective mass.<sup>18</sup> It was established that prerequisites for the ability to energetically resolve quantization effects are low temperatures as well as sufficiently long carrier relaxation times.<sup>18-20</sup> It was also recognized that materials of high quality are required because the carrier mean free path needs to exceed the thickness  $d$  of the film.<sup>18</sup> A systematic  $1/d^2$  dependence of the optical absorption in CdS films was observed<sup>21</sup> and compared to theoretical<sup>16</sup> predictions.

A qualitative breakthrough occurred when the development of molecular-beam epitaxy (MBE) in ultra-high vacuum,<sup>22</sup> used in combination with mass spectrometry, enabled the deposition of high-quality semiconducting thin films with precise control of thickness and composition. This made it possible to optically resolve multiple quantum states in thin ( $< 5$  nm) GaAs quantum wells formed between AlGaAs layers, after selective chemical etching to remove the GaAs substrate.<sup>23</sup> These observations received much attention in the semiconductor physics community because it had been previously considered impossible to make heterostructures with sufficient quality to observe quantum phenomena so clearly.

By the early 1980s, the experimental observation of quantum phenomena in thin films was well established. A theoretical understanding also was well developed, including that of the role of Coulomb interaction (exciton effects) that become particularly pronounced in low-dimensional structures such as quantum wells, where electron and hole wave functions are more likely to overlap.<sup>24, 25</sup> Semiconductor heterostructures proved to be highly useful material systems for high-speed and opto-electronics, as recognized by the Nobel Prize in Physics in 2000 to H. Kroemer and Z. I. Alferov.

However, the above observations concerned quantum size effects in structures embedded inside or on top of bulk materials, which could not be considered materials by themselves. The predictions pioneered by Fröhlich, that small particles should have size-dependent material properties, were not yet accessible to experimental test.

### **Quantum dots in a glass matrix**

The first discovery of quantum size effects in nanoparticles was made in the context of coloured glass. Historically, glassmakers knew very well that dopants such as gold, silver, cadmium, sulphur, and selenium could be used to change the optical properties of glass. For example, optical filters with different cut-off frequencies, so-called Schott glasses, were produced by controlling the type and amount of dopant as well as the details of the thermal process after melting of the

glass.<sup>26</sup> It was also understood that the glass properties were related to the inclusion of ‘colloidal particles’ in the glass, but the details of the mechanism had not been investigated.<sup>27</sup>

In 1979, **Aleksey Yekimov** began working on doped glasses at the S.I. Vavilov State Optical Institute.<sup>27</sup> He aimed to understand the chemical composition and structure of colloidal particles in coloured glasses, as well as the mechanism of their growth.<sup>27</sup> Using techniques familiar to him from his PhD training in semiconductor physics, he and his co-workers measured the optical absorption spectrum of heat-treated silicate glasses with additions of Cu and Cl of the order of a few percent, above the solubility limit of the matrix. At the cryogenic temperature of 4.2 K, the team found exciton lines similar to those observed in CuCl thin films, but the shapes of which varied with details of the heat treatment.<sup>28</sup> The researchers attributed this observation to the formation of a crystalline phase of CuCl in the glass matrix as a result of phase decomposition of a supersaturated solution during heat treatment. Furthermore, by varying temperature and duration of the heat treatment, they were able to control the average size of CuCl crystals forming in the glass melt.<sup>29</sup> Using small-angle X-ray scattering, they determined average crystal sizes in the range from a few nanometres to tens of nanometres and confirmed that crystal size varied with heat treatment time, as expected from a theoretical model<sup>30</sup> of recondensation growth that also predicted the observed narrow size distribution.<sup>29</sup>

Crucially, the wavelength of the observed CuCl exciton absorption lines varied systematically with the size of the nanocrystals: the position of the absorption line was increasingly blue-shifted for smaller crystals down to nanocrystals as small as a few nanometres.<sup>31,32</sup>

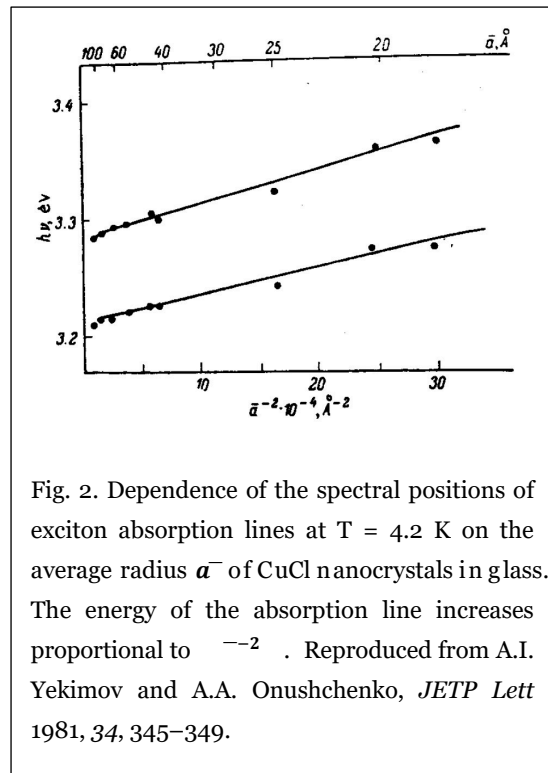


Fig. 2. Dependence of the spectral positions of exciton absorption lines at  $T = 4.2$  K on the average radius  $\bar{a}$  of CuCl nanocrystals in glass. The energy of the absorption line increases proportional to  $\bar{a}^{-2}$ . Reproduced from A.I. Yekimov and A.A. Onushchenko, *JETP Lett* 1981, 34, 345–349.

**Yekimov** immediately attributed this observation to quantum size effects,<sup>31,32</sup> giving reference to the observation of quantum size effects in MBE-grown, two-dimensional quantum wells a few years before.<sup>33</sup> As qualitatively expected from textbook quantum mechanics for a single particle confined in a spherical infinite well, the absorption line shifted with the inverse square of the average particle radius  $\bar{a}$  (Fig. 2).<sup>31,32</sup> Semiconductor quantum dots had been discovered.

