CORE CONCEPTS

Quantum dots

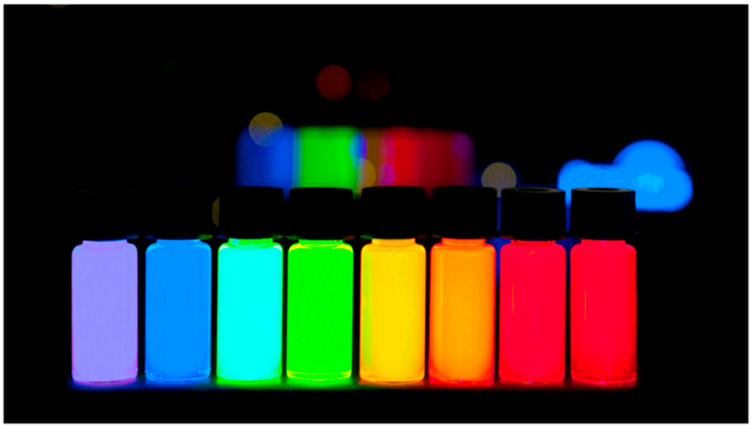
Stephen Ornes, *Science Writer*

In September 2015, Philips, an electronics company based in The Netherlands, unveiled a computer monitor that achieved a brilliant color display using quantum dots: semiconductor nanocrystals that can be tuned to glow in any color. The Philips monitor was the first of its kind, following on the heels of the television that uses quantum dots to enhance its backlighting—rolled out by Sony in 2013—and arriving a few months before the anticipated rollout of the first quantum dot-driven smartphone camera sensors, which the company InVisage announced would start appearing in phones in 2016. These screens have the same resolution as high-definition but can reportedly display a wider range of colors—and potentially at a lower cost—than existing devices.

The term "quantum dots," it seems, has gone mainstream. First identified 35 years ago (1), quantum dots have been evolving in the clean laboratories of curious physicists and engineers, out of sight of the general public, a revolutionary idea without a breakthrough application. They're tiny crystals, grown from or etched into semiconductor materials, with diameters ranging from one nanometer to a few dozen nanometers—on the order of a small virus. When excited by electricity or light, a quantum dot produces a brilliant, single-color glow.

Quantum dots occupy a sweet spot in the semiconductor size spectrum. They typically contain relatively few atoms, ranging from about 1,000 to 100,000. That means the crystals are large enough to be useful in the laboratory, but so small that they exhibit quantum behaviors associated with individual atoms. They're a classic example of "artificial atoms": semiconductor particles sufficiently tiny such that charge and energy levels are quantized. Movement of electrons is confined in all three directions so tightly that quantum dots are said to be "zero-dimensional." As a result, changing the size of a quantum dot controls how it absorbs and emits energy.

This behavior makes them appealing for a wide range of photonics and electronics applications. Some researchers think quantum dots will boost efficiency in LEDs and solar cells, or be used to create glowing paint. Others see potential for using quantum dots as quantum bits or "qubits" to store data in a quantum computer. Quantum bits also may be used as single-photon emitters, devices that would allow for the creation of quantum communication networks based on sending light signals from node to node (2). Their potential extends to other fields: biologists are using the fluorescence of quantum dots to tag cells of interest within a larger sample, an imaging technique that could be particularly useful in molecular cancer research by easily highlighting tumor cells or receptors on cells (3).



Quantum dots, here shown emitting colors from violet to deep red, have begun to evolve from a fascinating curiosity to a tool with potentially broad applications. Image courtesy of PlasmaChem.

Going to the Well

Quantum dots grew out of the study of quantum wells, devices that—like water wells do for water—were designed to restrict where electrons can go. They've been especially important in the advancement of optoelectronic devices, such as lasers. A quantum well is a sandwich of thin, stacked slices of semiconductor materials with different band gaps. The band gap is the energy required for an electron to jump from one energy level to another. In a quantum well, the central layer has the smallest band gap, which means the larger gaps of the outer layers act like barriers, restricting the electrons in the middle one. That structure vertically confines the energy levels of the middle layer in one dimension. By controlling the size of that layer, scientists realized in the 1970s that they could tune the wavelengths—corresponding to color—of photons emitted by the electrons. That realization led the development of quantum well lasers. The quantum confinement in quantum dots is similar to quantum wells, except that electrons are restricted in every direction.

 www.pnas.org/cgi/doi/10.1073/pnas.1601852113

"Quantum dots are like quantum wells, but electrons are confined in all three spatial dimensions, not just vertically," which means they can be tuned to only emit energy at certain frequencies, as colors, says Daniel Gammon, a physicist at the Naval Research Laboratory in Washington, DC. Gammon studies the optics of quantum dots and their potential use in light-based, quantum communication networks.

