Supplementary Materials

Explanation of Dramatic pH-Dependence of Hydrogen Binding on Noble Metal Electrode: Greatly Weakened Water Adsorption at High pH.

Tao Cheng, †, ‡ Lu Wang, § Boris V Merinov, † and William A Goddard III†, ‡*

† Joint Center for Artificial Photosynthesis (JCAP), California Institute of Technology, Pasadena, California 91125, United States

‡ Materials and Process Simulation Center (MSC) California Institute of Technology, Pasadena, California 91125, United States

§ Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China

AUTHOR INFORMATION

Corresponding Author

*E-mail: wag@wag.caltech.edu.
S1. Model and Methods

S1.1 Reactive Force Field Simulation
The reactive force field (ReaxFF) molecular dynamics simulation was carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) version of 11 Aug 2017 with user package of Reax/C. The interaction between Pt and water was described by Pt-O-H water ReaxFF. NVT simulations were performed with a time step of 0.25 fs, using the Nose-Hoover thermostat at 298 K with a damping parameter of 100 fs.

S1.2 Density Function Theory Calculation
Electronic structure calculations were performed within the density function theory (DFT) framework, as implemented in the Vienna ab initio simulation program (VASP), a plane-wave pseudopotential package. The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). Spin polarization does not have an appreciable effect on the overall energies, and is not included in the calculations to reduce computational demands. We used a plane-wave cutoff energy of 400 eV and the First order Methfessel-Paxton scheme with a smearing width of 0.2 eV. Dipole corrections were applied along the z-axis. The PBE-D3 method was employed to correct van der Waals interaction of water-water and water-Pt. We used a 1.2 fs time step in the Molecular Dynamics (MD) simulations with the hydrogen mass set to 2 atomic mass unit. These MD simulations used only the gamma point of the Brillouin zone with no consideration of symmetry. Nose-Hoover thermostat was applied to keep the temperature at 298 K with a temperature damping parameter of 100 fs.

S1.3 Molecular Dynamics Simulation
Here we simulate the water/Pt(100) interface using 36 to 60 explicit water molecules (3 to 6 layers) on a 4×4 Pt (100) surface slab (3 layers) with an area of 1.26 nm². The simulation box is 40 Å along the z-axis. To equilibrate the waters interacting with the interface, we carried out 2 ns of reactive molecular dynamics (RMD) simulations using the ReaxFF reactive force field for Pt and H₂O. The temperature and potential energies during the RMD simulation are shown in Figure S1a and S1b. Starting from this well-equilibrated interface; we carried out 10 ps of ab initio AIMD simulation at 298 K. The temperature and potential energies during the AIMD simulation are shown in Figure S1c and S1d.
Figure S1. (a) the temperature and (b) potential energy of 2 ns reactive force field molecular dynamics simulation (RMD); (c) the temperature and (d) potential energy of 10 ps Ab-initio molecular dynamics (AIMD) simulation.

S1.4 Adjust Applied Voltage

In the explicit scheme, we place one Na into the water (as shown in Fig.1b), which provides one extra electron to the electrode leaving Na\(^+\) solvated by water and reduces $U$ to 0.0 V. We find that including one extra Na solvated in the solution leads to a work function of 4.40 (±0.32) eV, which corresponds to 0.00 V (SHE). We intentionally put the Na\(^+\) in the third layer to prevent its adsorption to Pt electrode.

In the hybrid scheme, we employ 36 water molecules to explicitly simulate the first three layers of water, and incorporate the implicit solvation model to simulate the bulk water.\(^{10}\) The work function can be derived from the energy of fermi level ($E_{\text{fermi}}$) and electrostatic potential (reference fermi level to vacuum) as shown in Figure S2.
Figure S2. The profile of electrostatic potential along the direction perpendicular to the Pt (100) surface. The energy of fermi level is show as dashed line.

Taking -4.44 eV as the chemical potential of standard hydrogen electrode (SHE), the relationship between work function (Φ) and Voltage ($V_{SHE}$) is as follows:

$$V_{SHE} = \Phi - 4.44$$  \hspace{1cm} (S1)

Introducing extra electrons leads to the increase of $E_{\text{fermi}}$, thus decrease of $\Phi$, which, in turn, results in more negative voltage as show in Figure S3.

Figure S3. The extra electrons and the corresponded voltage of one snapshot from QMMD. Thus, we can control the number of electrons to reach the target $V_{SHE}$ at given pH at RHE scale. In QMMD simulations, the changes in configurations leads to the fluctuation of work functions. Thus, we extract at least 10 snapshots from the QMMD trajectories to calculate the average work function. Table S1 lists the number of extra electrons and the corresponded work function, voltage and pH.
Table S1. The number of extra electrons and the corresponded work function, voltage and pH.

