Supporting Information

Activation of CO_2 on Copper Surfaces: The Synergy Between Electric Field, Surface Morphology and Excess Electrons

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- **Dimensions of the supercells used for the calculations (all in Å):**

  - For constant potential method

    Cu (111): 12.76 × 13.26 × 30.00

    Cu (211): 12.78 × 12.52 × 30.00

    Cu (110): 10.84 × 15.34 × 30.00

    Cu (001): 10.84 × 14.46 × 30.00

  - For dipole sheet method

    Cu (111): 12.76 × 13.26 × 70.00

    Cu (211): 12.78 × 12.52 × 70.00

    Cu (110): 10.84 × 15.34 × 70.00

    Cu (001): 10.84 × 14.46 × 70.00

- **Details for making the dipole sheets**

Table S1- Corresponding surface area, charge and surface charge density on dipole sheets for an electric field of 1V/Å.

Surface	**A (Å ^{2})**	**q |e|**	**σ(C/m^2)**
Cu (111)	169.19	0.936	0.089
Cu (211)	160	0.887	0.089
Cu (110)	166.29	0.92	0.089
Cu (001)	156.75	0.87	0.089

Table S2- Corresponding surface area, charge and surface charge density on dipole sheets for an electric field of 1.5V/Å.

Surface	**A (Å ^{2})**	**q |e|**	**σ(C/m^2)**
Cu (111)	169.19	1.404	0.133
Cu (211)	160	1.33	0.133
Cu (110)	166.29	1.38	0.133
Cu (001)	156.75	1.30	0.133

- **Cross-checking: Calculation of the adsorption energy of the CO_2 molecule on Cu surfaces using both methods**

Cross-checking results for Cu (211) surface are shown in Figure S1. Furthermore, using constant potential method, and corresponding to the electric field strengths of $1.55\ V/\text{Å}$ and $1.44\ V/\text{Å}$ for Cu (001) and Cu (111), we got adsorption energies of CO_2 as $-0.90\ eV$ and $-0.59\ eV$, respectively. Employing charged plates and corresponding to the electric field strength of $1.5\ V/\text{Å}$ for both Cu (001) and Cu (111) we achieved adsorption energies of $-0.85\ eV$ and $-0.62\ eV$, respectively. Also, we have to mention that for each method we had to use different Poisson solvers ("Implicit"[1] for constant potential approach and "Martyna-Tuckerman (MT)"[2] for dipole sheet method) and slight difference in adsorption energies is a natural result of using different solvers. As we have emphasized in the manuscript, the trends for adsorption energy as a function of electric field strength are quite similar for both employed methods.

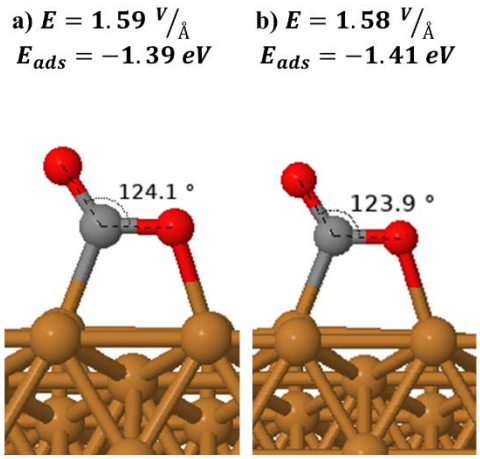

Figure S1- CO_2 adsorption on Cu (211) surface in the presence of external electric field imposed by a) charged plates and b) constant potential electrodes.

- **Electric field effect- Using constant potential approach**

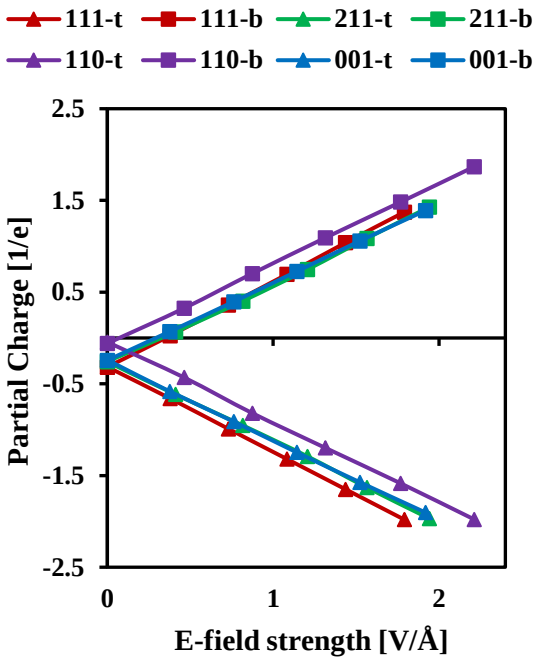

Figure S2- Aggregated surface partial charge versus electric field strength- "t" and "b" represent top and bottom layers of the Cu surfaces, respectively.

Figure S3 shows the potential distribution for the range of applied potential inside the simulation box. As we considered an electrode thickness of 5 Å in our simulations, the potential drops to zero around $z = 2.5$ Å inside the supercell.

