Supporting Information

-SR Removal or –R Removal? A Mechanistic Revisit on the Puzzle of Ligand Etching of $Au_{25}(SR)_{18}$ Nanoclusters during Electrocatalysis

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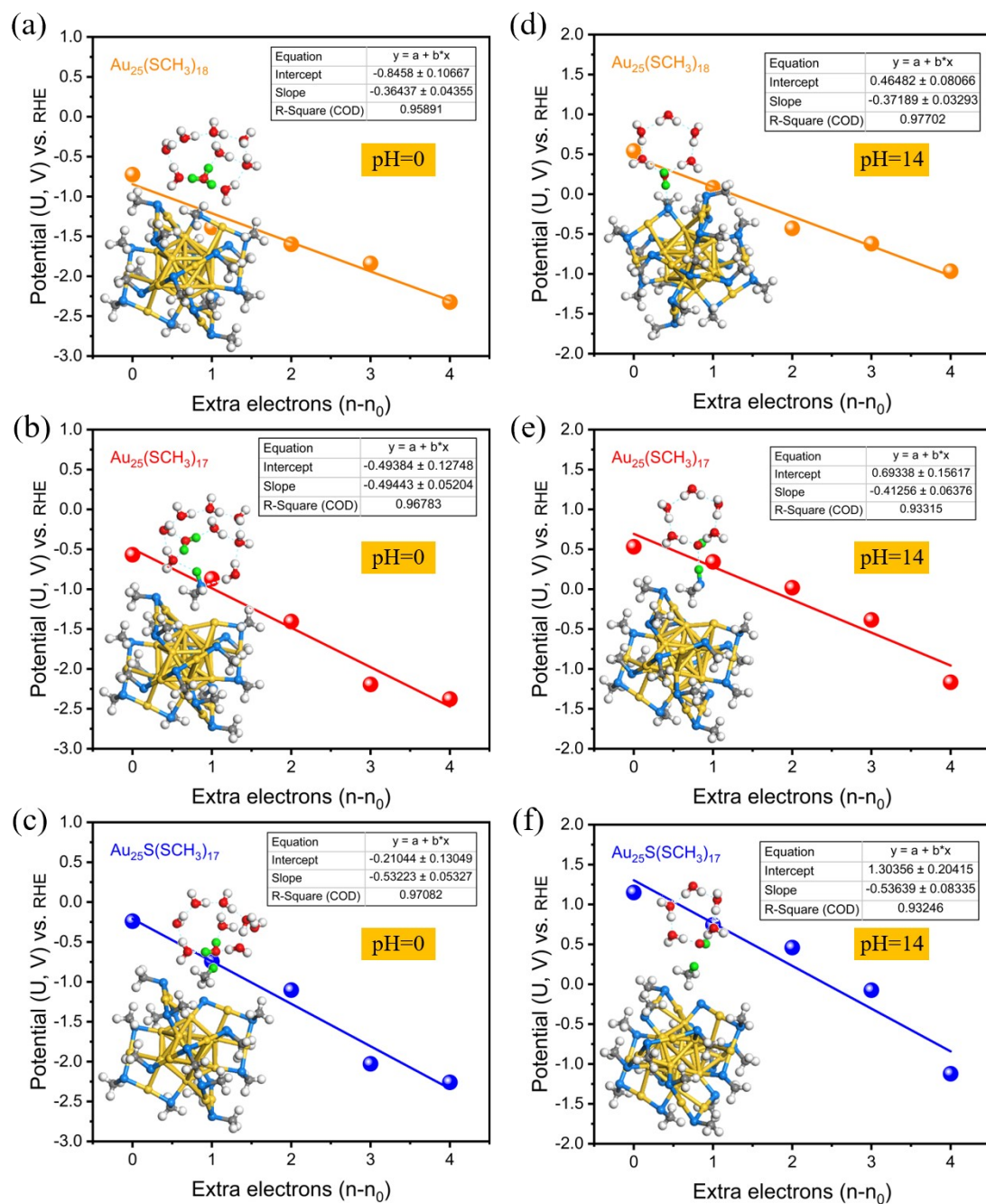[⊥] F.S. and L.Q. contributed equally to this work.

