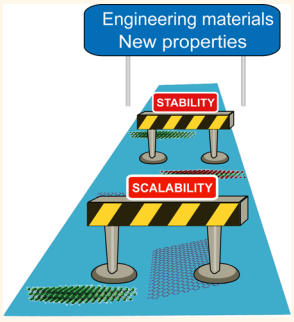
Bulk Nanostructured Materials Based on Two-Dimensional Building Blocks: A Roadmap

Jiayan Luo,[†,‡,⊥] Jun Gao,[§,⊥] Aoxuan Wang,[†,‡] and Jiaxing Huang*[,§]

[†]Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China, [‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China, and [§]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States. [⊥]These two authors contributed equally to this work.

ABSTRACT The family of two-dimensional (2D) materials, in particular MXenes, can now be greatly expanded based on a new "double metal" strategy as reported by Anasori, Xie, and Beidaghi *et al.* in this issue of *ACS Nano*. Now that a diverse array of well-defined nanoscale building blocks, especially the 2D systems, has become available, we are better prepared to think about scaling up nanomaterials in the broader context of materials science and engineering. In this Perspective, we construct a roadmap for assembling nanoscale building blocks into bulk nanostructured materials, and define some of the critical challenges and goals. Two-dimensional sheets are uniquely well-suited in this roadmap for constructing dense, bulk-sized samples with scalable material performance or interesting emergent properties.



"Bulk nanostructured materials" commonly refers to macroscopic dense materials with nanoscale grains.[1] This branch of nanomaterials research was initiated in metallurgy, where "top-down" processing techniques, such as extensive plastic deformation,[2] are typically employed to reduce the grain sizes of bulk metal pieces (Figure 1a), leading to significantly enhanced mechanical properties.[3] In this area, materials processing is largely based on thermal and mechanical means, and "nano" loosely refers to the microstructural features smaller than 100 nm. In a parallel branch of nanomaterials research, where materials processing strategies are more chemistry-driven, the structure–property relationships of isolated "nano" entities (loosely defined as objects with at least one dimension smaller than 100 nm) have been a major focus. By now, nanoparticles can be synthesized with well-defined sizes, shapes, and surface states.[4,5] There is strong interest in scaling up the syntheses of these nanoscale building blocks,[6,7] and studying them in "bulk" forms rather than as individual units. When these nanoscale building blocks are assembled into superstructures, new "collective" electronic, optical, magnetic, and ionic properties emerge that are not ascribable to the individual units.[8] In addition, nanomaterials are used in bulk quantities in applications such as batteries and ultracapacitors, and often need to be densely packed to achieve high overall performance. Close-packed superstructures and the high density bulk forms of nanomaterials can be treated and studied as bulk nanostructured materials since they are indeed made of nanostructured units.

> When nanostructures with better-than-bulk material performances are used in bulk form, it is critical that those extraordinary nanoscale properties can be scaled to the macroscopic level.

Bulk Nanostructure Materials: Collective Properties and Scalable Performance. Colloidal crystals are probably the best known example illustrating the collective properties that emerge from the close-packed assembly of

* Address correspondence to jiaxing-huang@northwestern.edu.

