

## Chemical Quantum Dots in Bell Laboratories

### Pioneer Account

Louis Brus



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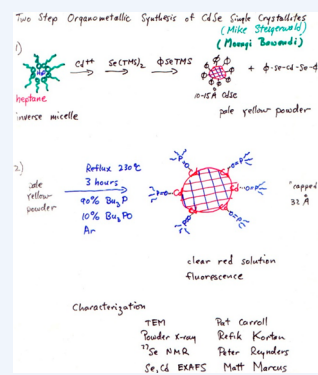
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**CONSPECTUS:** Chemical quantum dots are small semiconductor crystallites (1.5 to 5 nm in diameter). Too small to behave as bulk semiconductors, they have band gaps and luminescence colors that vary with size in a controllable and predictable manner. This is the quantum size effect. Quantum dots are essentially new classes of large molecules. This Account describes our efforts to synthesize, characterize, and understand them, starting in 1983 at the Bell Telephone Laboratories in Murray Hill, NJ. The culture and management style of Bell Laboratories was critical to the success of this effort. There was widespread collaboration among scientists of differing backgrounds and interests. Research was carried out entirely with internal AT&T corporate funding. It is doubtful this research could have been successfully carried out in an academic setting at that time.

We began with simple aqueous colloidal precipitations of II–VI salts such as CdS and ZnSe. To achieve better control and monodispersity, precipitations were done in the small water pools of inverse micelle solutions, using both inorganic and organometallic reagents. We found that with slow addition of reagents, existing particles would grow larger without nucleation of new particles. The particles were capped with phenyl radicals, causing them to become hydrophobic and enabling a powder of capped quantum dots to be recovered. CdSe/ZnS core/shell particles were made by sequential addition of ZnS reagents to an inverse micelle CdSe colloid. ZnS surface passivation greatly improved core CdSe luminescence by passivation of surface states. Quantum dot powders could be dissolved and refluxed at high temperature in Lewis base solvents such as tributyl phosphine oxide. High temperature annealing removed defects and improved structure and luminescence quantum yield, making high quality dots. We then focused on silicon because of its overwhelming importance in the computer and communications industry. To make dots of covalent, strongly bound silicon, a different synthesis was devised. Gaseous disilane in flowing He was cracked at 900 °C to make an aerosol of silicon crystallites of wide size distribution. This was bubbled through ethylene glycol to make a robust colloid. The smallest particles were separated by a combination of HPLC and size selective precipitation methods. These small oxide capped silicon dots emitted in the red range, about 0.9 eV above the bulk silicon band gap in the near IR. Despite this strong quantum size effect, and a large increase of band gap luminescence compared with bulk silicon, optical spectra showed that the fundamental transition remained dipole forbidden.



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- 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*, 4403–4409.<sup>2</sup> Theoretical article calculating the blue shift of the band gap due to both the quantum size effect and the size dependent electron–hole Coulomb attraction.
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- 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*, 1327–1332.<sup>4</sup> Synthesis of core/shell

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structure quantum dots, grown by slow sequential addition of reagents.

## ■ INTRODUCTION

At the request of editor Chris Chang, this is a personal account of my involvement in chemical quantum dot research in the 1980s at Bell Laboratories in Murray Hill, NJ. The [Key References](#) list several important developments.<sup>1–4</sup> Aspects of this research have been previously described in a long review written in 2021<sup>5</sup> and in a perspective on nonlocal dielectric effects in nanoscience written in 2023.<sup>6</sup> I also wrote a more complete autobiography for the Nobel Foundation just this year.

## ■ BELL LABORATORIES

As a young scientist in the 1970s, I had no intension of working on colloidal particles. I and most other chemists thought colloids were a dead subject that had been abandoned in the early 1900s. My PhD was in electronic spectroscopy and kinetics of small gas phase molecules. As a Lieutenant on active duty in the US Naval Research Laboratory, I continued to work in this area. However, my interests evolved when I was hired into the materials research area of Bell Laboratories in the summer of 1973. Bell Laboratories then was the famous corporate laboratory of the national telephone monopoly AT&T, with 1300 scientists in basic research alone—in materials, physics, communications, mathematics, and quantum electronics. It was focused on discovery and invention that would advance communications and computers. Chemistry supported materials research and was a minor part of the entire intellectual enterprise. As a corporate lab, there were no students and no tenure. Initially I had doubts I could survive in this environment. How could I do something at the same level as outstanding Bell Laboratories scientists? Why would they keep me?