Figure S1. The relationships between the extra electrons ($n-n_0$) and the corresponded electrode potential U_{RHE} in pH = 0 and pH = 14 on intact Au_{25} and its two removal systems. The corresponding snapshots for explicit + implicit model at local surface of $Au_{25}(SCH_3)_{18}$, $Au_{25}(SCH_3)_{17}$ and $Au_{25}S(SCH_3)_{17}$ can also be seen in the inset. Color codes: yellow, Au; blue, S; grey, C; white, H. Of note, the possible transferred H atoms from H_3O^+ and H_2O are highlighted in green. The same color scheme is used in the figures below.
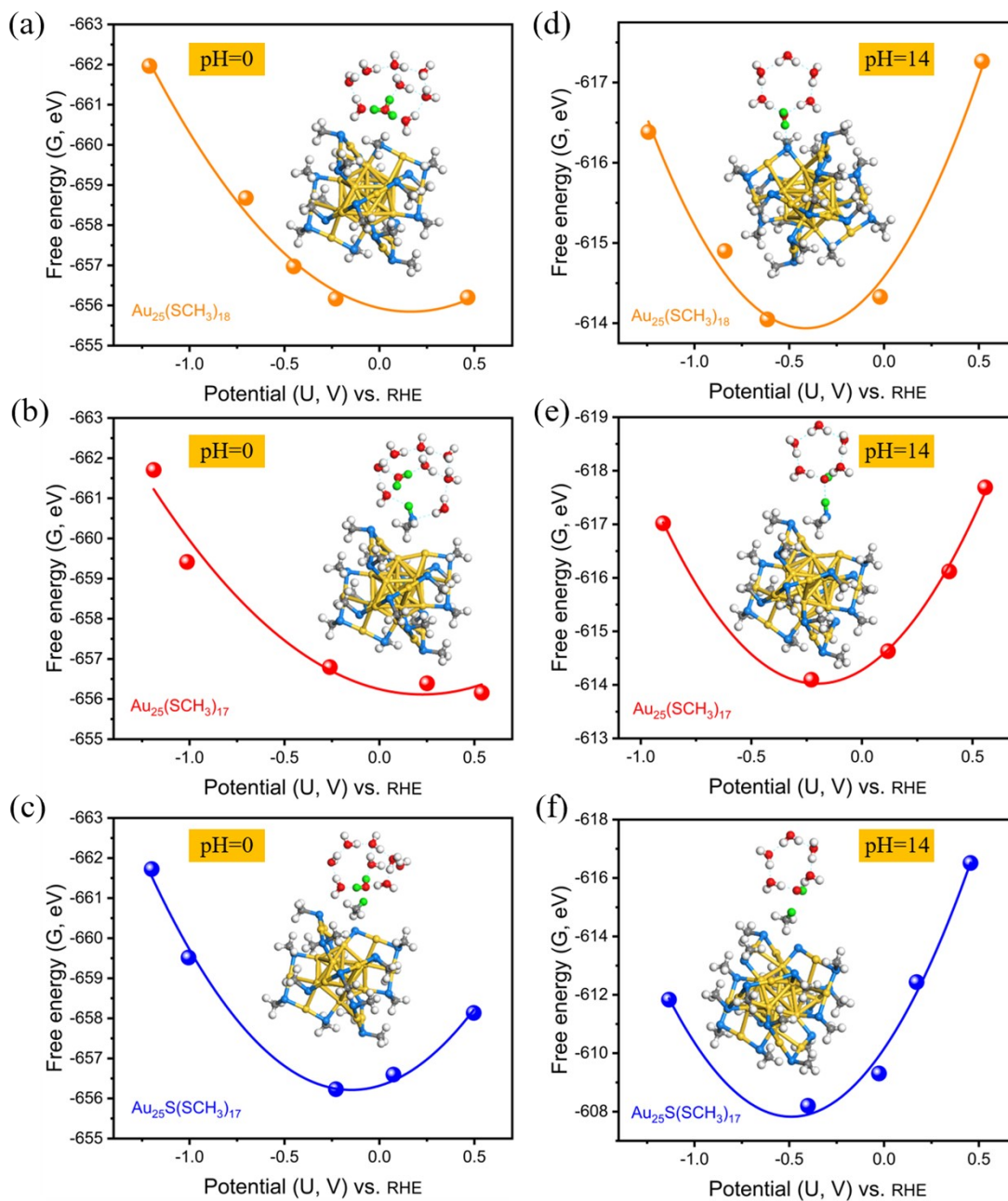
Figure S2. Calculated free energies (points) and polynomial fits (lines) of intact Au_{25} and its two removal systems as a function of potential U_{RHE} in pH = 0 and pH = 14, calculated using the constant potential method (cpm). The corresponding snapshots for explicit + implicit model at local surface of $Au_{25}(SCH_3)_{18}$, $Au_{25}(SCH_3)_{17}$ and $Au_{25}S(SCH_3)_{17}$ can be seen in the inset.
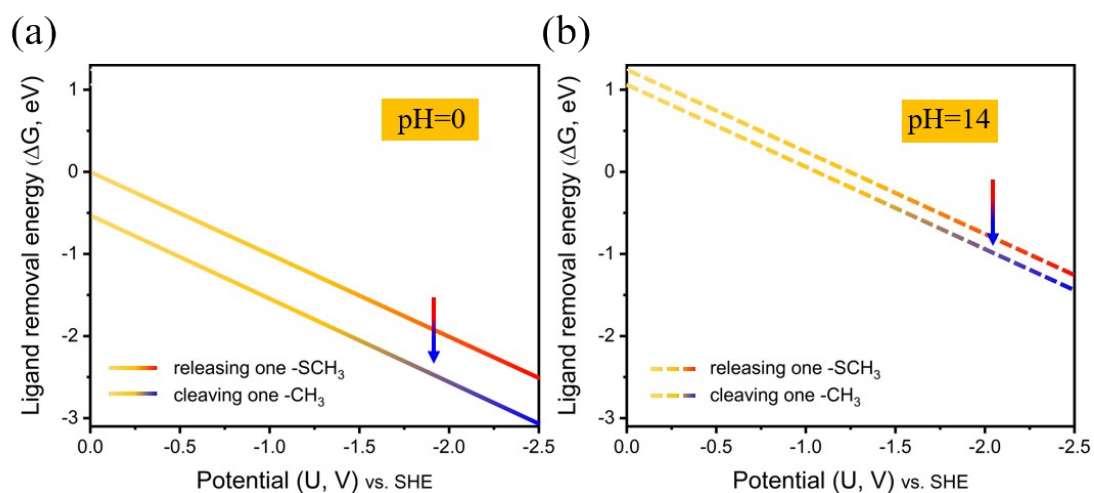
Figure S3. Based on the theoretical model in Figure 2a and 2b, calculated ligand removal energy ($\triangle G$) of the two cleaving modes as a function of potential by employing the CNM based on the CHE model.
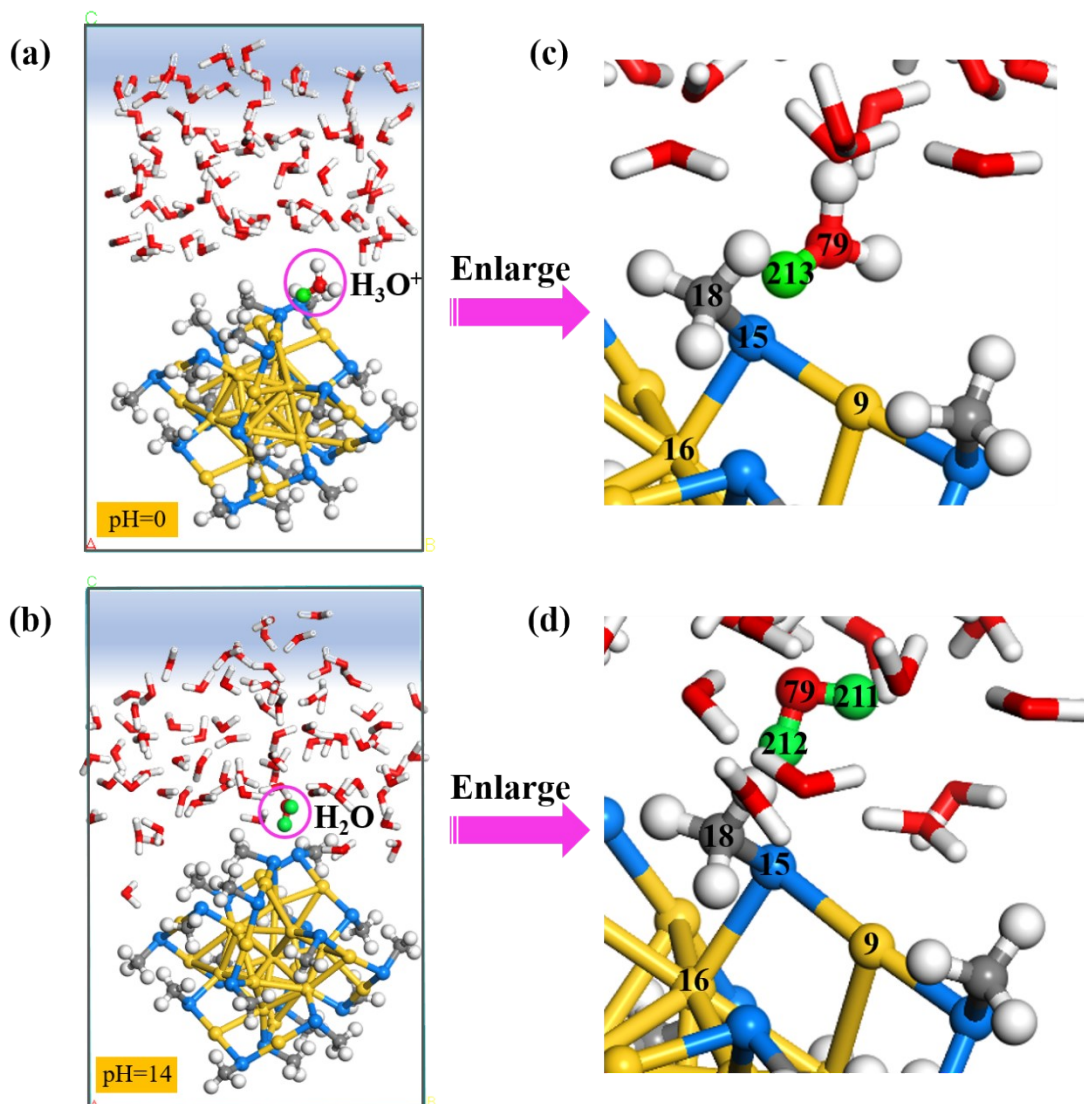
Figure S4. The theoretical model of (a) acid and (b) alkaline system at potential of zero charge (PZC) condition. The blue area