Optical excitations of metallic nanoclusters buried in TiO$_2$ for solar photochemistry

Fei Wang, Frank Womack, Phillip T. Sprunger, and Richard L. Kurtz
Department of Physics and Astronomy
Louisiana State University, Baton Rouge, LA 70803-4001

ABSTRACT

Ag deposited on TiO$_2$(110) forms nanoclusters ~5 nm across and 2 nm in height, shown by STM. These nanoclusters exhibit a plasmon loss at 3.8 eV as determined by EELS yet the substrate Fuchs-Kliewer phonon modes remain, indicating that the exposed TiO$_2$ is not perturbed by the Ag clusters. Titania is grown on top of these clusters by evaporation of Ti and subsequent oxidation and both EELS and optical measurements show that new excitations are produced in the 1.5-2 eV range, a much better match to the solar spectrum than the 3.8 eV Ag plasmon. AFM measurements indicate that the Ag clusters retain their morphology upon titania coating.

Keywords: TiO$_2$, plasmon excitation, solar photochemistry, Ag nanoclusters, buried clusters

1. INTRODUCTION

Water interactions with TiO$_2$ and other oxide surfaces have been thoroughly studied since Fujishima and Honda reported on its ability to split water by photolysis. The promise of using photolysis as a means of producing hydrogen fuel is a particularly attractive goal but there are significant challenges to enhancing the efficiency to the point where it can be a competitive process. As noted in recent DOE publications, the three major roadblocks to solar photoelectrolysis of water to produce hydrogen are the need for an efficient semiconducting absorber of light, a requirement of long-term stability of the semiconductor in the electrolytic environment, and suitable energetics in band matching so that photoexcited carriers efficiently react with the water.

We are investigating the means that metallic nanoclusters can be incorporated within our semiconductor to enhance the absorption of the solar spectrum by through utilizing their plasmon resonances. One challenge is that the plasmon resonances of metallic nanoclusters often absorb in the ultraviolet, falling outside of much of the solar spectrum, and are also only weakly dependent on cluster size. Secondly, metallic clusters adsorbed on an oxide surface are likely to be unstable within an oxidizing electrolyte.

Metallic nanoclusters on TiO$_2$ are well known to have unusual catalytic activities but they are also optically active and their inherent plasmon modes provide a potent means of absorbing radiation. Although the size distribution of the clusters on rutile can control the resonant absorption energy somewhat, we will show that placing them in a dielectric matrix causes a broadening and a red-shift allowing their photoresponse to be tailored to the solar spectrum. A natural dielectric to consider is to encapsulate these metal clusters supported on TiO$_2$ with an overlayer of TiO$_2$. Buried metallic nanoclusters (~5-50nm) within nanometers of the TiO$_2$ surface are a highly promising approach. Noble-metal clusters (Cu, Ag, Au) are known to be stable on TiO$_2$, and we show that they can be encapsulated intact within TiO$_2$.

The resulting structure shown schematically in Fig. 1 – nanoclusters beneath a thin layer of rutile – provides a valuable system to test the enhanced efficiency of photocatalytic reactions. When nanoclusters are located within the titania dielectric, their absorption bands shift and broaden due to the dielectric response of the matrix, matching a wide range of the solar spectrum, and this is key to enhancing efficiency. As efficient photoabsorbers in the near surface region, they can generate photoexcited e$^-$h$^+$ pairs near the active surface sites and more efficiently deliver charge to the reaction. This provides a competitive advantage over bulk doped titania where e$^-$h$^+$ pair production within the bulk can be quenched through recombination before the carriers can reach the surface.

Fig. 1. Structure studied in this work: Ag nanoclusters grown on a TiO$_2$(110) substrate buried beneath a nm-thick coating of titania.
Unprotected, however, these nanoclusters would quickly degrade in an electrochemical environment. By coating with a nanometer thin layer of TiO$_2$, which is stable in an electrolyte, we can protect these clusters from oxidizing radicals and produce a functionalized titania surface that incorporates these nanoscale “antennas” to absorb solar radiation. The excited carriers produced by the strong fields near these clusters are generated in close proximity to the sites for water cleavage, enhancing the efficiency of the photoelectrochemical cell.

