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Molecular and dissociative O_2 adsorptions on the $Cu_2O(111)$ surface

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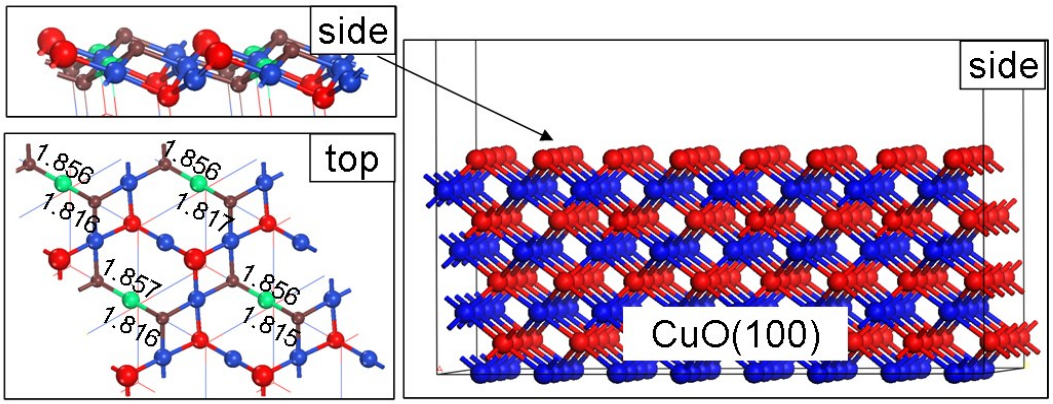
Fig. S1 (a) Most stable configuration of four O_2 adsorption on the $Cu_2O(111)$ surface and (b) CuO(100) surface. (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball.).



(a) 4 O_2 (b) CuO(100)

Fig. S2 Least stable configurations of one O_2 adsorption on the $Cu_2O(111)$ surface. (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

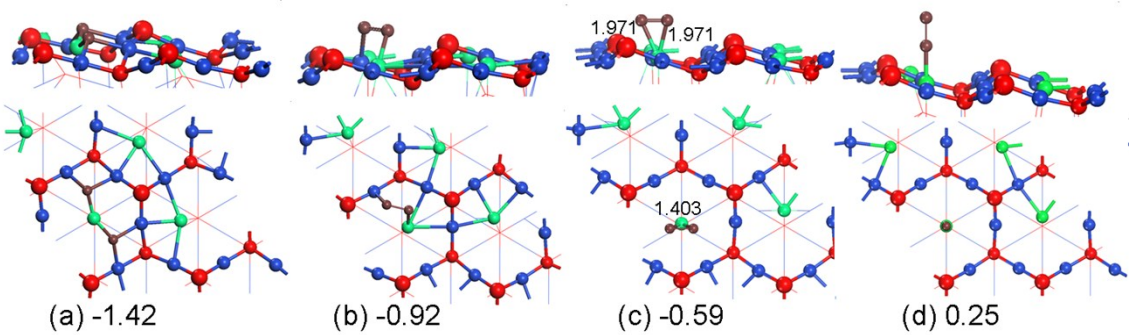


Fig. S3 Least stable configurations of the two O_2 adsorption on the $Cu_2O(111)$ surface (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