Published online September 21, 2015
10.1021/acsnano.5b05259

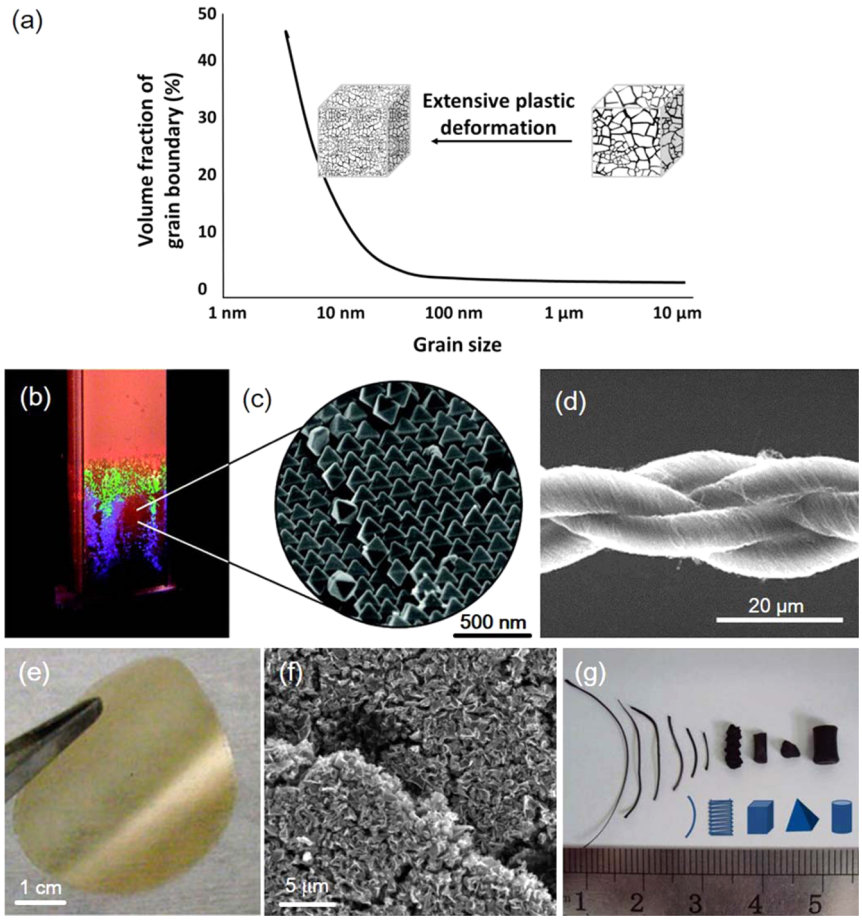


Figure 1. Bulk form of nanomaterials: Top-down and bottom-up. (a) Bulk nanostructured materials were initially demonstrated with metals processed by extensive plastic deformation, which significantly reduces their grain sizes, leading to unusual mechanical properties.[1,3] The curve illustrates the general trend of an increasing volume fraction of grain boundaries with decreased grain sizes. On the other hand, discrete nanoscale entities are often assembled into bulk forms for creating new properties or to be used in applications. Some examples include the following: (b) plasmonic colloidal crystals[9] with vibrant colors, tunable by the assembly of (c) octahedral Ag nanocrystals. Reprinted from ref 9. Copyright 2008 American Chemical Society. (d) Twisted yarns of carbon nanotubes[12] with extraordinary strength and toughness. Reprinted with permission from ref 12. Copyright 2004 American Association for the Advancement of Science. (e) Lamellar membrane made of exfoliated clay sheets[10] showing unipolar ionic transport and high ionic conductivity. Reprinted with permission from ref 10. Copyright 2015 Nature Publishing Group. (f) Pelletized powders of crumpled graphene balls[18] with scalable surface area. (g) Dense yet nanoporous graphene monoliths[19] with moldable shapes and extraordinary performance as supercapacitors. Reprinted with permission from ref 19. Copyright 2013 Nature Publishing Group.

monodisperse nanoscale building blocks from solution phase.[8] Plasmonic colloidal crystals[9] (Figure 1b) are a notable new addition to this group, made from close-packed arrays of plasmonic metal nanocrystals (Figure 1c). The optical properties of the bulk lattice are strongly dependent on the distance between the nanocrystal units, which can be potentially tuned by the assembly process. Another example of an unusual collective property is observed in a flexible membrane made by restacking exfoliated vermiculite clay sheets (Figure 1e).[10] When this membrane is hydrated, the stacked sheets become the walls that define massive arrays of parallel 2D nanofluidic ion channels.[11] When the sheet separation is smaller than the liquid's Debye length near its surface, the bulk lamellar-structured membrane exhibits unipolar ionic transport and significantly enhanced ionic conductivities.

