

Plasmonic response of composite graphene-Au nanopatterned systems

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Metallic nanostructures (NPs) under the influence of an incident electromagnetic (EM) field can undergo a resonant oscillation of their free-electron plasma, referred to as localized surface plasmon (LSP) resonance [1]. In correspondence of the LSP, the nanostructures exhibit enhanced cross sections for EM-field absorption and scattering and strong subwavelength concentration of the EM energy in the immediate proximity of the nanostructures' surface. The spectral structure of such LSP resonances are strongly sensitive to the local environment of the nanostructures, simultaneously offering a way to tune the resonance and making plasmonic systems excellent for sensing.

Coupling a plasmonic system to graphene leads to the realization of hybrid media where the mutual influence of plasmon resonances and graphene leads to the appearance of novel functionalities absent in the stand-alone materials. For example, graphene allows the active tuning of LSP resonances [2], while plasmonic particles may boost the otherwise weak optical absorption of graphene, and provide photoinduced hot-electron doping in graphene [3]. However, a detailed microscopic understanding of the dominant basic interaction mechanism of graphene and plasmonic materials that would allow for a more precise design of hybrid composites, is yet to be achieved. For this reason, the investigation of model systems that allow disentangling different physical ingredients of the graphene/plasmonic systems is strongly required.

Within this framework, we addressed the optical response of a hybrid graphene/plasmonic device consisting of a 2-dimensional gold nanoparticles (NPs) array, on top of which a single-layer-graphene foil was deposited. The Au NPs have a typical size below 20 nm and are arranged in the form of very-closely-spaced NP chains laid with a coherent orientation on a nanopatterned CaF₂(110) surface. The systems exhibited a strong absorption of electromagnetic (EM) radiation at $\lambda=580$ nm, indicative of a collective LSP, i.e. a plasmon resonance whose frequency depends from both the single-NP characteristics and the mutual EM coupling of the particles in the nanoarray.

The single-layer graphene sheets were fabricated by chemical vapour deposition on Cu foils [4], then transferred intact onto the Au-NP nanoarrays in aqueous solution. An atomic-force microscopy characterization showed that the graphene lies in direct contact with the Au NPs, showing a uniaxial corrugation due to the influence of the underlying Au-NP chains. Scanning electron microscopy shows that the Au NPs remain intact, in shape and spatial arrangement, following the graphene deposition (Fig.1).

The unique electronic properties of graphene in EM near-field coupling with metallic nanostructures lead to significant perturbation of the local distribution of electromagnetic field intensity, hence of the plasmonic response. Furthermore, injection of hot electrons from the plasmonic particles into the graphene can lead to indirect electron-mediated inter-particle coupling that affects the collective LSP.

The system showed indeed a remarkable LSP-resonance redshift as the graphene layer is transferred onto the gold nanoparticles. Interestingly, the uniaxial corrugation of graphene

induced a strong optical anisotropy in the system's plasmonic response, the LSP redshift being weaker/stronger whereupon the polarization of light is transverse/parallel to the graphene corrugation. This behavior can be understood mainly in terms of graphene-mediated electronic interaction between NPs in the nanoarray, allowing to discriminate between these phenomena and purely-EM coupling effects, possibly paving the way to the tailoring of plasmon/graphene hybrid systems' optical response [4].

References

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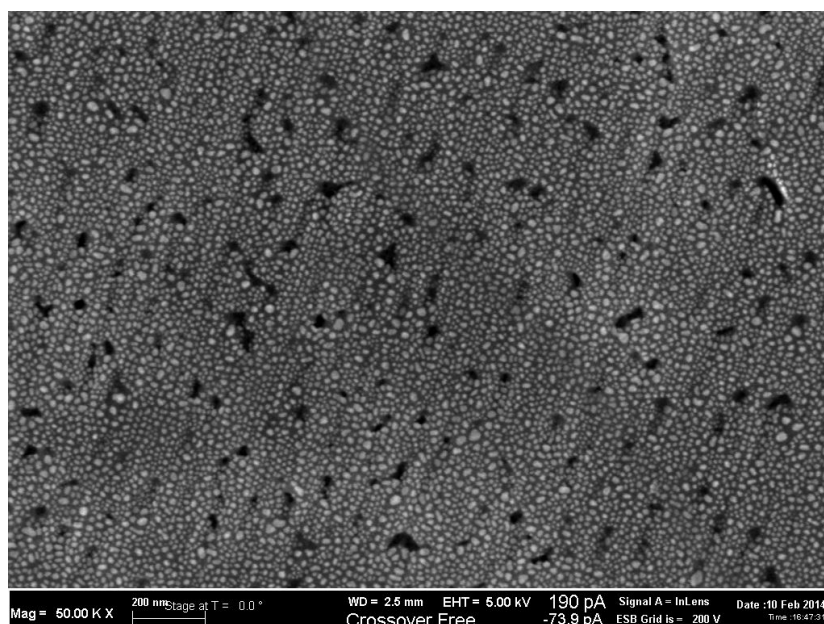


Figure 1: SEM image of Au NPs under a graphene layer.