

Au particle-in-a frame nanostructures (PIAFs) with sub-2 nm interior gap for enhanced plasmonic functions

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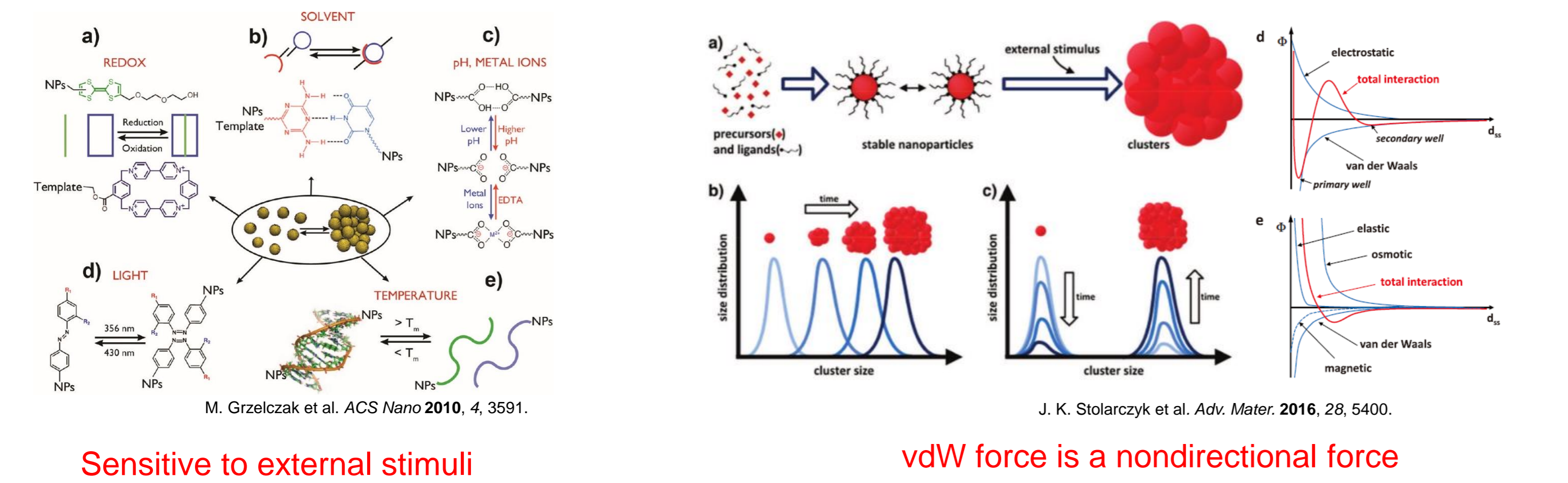
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Abstract

Designing hollow nanostructures with interior nanogaps is of paramount importance to fully exploit their inherent physicochemical properties. Here we report a new synthetic strategy for the realization of frame nanostructures with sub-2 nm interior gaps. The Au particle in a frame nanostructures (PIAFs) were successfully prepared by the fine controlled galvanic replacement of Ag nanoprisms with the controlled kinetic growth of nanoparticle. The prepared Au PIAFs showed remarkably enhanced plasmonic performance compared to Au nanoframe or Au solid nanostructure counterparts. The enhanced surface plasmon resonance (SPR) sensing performance and surface enhanced Raman scattering (SERS) efficiency demonstrated that the formation of interior nanogaps is a very effective route for improving plasmonic activities. Furthermore, In situ real-time SERS monitoring of the progress of a catalytic reaction proceeded on the surface of the PIAFs showed that frame nanostructures with interior gap successfully integrate the plasmonic and catalytic functions.

