

Aluminosilicate Nanotubes – Imogolite and Halloysite

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Abstract – Imogolite and Halloysite are naturally occurring aluminosilicate minerals with a predominantly hollow structure. In the present work we study the stability, electronic and mechanical properties of imogolite and halloysite nanotubes using the density-functional tight-binding (DFTB) method. The highest stability of all studied imogolite tubes has (12,0) chirality, in contrast to halloysite and conventional nanotubes where the stability decreases for larger radii (R) and the strain energy converges approximately as $1/R^2$. The results are in agreement with experimental data, as shown by comparison with the simulated XRD spectrum. An analysis of the electronic densities of states shows that all tubes are insulators.

In the last decade, inorganic nanotubes (NTs) such as MoS₂, TiO₂, have significantly attracted researchers attention, principally due to unusual physicochemical properties. Other inorganic nanotubes, like the clay minerals imogolite and halloysite, were rediscovered. Imogolite [1] and Halloysite [2] are naturally occurring aluminosilicate minerals with a predominantly hollow structure. Imogolite is composed of single walled nanotubes with stoichiometry of (Al₂SiO₃(OH)₄), where silanol (Si-OH) groups are in the inner part of the tube (Fig. 1-a). Halloysite have a 1:1 structure with stoichiometry (Al₂Si₂O₅(OH)₄.nH₂O), with silicate groups in the outside part of the tube (Fig. 1-b). The use of halloysite and imogolite offers significant advantages over other nanotubes. They are economically viable clay materials that can be mined from deposits as raw mineral. Such materials are attractive due to the vast range of applications, e.g., as catalyst support, molecular sieving material for membranes and adsorbents.

In this work we have calculated structure, stability, electronic and mechanical properties of imogolite and halloysite nanotubes using the self-consistent charge density-functional based tight-binding (SCC-DFTB) method [3]. Periodic boundary conditions were applied to the cells along tubes axes. For halloysite, we have considered *zigzag* and *armchair* NTs with diameters ranging from 15 to 46 Å, which correspond to (7,0)...(20,0) and (6,6)...(15,15) configurations. *Zigzag* (8,0)...(19,0) and *armchair* (5,5)...(14,14) imogolite tubes with diameter ranging from 14 to 40 Å have been studied. The highest stability of all studied imogolite tubes has (12,0) chirality, in contrast to halloysite and conventional nanotubes where the stability decreases for larger radii (R) and the strain energy converges approximately as $1/R^2$. This is in agreement with experimental data, as shown by comparison with simulated XRD spectrum. An analysis of the electronic densities of states shows that all tubes are insulators with a wide band gap.

A minimum in the strain energy is observed for imogolite (12,0) NT and not detected for halloysite NTs. The XRD simulations support the structural model proposed for imogolite and halloysite NTs, even though we are only studying halloysite single-walled tubes with smaller diameter than natural ones. Our results extend the theoretical understanding of aluminosilicate NTs, in perspective of potential applications.

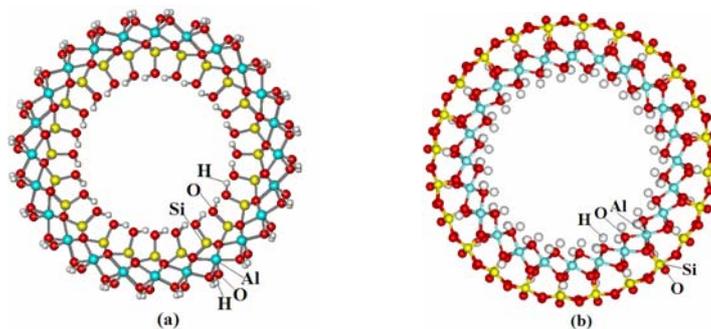


Figure 1 – Imogolite (a) and Halloysite Nanotubes (b).

References

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 [3] – Guimaraes, L. et al., *ACS Nano*, **2007**, 1, 362.