

Probing Plasmon Induced Chemical Mechanisms by Free Radical

NanoPhotopolymerization

Supporting Information

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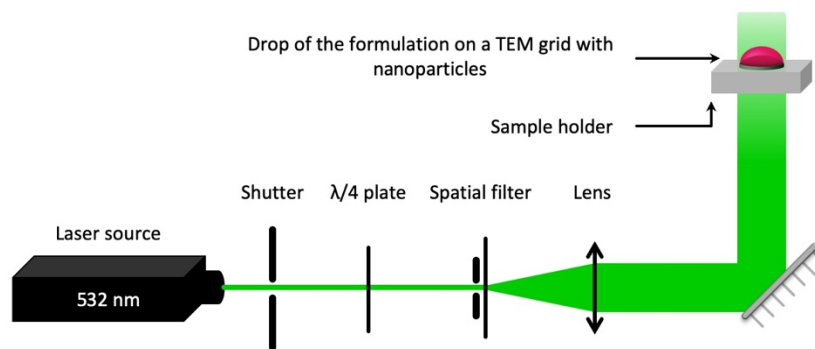


Figure S1: Schematic of the optical setup for LSPR polymerization

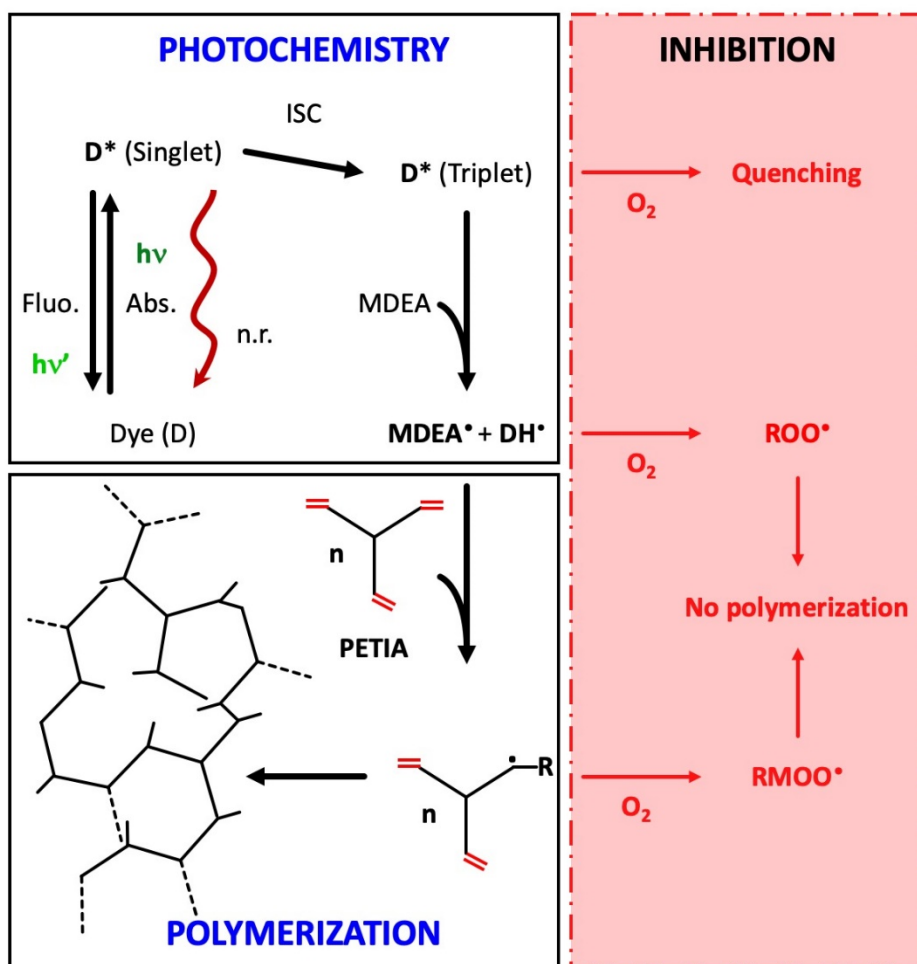


Figure S2: Schematic of the photopolymerization mechanism for EY-MDEA-PETA

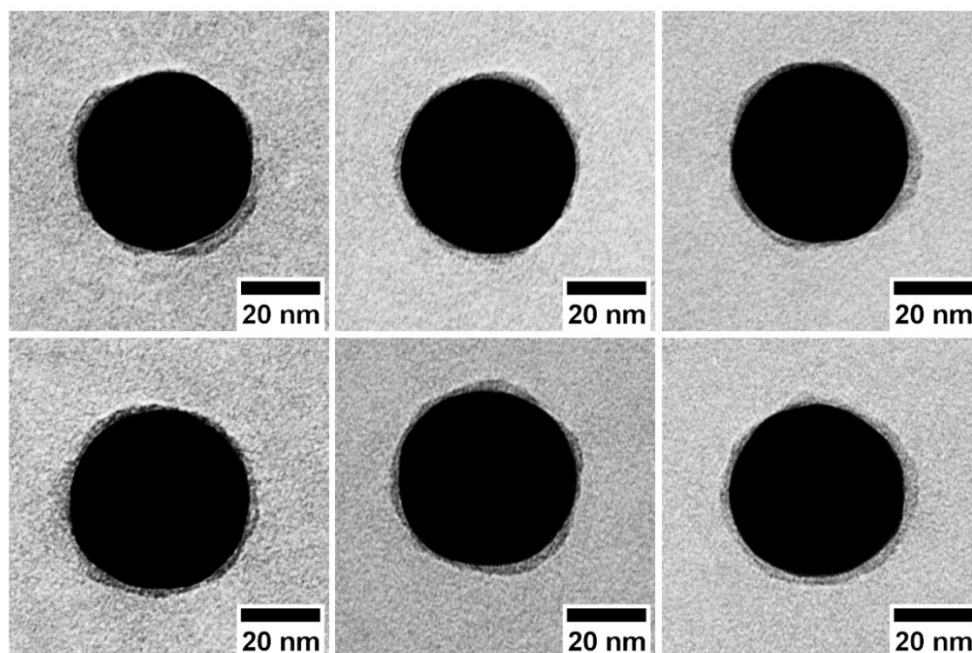


