Localized Surface Plasmon Assisted Oxygen Dissociation on Ag(111)

Casey Dudek, Blake Birmingham, and Zhenrong Zhang

***Abstract*— Thermal energy is used to pass the rate limiting step that oxygen's high activation barrier causes, but driving reactions using thermal energy can compromise efficiency or even dissociate other reactants. This study aims to observe another method used to achieve oxygen's activation barrier by coupling thermal energy with visible light to dissociate oxygen to atomic oxygen. Visible light incident on the substrate Ag(111) creates a plasmonic effect that aids in dissociating oxygen. Successful results were determined by the presence of oxygen adatoms present on the Ag(111) through a scanning tunneling microscope image after the prepared Ag(111) surface was dosed with O_2 molecules, heated by a filament, and shone with a laser. This confirms the viability of using the plasmonic effect to assist in oxygen dissociation on the level of a single isolated crystal, which will lead to a better understanding of a wider application of the plasmonic effect on catalytic oxidation reactions.**

***Index Terms*—activation barrier, plasmonic effect, scanning tunneling microscope**

I. Introduction

DISSOCIATION of gas requires high temperatures to excite the molecules into breaking their bonds. As such the prevalent method for dissociating gas molecules is to use a gas cracker. Oxygen is one particular gas that is dissociated using a gas cracker to create atomic oxygen. The rate limiting step in reactions is often set by oxygen, which needs a large amount of energy to dissociate its bonds. The current method to reach the activation barrier is to provide thermal energy, which is the driving principle behind gas crackers. The gas cracker normally reaches 1000° Celsius in order to create atomic oxygen [1]. This requirement for high temperatures limits the range and efficiency of reactions that can be carried out; high temperatures enable oxygen to reach its activation barrier but can dissociate or reduce the yield of other reactants [2], [3]. In a study on visible light enhanced catalytic oxidation reactions [2] it was first demonstrated that the temperatures for oxygen's rate limiting step could be reduced by the simultaneous use of thermal energy and low-intensity visible light. Low-intensity visible light was used to convert ethylene to ethylene oxide, oxidize CO to CO_2 and selectively oxidize NH_3 to N_2 on a silver catalyst through the use of the plasmonic effect.

This study examines the potential of using the plasmonic effect as an alternative method to a gas cracker for oxygen dissociation. Through the interaction of plasmons and oxygen this study aims to determine the potential of using the plasmonic effect to enable reactions that have been previously inaccessible.

The plasmonic effect happens when surface electrons are excited by a light source, such as a laser. The laser excites the electron cloud of a nanoparticle. The restoring force on the electron cloud due to the coulomb potential creates an oscillation, which is continuously driven by the incident laser. The nanoparticles' electron cloud begins a harmonic oscillation that is resonant with the electric field. This generates an enhancement of the incident electric field—a strong localized electric field of higher intensity than the incident driving electric field [4], [5]. The high energy electrons in the enhanced electric field are known as hot electrons. Plasmons are most easily achieved with materials that have many free surface electrons; these materials are plasmonically active.

The plasmonic effect assists in oxygen dissociation when oxygen is introduced to the surface of the plasmonically active sample [2]. The hot electrons that are generated from the plasmonic effect on the metal sample interfere with the oxygen and cause it to dissociate to atomic oxygen. The study on visible light enhanced catalytic oxidation reactions [2] showed that the excited silver surface plasmons allowed for a transfer of an electron to O_2 to create O_2^-. From there the combination of electron and thermal excitation caused the O_2 to dissociate to atomic oxygen. The study [2] confirmed the theory behind plasmon assisted dissociation through a wider observation of the effects of the light on the reaction. Their results found that the rate of the ethylene epoxidation increased nearly four times when laser illumination was provided.

This study is to investigate plasmon-assisted O_2 dissociation using single crystal Ag(111). It is structured to study the role of an isolated well-defined crystal structure to gain some insight into the mechanism of the plasmon assisted oxygen dissociation. The plasmonic effect acts to excite surface

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Casey Dudek is with Center for Astrophysics, Space Physics, and Engineering Research (CASPER), Baylor University, Waco, TX 76798 USA. She is an undergraduate student at Duke University, (e-mail: cmd47@duke.edu)

Blake Birmingham is with Baylor University, Waco, TX 76798 USA as a graduate student. (e-mail: blacke_birmingham@baylor.edu).

