<div align="center">**CSCI 595 Final Project Proposal**</div>

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<div align="center">**Title: "Synergistic Study of Interaction between Water Adsorbates and Solid Surfaces"**</div>

Objective

It is essential to understand the interaction between water and solid surface in surface chemistry and catalysis.[1, 2] In electrochemical water splitting cells, at hydrogen evolution reaction (HER) potentials, interfacial water behavior near single crystal catalysts is different from that of bulk water. The randomly oriented water molecules may form an ordered structure on the surface of those catalysts.[1] Furthermore, in photoelectrochemical (PEC) water splitting cells, light absorbers such as silicon or GaAs often undergo photocorrosion when immersed in aqueous solutions.[3-6] When coated with a thin oxide layer, such as TiO_2, the surface of those semiconductors is passivated and stabilized.[7] Understanding the reason why TiO_2 can inhibit photocorrosion and support water splitting is essential to search for better passivation candidate layers.

Research Plan

Project 1. Theoretical Study of Surface Reactivity with Water

 Atomistic simulation is an essential tool for predicting surface structures and reactivities. The techniques used in the atomistic simulation consist of energy minimization and molecular dynamics. The energy minimization method allows us to search for the most stable surface configurations and molecular dynamics simulates the temperature effects of the surface. The aim of project 1 is to model the surface structure and its interaction with water adsorbates. Since we

want to compare different surfaces in various materials, atomistic simulation is the most suitable choice because it does not require large amounts of calculations and can be easily parallelized.

Atomistic simulation is based on the Born model of solids, in which the interatomic forces between ions is a function of their atomic positions. The energy can be decomposed into two parts. One part considers the Coulombic contribution, and the other part incorporates the short-range force, such that the total lattice energy is given by

$$E_{Total} = \sum \left(\frac{q_1 q_2}{r_{ij}} + E_{short-range} \right) \tag{1}$$

where $E_{short-range}$ is the short-range energy between ions. The Coulombic energy describes the electrostatic interactions between pairs of ions. Usually, the charges of ions in the studies solids are predefined, so the quality of the model depends on how to calculate the short-range energy in the solids. The short-range potential should consider both attractive and repulsive forces. The repulsive force results from the electron cloud overlapping and the attractive force is due to instantaneous formation of dipoles. The formation of one dipole will induce dipoles in the neighboring ions with similar orientations, leading to ions to attract each other. This is so-called London dispersion force or Van der Waals force. The magnitude of the attraction force depends on the hardness or the polarizability of the ions.

Usually, $E_{short-range}$ consists of two body interaction, three body interaction (i.e., bond bending) and higher orders. In many ionic solids, two order interaction is the main contributor because of isotropic structures. Furthermore, the potential parameters used in modeling two body interaction are empirically fitted with experimental data so the residual many body interactions are implicitly included. Several analytical function can be used to describe the two body interactions. For the non-bonded interaction, $E_{short-range}$ can be modeled as Lennard-Jones potential:

$$E_{short-range} = \frac{A}{r^{12}} - \frac{B}{r^6} \qquad (2)$$

where A and B are parameters describing repulsive and attractive interactions, respectively. This potential is commonly used in modeling liquids and metals.[8] For ionic solids, the commonly used potential is Buckingham and Born-Mayer interaction:

$$E_{short-range} = Ae^{-r/\rho} - \frac{C}{r^6} \qquad (3)$$

where the terms A, ρ and C are three independent variables.[9] $Ae^{-r/\rho}$ describes the hard cation-anion repulsion and $-\frac{C}{r^6}$ incorporates attraction from polarization of the charge distribution. To find values of those parameters, we can vary the parameters iteratively until they give the best fit to the experimental values which are derived from the interaction energy, such as unit cell volume, lattice constants, dielectric and elastic constants. One disadvantage of this method is that the fitting of the parameters only depends on the equilibrium state of the materials, while most of the defects or surfaces states deviate largely from equilibrium interatomic positions. To overcome this shortcoming, we can fit the potential based on several different structures simultaneously. One common property of all the analytical forms of $E_{short-range}$ is that it must tend to zero when the interaction position approaches infinite. So, we can set up a cut off length to decrease the computational time within a reasonable duration. However, the cut off length must be reasonably long to maintain energy conservation.

