TiO_2 Nanocluster Modified-Rutile TiO_2 Photocatalyst: a First Principles Investigation.

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Supporting information:

The Supporting Information consists of

1. Figure S1: Relaxed, but less stable, adsorption structures for Ti_6O_{12} nanocluster on rutile (110) surface

2. Figure S2: Relaxed, less stable, adsorption structures for Ti_8O_{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_5O_{10}, (b)Ti_6O_{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.

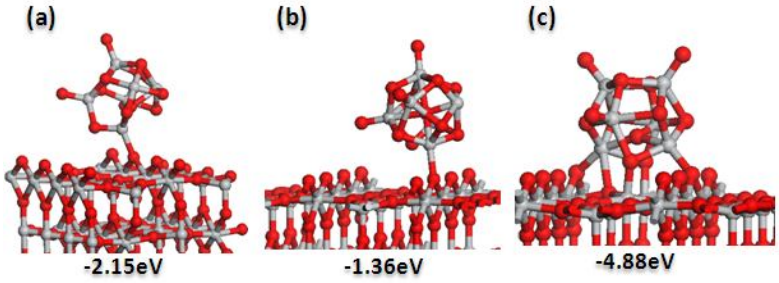


Figure S1 Relaxed adsorption structures with adsorption energies given in eV for different configurations of Ti_6O_{12} clusters on TiO_2 rutile (110).

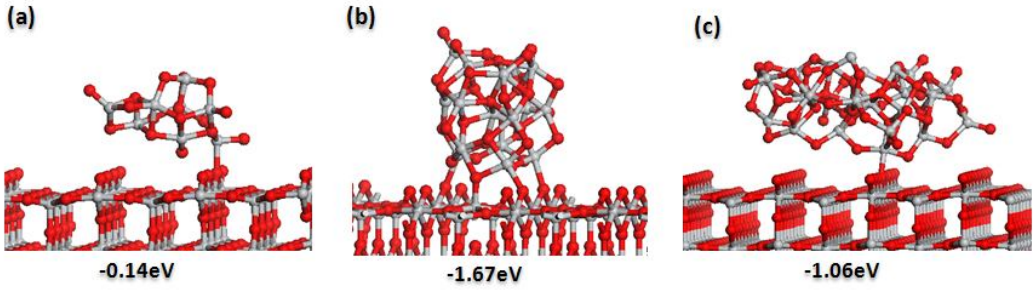


Figure S2 Relaxed adsorption structures with adsorption energies given in eV for (a)Ti_8O_{16}, (b)$Ti_{16}O_{32}$, (c)$Ti_{30}O_{60}$ clusters on TiO_2 rutile (110).

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 Ti6O12 compared to two Ti3O6 clusters on the same rutile (110) (2x4) surface