Two corrections to the simple textbook model were needed to achieve quantitative agreement between data and theory. The first was to include the attractive Coulomb interaction between

electron and hole, the so-called exciton effect, known to be strong when electron and hole are confined in the same space.<sup>25</sup> This resulted in the following expression<sup>32</sup> for the photon energy  $\hbar\omega$  of the exciton absorption line:

$$\hbar\omega = E_g - E_{ex} + \frac{\hbar^2\pi^2}{2M\bar{a}^2}$$

Here,  $E_g$  is the bulk material's semiconductor bandgap,  $E_{ex}$  is the exciton binding energy, and  $M$  is the charge carrier effective mass. The second correction was to also take into account the finite dispersion of particle sizes.<sup>34</sup> When doing so, the value of  $M$  that was needed to reproduce the observed slope of the data was in good agreement with the known value for CuCl.<sup>35</sup>

The initial observation of quantum size effects by **Yekimov** was determined to be in the so-called weak confinement regime, characterized by quantum size effects of the exciton as a whole, but not of the electron and hole individually.<sup>34</sup> Subsequently, also the intermediate and strong confinement regimes<sup>34</sup> were demonstrated.<sup>36</sup>

**Yekimov's** discovery of semiconductor quantum dots in a glass matrix showed that it was possible to observe profound signatures of quantum size effects not only in thin films but also in suspended, independent nanoparticles produced by a relatively simple traditional glass process. However, a limitation of **Yekimov's** groundbreaking discovery was that his team's quantum dots were 'frozen' in glass and not suitable for further processing.

### Colloidal quantum dots

An approach to synthesize quantum dots as colloids, in a sol-gel process, and thus suitable for further processing, emerged shortly later, independently of the discoveries by **Yekimov**.

During the 1970s, there was significant interest in using semiconductors for photoelectrochemistry, with the expectation that optical excitation of the semiconductor would create reactive charge carriers that could drive chemical reactions.<sup>37</sup> Of particular interest was the possibility to control electrical and optical properties of semiconductors by doping. A focus of the research was on the photophysics and surface redox chemistry of electrons and holes,<sup>4, 38-41</sup> on solar energy conversion by photoelectrolysis,<sup>42</sup> and on photovoltaics at the interface between semiconductor and electrolyte.<sup>43</sup>

Several groups worked on colloidal crystallites of CdS, ZnO, and TiO<sub>2</sub> because the energy levels in these materials were potentially suitable for photocatalysis.<sup>43</sup> For example, TiO<sub>2</sub> powder suspended in liquid was found to photocatalyse the decomposition of acetic acid to produce

methane,<sup>44</sup> and CdS microelectrodes prepared in the presence of a copolymer loaded with RuO<sub>2</sub> and Pt were found to be active catalysts for cleavage of H<sub>2</sub>O and H<sub>2</sub>S.<sup>38</sup>

Evidence of quantum size effects in colloidal nanoparticles was found in 1983 when **Louis Brus** and co-workers investigated CdS crystallites. Using previously known methods for the synthesis of nanoparticles,<sup>38</sup> they prepared relatively small CdS particles in solution in the presence of a styrene/maleic anhydride copolymer that helped prevent coagulation and flocculation.<sup>45, 46</sup> A freshly prepared colloid showed a narrow size distribution around 4.5 nm, as determined by transmission electron microscopy. However, when left to age for one day, crystallites dissolved and recrystallized to form larger particles with a broader size distribution around 12.5 nm (a process<sup>30</sup> also referred to as Ostwald ripening).<sup>45</sup> Using resonance Raman scattering and absorption spectroscopy to investigate the electronic states, **Brus** and co-workers found differences between fresh and aged particles. Whereas the larger aged particles featured an excitation spectrum like that expected for bulk CdS, the fresh smaller particles exhibited a blue shift and broadening of the exciton line. The authors attributed this difference between small and large particles to a quantum size effect moderated by electrostatic interaction between electron and hole.<sup>45</sup>

The bibliography of the early work by **Brus** and co-workers indicates that the USA-based team knew about the earlier observation of quantum size effects in two-dimensional quantum wells,<sup>23</sup> but were not aware of the discovery of semiconductor quantum dots in a glass matrix by **Yekimov** two years earlier in what was then the USSR.<sup>27</sup>

Following his team's experimental discovery of quantum size effects in colloidal nanoparticles, **Brus** presented a model describing the effect of particle size on electron and hole redox potentials for surface chemical reactions. Using an effective-mass approximation and a spherical model potential, and considering the polarization of the surrounding solution caused by the difference in dielectric constant between semiconductor and solution,<sup>47</sup> they predicted quantum size effects on photochemical redox potentials and on the lowest exciton energy for semiconductor crystals smaller than about 5 nm. In follow-up work soon after, **Brus** also included the Coulomb interaction between electron and hole.<sup>48</sup>

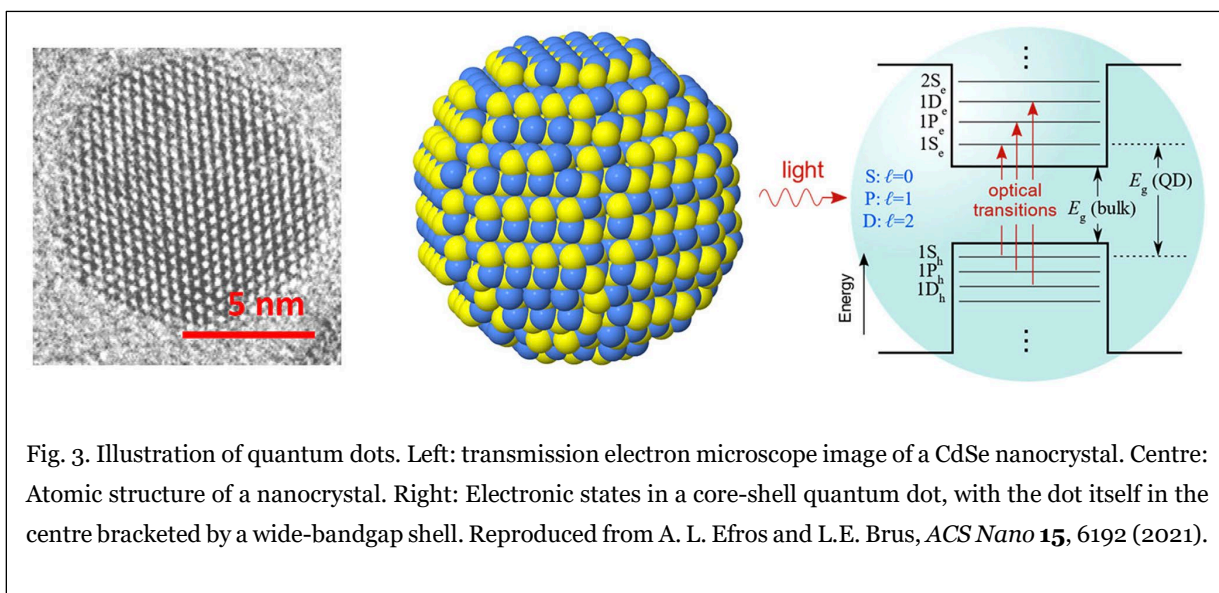
Quantum size effects in nanoparticles likely had been observed previously without being recognized as such. For example, studies of fine-grain suspensions of AgBr<sup>49</sup> and of AgI powders<sup>50</sup> in the late 1960s revealed variations in the exciton absorption coefficient that were dependent on crystal structure and grain size, but no systematic size-dependent observations of absorption wavelength or discussion of quantum size effects were reported. An observed systematic size dependence of the optical absorption in CdSe nanocrystals with radius less than 5 nm and embedded in glass was classified as an 'optical anomaly'.<sup>51, 52</sup> Observations of a size-dependent



