

Cluster-Inspired Design of High-Capacity Anode for Li-Ion Batteries

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S Supporting Information

ABSTRACT: One of the greatest challenges in next-generation Li-ion batteries (LIB) is to develop high charge capacity anodes with long cycle life. Inspired by the experimental observation of a magic $Ti_{13}C_{22}$ cluster and its layer-by-layer growth, we have constructed one-dimensional nanowires using Ti_9C_{13} clusters as well as those based on planar-tetracoordinate carbon-containing (ptC) Ti_8C_{12} metcar and TiC clusters with bulk cubic crystal structure. Using density functional theory and molecular dynamics we studied their energetic and thermal stability as well as their potential for LIB anode. The Ti_9C_{13} nanowire is found to be stable up to 2500 K and has a charge capacity five times larger than that of the graphite anode being used today. Furthermore, unlike silicon nanotube anode materials, the Ti_9C_{13} nanowire does not suffer from volume expansion/contraction during lithiation/ delithiation processes.

echargeable batteries are an indispensable part of modern society. Because of their several attractive properties, Li-ion batteries (LIB) have been the preferred choice for portable electronics, transportation, and energy storage devices. However, to meet future demand, considerable material challenges must be overcome to produce the next-generation LIB.^{1–3} Among these is the development of anodes with increased capacity, power density, cycle life, and safety. Because of stability and low cost,⁴ graphite-based materials are widely used for anode material,⁴ but their low specific capacity (372 mAh·g⁻¹) and poor cycle life limit further applications.^{5,6} Recent developments of one-dimensional (1D) materials such as 1D carbon and silicon nanotubes provide promising choices. For example, silicon nanotubes offer a high theoretical charge capacity of 4200 mAh \cdot g⁻¹, which is 11 times higher than that of the graphite anodes. Unfortunately, silicon expands volumetrically by up to 400% on full lithiation and contracts significantly with delithiation,⁷ creating stability issues. In addition, unstable solid electrolyte interphase limits the cycle life of silicon anodes to a few hundred cycles. Recently, Cui and co-workers⁸ designed a silicon nanotube anode coated with an ion-permeable silicon oxide shell that substantially improves cycle life while retaining more than 85% of its initial capacity. The coating layer also prevents the silicon nanotube from expanding outward. However, it will be ideal if one can develop high-capacity anode material, without a coating layer, that does not suffer from expansion and contraction during lithiation-delithiation processes.⁸



In the past, most 1D LIB anodes such as single-walled carbon, silicon, and germanium nanotubes were known to grow along the nanotube direction,9 and no 1D carbon-based structures that grow with a layer-by-layer process are known. In this Letter we discuss the design of such an anode composed of Ti and C. We drew inspiration from an early experiment by Wang and Cheng¹⁰ who observed an intense peak of the $Ti_{13}C_{22}^{-}$ cluster in the mass spectra and assigned a layer-bylayer growth for its structure. Clusters with such pronounced stability are referred to as magic clusters and have been considered as building blocks of a new class of cluster assembled materials. 11,12 A classic example of such materials is C_{60} fullerene.¹³ We wondered if it is possible to create a nanowire based on the $Ti_{13}C_{22}$ cluster motif. We recall that interest in very stable $Ti_x C_y$ clusters date back to the early 1990s when Castleman and co-workers observed a pronounced peak corresponding to Ti_8C_{12} in the mass spectra of $Ti_xC_y^+$ clusters.¹⁴ They termed this magic cluster "metcar" and proposed that it can be used as building blocks of clusterassembled materials, just as fullerides are created by assembling C₆₀ fullerenes. Successive experiments on other transition metal carbide clusters have observed the magic peak corresponding to metcar composition.^{15–17} However, materials with Ti_8C_{12} as building blocks have not yet been realized, and later studies showed that metcars are reactive and tend to coalesce.¹⁸ The

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Figure 1. (a) Geometry of Ti_9C_{13} with its perspective view. Layers A and B represent different layers; C_1 , C_2 , C_3 , Ti_1 , Ti_2 , and Ti_3 represent different nonequivalent atoms sites. (b) Cohesive energy of binary compounds with composition Ti_xC_{1-x} . The solid line links the cohesive energies of graphene (x = 0) and bulk Ti (x = 1). Formation energy, δF_i is positive (negative) above (below) the solid line.

