# Fluorescent semiconducting nanocrystals show their colours

When semiconductor materials are prepared in the form of nanometric crystals, their small particle size gives rise to quantum effects. When illuminated with ultraviolet light, these nanocrystals emit light, the colour of which varies according to their size, so that a complete colour spectrum can be obtained. Thanks to this property, semiconductor nanocrystals, often called *quantum dots*, can, for example, be used as luminescent markers of biological systems to monitor biological processes in living cells, or to mark valuable objects or merchandise.

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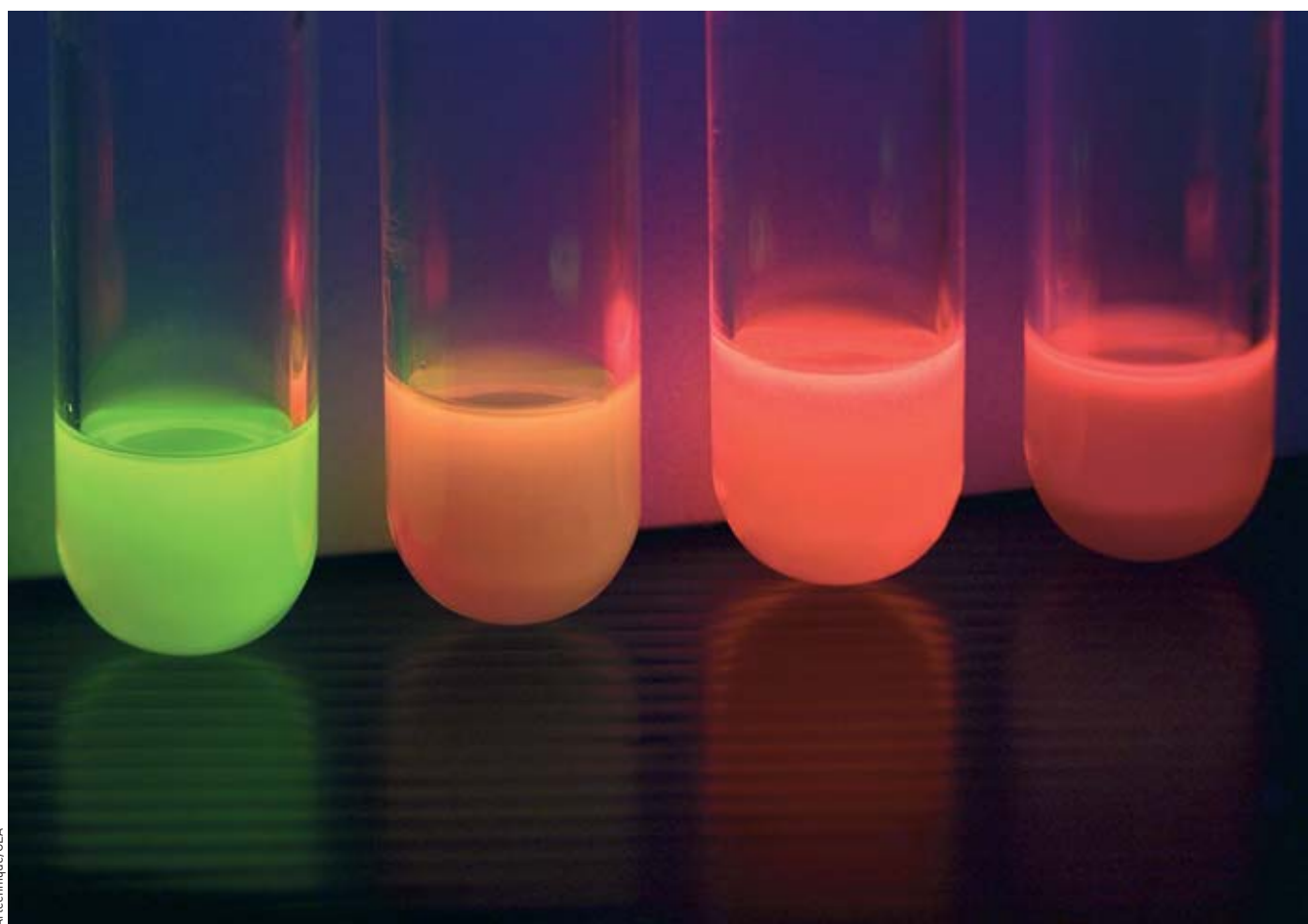
Semiconductor nanocrystals of different sizes illuminated with ultraviolet light.

Among the spectacular size-related properties of nano-objects are those arising from **quantum** confinement in nano**crystals** of **semiconductor** materials. As the size of a nanocrystal is reduced, its properties fall into a range between those of an isolated **atom**, which has **discrete** energy levels, and those of a macroscopic solid, in which these levels form **energy bands**. Nano-objects in this size range are termed *artificial atoms*. In particular, quantum confinement causes an increase in the energy **gap** between the topmost occupied energy level and the first empty level (box). The widening of this gap has a profound effect on optical properties. A semiconductor subjected to an excitation will return to its base energy level by emitting, by **fluorescence**, **photons** of energy equal to the gap energy.