shift in luminescence and Raman spectra of small CdS particles were attributed to quantum size effects but without comparison to theory.<sup>53</sup>

Rossetti and **Brus** had already reported above-bandgap absorption of 20-nm colloidal CdS particles in 1982.<sup>40</sup> Around the same time, Henglein observed a colour change in colloidal CdS deposited on 13-nm SiO<sub>2</sub>.<sup>39</sup> At the time, he attributed this effect to amorphous structure,<sup>39</sup> but later, following **Brus**' discoveries, established crystalline structure and attributed the colour changes to quantum size effects.<sup>54</sup>

A comprehensive review<sup>55</sup> from 1986 listed several works where quantum size effects in small metal nanoparticles likely had been observed, including in the Knight shift<sup>56</sup> and in the temperature dependence of the magnetic susceptibility<sup>57</sup> at low temperatures. The review concluded, however, that quantum size effects in optical properties of metal particles had not been observed.



### Improved synthesis of quantum dots

The discovery of quantum size effects in colloidal nanocrystals (Fig. 3) stimulated significant research efforts devoted to understanding their optical and photochemical properties, in the hope of being able to use size to design desirable physical and chemical properties.<sup>58-60</sup> However, progress was in part hampered by limited homogeneity and quality of the available nanocrystals, with variations in size, shape, crystallinity and surface electronic defects making it difficult to

isolate inherently size-dependent behaviour.<sup>58</sup> For example, luminescence from nanocrystals available in the late 1980s was typically limited by a quantum yield of only a few percent.<sup>59, 61</sup>

In 1993, **Moungi Bawendi** and co-workers developed a method for the synthesis of quantum dots with much more well-defined size and with high optical quality.<sup>62</sup> This discovery opened the door to the development of applications of colloidal quantum dots. Their synthesis begins with the injection and immediate pyrolysis of organometallic reagents (the precursors for the desired nanoparticles) into a hot coordinating solvent with a high boiling point. The rapid increase of reagent concentrations results in abrupt supersaturation and in nucleation that takes place at a well-defined moment. Injection is accompanied by a sudden drop in temperature and dilution of the precursors such that growth stops. After reheating to the desired growth temperature, a slow growth and annealing process takes place in the coordinating solvent that helps to stabilize the resulting colloidal dispersion. This principle of temporally discrete nucleation followed by controlled growth was known from the production of monodisperse lyophobic colloids.<sup>63</sup> Finally, particles can be selected using purification and size-dependent precipitation. The result is macroscopic quantities of nanoparticles with regular core structure and shape, with consistent surface derivation and electronically passivated semiconductor surface, and with a well-defined size that is determined by dynamic temperature control during the growth phase.<sup>62</sup> Relatively sharp optical absorption (Fig. 4) and emission spectra were observed at room temperature, with a luminescence quantum yield up to 10%. By removing aliquots during the growth process, an entire series of particle sizes can be obtained during a single growth run.<sup>62</sup>

The hot-injection synthesis method developed by **Bawendi** and co-workers constituted an adaptable and reproducible chemical strategy for synthesizing monodisperse nanoparticles using a wide range of material systems. It thus opened the door to the development of large-scale applications of quantum dots.

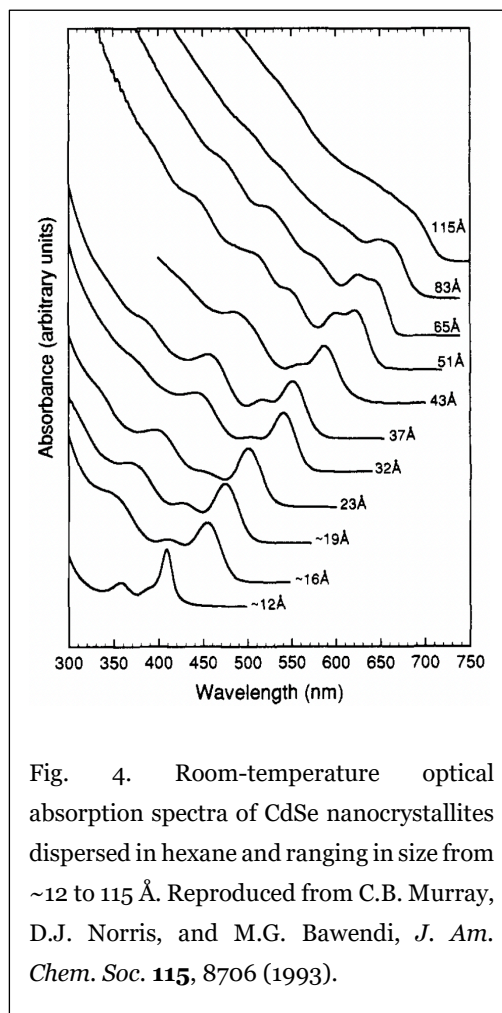


Fig. 4. Room-temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from ~12 to 115 Å. Reproduced from C.B. Murray, D.J. Norris, and M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).

## Further developments

Semiconductor quantum dots embedded in glass as discovered by **Yekimov** remain interesting to this day for use as nonlinear optical elements, for example for signal amplification in fibre-optic communication systems.<sup>64</sup>

Following the discoveries by **Yekimov** and **Brus**, quantum dots were produced using other methods. The name quantum dot was introduced by Mark Reed in 1986, to describe a completely confined zero-dimensional object, in the context of a top-down approach to define quantum dots in solids. His team used electron-beam lithography and etching to pattern an MBE-grown GaAs/AlGaAs quantum well to form a quantum dot.<sup>65</sup> “Quantum dot” followed the existing terminology for two-dimensional quantum wells and one-dimensional quantum wires.

