

## NANOWORLD in 3-D

By *Antonio Torrisi*

The 3-D version of James Cameron's last movie, "Avatar", has been considered a breakthrough in the cinematographic world and I, personally, still remember the strong impact of the experience of watching this film at the IMAX-3D cinema. The 3-D movies must all be grateful to the advent of stereoscopic photography, which dates back to 1838, when Sir Charles Wheatstone invented the first 3-D stereoscope. Stereoscopy creates an illusion of depth by using eyeglasses to combine two perspectives (2-D images) which differ by a minor deviation. Although it has only recently been applied for entertainment and in photogrammetry, its basic principles were already noted by the Greek Mathematician Euclid in 300 BC. As beautiful as it can be, it also reveals the great capacity for illusion in the human brain.

Interestingly, 3-D imaging is not limited only to cinema and photography. Another field in which vision is crucial and where 3-D imaging is fascinating and of enormous importance is electron microscopy. 3-D imaging is very important to study the world of nanoparticles, which consists of clusters of fifty to a few hundred atoms. Last February, a team of scientists from The Netherlands, Switzerland and Belgium, led by Gustaf Van Tendeloo and Kees J. Batemburg, succeeded in building a 3-D view of crystalline nanoparticles with a diameter of about 2 nm, reaching atomic resolution (Van Aert *et al.* 2011). This means that they not only successfully recreated the 3-D structure of the nanocluster, but could also count and distinguish individual atoms within the nanocluster and resolve their relative positions and distributions. The nanoclusters consist of silver atoms and are embedded in a matrix of aluminium. Using a particular type of electron microscopy technique called High-Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM), the group obtained high quality 2-D images of the silver nanoclusters, managing to distinguish the nanoclusters from the aluminium matrix. Combining the extremely high atomic resolution of the 2-D recorded images with the use of statistical analysis of the intensities of the spots corresponding to the atoms, they were able to distinguish the silver atoms inside the 2-D image of the cluster and, more importantly, to count the number of silver atoms along the atomic columns below each of the atoms observed in the 2-D image. Using this information and a mathematical method called discrete tomography the group was able to reconstruct the 3-D image of the nanocluster from a few recorded 2-D images at different orientations and could establish the position of each silver atom in the cluster with a confidence of 97%. The 3-D images are illustrated in Figure 1.

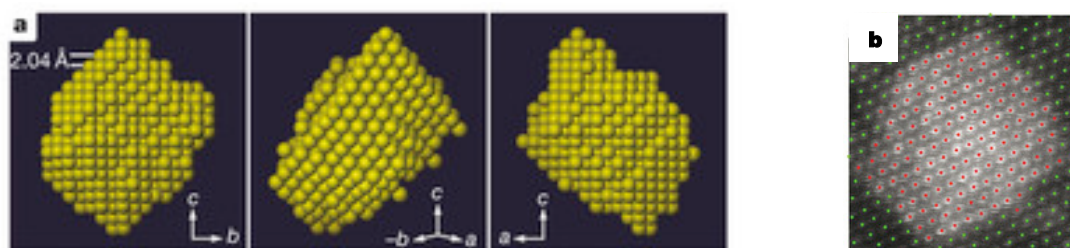


Figure 1. (a) The computed 3D reconstruction of the silver (Ag) nanocluster viewed along three different directions. (b) Magnification of the experimental HAADF STEM image of nanosized Ag clusters embedded in an aluminium (Al) matrix. Columns containing Ag are indicated by red markers. Images credit Nature (Van Aert *et al.* 2011).

This result is very exciting because it is the first time that atomic resolution has been achieved in 3-D imaging of particles. The road leading to this great success is a fascinating story which is worth being briefly recounted.

In the 17<sup>th</sup> century, scientists were able to see the microscopic world – from bacteria to viruses – for the first time, with the invention of optical microscopy by Anton Van Leeuwenhoek, extracting a huge amount of knowledge which set the fundamentals of modern biology. The optical microscope has a magnification power and resolution capability which allows us to see down to a few micrometers ( $10^{-6}$  m). This is still very far from the ability to see the ‘objects’ populating the nanoworld, such as proteins, macromolecules, nanoclusters and nanowires, not to mention molecules or single atoms. Typical dimensions in the nanoworld are of the order of nanometers ( $10^{-9}$  m); the ability of seeing a nanocluster (a cluster of 60-100 atoms) of, say, aluminium in 1 m of kitchen foil is equivalent to the possibility of recognising Murray and Federer playing a tennis match looking at an image of the Earth from the International Space Station. An optical microscope does not have sufficient power of magnification, nor of resolution.

