



Cluster Assembled Silicon-Lithium Nanostructures: A Nanowire Confined Inside a Carbon Nanotube

Walter Orellana¹, Ricardo Pino-Rios², Osvaldo Yañez^{3,4}, Alejandro Vásquez-Espinal⁵, Francesca Peccati⁶, Julia Contreras-García⁷, Carlos Cardenas^{8,9} and William Tiznado^{5*}

¹Departamento de Ciencias Físicas, Universidad Andres Bello, Santiago, Chile, ²Laboratorio de Química Teórica, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Santiago, Chile, ³Center of New Drugs for Hypertension (CENDHY), Santiago, Chile, ⁴Department of Pharmaceutical Science and Technology, School of Chemical and Pharmaceutical Sciences, Universidad de Chile, Santiago, Chile, ⁵Departamento de Ciencias Químicas, Computational and Theoretical Chemistry Group, Facultad de Ciencias Exactas, Universidad Andres Bello, Santiago, Chile, ⁶Center for Cooperative Research in Biosciences (CIC bioGUNE), Basque Research and Technology Alliance (BRTA), Bizkaia Technology Park, Derio, Spain, ⁷Sorbonne Universités, UPMC and CNRS, Laboratoire de Chimie Théorique (LCT), 75005, Paris, France, ⁸Departamento de Física, Facultad de Ciencias, Universidad de Chile, Santiago, Chile, ⁹Centro para el Desarrollo de la Nanociencias y Nanotecnología, CEDENNA, Avenida Ecuador, Santiago, Chile

OPEN ACCESS

Edited by:

Iwona Anusiewicz,
University of Gdansk, Poland

Reviewed by:

Fengyu Li,
Inner Mongolia University, China
Tanmoy Chakraborty,
Sharda University, India

*Correspondence:

William Tiznado
wtiznado@unab.cl

Specialty section:

This article was submitted to
Theoretical and Computational
Chemistry,
a section of the journal
Frontiers in Chemistry

Received: 30 August 2021

Accepted: 01 October 2021

Published: 12 November 2021

Citation:

Orellana W, Pino-Rios R, Yañez O,
Vásquez-Espinal A, Peccati F,
Contreras-García J, Cardenas C and
Tiznado W (2021) Cluster Assembled
Silicon-Lithium Nanostructures: A
Nanowire Confined Inside a
Carbon Nanotube.
Front. Chem. 9:767421.
doi: 10.3389/fchem.2021.767421

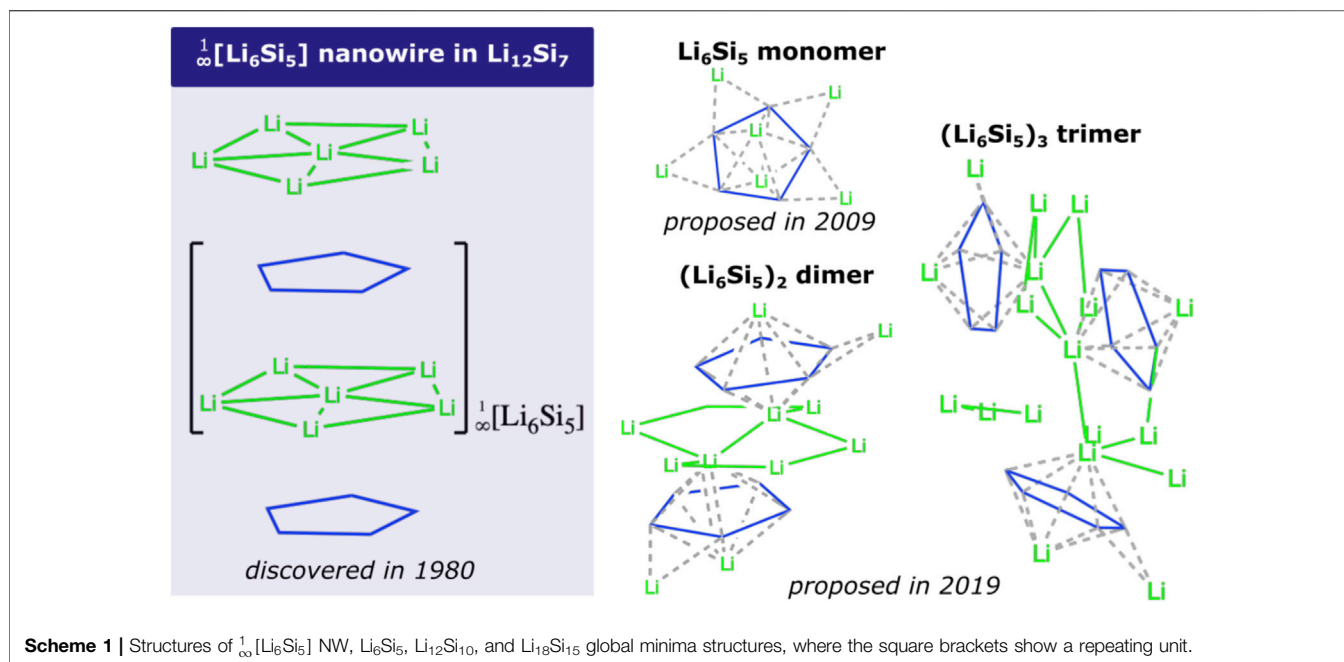
We computationally explore an alternative to stabilize one-dimensional (1D) silicon-lithium nanowires (NWs). The $\text{Li}_{12}\text{Si}_9$ Zintl phase exhibits the NW ${}_{\infty}[\text{Li}_6\text{Si}_5]$, combined with Y-shaped Si_4 structures. Interestingly, this NW could be assembled from the stacking of the Li_6Si_5 aromatic cluster. The ${}_{\infty}[\text{Li}_6\text{Si}_5]@\text{CNT}$ nanocomposite has been investigated with density functional theory (DFT), including molecular dynamics simulations and electronic structure calculations. We found that van der Waals interaction between Li's and CNT's walls is relevant for stabilizing this hybrid nanocomposite. This work suggests that nanostructured confinement (within CNTs) may be an alternative to stabilize this free NW, cleaning its properties regarding $\text{Li}_{12}\text{Si}_9$ solid phase, i.e., metallic character, concerning the perturbation provided by their environment in the $\text{Li}_{12}\text{Si}_7$ compound.

Keywords: nanowire, density functional theory, silicon-lithium clusters, carbon nanotube, metallic character

INTRODUCTION

The insertion of inorganic materials into single-walled carbon nanotubes (SWCNTs), hereinafter identified simply as CNT, enables the encapsulation of extreme nanowires (NWs) with diameters comparable to a unit cell of the parent material (Green, 1998; Sloan et al., 2002; Spencer et al., 2014). Although NWs of similar diameter can be produced using several templates, such as zeolites (Derouane, 1998), mesoporous phases (Alba-Simionesco et al., 2006; Ke et al., 2009), and metal-organic framework (MOF) (Lu et al., 2012) type materials, CNTs present many advantages as templates; they are atomically smooth, electron transparent, readily available, and can be filled by bulk infiltration to create milligram quantities of encapsulated nanowires, at least on a laboratory scale. Thus, encapsulated NW-CNT are scientifically interesting not only on their own but also as precursors to a wide range of other extreme nanowire materials.

