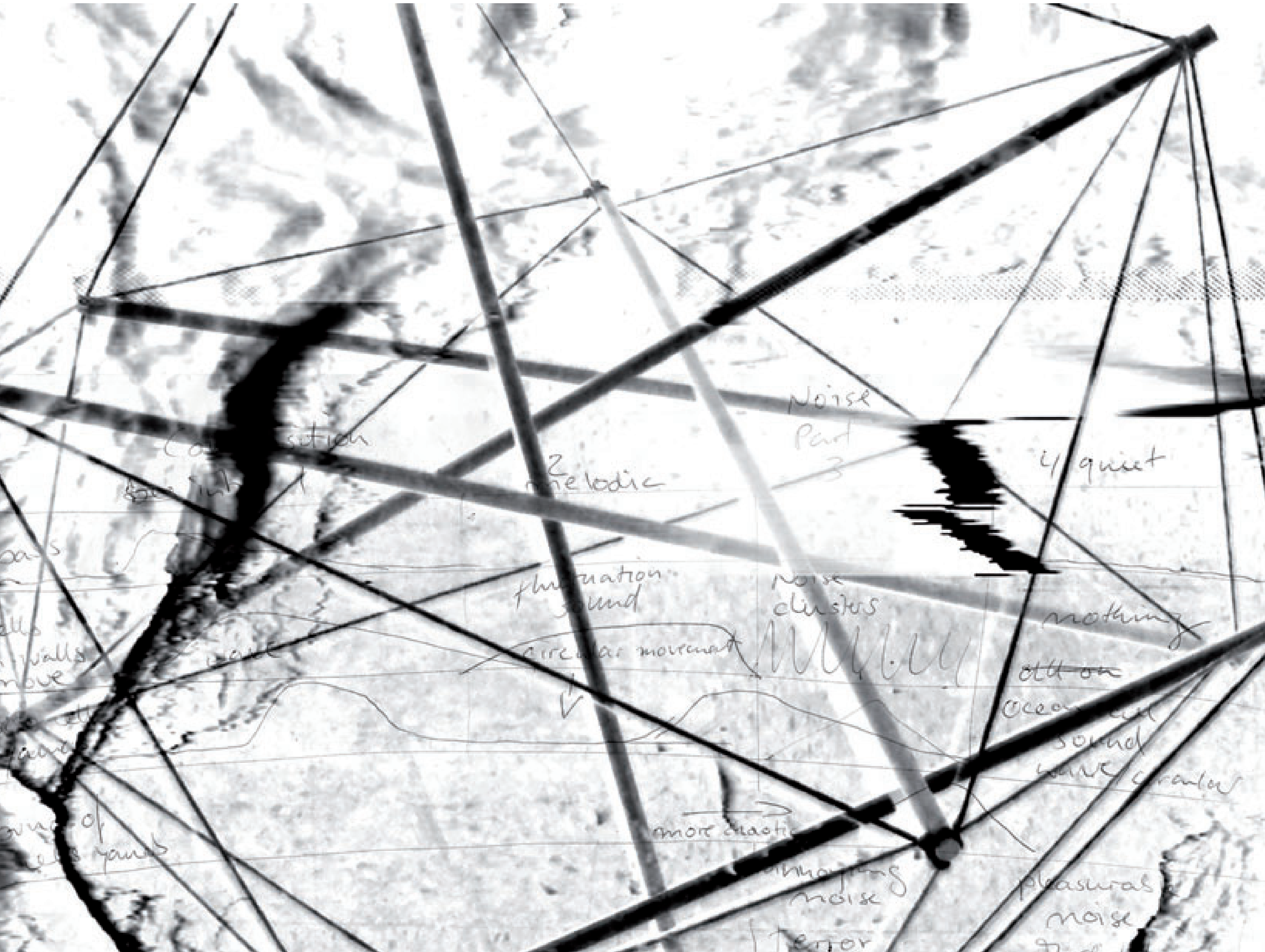



Anne Niemetz and Andrew Pelling. *Composition*, 2009. Digital collage, 30 x 22.5 cm.

