Tuning the optical properties of gold nanostars

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Plasmonic particles have many applications in catalysis,[1] nonlinear optics,[2] enhanced spectroscopy (i.e., SERS, MEF, and SEIRA),[3] biology,[4] and medicine,[5] because of their ability to generate strong electromagnetic fields at their surface upon excitation with the appropriate light. Both the energy and intensity of these fields, also denoted as localized surface plasmon resonances (LSPR), depend strongly on the material, the size, and especially the morphology of the particle.[6]
During the last years, the controlled synthesis of Au nanoparticles (NPs) has attracted the interest of many research groups. Thus, a remarkable success in the development of Au NPs has been achieved. Nowadays, it is possible to prepare quite homogeneous with a la carte dimensions structures like spheres, cubes, rods, decahedra or octahedra and therefore, controlling their optical properties.
Among all possible morphologies, spiked NPs such as nanostars (NSt), consisting of spherical cores with protruding sharp tips, are one of the most efficient plasmonic structures for a wide variety of applications ranging from sensing and imaging to photothermal treatments. In these NPs, the LSPR is highly confined at the tip of the spike, whereas the core acts as an electron reservoir.[7]
However, despite all the advances made in the synthesis of plasmonic nanostructures, there is still a lack of tunability in the optical properties of spiked NPs. Therefore, the ability to concentrate large electromagnetic fields at the apexes of the NSt tips upon illumination was till now restricted to concrete wavelengths and so were also, their possible applications.

In the presented work we demonstrate the possibility of tuning the concentration of the electromagnetic fields at the apexes of the NSt tips. It is presented an optimized bottom-up approach that allows the preparation of highly homogeneous plasmonic Au NSt with a la carte optical properties by means of a tunable LSPR response, by controlling the amount of reactants (i.e., gold seeds, reducing agent, and gold salt) and the reaction time. This synthesis enables the precise control over the tip reshaping which, in turn, allows for the fine tuning of the LSPR energy from the infrared to red. Produced Au NSt as shown in Figure 1, exhibit absorbance maximums that can be tuned from the visible to the infrared. [8]
Further, to demonstrate the effect of the LSPR tunability on the optical enhancing properties of the synthesized stars structures, the SERS intensities of the different materials was effectively tested for sensing using surface-enhanced Raman scattering spectroscopy (SERS) with visible and NIR lasers using a model analyte.

References

[1] Yu, S.; Wilson, A. J.; Kumari, G.; Zhang, X.; Jain, P. K. ACS EnergyLett. 2017, 2, 2058−2070.
[2] Sivis, M.; Pazos-Perez, N.; Yu, R.; Alvarez-Puebla, R.; García de Abajo, F. J.; Ropers, C. Comm. Phys. 2018, 1, 13.
[3] a) Ming, T.; Chen, H.; Jiang, R.; Li, Q.; Wang, J. J. Phys.Chem. Lett.2012,3, 191−202. (b) Schlücker, S. Angew. Chem., Int. Ed. 2014, 53, 4756−4795.
[4] Polo, E.; Navarro Poupard, M. F.; Guerrini, L.; Taboada, P.; Pelaz, B.; Alvarez-Puebla, R. A.; del Pino, P. Nano Today 2018, 20, 58−73.
[5] Xin, H.; Namgung, B.; Lee, L. P. Nat. Rev. Mater. 2018, 3, 228−243.
[6] Myroshnychenko, V.; Rodríguez-Fernández, J.; Pastoriza-Santos,I.; Funston, A. M.; Novo, C.; Mulvaney, P.; Liz-Marzán, L. M.; Garcíade Abajo, F. J. Chem. Soc. Rev. 2008, 37, 1792−1805
[7] Alvarez-Puebla, R.; Liz-Marzán, L. M.; García de Abajo, F. J. J. Phys. Chem. Lett. 2010, 1, 2428−2434.
[8] Pazos-Perez, N.; Guerrini, L.; Alvarez-Puebla, R., Plasmon Tunability of Gold Nanostars at the Tip Apexes. ACS Omega 2018, 3, 12, 17173–17179.

Figures

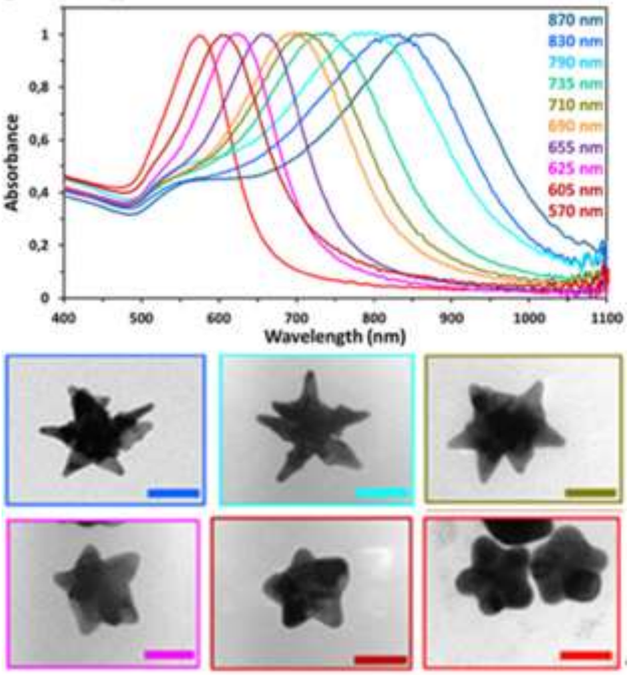

Figure 1. Normalized UV–vis spectra of different Au NSt solutions with plasmon resonances ranging from the visible to the infrared (top). TEM images of Au NSt corresponding to selected UV-vis spectra (right).