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E. Eizner and T. Ellenbogen

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Local excitation of strongly coupled exciton-surface plasmons polaritons by a single nanoantenna

E. Eizner^{a)} and T. Ellenbogen

Department of Physical Electronics, Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel

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We demonstrate experimentally local coupling of light from free space to exciton-surface plasmon polaritons (X-SPPs). This is achieved by using a single, sub-wavelength gold nanowire on top of a thin silver film which is covered with a 30 nm thick layer of J-aggregating dyes in polyvinyl alcohol. We show that the nanowire acts as an antenna that resonantly scatters light to X-SPPs states with a Rabi splitting of 0.1 eV. The locally excited X-SPPs properties are studied by angle resolved spectroscopy of the far-field leaky photons and are compared to the large-scale response through Kretschmann reflection measurements and to theoretical calculations. The nanowire scattering properties are studied by dark-field scattering measurements and finite-difference time-domain simulations. This method to locally excite X-SPPs can potentially be useful for future applications of hybrid light matter states. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4881717]

Surface plasmon polaritons (SPPs) are bound modes of electromagnetic fields coupled to oscillating charges which can be excited at the interface between a metal and a dielectric.¹ Their sub-wavelength confinement and strong dependence on the surface properties provide a way for focusing and guiding light at the nanoscale,^{2–4} enabling to develop new nano-optical devices. A main interest is to be able to make these devices active and controllable. One attractive approach is to couple SPPs with electrically and optically controllable materials such as semiconductors which allow formation of excitons.

The interaction between excitons (electron-hole pairs) and vacuum SPP fields has attracted great interest recently.⁵ When the interaction is weak, it can be treated as a perturbation leading to enhancement of the spontaneous emission rates, due to the modification of density of electromagnetic states.⁶ When the interaction is stronger, such that the energy exchange rate between the vacuum SPP and excitons becomes much faster than their individual decay and decoherence rate, the system is in the strong coupling regime and the excitations of the system are no longer SPPs or excitons but hybrid exciton-SPPs (X-SPPs) quasi-particles. These quasi-particles have mixed properties of light and matter particles which make them interesting both for fundamental research and applications.

In recent years, several groups demonstrated strong coupling between excitons in semiconductors or quantum dots and SPPs^{7,8} and some of their attractive properties were studied. For example, the coherent energy exchange between J-aggregate excitons and vacuum SPPs was measured in real time showing Rabi oscillations on a 10 fs timescale,⁹ demonstrating that the exciton population can be used as a nonlinear mechanism for manipulating light on the nanoscale. In addition, since unlike photons, these hybrid light matter modes can interact with each other due to their excitonic part,^{10,11} new device applications are possible, such as the generation of low threshold coherent emission at room temperature without the need for population inversion,^{12,13} low threshold, and ultra-fast all-optical switches.^{14,15}

The properties of excitons strongly coupled to localized surface plasmon resonance (LSPR) were studied in the past,^{16,17} however, so far the properties of propagating X-SPPs were mainly studied macroscopically. For the development of compact devices based on propagating X-SPP modes, it is of key interest to study their local properties and efficient ways to transfer energy locally into or out of these modes. In this work, we demonstrate and study local coupling of light from free space to strongly coupled X-SPPs modes on metal-organic semiconductor interfaces by using a single metallic nanoantenna. The nanoantenna supports LSPR which is used to enhance the local coupling to the propagating X-SPP modes.

Many features of X-SPPs, such as the energy dispersion and the vacuum Rabi splitting, can be understood in terms of two strongly coupled harmonic oscillators.^{7,18} Other features, such as the modes occupation statistics, require a quantum theory treatment.^{9,19} In the coupled oscillators model, the energies of the system can be written in the form of

$$E_{lp,up} = \frac{1}{2} \left[E_x + E_{SPP}(k) \pm \sqrt{4g_0^2 + (E_x - E_{SPP}(k))^2} \right], \quad (1)$$

where $E_{lp,up}$ are the lower and upper polaritons' energies, $E_{SPP}(k)$ is the vacuum SPP energy with k being the in-plane momentum, E_x is the excitons' energy, and g_0 is the coupling energy from the interaction between the vacuum SPPs and the excitons.

