

Conceptual design of a nanoleaf for artificial photosynthesis

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Abstract

Converting solar energy into chemical bonds is very attractive approach because energy is produced and stored without greenhouse gas emission. This perspective review covers the blueprint requirements paramount for the development of a nanoleaf containing plasmonic nanostructures as light absorber. The work is focused on d¹⁰ metals since their plasmonic resonances match the visible light spectrum.

Introduction

Converting solar energy into chemical bonds, in particular solar fuels, is very attractive because energy is produced and stored without greenhouse gas emission. Direct conversion of solar energy into fuel would satisfy our needs for storable energy on a large scale. Absorbing light and converting its energy to chemical energy by electron transfer can generate solar fuels. The electrons are used in the catalytic reduction of a cheap substrate with low energy content into a high-energy fuel, such as H₂. The holes are filled by oxidation of water, which is often seen as the only electron source available for large-scale solar fuel production [1].

The first significant breakthrough in converting light into chemical energy was published in 1972 by Fujishima and Honda, who reported the electrochemical photolysis of water assisted by a semiconductor under UV-A radiation [1]. However, despite all the scientific advances, it remains a significant challenge to construct a device capable to produce solar fuels, such as hydrogen, at a scale and cost able to compete with fossil fuels. Moreover, developments based on large band gap semiconductors (> 3 eV), such as TiO₂, are hampered by the fact that it requires UV-A irradiation to induce charge separation. Nevertheless, TiO₂ remains indisputably the best photo-catalyst to date [2]. Band gap manipulations by doping with elements, such as N, C and S to improve sunlight absorption often lead to decrease of the breadth of reactions that can be photo-catalyzed, as well as overall decrease in performance.

A more promising strategy to circumvent TiO₂ deficiency in absorbing visible light is to use sensitizers capable of harvesting solar light and introducing hot electrons into the TiO₂ conduction band (CB). O'Regan and Grätzel [3,4] developed dye-sensitized solar cells (DSSCs), in which the dye component harvests sunlight and readily injects electrons ($\tau_{inj} < 1$ ps) into the TiO₂ CB. The success of the dye system depends on fast electron injection and slow back electron transfer. However, organic dyes have low photo-stability, discrete absorption levels (narrow-band), and small optical cross-sections, thus requiring a high dye coverage, which diminishes the space available for photo-catalytic reactions. Besides, holes in oxidized dyes are unreactive,

which hinders hydrogen evolution since a sustainable process demands for equal consumption of electrons and holes. Herein, we cover the most recent aspects in using plasmonic nanostructures as integral components in the design of solar fuel production systems.

Challenges and advantages in designing nanoleaves based on localized surface plasmon resonance

Metallic nanoparticles (NPs) are interesting sensitizer candidates because of their large optical cross-sections related to the excitation of localized surface plasmon resonance (LSPR) [5,6]. The last is the combination of the charge motion in a surface plasmon and created electromagnetic field [7]. Gold group metals exhibit plasmonic resonances in the visible region, and their absorption can be easily tuned by changing nanoparticles morphology (shape and size), enabling a good match with the solar spectrum. Moreover, their d¹⁰ configuration bestows them chemical stability. Recently, the excitation of Au and Ag LSP nanostructures was shown to improve charge transfer from sensitizer to semiconductor [8-10], increase the photocurrents under solar irradiation [11-13], and enhance photo-initiated catalytic oxidations [14-18].

There are two main application of the LSPR phenomena in metallic NPs, which lead to the enhancement of the overall sensitizer/semiconductor performance for light harvesting, namely radiative and non-radiative. This reviews covers aspects solely related to solar fuel production, thus radiative processes are of no interest. In the non-radiative processes the LSPR relaxes by transferring energy to semiconductor via either hot electron transfer (HET) [19,20] or plasmon-induced resonant energy transfer (PIRET) [21]). Below is

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presented a brief explanation of both processes

(a) **HET**: Hot electron-hole pairs can be generated during non-radiative plasmon decay via Landau damping upon decoherence of the LSPR. In metallic nanostructures this could be realized by either interband excitations between occupied and unoccupied states or by intraband excitations of unoccupied states. Subsequently hot electrons with sufficient kinetic energy could be further injected to the semiconductor conduction band (CB) [22], until equilibrium in the Fermi levels is reached and if there is sufficient driving force for the electron transfer [23].

(b) **PIRET**: is implemented through the resonant energy transfer from the metal to the semiconductor via dipole-dipole coupling. Therefore, the electron-hole pairs below and near semiconductor band edge are being formed. PIRET is unaffected by separation distance between metal and semiconductor (for example insulating layer), in contrast to HET [24].

