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Seeing and measuring in colours: Electron microscopy and spectroscopies applied to nano-optics

Voir et mesurer en couleur: microscopie et spectroscopies électroniques pour la nano-optique

Mathieu Kociak, Odile Stéphan, Alexandre Gloter, Luiz F. Zagonel[1],
Luiz H.G. Tizei, Marcel Tencé, Katia March, Jean Denis Blazit, Zackaria Mahfoud,
Arthur Losquin, Sophie Meuret, Christian Colliex

Laboratoire de physique des solides, CNRS UMR 8502, Université Paris-Sud, 91405 Orsay, France

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A B S T R A C T

Over the past ten years, Scanning Transmission Electron Microscopes (STEM) fitted with Electron Energy Loss Spectroscopy (EELS) and/or Cathodoluminescence (CL) spectroscopy have demonstrated to be essential tools for probing the optical properties of nano-objects at sub-wavelength scales. Thanks to the possibility of measuring them at a nanometer scale in parallel to the determination of the structure and morphology of the object of interest, new challenging experimental and theoretical horizons have been unveiled. As regards optical properties of metallic nanoparticles, surface plasmons have been mapped at a scale unimaginable only a few years ago, while the relationship between the energy levels and the size of semiconducting nanostructures a few atomic layers thick could directly be measured. This paper reviews some of these highly stimulating recent developments.

R É S U M É

Au cours des dix années écoulées, les microscopes électroniques à transmission en balayage (STEM) equipés pour la spectroscopie de perte d'énergie d'électrons (EELS) et/ou la cathodoluminescence (CL) ont démontré leur capacité fondamentale pour une étude fine des propriétés optiques de nano-objets à l'échelle sub-longueur d'onde. Comme ils permettent de les mesurer au niveau du nanomètre en même temps que leur structure et morphologie au niveau atomique, de nouveaux champs d'étude aussi bien expérimentaux que théoriques ont ainsi pu être explorés. En ce qui concerne la réponse optique de nanoparticules métalliques, les plasmons de surface ont été cartographiés à une échelle qui aurait été inimaginable il y a encore quelques années, tandis que la relation entre les niveaux d'énergie et la taille de nanostructures semiconductrices épaisses de quelques couches atomiques a pu être directement établie. Cet article a pour but de présenter une revue rapide de quelques-uns des résultats récents les plus spectaculaires dans ce domaine.

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[1] Now at: Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas – UNICAMP, 13083-859 Campinas, SP, Brazil.

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1. Introduction

In recent years, the number of studies on the optical properties of nanoparticles or nanostructured materials has literally exploded. Most probably, this is due to the fact that these optical properties can be manipulated and designed at will by playing with the nanostructures sizes and shapes, and the skills and creativity of chemists and technologists have provided over the past years the physicist with an access to such on-purpose designed nano-objects.

Nowadays, the relevant scale can be as small as a nanometer for optical properties, and, since these are so dependent on the structure and morphology, these latter may have to be known with an atomic precision.

Indeed, many fundamental and more applied issues rely on the observation of optical properties at these scales. As an example, the behaviour of the light at distances much smaller than its wavelength is a fascinating and counterintuitive topic. Another example is the development of Light Emitting Diodes (LEDs), or the optimisation of photovoltaic devices, that heavily rely on the miniaturisation and nanostructuration of the materials they are made up of. It is thus an exciting challenge to explore and measure the optical properties variations of such important industrial devices at the relevant scale, i.e. over a few nanometers scale. Therefore, the fundamental limits of optical techniques relying on photons alone call for the introduction of disruptive methods and concepts, which have appeared these last years and which will be described in this review paper.

Needless to say, standard optical means—such as visible–UV spectroscopy or PhotoLuminescence, PL—, even in a confocal set-up, cannot go below the diffraction limit and can't address the issue efficiently. Stunning optical techniques, such as the STimulated Emission Depletion (STED), can now reach true nanometer resolution, optionally in 3D [1]. However, they are limited to specific applications, and cannot help at determining the structure or morphology of the objects of interest. Other alternatives, such as the PhotoEmission Electron Microscopy (PEEM) [2], despite their interest, have not yet demonstrated resolutions better than a few nanometers.

At the opposite, fast electron microscopies, such as Scanning (Transmission) Electron Microscopies—S(T)EM—, taking advantage of the very short de Broglie wavelength of accelerated electrons can produce nowadays sub-angström probes. They reveal the structure of nano-objects down to their atomic configuration. The optical properties can then be investigated in parallel through spectroscopic measurements.

However, before trying to understand how optical properties can be deduced from electron spectroscopies, let us remind that the notion of optical properties is not unique and that it depends on the way those properties are measured. In a traditional optical experiment, one sends a light beam on the sample of interest. Part of the light is scattered at the same energy, at a different one, or absorbed by the sample. This corresponds to the scattering, luminescence, or absorption optical properties. Finally, if after sending a light beam onto a sample, one observes the decrease of intensity along its path, one is dealing with the so-called extinction properties. All these properties, the measurement of which allows access to different information, are interconnected. The extinction cross section is the sum of the absorption, scattering and luminescence one.

How can we understand that an electron, which in free space would never interact with light, can help measuring optical properties? An heuristic point of view is as follows. A fast electron carries a Coulomb field. A nanoparticle close to the electron trajectory experiences a time-varying electric field pointing from the electron to the nanoparticle. When the electron is close to the nanoparticle, the interaction is strong and the electric field points roughly perpendicular to the electron trajectory, while when it is far, it is too weak to be relevant. Thus, the nanoparticle feels a pulse of electromagnetic radiation propagating along, and with an electrical field oriented mostly perpendicular to the electron axis. This resembles dramatically a plane wave packet of light propagating along the electron path. Since the pulse is relatively short in time (for a 10 nm thick nanoparticle and an electron travelling at half the speed of light, the interaction time is typically less than a fs), the spectrum of the electromagnetic field accompanying the electron is white. Furthermore, the field is concentrated on a very small volume (due to the localised Coulomb interaction it is made up of). One may then view the electron as a highly localised white source of light. In the following, it is this "light" which is absorbed, scattered or responsible for the luminescence phenomena—and not the electron itself!

Now, two different brands of spectroscopies are of interest when trying to unveil the optical properties of nano-objects with electrons. When a fast electron is sent onto or close to an object of interest, it can transfer some energy through Coulomb interaction. If one is able to measure the amount of energy lost by the electrons, one has access to the extinction properties of the object of interest. Luckily enough, such energy loss can be measured through Electron Energy Loss Spectroscopy (EELS), which is here intuitively cast as an extinction spectroscopy at the nanometer scale.

Of course, the energy transferred to the object has to be released. If by chance this happens in the form of a photon in the Infra Red/visible/Ultra Violet (IR/VIS/UV) range, then one have access to the luminescence or scattering properties through the so-called Cathodoluminescence (CL) spectroscopy.

The fact that both techniques can really reveal these properties at a few nanometers scale or less, is not straightforward as it implies both conceptual and technical issues. These issues have nowadays been partly solved, and have led to an impressive amount of work, both experimental and theoretical, and to conceptual advances in the study of plasmons in metallic nano-objects (through EELS and in a lesser extent CL) and of excitons in semiconducting structures (by CL). A comprehensive and excellent review, mainly devoted to plasmon and photonics excitations has been recently published [3]. This reference is a must for all those who aim at a deep understanding of the physics behind optical excitations at the nanometer level and how electrons can be used to explore them. However, since this publication, the field has kept growing very quickly and this is the intent of this paper to review these recent advances.