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$SrTiO_3$ Nanotubes with Negative Strain Energy Predicted from First Principles

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Motivation

- Nanostructures made of perovskite materials have recently attracted considerable interest because of demonstrated increase of ferroelectric ($BaTiO_3$, $Pb(Ti,Zr)O_3$), magnetic ($LaMnO_3$), photocatalytic (doped $SrTiO_3$) responses.

- Nanotubes made of $SrTiO_3$ have been proposed as Sr-delivery platforms for medical applications.

- Up to now, knowledge obtained on perovskite nanotubes are mainly from experimental site.

- The only pioneering theoretical study on ABO_3-nanotubes:
  Evarestov R.A., Bandura A.V., (2011) IOP Conf. Ser.: *Mater. Sci. Eng.* **23,** 012013.

- Due to its high symmetry simple cubic structure at room temperature $SrTiO_3$ is an excellent model material for the whole class of ABO_3 perovskites.

- In order to provide deeper understanding of atomic and electronic structure of the model ABO_3 nanotubes, in this contribution we perform comprehensive theoretical modeling of $SrTiO_3$ nanotubes taking into account all possible morphologies.

Objectives

- Define the atomic structure of the most energetically stable $SrTiO_3$ nanotube:
  - 2D morphology
  - Chirality indexes
  - Number of walls
- Theoretically predict its electronic structure and chemical properties:
  - Band edges positions
  - Net charges and bond populations

Computational details

Calculation method:

Hybrid exchange-correlation functional

$$E_{XC}^{B3PW} = E_{XC}^{LSDA} + a_0\left(E_X^{Fock} - E_X^{LSDA}\right) + a_X E_X^{B88} + a_C E_C^{PW} + (1 - a_C) E_C^{VWN}$$

$$a_0 = 0.20, \quad a_X = 0.72, \quad a_C = 0.81$$

A.D.Becke, *J.Chem.Phys.* **98** (7), 5648 (1993)

J.P.Perdew, Y.Wang, *Phys. Rev. B* **45** (23), 13244 (1992)

LCAO(CO)-GTF

Sr – (ECP)311d1G, Ti – (ECP)411d311G, O – 8-411d1G

Computer code:

CRYSTAL 2009

Dovesi R., Saunders V.R., Roetti C., *et al.* (2010) *CRYSTAL-2009 User Manual*: University of Turin, Italy.

