Supporting Information

Theoretical investigation of Cu$_5$/silicates deposited on rutile TiO$_2$ as a photocatalyst

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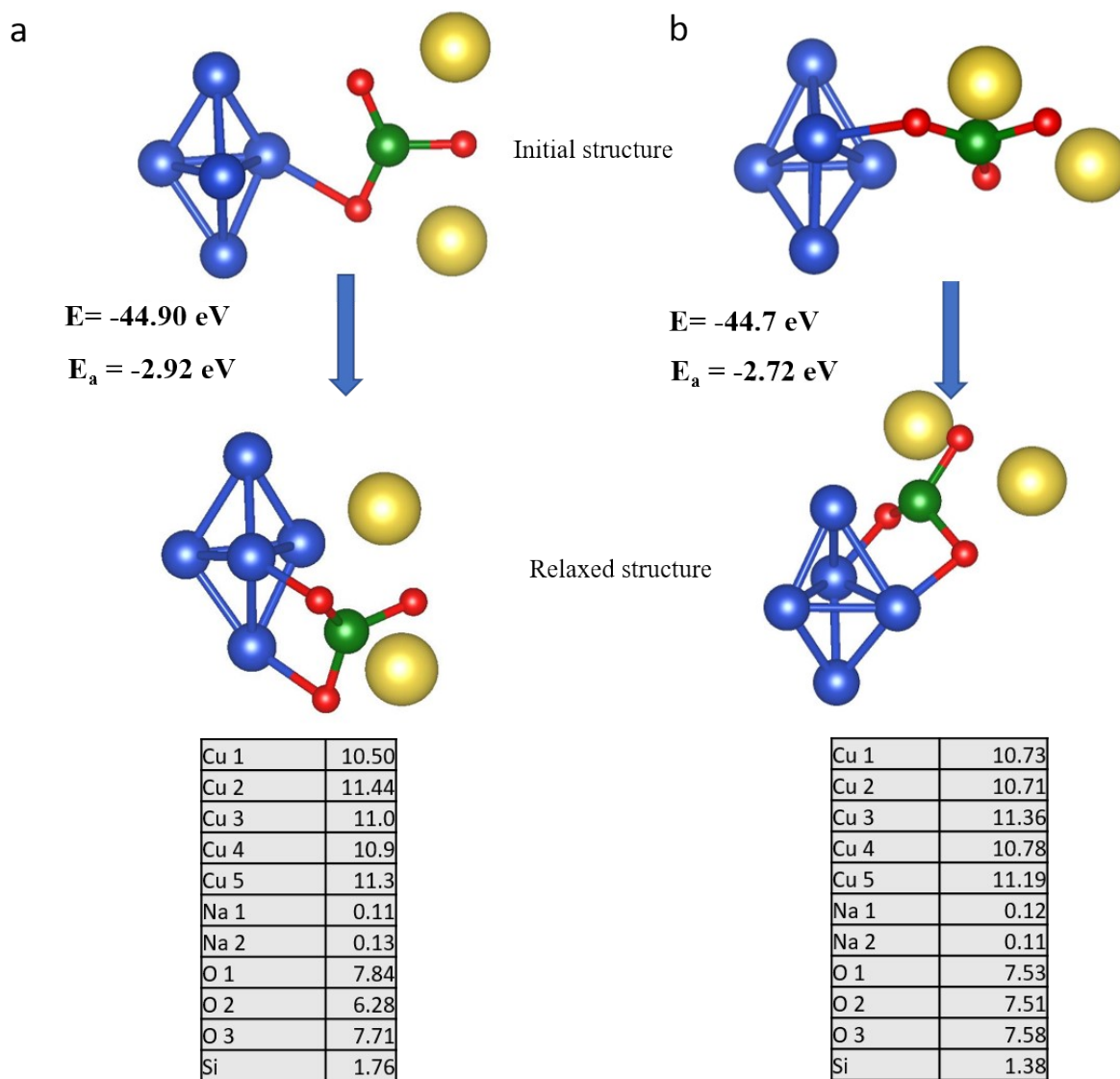
* denotes the corresponding authors.
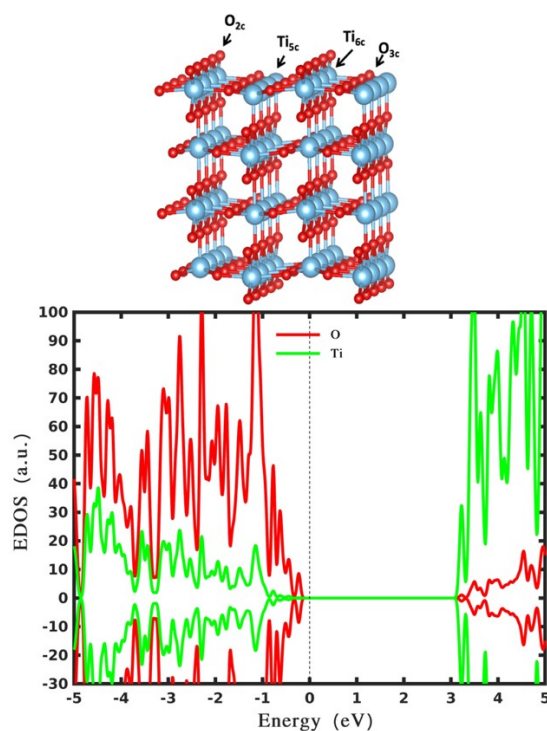
Fig. S1 Schematic of the rutile TiO$_2$(110) slab model and the corresponding density of states. Blue and red balls in the left panel represent titanium and oxygen atoms (the color scheme is used in the following figures). O$_{2c}$ denotes the two-fold coordinated oxygen atom while O$_{3c}$ represents the three-fold coordinated oxygen atom. Ti$_{2c}$ stands for the five-fold coordinated titanium atom while Ti$_{6c}$ is for the six-fold coordinated titanium atom. The green and red curves depict the projected density of states on titanium and oxygen atoms, while the black curve is the total density of states.
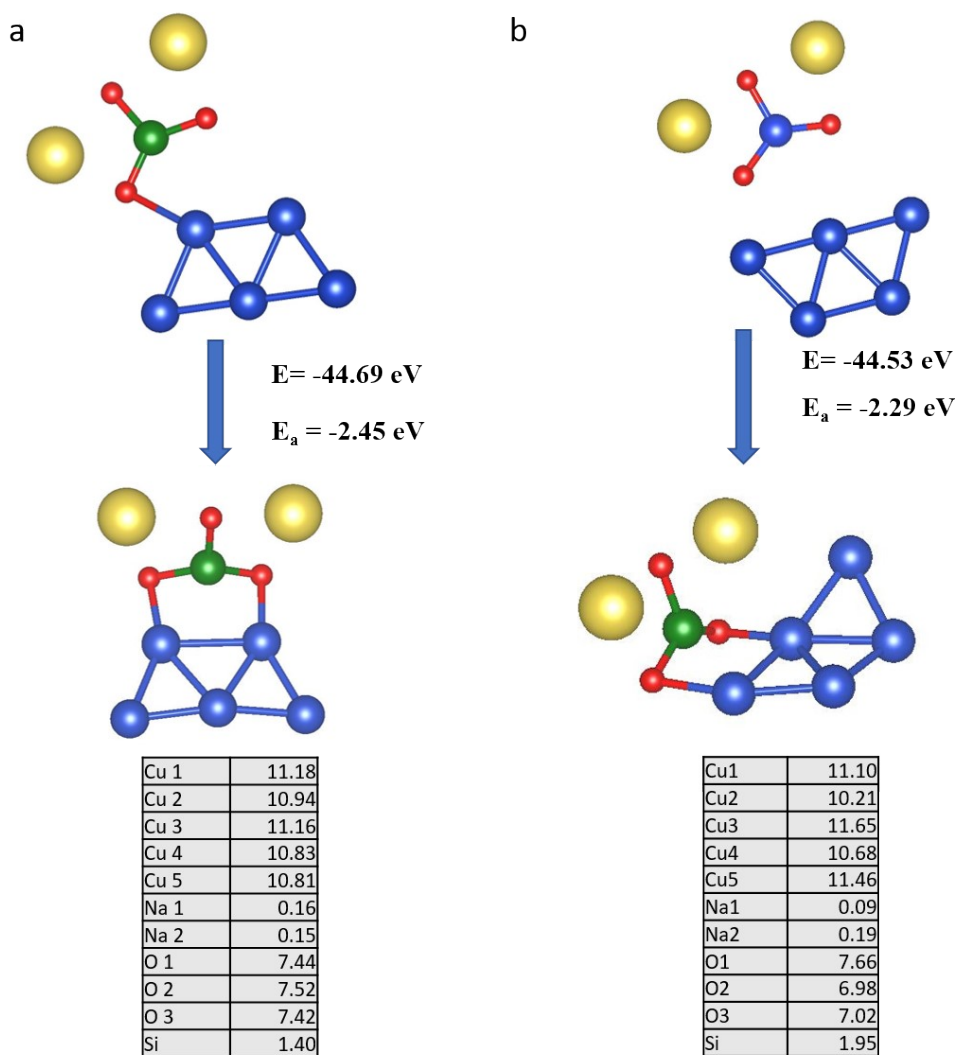
a   b