<table>
<thead>
<tr>
<th>Extra Electrons (N\text{e}^- - N_0\text{e}^-)</th>
<th>Work Function (\Phi, eV)</th>
<th>Voltage (V\text{SHE})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>4.73</td>
<td>0.29</td>
<td>0.2</td>
</tr>
<tr>
<td>1.94</td>
<td>4.34</td>
<td>-0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>3.06</td>
<td>4.11</td>
<td>-0.33</td>
<td>10.7</td>
</tr>
<tr>
<td>3.48</td>
<td>3.98</td>
<td>-0.46</td>
<td>12.8</td>
</tr>
</tbody>
</table>

S1.5 Widom’s Insertion

Widom’s insertion method is used to calculate the chemical potential of hydrogen adsorption. The chemical potential ($\mu$) has contribution from ideal gas contribution ($\mu_{\text{ideal}}$) and the excess part ($\mu_{\text{ex}}$).\(^{11}\)

$$\mu = \mu_{\text{ideal}} + \mu_{\text{ex}} \quad (S2)$$

Where

$$\mu_{\text{ideal}} = -k_B T \ln\left( \frac{V}{\Lambda^3 (N + 1)} \right) \quad (S3)$$

$$\mu_{\text{ex}} = -k_B T \ln \int dr_{N+1} \left\{ \exp\left[ -\beta (U_{N+1} - U_N) \right] \right\}_N \quad (S4)$$

Here, $k_B$ is the Boltzmann constant, $T$ is temperature, $V$ is volume, $N$ is the number of atoms, $\Lambda$ is the thermal de Broglie wavelength of the atoms, $U_N$ is the potential energy of the original system and $U_{N+1}$ is the potential energy after insertion. Because hydrogen is chemically adsorbed on surface, we only focus on $\mu_{\text{ex}}$, which can be obtained by approximated by evaluating particle insertions.

Furthermore, to improve the sampling efficiency, grid points are ranked based on bridge sites with a random displacement of 0.5 Å. Particle insertions were performed on 10 equilibrated configurations from 10 ps AIMD trajectory.

S1.6 XPS Prediction

The core levels of O1s was calculated in the initial state approximation, which was implemented in VASP.\(^{12}\)

S1.7 Two-Phase Thermodynamics Calculation

The production MD simulations were subjected to a further 10 ps of NVT MD simulations, saving the atomic coordinates and positions every 2.4 fs. For each 10 ps trajectory, the entropy of
the water molecules as well as the zero-point energy and heat capacity corrections to the enthalpy was calculated using an external code employing the Two-Phase Thermodynamics (2PT) methods of Goddard and coworkers18-20,13-15 employing the recent memory functions corrections.16
S2. Additional Simulation Results

S2.1 Interface Structure at $U = -0.90$ V

Figure S4. The snapshots with atomic details of the interfaces at $U = -0.90$ V (SHE). We highlight the water with OH parallel to the surface ($\text{H}_2\text{O}^*$) with yellow stars. The colors of atoms are Pt in silver, O in red and H in white.
S2.2 Simulations with HCl and NaOH

Figure S5. The QMMD snapshot of (a) water+HCl (57 H$_2$O + 1 H$_3$O + 1 Cl) and (b) water + NaOH (58 water + OH$^-$ + 1 Na$^+$).

In our simulations (~60 solvent molecules and 10 ps), we see no significant differences of water structure, as shown in Figure S6. Thus, we conclude that the impact of including explicit H$^+$ and OH$^-$ is minor for this simulation.
Figure S6. ZDF from 10 ps QMMD of water (59 H$_2$O, in red), water + HCl (57 H$_2$O + 1 H$_3$O + 1 Cl, in green) and water + NaOH (58 water + OH$^-$ + 1 Na$^+$, in blue).

Figure S7. (a) The minimum distance between Na and O ($r_{\text{Na-O}}$) and (b) the minimum distance between Pt and O ($r_{\text{Pt-O}}$) in 10 ps QMMD simulation. The average $r_{\text{Na-O}}$ and $r_{\text{Pt-O}}$ are shown as dashed line.
Figure S8. The Na trajectories (overlapped) in 10 ps QMMD simulation. The radius of the trajectories is ~1.3Å and the average distance to surface is ~8.4Å.
S2.3 Data Fitting

Figure S9. The HBE* from QMMD prediction (a) and Experiment (b). The slopes of pH dependent HBE* can be estimated by either fitting data covering full range of pH values (from 0 to 13, in solid black line) or only considering data from pH = 3 to pH = 13 (in dashed red line).
Figure S10. Density of state (DOS) of water with both OH parallel to the interface (H$_2$O$^-$, in black) with a comparison of bulk water (in green) from a separate calculation of bulk water. We decompose the DOS of bulk water into contributions from translation (red shaded), rotation (blue shaded) and vibration (purple shaded).
References