H. Freund recently reviewed the structure and optical properties of clusters adsorbed on insulating surfaces. It is well-known that the optical properties of metal clusters, such as those in stained glass, arise from plasmon excitations, giving rise to characteristic colors. Although plasmon energies of many bulk metals are not necessarily well-defined due to interband transitions that quickly damp them, they are well defined in nanoclusters. In nanoclusters, the classical Mie resonance gives way to quantized behavior due to quantum confinement within the cluster.\(^2\)

In considering clusters on surfaces, Freund has shown that Ag on Al$_2$O$_3$, excited with tunneling electrons from an STM show light emission at the bulk plasmon energy of 3.76 eV with some cluster size dependence, that can shift the resonance to \(~3.5\) eV in clusters 3-6 nm in size.\(^5\) Au clusters, also supported on Al$_2$O$_3$ show a similar sharp photon emission spectrum due to plasmons at \(~2.5\) eV while Au on TiO$_2$ emit at 2.25 eV.\(^7\) The relatively small dependence of this on cluster size, however, has motivated our investigation to study the potential of tuning the resonance by embedding within the dielectric, semiconducting matrix of defective titania.

As a byproduct of encapsulation, we anticipate that defect densities will be strongly enhanced nearby the clusters, and we investigate the impact of this on potential band-bending and charge separation. The nature of the defect sites near these nanoclusters are key to band-bending and efficient charge transfer, and they play a significant role in establishing the band-matching conditions required to match the electrolyte couple.\(^6,\,9\) We control and study the nature of these defects by varying the growth techniques applied as well as the associated kinetics. The first approach involves physical deposition using vacuum-based techniques for film growth (MBE, magnetron sputter-deposition, PLD) and the second is electrochemical. Both methods have proven to be able to produce co-deposited metallic and oxide components and we are working to refine methods for the current application. A better fundamental understanding of physical, chemical, and catalytic properties of the buried nanoclusters will be elucidated using surface and materials-analysis, synchrotron-based spectroscopies, and electrochemical techniques.

In this report we focus on the noble-metal Ag, which does not oxidize and readily form clusters on TiO$_2$.\(^10\) In this model study, we will use single-crystal TiO$_2$(110) as the substrate for arrays of Ag nanoclusters.\(^11\) A thin rutile layer will be grown on top via evaporation of Ti in an oxygen ambient and annealed under conditions that leave the noble-metal clusters intact. This allows us to separate the direct catalytic activity of the noble metal cluster from the effects due to the photoexcited carriers that are generated near the surface. The overcoating thickness, degree of epitaxy, and defect sites within it will be active areas of our investigation as we progress from the limit of nearly bare nanoclusters to thicker rutile coatings.

### 2. EXPERIMENTAL

Ag nanoclusters were grown on TiO$_2$(110) in a uhv vacuum chamber with a base pressure of \(1\times10^{-10}\) Torr. The TiO$_2$(110) crystal was cleaned by successive cycles of sputtering at \(5\times10^{-5}\) Torr with 1.5 keV Ne followed by annealing to 600°C. This treatment resulted in a surface with O-vacancies and regions of substoichiometric TiO$_2$. O$_2$-exposure is effective for oxidizing the surface O-vacancies but subsurface Ti-interstitials were not removed by room-temperature O$_2$ exposure.\(^12\)

Ag was deposited at \(~1\times10^{-9}\) Torr on a room-temperature TiO$_2$(110) surface using a simple evaporator consisting of a W filament wrapped with Ag wire. The Ag evaporator was maintained at 500°C when not evaporating to maintain cleanliness and minimize outgassing. Ti was deposited from an e-beam heated rod evaporator with an integral flux monitor.