Z. Zhang is Baylor University, Waco, TX 76798 USA (e-mail: Zhenrong_Zhang@baylor.edu).

electrons to raise the energy floor, thus reducing the amount of thermal energy needed to achieve oxygen dissociation.

II. Materials and Methods

A. Experiment Setup

The chamber used for the study has three sections: the experiment stage, preparation area, and the transfer chamber. The transfer chamber is used to introduce new tips for the STM into the chamber. The sample is moved back and forth between the preparation chamber and the experiment stage as needed. The sample used to create surface plasmon resonances and act as a substrate for the atomic oxygen to bond with is Ag(111).

1) Preparation Chamber: The sample is prepared through a sputtering and annealing cleaning cycle. During sputtering the sample surface is bombarded by high velocity ionized argon, and the top molecular layers of the sample are stripped away. Sputtering clears away any molecules that may have adsorbed on the silver surface. Argon ions are used for sputtering because they are effective in knocking off surface atoms while maintaining a low reactivity with the Ag(111). However, argon ions do become embedded in the surface, but the annealing process desorbs the argon ions.

To repair the damage to the sample surface that is caused by sputtering and desorb the argon ions, the sample is annealed by a tungsten filament that heats the surface of the sample to about 600 C. The heat allows the damaged surface to smooth back into the Ag(111) lattice structure that was preserved under that layers that were damaged by sputtering.

2) Experiment Chamber: The equipment at the stage are the oxygen doser, laser, tungsten heating filament, and scanning tunneling microscope (STM). These four elements are arranged to interact with the sample without inhibiting each other. The oxygen doser, laser, and STM scanhead are positioned to point to that same place on the sample.

a) Scanning Tunneling Microscopy: A scanning tunneling microscope (STM) is used to take images that can be resolved at an atomic level. Its scanning tip approaches the sample until they are within a fraction of a nanometer of each other. A bias voltage is applied between the tip and sample, and overlapping wavefunctions between the tip and sample surface lead to electron tunneling from the tip to the sample. The tunneling electrons are observed as current and converted to a voltage, which is compared to a reference value. Based on the relationship between the voltage from the tunneling current and the reference value the tip retracts or descends to maintain an equilibrium position away from the sample. The image provided by STM is the electronic structure of the surface with the lighter areas protruding more than the darker areas [6].

B. Final Stage

The sample is prepared by cycles of sputtering and annealing. The two step cleaning process of sputtering and annealing is balanced to achieve a rough enough surface for the oxygen to react with but smooth enough surface to use the STM with high enough resolution to confirm existence of atomic oxygen. The general nanoparticle size that meets these conditions ranges from ten to two hundred nanometers. The relative times for sputtering and annealing were set to be fifteen minutes and twenty minutes, respectively. This was qualitatively determined through use of the STM.

After a minimum of two cleaning cycles the sample is sputtered one more time for a longer period of thirty minutes, and then it is moved to the experiment stage. STM images are collected to verify the tip state of the STM and record the surface state of the sample.

If the sample is clean and the STM can produce images with atomic resolution, then the sample is heated to 450 K, shone with a 532nm laser, and dosed with oxygen for thirty minutes. After this the sample is scanned again with STM.

III. Results

Figure 1a) is an STM image of the sample before cleaning; after sputtering it was left in the chamber for three days.