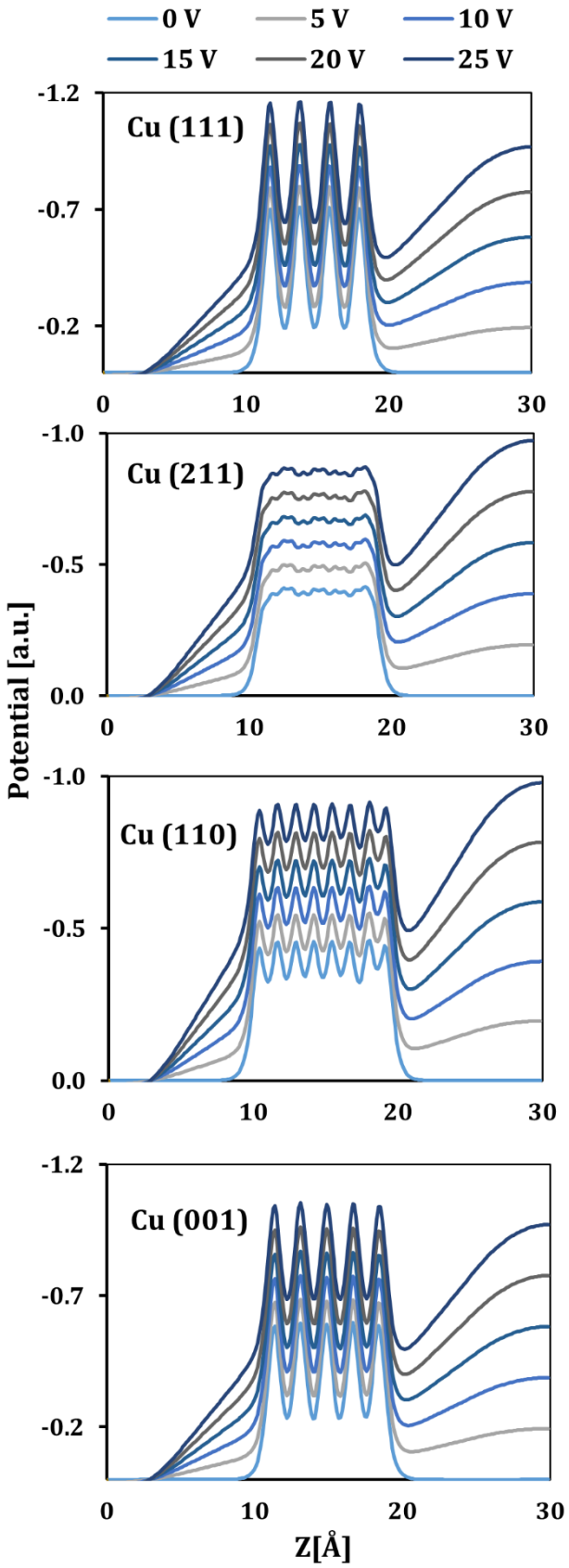

Figure S3- Electrostatic potential around the Cu surfaces for each applied voltage on the electrodes.

Table S3- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (111) as a function of applied potential.

V [V]	Structure	r(C-O)[Å]		OCO angle [˚]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0	physi.	1.17	1.17	179.9			-0.34
5	physi.	1.17	1.17	178.5			-0.34
10	physi.	1.17	1.17	176.7			-0.35
15	physi.	1.18	1.18	172.1			-0.40
20	chemi.	1.24	1.29	127.2	2.04	2.07	-0.59
25	chemi.	1.25	1.3	125.2	2.05	2.09	-0.90

Table S4-Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (211) as a function of applied potential.

V [V]	Structure	r(C-O)[Å]		OCO angle [˚]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0	physi.	1.17	1.18	179.5			-0.29
5	chemi.	1.23	1.25	137.4	2.05	2.12	-0.33
10	chemi.	1.23	1.28	130.7	2.01	2.03	-0.58
15	chemi.	1.24	1.29	127.0	2.00	2.03	-0.94
20	chemi.	1.25	1.3	123.9	2.01	2.03	-1.41
25	chemi.	1.27	1.31	121.4	2.03	2.04	-1.96

Table S5- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (110) as a function of applied potential.

V [V]	Structure	r(C-O)[Å]		OCO angle [˚]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0	physi.	1.17	1.18	179.8			-0.39
5	physi.	1.17	1.17	177.6			-0.36
10	chemi.	1.24	1.28	127.9	2.02	2.02	-0.62
15	chemi.	1.25	1.29	125.3	2.03	2.03	-0.96
20	chemi.	1.26	1.3	122.8	2.03	2.03	-1.38
25	chemi.	1.28	1.3	121.0	2.05	2.08	-1.96

Table S6- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (001) as a function of applied potential.

V [V]	Structure	r(C-O)[Å]		OCO angle [˚]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0	physi.	1.17	1.17	179.5			-0.35
5	physi.	1.17	1.17	177.9			-0.38
10	physi.	1.17	1.17	175.9			-0.38
15	chemi.	1.23	1.28	130.3	2.03	2.09	-0.56
20	chemi.	1.24	1.29	127.0	2.04	2.08	-0.90
25	chemi.	1.26	1.29	124.2	2.04	2.09	-1.31

- **Combined effect of electric field and excess electron- Using dipole sheet method**

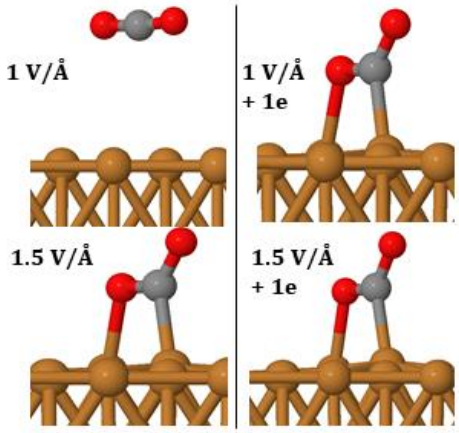

Figure S4- The most stable CO_2 adsorption mode on Cu (111).