Figure S3: TEM images of HNPs prepared at 90% t_r with EY-MDEA-PETA 2 mW/cm², 1.35 s

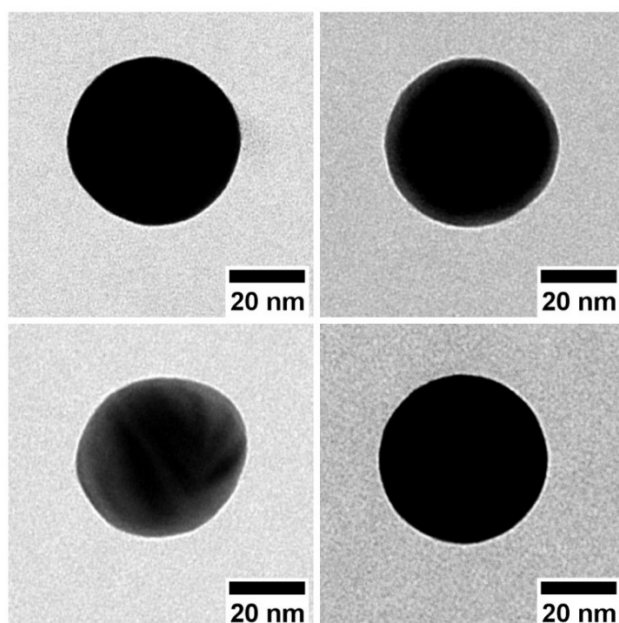


Figure S4: TEM images of NPs after irradiation at 90% t_r with MDEA-PETA 2 mW/cm², 1.35 s

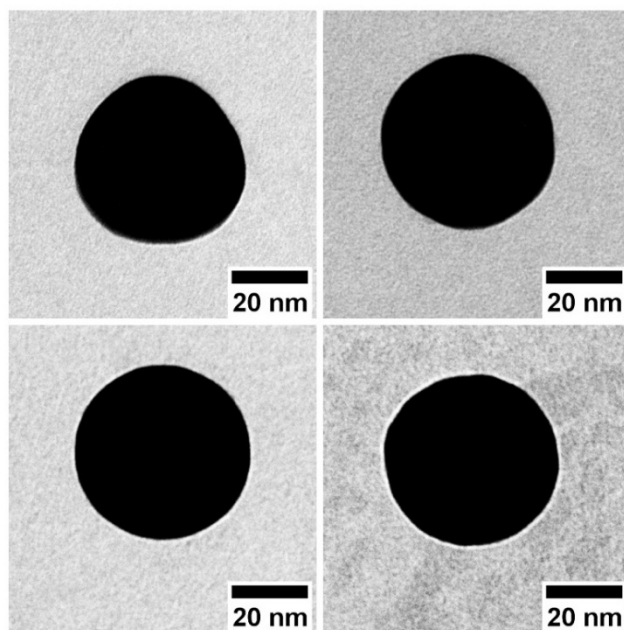


Figure S5: TEM images of NPs after irradiation at 90% t_r with EY-PETA 2 mW/cm², 1.35 s

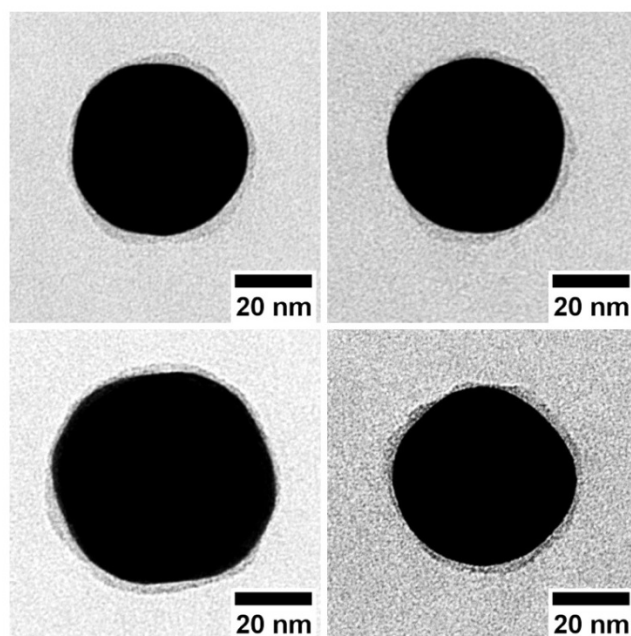


Figure S6: TEM images of NPs after irradiation 1000% t_r with MDEA-PETA 2 mW/cm², 15 s