# TININESS MAKES A HUGE IMPACT

## SEMICONDUCTING AND METALLIC NANOPARTICLES

Juan Martínez-Pastor, Guillermo Muñoz-Matutano and Rafael Abargues López

Defying the conventions of linguistic repetition, the prefix *nano* springs up in all languages with unusual force. Nanostructure, nanofibre, nanocrystals, nanowires, nanotubes, nanodevice… These are just a few examples, although you won't find them in the dictionary. These words have retained some meaning of the root from which they are derived, but should inescapably be contemplated, at best, as distant metaphorical reflections. The words *nanoparticle* and *nanocrystal* will be the focus of this article: What are nanoparticles? When is a nanoparticle a nanocrystal? When is a nanoparticle a quantum dot? What applications can we expect if they are semiconducting or metallic?

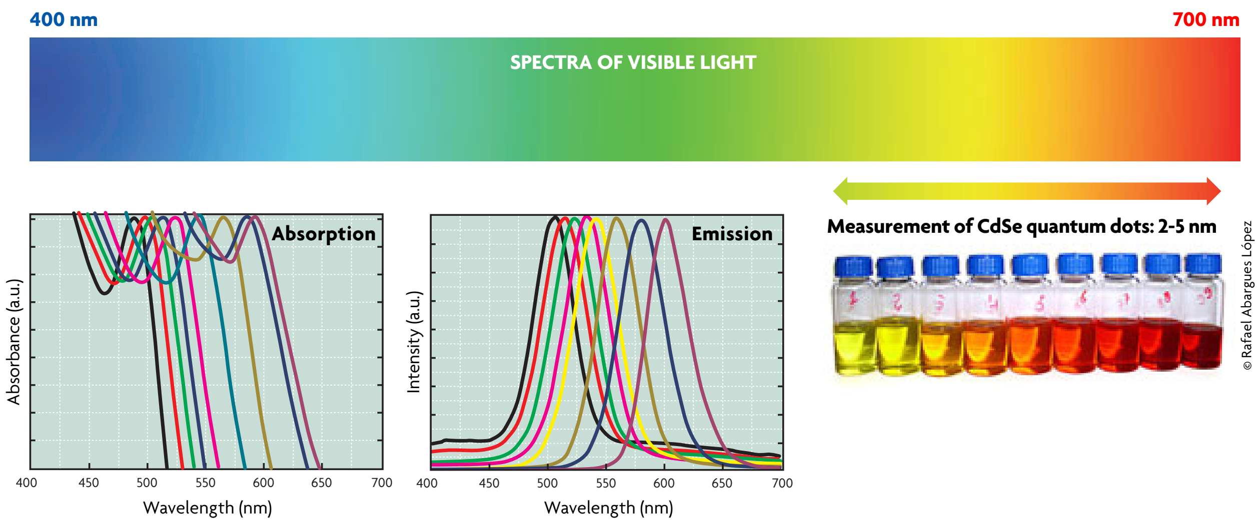
To define a word is to mirror its history, its use and the expectations it awakens. Quite a challenge in so few letters. Although there is no clear date marking the spark that triggered the nanotechnological race, today the nanoscopic world is gathering an awesome pace. One of the milestones most often cited is Scanning Tunnelling Microscopy (STM), developed by Binnig and Rohrer in 1981, which in turn gave rise to other microscopy techniques such as Atomic Force (AFM) and Near-field Scanning Optics (NSOM). STM was achieved by manipulating atoms one by one, bringing a new landscape into view: nanotechnology as a bottom-up approach, a procedure that starts off with small elements to build complex systems, to construct atomic aggregates and more complex materials.

However, accounts of the history of nanotechnology often forget research that took place throughout the twentieth century, for instance in the fields of inorganic chemistry, thermodynamics and surface physics. These disciplines provide the scientific foundations of growth methods and the development of many nanoconstructions, as is the case of nanoparticles. Depending on the fabrication procedure, the external parameters (pressure and temperature) and the electronic structure of the atoms, they will join together to form nanoparticles. If atoms group to form a particle size of between 1 and 10 nm, these are also known as *nanoclusters*. If the atoms are arranged in crystalline order, they are called *nanocrystals* and if they are deposited on semiconductor substrates, they are referred to as *nanostructures*.

Furthermore, if the nanocrystals are semiconductive or metallic in nature, with sizes small enough to give rise to quantum confinement of the valence electrons, the term most widely used is quantum dots. We could say that nanoparticles are a kind of «go-between», through which we can relate the properties of the nanoscopic world with perceptible effects on human beings, in a controlled and orderly way.

