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Published in:
ACS Applied Nano Materials

Link to article, DOI:
10.1021/acsanm.0c03358

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Hattori, Y., Gutiérrez Álvarez, S., Meng, J., Zheng, K., & Sá, J. (2021). Role of the Metal Oxide Electron Acceptor on Gold-Plasmon Hot-Carrier Dynamics and Its Implication to Photocatalysis and Photovoltaics. ACS Applied Nano Materials, 4(2), 2052–2060. https://doi.org/10.1021/acsanm.0c03358
Role of the Metal Oxide Electron Acceptor on Gold–Plasmon Hot-Carrier Dynamics and Its Implication to Photocatalysis and Photovoltaics

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ABSTRACT: The recent discovery that metal nanoparticles can generate hot carriers upon light excitation is seen as a breakthrough in the fields of plasmonics and photonics. However, the high expectations for a plasmonic revolution in applications have been dampened by the ultrafast energy dissipation of surface plasmon polariton modes. While research aimed at suppressing loss mechanisms is still pursued, another research direction has emerged where charges are harnessed before they relax. Despite the effort, efficiencies of devices based on hot carriers harnessed from plasmonics are typically very low (a few percent), which is somehow paradoxical since efficiencies for electron injection efficiency have been reported to be in the range from 25% to 40% and hole injection up to 85%. This indicates that the low device performance relates to the undesirable charge back-transfer process, which happens in the picosecond time scale. In this context, we performed a comparative ultrafast spectroscopy investigation with gold nanoparticles in direct contact with different metal oxides, namely, TiO₂, ZnO, SnO₂, and Al:ZnO. Electron dynamics revealed the decisive role of metal/semiconductor interfaces and semiconductor electronic structure in electron injection efficiency and recombination, with significant implications to the fields of photocatalysis and photovoltaics.

KEYWORDS: plasmon, hot-electron dynamics, metal/semiconductor interfaces, heterogeneous electron transfer, recombination suppression

INTRODUCTION

Nanostructures have a high density of free charge carriers and can concentrate incoming light to volumes much smaller than the diffraction limit. This outstanding phenomenon is a consequence of coherent oscillations of free electrons in a metal nanoparticle driven by the external electromagnetic waves commonly referred as localized surface plasmon resonance (LSPR) or localized surface plasmon polariton resonance. The excitation of LSPR results in strong enhancement of the electric and magnetic fields in the nanostructure vicinity, which are being explored for applications such as single-molecule spectroscopy, surface-enhanced Raman spectroscopy (SERS), biosensing, photovoltaics, photocatalysis, phototherapy, and many others.1–15

Following the excitation, the LSPR decays transferring the energy to form energetic electron–hole pairs in the femtosecond time scale known as hot carriers,16 a discovery seen as a breakthrough in the fields of plasmonics and photonics.17 However, the high expectations for a plasmonic revolution in applications have been dampened by the ultrafast energy dissipation of surface plasmon polariton modes.18,19 While research aimed at suppressing loss mechanisms is still pursued, another research direction has emerged where charges are harnessed before they relax by transferring them to accepting molecules20,21 and semiconductors.22–27 Despite the effort, efficiencies of devices based on hot carriers harnessed from plasmonics are typically very low (a few percent),15 which is somehow paradoxical since efficiencies for electron injection efficiency have been reported to be in the range from 25% to 40%22,34,35 and hole injection up to 85%.23 This indicates that the low device performance relates to the undesirable charge back-transfer process, which happens in the picosecond time scale. Despite the existence of a Schottky barrier at the interface of a metal–semiconductor, it is important to point out the basic fact that metals possess a continuous unoccupied density of states in the conduction band (CB) region of typical metal oxides (MOs) that can compete for charge recombination to the plasmonic metal through tunneling.