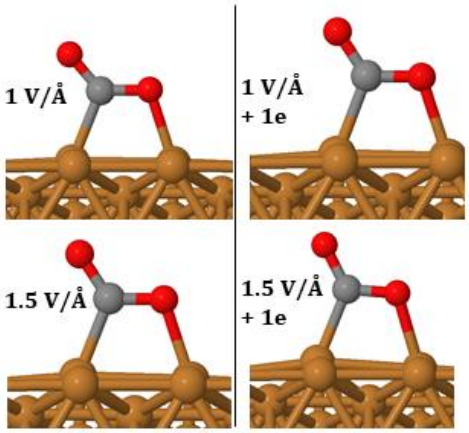

Figure S5- The most stable CO_2 adsorption mode on Cu (211).

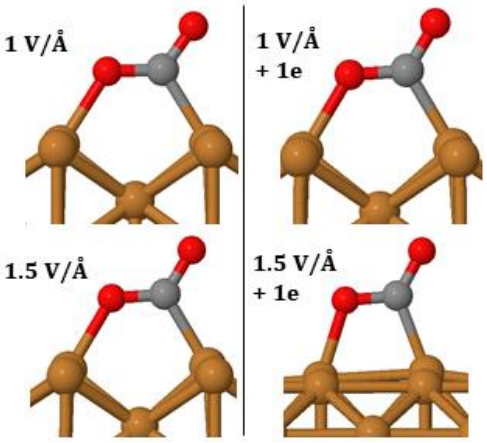

Figure S6- The most stable CO_2 adsorption mode on Cu (110).

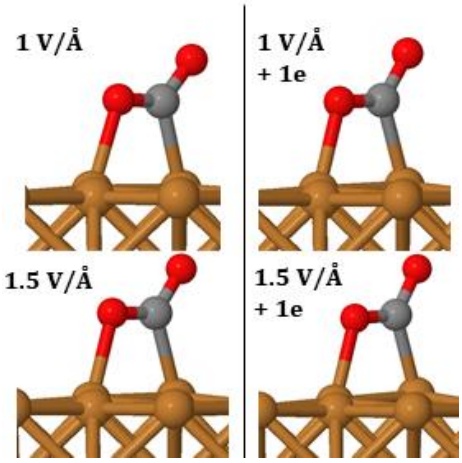

Figure S7- The most stable CO_2 adsorption mode on Cu (001).

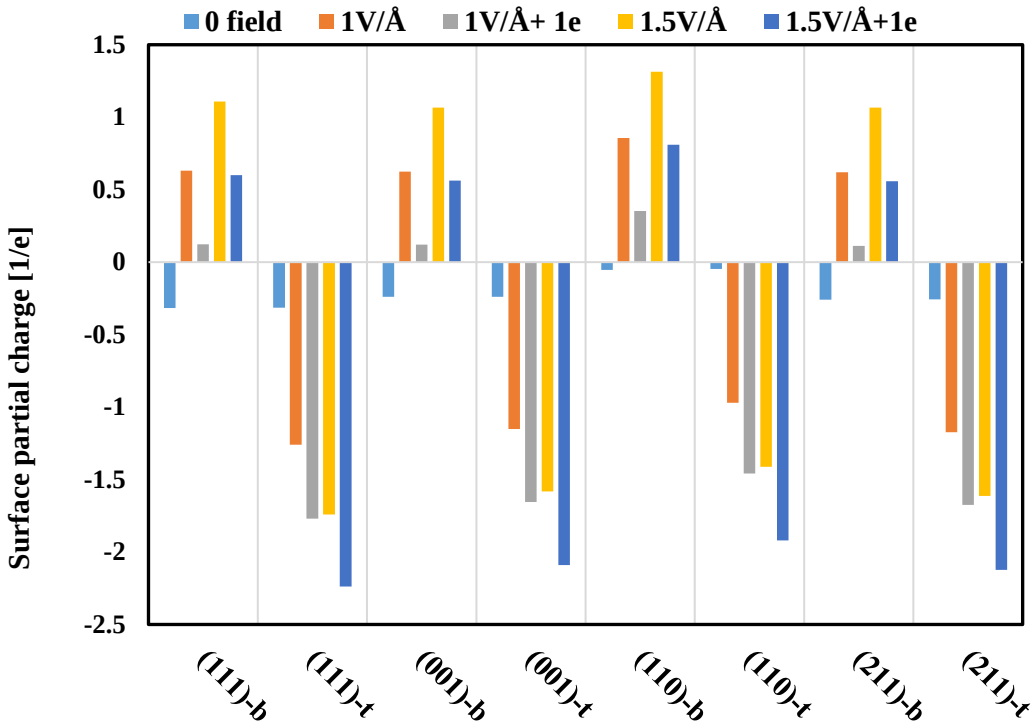

Figure S8- Surface partial charges as a function of field and excess electron combination- "b" and "t" are referred to bottom and top layers of the slabs, respectively.