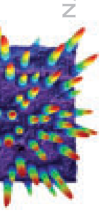
**«NANOPARTICLES ARE A KIND OF "GO-BETWEEN", THROUGH WHICH WE CAN RELATE THE PROPERTIES OF THE NANOSCOPIC WORLD WITH PERCEPTIBLE EFFECTS ON HUMAN BEINGS, IN A CONTROLLED AND ORDERLY WAY»**

The characteristics of light absorption and emission from nanoparticles can help us understand this path to controlling their properties. Any physical system, on surpassing the energy-balance tipping-point, tends to bounce back spontaneously. One way to disrupt a material to the point of imbalance is via light irradiation. Light is energy, and materials that can absorb this energy are thus brought to a state of imbalance. In certain materials, excess energy is converted into new light emission, going through an internal energy-loss process such that the emitted light differs in colour




On the right, a photo of colloids (particle suspensions in a liquid, like coffee for instance), each vial contains cadmium selenide semiconductor nanocrystals of different sizes. Each colloid contains nanocrystals of the same material but of different nanometric sizes (in the 2-5 nm range), which, in turn, correspond to differences in the colour of light they emit. Not only do the optical properties of nanoparticles depend on their size or shape, but so too do other physical (e.g. electrical and magnetic) or chemical (catalytic activity) properties. On the left, absorption and emission spectra of light in each colloid.





from the absorbed light. Normally, the characteristics of a material are linked to its composition, organization of its internal structure, etc.

The colour of light would not change so much if seen at one $cm^2$ of material as it would if seen at one $mm^2$, for example. But, what happens if we cut the size of our material down to a few nanometres? Indeed, the fact there is a direct relationship between a material's properties and its size comes as a great surprise: the colour of the material depends on the size of the particle. The changes that occur are of great importance in the scientific and technical domain, because the properties of materials can even be enhanced or augmented by reducing their dimensions below a certain size. For example, from the chemical viewpoint, the active surface of a material composed of nanoparticles will increase as its size decreases, thus increasing the catalytic activity of the material. Maximum catalytic performance is limited by the minimum size of the nanocluster, in which all the atoms determine the surface.

«THE FACT THERE IS A DIRECT RELATIONSHIP BETWEEN A MATERIAL'S PROPERTIES AND ITS SIZE COMES AS A GREAT SURPRISE»

## SEMICONDUCTOR NANOPARTICLE REVOLUTION

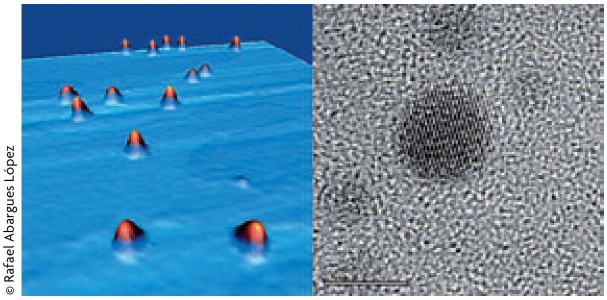
During the eighties, semiconductor research focused most of its efforts on the miniaturization of materials. It managed to reduce the thickness of thin semiconductor films via atomic resolution control using the MBE (Molecular Beam Epitaxy) technique, generating what was labelled a quantum well. The outcome of this thinning was that the outermost electrons of the atoms of the material were confined in that direction.

It was found that via this quantum confinement effect, as it came to be known, the wavelength of emitted light could be controlled just by increasing or decreasing the thickness, which led to the development of the first 780 nm laser diode for recording and reading CDs.

Later, structures were formed in which quantum confinement occurred in two spatial directions or even in three (using epitaxy techniques, in the case of nanostructures, and chemical synthesis, in the case of nanocrystals). The latter nanostructures and nanocrystals, which confined electrons in a nanoscopic volume, are called *quantum dots*.

Not only does the light emitted by quantum dots have the characteristic that it synchronizes as the size changes, but also resembles that emitted by the atoms themselves. We could say that their optical properties are similar to those of atoms, having come to be called artificial atoms, which can be synthesized or prepared in the lab at will.