Received: December 16, 2020
Accepted: February 3, 2021
Published: February 10, 2021
Herein, a comparative study was performed on the initial dynamics of the electron injected from gold nanoparticles (AuNPs) into different MOs, namely, titanium dioxide (TiO$_2$), zinc oxide (ZnO), stannic oxide (SnO$_2$), and aluminum-doped zinc oxide (AZO). The objective was to investigate the charge-transfer process and also elucidate the main factors that contribute for charge separation in semiconductors directly attached to AuNPs in the first few hundred picoseconds after plasmon excitation. TiO$_2$ is the most commonly used material in the field of dye-sensitized solar cells (DSSCs), and perovskite solar cells, ZnO, SnO$_2$, and AZO are alternative promising candidates because of their high electron bulk mobility.$^{36-38}$

In this study, the dynamics of the electron injected from AuNPs into the MOs was investigated using the transient infrared absorption spectroscopy (TIRAS) technique and AuNPs plasmonic response via transient absorption spectroscopy (TAS). We observed a delayed electron injection in all the investigated MOs, except for TiO$_2$, which was assigned to the occurrence of heterogeneous electron transfer (HET) that has not been reported for plasmonics materials. Similar electron injection delays have been observed in dye molecules on ZnO and SnO$_2$, which were attributed to the formation of intermediate states in the dye molecules. Since this is not possible in plasmonic systems, the behavior might be intrinsic to the surface properties of these MOs. Additionally, ZnO/AuNPs and AZO/AuNPs composites exhibited slow recombination dynamics compared to TiO$_2$/AuNPs and SnO$_2$/AuNPs, which we ascribed to a combination of Schottky barrier height, semiconductor CB density of states, and electron bulk mobility in the semiconductor. The insertion of an Al$_2$O$_3$ layer between the AuNPs and MOs prolonged the lifetime of electrons in the semiconductor’s CB, especially for ZnO and AZO. Despite the reduction of electron injection, the insertion of Al$_2$O$_3$ was indicated to be a promising strategy to improve the efficiency of plasmonic devices. The findings are important to fields that utilize directly the hot electrons, namely, photocatalysis and photovoltaics.

The films of AuNPs were fabricated according to Scheme 1. Briefly, a thin glass cover coated with the poly(diallyldimethylammonium chloride) polymer was immersed in a AuNPs colloidal solution prepared according to the Piella et al. methodology.$^{39}$ The capping ligand (citrate) and the polymer were then removed by heating the films up to 450 °C. The second layer, composed of ZnO (wurtzite), SnO$_2$ (rutile), and AZO (2.5 wt % Al-doped ZnO, wurtzite), was deposited by spin-coating followed by annealing at 200 °C for the former ones and 500 °C for the latter. The film containing TiO$_2$ (anatase according to Raman spectroscopy) was prepared by spray pyrolysis at 450 °C on top of AuNPs film followed by annealing at 500 °C. A sample containing only AuNPs covered with poly(methyl methacrylate) (PMMA) was also prepared as a reference. A detailed description of the films’ preparation can be found in Supporting Information.

Figure 1 shows a representative transmission electronic microscope (TEM) image of the AuNPs. The TEM shows that the AuNPs are highly homogeneous with an average particles size of 5 ± 2 nm. The size and surrounding environment affect hot-carrier formation.$^{40,41}$ Since this study objective is to determine the role of the metal/semiconductor interface in hot-electron collection, we opted for a particle size shown previously to be optimal for injection.$^{42}$

Figure 2a shows the schematic diagram of the energy levels of the CB and valence band (VB) of TiO$_2$, ZnO, and SnO$_2$, and the bulk Au Fermi level. Figure 2b shows the total transmission and reflection of the samples that were measured using an integrating sphere in order to determine their absorption. All the initial samples containing only AuNPs have the same absorption, and therefore, the distinct absorption peak wavelength and intensity observed is solely due to the different dielectric permittivities of the MOs. It is known that the surrounding medium plays an important role in the plasmon resonance through its refractive index, $n$, linked to the dielectric permittivity by $\epsilon_m = n^2$. Specifically, the polarizability is maximized when $|r + 2\epsilon_m| = 1$ is a minimum, leading to the Fröhlich condition, which is a good approximation for noble metals:

$$\text{Re}[\epsilon(\omega)] = -2\epsilon_m$$

(1)

