Three-dimensional imaging of localized surface plasmon resonances of metal nanoparticles

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The remarkable optical properties of metal nanoparticles are governed by the excitation of localised surface plasmon resonances (LSPRs). The sensitivity of each LSPR mode, whose character and resonant energy depend on the nanoparticle size, shape, composition and environment, has given rise to many potential photonic and opto-electronic applications [1]. However, the precise interplay between the three-dimensional (3D) nanoparticle structure and the 3D morphology and localization of each LSPR is not fully understood and a spectrally-sensitive 3D imaging technique is needed to visualise the excitation at the nanoscale. To reveal the delicate relationship between NP structure and LSPR at the nanoscale, electron energy-loss spectroscopy (EELS) in a monochromated scanning transmission electron microscope (STEM) offers an unrivalled combination of spatial and energy resolution [2]. The ability to provide nanometre resolution and to strongly excite LSPR modes with non-dipolar character ('dark' modes in optical spectroscopy) has led to a greater understanding of the plasmonic response of a range of NPs. The literature though, is limited only to two-dimensional (2D) LSPR maps as a result of projection of 3D excitations [3]. In this work we retrieve key information pertaining to the often critical third dimension, by probing the NP at different orientations through the combination of EELS with electron tomography (ET). In particular we apply STEM-EELS spectrum-imaging (SI) with a novel combination of non-negative matrix factorisation (NMF), compressed sensing and electron tomography and are thus able to reconstruct a 3D image of the dominant LSPR modes for an individual silver nanocube resting on a dielectric substrate.

Our results show that the peaks seen in STEM-EELS selected area spectra of a single silver nanocube resting on a 30 nm thick silicon nitride membrane have a strong variation in their intensity with position and tilt angle (Figure 1). This emphasizes the need to investigate the plasmonic response at multiple orientations. We thus acquired STEM-EELS SIs at 5 different tilt angles (ranging from -60° to 0°, with 15° step), tilting about a <100> cube axis perpendicular to the electron beam. Using non-negative matrix factorization (NMF) [4] we could perform a blind separation between the sources of peaks in the STEM-EELS SIs and obtained 5 dominant LSPRs for the silver nanocube and their corresponding 2D maps at each tilt angle. Using an iterative tomographic algorithm that harnesses compressed sensing [5] and taking advantage of the 4*mm* symmetry of the cube-substrate system, enabled ET reconstruction of the 3D morphology of the LSPRs from the small number of 2D maps (5 tilt angles). The 3D reconstructions shown in Figure 2 confirm the substrate-mediated hybridisation of dipolar and quadrupolar modes predicted by theory and optical spectroscopy [6], and reveal for the first time experimental 3D images of the dominant LSPR modes of a silver nanocube.

This work highlights how a powerful combination of electron microscopy, spectroscopy and tomography opens the way for 3D investigation of nano-optics. We believe these results will act as a catalyst for the study of LSPRs in three dimensions, leading to a deeper understanding of the optical properties of metallic nanostructures, and to the exploitation of three-dimensional LSPR morphology in future applications. [7]

