Spatially Mapping Energy Transfer from Single Plasmonic Particles to Semiconductor Substrates via STEM/EELS

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* Supporting Information

ABSTRACT: Energy transfer from plasmonic nanoparticles to semiconductors can expand the available spectrum of solar energy-harvesting devices. Here, we spatially and spectrally resolve the interaction between single Ag nanocubes with insulating and semiconductor substrates using electron energy-loss spectroscopy, electrodynamics simulations, and extended plasmon hybridization theory. Our results illustrate a new way to characterize plasmonic energy transfer at the nanoscale and bear impact upon the design of next-generation solar energy-harvesting devices.

KEYWORDS: STEM, EELS, energy transfer, plasmonics, photovoltaics, nanocubes

Local surface plasmon resonances (LSPRs), the collective and coherent optical-frequency excitations of a metal nanoparticle’s conduction band electrons, can localize light below the diffraction limit and generate intense electric near-fields.1 This unique property has been exploited in applications ranging from single-molecule spectroscopy2 to molecular sensing3 and photothermal cancer therapy.4 Beyond these applications, plasmonically active nanoparticles have been incorporated in the design of photovoltaic (PV) and photothermal cancer therapy.5

The interaction of metal nanoparticles with a dielectric substrate serves as a model for understanding the flow of plasmonic energy in solar devices. Experiments on related systems have shown that the addition of plasmonic nanoparticles improves the efficiency of solar light-harvesting via one or more of the following mechanisms: (1) the LSPR excitation leads to an increase in path length for incoming light via scattering, thereby increasing the probability of photon absorption by the substrate;10−12 (2) energy transfer from the decay of an LSPR directly creates an electron–hole pair in the neighboring semiconductor, a process known as plasmon-induced resonant energy transfer (PIRET);13−16 or (3) direct electron transfer (DET) from the nanoparticle to the substrate;17−21,27 in which an LSPR decays, through Landau damping,22 into an energetic electron (a so-called “hot” electron) that may then scatter into the semiconductor if it has sufficient energy. Though hot electrons carry energy away from the metal, it is not solely an energy transfer mechanism since it includes electron transport from the metal to the neighboring semiconductor and therefore leads to a change in the number of charge carriers. However, for the purpose of the work presented here, this distinction is of no consequence, and we refer to both as energy transfer pathways. Both PIRET and DET stem from the LSPR–substrate coupling and constitute light-harvesting mechanisms absent in nonplasmonic PV devices. These mechanisms can be further divided into radiative and nonradiative contributions; mechanism 1 involves the absorption of solar radiation by the semiconductor and is only effective for photon energies above the semiconductor band gap, while mechanisms 2 and 3 involve solar photons with energies below or above the band gap.14,15 Mechanisms 2 and 3 are of particular interest and importance as they expand the

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Figure 1. Correlation diagram of substrate-induced LSPR hybridization in the cube@substrate system and EELS experimental setup. (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 a 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 at a beam position far from the nanocube.
isolation of the D mode, it has no further impact on the experiment. Difficulties related to finding cube@substrate systems with similar substrate thickness, cube size, and low contamination levels make tilting each system to the same angle impractical.

To explore a variety of optical and electronic properties, we utilize both commercial and in-house fabricated TEM membranes. The employed substrates and their selected properties are listed in Table 1. The SiO\(_2\) membrane is a commercial product widely used for TEM. BP and a-Si membranes are fabricated via conventional TEM specimen preparation procedures. The edge lengths of the studied Ag nanocubes range from 71 to 77 nm. Details about substrate preparation, characterization, and planview TEM images of the studied cubes can be found in the Supporting Information.

The EEL spectra, Z-contrast images, and EEL probability maps of the cube@SiO\(_2\)/BP/a-Si systems are shown in Figure 2. Figure 2a displays EEL spectra acquired at the proximal and distal corners of the cube. The EEL spectra acquired far from the cube are also included to show the background signal due to the substrate. Figure 2b is a collection of Z-contrast images of the tilted cube@SiO\(_2\)/BP/a-Si systems, in which the background color is tuned from black to red, green, and blue, respectively, to increase the visibility of the cube edges. Figures 2c,d show the EEL probability map at the resonance energies of D and Q (\(E_D\) and \(E_Q\)) over the spatial ROI, showing the spatial distribution of the EEL probability.