The Laboratories managed basic research with a very light hand. Individual working scientists were essentially responsible for recognizing and exploiting new opportunities. In this respect, it was like a university. Yet it was different in that scientists did not have fixed budgets, did not write proposals, and devoted full time to research. Collaboration was often necessary to put together the expertise for a specific experiment. There was extensive internal discussion, particularly over lunch in the cafeteria. If someone came to you with a question or idea, you would take the time to talk to them at some length. In this way, I could come up to speed quickly, if I could find a relevant expert somewhere. The fundamental core strength of Bell Laboratories was the quality of the people. Experienced researchers could work on a hard problem that was too difficult for an academic group. Progress could be made quickly. Because we were immersed in communications and microelectronics, my colleagues and I were aware of a wider range of possible research problems than our friends in academic science. Vice President Arno Penzias said “We work in a problem rich environment”. My scientific horizons broadened as I absorbed the physics, microelectronics, and materials culture of the Laboratories, year by year. I made an effort to formally study solid state physics, coherent dynamics, and electromagnetic phenomena. I began to recognize connections between the physics and chemistry descriptions of bonding and dynamics.

Over time I made friends with and learned from Adam Heller and Barry Miller in electrochemistry; Fred Wudl, Ed Chandross, and Ed Wasserman in organic chemistry; Bob Cava, Frank DiSalvo, and Bob Laudise in solid state chemistry; and John

Tully and Frank Stillinger in theoretical chemistry. In theoretical physics, Stephen Schmit-Rink, Michael Schluter, and Mark Hybertsen tutored me. I followed the work of Walter Brown, Horst Stormer, Kumar Patel, Chuck Henry, Cherry Murray, and Lewis Rothberg in physics. In quantum electronics Chuck Shank, Steve Chu, and Daniel Chemla shared similar interests.

What should I work on? In retrospect, in the 23 years I was there, I was always searching for a better problem, at least in the back of my mind. As time went on, I began to think more about the long-term significance of what I was doing. Even if the experiments were a success, who would care? The structure of the Laboratories made it easy to change fields quickly. It took some time to stumble across and understand the possible advantage of working on semiconductor colloids. I was in my 10th year in the Laboratories when we first observed quantum size effects in colloids.

## ■ CdSe QUANTUM DOTS

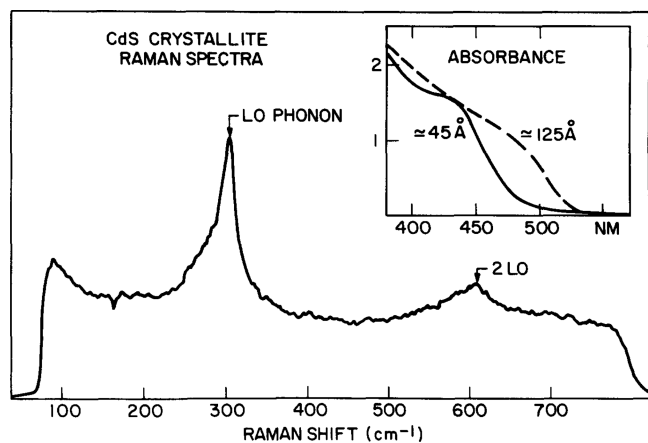
In 1981, I was trying to develop time-resolved resonance Raman spectroscopy as a method to observe the structure of short-lived intermediate species in organic photochemistry, using my picosecond laser system. It was critical to drive the underlying solvent Raman signal as low as possible, and for this reason, I began to read the aqueous micelle literature, as water shows weak Raman scattering. I came across articles on semiconductor colloids. Small semiconductor particles acted much like molecules: they could absorb light and then undergo photochemistry or emit. It was obvious that we might use our lasers to study them.

While postdoc Steven Beck continued to do organic photochemistry with the laser system, I myself began in late 1982 to make colloids using recipes from the literature. In the open air, I injected a dilute Na<sub>2</sub>S solution into a stirring Cd salt solution. As small CdS particles formed, the solution turned yellow. The resulting particle size and polydispersity depended very much on injection technique. Occasionally a colloid showed a blue-shifted band gap with a small peak, later identified to be an “exciton”. The Raman spectrum of the colloid showed the particles to be crystalline and not amorphous. Working with TEM expert Sho Nakahara, we found these particles were near 4.5 nm in diameter. Larger particles showed the normal bulk band gap as seen in [Figure 1](#).

