NANO LETTERS

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Fermi Level Equilibration at the Metal–Molecule Interface in Plasmonic Systems

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Cite This: *Nano Lett.* 2021, 21, 6592–6599 Read Online

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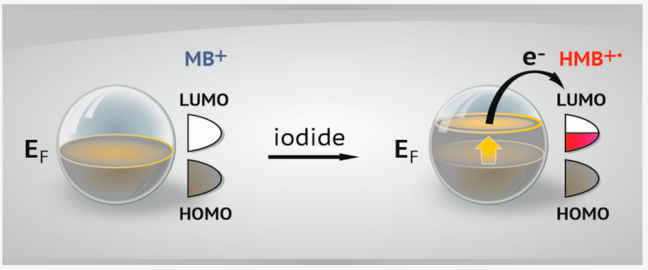
ABSTRACT: We highlight a new metal–molecule charge transfer process by tuning the Fermi energy of plasmonic silver nanoparticles (AgNPs) *in situ*. The strong adsorption of halide ions upshifts the Fermi level of AgNPs by up to ~0.3 eV in the order $Cl^- < Br^- < I^-$, favoring the spontaneous charge transfer to aligned molecular acceptor orbitals until charge neutrality across the interface is achieved. By carefully quantifying, experimentally and theoretically, the Fermi level upshift, we show for the first time that this effect is comparable in energy to different plasmonic effects such as the plasmoelectric effect or hot-carriers production. Moreover, by monitoring *in situ* the adsorption dynamic of halide ions in different AgNP–molecule systems, we show for the first time that the catalytic role of halide ions in plasmonic nanostructures depends on the surface affinity of halide ions compared to that of the target molecule.



KEYWORDS: *Photocatalysis, catalysis, Fermi level, charge transfer, SERS*

INTRODUCTION

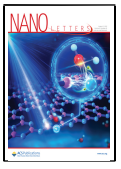
Plasmonic photocatalysis has recently emerged as a new paradigm in the sunlight-to-chemical energy conversion cycle.[1−7] However, our physicochemical understanding of the metal–molecule interface and its reactivity is still in its early stages.[8−11] We can gain further insight on how to manipulate and tune metal interfaces at the nanoscale by borrowing some concepts from more advanced fields such as heterogeneous catalysis, photocatalysis, electrocatalysis and surface science.[12−14] Let us focus on one of the simplest examples: a charge transfer process across the metal–molecule interface.

A molecule's donor and acceptor states are its occupied (HOMO) and unoccupied (LUMO) frontier orbitals, respectively. During chemisorption, the frontier orbital energies change relative to the free state (unbound molecule). The energy change of a molecule's frontier orbital when adsorbed to a surface, named energy level alignment, can either enable or inhibit spontaneous charge transfer with the solid.[15−18] Thus, during the chemisorption of a molecule on a metal substrate, charge transfer can occur between the metal and the molecule if the donor and acceptor energy states of the two partners are aligned. This process ends up changing the charge state of the adsorbed molecule (i.e., promoting its reduction or oxidation).[15,17,18] Accordingly, the surface metal atoms can be reduced or oxidized to equilibrate the energy levels in the metal–molecule system (i.e., redox potentials). This has been recently shown in dissolution experiments with silver nanoparticles (AgNPs).[19−21]

Even though the effect of tuning the Fermi energy of metal nanostructures through ligands has been known since the early 90s through the work of Henglein and co-workers,[22−24] it has not been explored extensively in the fields of plasmonic chemistry or surface-enhanced Raman scattering (SERS), being more commonly seen in the fields of molecular electronics[25] or quantum dots.[16,26,27] This concept could have a strong impact in plasmonic catalysis, as both the Fermi level of the NPs and the energy of the absorbed photon determine the energy of the generated hot-carriers.[28−31]

Here, we show a simple and straightforward approach to tune the Fermi level of AgNPs through the adsorption of Cl^-, Br^-, or I^-, which can block or promote the charge transfer to an adsorbed molecule. As a test system, we used the well-known adsorption of methylene blue (MB^+) on AgNPs.[32−36] We show that it is possible to reduce MB^+ to the $HMB^{+\bullet}$ form only by controlling and tuning the surface chemistry. Furthermore, we used SERS to monitor the surface dynamics of our target analyte, MB^+, and of halide ions, which allowed us to gain a mechanistic understanding on the different adsorption regimes of halide ions on the metal surface. The

Received: May 21, 2021
Revised: July 7, 2021
Published: July 22, 2021



https://doi.org/10.1021/acs.nanolett.1c02003
Nano Lett. 2021, 21, 6592–6599