This emitted energy depends on the semiconductor material. In nanocrystals it also depends on physical dimensions, which makes it possible to choose the colour of the emitted light over a complete range from **visible** to **infrared** by grading particle size.
Fluorescent semiconductor nanocrystals can be prepared using various physical techniques (**molecular beam epitaxy** [Box C], laser pyrolysis, etc.) or by **soft chemical** methods. The form in which they are obtained (deposited on a substrate or dispersed in a liquid phase) differs according to the method of synthesis, but the physical properties described above remain the same. Here we describe two examples of semiconductor nanocrystals prepared either as **colloids** by soft chemical methods, or by laser pyrolysis. These techniques

Size effects in semiconductor nanocrystals

In the macroscopic state, a non-doped semiconductor presents a full valence band and an empty conduction band separated by a bandgap, of width E_g. By light excitation with photons of energy $h\nu_{exc} \geq E_g$ (h, Planck's constant; ν, radiation frequency), it is possible to transfer an electron from the valence band to the conduction band and thereby create a hole in the valence band. The fluorescence corresponds to the radiative recombination of this electron-hole pair (or exciton) by emission of a photon of energy $h\nu_{fluo} = E_g$, the excess energy $h\nu_{exc} - h\nu_{fluo}$ being lost as heat. The fluorescence is more probable at lower temperatures and if the semiconductor contains few structural defects.

Because of the finite number of atoms and the quantum confinement, the energy bands of a nanocrystal are split into discrete levels, which widen as the radius r of the nanocrystal decreases. This is especially so for the levels that determine the gap (left-hand figure). To a first approximation, the gap E_g of the spheric nanocrystals is given by the formula:

$$E_g = E_g^{solid} + \frac{\hbar^2 \pi^2}{2r^2}\left(\frac{1}{m_e^* m_e} + \frac{1}{m_h^* m_e}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\frac{1}{r}.$$

In this equation, the first term E_g^{solid} corresponds to the gap of the macroscopic crystal. The second $1/r^2$ term, called *quantum confinement*, is calculated assuming a spherical nanocrystal in which are confined an electron and a hole of respective effective masses m_e^* and m_h^* (dimensionless variables). The effective mass is a corrective factor applied to the mass of the free electron to allow for the curve of the valence and conduction bands near the energy gap. m_e represents the mass of the electron ($m_e = 9.1 \cdot 10^{-31}$ kg) and $\hbar$ the quantum of angular moment ($\hbar = h/2\pi = 1.0546 \cdot 10^{-34}$ J·s). The last term accounts for the Coulomb attraction between the electron and the hole. ε (dimensionless) is the static dielectric permittivity of the material relative to that of a vacuum ε_0 ($\varepsilon_0 = 8.854$ pF/m). e is the electric charge of the electron ($e = -1.602 \cdot 10^{-19}$ C).

Quantum confinement increases the gap as r decreases, more steeply with a smaller r (variation with $1/r^2$). The equation gives E_g for nanocrystals of different semiconductors from macroscopic solid parameters (right-hand figure). With appropriate light excitation, nanocrystals can re-emit, by fluorescence, photons of energy equal to the gap value. With different semiconductors, a broad spectrum of gap energies is therefore covered, spanning a complete spectral range from near infrared to near ultraviolet.
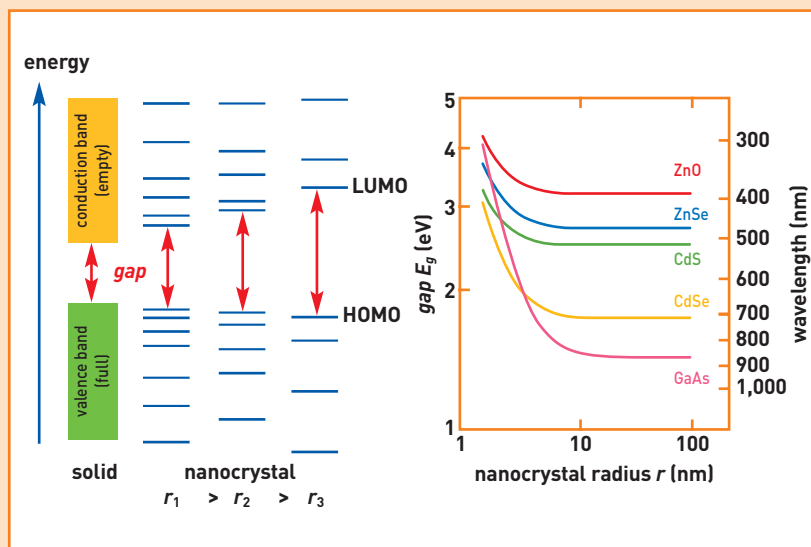

Figure.
Left, schematic evolution of the electronic structure between the macroscopic solid and nanocrystals of decreasing size (the filling of electron levels and energy bands is not indicated). HOMO and LUMO represent respectively the topmost occupied level and the bottommost empty level.
Right, theoretical variation of the gap calculated from the equation for the nanocrystals of different semiconductors: zinc oxide ZnO, zinc selenide ZnSe, cadmium sulphide CdS, cadmium selenide CdSe and gallium arsenide GaAs.

are used respectively by the Department of Fundamental Research on Condensed Matter (DRFMC: Département de recherche fondamentale sur la matière condensée) at CEA Grenoble and by the Solid State, Atoms and Molecules Research Department (Drecam: Département de recherche sur l'état condensé, les atomes et les molécules) at CEA Saclay. Lastly, special properties and some applications will be described.

