

Large area hexagonal boron nitride monolayer as efficient atomically thick insulating coating against friction and oxidation

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 Nanotechnology 25 105701

(<http://iopscience.iop.org/0957-4484/25/10/105701>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 160.39.166.188

This content was downloaded on 04/04/2015 at 20:16

Please note that [terms and conditions apply](#).

Large area hexagonal boron nitride monolayer as efficient atomically thick insulating coating against friction and oxidation

Xuemei Li¹, Jun Yin¹, Jianxin Zhou and Wanlin Guo

State Key Laboratory of Mechanics and Control of Mechanical Structures, Key Laboratory for Intelligent Nano Materials and Devices of the Ministry of Education and Institute of Nanoscience, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China

E-mail: wlguo@nuaa.edu.cn

Received 16 August 2013, revised 20 November 2013

Accepted for publication 25 November 2013

Published 14 February 2014

Abstract

Coating is the most widely applied technology to improve surface properties of substrates, and nanotechnology has been playing an important role in enhancing the coating performance. However, the tunability of surface properties by a single atomic layer remains poorly understood. Here we demonstrate that a chemical vapor deposited hexagonal boron nitride (h-BN) monolayer of large area and high quality can serve as a perfect coating to significantly improve friction, oxidation and electric resistance of the substrates. The exceptional low friction and insulation of h-BN monolayer coating facilitate the characterization of the h-BN film vividly by atomic force microscopy, showing the h-BN monolayer consists of domains with size within a few micrometers. This excellent coating performance together with the exceptional high thermal and chemical stability make the h-BN monolayer a promising coating material.

Keywords: hexagonal boron nitride monolayer, coating, friction, oxidation resistance, insulation

(Some figures may appear in colour only in the online journal)

1. Introduction

Two-dimensional (2D) atomic architectures are of particular interest for their distinct properties and attractive promise for a wide range of applications [1, 2]. In particular, due to the planar geometry, large in-plane size and atomic thickness, they can be facily adhered to any solid surfaces through efficient interfacial van der Waals interactions and serve as an atomically thick coating [3]. Comparing with traditional coatings composed of polymers, oxides, novel metals or nanocomposites, which would introduce changes of solid dimensions and optical properties of the solid surfaces, using

2D materials as coatings should have exceptional advantages [4, 5], but the efficiency remains a topic of high suspense [6, 7].

Monolayer h-BN, a single atomic layer consisting of an sp^2 hybridized boron and nitrogen compound in a honeycomb lattice [8], has become one of the most promising 2D materials with a wide range of applications, such as dielectric layers, transparent membranes and deep ultraviolet emitters [9–11]. The in-plane mechanical strength and thermal conductivity of the h-BN monolayer has been reported to be close to that of graphene, but h-BN presents significantly higher thermal and chemical stability than graphene and is insulating and optically transparent except for a narrow adsorption peak in the far ultraviolet wave region [12–15]. These properties make the h-BN monolayer a promising candidate for a unique coating

¹ These authors contributed equally to this work.

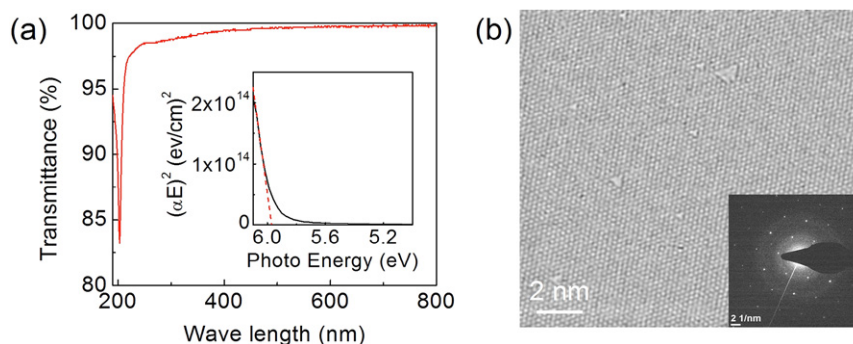


Figure 1. (a) UV–visible transmittance spectra of the BN sample. The inset shows analysis of the optical band gap. (b) Atomic-resolution TEM image showing the hexagonal atomic lattice of the h-BN monolayer and typical triangle defects induced by electron irradiation. The inset is the selected area electron diffraction pattern.

material. The growth of monolayer h-BN using chemical vapor deposition (CVD) has been reported since last year [13, 15–17]. However, its coating performance has rarely been probed, although a few studies on the films composed of boron nitride nanotubes and nanosheets have been reported [18–22].

