# Utilizing plasmonic hot electrons for bridging top-down and bottom-up nanofabrication and for sub-wavelength absorption imaging

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We demonstrate a novel approach towards the combination of top-down and bottom-up nanofabrication, based on controlled modification of the surface functionalization of plasmonic nanoantennas facilitated by hot electron bond cleaving.

Plasmon decay in sub-wavelength metallic nanostructures leads to the generation of energetic, "hot" electrons, which can catalyze chemical reactions at the nanoparticle's surface. Here we demonstrate two exciting applications of this phenomenon.

Firstly, we show how top-down nanofabrication of Au nanostructures ("nanoantennas") can be combined with bottom-up self-assembly of colloidal units, thereby generating hybrid structures that bridge both fabrication methodologies [1]. This is achieved via controlled cleaving of thiol bonds on molecularly functionalized nanoantennas, allowing for refunctionalization with a second molecular unit (see picture) that links to the colloidal system of choice. Exploiting polarization and wavelength degrees of freedom hence enables to assemble the colloidal units to selected parts of the nanoantenna.

Secondly, we demonstrate how the thiol-bond cleaving can be utilized to map absorption sites in complex metallic nanostructures, utilizing fluorescence-based super-resoluation localization microscopy on DNA-functionalized Au nanoantennas [2]. Spatially localized decay of hot electrons leads to thiol-bond cleaving only where optical absorption has occurred, allowing for spatial identification of absorption sites via monitoring changes in fluorescence.

These two examples demonstrate avenues to exploit plasmonic hot electrons beyond catalysis and Schottky-based photodetection. In particular, the combination of top-down and bottom-up nanofabrication facilitated by this approach should allow new approaches towards metasurface creation combining both nanoantennas and colloidal particles.

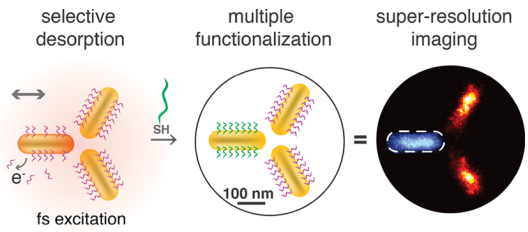


Figure 1. Thiol-bond cleaving via plasmonic hot electrons allows selective modification of nanoantenna surface functionalization

## References

[1] Simoncelli, S., Li, Y., Cortés, E., & Maier, S.A., ACS Nano 12, 2184 (2018)

[2] Simoncelli, S., Li, Y., Cortés, E., & Maier, S.A., Nano Letters 18, 3400 (2018)