

Introduction

- TiO₂ (Rutile) has promise as a photo-catalyst for photolysis, the separation of hydrogen gas from water using sunlight.
- By carefully evaporating silver onto the surface of TiO₂ we will form metallic nanoclusters that will act as nano-antennas enhancing the ability of TiO₂ to absorb the radiation of incident sunlight.
- This enhancement will occur due to the generation of electron hole pairs in the near surface region of TiO₂ that will then contribute to the photo-catalytic reaction.
- Metallic nanoclusters on TiO₂ 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 absorption energy somewhat, placing them in a dielectric matrix causes a broadening and a red-shift allowing their photo response to be tailored to the solar spectrum.
- A natural dielectric to consider is to encapsulate these noble metal clusters supported on TiO₂ with an overlayer of TiO₂.

Experimental Techniques

We use several surface characterization tools in these studies to investigate the surfaces. The morphology of the nanoclusters is given using scanning-tunneling microscopy. The reaction pathways (plasmon interactions) are found using electron energy loss spectroscopy. To fully characterize their electronic structures and reactions we use angle-resolved synchrotron-based photoemission spectroscopy.

Objective and Results

Our goal is to grow silver nanoclusters and arrays of clusters, study their optical properties, embed them in a protective TiO₂ matrix, and determine the best path to improved photo catalytic activity.

We have established techniques to produce TiO₂ surfaces with controlled densities of structures noble-metal nanoclusters and nanowires.

The surfaces that we use are bulk single crystal TiO₂ (110) oriented, vacuum annealed and sputter polished in Ultra High Vacuum.

Nanoclusters of Ag have been grown on these surfaces to investigate the effect of step edges and crystal defects (such as Oxygen vacancies) on clusters.

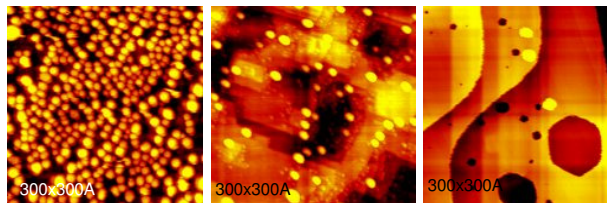
Currently we are developing techniques to overcoat with TiO₂ using e-beam evaporation of Ti in an oxygen ambient.

We evaluate the optical properties by measuring photocurrent induced in a biased-diode configuration. This is done as a function of wavelength using an IR/VIS/UV spectrometer (Hitachi U4000) at CAMD.

High Resolution Electron Energy Loss Spectroscopy is now being implemented to Determine plasmon excitation energies of all vibrational modes.

Once we grow the overlayer we will Investigate chemisorption effects This will be done as a function of overlayer thickness from 0 ML (bare clusters) to thick TiO₂ films.

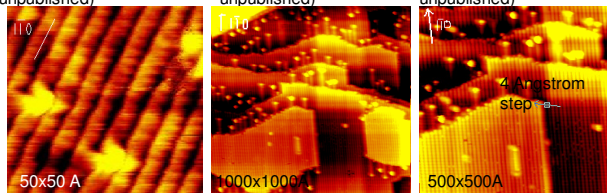
The final process will require a test cell using 1.5 AM sunlight and the dissociation of water as the gauge to maximize efficiency.



STM image showing 5 nm silver nanoclusters grown on TiO₂. A lower cluster density will be used for embedding (Kurtz & Sprunger, Wang, unpublished)

AG/TiO₂(110) STM image showing nucleation of silver nanoclusters on terrace step edges (Kurtz & Sprunger, Wang, unpublished)

AG/TiO₂(110) STM image of silver(111) terraces, notice the hexagonal shapes. (Kurtz & Sprunger, Wang, unpublished)



AG/TiO₂(110) STM image showing atomic Oxygen vacancies (Kurtz & Sprunger, Wang, unpublished)

TiO₂(110) 2 STM images showing bridging atomic Oxygen Vacancies and Stoichiometric Ti₂O₃ (Kurtz & Sprunger, Wang, unpublished)

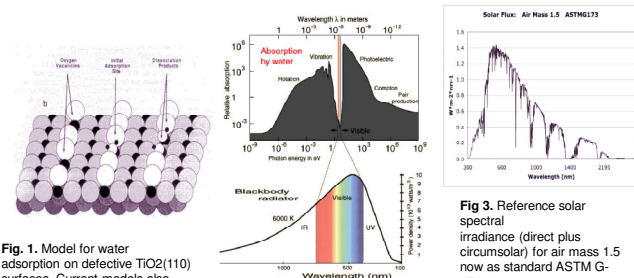


Fig. 1. Model for water adsorption on defective TiO₂(110) surfaces. Current models also conclude that the OH is located in the bridging rows. Kurtz, Ref 30.

Fig. 2. Water Window (Resonant frequency spectrum of water) http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf

Fig 3. Reference solar spectral irradiance (direct plus circumsolar) for air mass 1.5 now as standard ASTM G-173-03. The 300-1200 nm range is key for solar photochemistry, the target of this proposal. From NREL Renewable Ref. Data Center <http://redc.nrel.gov>.

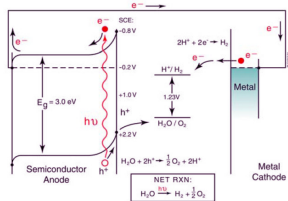
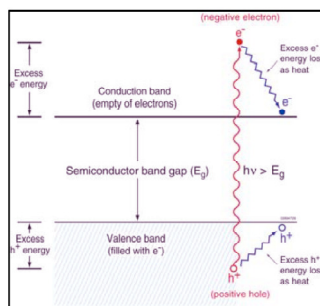


Figure 34 Photoelectrolysis cell
Basic Research Needs for the Hydrogen Economy
http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf



Basic Research Needs for Solar Energy Utilization
http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf

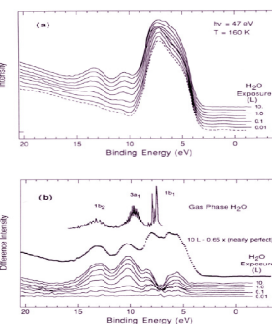
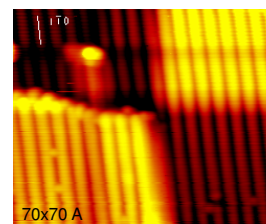


Fig. 4. Water adsorption on TiO₂(110) at 160K from Kurtz et al Ref 30.



TiO₂(110) STM image showing bridging atomic Oxygen Ligands and Stoichiometric Ti₂O₃ (Kurtz & Sprunger, Wang, unpublished)



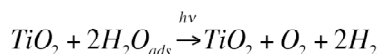
Picture of an STM chamber at LSU where Ag and Ti deposition do occur.



Picture of 2nd STM chamber at LSU where Ag and Ti deposition will occur.

Discussion

The resulting structure – nanoclusters beneath a thin layer of rutile – Will produce photocurrent at high efficiency when exposed to water with a byproduct of hydrogen gas which can be stored for later use in a fuel cell. Also, the structure provides a valuable system that can enhance the efficiency of other photo catalytic reactions. First, as efficient photo absorbers, they can generate photo excited e⁻ h⁺ pairs near the active surface sites and more efficiently deliver charge to a reaction. Second, their titanium encapsulation naturally protects them from highly oxidizing character of the radicals produced in many important reactions and naturally provides for longevity to the catalytic system.



Acknowledgements

We acknowledge the assistance of the LSU-CAMD synchrotron staff and the support of the LA-Board of Regents and the National Science Foundation