Substituting only the Drude dielectric function (Re) into eq 1 one obtains the expression for the surface plasmon frequency:

$$\omega_p = \sqrt{\frac{\omega^2_p}{1 + 2\epsilon_m} - \gamma^2}$$

(2)

where $\omega_p$ is the bulk plasmon frequency and $\gamma$ is the plasmon damping constant. Equation 2 further expresses the strong dependence of the dielectric environment observed in Figure 2b. The resonance red-shifts as $\epsilon_m$ is increased. Along with the
wavelength shift, the absorption intensity also becomes higher according to \( \varepsilon \sim \lambda^{3/2} \) as is known from the absorption coefficient equation of small nanoparticles \((d \ll \lambda)\). It is interesting to point out that the relation between frequency shift and intensity has the same behavior as that of a well-studied harmonic oscillator. Despite the fact that the AuNPs on the film are not embedded in a uniform medium, the sample configuration composed of MO/AuNPs/glass is similar for all samples, and thus, the previous discussion of the effect of the dielectric permittivity of the MOs on the plasmon resonance can be considered qualitatively valid.

The dynamics of the electron injected into the semiconductor upon light excitation of AuNPs was investigated by using the TIRAS technique. Free carriers have a strong absorption in IR spectra exhibiting a broad featureless signal. In this technique, the samples are excited at the resonance peak and the temporal evolution of the difference in absorption \((\Delta OD = OD_{pump} - OD_{unpump})\) is recorded through a broad probe light range \((4300-5200 \text{ nm})\) centered at 4800 nm.

While for the sample with TiO\(_2\) the expected ultrafast injection is observed,\(^{22}\) the samples with other MOs showed an injection time higher than our instrument response function (IRF) of ca. 95 fs (Figure S2). A convoluted fitting of the rising component resulted in 124 \(\pm\) 20 fs for SnO\(_2\)/AuNPs, 389 \(\pm\) 105 fs for AZO/AuNPs, and 368 \(\pm\) 43 fs for ZnO/AuNPs. It is widely established in the field of plasmonics that the formation of a highly energetic electron–hole pair through the plasmon decay happens in the time scale ranging from 1 to 100 fs.\(^{17}\)

Following the first generation of hot carriers they will redistribute their energy by \(e-e\) collisions. The \(e-e\) collision rate is proportional to the electron energy by \(\tau^{-1}_{e-e} = K(E - E_F)^2\), with \(K = 0.30 \text{ fs}^{-1} \text{ eV}^{-2}\).\(^{45}\) Therefore, the most energetic electrons are the first ones to transfer their energy by exciting new ones. In a rough approximation, for each \(e-e\) collision the hot electron will halve its energy, while the number of hot electrons is doubled, meaning only the electrons with one or a few scattering events will have enough energy to overcome the Schottky barrier that takes place in less than a femtosecond considering \(E = 2 \text{ eV}\) for the most energetic electron. The time interval is 2 orders of magnitude lower than the observed slow
rising component, i.e., electron injection occurs much later than the e−e scattering events in gold, and thus, potential changes in the process due to differences in MO support cannot justify the observed signal. Another possible explanation is that AuNPs transfer energy to the MOs via resonant energy transfer (RET). Cushing et al.48 also observed a slow rise component which they associated with the formation of an electron−hole pair on the Cu2O shell surrounding core AuNPs with a 5 nm SiO2 intermediate layer. However, the absence of overlap between the Au LSPR and the semiconductor absorption spectra (>3.4 eV) makes RET less probable. Moreover, we did not detect any steady-state and time-resolved photoluminescence (PL) from our samples when exciting at the plasmonic peak, which would be expected if the RET mechanism was involved, in particular for the ZnO sample because of its known PL quantum yield.47,48

A similar injection time trend, however with longer time components (Figure 3b), was observed when the same MOs were sensitized with a Z907 dye (Figure S1). Tiwana et al.49 investigated the same Z907 dye attached on TiO2, ZnO, and SnO2 mesoporous films by transient terahertz conductivity upon light excitation and compared the findings with the photovoltaic performance of those DSSCs. They concluded that factors such as the density of states, local binding, and orbital overlap of the sensitizer on the MOs surface are responsible for the slow injection component as well as charge generation efficiency, therefore being largely independent of the energetic positioning of the CB of the MOs.

