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

Supporting Information

First-Principles Study on the Mechanism of Photo- catalytic Reduction of Nitrobenzene on the Rutile $TiO_2(110)$ Surface

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1, Effects of the location of the excess electron on the Adsorption Energy of $ArNO_2$

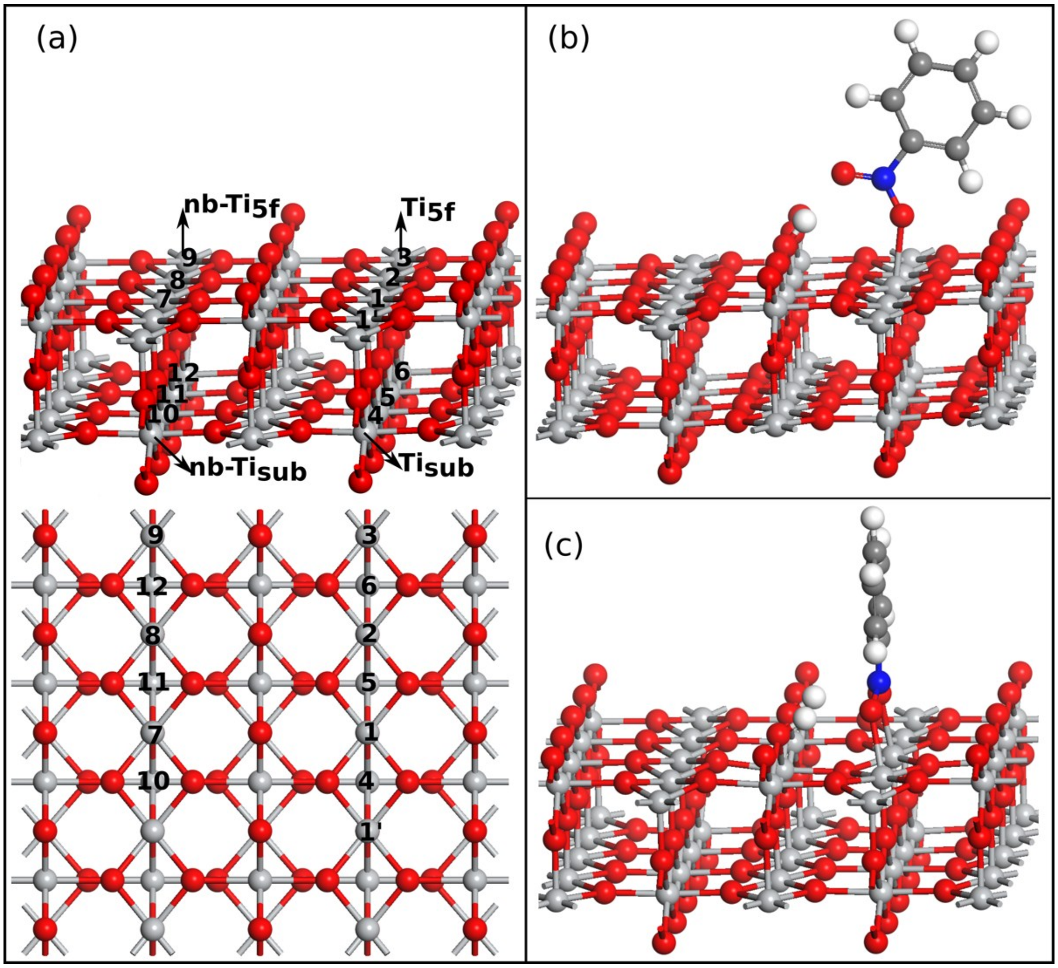

Fig. S1. (a) Structure of the rutile $TiO_2(110)$ surface, front and top view. (b) optimized structure of monodentate $ArNO_2$ on at T_{i5f} site with one excess electron injected by H_b. (c) optimized structure of bidentate $ArNO_2$ with two excess electrons injected by two H_b.

On the bare $TiO_2(110)$ surface, the most favorable site for the trapping of the excess electron in Ti_{sub} (Fig. S1 (a)). With two excess electrons, we can trap them at Ti_{sub} and nb-Ti_{sub}. However, in the presence of three excess electrons, we failed to trap two excess electrons at the same Ti row. Therefore, one was trapped Ti_{5f}, one at Ti_{sub} and the other at nb-Ti_{sub}.