In 2016, Ivanov et al. published a theoretical prediction of helix-shaped lithium-phosphorus nanowires encapsulated into single-walled carbon nanotubes ($\text{LiP}@\text{CNTs}$) (Ivanov et al., 2016). Note that helix-shaped Li_nP_n clusters ($n = 5-9$) had previously been reported as global minimum structures (Ivanov et al., 2012). Some solid phases consist of structural motifs like atomic clusters, i.e., in Zintl phases. This connection brings consistency to the use of models based on



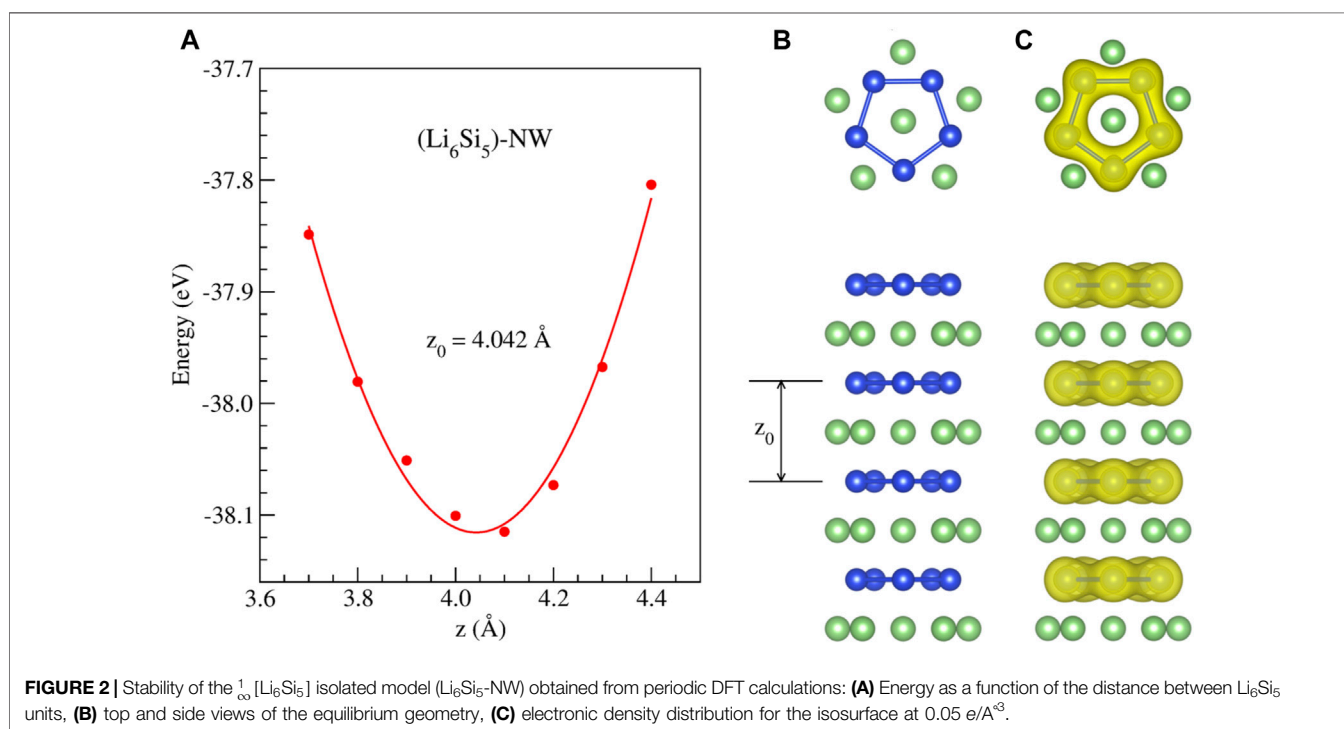
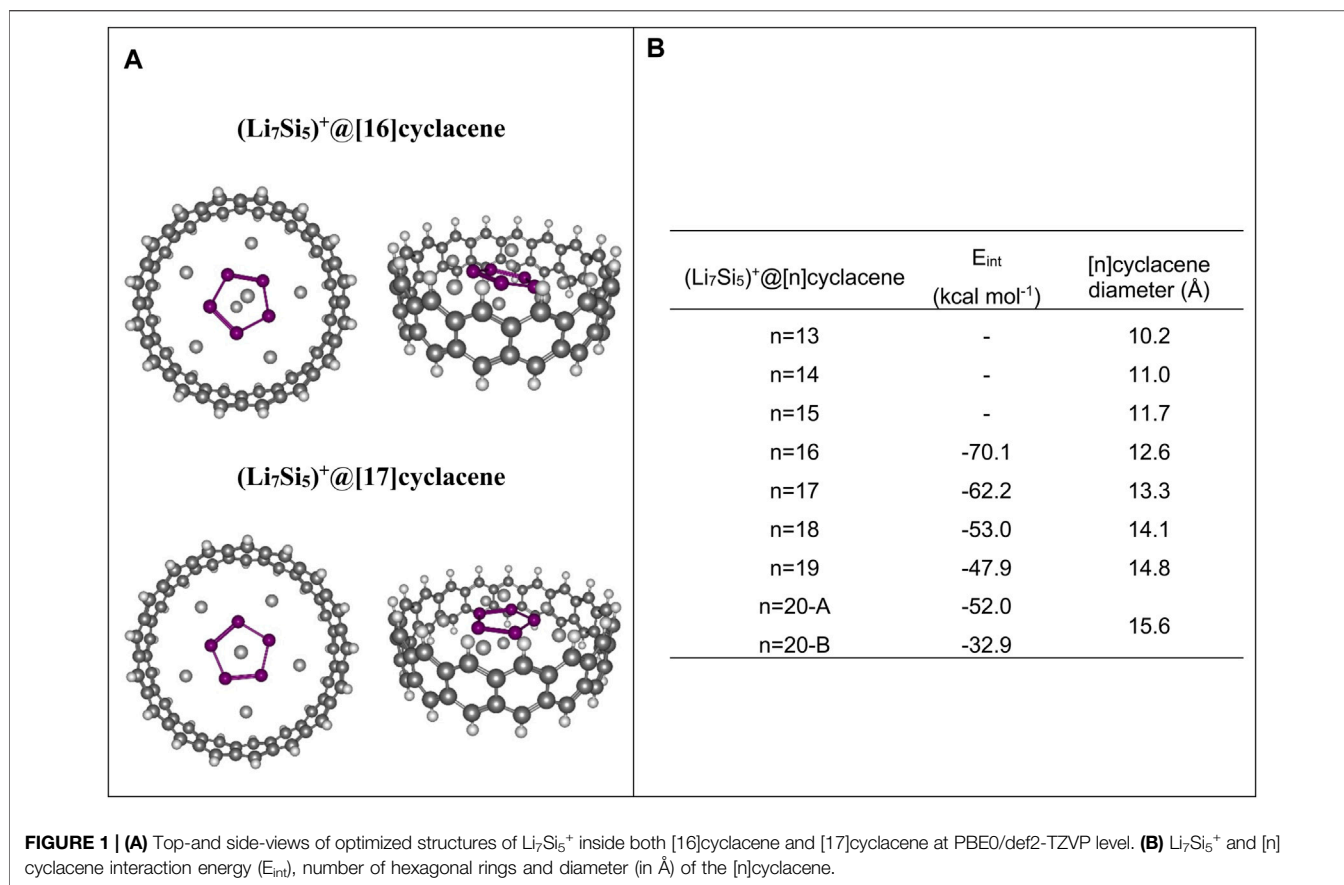
stable clusters to generate NWs inside nanotubes, as proposed in Ivanov's work (Ivanov et al., 2012). The study of these clusters inside CNTs can provide relevant information about these hybrid materials, for example, about their viability (stability analysis), their structural characteristics (geometry analysis), their physical and chemical properties (analysis of their electronic structure).

