

## Supporting Information

### Theoretical Investigation of Single-Atom Catalysts Anchored on Pure Carbon Substrate for Electroreduction of NO to NH<sub>3</sub>

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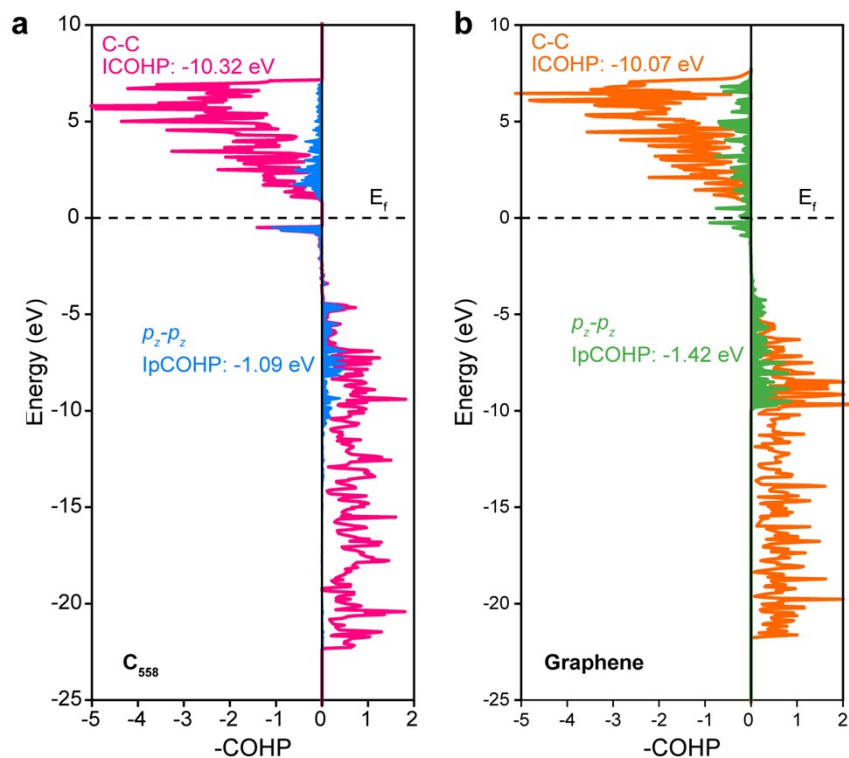
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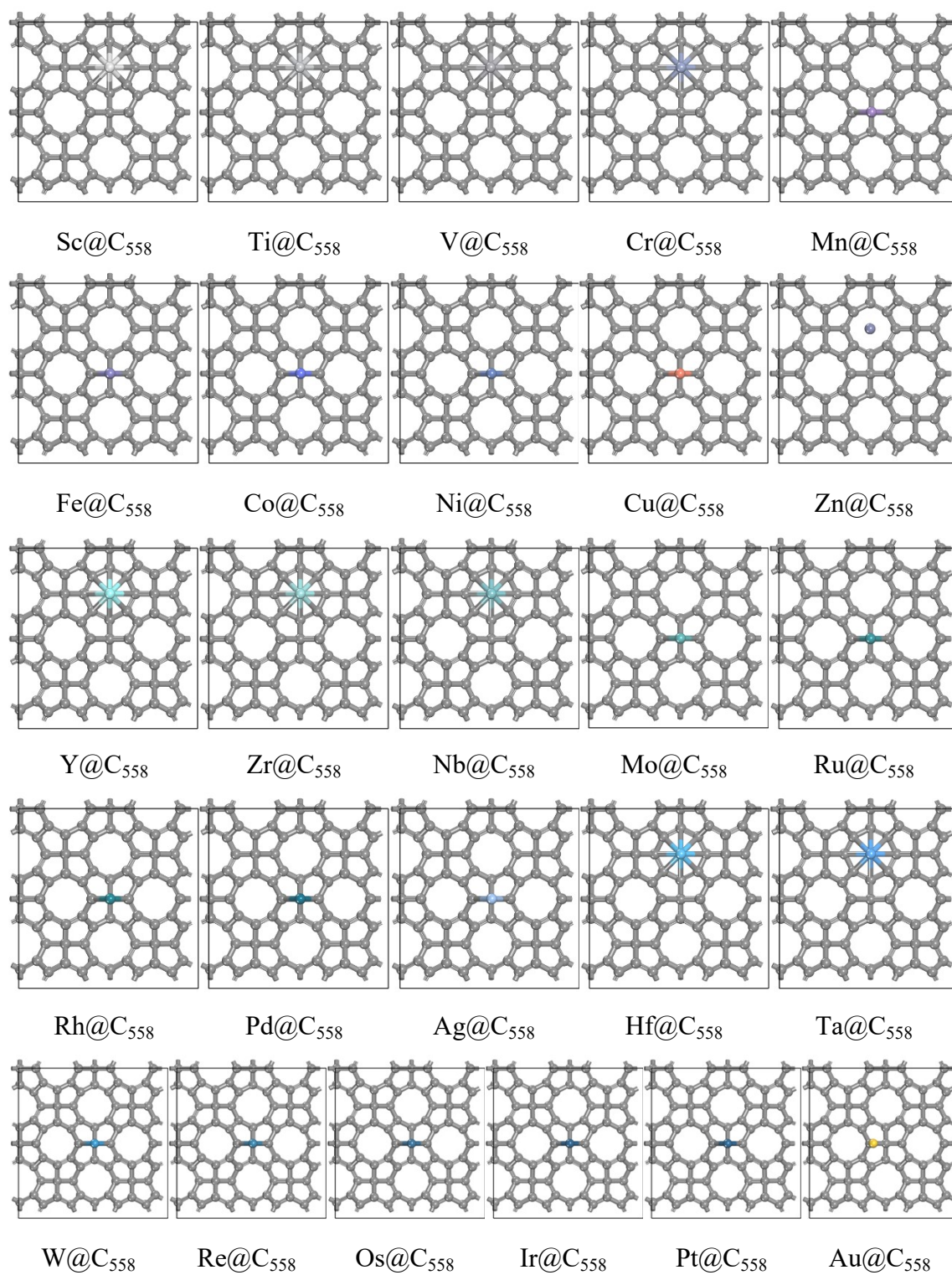
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**Table S1.** Calculated zero-point energies and entropies of key adsorbed intermediates.

