EFFECTS OF SURFACE DEFECTS ON HYDROPHOBICITY AT RARE-EARTH OXIDE INTERFACES USING MOLECULAR DYNAMICS SIMULATIONS DRIVEN BY *AB INITIO*-BASED DEEP NEURAL NETWORK POTENTIALS

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EXECUTIVE SUMMARY

Hydrophobic and superhydrophobic surfaces that are robust to harsh environments have immense potential to enhance the performance of a plethora of applications. However, the successful widespread commercialization of hydrophobic surfaces has been fraught with many challenges. The biggest challenge is the lack of mechanical, chemical, and thermal robustness.

Recent studies show that rare-earth oxides (REOs) are intrinsically hydrophobic and durable owing to their unique electronic structure. However, surface defects such as adatoms (single atoms lying on surfaces) and vacancies are ubiquitous and may change the wettability of REOs. Thus, in this project, the research team investigated the influence of the defects on hydrophobicity and elucidated the mechanism governing wettability by employing first-principle neural network potentials combined with molecular dynamics (MD) simulation. This work is significant for simulating and understanding the hydrophobicity of REOs at the molecular level and providing insights to identify ideal candidates with strong hydrophobicity when considering the presence of defects.

RESEARCH CHALLENGE

Water/solid interfaces have attracted significant attention owing to their central role in many fields such as electrochemistry, corrosion, and heterogeneous catalysis. Hydrophobic materials have immense potential in enhancing the performance of materials under harsh environments, ranging from reducing ice adhesion to eliminating corrosion. Although common metals are hydrophilic while general organic materials are hydrophobic, organic materials deteriorate easily and are not durable in harsh environments.

Recently, Azimi *et al.* [1] found that REOs are intrinsically hydrophobic owing to the saturation of electrons in their outer shells and their lower tendency to form hydrogen bonds. However, surface defects such as adatoms and vacancies are pervasive, which may change the hydrophobicity of REOs because of increasing surface reactivity and attracting structural arrangements. This project aims to investigate the influence of such defects on hydrophobicity with MD simulations.

Ab initio MD with electronic structure theory is the gold standard for simulations of solid–liquid interfaces owing to minimal assumptions made to describe interactions between water and surface. However, the relatively high computational cost limits the system size and timescale. High-dimensional neural network potentials (NNPs) based on density functional theory (DFT) data have the ability to enable efficient classical MD with accuracy close to *ab initio* MD. By combining classical MD with NNPs, the research team was able to perform long-timescale simulations with high accuracy.

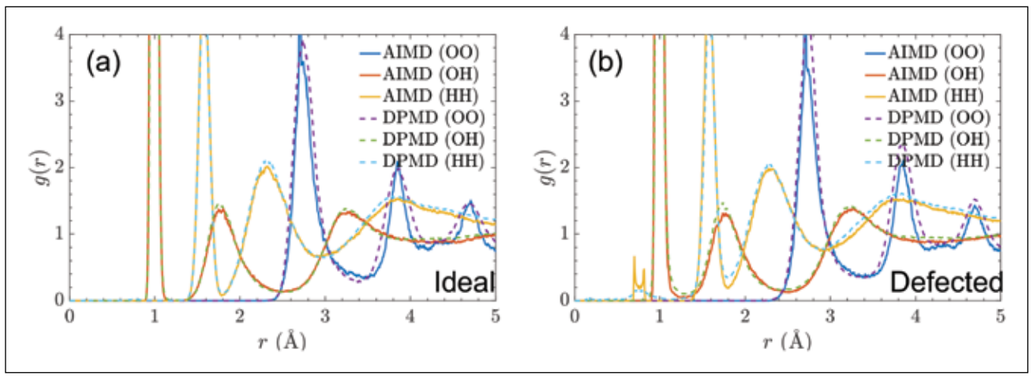

Figure 1: Comparison of the pair distribution function of O–O, O–H, H–H using *ab initio* MD (AIMD) and MD driven by neural network potentials (DPMD) at ideal ceria surface (a) and defected ceria surface (b).