As we mentioned before, the greatest advantage of the atomistic simulation method is that many different surfaces with high complexity can be analyzed and compared with experimental structural techniques, which we will discuss later. Right now, there are already good agreement between theoretical and experimental results for rutile, alumina and tungsten oxide, where surface reconstruction is analyzed for different indices of surfaces[10, 11] The surfaces having the lowest

energies are those of low Miller indices because these planes are usually closest packed and have the smallest surface area per unit cell. Since the volume of the unit cell is fixed, the interplane distance is usually largest and those planes are easily to be cleaved and exposed. There are usually three types of surfaces based on surface dipole moments.[12] Type I surface has repeating unit with charge neutral stoichiometry. Type II surface consists of charged layer but there is no dipole moment perpendicular to the surface, and type III surface has perpendicular dipole moment.

Here, we plan to model surfaces based on a two-region principle, where region I is adjacent to the water/solid interface and region II stands for the bulk of the material. In region I, the ions are allowed to move independently, while in region II, the ions are fixed relative to each other but can move as a whole. The reason why we include region II is to make sure all the ions in region I experience the forces from the rest of the crystal and lattice energy is conserved. Once the regions are clearly defined, we can apply energy minimization combined with molecular dynamics simulation. Energy minimization is used to adjust the ions in region I until the lattice energy in this region reaches a minimum. Using this, we can evaluate a range of surfaces and search for suitable candidate surfaces which will be further evaluated by molecular dynamics. In molecular dynamics, the ions in region I will be given a kinetic energy based on the studies temperature. The specific surface energy is defined as the extra energy per unit area needed to form the surface compared to the bulk:

$$\gamma = \frac{U_s - U_b}{A} \tag{4}$$

where U_s stands for the energy the region adjacent to the surface, U_b is the energy of the same number of atoms in the bulk, and A is the surface area. Furthermore, we will also calculate the hydration energy, which is the energy to adsorb water on the surface:

