Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Electron Injection Study of Photoexcitation Effects on Supported Subnanometer Pt Clusters for CO_2 Photoreduction

Chi-Ta Yang,[1] Brandon C. Wood,[2] Venkat R. Bhethanabotla,[3] Babu Joseph[4*]*

[1,3,4]Department of Chemical and Biomedical Engineering, University of South Florida, Tampa, FL, 33620, USA, [2]Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA.

[1*]chita@mail.usf.edu, [2]brandonwood@llnl.gov, [3]bhethana@usf.edu, [4*]bjoseph@usf.edu,

*To whom correspondence should be addressed: chita@mail.usf.edu; bjoseph@usf.edu.

1. Configurations and bond lengths of CO_2 adsorption sites on stoichiometry and reduced (oxygen vacancy) anatase TiO_2(101) surfaces in the presence of Pt octamers, hexamers, and tetramers upon one, two, and three electrons introduced in the model slabs.

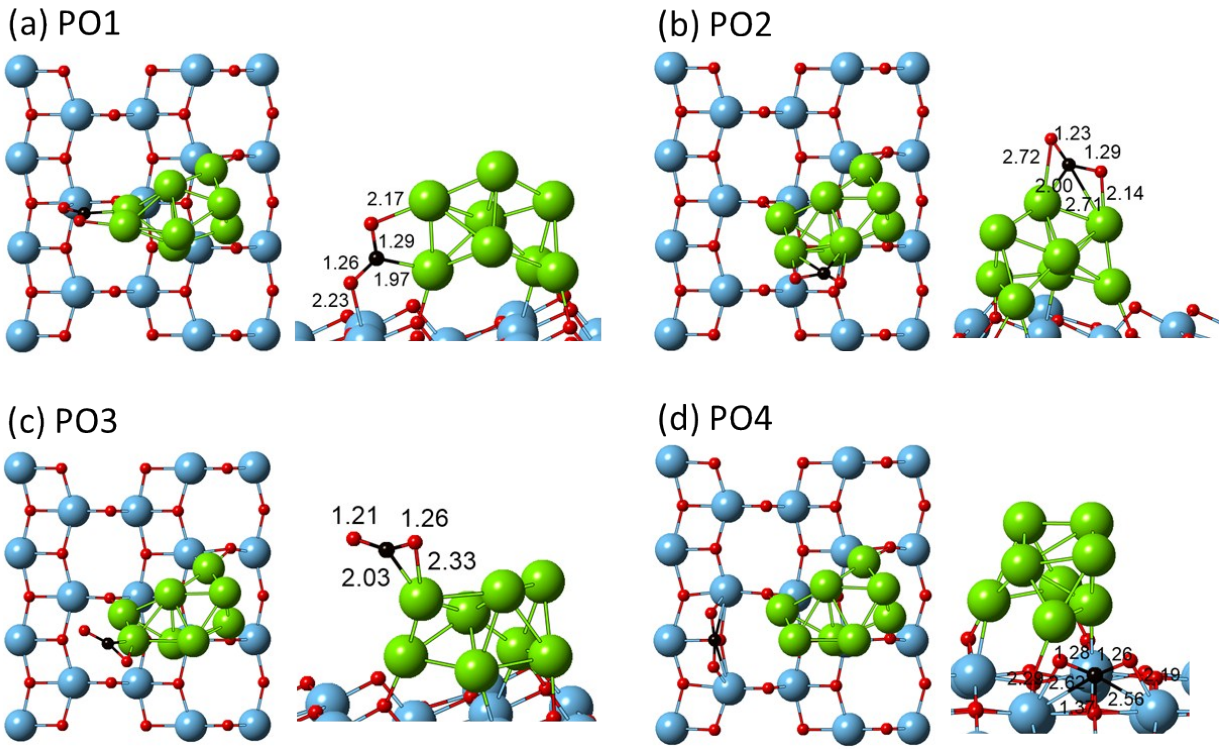

Figure S1. CO_2 adsorption configurations on anatase TiO_2(101) surface with Pt octamers upon one electron introduced in the model slabs (PO represents octamer; O in red, C in black, Ti in blue, and Pt in green; The numbers indicate the bond lengths in Å).