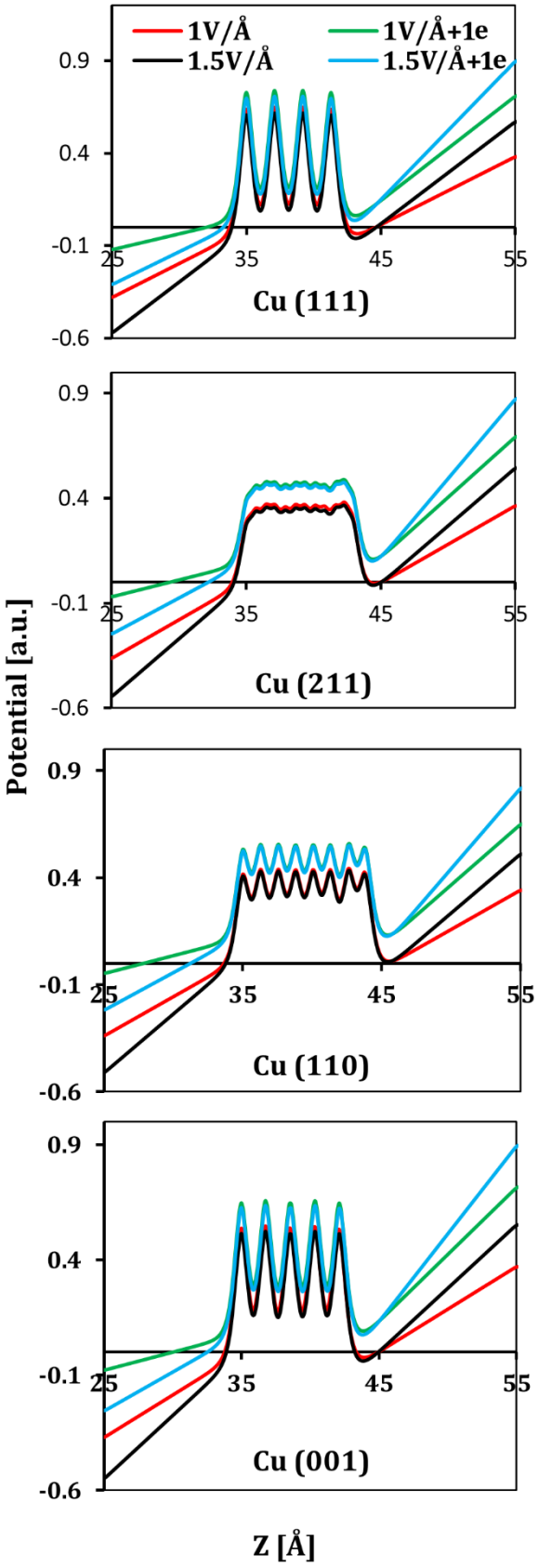

Figure S9- Potential distribution around the Cu surface for different combined electric field and excess electron situations.

Table S7- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (111).

E-field	Structure	r(C-O)[Å]		OCO angle [°]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0V/Å	physi.	1.17	1.17	179.9			-0.32
0V/Å+1e	physi.	1.17	1.17	177.7			-0.33
1V/Å	physi.	1.17	1.18	175.3			-0.39
1V/Å+1e	chemi.	1.24	1.29	127.5	2.04	2.08	-0.58
1.5V/Å	chemi.	1.24	1.29	127.0	2.04	2.07	-0.62
1.5V/Å+1e	chemi.	1.25	1.29	124.8	2.06	2.12	-1.07

Table S8- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (211).

E-field	Structure	r(C-O)[Å]		OCO angle [°]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0V/Å	physi.	1.17	1.18	179.5			-0.31
0V/Å+1e	physi.	1.17	1.17	176.4			-0.30
1V/Å	chemi.	1.24	1.29	128.9	2.00	2.02	-0.78
1V/Å+1e	chemi.	1.25	1.3	124.3	2.01	2.03	-1.45
1.5V/Å	chemi.	1.25	1.3	124.7	2.01	2.02	-1.30
1.5V/Å+1e	chemi.	1.27	1.31	121.2	2.03	2.05	-2.16

Table S9- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (110).

E-field	Structure	r(C-O)[Å]		OCO angle [°]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0V/Å	physi.	1.17	1.18	179.7			-0.34
0V/Å+1e	chemi.	1.23	1.27	131.3	2.02	2.02	-0.33
1V/Å	chemi.	1.24	1.29	127.3	2.02	2.01	-0.67
1V/Å+1e	chemi.	1.25	1.30	124.3	2.03	2.03	-1.12
1.5V/Å	chemi.	1.25	1.30	124.3	2.03	2.03	-1.11
1.5V/Å+1e	chemi.	1.26	1.30	122.6	2.04	2.06	-1.70

Table S10- Bond lengths, angles and adsorption energies for the most stable CO_2 adsorption mode on Cu (001).