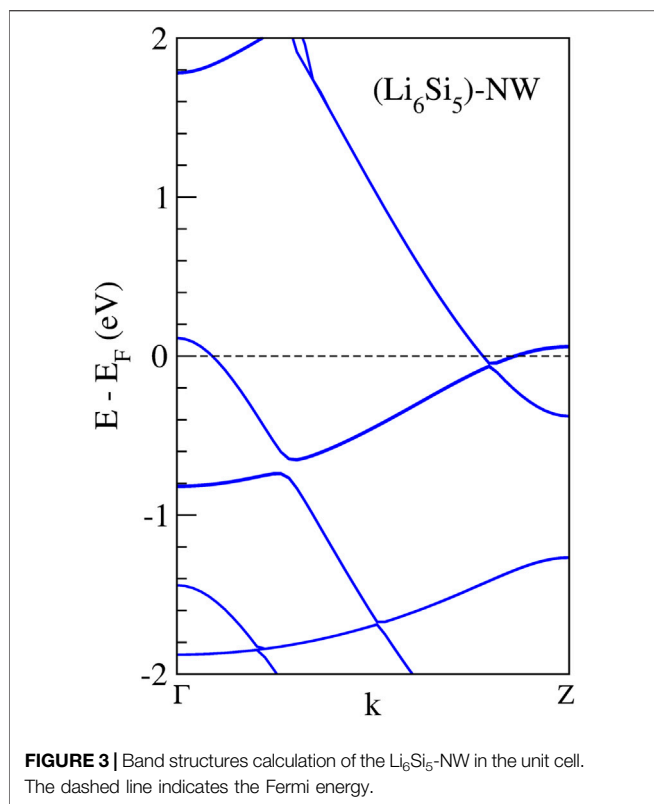
Due to its excellent energy storage capacity, Si has been extensively studied experimentally as a negative electrode material for Li-ion batteries (Gao et al., 2001; Ryu et al., 2004; Li et al., 2006, Li et al., 2008, Li et al., 2009; Obrovac et al., 2007; Song et al., 2014; Shin et al., 2020). Hence, Si lithifies at high temperature (415°C) in a LiCl-KCl melt, identifying potential plateaus evidencing the crystalline phases $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$ (Wen and Huggins, 1981). In particular, the binary (non-paramagnetic) Zintl-type $\text{Li}_{12}\text{Si}_7$ silicide contains semi-infinite sandwich-like ${}^1_{\infty}[\text{Li}_6\text{Si}_5]$ linear chains, consisting of Si_5 pentagons intercalated with Li atoms (see **Scheme 1**). Note that the unit cell of the Zintl $\text{Li}_{12}\text{Si}_7$ phase has been rationalized (Nesper, 1990; Chevrier et al., 2010; Köster et al., 2011; Kuhn et al., 2011a, Kuhn et al., 2011b) as $(\text{Li}_6^{6+}[\text{Si}_5]_6)_2$ ($\text{Li}_{12}^{10+}[\text{Si}_4]_{10}$)₂, with two well-defined silicon moieties: planar Si_5 rings and the Y-shaped Si_4 moiety. Such a structural pattern is justified by assigning 26 electrons (20 from 6Si + 6 from 6Li) to the Si_5^{6-} ring, favoring Hückel's aromaticity (Hückel, 1930, Hückel, 1931a, Hückel, 1931b; Zhao et al., 2017). This aromatic character is supported by experimental evidence of an upfield shift (to -17.2 ppm) of Li (at the center of the Li_6 fragment in **Scheme 1**) in the corresponding magic angle NMR (MAS) spectrum (Kuhn et al., 2011b; Köster et al., 2011). It is noteworthy that the Si_5^{6-} structural motif is also present in the ternary compound Li_8MgSi_6 (Nesper et al., 1986a). On the other hand, at the cluster level, our group has identified that the global minimum (GM) of the Li_6Si_5 cluster, consists of an aromatic Si_5^{6-} pentagon surrounded by 6 Li^+ counterions (Tiznado et al., 2009; Perez-Peralta et al., 2011; Contreras et al., 2013; Vásquez-Espinal et al., 2018). More

recently, we have identified the GM structures of the oligomers $(\text{Li}_6\text{Si}_5)_2$ and $(\text{Li}_6\text{Si}_5)_3$ (Yañez et al., 2019b; Manrique-de-la-Cuba et al., 2021), which also consist of aromatic Si_5 rings surrounded by Li's (see **Scheme 1**). However, the stacking of Li_6Si_5 units does not tend to form the nanowire identified in $\text{Li}_{12}\text{Si}_7$, suggesting that $\text{Li}_{12}^{10+}[\text{Si}_4]^{10-}$ component (with the Y-shaped Si_4 moiety) contributes decisively to the stabilization of this NW. In mentioned cluster studies, explorations of the potential energy surface have been performed by hybrid methods, including genetic algorithms (Yañez et al., 2019a, Yañez et al., 2020).

To build new class of materials with desirable properties, using atomic clusters instead of atoms as building blocks, is a remarkable possibility. However, it requires that atomic clusters must retain their identity when assembled, as Khanna and Jena first outlined when they coined the word "cluster-assembled materials" (CAMs) (Khanna and Jena, 1992). These authors argued that the clusters' coupling would have a unique effect on both the assembled material's electronic structure and mechanical properties, which is not possible when the assembly blocks are atoms (Khanna and Jena, 1995; Jena et al., 1996; Jena and Khanna, 1996; Claridge et al., 2009; Jena and Sun, 2018). For a more detailed and timely overview of advances in the assembly of materials from clusters, please refer to the following reviews: (Chakraborty and Pradeep, 2017; Jena and Sun, 2018; Pinkard et al., 2018; Zheng et al., 2019; Doud et al., 2020).

Given the above background, here we evaluated, *in silico*, the stability of the isolated ${}^1_{\infty}[\text{Li}_6\text{Si}_5]$ NW, as well as its electronic properties. In addition, we studied the hybrid material consisting of the NW confined in a CNT. The latter focused on identifying alternative ways to stabilize this conformation and to evaluate the effect of this association on NW electronic properties. Our density functional theory (DFT) calculations demonstrate that Li-Si@CNTs hybrid systems have excellent stability and thus have potential for experimental realization.





COMPUTATIONAL METHODS

In the finite models (clusters), geometry optimizations and frequency calculations were performed at the PBE0 (Adamo and Barone, 1999)/Def2TZVP (Weigend and Ahlrichs, 2005) level with the Gaussian 16 program (M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., 2016).

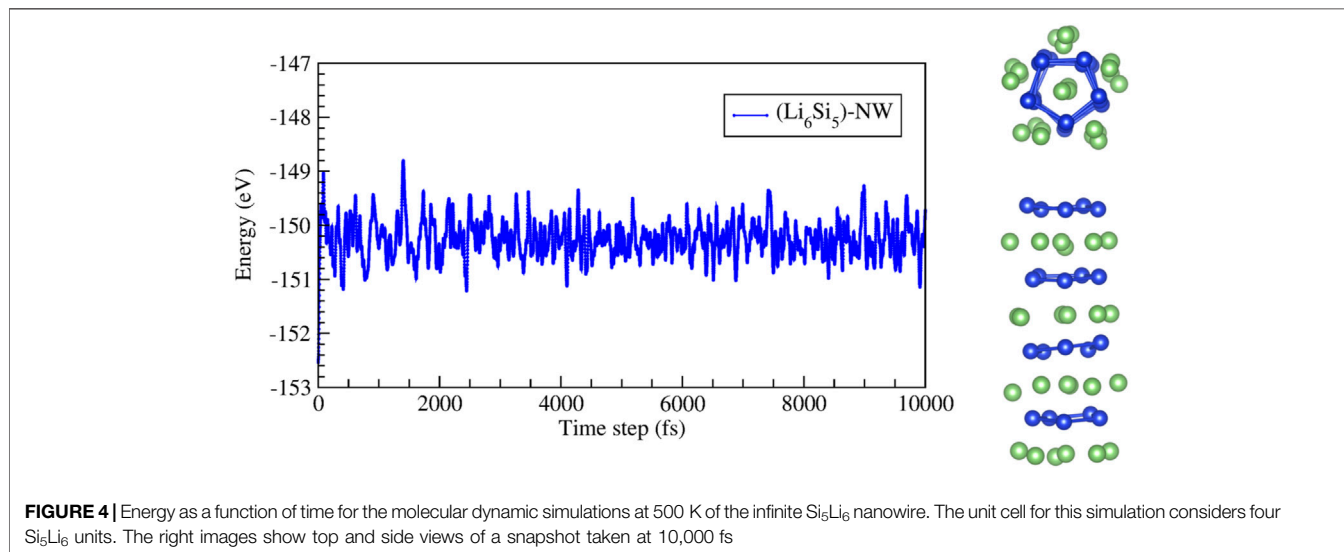
For the solid-state study, we performed first-principles calculations based on DFT (Sham and Kohn, 1966; Kohn