structure of metcars has been a topic of debate in the literature. Observation of very stable Ti₁₄C₁₃⁺ magic clusters^{19,20} suggested the existence of a cubic structure reminiscent of the cubic structure of TiC crystal. Wang and Cheng¹⁰ addressed this issue of cagelike or cubiclike structure of transition-metal carbide clusters using photoelectron spectroscopy when they observed a bimodal distribution of Ti_xC_y anion clusters with a pronounced peak in the spectrum at $Ti_{13}C_{22}$ -. Using density functional theory (DFT), they calculated the geometry of this cluster to be an ABA layered structure (see Figure 1a) where the A layer (Ti_4C_9) is formed with C_2 dimers at the cube corners, Ti atoms at the edge centers, and a lone C atom at the face-center. The B layer is composed of Ti₅C₄ with four Ti atoms occupying cube corner sites and the fifth Ti at the face-center site while the four C atoms occupy edge centers. The validity of this structure was confirmed by comparing the calculated photoelectron spectra with their experimental result. The authors further showed that such a layer-by-layer growth involving C₂ dimers can explain all the magic numbers in a multistage growth model previously proposed for large metal carbide clusters. They extended the layer-by-layer growth to include Ti₂₂C₃₅ (ABABA) motif and showed that such a cluster is highly stable and can form a novel class of 1D metallic quantum wire.

To go beyond the existing carbon-group 1D LIB morphology, we followed the above work and conceived the idea of building 1D nanowire by using Ti_xC_y clusters as building blocks. First, we used Ti_9C_{13} (layer AB stacking) to construct a 1D TiC nanowire. Before the potential of such a wire for an effective LIB anode can be tested, the following questions have to be addressed: Is the Ti_9C_{13} nanowire dynamically and thermally stable, and does it exceed the stability of its cluster motif? If so, what are the electronic and thermal properties of this nanowire? Can it be extended to study other 1D nanowires based on a metcar and clusters mimicking cubic TiC crystal structure and if so, do such structures possess properties different from that based on the Ti_9C_{13} motif? Do these nanowires offer advantages over carbon nanotube- or silicon nanotube-based 1D LIB anodes?

First, we optimized the crystal structure of 1D nanowire composed of Ti_9C_{13} cluster as the building block. The structure possesses $P\overline{4}m2$ symmetry (space group no. 115) with a tetragonal lattice of lattice constant 5.142 Å. There are three

nonequivalent Ti and C atoms in the unit cell: the one on the face center is termed "1", that on the edge center "2", and the central one "3" (see Figure 1). Here, the sp² hybridized C atoms of the C2 dimers on the edge can be transformed to each other by symmetry operations in Figure 1a. The bond lengths between different atoms are given in Table S1 of the Supporting Information. Note that all the Ti–C bond lengths are quite close to that in the bulk TiC, namely, 2.156 Å,²¹ and match with that of TiC bulk surface. Therefore, Ti₉C₁₃ nanowire could be thought of as growing on the [100] surface of TiC. This feature may be important for further device application because it has advantage over other 1D LIB anodes composed of carbon and silicon nanotubes which need to be attached covalently to base sheets to form seamless structures.²² The Ti₉C₁₃ nanowire has no such requirement because it can grow on the TiC surface. We have calculated the cohesive energy of 1D Ti₉C₁₃ nanowire and compared it with other Ti-C binary compounds, such as 1D Ti₈C₁₂ nanowire, Ti₁₃C₂₂ cluster, $\mathrm{Ti}_8\mathrm{C}_{12}$ cluster, and TiC bulk. We found 1D $\mathrm{Ti}_9\mathrm{C}_{13}$ nanowire to be energetically favorable over Ti13C22 cluster which has been observed in experiment (see Figure 1b). Details of our results are given in section I of the Supporting Information.

The phonon bands and density of states (DOS) given in Figure S1a confirm that the Ti_9C_{13} nanowire is dynamically stable. We also carried out molecular dynamics (MD) simulations to further study the stability of Ti_9C_{13} nanowire at elevated temperatures and found it to be stable at 2500 K. The results are given in section III, Figure S1b of the Supporting Information. On the basis of the phonon spectrum, we found that 1D Ti_9C_{13} nanowire exhibits large heat capacity and possesses a high Debye temperature; details are given in section IV, Figure S2 of the Supporting Information.

We next studied the electronic properties of Ti_9C_{13} nanowire by calculating its electronic band structure. To get an accurate description of the band gap we used the HSE06 functional.^{23,24} The results are plotted in Figure 2a. Note that the Ti_9C_{13} nanowire is metallic, which is further confirmed by orbital analysis. Energy bands near the Fermi level are dominated by Ti-3d states, while the C-2s and 2p make only a small contribution to the observed metallic behavior. For more details, we project the DOS onto the atomic orbitals of the Ti and C atoms. The electronic states near the Fermi level are



Figure 2. (a) Band structure and partial density of states (PDOS) of the Ti₉C₁₃ structure, with size of circles denoting the contribution from Ti and C, respectively. The high-symmetry k point path is $\Gamma(0,0) \rightarrow X(1,0)$. (b) Slices of ELF of the Ti₉C₁₃ panels are viewed from the y direction; (c, d) two different layers from the z direction.