$$E_{hyd} = \frac{U_w - (U_s + nE_{H_2O})}{n} \tag{5}$$

where E_{H_2O} is the water self-energy, U_w is the energy per surface area with water adsorbates, and n is the number of water molecules. Parker et $al.$ used this approach to study the surface reconfigurations of MgO (110) surface, which is shown in Figure 1.[13] MgO has the rock-salt crystal structure and in the bulk each cation and anion have coordination number of six. Here, the planar (110) surface shown in Figure 1a is reconstructed to two different surface morphologies to lower the lattice energy.
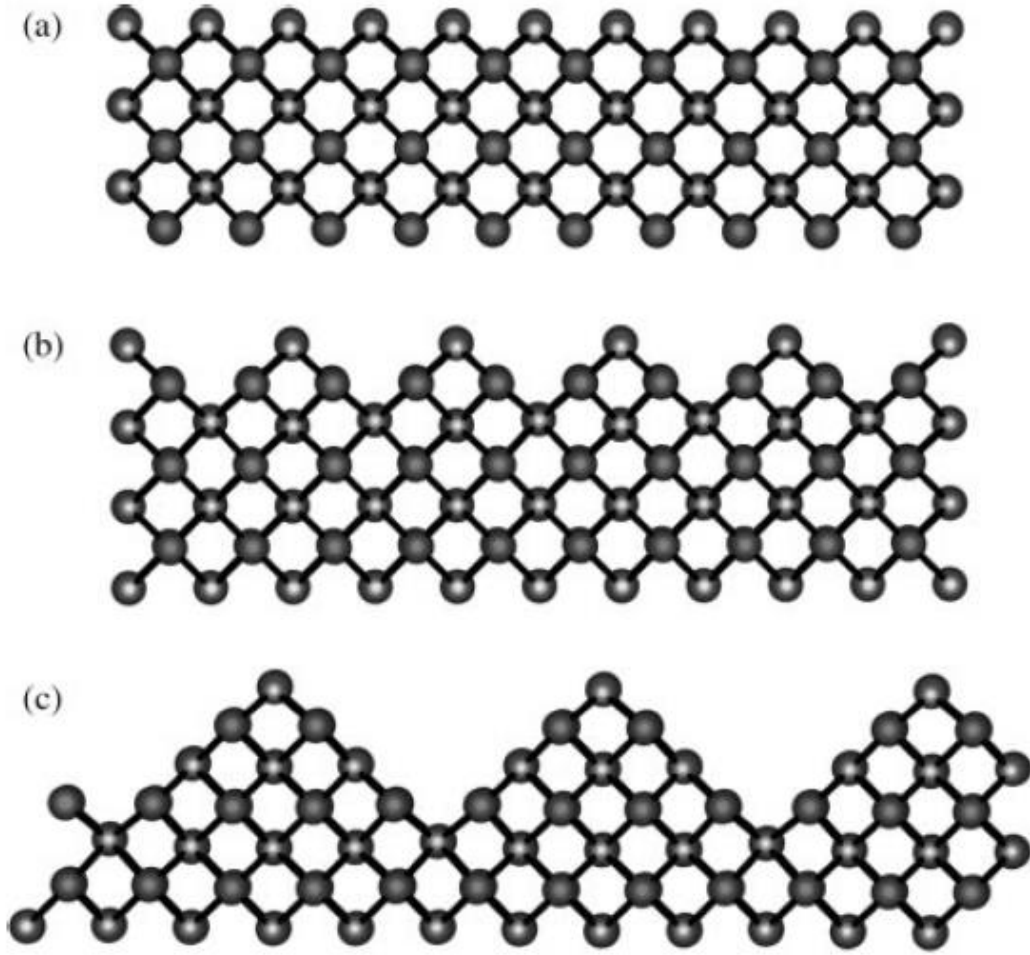
Figure 1. (a) unfaceted, (b) $(a_0\sqrt{2})/2$, and (c) $a_0\sqrt{2}$ reconstructed (110) surface of MgO, where a_0 stands for the lattice parameter.[13]

On the other hand, the structure of water at the liquid/solid interface can also be different from that of bulk water. To get more precise atomic structure of interfacial water, we plan to use Ab initio molecular dynamic (AIMD) method to simulate the liquid/solid interface.[14, 15] In AIMD, the potential energy can be calculated through density functional theory (DFT) using ready to use package, such as Vienna ab initio simulation pack (VASP). Wang *et al.* demonstrated modeling of Pd (111)-water interface and found that the interfacial water undergoes structural changes when

the applied potential on the Pd (111) is decreased.[2] Figure 2 shows their study of potential