Hallett-Tapley *et al.* [25] defended that the plasmon excitation could drive reactions via thermal, electronic and/or antenna processes. In the case of photocatalysis, the relevant process is the electronic one, in which hot electrons and holes formed upon plasmon excitation with visible light are used for the formation and/or rupture of chemical bonds [26].

Conceptually, plasmonic nanostructures can be used directly in photocatalysis, however the electron-hole pair is short lived (few femto-second), making it challenging to drive chemical reactions. Interfacial reactions are relatively slow with kinetics in the milliseconds range. To increase charge separation lifetime, the charges can be confined to spatially separated sites where reactions take place. For example, charge separation lifetime can be dramatically improved by coupling LSPR structures with a semiconductor [22], analogous to DSSCs [3,4].

There is however a significant challenge in using sensitizer/semiconductor combination, namely conciliation between the light-induce single electron transfer and multi-electron catalysis. A system employed in a direct solar fuel production must be able to accumulate electrons and holes provided by the sequential absorption of photons in order to complete the catalytic reactions. This process is termed *accumulative charge separation* [27] and it is considerably more complicated than charge separation on a single electron level. The distribution of the carriers on NPs depends on plasmon energy, particle size, symmetry of the plasmon mode, and metal electronic structure/density of states [23]. Metal NPs have a large amount of loosely bond electrons which allied to the fact that LSP excitation redirects the flow of light (Pointing vector) towards and into the NP (i.e. multi-photon absorption), it is conceivable that more than one electron is excited per particle, which suppresses the problem with multi-electron generation. It was demonstrated that metal NPs have the ability to store more than one electron per particle [28,29], thus fulfilling the demand for charge accumulation.

In general, plasmonic nanostructures provide variety of ways to manipulate light absorption with nanometer-scale precision and at sub-fs timescales. Most of the research efforts have been focused on gold group metals, and in particular on gold metal NPs. This is in part due to gold inertness and stability, allied to lower Schottky barrier in respect to TiO_2 CB (ca. 1.0 eV). However gold is very expensive and cannot be considered for practical applications. Silver is a promising alternative because it is cheaper, has a larger optical cross-section, and lower Ohmic losses than gold. Thus, higher scattering efficiency

and narrower plasmon linewidths are observed for Ag. Comparison of the optical constants of various metal candidates (Ag, Au, Cu, Al), strengthens above mentioned statement [30,31]. However, silver is potentially less stable and has a larger Schottky barrier in respect to TiO_2 CB (ca. 1.5 eV). The latter can be partially counteracted by Ohmic junction at the contact between Ag NPs and TiO_2 nanocrystals, which should help charge injection. The different work functions result in electrons flowing from Ag nanoparticles (the material with low work function $\phi_{\text{Ag}} = 4.26$ eV) to TiO_2 nanocrystals (the one with high work function $\phi_{\text{TiO}_2} = 5.5$ eV) until the Fermi levels on both sides line up (i.e., the system reaches the thermal equilibrium state), and thus positive charges are built up at the silver surface and an equal number of negative charges should be distributed over the depletion region near the surface of the TiO_2 nanocrystals (i.e., the space charge is established between Ag and TiO_2 nanocrystals). Once the space charge is formed, there is an electric field at the interface, which will further increase the potential energy difference between Ag and TiO_2 nanocrystals [32]. This is less noticeable on Au because of its larger work function ($\phi_{\text{Au}} = 5.1$ eV).

The final aspect relates to the catalysis itself. Semiconductors are not very good hydrogen evolution catalysts, thus one needs to add co-catalysts, such as platinum NPs, to improve catalytic efficacy. The hole in the plasmonic nanostructure is reactive but in many cases co-catalysts are added to improve catalytic activity and direct product formation. Mubeen *et al.* [33] prepared a proof-of-concept system conglomerating the findings on plasmonic nanostructures, water reduction and oxidation catalysts to produce simultaneously H_2 and O_2 under visible light irradiation. They use Pt NPs and CoP as reducing and oxidizing catalyst, respectively.

Fundamental understanding of nanoleaves

Despite plasmonic nanostructures potential, there are not many systems proposed in literature. This is primarily related to the fact that there is a void in the fundamental understanding of the process from light absorption to the catalytic process itself. In fact until recently there was no spectroscopic evidence that hot carriers are formed after photon absorption, which is essential process for the utilization of these structures in photo-catalysis.

