Supplementary Materials for

Exceptionally Stiff Two-Dimensional Molecular Crystal by Substrate-Confinement

MovieS1:

Selected frames from a series of STM images during *in-situ* CO deposition onto the Cu(100) surface at Liquid Nitrogen (LN_2) temperature to show the evolution of the CO adlayer. All frames have a size of 8.0 Å × 7.5 Å.

TableS1:

Structures	N_{Cu}	N_{CO}	Coverage (CO/atom)	Adsorption energy per CO (eV/molecule)	Adsorption energy per Cu (eV/atom)
Single CO				-0.626	
√2 ×√2	2	1	0.500	-0.541	-0.271
c(11√2×√2)	22	12	0.545	-0.529	-0.289
c(9√2×√2)	18	10	0.556	-0.521	-0.290
c(7√2×√2)	14	8	0.571	-0.508	-0.291
c(5√2×√2)	10	6	0.600	-0.490	-0.294
c(3√2×√2)	6	4	0.667	-0.426	-0.284
c(7√2×7√2)	100	64	0.640	-0.471	-0.302
c(5√2×5√2)	52	36	0.692	-0.426	-0.295
c(3√2×3√2)	20	16	0.800	-0.298	-0.238

Structures and the corresponding DFT calculated energy of different CO phases on Cu(100) surface. For a clear comparison, the results of three theoretical models of compressed phases that were not experimentally observed, *i.e.* (3√2×√2), c(5√2×5√2), and c(3√2×3√2) , were also

included.

TableS2:

Structures	N_{ND}	N_{DW}	N_{CI}	Coverage (CO/atom)	Adsorption energy (eV/molecule)	Site-specific adsorption energy (eV/molecule)		
						ND	DW	CI
Single CO					-0.626			
√2 ×√2	1			0.500	-0.541	-0.541		
c(11√2×√2)	8	4		0.545	-0.529			
c(9√2×√2)	6	4		0.556	-0.521			
c(7√2×√2)	4	4		0.571	-0.508	-0.569±5	-0.448±4	
c(5√2×√2)	2	4		0.600	-0.490			
c(3√2×√2)		4		0.667	-0.426			
c(7√2×7√2)	16	32	16	0.640	-0.471			-0.420±9
c(5√2×5√2)	4	16	16	0.692	-0.426			
c(3√2×3√2)			16	0.800	-0.298			

The site-specific adsorption energies of CO molecules for a series of adsorption phases on Cu(100). The site-specific adsorption energy, local electronic structures and other properties of the CO adlayer are contributed by the local structural relaxations of tilting and bending COs at the DWs and CIs.

Three distinct features have been identified in the temperature-programmed desorption (TPD) measurements of CO/Cu(100), with the peak desorption temperatures at approximately 135 K, 180 K and 220 K, respectively.[1] The 220 K feature was attributed to COs desorbed from the defect sites, which is most prominent at the lowest coverages. The 180 K feature can be assigned to COs on the flat (100) terraces, which has the largest intensity at saturation and corresponding to the adsorption energy of COs in ND (-569 meV to -541 meV). The adsorption

energy of COs in DW and CI (-448 meV to – 420 meV) is corresponding to a desorption temperature of ~ 135 K, which is only observed at the coverage of > 0.5 ML.[2,3]

For the other local electronic structures and other properties, we give an example of surface resistivity of CO/Cu(100).[1] Surface resistivity is not only a direct and powerful probe of adsorption kinetics and interadsorbate interactions, but also an important way to understand the atomic-scale friction, electromigraticon, and adsorbate effects on the electrical resistance of nanoobjects. All these are valuable in the corresponding fields of nanotribology, thin film electrics, and nanotechnology. The coverage-dependence of surface resistivity for the CO film on Cu(100) can be roughly understood from the calculated electronic states of DWs and CIs in Fig. 3 and Fig. 4, and a deeper discussion in the view of surface band structures of different CPs will be supplied in our following paper.

REFERENCES

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3. Vollmer, S.; White, G.; Woll, C. Determination of Site Specific Adsorption Energies of CO on Copper. *Catal. Lett.* **2001**, 77, 97-101.