dependent structural change of interfacial water in Pd (111) – water system through AIMD.
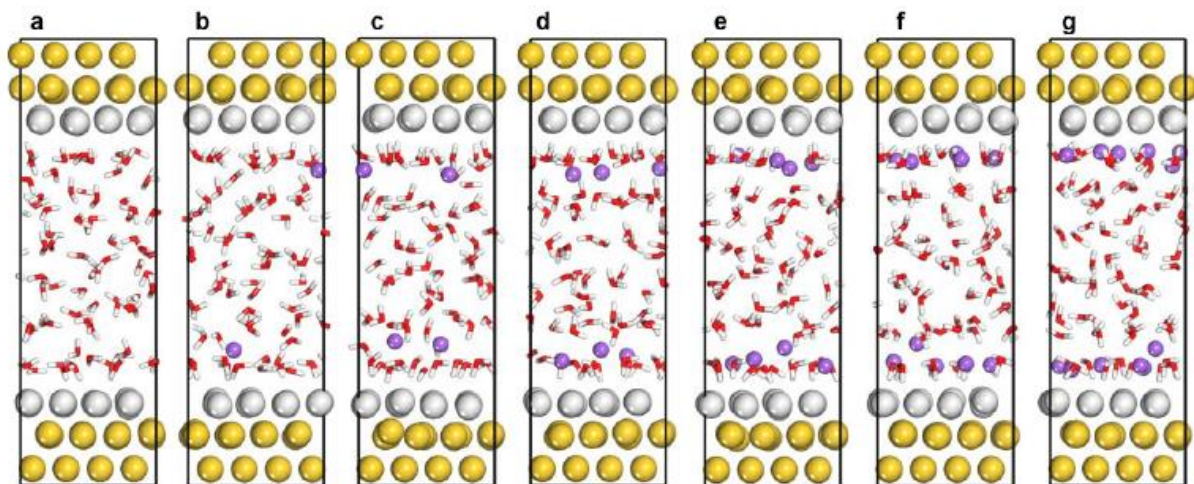

Figure 2. Potential dependent Pd (111) – water system, where Au, Pd, and Na atoms are represented by yellow, gray and purple spheres, with water molecules as red and white sticks. (a)-(g) correspond to the applied potential at 1.12, 1.01, 0.78, 0.38, -0.12, -0.65 and -1.07 V vs reversible hydrogen electrode (RHE) in 0.1 M NaCiO$_4$ aqueous solution, respectively.

In their study, as the applied potential decreased, the water adsorbates at the interface first form random structure, then form one-H-down orientation, which is followed by two-H-down configuration. In addition, the simulated Pd-H bonding length decreases with applied more negative potential on the electrode, which facilitates electron transfer efficiency and enhances the HER performance. So, AIMD is clearly a suitable tool to study the water phase reconstruction at the liquid/solid interface. In this research plan, we will use AIMD to study more surfaces from different materials to get a broader understanding of interfacial water phase reconstruction.

In conclusion, energy minimization combined with molecular dynamics will be used to study the solid surface reconfiguration and water adsorption energy on different indices of surfaces

of various materials, while AIMD will be applied to study the interfacial water behavior on those surfaces.

