Graphene as a Long-Term Metal Oxidation Barrier: Worse Than Nothing

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ABSTRACT Anticorrosion and antioxidation surface treatments such as paint or anodization are a foundational component in nearly all industries. Graphene, a single-atom-thick sheet of carbon with impressive impermeability to gases, seems to hold promise as an effective anticorrosion barrier, and recent work supports this hope. We perform a complete study of the short- and long-term performance of graphene coatings for Cu and Si substrates. Our work reveals that although graphene indeed offers effective short-term oxidation protection, over long time scales it promotes more extensive wet corrosion than that seen for an initially bare, unprotected Cu surface. This surprising result has important implications for future scientific studies and industrial applications. In addition to informing any future work on graphene as a protective coating, the results presented here have implications for graphene's performance in a wide range of applications.
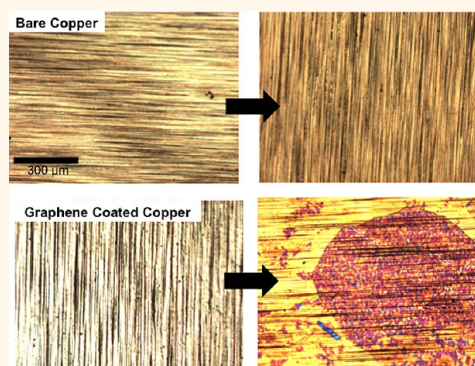
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Protective coatings, from paints to galvanization to plasma-sprayed ceramics, are essential treatments for most modern structures. Applications range from the gigantic (maintaining the integrity of steel bridges) to the microscopic (passivation in transistors). A highly promising new coating material is graphene, a strong, transparent single-atom-thick crystal of sp²-bonded carbon that can be directly grown on selected metals or transferred postgrowth to arbitrary substrates.[1,2] Graphene is highly impermeable to gases[3−5] and is itself robust against oxidation,[6,7] suggesting that mono- or few-layer graphene films could be effective anticorrosion barriers. We present a systematic study of graphene's performance as an anticorrosion and antioxidation barrier for Cu and Si substrates. Consistent with previous speculations and observations, we find that graphene indeed protects Cu from thermal oxidation reasonably well at high temperatures over relatively short time scales (minutes to hours). On the other hand, graphene greatly *promotes* galvanic corrosion of Cu at ambient temperature over long time scales (months to years) and

can in fact be a much worse long-term anticorrosion barrier than no coating at all.

Cu is a commonly used metal in numerous applications requiring corrosion mitigation. Fortuitously, monolayer graphene can be grown with relative ease directly on Cu (and many other metals) by chemical vapor deposition (CVD).[2,8−10] Recent studies[11−15] suggest that Cu coated by CVD-graphene is significantly more resistant to thermal oxidation and wet corrosion than bare, unprotected Cu (*i.e.*, Cu with only its native oxide coating), at least in the short term. We here examine the behavior of bare and graphene-coated Cu exposed to air both at elevated temperatures and short to moderate time scales and at ambient temperature over much longer time scales.

