Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Materials

Reduction of cupper oxides by carbon monoxide at applied potential

Nadezhda V. Dokhlikova, Andrey K. Gatin, Sergey Yu. Sarvadii, Sergey A. Ozerin, Vasiliy A. Kharitonov, Boris R. Shub, Maxim V. Grishin and Sergey V. Doronin

S1. Potential of charged Cu_2O and CuO slabs

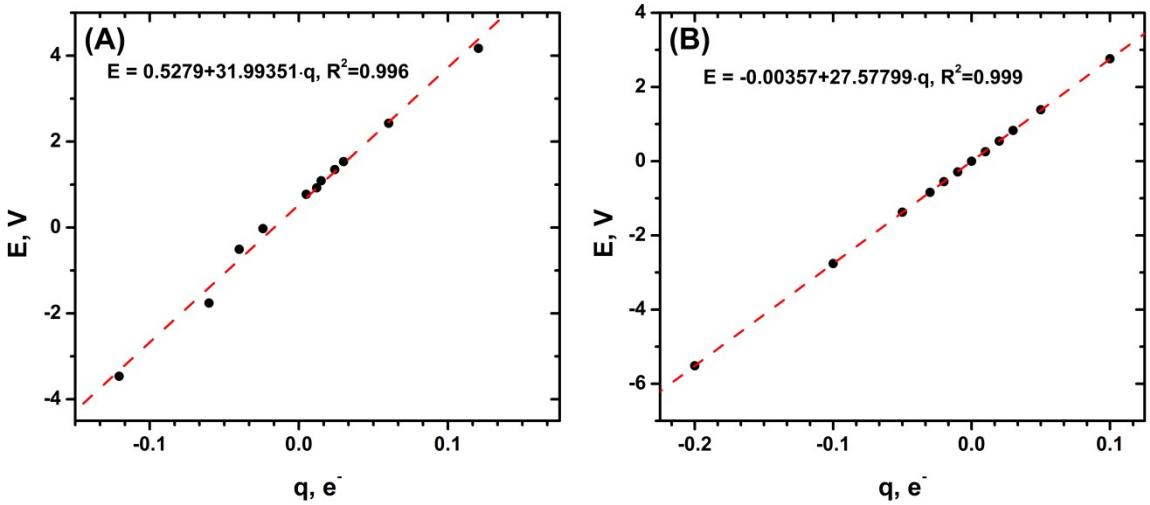

Fig. S1. Dependence of the applied potential calculated based on the Fermi level shift on the charge of Cu_2O **(A)** and CuO (Fm3m) **(B)** slabs.

S2. DOS of Cu_2O and CuO allotropes

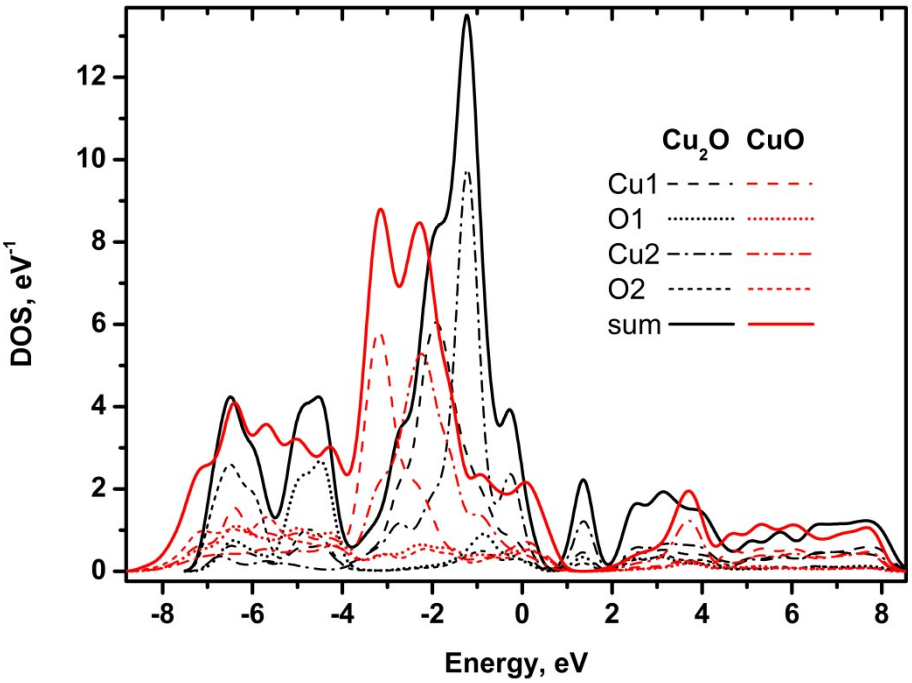

Fig. S2. Partial DOS для Cu_2O и CuO (Fm3m).

