New possibilities with sub-20meV spatially resolved STEM-EELS

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1. INTRODUCTION

In the past ten years, Electron Energy-Loss Spectroscopy (EELS) in a Scanning Transmission Electron Microscopy (STEM) has shown to be an invaluable technique for mapping optical excitations in the near infrared/visible/ultraviolet range with a nanometer spatial resolution, with a clear interest in mapping surface plasmons (SP) on small nanoparticles [1]. The new advances in monochromator technologies have made it possible to map surface plasmons of energy as small as 170 meV [2]. Very recently, phonons in hexagonal boron nitride (h-BN), with a peak energy around 160 meV, have been measured in a STEM [3]. Such technologies thus act as game changers for the investigation of physical effects at low energy (less than 100 meV) and high spectral resolution (less than 20 meV). In this contribution, we will present recent results acquired on the NION HERMES STEM at Arizona States University (ASU) from plasmonic nanoantennas and h-BN flakes. Hereafter, we illustrate the performances of this new instrument using the example of a noble metal nanowire.

2. RESULTS

We have used nanowires (NW) formed with a gold core and two elongated silver extremities [4]. These nanowires have been chosen because, given a diameter of typically 40 nm and lengths up to 1.8 microns, their aspect ratio can be as large as typically 30-45, ensuring the existence of low energy SP [1,2]. Also, as a test of the monochromator performances, their high crystallinity ensures minimal full width at half maxima (FWHM) as a result of low energy dissipation.

NW were sonicated in water and deposited on an Si_3N_4 membrane. Spectral imaging was performed in a HERMES NION operating at 60 keV and fitted with a Gatan HR Quantum spectrometer. Typical incident and acceptance semi-angles were 12 mrd and 14 mrd. Typical dispersion was 2 meV/channel.

Figure 1 presents the results of a spectrum image consisting of 193x29 points, with a spatial sampling of 10 nm. In these experimental conditions, the zero loss peak (ZLP) FWHM was 16 meV (not shown). The summed spectrum acquired on the nanowire exhibits a series of peaks related to excitation of multipolar SP [1,2] ranging from 237 meV to approximatively 1800 meV. Although SP of similar energies have already been measured [2], here the detrimental effect of the ZLP tail is absent. More importantly, these measurements reveal extremely low FWHM values (down to less than 50 meV) which are barely affected by the ZLP FWHM.

Such performances have never been reached to our knowledge in spatially resolved plasmonics. In the contribution, we will point out the physical implication of this technical performance, showing how it opens new avenues in plasmonics and nanophononics.



Figure 1: EELS spectrum summed on a AgAuAg bimetallic nanowire showing 10 distinct harmonic plasmon modes which are well fitted by multiple Lorentzians. Inset, HAADF of the nanowire (top), and EELS filtered map on energy windows centered on the zero-loss peak (middle) and on 237 meV (bottom). The latter clearly exhibits the intensity distribution of a dipolar mode.

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REFERENCES

- [1] Kociak, M. & Stéphan, O. Chem. Soc. Rev. 43, 3865–3883 (2014).
- [2] Rossouw, D. & Botton, G. A. Phys. Rev. Lett. 110, 066801 (2013).
- [3] Krivanek, O. L. *et al. Nature* **514**, 209–212 (2015).
- [4] Scarabelli, L. *et al.*, *in preparation*.