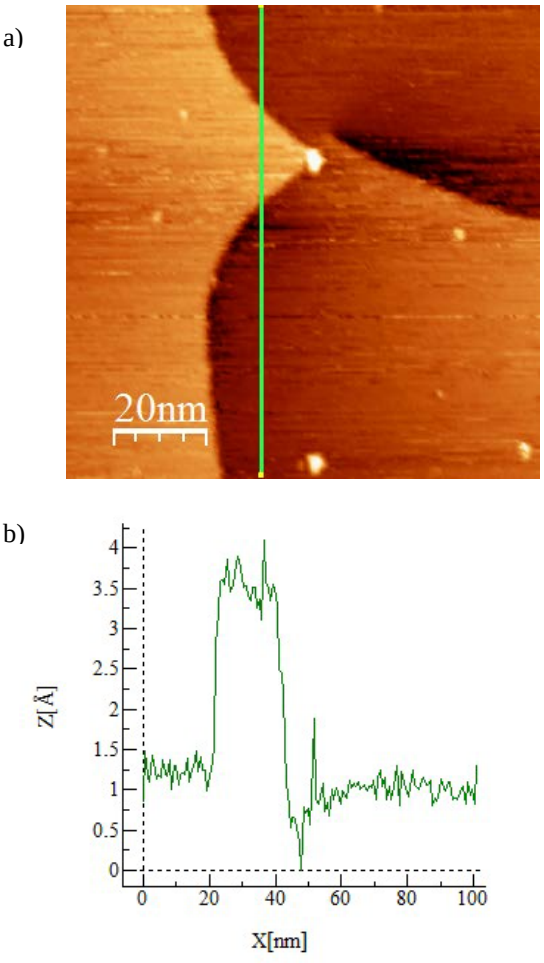
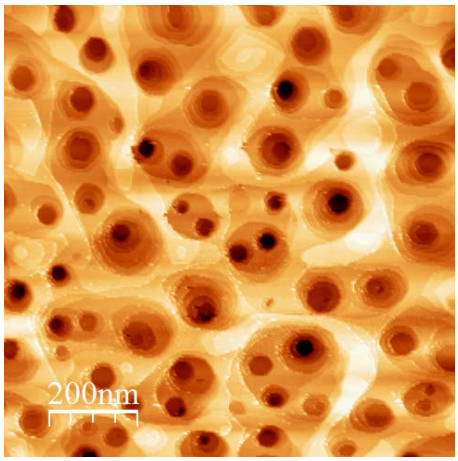


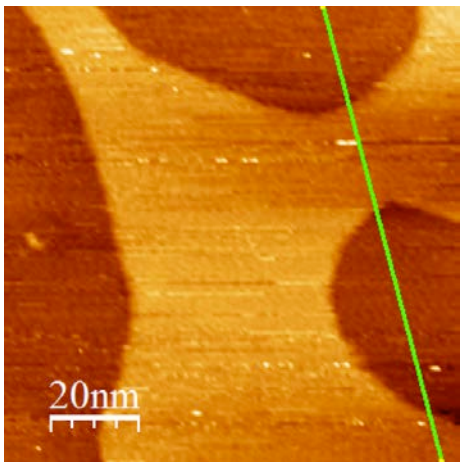
Fig 1. a) STM image of sample that has sat in the chamber for three days. Note the presence of adsorbed molecules. B) A line profile shows the heights of the two plateaus of nanostructure.

The results of sputtering can be seen in Figure 2. The surface was characterized by many holes gouged out of the silver surface.

a)



b)



c)

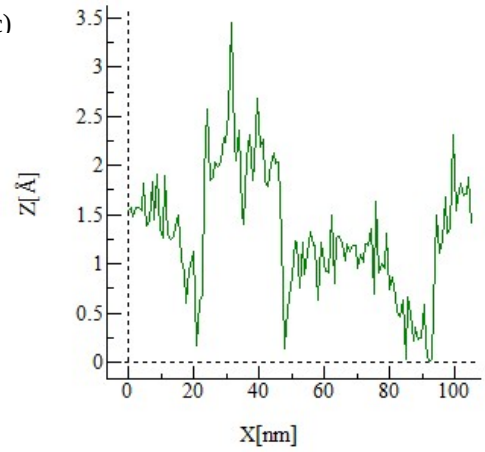
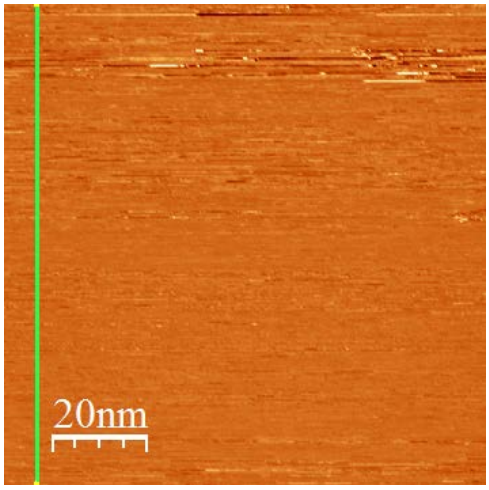