Semiconductor nanocrystals made by soft chemical methods

Among the various methods of synthesis by soft chemical methods, the *organometallic synthesis* pathway and its derivatives are the most efficient in terms of size control and nanocrystal brightness. This method, developed in 1993 in the US by the group of Moungi Bawendi (Massachusetts Institute of Technology MIT) for CdE nanocrystals (where E is a chalcogen; sulphur S, selenium Se or tellurium Te), has since been extended to other semiconductors; II-VI (zinc selenide ZnSe, mercury telluride HgTe, etc.) and III-V (indium phosphide InP, indium arsenide InAs, etc.). It is based

on the processes that take place between nucleation and seed growth (Figure 1a). An organometallic precursor and an appropriate chalcogen precursor for nanocrystals of the cadmium selenide (CdSe) type, are injected into a "coordinating" solvent at high temperature, close to 300 °C, so that their concentration rapidly exceeds the nucleation threshold. This causes supersaturation, which is relieved by crystal seed formation. Ideally, all the crystal seeds form simultaneously and grow identically until the precursors in the solution are expended. Other reagents can then be injected to increase average particle size. In most cases, initial growth is followed by a second process called *Ostwald maturation*, which causes the larger particles to grow at the expense of the smaller ones, owing to differences in surface energy. Ostwald maturation thus tends to broaden size distribution. By stopping the crystallization before this stage, nanocrystals with a size dispersion of a few percent are obtained with CdSe. A colloidal solution of nanoparticles is obtained, each with a crystalline core (CdSe…) passivated[(1)] by a layer of organic hydrophobic ligands. The fluorescence quantum yield, which corresponds to the probability of emission of a photon by fluorescence after excitation

of the nanocrystal by a first photon, is limited to a few percent at ambient temperature, because of the incomplete surface passivation by the ligands. The epitaxial growth around the nanocrystals of a shell of a semiconductor with a wider gap improves this passivation and affords quantum yields greater than 50% for nanocrystals of CdSe coated with ZnSe or ZnS. The growth of the shell takes place in solution, on the basis of the principles described above, on the nanocrystals, which act as seeds. In this way, complex multilayer constructions with specific photophysical properties can be built in successive steps. However, quantities remain limited to about 100 mg per run, and decrease with the number of steps in the sequence.

(1) Passivation: natural or artificial modification of the surface of a material that enables it to resist an active process. Here the passivation layer (organic ligands) wrapped around the core prevents the transfer of the excitation (the electron-hole pair) towards the non-radiative recombination centres located at the interface with the external medium.


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Synthesis of semiconductor nanocrystals. Here, coating of CdSe nanocrystals with a shell of ZnSe/ZnS to improve optical properties.
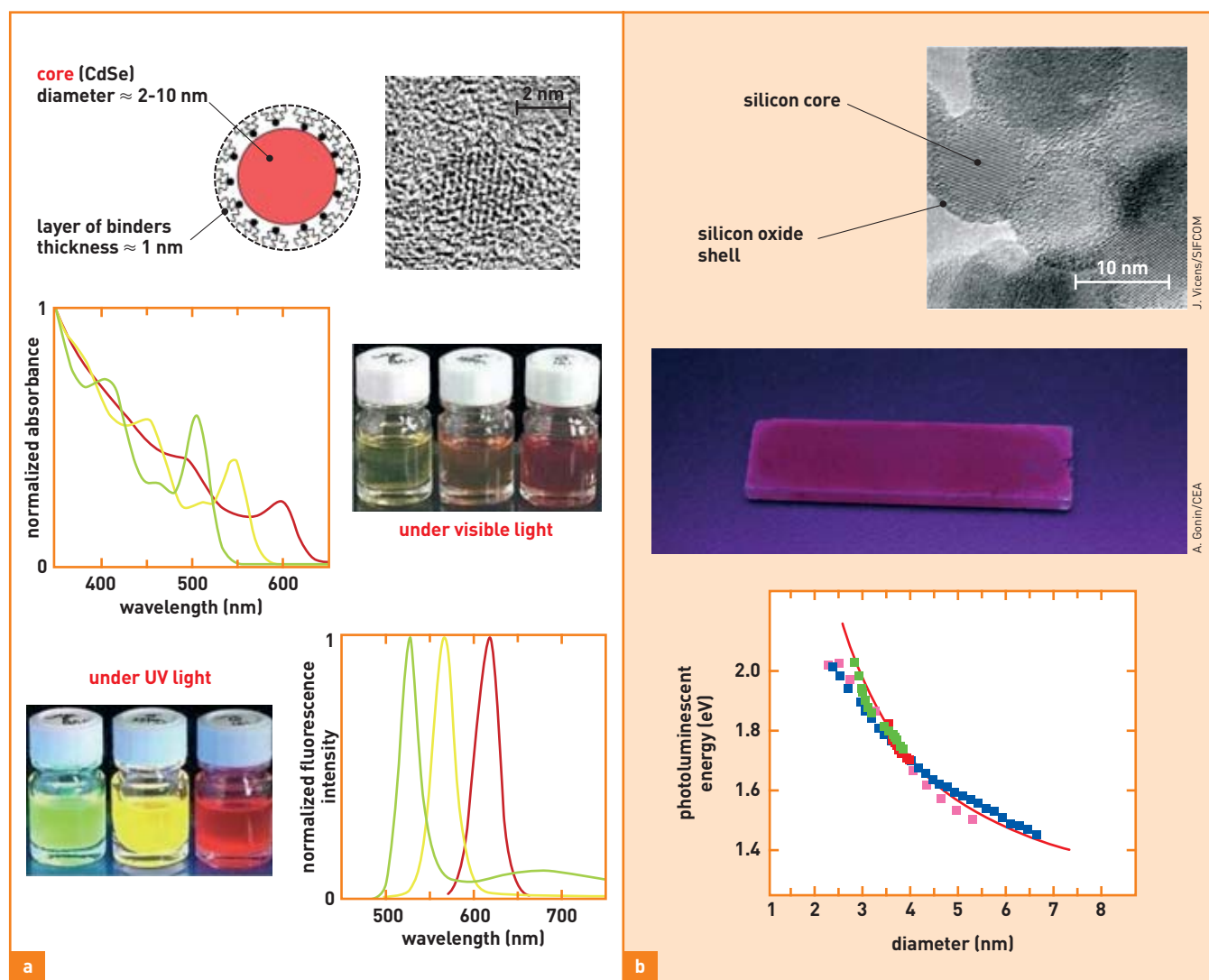
Figure 1.
a) Top: diagram and transmission electron microscope (TEM) image of a nanocrystal of CdSe (core only). Bottom: absorption and fluorescence spectra at ambient temperature of colloidal dispersions of CdSe nanocrystals of diameter 2.8 nm (green), 3.8 nm (yellow) and 5 nm (red) with facing vials.
b) Top: TEM image of silicon nanocrystals presenting a pure silicon core and a shell of silica (silicon oxide) linked to partial oxidation of the nanocrystal. Middle: photo showing the characterization of photoluminescent silicon crystals under ultraviolet light. Bottom: variation of photoluminescence peak energy as the size decreases (squares) compared with the prediction of the **model** of quantum confinement (unbroken line).
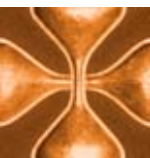
Silicon nanocrystals made by laser pyrolysis