above the water layer denotes an implicit solvation model. On the right are corresponding locally magnified images with some atomic markings.
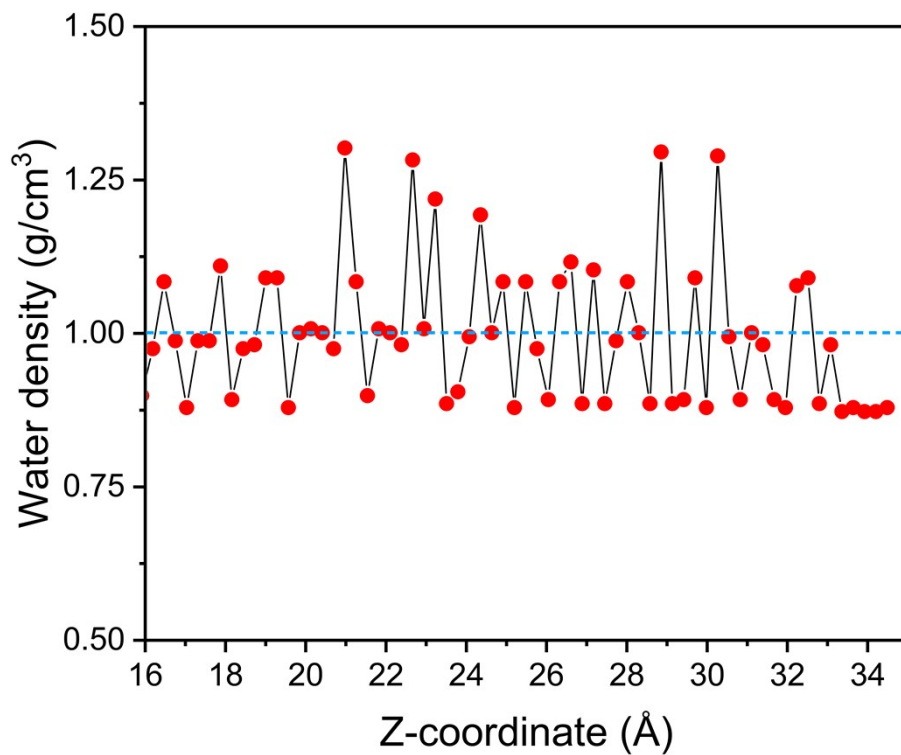
Figure S5. Water density along the z-axis of the water adsorption layers on Au_{25} NC during the structural relaxations. The 1-D density profiles of water were plotted by using the "Density Profile Tool" plugin implemented in VMD software.