Nanoparticle assemblies



New strategy for synthesis of assembled nanostructures

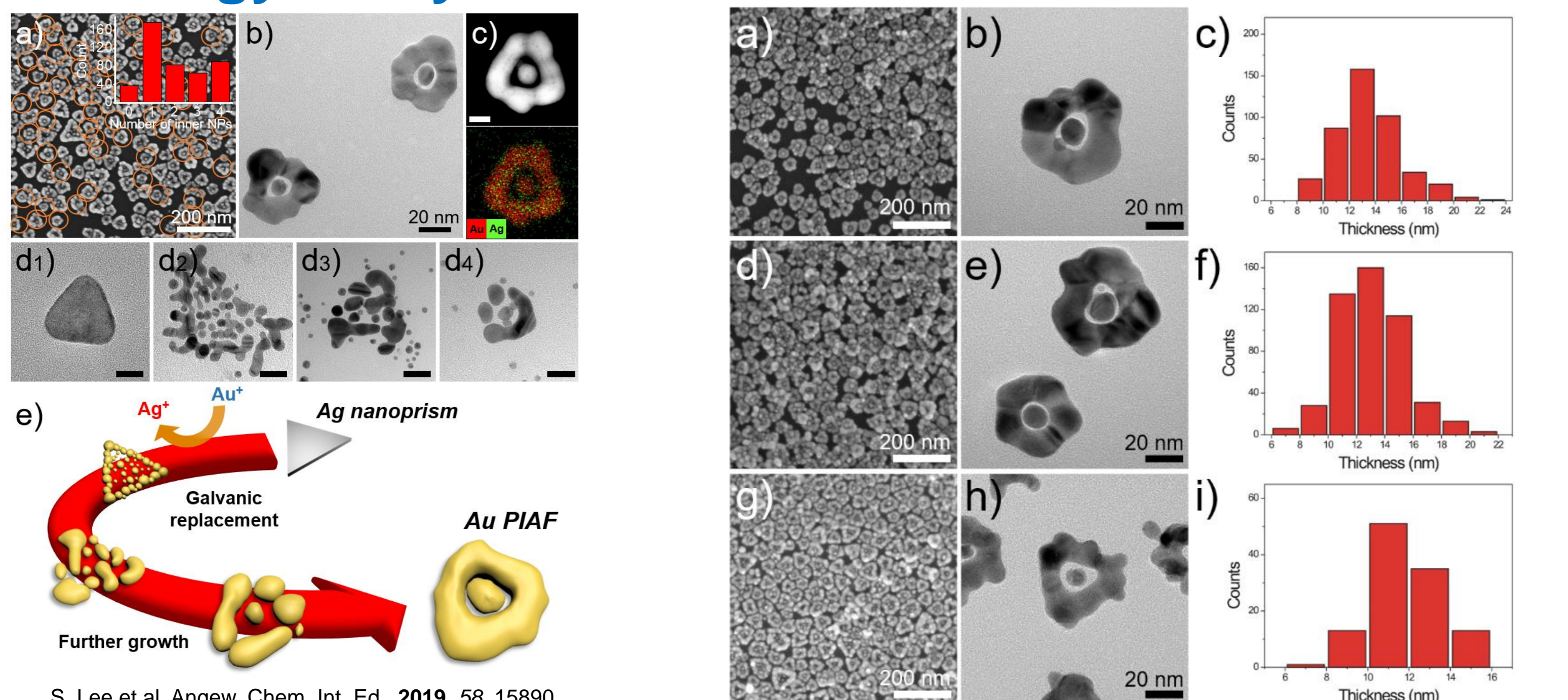


Figure 1. (a) SEM image of Au PIAFs. Au PIAFs containing one inner NP are marked by orange circles. Inset shows the TEM-determined distribution of the number of inner NPs per Au PIAF. (b) TEM image of Au PIAFs containing one inner NP. (c) HAADF-STEM image and corresponding EDS elemental mapping image of an Au PIAF (scale bar = 10 nm). (d) TEM images of samples collected at different reaction times during the formation of Au PIAFs: (d1) 0, (d2) 5, (d3) 60, (d4) 300 s. Scale bars indicate 20 nm. (e) Schematic illustration of the growth mechanism of Au PIAFs.

Figure 2. (a,d,g) SEM images, (b,e,h) TEM images, and (c,f,i) TEM-determined distributions of the frame thickness of Au PIAFs prepared with (a-c) 0.6, (d-f) 0.8, and (g-i) 1.2 mL of Ag nanoprism seed solution.

