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Anomalous spectral shifts in extreme plasmonic nano-cavities

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Abstract – **Nanoplasmonics have the ability to confine light in sub-wavelength cavities, with recent nano-fabrication developments allowing for the realization of nanometer and sub-nanometer plasmonic cavities. We show that for such extremely small nano-cavities, the correlation between the field enhancement resonance and the radiative (far-field) resonance breaks down. This dissociation dominated the excitation and interference of higher-order modes in these nano-cavities. We discuss and demonstrate the impact of this anomalous spectral behaviour for the strong coupling of quantum emitters with plasmonic nano-cavities, where it is imperative to have nano-sized cavities.**

I. Introduction

Plasmonic nanostructures have the ability to confine light in sub-wavelength volumes, which leads to large field enhancements. It was recently shown [1, 2] that by assembling a nanoparticle on a metallic surface (i.e. nanoparticle on mirror configuration- NPoM) figure 1(a), one can achieve extremely small nano-cavities whose dimensions are controlled with high accuracyby the molecular spacer between the nanoparticle and the metallic surface. Hence, nanoplasmonic cavities of just few nanometers [1, 2] and even sub-nanometer [3] dimensions have been realized, paving the route towards observing strong coupling [4] and intense surface-enhanced Raman scattering (SERS) [5] from just few molecules. It has been widely accepted so far that the localized field enhancement (near-field) of a plasmonic structure or antenna and its radiative far-field spectra are resonant at similar wavelengths, with the near-field resonance always slightly red-shifted from the far-field resonance [6]. This near-field red-shift has been assumed to be a universal plasmonic property [6]. However, we show, using a theoretical model, numerical calculations and experiments, that for tightly-coupled nanoplasmonics forming extremely small nano-cavities (of few nanometer and sub-nanometer dimensions), this correlation between the near- and far-field spectra breaks down. In fact, in such nano-cavities the near-field resonance is always significantly blue-shifted from the far-field spectra (see figure 1(b-d)) [5].

II. Near-field and far-field spectral correlation in nano-cavities

Direct measurements of the near-field plasmonic enhancement for the NPoM set-up and for a wide spectra regime are rather challenging due to the morphology of the structure that does not allow for probe-based techniques, and the unsuitability of single wavelength measurements (such as third harmonic generation). We employ a widely-tuneable SERS technique to measure the Raman signal of the molecules within the nano-cavity (i.e. field enhancement) and dark-field measurements (far-field) on single NPoM structures [5]. This set-up allows us to obtain the near-field spectra within the nano-cavity of NPoM, and directly compare it to the far-field spectra radiated from the same single NPoM structure [5]. Experimental results (see figure 1(b-c)) show the significant blue-shift of the near-field resonance with respect to the radiated spectra. The high reproducibility of our measurements confirms the robustness of the NPoM geometry, and the excellent control of the cavity size achieved with this nano-assembly procedure [5].

Using a theoretical analytical model, where we decompose the excited plasmonic modes in the system, we find that this spectral blue-shift of the near-field resonance is due to the excitation and strong interference of

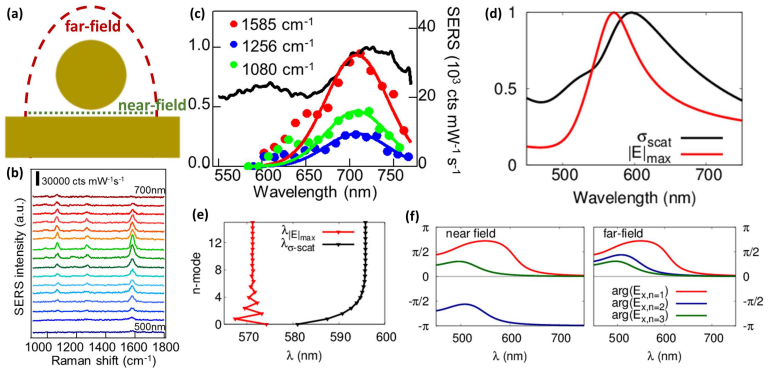

Fig. 1: (a) The nanoparticle on mirror (NPoM) configuration. (b) Experimental measurements of the Raman signal showing the field enhancement at different wavelength and (c) the normalized scattered intensity in the far-field obtained with dark-field measurements. (d) Numerical calculations for the normalized field enhancement and the scattering cross-section. (e) The near- and far-field resonance wavelength as higher-order modes are considered.(f) The E-field phase for the three first modes of the system in the near-field and the far-field.

higher-order modes within the nanocavity. Although higher-order modes in plasmonic structures are usually either too weak and/or non-radiative, their strong confinement in such extreme nano-cavities enhances them enough to interfere with the strongly radiative (bright) modes, shifting them [5]. One would expect though, that the higher order modes would impact the near- and far-field spectra in the same manner, preserving their correlation. However, consecutive modes within the nano-cavity are out of phase and therefore interfere destructively, but radiate in the far-field in phase (i.e. constructively), as shown in figure 1(f). This shifts the far-field spectra to more red wavelengths, leaving the near-field (field-enhancement) resonance to bluer wavelengths (see figure 1(e)). As the nanoparticle is moved away from the mirror, and the two plasmonic structures decouple, the higher-order modes become less prominent and the system reverts back to the universal state, where the near- and far-field spectra are resonant at close wavelengths.