Semiconductor nanocrystals are chemically synthesised using the method developed by La Mer and Dinegar in 1950. Via this procedure, nanoparticle precursors are injected above a critical temperature, leading to nucleation, and then cooled to the growth temperature at which nucleation is much less favoured. This process takes place in the presence of a chemical, normally organic, called a *ligand,* which controls and limits nanocrystal growth. The ligands are attached to the surface of these and determine the chemical properties of the nanoparticle, such as solubility (to keep them in colloidal form, for example) and their reactivity with other molecules (proteins, DNA, etc.), which is of great importance for nanomedical applications.



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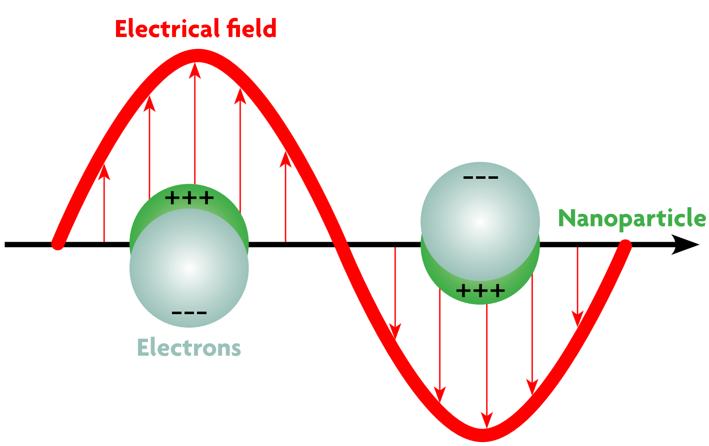
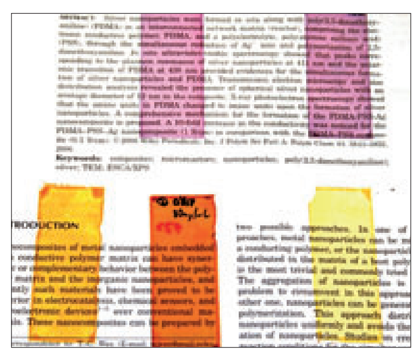
On the left, semiconductor nanostructures (quantum dots) of indium arsenide deposited on a gallium arsenide substrate by Molecular Beam Epitaxy (MBE image). On the right, Transmission Electron Microscopy (TEM) image of a gold crystal nanoparticle or nanocrystal (diffraction on atomic planes can be observed).

## METALLIC NANOPARTICLES LINKING PAST AND PRESENT

Light absorption in noble metal nanoparticles takes place via a physical mechanism which differs to that of quantum dots. In this case, light absorption and scattering is not defined by the quantum confinement effect of the electrons in the nanoparticle, but rather by the effect of the interaction of light with the collective vibration of free electrons. When light hits the nanoparticles, the area of the spectrum whose frequency is conducive to collective vibration, causes a resonance in the absorption of light. This peculiar oscillation of the electrons, together, has been called *plasmon* while the phenomenon of resonance with light is known as *Localized Surface Plasmon*

**«NOT ONLY DOES THE LIGHT EMITTED BY QUANTUM DOTS HAVE THE CHARACTERISTIC THAT IT SYNCHRONIZES AS THE SIZE CHANGES, BUT ALSO RESEMBLES THAT EMITTED BY THE ATOMS THEMSELVES»**