Plasmonic properties of PIAFs

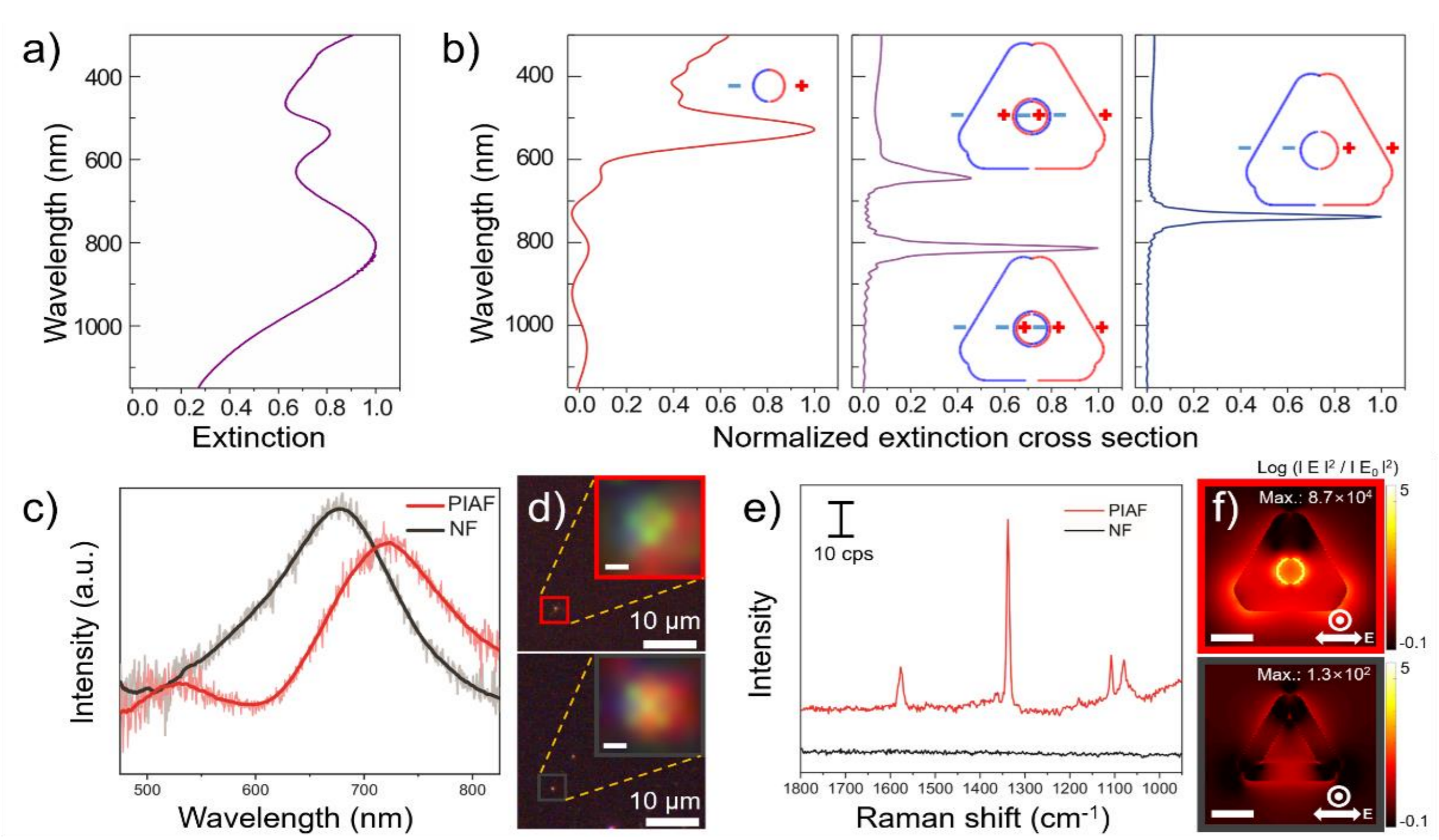


Figure 3. (a) Extinction spectrum of Au PIAFs in water. (b) FDTD-simulated extinction spectra of a model spherical Au NP (red), triangular Au NF (blue), and Au PIAF (purple) obtained by the excitation of each nanostructure with in-plane polarized light. The insets show the simulated charge distributions at the respective resonance wavelengths. (c) Dark-field scattering spectra of single Au PIAF and NF on glass substrates. (d) Dark-field micrographs of single Au PIAF (top) and NF (bottom). The insets show the high-magnification dark-field images of the nanostructures (scale bar = 200 nm). (e) SERS spectra of 4-NBT obtained with single Au PIAF and NF with a λ_{exc} of 633 nm. (f) FDTD-simulated $\log(|E|^2/|E_0|^2)$ distributions around the model Au PIAF (top) and NF (bottom) with the λ_{exc} of 633 nm. The scale bars indicate 20 nm.

