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Nanoscopic imaging of energy transfer from single plasmonic particles to semiconductor substrates via STEM/EELS

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Localized surface plasmon resonances (LSPRs), the collective oscillations of conduction electrons in metallic nanoparticles, can produce intense near-fields at the resonance wavelengths. Plasmonic nanoparticles have been incorporated in the design of photovoltaic (PV) and photocatalytic devices, where they have been shown to enhance solar energy harvesting efficiency. Research has shown that the addition of plasmonic nanoparticles improves the efficiency of solar light harvesting via one or more of the following mechanisms[1]: (1) LSPR excitation leads to an increase in path length for incoming light via scattering, thereby increasing light absorption by the semiconductors; (2) energy transfer from the decay of an LSPR directly creates an electron-hole pair in the semiconductor, a process known as plasmon-induced resonant energy transfer (PIRET). Its efficiency relies on the overlap between the LSPR emission and the band gap absorption of the semiconductor[2]; (3) direct electron transfer (DET) from the nanoparticle to a semiconductor, in which an LSPR decays, through Landau damping, into a "hot" electron that may then scatter into the semiconductor if it has sufficient energy to overcome the Schottky barrier formed at the interface[3]. Mechanism (1) is only effective for photon energies above the band gap, while mechanism (2) and (3) involve photons with energies below or above the band gap, therefore, are of particular interest and importance. However, despite its importance, little is known about how PIRET and DET operate at the nanoscale, particularly at the level of a single nanoparticle.

In this paper, we present a nanoscale EELS study of PIRET and DET on several Ag nanocube@substrate systems, where the cubes and substrates serve as plasmonic energy donors and acceptors, respectively. The substrates are carefully chosen to turn off or isolate the PIRET and DET energy transfer channels. To simplify the discussion, we focus on only the cube@silicon dioxide (SiO_2)/boron phosphide (BP)/amorphous silicon (a-Si) results. Figure 1(a) demonstrates the correlation diagram of substrate-induced LSPR hybridization without energy transfer. Figure 1(b) describes schematically the EELS experiments. By tilting the samples, we are able to probe how the energy transfer modifies the proximal (D) and distal (Q) corner LSPR modes[4] without the interferences from the edge and face modes. As are shown in Figure 2, SiO_2 does not damp either D or Q mode whereas BP and a-Si impair the D modes remarkably, leaving the Q mode unaffected. This is because SiO_2 is a transparent large band-gap (9 eV) insulator which is closed to both PIRET and DET; BP has the PIRET off (optically transparent) but the DET on (small band gap); a-Si has both PIRET and DET on. The efficiencies of PIRET and DET cause the D modes damp at different levels, but do not affect the Q modes which are far from the substrates.

The experiments are carried out in a monochromated Carl Zeiss LIBRA® 200MC (S)TEM operated at 200 kV (150 meV energy resolution). The edge lengths of the Ag nanocubes range from 70 nm to 77 nm, the corner radii range from 10.2 nm to 12.6 nm. The SiO_2 substrate is a commercial product, the BP and a-Si substrates are fabricated via conventional TEM specimen preparation procedures.

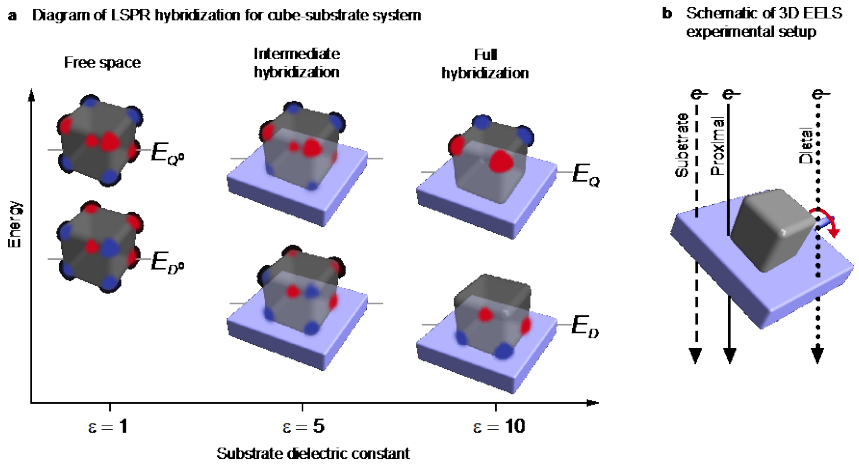

Figure 1. (a) Diagram of substrate-induced LSPR hybridization of a Ag nanocube. The evolution of the surface charge distributions of the D and Q eigenmodes of the nanocube is schematically displayed as function of increasing substrate dielectric constant. **(b)** Experimental EELS setup. The electron beam independently addresses the proximal and distal corners of the nanocube by tilting the composite system. The substrate is probed by a beam position far from the nanocube.

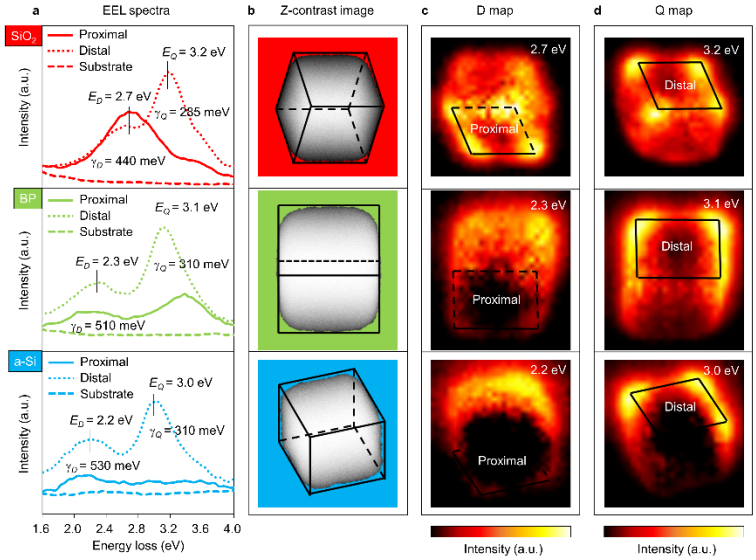

Figure 2. (a) Raw EEL spectra acquired at the proximal corner (solid lines), distal corner (dotted lines), and substrate (dashed lines), as described in Fig. 1b. E_D and E_Q denote the resonant energies, while γ_D and γ_Q denote the damping coefficients of the D and Q modes. **(b)** Z-contrast images of the tilted cubes. The solid lines represent the cube edges that are visible when viewed into the page, the dashed lines are cube edges that are blocked in the viewing direction. **(c, d)** D and Q EELS maps generated by plotting the spectral intensities over the spectrum image at E_D and E_Q. The proximal and distal faces are shown in the maps. *The D mode (proximal) is highly damped for nanocubes on BP and a-Si, indicating significant energy transfer to the substrate.*

References

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