Honored for the discovery and synthesis of quantum dots

The Nobel Prize in Chemistry goes to three nanoscientists

This year's Nobel Prize in Chemistry has been awarded to the three nanoscientists Professor Moungi G. Bawendi (MIT, Cambridge, MA, USA), Professor Louis E. Brus (Columbia University, New York, USA) and Dr. Alexei I. Ekimov (Nanocrystals Technology Inc., New York, USA). Their research has paved the way for the application of versatile nanocrystals known as quantum dots – that, like other nanostructures, are subject to the rules of quantum mechanics. We interviewed Professor Jonathan de Roo from the Department of Chemistry at the University of Basel to find out more about these special nanocrystals and about the nanocrystal applications he is exploring in his research.

SNI INSight: What are quantum dots and what's so special about them?

Jonathan de Roo: Quantum dots are colloidal – that is, finely dispersed – semiconductor crystals that measure only a few nanometers in diameter. These tiny particles contain just a few hundred or thousand atoms, and their properties vary depending on their size. One such property is their color when excited by exposure to light – for example, small quantum dots glow blue when excited with UV light, whereas medium-sized quantum dots emit green light, and larger quantum dots emit red light. By varying the size of the particles, it's therefore possible to define the emission wavelength of quantum dots and, accordingly, the energy or frequency of the light they emit.

SNI INSight: How can this phenomenon be explained in simple terms?

Jonathan de Roo: If we expose a quantum dot to light, the electrons in the semiconductor material absorb energy and rise to a higher energy level. When they fall back to their original energy level, they give off electromagnetic waves in the form of light. The color of this light de-

At the SNI's Annual Event, Jonathan de Roo described his work with colloidal nanocrystals.

Further information:

Webpage Nobel Prize
https://www.nobelprize.org

Research group Jonathan de Roo
https://deroo.chemie.unibas.ch/en/

Quantum dots are colloidal — that is, finely dispersed — semiconductor crystals that measure only a few nanometers in diameter. Depending on their size, they have different properties — for example, their color when excited with light. (Image: Stockphoto)

pends on the energy difference between the excited state and the ground state. Although quantum dots can absorb light with a wide range of energies, the color of emitted light then depends on the size of the crystals.

We can think of this as being like an organ, in the sense that a short organ pipe produces a high-pitched sound with a high frequency, whereas a long pipe produces a deep sound with a low frequency. If the crystals of the quantum dots are small, the emitted light is high-frequency and high-energy – and therefore blue. If the crystals are large, on the other hand, the emitted light has a lower frequency and a longer wavelength – and is red in color.

SNI INSight: What exactly did the three Nobel laureates investigate?

Jonathan de Roo: In the early 1980s, Alexei Ekimov studied glasses that contained finely dispersed copper chloride nanocrystals. Ekimov showed that the color of the glasses varied depending on the size of the copper chloride crystals and that this phenomenon was caused by quantum effects. He was able to control the size of the particles to some extent by varying the heating and cooling of the glass.

A few years later, Louis Brus was the first to investigate quantum dots made of cadmium sulfide crystals freely dispersed in fluids. Brus showed that the size of these crystals influenced not only the color of the emitted light but also other chemical and physical properties.

In 1993, Moungi Bawendi successfully applied the “hot injection method” to the chemical production of quantum dots with a homogeneous size for the first time – thereby achieving the fundamental prerequisite for practical applications of quantum dots.

To this end, Bawendi’s team injected organometallic cadmium compounds together with organic selenium compounds into a hot solvent that also contained surfactants. The high temperatures caused the organic parts of the organometallic molecules to break down, and the metal ions bonded with the selenium to form cadmium selenide nanocrystals. Meanwhile, the surfactants in the solution ensured that the crystals were finely dispersed. Although the crystals would continue to grow while the temperatures were still high (between 240 and 360°C) and sufficient source material was available, Bawendi repeatedly took samples and stopped the crystallization process within them. By doing so, he obtained a series of liquids each containing quantum dots of a specific size.

SNI INSight: The first chemical synthesis of homogeneous quantum dots was presented 30 years ago. What progress have researchers made since then?

Jonathan de Roo: Back then, the Nobel laureates were working with highly toxic compounds. Today, we can produce quantum dots from starting materials that are much less dangerous. For each new compound used to produce quantum dots, it’s necessary to redefine the conditions – even if some aspects of production remain very similar today.

In the last few decades, researchers have massively increased the quantum efficiency of quantum dots. This was initially around 5% – in other words, it took 20 photons of excitement to produce one photon of emitted light. In modern quantum dots, the efficiency stands at almost 100%. In part, this improvement was achieved by encasing the nanocrystals in an inorganic shell – like an onion having different layers.