SERS performance of PIAFs

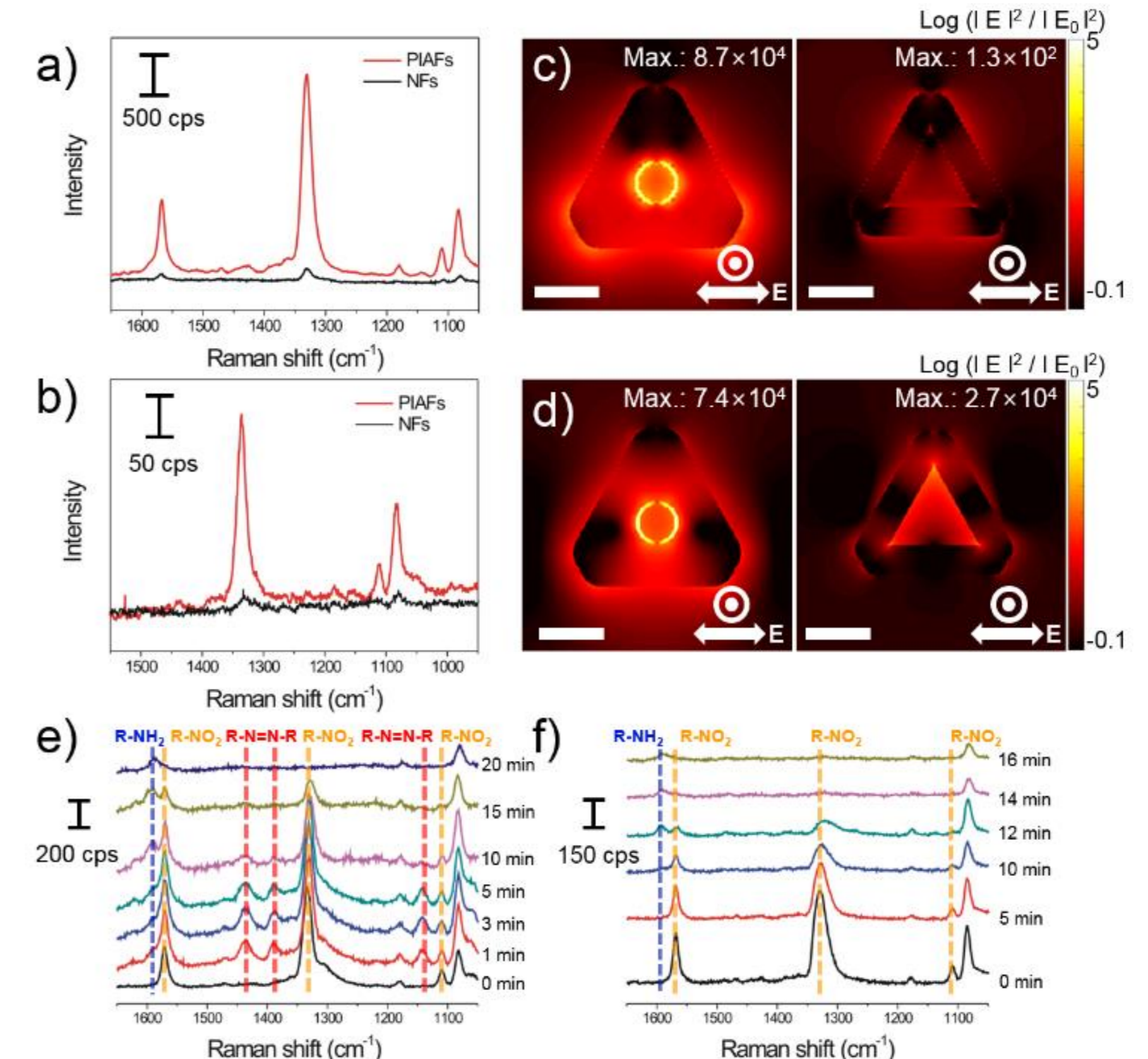


Figure 4. SERS spectra of 4-NBT obtained with Au PIAFs and NPs with a λ_{exc} of (a) 633 and (b) 785 nm. FDTD-simulated $\log(|E|^2/|E_0|^2)$ distributions around a model Au PIAF (left) and NF (right) with a λ_{exc} of (c) 633 and (d) 785 nm. The scale bars indicate 20 nm. Time-dependent SERS spectra collected during the Au PIAFs-catalyzed reduction of 4-NBT to 4-ABT (e) on a Si wafer and (f) in aqueous solution.