E-field	Structure	r(C-O)[Å]		OCO angle [°]	r(C-Cu) [Å]	r(O-Cu) [Å]	E_{ads}[eV]
0V/Å	physi.	1.17	1.17	179.4			-0.33
0V/Å+1e	physi.	1.17	1.18	176.8			-0.33
1V/Å	chemi.	1.23	1.27	131.9	2.03	2.08	-0.43
1V/Å+1e	chemi.	1.24	1.29	126.7	2.04	2.07	-0.89
1.5V/Å	chemi.	1.24	1.28	127.4	2.04	2.08	-0.85
1.5V/Å+1e	chemi.	1.26	1.29	124.0	2.04	2.09	-1.43

- **PDOS for combined electric field and excess electron effect**

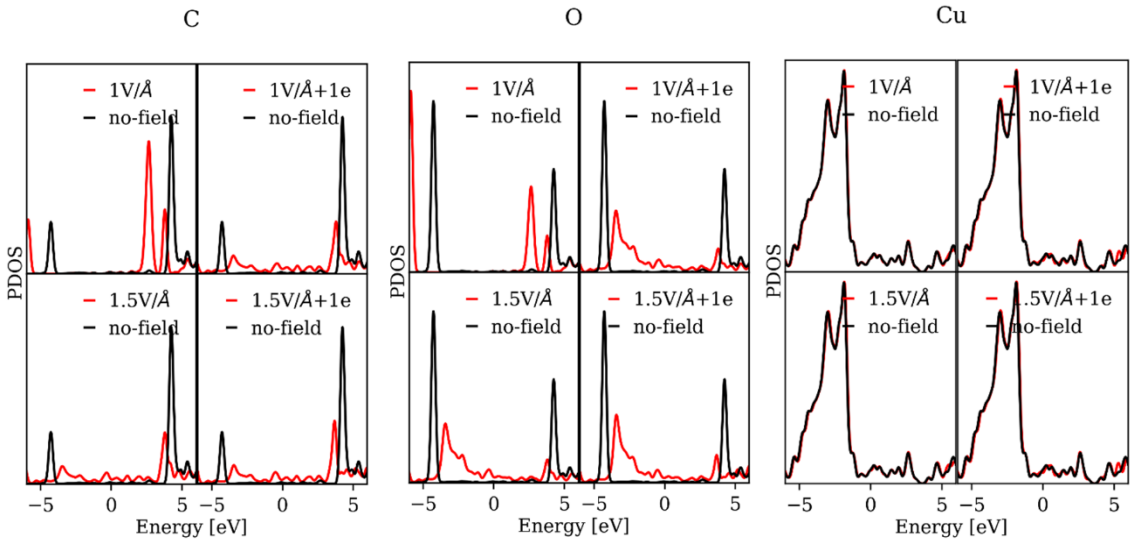

Figure S10- Projected density of states for CO_2 adsorption on Cu (111) surface.

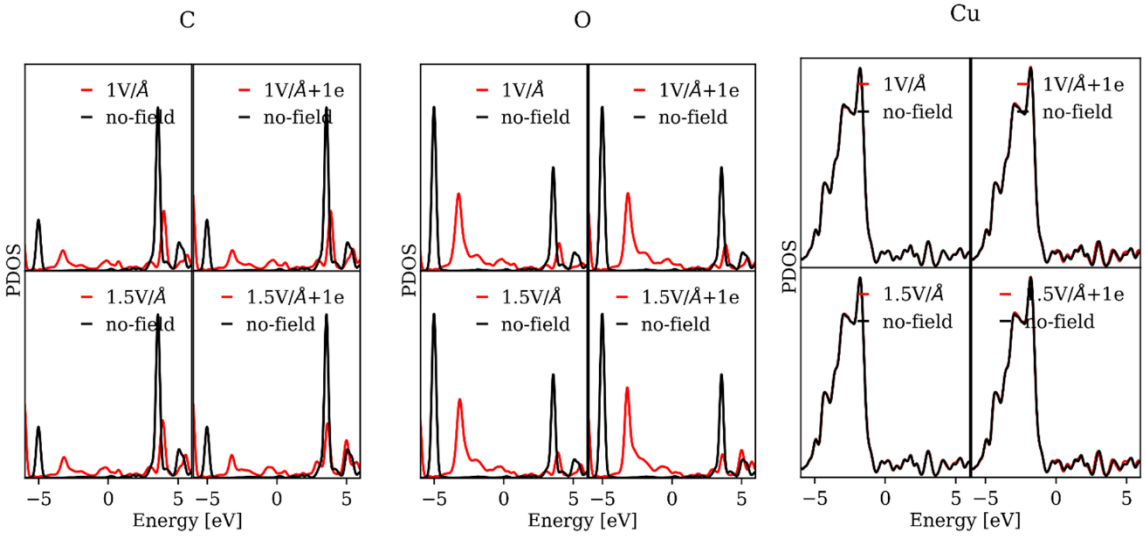

Figure S11- Projected density of states for CO_2 adsorption on Cu (211) surface.