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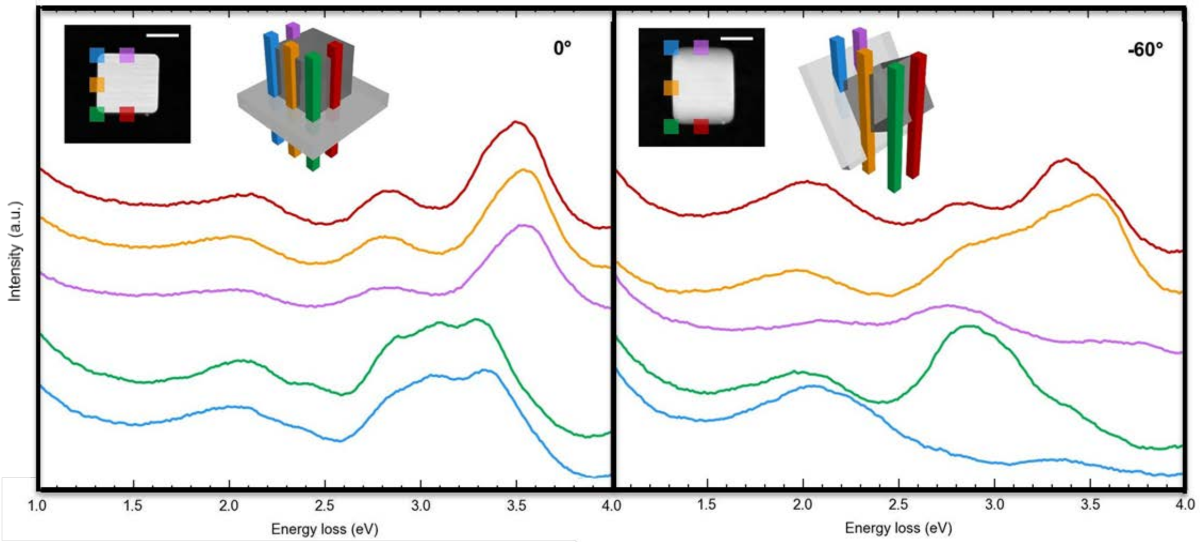

Figure 1. Selected area spectra of a silver nanocube. *Selected area spectra (unprocessed) corresponding to the areas highlighted in the insets, acquired at 0° tilt (left) and at -60° tilt (right). The selected area squares, and square prisms, in the schematics, highlight 25.4x25.4 nm^2 (18x18 pixels^2) areas from which individual spectra have been extracted and summed. Insets: High-Angle Annular Dark-Field (HAADF) STEM image of a silver nanocube resting on a 30 nm thick silicon nitride membrane at 0° tilt (left) and at -60° tilt (right). Inset scale bar: 50 nm.*

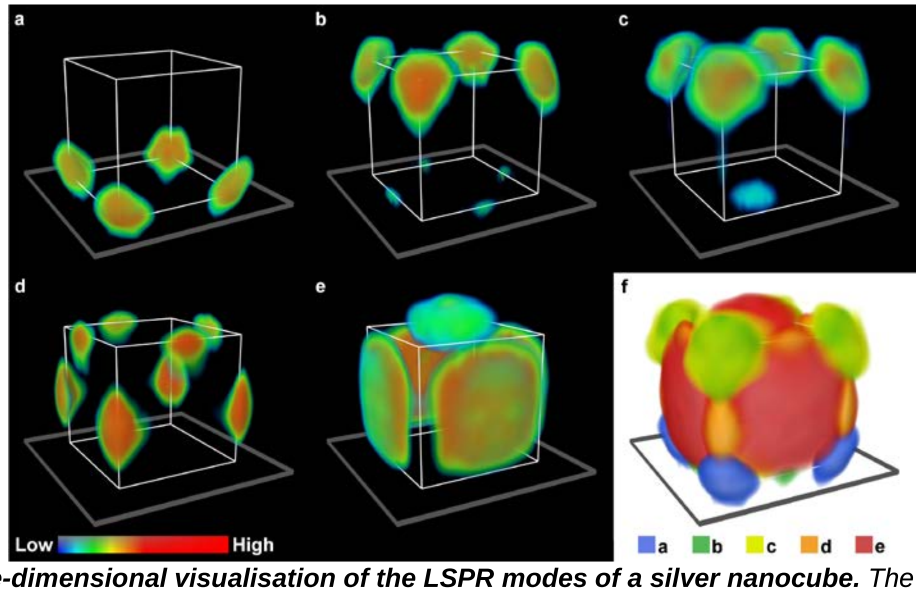

Figure 2. Three-dimensional visualisation of the LSPR modes of a silver nanocube. *The 3D images visualised in (a)-(e) were obtained by tomographic reconstruction of the EELS maps of the respective 5 LSPR modes identified by NMF. The visualisations are voxel projections of the reconstructed 3D volumes. The colour bar indicates the LSPR intensity. (f) Combined 3D rendering of all the modes.*