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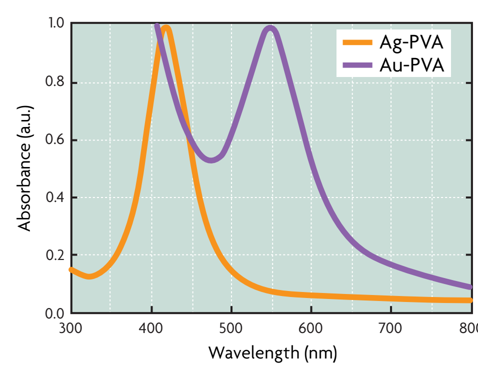
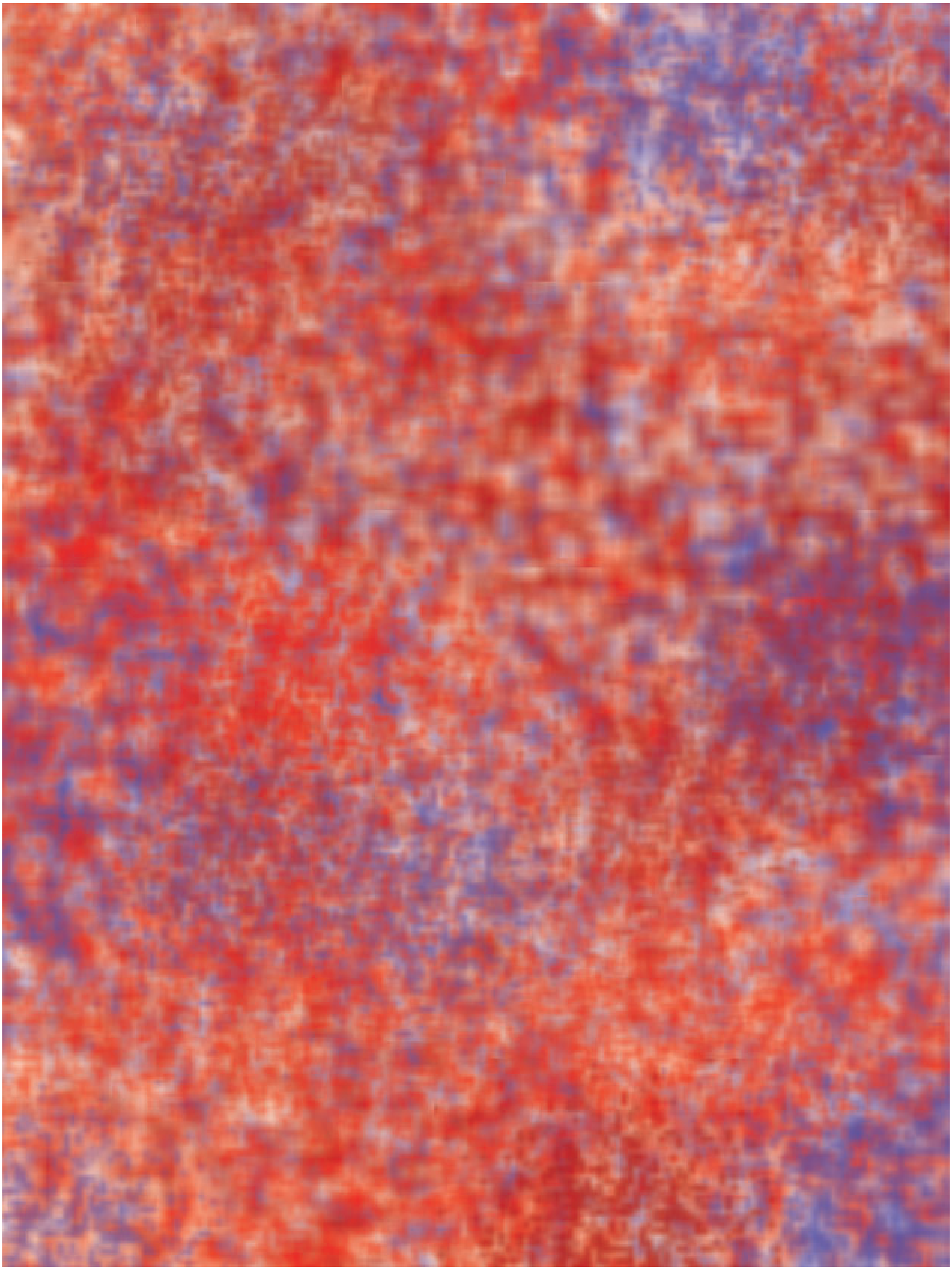



When light shines on noble metal nanoparticles, the area of the spectrum whose frequency favours this collective vibration prompts a resonance in light absorption. This vibration is known as *plasmon* while the light resonance phenomenon is termed *Localized Surface Plasmon Resonance* (LSPR) effect. On the left, diagram representing the LSPR effect, showing the oscillation of free electrons in the metallic nanoparticle in phase with the electromagnetic field of light. Top right, photo of two polymer layers containing spherical nanoparticles of silver (yellow) and gold (magenta), and below, absorption spectra explaining these colours under transmitted light (*i.e.*, in the case of silver nanoparticles, which absorb/scatter blue light, letting the rest of the visible spectrum pass).



Hugo Martínez-Tormo. *Nanopaper,* 2010. Digital creation, 21 x 28 cm.