Project 2. Experimental Study of Surface Reactivity with Water

In situ Raman Spectroscopy has been proven to be a useful tool for studying interfacial water structure, in which different water molecule vibrational modes are detected and analyzed while driving the hydrogen evolution reaction (HER) or oxygen evolution reaction (OER). Because the collected signal from the surface molecules is small, we plan to use surface-enhanced Raman scattering through shell-isolated nanoparticles (SHINs), where strong localized surface plasmon resonance is induced by the incident light. Wang *et al.* have demonstrated the study of interfacial water through this technique.[2] Figure 3a shows the device schematics they used in the research. Here, the working electrode consists of single layer of Pd on top of Au, and an ultra-thin layer of water is trapped between a quartz window and the electrode to minimize the influence from bulk water. During the in situ Raman measurement, various potentials are applied to the working electrode, and the whole cell is vertically placed to get rid of hydrogen bubbles. For shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), the collected Raman signal is semi linear to $|E|^4/|E_0|^4$, where E is the localized electric field and E_0 is the electric field of the incoming light. One of the greatest advantage of SHINERS is that the extremely strong $|E|^4/|E_0|^4$ comes from the gaps between nanoparticles and working electrode, where the number of interfacial water molecules is also highest. Figure 3b shows the electric field profile (i.e., $|E|^4/|E_0|^4$) through finite difference time domain (FDTD) simulation for 2 x 2 array of SHINs on the Pd/Au working electrode in aqueous environment, and as high as 10^8 enhancement of $|E|^4/|E_0|^4$ is observed between SHINs and the electrode.
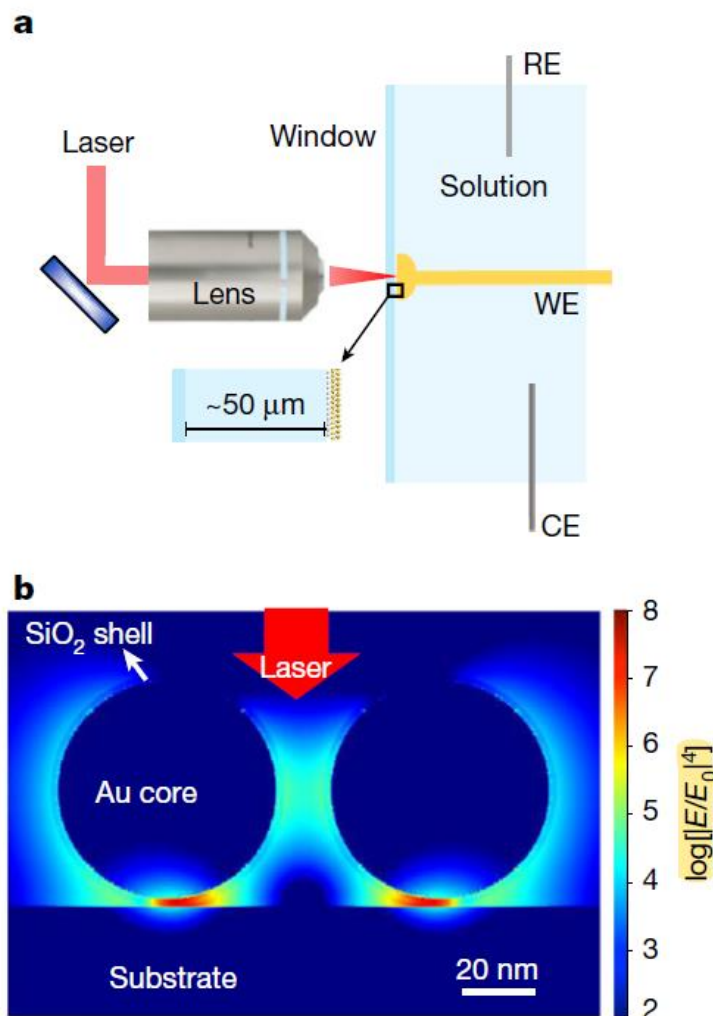
Figure 3. (a) Schematic of the in situ Raman spectroscopy with a standard 3-terminal electrochemical cell in $NaClO_4$ solution, where WE, RE and CE are working electrode, reference electrode, and counter electrode, respectively. (b) Three-dimensional FDTD simulation of electric field profile (i.e., $|E|^4/|E_0|^4$) of 2 x 2 array of SHINs on Pd/Au substrate.

In their findings, the intensity of Raman band at 550 cm^{-1} attributed to the libration vibration mode of water molecules increased when the applied potential decreases, indicating higher level of orderliness of the interfacial water structure.[16] Furthermore, the population of surface Na-H_2O increases with decreasing potential, which is caused by the electrostatic effect of

Na^+ cations moving to the electrode surface. These Na-H_2O molecules tend to form ordered orientation with respect to the electrode surface with a two-H-down type, further decreasing Pd-H bonding strength and increasing charge transfer efficiency.

So, SHINERS has been proven to be a valuable tool for interfacial water structural study. As most the previous research has been focused on HER, we will focus on the oxygen evolution reaction (OER) to get a deeper understanding of overall water splitting reaction. In this research plan, we will use this tool to study the interfacial water behavior in OER on difference surfaces of various materials.

Summary

In conclusion, we proposed a synergistic study of interaction between water molecules and solid surfaces both theoretically and experimentally for further enhancing HER and OER under different pH conditions. In terms of theoretical study, we plan to use energy minimization combined with molecular dynamics to understand solid surface reconstructions as well as water adsorption energy, and AIMD will be used to study water adsorbate reorientations. For experimental study, SHINERS will be applied to further study the effects of cations as well as applied potentials on the interfacial water behavior.

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