mainly contributed by Ti $3d_{z^2}$ and $3d_{yz}$ orbitals, while the hybridized C 2p and Ti 3d states are mainly distributed in the energy range from -1.5 to -2.5 eV, below the Fermi level. The

electronic structure was further studied by calculating the electron localization function (ELF) of Ti_9C_{13} nanowire. Slices parallel to the *y*-axis crossing Ti_3 atoms and those along the *z* direction crossing C_3 and Ti_3 atoms in Figure 1 are plotted in panels c and d of Figure 2, respectively. ELFs in the regions near Ti_1 , Ti_2 , C_1 , and C_2 atoms are delocalized, while those on Ti_3 and C_3 atoms are localized.

Having illustrated the origin of metallic behavior in the Ti_9C_{13} nanowire, we extended this study by removing both C_3 and Ti3 atoms in the unit cell to examine the stability and metallic behavior of Ti₈C₁₂ in the 1D phase. The corresponding structure of Ti₈C₁₂ nanowire is shown in Figure 3f; there are 8 titanium and 12 carbon atoms in the primitive cell. Analogous to the metcar (Ti_8C_{12}) cluster,¹⁷ Ti_8C_{12} nanowire shows chemical stability, and the binding energy of Ti₈C₁₂ nanowire is 5.21 eV per formula unit (0.261 eV per atom) lower than the that of Ti_8C_{12} cluster (T_d) shown in Figure 1b. Phonon spectra in Figure 3a confirm that 1D Ti₈C₁₂ nanowire is also dynamically stable. The high-frequency mode of Ti₈C₁₂ due to C_2 atoms is at 1700 cm⁻¹ lower than that in Ti₂C₁₃. A parallel study of the electronic structure reveals that the Ti_8C_{12} is also metallic, as seen in Figure 3b, and the bands near the Fermi Level are mainly contributed by Ti 3d orbitals. Ti 3d_{rv} and $3d_{x^2-y^2}$ orbitals mainly contribute to the metallic bands near the Fermi level. The ELF analyses shown in Figure 3c-e confirm that the delocalized charges come from Ti1, Ti2, C1, and C_2 atoms. Because there are no Ti_3 atoms, all the C_1 atoms become planar-tetracoordinated carbon, a concept put forth by Hoffmann et al. in 1970.²⁵ Subsequent bonding rules proposed by Boldyrev and co-workers in 1991²⁶ and further developed by



Figure 3. (a) Phonon dispersion and DOS of the Ti_8C_{12} structure, (b) band structure and PDOS of the Ti_8C_{12} nanowire, with size of circles denoting the contribution from Ti and C, respectively. The high-symmetry k point path is $\Gamma(0,0) \rightarrow X(1,0)$. (c) Slices of ELF of the Ti_8C_{12} panels are viewed from the y direction; (d, e) two different layers from the z direction. (f) Geometry of Ti_8C_{12} nanowire.



Figure 4. (a) Three optimized configurations of the Li-adsorbed Ti_9C_{13} nanowire $(Ti_{18}C_{26}Li)$ and their relative energies with respect to the lowest-energy configuration Li_{1} . (b) Considered migration paths of Li diffusion on the Ti_9C_{13} nanowire and (c) the corresponding diffusion energy barrier profiles.

Boldyrev and Wang in 2001²⁷ contributed greatly to the theoretical design of ptC molecules. Extended ptC systems have attracted much attention recently; however, nearly all of the predictions correspond to 2D materials, such as B_2C graphene²⁸ and its analogue Al_2C .^{29,30} No 1D nanowire built from ptC-network has yet been studied. Bader charge analysis of our predicted 1D Ti₈C₁₂ nanowire shows that the charges on C₁, C₂, Ti₁, and Ti₂ are 5.27, 4.75, 2.81, and 2.51*e*, respectively, and the charge on C₂ is less than that of imperfect ptC atom (5.60) in 2D TiC sheet.

Enhanced metallic behavior of the Ti₉C₁₃ nanowire provides an intrinsic advantage in electrical conductivity compared to those of chirality carbon,^{31,32} silicon nanotube,³³ and semiconducting or insulating transition-metal oxide nanotubes.^{34–36} Thus, Ti₉C₁₃ may be suitable as a LIB anode. While 2D metcars have been studied both theoretically³⁷ and experimentally³⁸ as candidates for LIB anode materials,^{39–42} the potential of 1D metcars as LIB anodes remains to be demonstrated.⁴¹ Considering that Ti₉C₁₃ nanowires are stable and possess a higher concentration of light atoms, we can expect it to have a large Li storage capacity. In the following, we systematically explore the potential of the Ti₉C₁₃ nanowire as a Li ion battery anode material by studying the Li adsorption and diffusion behavior as well as their relative electrochemical properties.