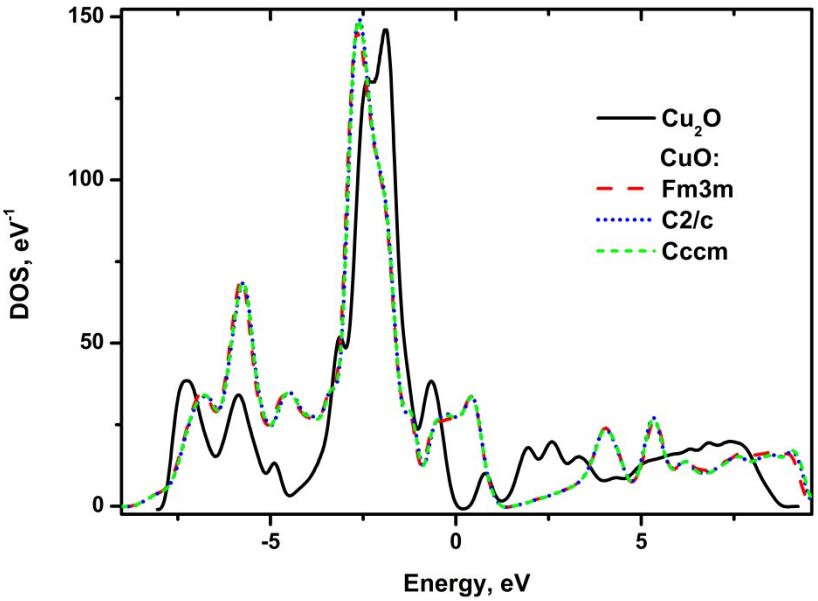

Fig. S3. Total DOS of copper oxides.

S3. CO interaction with cuprum oxides

Tab. S1. Binding energies ($\mathbf{E_{bind}}$) of CO and reduction reaction energy ($\mathbf{E_{reac}}$) on sites (Cu1, Cu2, O1, and O2) of copper oxides (Cu_2O and CuO Fm3m, C2/c, and Cccm).

Oxide	E, V	Cu1			Cu2			O1			O2		
		E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}
Cu_2O	-1	-0.574	0.567	0.693	-1.825	-0.684	-0.558	-1.492	-0.351	-0.225	-0.469	0.672	0.798
	0	-2.308	-1.011	-0.891	-2.268	-0.970	-0.851	-1.404	-0.107	0.013	-1.000	0.298	0.417
	1	-0.576	0.566	0.683	-1.785	-0.643	-0.526	-0.275	0.868	0.984	-0.461	0.682	0.798
CuO Fm3m	-1	-0.361	1.201	0.971	-0.608	0.954	0.724	-1.732	-0.170	-0.400	-0.607	0.955	0.725
	0	-0.362	1.188	0.922	-0.640	0.911	0.644	-1.735	-0.185	-0.451	-1.734	-0.183	-0.450
	1	-0.363	1.201	1.017	-0.614	0.950	0.766	-1.749	-0.185	-0.369	-0.303	1.260	1.076
C2c	-1	-0.121	1.267	1.014	-0.121	1.267	1.014	-1.503	-0.115	-0.367	-0.452	0.936	0.684
	0	-0.871	1.271	1.014	-1.205	0.938	0.681	-2.257	-0.114	-0.371	-1.206	0.937	0.680
	1	-0.127	1.265	1.005	-1.548	-0.643	-0.526	-1.517	-0.125	-0.384	-0.462	0.930	0.670
Cccm	-1	0.063	1.378	1.205	-0.133	1.181	1.008	-1.399	-0.084	-0.257	-0.133	1.181	1.008
	0	-0.805	0.644	0.229	-1.048	0.401	-0.014	-2.186	-0.737	-1.152	-1.048	0.402	-0.014
	1	0.053	1.380	1.202	-0.144	1.183	1.005	-1.414	-0.087	-0.264	-0.144	1.183	1.006