Soft chemical methods are more difficult for **silicon**. Silicon nanocrystals can be made from macroscopic silicon, for example by electrochemical treatment of a silicon **wafer**, but the most effective method is gas phase growth by laser pyrolysis of a silane flux (SiH_4). The heat of the infrared laser radiation used causes the silane to dissociate, forming a supersaturated silicon vapour phase in which nucleation and growth of nanocrystals take place (Figure 1b). This very efficient process allows control over the size of the nanocrystals formed by setting the partial pressure of the silicon in the reagent mixture. The size range is broader than that obtained by the soft chemical method, but it produces several grams per hour. These nanocrystals are surface-passivated by natural or controlled **oxidation**. They can then be dispersed in solution and **functionalized**.

Silicon has the particularity of being an **indirect gap** semiconductor. The emission (or absorption) of a photon is forbidden at the gap itself. The transition requires the intervention of a **phonon**, which is an appreciably slower process. Consequently, an **electron-hole pair**, once created, has a very long life expectancy in macroscopic silicon, of the order of a thousandth of a second, *i.e.*, a million times longer than **direct gap** semiconductors of the CdSe type. However, during this time, the **exciton** can meet a structural defect in the crystal that will cause the recombination of the electron-hole pair without emission of light. The probability of light emission is thus very low in macroscopic silicon. The situation is different in silicon nanocrystals. The restricted space in which the electron-hole pair is confined increases the probability of radiative de-excitation. Also, the number of structural defects is low (inversely proportional to the volume of the nanocrystal), and the surface defects are minimized by passivation. An increase in the quantum yield of several orders of magnitude is observed as the size decreases, reaching at least 10%. At the same time, the widening of the gap shifts the **photoluminescence** peak from infrared towards red and orange, and even blue for the smallest crystals. The lifetime of the excitons falls exponentially according to the value of the gap, but still remains very high, between 10 and 100 microseconds. These lifetimes, associated with high quantum yields, are useful for biological applications, because they allow selective observations over long time spans. The observation of the light emission can simply be slightly delayed after excitation to avoid the rapid interference emission in the medium.

Promising potential applications

Whatever their mode of synthesis, the coating of the nanocrystals determines their stability in different solvents. The nanocrystals of CdSe derived from organometallic synthesis are hydrophobic: by acting on the coating, for example by ligand exchange, it is possible to modify this property and add chemical functions for grafting to other **molecules**, biomolecules, **polymers**, etc. (see *Giving nano-objects new properties by molecular grafting*). The functionalization step can be delicate because it can strongly affect the photophysical properties of the nanocrystal.