Theoretical model

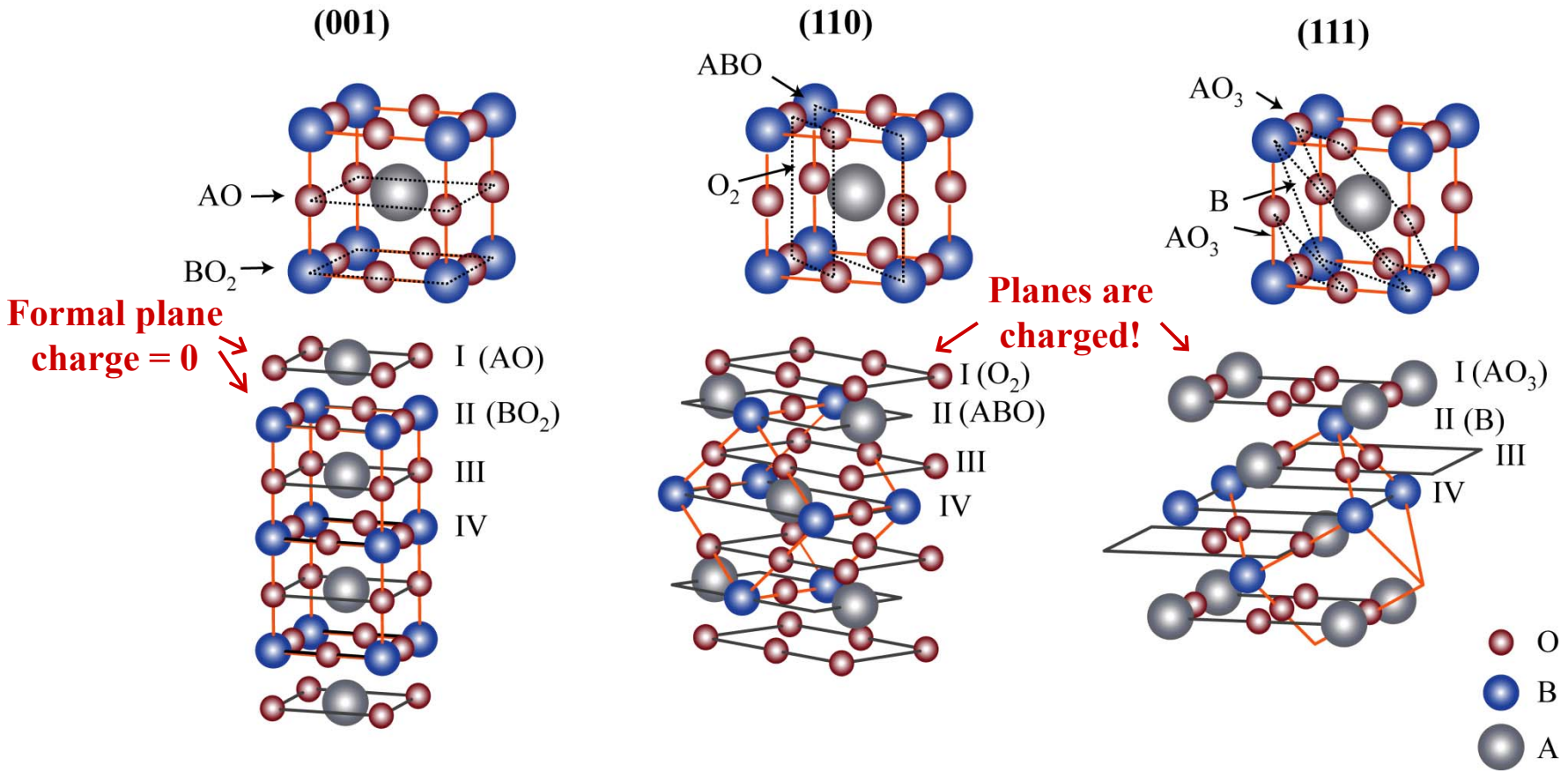
- In the labs $SrTiO_3$-nanotubes are synthesized through sophisticated thermochemistry processes using TiO_2-nanotubes as precursor. Most of them are polycrystalline structures having hundreds nanometers in diameter, however synthesis of monophasic $SrTiO_3$-nanotubes with smallest inner/outer diameter of 4/8 nm have been also reported:
  Y. Mao, S. Banerjee, S. Wong, *Chem. Commun.* **2003** (2003) 408

- Studied nanotubes are modeled using ***layer folding approach***, which means the formation builds of cylindrical nanotube structure by rolling up the stoichiometric 2D nanosheet cut from $SrTiO_3$ bulk parallel to its low index surfaces. In this respect the most stable nanotube should posses:

  - The lowest nanosheet formation energy with respect to the bulk and

  - The negative strain energy indicating stability of the nanotube relative to the corresponding flat nanosheet.