To determine the preferable adsorption site of Li on Ti₉C₁₃ nanowire, we created a supercell by doubling its size and depositing one Li atom on different adsorption sites. This corresponds to a supercell with chemical stoichiometry of Ti₁₈C₂₆Li. Three typical adsorption configurations (labeled as Li_I, Li_{II}, and Li_{III}) with high structural symmetry are considered, as shown in Figure 4a. We relaxed these configurations and calculated their total energies. Here, Li_I is the hollow site formed by three neighboring carbon atoms, Li_{II} the hollow site formed by two neighboring carbon atoms, and Li_{III} the bridge site of the C₂ dimer. Full geometry optimizations and total energy calculations are performed to identify their relative stability. Li_I is found to be the lowest-energy configuration which lies 0.316 and 0.093 eV lower than those of $\mathrm{Li}_{\mathrm{II}}$ and $\mathrm{Li}_{\mathrm{III}}$ sites, respectively. This suggests that Li atom prefers to occupy the Li_I configuration. Each adsorbed Li atom transfers 0.88

electrons to the neighboring C atoms, according to Bader charge analysis. The energy of the structure where Li is intercalated inside the Ti_9C_{13} nanowire is 0.738, 0.422, and 0.645 eV higher than that of the Li_J, Li_{IJ}, and Li_{III} configuration in Figure 4a, respectively, making it unlikely that Li can reside in the interior of the nanowire.

To evaluate the potential application of the $Ti_{18}C_{26}Li$ as an anode material for LIB, we investigate the possible diffusion paths of Li atom on its surface and their corresponding energy barriers. We considered four trial diffusion paths that connect the two neighboring most preferable Li adsorption sites with high structural symmetry, as indicated in Figure 4b. Pathway IV, which depicts a spiral diffusion route, is found to have the lowest diffusion barrier of 0.35 eV (Figure 4c). The magnitude of the energy barrier is less than half of those in carbon nanotubes and silicon nanotubes.

After investigating the adsorption site and the migration path, we studied the adsorption of Li with high concentration. For application, the storage capacity of electrode materials is the key indicator of battery performance. Hence, the average adsorption energies are calculated to investigate the storage capacity of Li on nanowires. We first increased the concentration of Li by depositing a single layer of Li atoms on the surface of the nanowire, leading to a stoichiometry of Ti₉C₁₃Li₂₀. The average adsorption energy for each Li ion in this situation is 0.98 eV. We then introduced a second layer of Li on the surface of the Ti₉C₁₃Li₂₀. The average adsorption energy corresponding to a chemical composition of Ti₉C₁₃Li₅₆ was found to be 0.86 eV for each Li ion. This value is the same as that in the 2D Li ion battery.^{38,39} Here, we see that the Ti₉C₁₃ nanowire has high Li storage capacity yet does not suffer volume expansion during lithiation (details are given in section V in the Supporting Information). This is different from silicon nanotube anodes where 400% volume expansion was noted after full lithiation.

We next calculated the average open-circuit voltage (OCV) as a function of Li coverage and the theoretical Li specific capacity, which are important electrochemical properties for an electrode material. Details of these calculations are given in section VI in the Supporting Information. For single-layer adsorption, the estimated OCV is 0.980 V and theoretical capacity is calculated to be 525 mAh·g⁻¹. When second-layer adsorption is considered, the OCV and the theoretical specific capacity of $Ti_9C_{13}Li_{56}$ are 0.858 V and 1542 mAh·g⁻¹(in Table 1), respectively. The later value is five times larger than that of the graphite anode currently used in LIB.

 Table 1. Comparison of Specific Capacity, Diffusion Barrier,

 OCV, and Volume Expansion of Candidate Anode Materials

 for Li Ion Battery^a

	specific capacity (mAh/g)				
material	theor	exptl	diffusion barrier (eV) (theor)	OCV (V) (theor)	volume expansions
Ti ₉ C ₁₃	1542	-	0.35	0.86	no
TiC nanowire	1019	-		1.13	no
C nanotube	515 ⁴⁵	450 ⁴⁶	10.12 ^{31,47}	3.97 ³²	yes
Si nanotube	1961 ⁴⁸	3247 ³³	1.41 ⁴⁹	1.98	yes
Ge nanotube	1384 ⁵⁰	963 ⁵¹	-	1.70	yes
TiO ₂ wire	275 ⁵²	305 ⁵³	0.48 ⁵⁴	1.10 ⁵⁵	no
Ti ₃ C ₂ metcar	320 ³⁷	410 ⁴¹	0.07 ³⁷	0.62	no
graphite	372 ⁴⁴	372	0.4 ⁴⁴	0.2	no
<i>a</i> "—" means data unavailable.					