With $ArNO_2$ adsorbed in a monodentate fashion at site 1 (Fig. S1(b), Fig. 2B), we calculated the energy of the system with the excess electron trapped at different Ti sites as in ref.[1] Note that some sites are equivalent because of the symmetry of the structure. The adsorption energy of $ArNO_2$ is summarized in Table SI. Trapping of an excess electron at Ti_{sub} (site 4, 5, 6) is about 0.09 eV more stable than trapping at Ti_{5f} (site 2, 3) but 0.02 eV less stable than trapping at site 1. As mentioned in the main text, this has also been observed in the presence of other adsorbates. However, trapping of the excess electron at the Ti_{sub} in the neighboring (nb-Ti_{sub}) row (site 10,11,12) is even more stable than trapping at site 1. And similar to the trapping of excess electron on the bare surface, trapping at nb-Ti_{sub} is 0.07 eV more stable than trapping at nb-Ti_{5f}.

Table SI, The adsorption energy (eV) of $ArNO_2$ in structure B and D in Fig. 1.

	1	2	3	4	5	6	7	8	9	10	11	12
B	-1.28	-1.17	-1.17	-1.26	-1.26	-1.25	-1.23	-1.22	-1.22	-1.29	-1.29	-1.29
D	-1.52	-1.49	-1.49	-1.55	-1.53	-1.56	-1.68	-1.68	-1.68	-1.70	-1.70	-1.71

For $ArNO_2$ adsorbed in a bidentate form (at site 1 and 1') with two excess electrons (Fig. S1 (c), Fig. 2D) . One excess electron is transferred to $ArNO_2$ with the other trapped at a Ti site. Similar to the adsorption of $ArNO_2$ in structure B, nb-Ti_{sub} is still the most favorable trapping site. But it is only 0.03 eV more stable than trapping at nb-Ti_{5f}. More importantly, trapping at site 1 is 0.03 eV than trapping at site 2 and 3, but is no longer more stable than trapping at Ti_{sub} (site 4, 5,6). We can see the adsorption energy is not sensitive to the trapping site if it is trapped at the same Ti row (same nb-Ti_{5f} row, nb-Ti_{sub} row, Ti_{sub} row and even Ti_{5f} row if it is not trapped at the adsorption site). And the trapping at the neighboring row is much more stable than trapping at the same row, especially for structure D probably because of the repulsion between the charged $ArNO_2$ and the trapped electron. Therefore, for other structures, we will only exam limited number of trapping sites of the excess electrons.

In the presence of three excess electrons, only one was transferred to $ArNO_2$ in structure E. we failed to trap the other two at the nb-Ti row. One is trapped at nb-Ti_{5f} (site 8) and the other is trapped at nb-Ti_{sub} (site 10) with an adsorption energy of -1.60 eV. It is 0.06 eV less table if one electron is trapped at Ti_{5f} (site 1) with the other at Ti_{sub}(site 11); it is 0.11 eV less stable if one electron is at Ti_{5f} (site 2) with the other at nb-Ti_{sub} (site 11), and it is 0.19 eV less stable if one electron is trapped at site 2 with the other at site 1'. In structure F, two excess electrons were transferred to $ArNO_2$. Trapping of the other excess electron at site nb-Ti_{sub} (site 12) is 0.03 eV more stable than trapping at nb-Ti_{5f} (site 8)

At the oxygen vacancy, the two excess electrons were trapped at Ti_{sub} and nb-Ti_{sub}. In structure G, none of them was transferred. In structure F, one is transferred to $ArNO_2$ with the other trapped nb-Ti_{sub}. It is 0.09 eV less stable if the other electron is trapping at Ti_{sub}.

2, Density of states of structures in Fig. 1

The location of the trapped excess electron can be found by looking at the site projected moment because the Ti^{3+} bares a larger magnetic moment.[2] The number of excess electrons transferred to the molecule can be obtained by counting the number of Ti^{3+}. Another method is to look at the density of states for the structures as shown in Fig. S2. For structure A, the HOMO of $ArNO_2$ is in the bandgap. Note that the peak of PDOS of $ArNO_2$ is lower than the corresponding peak in the Total DOS. This is because when doing the projection, DOS was projected into spheres, the sum of whose volumes is smaller than the total volume of the cell. Then the height of HOMO peak in the PDOS is lower than that in the Total DOS. For Structure B, the HOMO is in the bandgap, one additional peak in the gap comes from the Ti^{3+}. In this configuration, the excess electron is not transferred to $ArNO_2$. But in Structure C, we can see that the HOMO of $ArNO_2$ is split with the excess electron transfer to its spin-up component. Similarly, in structure D, one excess electron is transferred to $ArNO_2$ with the other trapped at Ti. In the presence of three excess electrons, only one of them is transferred to $ArNO_2$ in structure E with two Ti^{3+} peaks merged to one; in structure E, both spin components of HOMO was filled by an excess electron with the other one trapped at Ti. At the oxygen vacancy, in structure G, $ArNO_2$ is high above the vacancy. Therefore, the two excess is still trapped Ti with one high peak appears in the gap. Compare to DOS of structure A and B, we can see that the molecule's orbitals are shifted and broadened to a larger extent in A and B which suggests a stronger hybridization of the molecule's orbitals with TiO_2. This agrees with more negative adsorption energies of $ArNO_2$ in structure A and B. In structure H, similar to the DOS of structure D, one excess electron is transferred to $ArNO_2$ with the other trapped at Ti.