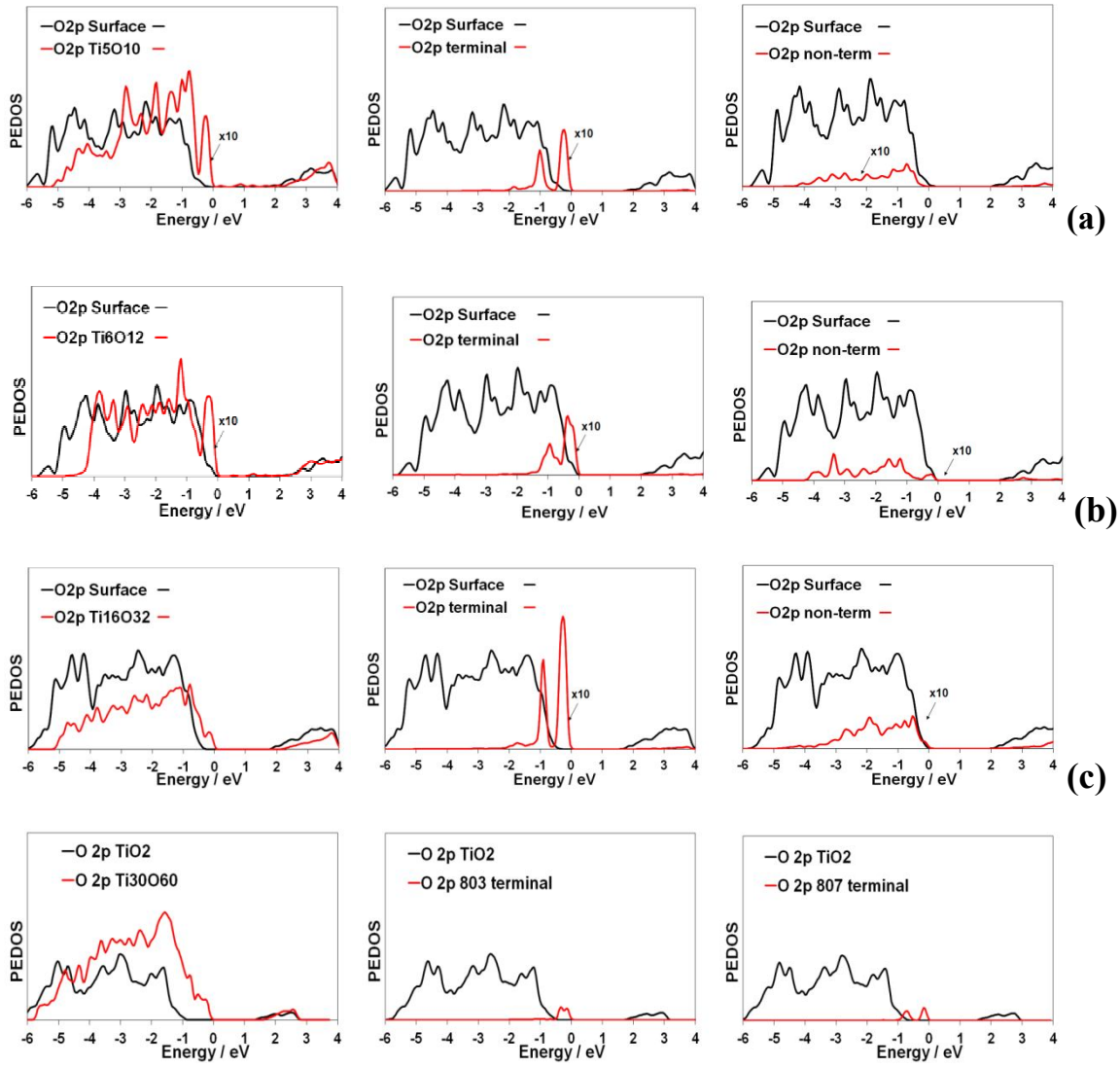
E{2(Ti3O6)-rutile (110) } = -4482.857 eV

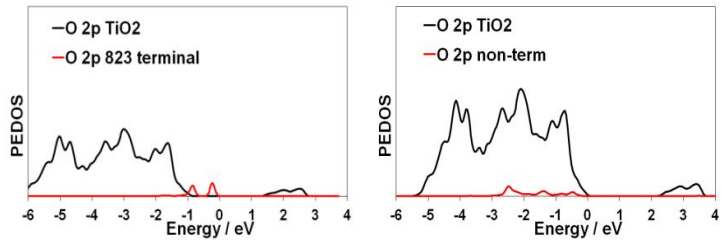
E{Ti6O12-rutile (110)} + E{rutile (110)} = -4477.507 eV

Formation of Ti16O32 compared to two Ti8O16 clusters on the same rutile (110) (4x4) surface

E{2(Ti8O16)-rutile (110)} = -6135.125 eV

E{Ti16O32-rutile (110)} + E{rutile(110)} = -6134.395 eV





(d)

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_5O_{10}, (b)Ti_6O_{12}, (c)$Ti_{16}O_{32}$, (d)$Ti_{30}O_{60}$ clusters on TiO_2 rutile (110) surface.

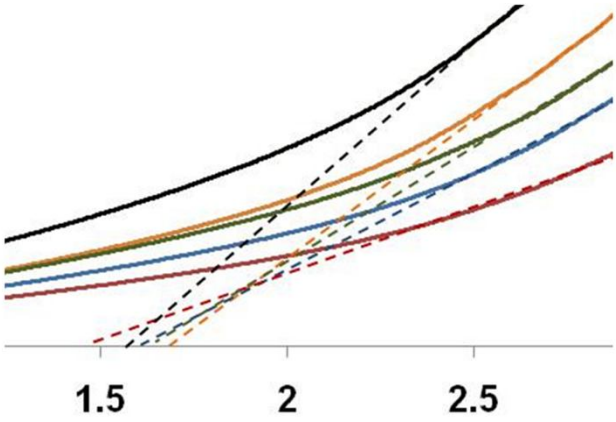


Figure S4: Absorption spectrum of nanocluster modified rutile (110) showing a zoom into the region around the photon energy corresponding to the extrapolated absorption energy.