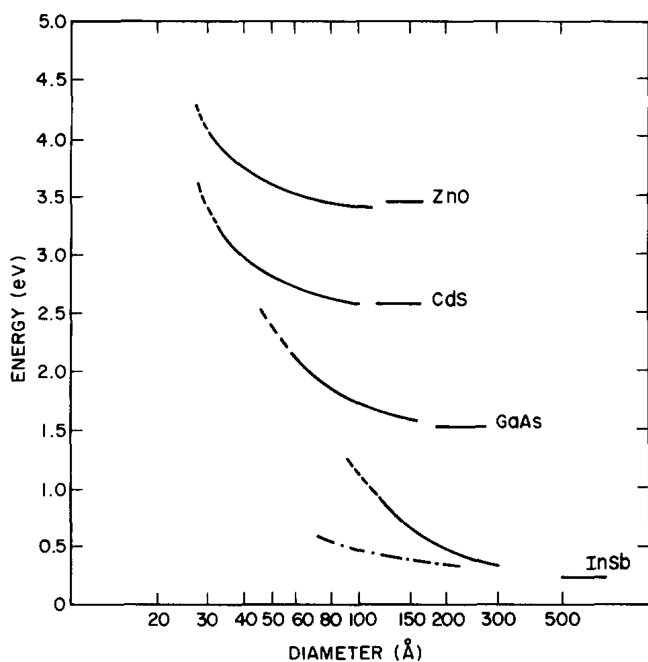
After some thought, I realized the basic wave functions in the particle were changing with size in this few nm regime. I did some simple theory on this evolution as shown in [Figure 2](#).

This question of the evolution of molecular to solid state properties with increasing size was certainly fundamental and of long-term interest to the microelectronics industry. What was the best way to study this? A number of groups around the world were using molecular beams to study cluster properties as a function of size. Famously, about this time Smalley and co-workers discovered C<sub>60</sub> in a carbon beam.<sup>7</sup> It was initially far from clear to me, and many others, that our uncontrolled colloids might prove to be a competitive or useful approach.

In exploratory mode, I extended these studies to other compounds and solvents: ZnS, PbS, ZnSe, and CdSe, in low temperature isopropanol, acetonitrile, and glass forming alcohol mixtures.<sup>8</sup> CdS precipitated at low temperature showed a greater blue shift, indicating we were making smaller particles. Particle growth occurred upon thermal cycling to room temperature and then back down to low temperature. We worked on selenides as their spectra showed a better match to our laser sources.



**Figure 1.** Blue shift of band gap at small size in CdS crystallites in water. The Raman spectrum shows that the particles are crystalline and not amorphous. Reproduced with permission from ref 1. Copyright 1983 AIP publishing.



**Figure 2.** Calculated increase in crystallite band gap with decreasing size. This calculation includes both the quantum size effect and size dependent electrostatics. Reproduced with permission from ref 2. Copyright 1984 AIP Publishing.

During this period, we were pursuing both organic photochemistry and small colloids. About 1985, I decided to focus full time on colloids as they presented a more-or-less unique problem and opportunity. If we could make, isolate, characterize, and understand macroscopic samples of crystallites in this size regime, there would be strong interest. Such crystallites (quantum dots) would be new classes of large molecules with systematic and predictable properties.

Paul Alivisatos came from Berkeley to be a postdoc in 1986. After a discussion of several days, we decided to try to find a way to make higher quality crystallites in a controlled fashion. Paul and I apprenticed ourselves to the young organometallic synthetic chemist Michael Steigerwald, who had just arrived after a postdoc at Princeton. Mike taught us Schlenk line and  $N_2$  dry box techniques to exclude water and oxygen. The three of us

worked side-by-side in his lab exploring possible ideas for making better particles. After a year or so, to increase our synthetic effort, I installed a Schlenk line and dry box in my lab and spent less time on ultrafast lasers. My fruitful collaboration with Mike has continued over many years, both in Bell Laboratories and here at Columbia.

We explored precipitation reactions in the small 5 nm water pools of hydrocarbon inverse micelle solutions. We made CdSe quantum dots by injecting an organoselenium reagent into an inverse micelle solution in which each water pool contained a small number of  $Cd^{2+}$  ions. One quantum dot formed in each micelle; the dots were protected against aggregation with other dots by the micelle structure. We could grow small dots, stop, and then grow larger dots by slowly adding more Cd and Se reagents. That is, with slow addition, the existing dots grew larger without nucleation of new dots. Growth was followed by the evolution in the optical spectra toward the bulk band gap at 700 nm. We further found that we could covalently bind phenyl radicals to the dot surface by adding a phenyl organoselenium reagent as a last step. The dots became hydrophobic and settled on the bottom of the flask. This quantum dot powder was recovered, dried, and characterized by powder X-ray scattering with Refik Kortan, TEM with Murray Gibson, NMR with Dean Douglass, and HPLC with Amy Muller. We also did Raman spectroscopy in a diamond anvil cell and low temperature optical hole burning spectroscopy.

