

# Density Functional Theory Study of Adsorption of Benzotriazole on Cu<sub>2</sub>O Surfaces

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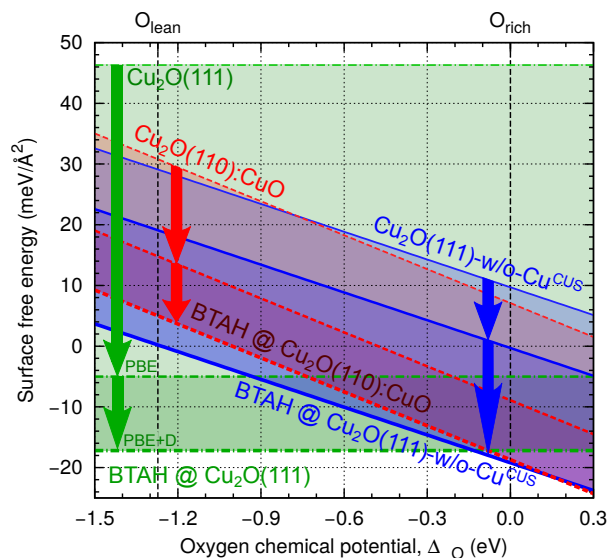
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## Supporting Information

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**Figure S1** Surface free energy,  $\gamma_{\text{surf}}$ , as a function of oxygen chemical potential and its stabilization due to molecular adsorption as calculated by PBE and PBE+D functionals.† For a given surface, the upper  $\gamma_{\text{surf}}$  line corresponds to a bare surface and the middle and bottom lines to a BTAH covered surface, i.e., middle line corresponds to PBE and bottom line to PBE+D calculated stabilization. This stabilization is also indicated by two consecutive vertical arrows: the first corresponds to PBE calculated adsorption stabilization and the second represents the stabilization due to dispersion correction.

### References and Notes

- (1) Peljhan, S.; Kokalj, A. DFT Study of Gas-Phase Adsorption of Benzotriazole on Cu(111), Cu(100), Cu(110), and Low Coordinated Defects Thereon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 20408–20417.
- (2) Peljhan, S.; Koller, J.; Kokalj, A. The Effect of Surface Geometry of Copper on Adsorption of Benzotriazole and Cl. Part I, *J. Phys. Chem. C* **2014**, *118*, 933–943.

†The PBE+D adsorption energy was calculated as  $E_{\text{ads}}(\text{PBE} + \text{D}) = E_{\text{ads}}(\text{PBE-D}') - E_{\text{disp}}^{\text{lateral}}(\text{PBE-D}') + E_{\text{disp}}^{\text{lateral}}(\text{PBE-D})$  and the total stabilization energy per unit area due to molecular adsorption as  $\epsilon_{\text{ads}}^{\text{tot}}(\text{PBE} + \text{D}) = nE_{\text{ads}}(\text{PBE} + \text{D})/A$ . For the meaning of labels refer to the manuscript.

**TABLE S1** PBE and PBE-D' binding energies and bond lengths of various BTAH<sub>(ads)</sub> and BTA<sub>(ads)</sub> modes on (111) and (110) surfaces of Cu<sub>2</sub>O (the PBE-D' data are stated in parentheses). For comparison also the corresponding data, as obtained on metallic Cu(111) and Cu(110), are stated.<sup>[1,2]</sup> For the meaning of the labels refer to the manuscript.

species	substrate	coverage ( $10^{-3}\text{\AA}^{-2}$ )	supercell	adsorption mode	shown in Figure	$E_b$ (eV)	$d_{N2-Cu}$ (\AA)	$d_{N3-Cu}$ (\AA)	$d_{H...O}$ (\AA)	ref
<b>BTAH<sub>(ads)</sub></b>										
Cu <sub>2</sub> O(111)-w/ $\alpha$ -Cu <sup>CUS</sup>		7.6	(2 × 2)	N2+N3	3a	-0.39 (-0.69)	2.16 (2.15)	2.33 (2.32)	/	this work
				N2+H1...O <sup>sub</sup>	3b	-0.39 (-0.84)	2.18 (2.15)	/	2.08 (2.03)	
				N2+H1...O <sup>up</sup>	3c	-0.32 (-0.58)	2.26 (2.13)	/	1.94 (1.90)	
	... + individual Cu <sup>CUS</sup> sites			N2@CUS+H1...O <sup>up</sup>	3f	-1.50 (-1.83)	1.93 (1.92)	/	1.63 (1.62)	
			N3@CUS+H4...O <sup>up</sup>	3g	-1.24 (-1.59)	/	1.94 (1.93)	2.18 (2.13)		
Cu <sub>2</sub> O(110):CuO		6.2	(3 × 2)	N2+H1...O <sup>surf</sup>	4a	-0.73 (-1.02)	2.06 (2.05)	/	1.64 (1.60)	
Cu(111)		6.8	(5 × 5)	N2+N3	/	-0.44 (-0.79)	2.13 (2.10)	2.11 (2.06)	/	1
Cu(110)		5.2	(5 × 4)	N2+N3	/	-0.84 (-1.21)	2.02 (1.99)	2.00 (1.99)	/	1
<b>BTA<sub>(ads)</sub></b>										
Cu <sub>2</sub> O(111)-w/ $\alpha$ -Cu <sup>CUS</sup>		7.6	(2 × 2)	N1+N2+N3	3d	-1.97 (-2.34)	2.05 (2.05)	1.94,2.16 <sup>a</sup> (1.94,2.15) <sup>a</sup>	/	this work
				N2+N3	3e	-1.78 (-2.10)	2.02 (2.01)	2.02 (2.01)	/	
				N2@CSA+N3@CUS	3h	-2.80 (-3.12)	1.93 (1.93)	1.91 (1.90)	/	
	... + individual Cu <sup>CUS</sup> sites			N2@CUS+N3@CSA	3i	-2.75 (-3.04)	1.91 (1.90)	1.95 (1.95)	/	
Cu <sub>2</sub> O(110):CuO		6.2	(3 × 2)	N2+N3	4b	-1.74 (-2.04)	1.98 (1.98)	1.98 (1.97)	/	
Cu(111)		10.7	(4 × 4)	N2+N3	/	-2.78 (-3.21)	2.01 (2.01)	1.98 (1.98)	/	2
Cu(110)		8.7	(4 × 3)	N2+N3 <sup>b</sup>	/	-3.27 (-3.66)	1.99 (1.96)	1.95 (1.96)	/	2

<sup>a</sup>N1-Cu and N3-Cu distances.

<sup>b</sup>Upright adsorption mode.