

Plasmonic Enhancement of Photocatalytic Reactions

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Introduction

Solar energy is an important renewable energy source to supplement and possibly replace fossil fuels. As a result of the global energy crisis, photocatalysis, which uses photonic energy instead of thermal energy to drive chemical reactions, has attracted much attention. The direct conversion of solar energy to electricity is problematic because of our inability to store large amounts of electricity. Photocatalysis offers the ability to convert solar energy directly into chemical bonds, which can be stored indefinitely for later use. Photocatalytic water splitting and conversion of carbon dioxide into hydrocarbons have been of great interest since the early 1970s, after the first demonstration under ultraviolet radiation by Fujishima and Honda.¹ While TiO₂ is one of the most promising photocatalysts, it does not absorb light in the visible region of the electromagnetic spectrum. Because of TiO₂'s short wavelength cutoff, there are very few solar photons (~4%) that can be used to drive this photocatalyst.

Plasmon resonant nanostructures have gained considerable interest in many fields, including near-field optics,² surface enhanced spectroscopy,³ solar cells,⁴ and medicine.⁵ More recently, researchers have explored the applicability of plasmonic processes in the field of photocatalytic chemistry for organic molecule decomposition,⁶ CO oxidation,⁷ and even materials synthesis.⁸

In this paper, we discuss our recent demonstration of enhanced photocatalytic water splitting and photocatalytic conversion of carbon dioxide into hydrocarbons under visible illumination in TiO₂ films with strongly plasmonic Au nanoparticles. Here, we utilize plasmonic near-field coupling to improve TiO₂ photocatalysis in the visible wavelength range.

Experimental

We prepare TiO₂ in the anatase crystalline phase by electrochemically oxidizing titanium foils (ATO) and by the sol-gel method.⁹ We then evaporate a gold film with a nominal thickness of 5 nm on the surface of the TiO₂. This thin gold film is known to form island-like growth that is strongly plasmonic and serves as a good substrate for surface enhanced Raman spectroscopy (SERS).^{3b, c} We measured the photocatalytic water splitting reaction rates of TiO₂ with and without Au nanoparticles in a 1 M KOH solution using a three-terminal potentiostat. Photocurrent spectra were measured using a Fianium supercontinuum white light source in conjunction with a Princeton Instruments double grating monochromator, providing continuously tunable monochromatic light (10 nm FWHM) from 400 nm to 1600 nm.¹⁰ The photocatalytic reduction of CO₂ and H₂O are carried out in a sealed 51.6 ml stainless steel reactor with a quartz window. Reaction products are analyzed using a Varian gas chromatograph (GC) equipped with TCD and FID detectors.¹¹

Results and Discussion

Figure 1 shows the photocurrent of anodic TiO₂ with and without Au nanoparticles irradiated with visible light (7 W/cm² @ 532 nm) for 22 seconds. Under visible irradiation ($\lambda = 532$ nm), the addition of gold nanoparticles results in a 5-fold increase in the photocurrent due to the large plasmonic enhancement of the local

electromagnetic fields.¹⁰ The transient decay observed in Figure 1 is the result of trapped surface charge that is released upon irradiation.¹²

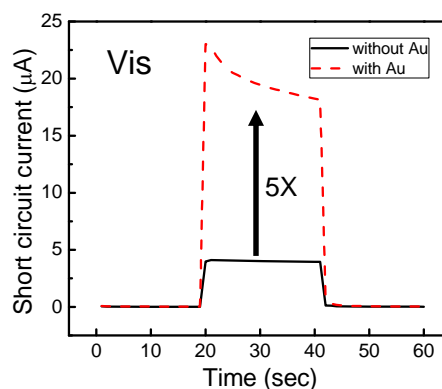


Figure 1. Photocurrent of anodic TiO₂ with and without Au nanoparticles at zero bias voltage irradiated with visible ($\lambda = 532$ nm) light for 22 seconds. (Reprinted with permission from Ref 28. Copyright (2011) American Chemical Society.)

The photocatalytic enhancement observed under 633 nm wavelength illumination is shown in Figure 2. For bare TiO₂ with no nanoparticles, a small photocurrent of 4.5 nA can be seen just above the noise signal. Here, a significant enhancement in the photocurrent (66X) is evident for the sample with plasmonic Au nanoparticles, resulting in a photocurrent of 0.3 μ A. While this irradiation (1.96 eV) is significantly below the bandgap of TiO₂ (3.2 eV), the photocatalytic enhancement is considerably larger than that observed at 532 nm (2.42 eV).¹⁰

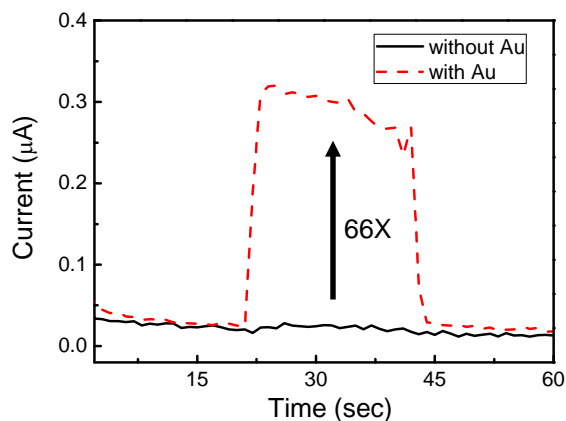


Figure 2. Photocurrent of anodic TiO₂ with and without Au nanoparticles irradiated with $\lambda = 633$ nm light for 22 seconds. (Reprinted with permission from Ref 28. Copyright (2011) American Chemical Society.)