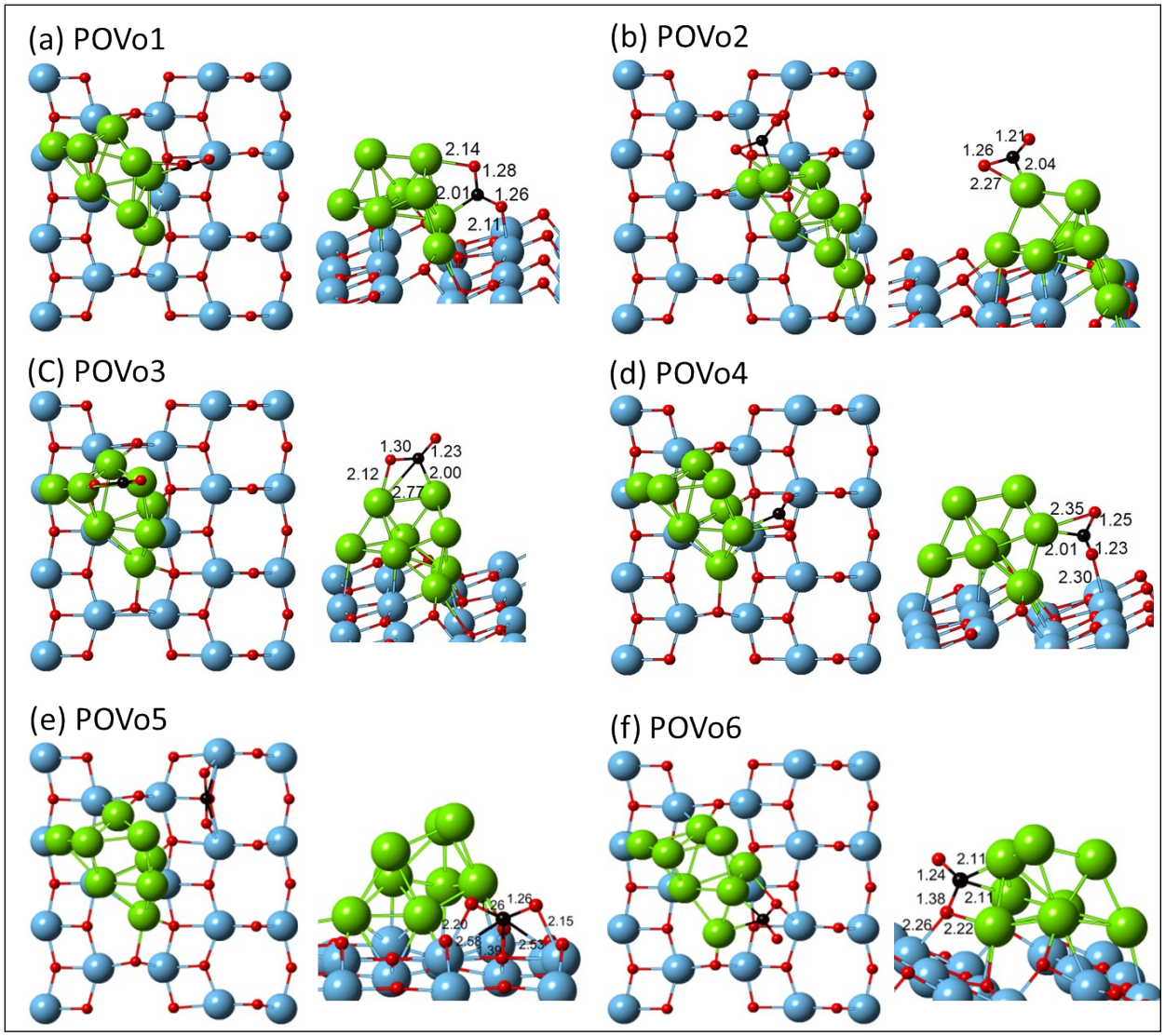

Figure S2. CO_2 adsorption configurations on anatase TiO_2(101) surface with Pt octamers upon one electron introduced in the model slabs (PO represents octamer; Vo represents an oxygen vacancy; O in red, C in black, Ti in blue, and Pt in green; The numbers indicate the bond lengths in Å).