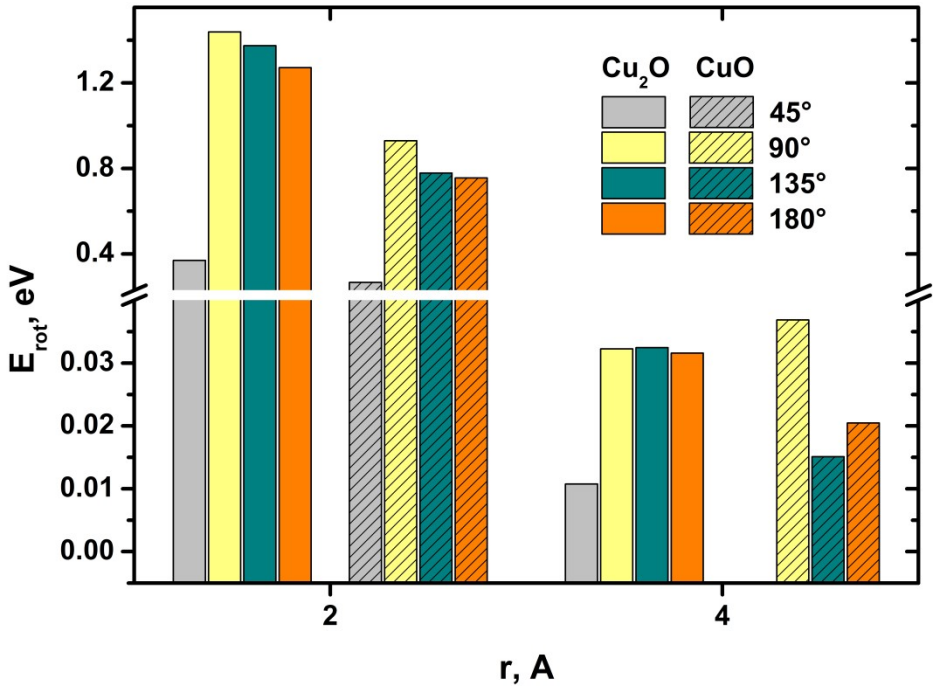

Fig. S4. Energies of the CO molecule rotation at distances **r** = 2 and 4 Å from the Cu2 site on the Cu_2O and CuO (Fm3m) surfaces.

Tab. S2. Energy of the CO molecule rotation by the angle α on the copper oxides surface. **r** is the distance between the carbon (CO) and Cu2 at α < 90°, oxygen (CO) and Cu2 at α > 90°.

Oxide	r, Å	E = -1 V				E = 0 V				E = +1 V			
		α = 45°	90°	135°	180°	45°	90°	135°	180°	45°	90°	135°	180°
Cu2O	2	0.369	1.436	1.357	1.253	0.370	1.438	1.375	1.271	0.370	1.441	1.378	1.275
	4	0.009	0.026	0.022	0.019	0.011	0.032	0.032	0.032	0.013	0.038	0.042	0.043
	6	-0.0011	-0.0035	-0.0080	-0.0088	0.0006	0.0021	0.0018	0.0027	0.0022	0.0075	0.0081	0.0133
	8	-1.70E-03	-5.29E-03	-9.75E-03	-1.04E-02	-6.35E-05	3.68E-04	-3.05E-05	1.04E-03	1.51E-03	5.71E-03	9.04E-03	1.16E-02
CuO (Fm3m)	2	0.261	0.925	0.774	0.755	0.267	0.930	0.778	0.755	0.273	0.935	0.783	0.755
	4	-0.007	0.034	0.011	0.015	-0.006	0.037	0.015	0.020	-0.005	0.040	0.020	0.026
	6	-0.0006	0.0028	-0.0021	-0.0028	0.0001	0.0052	0.0021	0.0021	0.0008	0.0077	0.0064	0.0071
	8	-6.90E-05	-4.96E-04	-3.37E-03	-4.72E-03	6.17E-04	1.88E-03	7.56E-04	1.44E-04	1.37E-03	4.42E-03	5.04E-03	5.12E-03

S4. Reaction of CO with cumprum oxides

Tab. S3. CO binding energies ($\mathbf{E_{bind}}$) and reduction reaction energy ($\mathbf{E_{reac}}$) on the Cu1, Cu2, O1, and O2 sites of copper oxides (Cu_2O, CuO Fm3m, C2/c, and Cccm).