Na	0.04
Na	0.06
O	7.10
O	7.82
O	7.79
Si	1.20

Cu	10.07
O	7.32
O	7.12
O	7.40
Si	1.09
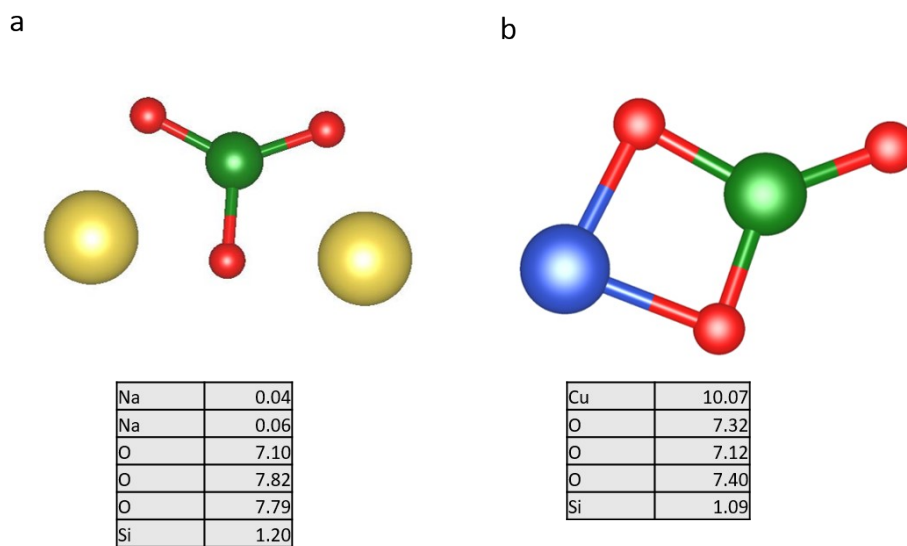
Fig. S2 Simulations for neutral system Na$_2$SiO$_3$ (a) and CuSiO$_3$ (b). The yellow ball represents Na atom, the blue represents Cu atom, the red represents O atom, and the green represents Si atom. The bottom tables show the number of valence electrons for each atom.

E_{ads} = -1.75 eV E_{ads} = -2.1 eV
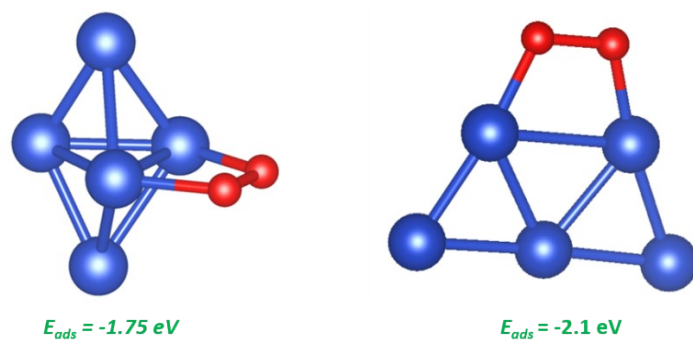
Fig. S3 One oxygen dimers adsorbed on a pyramidal (a) and trapezoidal (b) Cu$_5$ AQC. the green numbers show the adsorption energies of the most stable configurations of oxygen.

a

b

Initial structure

E= -44.90 eV

E_a = -2.92 eV

E= -44.7 eV

E_a = -2.72 eV

Relaxed structure

Cu 1	10.50
Cu 2	11.44
Cu 3	11.0
Cu 4	10.9
Cu 5	11.3
Na 1	0.11
Na 2	0.13
O 1	7.84
O 2	6.28
O 3	7.71
Si	1.76

| Cu 1	10.73
Cu 2	10.71
Cu 3	11.36
Cu 4	10.78
Cu 5	11.19
Na 1	0.12
Na 2	0.11
O 1	7.53
O 2	7.51
O 3	7.58
Si	1.38

Fig. S4 Configurations, adsorption energies, and total energy of SiO_3^{2-} adsorbed on a bipyramidal Cu_5 cluster. Most sable (a), metastable (b). The bottom tables show the number of electrons in the valance bands for each atom.

