Free-radical photopolymerization triggered by localized surface plasmons

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Over the past ten years, localized surface plasmons have been exploited for triggering and controlling photochemical and photophysical reactions. Achieving hybrid nanosystems that couple metal nanostructures to organic dyes or polmyers with enhanced effect is a major challenge for applications in nanophotonics, sensors or spectroscopy. [1]

In our case, surface plasmon dipolar resonance of individual metal nanoparticles was used as an optical near-field source to locally trigger free radical polymerization of an acrylic monomer via excitation of appropriate photoinitiator: metal nanoparticles embedded in a photopolymer sensitive at the resonance wavelength are irradiated under the polymerization threshold but close enough to this threshold to initiate the free-radical polymerization thanks to electromagnetic near-field enhancement. [2]

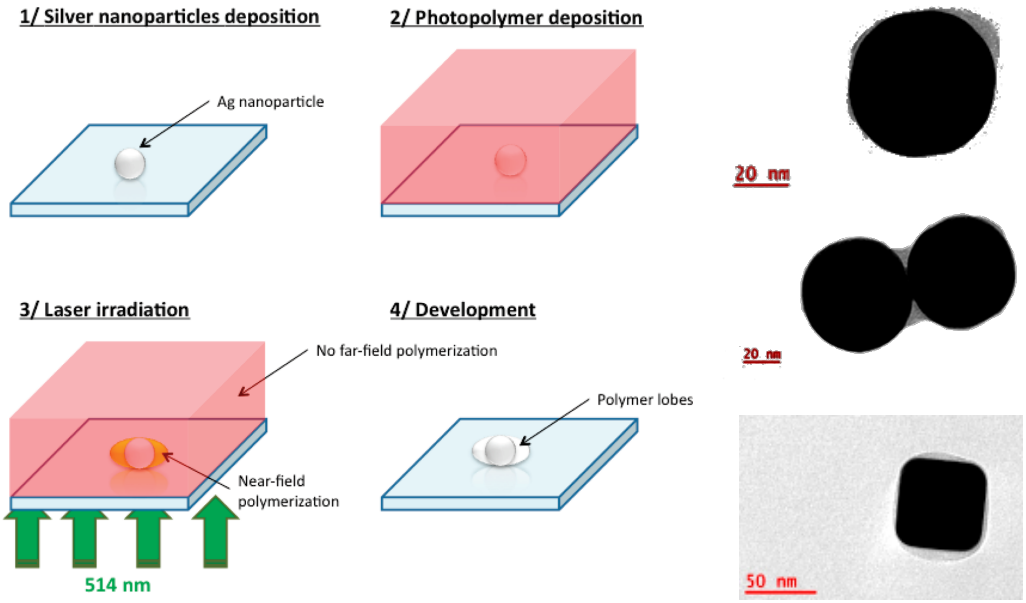

Figure : Schematic description of the procedure for near-field photopolymerization around Ag nanoparticles leading to the hybrid metal/polymer particle and examples of hybrids nanostructures visualized in TEM (metal nanoparticle and polymer appear resp. in black and in grey).

We report on the physicochemical and optical parameters controlling the photopolymerization process in near-field. Kinetic parameters were shown to be of paramount importance to

control the polymerization in highly confined space. Indeed, the number of photoinitiator molecules is so limited that unconventional response to photonic parameters was recorded. Light polarization was also found to be important not only for the shape of hybrid particles but also for the energy transfer efficiency from nanoparticles to photopolymer.

Finally, this method is very interesting to fabricate hybrid metal/polymer nanosystems with original optical properties and also investigating photopolymerization at the nanoscale.

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