et al., 1996) as implemented in the Vienna Ab Initio Simulation Package (VASP) (Kresse and Furthmüller, 1996). The exchange-correlation energies were calculated at PBE-D3 level (Ernzerhof and Perdew, 1998; Grimme et al., 2010). Plane-wave basis set with a kinetic energy cutoff of 400 eV, and the projector augmented-wave method for the core-valence interaction was employed (Blöchl et al., 1994). The ${}^1_{\infty}[\text{Li}_6\text{Si}_5]$ NWs were simulated in a large unit cell with volume $(20 \times 20 \times z_0) \text{ \AA}^3$, considering periodic boundary conditions along the NW direction, where z_0 is the periodicity. Within this supercell, the lateral distance between NW images is set to 15 Å. We use a $(1 \times 1 \times 10)$ Monkhorst-Pack k-point mesh (Monkhorst and Pack, 1976). We also study finite $(\text{Li}_6\text{Si}_5)_4$ structures in the free space, also inside both an armchair and a zigzag single-walled carbon nanotube (SWCNTs). We consider armchair CNTs with chiral indexes (8,8), (9,9), and (10,10), which have diameters of 10.93, 12.27, and 13.63 Å, and zigzag CNTs with chiral indexes (14,0), (15,0), and (16,0) which have diameters of 11.04, 11.80, and 12.59 Å, respectively. For $(\text{Li}_6\text{Si}_5)_4@\text{CNT}$ simulation, $(22 \times 22 \times z_0) \text{ \AA}^3$ volume was used, where z_0 is the periodicity chosen for the CNTs. All studied structures were allowed to freely relax without any constraint until forces on each atom were smaller than 25 meV/Å. To gain insights on the stability of the NW models in the free space and inside the SWCNTs, we performed Born-Oppenheimer ab initio molecular dynamics (BO-AIMD) simulations within the NVT ensemble at different temperatures, over a total simulation time of 10 ps, considering a time step of 1 fs.

RESULTS AND DISCUSSION

Finite Model Tests to Estimate the Optimal Width of SWNTs

The first question that arises is which is the optimal SWCNT width to favor the ${}^1_{\infty}[\text{Li}_6\text{Si}_5]$ NW grown? This is a relevant question, considering that the electronic structure of group 1 elements, such as Li, is particularly sensitive to confinement



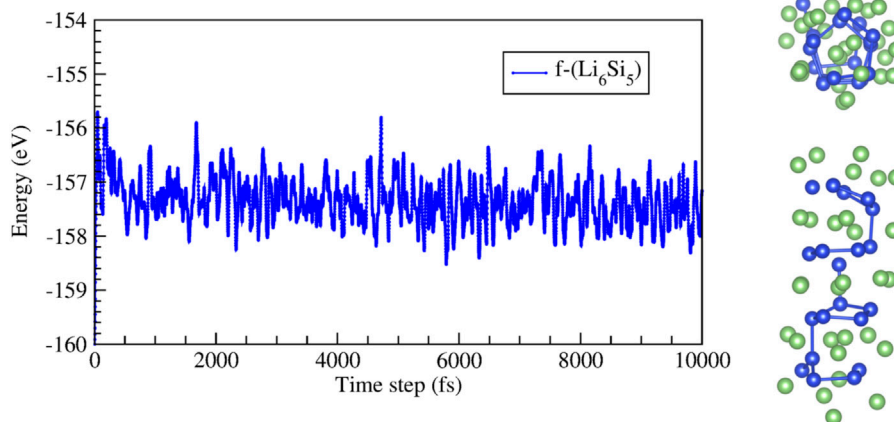


FIGURE 5 | Energy as a function of time for molecular dynamic simulations at 500 K for the finite Li_6Si_5 structure ($f\text{-Li}_6\text{Si}_5$). The right images show top and side views of a snapshot taken at 10,000 fs

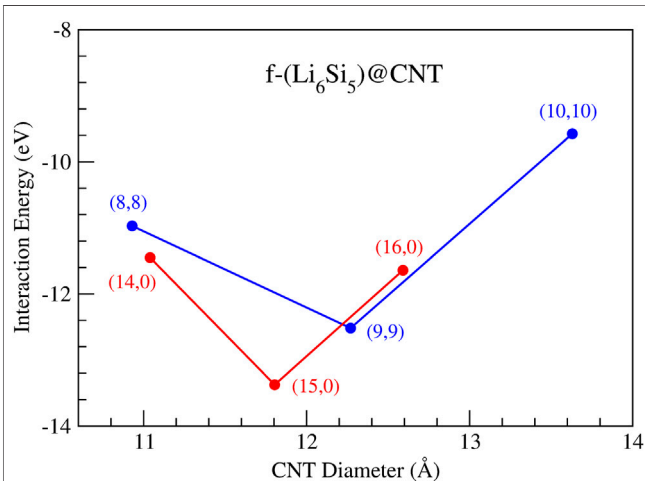


FIGURE 6 | Interaction energy as a function of the nanotube diameters for the finite Li_6Si_5 structures inside armchair CNTs with chiral indexes (8,8), (9,9), and (10,10) and zigzag CNTs with chiral indexes (14,0), (15,0), and (16,0).

(Robles-Navarro et al., 2020). To get an idea of the nanotube widths to be considered in our study, we first performed a finite model analysis. This model consists of $[n]$ cyclacenes ($n = 13\text{--}20$) in their optimal structure (at the PBE0/Def2TZVP level), covering the diameter range from 10.2 to 15.6 Å. Then the Li_7Si_5^+ cluster was placed, centering it on emulating the growth pattern towards the nanowire (see **Scheme 1**). We choose the star-shaped $\text{D}_{5h}\text{-Li}_7\text{Si}_5^+$ cluster as a suitable model for projecting the nanowire inside the CNT due to its high symmetry and its analogy in electronic structure with the Li_6Si_5 unit. In this study, we have kept the $[n]$ cyclacene structure rigid, allowing only the optimization of the Li_7Si_5^+ structure (at the PBE0/Def2TZVP level).

In the case of small $[n]$ cyclacenes ($n = 13\text{--}15$), Li_7Si_5^+ cluster undergoes noticeable changes in the optimization process due to the

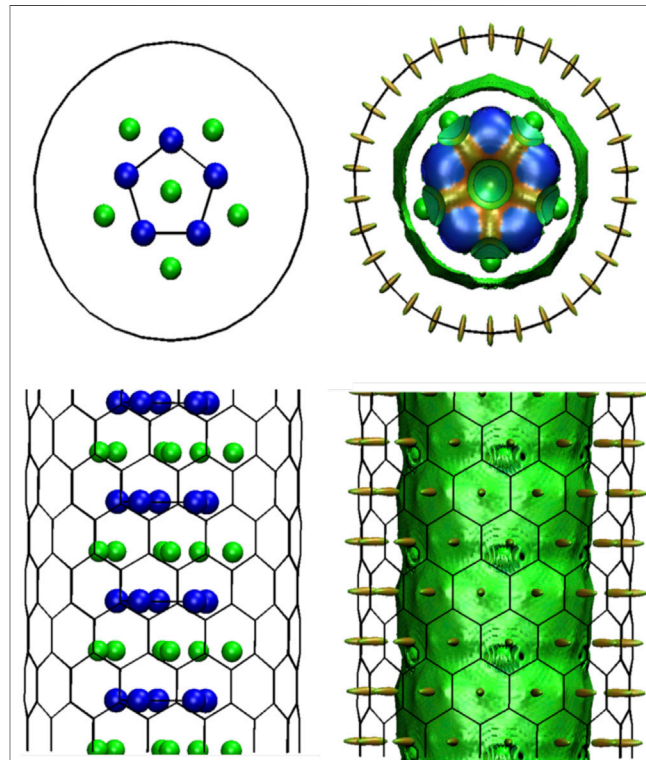


FIGURE 7 | $f\text{-Li}_6\text{Si}_5\text{@NTC}$ optimized structure, for zigzag CNTs with chiral indexes (15,0), with NCI surfaces ($s = 0.3$, color range: -0.03 to 0.03 a.u.). Geometries and electron density were taken from solid state computations.

confinement effects. In contrast, when $[n]$ cyclacenes with $n = 16\text{--}20$ are used, the Li_7Si_5^+ cluster maintains its structure at the end of the optimization process, leading to the best interaction energy, $[E_{\text{int}} = E(\text{Li}_7\text{Si}_5^+@n[\text{cyclacene}]) - E(\text{Li}_7\text{Si}_5^+) - E(n[\text{cyclacene}])]$, with [16] cyclacene ($-70.1 \text{ kcal mol}^{-1}$ at PBE0/Def2TZVP level). Since this