TAS measurements on ZnO/AuNPs and AZO/AuNPs excited at 330 nm (semiconductor band gap excitation) or the Au resonance peak and probed in the UV to the near-IR range are shown in Figure 4. The kinetics at the band edge bleach wavelength of ZnO and AZO when excited at 330 nm showed the formation of a signal maximum signal with a time constant within our IRF, while excitation at the Au LSPR peak resulted in a slower component. The observation strongly suggests that the slow injection observed in some of our Au/MOs system is related to the interface of MOs and not to the bulk electronic property. It was not possible to observe the band edge bleach for TiO2 and SnO2 due to the low signal. However, it is clear that in the case of TiO2 the rising edge component is almost the same after band gap excitation or Au LSPR excitation (Figure 4, bottom panel).

In order to further investigate the origin of the slow rise component, we prepared samples with 1 nm of Al2O3 between the AuNPs and the MOs by using atomic layer deposition (ALD) with trimethylaluminum (TMA) as the precursor; the absorption spectra of each sample can be found in the Supporting Information (Figure S5). TIRAS measurements on these samples indicated that, while the insulating layer reduced the injected electrons as indicated by a lower absorption maximum, the rising component line shape is similar to the ones presented in Figures 3b and 5. In previous studies related to HET, it has been suggested that interface states are created through the formation of the chemical bonds between the dye molecules and the semiconductor surface.50−52 Stockwell et al.53 attributed the delayed electron injection on ZnO to the formation of an interface-bound charge-separated pair intermediate that depends on the nature of both the semiconductor and adsorbates. More specifically, they suggest that the Coulombic interaction between the oxidized adsorbate and the surface-bound electron at the interface and/or the Zn4+−based electron-accepting states that weaken their coupling with the bulk CB states are mainly responsible for the long-lived interface-bound charge-separated pair, which slows down the escape of electrons to the bulk states.

Strothkämper et al.52 investigated perylene derivatives linked to ZnO with different bridge prolongations that slowed down the injection rate, which contested the effect of the electrostatic screening due to different permittivities of the MOs. TIRAS measurements without (Figure 3a) and with the presence of 1 nm of Al2O3 (Figure 5) show that indeed the electrostatic screening plays a minor role on the delayed formation of free charge on the MOs. In addition, it also indicates that the observed delay is intrinsic to the electronic property of the surface states of the MOs, since the presence of the insulating layer avoids or at least decreases considerably the

**Figure 4.** Transient absorption spectroscopy measurements: band edge bleach kinetics of samples with ZnO and AZO excited at 330 nm and at the LSPR peak wavelength; kinetics at 4800 nm of the sample with TiO2 excited at the LSPR peak and at 330 nm (bottom). The narrow positive peaks in the ZNO and AZO traces are ascribed to cross-phase modulation in the sample.

**Figure 5.** Kinetic traces extracted at 4800 nm of MOs/Al2O3(1 nm)/AuNPs.
wave function overlap of the surface states between AuNPs and MOs. The same samples but with 3 nm of Al2O3 were also prepared and measured (Figure S7). All the other samples, except SnO2, had signals commensurate with the noise along with the appearance of cross-phase modulation that prevented the observation of the signal rise component. The observation indicates that in these MO hot electrons are prevalent from direct plasmon decay, not via indirect plasmon-induced energy transfer. The SnO2/AuNPs sample presented the highest signal where the delayed electron injection is still apparent. The observation suggests that the optimal insulator layer thickness is substrate-dependent and that electrons can tunnel through layers significantly thicker than 1 nm. Moreover, the involvement of RET or other indirect plasmon-induced energy transfer processes can be speculated, but we found no additional evidence to substantiate its involvement, such as photoluminescence resultant from electron–hole pair recombination.

