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Supporting Information

Spatial charge separation and high-index facet dependence in polyhedral Cu_2O type-II surface heterojunctions for photocatalytic activity enhancement

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Experimental Section

Computational details. Utilizing the projected augmented wave (PAW) method to study density functional calculations, executed in the Vienna *ab* initio simulation package (VASP) code.[1] The exchange-correlation functional adopted the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE).[2] In order to minimize the interaction between adjacent slabs, the periodic boundary condition with a vacuum space of 15 Å was used. The kinetic energy cutoff was programmed to be 400 eV. Monkhorst–Pack uncommon k-point meshes[3] of 3×3×1 and 1×2×1 was recommended to {001} and {332} facets in the optimization process, while 7×7×1 and 3×7×1 were embraced by DOS calculations.

The surface free energy of Cu_2O {111} and {332} facets was calculated by ab initio thermodynamic approach, according to the surface linking with an oxygen atmosphere, which was described by an oxygen pressure, *p*, and temperature, *T*. Since surface system is modeled by symmetrical slabs with two equivalent surfaces, the surface free energy at given (T, p) can be expressed as:

$$\gamma_{\mathrm{sur}f}(T,p)=\frac{1}{2A}[G_{slab}(T,p,N_{Cu},N_O)-N_{Cu}\mu_{Cu}(T,p)-N_O\mu_O(T,p)] \qquad (1)$$

Here, A is the area exposed to a unit cell, G_{slab} is the Gibbs free energy of the slab, μ_{Cu} and μ_O are the chemical potentials of copper and oxygen, while N_{Cu} and N_O are the number of Cu and O atoms. Thermodynamically the surface with the lowest $\gamma_{\mathrm{surf}}(T,\mathrm{p})$ under certain conditions (T, p) corresponds to the most stable surface.

It has been proved in eq (1)[4,5] that Gibbs free energies of solids can be expressed as a first approximation total energies. Thus $\gamma_{\mathrm{surf}}(T,\mathrm{p})$ can be approximated by:

$$\gamma_{\text{surf}}(T,p) \approx \frac{1}{2A}\left[E_{slab} - \frac{N_{Cu}}{2}E^{bulk}_{Cu_2O} - \Delta N^{stoich}_{O}\mu_O(T,p)\right] \tag{2a}$$

where

$$\Delta N^{stoich}_{O} = (N_O - \frac{N_{Cu}}{2}) \text{ and} \tag{2b}$$

$$E^{bulk}_{Cu_2O} \approx 2\mu_{\text{Cu}}(T,p) + \mu_O(T,p). \tag{2c}$$

The E_{slab} and $E^{bulk}_{\text{Cu}_2O}$ are total energies of the slab and of the formula unit of Cu_2O bulk, respectively. The ΔN^{stoich}_{O} is the number of excess O atoms.

Before establishing the function between oxygen chemical potential (μ_O) and $\gamma_{\text{surf}}(T,\text{p})$, the oxygen poor limit (O_{lean}) and oxygen rich limit (O_{rich}) should be considered. The O_{lean} can be regarded as μ_O corresponding to the decomposition of bulk Cu_2O into bulk Cu and O_2 gas, nevertheless at O_{rich} oxygen gas condenses on the surface. The O_{lean} and O_{rich} limits are determined by eqs (3a) and (3b), respectively.

$$\mu_O^{\min} = E^{\text{bulk}}_{\text{Cu}_2O} - E^{\text{bulk}}_{\text{Cu}} \text{ and } \mu^{\max}_{\text{Cu}} = E^{bulk}_{Cu} \tag{3a}$$

$$\mu_O^{\max} = \frac{1}{2}E_{O_2} \text{ and } \mu^{\min}_{\text{Cu}} = \frac{1}{2}\left[E^{bulk}_{Cu_2O} - \frac{1}{2}E_{O_2}\right] \tag{3b}$$

where E^{bulk}_{Cu} and E_{O_2} are total energies of Cu atom in the Cu-bulk and isolated O_2 molecule, respectively. Half the total energy of O_2 molecule is chosen as the zero reference for $\mu_O(p,T)$.

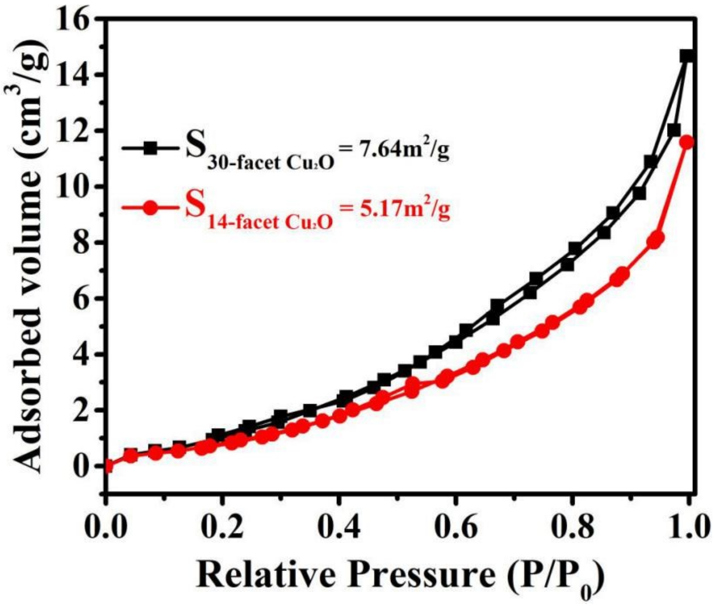

Fig. S1 N_2 adsorption/desorption isotherms for the 30-facet and 14-facet Cu_2O, respectively.

References

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