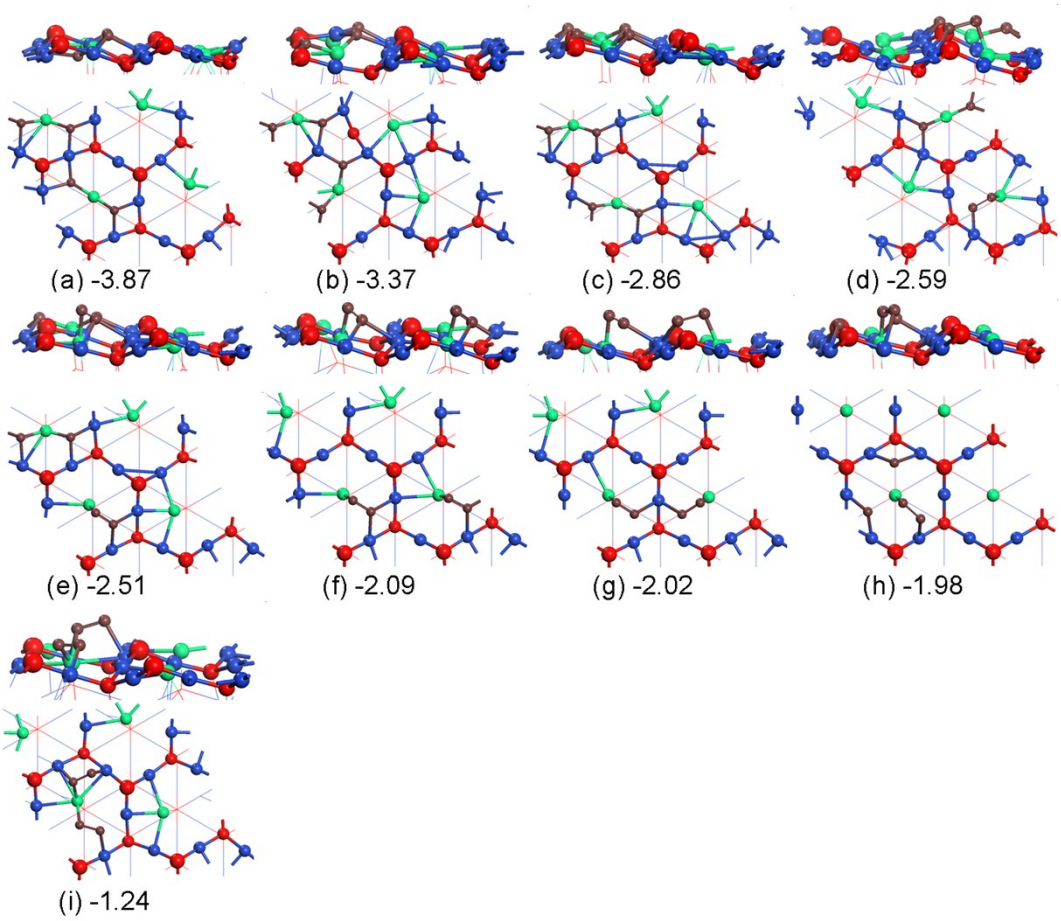


Fig. S4 Metastable configurations of the three O_2 adsorption on the $Cu_2O(111)$ surface. (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

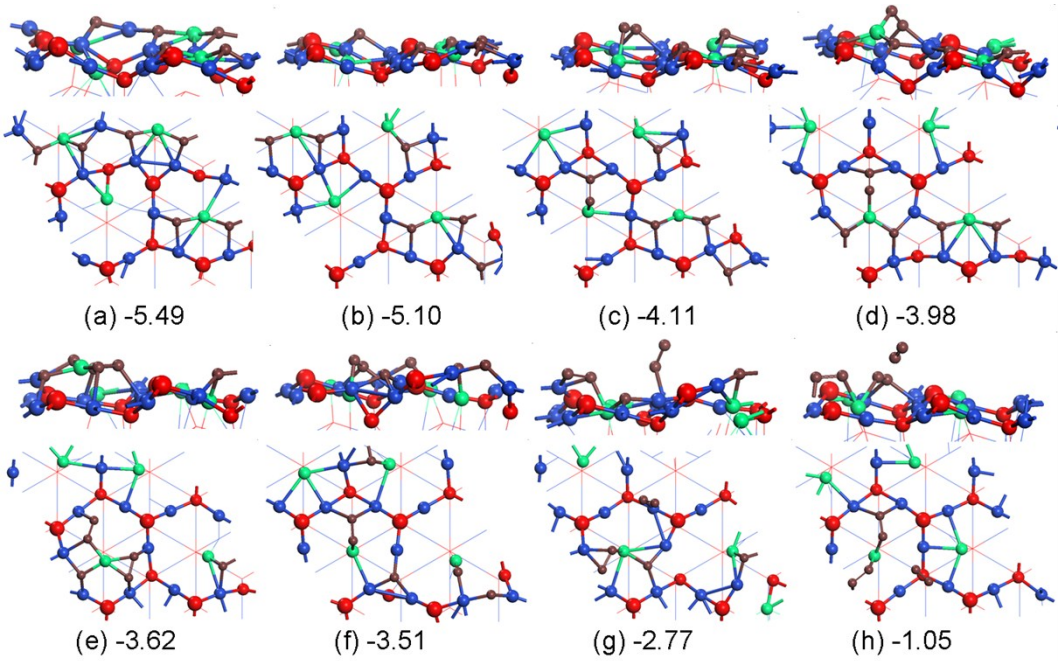


Fig. S5 Metastable configurations of the four O_2 adsorption on the $Cu_2O(111)$ surface (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