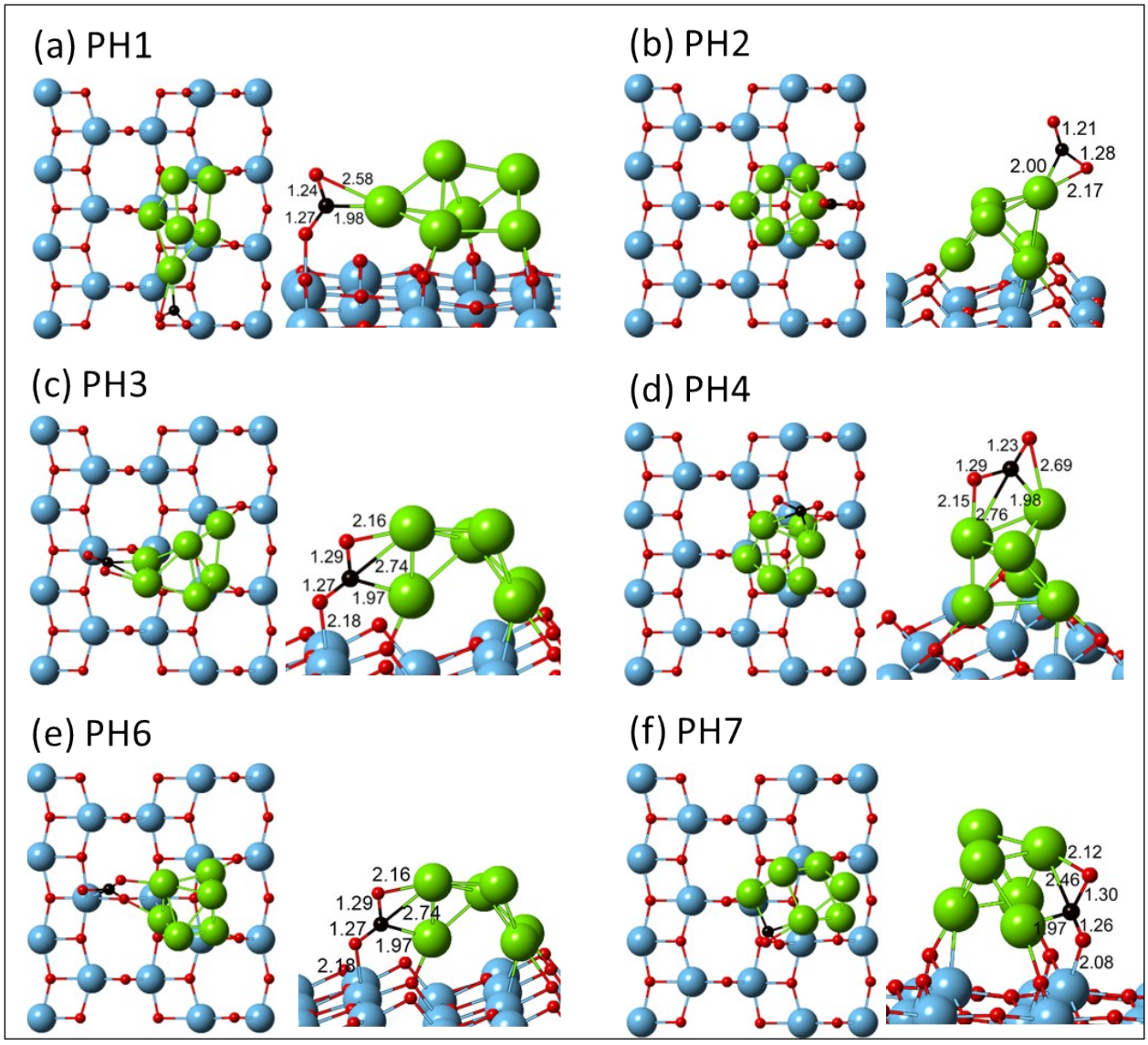

Figure S3. CO_2 adsorption configurations on anatase TiO_2(101) surface with Pt hexamers upon one electron introduced in the model slabs (PH represents hexamer; O in red, C in black, Ti in blue, and Pt in green. The numbers indicate the bond lengths in Å).