The potential applications of fluorescent semiconductor nanocrystals are numerous. First, these entities are inorganic fluorophores[2] with flexible optical properties in terms of excitation and fluorescence. They are as bright as organic fluorophores and, importantly, much more resistant to **photobleaching**. When permanently illuminated, the fluorescence of nanocrystals persists for several hours, whereas it fades in a few minutes for the best organic fluorophores such as Alexa Fluor®. Nanocrystals thus represent an advan-

[2] Fluorophore: molecule or nano-object able to emit light by fluorescence at longer wavelengths than that of the absorbed radiation.
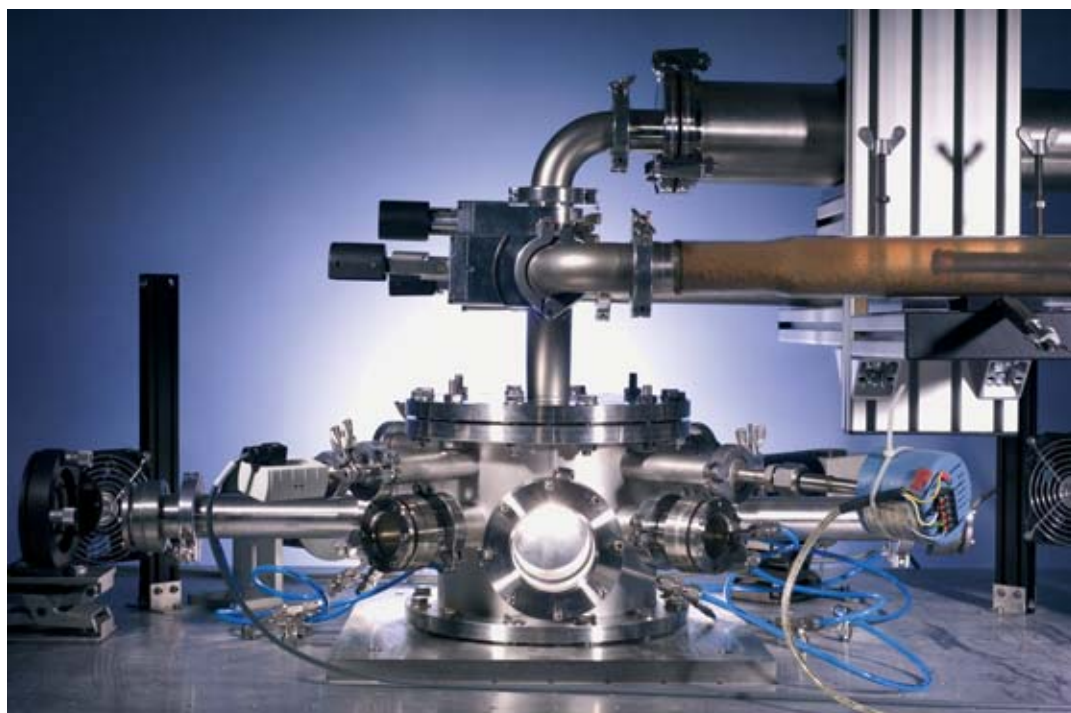
Reactor for the synthesis of fluorescent nanocrystals by laser pyrolysis.
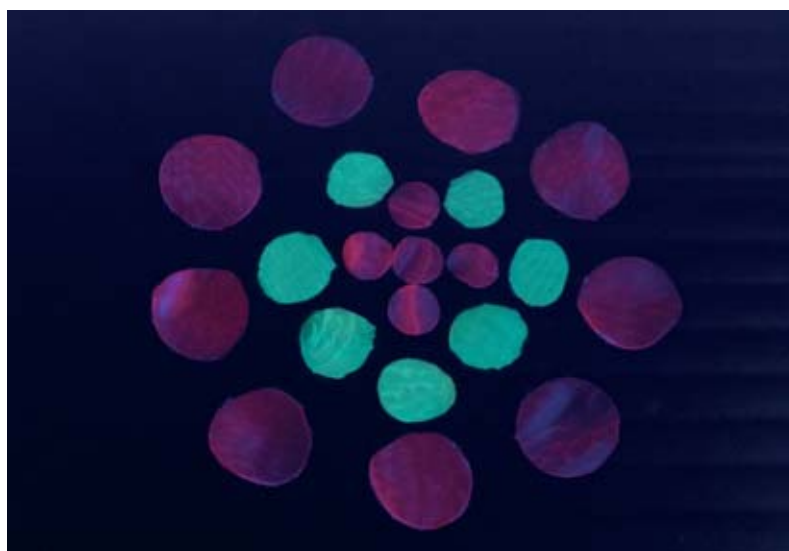
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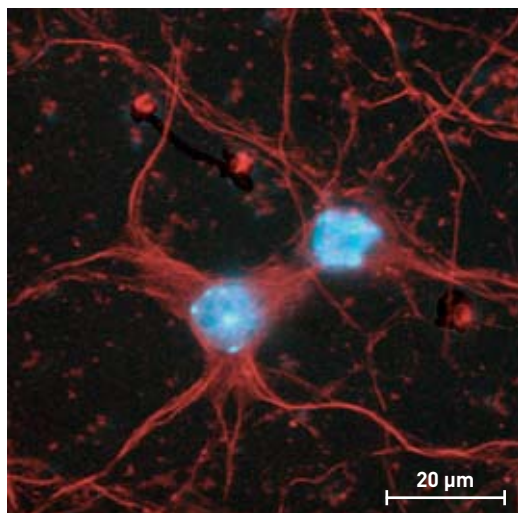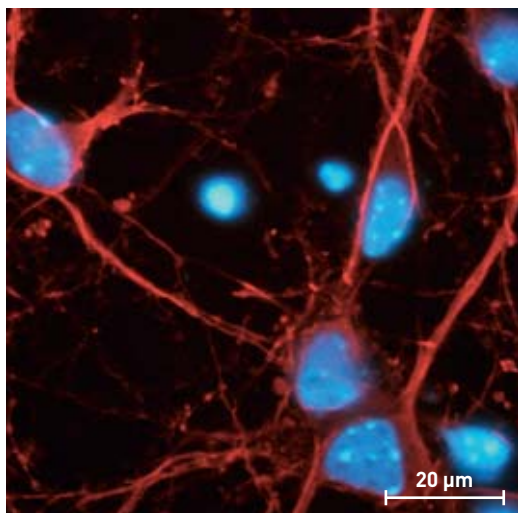
Fluorescence microscopy images (sham colours) of neurone cells in a mouse embryo labelled with; left, an organic fluorophore routinely used in biology, cyanine-3, and right, fluorescent semiconductor CdSe nanocrystals wrapped in a ZnSe shell. In both cases, the nuclear **DNA** is labelled with another organic fluorophore (blue).

