Molecular and dissociative O\textsubscript{2} adsorptions on the Cu\textsubscript{2}O(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.).
Fig. S2 Least stable configurations of one O₂ adsorption on the Cu₂O(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 O₂ in small brown ball. Adsorption energies in eV).
**Fig. S3** Least stable configurations of the two O$_2$ adsorption on the Cu$_2$O(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$_2$O(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\(_2\)O(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$_2$O(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 $\text{O}_2$ adsorption on the Cu$_2$O(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$_2$O(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 ($\Delta G$) of $n$O$_2$ adsorption on the Cu$_2$O(111) surface is chose as the criterion and defined as:

$$
\Delta G_{\text{ads}}^{\text{Cu}_2\text{O}}(T, P, n\text{O}_2) = G[n\text{O}_2/\text{Cu}_2\text{O}(111)] - G[\text{Cu}_2\text{O}(111)] - nG_{\text{O}_2}(T, p_{\text{O}_2})
$$

(1)

where $G[n\text{O}_2/\text{Cu}_2\text{O}(111)]$, $G[\text{Cu}_2\text{O}(111)]$ and $G_{\text{O}_2}(T, p_{\text{O}_2})$ are the Gibbs free energies of adsorbed system, support and adsorbates, respectively, $n$ is number of adsorbed O$_2$ molecules, $T$ is the temperature, $p_{\text{O}_2}$ is the partial pressure of O$_2$ in the gas atmosphere. It is clear that a more
negative $\Delta G$ indicates the more stable adsorption structure. We can write $G_{O_2}(T, p_{O_2})$ as:

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

(2)

where $E_{O_2}^{total}$ is the total energy of $O_2$ molecules including zero point vibration energy, $\mu_{O_2}(T, p^0)$ term includes vibrational and rotational contributions for $O_2$ gas, and can be taken from tables of thermodynamic data. $k_B T \ln(p / p^0)$ 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 large entropy contribution 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:

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

(3)

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

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

(4)

Each adsorption configuration 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, $\Delta E$ 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: