Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Reduction Mechanisms of the CuO(111) surface through surface oxygen vacancy formation and hydrogen adsorption

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The electronic supplementary information consists of the following:

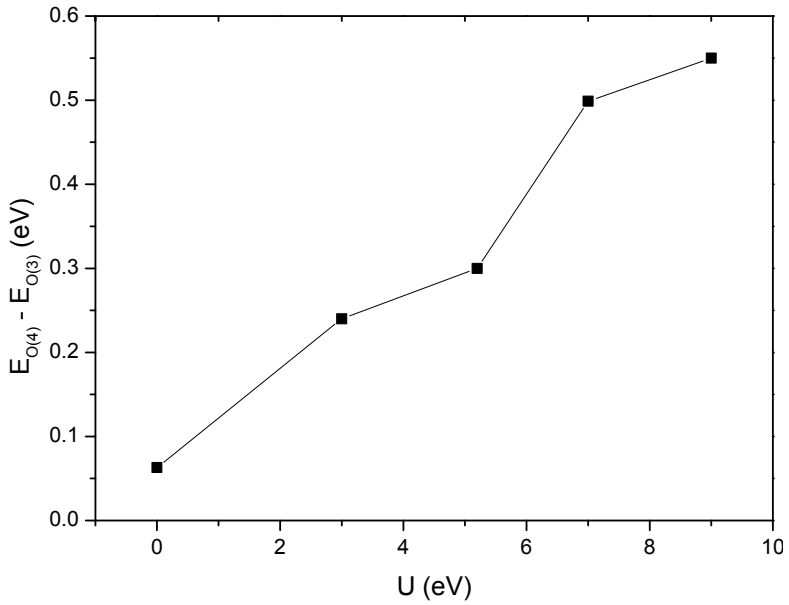


Figure S1. Energetic preference of $V_{O_3^{surf}}$ and $V_{O_4^{surf}}$ structure as the function of U.

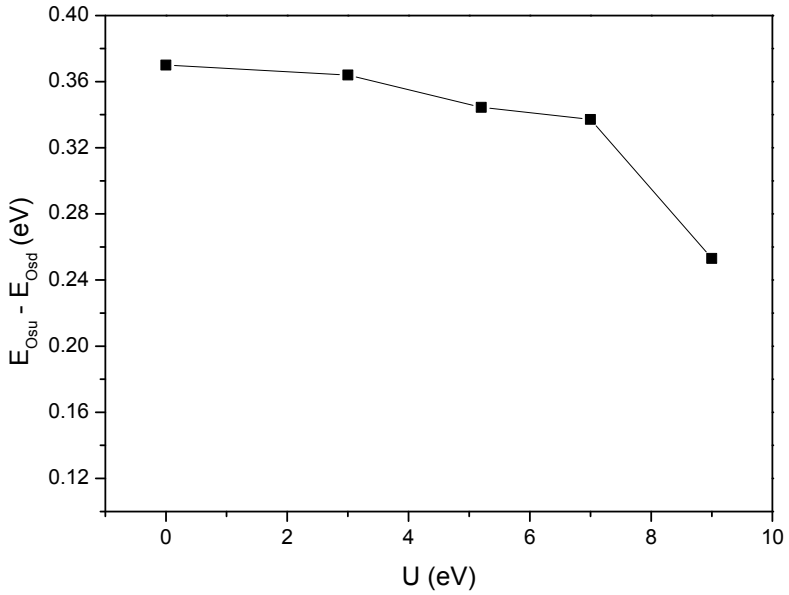


Figure S2 Energetic preference of surface $V_{O_3^{surf}}$ and sub-surface $V_{O_u^{sub}}$ structure as the function of U.