tageous alternative to organic fluorophores in applications that require fluorescent labelling as in biology, biotechnology (*e.g.*, **biochips**) or medical imaging (optical detection of certain cancerous tumours). When incorporated in **micrometric** plastic beads they can be used to create discrete barcodes to mark valuables or commercial goods.

In addition, nanocrystals enter into the composition of new materials for applications in optoelectronics. Coupling to conducting polymers such as polythiophene, which are in fact organic semiconductors, produces inorganic-organic hybrid materials that convert sunlight into electric current. These materials combine the flexible optical properties of nanocrystals with the easy fabrication of polymer structures. In different coupling conditions, such materials can serve as active components in electroluminescent **diodes** for information display. Nanocrystals can also be used as a basis for active materials in devices such as lasers.

A broader range of nanocrystals

The examples presented concern spherical nanocrystals, which are prototypes of zero-dimensional (0D) point objects. Improved soft chemical methods can be used to prepare nanocrystals with a wide range of shapes (nanowires, tetrapods, etc.) intermediate between 0D and 1D objects, and made of one or several materials. Similarly, several teams have described the formation of silicon nanowires. Work in this area can be expected to continue, providing an ever-greater control over topology, composition and even crystalline structure.

As regards applications, nanocrystals suitable for fluorescent marking are already commercially available. In **photovoltaic** applications, solar cells based on nanocrystals are still restricted to laboratory use. However, research in this area is very active, and so we can expect to see the exciting properties of nano-objects continue to inspire further novel applications in the future.

Soft chemical methods can be used to construct fluorescent semiconductor nanocrystals in a wide range of shapes.

> **Frédéric Chandezon*** and **Cécile Reynaud****
Materials Science Division
*CEA Grenoble Centre
**CEA Saclay Centre

A From the macroscopic to the nanoworld, and vice versa...

In order to gain a better idea of the size of microscopic and nanoscopic* objects, it is useful to make comparisons, usually by aligning different scales, *i.e.* matching the natural world, from molecules to man, to engineered or fabricated objects (Figure). Hence, comparing the "artificial" with the "natural" shows that artificially-produced **nanoparticles** are in fact smaller than red blood cells.

Another advantage of juxtaposing the two is that it provides a good illustration of the two main ways of developing nanoscale systems or objects: *top-down* and *bottom-up*. In fact, there are two ways

* From the Greek *nano meaning* "very small", which is also used as a prefix meaning a billionth (10^{-9}) of a unit. In fact, the **nanometre** (1 nm = 10^{-9} metres , or a billionth of a metre), is the master unit for nanosciences and nanotechnologies.

Artechnique

300-mm silicon wafer produced by the Crolles2 Alliance, an illustration of current capabilities using top-down microelectronics.

into the nanoworld: molecular manufacturing, involving the control of single **atoms** and the building from the ground up, and extreme miniaturization, generating progressively smaller systems.

Top-down technology is based on the artificial, using macroscopic materials that we chip away using our hands and our tools: for decades now, electronics has been applied using **silicon** as a substrate and what are called "**wafers**" as workpieces. In fact, microelectronics is also where the "top-down" synthesis approach gets its name from. However, we have reached a stage where, over and above simply adapting the miniaturization of silicon, we also
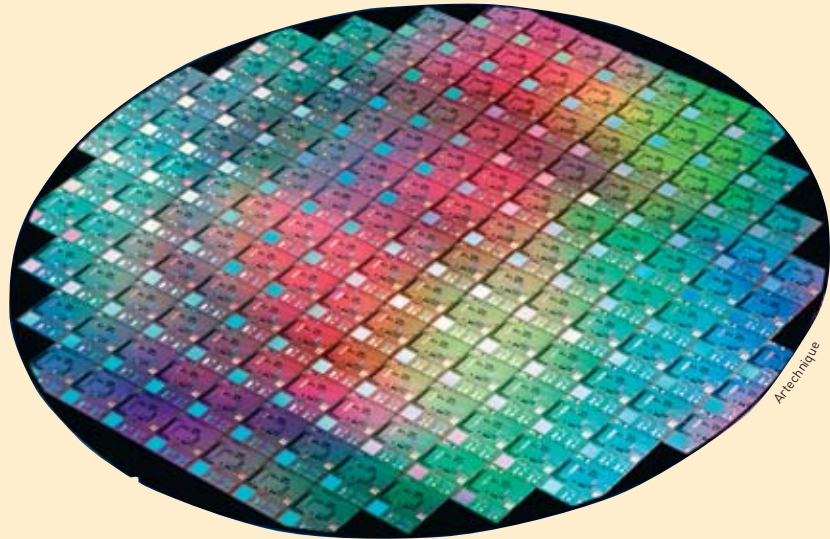
have to take on or use certain physical phenomena, particularly from **quantum** physics, that operate when working at the nanoscale.

The bottom-up approach can get around these physical limits and also cut manufacturing costs, which it does by using component **self-assembly**. This is the approach that follows nature by assembling molecules to create **proteins**, which are a series of amino acids that the super-molecules, *i.e.* **nucleic acids** (**DNA**, **RNA**), are able to produce within cells to form functional structures that can reproduce in more complex patterns. Bottom-up synthesis aims at structuring the material using

"building blocks", including atoms themselves, as is the case with living objects in nature. Nanoelectronics seeks to follow this assembly approach to make functional structures at lower manufacturing cost.

The **nanosciences** can be defined as the body of research into the physical, chemical or biological properties of nano-objects, how to manufacture them, and how they self-assemble by auto-organisazation.

Nanotechnologies cover all the methods that can be used to work at molecular scale to reorganize matter into objects and materials, even progressing to the macroscopic scale.

natural world

bottom-up

molecule
a few Å

DNA ,
3.4 nm

virus,
0.1 μm

red blood cell,
5 μm

pollen grain,
10 μm to 20 μm

a hair, 50 μm
(diameter)

flea,
1 mm

ant,
1 cm

butterfly,
5 cm

man,
2 m

0.1 nm	1 nm	10 nm	100 nm	1 μm	10 μm	100 μm	1 mm	1 cm	10 cm	1 m

nanoworld

10^{-10} m	10^{-9} m	10^{-8} m	10^{-7} m	10^{-6} m	10^{-5} m	10^{-4} m	10^{-3} m	10^{-2} m	10^{-1} m

atome,
0.1-1 nm

quantum dot,
5 nm

nanoparticle,
10 nm

nanotransistor,
20 nm

"Cooper"
transistor,
1 μm

integrated circuit
interconnects,
1 to 10 μm

microsystem,
10 to 100 μm

card chip,
1 cm

mobile phone,
10 cm

private vehicle,
2 m

top-down

artificial world

B A guide to quantum physics

Quantum physics (historically known as quantum mechanics) covers a set of physical laws that apply at microscopic scale. While fundamentally different from the majority of laws that appear to apply at our own scale, the laws of quantum physics nevertheless underpin the general basis of physics at all scales. That said, on the macroscopic scale, quantum physics in action appears to behave particularly strangely, except for a certain number of phenomena that were already curious, such as superconductivity or superfluidity, which in fact can only explained by the laws of quantum physics. Furthermore, the transition from the validating the paradoxes of quantum physics to the laws of classical physics, which we find easier to comprehend, can be explained in a very general way, as will be mentioned later.

Quantum physics gets its name from the fundamental characteristics of quantum objects: characteristics such as the angular momentum (spin) of discrete or discontinuous particles called quanta, which can only take values multiplied by an elementary quantum. There is also a quantum of action (product of a unit of energy multiplied by time) called Planck's cons-
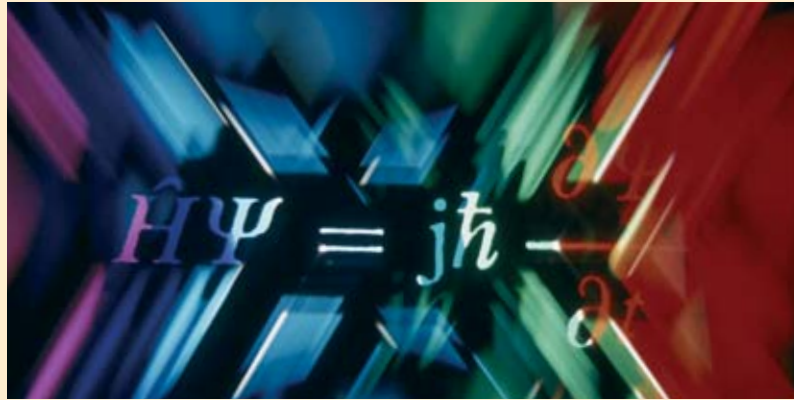
An "artist's impression" of the Schrödinger equation.

D. Sarraute/CEA

tant (symbolized as h) which has a value of 6.626×10^{-34} joule·second.
While classical physics separates *waves* from *particles*, quantum physics somehow covers both these concepts in a third group, which goes beyond the simple wave-particle duality that Louis de Broglie imagined. When we attempt to comprehend it, it sometimes seems closer to waves, and sometimes to particles. A quantum object cannot be separated from how it is observed, and has no fixed attributes. This applies equally to a particle - which in no way can be likened to a tiny little bead following some kind of trajectory - of light (photon)

or matter (electron, proton, neutron, atom, etc.).
This is the underlying feature behind the Heisenberg uncertainty principle, which is another cornerstone of quantum physics. According to this principle (which is more *indeterminacy* than *uncertainty*), the position and the velocity of a particle cannot be measured *simultaneously* at a given point in time. Measurement remains possible, but can never be more accurate than *h*, Planck's constant. Given that these approximations have no intrinsically real value outside the observation process, this simultaneous determination of both position and velocity becomes simply impossible.

