TiO$_2$ Nanocluster Modified-Rutile TiO$_2$

Photocatalyst: a First Principles Investigation.

Anna Iwaszuk$^a$, P. A. Mulheran$^b$ and Michael Nolan$^a$*

a: Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland

b: Department of Chemical Engineering, University of Strathclyde, Glasgow G1 1XQ, Scotland, UK

Supporting information:

The Supporting Information consists of

1. Figure S1: Relaxed, but less stable, adsorption structures for Ti$_6$O$_{12}$ nanocluster on rutile (110) surface

2. Figure S2: Relaxed, less stable, adsorption structures for Ti$_{10}$O$_{16}$, Ti$_{16}$O$_{32}$, Ti$_{30}$O$_{60}$ clusters on rutile (110).

3. Details of calculation of energetics in cluster aggregation

4. Figure S3: PEDOS of O 2p states in the adsorbed nanocluster for terminal oxygen (denoted O 2p terminal) and non-terminal oxygen (denoted O 2p non-term) for: (a)Ti$_5$O$_{10}$, (b)Ti$_6$O$_{12}$, (c)Ti$_{16}$O$_{32}$, (d)Ti$_{30}$O$_{60}$ clusters on TiO$_2$ rutile (110) surface.

5. Figure S4: Absorption spectrum of nanocluster modified rutile (110) showing a zoom into the region around the photon energy corresponding to the extrapolated absorption energy.
Figure S1 Relaxed adsorption structures with adsorption energies given in eV for different configurations of Ti₆O₁₂ clusters on TiO₂ rutile (110).

Figure S2 Relaxed adsorption structures with adsorption energies given in eV for (a) Ti₆O₁₆, (b) Ti₁₆O₃₂, (c) Ti₃₀O₆₀ clusters on TiO₂ rutile (110).

**Calculations on energetics in nanocluster aggregation**

1. Free Nanoclusters

**Formation of Ti₈O₁₆ from 2x Ti₄O₈:**

E(Ti₈O₁₆) = -168.443 eV

E(2xTi₄O₈) = -161.232 eV

**Formation of Ti₁₆O₃₂ from 2x Ti₈O₁₆**

E(Ti₁₆O₃₂) = -344.417 eV

E(2x Ti₈O₁₆) = -336.886 eV

**Formation of Ti₃₀O₆₀ from Ti₆O₁₂+Ti₈O₁₆+Ti₁₆O₃₂**

E(Ti₃₀O₆₀) = -647.250 eV

E(Ti₆O₁₂ + Ti₈O₁₆ + Ti₁₆O₃₂) = -635.088 eV

2. Aggregation of Nanoclusters Supported on TiO₂
Formation of Ti$_6$O$_{12}$ compared to two Ti$_3$O$_6$ clusters on the same rutile (110) (2x4) surface

$E\{2(Ti_3O_6)\text{-rutile (110)}\} = -4482.857 \text{ eV}$

$E\{Ti_6O_{12}\text{-rutile (110)}\} + E\{\text{rutile (110)}\} = -4477.507 \text{ eV}$

Formation of Ti$_{16}$O$_{32}$ compared to two Ti$_8$O$_{16}$ clusters on the same rutile (110) (4x4) surface

$E\{2(Ti_8O_{16})\text{-rutile (110)}\} = -6135.125 \text{ eV}$

$E\{Ti_{16}O_{32}\text{-rutile (110)}\} + E\{\text{rutile (110)}\} = -6134.395 \text{ eV}$
Figure S3: Electronic density of states projected (PEDOS) on O 2p states with terminal oxygen (denoted O 2p terminal) and non-terminal oxygen (denoted O 2p non-term) for: (a)Ti$_{16}$O$_{32}$, (b)Ti$_{6}$O$_{12}$, (c)Ti$_{16}$O$_{32}$, (d)Ti$_{30}$O$_{60}$ clusters on TiO$_2$ rutile (110) surface.

Figure S4: Absorption spectrum of nanocluster modified rutile (110) showing a zoom into the region around the photon energy corresponding to the extrapolated absorption energy.