The EEL probability maps (Figure 2c,d) for the cube@SiO\(_2\) system are in agreement with previous studies of cube@insulator systems, showing substrate- and vacuum-localization for the D and Q mode, respectively. Interestingly, both D-mode maps (Figure 2c) for the cube@BP and cube@a-Si systems exhibit almost zero EEL probability near the proximal corners, in sharp contrast to the substrate localization seen in the cube@SiO\(_2\) system. As will be demonstrated in the following, we interpret the low EEL probability of the D mode at the proximal corners in the cube@BP and cube@a-Si systems as a near-field signature of energy transfer.

### Table 1. Selected Properties of Employed Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(\varepsilon_1)</th>
<th>(\varepsilon_2)</th>
<th>(E_g) (eV)</th>
<th>(E_{\text{opt}}) (eV)</th>
<th>(d_t) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>2.3</td>
<td>0</td>
<td>9.0</td>
<td>10.6</td>
<td>30</td>
</tr>
<tr>
<td>BP</td>
<td>9.6</td>
<td>0</td>
<td>2.1</td>
<td>4.3</td>
<td>38</td>
</tr>
<tr>
<td>a-Si</td>
<td>17.5</td>
<td>3.4</td>
<td>1.7</td>
<td>1.7</td>
<td>26</td>
</tr>
</tbody>
</table>

\(\varepsilon_1\) and \(\varepsilon_2\) are the real and imaginary parts of the dielectric constant at 633 nm, respectively. \(E_g\) is the band gap of the substrate material. \(E_{\text{opt}}\) is the optical or the lowest direct band gap of the substrate material. \(d_t\) is the calculated substrate thickness (Supporting Information).

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Figure 2. EEL spectra, Z-contrast images, and EEL probability maps. (a) EEL spectra acquired at the proximal (solid lines) and distal (dotted lines) corners of the cube and substrate (dashed lines), as described in Figure 1b. These spectra are normalized by corresponding zero-loss intensities. The impact parameter for the proximal and distal EEL spectra is approximately 1 pixel (4 nm) from the cube surface in all cases. The substrate EEL spectra are acquired at a beam position far from the cube. \(E_D\) and \(E_Q\) denote the resonant energies, while \(\Gamma\) denotes the line width of the D mode. (b) Z-contrast images of the tilted cubes. The solid lines represent the cube edges that are visible when viewed into the page, whereas the dashed lines represent cube edges that are blocked in the viewing direction. (c, d) Experimental D- and Q-mode EEL probability maps generated by plotting the spectral intensity over the ROI at \(E_D\) (c) and \(E_Q\) (d). The proximal and distal faces are shown in the maps. The near-zero EEL probability in the D-mode map at the cube@BP and cube@a-Si interfaces is a signature of energy transfer to the substrate.
As was mentioned above, only the substrate-localized D mode significantly contributes to energy transfer, making the Q mode irrelevant to the subsequent discussion. However, as can be seen in Figure 2a, the Q mode is a prominent feature in the distal EEL spectra. For this reason, we include the Q-mode maps to show consistency between our work and previous studies. To gain a metric for energy transfer, we fit the lowest energy peak in each distal EEL spectra to obtain an empirical measure of the D-mode line width, $\Gamma$. (Figure 2a).

We begin by exploring theoretically the signature of PIRET in the D-mode map (Figure 2c). PIRET arises from the near-field coupling between a metal nanoparticle LSPR and an adjacent semiconductor and is similar to the well-studied Förster resonant energy transfer (FRET) mechanism. The plasmonic dipole moment induces a transition dipole moment in the nearby semiconductor, which, through induced dipole–dipole coupling, results in the decay of an LSPR into a bound electron–hole pair in the substrate.

To understand how the EEL probability map and EEL spectra of the D mode is affected by PIRET, we now construct two different theoretical models. First, we calculate the D-mode map and EEL spectra of a model cube@substrate system using e-DDA simulations. The optical response of the cube is parametrized by experimental dielectric data for Ag, while the substrate is characterized by a Lorentz oscillator dielectric function $\epsilon(\alpha; E_{\text{opt}}/h) = 1 + \frac{\alpha^2}{E_{\text{opt}} - i \omega}$. A driving frequency of $\omega$ is set.

In contrast to the cube@insulator map, but in qualitative agreement with the cube@BP/a-Si D-mode maps (Figure 2c). PIRET arises from the near-field coupling between a metal nanoparticle LSPR and an adjacent semiconductor and is similar to the well-studied Förster resonant energy transfer (FRET) mechanism. The plasmonic dipole moment induces a transition dipole moment in the nearby semiconductor, which, through induced dipole–dipole coupling, results in the decay of an LSPR into a bound electron–hole pair in the substrate.

