

Final Report for the grant FA2386-08-1-4064
(AOARD grant 084064)

“Increasing the efficiency of gold-ceria catalyst for the massive production of hydrogen”

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Abstract:

We have studied the adsorption of molecular water at the (111) surface of cerium dioxide (CeO_2) single crystals by means of atomic force microscopy (AFM) working with atomic resolution. Our AFM data reveal that single molecular water does not dissociate upon adsorption at the bare $\text{CeO}_2(111)$ surface, but it remains stably adsorbed at the surface over the temperature range in which we have performed this study (300K to 10K). We have been able to manipulate individual water molecules with the tip of the AFM and positioning them at will on the $\text{CeO}_2(111)$ surface. By using this technique, we have studied the interaction between individual water molecules and surface oxygen vacancies, finding a considerable energy barrier for individual water molecules to enter into oxygen vacancies. We have also deposited atomic gold on the $\text{CeO}_2(111)$ surface and studied this system with AFM. Deposition of atomic Au over the $\text{CeO}_2(111)$ surface at a 77K temperature yielded the formation of small clusters of Au atoms sparsely distributed on the surface and nucleated over intrinsic defect of the surface as well as at kink positions at the step edges. By using atom manipulation techniques, we produced and investigated the selective dissociation of water molecules over Au clusters deposited over the $\text{CeO}_2(111)$ surface. The elucidation of the atomistic mechanism for the selective dissociation of molecular water is pending of corroboration of our experimental observations by first principle simulations that are currently carrying out our collaborators.

Introduction:

Ceria (cerium dioxide, CeO_2) is a material of tremendous potential in several industrial applications with important repercussions in environmental and energy related issues. One of these applications is the massive production of hydrogen through the enhancement of the water-gas shift (WGS) reaction [$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$]. It has been demonstrated that the performance of this reaction is considerably enhanced upon the presence of a catalyst combining gold and ceria, yet the mechanisms for the reduction of water by this catalytic system are still unknown.

In this project, we wanted to optimize the efficiency of the WGS reaction by characterizing the performance of the gold-ceria catalytic system at atomic scale using atomic force microscopy. To accomplish this task, we focused on the production and clarification of the dissociation of individual water molecules –the most relevant process in the WGS reaction– on the two most efficient systems currently known for enhancing this chemical reaction: gold nanoclusters on ceria and ceria nanoclusters on gold.

To clarify the atomistic processes involved in the water dissociation and the role that gold plays in the process, we applied the atomic manipulation and single atom chemical identification tools we have developed for atomic force microscopy working with true atomic resolution.

Experiment:

The experiments were performed in an atomic force microscope (AFM) working at cryogenic temperatures (either 77K cooling with liquid nitrogen or 10 K cooling with liquid helium) and in ultra high vacuum environment (UHV). The AFM is based on an optical-fiber interferometric detection scheme, and it is specially designed for atomic resolution experiments. We have also used the X-ray photoelectron spectroscopy (XPS) common facilities of NIMS for the characterization of the atomic

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14. ABSTRACT This is the report on the adsorption of molecular water at the (111) surface of cerium dioxide (CeO2) single crystals by means of atomic force microscopy (AFM) working with atomic resolution.					
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impurities at the surface of the CeO₂(111) single crystals in which we were carrying out our experiments.

Results and Discussion:

In an initial stage, we carried out a characterization of our ceria single crystals with (111) and (110) surface terminations by performing imaging and force spectroscopy experiments with the AFM in UHV and at 77K tip-surface temperature. We detected a possible contamination of the surface by fluorine. We performed an elemental composition analysis of our samples by using XPS experiments, and found that the sample holder we were using produced a contamination of fluorine during the annealing process that follows the Ar ion sputtering of the crystals during the sample preparation.

After solving the fluorine contamination problem, we started adsorbing molecular water on the CeO₂(111) surface at 77K and at 4K sample temperatures, respectively. Our AFM data reveal that single molecular water does not dissociate upon adsorption at the bare CeO₂(111) surface, but it remains stably adsorbed at the surface over the temperatures range in which we have performed the experiments (300K to 10K). In our AFM images, single molecular water appears as a triangular protrusion extending over three adjacent oxygen positions at the CeO₂(111) surface. We interpret this triangular protrusion as the water molecule anchored on a position corresponding to a Ce atom of the second surface layer and jumping over three equivalent adsorption sites much faster than our scanning speed. The superposition of the molecule adsorbed on these three equivalent sites yields to a triangular shape. Surprisingly, this triangular shape is preserved even at the lowest temperatures we can reach (10K); meaning that either the energy barrier for the diffusion of the water molecule over these three equivalent adsorption sites is very small or that the presence of the AFM tip perturbs the dynamics of the molecule at the surface during imaging.

