Nano-Micro Letters

Supporting Information for

# Exploring the Cation Regulation Mechanism for Interfacial Water Involved in the Hydrogen Evolution Reaction by in situ Raman Spectroscopy

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## Supplementary Figures

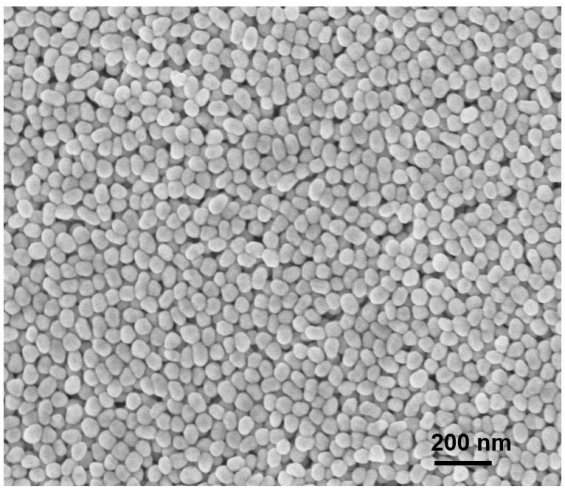


**Fig. S1** SEM image of Au NPs

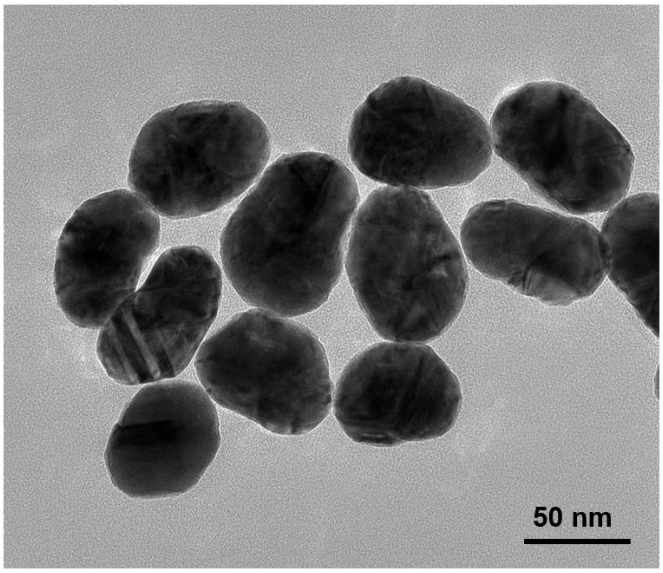


**Fig. S2** TEM of image of Au@Pd NPs

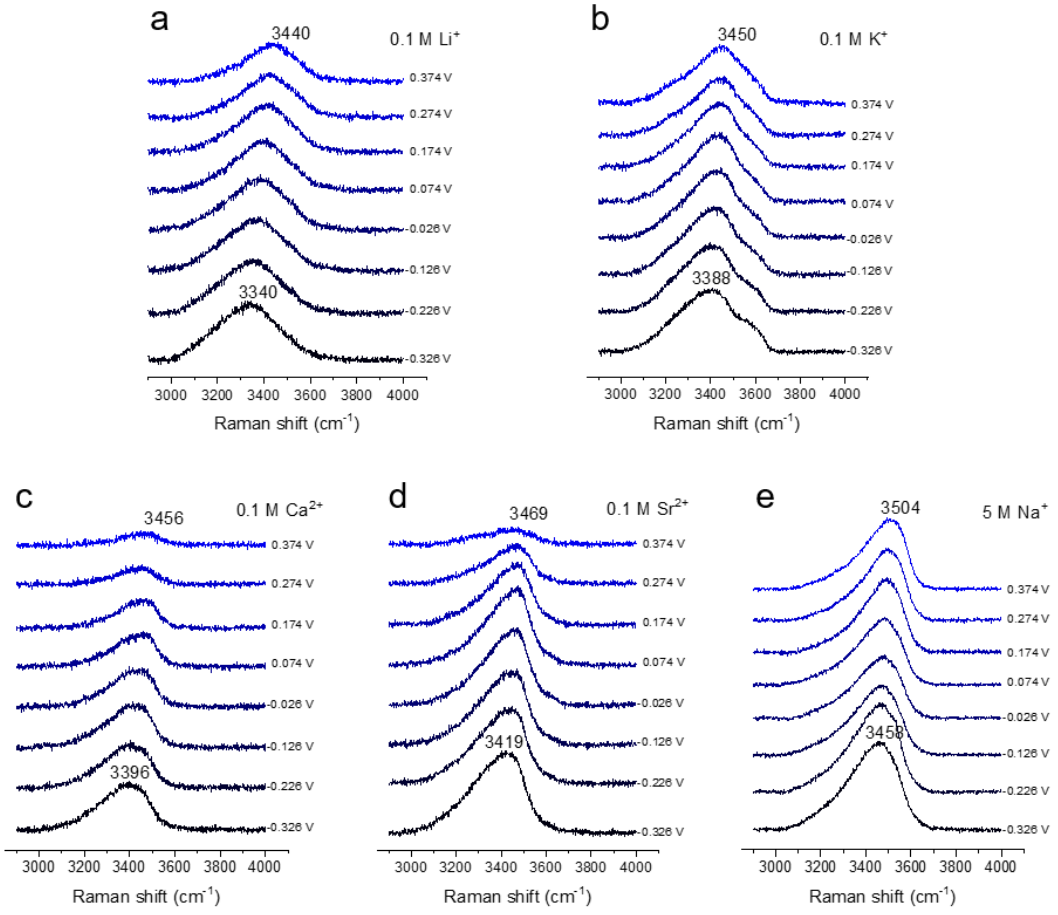


**Fig. S3** In situ Raman spectra of interfacial water on Au@Pd surface in alkaline electrolytes solutions (pH 12) containing **a** 0.1 M $LiClO_4$, **b** 0.1 M $KClO_4$, **c** 0.1 M $Ca(ClO_4)_2$, **d** 0.1 M $Sr(ClO_4)_2$, and **e** 5 M $NaClO_4$

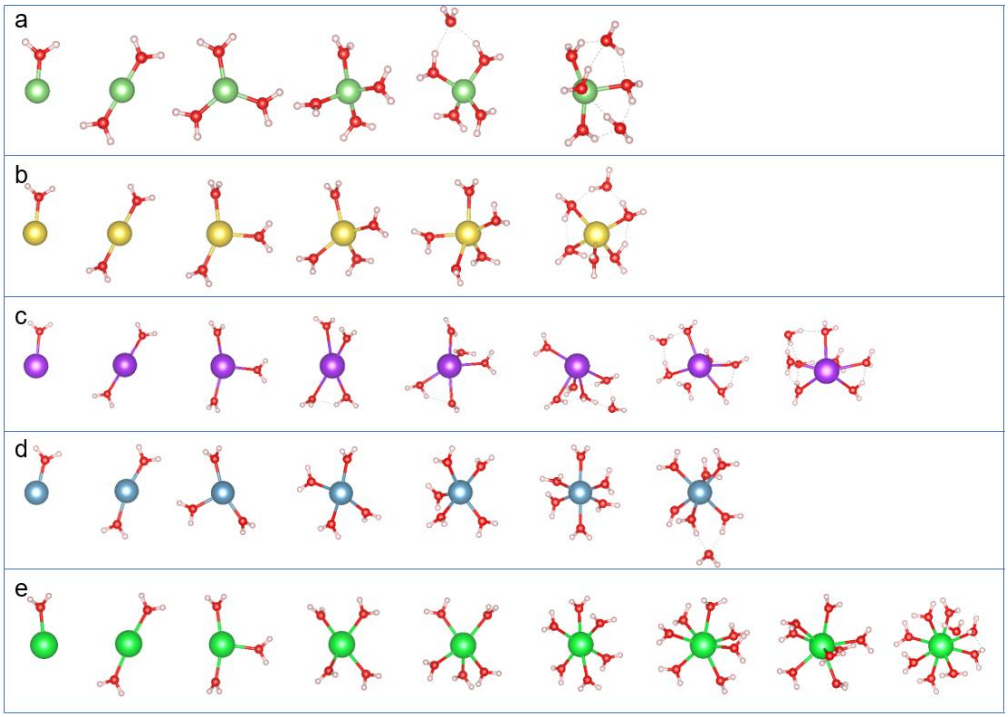


**Fig. S4** Geometrical structure of cations (**a-e**: $Li^{+}$, $Na^{+}$, $K^{+}$, $Ca^{2+}$, and $Sr^{2+}$) and water molecule with various coordination number

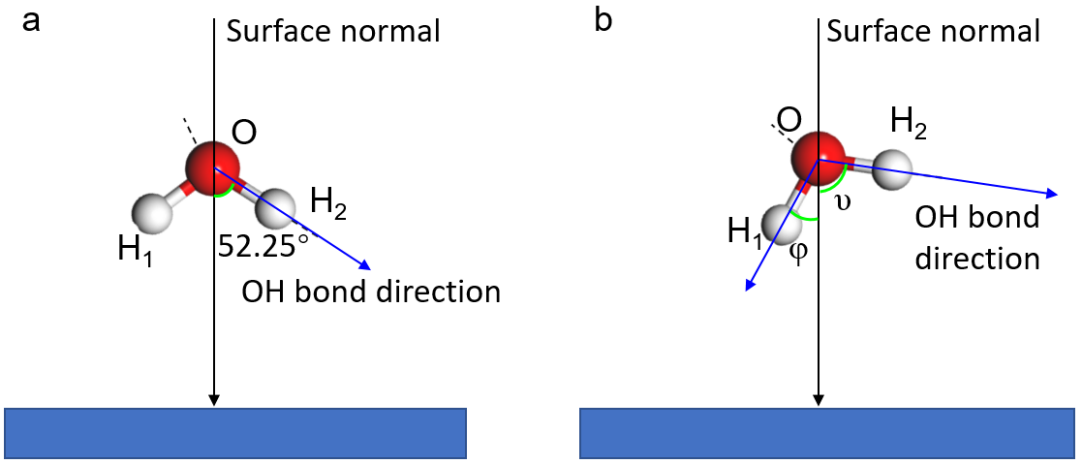


**Fig. S5** The angle (**a**: 52.25°; **b**: φ / υ angles) between the OH bond direction of water molecules and the surface normal

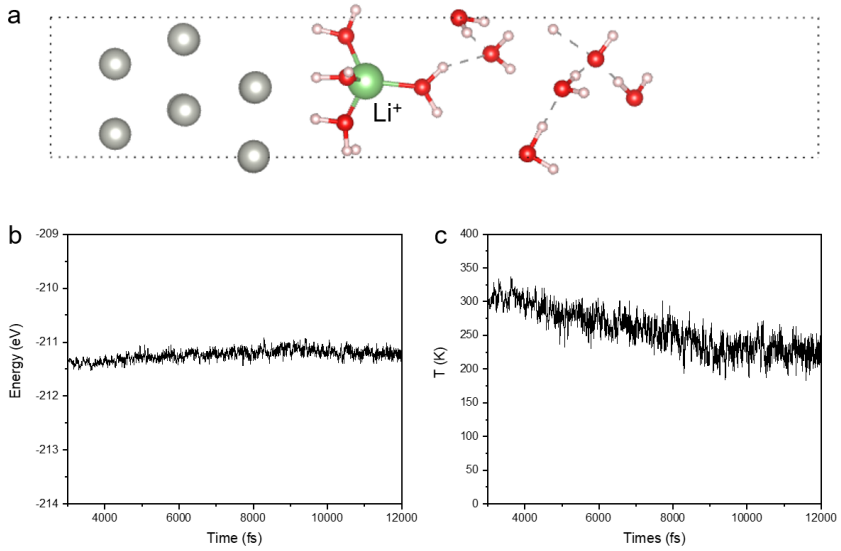


**Fig. S6** AIMD results of $Li^+$ system showing **a** a snapshot of a typical of $Li^+ – H_2O$ structure on a Pd(111) surface along with the **b** energy and **c** temperature curves