The creation of electron-hole pairs during illumination due to LSPR excitation was measured by high-resolution X-ray absorption spectroscopy at the Au L_{III} -edge, which determines Au 5d unoccupied electronic states. LSP excitation led to an upward shift of the ionization energy threshold by ca. 1.0 eV, and an increase of Au d-band hole population, consistent with hot electrons formation, and their promotion to high-energy states (Figure1a) [22]. The fundamental understanding of the process commanding steps of electron injection and dynamics could be performed by pump-probe ultrafast infrared (IR) spectroscopy, which probes simultaneously electron in the semiconductor CB (broad mid-IR absorption) and/or stabilized in the organic linker by following the changes in absorption of its functional groups fundamental vibration bands.

To evaluate if the hot electrons possess sufficient energy to be injected into TiO_2 CB, the transient broadband mid-IR spectroscopy was performed [34]. Free and trapped electrons in a semiconductor conduction band produce a broad mid-IR band. Upon excitation, a broad mid-IR band appeared confirming the presence of electrons in the TiO_2 CB. The minimum in transmittance was observed at $t = 0$ ps for both systems, which is the best possible overlap between pump and probe pulses (Figure 1b). Thus, confirming fast injection into the TiO_2

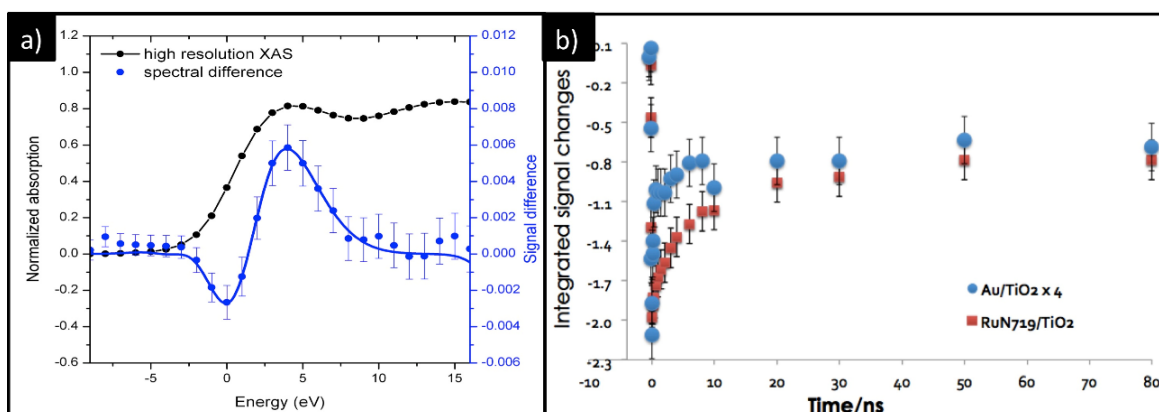


Figure 1. a) Au L_{III} -edge HR-XAS differences induced by CW laser excitation of LSP at 532 nm, with 100 mW power. Ground state HR-XAS and spectral difference due to Au NPs excitation. b) Transient mid-IR measurements of TiO_2 coated with a light absorber irradiated at 532 nm, 100 ps pump pulses (33 mW). The spectral changes were probed with 100 ps broad mid-IR pulses at a spectral resolution of 32 cm^{-1} . Integrated mid-IR transient signal for Au/ TiO_2 and RuN719/ TiO_2 . Reproduced from elsewhere with permission [11].

and consequently increase in electron lifetime from few fs to 100s of ns. The result corroborates Furube *et al.* [35] speculated mechanism and more importantly, it endorses that these NPs can drive photo-catalytic reactions under solar irradiation.

Additional powerful approaches are transient absorption spectroscopy (TAS) and transient photoluminescence (TrPL) methods [36]. One of the first examples of a femtosecond spectroscopy application studies of the metal NPs effect, was examined in [9]. TAS data analysis of Au@ TiO_2 /Z907 (dye) system revealed an increase in amplitude of transient absorption in the presence of metal NPs, assigning the plasmonic enhancement of photocurrent due to transfer of carriers from photoexcited dye into TiO_2 faster than decoherence of plasmons occurred. Zhao *et al.* have observed a faster decay in the presence of the Au@ SiO_2 NPs by TrPL [37]. Temperature dependence studies reveal rapid PL quenching upon higher temperatures due to a decrease in exciton binding energy for the plasmon-enhanced samples.