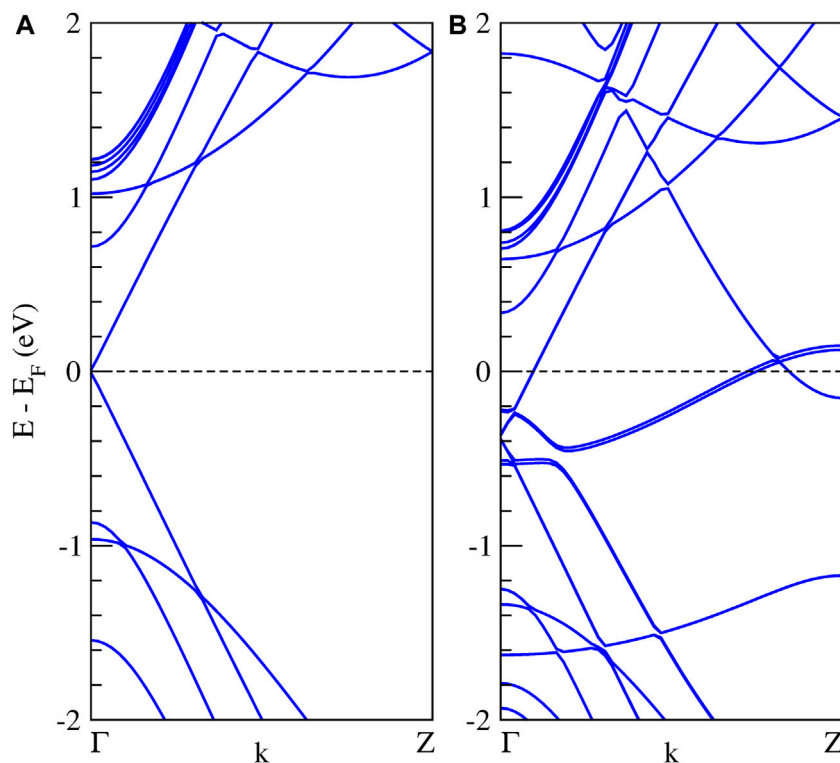


FIGURE 8 | Band structure calculations of the infinite Li_6Si_5 -NW inside the zigzag carbon nanotubes, **(A)** the isolated (15,0) CNT, and **(B)** the Li_6Si_5 -NW@CNT system. The dashed line indicates the Fermi energy.

analysis is only a reference for estimating the most suitable nanotube diameters to explore in the periodic calculations, we have not included basis set superposition error (BSSE) corrections. The most stable structures, as well as the E_{int} , are shown in **Figure 1**. The structures for the other complexes are shown in **Supplementary Figure S1** and their Cartesian coordinates in **Supplementary Table S1**. These results guided us to use CNTs with diameters in the range of 11–14 Å in next steps of our research.

Insights on the stability of free $1/\infty [\text{Li}_6\text{Si}_5]$ NW.

We first studied the stability of periodically repeated Li_6Si_5 units (Li_6Si_5 -NW), which are stacked along the z direction, forming a one-dimensional structure, as shown in **Figure 2**.

We found a stable structure with an equilibrium distance between Si_5 rings of 4.04 Å which is the periodicity of the Li_6Si_5 unit cell. In the equilibrium geometry, the distance between Li atoms of the border is 3.33 Å while the distance with respect to the center one is 2.83 Å. The Si-Si distance between neighboring atoms is 2.37 Å, very close to the ones in Li_6Si_5 monomer (between 2.30 and 2.35 Å). Our computations of the electronic band structure of the Li_6Si_5 -NW in the primitive unit cell suggest a metallic character (see **Figure 3**). Note that the bandgaps of $\text{Li}_{12}\text{Si}_7$ was reported from conductivity-temperature experimental measurements and found to be 0.6 eV (Nesper et al., 1986b).

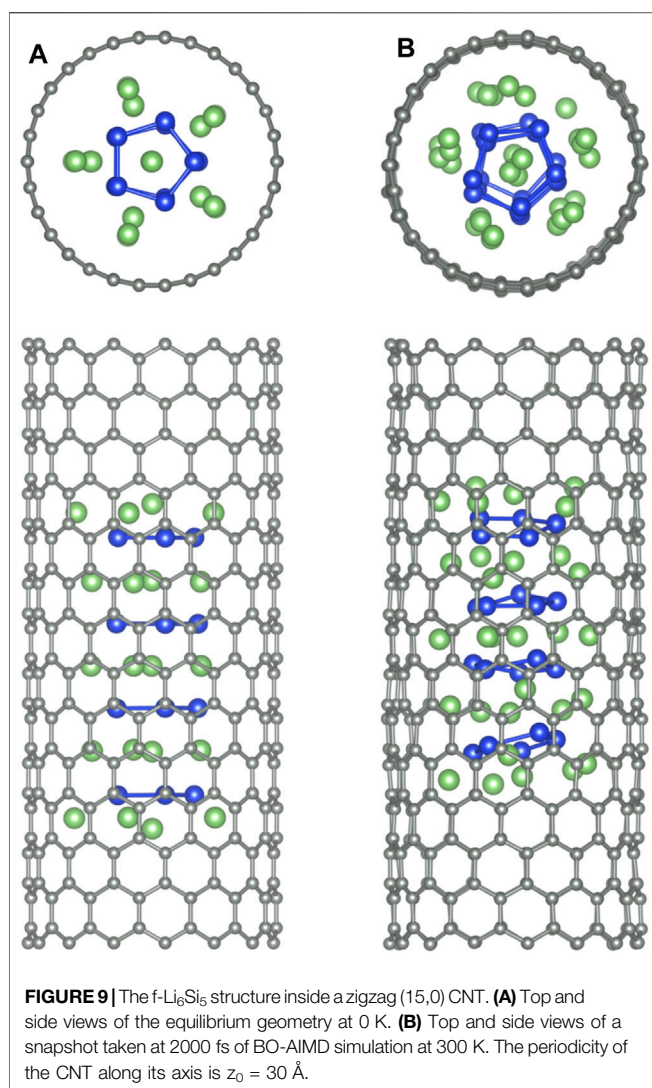
The stability of the Li_6Si_5 -NW was also verified by BO-AIMD simulations at 300 K and 500K, during a simulation time of 10 ps.

The simulation was performed by considering four Li_6Si_5 units in the periodic unit cell, as shown in **Figure 4**. We observe that at 500 K the Si_5Li_6 NW preserves its stability, showing energy fluctuations of around 2 eV. Supporting information contains short movies extracted from the BO-AIMD simulations.

Stability of the Li_6Si_5 -NW Inside the CNTs

Next, we studied a finite Li_6Si_5 structure ($f\text{-Li}_6\text{Si}_5$) in the free space and encapsulated it inside both armchair and zigzag carbon nanotubes ($f\text{-Li}_6\text{Si}_5\text{@CNT}$). For the $f\text{-Li}_6\text{Si}_5$ structure, we consider four Si_5 rings surrounded by five Li_6 moieties. BO-AIMD simulations provide insights on the stability of the $f\text{-Li}_6\text{Si}_5$ system in the free space at 300 K and 500 K. We find that at 300 K, the $f\text{-Li}_6\text{Si}_5$ structure preserves its stability. Still, at 500 K, it tends to form Si-Si bonds between adjacent Si rings without losing its one-dimensional array, as shown in **Figure 5**. However, it is important to note that this model does not have the exact stoichiometry of NW because, to maintain symmetry, an extra Li_6 unit group is added, i.e., $[(\text{Li}_6)_5(\text{Si}_5)_4]$.

To study the $f\text{-Li}_6\text{Si}_5$ structure inside the CNTs, we consider three armchair CNTs with chiral indexes of (8,8), (9,9), and (10,10), and three zigzag CNTs with chiral indexes of (14,0), (15,0), and (16,0). With this choice, we seek to find the CNT size that best accommodates the Li_6Si_5 -NW inside. Note that we selected these CNTs according to our preliminary findings from the $\text{Li}_7\text{Si}_5^+\text{@}[n]\text{cyclacene}$ model, suggesting diameters between 12 and 15 Å. The CNTs were simulated with periodic boundary conditions along its axis with a periodicity of $z_0 = 30$ Å.



