

Absorption engineering in stacked Au-SiO₂-Pd nanostructures

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Abstract

Nonradiative decay of localized surface plasmon resonance (LSPR), i.e. *absorption*, leads to the formation of energetic electron-hole pairs and, if not otherwise utilized, subsequent decay into heat. In a photocatalysis application such energetic electrons can be used to enhance a chemical reaction on the surface of the plasmonic nanoparticle [1]. This concept has been demonstrated in a number of studies but is to date focused entirely on Au or Ag particles, owing to their favourable plasmonic properties. This greatly limits the number of possible reactions since Ag and Au surfaces are catalytically not very active (exceptions exist). Other classical metals in catalysis with high activity, e.g. palladium (Pd), have not been considered since they show rather weak LSPR in the UV-visible spectral range [2], due to a strong presence of interband transitions.

In this work [3, 4] we combine the strong LSPR of Au with a more catalytically active metal, Pd, in order to “make use of the best from both worlds” by exploiting a novel *generic absorption engineering strategy*. Our model structure, to demonstrate the effect, is a stack consisting of Au and Pd nanodisks separated by a SiO₂ spacer layer, see Fig. 1. As we show, by varying the spacer layer thickness, the coupling strength between the plasmonic excitations in the Au and Pd disks can be tailored and the dissipation of the absorbed energy *locally* optimized in the structure.

For our experiments amorphous arrays of Au-SiO₂-Pd sandwich structures with various spacer thicknesses are fabricated using hole-mask colloidal lithography [5]. Their optical properties are evaluated using a spectrophotometer with integrating sphere detector, allowing for both extinction and absorption measurements. The experimental data are compared to electrodynamic simulations obtained using the FDTD method and analyzed qualitatively by an analytical coupled-oscillator/dipole model. In our analysis we put particular focus on “dissecting” the structure to identify *where* in the stack light absorption is taking place.

As the main result of our study we find that the local light absorption in the Pd in the stack arrangement is significantly enhanced. Assuming a flat light intensity profile and integrating the total light absorption in the range 400 – 900 nm we find an enhancement of ca. two. For a specific wavelength the maximum absorption enhancement is six-fold. We attribute this novel effect of *absorption enhancement*, in a mechanistic picture, to the fact that the Au disk in the stack is an efficient antenna, which captures energy from the incoming light. Due to the coupling and the specific damping mechanisms in the Au and Pd disks this energy is dissipated predominantly in the Pd disk.

We argue that our absorption engineering concept constitutes a general blueprint for optimization of light absorption in heterometallic plasmonic structures. As the key feature one element in such a structure is an efficient plasmonic antenna; such as Au, Ag or Al; and the other one is “lossy”, i.e. features interband transitions in the visible range; such as Pd, Pt, Ni, Ru, Re, Co, or Fe. We predict that this novel concept will facilitate LSPR-enhanced chemical reactions on a wide range of metal catalysts beyond Au or Ag.

References

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Figures

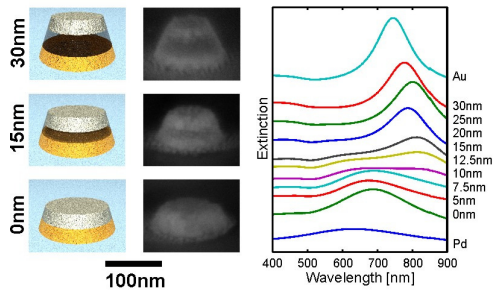
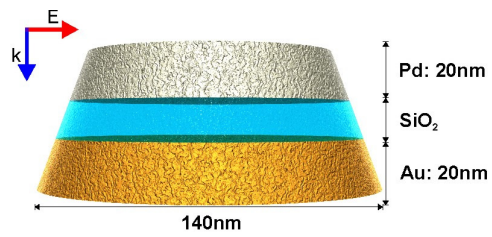


Fig. 1: Sketch of the Au-SiO₂-Pd structures used in this work. Also shown are extinction spectra for structures with different spacer thicknesses, as well as for the individual Au and Pd disks. Figure from [3].