At any moment in time, the quantum object presents the characteristic of *superposing* several states, in the same way that one wave can be the *sum* of several others. In quantum theory, the amplitude of a wave (like the peak, for example) is equal to a **probability amplitude** (or probability wave), a complex number-valued function associated with each of the possible sates of a system thus described as quantum. Mathematically speaking, a physical state in this kind of system is represented by a **state vector**, a function that can be added to others *via* superposition. In other words, the sum of two possible state vectors of a system is *also* a possible state vector of that system. Also, the product of two vector spaces is also the sum of the vector products, which indicates **entanglement**: as a state vector is generally spread through space, the notion of local objects no longer holds true. For a pair of entangled particles, *i.e.* particles created together or having already interacted, that is, described by the *product* and not the *sum* of the two individual state vectors, the fate of each particle is linked - entangled - with the other, regardless of the distance between the two. This characteristic, also called *quantum state entan-glement*, has staggering consequences, even before considering the potential applications, such as quantum cryptography or - why not? - teleportation. From this point on, the ability to predict the behaviour of a quantum system is reduced to probabilistic or statistical predictability. It is as if the quantum object is some kind of "juxtaposition of possibilities". Until it has been measured, the measurable size that supposedly quantifies the physical property under study is not strictly defined. Yet as soon as this measurement process is launched, it destroys the **quantum superposition** through the "collapse of the wave-packet" described by Werner Heisenberg in 1927. All the properties of a quantum system can be deduced from the equation that Erwin Schrödinger put forward the previous year. Solving the **Schrödinger equation** made it possible to determine the energy of a system as well as the **wave function**, a notion that tends to be replaced by the probability amplitude.

According to another cornerstone principle of quantum physics, the **Pauli exclusion principle**, two identical half-spin ions (**fermions**, particularly electrons) cannot simultaneously share the same position, spin and velocity (within the limits imposed by the uncertainty principle), *i.e.* share the same *quantum state*. **Bosons** (especially photons) do not follow this principle, and can exist in the same quantum state.

The coexistence of **superposition states** is what lends **coherence** to a quantum system. This means that the theory of **quantum decoherence** is able to explain why macroscopic objects, atoms and other particles, present "classical" behaviour whereas microscopic objects show quantum behaviour. Far more influence is exerted by the "environment" (air, background radiation, etc.) than an advanced measurement device, as the environment radically removes all *superposition of states* at this scale. The larger the system considered, the more it is coupled to a large number of degrees of freedom in the environment, which means the less "chance" (to stick with a probabilistic logic) it has of maintaining any degree of quantum coherence.

c Molecular beam epitaxy

Quantum wells are grown using Molecular Beam Epitaxy (from the Greek *taxi*, meaning order, and *epi*, meaning over), or MBE. The principle of this physical deposition technique, which was first developed for growing III-V semiconductor crystals, is based on the evaporation of ultra-pure elements of the component to be grown, in a furnace under ultra-high vacuum (where the pressure can be as low as $5 \cdot 10^{-11}$ mbar) in order to create a pure, pollution-free surface. One or more thermal beams of atoms or molecules react on the surface of a single-crystal wafer placed on a substrate kept at high temperature (several hundred °C), which serves as a lattice for the formation of a film called epitaxial film. It thus becomes possible to stack ultra-thin layers that measure a millionth of a millimetre each, *i.e.* composed of only a few atom planes.

The elements are evaporated or sublimated from an ultra-pure source placed in an **effusion cell** (or Knudsen cell; an enclosure where a molecular flux moves from a region with a given pressure to another region of lower pressure) heated by the Joule effect. A range of structural and analytical probes can monitor film growth *in situ* in real time, particularly using surface quality analysis and grazing angle phase transitions by LEED (*Low energy electron diffraction*) or RHEED (*Reflection high-energy electron diffraction*). Various **spectroscopic** methods are also used, including Auger **electron** spectroscopy, secondary **ion** mass spectrometry (SIMS), **X-ray** photoelectron spectrometry (XPS) or **ultraviolet** photoelectron spectrometry (UPS).
As *ultra-high-vacuum* technology has progressed, molecular beam epitaxy has branched out to be applied beyond III-V semiconductors to embrace metals and insulators. In fact, the vacuum in the growth chamber, whose design changes depending on the properties of the matter intended to be deposited, has to be better than 10^{-11} mbar in order to grow an ultra-pure film of exceptional crystal quality at relatively low substrate temperatures. This value corresponds to the vacuum quality when the growth chamber is at rest. Arsenides, for example, grow at a residual vacuum of around 10^{-8} mbar as soon as the arsenic cell has reached its set growth temperature.
The pumping necessary to achieve these performance levels draws on several techniques using ion pumps, cryopumping, titanium sublimation pumping, diffusion pumps or turbomolecular pumps. The main impurities (H_2, H_2O, CO and CO_2) can present partial pressures of lower than 10^{-13} mbar.