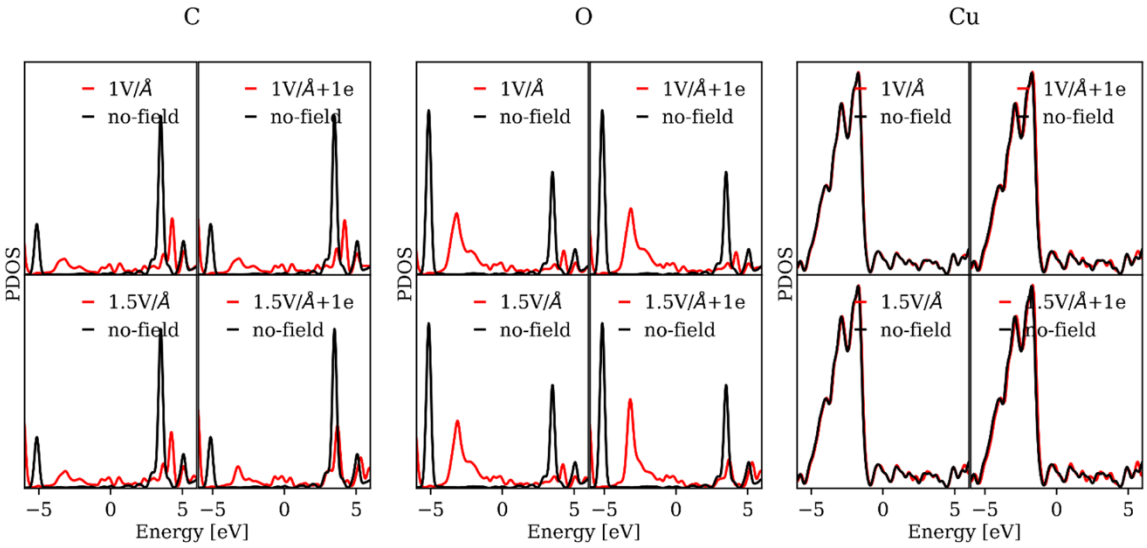

Figure S12- Projected density of states for CO_2 adsorption on Cu (110) surface.

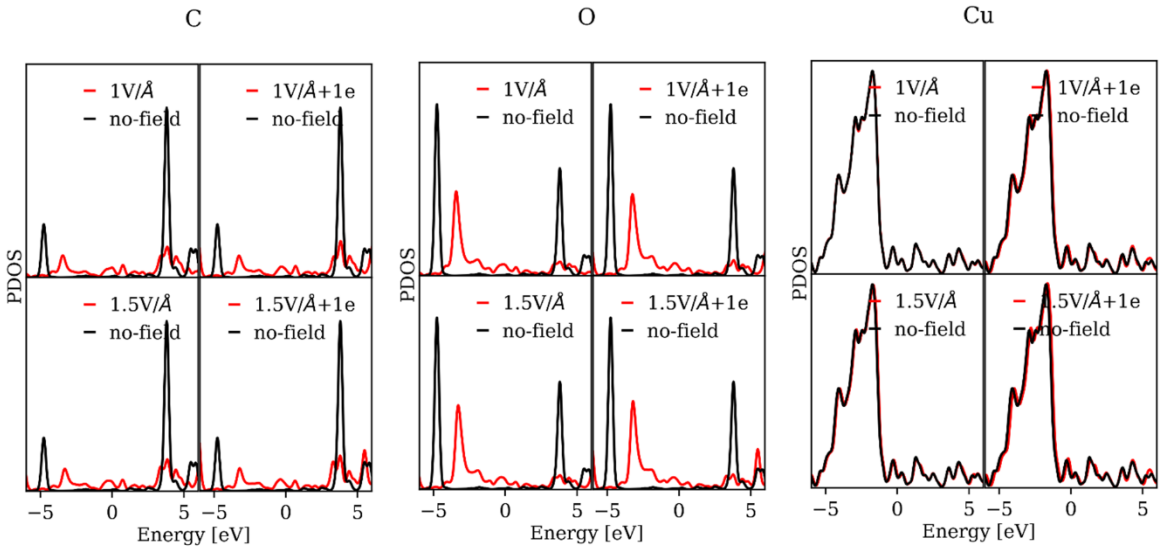

Figure S13- Projected density of states for CO_2 adsorption on Cu (001) surface.

- **Hirshfeld charges of the surface atoms and adsorbed molecule using dipole sheet method**

Table S11- Partial charges of the top layer atoms of the Cu (111) and the adsorbed CO_2 molecule- bonded atoms from the molecule and the surface are indicated in same colors.

Atom	0V/Å	0V/Å +1e	1V/Å	1V/Å +1e	1.5V/Å	1.5V/Å +1e
Cu	0.011	0.011	-0.045	-0.051	-0.05	-0.064
Cu	0.01	0.011	-0.04	-0.053	-0.053	-0.065
Cu	0.011	0.011	-0.04	-0.024	-0.025	-0.036
Cu	0.011	0.011	-0.042	-0.033	-0.029	-0.045
Cu	0.011	0.011	-0.04	-0.055	-0.053	-0.068
Cu	0.01	0.011	-0.041	-0.05	-0.049	-0.063
Cu	0.01	0.011	-0.04	-0.021	-0.024	-0.025
Cu	0.011	0.011	-0.03	-0.013	-0.011	-0.025
Cu	-0.01	-0.025	-0.031	-0.255	-0.258	-0.261
Cu	-0.01	-0.027	-0.04	-0.048	-0.047	-0.06
Cu	-0.01	-0.026	-0.04	-0.035	-0.03	-0.044
Cu	0.011	0.011	-0.041	-0.005	-0.002	-0.011
Cu	0.011	0.011	-0.04	-0.052	-0.051	-0.064
Cu	0.011	0.011	-0.041	0.02	0.018	0.025
Cu	0.01	0.011	-0.041	-0.054	-0.052	-0.067
Cu	0.011	0.011	-0.04	-0.051	-0.048	-0.065
Cu	0.011	0.011	-0.042	-0.051	-0.05	-0.065
Cu	-0.01	-0.024	-0.041	-0.051	-0.048	-0.065
Cu	-0.01	-0.026	-0.041	-0.03	-0.031	-0.038
Cu	-0.011	-0.027	-0.033	-0.047	-0.048	-0.059
Cu	0.001	-0.012	-0.029	-0.052	-0.051	-0.066
Cu	0.011	0.011	-0.04	-0.012	-0.012	-0.025
Cu	-0.011	-0.027	-0.041	-0.051	-0.05	-0.065
Cu	-0.011	-0.027	-0.041	-0.052	-0.051	-0.065
Cu	-0.012	-0.028	-0.04	-0.052	-0.051	-0.064
Cu	-0.011	-0.026	-0.041	-0.052	-0.052	-0.066
Cu	-0.011	-0.027	-0.04	-0.053	-0.052	-0.067
Cu	-0.011	-0.027	-0.041	-0.054	-0.052	-0.068
Cu	-0.01	-0.026	-0.023	-0.051	-0.05	-0.065
Cu	-0.011	-0.027	-0.031	-0.053	-0.052	-0.066
C	1.525	1.52	1.454	1.401	1.396	1.369
O	-0.791	-0.8	-0.777	-0.745	-0.74	-0.778
O	-0.783	-0.799	-0.78	-0.96	-0.961	-1.027
Total partial charge of the molecule	-0.049	-0.079	-0.103	-0.304	-0.305	-0.436

