Probing Resonant Photonic Modes in Oxide Nanoparticles with Focussed Electron Beams

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Controlling the nanolocalization of light through engineering optical responses in dielectric structures has drawn ever increasing interest, since it can be applied to enhance light absorption in solar cells, detect unlabeled molecules), and optimize cavity quantum electrodynamics (QED) systems. Such applications cannot be fully achieved without a fundamental understanding of the resonance effects and optical behaviors of dielectric materials confined to micro- to nanoscale dimension. It is precisely in these size regimes where highly localized measurements that correlate the detailed structures of the observed materials with their optical responses are needed. Electron energy-loss spectroscopy (EELS) coupled to a scanning transmission electron microscope (STEM) provides a unique approach for locally probing a materials' optical properties with nanometer-scale spatial resolution. Recent developments in monochromators has improved the energy resolution of EELS to ~10 meV, contributing to a significantly reduced background from the tails of the elastic peak[1]. The improved signal-to-background allows subtle features in the low-loss region of the spectrum to be observable, thus opening up new opportunities such as detecting local vibrational signals and features within the bandgap of semiconductors and insulators [2-6]

Here we employ monochromated EELS for detection of local geometric resonance modes with energies in the infrared-visible range and peak widths on the order of one hundred meV. The particular focus of this work is on investigating the behavior of the latter geometric resonant modes on catalytically relevant oxide nanoparticles such as TiO_2, Ta_2O_5, CeO_2, and MgO using monochromated Nion UltraSTEM. Figure 1 shows the valence loss spectrum from a CeO_2 nanocube showing pronounced resonance modes below the bandgap. To interpret the spectral features detected, theoretical models and numerical simulations based on classical electrodynamics are performed (see Figure 2). The role of particle shape and particle coupling between modes will be discussed.

References:
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[7] We gratefully acknowledge support from DOE (DE-SC0004954), NSF CHE-1253775 and the use of NION microscope at John M. Cowley Center for Microscopy at Arizona State University are greatly acknowledged.

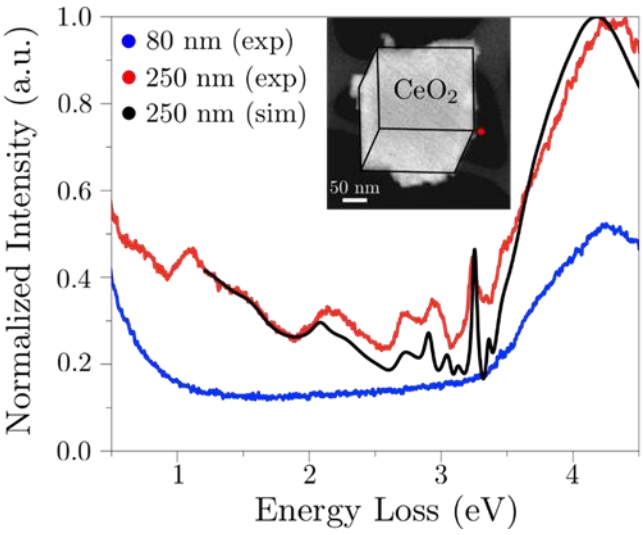

Figure 1: Experimental (red) and computed (black) aloof EEL spectra with the electron beam positioned 4 nm from the corner of a well-defined CeO_2 cube of 250 nm in size. The aloof beam EEL spectrum (blue) from an isolated 80 nm CeO_2 cube shows a featureless bandgap. The inset is the HAADF image of the 250 nm cube with beam position denoted by the red bullet.

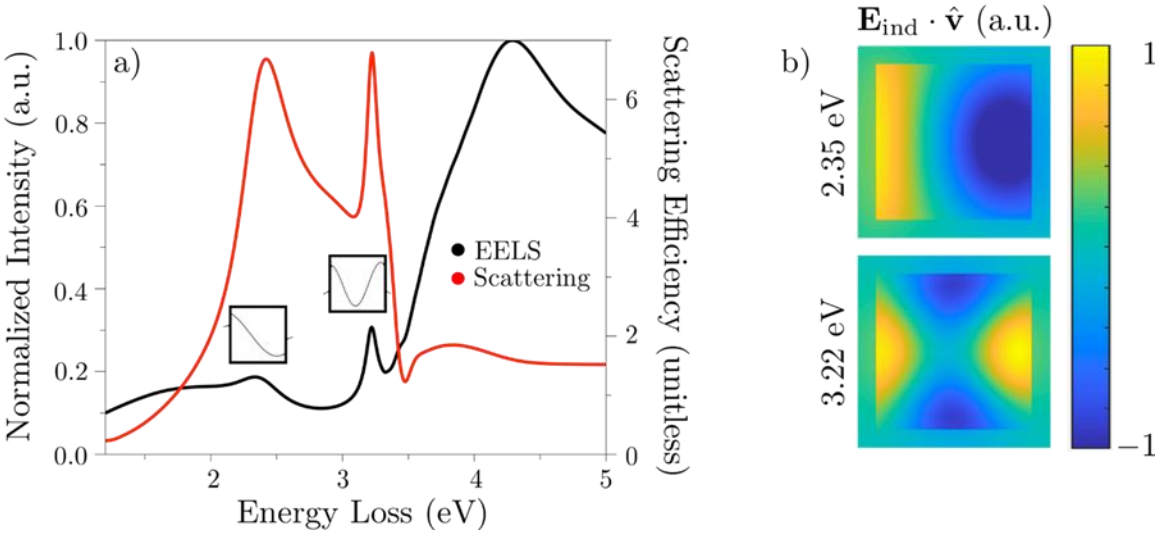

Figure 2: Simulated aloof EEL (black) and optical scattering (red) spectra of a 160 nm CeO_2 nanocube. The electron beam is directed down the cube face in the aloof geometry and the plane-wave light field polarized normal to the cube face. The two insets display the electric field intensity profiles within the cube at the band-gap resonances. (b) The field maps show the electron-driven electric field distributions associated with the cavity modes at 2.37 eV (top) and 3.22 eV (bottom).