Oxide	E, V	Cu1			Cu2			O1			O2		
		E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}	E_{bind}	E_{reac1}	E_{reac2}
Cu_2O	-1	-0.574	0.567	0.693	-1.825	-0.684	-0.558	-1.492	-0.351	-0.225	-0.469	0.672	0.798
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	1	-0.363	1.201	1.017	-0.614	0.950	0.766	-1.749	-0.185	-0.369	-0.303	1.260	1.076
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	0	-0.871	1.271	1.014	-1.205	0.938	0.681	-2.257	-0.114	-0.371	-1.206	0.937	0.680
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	1	0.053	1.380	1.202	-0.144	1.183	1.005	-1.414	-0.087	-0.264	-0.144	1.183	1.006

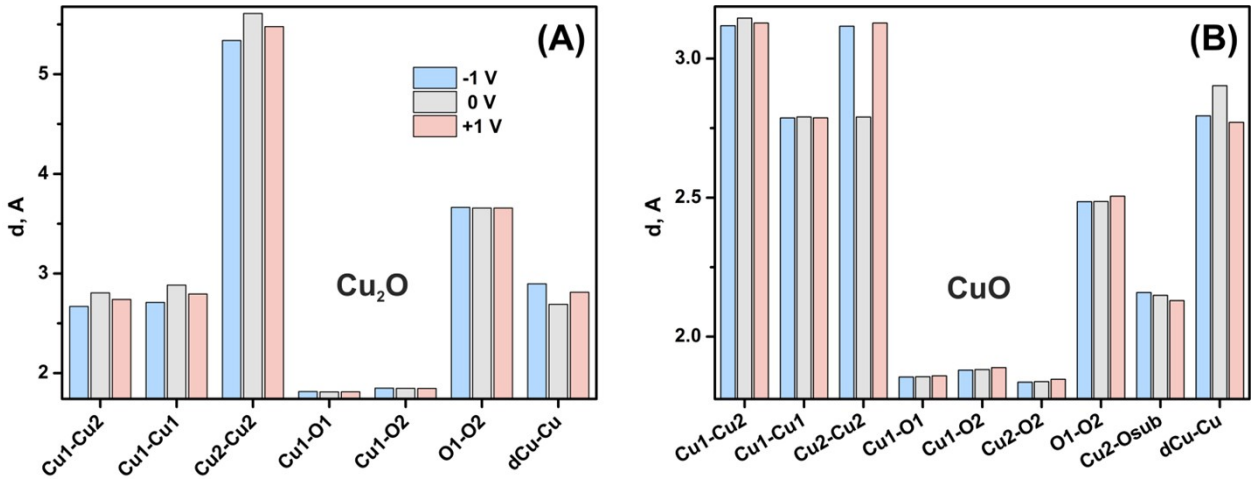

Fig. S5. Bond length changes for Cu_2O **(A)** and CuO Fm3m **(B)** copper oxides at potentials ±1V. Notation: O_{sub} is the subsurface oxygen lying below O2, d_{Cu-Cu} is the distance between the layers formed by the copper atoms; the other designations correspond to **Fig. 1** and **Fig. S6**.