Trustees of the British Museum

The Lycurgus Cup (fourth century AD), which is held at the British Museum, contains gold nanoparticles dispersed within the glass, causing the colour to change on interacting with light. On the left, the effect of light scattering on the cup's surface emits green hues. On the right, the effect of light shining through the glass, in which case the LSPR effect produces a reddish glow.

*Resonance* (LSPR) effect. This strong resonance causes nano-scale gold and silver particles to appear reddish and yellowish in colour, respectively, when light passes through them (transmitted light) provided their shape is spherical. The use of gold nanoparticles dates back some 1700 years, as witnessed by the Lycurgus cup, preserved in the British Museum. It would appear that Faraday was the first, in 1857, to try to explain that the red colour of the gold present in the stained glass windows of churches was associated with an effect of size, although he was unable to prove it. However, this was proven by Mie fifty years later in Germany. Faraday was also the first to synthesize gold colloid nanoparticles in the laboratory, using a reduction reaction of $AuCl_4$ ions with phosphorus.

During the next two decades, similar reactions were used to develop photographic plates (based on silver halide emulsions), whose pixels were just silver nanoparticles produced in these reduction reactions favoured by light exposure. At present, there are a host of chemical and physical methods used to synthesise these types of nanoparticles, each being more or less appropriate depending on the final application.

## FROM NANOHOSPITAL TO INTELLIGENT MEDICINES

In the coming years, the marriage of microelectronics and photonics with nanochemistry and biotechnology may lead to important progress in intelligent systems on-chip technology, both from the viewpoint of measurement and medical diagnosis. It has been shown that biomolecules of interest can be identified down to a single molecule when labelled with fluorescent nanoparticles under high-resolution optical microscopy. Currently large external microscopes are used, as well as laser excitation and complex detection systems, so efforts are being directed towards miniaturization of these optical systems and their integration into functional chips. Moreover, nanoparticles themselves can also be used as biomarkers in high sensitivity imaging techniques for biomedicine, such as those needed for early detection of cancerous tumours.

Both metallic and semiconductor nanoparticles have been proposed as physical systems for use in biomedicine (or nanomedicine) with a view to developing screening techniques for early detection.

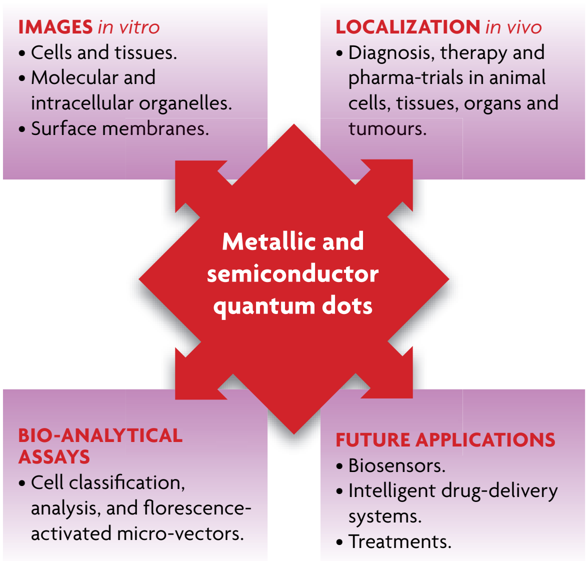



Figure outlining the applications in the field of biology, biomedicine or nanobiomedicine, based on the control and use of semiconductor and metallic quantum dots.

The wavelength range 600-1000 nm is important when using semiconductor nanoparticles as biomarkers, as this is where human tissue is the most transparent. In this range CdSe, CdTe, PbS, PbSe or PbTe quantum dots of the appropriate diameter could be used. The use of heavy metals in these applications is not significantly hazardous because most of the nanoparticles used in a trial would be eliminated. Nanoparticles that are not deposited in the infected cells would be eliminated through the body's excretory system. Those that are deposited would be eliminated during therapy along with the diseased cells. Furthermore, significant progress is being made in the encapsulation of semiconductor nanoparticles using a coating of some hundred nm of $SiO_2$, which is not harmful to the body. The increase in size produced by this envelope greatly reduces the probability that a cell can *swallow* it, which diminishes the danger and toxicity of nanoparticles in the human body to almost zero. The use of nanoparticles in this field goes hand in hand with the development of molecular markers which are suitable for the recognition of diseased cells, as well as others that serve to anchor these cells, once found, without losing their luminescent properties. All these strategies are difficult to achieve using conventional molecular architecture, hence the boom in the use of nanoparticles in nanobiomedicine.