The latter allows a vacuum region for the encapsulated $f\text{-Li}_6\text{Si}_5$ structure of 14 \AA , allowing the atomic movement inside the CNT. Next, we calculate the E_{int} between encapsulated $f\text{-Li}_6\text{Si}_5$ and the CNTs by the equation:

$$E_{\text{int}} = E_{\text{tot}}(f\text{-Li}_6\text{Si}_5@CNT) - E_{\text{tot}}(f\text{-Li}_6\text{Si}_5) - E_{\text{tot}}(CNT),$$

where $E_{\text{tot}}(f\text{-Li}_6\text{Si}_5)$ and $E_{\text{tot}}(CNT)$ are the total energies of the isolated $f\text{-Li}_6\text{Si}_5$ and the CNT, respectively, and $E_{\text{tot}}(f\text{-Li}_6\text{Si}_5@CNT)$ is the total energy of $f\text{-Li}_6\text{Si}_5$ unit inside the CNT. Our results for the E_{int} are shown in **Figure 6**. The armchair (9,9) and the zigzag (15,0) CNTs of 12.3 and 11.8 \AA in diameter, respectively, exhibit the more stabilizing E_{int} , being the best candidates to accommodate the $f\text{-Li}_6\text{Si}_5$ inside. In addition, the $f\text{-Li}_6\text{Si}_5$ is better stabilized inside the zigzag (15,0) CNT than inside the armchair (9,9) CNT by 0.9 eV . Noteworthy, the larger-diameter CNTs are energetically less favorable to encapsulate the $f\text{-Li}_6\text{Si}_5$, as shown in **Figure 6**, in agreement with the $\text{Li}_7\text{Si}_5^+@n$ cyclacene model. This behavior is presumable due to the van der Waals (vdW) interaction between the $f\text{-Li}_6\text{Si}_5$ and the CNT internal walls, stabilizing the system. The non-covalent

interaction index (NCI) plots confirm the non-covalent character of $f\text{-Li}_6\text{Si}_5$ with the CNT [$f\text{-Li}_6\text{Si}_5$ inside the zigzag (15,0) CNT]. In the NCI method (Johnson et al., 2010; Contreras-García et al., 2011), an isosurface of the reduced density gradient (s) is colored with the density times the sign of the second eigenvalue of the electron density Hessian matrix, λ_2 , to distinguish between attractive and repulsive interactions. The following color code is used: blue for attractive such as hydrogen bonds, green for very weak interactions such as vdW and red for steric repulsion. **Figure 7** depicts the second one (vdW) between $f\text{-Li}_6\text{Si}_5$ and the walls of the CNT.

We also calculate the band structure of the $\text{Li}_6\text{Si}_5\text{-NW}$ inside the zigzag (15,0) CNT. It is important to note that the unit cells of the $\text{Li}_6\text{Si}_5\text{-NW}$ and the CNT have a mismatch of 5.7% , which means that the $\text{Li}_6\text{Si}_5\text{-NW}$ is not in its equilibrium geometry in the $\text{Li}_6\text{Si}_5\text{-NW}@CNT$ unit cell, where the distance between the Si_5 rings increases by 0.23 \AA . However, this mismatch is relatively small and should not affect the electronic properties of the system. For the isolated CNT we find a small bandgap of 0.02 eV as shown in **Figure 8A**, which is in good agreement with the measured value of $0.029 \pm 0.004 \text{ eV}$ (Ouyang et al., 2001). Whereas the $\text{Li}_6\text{Si}_5\text{-NW}@CNT$ system exhibits metallic properties as shown **Figure 8B**, suggesting that the $\text{Li}_6\text{Si}_5\text{-NW}$ would preserve its electronic properties inside the CNT as can be compared with **Figure 3**.

Finally, we study the stability of the $f\text{-Li}_6\text{Si}_5$ structure inside both zigzag (15,0) and armchair (9,9) CNTs by performing BO-AIMD simulations. **Figure 9A** shows the equilibrium geometry of the $f\text{-Si}_5\text{Li}_6$ structure inside the (15,0) CNT. We find that the structure remains almost unchanged with respect to $f\text{-Si}_5\text{Li}_6$ in the free space, showing that the CNT would have a small influence in the Li_6Si_5 NW stability. We only note a small displacement of the Li ions at the extreme of the $f\text{-Li}_6\text{Si}_5$ structure which move toward the CNT wall. The integrity of the $f\text{-Li}_6\text{Si}_5$ structure inside the (15,0) and (9,9) CNTs was investigated by BO-AIMD simulations at 300 K . We find that the $f\text{-Si}_5\text{Li}_6$ structure preserves its stability where the Li ions move around the Si_5 ring without detaching. Similar results are found for the $f\text{-Li}_6\text{Si}_5$ structure inside the armchair (9,9) CNT, indicating that the formation and stability of the Li_6Si_5 NW inside the CNTs is independent of its chirality. This result suggests that $\text{Li}_6\text{Si}_5\text{-NW}$ are likely to form inside CNTs in a compact form, which would allow efficient storage of Li ions into CNTs mediated by Si_5 rings. **Supplementary Figure S2** shows the variation of the total energy for the BO-AIMD simulation of $f\text{-Li}_6\text{Si}_5$ inside the (15,0) and (9,9) CNTs at 300 K . We observe energy fluctuation of around 5 eV in both CNTs, preserving the stability of the $f\text{-Li}_6\text{Si}_5$ structure.

CONCLUSION

Using periodic DFT calculations and Born-Oppenheimer *ab initio* molecular dynamic simulations, we have shown that Li_6Si_5 units can be stacked one above the other, forming a one-dimensional structure linked together by Coulomb interactions. This study complements previous findings, where we

demonstrated that Li_6Si_5 , $(\text{Li}_6\text{Si}_5)_2$, and $(\text{Li}_6\text{Si}_5)_3$ lowest energy structures contain one, two, and three Si_5^{6-} aromatic rings stabilized by Li^+ counterions. Additionally, the ${}^1_{\infty}[\text{Li}_6\text{Si}_5]$ nanowire was identified in the Zintl $\text{Li}_{12}\text{Si}_7$ compound but coexisting with Y-shaped Si_4 moieties. In this case, we support the stability of the isolated Si-Li-nanowire—additionally, the relaxed structure (at room temperature) exhibits metallic characteristics.

We also found that finite $(\text{Li}_6\text{Si}_5)_4$ systems are stable inside both armchair and zigzag carbon nanotubes of around 12 Å in diameter, preserving its stability at room temperature, supporting the viable formation of Li_6Si_5 -NW inside the CNTs. Interestingly, the Li_6Si_5 -NW@CNTs hybrid nanocomposite maintains the metallic character. Finally, in the Li_6Si_5 -NW, the Li_6Si_5 units are connected by strong electrostatic interactions (Si_5^{6-} aromatic pentagons intercalated with the Li_6^{6+} moiety) in agreement with the Zintl ion concept. In the $[\text{Li}_6\text{Si}_5\text{-NW}]@\text{CNTs}$, NCI predicts that Li_6Si_5 -NW interacts with the CNT walls by van der Waals interactions Frisch et al., 2016.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