There is a plethora of open questions when one considers nanoleaves containing plasmonics nanostructures as light harvesting components. Some of them are enumerated below:

- what is the energy of the hot electrons?
- what is the efficacy of the injection process?
- what is the periodicity of the plasmonic resonance?
- how does the plasmonic resonance gets quench?
- how fast is the quenching process?
- is the process a single- or a multi-photon process?

The design of efficient structures requires that some solving at least some of the questions highlighted above.

Theoretical studies on LSPR: from classical to quantum mechanical approaches

LSPR on metal NPs can be conceptually and accurately understood from the point of view of the classical theory, even for NPs dimensions as small as a few nanometers. Starting from a simple Drude model for metals, the concept of plasmon excitation can be introduced. Thenceforth, the plasmon is studied by confining in two and three dimensions, leading to strong resonances at particular frequencies. In short, the classical models are all based on solving Maxwell's equations

subject to appropriate boundary conditions. For a homogeneous nanosphere, Mie theory [38] gives an analytical solution for the space inside and outside of the spherical boundary, allowing to obtain the scattering and absorption cross section of spherical particles with sizes between ca. 10 and 100 nm. Numerical methods have been developed for more complicated shapes, for instance, the discrete dipole approximation (DDA) [39,40], finite difference time domain (FDTD) [41], and the finite element method (FEM) [42]. A very popular software code that applies the DDA approximation is the DDSCAT, which calculates the scattering and absorption of light by irregular particles and periodic arrangement of irregular particles [40,43,44].

However, as the size of metal nanoparticles shrinks on the order of few nanometers the classical method starts failing due to the lack of nonlocal response in the dielectric function and interband transitions. Therefore, a quantum-mechanical description using first principles calculation becomes necessary. The method that is most commonly used is the time-dependent density functional theory (TDDFT) [45]. Recently, simulations on nanoclusters up to several hundred atoms using local-orbital or real-space grids were performed [46,47]. Those works investigate the cluster-size dependence of LSPR for Au and Ag NPs since these materials display strongest absorption peaks. It should be mentioned that these are highly demanding simulations from computationally point of view and often restricted to nanoclusters size about 2 nm in diameter. Iida *et al.*, [47] simulated a cluster of Au using 1414 atoms (3.9 nm diameter) consisting of 15554 electrons, which is unprecedentedly large.

Kuisma *et al.* [46] showed that the LSPR frequencies and intensities in icosahedral Ag nanoparticles enter in asymptotic region already around of 2 nm. The optical response converges close to the classical limit of 3.43 eV for icosahedral Ag nanoparticles obtained using quasistatic (QS) version [48] of the FDTD method. This agreement suggests that the quantum mechanical model correctly describes the shape effect of the nanoparticle.

Most of the published work concerns materials optical absorptions, rather than the interplays and energy transfer between the plasmon and single-particle excitations. In a recent work, Ma *et al.* [49] described both the plasmon and the single-particle excitation (hot carriers) by deriving a method based on band to band transitions coefficients, which allows processes differentiation. Furthermore, they showed that if the single-particle d-to-s excitations are resonant to the plasmon frequency, then most of the plasmon energy will be converted to hot

carriers, and the overall hot-carrier generation is enhanced by the plasmon. Otherwise, the total energy will go back and forth between the plasmon and the single particle excitation and the plasmon decays slowly and may exhibit Rabi oscillations.

To illustrate this fact, a negatively charged cluster of (Ag55)⁻ was simulated to show what would occur if these transitions are blocked. Indeed, by adding one electron most of the hot-carrier generation channels are obstructed in (Ag55)⁻, and thus the plasmon decay becomes much slower. But for large nanoclusters, adding only one electron may not block the major plasmon decay or dramatically affect the dynamics. Experimentally, the change in the system may be realized by alloying with other metals, changing the nanocluster size and shape, or using some dielectric medium. Therefore, in order to elucidate the fundamentals process underlying plasmon energy conversion to hot carriers and enhancement of the hot carrier generation rate one needs a unified quantum mechanical framework using first principles calculations.

Conclusion

In conclusion, the use of plasmonic nanostructures from group 11 is a promising solution for solar fuel production because of their large optical cross-sections in the visible domain related to the excitation of localized surface plasmon resonance (LSPR). The photocatalytic efficiency can be improved by adding co-catalysts and charge lifetime enhancer material, such as semiconductors. However, the existing lack in understating of the commanding processes precludes the rapid development of the area. Nevertheless, we believe this will become a dominant research area in the field of solar energy in the near future spurred by the recent spectroscopic developments that enable us answering the currently unknown questions, and the relentless discoveries and developments in the nanoscience related fields.

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