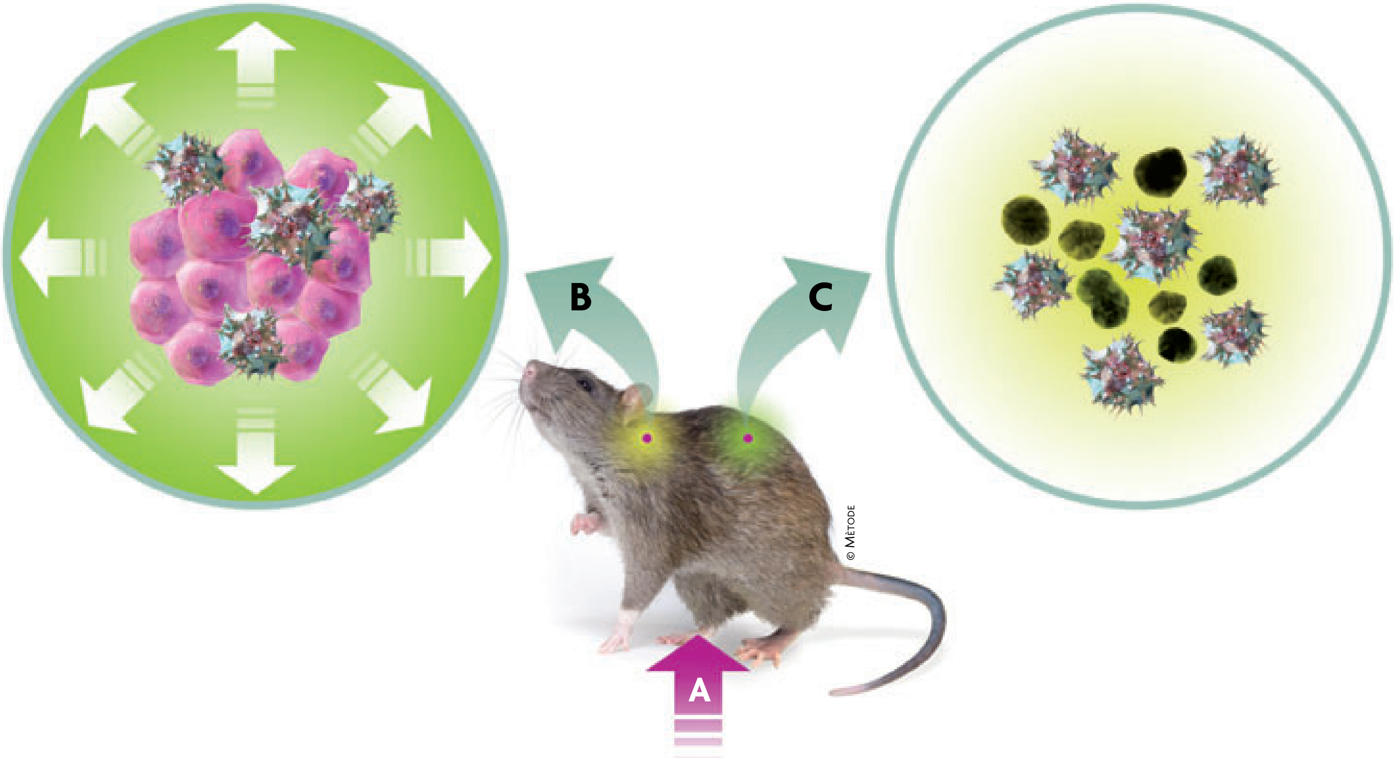
While the free surface of metallic nanoparticles is already the base for catalysis, the effects described for resonant interaction with light are of great interest in various fields of application, such as bioassays *in-vivo*/*in vitro* (biosensors), diagnosis *in vivo* and cancer therapy. In this case the idea is to incorporate cancer-cell recognition molecules within the metallic nanoparticles and, once anchored in them selectively, on controlling reactivity, scan the identified area with a laser whose wavelength is resonant with surface plasmon (LSPR effect). If this wavelength is not absorbed by other tissues it would be possible to develop non-surgical therapies. When laser light of appropriate wavelength is focussed on the nanoparticle-treated area, the light that is scattered/absorbed by these is transformed into heat, with temperature increases of up to 80 ºC. This local increase in temperature would kill the cancer cells that have nanoparticles bound to them.