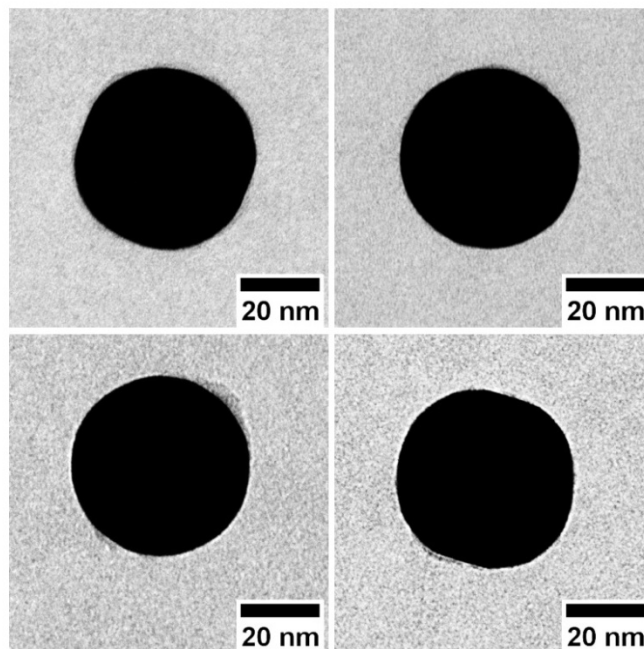


Figure S7: TEM images of NPs after irradiation at 1000 % t_r with EY-PETA 2 mW/cm², 15 s

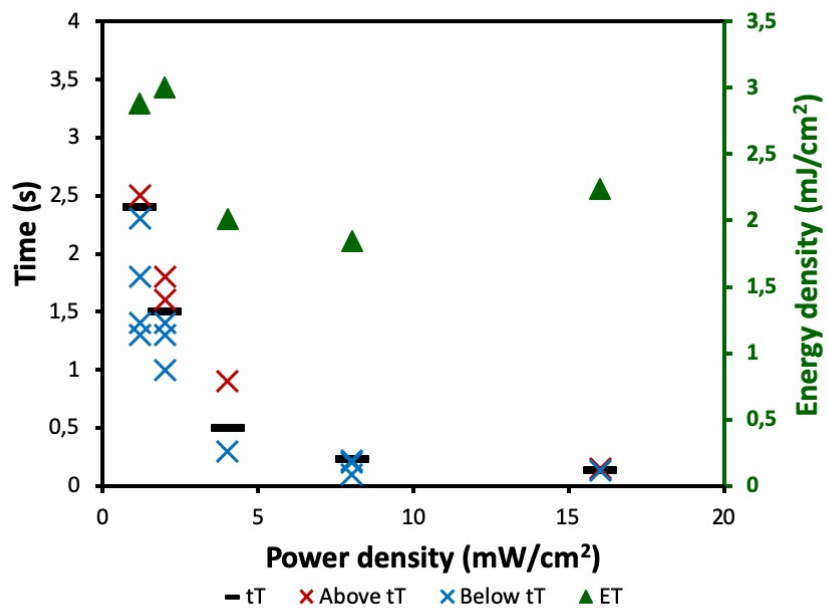


Figure S8: Threshold time and Threshold Energy of polymerization as a function of light power density (EY-MDEA-PETA)

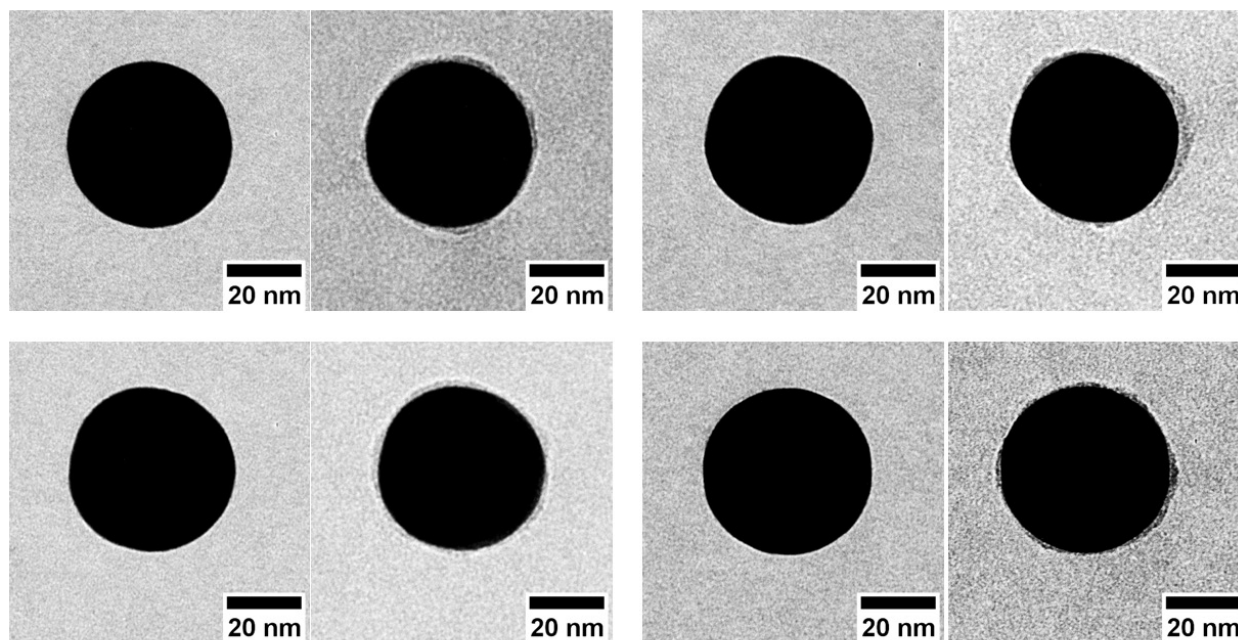


Figure S9: TEM images of NPs before and after irradiation at 90 % t_1 with EY-MDEA-PETA (1.2 mW/cm², 1,26 s)