This is fundamentally due to the fact that visible light has a limiting wavelength of about 400 nm, which is larger than the dimensions of nanoparticles and other objects in the nanoworld. According to quantum mechanics, a particle of extremely small dimensions (e.g. an electron or a proton) is not only an object with an associated mass but can undergo a sort of metamorphosis, which enables it to behave as a wave; the converse also applies. This theory not only predicts that light can behave as a train of particles (photons), but also implies that electrons can behave as waves. In 1927, the physicist De Broglie published his hypothesis that electrons possess a wavelength which is closely related to its velocity. This wavelength appeared to be 10,000 times smaller than the wavelength of visible light. A few years later, in 1933, following the work on cathode ray (electron) oscilloscopes at the Technological University in Berlin, Ernst Ruska developed the first Transmission Electron Microscopy (TEM) that had greater resolution than optical microscopy, of the order of a few nanometers: the electron microscopy had opened the doors to the nanoworld.

The TEM is a very complex instrument, which is schematically and fundamentally very similar to the optical microscope, but much more flexible and powerful. The structure consists of vertical columns as illustrated in Figure 2. The main character is no longer light, but electrons, which are produced via thermo-ionic effects in a metallic filament; very strong heating results in the extraction of electrons from the metal. The electrons are formed into an electron beam by utilising the fact that electrons can interact with electric and magnetic fields. Electromagnetic fields can also be used to manipulate the electron beam, focusing it on the sample or to correct eventual beam distortions. The beam interacts with the sample located approximately in the centre of the column and it can be magnified, corrected and finally expanded onto the imaging screen. The interpretation of TEM images is far more complex than those from an optical microscope; in fact, they are the result of the interaction of the electron wave-function and the sample, which can change either in intensity or in phase.

The information provided by TEM is typically related to crystal structure, crystal plane distances, and presence of defects. All of these features are clearly visible within the resolution limits of 200 picometers ( $1\text{pm} = 10^{-12}$  m). Because the atomic dimensions are typically on the order of a few ångströms ( $10^{-10}$  m), atomic resolution was not possible. For decades, TEM resolution was limited by the presence of spherical and chromatic aberrations: the first is due to an excess of refraction of the electron beam when this hits the sample at the edge, while chromatic aberration is due to a failure to focus all the electrons in the beam to the same converging point. Only in 2002-2003 were these aberrations fully corrected and sub-ångstrom atomic resolution achieved (Batson, Dellby, Krivanek 2002).



Figure 2. Example of a typical TEM with voltage of 200 kV.

In the meantime, mathematicians since the 1980s have been developing the field of discrete tomography. Beginning from a few 2-D projections, it aims to reconstruct 3-D images by processing them in thousands of units (pixels) and using iterative binary algorithms, in which only values of either 0 or 1 are assigned to each pixel (Batenburg 2006). The more complex the image, the more accurate and fast the reconstruction. In the case of very complex images, the accuracy strongly depends on the number of projections used. A fundamental procedure for the 3-D image reconstruction is the recording of a series of projections of the sample at different orientations. This is achieved by tilting the sample at a range of angles. This is still limited and it can generate the so called ‘missing edge’ artefact which is essentially a lack of information at the edges of the sample. This problem can be overcome by tilting the sample along two axes. Furthermore the use of mathematical algorithms which combine continuous and discrete 3-D binary reconstructions can help in recovering the loss of information due to the “missing edge”. In the last 20 years mathematicians and material scientists have joined forces to produce 3-D images of objects in the nanoworld, demonstrating success in reconstructing 3-D images of gold nanoparticles, magnetotactic bacteria, porous environment in zeolites, but none of the 3-D images had ever reached the atomic resolution.

The recent success in reconstructing the 3-D structure of silver nanoclusters with atomic resolution can provide a huge source of knowledge to scientists for the study of the detailed structures of biological molecules such as proteins or peptides and the study of nano-semiconductors and catalysts in which the three-dimensional features and morphology plays a fundamental role in determining their chemical reactivity and physical properties.

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