## LIGHT AS A SOCIAL CURRENT

Semiconductor technology has been, and still is, the basis for most devices and technologies that relate the fields of optics and electronics. Currently, some of them are based on miniaturization in one of the spatial directions, as in the case of light-emitting diodes and lasers, and some types of photodetectors and even solar cells based on quantum dots (still under development). Nowadays, thoughts are turning to how to build new devices that incorporate the advantages of using quantum dots. Significant progress has been made in the construction of nano-LEDs (Light-Emitting Diodes), although this technology is still far from being well established.

Something similar is happening in the field of photodetection and solar cells, in which the Bawendi group at MIT is one of the most active, besides being a pioneer in the synthesis of CdSe nanocrystals and their application in optoelectronics. The idea behind these devices is to enclose a layer of quantum dots, measuring just a few tens of nm, between electrodes suitable for injection or transport of electrons and holes. In a nano-LED device, electron-hole pairs that give rise to photons (light) are electrically injected through these electrodes.

«THE MARRIAGE OF MICROELECTRONICS AND PHOTONICS WITH NANOCHEMISTRY AND BIOTECHNOLOGY MAY LEAD TO IMPORTANT PROGRESS IN INTELLIGENT SYSTEMS ON-CHIP TECHNOLOGY»




Application of anti-cancer imaging and therapy *in vivo* in a mouse, which has assimilated semiconductor nanoparticles and metallic nanoparticles. The laser light (A) reaches two zones of the mouse. In Zone B, we can see how semiconductor nanoparticles with cancer-cell-sensitive ligands can bind to a tumour, so that the incident laser light will lead to the luminescence of semiconductor nanoparticles, thus enabling the malignant tumour to be located. In Zone C we can see how the metallic nanoparticles, which can also be anchored to a tumour, can cause increased local temperature (shaded yellow) triggered by the plasmon interaction with laser light (A) and this increase in temperature can destroy the tumour.



In the case of photodetectors or solar cells, electron-hole pairs are generated in the quantum dots when they absorb the incident light and on applying an electric current between the electrodes, the positive and negative charges should be pulled and separated, thereby feeding an external circuit. The simplicity and low manufacturing costs represent an advantage of this and similar technology using polymer-nanoparticle *composites* or organic-inorganic hybrid materials. There is still much ground to cover before achieving the desired goal, but huge progress is to be expected.

Nanoparticles. A simple word linking past, present and future, tracing a continuous and trans-disciplinary path throughout history; spanning more than 1700 years –from the Greek myths, embodied in the Lycurgus cup, through the golden glow of Paterna ceramics to highly futuristic applications in nanobiomedicine.

Research in this field points towards alluring prospects for physicists, chemists, biologists, physicians or engineers, and even for specialists in the area of humanities and art; research that opens up a window through which to gaze upon the nanoworld.

As in the stained-glass windows of the old medieval cathedrals, the light shining through this metaphoric window might project a far richer, more varied society with greater opportunities. Not only will this depend upon technicians and specialists, but also on every eye that is able to perceive the mysterious and powerful light glowing from nanoparticles.

BIBLIOGRAPHY

Edwards, S. A., 2006. *The Nanotech Pioneers*. Wiley-VCH. Weinheim.

Faraday, M., 1857. «The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light». *Philosophical Transactions of the Royal Society of London*, 147: 145-181.

La Mer, V. K. & R. H. Dinegar, 1950. «Theory, Production and Mechanism of Formation of Monodispersed Hydrosols». *J. Am. Chem. Soc.*, 72: 4847-4854.

Mie, G., 1908. «Beiträge zur optik trüber Medien speziell kolloidaler Metallösungen». *Ann. Phys.*, 25: 377.

Ozin, G. A. *et al.*, 2005. *Nanochemistry: A Chemical Approach to Nanomaterials*. The Royal Society of Chemistry. Cambridge.

Schmid, G. (ed.), 2004. *Nanoparticles: From Theory to Application*. Wiley-VCH. Weinheim.

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