Computational study of anatase TiO_2 as an anode material for energy storage devices

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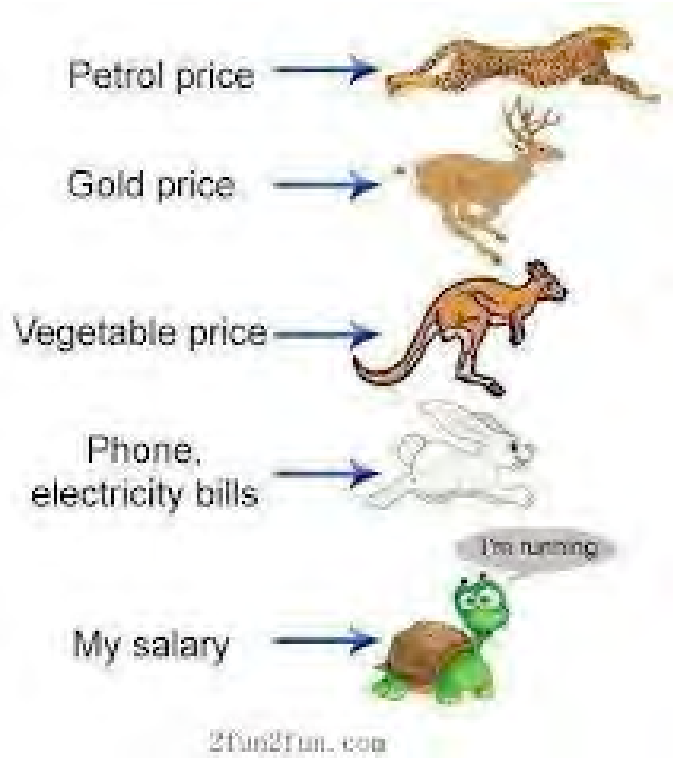
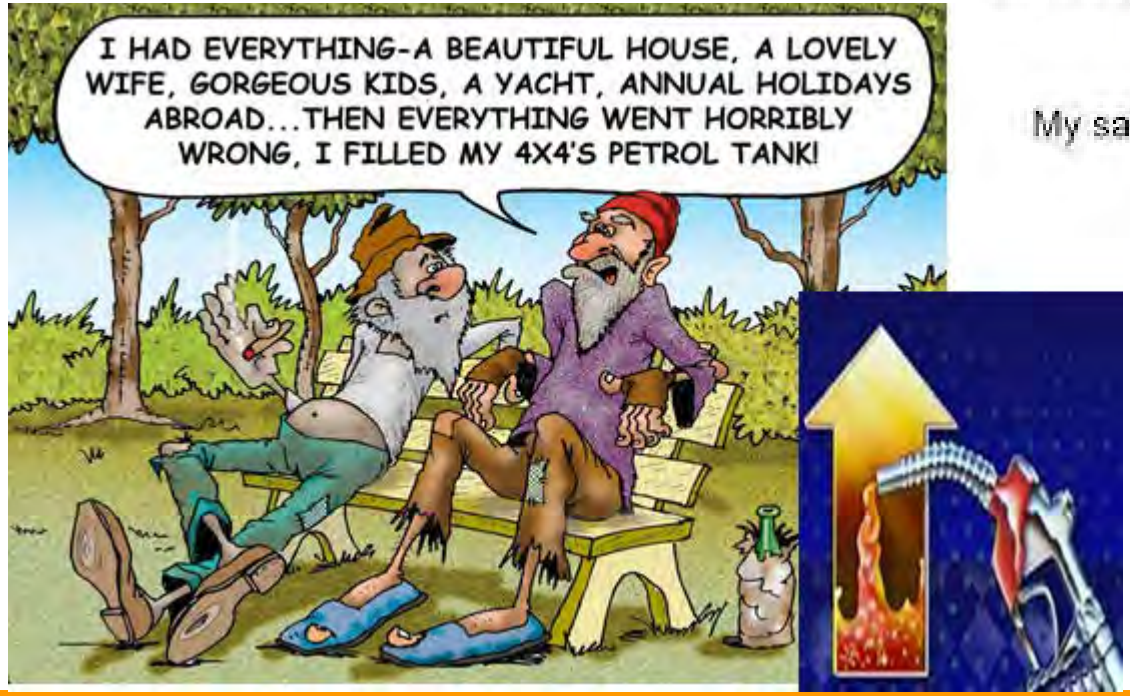
World without batteries