a

b

E= -44.69 eV

E_a = -2.45 eV

E= -44.53 eV

E_a = -2.29 eV

Cu 1	11.18
Cu 2	10.94
Cu 3	11.16
Cu 4	10.83
Cu 5	10.81
Na 1	0.16
Na 2	0.15
O 1	7.44
O 2	7.52
O 3	7.42
Si	1.40

Cu1	11.10
Cu2	10.21
Cu3	11.65
Cu4	10.68
Cu5	11.46
Na1	0.09
Na2	0.19
O1	7.66
O2	6.98
O3	7.02
Si	1.95

Fig. S5 Configurations, adsorption energies, and total energy of SiO_3^{2-} adsorbed on a trapezoidal Cu_5 cluster. Most sable (a), metastable (b). The bottom tables show the number of electrons in the valance bands for each atom.
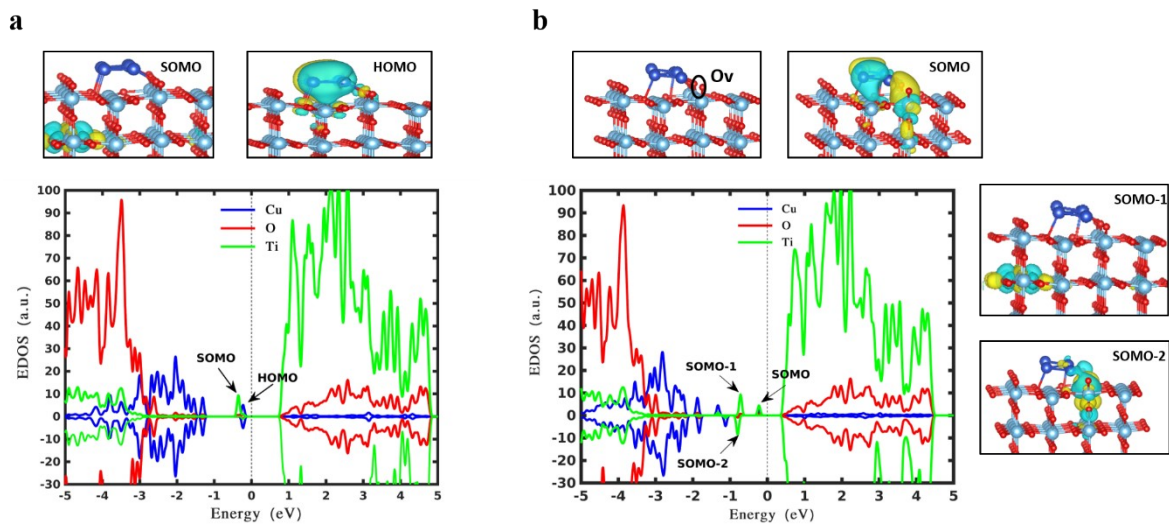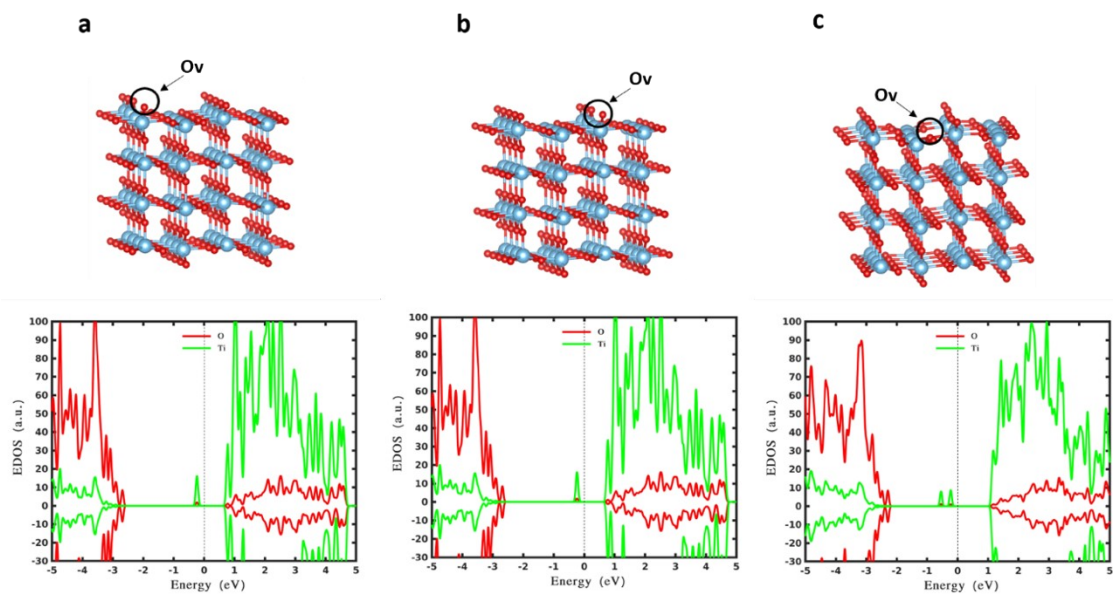
Fig. S6. Frontier molecular orbitals and spin density of states of the metastable trapezoidal Cu_5 cluster deposited on a pristine (a) and reduced (b) rutile $TiO_2(110)$. The green, red, and blue curves represent the states located on titanium, oxygen, and copper atoms respectively. Bader charge analysis