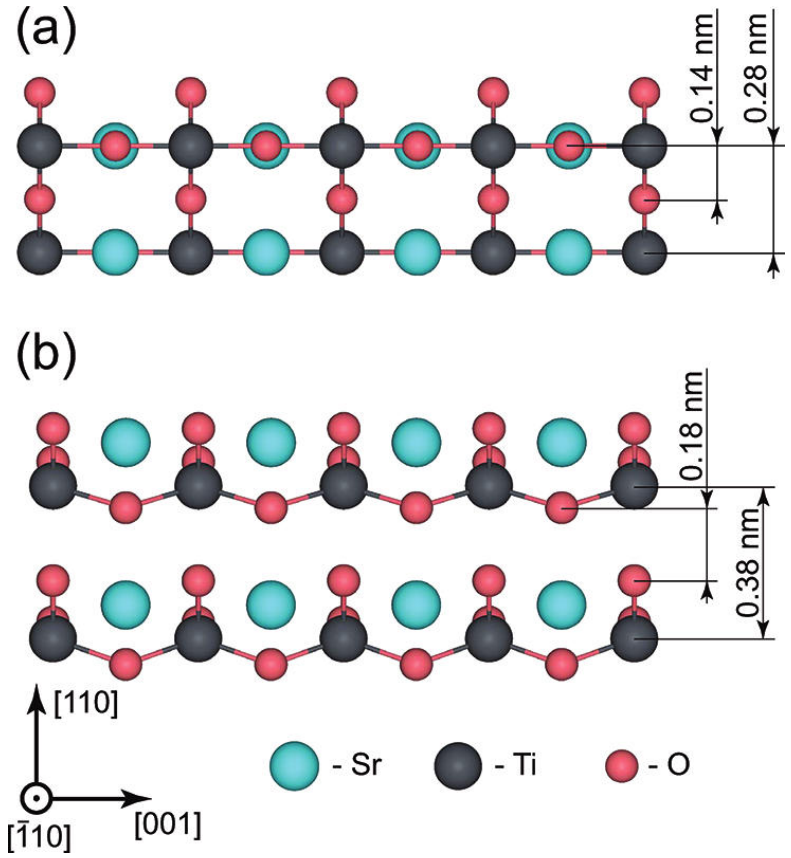
Surfaces of cubic ABO_3 perovskites



$SrTiO_3$-nanosheet energy of formation

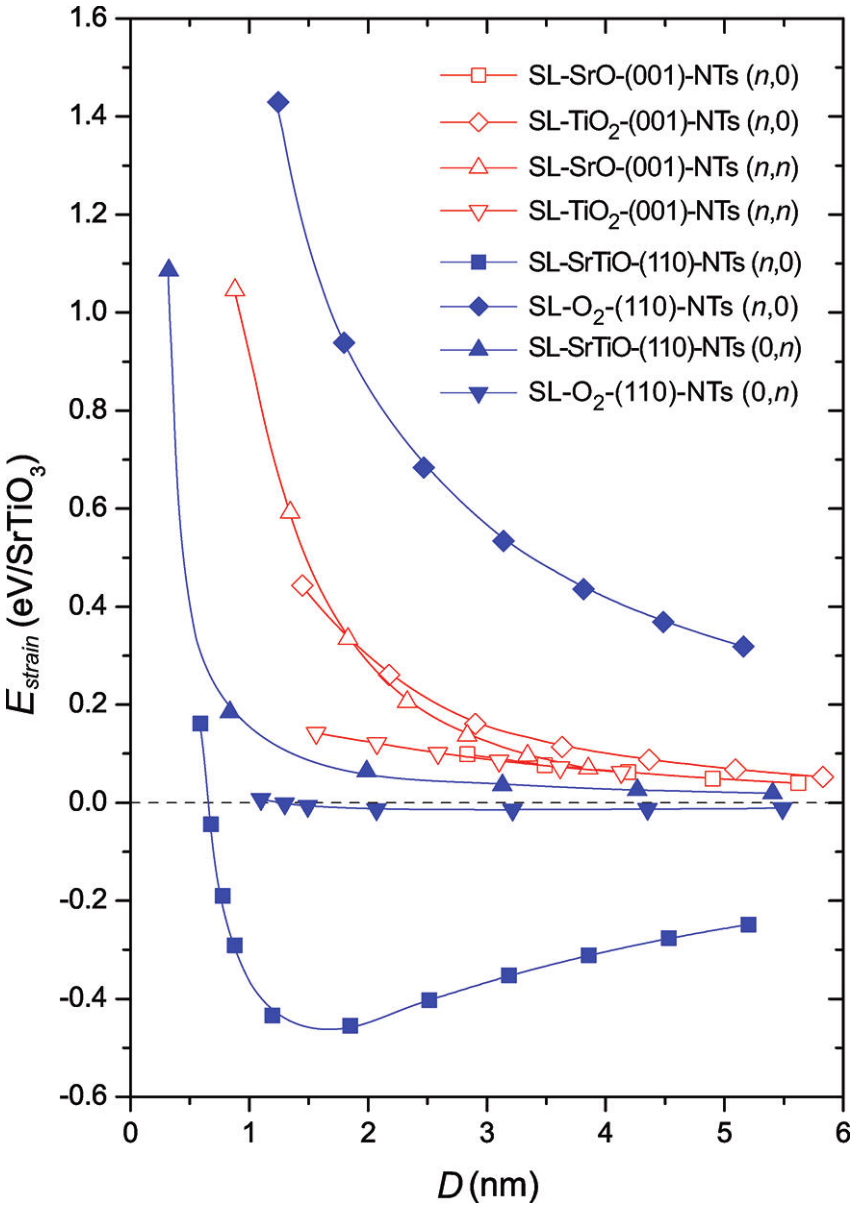
$SrTiO_3$-nanosheet	Lattice morphology	E_{form}, eV/$SrTiO_3$
Single-layer (001)	Square	**1.84**
Double-layer (001)	Square	**1.10**
Single-layer (110)	Rectangular	**1.81**
Double-layer (110)	Rectangular	**1.41**
Single-layer (111)	Reconstruction to SL-(110)-NS	
Double-layer (111)	Hexagonal	2.83

$SrTiO_3$ (110) nanosheet:



Schematic representation of DL-(110)-NS: (a) as cut from the bulk and (b) after full atomic relaxation without symmetry constraints.

