Electron Energy-Loss Spectroscopy of Coupled Plasmonic Systems: Beyond the Standard Electron Perspective

G. D. Bernasconi[a], V. Flauraud[b], D. T. L. Alexander[c], J. Brugger[b], O. J. F. Martin[a], J. Butet [*a]
[a] Nanophotonics and Metrology Laboratory (NAM), Swiss Federal Institute of Technology Lausanne (EPFL), 1015, Lausanne, Switzerland
[b] Microsystems Laboratory, Swiss Federal Institute of Technology Lausanne (EPFL), 1015 Lausanne, Switzerland.
[c] Interdisciplinary Center for Electron Microscopy (CIME), Swiss Federal Institute of Technology Lausanne (EPFL), 1015 Lausanne, Switzerland.

ABSTRACT

Electron energy-loss spectroscopy (EELS) has become an experimental method of choice for the investigation of localized surface plasmon resonances, allowing the simultaneous mapping of the associated field distributions and their resonant energies with a nanoscale spatial resolution. The experimental observations have been well-supported by numerical models based on the computation of the Lorentz force acting on the impinging electrons by the scattered field. However, in this framework, the influence of the intrinsic properties of the plasmonic nanostructures studied with the electron energy-loss (EEL) measurements is somehow hidden in the global response. To overcome this limitation, we propose to go beyond this standard, and well-established, electron perspective and instead to interpret the EELS data using directly the intrinsic properties of the nanostructures, without regard to the force acting on the electron. The proposed method is particularly well-suited for the description of coupled plasmonic systems, because the role played by each individual nanoparticle in the observed EEL spectrum can be clearly disentangled, enabling a more subtle understanding of the underlying physical processes. As examples, we consider different plasmonic geometries in order to emphasize the benefits of this new conceptual approach for interpreting experimental EELS data. In particular, we use it to describe results from samples made by traditional thin film patterning and by arranging colloidal nanostructures.

Keywords: Electron-energy loss spectroscopy, EELS, Numerical methods, Advanced nanofabrication, Plasmonic, Near-field imaging, Nanoantenna

1. INTRODUCTION

Electron energy-loss spectroscopy (EELS) is a method of choice for the characterization of both the spatial and spectral properties of localized surface plasmon resonances.[1] Contrary to optical far-field excitation, for which the beam size cannot be smaller than the diffraction-limit, using swift electrons allows researchers to map localized surface plasmon resonances with a nanometric spatial resolution.[2] Nanostructures with various geometries have been investigated using EELS, such as nanotriangles,[3] nanorods,[4] and nanowires[5] for example. Interestingly, modes that are weakly optically active, the so-called dark modes, are observable using EELS.[6] In order to explain the experimental observations, modelling approaches, based on different numerical methods used for solving the Maxwell's equations at the nanoscale,[7] have been proposed. All these methods are based on the evaluation of the work done by the Lorentz force acting on the electron.[8] Furthermore, the relation between EELS and the local density of state (LDOS) has been discussed and schemes for the 3D reconstruction of the LDOS have been proposed.[9] The symmetry properties of the modes and the influence of the electron beam position on their observations in the electron energy loss (EEL) spectra have been widely addressed in the past.[10] However, even if modelling methods that reproduce the EEL spectra are available, the insights they give into the direct role of the plasmonic nanostructures are quite limited.

To go beyond this statement, we propose to interpret the EELS data using directly the intrinsic properties of the nanostructures, without any evaluation of the Lorentz force acting on the electron. This antenna perspective is particularly well-suited for the description of coupled plasmonic systems, since the role played by each individual nanoparticle can now be clearly identified in the observed EEL spectrum. As a convincing example, we consider here a heterodimer made with e-beam lithography and composed of a gold nanodisc and a silver nanodisc, see Figure 1.

*jeremy.butet@epfl.ch

Nanoimaging and Nanospectroscopy IV, edited by Prabhat Verma, Alexander Egner, Proc. of SPIE Vol. 9925, 99250N · © 2016 SPIE · CCC code: 0277-786X/16/$18 · doi: 10.1117/12.2237571

STEM-EELS data were acquired using a FEI Titan Themis 80-300 equipped with a Wien-type monochromator and a Gatan GIF Quantum ERS spectrometer. A 300 keV incident electron beam was used in this case. The EEL spectrum for an electron beam passing through the nanogap center is shown in Figure 1, revealing a localized surface plasmon mode resonant at 2.17 eV in energy loss. The corresponding EELS map, recorded at this energy (2.17 eV) using a ? eV window, is shown in the inset of Fig. 1. Before discussing the antenna perspective, we consider the standard approach for the interpretation of this EEL spectrum, in order to use it as a benchmark.