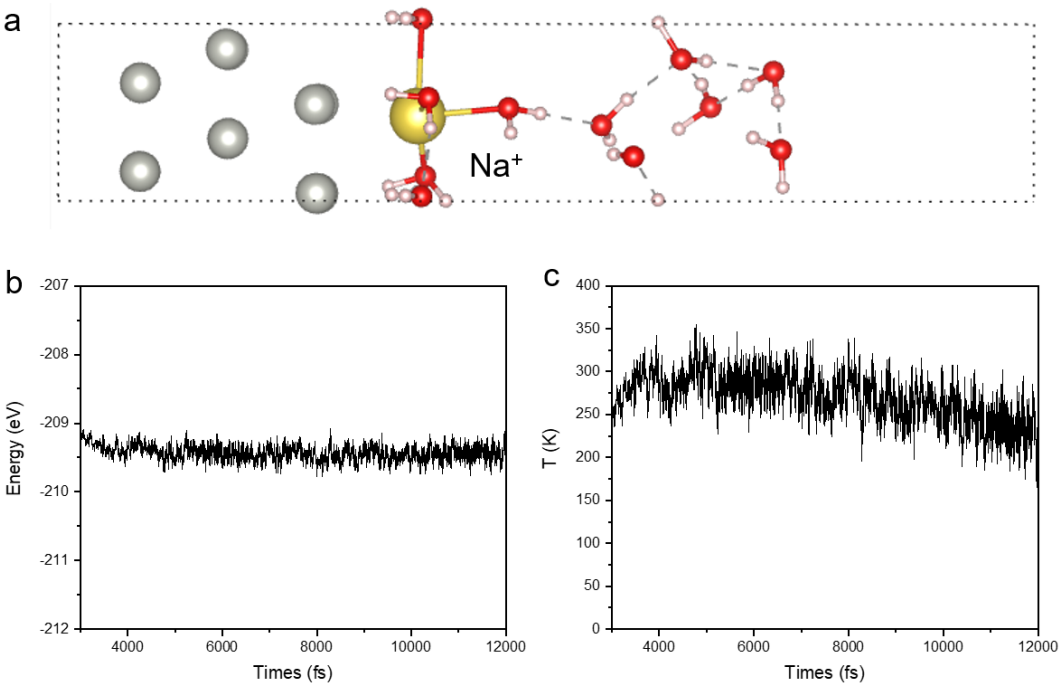


**Fig. S7** AIMD results of $Na^+$ system showing **a** a snapshot of a typical $Na^+ – H_2O$ structure on the Pd(111) surface along with the **b** energy and **c** temperature curves