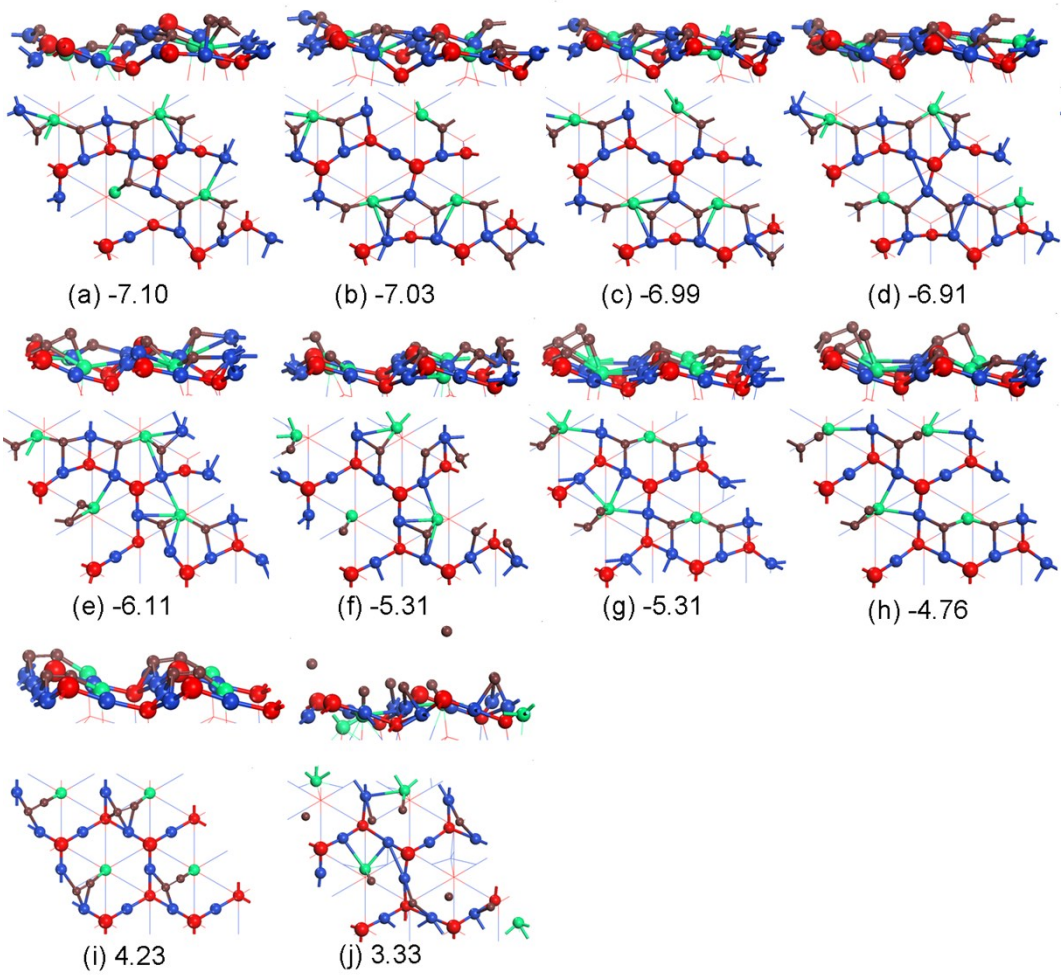


Fig. S6 Metastable configurations of the five O_2 adsorption on the $Cu_2O(111)$ surface (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