reveals that 1.03 electrons (a) ,and 0.77 electrons (b) electrons are transferred from Cu_5 to the support. The dashed line indicates the Fermi energy level of 0 eV.
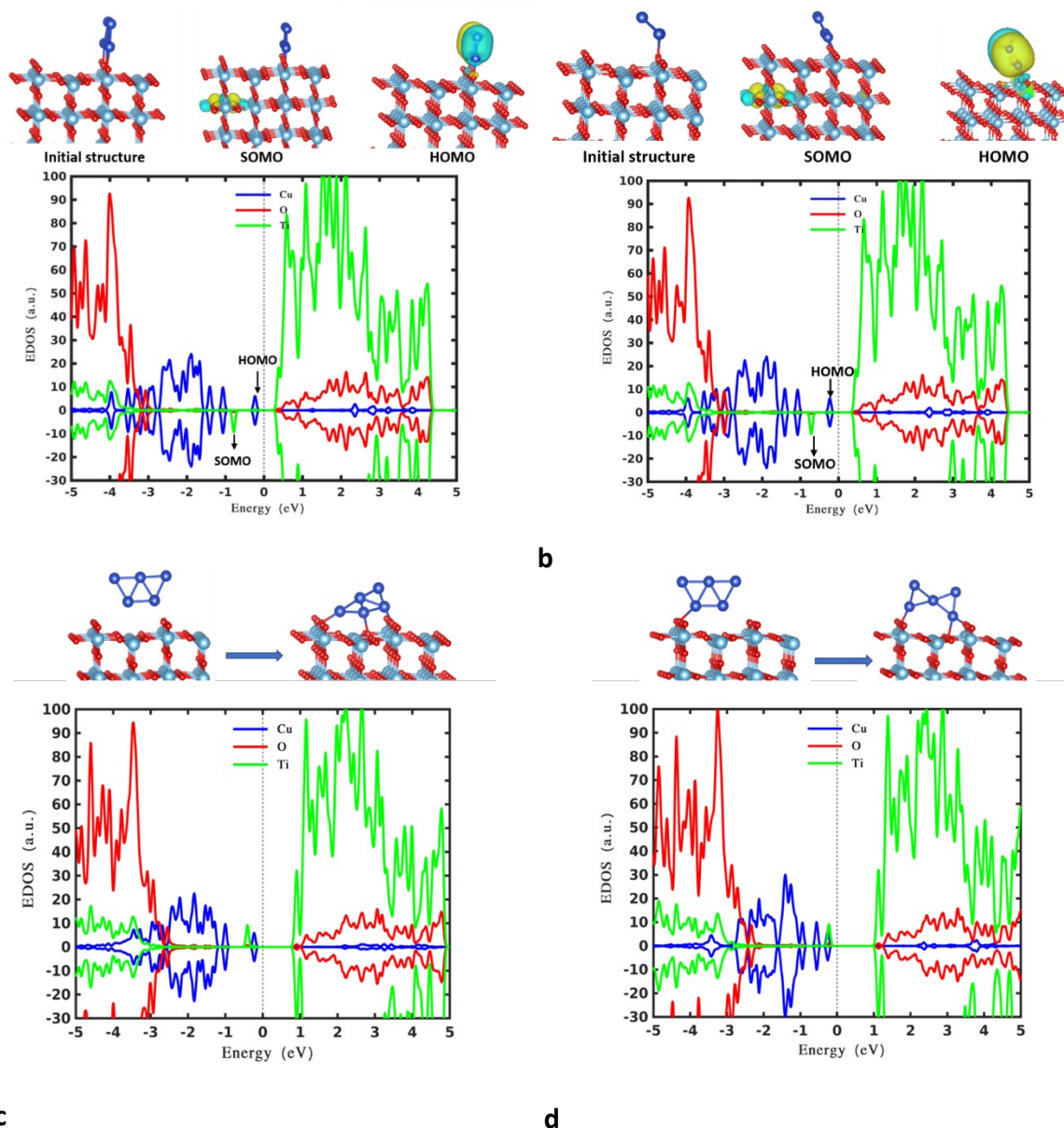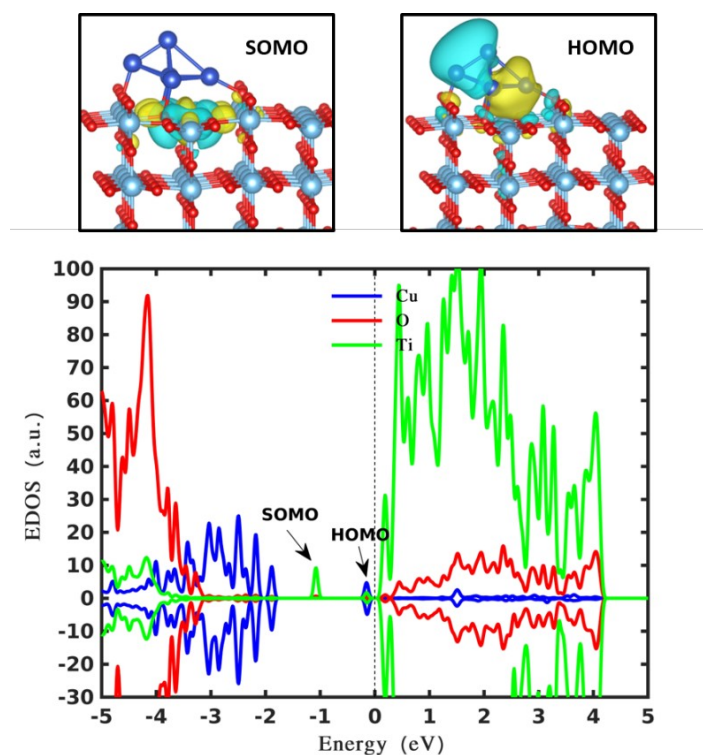
Fig. S7 Molecular orbitals of trapezoidal (a), and tilted trapezoidal (b) Cu$_5$ cluster deposited on rutile TiO$_2$ (110) surface, and 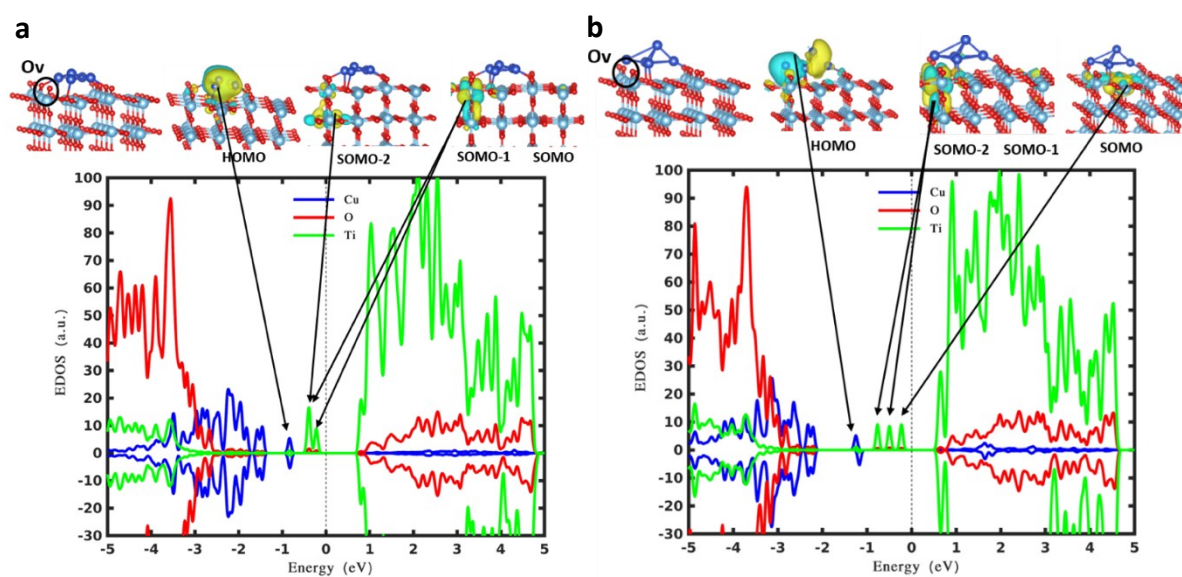their corresponding spin densities of states. The SOMO and HOMO orbitals are presented in the top panels (HOMO: highest occupied molecular orbital). The green, red and blue curves represent the states located on titanium, oxygen, and copper atoms respectively. Bader charge analysis reveals that 0.8 electrons (a), 0.79 electrons (b), 0.87 electrons(c), and 0.8 (d) electrons are transferred from Cu$_5$ to the support. The dashed line indicates the Fermi energy level of 0 eV.