Here we reveal the coating performance of the CVD-deposited h-BN monolayer through comprehensive experimental investigations. We found that with monolayer h-BN coating the friction of the Cu surface can be reduced by a factor of tens even at normal pressure up to 46 MPa, showing excellent anti-friction performance. The separated h-BN domains can be distinguished from the bare surface of the copper substrate in both friction and current imaging modes by an atom force microscope (AFM) owing to the significant reduction in friction and contact current by a monolayered h-BN coating. Even some grain boundaries of the h-BN monolayer grown on copper substrate can be distinguished in the current image. The oxidation resistance of the h-BN monolayer coated Cu surface is also demonstrated at elevated temperature. This outstanding coating performance of the h-BN monolayer, combined with its intrinsic wide spectrum transparency [15, 16], promise great potential in developing atomic thin coating technology.

2. Experimental section

In this work, a high quality h-BN monolayer was grown in a large area directly on Cu foil using ammonia borane as source by CVD under low pressure [15]. The as-grown h-BN samples were then transferred onto quartz for UV–visible characterization and TEM grids for TEM characterization using polymethyl methacrylate (PMMA) as the mediator, similar to the transferring of graphene [3]. The quality of our h-BN monolayer samples was characterized by UV–visible spectroscopy (TU 1901 UV–Vis) as well as aberration-corrected high resolution transmission electron microscopy (HRTEM). HRTEM was carried out using an image aberration-corrected TEM (FEI Titan 80–300 operating at 80 kV), and images were recorded by a charge-coupled device camera (Gatan UltraScan™ 1000) with an exposure time of 1–2 s. The friction property was measured on an AFM (Seiko Instruments, SPA-300HV) using a silicon probe (SPI Si-DF3, normal force

contact $k_N \sim 1.5 \text{ N m}^{-1}$, lateral force contact $k_L \sim 508 \text{ N m}^{-1}$, calibrated using the Sadder method). All the friction force in this report was recorded at a velocity of 90 nm s^{-1} , and the presented friction data represent an average of ten different measurements. Current images were taken in the contact mode using a silicon probe coated with platinum under an applied bias. The element analysis was performed using an SEM (Zeiss EVO 18) equipped with x-ray energy dispersive analysis (Bruker QM100).

3. Results and discussion

The UV–visible transmittance spectrum of h-BN monolayer presented in figure 1(a) exhibits almost complete transmittance in the visible range, which is sharply reduced to around 84% at 203 nm, showing the intrinsic wide spectrum transparency of the h-BN film. The corresponding optical band gap is calculated to be around 5.97 eV [23, 24], which is very close to that predicted by theoretical calculations for an isolated h-BN monolayer (6.0 eV) [25], indicating the majority monolayer character of our sample. The atomic resolution image of the h-BN film and the inserted selected area electron diffraction pattern shown in figure 1(b) indicate the high crystalline quality of our h-BN sample. Moreover, the sharp edges of the typical electron irradiation induced triangle defects [26–28] confirm the monolayer character of the obtained h-BN film, and the same orientation of the irradiation induced defects suggests a single crystal in the image area.

The coating performance in tuning the friction behavior of the Cu foil by a covering h-BN monolayer was then explored by friction force measurement on an AFM. Although the tip–sample adhesion forces determined by force–displacement spectroscopy were comparable for the h-BN and bare Cu substrate annealed at $1000 \text{ }^\circ\text{C}$ in H_2 environment, a monolayered h-BN coating can reduce the friction force of the Cu surface significantly. Figure 2(a) shows the typical friction force curves taken on bare and h-BN monolayer coated Cu surfaces at an applied normal force of 40 nN. The friction curve on the bare Cu surface shows a large difference between the steady-state value in the forward and reverse scans, indicating a large friction force of the bare Cu, and remarkable amplitude of stick–slip motion. In sharp contrast, the friction force curve on

