Supplementary information

A DFT study of the effect of SO$_4$ groups on the properties of TiO$_2$ nanoparticles

Olga Miroshnichenko[*a,b], Sergei Posysaev[a,b], Matti Alatalo[a]

[a] University of Oulu, Theoretical Physics Research Unit, PL 3000, FI–90014 Oulu, Finland;

[b] Peter the Great St. Petersburg Polytechnic University, Department of Theoretical Mechanics, Polytechnicheskaya 29, 195251 St. Petersburg, Russian Federation.
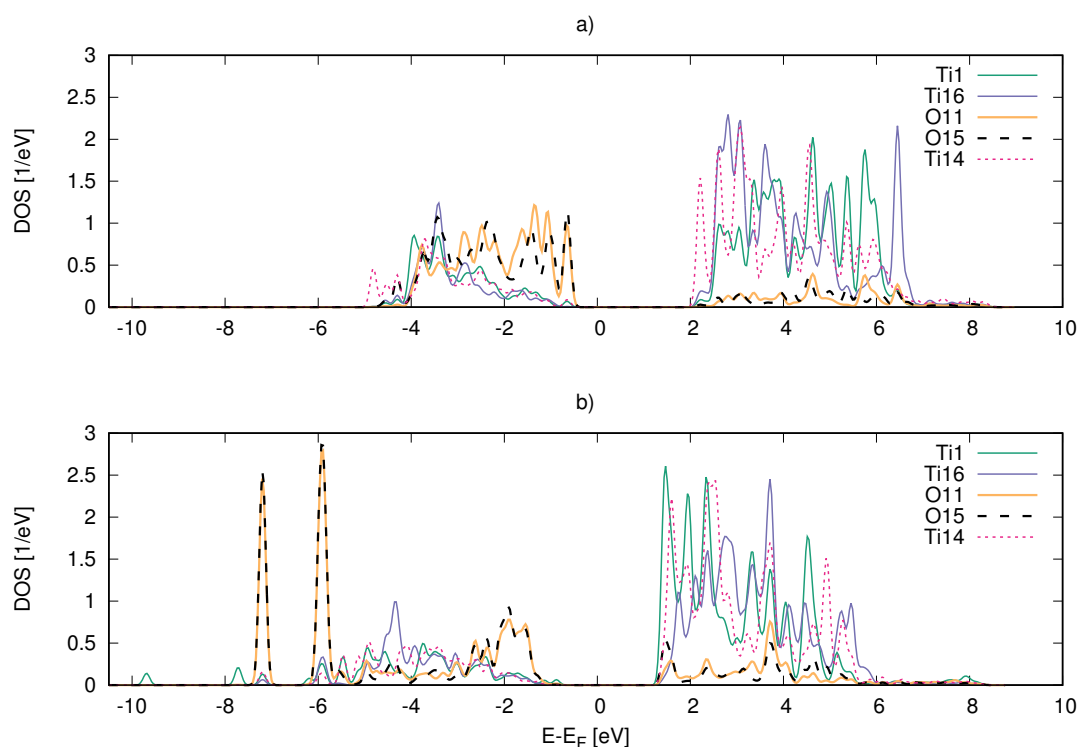
E-mail: olga.miroshnichenko@oulu.fi

Figure S1: LDOS before (a) and after (b) the adsorption of 1 SO$_4$ group for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 d.