Fig. S8 Relaxed configurations of reduced TiO$_2$ for different positions of Oxygen vacancy, and their corresponding spin densities of states.

Fig. S9 Frontier molecular orbitals and spin density of states of the metastable pyrmidal Cu$_5$ cluster deposited on a pristine rutile TiO$_2$(110). The green, red, and blue curves represent the states located on titanium, oxygen, and copper atoms respectively. The dashed line indicates the Fermi energy level of 0 eV.

Fig. S10 Molecular orbitals of trapezoidal (a), and pyramidal (b) Cu$_5$ cluster deposited on reduced rutile TiO$_2$(110) surface, and their corresponding spin densities of states. The SOMO and HOMO orbitals are presented in the top panels (HOMO: highest occupied molecular orbital). The green, red and blue curves represent the states located on titanium, oxygen, and copper atoms respectively, while the two green peaks between − 1 ~ 0 eV stand for the polaronic states located on one 5-fold coordinated Ti3+(3d) atom in the surface and one 6-fold coordinated Ti3+(3d) in the subsurface. The dashed line indicates the Fermi energy level of 0 eV.
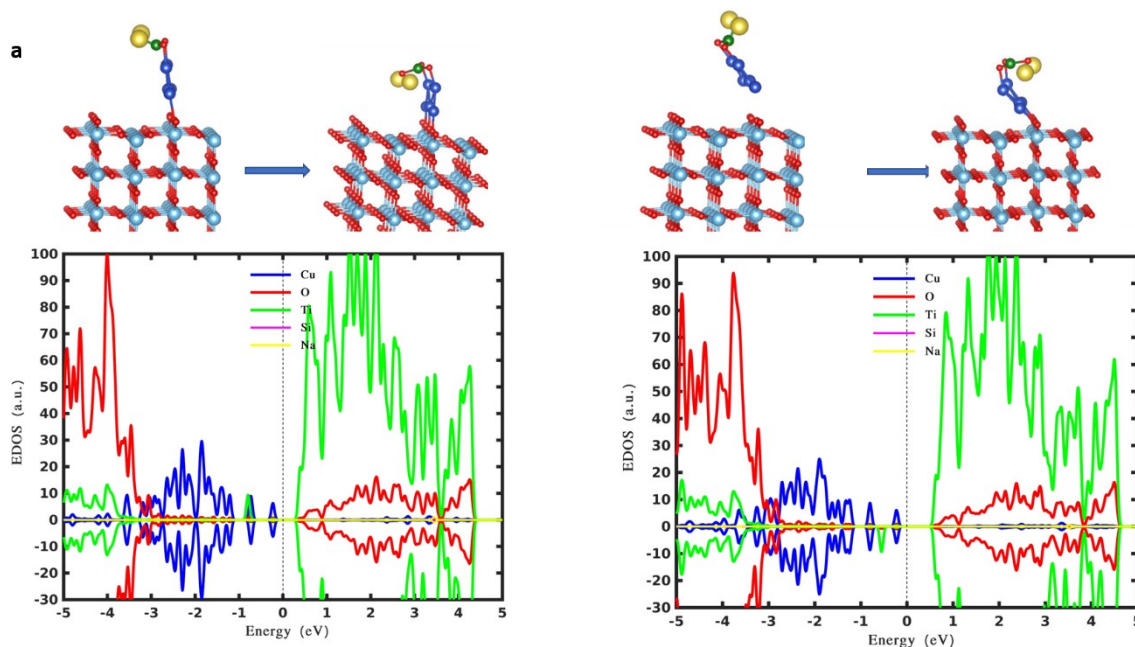