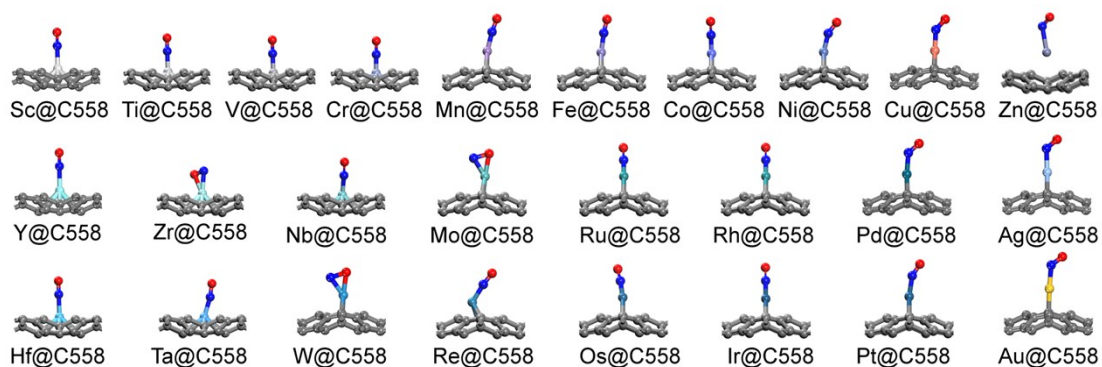
Intermediates	ZPE (eV)	TS (eV)
*NO	0.17	0.18
*NHO	0.46	0.20
*N*OH	0.46	0.15
*NHOH	0.78	0.23
*NH <sub>2</sub> O	0.80	0.22
*NH*OH	0.71	0.20
*NH <sub>2</sub> OH	1.09	0.16
*NH <sub>2</sub> *OH	1.01	0.20
*NH <sub>2</sub>	0.65	0.16
*NH <sub>3</sub>	1.02	0.15
*OH	0.33	0.14