X-SPPs have higher momentum than free space photons with the same frequency, resulting from their SPP component. In order to couple to X-SPPs modes from free space, the energy and momentum must be conserved in the transition. There are a few well established approaches to provide the missing momentum. One approach is to use a high index glass in Kretschmann's or Otto's configurations. Another approach is to use periodic gratings.²⁰ However, in these

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^{a)}Electronic mail: eladeiz@post.tau.ac.il





FIG. 1. (a) Illustration of local coupling of light to X-SPP surface modes. (b) Layer diagram of the fabricated sample. (c) Absorption of a 30 nm layer of PVA-TDBC solution. The inset shows the chemical formula of TDBC. (d) Scanning Electron Microscope image of the nanowire.

techniques, the coupling is on a length scale much larger than the wavelength. For a local coupling, methods using near field optics can be used, e.g., near field scanning microscopy (NSOM) tip excitation,²¹ emission from quantum emitters close to the surface,²² free electron beams,²³ and by use of sub-wavelength light scatterers.^{24–27} In our work, local coupling is achieved by using a single metallic nanowire which acts as a nanoantenna launching the propagating X-SPPs (see illustration in Fig. 1(a)). We chose a nanowire since it can support launching of quasi-plane-waves.

To fabricate our sample (illustrated in Fig. 1(b)), 70 nm of silver was evaporated on indium tin oxide covered glass substrate. On top of the silver film, a 300 nm wide, 100 μ m long nanowire was fabricated using electron-beam lithography of polymethyl methacrylate (PMMA) followed by evaporation of 60 nm of gold layer and a lift-off process. A thin 3 nm layer of titanium was evaporated and then oxidized in air²⁸ to protect the silver layer and improve the adhesion of the organic layer.^{7,29,30} The organic-semiconductor layer consisted an aqueous solution of 0.72% polyvinyl alcohol (PVA) mixed in a 3:1 ratio with a aqueous solution containing 4×10^{-5} mol cyanine dye molecules (resulting in 2×10^{-3} mol/l molecules concentration for the mixed solution) which was spin coated at 6000 rpm resulting in a film of 30 nm thickness. The cyanine dye molecules were 5,5', 6,6'-tetrachloro-1-1'-diethyl- 3,3'-di(4-sulfobuthyl)-benzimidazolocarbocyanines (TDBC), which are known to form linear chains of J-aggregating molecules at low concentrations $(>10^{-5} \text{ mol/l}).^{30,3}$

Molecular aggregates have remarkable optical properties, including a delocalization of the excitation, narrow absorption, and emission spectra, and large oscillator strengths,⁵ making them susceptible to couple strongly to electromagnetic fields. The PVA concentration in the solution has a large effect on the layer thickness. By modifying the concentration along with the spin coating speed, one can control the layer thickness from a few tens to hundreds of nm, allowing to tailor the coupling strength or to support waveguide modes.^{32,33} The absorption of a 30 nm layer of PVA-TDBC film on glass is presented in Fig. 1(c), which shows a strong absorption peak (at the J-band at 2.113 eV (587 nm) and with a 60 meV full width at half maximum) and proves that the molecules formed aggregates.

The experimental setup is illustrated in Fig. 2. The sample was attached to a right angle glass prism using index matching oil and was excited by three separate pathways (marked I–III). Pathway I was used for bright-field imaging and leaky photons experiments, pathway II was used for dark-field imaging and scattering measurements, and pathway III was used for reflectometry in Kretschmann's configuration. The objective lens was a $50 \times \log$ working distance objective with numerical aperture of 0.42. For excitation, we used either Xenon arc lamp or super-continuum laser source (SuperK Compact), for imaging, we used either conventional CCD camera or a cooled EMCCD camera (Newton 970) and