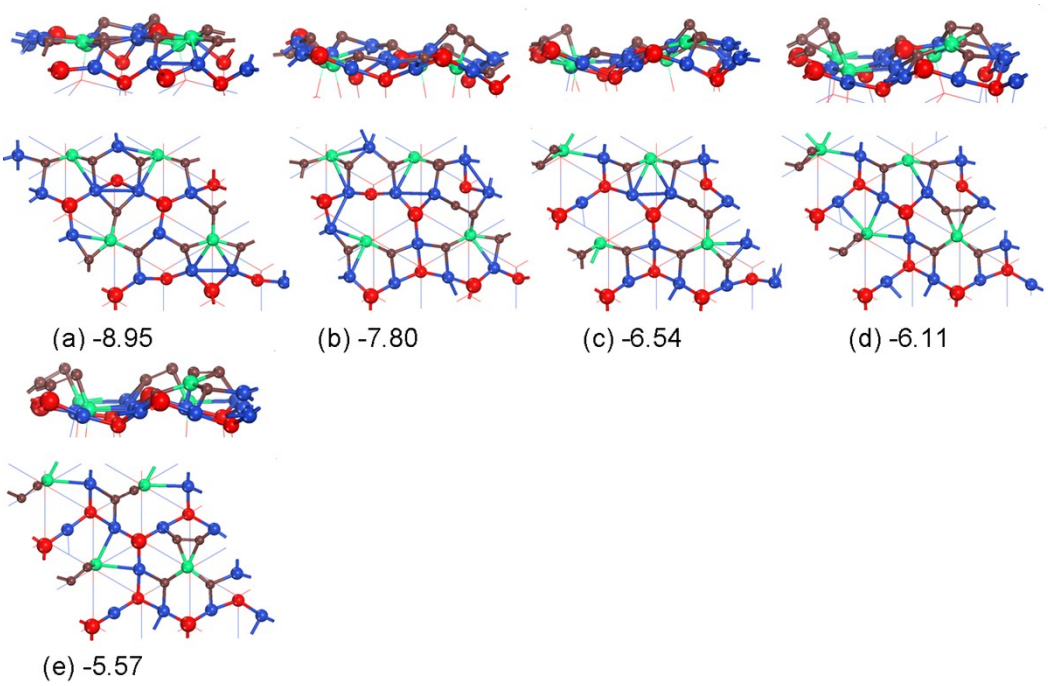


Fig. S7 Metastable configurations of the six O_2 adsorption on the $Cu_2O(111)$ surface (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).

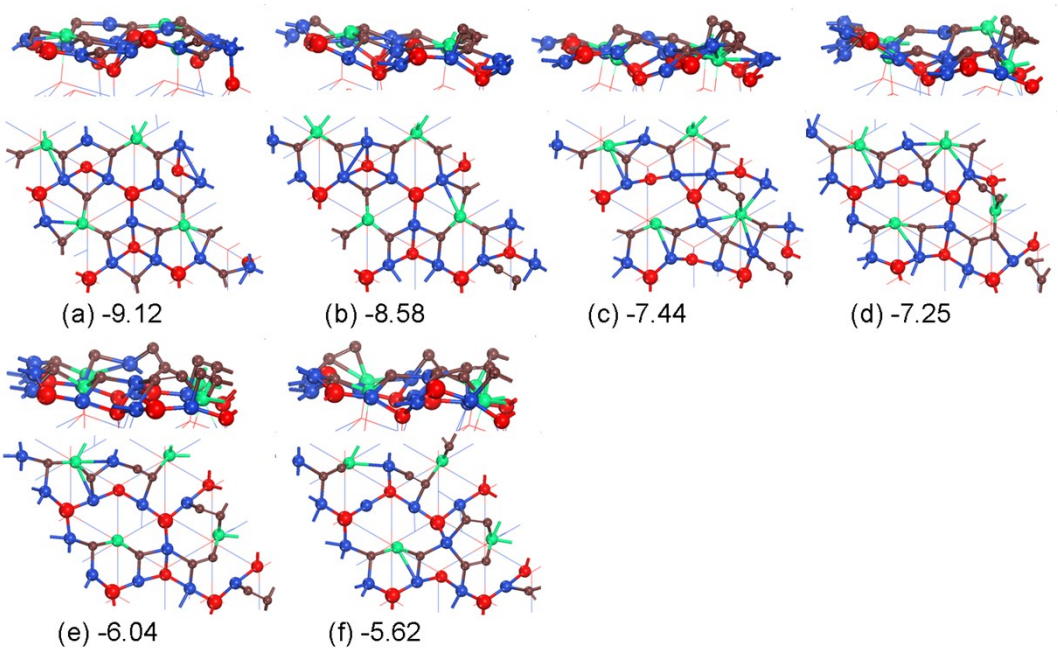
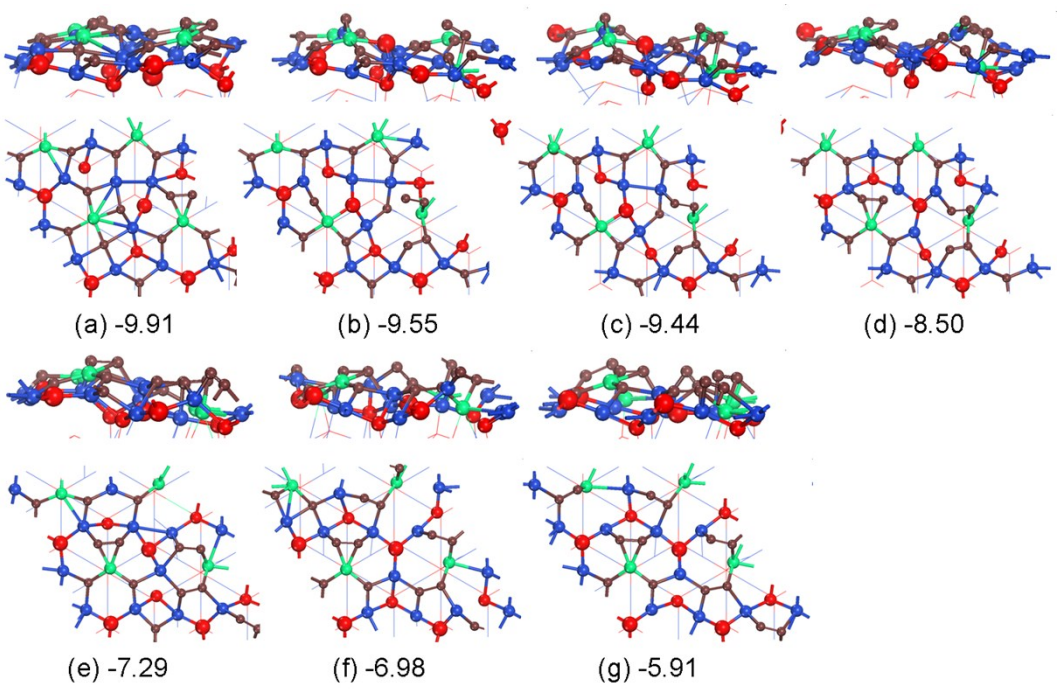