Strain energy *vs.* nanotube's diameter and chirality

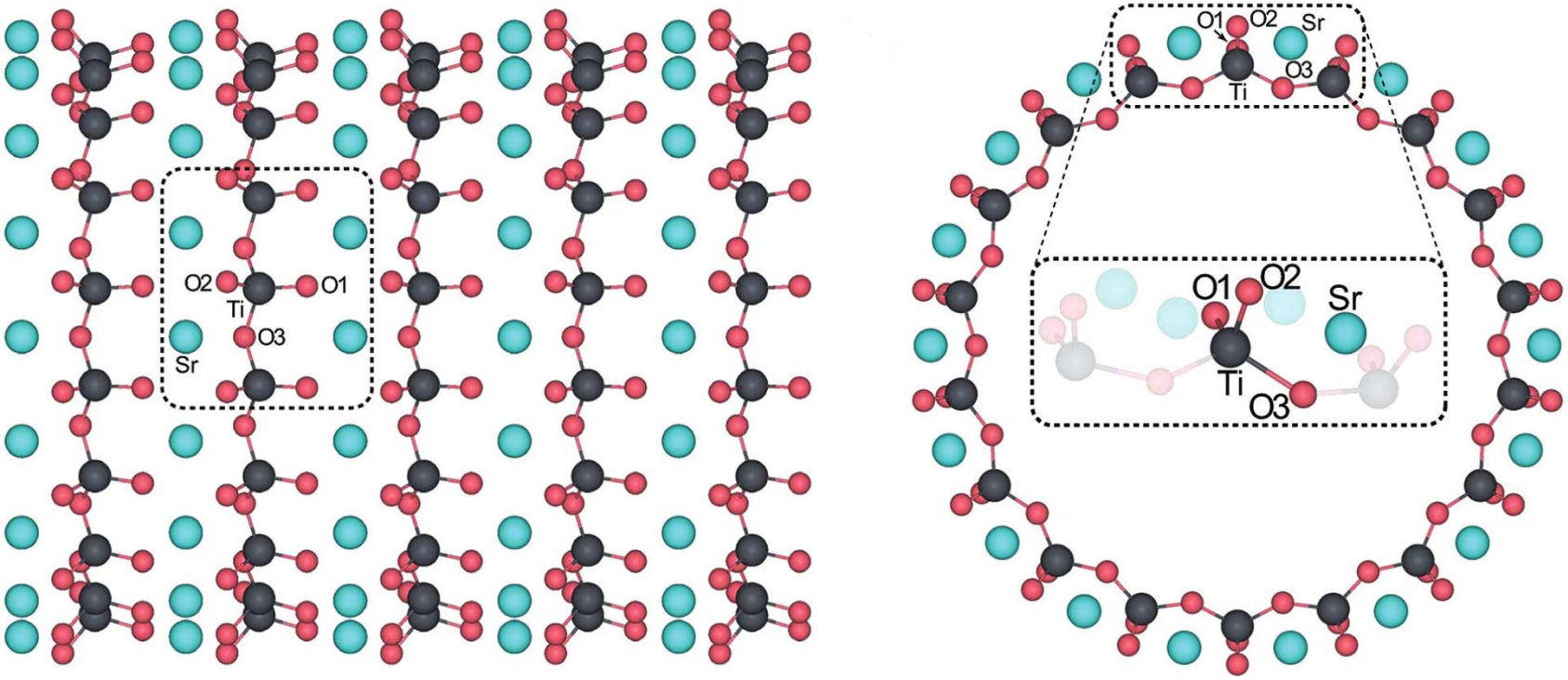


Calculated strain energies (Estrain) of nanotubes as a function of the nanotube inner diameter (D). Strain energy per $SrTiO_3$ formula unit is defined as the difference between the total energies calculated for the nanotube and the corresponding flat nanosheet.