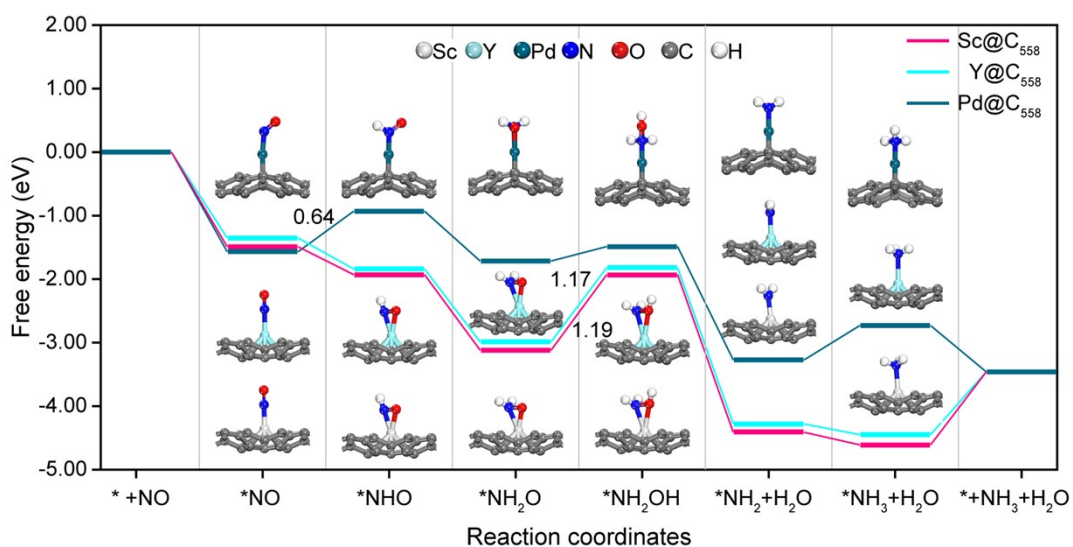
**Figure S1.** The crystal orbital overlap population (COHP) analysis of C-C bonds in octagonal rings of  $C_{558}$  and graphene. The contribution of  $p_z$  orbitals to the C-C bond is also shown.  $E_f$  means the Fermi level and is set to be 0 eV. The bonding and antibonding contributions are shown on the right and left of the line  $x = 0$ , respectively. The values of integrated COHP (ICOHP, in eV) of the C-C bonds and integrated projected COHP (lpCOHP, in eV) of the  $p_z-p_z$  orbitals are listed.



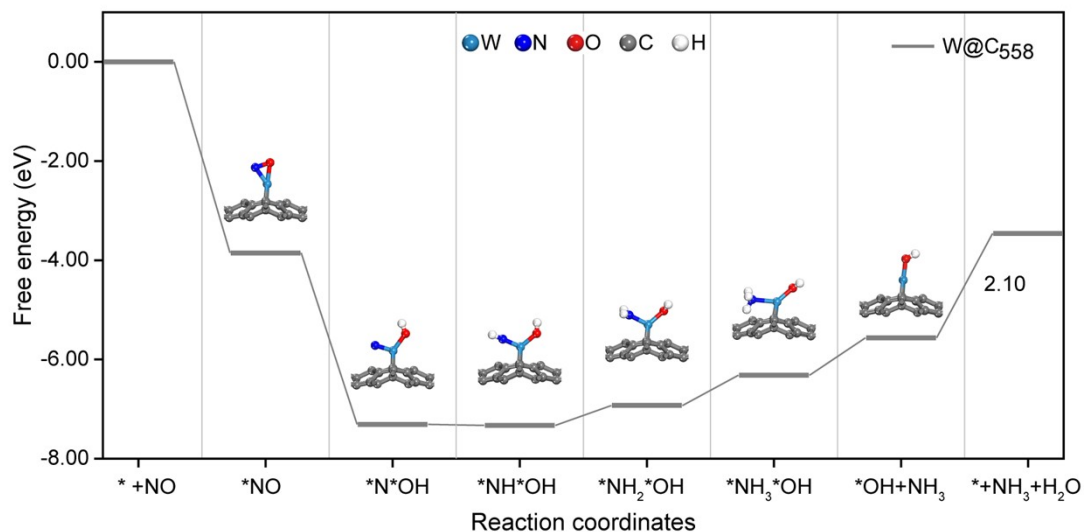
**Figure S2.** The most stable structures of 26 transition metal atoms anchored on  $C_{558}$ .



