High Resolution Energy Loss Spectroscopy of Plasmonic Hybridization in Silver Nanostructures

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1. INTRODUCTION

La Surface plasmon resonances (SPR) in metallic nanostructures arise from the collective oscillation of conduction electrons, which create strong confined electric fields around the nanostructures. This confinement of electromagnetic (EM) energy at nanoscale dimensions holds potential towards the miniaturization of photonic devices [1]. Tremendous effort has been devoted towards optimization and design of nanostructures for several applications [2,3,4]. Most of these applications involve arrays of closely-spaced nanostructures: the plasmonic properties of the array differ from those of its isolated parts due to the interaction of evanescent fields. The study of SPR in these arrays, in particular the coupling of resonant modes, requires a characterization technique with both high spatial and energy resolution. Electron energy loss spectroscopy (EELS) meets these requirements, but has previously been limited to energies in the range of visible light or higher, mainly because of the relative intensities of the zero loss peak (ZLP) and low energy loss signal.

2. RESULTS

In this work, we use electron beam lithography to fabricate circular arrays of rods (Fig. 1) and 30 nm high silver nano-square dimers (Inset Fig. 2) 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 80 meV. To further increase the energy resolution and reduce the contribution of the ZLP, extending the range of detectable energies down to the mid-infrared region of the EM spectrum, we apply the iterative Richardson-Lucy deconvolution [5]. With this method, we obtain an effective energy resolution of 40 meV.

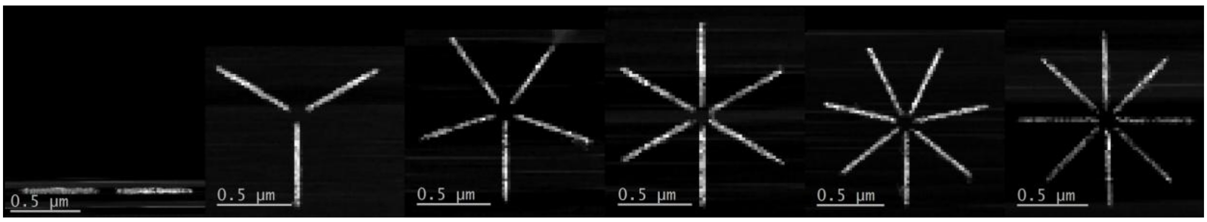

Figure 1. Annular dark-field images of the nanorod arrays.

The nano-square dimers are separated by 100 nm, as shown in the inset of Fig. 2. Due to the proximity of the two squares the structures couple through their evanescent fields, creating new modes that can be understood as the hybridization of the individual silver square SPR [6]. The result of the hybridization is the formation of multiple resonances that are energetically close to each other and can only be resolved by high energy resolution EELS. Figure 2 shows the deconvoluted spectra after 39 iterations at several positions on the dimer. Eleven plasmon peaks can be clearly identified, with the first peak at an energy of 0.28 eV, corresponding to the mid-infrared region on the EM spectrum. After deconvolution, we can identify peaks that are as close as 70 meV.

As previously demonstrated, nanoantennas are able to efficiently transform optical radiation into SPR [7]. Far field radiation can excite short-range surface plasmon-polaritons (SR-SPP) in silver nanorods, which act as nanoantennas where the spatial distribution of the electromagnetic fields is correlated with the nanorod structure [2,3,7]. In this work, we also studied the coupling and hybridization of SPR in nanoantennas. We extracted high-resolution images and energy-filtered maps of hybrid SPR of 500 nm long nanorods in circular arrays with an inner gap radius of 50 nm; the number of rods in the array varies from two to eight. In these structures, we observe SP enhancement effects in the center for one or sometimes two of the low energy modes, despite minor asymmetries in the nanoantennas which may shift their individual resonant frequencies. Results suggest that these arrays do not require perfect resonance matching for enhancement effects to be observable. Calculations of the plasmonic response have been carried out and are used to identify the modes and the hybridization.

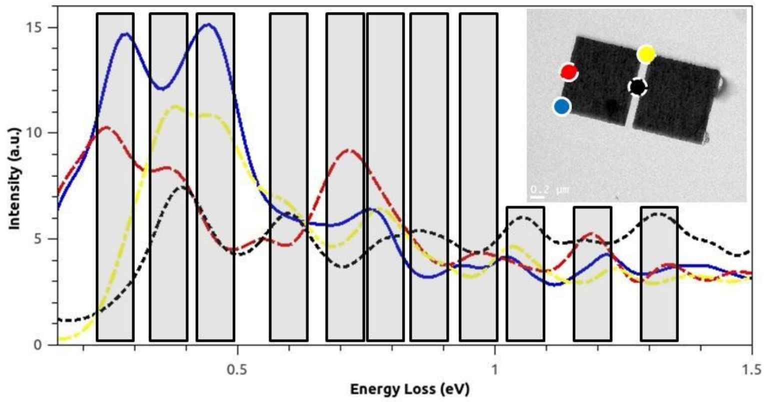

Figure 2. Spectra showing the multiple hybrid plasmon resonances peaks of the two silver squares. The spectra were extracted from four positions color coded in the inset.

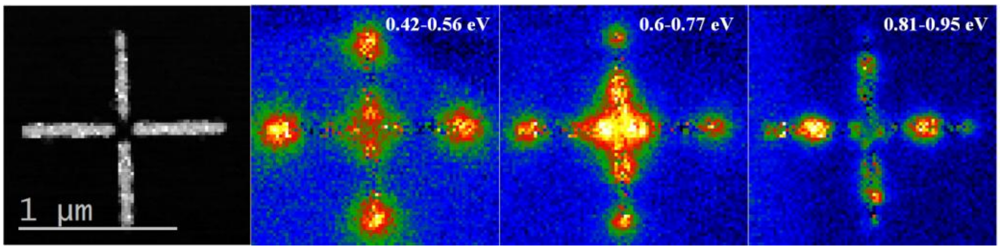

Figure 3. Annular dark-field image of a circular array of four 500 nm rods (left) and its SPR showing the coupling and formation of hybrid modes from the multipolar resonances of the individual nanoantennas.

3. CONCLUSION

We have shown that electron energy loss spectroscopy provides the necessary spatial resolution to observe subtle field enhancements and hybridization effects in a variety of structures, even visible in the mid-IR regime of the electromagnetic spectrum. Different structures and coupling will be discussed together with calculations to verify the nature of the modes and coupling between the nanostructures.

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