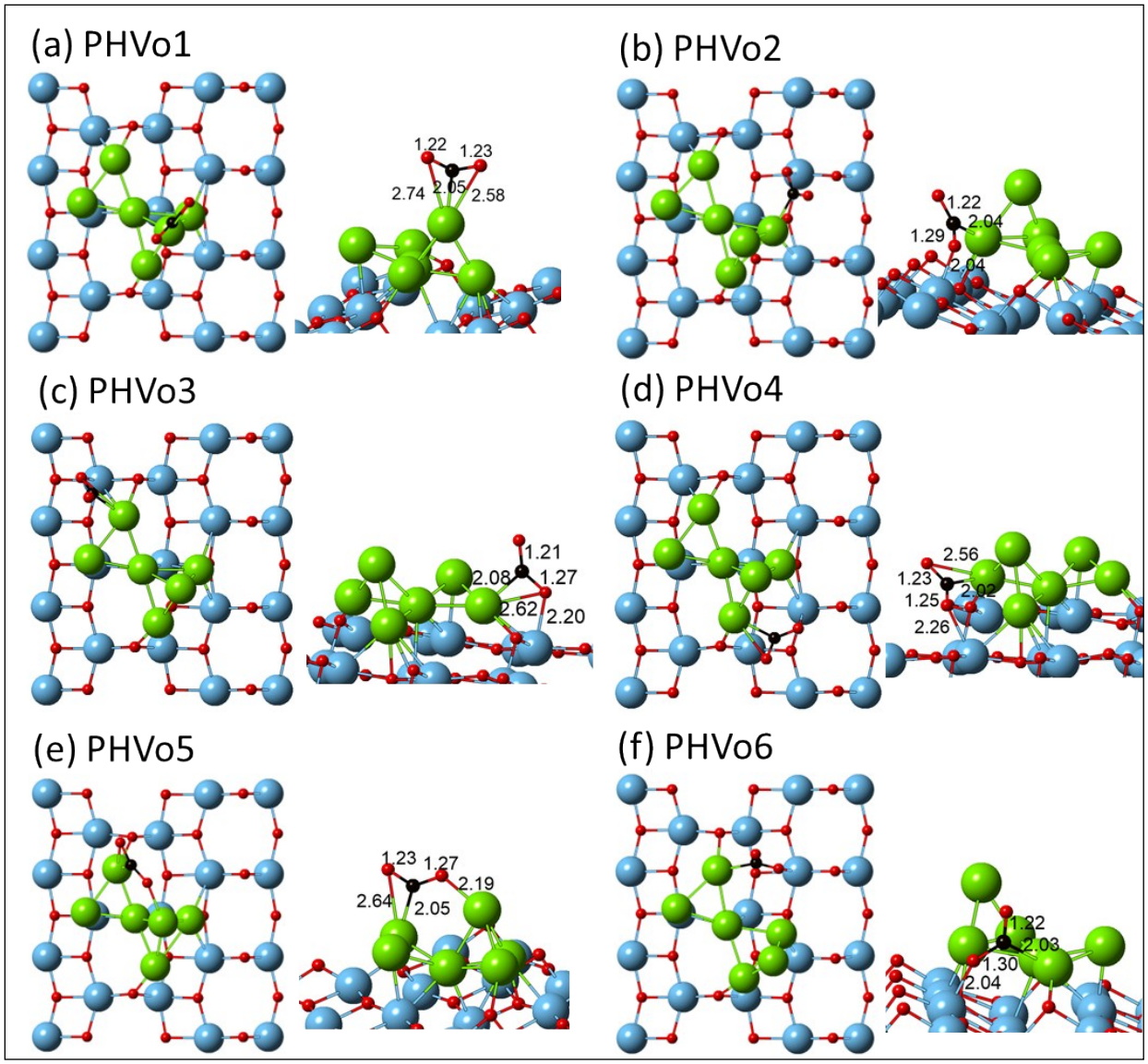

Figure S4. CO_2 adsorption configurations on anatase TiO_2(101) surface with Pt hexamers upon one electron introduced in the model slabs (PH represents hexamer; Vo represents an oxygen vacancy; O in red, C in black, Ti in blue, and Pt in green. The numbers indicate the bond lengths in Å).