Table S1: Detailed electronic states for Ti$_{16}$O$_{32}$ with 1 SO$_4$

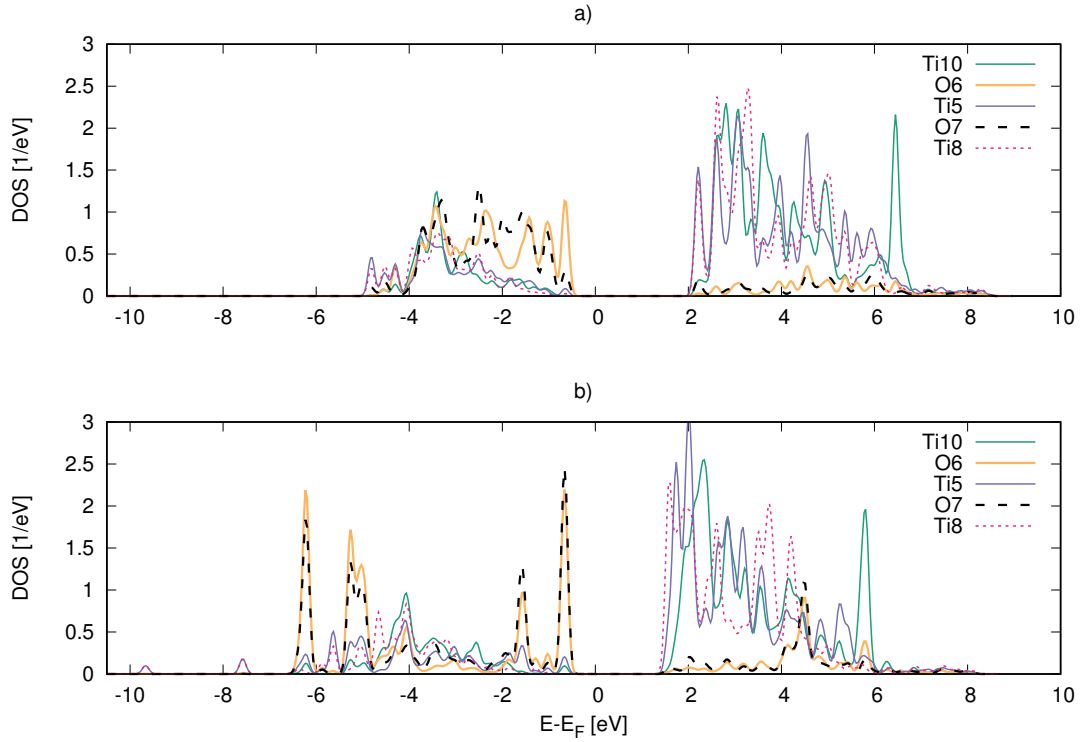| state/eV	atom and orbital	comments
-9.681	Ss	
-7.706	Sp	
-7.204	O11p-O15p	O-O bond
-6.199	Sp	
-5.931	O11p-O15p	O-O bond
-5.529	Sp	
-0.880	O25p, O26p	HOMO level. Double bonded O atoms in the SO$_4$ group
1.448	Ti1d	LUMO level. One of the atoms to which the SO$_4$ group is attached

Figure S2: LDOS before (a) and after (b) the adsorption of 2 SO_4 groups for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 e.
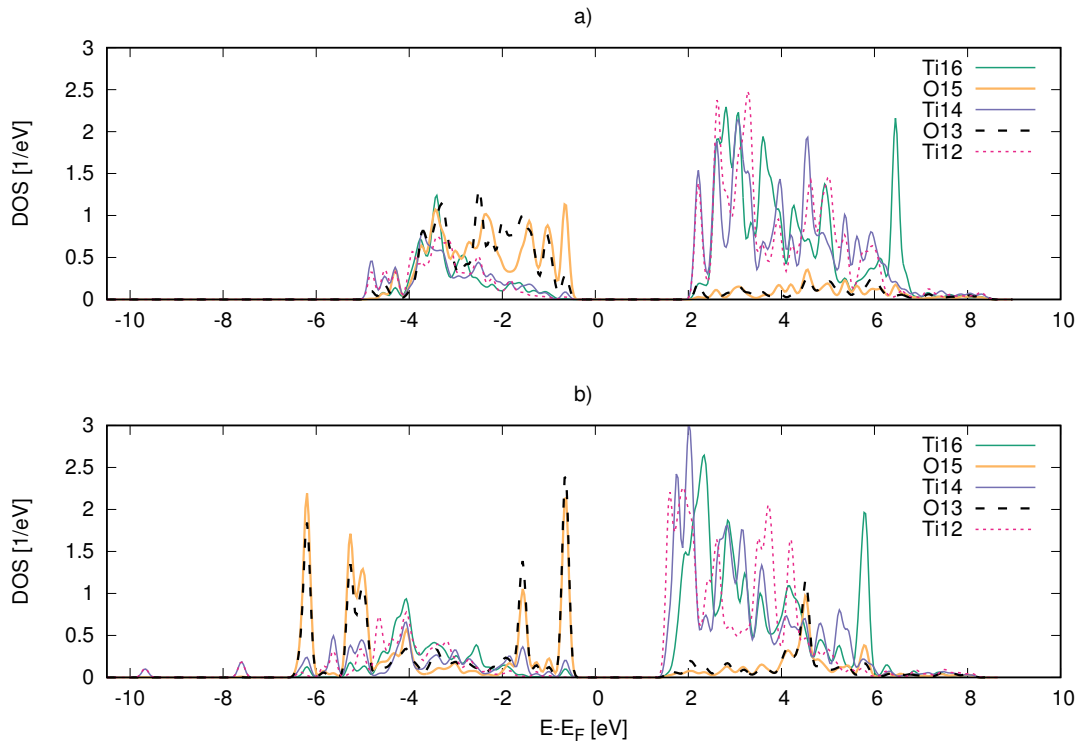