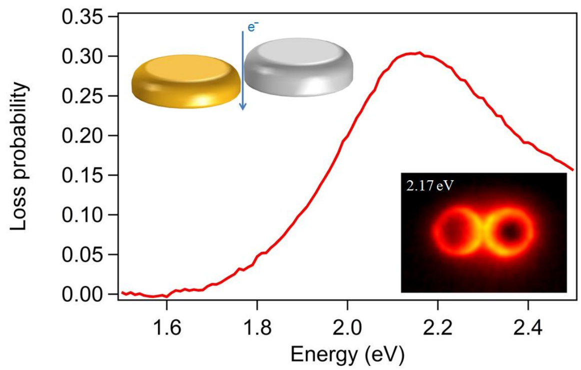

Figure 1: EELS of a heterodimer composed of a gold nanodisc (diameter d = 105 nm and thickness t = 25 nm) and a silver nanodisc (diameter d = 105 nm and thickness t = 30 nm) separated by a 9 nm gap. The EEL spectrum is measured for an electron beam passing through the nanogap center. The inset shows the EELS map for an energy loss of 2.17 eV integrated over a 0.1 eV window.

2. STANDARD FORMULATION

In the present work, we used a surface integral equation method (SIE) for all the numerical computations.[11] This method has been proven to be very accurate for the evaluation of the electromagnetic properties of plasmonic nanostructures, especially in the near-field region, and is therefore suitable for the evaluation of the EEL spectra. The electromagnetic field induced by an impinging electron with an energy of 300 keV is used to describe the excitation condition. Using the SIE, the induced electric field $E^{ind}(r,\omega)$ can be evaluated everywhere, inside and close to the nanodimers, and at different frequencies. The spectral loss probability – the quantity measured in standard EELS experiments – is in general expressed by invoking the Lorentz force exerted by the induced electric field $E^{ind}(r,\omega)$ on the incident electron. Considering a straight line trajectory $r_e(t)$ and a constant electron velocity v (the so-called non-recoil approximation)[1], the energy loss is expressed as[8]

$$\Delta E = e\int dt\,\mathbf{v}\cdot\mathbf{E}^{ind}(\mathbf{r},t) = \int_0^\infty \hbar\omega\Gamma(\omega)d\omega, \tag{1}$$

where

$$\Gamma(\omega) = \frac{e}{\pi\hbar\omega v}\int \mathrm{Re}\left\{\left(\mathbf{v}e^{-i\omega t}\right)\mathbf{E}^{ind}(\mathbf{r},\omega)\right\}dl \tag{2}$$

is the loss probability given per unit of frequency ω. The so computed EEL spectrum is shown in Figure 2, revealing a high intensity loss probability close to 2.2 eV, in agreement with the experimental EEL spectrum. Note that the computations are performed without any substrate, explaining the slight differences between both spectra. Here, the substrate contribution is instead mimicked by using a refractive index of the surrounding medium higher than that of vacuum (n = 1.34). Despite this confirmation of the experimental observation, the standard formulation does not provide further information about the role played by each nanoparticle in the energy dissipation. In the present case, the electron beam is equidistant from the two nanoparticles and the amplitude of the electromagnetic field driving each of them is the same. Furthermore, the Lorentz force acting on the electron is evaluated along its trajectory, which is also equidistant from the two nanodiscs. *A priori*, the electric field acting on the electron is induced by both nanoparticles. However, because of the different electronic properties of gold and silver, one can expect that the two nanodiscs play a different role, *i. e.* is the contribution of one more important than that of the other one at a given energy? This question cannot be answered directly using the standard formulation of EELS modelling used above. For this reason, we propose another approach for the evaluation of the EEL spectra, based on the antenna theory and energy conservation, as discussed below.