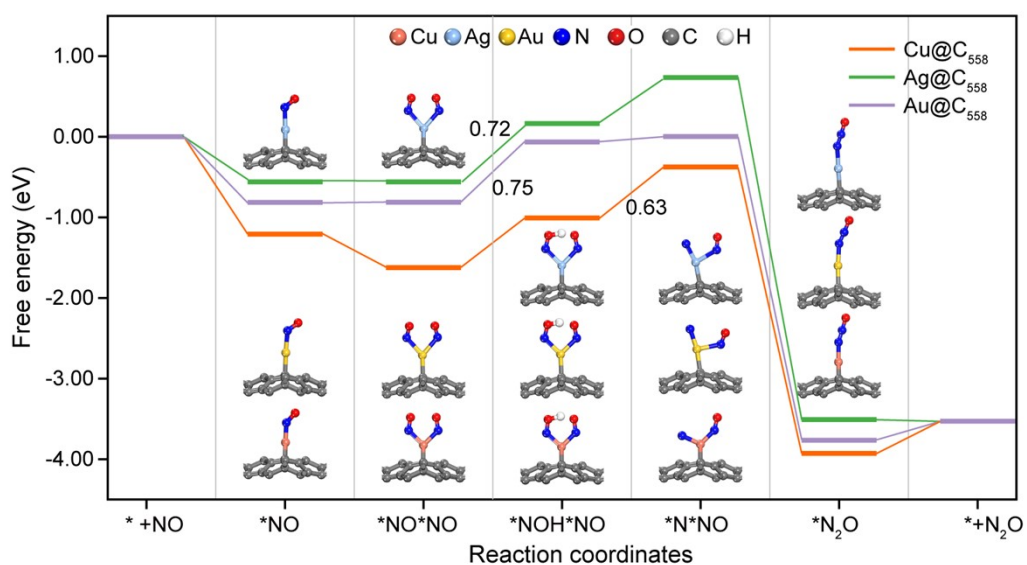
**Figure S3.** The favorable adsorption configurations of NO adsorbed on transition metal sites of 26 single-atom catalysts.



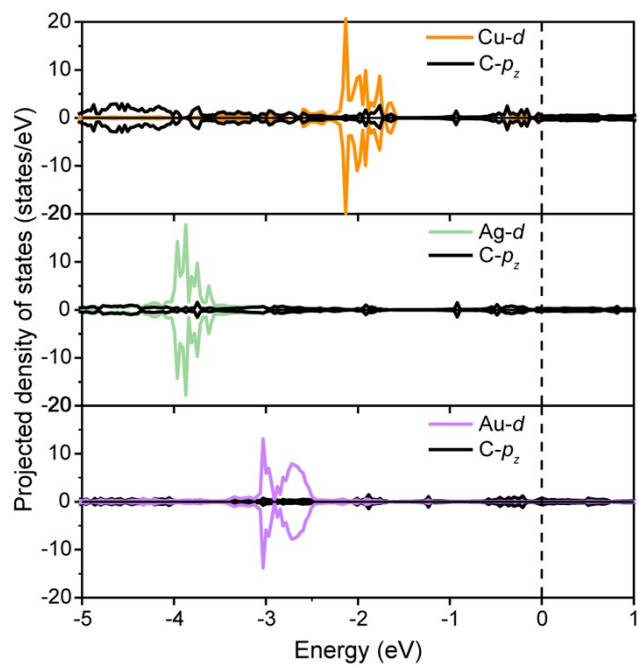
**Figure S4.** Free energy diagrams of the NOER on Sc- and Y- and Pd@C<sub>558</sub> via the most favorable reaction pathways. The free energy changes of potential determining steps are labelled.