Fig. Molecular orbitals of trapezoidal (a), and tilted trapezoidal (b) Cu$_5$ cluster in the presence of SiO_3^{2-} deposited on rutile TiO$_2$(110) surface, and their corresponding spin densities of states. The SOMO and HOMO orbitals are presented in the top panels (HOMO: highest occupied molecular orbital). The green, red and blue curves represent the states located on titanium, oxygen, and copper atoms respectively. Bader charge analysis reveals that 0.7 electrons (a) and 0.8 electrons (b) are transferred from Cu$_5$ to the support. The dashed line indicates the Fermi energy level of 0 eV.
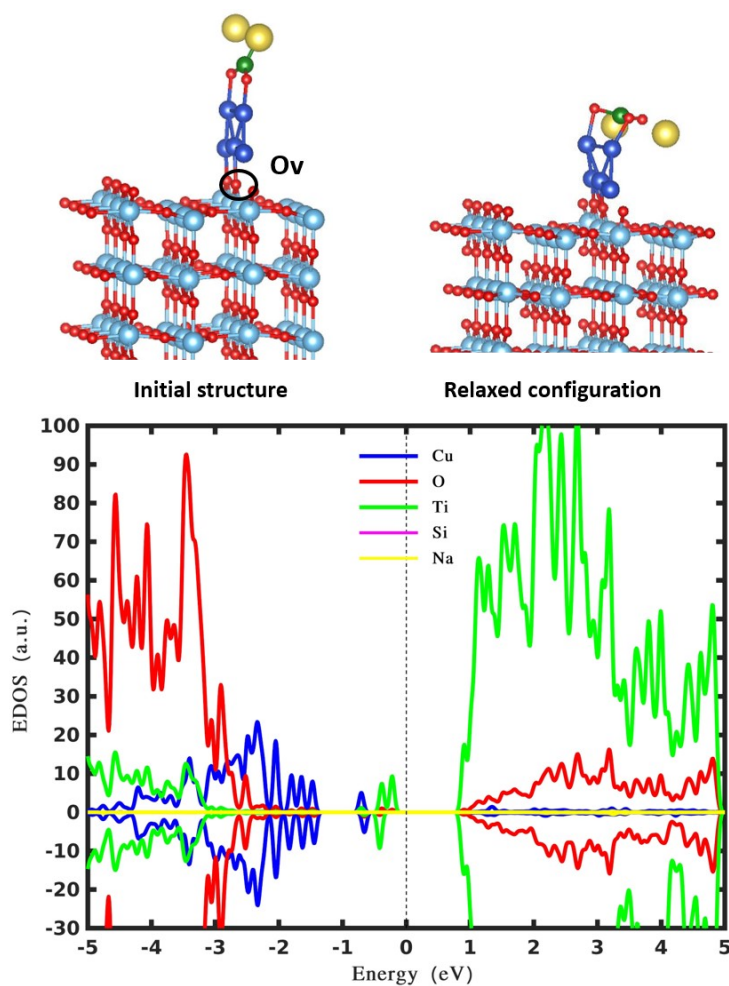
Fig. S12 Configurations of trapezoidal Cu$_5$/SiO_3^{2-} deposited on rutile TiO$_2$(110) and the corresponding density of states. The green, red and blue curves represent the states located on Titanium, oxygen, and copper atoms. The dashed line indicates the Fermi energy level of 0 eV.
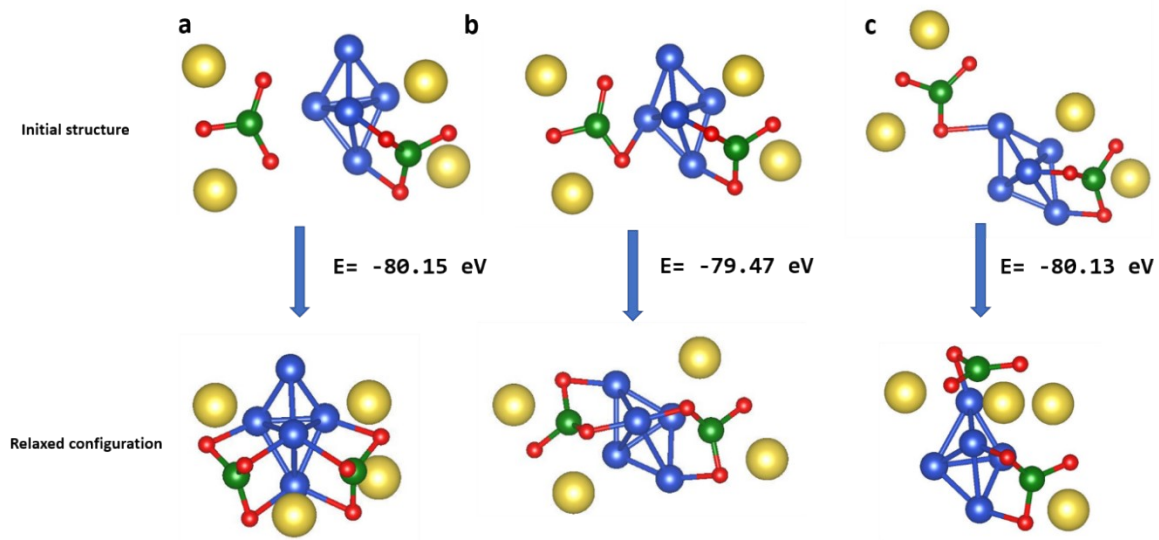
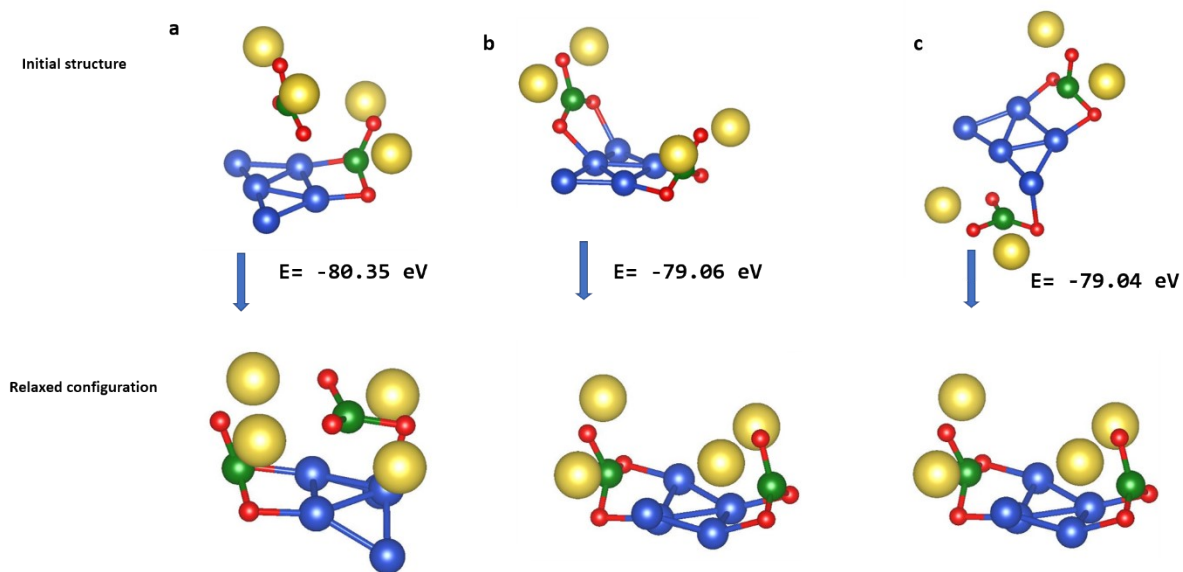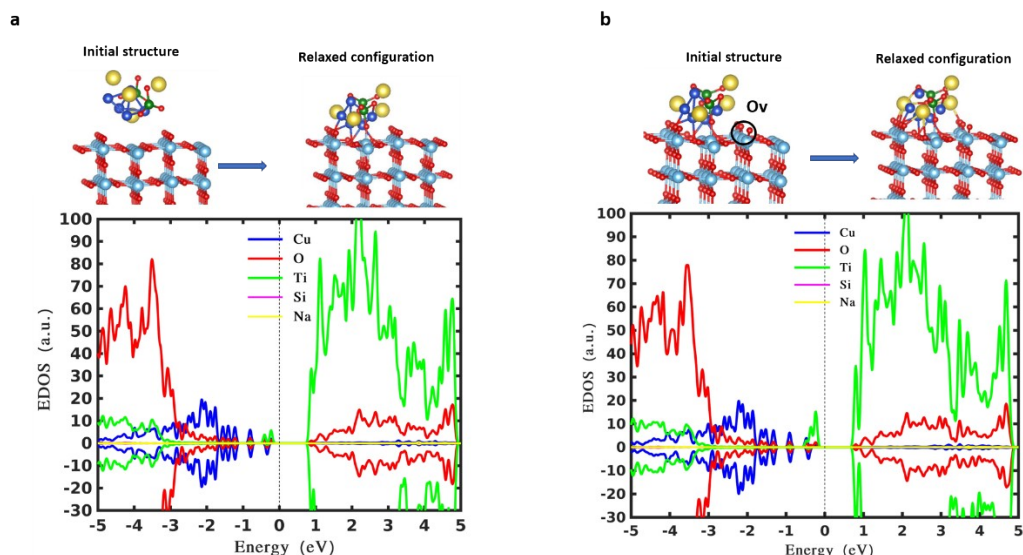**Fig. S13 Configurations and total energy of SiO_3^{2-} adsorbed on a pyramidal Cu$_5$ cluster.**