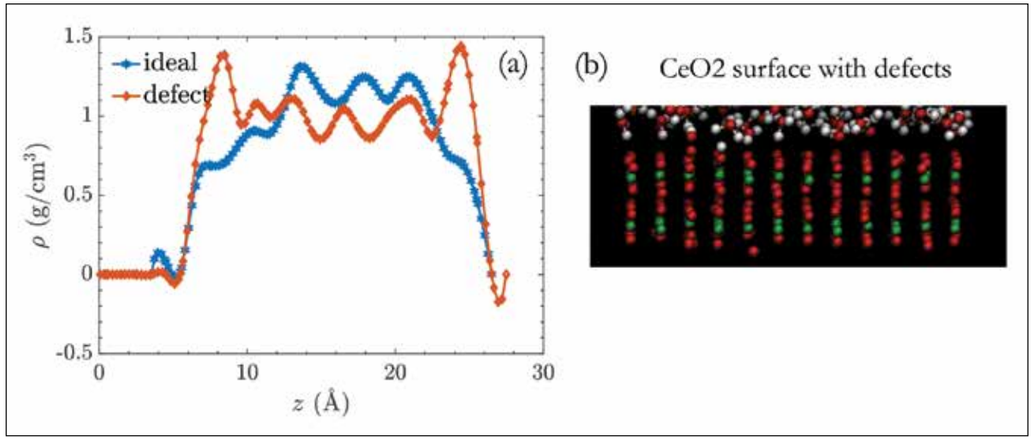

Figure 2: (a) Water density along z directions at both the ideal and defected ceria surface. (b) Snapshot of the water dissociation at the defected ceria surface.

METHODS & CODES

Starting from bulk water, a specific bulk REO such as ceria (CeO_2), and a wide range of REO–water interfaces, the team carried out DFT reference calculations using VASP [2]. Projector augmented waves with a plane wave energy cutoff of 700 eV to converge the results were used to describe the electron-core interaction in the DFT calculations. Furthermore, more uncorrelated structures for DFT calculations were generated by taking snapshots of *ab initio* MD simulation trajectories. The calculated energy and force were related with a vector of atom-centered symmetry functions defined by atomic environment. For each atom, the symmetry function vector was fed into an individual atomic neural network and the neural network was constrained to have the same architecture and parameters for each element in the system. Using these symmetry functions related to each kind of atom and energy, the reference data were split into training sets to determine the fitting parameters for each type of atom and test sets to verify the transferability of those parameters. An iterative gradient-based fitting process was used to determine the fitting parameters by minimizing the error function until a set of parameters could accurately reproduce the reference energies and forces and a converged neural network potential energy surface was obtained. Using the generated potentials, the research team performed MD simulations to collect trajectories to quantify the level of hydrophobicity.

RESULTS & IMPACT

By performing MD simulations with constructed neural network potential, both structural and dynamics properties can be calculated efficiently for ideal and defected systems. The accuracy using neural network potentials is close to DFT calculation and *ab initio* MD. Upon comparing the hydrophobicity in both the ideal and defected ceria–water interface, the researchers found that the interaction of water with the surface increases and water dissociates in the presence of the defects, suggesting the rare-earth oxides interface becomes hydrophilic when there are defects in the surface.

Using efficient and accurate *ab initio*-based neural network potentials makes it possible to explore the general structural and dynamical characterization of large-scale solid–liquid interfaces with first-principle accuracy. In the future, this work will help to identify ideal candidates with strong hydrophobicity by using a closed-loop characterization.

WHY BLUE WATERS

Collecting high-quality data requires computationally expensive DFT and *ab initio* MD simulations. To ensure the convergence of the properties, a reasonable system size of 500 atoms is essential. Tens of nodes are required to fulfill the memory and speed requirements of the calculations. Access to the Blue Waters system made the calculations possible. Furthermore, the VASP code can run efficiently on Blue Waters, and the project staff were very helpful and responded quickly to solve any computational issues.