A first-principles investigation of CO_2 interaction with nano-cluster modified TiO_2 rutile(110) and anatase(101) surfaces

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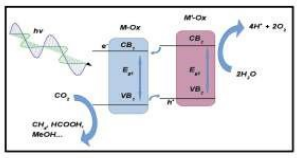
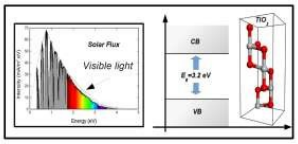
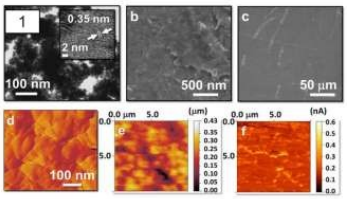
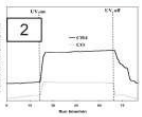
Abstract

Growing global energy demands and the depletion of fossil fuel resources, together with the risk of global warming, makes the use of incident solar radiation and photo-active materials to transform CO_2 into fuels an active and exciting research topic with much interest and high potential for impact.
In this context, TiO_2 has long been known to have many useful characteristics for use as photo-catalyst. It shows good stability, catalytically active surfaces and a relatively high photo-sensitivity.[1-5] However, there are some issues that have to be addressed in order to design an efficient photo-catalyst material. First TiO_2 photo-absorbance is still low due to its large band gap that lies in the UV region. Second, efficient activation and reduction of CO_2, due to the high chemical stability of this molecule, remains an issue.
In this poster, we will present results from density functional theory simulations to study novel metal oxide nano-cluster modified TiO_2 anatase (101) and rutile (110) surfaces. In particular we focus on (1) the effect of the nano-cluster modification on band gap reduction, (2) electron-hole separation, (3) the role of "wet surfaces" and (4) present the first results on the interaction of such surfaces with CO_2 to assess if CO_2 activation and reduction is possible.

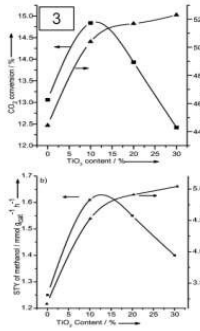








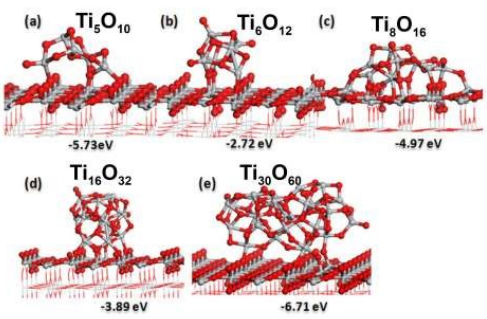
Target
- **Visible Light harvest**
- **Efficient Charge separation**
- **Enhancement of Catalytic activity**



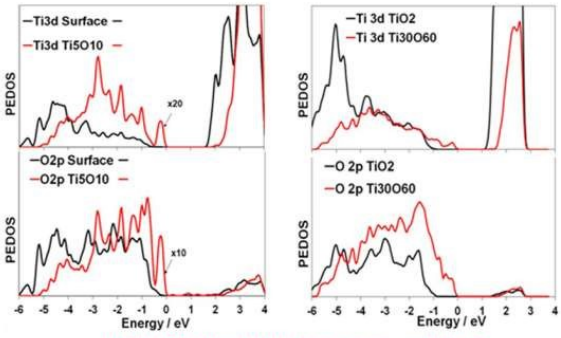
[1] Scanning TEM image indicates 15–20 nm crystallites. High-resolution TEM (inset) confirms the presence of crystalline anatase. (b) Magnified SEM image of the film. (c) Large area SEM image of the film. (d) AFM image showing 100–200 nm self-sintered TiO2 grains. (e) Conductive AFM topography map. (f) Conductive AFM current map.