Figure S3: LDOS before (a) and after (b) the adsorption of 2 SO_4 groups for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 f.

Table S2: Detailed electronic states for $Ti_{16}O_{32}$ with 2 SO_4

| state/eV	atom and orbital	comments
-9.666	Ss, Ss	
-7.598	Sp, Sp	
-6.264	O6p-O7p, O15p-O13p	O-O bonds
-5.863	Sp, Sp, O27p, O28p	O: double bonded O atoms in the SO_4 groups
-5.630	O21p, O22p	O atoms between the titanium atoms to which SO_4 groups are attached
-5.063	O23p, O24p, O21p, O22p	
-0.643	O13p, O7p, O15p, O6p	HOMO level. O-O bonds
1.577	Ti8d, Ti12d	LUMO level. Ti atoms, to which different SO_4 groups are attached
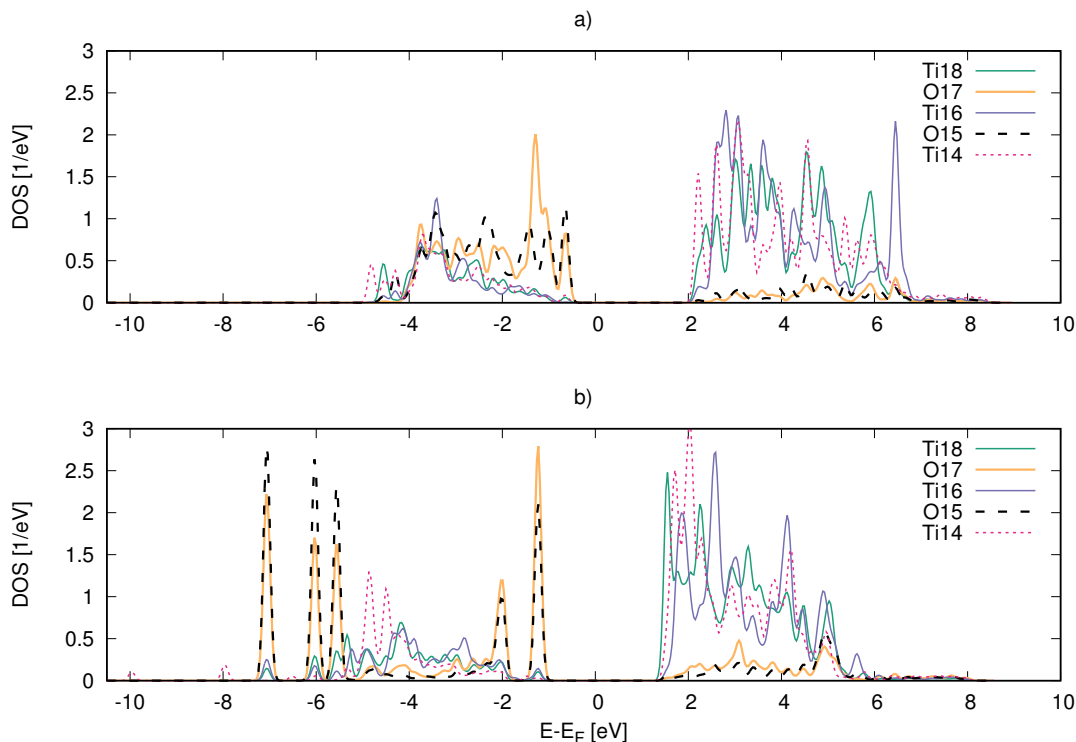
Figure S4: LDOS before (a) and after (b) the adsorption of 3 SO_4 groups for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 i.

