

## Editorial

# Mechanisms Behind Plasmonic Enhancement of Photocurrent in Metal Oxides

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**Abstract**

Surface plasmon resonance (SPR) of metal nanostructures has been proposed as a promising strategy to enhance the photoactivity of metal oxides for photovoltaic and photoelectrochemical applications. While several studies have suggested that metal nanostructures could act as photosensitizers to improve the photocurrent of metal oxides, the mechanism behind is still not well established. Here we briefly review some of the recent research progress and discuss several possible mechanisms underlying the observed plasmonic enhancement of photocurrent in metal-metal oxide systems.

**Introduction**

Photoelectrical conversion is a promising and environmentally friendly technology to solve faced energy crisis because sunlight delivers a power of  $10^6$  TW/year continuously [1,2]. In photoelectrical conversion, semiconductors play an important role in capturing light to generate electron-hole pairs for subsequent electricity or chemical fuel production [3]. For instance, since Fujishima and Honda demonstrated the photocatalytic water splitting using a  $\text{TiO}_2$  photoanode in a photoelectrochemical (PEC) cell [4], an enormous amount of work has been carried out in order to achieve photoassisted water splitting and develop sustainable methods for producing chemical fuel [5-10]. Metal oxide (MO) semiconductors afford advantages of low cost, high stability, and suitable oxidation potential for water oxidation. However, the limitation of most MOs is the intrinsically wide bandgap, resulting in poor ability to capture solar energy in the visible and near-infrared (NIR) regions. It is thus highly desired to develop MOs with small bandgaps or strategies for sensitizing MOs with large bandgaps so they can respond effectively to sunlight for enhancing solar energy conversion.

Surface plasmon resonance (SPR) is a unique optical property of noble metal nanoparticles (NPs) such as Au, Ag and Cu, and it arises from collective coherent oscillation of electrons in the NPs induced by light irradiation [11]. The SPR oscillation frequency is highly sensitive to the size and shape of the metal NPs as well as the dielectric constant of the surrounding environment, which often manifests as strong absorption in the visible and NIR regions [12,13]. One interesting question is: can metal NPs with strong SPR in the visible sensitize MO semiconductors for enhancing photoelectrical conversion applications?

To answer this question, a number of studies have been carried out with focus on interface charge transfer [14,15] as well as photoelectron conversion using plasmonic metal-MO nano heterostructures [16-19]. Several studies suggested that some of the hot electrons from SPR excitation can participate in chemical reactions. For example, Au-MO or Ag-MO nanocomposites have been proposed as visible light driven photocatalysts to degrade pollutant [20-23]. Likewise, plasmonic metal NPs have been demonstrated to sensitize MOs to generate photocurrent in photovoltaic (PV) cells [24-26].

Incident-photon-to-current efficiency (IPCE) of optimized Au- $\text{TiO}_2$  and electrolyte based PV as high as 26% under SPR excitation was reported [24]. In addition, a solid-state plasmonic solar cell fabricated using metal NPs,  $\text{TiO}_2$  and hole conductor Spiro-OMeTAD showed photocurrent density of  $\sim 2.5$  mA/cm<sup>2</sup> as compared to dye sensitized solid-state solar cell (0.5 mA/cm<sup>2</sup>) under high intensity visible LED illumination [26]. On the other hand, the same effect of photosensitization of MOs using metal NPs based on hot electron injection has also been proposed for application in PECs [27-29]. Lee *et al.* reported that the plasmonic photoanode made by a dense array of Au nanorods capped with  $\text{TiO}_2$  could generate photocurrent and produce  $\text{H}_2$  under visible light illumination [29]. Fuel production efficiency is up to 20-fold higher in the visible region than in the UV region. In another study, plasmonic Au NPs were found to play dual roles in enhancing the efficiency of CdS-Au- $\text{TiO}_2$  PEC for hydrogen generation [30]. As the incident light shorter than 525 nm, Au NP served as an electron relay to facilitate the charge transfer between CdS and  $\text{TiO}_2$ . For wavelength from 525 nm - 725 nm, the Au NP acted as a photosensitizer to improve solar-to-hydrogen conversion. Likewise, Au-decorated  $\text{TiO}_2$  nanowire (NW) electrodes for PEC water oxidation have been investigated recently [31]. Enhancement in photocurrent was observed in the entire UV-Vis region from 300 to 800 nm by controlling the cover density and shape of the decorating Au nanostructures including both Au NPs and nanorods (NRs). Although the most improved photoactivity of  $\text{TiO}_2$  was found in the UV region, which is attributable to effective surface states passivation by Au NPs, the enhancement in visible region of  $\text{TiO}_2$  photoelectrodes matched well the SPR absorption of Au NPs and Au NRs. The mixture of Au NPs and NRs on  $\text{TiO}_2$  was able to enhance the photocurrent in the entire UV-Vis region from 300 to 800 nm, even though the efficiency of photoelectron conversion efficiency was very low, just  $\sim 0.01$ - $0.02\%$  in IPCE measurements.

