Birth of a Nanoscience Building Block

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ABSTRACT The first Kavli Prize in Nanoscience has recognized two giants of the field, Louis Brus and Sumio Ijima, who have helped to lay the foundation of the field of nanoscience through their efforts to develop two of the most fundamental nanoscience building blocks: colloidal quantum dots and the carbon nanotube. In this Focus, I provide a brief history on the birth of the field of semiconductor nanoparticles, or quantum dots, and outline the contributions that Louis Brus has made in this area, which have served to advance the field of nanoscience in vast and far-reaching ways.

The field of nanoscience continues to grow in remarkable ways. Now in its third decade, it is broadening, with increasing impact in fields as diverse as the life sciences, energy, and environmental sciences, while becoming ever deeper, with increased understanding of fundamental scaling laws and the basic physics and chemistry that form its base. The importance of artificial building blocks for the field of nanoscience can hardly be overstated. It is the very premise of the field that nanoscience will enable us to make completely new materials through rational design, materials that will rival or perhaps even exceed the remarkable complexity and functionality of those we can see before us in living systems. This vision was only really set in motion when those first nanoscience building blocks emerged and became widely available to a broad range of scientists, who could then start to build with them. As in most fields of science, we can see here the twin influences of discovery and invention: the nanotube was first discovered, and then a remarkable science developed around it;[1] the quantum dot, on the other hand, was really invented—it is a wholly human construct. Since I had the honor personally to work closely with Louis Brus as a postdoc at Bell Laboratories in the mid-1980s, I had the opportunity to observe and participate in early stages of this development, and it is a great pleasure and honor to prepare this Focus on the birth of the colloidal quantum dot as a nanoscience building block.[2−5]

Today it is commonplace to see the familiar picture of vials lined up in a row on top of a UV lamp, each containing a different size of colloidal semiconductor nanocrystal, and beautifully luminescent with a rainbow of colors across the visible spectrum (Figure 1). These can be seen on Web sites, in research papers, in product catalogs, school and lecture demonstrations kits, and in ever so many grant proposals. It is a nanoscience icon, and it had its origin in Bell Laboratories in the 1980s.

The concepts of quantum confinement and dimensional control of the density of electronic states of a semiconductor material emerged from condensed matter physics in the late 1970s and early 1980s, with work on artificially grown semiconductor materials, especially quantum wells, made by molecular beam epitaxy.[6,7] A visitor to the office of Louis Brus at the Murray Hill site of Bell Laboratories at that time would have had to walk past corridor after corridor of sophisticated vacuum apparatus dedicated to the creation of such novel structures. Ever since the work of Esaki,[8,9] it was a major goal to create artificial quantum materials, in which the potentials that electrons experi-

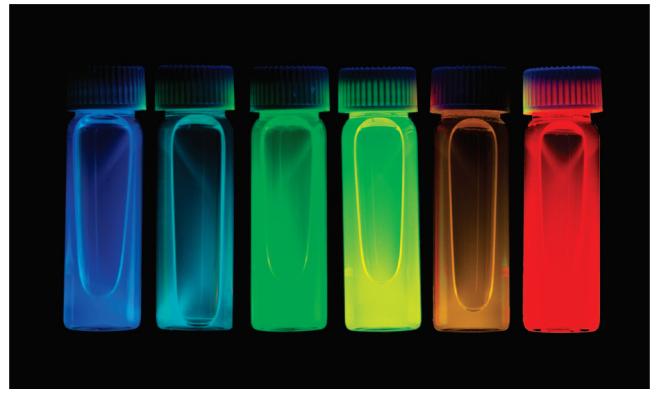

Figure 1. The emission wavelength of CdSe quantum dots can be tuned on the basis of particle size. Image used with permission from Felice Frankel and based on research by M. Bawendi.

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Among piles of research papers, monographs, and very neat pieces of paper with detailed calculations laid out on them, a visitor to Bell Laboratories at that time could find Louis Brus immersed in thought about the basic physics of quantum confinement. He understood it deeply, enough so that he made a further leap when he showed that this same basic physics could be manifested in an entirely new type of system, a colloidal nanoparticle. A short while later, Louis Brus could be found in his laser laboratory; there, in a corner hood, he was working to make colloidal semiconductor particles. He could show that quantum size effects were clearly influencing the optical properties of these particles prepared in liquid solution, and he worked out the basic scaling laws that describe the evolution of the optical spectra *versus* size (Figure 2).[3]

When I came to interview for a postdoctoral position at Bell Laboratories in 1986, I was immediately captivated by this research, which sat so squarely at the intersection between physics, chemistry, and materials science. I enthusiastically signed up to work on the development of these materials. In those earliest days, the colloidal particles produced were stable only for the briefest period of time, and they had (by today's standards) positively appalling size and shape distributions, although we were only dimly aware of this as it was rather difficult even to deposit the particles onto a grid to perform electron microscopy. In many ways, the practical birth of the colloidal quantum dot as a nanoscience building block awaited the further development of suitable chemistry to bring the properties of these newly emerging materials under control.