When nanostructures with better-than-bulk material performances are used in bulk form, it is critical that those extraordinary nanoscale properties can be scaled to the macroscopic level. Many works have aimed to address this challenge. For example, to scale up the properties of carbon nanotubes, they can be twist-spun to form continuous yarns with macroscopic lengths.[12] Such yarns have been found to have extraordinary mechanical properties, including high strength and high toughness, in addition to their electrical conductivity and thermal stability at extreme temperatures. Rapid progress has been made over the past decade to improve the quality of the yarns and scale up the production.[13,14] Carbon nanotube-based engineering fiber materials[15] have now emerged. In another example, graphene-based sheets have

attracted tremendous interest as electrode materials for supercapacitors.[16] In such devices, the active materials need to be densely packed to maximize both mass- and volume-based capacitance. However, this has proven to be challenging because graphene-based sheets are highly prone to aggregation, which leads to reduced surface area and degraded device performances as their mass loading level increases.[17] Figure 1f,g illustrates two strategies to overcome this problem and achieve scalable device performance. In the first approach, an aggregation-resistant form of graphene particles is created, which resembles crumpled paper balls in appearance (Figure 1f).[18] Crumpling is achieved by capillary compression of the flat sheets suspended in evaporating aerosol droplets. Particles with such shapes have weak attractive interactions, and can maintain relatively high surface areas while being densified, leading to scalable supercapacitor performance. In the second approach, high-density graphene monoliths are made, also by capillary compression, through slow drying of preformed hydrogels.[19] The resulting monoliths were found to be nanoporous, with extraordinary volumetric capacitance. By molding the hydrogel precursor, graphene monoliths can be made in many different shapes (Figure 1g).

Two-Dimensional Building Blocks: The Tip of an Iceberg. Two-dimensional sheets are exciting new nanomaterials with fascinating properties and potential applications.[20] Graphene and transitional metal dichalcogenides (TMDC) sheets are being hotly studied for electronic applications. The flat, high-aspect-ratio geometry of 2D nanomaterials suggests that they should naturally integrate into planar devices or coating applications. Compared to other nanomaterials, this is a fundamental material-processing advantage of all 2D sheets, regardless of their chemical composition. Therefore, materials scientists continue to search for, and even to design, new 2D materials to expand this family of materials and increase its diversity. In addition to clays, graphene, and TMDCs, many other 2D materials have captured the spotlight, including, but not limited to, silicene, germanene, stanene, phosphorene, boron nitride, metal oxides, and metal hydroxides.[20]

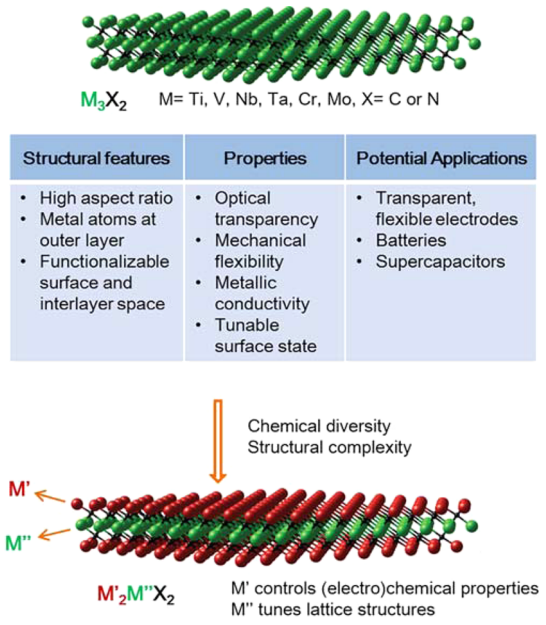


Figure 2. Structure–properties relationship of MXenes (top) and the evolution from single metal MXenes M_3X_2 to double metal $M'_2M''X_2$ (bottom) and $M'_2M''_2X_3$ (not shown).

> Two-dimensional sheets are exciting new building blocks for constructing bulk nanostructured materials with scalable performance and emerging properties.