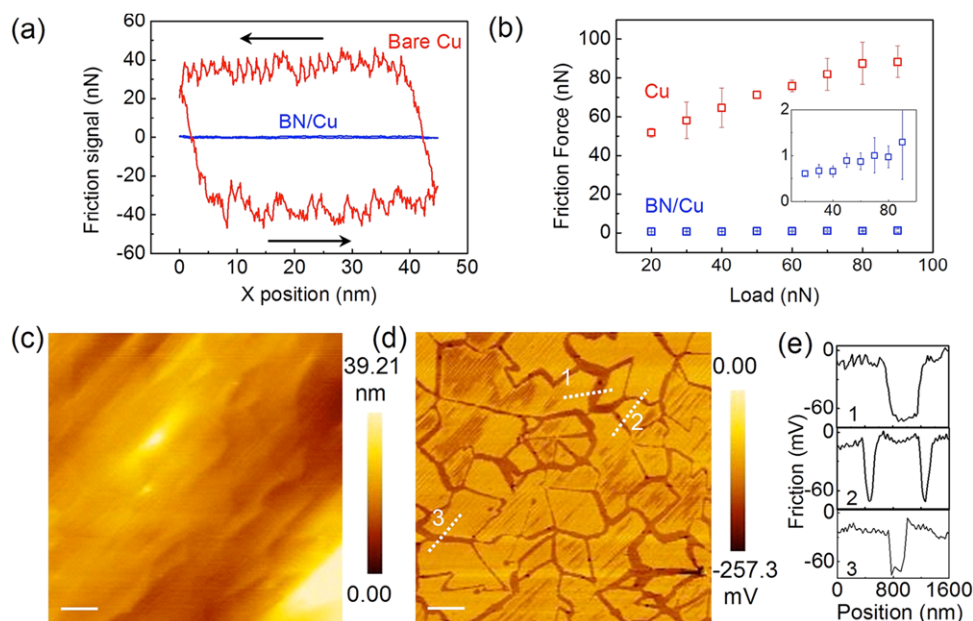


Figure 2. (a) Friction force signal taken on the bare Cu surface and h-BN monolayer coating on Cu at an applied load of 40 nN. (b) The deduced friction force as a function of the applied load. (c), (d) Topographic (c) and friction images (d) taken simultaneously by AFM. Scale bar, 1 μm . (e) Friction signature curves across three gaps between neighboring h-BN coating domains along the dashed lines marked in (d).

the h-BN monolayer coated Cu surface is shrunken into nearly a single smooth line. The measured friction force presented in figure 2(b) shows that a monolayer h-BN coating can reduce the friction force of Cu surface more than 40-fold in a wide range of applied normal load. As the curvature radius of the AFM tip is estimated at around 50 nm, the average normal pressure at 90 nN is about 46 MPa, suggesting an excellent anti-friction property of the h-BN coating only one atom thick.

It is exciting that the distinctive low friction performance of the monolayer h-BN coating can be used to characterize the quality of an h-BN sample grown on a Cu surface with unexpected efficiency, as shown by the friction force image in figure 2(d), where the dark regions are the bare Cu surface with high friction, while the bright regions represent the h-BN monolayer coated surface with distinctive low friction. In contrast, it is difficult to distinguish the h-BN coated domains from the bare Cu surface by the traditional topographic image (figure 2(c)). The partially covered h-BN sample used here was intentionally synthesized by reducing the supplied precursor gas, leading to isolated h-BN domains about 2 μm in size. Figure 2(e) draws the specific friction signature curves measured across three different gaps between BN-coating domains along the dashed lines marked in figure 2(d). The friction signal decreases dramatically in the gaps of the BN domains where the copper surface remains uncovered.

As h-BN is an insulator with a wide band gap of about 6.0 eV [9, 29], it should be interesting to see if an h-BN monolayer coating can tune the contact resistance of a metal surface. We have taken a current image of the copper foil partially covered with h-BN flakes at a bias of 0.5 V on the AFM, as shown in figure 3(b). It is found that an h-BN monolayer can efficiently reduce the contact current of the copper foil in the vertical orientation from around 10 pA

to almost zero. Therefore, the h-BN covered regions (puce regions) can be facily distinguished from the uncovered copper surface (light brown regions) from the current image, in contrast to the featureless topography image (figure 3(a)). Comparing to the image of the sample in figure 2(d) obtained in friction force mode, the h-BN flakes in figure 3(b) have much smaller size but higher density. This can be attributed to the large number of valleys and peaks appearing in the topography image (figure 3(a)), where the nucleation energy of h-BN could be greatly reduced comparing to the flat copper surface shown in figure 2(c), similar to the graphene case [30].