We also calculated the structure, stability, and properties of 1D TiC nanowire using a cluster motif that mimics its bulk cubic structure. Note that recently PbS clusters⁴³ were found to grow with the geometry reminiscent of its bulk structure. The cubic TiC nanowire is energetically nearly degenerate with that based on the Ti_9C_{13} motif discussed before. The details of our results on cubic TiC nanowire are given in sections V and VI of the Supporting Information. The calculated LIB specific capacity of the cubic TiC nanowire is 1019 mAh·g⁻¹, which is smaller than that in the Ti_9C_{13} nanowire.

In conclusion, inspired by the experimental observation of layered growth of Ti_xC_y clusters, we carried out systematic studies of the equilibrium geometry and stability of 1D nanowires based on Ti₉C₁₃, Ti₈C₁₂, and cubic TiC cluster motifs. We also examined the potential of the Ti₉C₁₃ nanowire as an effective anode material for Li-ion batteries. The following are the major conclusions of our Letter: (1) While all the above nanowires were found to be dynamically stable, not only was $Ti_{9}C_{13}$ nanowire found to be more stable than its cluster analogues as well as that constructed from a Ti₈C₁₂ metcar motif, but also it is thermally stable up to 2500 K. (2) Ti_9C_{13} exhibits metallic properties and high heat capacity. (3) To the best of our knowledge, Ti₉C₁₃ nanowire is the first planartetracoordinated carbon (ptC)-containing 1D nanowire with metallic properties. (4) Compared to other carbon and silicon nanotube-based anodes for Li ion batteries, not only does the Ti₉C₁₃ nanowire offer great advantage, but also, due to lattice matching, it can grow seamlessly on TiC surface. (5) Unlike carbon and silicon nanotube anodes, there is no thermal expansion/contraction following lithiation/delithiation. In addition, the specific capacity of Ti₉C₁₃ nanowire-based LIB is five times bigger than that of graphite anodes, thus making TiC a promising material for anode design in Li-ion batteries. (6) Although 1D TiC cubic nanowire is energetically nearly

degenerate with the Ti_9C_{13} nanowire, its specific capacity as a LIB anode is not as large as that of the Ti_9C_{13} nanowire. We hope that these results will motivate experimentalists to synthesize these nanowires and examine their potential for next-generation LIB anodes.

COMPUTATIONAL METHODS

Atomic structures and electronic properties are calculated using density-functional theory as implemented in Vienna ab initio simulation package (VASP).⁵⁶ The projector augmented wave (PAW) method³⁷ and Perdew-Burke-Ernzerhof (PBE)⁵⁸ exchange correlation functional within the generalized gradient approximation (GGA) are used. The 2s1, 2s2p2 and 3d24s2 atomic orbitals are treated as valence states for Li, C, and Ti, respectively. A plane-wave cutoff of 500 eV is used for all the calculations. The convergence criteria for total energy and Hellmann-Feynman force are set to 10^{-4} eV and 10^{-2} eV/Å, respectively. A vacuum space of 20 Å in the radial directions (xand y) is kept to avoid mirror interactions. In all calculations, the k-point grid is sampled by a $1 \times 1 \times 9$ mesh using the Monkhorst-Pack scheme.⁵⁹ To check the dynamic stability, Phonopy code⁶⁰ is used to calculate the vibrational spectra. Ab initio molecular dynamics (AIMD) simulations are performed to assess the thermal stability of the nanowire. Canonical ensemble (NVT) is adopted using the Nosé heat bath method.⁶¹ Bader charge analysis⁶² is carried out to study charge transfer. By using the nudged elastic band (NEB) method,⁶³ we calculate the diffusion energy barrier and the minimum energy pathways for Li diffusion on the nanowire.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.6b00120.

Stability relative to other Ti–C compounds, dynamic stability, thermal stability, thermodynamic properties, volume expansion/contraction during lithiation/delithiation process, open-circuit voltage, and specific capacity (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Idota, Y.; Kubota, T.; Matsufuji, A.; Maekawa, Y.; Miyasaka, T. Tin-Based Amorphous Oxide: A High-Capacity Lithium-Ion-Storage Material. *Science* **1997**, *276*, 1395–1397.

(2) Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? *Science* **2014**, *343*, 1210–1211.

(3) Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* 2008, 451, 652–657.

(4) Dahn, J. R.; Zheng, T.; Liu, Y.; Xue, J. S. Mechanisms for Lithium Insertion in Carbonaceous Materials. *Science* **1995**, *270*, 590–593.

(5) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novák, P. Insertion Electrode Materials for Rechargeable Lithium Batteries. *Adv. Mater.* **1998**, *10*, 725–763.