Recently, a new subset of 2D materials named "MXenes" was discovered (Figure 2, top).[21] They are prepared by etching of the "A" layers from the layered carbides or carbonitrides known as MAX phases, in which M is a transition metal, A is usually a group III-A or IV-A element (such as Al, Ga, Si, or Ge), and X is C and/or N.[22] The A layers have higher chemical reactivity, allowing them to be selectively etched from the MAX phases by aqueous hydrofluoric acid (HF) at room temperature. The removal of the bridging A atoms generates weakly bonded MX layers that can now be readily exfoliated. After etching, the M atoms on the outer surface are modified with functional groups (OH, O, or F). These unique structural characteristics make MXene both metallic and hydrophilic, a combination rarely observed in 2D materials. It is also possible to use additional surface functional groups to tune the electrical properties of the MXene sheets. It has been found that many types of cations including H^+, Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, and Al^{3+}, and neutral molecules such as hydrazine, urea, and dimethyl sulfoxide can intercalate between the MXene layers. MXenes have been found to be promising for making high-power electrodes for batteries and supercapacitors, as well as for sensing and electrochromic applications.[22,23] In this issue of *ACS Nano*, Anasori, Xie, and Beidaghi *et al.* report yet another breakthrough. First, using density functional theory (DFT), they predicted

and then they experimentally verified two new groups of 2D double transition metal carbides: $M'_2M''C_2$ and $M'_2M''_2C_3$, in which the inner M'' layers help to stabilize the 2D lattice and the outer M' layers control the chemical and electrochemical properties (Figure 2, bottom).[24] Two model systems were created where M' and M'' are Mo or Cr, and Ti, respectively. The success of this double metal strategy suggests that there are likely many *more* types of 2D MXenes waiting to be discovered. For example, one cannot stop wondering whether trimetal, "Janus" MXenes sheets could exist, where three different metals occupy three different layers. These double-metal MXenes have uncovered the tip of an iceberg of numerous opportunities for new materials discoveries.

Bottom-Up Assembly to Bulk Nanostructured Materials: A Roadmap. Bottom-up processing approaches, such as consolidation of ultrafine particles, have been employed in powder metallurgy to make nanostructured metals.[1] However, since a diverse array of well-defined nanoscale building blocks, especially 2D systems, have become available, we are now much better prepared to rethink bottom-up strategies to assemble them into bulk-sized, engineering materials. The roadmap shown in Figure 3 is an attempt to define the critical challenges and outcomes along the pathway toward assembling nanoscale entities into high-density, bulk-sized, processable engineering materials that can meet the requirements of modern applications. Note that bulk-sized aerogels and foams of nanomaterials with low densities are also of great interest for a number of applications. They may be categorized as bulk nanostructured materials with low-density form factors, but we place them beyond the scope of this discussion. If such bulk nanostructured materials are successfully made, there are two appealing outcomes. We could have high-performance bulk materials where the extraordinary properties of their nanoscale units are maintained and accessible. We could also have novel bulk materials with new useful properties that transcend those of their individual building blocks. Note that in metallurgy, nanostructured metals need to have high, near-theoretical density values to maintain structural integrity and to exhibit enhanced mechanical properties. For the new bulk nanostructured materials at the end of the roadmap, higher density is certainly needed to ensure mechanical integrity of the final products and is likely more desirable in many applications. Of course, the critical density value is determined by the material requirements of specific applications.

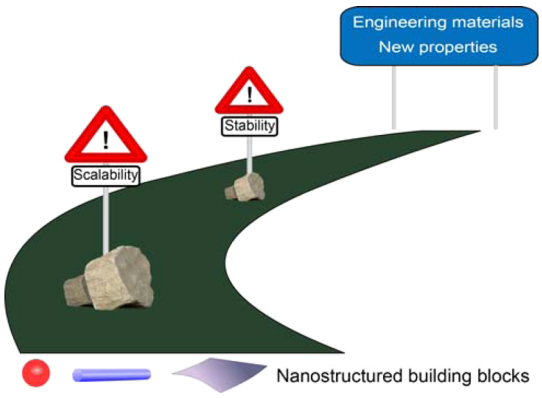


Figure 3. A roadmap showing bottom-up assembly route toward new bulk nanostructured materials, highlighting the challenges of scalability and stability.

In this issue of *ACS Nano*, Anasori, Xie, and Beidaghi *et al.* predicted and then experimentally verified two new groups of 2D double transition metal carbides.