Fig. S14 Configurations and total energy of SiO_3^{2-} adsorbed on a trapezoidal Cu$_5$ cluster.
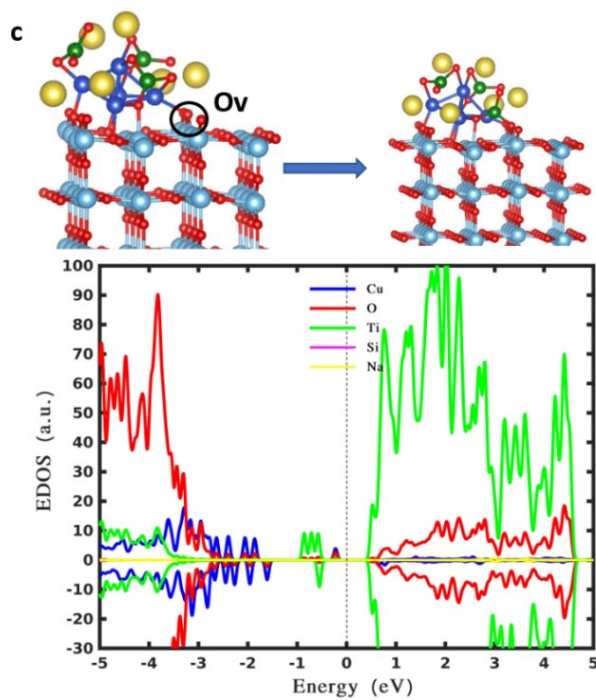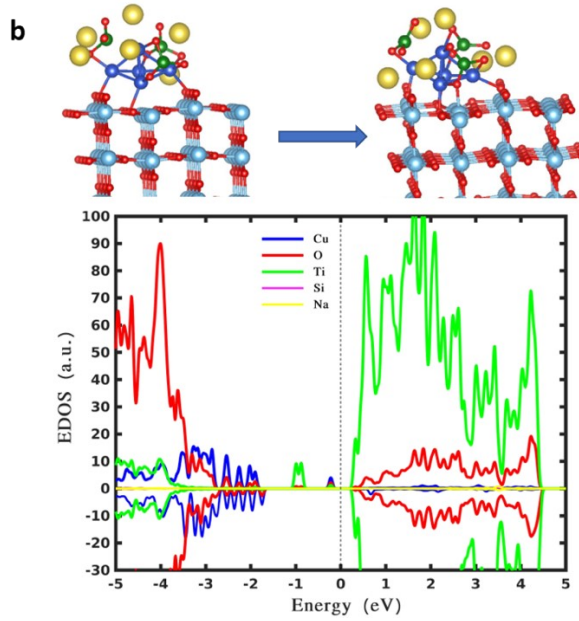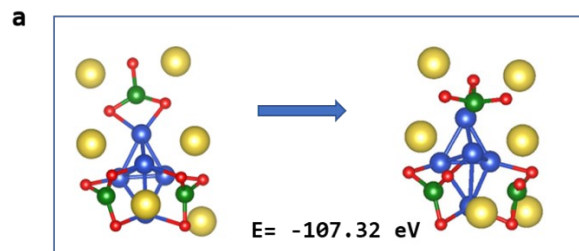
Fig. S15 Configurations of pyramidal Cu$_5$/SiO_3^{2-} deposited on perfect (a) and reduced (b) rutile TiO$_2$(110), and the corresponding density of states. The green, red and blue curves represent the states located on Titanium, oxygen, and copper atoms. Bader charge analysis reveals that 1.3 electrons (a) and 1.3 electrons (b) are transferred from Cu$_5$ to the support. The dashed line indicates the Fermi energy level of 0 eV.
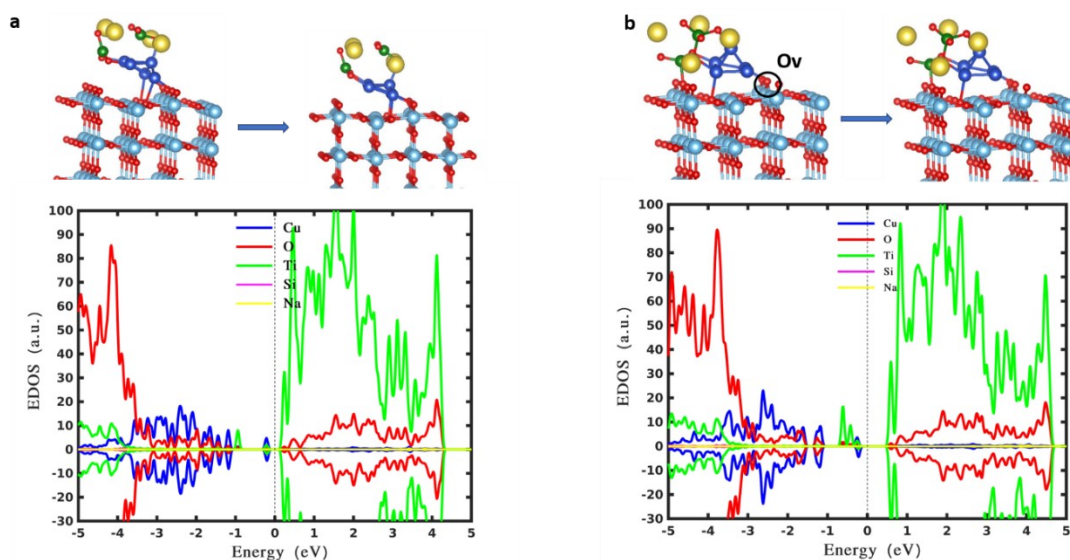
Fig. S16 Configurations of pyramidal Cu$_5$/SiO_3^{2-} deposited on perfect (a) and reduced (b) rutile TiO2(110), and the corresponding density of states. The green, red and blue curves represent the states located on Titanium, oxygen, and copper atoms. Bader charge analysis

reveals that 1 electron (a) and 0.8 electrons (b) are transferred from Cu_5 to the support. The

dashed line indicates the Fermi energy level of 0 eV.