The suggestion of metal NP-sensitized MOs with high IPCE in PV is at first somewhat surprising since the lifetime of hot electrons in Au and Ag NPs are usually very short, only 1-2 ps [32]. Thus, for photosensitization or hot electron transfer to be effective, the charge transfer rate has to be much faster than 1-2 ps. Indeed, plasmon-induced electron transfer from Au to  $\text{TiO}_2$  was reported to be 240 fs based on transient absorption spectroscopy with an IR probe [14].

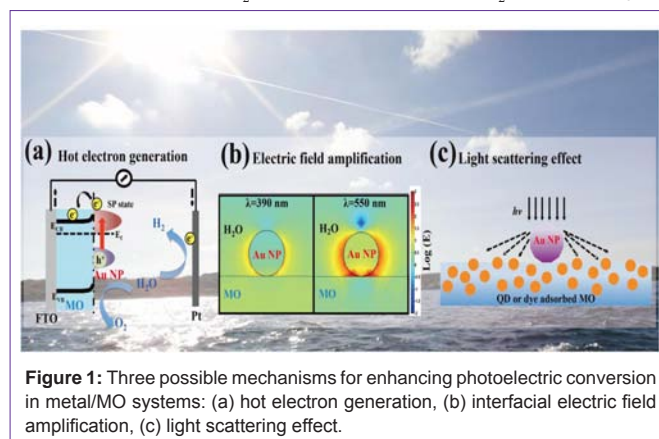
Similarly, the half-lifetime of intra-band signal of hot electron from Au to CdS nanorod by SPR excitation was recently demonstrated to be  $1.83 \pm 0.22$  ps [33]. While ultrafast charge transfer seems to be possible, its branching ratio or quantum yield with respect to other hot electron relaxation processes, such as photothermal conversion through electron-phonon coupling, is often not determined unambiguously. We have investigated the charge carrier dynamics in Au NP-decorated ZnO NWs by ultrafast transient pump-probe spectroscopy with the attempt to determine if there is direct evidence for hot electron injection from Au to ZnO [34]. The observed hot electron lifetime of Au NP on ZnO NWs ( $3.2 \pm 0.5$  ps) did not change noticeably from that of Au NPs alone. Moreover, the exciton lifetime in ZnO is essentially the same with and without Au decoration. The results indicate no charge transfer between ZnO NW and Au NPs or weak interaction between them. Based on the ultrafast study of hot electron lifetime in ZnO, we estimate that the quantum yield of hot electron injection is no more than 10%, based on the uncertainty of our measurement. This is consistent with the low photocurrent observed in our Au-TiO<sub>2</sub> work that also suggests a very low yield of hot electron injection, if injection is indeed responsible for the photocurrent observed in the visible [31]. Our results seem to be in interesting contrast to the much higher IPCE reported by others, as discussed earlier, which suggest that other possible enhancement mechanisms may be involved when high IPCE is observed or the IPCE may be very sensitive to the detailed experimental conditions that can easily differ for different systems studied.

In the hot electron generation mechanism, metal nanostructures serve as photosensitizers, similar to dyes or quantum dots (QDs), that generates high energy or hot electrons with enough energy to overcome the Schottky barrier upon SPR excitation and be injected into the conduction band of MO semiconductors (Figure 1a). Hot electron injection from metal to MOs will likely occur when the metal and MOs are strongly coupled. SPR excited Au nanostructures have been found to generate hot electrons in Au-ZnO photoanode under visible light irradiation based on in-situ X-ray absorption measurements [35]. As mentioned above, based on the very short lifetime of hot electrons, the probability of electron injection should be low if possible at all. Several studies have focused on improving the hot electron injection efficiency of plasmonic metal-MO systems by optimizing the detailed structures of MOs. For instance, three-dimensional (3D) hierarchical MO nanostructures have been designed and demonstrated to exhibit not only high interfaces between metal, MO and electrolyte, but also strong light harvesting in improving the performance of PEC performance [36,37]. The plasmonic metal combined with geometric 3D-MO nanostructures showed high photoactivity in the visible region, with photocurrent density  $\sim 0.125$  mA/cm<sup>2</sup> (0.5 V vs. Ag/AgCl) and  $\sim 0.4$  mA/cm<sup>2</sup> (1 V vs. reversible hydrogen electrode or RHE, IPCE = 5.5 % at 550 nm) in dendritic Au-TiO<sub>2</sub> nanorods and Au-ZnO branched nanowires, respectively [36,37]. Similarly, the combined 3D MO structures or photonic crystals with plasmonic metal NP-MO systems were claimed to generate hot electrons for enhancing PEC performance [38-40].