We reproduced our previous experimental results on the manipulation of molecular water on the CeO₂(111) surface, being able to positioning a water molecule on the surface at will. This capability allowed us to study the interaction of a water molecule with intrinsic defects of the CeO₂(111) surface, and in particular, with single atomic oxygen vacancies that can be sporadically found at the surface. It has been theoretically predicted that a water molecule should immediately dissociate inside an oxygen vacancy of the CeO₂(111) surface. Our results show that molecular water stably adsorbs in the vicinity of oxygen vacancies. We tried to produce the dissociation of a water molecule by manipulating single molecules towards oxygen vacancies. Surprisingly, we have found a considerable energy barrier for the water molecule entering inside an oxygen vacancy that has frustrated all our attempts to produce and observe the dissociation of water molecules at oxygen vacancies. Due to this considerable energy barrier, the water molecule prefers to adsorb in a position corresponding to Ce atoms of the second surface layer near the vacancy instead of getting inside the vacancy.

After the characterization of the interaction of molecular water with intrinsic defects of the CeO₂(111) surface, we proceeded to study the adsorption of gold on ceria. In a first stage, the gold evaporator was precisely calibrated to obtain a deposition rate of one Au atom per 50 nm² per minute of exposure. We deposited Au atoms over the CeO₂(111) surface in situ at a temperature of 77K. We observed the formation of clusters of Au atoms sparsely distributed on the surface and nucleated at preferential positions —over intrinsic defect of the surface and at kink positions at the step edges. The formation of Au clusters at the CeO₂(111) surface at 77K indicates that the diffusion energy barriers of Au on this surface are very small. This result compelled us to use lower sample temperatures for the observation of individual Au atoms at the CeO₂(111) surface.

We proceeded to the deposition Au at very low coverage on the CeO₂(111) surface at a sample temperature of 10K, cooling the system with liquid helium, for the observation of individual Au atoms on the CeO₂(111) surface with the AFM. Preparation of the sample was successful, but we obtained a negative result concerning the observation of the Au atoms: the interaction with the AFM tip was too intrusive, and we were uncontrollably moving and picking up Au atoms with the AFM tip even at the lowest tip-surface interaction forces we are able to detect, yielding to unstable imaging and a poor quality images.

In an effort to improve our force detection capabilities, we invested considerable portion of time and budget of the second year of the project on increasing the resolution of the optical-fiber-based interferometer that we use for the detection of the deflection and dynamics of the cantilever. We succeeded in improving it, and we are now in the process of testing the new detection system for the observation of individual Au atoms adsorbed at the CeO₂(111) surface at 10K.

In parallel to the improvement of our optical interferometer, we conducted experiments on the manipulation of individual water molecules towards small Au clusters —of unknown number of atoms— formed by the deposition of Au on the CeO₂(111) surface at a temperature of 77K, aiming to produce and investigate the dissociation of water molecules. We succeeded in observing the selective dissociation of water molecules upon manipulation towards some clusters, but the process did not occur in the case of some other clusters. We are now in the process of elucidating the atomistic mechanisms behind our experimental observations by means of comparison with the results obtained from theoretical simulations performed by our collaborators in Europe, which are experts in first principles calculations. Unfortunately, the correct treatment of the charge localization at the *f* orbitals of the cerium atoms seems to be a very challenging issue, and it is taking a considerable amount of time for the simulations to reproduce our observations and to clarify the atomistic process involved in the dissociation of molecular water in the presence of Au clusters at the CeO₂(111) surface.

Due to several difficulties experienced during the development of the project and during the execution on the experiments on the CeO₂(111) surface (the extreme roughness of the surface of our crystals compels us to sometimes expend days looking for a flat enough surface area to perform the experiments), a serious delay has compromised the realization of the works initially planned for the CeO₂(110) surface and the CeO₂/Au(111) system in the time frame initially specified. These research activities are left for the future.

We suspect that the preferential dissociation of molecular water only for some clusters is closely related to the accumulation of charge in the Au cluster. In the near future, we are going to perform Kelvin probe force microscopy (KPFM) experiments on Au clusters deposited on the CeO₂(111) surface at 77K. These experiments will allow us to quantify the charge of the Au cluster by measuring variations of the local contact potential difference between tip and surface. We will try to correlate the accumulation of charge at the Au clusters with the selective dissociation of the water molecules. Furthermore, similar experiments to the ones reported here will be performed at ceria single crystals of different orientations, namely the (110) and the (100), currently available at the laboratory.