An investigation of the electron dynamics at the ZnO(1010) surface using time-resolved two-photon photo-emission (TR-2PPE) showed a quasi-continuum of defect-derived surface states located in the vicinity of the CB minimum with decreasing density of surface states within the band gap (ca. 0.3 eV below the CB minimum). The 1010-terminated surface of zinc oxide is the energetically most favorable surface, and therefore, it likely constitutes a large fraction of the surface area in sintered ZnO nanoparticle films. Hence, one likely explanation is that injected electrons from AuNPs into ZnO are initially trapped in the surface states which only upon filling are able to escape to the bulk. Surface states in the band gap of TiO2 have such as atom vacancies are known to exist; however, they affect electron dynamics differently, namely, they affect charge recombination not injection. Ultimately, the results show that in ZnO, AZO, and to a minor extent SnO2 electron transfer occurs via an HET process, while in the case of TiO2 it is primarily via direct transfer that is not significantly affected by surface states.

Following the stage of maximum signal amplitude in TIRAS, each sample has distinct electron kinetics in their respective materials. Clearly, ZnO/AuNPs and AZO/AuNPs have the slowest recombination rate followed by SnO2/AuNPs and TiO2/AuNPs (Figure 6). One important factor that affects the recombination rate is the metal–semiconductor Schottky barrier height that has been reported to be $0.62–0.67$, $0.9–1.2$, $0.85–0.86$ and $<0.33$ eV for ZnO, TiO2, and SnO2, respectively. Between the MOs used, TiO2 has the highest effective mass of about $5–10$ and electron bulk mobility of ca. $1$ cm$^2/(V·s)$, in contrast to $0.3$ and electron bulk mobility of $205$ cm$^2/(V·s)$ for ZnO and $200$ cm$^2/(V·s)$ for SnO2. This considerable difference in the effective mass and bulk mobility is related to the density of states in the CB region, which is almost $2$ orders of magnitude higher than TiO2. The high density of states in TiO2 is a consequence of the empty $3d$-orbital nature, whereas the other MO’s CBs are mainly derived from the empty $s$ and $sp$ orbitals of the metal atoms. It is evident that the Schottky barrier height cannot only be taken to account, otherwise the sample containing TiO2 would have to have the slowest recombination rate. We tentatively associate the slower decay kinetics of MOs/AuNPs to the higher electron bulk mobility, as it decreases the recombination probability due to fast escape from the interface. Although the aforementioned MOs have similar electron bulk mobility, the faster electron recombination observed for SnO2 can be attributed to the lower Schottky barrier height. In summary, we suggest that the interplay between the Schottky barrier height and electron bulk mobility plays the main role of the electron dynamics at this short time scale.

The change in the electron decay kinetics with the insertion of $1$ nm of Al2O3 can be clearly observed for the samples containing ZnO and AZO and less obviously for SnO2 and TiO2. The relative electron injection efficiency (RIE), i.e., the injection efficiency in respect to the samples without Al2O3, was calculated by accounting the $\Delta OD_{max}$ signal for a specific absorbed fluence (Figure S6) compared with the dependence of the absorbed fluence with $\Delta OD_{max}$ of the samples without Al2O3 (Figure 6a, inset). The normalized signal at $400$ ps was also compared with the samples with $1$ nm of Al2O3 by multiplying with the RIE for each sample (Table 1). Curiously, the sample with TiO2 is the one with the lowest RET that also did not improve in the charge separation. However, this could be due to the highest Schottky barrier value reported for TiO2/AuNPs, and therefore wider depletion layer, that suppresses electron recombination more than the insulating layer.

Figure 6. Kinetic traces extracted at $4800$ nm up to $400$ ps of AuNPs attached to MOs without (a) and with (b) $1$ nm of Al2O3. Inset: absorbed fluence vs $\Delta OD_{max}$. 