a

E= -107.32 eV

b

c

Fig. S17 Configurations of pyramidal Cu$_5$/ SiO^{2-}_3 (a) deposited on perfect (b) and reduced (c) rutile TiO$_2$(110), and the corresponding density of states. The green, red and blue curves represent the states located on Titanium, oxygen, and copper atoms. Bader charge analysis reveals that 1.5 electrons (a) and 1.5 electrons (b) are transferred from Cu$_5$ to the support. The dashed line indicates the Fermi energy level of 0 eV.
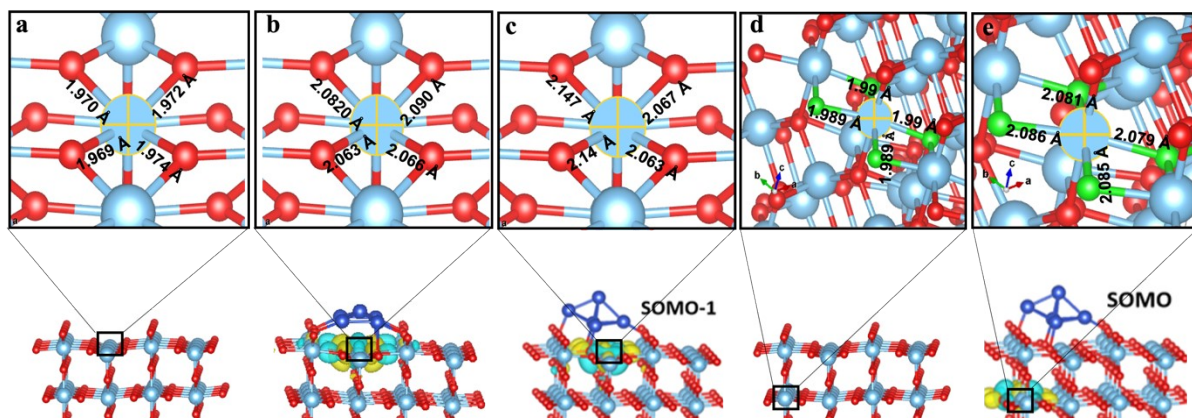
Fig. S18. Lattice structural distortions induced by the excess electron donated from Cu$_5$. (a, d) A bare and pristine surface and subsurface as references. (b, c, e) Elongated Ti-O bond lengths due to the excess electron transferred from Cu$_5$ with different shapes.
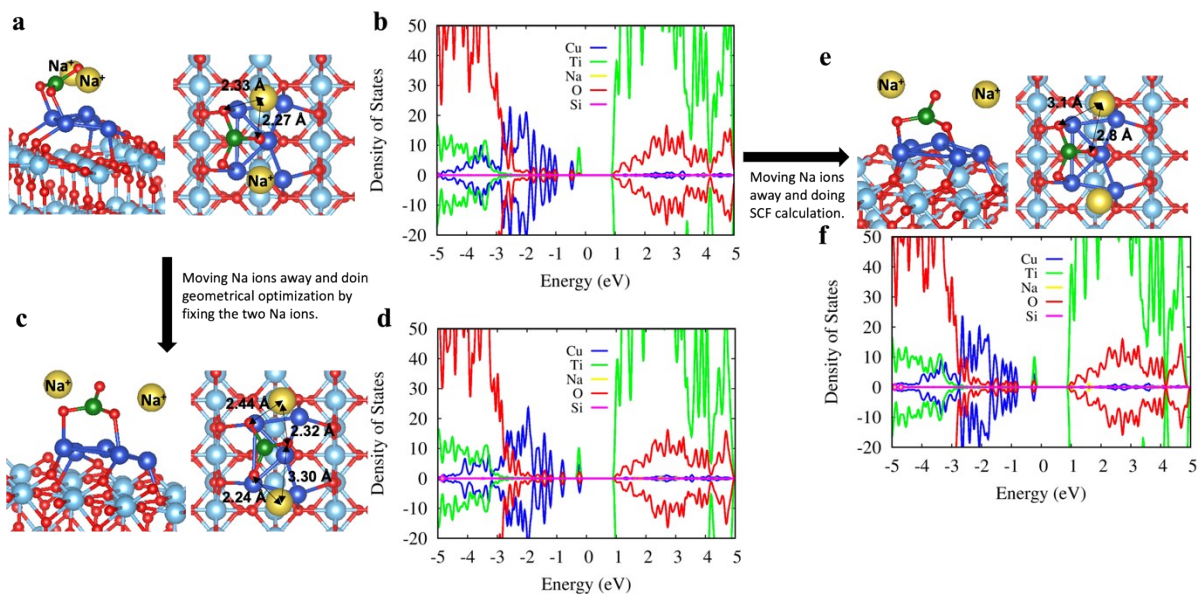
Figure S19. Influence of changing the distance of Na ions from silicate ions. Changing the distance between one of the two Na ions and one of the three O atoms from 2.33Å (a) to 3.1Å (e) produces a negligible change in the density of states. During this process, the charge of Na needs to remain +1 (donating one electron to the system). This means that the Na should not be moved too far away, otherwise the +1 charge state would not persist, and the simulation would be unphysical.
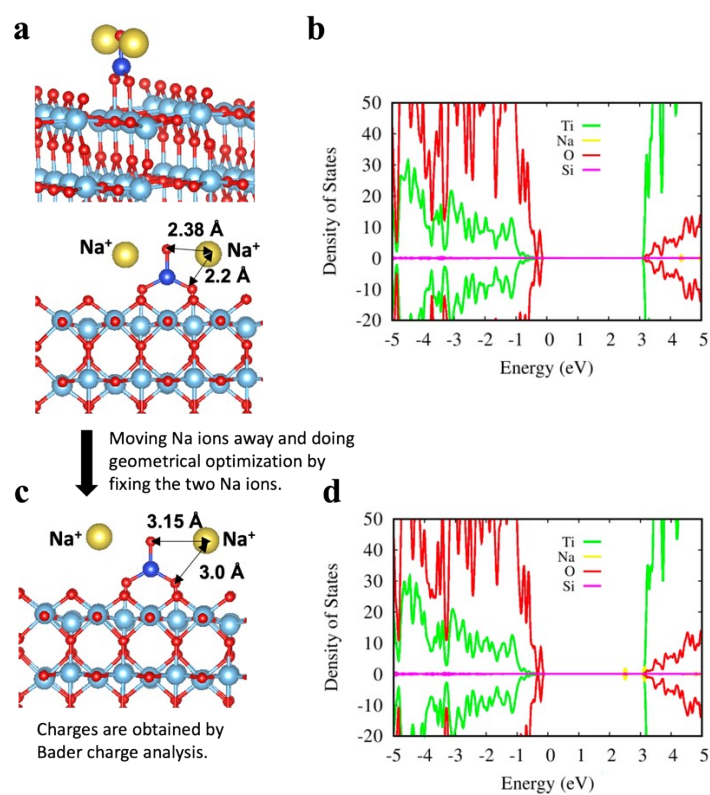

Figure S20. Impact of silicates adsorbed on TiO_2(110) surface. Different distances between Na ions and silicate (a, c) were tested and negligible impact is observed in terms of the density of states (b, d).