Electric Vehicle

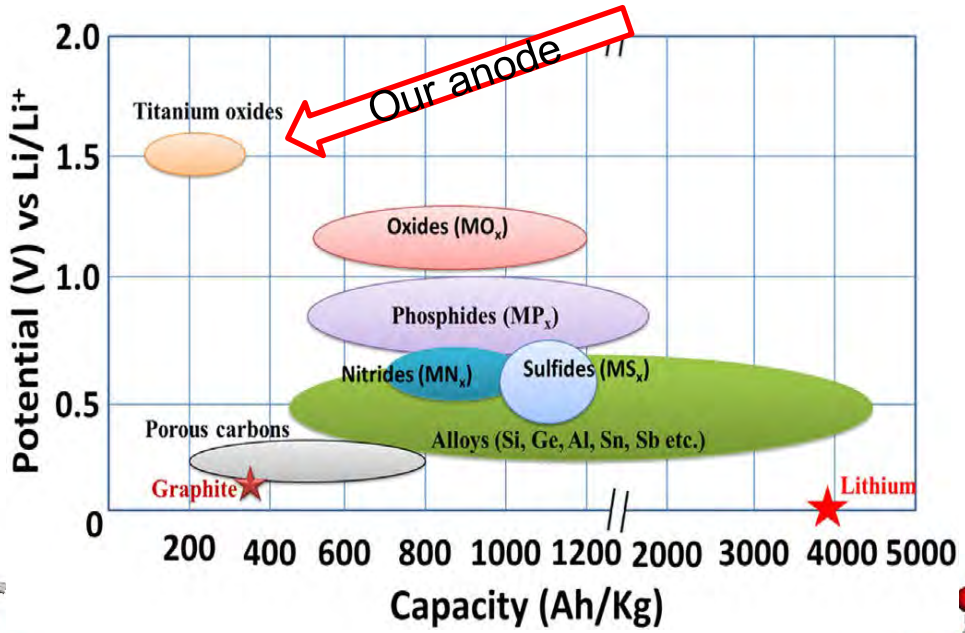


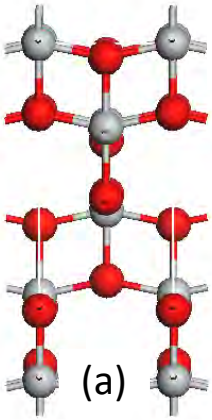


LIB anode material conditions

- Low initial irreversible capacity loss
- High electric conductivity and ion diffusion rates within active materials
- Less change in volume by intercalation/deintercalation of lithium
- Eco-friendliness
- Easy manufacturing process and low prices

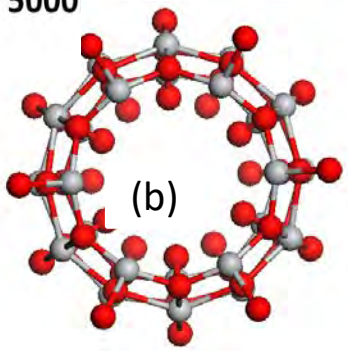
Systems





Titanium

Oxygen



(a) Bulk anatase TiO_2 with a space group141 ($I4_1/amd$) Tetragonal and (b) Anatase TiO_2 nanotube

[1] Z. Hong, M. Wei, J. Mater. Chem. A1, 4403-4414, (2013).
[2] A. Moretti, G.-T. Kim, D. Bresser, K. Renger, E. Paillard, R. Marassi, M. Winter, S. Passerini, J. Power Sources 221, 419-426, (2013).