List of Publications:

Publications:

During the period in which the principal investigator was funded by the grant FA2386-08-1-4064, a total of three papers were published:

- 3) Sascha Sadewasser, Pavel Jelinek, Chung-Kai Fang, Oscar Custance, Yoshiaki Sugimoto, Masayuki Abe and Seizo Morita,
***Phys. Rev. Lett.* 103, 266103 (2009)**
“*New Insights on Atomic-Resolution Frequency-Modulation Kelvin-Probe Force-Microscopy Imaging of Semiconductors*”
- 2) Oscar Custance, Ruben Perez and Seizo Morita,
***Nature Nanotechnology* 4, 803-810 (2009)**
“*Atomic force microscopy as a tool for atom manipulation*”
- 1) Yoshiaki Sugimoto, Pablo Pou, Oscar Custance, Pavel Jelinek, Masayuki Abe, Ruben Perez and Seizo Morita,
***Science* 322, 413-417 (2008)**
“*Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy*”

Publication of the results obtained during this project is pending on the agreement between our experimental observations and the first-principles simulations that our collaborations are currently carrying out. Upon agreement of experiments and simulations, publication of the results

in high-profile journals is expected.

Presentations at conferences:

During the period in which the principal investigator was funded by the grant FA2386-08-1-4064, a total of seven talks were given at international meetings, six of them as an invited speaker.

- 7) First European Nanomanipulation Workshop, European Science Foundation; Cascais (Portugal), May 2010 (Invited talk)
- 6) MRS Fall Meeting 2009; Tutorial on Dynamic Scanning Probes: Imaging, Characterization and Manipulation; Materials Research Society; Boston (US), November 2009 (Invited talk)
- 5) Energy Dissipation in Nanocontacts and Molecular Bonds; Max Planck Institute for the Physics of Complex Systems; Dresden (Germany), September 2009 (Invited talk)
- 4) Nanostructures at Surfaces; Ascona (Switzerland), September 2009 (Invited talk)
- 3) APS March meeting 2009; American Physical Society; Pittsburgh (US), March 2009 (Invited talk)
- 2) The 11th International Conference on Non-contact Atomic Force Microscopy, NC-AFM 2008; Madrid (Spain), September 2008
- 1) "Seeing at the nanoscale VI" conference; Humboldt University Berlin; Berlin (Germany), July 2008 (Invited talk)

Awards:

During the period in which the principal investigator was funded by the grant FA2386-08-1-4064, the principal investigator received two awards:

- 1) The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology 2009. Prizes for Science and Technology. Research Category.
- 2) 2009 Foresight Institute Feynman Prize in Nanotechnology. Section: Experimental work. Foresight Institute, Palo Alto, California (USA).
Upon winning this award, the AOARD was proud to publically advertise financial support to this project. See a copy of the advertisement at the end of the document.

Patents:

During the period in which the principal investigator was funded by the grant FA2386-08-1-4064, no patents applications have been submitted.



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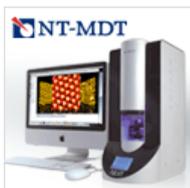
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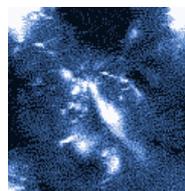
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[Air Force](#)-funded researcher, Dr. Oscar Custance from the National Institute for Materials Science in Japan has been chosen for the 2009 Feynman Prize for Experimental Work in Nanotechnology for his research in atomic-scale precision.

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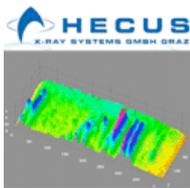


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The results of this research could someday lead to more effective catalysts for the production of hydrogen fuel.

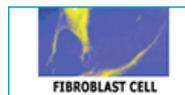
This year's prize for experimental work will be awarded in January 2010 near Palo Alto, California along with a prize for theory. Both have been awarded annually since 1993 by the Foresight Institute in honor of Nobel Laureate Richard Feynman.



The Feynman Prizes in Nanotechnology recognize researchers whose recent work has most advanced the field toward the achievement of Feynman's vision for nanotechnology: molecular manufacturing -- the construction of atomically-precise products through the use of molecular machine systems.



For the past two years, the Asian Office of Aerospace Research and Development (AOARD), an international detachment of the Air Force Office of Scientific Research, has been supporting Custance's research to develop catalysts that use an atomic-scale-precision technique to place active gold atoms at an exact location on or near the surface of a model system. For the purpose of this research, Custance is studying the system of gold on cerium dioxide, or ceria.



"Gold has become an exciting element to study for its catalytic properties," explains Dr. Thomas Erstfeld, AOARD program manager. "It was once thought of as relatively inert, but in the past couple of years, it has been discovered that nano-sized gold particles are excellent catalysts."

Custance will share the award with Professors Yoshiaki Sugimoto and Masayuki Abe of Osaka University in recognition of their pioneering experimental demonstrations of mechanosynthesis for vertical and lateral manipulation of single atoms on semiconductor surfaces.

Their work, published in Nature, Science and other prestigious scientific journals, has demonstrated a level of control over the ability to identify and position atoms on surfaces at room temperature, which opens up new possibilities for the manufacture of atomically precise structures.

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