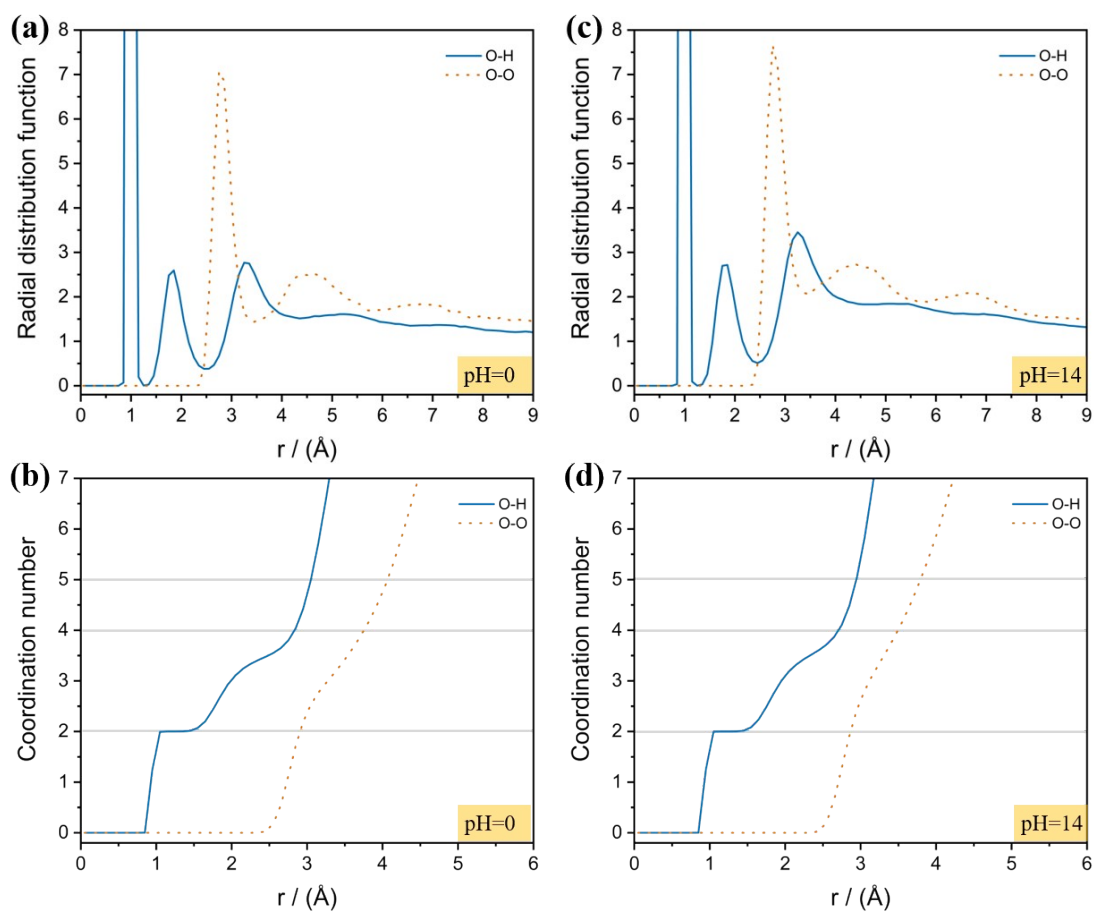
Figure S6. (a, b) Radial distribution function (RDF) and (c, d) integrated coordination number of O-O and O-H pairs of water from equilibrated AIMD trajectory in acid and alkaline system.
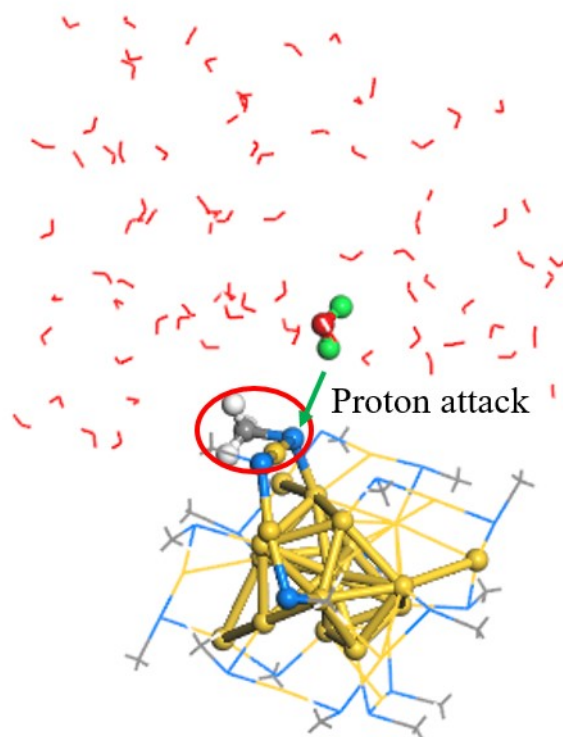
Figure S7. Schematic illustration for proton attack. Most protecting motifs and water molecules are shown in line mode.