Another approach to creating quantum dots on a solid substrate is the so-called Stranski-Krastanov<sup>66</sup> growth method. It makes use of the formation of islands or droplets during the deposition of one material on top of a substrate that is not lattice-matched.<sup>67</sup> By covering the resulting ‘island’ with an additional layer of material with a higher bandgap, heterostructure quantum dots with defined optical properties can be created in a self-organized manner. Heterostructure quantum dots embedded into a solid matrix of other materials, as described above, can be electrically contacted; they are used in a variety of applications, for example in quantum dot lasers for optical communication.<sup>68</sup>

Today, ‘quantum dot’ refers to a nanostructure in which quantum mechanical effects manifest themselves in the electronic structure, either through quantum size effects, many-body interactions (excitonic states) or high surface-to-volume ratio such that surface states dominate the electronic structure. In addition to a small size comparable to the carriers’ de Broglie wavelength, it is now recognized that the quantum phase coherence length (typically limited by inelastic scattering) needs to exceed the system size.

The discovery of colloidal quantum dots and their controlled synthesis by **Brus** and **Bawendi** and their colleagues initiated significant efforts to further improve the quality and optical properties of colloidal quantum dots, and to explore possible applications such as light-emitting diodes.<sup>69</sup> A drastic increase in the optical quality of colloidal quantum dots was enabled by the development of core-shell quantum dots,<sup>70, 71</sup> to realize passivation methods well known from semiconductor optics. Core-shell nanoparticles were created that consisted of a wide-bandgap shell, such as ZnS, to confine electrons and holes to a small-bandgap core (such as CdSe). In this way, the charge carriers in the core were separated from surface states, such as unsaturated bonds, that are detrimental to optical performance. Adding such an additional layer in the same reaction became possible by making modifications<sup>72</sup> to the hot-injection synthesis method to avoid size-selective precipitation to achieve near monodisperse nanocrystal synthesis.<sup>71</sup> The resulting



CdSe/ZnS core-shell quantum dots had a luminescence quantum yield at room temperature of up to 50%, with better long-term stability and reduced bleaching compared to uncapped quantum dots.<sup>71</sup>

The integration of inorganic quantum dots with biological systems was made possible with the synthesis of water-soluble quantum dots with high optical quality. This achievement was important because luminescent quantum dots up to that point were prepared in organic non-polar solvents. Two methods for achieving water solubility were demonstrated simultaneously for core-shell quantum dots. One added a third layer of silica to enable further functionalization using polysilanes.<sup>73</sup> The other approach used a bifunctional ligand – a molecule with a thiol and a carboxylic acid terminus – to change the polarity of ZnS-shelled CdSe quantum dots. The thiol group bonded to Zn on the quantum dot, displacing an organic ligand and exposing the polar carboxylic acid group to render the quantum dots water soluble.<sup>74</sup> Both methods also allowed covalent coupling to functional biomolecules such as proteins, peptides, and nucleic acids. Such functionalized quantum dots retained much of their advantageous optical properties, offering a new tool for labelling biomolecules outside and inside of cells, with better stability and with a wide range of available excitation and emission wavelengths.<sup>73, 74</sup>

Subsequent work widely expanded the scope of quantum dots and included the exploration of different materials and improved understanding of the growth process,<sup>75</sup> synthesis of quantum rods with elongated shape or branches,<sup>76, 77</sup> and of platelets with atom-scale thickness control.<sup>78</sup> Widely explored application areas of quantum dots include use in photovoltaics<sup>79</sup> and other forms of energy conversion,<sup>80, 81</sup> in photodetectors,<sup>82</sup> in biomedical imaging and nanomedicine,<sup>5, 81</sup> and generally in infrared technology,<sup>81</sup> where quantum dots may give access to bandgap ranges not easily accessible with other materials.

An important consideration is the toxicity of some quantum dots and their precursor materials. Health effects of quantum dots have been explored, not the least in the context of potential medical applications,<sup>5</sup> and ongoing research efforts aim to find production processes with less toxic reagents, and to find ways to avoid altogether the use of heavy metals such as cadmium, lead, or mercury in quantum dots.

### **Seeds of nanoscience**

The discovery of quantum dots was an important step in the development of nanoscience, and it inspired many chemists to engage in this interdisciplinary field.

Nanoscience is about studying phenomena that occur when materials are structured or patterned on a scale of less than about 100 nm. This size range includes, for example, the wavelength of light, the de Broglie wavelength of charge carriers, the size where plasmonic resonance occurs, as



well as the size of large biomolecules. Nanostructures also have a large surface area in relation to their volume, which also leads to new properties. Nanotechnology is about harnessing such new properties for improving the performance of materials or for enabling entirely new applications.

The large variety of relevant phenomena and the wide range of materials and applications that can be explored make nanoscience a very rich field with many different branches. Nanotechnology uses the tools of semiconductor physics, organic and inorganic chemistry, molecular biology, and biotechnology. Applications range from modern electronics to industrial scale catalysis, and from precision medicine to quantum technology. Today, most large research universities have centres or departments dedicated to nanoscience and nanotechnology.

In a sense, nanotechnology and nanoparticles have been used for many centuries.<sup>52</sup> For example, a hair-blackening recipe originating from the Greco-Roman period has been shown to work by the formation of 5-nm PbS nanocrystals inside the hair cortex,<sup>83</sup> and the famous Roman Lycurgus cup has been shown to derive its red colour from enclosed Au particles in the size range 5–60 nm.<sup>84</sup> Classical Mie scattering changes the colour of transmitted light.<sup>85</sup> It also was known for a long time that the colouring of glass by adding CdS or CdSe to silicate glass in amorphous, supersaturated solutions was due to nucleation and growth of crystallites, and that glass colour could be varied by changing the synthesis and annealing procedures.<sup>86</sup>

However, the modern field of nanoscience requires precise and ideally atom-level control of the synthesis of nanostructures. Therefore, the ability to fabricate materials at nanometre size and with sub-nanometre precision and high fidelity, safely, in benchtop chemical batch reactions, represents a key milestone in the development of the field of nanoscience. This year's Laureates played a central role in establishing these capabilities and in this way provided seeds for the rich field of nanoscience to grow.

*Heiner Linke*

Professor of Nanophysics

Member of the Royal Swedish Academy of Sciences

Member of the Nobel Committee for Chemistry

### Further reading

**History:** Montanarella, F.; Kovalenko, M. V. Three Millennia of Nanocrystals. *ACS Nano* **2022**, *16* (4), 5085-5102.