Scanning-tunneling microscopy (STM) was performed at room temperature using an Aarhus-type STM using W tips.\(^13\) High-resolution electron energy loss (EELS) was performed in an electron spectrometer manufactured by LK Technology.\(^14\) Primary electron beam energies varied from \(~6-30\) eV and spectra were taken with energy resolution of 15-30 meV as determined from the width of the primary elastically-scattered peak.

We will use several surface characterization tools in these studies. We will investigate the morphology of the nanoclusters using scanning-tunneling microscopy (STM) and verify that the clusters retain their identity following
encapsulation using conductive-probe atomic force microscopy (AFM). High-resolution electron energy loss spectroscopy (EELS) has been used to characterize vibrational excitations and at lower resolutions, can be used to extract electronic excitations. Electronic structures and reactions have been characterised using synchrotron-based photoelectron spectroscopy and synchrotron-based infrared spectroscopy to better understand reaction pathways.

3. RESULTS

Figure 2 shows STM images from TiO$_2$(110). These images were obtained in constant-current mode from surfaces that have been prepared as indicated above. In Fig. 2(a) we show a 50×50 nm scan showing terraces of TiO$_2$ with a variety of defects. As indicated near the center of 2(a) with a circle, the terraces are decorated with a number chains of a TiO$_x$ suboxide that terminates in an oxide cluster. Note that these surfaces are clean as determined by Auger spectroscopy, containing only Ti and O so that the chains and clusters are titania.

Fig 1(b) shows a 7×7 nm scan giving much better detail and atomically resolving several types of defects. The bright rows in this image are 5-fold coordinated Ti cations and the dark rows are the bridging-O rows on top of 6-fold coordinated Ti. The chain of TiO$_x$ suboxide extending from the upper terrace ends in a cluster and a recent combination of STM and density-functional theoretical calculations indicate that its nominal composition is TiO$_2$ and while the coordination departs from that of rutile, it is related.

Fig 1(b) also shows two other recognizable defects indicated by the arrows. The black arrow shows a bright spot on the dark row, identified as a bridging-O vacancy. This leaves two of the underlying Ti under-coordinated and the charge localized in this area gives a larger tunneling current. Several other of these point defects are visible. The white arrow shows a dark region in the bright row and this is identified as an adsorbed hydroxyl (OH$^-$) species. Ultimately our interest is to understand the role that these and other defects play in the interaction of H$_2$O with the surface.

In Fig. 1(c) we present a 100×100 nm scan following deposition of ~0.3 monolayer (ML) of Ag in uhv at room temperature. We note that the Ag spontaneously forms clusters ~5nm across and 2nm high, minimizing its surface free energy. The nanoclusters appear to preferentially decorate step edges and kink sites. Additional deposition of Ag giving ~3 ML equivalent coverage results in the array of nanoclusters shown in Fig. 1(d). Close inspection of the images between the nanoclusters show that the characteristic rows in TiO$_2$(110), such as those in 1(b), remain unperturbed by the addition of the Ag clusters.
subsequently oxidizing the Ti. Fig. 4 presents high-resolution electron energy loss (EELS) spectra from clean TiO$_2$(110) and from a TiO$_2$(110) surface that has 3 ML equivalent of Ag, producing adsorbed nanoclusters. The energy loss range of 0-350 meV and probes the Fuchs-Kliewer phonon modes of the oxide lattice.\textsuperscript{14} The primary energy is 30 eV and a resolution of $\pm$30 meV is obtained, and the intensities are scaled to give equal peak heights to facilitate comparison of shapes. The key observation of this data set is that although there is an overall reduction in intensity with Ag clusters, as seen by the reduced signal to noise, the shape of the phonon losses remain unchanged by the addition of the clusters. This is another means that suggests that the bonding to the surface is weak and the perturbation of the underlying TiO$_2$(110) is minimal. Note that the reduction in signal to noise is due to the reduced amount of TiO$_2$(110) surface area exposed after the adsorption of Ag and increased scattering from the clusters, reducing overall intensity.