Methodology

- The anatase TiO_2 nanotubes were created using the MedeA® Software environment .[1]

- MD calculations and geometry optimizations were carried out with the DFTB+ program .[2]

- MD calcutions−Time step=0.1fs

  −Total simulation time=10ps

- Bulk anatase TiO_2 structures were simulated with 4×4×2 Monkhorst-Pack [3] grids for k-point sampling.

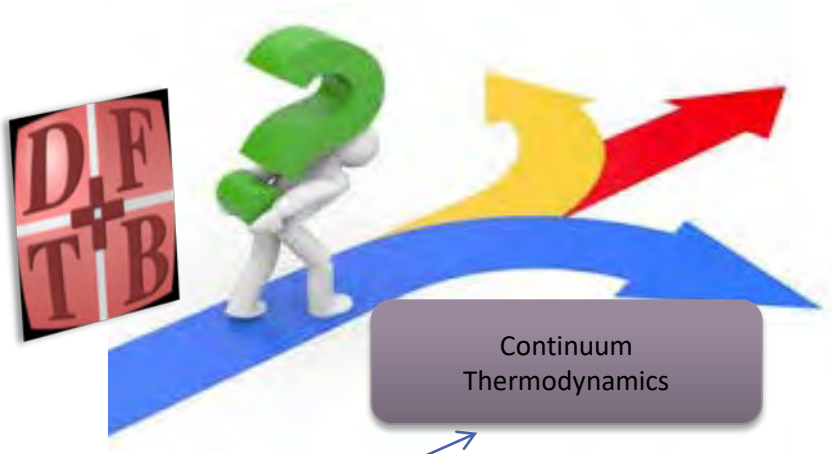
- The total energy expression is given by :

  $E_{tot}=E_{BS}+E_{rep}+E_2(n, \Delta n)$,

  Where E_{BS} is the band structure, E_{rep} is the short range repulsive term, and $E_2(n, \Delta n)$ is an electrostatic-interaction term that account for the charge fluctuations. [4]

1. MedeA, v2.8,Materials Design, Inc., Angel Fire NM USA, 2012.
2. B. Aradi, B. Hourahine, T. Frauenheim, Matrix-Based Implementation of the DFTB Method, *J. Phys. Chem. A 111* (26), 5678–5684 *(*2007).
3. H. Monkhorst, J.D. Pack, Phys. Rev. B 13, 5188, (1976).
4. M. Eltsner, T. Frauenheim, S. Suhai, J. Mol. Struct. (THEOCHEM) 632, 29-41, (2003).

Hierarchies of models in Materials Research



Discipline

Engneering

Materials

Chemistry

Physics

Continuum Thermodynamics

Microstructural

Classical MM

Mesoscopic scale – 1 000 000 atoms and more

DFTB

Model structures – up to 10 000 atoms

Electronic ab initio DFT

Model structures – few 100 atoms

nm

µm

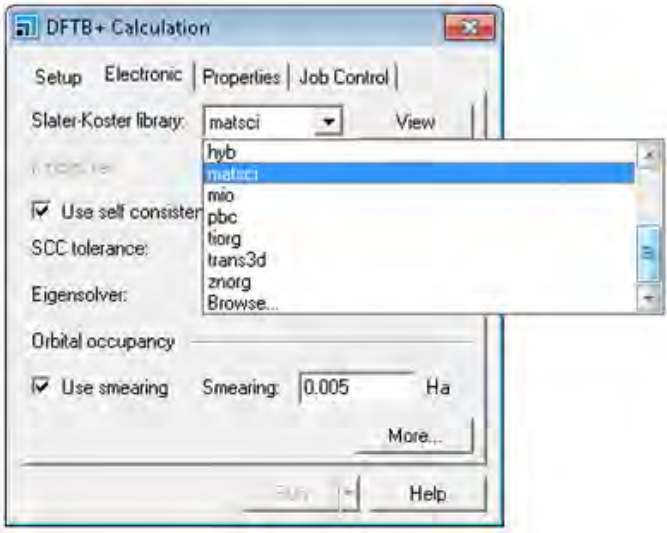
mm

m

Time scale

Implementation of the DFTB technique

- The Density Functional based Tight Binding (DFTB) method requires atomic parameters for calculations
- Two ways to start a DFTB+ calculation
  - Use the set of parameters provided by Material Studio
  - Develop new parameters for the targeted structure