**Applications in medicine:** Abdellatif, A. A. H.; Younis, M. A.; Alsharidah, M.; Al Rugaie, O.; Tawfeek, M. H. Biomedical Applications of Quantum Dots: Overview, Challenges, and Clinical Potential. *Int J Nanomed* **2022**, *17*, 1951-1970.



**Review articles:** Yekimov, A. I. Optical-Properties of Semiconductor Quantum Dots in Glass Matrix. *Phys Scripta* **1991**, T39, 217-222; Efros, A. L.; Brus, L. E. Nanocrystal Quantum Dots: From Discovery to Modern Development. *ACS Nano* **2021**, 15 (4), 6192-6210.

### Related Nobel Prizes

The Nobel Prize in Chemistry 1996 – “for their discovery of fullerenes”, molecules that approach the size of quantum dots ( $C_{60} \approx 0.71$  nm)

The Nobel Prize in Physics 2000 – “for developing semiconductor heterostructures used in high-speed- and opto-electronics”

The Nobel Prize in Physics 2010 – “for groundbreaking experiments regarding the two-dimensional material graphene”

### References

- (1) Brus, L. E. A Simple-Model for the Ionization-Potential, Electron-Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites. *J Chem Phys* 1983, 79 (11), 5566-5571. DOI: Doi 10.1063/1.445676.
- (2) Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. Melting in Semiconductor Nanocrystals. *Science* 1992, 256 (5062), 1425-1427. DOI: DOI 10.1126/science.256.5062.1425.
- (3) Tolbert, S. H.; Alivisatos, A. P. High-Pressure Structural Transformations in Semiconductor Nanocrystals. *Annu Rev Phys Chem* 1995, 46, 595-625. DOI: DOI 10.1146/annurev.physchem.46.1.595.
- (4) Quantum Dot Market; 2021. [https://www.marketsandmarkets.com/Market-Reports/quantum-dots-qd-market-694.html?gclid=EA1aIQobChMI76Ws1fGLgQMVcZGDBx2JcQTEEAAYASAAEgJD3\\_D\\_BwE](https://www.marketsandmarkets.com/Market-Reports/quantum-dots-qd-market-694.html?gclid=EA1aIQobChMI76Ws1fGLgQMVcZGDBx2JcQTEEAAYASAAEgJD3_D_BwE).
- (5) Abdellatif, A. A. H.; Younis, M. A.; Alsharidah, M.; Al Rugaie, O.; Tawfeek, M. H. Biomedical Applications of Quantum Dots: Overview, Challenges, and Clinical Potential. *Int J Nanomed* 2022, 17, 1951-1970. DOI: 10.2147/Ijn.S357980.
- (6) Condon, E. U.; Morse, P. M. *Quantum Mechanics*; McGraw-Hill, 1929. DOI: <https://babel.hathitrust.org/cgi/pt?u=1&id=uc1.%24b568098&num=44&seq=64>
- (7) Sommerfeld, A. Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik. *Z Phys* 1928, 47 (1-2), 1-32. DOI: Doi 10.1007/Bf01391052.
- (8) Bloch, F. About the Quantum mechanics of Electrons in Crystal lattices. *Z Phys* 1929, 52 (7-8), 555-600. DOI: Doi 10.1007/Bf01339455.
- (9) Kronig, R. D.; Penney, W. G. Quantum mechanics of electrons on crystal lattices. *P R Soc Lond a-Conta* 1931, 130 (814), 499-513. DOI: DOI 10.1098/rspa.1931.0019.





- (10) Sommerfeld, A. On the specific heat of metal electrons. *Ann Phys-Berlin* 1937, 28 (1), 0001-0010.
- (11) Fröhlich, H. Die spezifische Wärme der Elektronen kleiner Metallteilchen bei tiefen Temperaturen. *Physica* 1937, IV (5), 406 - 412.
- (12) Landau, L. Diamagnetism of metals. *Z Phys* 1930, 64 (9-10), 629-637. DOI: Doi 10.1007/Bf01397213.
- (13) de Haas, W. J.; van Alphen, P. M. The dependence of the susceptibility of diamagnetic metals upon the field. *P K Akad Wet-Amsterd* 1930, 33 (6/10), 1106-1118.
- (14) Lifshitz, I.; Kosevich, A. On the oscillations of the thermodynamic parameters of a degenerate Fermi gas at low temperatures. *Bull. of the Acad. Sciences USSR Phys. Ser.* 1955, 19, 353.
- (15) Kubo, R. Electronic properties of metallic fine particles. *J. Phys. Soc. Jap.* 1962, 17, 975-987.
- (16) Sandomirskii, V. B. Dependence of the Forbidden-Band Width of Semiconducting Films on Their Thickness and Temperature. *Sov Phys JETP-USSR* 1963, 16 (6), 1630-1631.
- (17) Lutskii, V. N.; Kulik, L. A. Features of Optical Characteristics of Bismuth Films under Conditions of Quantum Size Effect. *Jetp Lett-Ussr* 1968, 8 (3), 80-+. Tavger, B. A.; Demikhov, V. Y. Quantum Size Effects in Semiconducting and Semimetallic Films. *Sov Phys Uspekhi* 1969, 11 (5), 644-+. DOI: DOI 10.1070/PU1969v011n05ABEH003739.
- (18) Ogrin, Y. F.; Lutskii, V. N.; Elinson, M. I. Observation of Quantum Size Effects in Thin Bismuth Films. *JETP Lett-USSR* 1966, 3 (3), 71-&.
- (19) Fowler, A. B.; Fang, F. F.; Howard, W. E.; Stiles, P. J. Magneto-Oscillatory Conductance in Silicon Surfaces. *Phys Rev Lett* 1966, 16 (20), 901-&. DOI: DOI 10.1103/PhysRevLett.16.901.
- (20) Elinson, M. I.; Volkov, V. A.; Pinsker, T. N.; Lutskij, V. N. Quantum Size Effect and Perspectives of Its Practical Application. *Thin Solid Films* 1972, 12 (2), 383-+. DOI: Doi 10.1016/0040-6090(72)90102-2.
- (21) Stasenko, A. G. Dependence of Forbidden Energy Gap in Cadmium Sulfide Films on Film Thickness. *Fiz Tverd Tela+* 1968, 10 (1), 186-+.
- (22) Arthur, J. R. Interaction of Ga and As<sub>2</sub> Molecular Beams with Gaas Surfaces. *J Appl Phys* 1968, 39 (8), 4032-&. DOI: Doi 10.1063/1.1656901. Cho, A. Y. Film Deposition by Molecular-Beam Techniques. *J Vac Sci Technol* 1971, 8 (5), S31-&. DOI: Doi 10.1116/1.1316387.
- (23) Dingle, R.; Wiegmann, W.; Henry, C. H. Quantum States of Confined Carriers in Very Thin Al<sub>x</sub>Ga<sub>1-x</sub>As-GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As Heterostructures. *Phys Rev Lett* 1974, 33 (14), 827-830. DOI: DOI 10.1103/PhysRevLett.33.827.
- (24) Weisbuch, C.; Dingle, R.; Gossard, A. C.; Wiegmann, W. Optical Characterization of Interface Disorder in GaAs-Ga<sub>1-x</sub>Al<sub>x</sub>As Multi-Quantum Well Structures. *Solid State Commun* 1981, 38 (8), 709-712. DOI: Doi 10.1016/0038-1098(81)90401-4. Miller, R. C.; Kleinman, D. A.; Tsang, W. T.; Gossard, A. C. Observation of the Excited-Level of Excitons in GaAs Quantum Wells. *Phys Rev B* 1981, 24 (2), 1134-1136. DOI: DOI 10.1103/PhysRevB.24.1134.
- (25) Ando, T.; Fowler, A. B.; Stern, F. Electronic-Properties of Two-Dimensional Systems. *Rev Mod Phys* 1982, 54 (2), 437-672. DOI: DOI 10.1103/RevModPhys.54.437.
- (26) Borelli, N. Photonic applications of semiconductor-doped glasses. In *Ch.1, Semiconductor nanocrystals, from basic principles to applications*, Efros, A., Lockwood, D., Tsybeskov, L. Eds.; Nanostructure Science and Technology, Springer Science + Business Media, LLC, 2003; pp 1-51.