SPR sensing

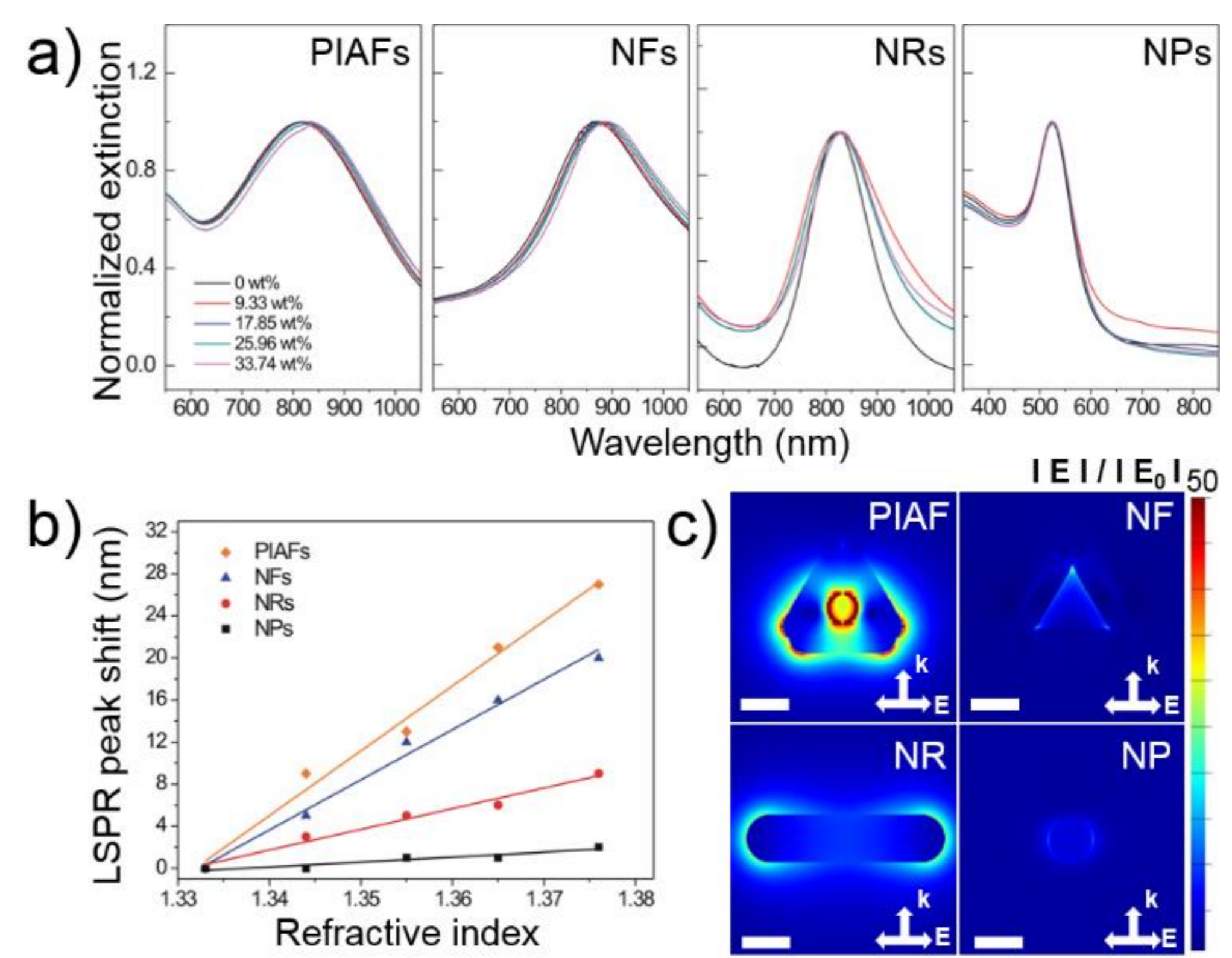


Figure 5. (a) Extinction spectra of Au PIAFs, NFs, NRs, and NPs in water containing different amounts of glycerol. (b) LSPR peak shifts of the different nanostructures as a function of the refractive index of the dielectric medium. (c) FDTD-simulated $|E|^2/|E_0|^2$ distributions around a model Au PIAF, NF, NR, and NP with a λ_{exc} of 811, 870, 826, and 522 nm, respectively, which are the LSPR peak positions of the respective nanostructures in water. The scale bars indicate 20 nm.

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Conclusion

In summary, we have presented a novel synthesis strategy to realize a new class of nanoframe structures, i.e., particle-in-a-frame nanostructures, which have well-defined interior nanogaps between the constituent inner nanoparticles and outer nanoframes. The formation of the unprecedented nanostructures was made possible by fine control over the galvanic replacement of Ag nanoprisms with Au precursors. The prepared nanostructures showed promising performance in LSPR-based sensing and SERS applications due to their interior nanogaps, which give the nanostructures highly localized interior-field confinement. We envision that the present strategy can provide a new direction toward the development of efficient plasmonic platforms with interior hot spots for various applications, such as bio/chemical sensing, photocatalysis, and solar energy conversion.

Acknowledgements

This work was supported by the Basic Science Research Program (2015R1A3A2033469) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (MSIP). E.C acknowledge funding and support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2089/1 – 390776260, the Bavarian program Solar Energies Go Hybrid (SolTech), the Center for NanoScience (CeNS) and the European Commission through the ERC Starting Grant CATALIGHT (802989).