[2] Photo-Catalytic activity conversion of CH_4

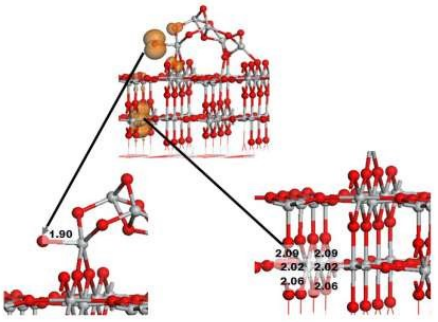
[3] CO_2 conversion and Methanol selectivity as a function of the TiO_2 content



$Ti_{30}O_{60}$ **1.5 nm => experimental cluster size**

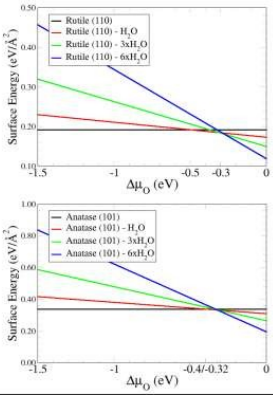


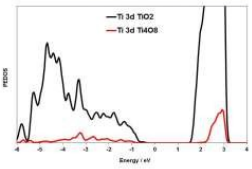
Push VB edge to higher energy – red shift



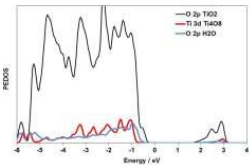
After excitation – electron on TiO_2 surface and hole on titanyl oxygen of TiO_2 Nanocluster

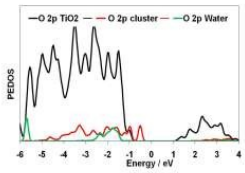
What Happens with Water?



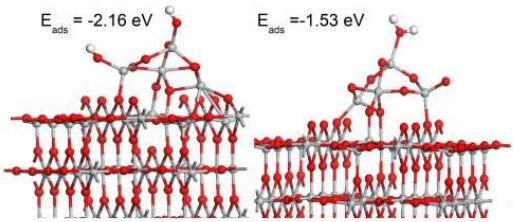


No change in the VB edge on the wet surface Different from Nanocluster on the dry TiO_2 surface





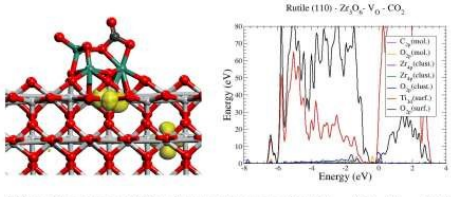
Water interacting with TiO_2 nanocluster



Dissociative adsorption more favourable
No change in the VB upshift

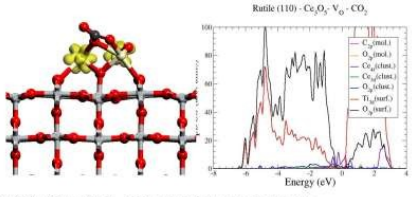
CO_2 adsorption on TiO_2 Rutile Modified with Oxide Nanoclusters

Zr_3O_6 - V_O - Rutile (110)

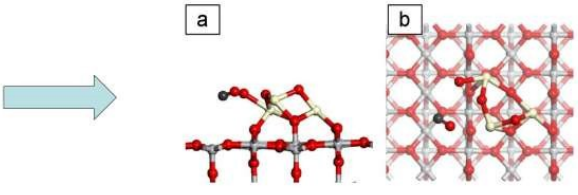


We observe a CO_3 formation on Zr_3O_6 - Ce_3O_5 Rutile (110) after CO_2 adsorption ot oxygen vacancy site

Ce_3O_5 - V_O - Rutile



CO formation on Ce_3O_5 - V_O - Rutile (110)



We observe a CO formation and desorption on Ce_3O_5 Rutile (110) after CO_2 adsorption at oxygen vacancy site

References

[1] B. Reeja-Jayan, Katharine L. Harrison, K. Yang, Chih-Liang Wang, A. E. Yilmaz and Arumugam Manthiram *Scientific Reports* **2**, 1003 (2012)
[2]U. Diebold. Appl. Phys. A Mater. Sci. Process., 76:681–687, 2003. [3] A. Fuerte, M. D. Hernandez-Alonso, A. J. Maira, A. Martinez-Arias, M. Fernandez-Garcia, J. C. Conesa, and J. Soria. Chem. Commun., (24):2718–2719, dec 2001. [4] Wenxian Li. Phys. status solidi - Rapid Res. Lett., 9(1):10–27, 2015. [5] Masakazu Anpo. Pure Appl. Chem., 72(9):1787–1792, January 2000.