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.


- 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

\[ E_{XC}^{B3PW} = E_{XC}^{LSDA} + a_0 \left( E_{X}^{Fock} - E_{X}^{LSDA} \right) + a_X E_{X}^{B88} + a_C E_{C}^{PW} + (1 - a_C) E_{C}^{VWN} \]

\[ a_0 = 0.20, \quad a_X = 0.72, \quad a_C = 0.81 \]


LCAO(CO)-GTF

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

Computer code:

CRYSTAL 2009

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

Formal plane charge = 0

Planes are charged!
**SrTiO$_3$-nanosheet energy of formation**

<table>
<thead>
<tr>
<th>SrTiO$_3$-nanosheet</th>
<th>Lattice morphology</th>
<th>$E_{\text{form}}$, eV/SrTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer (001)</td>
<td>Square</td>
<td>1.84</td>
</tr>
<tr>
<td>Double-layer (001)</td>
<td>Square</td>
<td>1.10</td>
</tr>
<tr>
<td>Single-layer (110)</td>
<td>Rectangular</td>
<td>1.81</td>
</tr>
<tr>
<td>Double-layer (110)</td>
<td>Rectangular</td>
<td>1.41</td>
</tr>
<tr>
<td>Single-layer (111)</td>
<td>Reconstruction to SL-(110)-NS</td>
<td></td>
</tr>
<tr>
<td>Double-layer (111)</td>
<td>Hexagonal</td>
<td>2.83</td>
</tr>
</tbody>
</table>
SrTiO₃ (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 ($E_{strain}$) 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

<table>
<thead>
<tr>
<th></th>
<th>$Q_{\text{Sr}}$</th>
<th>$Q_{\text{Ti}}$</th>
<th>$Q_{\text{O1}}$</th>
<th>$Q_{\text{O2}}$</th>
<th>$Q_{\text{O3}}$</th>
<th>$l_{\text{Ti-O1}}$</th>
<th>$l_{\text{Ti-O2}}$</th>
<th>$l_{\text{Ti-O3}}$</th>
<th>$P_{\text{Ti-O1}}$</th>
<th>$P_{\text{Ti-O2}}$</th>
<th>$P_{\text{Ti-O3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL-SrTiO-(110)-NT</td>
<td>1.85</td>
<td>2.22</td>
<td>-1.40</td>
<td>-1.34</td>
<td>-1.32</td>
<td>0.178</td>
<td>0.177</td>
<td>0.188</td>
<td>138</td>
<td>136</td>
<td>106</td>
</tr>
<tr>
<td>SL-(110)-NS</td>
<td>1.83</td>
<td>2.22</td>
<td>-1.38</td>
<td>-1.31</td>
<td>-1.37</td>
<td>0.177</td>
<td>0.176</td>
<td>0.195</td>
<td>156</td>
<td>150</td>
<td>102</td>
</tr>
<tr>
<td>Bulk</td>
<td>1.87</td>
<td>2.35</td>
<td>-1.41</td>
<td>-1.41</td>
<td>-1.41</td>
<td>0.196</td>
<td>0.196</td>
<td>0.196</td>
<td>88</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>

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/SrTiO$_3$ 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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