REFERENCES

- Adamo, C., and Barone, V. (1999). Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* 110, 6158–6170. doi:10.1063/1.478522
- Alba-Simionesco, C., Coasne, B., Dosseh, G., Dudziak, G., Gubbins, K. E., Radhakrishnan, R., et al. (2006). Effects of Confinement on Freezing and Melting. *J. Phys. Condens. Matter* 18, R15–R68. doi:10.1088/0953-8984/18/6/r01
- Blöchl, P. E., Jepsen, O., and Andersen, O. K. (1994). Improved Tetrahedron Method for Brillouin-Zone Integrations. *Phys. Rev. B* 49, 16223–16233. doi:10.1103/physrevb.49.16223
- Chakraborty, I., and Pradeep, T. (2017). Atomically Precise Clusters of noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* 117, 8208–8271. doi:10.1021/acs.chemrev.6b00769
- Chevrier, V. L., Zwanziger, J. W., and Dahn, J. R. (2010). First Principles Study of Li-Si Crystalline Phases: Charge Transfer, Electronic Structure, and Lattice Vibrations. *J. Alloys Compd.* 496, 25–36. doi:10.1016/j.jallcom.2010.01.142
- Claridge, S. A., Castleman, A. W., Jr, Khanna, S. N., Murray, C. B., Sen, A., and Weiss, P. S. (2009). Cluster-assembled Materials. *ACS Nano* 3, 244–255. doi:10.1021/nn800820e
- Contreras, M., Osorio, E., Ferraro, F., Puga, G., Donald, K. J., Harrison, J. G., et al. (2013). Isomerization Energy Decomposition Analysis for Highly Ionic Systems: Case Study of Starlike E5Li7^+ Clusters. *Chem. Eur. J.* 19, 2305–2310. doi:10.1002/chem.201203329
- Contreras-García, J., Johnson, E. R., Keinan, S., Chaudret, R., Piquemal, J.-P., Beratan, D. N., et al. (2011). NCIPLLOT: A Program for Plotting Noncovalent Interaction Regions. *J. Chem. Theor. Comput.* 7, 625–632. doi:10.1021/ct100641a
- Derouane, E. G. (1998). Zeolites as Solid solvents. Paper Presented at the International Symposium 'Organic Chemistry and Catalysis' on the Occasion of the 65th Birthday of Prof. H. Van Bekkum, Delft, Netherlands, 2-3 October 1997.1. *J. Mol. Catal. A: Chem.* 134, 29–45. doi:10.1016/s1381-1169(98)00021-1
- Doud, E. A., Voevodin, A., Hochuli, T. J., Champsaur, A. M., Nuckolls, C., and Roy, X. (2020). Superatoms in Materials Science. *Nat. Rev. Mater.* 5, 371–387. doi:10.1038/s41578-019-0175-3

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

FUNDING

We thank the financial support of National Agency for Research and Development (ANID) through ECOS170045, FONDECYT projects 1211128 (W.T.), 1181121 (C.C.), and 1170480 (W.O.). FONDECYT Postdoctorado 3180119 (R.P.-R.), ANID/PIA ACT192144 (O.Y.). Powered@NLHPC: This research was partially supported by the supercomputing infrastructure of the NLHPC (ECM-02) of the Universidad de Chile. Computational resources for periodic DFT calculations and BO-AIMD simulations were provided by Fenix HCP of the Universidad Andres Bello. C.C. acknowledges Center for the Development of Nanoscience and Nanotechnology CEDENNA AFB180001.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2021.767421/full#supplementary-material>

- Ernzerhof, M., and Perdew, J. P. (1998). Generalized Gradient Approximation to the Angle- and System-Averaged Exchange Hole. *J. Chem. Phys.* 109, 3313–3320. doi:10.1063/1.476928
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scalmani, G., Robb, M. A., Cheeseman, J. R., et al. (2016). *Gaussian 16, Inc.Revis. B.01.* (Wallingford CT: Gaussian).
- Gao, B., Sinha, S., Fleming, L., and Zhou, O. (2001). Alloy Formation in Nanostructured Silicon. *Adv. Mater.* 13, 816–819. doi:10.1002/1521-4095(200106)13:11<816::aid-adma816>3.0.co;2-p
- Green, M. H. (1998). The Opening and Filling of Single Walled Carbon Nanotubes (SWTs). *Chem. Commun.* (3), 347–348. doi:10.1039/a707632k
- Grimme, S., Antony, J., Ehrlich, S., and Krieg, H. (2010). A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* 132, 154104. doi:10.1063/1.3382344
- Hückel, E. (1931a). Quantentheoretische Beiträge Zum Benzolproblem. *Z. Physik* 72, 310–337. doi:10.1007/BF01341953
- Hückel, E. (1931b). Quantentheoretische Beiträge Zum Benzolproblem. *Z. Physik* 70, 204–286. doi:10.1007/BF01339530
- Hückel, E. (1930). Zur Quantentheorie der Doppelbindung. *Z. Physik* 60, 423–456. doi:10.1007/BF01341254
- Ivanov, A. S., Kar, T., and Boldyrev, A. I. (2016). Nanoscale Stabilization of Zintl Compounds: 1D Ionic Li-P Double helix Confined inside a Carbon Nanotube. *Nanoscale* 8, 3454–3460. doi:10.1039/c5nr07713c
- Ivanov, A. S., Morris, A. J., Bozhenko, K. V., Pickard, C. J., and Boldyrev, A. I. (2012). Inorganic Double-Helix Structures of Unusually Simple Lithium-Phosphorus Species. *Angew. Chem. Int. Ed.* 51, 8330–8333. doi:10.1002/anie.201201843
- Jena, P., and Khanna, S. N. (1996). Physics of Cluster Assembled Materials. *Mater. Sci. Eng. A* 217–218, 218–222. doi:10.1016/s0921-5093(96)10361-0
- Jena, P. K., Khanna, S. N., and Rao, B. K. (1996). Stability and Electronic Structure of Cluster Assembled Materials. *Msf* 232, 1–26. doi:10.4028/www.scientific.net/msf.232.1
- Jena, P., and Sun, Q. (2018). Super Atomic Clusters: Design Rules and Potential for Building Blocks of Materials. *Chem. Rev.* 118, 5755–5870. doi:10.1021/acs.chemrev.7b00524