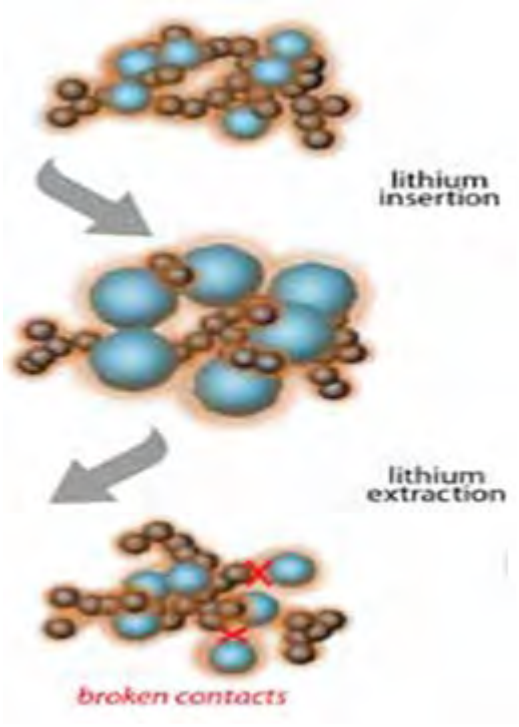


Examples of available Slater-Koster libraries in Material Studio

Name	Requires	Elements	Short description
hyb	mio	Ag-O-C-H Ga-As-S-H Ga-S-O-C-H Ga-As-Si-S Ag-Si	SCC files for organic/inorganic hybrid systems
chalc	mio	As-S-H	chalcogenide glasses
trans3d	mio	(Sc,Ti,Fe,Co,Ni)-(H-C-N-O)	Transition metal elements in biological systems
tiorg	mio	Ti-(H-C-N-O-S)	Ti bulk, TiO_2 bulk, TiO_2 surfaces, TiO_2 with organic molecules

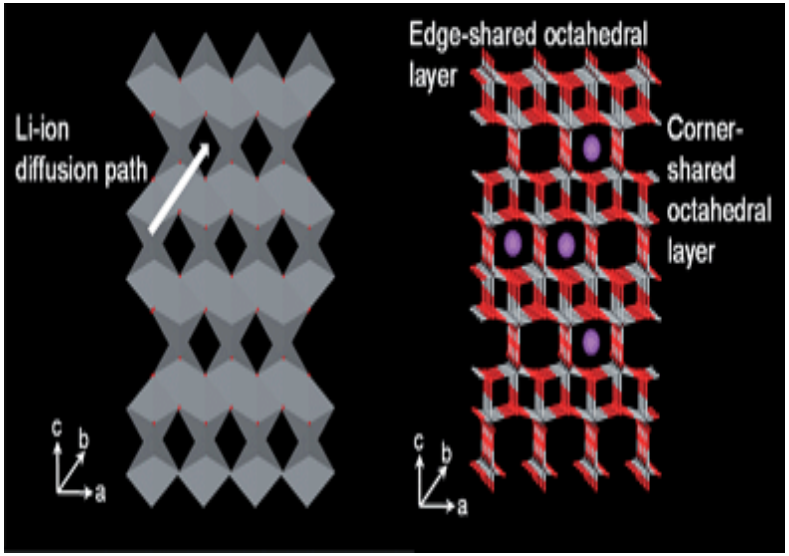
Comparison of anode materials

Silicon



Credit : Lawrence Berkeley National Lab(LBNL)

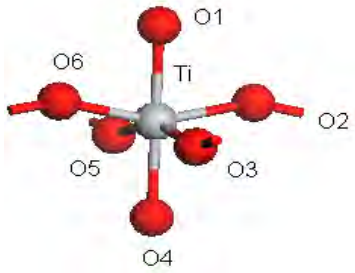
Anatase



Structural parameters

The calculated structural parameters, a (Å), c (Å), Ti—O bond length D_{eq} (Å) and D_{ap} (Å).