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With the purpose of investigating the relative efficiency of electron injection of AuNPs into the MOs, an excitation fluence dependence in function of the e−ph relaxation time was carried out. Transient absorption measurements of plasmonic nanoparticles give rise to the typical features with a bleach region at the absorbance peak with two positives “winglets” on its side both mainly governed by e−ph scattering events with a characteristic decay time known as the electron−phonon relaxation time \( \tau_{e\text{-}ph} \) (Figure 7a), which is sensitive to the gold electronic density and thus different for each system. Additionally, there are signals below 400 nm associated with changes in the semiconductor band gap excitation due to electron injection. The maximum transient signal intensity of the plasmonic nanoparticles reflects the establishment of an electron temperature, whose energy is subsequently transferred to the metal lattice by e−ph interactions, leading to thermal equilibrium between the metal electron gas and the lattice. The signal decay probed at each fluence value was fitted with a monoexponential decay function at the bleach peak wavelength, as expected from the well-accounted two-temperature model. The obtained slopes from Figure 7b are listed in the Table 2. For the PMMA/AuNPs sample that is used as a reference, since no electron injection takes place, the slope is the highest value of 0.158 ± 0.03 ps cm\(^2\)/\( \mu \)J. The shallower slope of the MOs/AuNPs sample in comparison to PMMA/AuNPs reflects the decrease in the electron temperature due to hot-electrons injection. In particular, TiO\(_2\) showed the shallower slope as expected, followed by ZnO, SnO\(_2\), and AZO. The higher Fermi level position of AZO in comparison to ZnO can be used to explain the lower injection efficiency observed in the former.

### Table 1. Relative Injection Efficiency (RIE) and Comparison of the ΔOD Signal at 400 ps with and without 1 nm of Al\(_2\)O\(_3\)

| MO      | TiO\(_2\) | SnO\(_2\) | ZnO | AZO |
|---------|-----------|-----------|-----|-----|
| RIE (%) | 24.7      | 80.0      | 69.9| 65.6|
| ΔΔOD\(_{400}\) (%) without Al\(_2\)O\(_3\) | 3.4 | 2.8 | 23.2 | 20.2 |
| ΔΔOD\(_{400}\) × RIE (%) with 1 nm of Al\(_2\)O\(_3\) | 1.2 | 8.2 | 38.4 | 41.0 |

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### Table 2. Obtained Slope Values for Each MO/AuNPs System Using the TAS Measurements Presented in Figure 7b

| Sample          | Slope (ps cm\(^2\)/\( \mu \)J) |
|-----------------|---------------------------------|
| PMMA/AuNPs      | 0.158 ± 0.017                   |
| TiO\(_2\)/AuNPs | 0.075 ± 0.005                   |
| SnO\(_2\)/AuNPs | 0.126 ± 0.007                   |
| ZnO/AuNPs       | 0.113 ± 0.016                   |
| AZO/AuNPs       | 0.135 ± 0.031                   |

**Figure 7.** (a) Transient absorption excited at their respective LSPR peak wavelength. (b) Electron−phonon relaxation time in function of the absorbed fluence.
further improving efficiencies of photodevices that utilize charged particles.

**ASSOCIATED CONTENT**

• Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnanomater.0c03358.

Detailed description of the sample preparation, structural characterization, transient absorption experiments, and catalytic experiments (PDF)

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**Author Contributions**

Y.H. conceived and planned the project in liaison with J.S. The experimental work was performed by Y.H., S.G.A., and J.M. Y.H. analyzed and treated the data and prepared the figures in liaison with J.S. The manuscript was drafted by Y.H. and J.S. with input from all authors. The final version was read and agreed upon by all the authors.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to thank the photovoltaic unit of the Physical Chemistry Division, Department of Chemistry—Angstrom, Uppsala University for the access and support using their material preparation systems. The authors would like to thank Uppsala University for financial support. J.S. acknowledges the support by the Swedish Research Council (nos. 2015-03764 and 2019-03597). K.Z. acknowledges the support by the Danish Council for Independent Research, no. 7026-0037B, and the Swedish Research Council, no. 2017-05337.

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