On the other hand, for a high quality sample completely covered with CVD grown h-BN on a copper foil, the contact current image taken at a larger bias of 5 V shows a sharply different picture, as can be seen in figure 3(d). At the much higher bias voltage, the monolayer h-BN coated background area is shown in uniform bright golden yellow, and the darkened dots represent the multilayered h-BN flakes. Surprisingly, even some of the fine grain boundaries of the h-BN monolayer coating can be revealed clearly by the current image, as indicted by the arrows in figure 3(d). There are several possibilities for the visible grain boundary in the contact current image: change of electric property at the grain boundary [31], adsorbates preferring to locate at the more active grain boundary, and possible overlap between neighboring h-BN monolayer domains. At the dots of multilayered h-BN, significantly reduced current, from 70 pA to almost zero, shows enhanced contact resistance by additional BN layers. Some multilayered regions as circled by dashed rings take triangular shape, contributing to the lower edge energy of nitrogen-terminated triangles than of boron-terminated ones as reported previously [32]. However, no triangle h-BN flakes were found during the growth of the first layer of h-BN, which

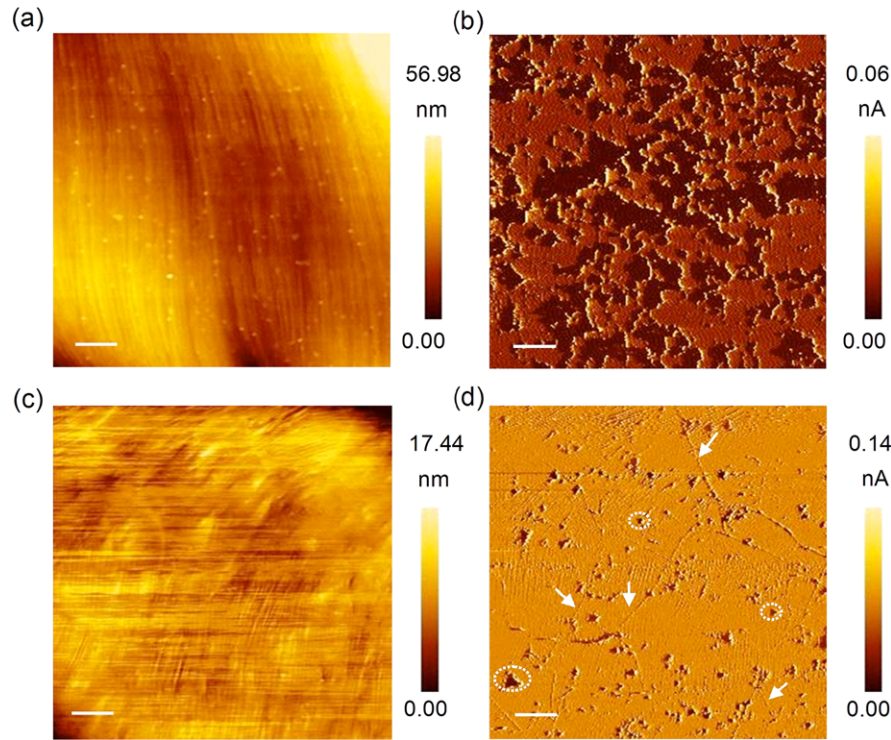


Figure 3. ((a), (b)) Topography image (a) and simultaneously recorded contact current image (b) of partially grown h-BN monolayer on Cu foil taken at a bias of 0.5 V. ((c), (d)) Topography image (c) and contact current image (d) of fully grown h-BN monolayer on Cu foil taken at a bias of 5 V, with dots of small multilayer h-BN flakes on the sample. The arrows indicate grain boundaries, and in the dashed small circles are typical triangle multilayer flakes. Scale bars, 1 μm .

