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Very High Resolution Energy Loss Spectroscopy: Applications in Plasmonics

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The development of monochromators in commercial instruments [1] has lead to a surge in interest in high-energy resolution electron energy loss spectroscopy (EELS). While the early applications were focused on the use of high-resolution EELS for the study of EELS Near-Edge Structures (ELNES) [2], one of the most fruitful applications of such devices has been in the field of plasmonics, spurred by the first results obtained with non-monochromated cold-field emission electron sources, which demonstrated the detection of surface plasmon resonances in Au and Ag nanostructures [3,4]. Energy resolution (measured at the full width-half maximum) of the Zero-Loss Peak (ZLP) in the range of 0.1 to 0.2 eV has been typically considered sufficient for ELNES work because of the intrinsic width of spectral features due to the broadening arising from the lifetime of the core hole and the excited states, even for edges at relatively low energy losses (e.g. the C and B K edges). However, interests in the measurements of bandgaps [e.g. 5] and the recent demonstration of detection of phonons [6, 7] have spurred interest towards much improved energy resolution capabilities. Here we present some examples of applications in high-resolution EELS achieved through a combination of monochromators and numerical deconvolution methods providing in principle an effective resolution in the range between 10 to 30 meV thus making it possible to detect very low energy features arising from surface plasmon resonances (SPR) in metallic nanostructures [8]. Improved resolution is shown to make it possible to detect and subsequently map subtle spectroscopic features due to coupling of excitation modes and very low intrinsic resonance energies in very large size structures.

To highlight these effects, we have used electron beam lithography to fabricate large structures such as 30 nm thick silver squares and triangles on 50 nm thick silicon nitride membranes. Using an ultrastable STEM-TEM (FEI Titan 80-300) system, operated at 80 keV and equipped with an electron monochromator and high-resolution electron energy loss spectrometer, we acquire spectral images of SPR modes with an energy resolution of 70-80 meV. To further enhance the energy resolution and reduce the contribution of the ZLP tails due to the point-spread function of the detector, we have applied the iterative Richardson-Lucy deconvolution [8]. With this method, we have shown an effective energy resolution potentially reaching 10 meV using stable algorithms that consider the noise evolution due to the increased number of iterations.

In Ag squares, we have been able to show the presence of very high order *edge* as well as low probability *cavity* modes not detected previously in such structures (Fig. 1b). The experimental results are supported by theoretical calculations that allow a detailed interpretation of the measurements [9]. Similar antinode distribution is found on high-order edge modes for a 2 µm side equilateral triangle (Fig. 1a). Also, in measurements of a plasmon mode localized at the tip of micrometer-sized isosceles triangle we show that the improved resolution allows the detection of features as low as 150 meV that correspond to the lower energy region of the mid-infrared spectrum. With such a resolution, we have been able to study the splitting of spectral features arising from the coupling of nanosquare dimers with gaps between 50 to 100 nm (Fig. 2). Our results show the formation of 14 hybrid resonant modes, including peaks separated by only 60 meV. These peaks are not visible without data deconvolution, suggesting the need for improved resolution and confirming the efficacy of our processing method.

With these experimental and numerical capabilities, we have explored a variety of coupling phenomena in Ag nanostructures, for example, we demonstrate the suppression or enhancement of the modes formed by coupling of silver nanorods by adjusting the length of the coupling region [10]. Further examples will be shown highlighting the benefits of improved resolution in new instruments to detect subtle electron interaction phenomena with plasmons [11].

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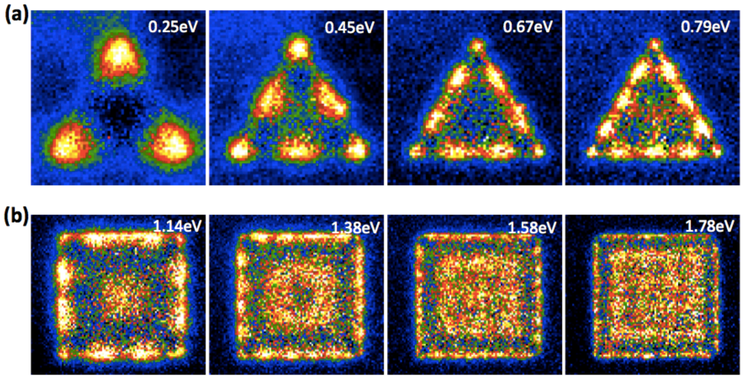

Figure 1. EELS maps of the edge multipolar plasmon modes present in a 2 μm side solid Ag triangle (a). EELS maps of cavity plasmon modes of silver nanosquares with 850 nm lateral size. Based on the symmetry of the structure, the modes can be classified as (1,1), (1,2), (1,3), and (1,4), from left to right respectively (b). Adapted from [9].

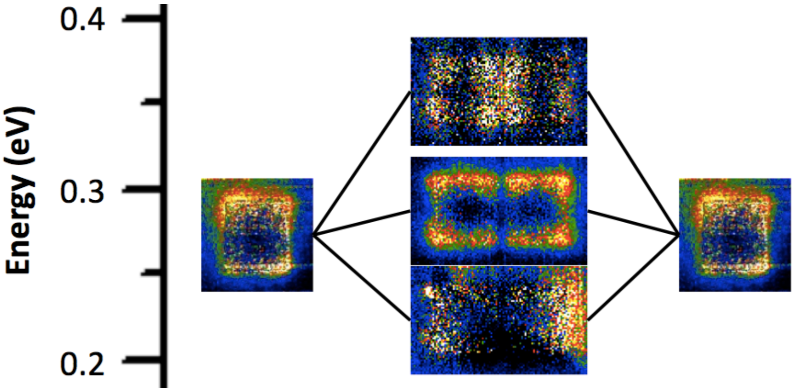

Figure 2. Diagram showing the splitting of the dipolar mode of a 1 μm nanosquare into three modes by plasmonic coupling.