By taking the ratio of the photocurrent spectra of anodic TiO₂ with and without Au nanoparticles (Figure 3), an enhancement in the photocurrent of TiO₂ with Au nanoparticles can be seen for wavelengths above 500 nm, with a maximum enhancement occurring around 650 nm.¹⁰

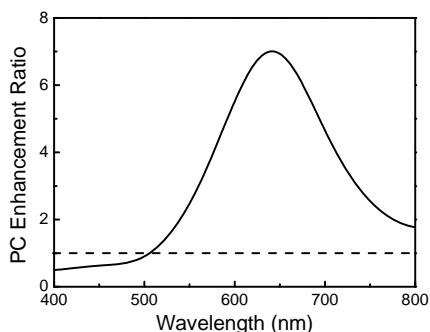


Figure 3. Photocurrent enhancement ratio spectrum of anodic TiO₂ with and without Au nanoparticles. (Reprinted with permission from Ref 28. Copyright (2011) American Chemical Society.)

Figure 4 shows the GC signal of the photoreduction of aqueous CO₂ after 15 h visible (532 nm laser) illumination. Here, methane is the only product detected by the FID detector of the GC. These reactions can be understood by comparing the conduction and valence band energies of TiO₂ with the reduction potentials of CO₂ for the three reduction products CH₄, HCHO, and CH₃OH, as shown in Figure 5. Since the conduction band of TiO₂ lies above the reduction potential of CO₂/CH₄,¹³ it is energetically favorable for electrons from the conduction band of TiO₂ to transfer to CO₂ to initiate the reduction of CO₂ with H₂O producing CH₄.¹⁴ Methane is the only favorable product since the reduction potentials of CO₂/HCHO and CO₂/CH₃OH lie above the conduction band of TiO₂.^{1b, 15} For the bare TiO₂-catalyzed reduction, only a small amount of methane is detected by GC since the energy of the 532 nm wavelength light (2.41 eV) is significantly lower than the bandgap of TiO₂ (3.2 eV). The yield is finite, yet small (0.93 μmol/m²-cat.), because of electronic transitions excited to and from defect states in the bandgap of TiO₂. On the other hand, the yield of Au nanoparticle/TiO₂-catalyzed reduction is 22.4 μmol/m²-cat., a 24-fold enhancement over the bare constituent materials. This enhancement in sub-bandgap absorption/photocatalysis is consistent with the water splitting results shown above, wherein the intense local fields produced by the plasmonic nanoparticles couple light very effectively from the far-field to the near-field, short-lived defect states at the TiO₂ surface.¹⁶

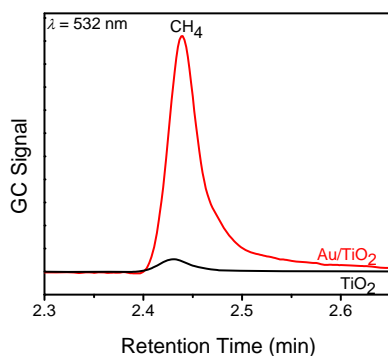


Figure 4. GC signal of sol-gel TiO₂ with and without Au nanoparticles irradiated with visible ($\lambda = 532$ nm) light for 15 h. (Reprinted with permission from Ref 28. Copyright (2011) American Chemical Society.)

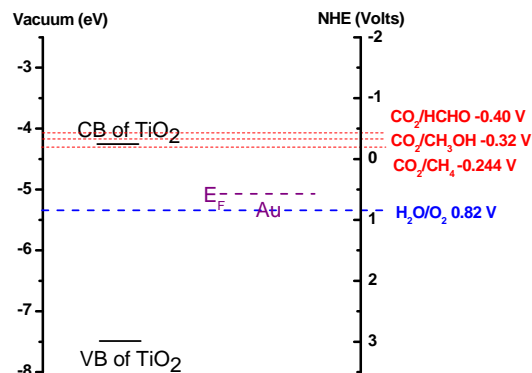


Figure 5. Energy band alignment of anatase TiO₂, Au, and the relevant redox potentials of CO₂ and H₂O under visible illumination. (Reprinted with permission from Ref 28. Copyright (2011) American Chemical Society.)

We can understand the photocatalytic enhancement observed under visible illumination by simulating the electromagnetic response of the Au nanoparticle/TiO₂ composite film using the finite-difference time-domain (FDTD) method.¹⁷ The electromagnetic response of the film is dominated by local hot spots where the electric field intensity reaches 1000 times that of the incident electric field at the TiO₂ surface.^{10, 18} This means that the electron-hole pair generation rate is 1000 times that of the incident electromagnetic field. Thus, an increased amount of charge is induced locally in the TiO₂ due to the local field enhancement of the plasmonic nanoparticles.

Conclusions

In conclusion, we demonstrate plasmon enhancement in the photocatalytic splitting of water and conversion CO₂ to hydrocarbon fuels in the visible region of the electromagnetic spectrum by exploiting the surface plasmon resonance of gold nanoparticles. The intense local fields produced by the surface plasmons couple light efficiently to the surface of the TiO₂. This enhancement mechanism is particularly effective because of anodic TiO₂'s short minority carrier diffusion length, which would otherwise limit its photocatalytic activity. Enhancements in the photocatalytic activity of 5X and 24X are observed at wavelengths of 532 nm for water splitting and conversion CO₂ to hydrocarbons, respectively. Electromagnetic simulations of this process suggest that enhancement factors many times larger than this are possible if this mechanism can be optimized. The experimental data and fundamental understanding described here provide a path toward resolving the photon absorption/electron diffusion length mismatch that has made photovoltaics and direct photocatalysts far too expensive to find broad applicability in our energy infrastructure. For photocatalysis, this area is especially exciting because it presents a possible route to direct solar to fuels production.^{10, 16}

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