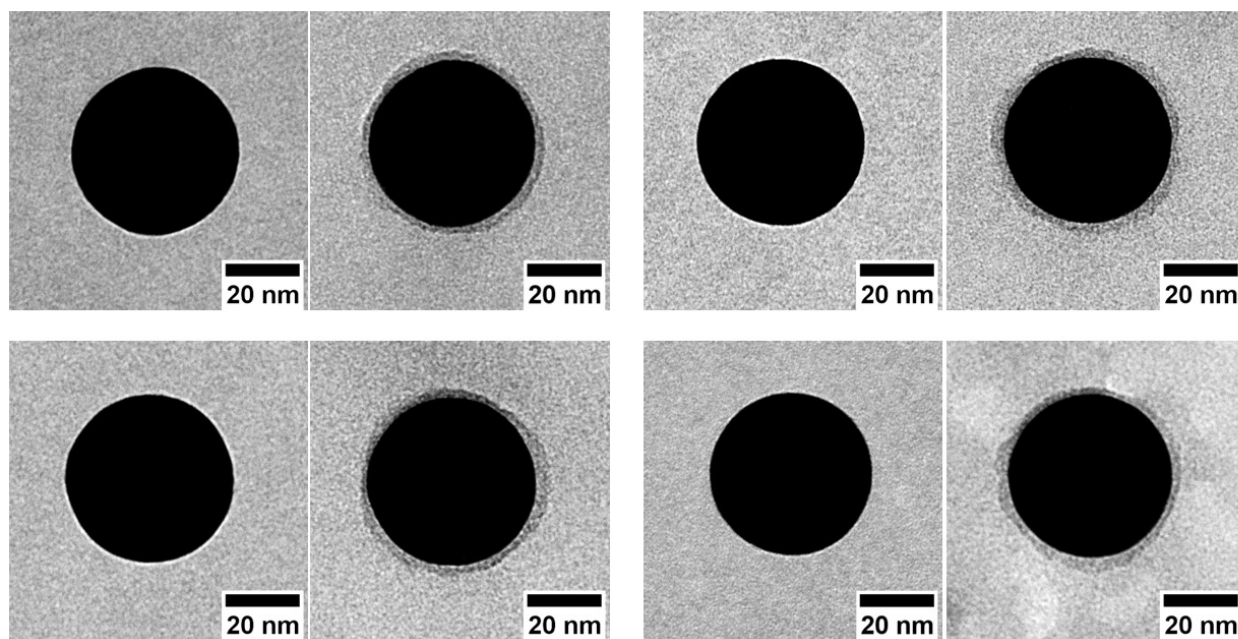


Figure S10: TEM images of NPs before and after irradiation at 90 % t_1 with EY-MDEA-PETA (4 mW/cm², 0,45 s)

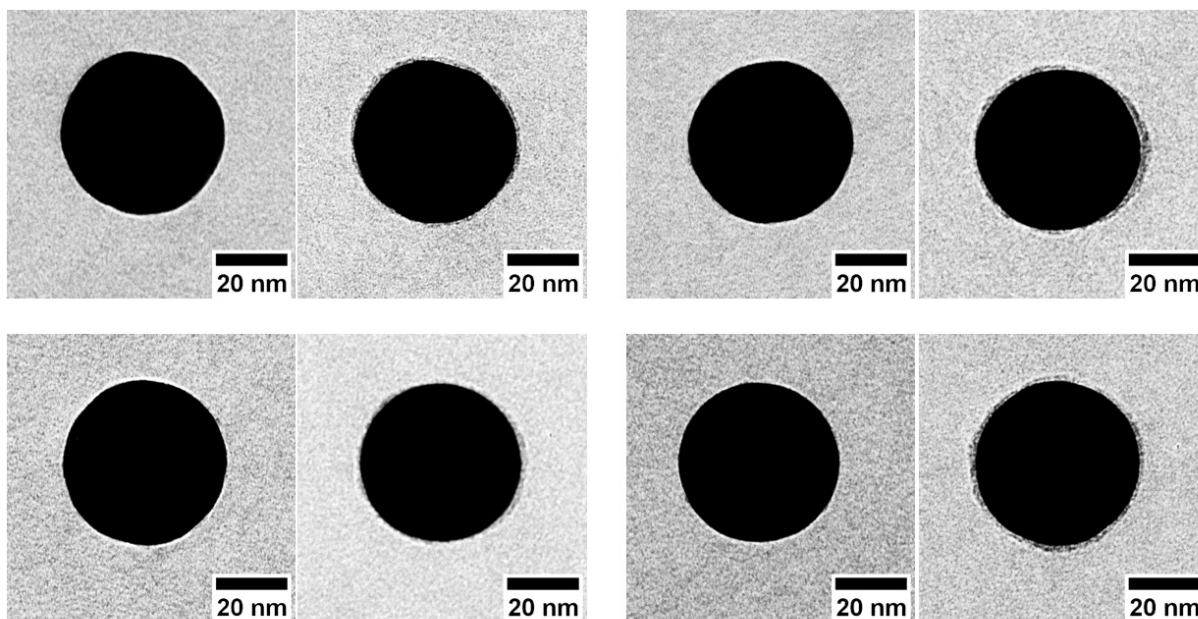


Figure S11: TEM images of NPs before and after irradiation at 90 % t_r with EY-MDEA-PETA (8 mW/cm², 0.18 s)