In principle, besides hot electron injection, there are other possible mechanisms that may be responsible for enhancing photoelectric conversion of MOs by metal nanostructures. For example, metal nanostructures may increase photocurrent by local electric field

enhancement. SPR of metal NPs could amplify the electric field near semiconductor surfaces, resulting in an increase of the light absorption rate by the semiconductor (Figure 1b). The enhancement should be observed only when the SPR of the metal spectrally overlaps with the absorption of the semiconductor. For instance, an enhancement factor of 3~4 around 600~700 nm was reported in the case of hematite coated on Au nanopillars [41,42]. Similarly, the efficiency of an N719 dye-sensitized solar cell (DSSC) was enhanced from 9.3% to 10.2% when SiO<sub>2</sub>-capped Au NPs were used as a localized electric field amplifier [43]. The increased absorption of dyes by SPR resulted in the improved photocurrent and IPCE of DSSC in the visible region. In related studies, it was suggested that the negative shift of Fermi level in the Au/TiO<sub>2</sub> nanocomposite could increase open-circuit voltage of DSSC or improve charge separation in PEC [44]. On the other hand, the band edge absorption of most wide bandgap MOs could not overlap with the SPR of metals, such as TiO<sub>2</sub>, ZnO and SnO<sub>2</sub>, while the enhancements in PEC cells were still observed after metal NP decoration. For example, the performance of Au-deposited TiO<sub>2</sub> films under visible light illumination for PEC water splitting was enhanced around 66-fold at 633 nm [45]. The proposed enhancement mechanism in this study was that the electrical field of SPR could amplify the contribution of absorption due to defect and impurity state within the bandgap.

In addition, metal nanostructures can serve as light scattering centers to increase the average photon path length, resulting in improved absorption and electron-hole pair formation in semiconductors (Figure 1c) [46,47]. For example, enhanced coupling of light into semiconductor thin films by scattering from plasmonic metal nanoparticle arrays has been demonstrated [48]. Within incorporation of Au, Ag or Cu dense nanoparticle arrays into Si-on-insulator photodetector, a 20-fold increase in photocurrent was observed. Likewise, light scattering due to plasmonic metal nanostructures was also observed for single-crystalline Si [49], amorphous Si [50] and GaAs [51] solar cells [52]. The scattering effect is expected to become more important for larger sized metal NPs. For instance, nanorods, nanowires, and aggregates tend to exhibit stronger scattering effect. Since light scattering can occur from far field, it can happen when the metal NPs are not near or strongly coupled with the semiconductor MOs. For example, in a study of CdSe QD-sensitized Au/TiO<sub>2</sub> hybrid mesoporous electrode for PEC applications [53], it was found that without CdSe QDs, the photocurrent of Au/TiO<sub>2</sub> was lower than that of TiO<sub>2</sub> in the UV region,



**Figure 1:** Three possible mechanisms for enhancing photoelectric conversion in metal/MO systems: (a) hot electron generation, (b) interfacial electric field amplification, (c) light scattering effect.

suggesting trapping of electrons photogenerated in TiO<sub>2</sub> by Au NPs, which is expected. However, the combination of Au NPs, CdSe QDs and TiO<sub>2</sub> nanostructures showed substantial increase in photocurrent due to Au NPs in the visible region (350–600 nm). The increase was stronger with higher Au NP loading and at shorter wavelength. The enhancement was attributed to enhanced absorption of CdSe QDs due to increased light scattering by Au NPs. The same mechanism may also be responsible for the enhancement photocurrent observed for TiO<sub>2</sub> with Au NPs and NRs we reported recently, where the TiO<sub>2</sub> bandgap state absorption may be enhanced due to scattering of the Au NPs and/or NRs [31].

In summary, the possibility of photosensitization of MOs using plasmonic metal NPs is tantalizing. While there is increasing evidence for hot electron injection, there is no general consensus to date. Further research is necessary to more firmly establish the possibility. In addition, better determination of the quantum yield or branching ratio for photosensitization with respect to other competing processes such as photothermal conversion needs to be made, which requires more quantitative studies. More work is also needed to better understand what factors determine the mechanism of operation. The strengthen of interaction between the metal NP and MOs is likely a critical factor, which may in turn depends on the detailed structures of both constituents down to the molecular or atomic level. Control and optimization of charge carrier dynamics at the interface of metal NPs and MOs will be very important for possible hot electron injection as well as other possible enhancement mechanisms such as local electric field amplification and light scattering. Both experimental and theoretical works will be needed before a complete understanding can be achieved and the full potential for application can be realized.

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