Researchers unveil mechanism to obtain metal 'nanoscrews'

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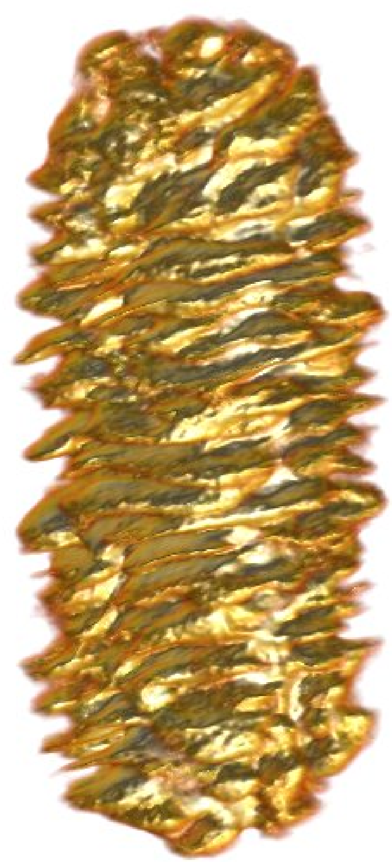

3D visualizations (obtained by electron tomography) of gold nanoparticles with chemically-grown quasi-helical (chiral) features, which provide them with a peculiar ability to interact with circularly polarized light. Credit: Adrián Pedrazo Tardajos, University of Antwerp.

Led by the Ikerbasque professor Luis Liz-Marzán, researchers at the Centre for Cooperative Research in Biomaterials CIC biomaGUNE have developed a mechanism by which gold atoms are deposited by means of chemical reduction onto previously formed gold nanorods to produce a quasi-helicoidal structure (the particles acquire chirality). This geometry enables these "nanoscrews" to interact with circularly polarized light much more efficiently than what is achieved with any other known object. These properties could lead to the detecting of biomolecules in a very selective and very sensitive way. What we have here is a versatile, reproducible mechanism that is scalable for the fabrication of nanoparticles with strong chiral optical activity. This piece of research has been published in the prestigious scientific journal *Science*.

There are many fields in which the interaction between light and material is used to detect substances. Basically, light shines on the material and is absorbed or reflected either very brightly or very selectively, depending on the size and geometry of the particle and the type of incident light. The research group led by Luis Liz-Marzán, which works in the field known as nanoplasmonics, uses nanoparticles of noble metals, such as gold or silver, "because light interacts in a special way with particles of this type and size," explained Liz-Marzán, Scientific Director of CIC biomaGUNE. "In this case, we studied the interaction between these chiral gold nanoparticles and circularly polarized light."

Light is not normally polarized, in other words, the waves expand in practically any orientation within the beam of light. "When it is polarized, the wave only goes in one direction; when it is circularly polarized the wave rotates, either clockwise or anti-clockwise," added the researcher. "Chiral substances tend to absorb light with a specific circular polarization, rather than light polarized in the opposite direction."

Chirality is a phenomenon that occurs on all scales: a chiral object cannot have its mirror image superimposed on it; for example, one hand is the mirror image of the other, they are identical, but if one is superimposed on the other, the position of the fingers does not coincide. The same thing occurs "in some biomolecules; and the fact that a molecule cannot be superimposed on its mirror image gives rise to many biological processes. For example, some diseases arise due to the loss of recognition of one of the two forms of the chiral substance that is responsible for a specific action," said Liz-Marzán.

Three-dimensional fabrication onto a nanometric object

As the Ikerbasque professor explained, "what we have done is look for a mechanism to guide the deposition of gold atoms onto nanoparticles fabricated in advance in the form of a rod so that these atoms are deposited according to a practically helicoidal structure, a kind of 'nanoscrew." That way the particle itself acquires a chiral geometry. This new strategy is based on a supramolecular chemical mechanism, in other words, on structures obtained through molecules associating with each other without forming chemical bonds." Liz-Marzán asserts that "this really means being able to control the structure of the material on a nanometric scale, but inside one and the same nanoparticle; in other words, it involves three-dimensional fabrication on top of a nanometric object. In actual fact, it is almost like deciding where they have to be positioned atom by atom to obtain a structure that is truly complicated."