Table S12- Partial charges of the top layer atoms of the Cu (211) and the adsorbed CO_2 molecule - bonded atoms from the molecule and the surface are indicated in same colors.

Atom	0V/Å	0V/Å +1e	1V/Å	1V/Å +1e	1.5V/Å	1.5V/Å +1e
Cu	-0.013	-0.017	-0.008	-0.007	-0.008	-0.009
Cu	-0.013	-0.015	-0.014	-0.016	-0.016	-0.017
Cu	-0.012	-0.015	-0.016	-0.017	-0.017	-0.017
Cu	-0.012	-0.015	-0.016	-0.018	-0.018	-0.019
Cu	-0.013	-0.017	-0.007	-0.008	-0.008	-0.011
Cu	-0.012	-0.015	-0.016	-0.018	-0.018	-0.019
Cu	-0.013	-0.016	-0.016	-0.017	-0.018	-0.018
Cu	-0.012	-0.015	-0.017	-0.018	-0.019	-0.02
Cu	-0.012	-0.016	-0.016	-0.018	-0.018	-0.019
Cu	-0.012	-0.016	-0.017	-0.019	-0.019	-0.02
Cu	-0.015	-0.025	-0.023	-0.031	-0.032	-0.041
Cu	-0.01	-0.024	-0.019	-0.025	-0.025	-0.03
Cu	-0.015	-0.027	-0.021	-0.029	-0.029	-0.037
Cu	-0.014	-0.025	-0.029	-0.038	-0.038	-0.048
Cu	-0.021	-0.031	-0.012	-0.015	-0.015	-0.02
Cu	-0.013	-0.024	-0.029	-0.039	-0.039	-0.047
Cu	-0.014	-0.025	-0.024	-0.033	-0.033	-0.042
Cu	-0.014	-0.025	-0.022	-0.031	-0.03	-0.038
Cu	-0.014	-0.025	-0.031	-0.041	-0.041	-0.05
Cu	-0.014	-0.025	-0.032	-0.042	-0.041	-0.05
Cu	-0.008	-0.041	-0.285	-0.309	-0.304	-0.304
Cu	0.004	-0.023	0.004	-0.017	-0.017	-0.043
Cu	-0.003	-0.039	-0.05	-0.089	-0.077	-0.114
Cu	-0.002	-0.037	-0.045	-0.073	-0.07	-0.097
Cu	0.017	-0.01	0.001	0.002	0.001	0.003
Cu	-0.001	-0.035	-0.041	-0.067	-0.064	-0.092
Cu	-0.006	-0.038	-0.054	-0.082	-0.078	-0.107
Cu	-0.002	-0.037	-0.046	-0.076	-0.073	-0.102
Cu	0.009	-0.027	-0.018	-0.043	-0.039	-0.063
Cu	-0.003	-0.037	-0.047	-0.077	-0.074	-0.102
C	1.528	1.522	1.422	1.381	1.385	1.27
O	-0.768	-0.782	-0.906	-0.994	-0.983	-1.044
O	-0.77	-0.786	-0.716	-0.742	-0.738	-0.738
Total partial charge of the molecule	-0.01	-0.046	-0.2	-0.355	-0.336	-0.512

Table S13- Partial charges of the top layer atoms of the Cu (110) and the adsorbed CO_2 molecule - bonded atoms from the molecule and the surface are indicated in same colors.