- (27) Efros, A. L.; Brus, L. E. Nanocrystal Quantum Dots: From Discovery to Modern Development. *ACS Nano* 2021, 15 (4), 6192-6210. DOI: 10.1021/acsnano.1c01399.
- (28) Yekimov, A.; Onushchenko, A. A.; Tsekhomskii, V. Exciton light absorption by CuCl microcrystals in glass matrix. *Sov. Glass Phys. Chem.* 1980, 6, 511-512.
- (29) Golubkov, V. V.; Yekimov, A. I.; Onushchenko, A. A.; Tsekhomskii, V. A. Growth kinetics of CuCl microcrystals in a glassy matrix. *Fizika i Khimiya Stekla* 1980, 7, 397-401.
- (30) Lifshitz, I. M.; Slezov, V. V. Kinetics of Diffusive Decomposition of Supersaturated Solid Solutions. *Sov Phys JETP-USSR* 1959, 8 (2), 331-339.
- (31) Yekimov, A. I.; Onushchenko, A. A. Quantum Size Effect in Three-Dimensional Microscopic Semiconductor Crystals. *JETP Lett+* 1981, 34 (6), 345-349.
- (32) Yekimov, A. I.; Onushchenko, A. A. Quantum Size Effect in the Optical-Spectra of Semiconductor Micro-Crystals. *Sov Phys Semicond+* 1982, 16 (7), 775-778.
- (33) Dingle, R. Confined carrier quantum states in ultrathin semiconductor heterostructures. In *Festkörperprobleme: Advances in Solid State Physics*, Queisser, H. Ed.; Vol. XV; Vieweg, 1975; p 21.
- (34) Efros, A. L.; Efros, A. L. Interband Absorption of Light in a Semiconductor Sphere. *Sov Phys Semicond+* 1982, 16 (7), 772-775.
- (35) Yekimov, A. I.; Onushchenko, A. A.; Plyukhin, A. G.; Efros, A. L. Size Quantization of Excitons and Determination of Their Energy-Spectrum Parameters in CuCl. *Sov. Phys. JETP* 1985, 61 (4), 891-897.
- (36) Efros, A. L.; Rosen, M. The electronic structure of semiconductor nanocrystals. *Annu Rev Mater Sci* 2000, 30, 475-521. DOI: DOI 10.1146/annurev.matsci.30.1.475.
- (37) Brattain, W. H.; Garrett, C. G. B. Experiments on the Interface between Germanium and an Electrolyte. *At&T Tech J* 1955, 34 (1), 129-176. DOI: DOI 10.1002/j.1538-7305.1955.tb03766.x.
- (38) Kalyanasundaram, K.; Borgarello, E.; Duonghong, D.; Gratzel, M. Cleavage of Water by Visible-Light Irradiation of Colloidal Cds Solutions - Inhibition of Photocorrosion by RuO<sub>2</sub>. *Angew Chem Int Edit* 1981, 20 (11), 987-988. DOI: DOI 10.1002/anie.198109871.
- (39) Henglein, A. Photo-Degradation and Fluorescence of Colloidal-Cadmium Sulfide in Aqueous-Solution. *Ber Bunsen Phys Chem* 1982, 86 (4), 301-305. DOI: DOI 10.1002/bbpc.19820860409.
- (40) Rossetti, R.; Brus, L. Electron-Hole Recombination Emission as a Probe of Surface-Chemistry in Aqueous Cds Colloids. *J Phys Chem-Us* 1982, 86 (23), 4470-4472. DOI: DOI 10.1021/j100220a003.
- (41) Kuczynski, J.; Thomas, J. K. Photochemistry at the Surface of Colloidal Cadmium-Sulfide. *Chem Phys Lett* 1982, 88 (5), 445-447. DOI: Doi 10.1016/0009-2614(82)83150-3.
- (42) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972, 238 (5358), 37-+. DOI: DOI 10.1038/238037a0.
- (43) Nozik, A. J. Photoelectrochemistry - Applications to Solar-Energy Conversion. *Annu Rev Phys Chem* 1978, 29, 189-222. DOI: DOI 10.1146/annurev.pc.29.100178.001201.
- (44) Kraeutler, B.; Bard, A. J. Heterogeneous Photocatalytic Synthesis of Methane from Acetic-Acid - New Kolbe Reaction Pathway. *J Am Chem Soc* 1978, 100 (7), 2239-2240. DOI: DOI 10.1021/ja00475a049.