To make these nanoparticles grow, "the cylindrical particles are surrounded by soap molecules, by a surfactant. In the middle of the ordinary soap molecules we have placed additives with molecular chirality, so that the supramolecular interaction causes them to become organized on the surface of the metal rod with an almost helicoidal structure, in turn guiding the growth of the metal with that same structure which gives it the chirality we are seeking. As a result, we can practically obtain the greatest efficiencies ever achieved in spectrometric detection with circularly polarized light."

Liz-Marzán confirmed that the process can be generalized to other types of materials: "We have seen that when the same strategy is applied, platinum atoms can be deposited onto gold nanorods with the same helicoidal structure. A whole host of possibilities is thus opened up both in applications of their optical properties and in others in the field of catalysis (platinum is a very efficient catalyst). At the same time, it could lead to a huge improvement in the synthesis of chiral molecules that would be of biological and therapeutic importance." This mechanism could also be applied to new biomedical imaging techniques, for the manufacture of sensors, etc. "We believe that this work is going to open up many paths for other researchers precisely because of the generalization of the mechanism that can be used with many different molecules. A lot of work lies ahead," he said.

The research was conducted and coordinated by CIC biomaGUNE, but they had the collaboration of research groups from other organizations. These include the Complutense University of Madrid (computer calculations showing the formation of the helicoidal structures when the two types of surfactants are blended), the University of Vigo and the University of Extremadura (theoretical calculations of the optical properties of the particles), and the University of Antwerp (obtaining of three-dimensional electron microscopy images and the animated reconstructions of the particles fabricated).

Mapping nano chirality in three dimensions

Essential to understanding the behavior of these complex nanoparticle assemblies is to intimately understand their structure. When handling such intricate three-dimensional morphologies, imaging in two dimensions simply will not do. The EMAT team lead by Prof. Sara Bals at the University of Antwerp is the world leading electron microscopy group for imaging nanoparticles in three dimensions. By taking a series of two-dimensional images collected at many viewing angles they can be combined with specially designed computer code to generate a three-dimensional representation of the particle. This is the so-called transmission electron tomography method, which is an essential tool in nanoscience, helping researchers from around the world to visualize nanoparticles and understand their structure and how they are formed.

The EMAT team has gone one step further to understand the origin of the chiral properties these unprecedented nanorods display. By developing a method to study the three-dimensional periodicity of the individual particles using a 3-D Fast Fourier Transform on the tomography previously obtained, repetitive patterns have been discovered in the structure. "The nanoparticles appeared to show a long-range chiral structure, but how can we identify this in a meaningful way to understand the nanoparticle's properties?" asks Prof. Bals. By mapping the periodic structure using this technique, a characteristic X-shape appeared within the 3-D FFT pattern. Scientists have seen this characteristic fingerprint before; in the revolutionary X-ray diffraction experiment leading to the discovery of the most known chiral structure—our DNA.

Using that characteristic pattern as an input, regions in the reconstruction with helicoidal features were identified. In addition, "Our developed technique not only allows us to identify a chiral structure, but can also tell us the chiral handedness of each individual nanoparticle," says Prof.

Bals.

The preparation and characterization of such complex chiral nanoparticles is an important step in reaching a key scientific milestone. It was once believed that the complexity of biological superstructures could not be artificially prepared. However, with increasing understanding of nanostructure design and growth, scientists can prepare atom-by-atom designed materials that are tailor-made for a desired application, and in doing so—continuously push the frontier of material design.

More information: Micelle-directed chiral-seeded growth on anisotropic gold nanocrystals. *Science* (2020). science.sciencemag.org/cgi/doi … 1126/science.aba0980

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