Investigating photopolymerization at the single molecule scale

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Optical near-field at the vicinity of metal nanoparticles generates highly confined electromagnetic fields that can be used to trigger polymerization reaction at their surface.[1] This strategy has been used to fabricate hybrid metal/polymer nanoparticles.[2] We recently demonstrated that this configuration is associated to very specific physico-chemical phenomena that result from the limited number of excitable initiator molecules in the exalted volume.[3]

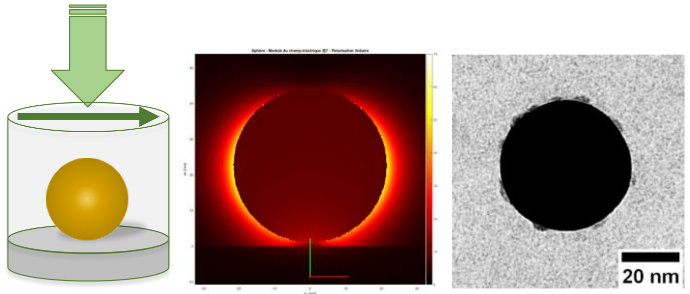

Figure: (Left) Schematic view of a metal nanoparticle in the photopolymerization under irradiation. (Center) Simulated electro-magnetic field around the nanoparticle showing the exaltation and confinement of the field near the nanoparticle surface. (Right) TEM image after polymerization showing single macromolecules grafted at the surface of the metal nanoparticle.

The first objective of this PhD thesis is to further investigate the physico-chemical phenomena involved by monitoring the polymerized volume versus different experimental conditions. By using a methodology based on the observation of the hybrid nanoparticles by Transmition Electron Microscopy, the impact of photonic and chemical parameters can be directly observed. In particular, we have shown in recent studies that very small polymer parts can be generated.[4] They correspond to single macromolecules generated by the excitation of a single photoinitiator molecule, in specific irradiation conditions (see figure).

The second objective is to develop new nanomaterials compatible with the near-field photopolymerization process. In particular, sensing materials will be grafted to the metal center and the material will be interogated through spectroscopic (SERS) or refractive index changes. The hybrid nanoparticles will be then used optical nanosensors. Combination with living photopolymerization will be further also developed for advanced hybrid functional nanostructures.[4]

[1] Zhou, X. et al, *Journal of Optics* **2014,** *16*, 114002.
[2] Deeb, C. et al, Acs Nano **2010**, 4 (8), 4579-4586.
[3] Deeb, C. et al, J Am Chem Soc **2011**, 133 (27), 10535-10542.
[4] Kameche, F. et al, submitted.