Electronic Supplementary Information

Fundamentals and applications of photo-thermal catalysis

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Localized surface plasmon resonance theories.

According to the Drude model, inside bulk metals, free electrons oscillate in response to the applied electromagnetic field against a fixed background of positive ion cores, thus creating an electron cloud whose motion is the sum of the motion of all individual electrons.[1] Equation (1) can describe the motion of one individual electron where *m* is the mass of the electron; *v* is the electron speed, *e* the charge of the electron and *E* the electric field:

$$m\frac{d^2x}{dt^2} + m\Gamma\frac{dx}{dt} = eE(t) \quad (1)$$

The second term in the equation above corresponds to a damping term due to electronic collisions with the ionic background, being Γ the corresponding damping constant.[1] If we assume a harmonic behavior of the driving field, from the resolution of this expression it is possible to obtain the plasma frequency (ω_P) of the sinusoidal motion of the free electron gas in the bulk metal as follows (Equation (2)):

$$\omega_P^2 = \frac{ne^2}{\varepsilon_0 m} \quad (2)$$

where *n* is the electron density, *e* the charge of the electron, ε_0 the electric permittivity of vacuum and *m* the mass of the electron.

In order to adapt this model to the particular case of metal NPs and determine the resonant conditions, the *quasi*-static regime approximation is applied following the approach developed by Moores and Goettman.[1, 2] In line with this hypothesis, because nanoparticle size is very small compared to the irradiation wavelength, one can consider that all electrons confined in a nanoparticle are subjected to the same electric field at a given time, *t*. The movement of the electron cloud under the effect of the electric field leads to the generation of accumulated charges in the nanoparticle surface, positive where the cloud is missing, negative where it is concentrated. This dipolar charge distribution introduces a new force on the electron cloud and

electrons are exposed to a restoring force that opposes to the external electric field. The position of an electron oscillating into an irradiated plasmonic nanoparticle can be then described by Equation (3):

$$m\frac{d^2x}{dt^2} + m\Gamma\frac{dx}{dt} + m\omega_0^2 x = eE(t) \quad (3)$$

where ω_0 is the plasmon resonant frequency (related to the bulk plasma frequency ω_P as $\omega_0 = \omega_P/\sqrt{3}$), and E is the external field driving the charge movement.[2]

Of great importance, if the external field (E) oscillates at the frequency of the resonant mode of the electron cloud (ω_0) both external and restoring field synchronize, and the interaction between the resonant photons and the accumulated surface electrons leads to the creation of strong electric fields close to the surface of plasmonic NPs.[3] The amplification of the electric field in these regions, also known as "plasmonic hot spots", maximizes nanoparticle extinction cross section (*i.e.* light absorption and scattering).[4] This enhancement of the electric field is one of the key features of LSPR and it has led to a wide variety of applications including biological and chemical sensing, surface enhanced Raman scattering and plasmon-enhanced fluorescence. [5-8]

After excitation, plasmon energy can relax either radiatively as re-emitted photons or non-radiatively as electron-electron collisions (ultimately dissipating the energy as heat) or electron-hole pair excitations. In order to have a better understanding of the different electronic excitations arising from plasmon decay, it is first convenient to revise some fundamentals of light absorption in metal NPs. Among the many models that have tried to theorize the optical properties of metal NPs, the general theory presented by Mie provides an appropriate tool to calculate the intensity of the interaction of light with small spherical metal NPs. According to Mie's theory, the extinction cross section (σ_{ext}) is associated to the complex dielectric function of the metal as follows (Equation (4)):

$$\sigma_{ext} \sim \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m) + \varepsilon_2^2} \quad (4)$$

where ε_m is the dielectric function of the medium, ε_1 is the real part of the dielectric function of the metal and ε_2 the imaginary part of the dielectric function of the metal. [1] As commented above, under resonant conditions the extinction cross section is maximum as the denominator comes into zero. This means that the plasmon resonance condition is fulfilled when $\varepsilon_1 \approx -2\varepsilon_m$ and ε_2 is small.