Fig. S8 Metastable configurations of the seven O_2 adsorption on the $Cu_2O(111)$ surface (coordinated saturated Cu atoms in blue ball, coordinated unsaturated Cu atoms in green ball, first layer coordinated unsaturated O atoms in big red ball, third coordinated saturated O atoms in red ball, O atoms of adsorbed O_2 in small brown ball. Adsorption energies in eV).



The full description of Boltzmann statistics and atomistic thermodynamics is shown as follows.

According to atomic thermodynamics, the Gibbs free energy (ΔG) of $n$$O_2$ adsorption on the $Cu_2O(111)$ surface is chosed as the criterion and defined as:

$$\Delta G^{ads}_{Cu_2O}(T,P,nO_2) = G[nO_2/\mathrm{Cu_2O(111)}] - G[\mathrm{Cu_2O(111)}] - nG_{O_2}(T,p_{O_2}) \quad (1)$$

where $G[nO_2/\mathrm{Cu_2O(111)}]$, $\mathrm{G[Cu_2O(111)]}$ and $\mathrm{G}_{O_2}(T,p_{O_2})$ are the Gibbs free energies of adsorbed system, support and adsorbates, respectively, n is number of adsorbed O_2 molecules, T is the temperature, p_{O_2} is the partial pressure of O_2 in the gas atmosphere. It is clear that a more

negative ΔG indicates the more stable adsorption structure. We can write $G_{O_2}(T, p_{O_2})$ as:

$$G_{O_2}(T, p_{O_2}) = E_{O_2}^{\text{total}} + \mu_{O_2}(T, p^0) + k_B T \ln(p / p^0) \quad (2)$$

where $E_{O_2}^{\text{total}}$ is the total enery of O_2 molecules including zero point vibration energy, $\mu_{O2}(T, p^0)$ term includes vibrational and rotational contributions for O_2 gas, and can be taken from tables of thermodynamic data [1]. $k_B T \ln(p / p^0)$ is the contribution of temperature and O_2 partial pressure to the H_2 chemical potential and k_B is the Boltzmann constant. The vibration contribution of the $Cu_2O(111)$ surface with adsorbed O_2 was included in the DFT-calculated total energy to substitute the Gibbs free energies of the solid surface since frequency motions of the surface slab have a large entropy contribution to the surface. Then, equation (1) can be rewritten as:

$$\Delta G_{Cu_2O}^{ads}(T, P, nO_2) = G[nO_2/\mathrm{Cu_2O}(111)] - E[\mathrm{Cu_2O}(111)] - nG_{O_2}(T, p_{O_2}) \quad (3)$$

Inserting equation (2) into (3), we can derive:

$$\Delta G_{Cu_2O}^{ads}(T, P, nO_2) = G[nO_2/\mathrm{Cu_2O}(111)] - E[\mathrm{Cu_2O}(111)] - nE_{O_2}^{\text{total}} - n\mu_{O_2}(T, p^0) - nk_B T \ln(p / p^0) \quad (4)$$

Each adsorption configutation has a probability of occurrence, P_m, which is a function of the temperature: $P_m = 1/Z\exp[-\Delta E/(k_B T)]$, where Z is the canonical partition function, ΔE is the adsorption energy of a single O_2 adsorption on the $Cu_2O(111)$ surface, and k_B is the Boltzmann constant, respectively.

References:

(1) Stull, D. R.; Prophet, H. *JANAF thermochemical tables*, DTIC Document, 1971.