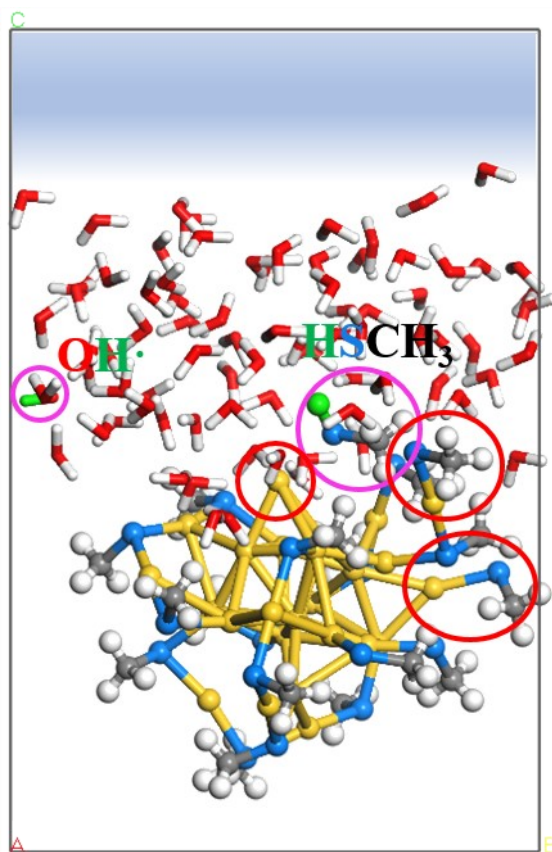
Figure S8. Representative AIMD snapshot of the Au_{25}/H_2O interface at U_{RHE}= -1.10 V for an alkaline system.
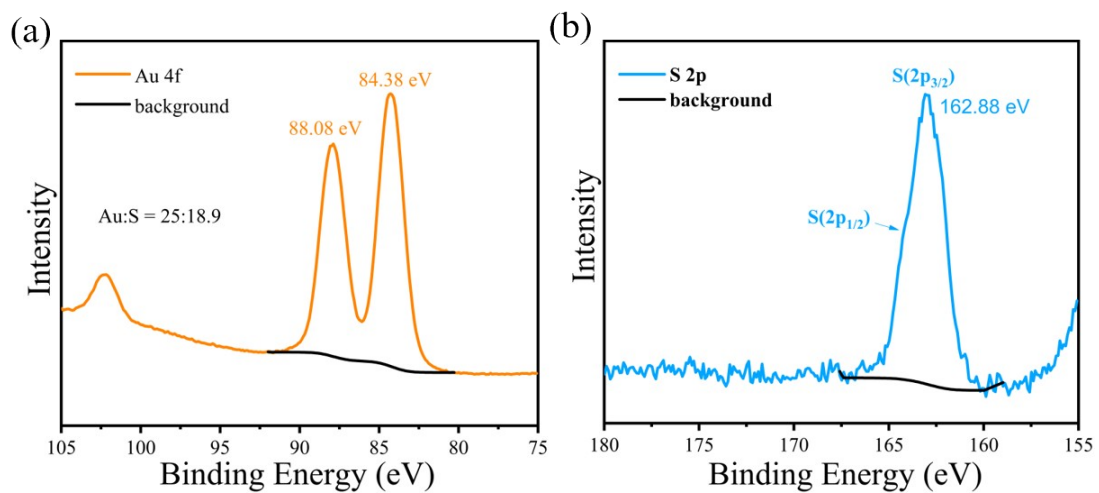
Figure S9. XPS spectra of Au$_{25}$(SR)$_{18}$. The core-level XPS spectra of the Au 4f (a) and S 2p (b) levels.