It is also important to adjust the reaction conditions so that particles reach the target size at the end of the reaction. To obtain small quantum dots, I can obviously take my samples right at the start of the reaction and halt crystal growth – but then I lose most of the reagents. The aim is to choose components and conditions with a view to maximizing yield by making optimum use of the starting materials. This is another area where researchers have made considerable progress.

SNI INSight: What are quantum dots used for?

Jonathan de Roo: Today, quantum dots are used in numerous areas. For example, they are responsible for the brilliant colors in QLED televisions, where blue light is emitted by a gallium nitride light source and then converted into green and red by the various quantum dots. These three primary colors can then be combined to produce the full color palette.

In QLED lamps, quantum dots convert colors more efficiently than is the case with traditional LEDs, although these QLED lamps are not yet commercially available. It is first necessary to improve the stability of the quantum dots because, unlike a TV screen, an LED lamp becomes very hot and can therefore cause the quantum dots to "die off."

In the future, quantum dots or nanocrystals may also play a key role in medical applications – for example, in order to visualize certain tissues. This is another focal point of our research.

SNI INSight: Does your team also work with quantum dots?

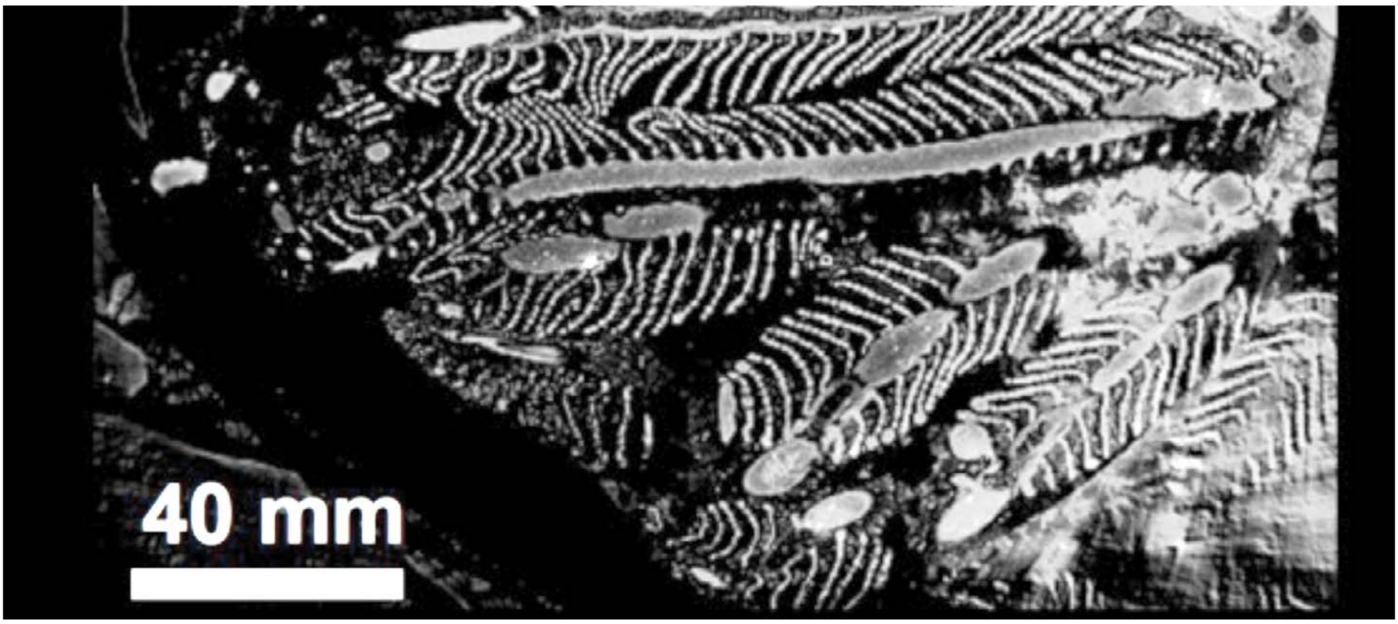
Jonathan de Roo: We don't work with quantum dots, but we do use non-toxic colloidal nanocrystals made of zirconium and hafnium oxide. These are close relatives of quantum dots and are produced in a similar manner.

SNI INSight: What applications are you exploring for these nanocrystals?

Jonathan de Roo: We want to use the nanocrystals for diagnostic imaging.

