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

Energetics of native defects in anatase TiO_2: A hybrid density functional study

Adisak Boonchun, Pakpoom Reunchan and Naoto Umezawa

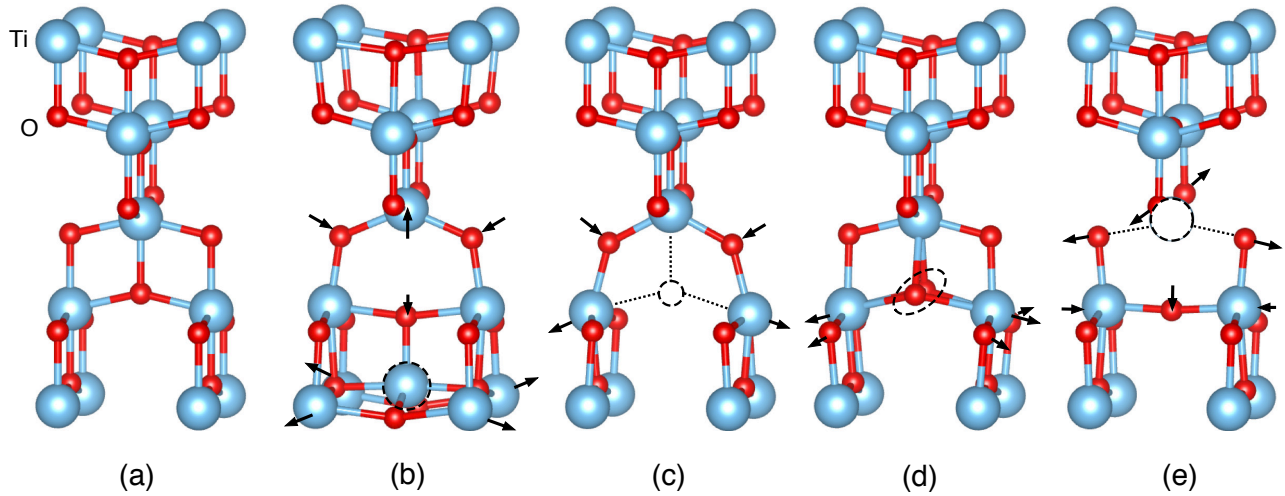

Figure S1 The optimized atomic structure of (a) bulk (b) Ti_i^{4+} (c) V_O^2 (d) $O_{i,db}$ and (e) V_{Ti}^{4-} defect. The large gray spheres are Ti atoms and the small red spheres are the O atoms. Relaxation around neighboring defect atoms are indicated by the arrows.

In Equation 3, the thermodynamic transition levels which the formation energy of the two charge states are equal can be derived as following equation:

$$E_f(D^q) = E_{tot}(D^q) - E_{tot}(\mathrm{TiO_2}) - n_i\mu_i + q(\varepsilon_F + E_V) \tag{1}$$

$$E_f(D^{q'}) = E_{tot}(D^{q'}) - E_{tot}(\mathrm{TiO_2}) - n_i\mu_i + q'(\varepsilon_F + E_V). \tag{2}$$

The formation energy of the two charge states are equal;

$$E_f(D^{q'}) - E_f(D^{q'}) = 0 \tag{3}$$

Then,

$$E_f(D^{q'}; \varepsilon_F = 0) - E_f(D^{q'}; \varepsilon_F = 0) + (q - q')\varepsilon_F = 0 \tag{4}$$

Finally,

$$\varepsilon(q/q') = \frac{E_f(D^{q'}; \varepsilon_F = 0) - E_f(D^{q'}; \varepsilon_F = 0)}{q' - q}, \tag{5}$$

where

$$E_f(D^{q'}; \varepsilon_F = 0) = E_{tot}(D^q) - E_{tot}(\mathrm{TiO_2}) - n_i\mu_i + qE_V$$