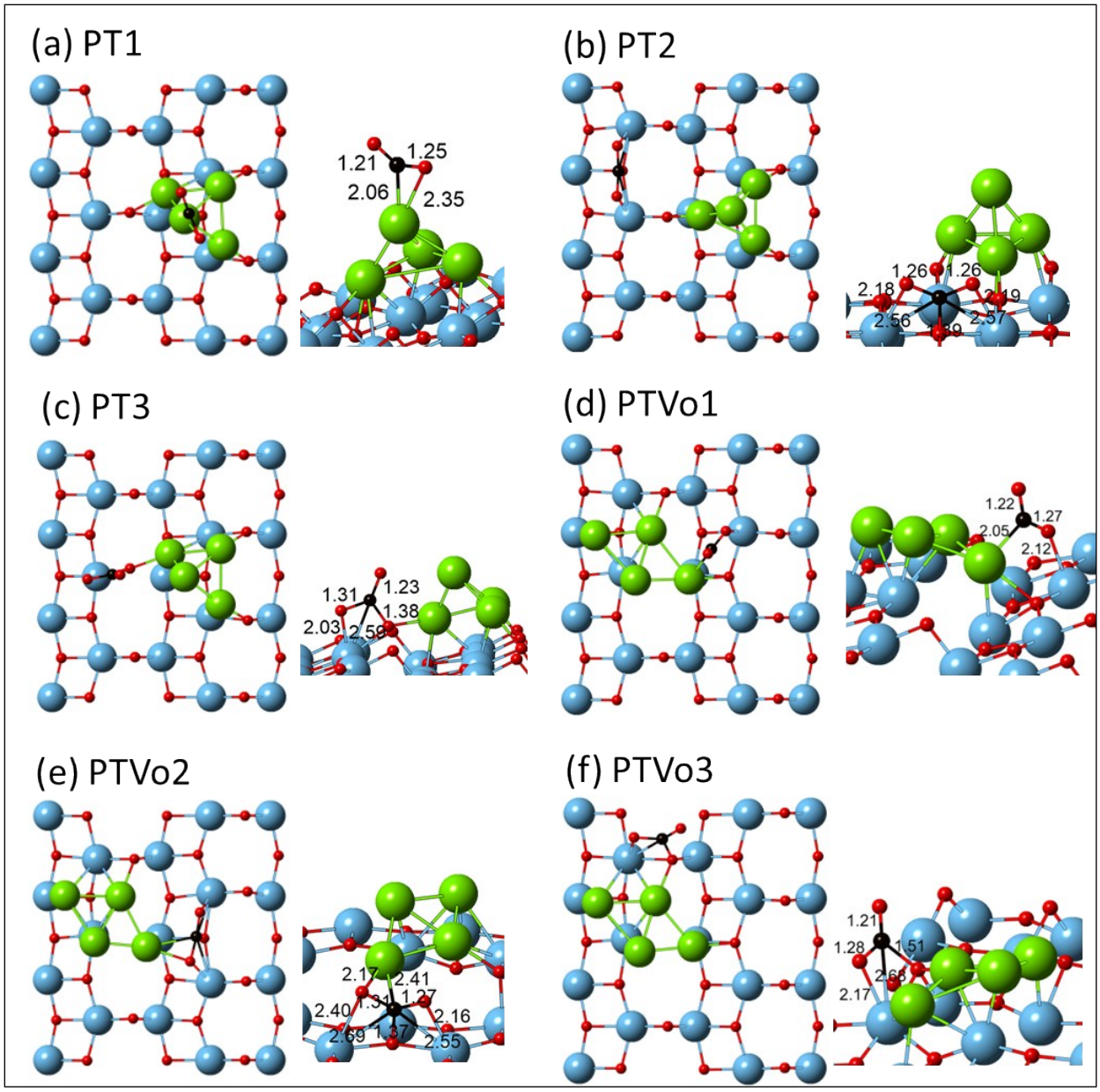

Figure S5. CO_2 adsorption configurations on anatase TiO_2(101) surface with Pt tetramers upon one electron introduced in the model slabs (PT represents tetramer; Vo represents an oxygen vacancy; O in red, C in black, Ti in blue, and Pt in green. The numbers indicate the bond lengths in Å).

Table S1. Interface edge CO_2 adsorption sites on stoichiometry anatase TiO_2(101) surfaces in the presence of Pt clusters upon one, two, and three electrons introduced into the model slabs.

	d(C-O)(Å)		d(O-Pt)(Å)	d(C-Pt)(Å)	d(O-Ti)(Å)
PO1	1.28	1.26	2.17	1.97	2.20
PO1(1e)	1.29	1.26	2.17	1.97	2.23
PO1(2e)	1.29	1.26	2.16	1.96	2.18
PO1(3e)	1.29	1.27	2.14	1.96	2.14
PH1	1.26	1.23	2.20	1.99	2.19
PH1(1e)	1.24	1.27	2.58	1.98	2.04
PH1(2e)	1.24	1.29	2.75	2.00	2.01
PH1(3e)	1.24	1.30	2.81	2.01	1.99
PH3	1.29	1.27	2.13	1.97	2.16
PH3(1e)	1.29	1.27	2.16	1.97	2.18
PH3(2e)	1.29	1.27	2.17	1.96	2.20
PH3(3e)	1.30	1.27	2.19	1.95	2.20
PH7	1.30	1.27	2.12	1.97	2.06
PH7(1e)	1.30	1.26	2.11	1.97	2.08
PH7(2e)	1.30	1.27	2.13	1.97	2.06
PH7(3e)	1.31	1.27	2.13	1.97	2.08

d(C-O): the bond distance of C-O in CO_2; d(O-Pt): the bond distance of O (of CO_2) and Pt; d(C-Pt): the bond distance of C (of CO_2) and Pt; d(O-Ti): the bond distance of O (of CO_2) and surface Ti; PH and PO represent Pt hexamer and octamer, respectively; 1e, 2e, and 3e in the parenthesis indicate the introduction of 1, 2, and 3 electrons in the model systems.

Table S2. Interface edge CO_2 adsorption sites on anatase TiO_2(101) surfaces with an oxygen vacancy in the presence of Pt clusters upon one, two, and three electrons introduced into the model slabs.

	d(C-O)(Å)		d(O-Pt)(Å)	d(C-Pt)(Å)	d(O-Ti)(Å)
POVo1	1.28	1.26	2.13	2.01	2.09
POVo1(1e)	1.28	1.26	2.14	2.01	2.11
POVo1(2e)	1.28	1.26	2.15	2.00	2.12
POVo1(3e)	1.29	1.26	2.18	1.99	2.11
POVo4	1.25	1.23	2.33	2.01	2.28
POVo4(1e)	1.25	1.23	2.35	2.01	2.30
POVo4(2e)	1.25	1.21	2.31	2.05	3.09
POVo4(3e)	1.26	1.21	2.31	2.04	3.50
POVo6	1.24	1.39	2.22	2.114 2.104	2.24
POVo6(1e)	1.24	1.38	2.22	2.109 2.108	2.26
POVo6(2e)	1.24	1.39	2.27	2.098 2.115	2.21
POVo6(3e)	1.25	1.38	2.28	2.097 2.120	2.24
PHVo2	1.22	1.29	2.82	2.04	2.02
PHVo2(1e)	1.22	1.29	2.82	2.04	2.04
PHVo2(2e)	1.23	1.29	2.84	2.04	2.03
PHVo2(3e)	1.25	1.28	2.81	2.01	2.05

d(C-O): the bond distance of C-O in CO_2; d(O-Pt): the bond distance of O (of CO_2) and Pt; d(C-Pt): the bond distance of C (of CO_2) and Pt; d(O-Ti): the bond distance of O (of CO_2) and surface Ti; PH and PO represent Pt hexamer and octamer, respectively; Vo represents an oxygen vacancy; 1e, 2e, and 3e in the parenthesis indicate the introduction of 1, 2, and 3 electrons in the model systems.