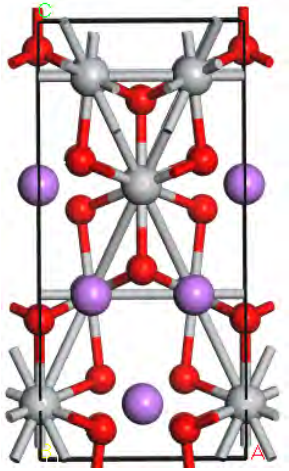
Anatase	a	c	D_{eq}	D_{ap}
Our Results	3.840	9.512	1.93	1.97
Yin et al. [1]	3.819	9.688	1.95	2.00
Experimental [2]	**3.782**	**9.502**	—	—



1. W. Yin, S. Chen, J. Yang, X. Gong, Y. Yan, S. Wei, APPLIED PHYSICS LETTERS **96**, 221901, (2010).
2. D. Szieberth, A.M. Ferrari, Y. Noel, M. Ferrabone, The Royal Society of Chemistry Nanoscale 2, 81, (2010).

Structural parameters cont…

	Method	Lattice parameters (Å)		
		a	b	c
Anatase	DFTB+	4.076	–	8.954
($I4_1/amd$)	Exp.	4.043	–	8.628



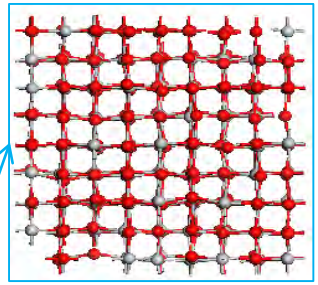
[1] M. Wagemaker, W. J. H. Borghols and F. M. Mulder, J. Am. Chem. Soc, 129(14), 4323–4327 ., (2007).

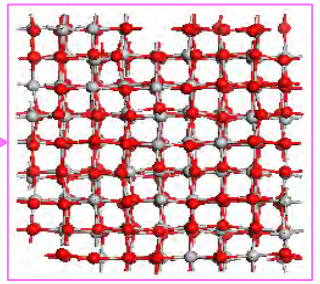
Band gap energies (bulk TiO_2 polymorphs)

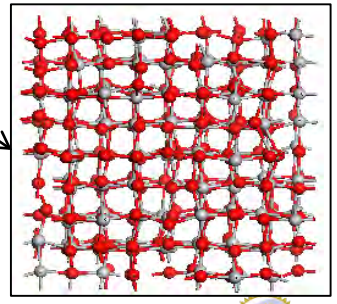
TiO_2 polymorphs	E_{gap}^{DFTB}	E_{gap} [16]	% error
Anatase	3.183	3.21	0.8
Rutile	3.095	3.00	3.2
Brookite	3.113	3.13	0.5