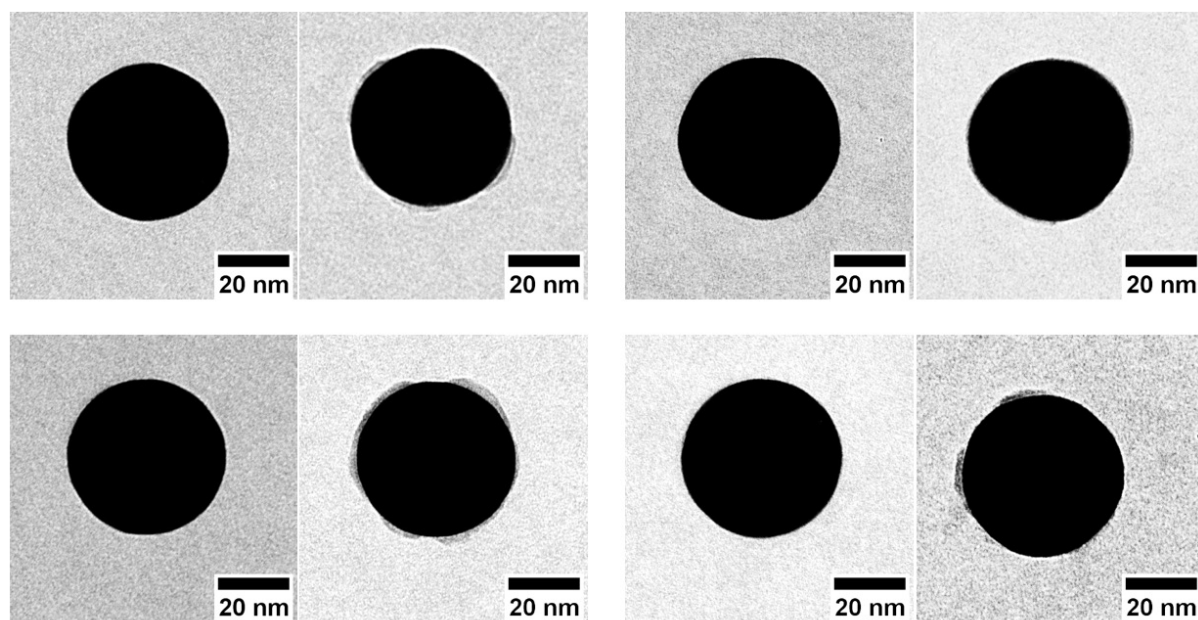


Figure S12: TEM images of NPs before and after irradiation at 90 % t_r with EY-MDEA-PETA (16 mW/cm², 0.117 s)