When $\sim$3ML Ag is evaporated onto the TiO$_2$(110) surface, the EELS spectra change dramatically as shown in Fig. 4(b). The overall modulation of loss intensity with a minimum near $\sim$3 eV is still present but there is a new loss peak that is clearly evident at $\sim$3.8 eV. Concurrent with the growth of this feature, there is a dramatic loss of intensity in the region below 2 eV, indicating that the defect state losses are quenched by the addition of Ag nanoclusters to the surface. This is most easily explained if the defect losses are primarily due to surface O point vacancy defects. In this case Ag clusters interact with the defects, pulling the excess charge to the cluster and quenching the losses. We have photoluminescence evidence, not shown here, that this is indeed the case as the electronic states of the first ML of Ag occur at a lower binding energy than they do for successive layers.

The 3.8 eV loss is identified as a plasmon excitation of the nanocluster, very similar to the Mie resonance observed for free Ag clusters and the surface plasmon of single-crystal Ag. This is also close to the surface plasmon energy of Ag that occurs at 3.7 eV at the zone center, $\Gamma$, on Ag(111).\textsuperscript{17}

Since we are interested in investigating the behavior of these clusters when encapsulated in a layer of TiO$_x$ (where $x$~2), we have grown TiO$_x$/Ag clusters/TiO$_2$(110) by depositing elemental Ti from an e-beam heated evaporator and subsequently oxidizing the Ti. Fig. 4(c) shows the EELS data acquired after evaporating $\sim$5ML Ti on the surface of 4(b). The Ag plasmon intensity is clearly attenuated.
Auger electron data in Fig. 5 shows that there is some alloying of the Ti and Ag. Fig. 5(a) shows the data for ~3 ML Ag on the surface giving isolated nanoclusters, and a Ti:O:Ag ratio of 1:1.9:1.87, normalizing to the Ti peak at 387 eV. Following a dose of ~3.5 ML Ti, Fig. 5(b), the ratios change to 1:0.83:1.62. This shows that the O in the substrate is attenuated by 56% while the Ag is only attenuated by 13%. If the Ti were to evenly coat the clusters and the substrate, the O and Ag should be attenuated by the same percentage. Since this is not the case, either the Ti is deposited only between clusters, which we believe unlikely, or Ti and Ag are alloying, keeping a larger amount of Ag at the surface than would be expected without alloying. The two are known to alloy in the bulk but at the surface we expect that the much higher heat of formation of Ti oxides compared to Ag oxides will allow us to preferentially oxidize the Ti. This will be more likely if we start with a thin Ti film, and oxidize to form a thin TiO\textsubscript{x} layer that passivates the surface of the Ag clusters, and allow successive depositions of Ti and oxidation to form thicker TiO\textsubscript{2} films.

In Fig. 4(d) the result of oxidizing the 5 ML Ti with a dose of 50L O\textsubscript{2} is shown. Several important observations can be made from this spectrum. First the broad interband absorption characteristic of TiO\textsubscript{2} is seen to return for energy losses above 4 eV, as seen in Fig 4(a). This suggests that additional oxide is formed on the surface, and presumably on the surface of the clusters. Second, the 3.8 eV plasmon also returns, suggesting that some of the Ag clusters are providing excitations unchanged from the bare clusters in Fig. 4(b). This enhancement could arise from the de-alloying of Ti/Ag as the TiO\textsubscript{x} oxide skin forms. Perhaps the most important observation of this spectrum is the enhanced intensity of losses producing a distinct, broad peak below 2 eV. We propose that these losses are due to plasmon excitations of Ag clusters that are surrounded by a dielectric – the TiO\textsubscript{x} matrix – but is also likely that some of these losses are due to excitations of defects within the TiO\textsubscript{x}.

Figure 4(e) shows the spectrum that results following additional Ti dosing and oxidation. The 3.8 eV plasmon is essentially removed from the spectrum and the losses between 1 and 2.5 eV are substantially enhanced. The result of this surface treatment is an enhancement in optical excitations within the region of the solar spectrum that provides the most intense radiation, accomplishing the first goal of this investigation.

