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## Renewable energy nanosources for sustainable biomass conversion

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The use of light as primary energy source in chemical transformations is one major pillar of the forthcoming energy transition. In this issue of CHEM, Han and co-workers design a quite sophisticated antenna-reactor complex which selectively catalyzes the reductive cleavage of C-O bonds in aryl ethers under mild conditions.

The interaction between light and matter has fascinated scientists for centuries. In particular, the collective oscillation of conduction electrons triggered by incident light in plasmonic nanoparticles has attracted much interest.<sup>1,2</sup> This phenomenon, referred to as localized surface plasmon resonance (LSPR), indeed increases the electromagnetic field intensities around illuminated nanoparticles. This nanosource of energy can be harvested in many ways by neighboring functional nanostructures.

It can be transferred to adsorbed molecules and transformed into vibrational energy, which has been exploited in detection and sensing applications. It can be absorbed by a semiconductor (SC), provided the optical absorption of the SC matches the emitted energy levels, which has contributed to the development of the SC-based photocatalysis field by drastically enhancing the number of active species (electron-hole pairs) generated within the SC. More recently, the electromagnetic energy from LSPR can be absorbed by a neighboring heterometal, inducing peculiar absorption properties in the receiving metal, which is currently being exploited in the photo-induced catalysis field.<sup>3</sup>

Besides the primary LSPR-induced effect, known as near-field enhancement, another way of extracting energy from LSPR has been attracting increasing attention over the last few years. That is during its decay. In particular, the non-radiative decay of LSPR, also known as Landau damping, generates a Fermi-Dirac distribution of hot charge carriers (electron-hole pairs) within the plasmonic nanostructure.<sup>4</sup> These hot charge carriers can in principle be harvested as such in the femto- to pico-second timescale, or as a source of localized heat after thermalization, before all the LSPR energy is dissipated. For example, hot electrons are believed to be responsible for the peculiar features of the few plasmonic catalytic (and photocatalytic<sup>5</sup>) reactions studied so far.<sup>6</sup> By reaching energy levels far above the Fermi level of the metal, hot electrons could in principle populate antibonding orbitals of molecules directly adsorbed on the plasmonic nanoparticle, thereby destabilizing and ultimately breaking internal bonds in the adsorbate.

In pioneer work by Linic and coworkers, such light-induced cleavage of the oxygen molecule was used to epoxidize ethylene into ethylene oxide at a significantly higher rate than that observed over the externally heated system. By facilitating the rate-limiting O<sub>2</sub> dissociation step, light-activated silver nanoparticles could lower the overall temperature required to produce ethylene oxide, i.e. the consumption of non-renewable energy.<sup>4</sup>

This is one of the rare examples in which the catalytic reaction is completed directly on the surface of the plasmonic nanoobject. In most other examples, plasmonic and catalytic functions are decoupled, i.e., they occur on two distinct metals in close proximity. In this antenna-reactor design, light is absorbed by the plasmonic metal (antenna) and hot charge

carriers may be generated directly within the catalytic nanostructure (reactor) by near-field enhancement effects.<sup>3</sup> This offers the advantage of harvesting visible light, by using one of the few metals exhibiting a LSPR in the visible range (Cu, Ag, Au, Al) as the antenna while broadening the scope of catalytic transformations achievable by light by using a catalytic metal of interest for the target reaction (among those having a LSPR with a large imaginary part in the near-visible range). In such configuration, both components can be designed and optimized independently, which should contribute to faster progress in the development of light-activable catalytic nanostructures.

In a pioneer example, Swearer *et al.*<sup>3</sup> showed that heterometallic Al-Pd nanoparticles exhibited a much higher ethene-versus-ethane selectivity in the light-induced partial hydrogenation of acetylene (another high profile reaction of the petrochemical industry) than those observed under external thermal activation. In this case, hot electrons are believed to destabilize Pd-H bonds and facilitate associative desorption of H<sub>2</sub>, thereby decreasing the surface concentration of active atomic hydrogen, and in turn, the probability for ethene hydrogenation (acetylene overhydrogenation) to ethane.

Other heterometallic nanostructures, such as Ag@Pt,<sup>4</sup> Cu@CuRu,<sup>7</sup> have been probed as heterogeneous plasmonic catalysts. In general, the higher levels of energy attained by hot electron-activated intermediates are believed to bring the intermediate closer to the activation barrier, thereby decreasing the energy input required for overcoming the barrier of the corresponding reaction step (Figure 1). When this relates to the rate-limiting step of the reaction, the overall apparent activation energy will be decreased, accounting for the higher rates observed in light-activated processes at one given external temperature. When this relates to a multi-step reaction with competitive pathways, the preferential facilitation of one of the pathways will explain the higher selectivities achievable in light-mediated processes. Overall, results are often explained in terms of facilitation of desorption of adsorbates (reactants, intermediates or products).<sup>3,4,6,7</sup>