Atom	0V/Å	0V/Å +1e	1V/Å	1V/Å +1e	1.5V/Å	1.5V/Å +1e
Cu	0.001	0.002	0.002	0.002	0.002	0.002
Cu	0.001	0.001	0.001	0.002	0.001	0.002
Cu	0.001	-0.003	-0.004	-0.003	-0.004	0.005
Cu	0.001	0.001	0.001	0.002	0.001	0.002
Cu	0.001	-0.003	-0.004	-0.003	-0.004	0.003
Cu	0.001	0.002	0.002	0.002	0.002	0.002
Cu	0.001	0.001	0.001	0.003	0.002	0.002
Cu	0.001	0.002	0.001	0.002	0.001	0.002
Cu	-0.006	0.008	0.011	0.011	0.011	0.004
Cu	0.001	0.001	0.001	0.003	0.002	0.002
Cu	-0.003	0.009	0.011	0.011	0.012	0.003
Cu	0.001	0.001	0.001	0.003	0.002	0.002
Cu	0.001	0.001	0.002	0.001	0.002	0.002
Cu	0.001	0.001	0.001	0.001	0.002	0.002
Cu	0.001	-0.001	-0.002	-0.002	-0.003	0.001
Cu	0.001	0.001	0.001	0.001	0.002	0.002
Cu	0.001	-0.001	-0.002	-0.002	-0.002	0.002
Cu	0.001	0.001	0.002	0.001	0.002	0.002
Cu	0.011	0.013	-0.002	-0.02	-0.018	0.01
Cu	-0.003	-0.022	-0.041	-0.067	-0.064	-0.052
Cu	-0.004	-0.016	-0.033	-0.059	-0.054	-0.057
Cu	-0.005	-0.027	-0.05	-0.074	-0.073	-0.084
Cu	-0.003	0.025	0.017	0.014	0.013	-0.289
Cu	-0.003	-0.026	-0.046	-0.073	-0.07	-0.093
Cu	-0.002	-0.008	-0.022	-0.048	-0.041	-0.056
Cu	-0.004	-0.033	-0.058	-0.081	-0.082	-0.098
Cu	-0.012	0.013	0.002	-0.015	-0.014	-0.037
Cu	-0.004	-0.017	-0.032	-0.058	-0.053	-0.071
Cu	-0.005	-0.022	-0.041	-0.066	-0.063	-0.087
Cu	-0.005	-0.028	-0.049	-0.073	-0.072	-0.09
Cu	-0.013	-0.004	-0.019	-0.034	-0.032	-0.06
Cu	-0.007	-0.02	-0.039	-0.064	-0.06	-0.085
Cu	0.025	-0.231	-0.243	-0.26	-0.261	-0.059
Cu	-0.005	-0.023	-0.042	-0.07	-0.066	-0.098
Cu	0.007	-0.006	-0.014	-0.03	-0.03	-0.072
Cu	-0.004	-0.02	-0.038	-0.063	-0.06	-0.09
C	1.463	1.422	1.327	1.309	1.307	1.276
O	-0.734	-0.827	-0.864	-0.94	-0.938	-0.742
O	-0.739	-0.715	-0.702	-0.725	-0.725	-1.029
Total partial charge of the molecule	-0.01	-0.12	-0.239	-0.356	-0.356	-0.495

Table S14- Partial charges of the top layer atoms of the Cu (001) and the adsorbed CO_2 molecule - bonded atoms from the molecule and the surface are indicated in same colors.

Atom	0V/Å	0V/Å +1e	1V/Å	1V/Å +1e	1.5V/Å	1.5V/Å +1e
Cu	-0.011	-0.031	-0.042	-0.06	-0.058	-0.074
Cu	-0.011	-0.032	-0.046	-0.066	-0.062	-0.081
Cu	-0.012	-0.032	-0.038	-0.057	-0.053	-0.071
Cu	-0.009	-0.026	-0.025	-0.040	-0.038	-0.053
Cu	-0.012	-0.031	-0.038	-0.055	-0.053	-0.069
Cu	-0.011	-0.031	-0.039	-0.063	-0.056	-0.079
Cu	-0.011	-0.031	-0.039	-0.062	-0.056	-0.078
Cu	-0.010	-0.029	-0.034	-0.050	-0.048	-0.064
Cu	-0.012	-0.032	-0.036	-0.056	-0.052	-0.071
Cu	-0.011	-0.032	-0.04	-0.062	-0.055	-0.079
Cu	-0.005	-0.026	-0.022	-0.035	-0.032	-0.049
Cu	-0.012	-0.025	-0.011	-0.016	-0.016	-0.028
Cu	-0.013	-0.037	-0.023	-0.032	-0.032	-0.042
Cu	-0.011	-0.032	-0.042	-0.059	-0.056	-0.073
Cu	-0.009	-0.03	-0.035	-0.049	-0.049	-0.064
Cu	-0.001	-0.002	0.007	0.008	0.006	0.012
Cu	-0.009	-0.03	-0.031	-0.044	-0.044	-0.057
Cu	-0.011	-0.031	-0.033	-0.047	-0.048	-0.062
Cu	-0.012	-0.033	-0.008	-0.018	-0.019	-0.026
Cu	-0.003	-0.033	-0.245	-0.266	-0.261	-0.279
Cu	0.001	-0.018	-0.003	-0.018	-0.017	-0.030
Cu	-0.011	-0.031	-0.042	-0.059	-0.057	-0.073
Cu	-0.012	-0.033	-0.042	-0.058	-0.057	-0.072
Cu	-0.013	-0.032	-0.025	-0.033	-0.032	-0.041
C	1.524	1.521	1.438	1.397	1.403	1.369
O	-0.777	-0.795	-0.737	-0.757	-0.757	-0.783
O	-0.778	-0.796	-0.893	-0.975	-0.963	-1.047
Total partial charge of the molecule	-0.031	-0.07	-0.192	-0.335	-0.317	-0.461

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