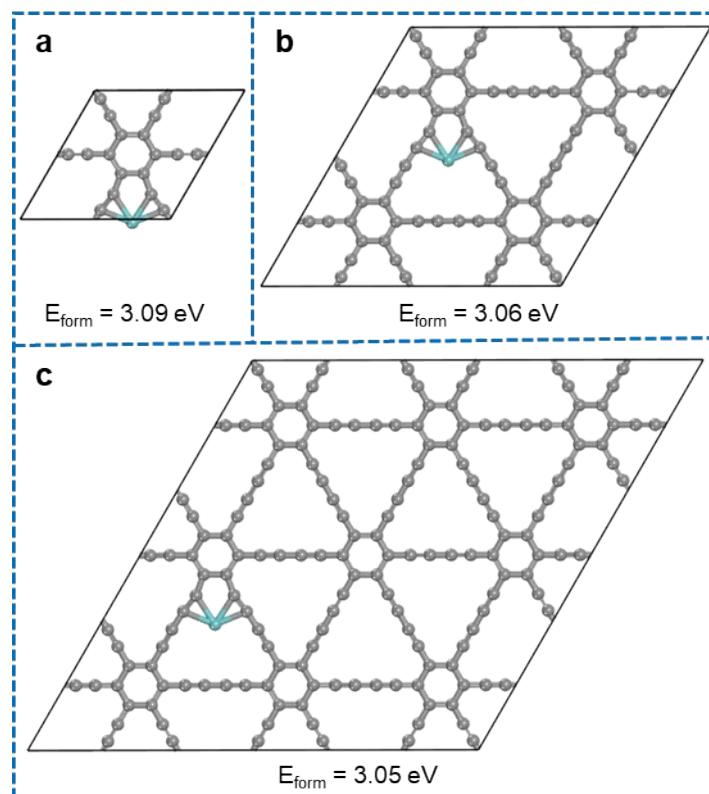
**Figure S5.** The lowest free energy diagram of NOER on  $W@C_{558}$ . The free energy change of the potential determining step is labelled.