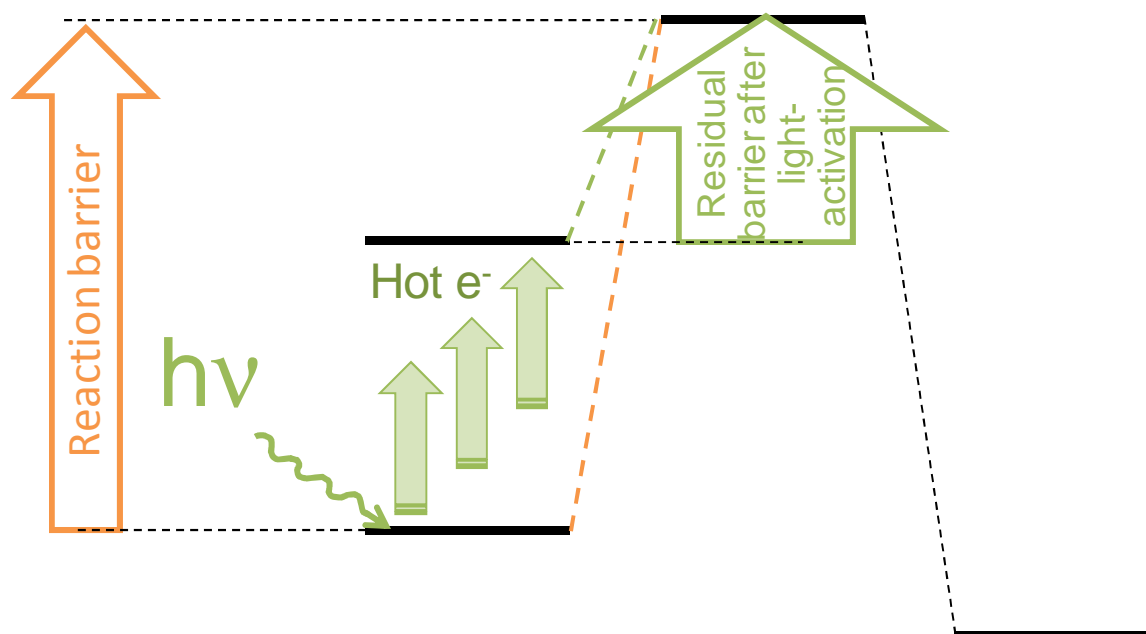


Figure 1. Schematic diagram of the impact of hot electrons generation on the energetics of a catalytic reaction.

The actual mechanisms of action of these hot electrons (and corresponding hot holes) are, however, elusive. Even the fact that these act as charge carriers or as thermalizers at the

nanoscale is not completely clear yet. Hence, in the absence of clear-cut understanding of the nature of the energy transfer (charge or heat transfer), the design of such bi-functional plasmonic-catalytic nanoobjects, particularly the design of the interface between the two components that controls the efficiency of the energy transfer, remains a challenge.<sup>1</sup> Besides, the low irradiance of the light sources that are intended to be used, and ultimately solar illumination ( $< 1 \text{ W/cm}^2$ ), adds additional material requirements inspired from nanophotonics: the concentration of light directly at the surface or in direct proximity of the plasmonic nanostructures, i.e., the engineering of so-called hot spots (plasmonic nanogaps).

In this issue of Chem, Han et al. combine plasmonic silver or gold nanoparticles and heterogenized Ni(II) complexes to successfully tackle challenges in biomass upgrading with soft-light activation.<sup>8</sup>

Specifically, catalytic transfer hydrogenolysis of the  $\alpha$ -O-4 linkage of benzyl phenyl ether is achieved selectively, i.e., *without* hydrogenation of the aromatic rings, under mild conditions.<sup>9</sup> In this bifunctional architecture, the two sites operate in tandem.<sup>10</sup> Plasmonic nanoparticles provide not only hot electrons and holes, but also active sites for the oxidation of the mild hydrogen donor (isopropanol), leading to the release of the active H species. Hydrogenolysis of the C-O bond into phenol and toluene is subsequently achieved by the reduced Ni(0) site as a result of hot electron transportation<sup>1</sup> from plasmonic nanoparticles (M) to Ni(II) complexes via the supposedly bridging aromatic substrate molecule. Direct energy transfer from M to Ni(II) *via* near-field enhancement effects could also contribute to the reaction.

The probability of occurrence of M-Ni(II) dual sites (short M-Ni(II) distance) inside hotspots (short interM distance) is enhanced by the association between a high coverage of grafted Ni complexes and a non-homogeneous distribution of plasmonic nanoparticles over the alumina support. An increase in substrate local concentration within hot spots and plasmon-enhanced chemisorption are emphasized, bringing new perspectives to plasmonic catalysis, including the potentiality for an aromatic substrate to promote its own transformation.

By providing useful energy *via* one of its decay pathways in addition to its primary energy release, LSPR can be seen as the next generation nanosource of energy. However, smart architectures will need to be designed in order to effectively harvest and use this new sustainable energy nanosource. In this regard, this new statistical combination of plasmonic metals and immobilized metal complexes proposed by Han et al. constitutes a key contribution to this grand scientific and societal challenge, as it expands the scope of light-activated catalytic reactions and demonstrates a further practical example for the transition towards more sustainable energy sources.

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