For this reason, we include the Q-mode map for the cube@insulator (PIRET off), and cube@semiconductor (PIRET on, lower panel) model systems. The cube@insulator system ($E_{\text{opt}} \gg E_D$) shows highest EEL probability at the proximal corners of the cube (substrate localization). The cube@semiconductor system ($E_{\text{opt}} = 2.75$ eV) shows a sharp reduction in EEL probability at the proximal corners, a signature of energy transfer and consistent with the experimental observations. The white lines are outlines of the cube and the substrate.

Figure 3. Theoretical study of the effect of PIRET on D-mode map, EEL spectra, and line width. (a) Simulated D-mode EEL probability map for the cube@insulator (PIRET off, upper panel) and cube@semiconductor (PIRET on, lower panel) model systems. The cube@insulator system ($E_{\text{opt}} \gg E_D$) shows highest EEL probability at the proximal corners of the cube (substrate localization). The cube@semiconductor system ($E_{\text{opt}} = 2.75$ eV) shows a sharp reduction in EEL probability at the proximal corners, a signature of energy transfer and consistent with the experimental observations. The white lines are outlines of the cube and the substrate. (b) Simulated EEL spectra for cube@insulator and cube@semiconductor systems for a proximal beam position. The difference in line width between the PIRET off (red curve) and PIRET on (green curve) spectra is due to energy transfer. The D-mode line width for the cube@semiconductor system ($\Gamma_D = 290$ meV) is approximately 3 times greater than the cube@insulator D-mode line width ($\Gamma_D = 105$ meV); this effect is accompanied by a drop in EEL probability intensity. (c) Extended plasmon hybridization model of the D-mode line width ($\Gamma_D$) is plotted as a function of $E_D$ for PIRET off (red curve) and PIRET on (green curve). At $E_{\text{opt}} \approx E_D$, the PIRET on system exhibits the maximum amount of line width broadening due to PIRET. The line width predicted by the hybridization model is in good agreement with the simulation results shown in (b); the green and red dots correspond to the simulated D-mode energies for PIRET on and PIRET off, respectively.

Here, $Q$ is the quality factor of the cube@insulator D mode, $\alpha_{sp}$ is the static polarizability of the cube, $d$ is the distance between the LSPR and its image in the substrate, and $\Gamma$ is the cube@insulator D-mode line width discussed above (PIRET off), which serves as a baseline to estimate PIRET-induced line width broadening. Equation 1 is plotted in Figure 3c as a function of $E_D$ and has a resonance when $E_D \approx E_{\text{opt}}$. This resonance corresponds to a maximum amount of line width broadening due to PIRET and therefore a maximum amount of energy transfer from the cube to the semiconductor. As shown in Figure 3c, the amount of PIRET-induced line width broadening predicted in the analytical model is in good agreement with the e-DDA simulations of the model cube@substrate system described above (Figure 3b). The conclusions drawn from both approaches are that the intensity reduction in the D-mode map at the proximal corners of the cube and the associated line width broadening in the EEL spectra are
Figure 4. Band diagrams and available energy transfer pathways for cube@SiO$_2$/BP/a-Si systems. The cube@SiO$_2$ system (left) has both DET and PIRET channels closed due to the insulating properties of SiO$_2$. $\Phi_b$ is the Schottky barrier and denoted by a black dot in each system. The cube@BP system (center) has DET open ($\Delta = +2.9$ eV) but PIRET closed because of the negligible absorbance of BP in the optical range. The cube@a-Si system (right) has both DET ($\Delta = +1.7$ eV) and PIRET channels open.

- **265 signatures of PIRET. Though neither the classical e-DDA simulations nor the analytical model take the quantum-mechanical DET mechanism into account, it is known to lead to a similar line width broadening. In the DET process, hot electrons are generated through the Landau damping of LSPRs, with a resulting electron energy distribution centered about the resonance energy of the plasmon. These nascent hot electrons may then scatter into the conduction band of the nearby semiconductor if they have sufficient energy to overcome the Schottky barrier ($\Phi_b$). The difference in energy between the LSPR and the Schottky barrier ($\Phi_b$) determines whether or not DET can occur, and the "hotter" an electron is with respect to $\Phi_b$, the higher the probability that it will scatter into the semiconductor. For the cube@substrate systems considered here, it is the decay of the D mode that provides the flux of hot electrons, and the energy difference $\Delta = E_D - \Phi_b$ determines the likelihood of DET. We assume DET to be an open channel if $\Delta$ is positive.