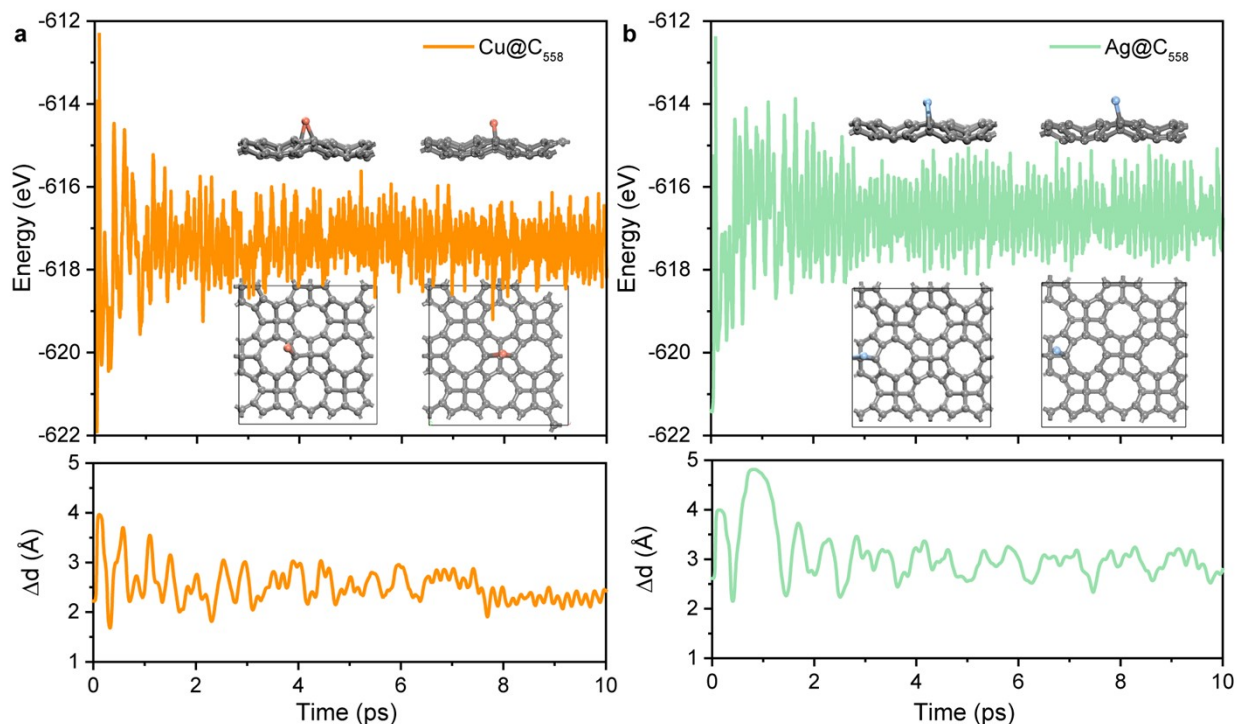
**Figure S6.** Reaction pathways of NOER to  $N_2O$  on Cu-, Ag- and Au@ $C_{558}$ . The free energy changes of potential determining steps are labelled.



**Figure S7.** Projected density of states of  $d$  orbital of Cu, Ag and Au and  $p_z$  orbitals of their neighboring carbon atoms in Cu, Ag and Au @C<sub>558</sub>. The Fermi energy is set as zero and marked with the dashed line.



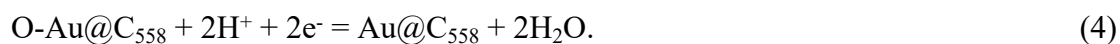
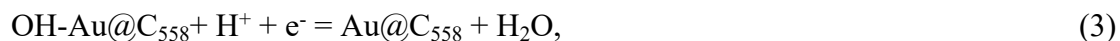
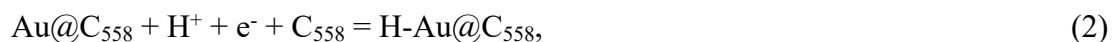
**Figure S8.** The most stable structures of single-atom Mo located on (a)  $(1 \times 1)$ , (b)  $(2 \times 2)$  and (c)  $(3 \times 3)$  graphdiyne supercells. The carbon and Mo atoms are drawn with gray and baby blue balls. The formation energy,  $E_{\text{form}}$ , is also listed.



**Figure S9.** The ab initio molecular dynamics simulation of (a) Cu- and (b) Ag@C<sub>558</sub> at 500 K. The inset pictures are structures of Cu- and Ag@C<sub>558</sub> at the 5 ps (left) and 10 ps (right) of AIMD simulation from the side and top views. The lower pictures show the distances ( $\Delta d$ , Å) between the carbon substrate and the Cu and Ag atom in Cu- and Ag@C<sub>558</sub> during the AIMD at 500 K. The  $z$ -coordinates of all the carbon atoms are averaged as the position of the carbon layer.