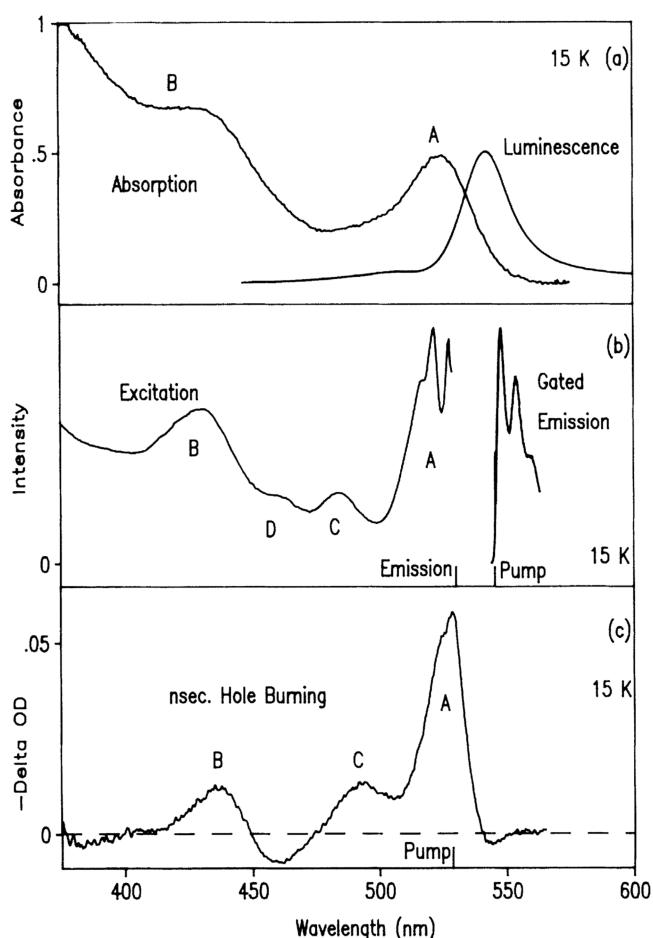
In 1988, Paul Alivisatos left to join the Berkeley faculty, and Mounji Bawendi arrived as a postdoc. We then used this idea of sequential growth to make putative core/shell quantum dots of ZnS on CdSe. If ZnS was slowly grown on CdSe quantum dots in inverse micelles, the core CdSe luminescence changed from weak trap emission to order-of-magnitude stronger near band gap emission in the ZnS capped dots. This result showed that the higher band gap ZnS was passivating surface traps on CdSe and that electrons and holes in CdSe did not penetrate far into the ZnS shell. In subsequent years, a higher band gap shell became a standard structure for strong luminescence. This core/shell powder was also recovered and characterized. We theoretically modeled the expected optical spectra and X-ray patterns for core/shell structure. The interface between the two materials was studied by Auger and Energy Dispersive Spectroscopy with Bob Opila. I spent many hours taking data in Bob's lab.

Our CdSe dots had phenyl bonded to surface Se atoms. We added the Lewis base pyridine, thinking at that time that it would make donor–acceptor bonds to bare surface Cd atoms and thus increase solubility. Pyridine did prove to be a good solvent for quantum dot powders. CdSe dots were refluxed in 4-ethyl pyridine at 169 °C. This markedly improved the X-ray powder patterns so that they were close to those expected for single crystal zinc-blende quantum dots. That is, high temperature refluxing annealed out defects present in the initial dots made at room temperature. The optical absorption spectra sharpened as well. We modeled both zinc-blende and wurtzite structures using the Debye formula.

Refluxing in mixtures of tributyl phosphine and tributyl phosphine oxide at roughly 220 °C made wurtzite CdSe dots of about 3.2 nm diameter.<sup>9</sup> The hand drawn figure in the conspectus shows the chemical synthesis procedure as we understood it in 1989. These dots were of sufficient quality that we did detailed spectroscopic characterization. In a colloid, there are a range of sizes around the average diameter. Larger particles have red-shifted spectra. The observed spectrum is broadened by the distribution in sizes. In an attempt to observe the true



spectra of a single size, transient hole burning and photoluminescence excitation experiments were done with Lewis Rothberg and Bill Wilson. In the near single size spectrum in Figure 3, we observed several higher exciton states in absorption and weak LO phonon side bands in emission.



