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Supplementary Materials

Mechanism of H adatom improving O_2 reduction reaction on Zn-modified anatase TiO_2 (101) surface studied by first principle calculation

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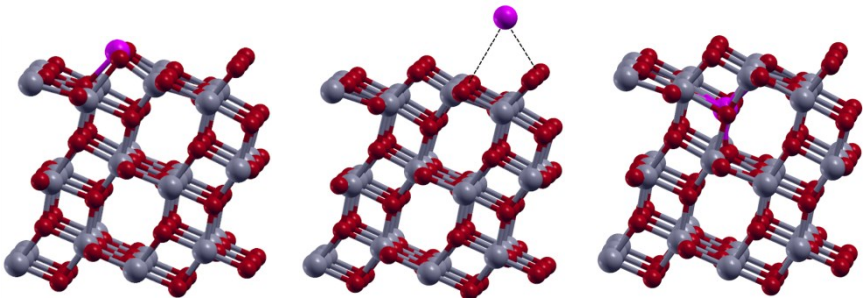
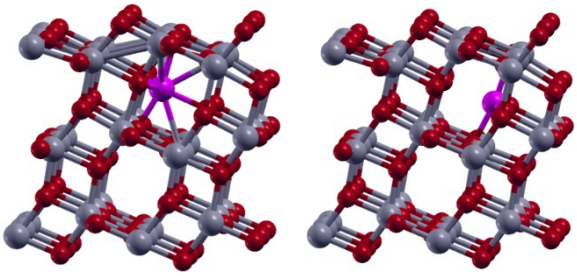


(a) S1 (b) S2 (c) S3



(d) S4 (e) S5

Fig S1: Different possible Zn interstitial sites on and near the A-TiO (101) surface. Ti: grey; O: red; and Zn interstitial: purple.

The formation energy of a Zn dopant (ΔE_{Zn}) is calculated by the equation [1]:

$$\Delta E_{Zn} = E_{surf+Zn} - E_{surf} - \Delta n_x \mu_x$$

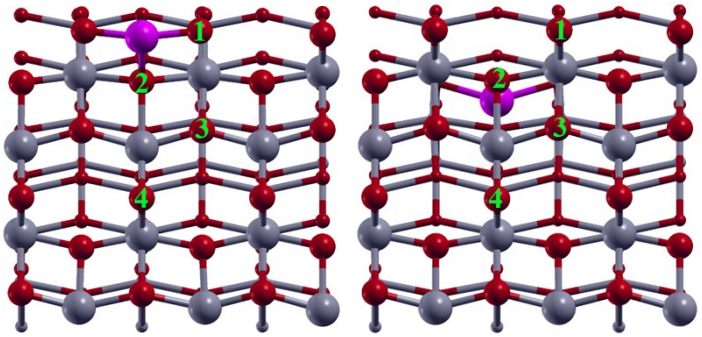
$$\mu_{Zn} = E_{(ZnO)} - 1/2\ E_{O2},\ \mu_{Ti} = E_{(TiO2)} - E_{O2}$$

here, $E_{surf+Zn}$ is the system energy of TiO_2 surface with a Zn dopant; E_{surf} is the system energy of the clean TiO_2 surface; μ_{Zn} and μ_{Ti} are the chemical potentials of the Zn atom and Ti atom respectively; Δn_x is the number of X removed from or added into

the TiO_2 surface; $\Delta E_{(ZnO)}$ is the formation energy of the wurzite ZnO. E_{O2} is the energy of an O_2 molecule in gas phase.

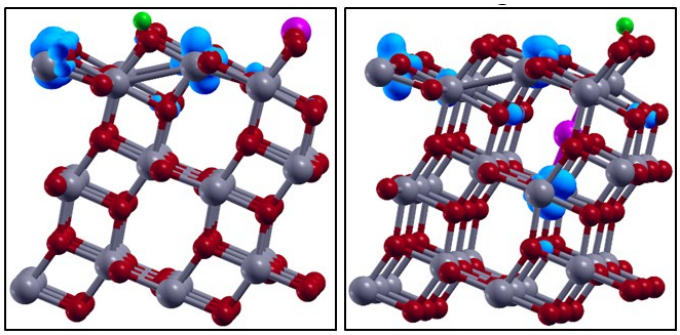
Table S1: The formation energy of a Zn interstitial on and near the A-TiO_2 (101) surface

Site	S1	S2	S3	S4	S5
ΔE_{Zn} (eV)	3.47	3.98	4.39	4.20	3.49



(a) S1 (b) S5

Fig. S2: Different H adsorption sites on S1 and S5 surface are marked from 1 to 4, which are the four surface O atoms around the Zn interstitial.



(a) $S1_H$ charge distribution (b) $S5_H$ charge distribution

Fig S3: (a) and (b) show the distribution of three excess electrons induced by the Zn and H interstitials on the A-TiO_2 (101) surface.

After a H atom is adsorbed on the Zn-modified anatase (101) surface, another one excess electron is induced into the S1 or S5 surface. The Fig. 3S (a) and (b) show that for $S1_H$ and $S5_H$ surfaces, the electron induced by the H atom mainly distributes on a surface Ti_{5c} lattice, and thus more excess electrons would transfer to adsorbed O_2 molecule.

The adsorption energy of a H atom (ΔE_H) on the S1 and S5 surface is calculated based on the equation [2]:

$$\Delta E_H = E_{surf+H} - (E_{surf} + \Delta\mu_H)$$

where E_{surf+H} is the system energy of the TiO_2 surface with a H atom; E_{surf} is the

system energy of TiO_2 surface without H atom; $\Delta\mu_H$ is the energy of a H atom.

Table S2: The adsorption energy of a H atom on S1 and S5 surface

S1	ΔE_H (eV)	S5	ΔE_H (eV)
1	2.07	1	2.17
2	unadsorbed	2	1.75
3	1.75	3	1.73
4	2.27	4	2.11

Reference

[1] Han, X. and Shao, G. *Phys. Chem. Chem. Phys.*, **15**, 9581 (2013).

[2] Aschauer, U and Selloni, A. *Phys. Chem. Chem. Phys.* 12, 16595 - 16602 (2012).