Table S3: Detailed electronic states for $Ti_{16}O_{32}$ with 3 SO_4

| state/eV	atom and orbital	comments
-9.948	Ss from SO_4#1 and #3	
-9.714	Ss from SO_4#2	
-7.943	Sp from SO_4#1	
-7.742	Sp from SO_4#2	
-7.375	O6p-O7p	η^2-O_2
-7.074	O15p-O17p	O-O bond (Fig. 1 i, Fig. S4)
-6.539	Sp from SO_4#1 and #2	
-6.038	O15p	the O atom from O-O bond
-5.570	O15p	the O atom from O-O bond
-5.302	O22p	Atom between the Ti atoms, to which SO_4#3 group is attached
-1.190	O7p-O6p, O17p	HOMO level. η^2-O_2 and the O from O-O bond
-1.167	O6p-O7p	LUMO level. η^2-O_2
1.551	Ti18d	Ti atom, to which O15-O17 is connected
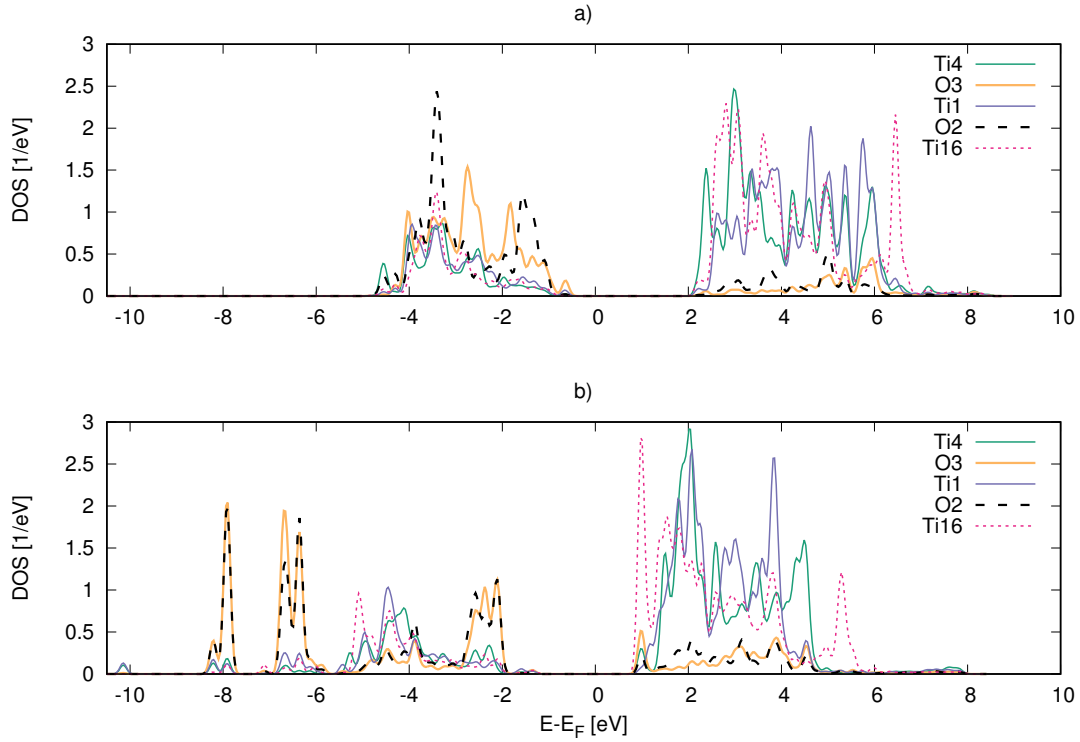
Figure S5: LDOS before (a) and after (b) the adsorption of 4 SO_4 groups for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 j.