All nanotubes folded from (001) nanosheet have positive E_{strain}.

Double layered nanotubes demonstrate extremely high strain energy.

$SrTiO_3$ (110) nanotube (18,0):



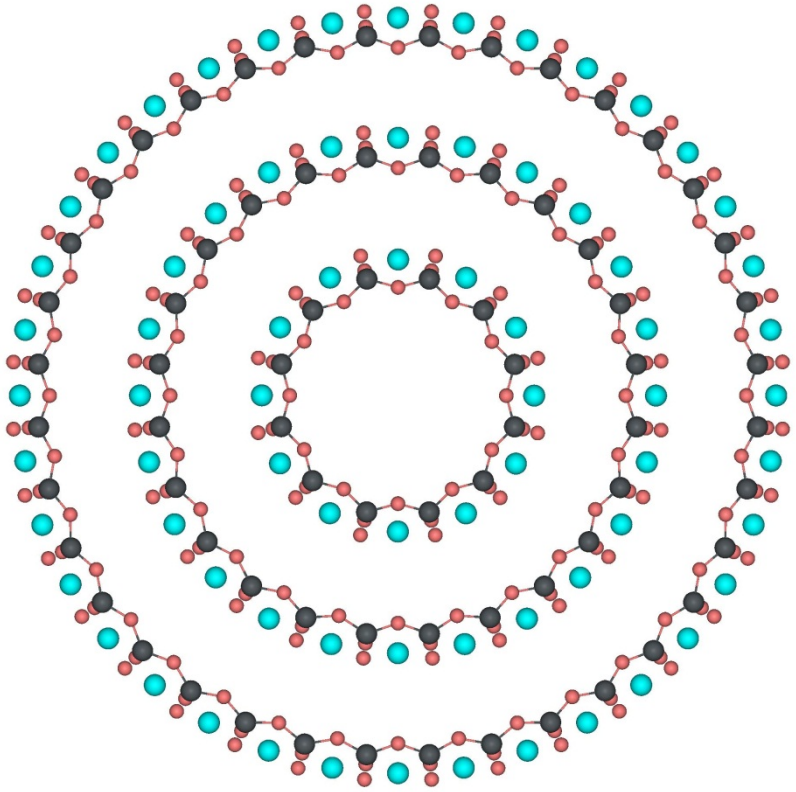
Side view (left) and front view (right) of single layered SrTiO-terminated (inner side) $SrTiO_3$(110) nanotube (18,0). Unshaded area of inset depicts irreducible atoms of nanotube unit cell. Calculated band gap 6.10 eV *vs.* 3.64 eV in the bulk.

Mulliken population analysis

	Q_{Sr}	Q_{Ti}	Q_{O1}	Q_{O2}	Q_{O3}	l_{Ti-O1}	l_{Ti-O2}	l_{Ti-O3}	P_{Ti-O1}	P_{Ti-O2}	P_{Ti-O3}
SL-SrTiO-(110)-NT	1.85	2.22	-1.40	-1.34	-1.32	0.178	0.177	0.188	138	136	106
SL-(110)-NS	1.83	2.22	-1.38	-1.31	-1.37	0.177	0.176	0.195	156	150	102
Bulk	1.87	2.35	-1.41	-1.41	-1.41	0.196	0.196	0.196	88	88	88

Calculated Effective Mulliken Charges (Q in e), TiO Bond Lengths (l in nanometers), and TiO Bond Populations (P in milli e) of SL-SrTiO-(110)-NT (18,0), SL-(110)-NS, and $SrTiO_3$ Bulk.

Multiwalled $SrTiO_3$ (110) nanotube (12,0)@(24,0)@(36,0):



Inner diameter 1.19 nm, outer diameter 4.26 nm, interwall distance 0.46 nm. Band gap 3.72 eV *vs.* 3.64 eV calculated for $SrTiO_3$ bulk. Energy gain 0.013 eV/SrTiO3 relative to constituents.

Summary and conclusions

- **Our calculations allows us to predict that the most energetically stable (multiwalled) nanotubes made of $SrTiO_3$ (ABO_3) perovskite can be rolled up from (110) nanosheet of rectangular morphology;**
- **Quantum confinement effect lead to the widening of the nanotube band gap making them attractive for further doping (photocatalysis);**
- **The increase of the TiO bond covalency in the outer nanotube shell may lead to an enhancement of adsorption properties.**

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