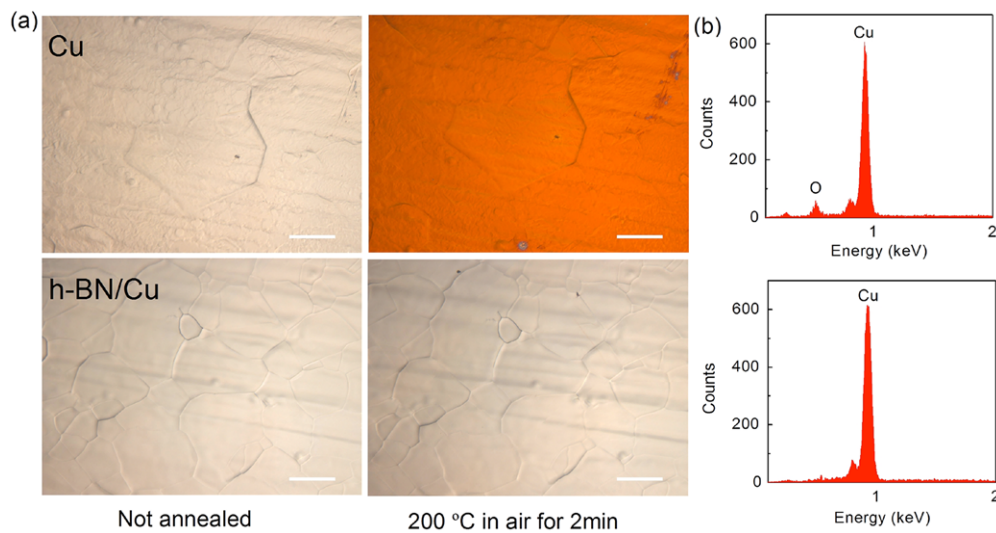


Figure 4. (a) Optical image of bare surface Cu foil (upper) and h-BN monolayer coated Cu surface (lower) taken before (left) and after (right) annealing in air at 200 °C. Scale bars, 50 μm . (b) Energy dispersive x-ray spectroscopy (EDX) for the bare (upper) and h-BN monolayer coated (lower) Cu samples taken after annealing in air at 200 °C.

may suggest that a much lower growth speed would be required for the formation of triangle h-BN domains.

We further demonstrated that an h-BN monolayer coating can efficiently protect the Cu surface from oxidation in air at elevated temperature. Figure 4(a) shows *in situ* optical observation of Cu foil before and after annealing in air at 200 °C for 2 min, without (top) and with (bottom) monolayer

h-BN coating. In contrast to the barely visible change of the h-BN monolayer coated Cu surface, the appearance of the uncoated Cu surface changes dramatically after the annealing. Figure 4(b) shows the average energy dispersive x-ray spectroscopy taken on a $700 \times 500 \mu\text{m}^2$ Cu foil surface with and without h-BN monolayer coating after annealing in air. An oxygen peak was obviously detected in Cu foil without

h-BN coating, but does not appear in the h-BN coated Cu, indicating that the bare Cu has been severely oxidized while h-BN monolayer coating can provide effective protection to the Cu surface against oxidization even at elevated temperature. It needs to be noted that the h-BN can protect the copper foil from oxidization even at the grain boundary of the copper foil (figure 4(a)), suggesting that the h-BN monolayer can grow perfectly across the grain boundary. The excellent oxidization resistance of h-BN is attributed to the unique physical and chemical properties of the h-BN monolayer. Its sp^2 structure efficiently prevents the diffusion of oxygen through h-BN to react with copper, and the thermal and chemical stability make the h-BN monolayer able to survive at high temperature. Additionally, it is reasonable to claim that molecular oxygen cannot diffuse even through the h-BN boundaries, as the h-BN film is composed of BN domains of several micrometers as mentioned above. Although h-BN is stable in air up to 1000 °C [33], it was found that the Cu surface can be gradually oxidized at temperature higher than 300 °C. This must be caused by the inevitable grain boundaries and defects in the CVD-grown h-BN monolayer, and further efforts to grow an h-BN monolayer with larger grain size should improve its coating performance to protect the metal surface from oxidation at higher temperature.

4. Conclusion

In conclusion, we have demonstrated the excellent performance of an h-BN monolayer as an atomically thick coating against friction, contact current and oxidation. It is also shown that the exceptional low friction and insulation of the h-BN monolayer can be used to characterize the quality of a CVD grown h-BN monolayer vividly on an AFM. This excellent performance of the h-BN monolayer makes it a promising candidate for a coating material with atomic thickness.