(6) Meini, S.; Elazari, R.; Rosenman, A.; Garsuch, A.; Aurbach, D. The Use of Redox Mediators for Enhancing Utilization of Li_2S Cathodes for Advanced Li–S Battery Systems. *J. Phys. Chem. Lett.* **2014**, *5*, 915–918.

(7) Beaulieu, L. Y.; Eberman, K. W.; Turner, R. L.; Krause, L. J.; Dahn, J. R. Colossal Reversible Volume Changes in Lithium Alloys. *Electrochem. Solid-State Lett.* **2001**, *4*, A137–A140.

(8) Wu, H.; Chan, G.; Choi, J. W.; Ryu, I.; Yao, Y.; McDowell, M. T.; Lee, S. W.; Jackson, A.; Yang, Y.; Hu, L.; Cui, Y. Stable Cycling of Double-Walled Silicon Nanotube Battery Anodes through Solid-Electrolyte Interphase Control. *Nat. Nanotechnol.* **2012**, *7*, 310–315.

(9) Kang, L.; Hu, Y.; Liu, L.; Wu, J.; Zhang, S.; Zhao, Q.; Ding, F.; Li, Q.; Zhang, J. Growth of Close-Packed Semiconducting Single-Walled Carbon Nanotube Arrays Using Oxygen-Deficient TiO₂ Nanoparticles as Catalysts. *Nano Lett.* **2015**, *15*, 403–409.

(10) Wang, L.-S.; Cheng, H. Growth Pathways of Metallocarbohedrenes: Cagelike or Cubic? *Phys. Rev. Lett.* **1997**, *78*, 2983–2986.

(11) Khanna, S. N.; Jena, P. Assembling Crystals from Clusters. *Phys. Rev. Lett.* **1992**, *69*, 1664–1667.

(12) Khanna, S. N.; Jena, P. Atomic Clusters: Building Blocks for a Class of Solids. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *51*, 13705–13716.

(13) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C_{60} : Buckminsterfullerene. *Nature* **1985**, *318*, 162–163.

(14) Guo, B. C.; Kerns, K. P.; Castelman, A. W. $Ti_8C_{12}^+$ -Metallo-Carbohedrenes: A New Class of Molecular Clusters? *Science* **1992**, 255, 1411–1413.

(15) Pilgrim, J. S.; Duncan, M. A. Metallo-Carbohedrenes: Chromium, Iron, and Molybdenum analogs. J. Am. Chem. Soc. 1993, 115, 6958–6961.

(16) Baruah, T.; Pederson, M. R. Stability, Electronic Structure, and Vibrational Modes of the Ti_8C_{12} Dimer. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 241404.

(17) Guo, B. C.; Wei, S.; Purnell, J.; Buzza, S.; Castleman, A. W. Metallo-Carbohedrenes $[M_8C_{12}+(M=V, Zr, Hf, and Ti)]$: A Class of Stable Molecular Cluster Ions. *Science* **1992**, 256, 515–516.

(18) Rohmer, M.-M.; Bénard, M.; Poblet, J.-M. Structure, Reactivity, and Growth Pathways of Metallocarbohedrenes M_8C_{12} and Transition Metal/Carbon Clusters and Nanocrystals: A Challenge to Computational Chemistry. *Chem. Rev.* **2000**, *100*, 495–542.

(19) Pilgrim, J. S.; Duncan, M. A. Beyond Metallo-Carbohedrenes: Growth and Decomposition of Metal-Carbon Nanocrystals. J. Am. Chem. Soc. **1993**, 115, 9724–9727.

(20) Jena, P.; Castleman, A. W., Jr Mass Spectrometry and its Role in Advancing Cluster Science. *Int. J. Mass Spectrom.* **2015**, 377, 235–247. (21) Arya, A.; Carter, E. A. Structure, Bonding, and Adhesion at the TiC(100)/Fe(110) Interface from First Principles. *J. Chem. Phys.* **2003**, *118*, 8982–8996.

(22) Novaes, F. D.; Rurali, R.; Ordejón, P. Electronic Transport between Graphene Layers Covalently Connected by Carbon Nanotubes. *ACS Nano* **2010**, *4*, 7596–7602.

(23) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals based on a Screened Coulomb Potential. J. Chem. Phys. 2003, 118, 8207–8215.

(24) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: "Hybrid Functionals based on a Screened Coulomb Ppotential" [J. Chem. Phys. 118, 8207 (2003)]. J. Chem. Phys. 2006, 124, 219906.

(25) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. Planar Tetracoordinate Carbon. J. Am. Chem. Soc. **1970**, 92, 4992–4993.

(26) von Rague Schleyer, P.; Boldyrev, A. I. A New, General Strategy for Achieving Planar Tetracoordinate Geometries for Carbon and other Second Row Periodic Elements. *J. Chem. Soc., Chem. Commun.* **1991**, 1536–1538.