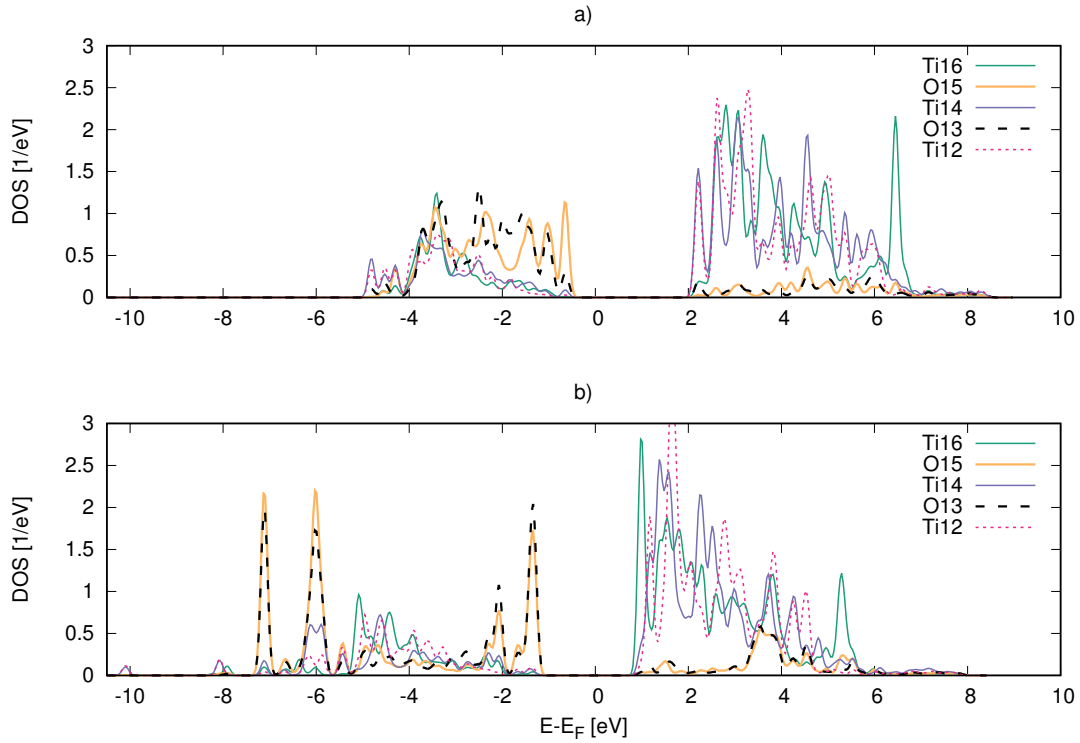

Figure S6: LDOS before (a) and after (b) the adsorption of 4 SO_4 groups for the p-orbitals of O atoms, forming O-O bond and the d-orbitals of neighboring Ti atoms. The atoms are emphasized in Fig. 1 l.

Table S4: Detailed electronic states for $Ti_{16}O_{32}$ with 4 SO_4

state/eV	atom and orbital	comments
-10.079	Ss from SO_4#1, #3, #4	
-8.036	Sp from SO_4#3 and #4	
-7.433	O9p-O6p	η^2-O_2
-7.132	O15p-O13p	O-O bond (Fig. 1 l, Fig. S6)
-6.663	Ti1p, O3p, Sp from SO_4 #1-4	Ti: one of the atoms to which the SO_4 #2 is attached, connects to O2-O3 bond (Fig. S5)
-6.127	Ti14p	
-5.424	O21p	O between Ti atoms, to which SO_4 #1 is attached
-1.320	O9p-O6p	HOMO level. η^2-O_2
-1.274	O9p-O6p	LUMO level. η^2-O_2
0.978	Ti16d	Ti atom, to which O2-O3 is connected