**Figure 3.** Low temperature optical characterization of 3.2 nm diameter wurtzite CdSe quantum dots. Reproduced with permission from ref 9. Copyright 1990 APS publishing.

## SILICON QUANTUM DOTS

It now seemed clear that Lewis base solvents at high temperature would be a fruitful general synthesis approach for II–VI dots. In 1990, Mounji Bawendi left to join the MIT faculty. Both Alivisatos and Bawendi were pursuing CdSe type dots in academic life. With newly arrived postdoc Karl Littau, we changed our focus. We would try to make silicon quantum dots. Silicon was and remains by far the most important semiconductor in the electronics industry. Silicon transistors on computer chips become smaller each year and are now in the nanometer range. Silicon dots also pose different scientific questions than CdSe dots. In bulk CdSe, the band gap optical transition is allowed, and emission is strong. In bulk silicon, this transition is forbidden by symmetry, and emission is extremely weak.

Strongly bound covalent silicon required a different synthetic approach. We doubted we could make crystalline dots using the available Lewis base solvents at ca. 300 °C or less. In industry, crystalline silicon wafers are made above 1000 °C. We built a

quartz apparatus in which the gas disilane diluted in He was decomposed at 900 °C to make partially aggregated Si crystallites with a wide size distribution.<sup>10</sup> In a second chamber oxygen was introduced to form a passivating SiO<sub>2</sub> layer on each particle. This aerosol was then bubbled through ethylene glycol to form a robust colloid. We were able to separate the smallest particles by using a combination of HPLC and size selective precipitation, which occurs when the nonsolvent tetrahydrofuran is slowly added to the colloid. With Bill Wilson, we found that the smallest particles had an emission quantum yield of near 50% near 600 nm at low temperature.<sup>11</sup> This was a strong quantum size effect and luminescence increase, with emission occurring about 0.9 eV above the bulk silicon band gap in the near IR. As suggested by Ed Chandross, these particles had been refluxed at acidic pH to passivate any remaining surface dangling bonds with hydrogen atoms. A dangling bond could trap an excited electron or hole and thus deactivate luminescence. However, the excitation spectra showed that the band gap transition remained strongly forbidden, which implied that the emission rate was very slow. The quantum yield is high as electron and hole are confined on top of each other in each crystallite and cannot separate as would occur in the bulk crystal. Even though the luminescence rate is slow, the excited state lifetime is long enough that with good passivation the quantum yield is high.

About 1994 my colleagues Jay Trautman, Tim Harris, and Eric Betzig were developing near-field and confocal optical methods for observation of single molecules. Tim, Jay and I, working with postdoc John Macklin, studied the luminescence of individual core/shell CdSe/ZnS quantum dots on surfaces in ambient conditions.<sup>12</sup> Under continuous illumination the emission blinked on and off, showing that the dot emitted as a single quantum entity, similar to a molecule. Blinking decreased for thicker ZnS shells, showing that the higher band gap shell retarded penetration of the electron and hole toward dangling bond traps on the surface.

The work described in this Account was a “golden period” in my research. It was possible because the Laboratories encouraged broad collaboration and also supported research that was not yet recognized as important in university circles. However, our funding progressively decreased as the Bell system was broken up. It became clear I would have to leave if I wanted to continue research. In 1996, I returned to Columbia University where I had earned my PhD 27 years earlier. I made new friends and found new problems. Tony Heinz, Horst Stormer, and I worked to build a culture of collaboration among the chemistry, physics, and engineering departments at Columbia, similar to what we had known at IBM and Bell Laboratories. I entered a second productive period as we worked on different nanoscience problems: strong electron correlation in carbon nanotubes and graphene, single molecule SERS (Surface Enhanced Raman Scattering), and photocatalysis from optical excitation of plasmons in metal nanoparticles.

## AUTHOR INFORMATION

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## Notes

The author declares no competing financial interest.

## Biography

**Louis Brus** earned a BA at Rice University and a PhD at Columbia University, both in chemical physics. Over the years, he has done research at the US Naval Research Laboratory, AT&T Bell Laboratories, and Columbia University, where he is now the Samuel Latham Mitchill Professor Emeritus. He served on the Board of Trustees of the Gordon Research Conferences and was an advisor to the Dreyfus Foundation.

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