Table S3. Interface edge CO_2 adsorption sites on anatase TiO_2(101) surfaces with an oxygen vacancy in the presence of Pt clusters upon one, two, and three electrons introduced into the model slabs.

	d(C-O)(Å)		d(O-Pt)(Å)	d(C-Pt)(Å)	d(O-Ti)(Å)
PHVo3	1.20	1.26	2.57	2.10	2.23
PHVo3(1e)	1.21	1.27	2.62	2.08	2.20
PHVo3(2e)	1.22	1.28	2.69	2.04	2.14
PHVo3(3e)	1.23	1.28	2.69	2.04	2.15
PHVo4	1.23	1.24	2.52	2.02	2.25
PHVo4(1e)	1.23	1.25	2.56	2.02	2.26
PHVo4(2e)	1.23	1.26	2.67	2.02	2.20
PHVo4(3e)	1.24	1.26	2.70	2.02	2.20
PHVo6	1.22	1.30	2.79	2.04	2.03
PHVo6(1e)	1.22	1.30	2.79	2.03	2.04
PHVo6(2e)	1.23	1.30	2.80	2.01	2.03
PHVo6(3e)	1.23	1.30	2.80	2.01	2.03
PTVo1	1.22	1.26	2.73	2.07	2.10
PTVo1(1e)	1.22	1.27	2.74	2.05	2.12
PTVo1(2e)	1.23	1.27	2.76	2.04	2.15
PTVo1(3e)	1.23	1.27	2.76	2.03	2.14

d(C-O): the bond distance of C-O in CO_2; d(O-Pt): the bond distance of O (of CO_2) and Pt; d(C-Pt): the bond distance of C (of CO_2) and Pt; d(O-Ti): the bond distance of O (of CO_2) and surface Ti; PT and PH represent Pt tetramer and hexamer, respectively; Vo represents an oxygen vacancy; 1e, 2e, and 3e in the parenthesis indicate the introduction of 1, 2, and 3 electrons in the model systems.

Table S4. Pt only CO_2 adsorption sites on stoichiometry anatase TiO_2(101) surfaces in the presence of Pt clusters upon one, two, and three electrons introduced into the model slabs.

	d(C-O)(Å)		d(O-Pt)(Å)	d(C-Pt)(Å)	d(O-Ti)(Å)
PO3	1.21	1.24	2.39	2.08	148.40
PO3(1e)	1.21	1.26	2.33	2.03	144.09
PO3(2e)	1.22	1.27	2.34	2.01	140.98
PO3(3e)	1.23	1.27	2.38	2.00	138.32
PH2	1.20	1.27	2.14	2.03	146.572
PH2(1e)	1.21	1.28	2.17	2.00	142.974
PH2(2e)	1.22	1.28	2.20	1.97	139.66
PH2(3e)	1.23	1.29	2.26	1.98	134.596
PT1	1.20	1.25	2.28	2.11	151.15
PT1(1e)	1.21	1.25	2.35	2.06	146.007
PT1(2e)	1.22	1.28	2.27	2.02	139.32
PT1(3e)	1.23	1.28	2.33	2.01	135.934
PO2	1.28	1.23	2.15 2.66	2.69 2.01	135.90
PO2(1e)	1.29	1.23	2.14 2.72	2.71 2.00	132.84
PO2(2e)	1.30	1.24	2.14 2.77	2.74 2.00	130.32
PO2(3e)	1.31	1.25	2.15 2.83	2.77 1.99	127.47
PH4	1.27	1.23	2.16 2.54	2.75 1.97	136.566
PH4(1e)	1.29	1.23	2.15 2.69	2.76 1.98	132.899
PH4(2e)	1.29	1.24	2.16 2.76	2.77 1.98	130.362
PH4(3e)	1.31	1.25	2.16 2.81	2.80 1.97	127.267

d(C-O): the bond distance of C-O in CO_2; d(O-Pt): the bond distance of O (of CO_2) and Pt; d(C-Pt): the bond distance of C (of CO_2) and Pt; d(O-Ti): the bond distance of O (of CO_2) and surface Ti; PT, PH, and PO represent Pt tetramer, hexamer, and octamer, respectively; 1e, 2e, and 3e in the parenthesis indicate the introduction of 1, 2, and 3 electrons in the model systems.