### The surface Pourbaix picture

The following electrochemical steps on Au@C<sub>558</sub> were considered to build the surface Pourbaix picture:



In the equation (1), the Au metal dissolution potential from the carbon substrate was analyzed according to the reported method (Dobrota et al. *Electrochim. Acta*, 2017, 250, 185-195.), where a hypothetical electrochemical cell was taken: one electrode was



the metallic Au with the other one was Au@C<sub>558</sub>. The electromotive forces for the equation (2) to (4) were calculated as  $E = -\Delta G/nF$ , where  $\Delta G$  was the free energy changes,  $n$  was the number of electrons transferred in the reaction and  $F$  was the Faraday constant. To obtain the surface Pourbaix picture, the relation between applied potential,  $E$ , and pH was analyzed as:

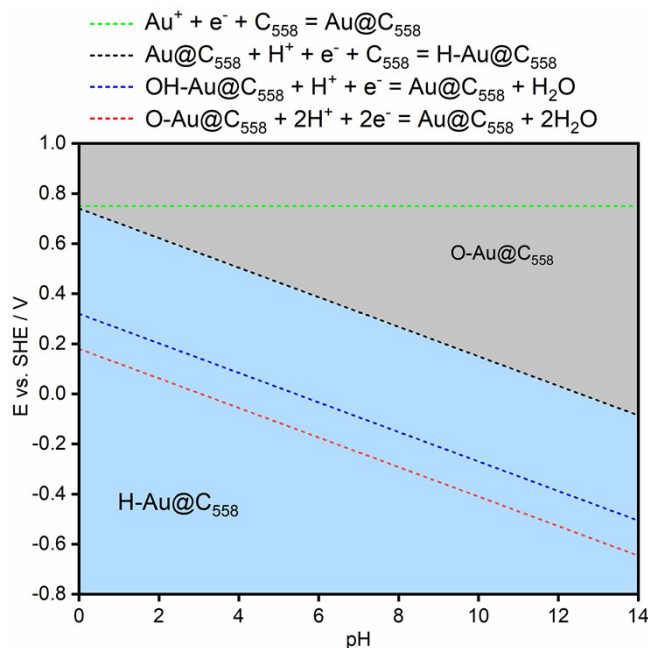
$$E(\text{Au}^+/\text{Au}@C_{558}) = E^0(\text{Au}^+/\text{Au}@C_{558}) - 0.059 * \log(\text{Au}^+) \quad (5)$$

$$E(\text{Au}@C_{558}/\text{H-Au}@C_{558}) = E^0(\text{Au}@C_{558}/\text{H-Au}@C_{558}) - 0.059 * \text{pH} \quad (6)$$

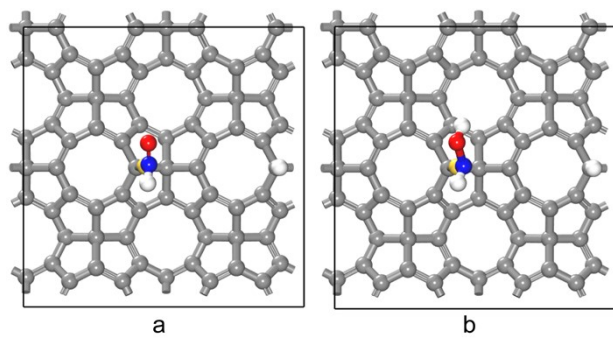
$$E(\text{OH-Au}@C_{558}/\text{Au}@C_{558}) = E^0(\text{OH-Au}@C_{558}/\text{Au}@C_{558}) - 0.059 * \text{pH} \quad (7)$$

$$E(\text{O-Au}@C_{558}/\text{Au}@C_{558}) = E^0(\text{O-Au}@C_{558}/\text{Au}@C_{558}) - 0.059 * \text{pH} \quad (8)$$

The activity of Au<sup>+</sup> was set as  $1 \times 10^{-8}$  mol/L at T = 298 K. The metal dissolution potential was not correlated with pH and was parallel to the pH axis (Figure S10).



**Figure S10.** The surface Pourbaix picture for Au@C<sub>558</sub>. The dashed lines exhibit the values for the equilibrium potentials for reactions listed on the top of the picture. The stable phases are labelled on the pictures. The activity of Au<sup>+</sup> was set as  $1 \times 10^{-8}$  mol/L at T = 298 K.



**Figure S11.** Structures of (a) \*NHO and (b) \*NHOH on the Au@C<sub>558</sub> with the presence of \*H on the C<sub>558</sub> substrate.