- (45) Rossetti, R.; Nakahara, S.; Brus, L. E. Quantum Size Effects in the Redox Potentials, Resonance Raman-Spectra, and Electronic-Spectra of Cds Crystallites in Aqueous-Solution. *J Chem Phys* 1983, 79 (2), 1086-1088. DOI: Doi 10.1063/1.445834.
- (46) Rossetti, R.; Ellison, J. L.; Gibson, J. M.; Brus, L. E. Size Effects in the Excited Electronic States of Small Colloidal Cds Crystallites. *J Chem Phys* 1984, 80 (9), 4464-4469. DOI: Doi 10.1063/1.447228.
- (47) Brus, L. E. A Simple-Model for the Ionization-Potential, Electron-Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites *J Chem Phys* 1983, 79 (11), 5566-5571. DOI: Doi 10.1063/1.445676.
- (48) Brus, L. E. Electron Electron and Electron-Hole Interactions in Small Semiconductor Crystallites - the Size Dependence of the Lowest Excited Electronic State. *J Chem Phys* 1984, 80 (9), 4403-4409. DOI: Doi 10.1063/1.447218. Brus, L. Electronic Wave-Functions in Semiconductor Clusters - Experiment and Theory. *J Phys Chem-Us* 1986, 90 (12), 2555-2560. DOI: DOI 10.1021/j100403a003.
- (49) Berry, C. R. Effects of Crystal Surface on Optical Absorption Edge of Agbr. *Phys Rev* 1967, 153 (3), 989-&. DOI: DOI 10.1103/PhysRev.153.989.
- (50) Berry, C. R. Structure and Optical Absorption of Agi Microcrystals. *Phys Rev* 1967, 161 (3), 848-&. DOI: DOI 10.1103/PhysRev.161.848.
- (51) Katzschmann, R.; Kranold, R.; Rehfeld, A. Optical-Anomaly of Small Particles in Glasses. *Phys Status Solidi A* 1977, 40 (2), K161-K161. DOI: DOI 10.1002/pssa.2210400255.
- (52) Montanarella, F.; Kovalenko, M. V. Three Millennia of Nanocrystals. *ACS Nano* 2022, 16 (4), 5085-5102. DOI: 10.1021/acsnano.1c11159.
- (53) Papavassiliou, G. C. Luminescence Spectra and Raman Excitation Profiles in Small Cds Particles. *J Solid State Chem* 1981, 40 (3), 330-335. DOI: Doi 10.1016/0022-4596(81)90399-6.
- (54) Henglein, A. Catalysis of Photochemical-Reactions by Colloidal Semiconductors. *Pure Appl Chem* 1984, 56 (9), 1215-1224. DOI: DOI 10.1351/pac198456091215.
- (55) Halperin, W. P. Quantum Size Effects in Metal Particles. *Rev Mod Phys* 1986, 58 (3), 533-606. DOI: DOI 10.1103/RevModPhys.58.533.
- (56) Nomura, K.; Kobayashi, S. I.; Sasaki, W. NMR-Study of Al Small Particle. *J Phys Soc Jpn* 1980, 48 (1), 37-41. DOI: Doi 10.1143/Jpsj.48.37. Yee, P.; Knight, W. D. Quantum Size Effect in Copper - Nmr in Small Particles. *Phys Rev B* 1975, 11 (9), 3261-3267. DOI: DOI 10.1103/PhysRevB.11.3261. Kobayashi, S. Nuclear relaxation in metallic small particles. *Journal de Physique Colloques* 1977, 38, 121-123.
- (57) Kimura, K.; Bandow, S.; Sako, S. Magnetic-Susceptibilities of Small Particles of Magnesium and Beryllium. *Surf Sci* 1985, 156 (Jun), 883-887. DOI: Doi 10.1016/0039-6028(85)90262-6.
- (58) Brus, L. Quantum Crystallites and Nonlinear Optics. *Appl Phys A-Mater* 1991, 53 (6), 465-474. DOI: Doi 10.1007/Bf00331535.
- (59) Henglein, A. Mechanism of Reactions on Colloidal Microelectrodes and Size Quantization Effects. *Top Curr Chem* 1988, 143, 113-180.
- (60) Wang, Y.; Herron, N. Nanometer-Sized Semiconductor Clusters - Materials Synthesis, Quantum Size Effects, and Photophysical Properties. *J Phys Chem-Us* 1991, 95 (2), 525-532. DOI: DOI 10.1021/j100155a009.