(27) Boldyrev, A. I.; Wang, L.-S. Beyond Classical Stoichiometry: Experiment and Theory. J. Phys. Chem. A 2001, 105, 10759–10775.

(28) Wu, X.; Pei, Y.; Zeng, X. C. B₂C Graphene, Nanotubes, and Nanoribbons. *Nano Lett.* **2009**, *9*, 1577–1582.

(29) Dai, J.; Wu, X.; Yang, J.; Zeng, X. C. AlxC Monolayer Sheets: Two-Dimensional Networks with Planar Tetracoordinate Carbon and Potential Applications as Donor Materials in Solar Cell. *J. Phys. Chem. Lett.* **2014**, *5*, 2058–2065.

(30) Li, Y.; Liao, Y.; Schleyer, P. v. R.; Chen, Z. Al₂C Monolayer: the Planar Tetracoordinate Carbon Global Minimum. *Nanoscale* **2014**, *6*, 10784–10791.

(31) Meunier, V.; Kephart, J.; Roland, C.; Bernholc, J. Ab Initio Investigations of Lithium Diffusion in Carbon Nanotube Systems. *Phys. Rev. Lett.* **2002**, *88*, 075506.

(32) Jaber-Ansari, L.; Iddir, H.; Curtiss, L. A.; Hersam, M. C. Influence of Electronic Type Purity on the Lithiation of Single-Walled Carbon Nanotubes. *ACS Nano* **2014**, *8*, 2399–2409.

(33) Park, M.-H.; Kim, M. G.; Joo, J.; Kim, K.; Kim, J.; Ahn, S.; Cui, Y.; Cho, J. Silicon Nanotube Battery Anodes. *Nano Lett.* **2009**, *9*, 3844–3847.

(34) Wang, J.-Z.; Lu, L.; Lotya, M.; Coleman, J. N.; Chou, S.-L.; Liu, H.-K.; Minett, A. I.; Chen, J. Development of MoS_2 -CNT Composite Thin Film from Layered MoS_2 for Lithium Batteries. *Adv. Energy Mater.* **2013**, *3*, 798–805.

(35) Zhu, C.; Mu, X.; van Aken, P. A.; Yu, Y.; Maier, J. Single-Layered Ultrasmall Nanoplates of MoS₂ Embedded in Carbon Nanofibers with Excellent Electrochemical Performance for Lithium and Sodium Storage. *Angew. Chem., Int. Ed.* **2014**, *53*, 2152–2156.

(36) Niu, C.; Meng, J.; Han, C.; Zhao, K.; Yan, M.; Mai, L. VO₂ Nanowires Assembled into Hollow Microspheres for High-Rate and Long-Life Lithium Batteries. *Nano Lett.* **2014**, *14*, 2873–2878.

(37) Tang, Q.; Zhou, Z.; Shen, P. Are MXenes Promising Anode Materials for Li Ion Batteries? Computational Studies on Electronic Properties and Li Storage Capability of Ti_3C_2 and $Ti_3C_2X_2$ (X = F, OH) Monolayer. J. Am. Chem. Soc. **2012**, 134, 16909–16916.

(38) Xie, Y.; Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y.; Yu, X.; Nam, K.-W.; Yang, X.-Q.; Kolesnikov, A. I.; Kent, P. R. C. Role of Surface Structure on Li-Ion Energy Storage Capacity of Two-Dimensional Transition-Metal Carbides. *J. Am. Chem. Soc.* **2014**, *136*, 6385–6394.

(39) Xie, Y.; Dall'Agnese, Y.; Naguib, M.; Gogotsi, Y.; Barsoum, M. W.; Zhuang, H. L.; Kent, P. R. C. Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries. *ACS Nano* **2014**, *8*, 9606–9015.

(40) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti₃AlC₂. *Adv. Mater.* **2011**, 23, 4248–4253.

(41) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* **2014**, *26*, 992–1005.

(42) Zhao, T.; Zhang, S.; Guo, Y.; Wang, Q. TiC_2 : a New Two-Dimensional Sheet Beyond MXenes. *Nanoscale* **2016**, *8*, 233–242.

(43) Kiran, B.; Kandalam, A. K.; Rallabandi, R.; Koirala, P.; Li, X.; Tang, X.; Wang, Y.; Fairbrother, H.; Gantefoer, G.; Bowen, K. PbS)₃₂: A Baby Crystal. *J. Chem. Phys.* **2012**, *136*, 024317.