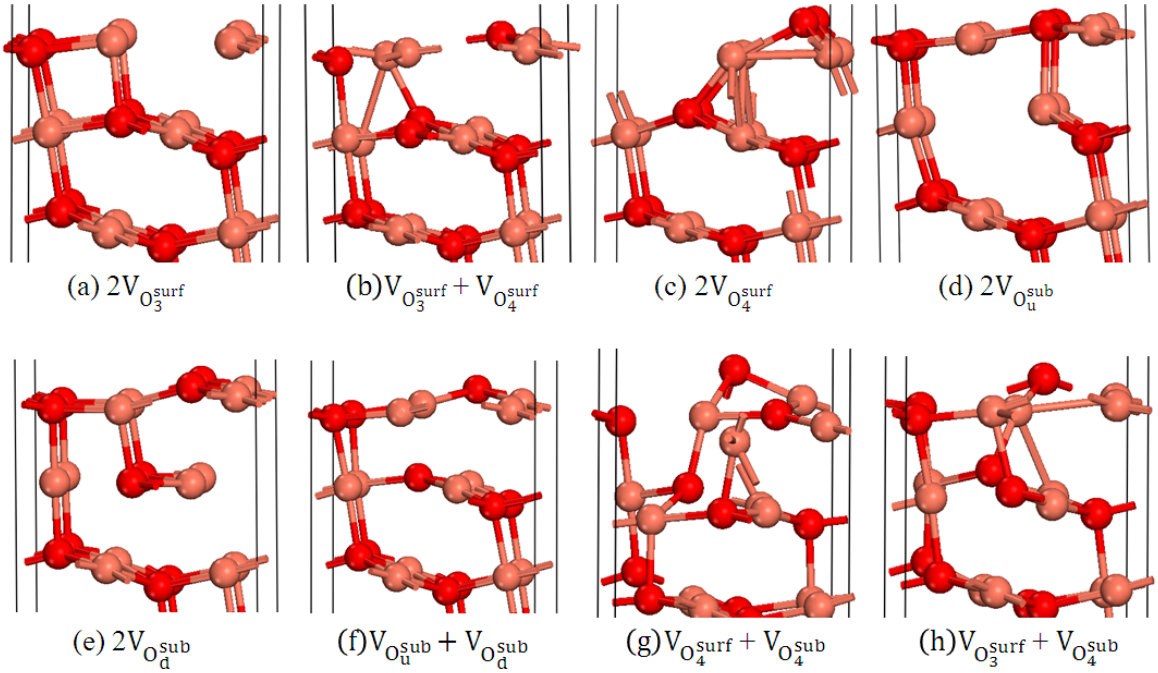


Figure S3. Optimized structures of CuO(111) with Θ=1/2.

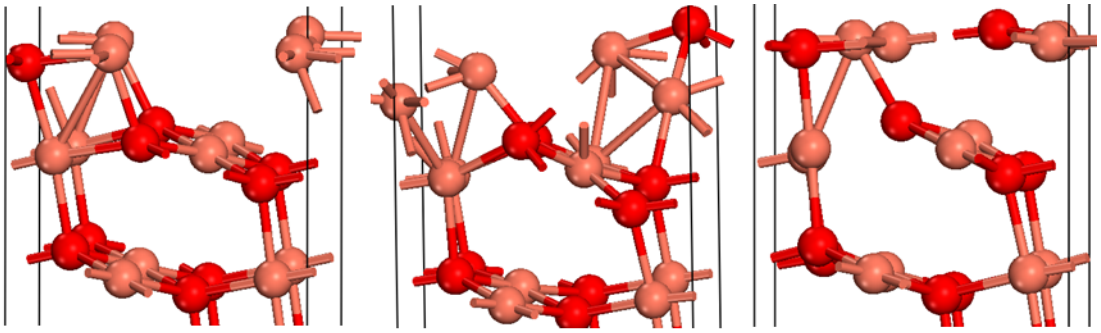
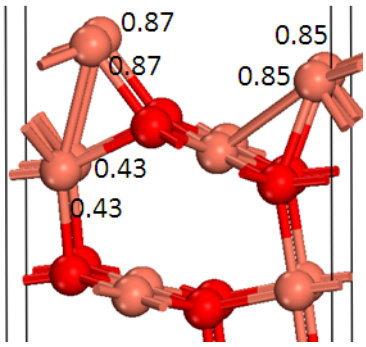


Figure S4. Optimized structures of CuO(111) with Θ=3/4.



(a) $2V_{O_3}^{surf} + 2V_{O_4}^{surf}$

Figure S5. Optimized structures of the $2\mathbf{V_{O_3}^{surf}} + \mathbf{2V_{O_4}^{surf}}$ structure with Θ=1 on the surface layer, The net Bader charge is given relative to the stoichiometric CuO(111) surface.

Table S1. The energies (ΔE) relative to the most stable structures of each coverage.

structure	ΔE(eV)
Θ=1/2	
$2V_{O_3}^{surf}$	2.03
$2V_{O_4}^{surf}$	2.11
$2V_{O_u}^{sub}$	0.69
$2V_{O_d}^{sub}$	1.98
$V_{O_3}^{surf} + V_{O_u}^{sub}$	1.26
$V_{O_4}^{surf.} + V_{O_d}^{sub}$	2.07
$V_{O_4}^{surf} + V_{O_u}^{sub}$	1.51
$V_{O_3}^{surf} + V_{O_d}^{sub}$	1.98
Θ=3/4	
$2V_{O_3}^{surf.} + V_{O_4}^{surf}$	1.09
$V_{O_3}^{surf.} + 2V_{O_4}^{surf}$	0.70
$V_{O_3}^{surf.} + V_{O_4}^{surf} + V_{O_u}^{sub}$	0.39
Θ=1	
$2V_{O_3}^{surf} + 2V_{O_4}^{surf}$	1.86