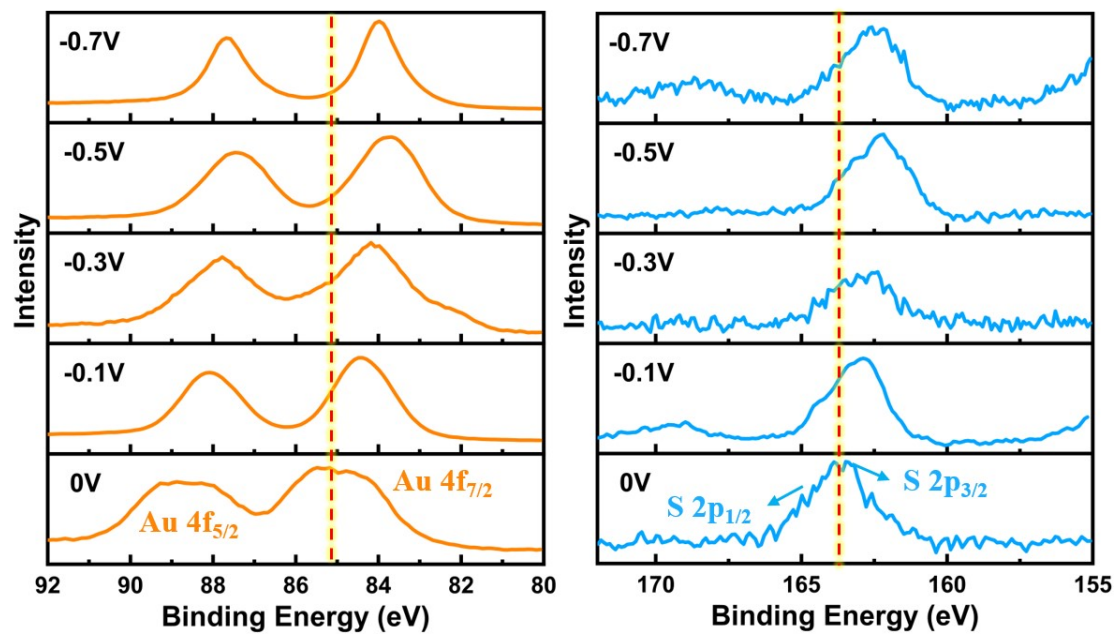
Figure S10. XPS spectra of Au_{25} in neutral medium after 1 h reaction at different potentials. The core level XPS spectra of the Au 4f and S 2p levels.
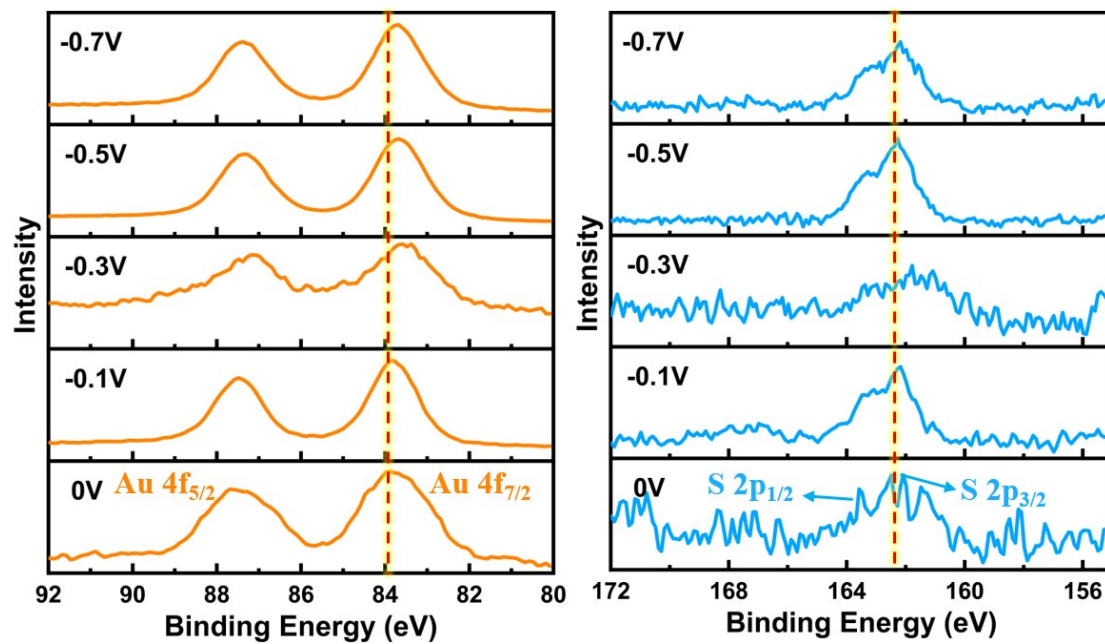
Figure S11. XPS spectra of Au_{25} in alkaline medium after 1 h reaction at different potentials. The core-level XPS spectra of the Au 4f and S 2p levels.