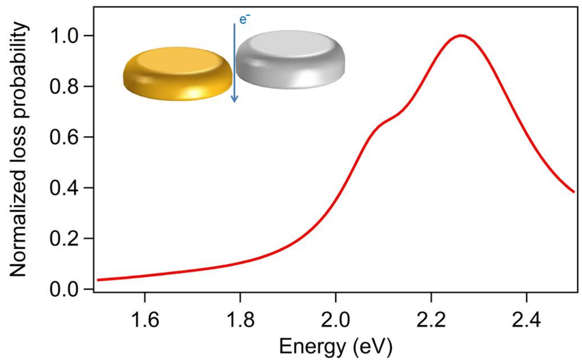

Figure 2: Modelled EEL spectrum of a heterodimer composed of a gold nanodisc (diameter d = 105 nm and thickness t = 25 nm) and a silver nanodisc (diameter d = 105 nm and thickness t = 30 nm). The EEL spectrum is computed for an electron passing through the nanogap center using the standard formalism.

3. AN ANTENNA PERSPECTIVE

In this part, EELS is described considering a new perspecive, based on the nanoantenna properties, by considering that the unique possibility for the electron to loose energy is through its interaction with this nanostructure. Note that the Cerenkov radiation is not considered here. Furthermore, the energy transferred from the electron to the nanostructure can be either dissipated by Joule effect or radiated into the far-field. In the case of the heterodimer, the EEL corresponds to three channels: the absorption in the gold nanoparticle; the absorption in the silver nanoparticle; and the scattering from the complete structure. Considering that the time separating two impinging electrons is much longer than the dissipation of the energy generated in the nanostructure by one electron, the power lost by the electron beam $P_{loss}(\omega)$ can be written as

$$P_{loss} = P_{sca} + P_{gold} + P_{silver}, \qquad (3)$$

where P_{sca} is the power scattered by the nanostructure, P_{gold} is the power absorbed in the gold nanodisc, and P_{silver} is the power absorbed in the silver nanodisc. The absorption in the metallic nanoparticles corresponds to ohmic losses. In this framework, the loss probability $\Gamma(\omega)$ per unit of frequency ω is proportional to the total lost power divided by the frequency squared. The EEL spectrum of the same heterodimer has been computed using the antenna perspective, see Figure 3(a). This spectrum shows an excellent agreement with the one obtained with the standard Lorentz force based formulation, confirming the validity of the new method that we propose for the evaluation of EEL spectra. To determine how the energy is lost by the electron beam, the scattered power as well as the power absorbed in the gold and silver nanodiscs are shown as functions of the energy in Figure 3(b). The results clearly demonstrate that the energy lost by the electron beam is mainly absorbed in the gold nanoparticle, even though the electron beam is equidistant from the two nanodiscs. This difference is explained by the electronic properties of gold and silver. For an energy between 2 eV and 2.5 eV, the imaginary part of the dielectric constant of gold is much higher than that of silver, resulting in higher ohmic losses in gold than in silver. Furthermore, it is interesting to note that the scattered power is even higher than the power absorbed in the silver nanodisc. This point emphasises that these two kinds of dissipative processes not only have to be considered in order to reproduce the EEL spectra and but also actually occur during EELS.

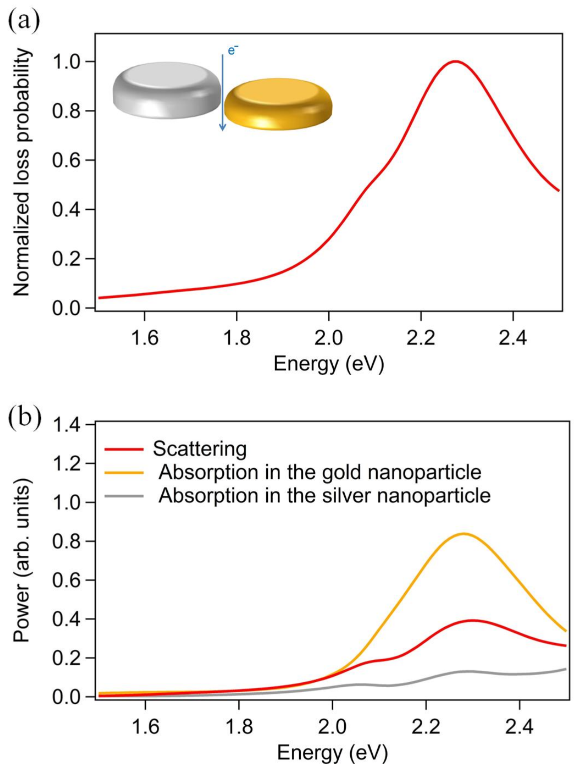

Figure 3: EELS of a heterodimer composed of a gold nanodisc (diameter d = 105 nm and thickness t = 25 nm) and a silver nanodisc (diameter d = 105 nm and thickness t = 30 nm). (a) The EEL spectrum is computed for an electron passing through the nanogap center using the antenna perspective. (b) The absorbed power in the gold nanodisc and in the silver nanodisc and the scattered power shown as functions of energy loss.