On the one hand, the real part of the dielectric function (ε_1) describes the polarizability of the metal as a function of the wavelength and, as shown in Fig. S1a, it is commonly negative for metals along a wide range of wavelengths. In view of this, one can consider that the first condition for plasmon excitation ($\varepsilon_1 \approx -2\varepsilon_m$) can be settled for many metals in air at UV-visible wavelengths. [9]

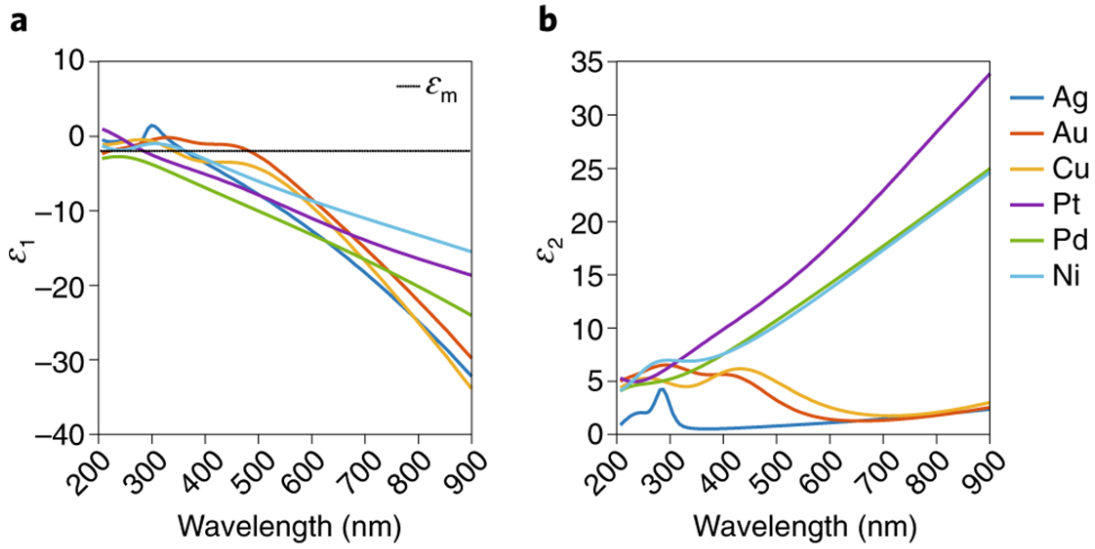

Fig. S1 Dielectric properties of metals. (a) The real part of the dielectric function for the plasmonic metals (Ag, Cu, Au) and other transition metals. The black line represents the case where $\varepsilon_1 = -2\varepsilon_{m,air}$. (b) The imaginary part of the dielectric function for the plasmonic metals and other transition metals. Reproduced with permission from ref. 9. Copyright (2018) Springer Nature.

On the other hand, the imaginary part of the dielectric function (ε_2) is associated to the probability of photon absorption in a metal at a particular wavelength (Fig. S1b). As typical plasmonic metals feature sp-bands

and d-bands, under illumination two different transitions can take place. One of the possible electron excitation paths upon plasmon decay involves the electron transition from filled *s* states below the Fermi level to empty *s* states above the Fermi level (intraband transitions). Unlike other types of electronic excitations, these electrons are not in thermal equilibrium with the material so they are considered as high-energy "hot electrons". Importantly for catalysis, hot electrons are able to escape from plasmonic structures and either interact with adsorbates or overcome Schottky barriers in plasmonic metal-semiconductor junctions, as we will discuss in section 3 of the main manuscript.[10] In addition to this, in many transition metals with deep d-bands electrons can undergo direct photoexcitation to *s* states above the Fermi level (interband transitions). Although they are not strictly based on the plasmonic effect, common plasmonic metals also feature these interband transitions, but typically at different excitation wavelengths from intraband transitions.[11] However, at the low energy limit of interband transition bands, the excited electrons commonly possess energies close to the Fermi level and they are not able to traverse Schottky barriers.[11] Nevertheless, interband transitions can generate holes with a very low energy in the absolute scale, thus being very reactive for oxidation reactions.[12, 13]

In summary, under resonant conditions the electric field on the surface of plasmonic NPs maximizes, thus enhancing light absorption and scattering. Eventually, LSPR decays and the non-radiative relaxation can produce either local heating at the vicinity of the NPs or the generation of hot carriers *via* intraband or interband transitions, altogether contributing to the photo-thermal effect.

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