FIG. 2. Experimental setup (RS- rotating stage; BS- beam splitter).

for spectral measurement light was collected with a fiber bundle into a spectrometer (Shamrock 303i). To study the local coupling effect, we simulated the system with 2D finite-difference time-domain (FDTD) simulation. Johnson and Christy data³⁴ were used for gold and silver permittivity. We used the following single Lorentzian oscillator model for the permittivity of the PVA-TDBC layer:

$$\epsilon_{Lorentz}(\omega) = \epsilon_{\infty} + \frac{f\omega_o^2}{\omega_0^2 - \omega^2 - i\gamma\omega},$$
(2)

where ϵ_{∞} is the PVA bound electrons permittivity ($\epsilon_{\infty} = 2.56$), ω_0 is the oscillator frequency ($\omega_0 = 3.212 \times 10^{15} \,[\text{rad/s}]$), γ is the damping constant ($\gamma = 9.1 \times 10^{13} \, [rad/s]$), and f is the oscillator strength (f = 0.04). These parameters were calculated from the PVA-TDBC absorption (Fig. 1(c)) and theoretical fit to the reflectometry experiments (discussed later and shown in Fig. 4). The numerical method which was used to study the system includes separating the simulation to a total field region, which includes the sum of the incident field wave plus the scattered field (within the dashed lines in Fig. 3(a)) and a scattered field region (outside the dashed lines). Fig. 3(a) shows the real part of the z component of the magnetic field using plane wave excitation at a free space wavelength of 620 nm polarized at the plane of incidence and launched from above. In resonance, the nanowire acts as an optical antenna, scattering light with a larger cross section than its geometrical cross-section. Coupling to X-SPPs will occur for scattered light with matching in-plane momentum. One can see the magnetic field enhancement close to the nanowire edges at the total field regime and surface waves launched away from the nanowire. These surface waves are the X-SPPs of interest in our work.

In order to check this mechanism experimentally, we first studied the scattering properties of the nanowire by dark-field scattering measurements. The sample was shined at oblique incidence at 45° with respect to the surface (pathway II). The scattered light was collected by the objective lens and either imaged on a CCD camera or analyzed spectrally. The inset in Fig. 3(b) shows a dark-field image of a small section of the nanowire. The measured normalized scattering from the nanowire with respect to surface scattering is presented as the blue line in Fig. 3(b) which shows

maximal scattering at 635 nm due to the nanowire resonance. The simulated scattering from a nanowire embedded in PVA and a nanowire embedded in PVA-TDBC are shown as the green line and green dashed line in Fig. 3(b), respectively. No temporal filtering was used to obtain the results. The experimental results agree with simulated results of uncoupled nanowire scattering (green line in Fig. 3(b)) except of a red shift in the experiment which can result from various reasons, such as the PVA-TDBC layer inhomogeneity at close vicinity to the nanowire and the nanowire actual geometrical shape. The experimental spectrum does not show the splitting as in the dashed line simulation, possibly due to larger dissipation of the localized modes compared to theory, exceeding the interaction energy or weak linking of the J-aggregates to the gold surface. Nevertheless, as shown next, light still couples locally to X-SPP modes. The thickness of the silver in our sample was chosen to be 70 nm to allow input and output coupling of propagating X-SPP modes from and to the glass side. To study the non-local, large scale response of the system, we performed reflectometry experiments in Kretschmann's configuration²⁰ with spot radius of approximately 0.5 cm (pathway III). We simulate the reflection response, using Fresnel's reflection calculations for five-layers with the same materials' permittivities and layer thicknesses as in the FDTD simulations. The angle resolved spectral reflection measurements and simulation, R_{tm}/R_{te} results appear in Figs. 4(a) and 4(b), respectively, where θ in all figures is the incident angle of light in the prism. The measured splitting which agrees with simulation results indicates that the probed modes are indeed X-SPPs.' The experimental spectral width of the modes is larger than the theoretical calculations, which can be accounted to the sample roughness, surface related dissipation, and inhomogeneity.