Table S5. Pt only CO_2 adsorption sites on stoichiometry anatase TiO_2(101) surfaces with an oxygen vacancy in the presence of Pt clusters upon one, two, and three electrons introduced into the model slabs.

	d(C-O)(Å)		d(O-Pt)(Å)	d(C-Pt)(Å)	d(O-Ti)(Å)
POVo2	1.26	1.20	2.23 3.00	2.06	147.607
POVo2(1e)	1.26	1.21	2.27 2.98	2.04	144.782
POVo2(2e)	1.23	1.24	2.77 2.64	2.03	141.632
POVo2(3e)	1.23	1.26	2.94 2.50	2.02	137.276
PHVo1	1.21	1.22	2.70 2.60	2.10	154.734
PHVo1(1e)	1.22	1.23	2.74 2.58	2.05	148.08
PHVo1(2e)	1.28	1.22	2.29 3.00	2.01	139.666
PHVo1(3e)	1.28	1.22	2.32 3.00	2.00	137.375
POVo3	1.29	1.22	2.74 2.11	2.01 2.75	134.222
POVo3(1e)	1.30	1.23	2.78 2.12	2.00 2.77	131.729
POVo3(2e)	1.30	1.23	2.81 2.15	2.00 2.79	129.178
POVo3(3e)	1.31	1.24	2.85 2.17	2.00 2.81	126.974
PHVo5	1.24	1.30	2.58 2.07	1.98 3.01	126.93
PHVo5(1e)	1.23	1.27	2.64 2.19	2.05 3.11	132.073
PHVo5(2e)	1.25	1.29	2.60 2.14	1.99 2.97	126.868
PHVo5(3e)	1.25	1.30	2.62 2.14	1.99 2.98	125.502

d(C-O): bond distances of C-O in CO_2; d(O-Pt): bond distance of O (of CO_2) and Pt; d(C-Pt) :bond distance of C (of CO_2) and Pt; d(O-Ti): bond distance of O (of CO_2) and surface Ti; PH and PO represent Pt hexamer and octamer, respectively; Vo represents an oxygen vacancy; 1e, 2e, and 3e in the parenthesis indicate the introduction of 1, 2, and 3 electrons in the model systems.