When a quantum dot is stimulated by electricity or light, electrons jump to a higher energy level. As they return to their ground state—the lowest energy state—quantum dots release light in single photons. The color of that light depends on the size, composition, and shape of the crystal. Smaller crystals glow with light toward the blue end of the spectrum. Larger crystals produce more reddish light. Quantum dots can be easily tuned to produce a particular color.

Russian physicist Alexey Ekimov first observed quantum dots, in glass, in 1981 (1). Throughout the 1980s, and especially in the 1990s, research into the materials accelerated as scientists realized that, because quantum dots behave like atoms, they could use findings from atomic physics as inspiration for new ways to probe the possibilities of quantum dots. By the turn of the century, the technology had spilled out from physics laboratories into other areas, leading to interdisciplinary collaborations.

Body Bound?

Quantum dot research has excited biologists in particular, says Massachusetts Institute of Technology chemist Moungi Bawendi, who has worked on both the manufacture and varied uses of quantum dots. Bawendi says that as a way to study cells and molecular structures, quantum dots are brighter and more stable than other types of dyes in use today.

For more than a decade, Bawendi has collaborated with Rakesh Jain at Harvard University, who trained as a chemical engineer and now investigates tumor microenvironments, the networks of healthy blood vessels and cells that surround a cancerous growth. Tumors interact with their environment in many ways: blood vessels feed the tumor, and the tumor may release chemical signals or other cancer cells into the rest of the body. Jain thinks quantum dots will help inform the design of drugs that can travel through the often-leaky blood vessels of tumors and reach malignant cells directly (4). The method starts by injecting quantum dots of different sizes into animal cancer models. Because different-sized dots have different colors, Jain can estimate the sizes of blood vessels by observing which colored dots get into the tumor.

"What is the right size of the car," Jain asks, "once you know the size of the road?" In other words, he's seeking the right sized nano therapeutic, one that can be effectively delivered to target the cancer of interest.

Quantum dots as they exist today will probably never be used in humans... Right now there is no formulation that is nontoxic.

—Moungi Bawendi

Other cancer researchers are investigating ways to use the glowing dots to identify cancerous cells in pathology studies by tagging cells that have particular receptor types on their surfaces, which may show that the tumor is vulnerable to targeted therapies. Still others argue that quantum dots may even play a role one day as a drug delivery system, by ferrying treatment directly to the cancer cells.

Bawendi, though, has serious doubts about sending quantum dots into the human body, citing major toxicity challenges. "Quantum dots as they exist today will probably never be used in humans," he says. "Right now there is no formulation that is nontoxic." Although quantum dots can be made from many different semiconductors, many require heavy metals, like cadmium, that are toxic to living cells. Even so, researchers are looking to develop nontoxic shells to protect the quantum dots and prevent leakage; some have demonstrated long-lasting nontoxicity in animal models.

Bawendi has spent most of his career with quantum dots: creating them and pushing them into new uses. In the 1980s and 1990s, the research was "purely curiosity driven, and driven by beautiful quantum mechanics," he says. "Today, they're in televisions."

1 Ekimov AI, Onushchenko AA (1981) Quantum size effect in three-dimensional microscopic semiconductor crystals. *JETP Lett* 34(6): 345–349.

2 Heinze D, Breddermann D, Zrenner A, Schumacher S (2015) A quantum dot single-photon source with on-the-fly all-optical polarization control and timed emission. *Nat Commun* 6:8473.

3 Fang M, Peng CW, Pang D-W, Li Y (2012) Quantum dots for cancer research: Current status, remaining issues, and future perspectives. *Cancer Biol Med* 9(3):151–163.

4 Stroh M, et al. (2005) Quantum dots spectrally distinguish multiple species within the tumor milieu in vivo. *Nat Med* 11(6):678–682.