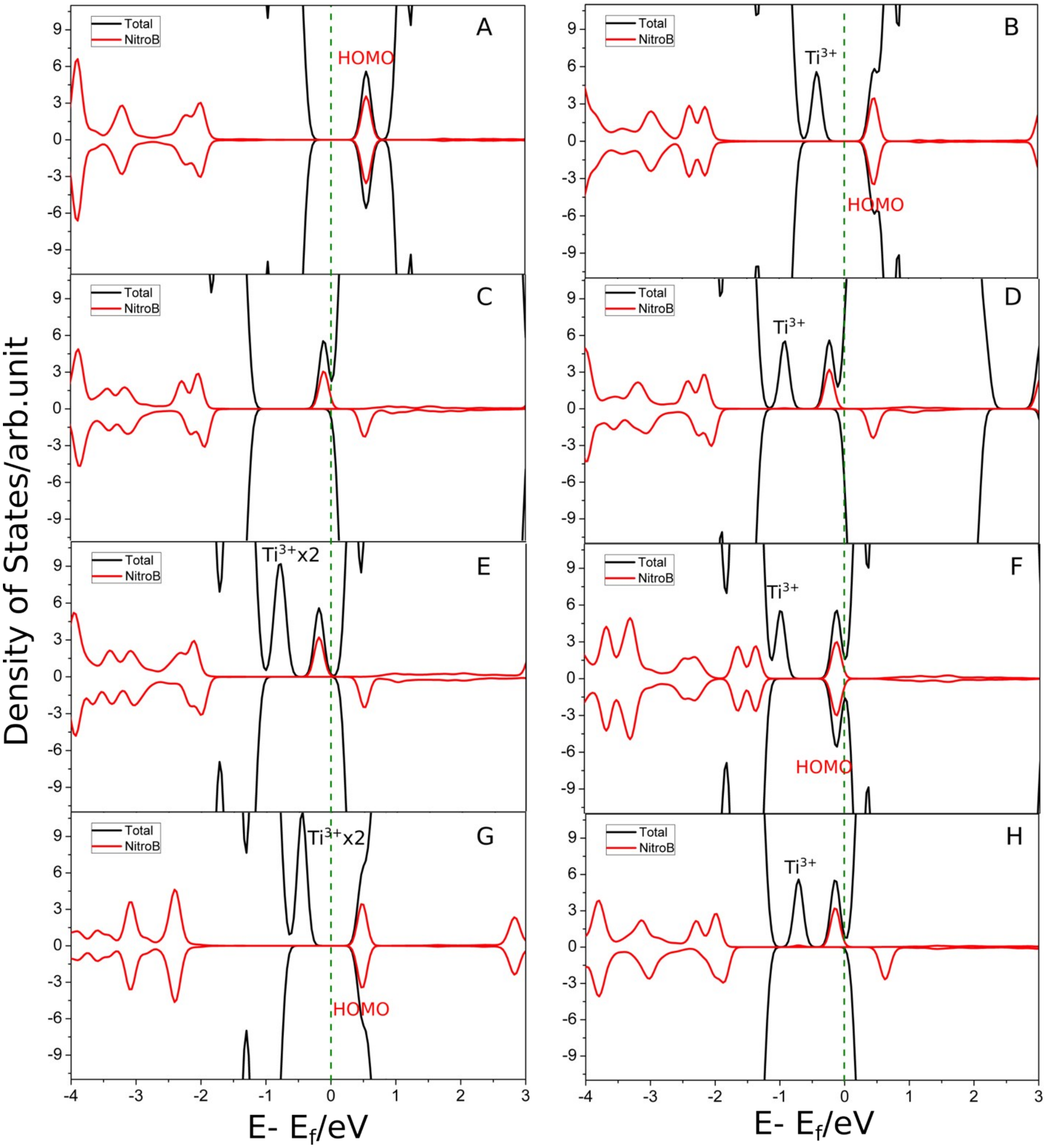

Fig. S2, Density of states (DOS) of structure A-H in Fig. 1. Black: total DOS; red: DOS projected to $ArNO_2$. Red dotted line presents the position of the calculated fermi level. Peaks related to HOMO of $ArNO_2$ and Ti^{3+} was labeled.

References

1. Deskins, N. A., Rousseau, R. & Dupuis, M.. *J. Phys. Chem. C* **114**, 5891–5897 (2010).

2. Ji, Y., Wang, B. & Luo, Y. *J. Phys. Chem. C* **116**, 7863–7866 (2012).