- **282 We summarize the available energy transfer pathways for all three cube@substrate systems in Figure 4. The cube@SiO$_2$ system is not expected to exhibit energy transfer since it is an optically transparent large band gap insulator ($E_{gap} \gg E_D$, $\Delta = -0.7$ eV). The cube@BP system is particularly interesting as BP is transparent at optical frequencies ($E_{gap} > E_D$); i.e., it has a static dielectric response, leaving DET as the only open energy transfer pathway. Furthermore, $\Delta_{BP} = +2.9$ eV suggests that DET will be an efficient channel. The cube@a-Si system has both energy transfer pathways open as a-Si has a small optical band gap ($E_{gap} < E_D$) and a value of $\Delta_{a-Si} = +1.7$ eV.

- **294 With the theoretical descriptions of energy transfer in mind, we return to the analysis of the data. As expected, the cube@SiO$_2$ system shows a clearly substrate-localized D mode (Figure 2c). The lack of energy transfer in the cube@SiO$_2$ system provides a baseline from which to compare other configurations. The energy transfer supporting systems, cube@BP and cube@a-Si, show highly damped D-mode maps with near-zero EEL probability at the proximal corners of the cubes. This is a signature of energy transfer and allows us to determine where the energy transfer occurs with nanoscale spatial resolution. To our knowledge, this is the first report of the STEM/EELS spatial mapping of energy transfer in coupled LSPR–semiconductor systems.

- **307 To further interpret these observations, we compute the EEL spectra using e-DDA for both the cube@BP and cube@a-Si systems (Supporting Information Figure 5) and obtain the simulated values of $\Gamma = 330$ meV for BP and $\Gamma = 410$ meV for a-Si. The dielectric data for both Ag and substrate materials are taken from experiments. The simulation results are less than half the value obtained from experiment ($\Gamma = 760$ meV for BP, $\Gamma = 900$ meV for a-Si). Since the PIRET pathway is accounted for in the classical e-DDA simulations, we attribute the large difference in line width between theory and experiment to DET. This suggests that the DET channel plays a dominant role in both systems, even though the cube@a-Si system has both channels open. This conclusion is supported by the excellent agreement between the full wave e-DDA simulations and the experimental EELS data in the cube@SiO$_2$ system, where all energy transfer channels are closed (compare $\Gamma = 700$ meV from experiment to $\Gamma = 670$ meV from simulation). The results for BP suggest that optically transparent materials could be used to fabricate PV devices that rely solely on plasmonic energy transfer via DET, in contrast to the usual electron–hole pair generation mechanism found in traditional devices.

The approach presented here can be extended in many directions beyond solar devices. For example, the semiconductor can be replaced with redox-active molecules, harvesting the hot electrons produced by the nanoparticle to drive plasmon-assisted catalysis. The localization of the D and Q modes could be exploited to act as an energy transfer switch by tuning the excitation energy, for example, in a semiconductor/cube/semiconductor interface. The nanocube shares a flat surface with the adjacent semiconductor and other geometries such as disks, truncated spheres, or pyramids should be explored to further understand the role of contact area in DET. In this same vein, this work can be extended to investigate the dependence of LSPRs on nanoparticle geometry to determine the role of morphology in energy transfer, a task to which EELS is well suited. Additionally, the dependence of energy transfer pathways on the surface electronic structure of doped semiconductors can be optimized.

In conclusion, we have demonstrated the ability of STEM/EELS experiments to elucidate the nanoscopic flow of energy from a light-harvesting plasmonic nanostructure into its semiconducting substrate. We correlated our experiments with full-wave electrodynamics simulations and extended plasmon hybridization theory to demonstrate that the EEL probability map can provide a spatial profile of energy transfer at the single-particle level. The work presented here provides researchers with new methods to probe competing energy.
transfer mechanisms in hybrid nanoparticle@semiconductor systems. The fundamental understanding of plasmonic energy transfer that we provide will help improve the efficiency of future PV and photocatalytic devices.

**ASSOCIATED CONTENT**

Supporting Information

Information on (i) Ag nanocube synthesis, (ii) TEM substrate preparation and characterization, (iii) EELS experiments and EEL probability map generation, (iv) e-DDA simulations, and (v) extended plasmon hybridization model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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