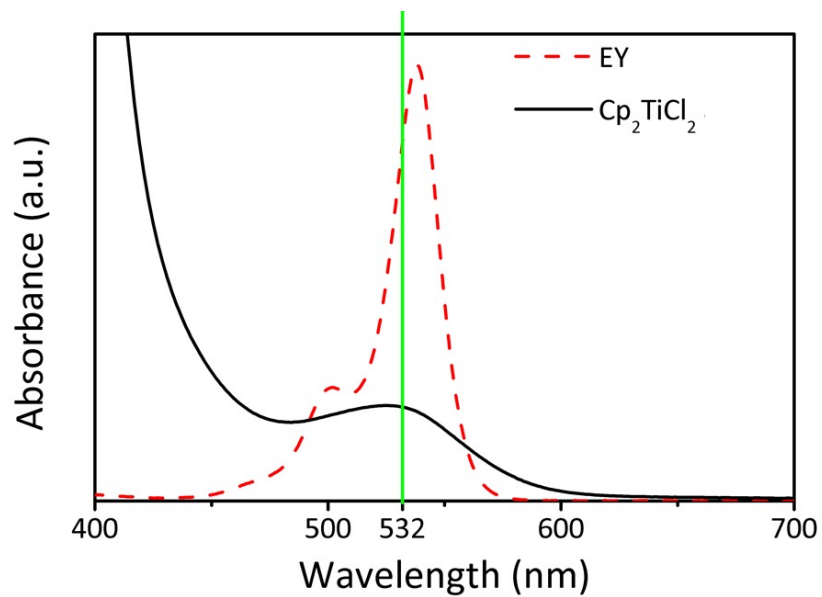


Figure S13: UV-visible spectra of EY and Cp_2TiCl_2 in acetonitrile

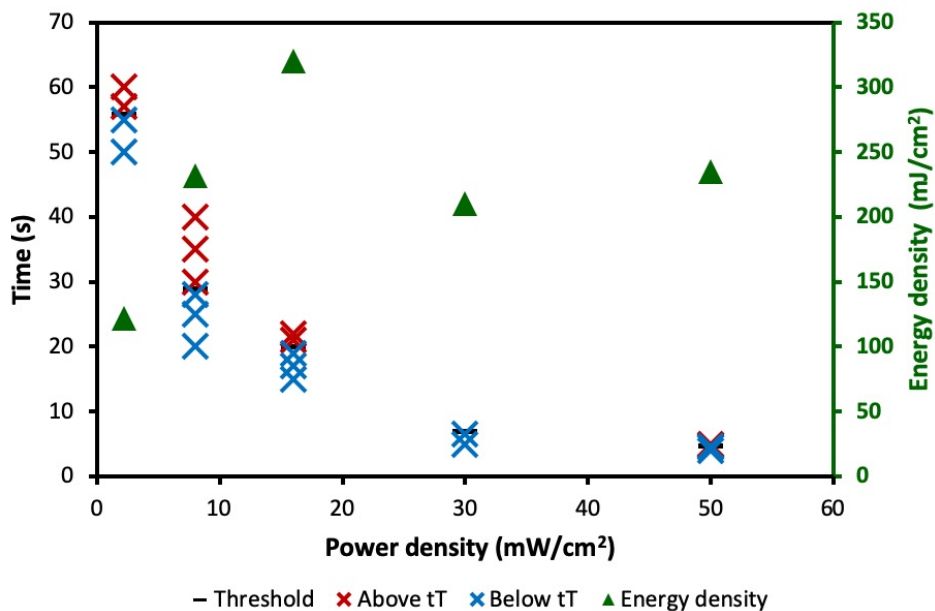


Figure S14: Threshold time and Threshold Energy of polymerization as a function of light power density (Cp_2TiCl_2 -PETA)

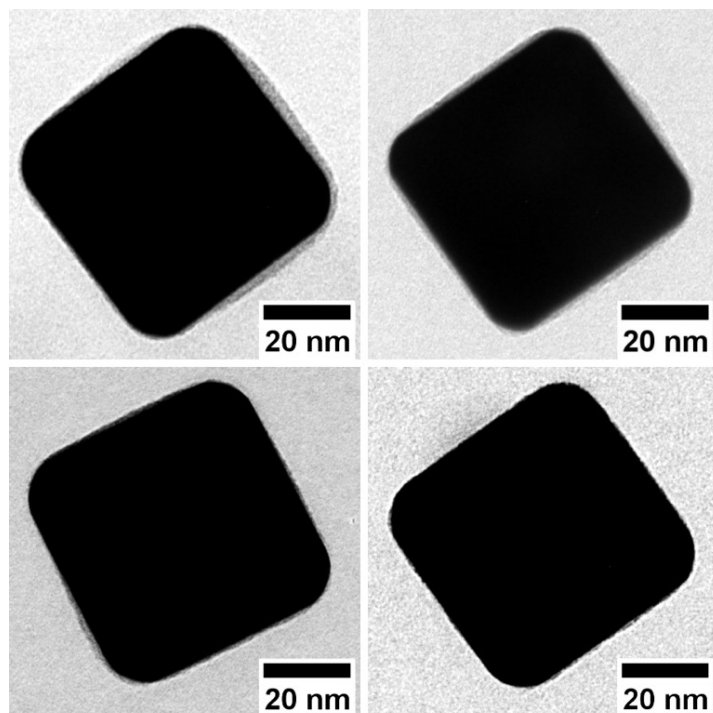


Figure S15: TEM images of 57 nm Au nanocubes prepared at 90% t_r with EY-MDEA-PETA (2 mW/cm², 1.35 s)

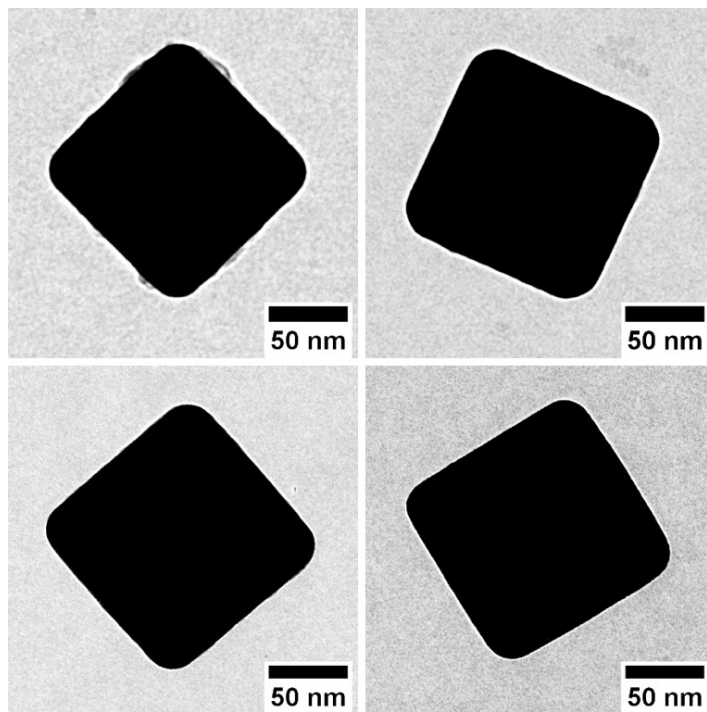


Figure S16: TEM images of 130 nm Au nanocubes prepared at 90% t_r with EY-MDEA-PETA (2 mW/cm², 1.35 s)

BEM simulations, maps of the electric field.

The enhancements and spatial distributions of the optical near field around Au NPs are determined by numerical simulations based on the *boundary element method* (BEM) via its implementation in the *multiple nanoparticles* MNPBEM toolbox.^{1,2} The different nanoparticles are modeled on an infinite Si_3N_4 substrate. The distance between the Au NP and the substrate is fixed at 1 nm. The NPs are covered by a monomer formulation with a refractive index $n = 1.48$, that of the Si_3N_4 substrate is fixed at $n_{\text{Si}_3\text{N}_4} = 2.0559$.³ All considered objects are made of Au, whose refractive index of is taken from Johnson and Christy.⁴ Illumination is carried out from the wide band gap semiconductor substrate side under normal incidence with a circular polarized light source at 532 nm wavelength. The simulations are carried out in retarded field approximation. Maps of the squared modulus of the optical near electric field $|\mathbf{E}_{\text{nf}}|^2$ around Au NPs are determined.