2. Negative charges transfer to CO_2 adsorption sites directly on TiO_2 w/wo Pt clusters upon the addition of electrons.

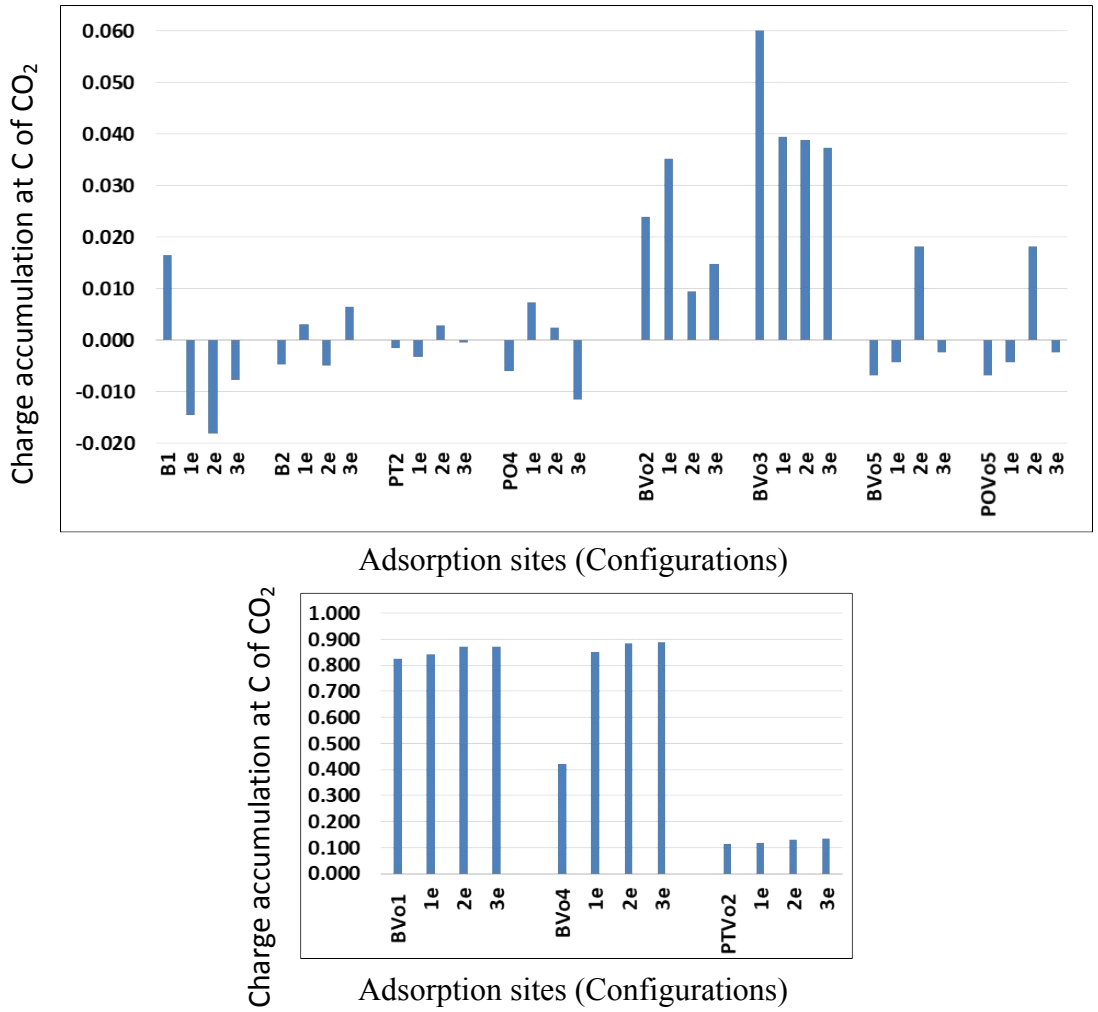

Figure S6. Negative charge accumulation at C of bound CO_2 of sites on anatase TiO_2(101) surfaces w/wo Pt clusters upon the addition of electrons (B represents TiO_2(101) surface without cluster; PT and PO represent Pt tetramer and octamer, respectively; Vo represents an oxygen vacancy; 1e-3e representing the addition of 1-3 electrons; the configurations investigated can be found in Figure S1-S5 except B1, B2, and BVo1-BVo5 in Ref. 18 of the main text).

3. Correlations of vibrational frequencies with negative charge accumulation at C of CO_2 adsorbed on Pt clusters and with their O-C-O angles (neutral and electrons injected model slabs).

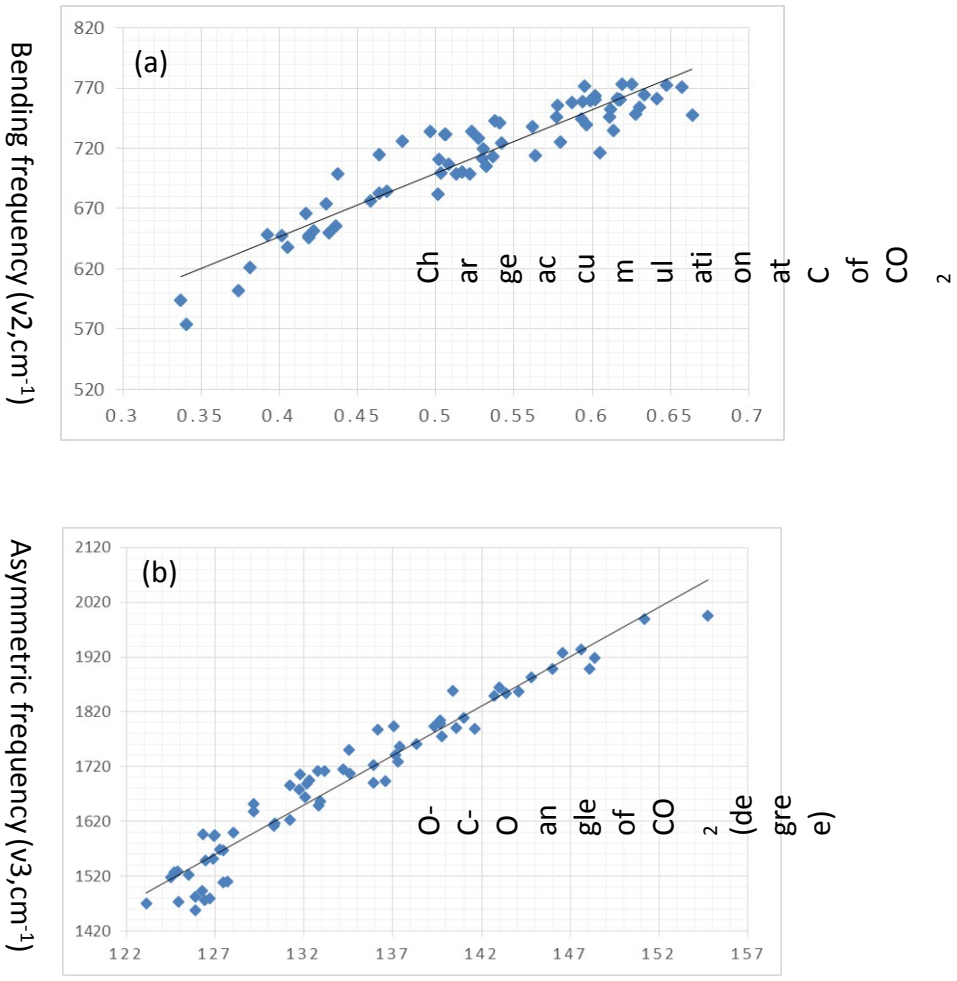

Figure S7. Correlations between (a) the bending frequency (ν2) and the negative charge accumulation at C of adsorbed CO_2, and between (b) the asymmetric stretching frequency (ν3) and the O-C-O angle of those CO_2. Adsorbed CO_2 binding sites are associated with Pt tetramer, hexamer, and octamer with neutral and electrons injected (1-3 electrons) model slabs.