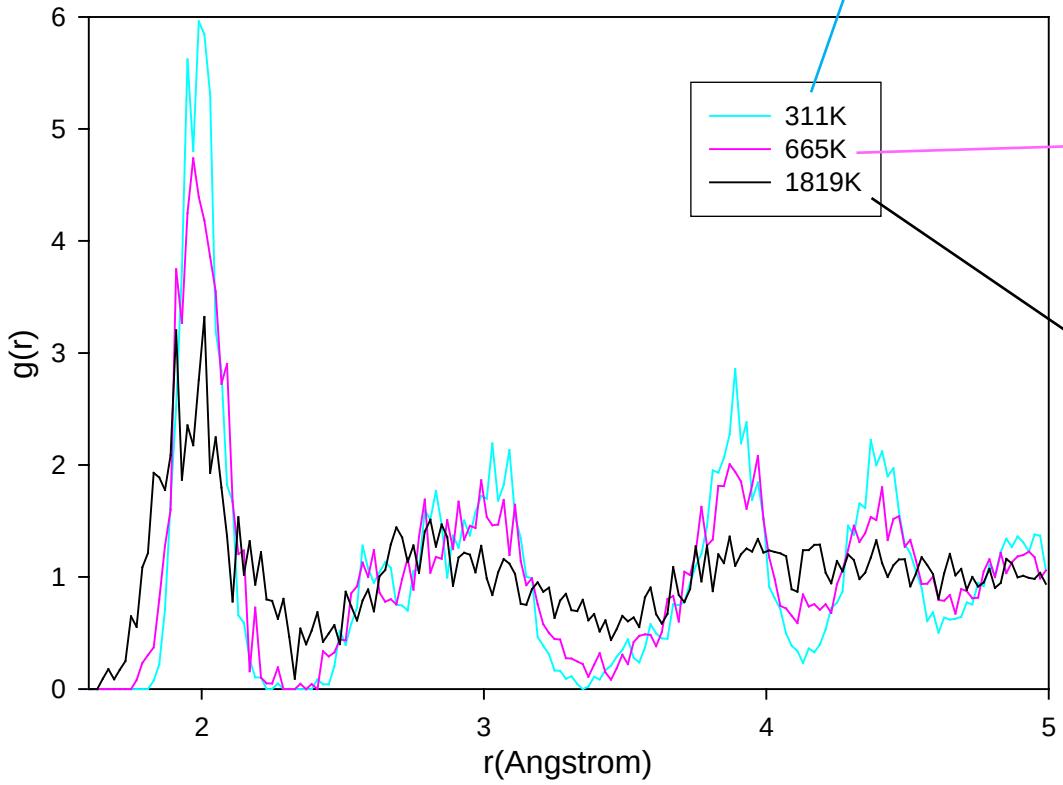
[1] D. Reyes-Coronado, G. Rodriguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. D. Coss, G. Oskam, *Nanotechnology*, vol. 19, 145605, (2008).