Acknowledgments

This work was supported by the 973 program (2013CB932604, 2012CB933403), the National and Jiangsu Province NSF (91023026, 51002076, BK20130781) of China, Funding of the Jiangsu Innovation Program for Graduate Education (CXZZ13_0150, CXLX12_0136), Funding for Outstanding Doctoral Dissertation in NUAA (BCXJ12-02) and the Fundamental Research Funds for the Central Universities (NJ20120016, NP2013309). We thank L T Sun of Southeast University for the TEM characterization and Z L Wang of Georgia Tech. for helpful discussions.

References

- [1] Novoselov K S, Falco V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 *Nature* **490** 192
- [2] Schwierz F 2010 *Nature Nanotechnol.* **5** 487
- [3] Li X, Zhu Y, Cai W, Borysiak M, Han B, Chen D, Piner R D, Colombo L and Ruoff R S 2009 *Nano Lett.* **9** 4359
- [4] Rafiee J, Mi X, Gullapalli H, Thomas A V, Yavari F, Shi Y, Ajayan P M and Koratkar N A 2012 *Nature Mater.* **11** 217
- [5] Chen S *et al* 2011 *ACS Nano* **5** 1321
- [6] Shih C J, Wang Q H, Lin S, Park K C, Jin Z, Strano M S and Blankschtein D 2012 *Phys. Rev. Lett.* **109** 176101
- [7] Raj R, Maroo S C and Wang E N 2013 *Nano Lett.* **13** 1509
- [8] Pease R S 1950 *Nature* **165** 722
- [9] Kubota Y, Watanabe K, Tsuda O and Taniguchi T 2007 *Science* **317** 932
- [10] Watanabe K, Taniguchi T, Niiyama T, Miya K and Taniguchi M 2009 *Nature Photon.* **3** 591
- [11] Watanabe K, Taniguchi T and Kanda H 2004 *Nature Mater.* **3** 404
- [12] Kho J G, Moon K T, Kim J H and Kim D P 2000 *J. Am. Ceram. Soc.* **83** 2681
- [13] Song L *et al* 2010 *Nano Lett.* **10** 3209
- [14] Zhi C, Bando Y, Tang C, Kuwahara H and Golberg D 2009 *Adv. Mater.* **21** 2889
- [15] Kim K K *et al* 2011 *Nano Lett.* **12** 161
- [16] Kim G, Jang A R, Jeong H Y, Lee Z, Kang D J and Shin H S 2013 *Nano Lett.* **13** 1834
- [17] Shi Y *et al* 2010 *Nano Lett.* **10** 4134
- [18] Yu J, Qin L, Hao Y, Kuang S, Bai X, Chong Y M, Zhang W and Wang E 2010 *ACS Nano* **4** 414
- [19] Pakdel A, Zhi C, Bando Y, Nakayama T and Golberg D 2011 *ACS Nano* **5** 6507
- [20] Lee C H, Drelich J and Yap Y K 2009 *Langmuir* **25** 4853
- [21] Li L H and Chen Y 2009 *Langmuir* **26** 5135
- [22] Boinovich L B, Emelyanenko A M, Pashinin A S, Lee C H, Drelich J and Yap Y K 2011 *Langmuir* **28** 1206
- [23] Gao Y, Ren W, Ma T, Liu Z, Zhang Y, Liu W, Ma L, Ma X and Cheng H 2013 *ACS Nano* **7** 5199
- [24] Yuzuriha T H and Hess D W Q 1986 *Thin Solid Films* **140** 199
- [25] Blase X, Rubio A, Louie S G and Cohen M L 1995 *Phys. Rev. B* **51** 6868
- [26] Meyer J C, Chuvilin A, Algara-Siller G, Biskupek J and Kaiser U 2009 *Nano Lett.* **9** 2683
- [27] Kotakoski J, Jin C H, Lehtinen O, Suenaga K and Krashennnikov A V 2010 *Phys. Rev. B* **82** 113404
- [28] Alem N, Erni R, Kisielowski C, Rossell M D, Gannett W and Zettl A 2009 *Phys. Rev. B* **80** 155425
- [29] Blase X, Rubio A, Louie S G and Cohen M L 1995 *Phys. Rev. B* **51** 6868
- [30] Yan Z *et al* 2012 *ACS Nano* **6** 9110
- [31] Li X, Wu X, Zeng X C and Yang J 2012 *ACS Nano* **6** 4104
- [32] Liu Y, Bhowmick S and Yakobson B I 2011 *Nano Lett.* **11** 3113
- [33] Yin J, Li X, Zhou J and Guo W 2013 *Nano Lett.* **13** 3232