- Johnson, E. R., Keinan, S., Mori-Sánchez, P., Contreras-García, J., Cohen, A. J., and Yang, W. (2010). Revealing Noncovalent Interactions. *J. Am. Chem. Soc.* 132, 6498–6506. doi:10.1021/ja100936w
- Ke, J., Su, W., Howdle, S. M., George, M. W., Cook, D., Perdjon-Abel, M., et al. (2009). Electrodeposition of Metals from Supercritical Fluids. *Proc. Natl. Acad. Sci.* 106, 14768–14772. doi:10.1073/pnas.0901986106
- Khanna, S. N., and Jena, P. (1992). Assembling Crystals from Clusters. *Phys. Rev. Lett.* 69, 1664–1667. doi:10.1103/physrevlett.69.1664
- Khanna, S. N., and Jena, P. (1995). Atomic Clusters: Building Blocks for a Class of Solids. *Phys. Rev. B* 51, 13705–13716. doi:10.1103/physrevb.51.13705
- Kohn, W., Becke, A. D., and Parr, R. G. (1996). Density Functional Theory of Electronic Structure. *J. Phys. Chem.* 100, 12974–12980. doi:10.1021/jp960669l
- Köster, T. K.-J., Salager, E., Morris, A. J., Key, B., Seznec, V., Morcrette, M., et al. (2011). Resolving the Different Silicon Clusters in Li₂Si₇ by ²⁹Si and ⁶Li Solid-State NMR Spectroscopy. *Angew. Chem. Int. Ed.* 50, 12591–12594. doi:10.1002/anie.201105998
- Kresse, G., and Furthmüller, J. (1996). Efficient Iterative Schemes For Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* 54, 11169–11186. doi:10.1103/physrevb.54.11169
- Kuhn, A., Sreeraj, P., Pöttgen, R., Wiemhöfer, H.-D., Wilkening, M., and Heitjans, P. (2011a). Li Ion Diffusion in the Anode Material Li₁₂Si₇: Ultrafast quasi-1D Diffusion and Two Distinct Fast 3D Jump Processes Separately Revealed by ⁷Li NMR Relaxometry. *J. Am. Chem. Soc.* 133, 11018–11021. doi:10.1021/ja2020108
- Kuhn, A., Sreeraj, P., Pöttgen, R., Wiemhöfer, H.-D., Wilkening, M., and Heitjans, P. (2011b). Li NMR Spectroscopy on Crystalline Li₁₂Si₇: Experimental Evidence for the Aromaticity of the Planar Cyclopentadienyl-Analogous Si₅–Rings. *Angew. Chem. Int. Ed.* 50, 12099–12102. doi:10.1002/anie.201105081
- Li, J., Christensen, L., Obrovac, M. N., Hewitt, K. C., and Dahn, J. R. (2008). Effect of Heat Treatment on Si Electrodes Using Polyvinylidene Fluoride Binder. *J. Electrochem. Soc.* 155, A234. doi:10.1149/1.2830545
- Li, J., Lewis, R. B., and Dahn, J. R. (2006). Sodium Carboxymethyl Cellulose: A Potential Binder for Si Negative Electrodes for Li-Ion Batteries. *Electrochem. Solid State Lett.* 10, A17. doi:10.1149/1.2398725
- Li, J., Smith, A., Sanderson, R. J., Hatchard, T. D., Dunlap, R. A., and Dahn, J. R. (2009). *In Situ* [sup 119]Sn Mössbauer Effect Study of the Reaction of Lithium with Si Using a Sn Probe. *J. Electrochem. Soc.* 156, A283. doi:10.1149/1.3073879
- Lu, G., Li, S., Guo, Z., Farha, O. K., Hauser, B. G., Qi, X., et al. (2012). Imparting Functionality to a Metal-Organic Framework Material by Controlled Nanoparticle Encapsulation. *Nat. Chem* 4, 310–316. doi:10.1038/nchem.1272
- Manrique-de-la-Cuba, M. F., Leyva-Parra, L., Inostroza, D., Gomez, B., Vásquez-Espinal, A., Garza, J., et al. (2021). Li₈Si₈, Li₁₀Si₉, and Li₁₂Si₁₀: Assemblies of Lithium-Silicon Aromatic Units. *ChemPhysChem* 22 (10), 906–910. doi:10.1002/cphc.202001051
- Monkhorst, H. J., and Pack, J. D. (1976). Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* 13, 5188–5192. doi:10.1103/physrevb.13.5188
- Nesper, R., Curda, J., and Von Schnering, H. G. (1986a). Li₈MgSi₆, a Novel Zintl Compound Containing Quasi-Aromatic Si₅ Rings. *J. Solid State. Chem.* 62, 199–206. doi:10.1016/0022-4596(86)90232-x
- Nesper, R. (1990). Structure and Chemical Bonding in Zintl-Phases Containing Lithium. *Prog. Solid State. Chem.* 20, 1–45. doi:10.1016/0079-6786(90)90006-2
- Nesper, R., von Schnering, H. G., and Curda, J. (1986b). Li₁₂Si₇, eine Verbindung mit trigonal-planaren Si₄-Clustern und isometrischen Si₅-Ringen. *Chem. Ber.* 119, 3576–3590. doi:10.1002/cber.19861191207
- Obrovac, M. N., Christensen, L., Le, D. B., and Dahn, J. R. (2007). Alloy Design for Lithium-Ion Battery Anodes. *J. Electrochem. Soc.* 154, A849. doi:10.1149/1.2752985
- Ouyang, M., Huang, J.-L., Cheung, C. L., and Lieber, C. M. (2001). Energy Gaps in "Metallic" Single-Walled Carbon Nanotubes. *Science* 292, 702–705. doi:10.1126/science.1058853
- Perez-Peralta, N., Contreras, M., Tiznado, W., Stewart, J., Donald, K. J., and Merino, G. (2011). Stabilizing Carbon-Lithium Stars. *Phys. Chem. Chem. Phys.* 13, 12975–12980. doi:10.1039/C1CP21061K
- Pinkard, A., Champsaur, A. M., and Roy, X. (2018). Molecular Clusters: Nanoscale Building Blocks for Solid-State Materials. *Acc. Chem. Res.* 51, 919–929. doi:10.1021/acs.accounts.8b00016
- Robles-Navarro, A., Fuentealba, P., Muñoz, F., and Cardenas, C. (2020). Electronic Structure of First and Second Row Atoms under Harmonic Confinement. *Int. J. Quan. Chem.* 120, e26132.
- Ryu, J. H., Kim, J. W., Sung, Y.-E., and Oh, S. M. (2004). Failure Modes of Silicon Powder Negative Electrode in Lithium Secondary Batteries. *Electrochem. Solid-state Lett.* 7, A306. doi:10.1149/1.1792242
- Sham, L. J., and Kohn, W. (1966). One-particle Properties of an Inhomogeneous Interacting Electron Gas. *Phys. Rev.* 145, 561–567. doi:10.1103/physrev.145.561
- Shin, H.-J., Hwang, J.-Y., Kwon, H. J., Kwak, W.-J., Kim, S.-O., Kim, H.-S., et al. (2020). Sustainable Encapsulation Strategy of Silicon Nanoparticles in Microcarbon Sphere for High-Performance Lithium-Ion Battery Anode. *ACS Sustain. Chem. Eng.* 8, 14150–14158. doi:10.1021/acssuschemeng.0c04828
- Sloan, J., Kirkland, A. I., Hutchison, J. L., and Green, M. L. H. (2002). Integral Atomic Layer Architectures of 1D Crystals Inserted into Single Walled Carbon Nanotubes. *Chem. Commun.* 2010, 1319–1332. doi:10.1039/b200537a
- Song, T., Hu, L., and Paik, U. (2014). One-dimensional Silicon Nanostructures for Li Ion Batteries. *J. Phys. Chem. Lett.* 5, 720–731. doi:10.1021/jz4027979
- Spencer, J. H., Nesbitt, J. M., Trehwhitt, H., Kashtiban, R. J., Bell, G., Ivanov, V. G., et al. (2014). Raman Spectroscopy of Optical Transitions and Vibrational Energies of ~1 Nm HgTe Extreme Nanowires within Single Walled Carbon Nanotubes. *ACS Nano* 8, 9044–9052. doi:10.1021/nn5023632
- Tiznado, W., Perez-Peralta, N., Islas, R., Toro-Labbe, A., Ugalde, J. M., and Merino, G. (2009). Designing 3-D Molecular Stars. *J. Am. Chem. Soc.* 131, 9426–9431. doi:10.1021/ja903694d
- Vásquez-Espinal, A., Palacio-Rodríguez, K., Ravell, E., Orozco-Ic, M., Barroso, J., Pan, S., et al. (2018). E5M7+ (E= C–Pb, M= Li–Cs): A Source of Viable Star-Shaped Clusters. *Chem. Asian J.* 13, 1751–1755. doi:10.1002/asia.201800654
- Weigend, F., and Ahlrichs, R. (2005). Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 7, 3297–3305. doi:10.1039/b508541a
- Wen, C. J., and Huggins, R. A. (1981). Chemical Diffusion in Intermediate Phases in the Lithium-Silicon System. *J. Solid State. Chem.* 37, 271–278. doi:10.1016/0022-4596(81)90487-4
- Yañez, O., Báez-Grez, R., Inostroza, D., Rabanal-León, W. A., Pino-Rios, R., Garza, J., et al. (2019a). AUTOMATON: a Program that Combines a Probabilistic Cellular Automata and a Genetic Algorithm for Global Minimum Search of Clusters and Molecules. *J. Chem. Theor. Comput.* 15, 1463–1475. doi:10.1021/acs.jctc.8b00772
- Yañez, O., García, V., Garza, J., Orellana, W., Vásquez-Espinal, A., and Tiznado, W. (2019b). (Li₆Si₅)₂₋₅: The Smallest Cluster-Assembled Materials Based on Aromatic Si₅–Rings. *Chem. Eur. J.* 25, 2467–2471. doi:10.1002/chem.201805677
- Yañez, O., Inostroza, D., Usuga-Acevedo, B., Vásquez-Espinal, A., Pino-Rios, R., Tabilo-Sepulveda, M., et al. (2020). Evaluation of Restricted Probabilistic Cellular Automata on the Exploration of the Potential Energy Surface of Be₆B₁₁–. *Theor. Chem. Acc.* 139, 41. doi:10.1007/s00214-020-2548-5
- Zhao, L., Grande-Aztatzi, R., Foroutan-Nejad, C., Ugalde, J. M., and Frenking, G. (2017). Aromaticity, the Hückel 4 N+2 Rule and Magnetic Current. *ChemistrySelect* 2, 863–870. doi:10.1002/slct.201602080
- Zheng, X.-Y., Xie, J., Kong, X.-J., Long, L.-S., and Zheng, L.-S. (2019). Recent Advances in the Assembly of High-Nuclearity Lanthanide Clusters. *Coord. Chem. Rev.* 378, 222–236. doi:10.1016/j.ccr.2017.10.023

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2021 Orellana, Pino-Rios, Yañez, Vásquez-Espinal, Peccati, Contreras-García, Cardenas and Tiznado. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.