For the case of a sphere, a polar side view is considered (figure S17). The field map in the polar plane (xz) exhibits maxima close to the equatorial plane of the sphere and minima along its polar axis. The maximum and minimum of the square modulus of the field are respectively $|\mathbf{E}_{\text{nf}}|^2 = 26.6$ and $7.7 \text{ V}^2/\text{m}^2$.

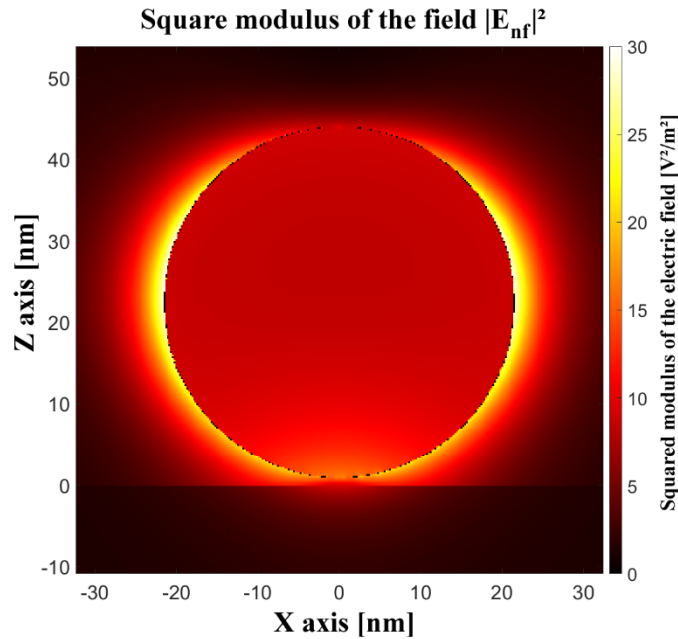


Figure S17. Au Sphere. Map of the squared modulus of the electric field as computed by BEM. Excitation wavelength 532 nm, circular polarization, infinite substrate Si_3N_4 . Polar plane view.

For the cubic geometry, the electric field maps are calculated at a distance of +0.5 nm from the cube faces. The cubes have rounded corners in agreement with cross sections measured in TEM images. Adopted curvature radii are $R_c = 13.25$ nm and $R_c = 19.5$ nm for the 57 and 130 nm edge length cubes respectively. Figure S18 displays the field maps for top and lateral faces of the 57 nm cube. Figure S19 displays similar information for the 130 nm cube. Under normal excitation, the plasmon dipolar resonance of a cube consists of two eigenstates of polarizations aligned on the diagonal planes.⁵ The field map in Figure S18.a shows four field hotspots at the cube corner positions as expected from the simultaneous excitation of both diagonal eigenstates even for the non-resonance conditions considered here. The maxima of the square modulus of the field are respectively $|E_{nr}|^2 = 16.3$ V²/m² on the top face and 20.9 V²/m² on the lateral face. The corresponding values for the 130 nm cube amount to $|E_{nr}|^2 = 8.35$ V²/cm² (top face) and $|E_{nr}|^2 = 8.88$ V²/cm² (lateral face), see Figure S18.

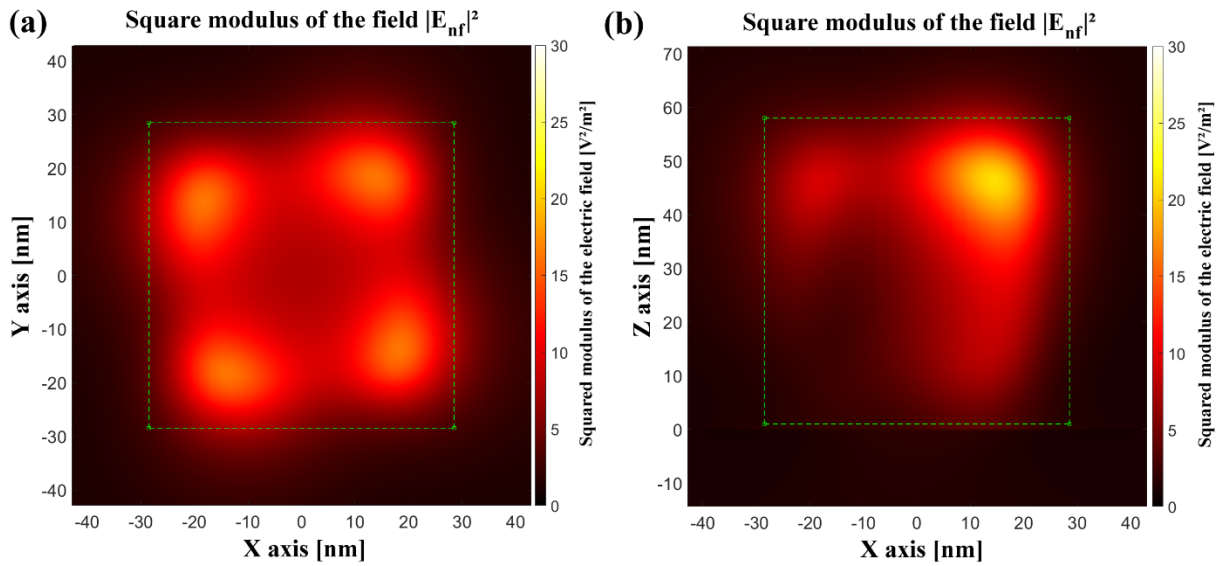


Figure S18. Au Cube, edge length 57 nm. Map of the squared modulus of the electric field as computed by BEM. Excitation wavelength 532 nm, circular polarization, infinite substrate Si₃N₄. (a) top view, (b) lateral view.