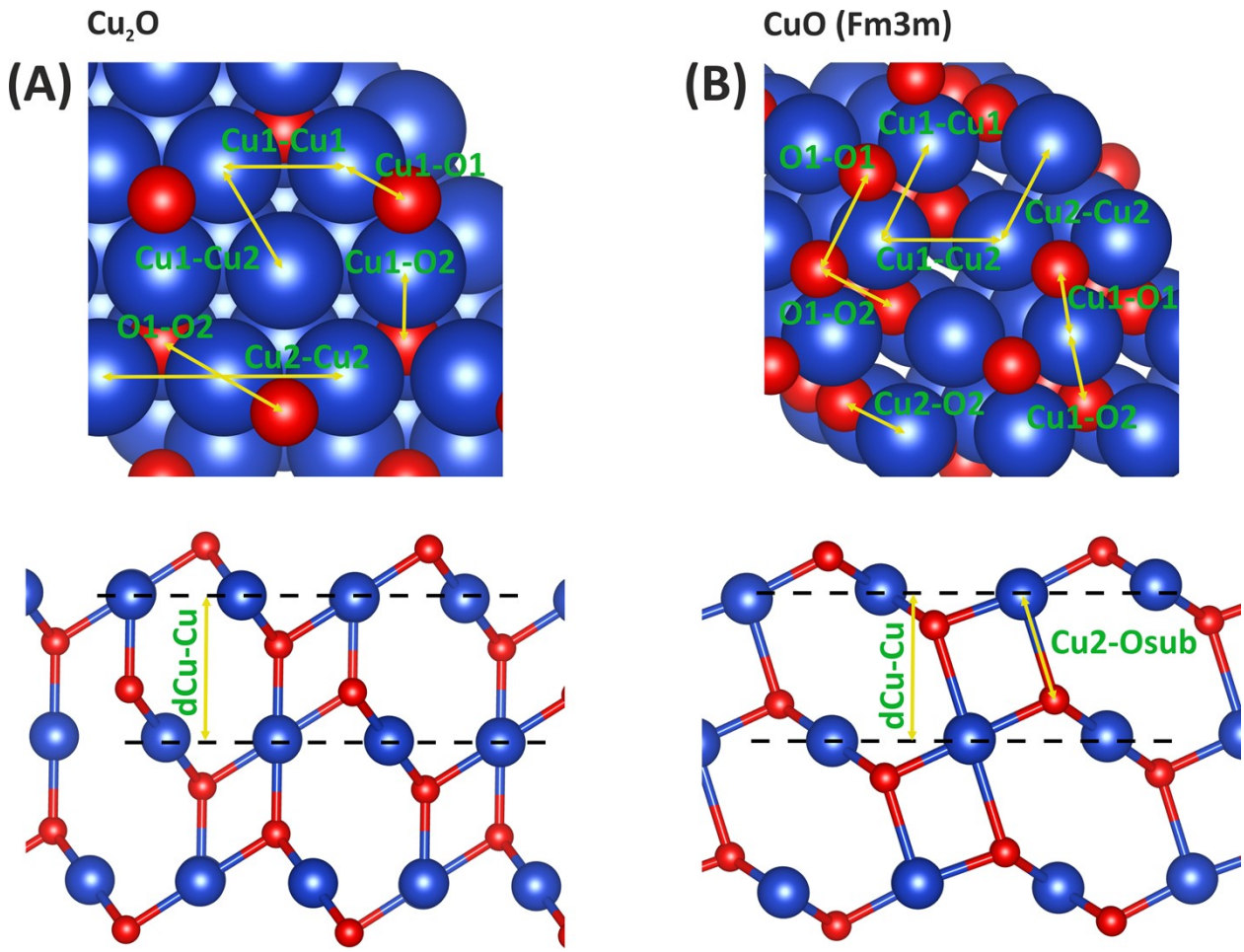

Fig. S6. Bonds from **Fig. S5** for Cu_2O **(A)** and CuO Fm3m **(B)** copper oxides.

Tab. S4. Bond length changes for Cu_2O at potentials ±1V.

	Distances, Å		
	-1 V	**0 V**	**+1 V**
Cu1-Cu2	2.670	2.806	2.739
Cu1-Cu1	2.711	2.884	2.795
Cu2-Cu2	5.340	5.610	5.478
Cu1-O1	1.815	1.811	1.812
Cu1-O2	1.850	1.847	1.846
O1-O2	3.664	3.656	3.658
dCu-Cu	2.897	2.691	2.812

Tab. S5. Bond length changes for CuO Fm3m copper oxides at potentials ±1V.

	Distances, Å		
	-1 V	**0 V**	**+1 V**
Cu1-Cu2	3.118	3.146	3.128
Cu1-Cu1	2.787	2.791	2.787
Cu2-Cu2	3.117	2.790	3.128
Cu1-O1	1.855	1.856	1.859
Cu1-O2	1.879	1.881	1.889
Cu2-O2	1.836	1.839	1.847
O1-O2	2.486	2.486	2.505
Cu2-Osub	2.159	2.149	2.130
dCu-Cu	2.794	2.903	2.771