Fig 2. a) STM image of the sample that has been sputtered for ninety minutes to show an extremely damaged Ag(111) surface. b) STM image of sample that has been sputtered for thirty minutes. c) Line profile of sample from b) showing the different heights in plateaus created by argon ion bombardment

In contrast to the sputtered image was the annealed image of the sample. The surface structure was much more planar as the damaged, pocked surface was transformed into large and flat terraces.

a)



b)

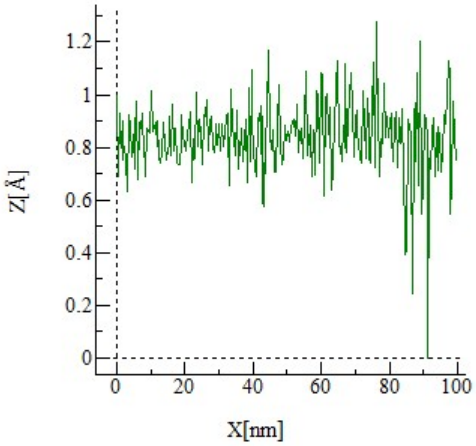


Fig 3. a) STM image of sample that has been annealed for fifteen minutes b) line profile of sample showing flat surface

After the sample was prepared and then sputtered for an additional thirty minutes it was simultaneously with dosed oxygen, heated, and hit by a laser. The results are shown on the silver sample in the STM image of Figure 4. Atomic oxygen can be confirmed by the presence of the black specks that were not present after either the sputtering or the annealing.

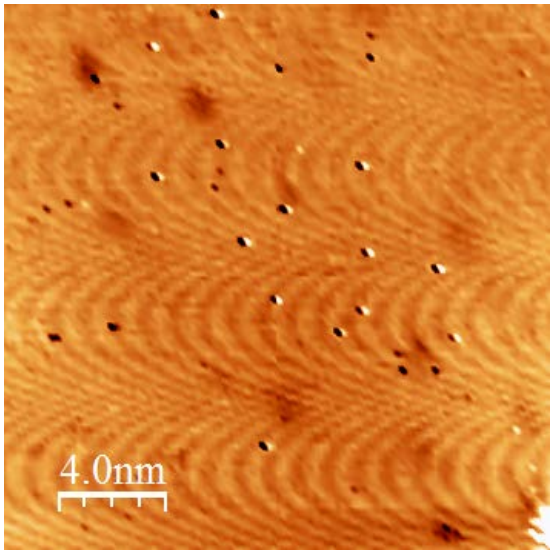


Fig 4. STM of Ag(111) showing oxygen adatoms, which are the black specks on the surface.

IV. Discussion

This study was conducted to determine if the plasmonic effect could reduce the activation temperature for oxygen dissociation. Based on the presence of atomic oxygen in the STM images, plasmons can assist in oxygen dissociation. The image of the atomic oxygen from the results was compared with an image of atomic oxygen from a cracker, which also showed a field of black specks on a silver sample surface. With the corroboration of two images of atomic oxygen—one from a gas cracker and one created with plasmon assistance—it is demonstrated that oxygen dissociation can be driven with a coupling of thermal energy and the plasmonic effect. With a better understanding of the plasmonic effect in driving oxidation and dissociation, the joint use of thermal energy and light can be applied to a wider range of reactions whose efficiency is severely limited by oxygen's high activation barrier. Also, the plasmonic effect is not limited to Ag(111) and the results gained here could theoretically be repeated with other plasmonically active samples.

However, as the results in this study are preliminary, the next step would be to confirm their reproducibility. After that, to gain more insight on the relationship between the plasmonic effect and oxygen dissociation, the effect of the laser wavelength and power on the oxygen dissociation process should be studied.

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