To excite X-SPPs locally, we used pathway I to focus light on the nanowire. To probe the excited modes, we measured the leaky photons which were coupled out to the far field using a glass prism. The leaky photons were collected by an optical fiber mounted on a rotating stage with 2° resolution and directed to a spectrometer. This way angle resolved spectroscopy of the leaky photons was performed. The spectral results, normalized between 0 and 1 for each angle are shown in Fig. 4(c). The measured leaky photons



FIG. 3. (a) 2D FDTD simulation of scattering incident field to surface modes by the nanowire. Magnetic field distribution [Real (H_z)] at wavelength of 620 nm. Arrow marks the incident light polarization. The scale-bar is normalized to have a minimum value of -1. (b) Dark-field (DF) scattering. Blue solid line: dark-field measurement of the scattered light by the nanowire, normalized with scattered light from a surface area without the nanowire. Green solid and dashed lines present simulation results of dark-field scattering spectrum normalized to the light source power with an excitonic layer (dashed) and with a normal dielectric layer (solid). The inset shows the dark-field image of the scattered light from the nanowire in false colors.



FIG. 4. (a) Reflectometry experiments in Kretchmann configuration. (b) Fresnel reflection simulation. (c) Angle resolved spectroscopy of leaky photons (d) Dispersion relations. Red circles: Energy dispersion of the locally excited X-SPPs taken from leaky photons experiments. Blue triangles: Energy dispersion of X-SPPs taken from the non-local reflectometry in Kretchmann configuration. Dashed lines are the uncoupled excitons absorption and the SPPs dispersion, the latter was calculated from Fresnel reflection simulation. Solid line was calculated from the coupled oscillator model with $g_0 = 0.05 \text{ eV}$.

were TM polarized, as expected from the polarization of the surface polaritons. We clearly observe two distinct branches in Fig. 4(c) spectrum due to existence of strongly coupled modes. This gives an excellent evidence that we were able to use the nanowire to locally excite X-SPPs. To make sure that these are indeed X-SPPs, we calculated the dispersion relation, E(k), obtained by the different measurements and by the simulation. The wave-vector $k = \frac{2\pi n}{\lambda} \sin(\theta)$, where n is the refractive index of the prism. The energy for each wave vector was derived from the peaks or dips in the measurements and simulation. The dispersion relations obtained by the different methods are plotted as Fig. 4(d). At energies detuned from the excitons and SPPs crossing there is an excellent agreement between the two data sets, suggesting that the local and the large-scale SPP properties are not so variant, and that the local PVA-TDBC layer thickness is approximately the average thickness in the sample. In the X-SPP region around the crossing of the exciton and SPP dispersions, the large-scale response exhibits stronger splitting, indicating that the interaction between the excitons and SPPs is stronger compared to the local case. We believe that the weaker interaction results from exciton bleaching due to strongly focusing the light on the nanowire. We noticed some color change in the sample at the nanowire area after performing the experiment which supports this assumption. The overall agreement between the different measurements and simulations indicates that all the different measurements probe X-SPPs. The uncoupled exciton and SPPs are at resonance when $k = 0.013 \text{ (nm}^{-1})$, where the two LP and UP energies have the minimum separation, with vacuum Rabi splitting of $\hbar \Omega = 2g_0 = 0.1 \,\mathrm{eV}$.

is obtained by a metallic nanowire which acts as a resonant antenna. At the antenna resonance, strongly coupled X-SPP modes are efficiently excited. We confirmed that the excited modes were X-SPP by comparing their energy dispersion to those of X-SPP probed by Kretchmann geometry, by numerical simulations and analytical calculations. For the use of X-SPPs, in all-optical nanophotonic devices, their local properties and efficient ways to transfer energy into these modes locally are of key interest. This work provides a way to locally couple into and out of X-SPP modes and opens the door to examine other properties such as their propagation distances and local population dependent nonlinearities.

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In conclusion, we experimentally demonstrated local coupling of light to propagating X-SPPs. The local coupling

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