There are also a number of challenges for constructing bulk nanostructured materials using bottom-up approaches, which can be summarized as *scalability* and *stability*. Scalability refers to both scalable synthesis of high-quality processable nanoscale building blocks,[6,7] and scalable material performance,[17] where the properties of the nanoscale units are still accessible in the final bulk pieces. Stability of the building blocks is also important, because they should not sinter into large grains or chemically transform into less useful materials during processing or application. For example, bulk nanostructured Si has attracted significant interest as a high-performance electrode material for Li ion batteries. However, an *in situ* transmission electron microscopy (TEM) study revealed that Si nanostructures can be unstable during charging and discharging, and subject to abrupt electrochemical sintering, turning into much larger grains and losing the advantages of being nanostructured.[25] Nanomaterials need to pass the following tests to reach their destination on the roadmap: Can they be made in sufficient quantities and qualities? Can they maintain their properties and deliver comparable performance when used in bulk form? Are they sufficiently stable, in terms of chemical composition, surface state, and morphology, to survive the material processing or assembly steps, and in the target applications?

In regard to scalability and stability, 2D nanomaterials have both unique advantages and challenges. Many types of 2D sheets can be prepared by exfoliating powders of layered materials, which is already

a scalable type of synthesis. The exfoliation-reassembly process simply transforms the discrete particles into a continuous, bulk form of materials with the same structural units. However, due to their ease of aggregation, scalable performance, such as in energy storage applications, could be challenging. Figure 1f,g shows two strategies to address this challenge. Two-dimensional sheets are capable of forming intimate face-to-face contact, and they can bend, wrinkle, or crumple during assembly. Some can even plastically deform at the single layer level.[26] Therefore, they can construct high-density bulk samples with tunable free volumes and porosities. In terms of stability, if the parent layered materials are thermodynamically stable, then we might expect the exfoliated 2D sheets to be sintering-resistant and capable of maintaining their single- or few-layer thickness. However, their high surface area also leads to higher chemical reactivity than in bulk materials, which should be addressed for target applications. Proper encapsulation or surface passivation could help to mitigate this problem without sacrificing performance. Therefore, 2D materials are probably the most promising group of well-defined nanoscale building blocks for constructing bulk nanostructured engineering materials.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. J.H. thanks the John Simon Guggenheim Memorial Foundation for a Guggenheim Fellowship, and the support of Office of Naval Research (ONRN000141310556) for some prior results leading to new thoughts described here. We also thank A.R. Koltonow for helping to improve the manuscript.