4. CONCLUSIONS

In summary, we have presented a new method for the evaluation and the interpretation of EELS of plasmonic nanostructures. Considering a heterodimer composed of gold and silver nanodiscs as an example, it was demonstrated that the antenna perspective gives results in agreement with the standard formulation based on the evaluation of the Lorentz force acting on the incident swift electron. Furthermore, using a simple case, it was emphasized how this new method provides a deep insight into the different mechanisms involved in EELS, enabling one to quantify the relative weight of scattering and absorption in the energy loss process. In conclusion, the antenna perspective is very promising for the interpretation of EEL spectra and we plan to use it to support our future EELS investigations of complex plasmonic nanostructures, including bi-metallic dimers with various nanoparticle shapes and composed of different metals, self-assembled nanoparticles, and extended nanostructures. It will also be interesting to combine this antenna perspective with eigenmodes analysis, as recently done in nonlinear plasmonics.[12]

ACKNOWLEDGMENTS

The authors thank the staff of the Center of Micro/Nanotechnology (CMI) of EPFL for the valuable discussions and support. This research was funded by the European Commission (FP7-ICT-2011-7, NANO-VISTA, under Grant Agreement No. 288263), and the Swiss National Science Foundation project 200020_153662.

REFERENCES

[1] García de Abajo, F. J., “Optical Excitations in Electron Microscopy” Rev. Mod. Phys. 82, 209-275 (2010).
[2] Kociak, M., and Stéphan, O., “Mapping Plasmons at the Nanometer Scale in an Electron Microscope” Chem. Soc. Rev. 43, 3865-3883 (2014).

[3] Nelayah, J., Kociak, M., Stéphan, O., García de Abajo, F. J., Tencé, M., Henrard, L., Taverna, D., Pastoriza-Santos, I., Liz-Marzán, L. M., and Colliex, C., "Mapping Surface Plasmons on a Single Metallic Nanoparticle" Nature Phys. 3, 348-353 (2007).

[4] Guiton, B. S., Iberi, V., Li, S., Leonard, D. N., Parish, C. M., Kotula, P. G., Varela, M., Schatz, G. C., Pennycook, S. J., and Camden, J. P., "Correlated Optical Measurements and Plasmon Mapping of Silver Nanorods" Nano Lett. 11, 3482-3488 (2011).

[5] Rossouw, D., Couillard, M., Vickery, J., Kumacheva, E., and Botton, G. A., "Multipolar Plasmonic Resonances in Silver Nanowire Antennas Imaged with a Subnanometer Electron Probe" Nano Lett. 11, 1499-1504 (2011).

[6] Schmidt, F. P., Ditlbacher, H., Hohenester, U., Hohenau, A., Hofer, F., and Krenn, J. R.,"Dark Plasmonic Breathing Modes in Silver Nanodisks" Nano Lett. 12, 5780–5783 (2012).

[7] Gallinet, B., Butet, J., and Martin, O. J. F., "Numerical Methods for Nanophotonics: Standard Problems and Future Challenges" Laser. Phot. Rev. 9, 577-603 (2015).

[8] Ritchie, R. H., "Plasma Losses by Fast Electrons in Thin Film." Phys. Rev. 106, 874-881 (1957).

[9] Hörl, A., Trügler, A., and Hohenester, U., "Full Three-Dimensonal Reconstruction of the Dyadic Green Tensor from Electron Energy Loss Spectroscopy of Plasmonic Nanoparticles" ACS Photonics 2, 1429-1435 (2015).

[10] Hohenester, U., Ditlbacher, H., and Krenn, J., "Electron Energy Loss Spectroscopy of Plasmonic Nanoparticles" Phys. Rev. Lett. 103, 106801 (2009).

[11] Kern, A. M., and Martin, O. J. F., "Surface Integral Formulation for 3D Simulation of Plasmonic and High Permittivity Nanostructures" J. Opt. Soc. Am. A 26, 732-740 (2009).

[12] Bernasconi, G. D., Butet, J., and Martin, O. J. F. "Mode Analysis of Second-Harmonic Generation in Plasmonic Nanostructures" J. Opt. Soc. Am. B 33, 768-779 (2016).