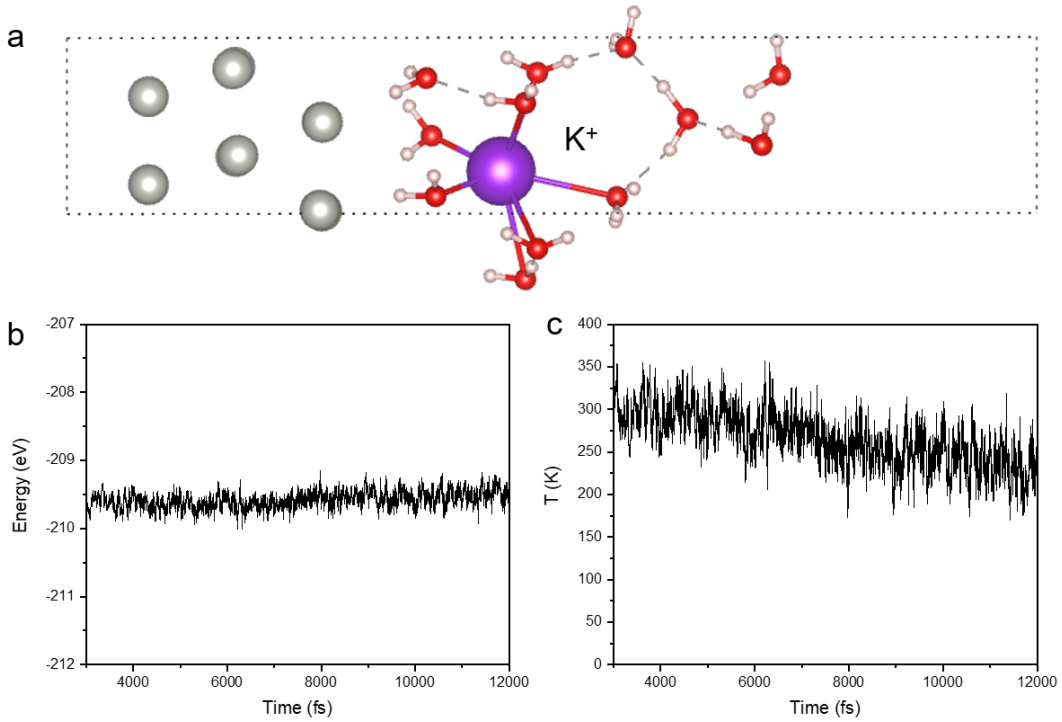


**Fig. S8** AIMD results of $K^+$ system showing **a** a snapshot of a typical structure of $K^+$ – $H_2O$ structure on the Pd(111) surface along with the **b** energy and **c** temperature curves

**Table S1** The distribution of φ and υ angles

| | Angle distribution | | | | | | | | | | Ave. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2O$-1 | | $H_2O$-2 | | $H_2O$-3 | | $H_2O$-4 | | $H_2O$-5 | | | |
| | φ | υ | φ | υ | φ | υ | φ | υ | φ | υ | φ | υ |
| $Li^+$ | 4.35 | 127.07 | 20.18 | 101.48 | 20.30 | 87.98 | | | | | 14.94 | 105.51 |
| $Na^+$ | 13.23 | 115.07 | 16.09 | 106.54 | 24.76 | 89.20 | 25.43 | 76.51 | 29.39 | 69.97 | 21.78 | 91.46 |
| $K^+$ | 15.75 | 135.22 | 23.50 | 95.79 | 24.83 | 84.12 | 27.78 | 78.22 | 31.14 | 72.04 | 24.60 | 93.08 |
| $Ca^{2+}$ | 12.86 | 126.75 | 16.43 | 120.27 | 25.35 | 90.30 | 32.38 | 86.34 | 42.36 | 53.60 | 25.88 | 95.45 |
| $Sr^{2+}$ | 15.31 | 125.57 | 15.32 | 94.81 | 20.45 | 86.54 | 23.76 | 78.66 | 40.98 | 55.04 | 23.16 | 88.12 |

# Supplementary Notes

### Electromagnetic field simulation

The finite element method (FEM) was widely used to investigate the near and far-field

optical properties of the plasmonic characteristics, such as electromagnetic field enhancement, light scattering, and light absorption. FEM simulations were performed using a commercial software (COMSOL Multiphysics) to probe the electromagnetic field distribution of Au@Pd, which was modeled with a heptamer on the Pd substrate. The perfectly matched layer was applied to all the simulation boundaries for absorbing incident light with minimal reflections. Specifically, the Au core is 55 nm in diameter with a 1-nm thick Pd shell, and the interparticle distance is set to 0 nm. The refractive index of background was set to 1.33, corresponding to the surrounding water in the system. The frequency dependent optical constant of Au and Pd was obtained from literature references [S1, S2].

## Supplementary References

[S1] P. Johnson, R. Christy. Optical constants of transition metals: Ti, V, Cr, Mn, Fe, Co, Ni, and Pd. Phys. Rev. B **9**(12), 5056-5070 (1974). https://doi.org/10.1103/PhysRevB.9.5056

[S2] P. B. Johnson, R. W. Christy. Optical constants of the noble metals. Phys. Rev. B **6**(12), 4370-4379 (1972). https://doi.org/10.1103/PhysRevB.6.4370