This was a process in which I had the opportunity to participate, working as a postdoc with Louis Brus and with another great Bell Laboratories scientist, Mike Steigerwald, who opened up his synthetic chemistry laboratory which became headquarters for the quest for new chemical routes to colloidal dots.[10] With a strong background in both quantum chemistry and synthetic organometallic chemistry, and a great spirit of adventure, Steigerwald taught us much about how to approach this problem. A year later, Moungi Bawendi joined the effort, and his remarkable talent and insight led to many further deep discoveries.[11] During that time, 1987 to 1989, this team led by Louis Brus developed many key concepts of photophysics and materials synthesis that underlie the colloidal quantum dot building block of today's nanoscience. When I left for Berkeley in 1988, and Moungi for MIT a year later, two research groups spun out and blossomed. The two groups attracted and trained some of the finest scientists working in the field today, and they in turn have propelled the field further.

As with all important scientific accomplishments, Louis Brus had contemporary colleagues from other institutions who made important contributions, significantly influencing the development of quantum dots. Alexei Ekimov of the Ioffe Institute in St. Petersburg performed a remarkable study of quantum confinement effects on semiconductor nanoparticles embedded in glass;[12] Sasha Efros, now of the Naval Research Laboratory, provided early theoretical understanding of the physics that underlies the materials.[13] Arnim Henglein and his student, Horst Weller, of the Hahn Meitner Institute in Berlin performed beautiful work on colloidal "Q-particles," as they called them;[14] later, Horst Weller established one of the most productive research groups worldwide in this field.[15]

The work from the Bell Laboratories team led by Louis Brus had special impact, owing to the mixing of physics and chemistry, and intellectual freedom and rigor, all in just the right proportions. The methods and approaches of that research have now been so widely adopted they are simply part of the fabric of today's nanoscience. This success owed to the guiding hand of Louis Brus as well as to the remarkable multidisciplinary environment tuned to materials discovery that Bell Laboratories fostered. It is worth recalling some aspects of that world.

In the Bell Laboratories of that time, scientists had an extraordinary degree of freedom to pursue new and perhaps unpopular or very early-stage ideas. I recall in particular a lunch early on in my time there as a postdoc, when several

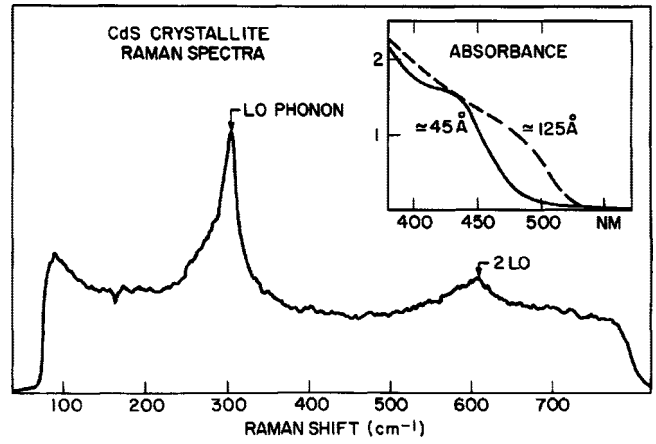

Figure 2. Resonance Raman spectra for CdS crystallites stabilized with a styrene/maleic anhydride copolymer. The inset is an optical absorbance spectra for freshly prepared (solid line) and aged colloid (dotted line). Reprinted with permission from ref 2. Copyright 1983, American Institute of Physics.

condensed matter physicists expressed to me their firm view that the colloidal particle research was a waste of time, and that the quality of semiconductor material that could be produced in a flask could never rival what was produced in a vacuum chamber. This was a place where people really knew how to say what was on their minds directly, and I left that lunch chastised but determined to work even harder to prove them wrong. A strong difference of opinion was allowed to run its course in that environment; indeed, that type of debate and the ensuing pursuit of differing points of view was a regular feature of the institution; part of the fun, really, once you came to understand this. Of course, it turns out there are very fundamental reasons why high-quality semiconductor nanocrystals can be grown in a flask, but these simply were not known nor anticipated nor appreciated properly at the time. If support for the work had been subjected to today's peer review system, I fear the doubts expressed by those colleagues would have been amplified negatively, and the research would never have had a chance to take off and grow as it did.

At Bell Laboratories, fundamental science was stimulated by the information and communications technology environment that it was steeped in. Chemists at universities then certainly would not have recognized the problem of colloidal nanocrystal science as one of any special interest; subsequently, the research opportunities were not widely known. A close connection to "real-world" problems provided a tremendous stimulus to the fundamental work, and Louis Brus was extremely aware of this as he sought a problem to work on. I suspect that the research was supported precisely because it did have such a potential connection. Yet if someone had pressed too hard, insisting early on that a truly credible application be clearly identified, I fear again the work would never have come to fruition.

It will be a double gift to nanoscience if the Kavli Prize[16] leads us to look back at how the quantum dot research was initiated at Bell Laboratories, and then to make changes that empower and stimulate talented scientists toward making new discoveries in the future. Louis Brus himself has dedicated much of his time and effort at Columbia University to this cause, and our community owes him much for this.

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It is wonderful to be able to celebrate the scientific achievements of Louis Brus, a person who so completely embodies the ideals most cherished by the science community. As all those who know him can attest, Louis Brus has a fierce dedication to science, and is able to cut to the essence of a problem quickly, frequently performing the experiment that sets a long-standing issue to rest. This comes from a dedication to the study of fundamental physics, combined with an adventurous and yet very quantitative experimental spirit, and a dedication to his home discipline of chemistry. Does not that sound like the description of a pioneering nanoscientist? At the same time, he is self-effacing, modest, and never boastful of his tremendous accomplishments. We have much to learn from his example, and I am very grateful to have had the opportunity to work so closely with him during those years and to be able to count him as my mentor.

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