- (61) Dannhauser, T.; Oneil, M.; Johansson, K.; Whitten, D.; Mclendon, G. Photophysics of Quantized Colloidal Semiconductors Dramatic Luminescence Enhancement by Binding of Simple Amines. *J Phys Chem-Us* 1986, 90 (23), 6074-6076. DOI: DOI 10.1021/j100281a004.
- (62) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse Cde (E = S, Se, Te) Semiconductor Nanocrystallites. *J Am Chem Soc* 1993, 115 (19), 8706-8715. DOI: DOI 10.1021/ja00072a025.
- (63) Lamer, V. K.; Dinegar, R. H. Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *J Am Chem Soc* 1950, 72 (11), 4847-4854. DOI: DOI 10.1021/ja01167a001.
- (64) Xia, M. L.; Luo, J. J.; Chen, C.; Liu, H.; Tang, J. Semiconductor Quantum Dots-Embedded Inorganic Glasses: Fabrication, Luminescent Properties, and Potential Applications. *Adv Opt Mater* 2019, 7 (21). DOI: ARTN 190085110.1002/adom.201900851.
- (65) Reed, M. A.; Bate, R. T.; Bradshaw, K.; Duncan, W. M.; Frensley, W. R.; Lee, J. W.; Shih, H. D. Spatial Quantization in Gaas-Algaas Multiple Quantum Dots. *J Vac Sci Technol B* 1986, 4 (1), 358-360. DOI: Doi 10.1116/1.583331. Reed, M. A.; Randall, J. N.; Aggarwal, R. J.; Matyi, R. J.; Moore, T. M.; Wetsel, A. E. Observation of Discrete Electronic States in a Zero-Dimensional Semiconductor Nanostructure. *Phys Rev Lett* 1988, 60 (6), 535-537. DOI: DOI 10.1103/PhysRevLett.60.535.
- (66) Krastanow, L.; Stranski, I. N. Short notifications and notes. On the crystallisation of alkali halogenide crystals on fluorite. *Z Kristallogr* 1938, 99 (5), 444-448.
- (67) Leonard, D.; Pond, K.; Petroff, P. M. Critical Layer Thickness for Self-Assembled Inas Islands on Gaas. *Phys Rev B* 1994, 50 (16), 11687-11692. DOI: DOI 10.1103/PhysRevB.50.11687.
- (68) Arakawa, Y.; Sakaki, H. Multidimensional Quantum Well Laser and Temperature-Dependence of Its Threshold Current. *Appl Phys Lett* 1982, 40 (11), 939-941. DOI: Doi 10.1063/1.92959. Kirstaedter, N.; Ledentsov, N. N.; Grundmann, M.; Bimberg, D.; Ustinov, V. M.; Ruvimov, S. S.; Maximov, M. V.; Kopev, P. S.; Alferov, Z. I.; Richter, U.; et al. Low-Threshold, Large T-O Injection-Laser Emission from (Inga)as Quantum Dots. *Electron Lett* 1994, 30 (17), 1416-1417. DOI: DOI 10.1049/el:19940939. Norman, J. C.; Jung, D.; Zhang, Z. Y.; Wan, Y. T.; Liu, S. T.; Shang, C.; Herrick, R. W.; Chow, W. W.; Gossard, A. C.; Bowers, J. E. A Review of High-Performance Quantum Dot Lasers on Silicon. *Ieee J Quantum Elect* 2019, 55 (2). DOI: Artn 200051110.1109/Jqe.2019.2901508.
- (69) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Light-Emitting-Diodes Made from Cadmium Selenide Nanocrystals and a Semiconducting Polymer. *Nature* 1994, 370 (6488), 354-357. DOI: DOI 10.1038/370354a0.
- (70) Eychmuller, A.; Hasselbarth, A.; Katsikas, L.; Weller, H. Fluorescence Mechanism of Highly Monodisperse Q-Sized Cds Colloids. *J Lumin* 1991, 48-9, 745-749. DOI: Doi 10.1016/0022-2313(91)90232-K. Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. Nucleation and Growth of Cdse on Zns Quantum Crystallite Seeds, and Vice Versa, in Inverse Micelle Media. *J Am Chem Soc* 1990, 112 (4), 1327-1332. DOI: DOI 10.1021/ja00160a005.
- (71) Hines, M. A.; Guyot-Sionnest, P. Synthesis and characterization of strongly luminescing ZnS-Capped CdSe nanocrystals. *J Phys Chem-Us* 1996, 100 (2), 468-471. DOI: DOI 10.1021/jp9530562.
- (72) Katari, J. E. B.; Colvin, V. L.; Alivisatos, A. P. X-Ray Photoelectron-Spectroscopy of Cdse Nanocrystals with Applications to Studies of the Nanocrystal Surface. *J Phys Chem-Us* 1994, 98 (15), 4109-4117. DOI: DOI 10.1021/j100066a034.



- (73) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor nanocrystals as fluorescent biological labels. *Science* 1998, 281 (5385), 2013-2016. DOI: DOI 10.1126/science.281.5385.2013.
- (74) Chan, W. C. W.; Nie, S. M. Quantum dot bioconjugates for ultrasensitive nonisotopic detection. *Science* 1998, 281 (5385), 2016-2018. DOI: DOI 10.1126/science.281.5385.2016.
- (75) Peng, X. G.; Wickham, J.; Alivisatos, A. P. Kinetics of II-VI and III-V colloidal semiconductor nanocrystal growth: "Focusing" of size distributions. *J Am Chem Soc* 1998, 120 (21), 5343-5344. DOI: DOI 10.1021/ja9805425.
- (76) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. Shape control of CdSe nanocrystals. *Nature* 2000, 404 (6773), 59-61. DOI: Doi 10.1038/35003535.
- (77) Milliron, D. J.; Hughes, S. M.; Cui, Y.; Manna, L.; Li, J. B.; Wang, L. W.; Alivisatos, A. P. Colloidal nanocrystal heterostructures with linear and branched topology. *Nature* 2004, 430 (6996), 190-195. DOI: 10.1038/nature02695.
- (78) Ithurria, S.; Tessier, M. D.; Mahler, B.; Lobo, R. P. S. M.; Dubertret, B.; Efros, A. Colloidal nanoplatelets with two-dimensional electronic structure. *Nat Mater* 2011, 10 (12), 936-941. DOI: 10.1038/Nmat3145.
- (79) Nozik, A. J. Quantum dot solar cells. *Physica E* 2002, 14 (1-2), 115-120. DOI: Pii S1386-9477(02)00374-0 Doi 10.1016/S1386-9477(02)00374-0. Semonin, O. E.; Luther, J. M.; Beard, M. C. Quantum dots for next-generation photovoltaics. *Mater Today* 2012, 15 (11), 508-515. DOI: Doi 10.1016/S1369-7021(12)70220-1.
- (80) Lu, H. P.; Huang, Z. Y.; Martinez, M. S.; Johnson, J. C.; Luther, J. M.; Beard, M. C. Transforming energy using quantum dots. *Energ Environ Sci* 2020, 13 (5), 1347-1376. DOI: 10.1039/c9ee03930a.
- (81) Lu, H. P.; Carroll, G. M.; Neale, N. R.; Beard, M. C. Infrared Quantum Dots: Progress, Challenges, and Opportunities. *ACS Nano* 2019, 13 (2), 939-953. DOI: 10.1021/acsnano.8b09815.
- (82) Gao, J. B.; Nguyen, S. C.; Bronstein, N. D.; Alivisatos, A. P. Solution-Processed, High-Speed, and High-Quantum-Efficiency Quantum Dot Infrared Photodetectors. *ACS Photonics* 2016, 3 (7), 1217-1222. DOI: 10.1021/acsp Photonics.6b00211.
- (83) Walter, P.; Welcomme, E.; Hallegot, P.; Zaluzec, N. J.; Deeb, C.; Castaing, J.; Veysiere, P.; Breniaux, R.; Leveque, J. L.; Tsoucaris, G. Early use of PbS nanotechnology for an ancient hair dyeing formula. *Nano Lett* 2006, 6 (10), 2215-2219. DOI: 10.1021/nl061493u.
- (84) Wagner, F. E.; Haslbeck, S.; Stievano, L.; Calogero, S.; Pankhurst, Q. A.; Martinek, P. Before striking gold in gold-ruby glass. *Nature* 2000, 407 (6805), 691-692. DOI: Doi 10.1038/35037661.
- (85) Nishi, H.; Tatsuma, T. Full-Color Scattering Based on Plasmon and Mie Resonances of Gold Nanoparticles Modulated by Fabry-Perot Interference for Coloring and Image Projection. *ACS Appl Nano Mater* 2019, 2 (8), 5071-5078. DOI: 10.1021/acsanm.9b00990.
- (86) Rooksby, H. P. The Colour of Selenium Ruby Glasses. *J. Soc. Glass Techn* 1932, 16, 171.