Figure 6 shows an atomic force microscopy image (AFM) acquired in air of a surface with ~5 ML Ag nanoclusters that
Fig. 8. Optical data taken in transmission from (a) TiO$_2$(110) that was unreduced and transparent/yellow with the 3 eV bandgap clearly evident. (b) From 3 ML Ag on TiO$_2$(110) (c) TiO$_2$/Ag/TiO$_2$(110). In (d) we present a difference spectrum highlighting the new absorption (decrease in transmission) that occurs between 1 and 2 eV following TiO$_2$ overcoating. Curves are offset for clarity.

transmission of light for 0–3 eV. When Ag clusters are grown on the surface, Fig. 8(b) with a 3 ML Ag dose, the transmission is reduced and the region from 0–3 eV shows a linear dependence on the transmission. Ag metal films have a nearly flat, 90–100% reflectivity in this region but this is not what we observe for these clusters in air. In Fig. 8(c) we show the transmission following overcoating with TiO$_2$. The roughly flat transmission between 2 and 3 eV returns, similar to the transmission of TiO$_2$(110) but is a clear dip in the transmission, consistent with enhanced absorption in the region below 2 eV. This enhanced absorption is also consistent with the observations provided by the EELS data in Fig. 4.

Since transmission measurements are sensitive to mostly bulk absorption properties, we have also made measurements in reflection for the nanoclusters encapsulated in TiO$_2$. Figure 9 presents the data from these same surfaces, showing the effect on the reflectivity. Fig 9(a) shows the reflectance of TiO$_2$(110) which exhibits a rise beginning 2.5–3 eV, a distinct maximum at 4 eV and a decrease in reflectivity at higher photon energies. When Ag nanoclusters are deposited on the surface, the reflectivity changes dramatically as shown in Fig. 9(b). Two distinct peaks are found at 3.7 eV and a second at 1.5 eV. There is a very strong dip in reflectivity at 4 eV, where the bare TiO$_2$ surface exhibited a maximum, and again rises at ~4.8 eV. Following encapsulation in TiO$_2$, the peak at 3.7 eV shifts to ~3.6 eV while the 1.5 eV peak is also consistent with enhanced absorption in the region below 2 eV.

In Fig. 7 we present a conductive-probe image of the same surface. This measurement uses the AFM to acquire a constant-height measurement while at the same time measuring the conductivity of the surface through the tunneling current to the tip. From this image it is clearly evident that a larger negative conductivity is observed in the regions of the clusters and a significantly reduced current in the regions between clusters. This is consistent with the notion that the Ag clusters retain their metallic nature following coating. Furthermore, we expect that the oxide coating at the cluster surface is highly defective, resulting in states within the bandgap and enhancing the conductivity of the oxide. At regions between the clusters, the oxide is more likely to approach stoichiometry and therefore is more insulating.

Figure 8 shows optical data taken in transmission from TiO$_2$(110), Ag nanoclusters on TiO$_2$(110), and TiO$_2$/Ag/TiO$_2$(110). Although we expect that transmission measurements will be insensitive to the very thin surface layers that we produce in this treatment, the films are visible by eye on the single-crystal substrate. Fig. 8(a) shows the 3 eV bandgap of bulk TiO$_2$(110) with strong absorption of all light at energies exceeding 3 eV. At energies below 3 eV, optical interband excitations are not possible so that there is a significant difference (c)–(a)
eV peak increases in intensity substantially and shifts slightly to ~1.6 eV. These data show that encapsulating the Ag nanoclusters within the TiO$_2$ matrix has changed the optical response within the 1-3 eV energy range relevant to solar-stimulated photochemistry. As mentioned previously, the reason for this change can be ascribed to several potential mechanisms and it is likely that more than one are in play. First, we expect that the response of the Ag nanoclusters to incident light will change when they are encapsulated in a dielectric medium such as titania. Secondly, we expect that the oxide will have additional defects, particularly in the region surrounding the Ag nanoclusters and these defects will give rise to states within the 3 eV bandgap of TiO$_2$, and give rise to additional optical excitation channels. Through the enhanced absorption, we have the potential for generating hot e$^-$–h$^+$ pairs to stimulate photochemistry with the added benefit that they are being created within nanometers of the surface.