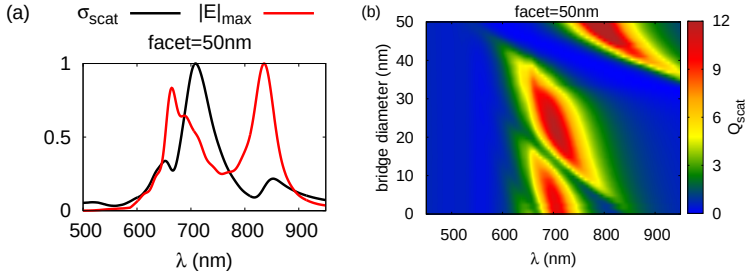

Fig. 2: (a) The normalized scattering cross-section and field enhancement spectra for a faceted NPoM with facet$=50nm$. (b) The scattering efficiency of a faceted NPoM as a bridge is formed within the nano-cavity.

Since higher-order modes change the correlation between the near- and far-field resonances, the geometry of the nanocavity that determines their excitation wavelength, also dominates the two spectra. Fabricated nanoparticles of diameter $< 100nm$ are not perfect spheres, but actually polyhedrals (or faceted spheres), and when assembled into a NPoM set-up they therefore produced nano-cavities of various geometries [7]. Through UV-laser irradiation, we grow and control the size of the facet and therefore the shape of the nano-cavity [3]. We observe that the plasmonic mode dominating the field enhancement in the nano-cavity, is not necessarily always the mode that radiates strongly to the far-field (see figure 2(a)), breaking down even further the correlation between the near- and far-field spectra [3]. In fact, we commonly observe that the facet NPoM radiates in the far-field with a higher-order mode than the mode providing the field enhancement in the cavity. This anomalous behaviour is dependent on the size and geometry of the nanoparticle's facet, which forms the nano-cavity [7]. It leads to sharp discontinuities in the far-field spectra as the NPoM becomes more faceted with UV-laser irradiation [3, 7]. Furthermore, by steadily

bridging (i.e. destroying) the nano-cavity, the dominant radiative mode gradually transitions back to a lower order (see figure 2(b)), and the plasmonic system reverts back to the universal state with the near- and far-field closely correlated.

III. Strong coupling in extreme plasmonic nano-cavities

The anomalous spectral shifts in extremely small nano-plasmonic cavities have a profound impact on optimizing and tuning SERS devices and plasmonic sensors. Most importantly though, the distinct differences between the field-enhancement in nano-cavities and radiative spectra have strong implications in quantum plasmonics, and in particular for observing and understanding strong coupling processes between nanoplasmonic structures and quantum emitters, where extremely small cavity are a necessity. It is evident from the discussion above and figure 2(a) that a quantum emitter placed within such nano-cavities, experiences the largest field enhancement (i.e. near-field resonance) at a different wavelength than the radiative wavelength of the nanopalsmonic structure. Furthermore, the plasmonic resonances are not spectrally isolated, and therefore the quantum emitters are actually interacting with multiple plasmons of different coherence. Finally, it should be noted that in these nano-cavities not all strong coupling processes can be carried and therefore measured in the far-field. Hence, a rather complex interaction occurs between the quantum emitters and the plasmons of such nano-cavities that has so far been ignored.

IV. Conclusion

Extremely small plasmonic nano-cavities of nanometer and sub-nanometer dimensions exhibit anomalous spectral shifts between their field enhancement resonance and their radiative resonance. For tightly-coupled spherical NPoM configurations, the near-field resonance is always blue-shifted with respect to the far-field resonance. As the two structures decouple, the system reverts back to its universal plasmonic state, where the near-field resonance is slightly red-shifted with respect to far-field resonance. Faceted NPoM create nano-cavities of varying geometry, where we demonstrate that the plasmonic mode driving the field-enhancement in the cavity does not necessarily carry the radiative fields to the far-field, leading to a complete break-down to the correlation between near- and far-field spectra. This anomalous spectral behaviour significantly impacts measurements of strong coupling for quantum plasmonics where extremely small nano-cavities are a necessity.

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