(44) Persson, K.; Sethuraman, V. A.; Hardwick, L. J.; Hinuma, Y.; Meng, Y. S.; van der Ven, A.; Srinivasan, V.; Kostecki, R.; Ceder, G. Lithium Diffusion in Graphitic Carbon. *J. Phys. Chem. Lett.* **2010**, *1*, 1176–1180. (45) Zhao, J.; Buldum, A.; Han, J.; Ping Lu, J. First-Principles Study of Li-Intercalated Carbon Nanotube Ropes. *Phys. Rev. Lett.* **2000**, *85*, 1706–1709.

(46) Gao, B.; Kleinhammes, A.; Tang, X. P.; Bower, C.; Fleming, L.; Wu, Y.; Zhou, O. Electrochemical Intercalation of Single-Walled Carbon Nanotubes with Lithium. *Chem. Phys. Lett.* **1999**, 307, 153– 157.

(47) Nishidate, K.; Hasegawa, M. Energetics of Lithium Ion Adsorption on Defective Carbon Nanotubes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 245418.

(48) Wang, C.-M.; Li, X.; Wang, Z.; Xu, W.; Liu, J.; Gao, F.; Kovarik, L.; Zhang, J.-G.; Howe, J.; Burton, D. J.; Liu, Z.; Xiao, X.; Thevuthasan, S.; Baer, D. R. In Situ TEM Investigation of Congruent Phase Transition and Structural Evolution of Nanostructured Silicon/ Carbon Anode for Lithium Ion Batteries. *Nano Lett.* **2012**, *12*, 1624–1632.

(49) Kulish, V. V.; Ng, M.-F.; Malyi, O. I.; Wu, P.; Chen, Z. Enhanced Li Adsorption and Diffusion in Single-Walled Silicon Nanotubes: An ab Initio Study. *ChemPhysChem* **2013**, *14*, 1161–1167. (50) Song, T.; Cheng, H.; Choi, H.; Lee, J.-H.; Han, H.; Lee, D. H.; Yoo, D. S.; Kwon, M.-S.; Choi, J.-M.; Doo, S. G.; Chang, H.; Xiao, J.; Huang, Y.; Park, W. I.; Chung, Y.-C.; Kim, H.; Rogers, J. A.; Paik, U. Si/Ge Double-Layered Nanotube Array as a Lithium Ion Battery Anode. *ACS Nano* **2012**, *6*, 303–309.

(51) Seo, M.-H.; Park, M.; Lee, K. T.; Kim, K.; Kim, J.; Cho, J. High Performance Ge Nanowire Anode Sheathed with Carbon for Lithium Rechargeable Batteries. *Energy Environ. Sci.* **2011**, *4*, 425–428.

(52) Armstrong, A. R.; Armstrong, G.; Canales, J.; Bruce, P. G. TiO₂-B Nanowires. *Angew. Chem., Int. Ed.* **2004**, *43*, 2286–2288.

(53) Armstrong, A. R.; Armstrong, G.; Canales, J.; García, R.; Bruce, P. G. Lithium-Ion Intercalation into TiO₂-B Nanowires. *Adv. Mater.* **2005**, *17*, 862–865.

(54) Wilkening, M.; Lyness, C.; Armstrong, A. R.; Bruce, P. G. Diffusion in Confined Dimensions: Li+ Transport in Mixed Conducting TiO_2 -B Nanowires. J. Phys. Chem. C **2009**, 113, 4741–4744.

(55) Goriparti, S.; Miele, E.; Prato, M.; Scarpellini, A.; Marras, S.; Monaco, S.; Toma, A.; Messina, G. C.; Alabastri, A.; Angelis, F. D.; Manna, L.; Capiglia, C.; Zaccaria, R. P. Direct Synthesis of Carbon-Doped TiO₂-Bronze Nanowires as Anode Materials for High Performance Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, 7, 25139–25146.

(56) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169.

(57) Gajdoš, M.; Hummer, K.; Kresse, G.; Furthmüller, J.; Bechstedt, F. Linear Optical Properties in the Pprojector-Augmented Wave Methodology. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 045112.

(58) Perdew, J. P.; Burke, K.; Ernzerhof, M. Projector Augmented-Wave Method. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(59) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(60) Togo, A.; Oba, F.; Tanaka, I. First-Principles Calculations of the Ferroelastic Transition between Rutile-Type and CaClSiO₂ at High Pressures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78*, 134106.

(61) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. J. Chem. Phys. **1984**, 81, 511–519.

(62) Tang, W.; Sanville, E.; Henkelman, G. A Grid-based Bader Analysis Algorithm without Lattice Bias. J. Phys.: Condens. Matter 2009, 21, 084204.

(63) Mills, G.; Jónsson, H. Quantum and Thermal Effects in H_2 Dissociative Adsorption: Evaluation of Free Energy Barriers in Multidimensional Quantum Systems. *Phys. Rev. Lett.* **1994**, *72*, 1124–1127.