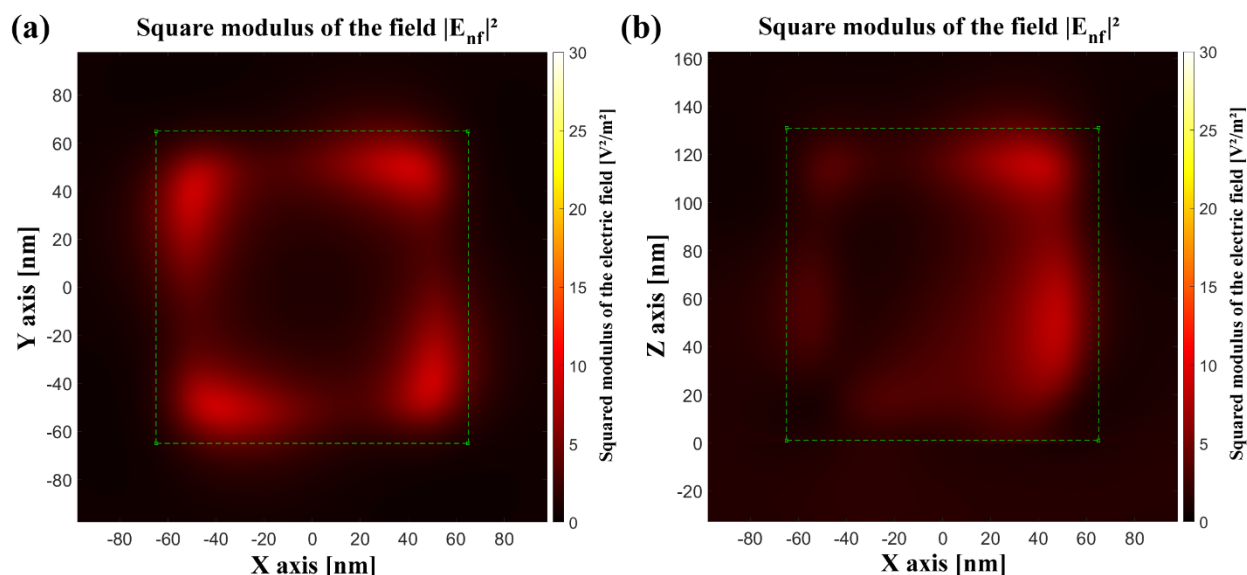


Figure S19. Au Cube, edge length 130 nm. Map of the squared modulus of the electric field as computed by BEM. Excitation wavelength 532 nm, circular polarization, infinite substrate Si_3N_4 . (a) top view, (b) lateral view.

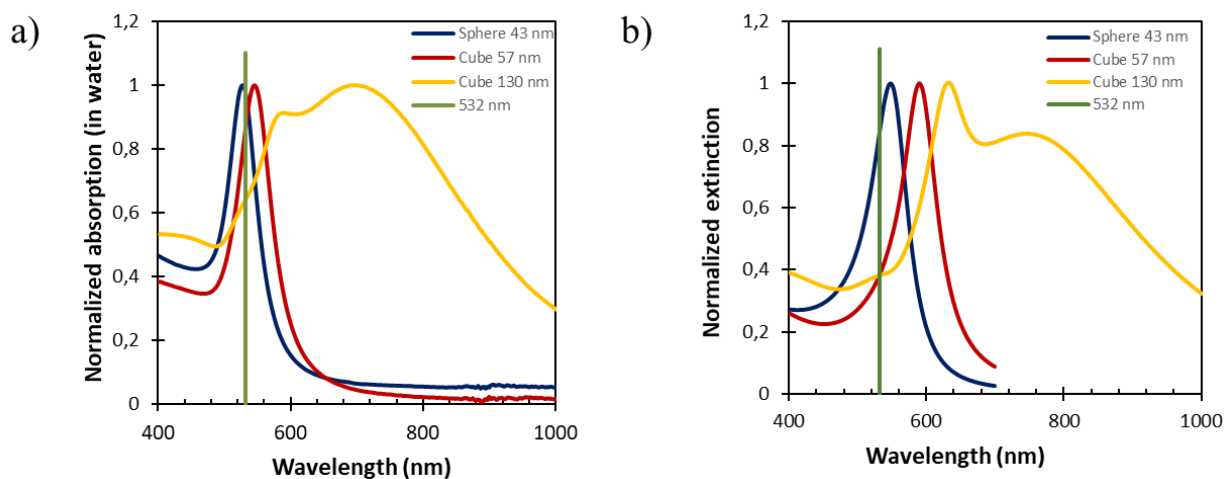


Figure S20: a) Experimental extinction spectrum of the NPs used in this study (Au nanospheres $2R = 43$ nm, Au nanocubes 57 nm and 130 nm) and b) BEM simulated spectra of the NPs on the Si_3N_4 substrates, surrounded by the photopolymer formulation ($n = 1.48$). Extinction spectra are normalized to their respective maxima.

References

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- ² Waxenegger, J.; Trügler, A.; Hohenester, U. Plasmonics simulations with the MNPBEM toolbox: Consideration of substrates and layer structures. *Comput. Phys. Commun.*, 2015, 193, 138-150
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- ⁴ Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B*, 1972, 6, 4370-4379
- ⁵ S. Mitiche, S. Marguet, F. Charra, L. Douillard, L. Near-field localization of single Au cubes: a group theory description. *J. Phys. Chem. C* 2017 121, 4517-4523.