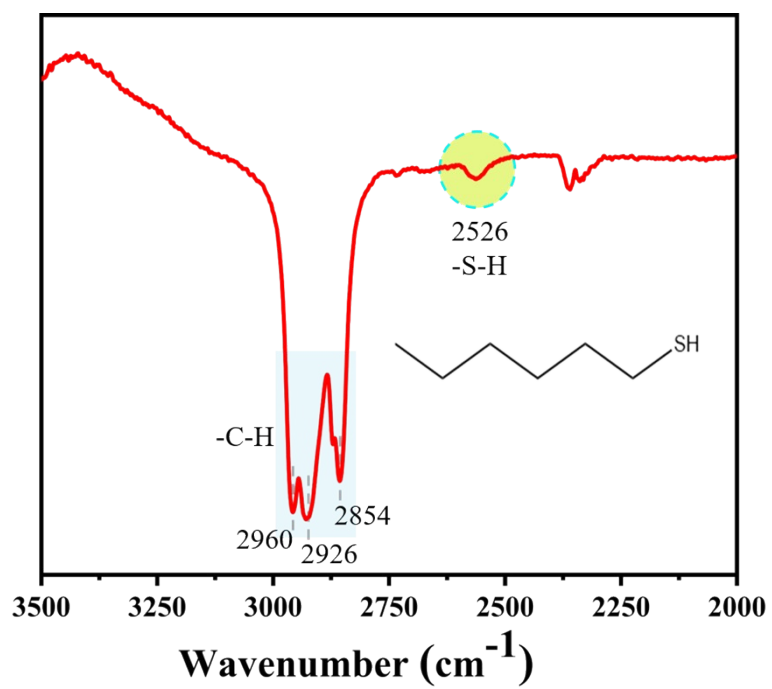
Figure S12. Fourier transform infrared spectrum of hexyl mercaptan.

Table S1. Bader charge analysis on Au atom at different potentials based on the AIMD simulations for the acid system and alkaline system. Orange highlights the Bader charge of naked under-coordinated Au atoms.

Atom	pH=0, -0.1V	pH=0, -0.44V	pH=0, -0.63V	pH=14, 0.05V	pH=14, -0.36V	pH=14, -0.88V
Au^1	0.04	0.02	0.00	0.03	0.02	0.00
Au^2	0.04	0.04	0.03	0.04	0.02	0.01
Au^3	0.05	0.03	0.01	0.05	0.04	0.04
Au^4	0.04	0.01	0.01	0.05	0.01	0.01
Au^5	0.01	0.01	0.04	0.02	0.04	0.01
Au^6	0.07	0.04	0.07	0.08	0.07	0.05
Au^7	0.07	0.06	0.04	0.07	0.03	0.00
Au^8	0.06	0.06	0.04	0.07	0.05	0.05
Au^9	0.09	-0.04	-0.08	0.15	-0.02	-0.17
Au^{10}	0.05	0.05	0.03	0.05	0.03	0.03
Au^{11}	0.07	0.05	0.06	0.08	0.06	0.06
Au^{12}	0.08	0.06	0.07	0.04	0.08	0.03
Au^{13}	0.03	0.03	0.01	0.04	0.00	0.00
Au^{14}	0.03	0.06	0.02	0.05	0.04	0.02
Au^{15}	0.05	0.00	0.01	0.04	0.01	0.01
Au^{16}	-0.08	-0.10	-0.27	0.01	-0.13	-0.14
Au^{17}	0.02	0.03	0.02	0.01	0.01	0.02
Au^{18}	0.05	0.09	0.06	0.06	0.06	0.04
Au^{19}	0.07	0.07	0.05	0.09	0.04	0.06
Au^{20}	0.08	0.03	0.05	0.07	0.06	0.03
Au^{21}	0.09	0.06	0.06	0.09	0.06	0.06
Au^{22}	0.07	0.03	0.04	0.04	0.03	0.00
Au^{23}	0.06	0.05	0.04	0.07	0.04	0.04
Au^{24}	0.08	0.06	0.07	0.06	0.05	0.03
Au^{25}	0.04	0.08	0.05	0.05	0.06	0.01