Bulk TiO_2 RDF



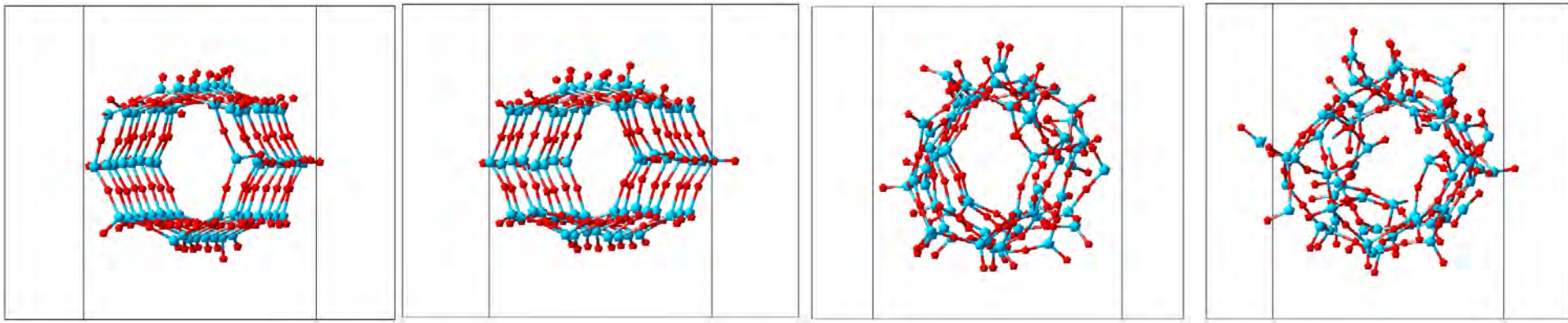






Molecular Dynamics

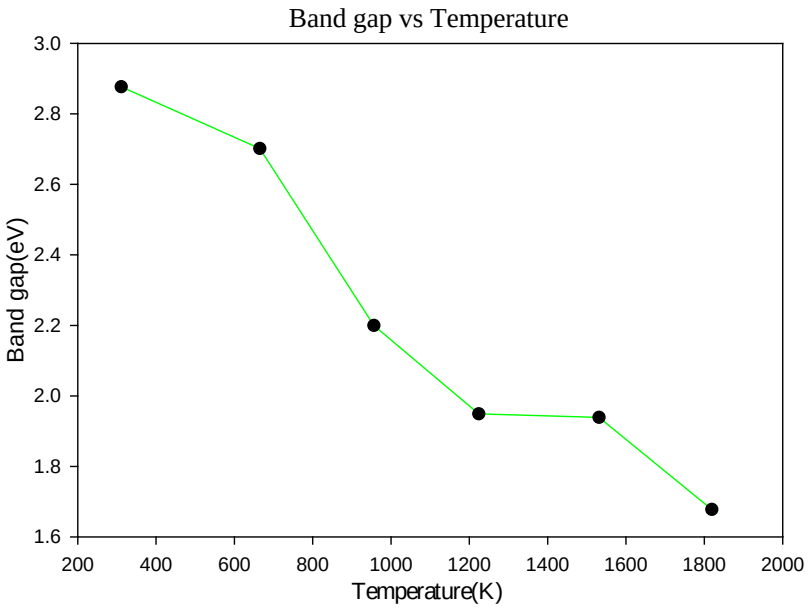
300K 400K 500K 600K



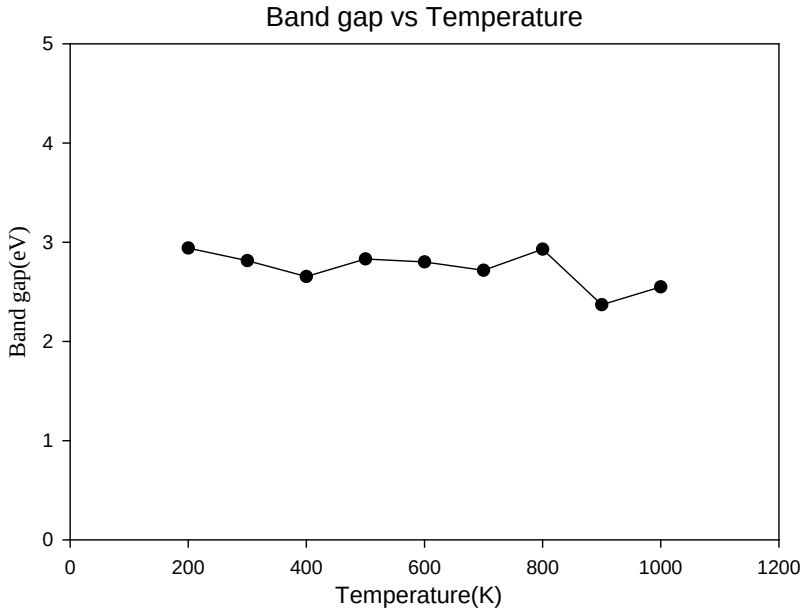
Molecular Dynamics for TiO_2 nanotube at different temperatures using NVT ensemble.

Bulk and Nanotube Band Gaps

Bulk anatase TiO_2



Anatase TiO_2 nanotube



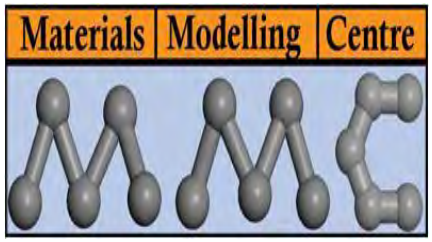
Conclusions

- Structural parameters of this bulk anatase TiO_2 are in good agreement with reference to experimental, and theoretical calculated results.

- Anatase TiO_2 nanotubes can work under extreme temperature without compromising its conductivity capability.

Acknowledgements

Faculty of Science and Agriculture



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Thank You