SERS in the ultra-small limit: size and interparticle distance effects

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We have studied the amplification by very small Ag NPs (r=2nm) of the Raman signal from Graphene and Rhodamine 6G (R6G). The Ag NPs, deposited on glass with a gas aggregation technique, present a very narrow size distribution (2 ± 2 nm) and surface free of organics. We have evaluated the suitability of ultra-small Ag Np as SERS[1] substrate. Although the electric field amplification factor for isolated ultra-small NPs is hampered by size effects[1,2], the increase in the density of available hotspots[2] may benefit the overall amplification for organic molecules.

We present experimental results on the dependence as a function of the NPs density of the plasmon and of the Raman amplification factors for an underlying SL graphene and for spin coated R6G. Numerical simulations (Lumerical FDTD Solutions) of close-packed NPs are used to reproduce the experimental results and obtain general trends. The observed energy and shape modifications of the plasmon are not related to the NPs size distribution, very narrow in this case, but to the presence of interacting NPs with varying distributions of inter-particle distances as their density is increased. The obtained amplification factors for these 2 nm NPs (when normalized to the silver mass present in the platforms) is higher than those corresponding to larger (r= 10-15 nm) Ag Nps. The amplification for R6G increases exponentially with NPs density due to the enhanced electric fields as the inter-particle distance is reduced, being larger at the equatorial planes of the NPs (Figure), where some R6G may be present, this effect however doesn't affect the Raman signal of the underlying graphene.

References

[1] Schatz G.C., Young M.A., Van Duyne R.P. (2006) Electromagnetic Mechanism of SERS. In Surface-Enhanced Raman Scattering. Topics in Applied Physics, vol 103. Springer

[2] Ref Ultrahigh-Density Array of Silver Nanoclusters for SERS Substrate with High Sensitivity and Excellent Reproducibility. Won Joon Cho, Youngsuk Kim, and Jin Kon Kim *ACS Nano* **2012** *6* (1), 249-255

Figures

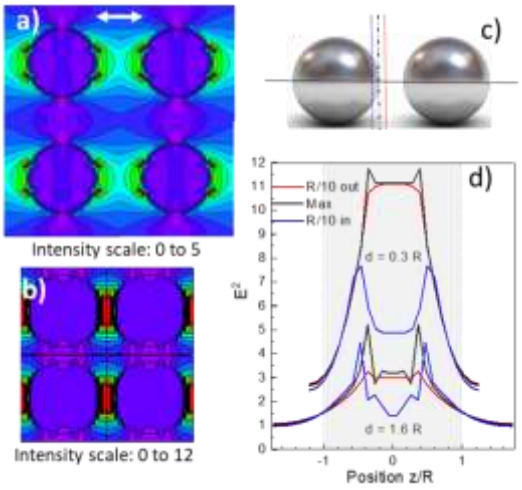

Figure 1. Electric field amplification of a periodic array of Ag NPs for to interparticles distances.