In a project with colleagues from Ghent University Hospital (Belgium), we're investigating whether the crystals can be used to boost soft-tissue contrast in X-ray examinations. By doing so, we hope to pave the way for the clear identification of "sentinel lymph nodes" in breast cancer patients during surgery. To this end, the nanocrystals are injected into the tumor, the liquid containing the nanocrystals flows through the lymph system to the first lymph node in the armpit, and this sentinel lymph node becomes visible in the X-ray image. As the solution carries a dye, the surgeons can then visualize the sentinel lymph nodes for removal during surgery.

In an SNI project, we're working with colleagues from the PSI in order to use our nanocrystals to spot rejection at an early stage in transplant patients. First, we equip the nanocrystals with certain antibodies that bind specifically to immune cells. Then, if we add our antibody



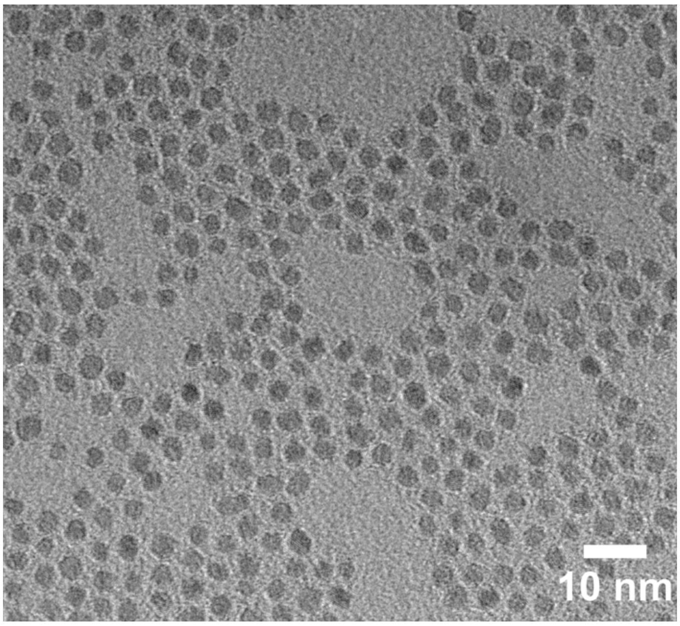
The nanocrystals from the de Roo team can be used to produce detailed images of even the finest blood vessels in the gills of a zebrafish. (Image: Department of Chemistry, University of Basel) nanocrystals to transplanted organ tissue obtained in a biopsy, the antibodies will bind to any immune cells. This allows us to determine whether a large quantity of immune cells are present in the tissue – which would point to the initial stages of rejection.

SNI INSight: What challenges affect the production of nanocrystals?

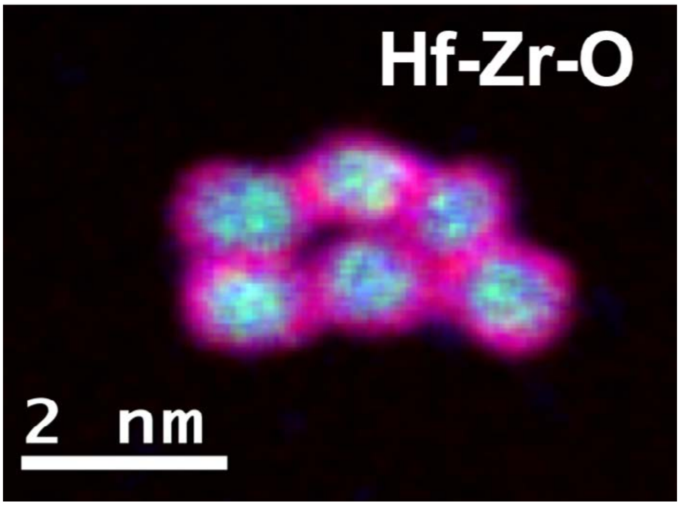
Jonathan de Roo: The oxide nanocrystals that we're investigating are even harder to produce than quantum dots. Zirconium and hafnium carry a multiple positive charge, and their oxides are difficult to produce because they have strong bonds that are not easily broken. At the same time, however, breaking bonds is a prerequisite for repairing defects in the crystals. Once they are produced, the crystals are extremely stable.

We're also studying complex shells of the crystals – which resemble layers of an onion – to further optimizing their properties. On top of that, we're working on producing oxide clusters, which are even smaller than nanocrystals and, above all, atomically precise – unlike the nanocrystals.

In any case, there's plenty of work to do and we still have numerous ideas about how we can provide various colloidal nanocrystals for different applications.



Producing nanocrystals of uniform size is the prerequisite for putting them to use. (Image: Department of Chemistry and Nano Imaging Lab, University of Basel)



Jonathan de Roo's group is investigating hafnium/zirconium oxide nanocrystals (zirconium core and hafnium shell) for use in diagnostic imaging. (Image: Department of Chemistry, University of Basel)