REFERENCES AND NOTES

1. Zehetbauer, M.; Zhu, Y. T. *Bulk Nanostructured Materials*; Wiley-VCH: Weinheim, 2009; p 710.
2. Valiev, R. Nanostructuring of Metals by Severe Plastic Deformation for Advanced Properties. *Nat. Mater.* **2004**, *3*, 511–516.
3. Palumbo, G.; Thorpe, S.; Aust, K. On the Contribution of Triple Junctions to the Structure and Properties of Nanocrystalline Materials. *Scr. Metall. Mater.* **1990**, *24*, 1347–1350.
4. Xia, Y. N.; Xiong, Y. J.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem., Int. Ed.* **2009**, *48*, 60–103.
5. Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* **2005**, *105*, 1025–1102.
6. Park, J.; An, K. J.; Hwang, Y. S.; Park, J. G.; Noh, H. J.; Kim, J. Y.; Park, J. H.; Hwang, N. M.; Hyeon, T. Ultra-Large-Scale Syntheses of Monodisperse Nanocrystals. *Nat. Mater.* **2004**, *3*, 891–895.
7. Skrabalak, S. E.; Xia, Y. N. Pushing Nanocrystal Synthesis toward Nanomanufacturing. *ACS Nano* **2009**, *3*, 10–15.
8. Murray, C. B.; Kagan, C. R.; Bawendi, M. G. Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.
9. Tao, A. R.; Ceperley, D. P.; Sinsermsuksakul, P.; Neureuther, A. R.; Yang, P. D. Self-Organized Silver Nanoparticles for Three-Dimensional Plasmonic Crystals. *Nano Lett.* **2008**, *8*, 4033–4038.
10. Shao, J. J.; Raidongia, K.; Koltonow, A. R.; Huang, J. X. Self-Assembled Two-Dimensional Nanofluidic Proton Channels with High Thermal Stability. *Nat. Commun.* **2015**, *6*, 7602.
11. Raidongia, K.; Huang, J. X. Nanofluidic Ion Transport through Reconstructed Layered Materials. *J. Am. Chem. Soc.* **2012**, *134*, 16528–16531.
12. Zhang, M.; Atkinson, K. R.; Baughman, R. H. Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology. *Science* **2004**, *306*, 1358–1361.
13. De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339*, 535–539.
14. Lima, M. D.; Li, N.; de Andrade, M. J.; Fang, S. L.; Oh, J.; Spinks, G. M.; Kozlov, M. E.; Haines, C. S.; Suh, D.; Foroughi, J.; et al. Electrically, Chemically, and Photonically Powered Torsional and Tensile Actuation of Hybrid Carbon Nanotube Yarn Muscles. *Science* **2012**, *338*, 928–932.
15. Di, J. T.; Wang, X.; Xing, Y. J.; Zhang, Y. Y.; Zhang, X. H.; Lu, W. B.; Li, Q. W.; Zhu, Y. T. T. Dry-Processable Carbon Nanotubes for Functional Devices and Composites. *Small* **2014**, *10*, 4606–4625.
16. Stoller, M. D.; Park, S. J.; Zhu, Y. W.; An, J. H.; Ruoff, R. S. Graphene-Based Ultracapacitors. *Nano Lett.* **2008**, *8*, 3498–3502.
17. Luo, J. Y.; Jang, H. D.; Huang, J. X. Effect of Sheet Morphology on the Scalability of Graphene-Based Ultracapacitors. *ACS Nano* **2013**, *7*, 1464–1471.
18. Luo, J. Y.; Jang, H. D.; Sun, T.; Xiao, L.; He, Z.; Katsoulidis, A. P.; Kanatzidis, M. G.; Gibson, J. M.; Huang, J. X. Compression and Aggregation-Resistant Particles of Crumpled Soft Sheets. *ACS Nano* **2011**, *5*, 8943–8949.
19. Tao, Y.; Xie, X. Y.; Lv, W.; Tang, D. M.; Kong, D. B.; Huang, Z. H.; Nishihara, H.; Ishii, T.; Li, B. H.; Golberg, D.; et al. Towards Ultrahigh Volumetric Capacitance: Graphene Derived Highly Dense but Porous Carbons for Supercapacitors. *Sci. Rep.* **2013**, *3*, 2975.
20. Butler, S. Z.; Hollen, S. M.; Cao, L. Y.; Cui, Y.; Gupta, J. A.; Gutierrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J. X.; Ismach, A. F.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. *ACS Nano* **2013**, *7*, 2898–2926.
21. Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall'Agnese, Y.; Rozier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide. *Science* **2013**, *341*, 1502–1505.
22. Naguib, M.; Gogotsi, Y. Synthesis of Two-Dimensional Materials by Selective Extraction. *Acc. Chem. Res.* **2015**, *48*, 128–135.
23. Ghidiu, M.; Lukatskaya, M. R.; Zhao, M. Q.; Gogotsi, Y.; Barsoum, M. W. Conductive Two-Dimensional Titanium Carbide 'Clay' with High Volumetric Capacitance. *Nature* **2014**, *516*, 78–81.
24. Anasori, B.; Xie, Y.; Beidaghi, M.; Lu, J.; Hosler, B. C.; Hultman, L.; Kent, P. R.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional, Ordered, Double Transition Metals Carbides (MXene). *ACS Nano* **2015**, 10.1021/acsnano.5b03591.
25. Luo, L. L.; Wu, J. S.; Luo, J. Y.; Huang, J. X.; Dravid, V. P. Dynamics of Electrochemical Lithiation/Delithiation of Graphene-Encapsulated Silicon Nanoparticles Studied by *in-Situ TEM*. *Sci. Rep.* **2014**, *4*, 3863.
26. Wei, X.; Mao, L.; Soler-Crespo, R. A.; Paci, J. T.; Huang, J.; Nguyen, S. T.; Espinosa, H. D. Plasticity and Ductility in Graphene Oxide through a Mechanochemically Induced Damage Tolerance Mechanism. *Nat. Commun.* **2015**, *6*, 8029.