In order for this material to be effective, band-bending effects between the defective titania and the TiO$_2$ substrate will need to allow us to separate charges prior to recombination. It may be possible to tailor these properties through kinetic control of titania growth and subsequent defect densities and characters, or through layering different oxide films to induce band bending at the surface.

When light is incident on this buried cluster/semiconductor matrix, some fraction will be reflected, some absorbed, and some transmitted. Neither the transmitted nor the bulk-absorbed light will be useful to stimulate surface chemistry. The reflected light is due to dielectric response of the electron gas within the nanoclusters, and at a particular frequency dependent on the charge density, a collective oscillation known as a plasmon can be excited. In general the reflectivity can be related to the electronic structure of the material. In discussing the origin of the features in the optical data, we first note that bulk Ag exhibits an interband absorption spectrum with transitions beginning at about 4 eV. This is associated with a very strong dip in the reflectivity at about the same energy. The broadening of this peak, as seen in Fig. 8(c) has been anticipated previously and is thought to depend on the details of the chemical environment at the interface surrounding the cluster, and can depend on the polarization of the light.

The new peak that appears between 1-2 eV is similar to the shifted plasmon that occurs for Ag nanoclusters embedded within a Si matrix. The details of the position of this peak, as well as its width, will depend on the local dielectric properties of the surrounding titania. Voids and defects will tend to decrease the dielectric response, giving a plasmon oscillation that is closer to the bare-surface value while improved encapsulation will tend to result in a larger red-shift into the solar spectrum. Since the surrounding oxide matrix is perturbed by the presence of the cluster, it will intrinsically be defective. The specifics of the densities of these defects will determine the details of the optical response.

Furthermore, these excitations have the potential for stimulating the production of e$^-$–h$^+$ pairs. The plasmon is essentially a collective electronic excitation of states near $E_F$, and this oscillation of charge can produce large local electric fields, particularly near regions of the cluster with a sharp radius of curvature. These electric fields, in turn, can produce excitations of the substrate or within a surrounding matrix, and generate electron-hole pairs. Since the surrounding oxide is highly defective in the region of the clusters, the additional bandgap states associated with these defects are spatially localized in the region of these large electric fields.

Clearly the separation of these pairs within the semiconducting substrate will determine whether this mechanism can effectively drive surface chemistry. In principle, it may be possible to further tailor the optical absorption through thermal treatments during oxidation that result in specific interface configurations. This will be particularly important in determining the nature of the nearby semiconductor and whether the defects act more as sites for stimulating photochemistry or as traps for recombination and quenching.

4. CONCLUSIONS

We have undertaken a study to enhance photoelectrolysis of water using TiO$_2$ modified with buried metallic nanoclusters, a system that has the potential to address some of the roadblocks to solar photolysis. We have shown that by embedding Ag within a dielectric medium, we produce new excitations within the photon energy range relevant to solar photochemistry. Noble-metal clusters (Cu, Ag, Au) are known to be stable on TiO$_2$ and when nanoclusters are located within a dielectric, like titania, their absorption bands shift and broaden, matching a wide range of the solar spectrum. The morphology of the clusters has been studied with STM and their encapsulation has been observed with AFM and suggests that the clusters retain their identity following overgrowth of titania. The optical properties have been studied with EELS as well as optical reflection and transmission measurements and all three methods observe new excitations within the 1-3 eV range that is relevant for solar photochemistry.
Unprotected, these nanoclusters would quickly degrade in an electrochemical environment. By coating with a thin layer of TiO$_2$, we expect that it will protect these clusters from oxidizing radicals and produce a functionalized titania surface that incorporates these nanoscale “antennas” to absorb solar radiation. The excited carriers produced by the strong fields near these clusters are generated in close proximity to the sites for water cleavage, enhancing the efficiency of the photovoltaic cell. We are currently investigating the application of these functionalized surfaces with electrochemical studies to assess their performance under illumination.

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6. REFERENCES