Cu foils (99.8%, Alfa Aesar No. 13382) are initially annealed with H_2 gas to reduce all native oxide. Samples termed "bare" receive no further treatment. Graphene-coated samples are subsequently coated with monolayer graphene using CVD (see Supporting Information for details). We employ optical micrographs as one diagnostic for degree of oxidation; oxide films of increasing thickness lead to optical
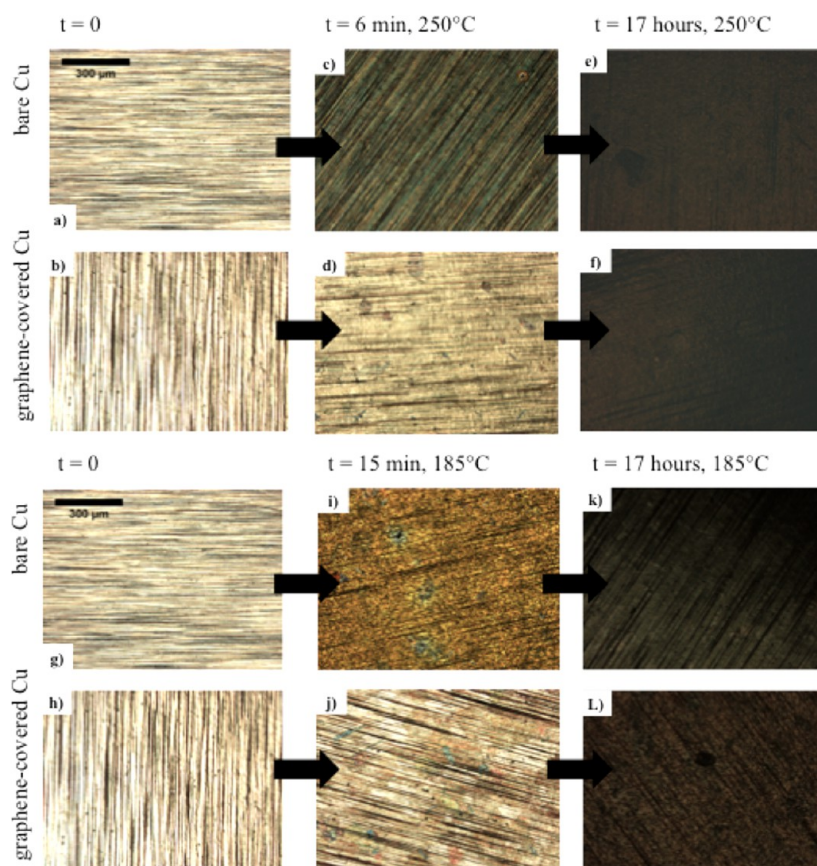
Figure 1. Graphene's impressive but limited short-term performance as an oxidation barrier. Panels a, b, g, and h show bare and graphene-coated Cu before treatment. Panels c and d show bare and graphene-coated Cu, respectively, after being heated in ambient pressure, low humidity air for 6 min at 250 °C. Panels i and j show bare and graphene-coated Cu, respectively, after being heated in air for 15 min at 185 °C. Graphene grown on the Cu prevents significant oxidation at these elevated temperatures for a short period of time. Panels e and f are bare and graphene-coated Cu, respectively, after being heated in air for 17 h at 250 °C, and panels k and L are bare and graphene-coated Cu, respectively, after 17 h at 185 °C. On this time scale, graphene does not protect effectively against thermal oxidation. All photos were taken with the same exposure with the exception of photos taken after 17 h, for which a longer exposure time was used to make details more visible.

interference effects and pronounced color changes. Additionally, energy dispersive X-ray spectroscopy (EDAX) is employed to determine the oxide phase and as an approximate gauge of thickness.

RESULTS AND DISCUSSION

Figure 1 shows a time evolution of optical images of the Cu foils for two selected high oxidation temperatures, 250 °C (upper six panels) and 185 °C (lower six panels). Panels a, b, g, and h show the foils just after preparation; the bare and monolayer-graphene-coated samples are uniformly colored and shiny, nearly indistinguishable by eye. We first investigate samples heated at 250 °C. After 6 min, the bare Cu sample (panel b) is significantly oxidized, while the graphene-coated Cu sample (panel e) shows little oxidation. This confirms that at very high temperatures and short times (several minutes), graphene serves as an impressive oxidation barrier for Cu, likely due to the low permeability of graphene to gases. At longer times, the graphene-coated Cu succumbs to thermal oxidation, likely due to the migration of oxygen through defects in the graphene. After 17 h at 250 °C, graphene-coated Cu

(panel f) is heavily oxidized and indistinguishable from the bare Cu subjected to the same conditions (panel c).

It stands to reason that if graphene partially protects Cu from thermal oxidation at 250 °C, it should also be protective at 185 °C. This is indeed the case, as demonstrated in Figure 1, panels g to L. After 15 min at 185 °C, the bare Cu sample is partially oxidized (panel h), while the monolayer-coated Cu sample is close to its pristine state (panel k). After 17 h in air at 185 °C, both the bare Cu (panel i) and the monolayer-graphene-coated Cu (panel L) are heavily oxidized. The effective time scale for effective thermal oxidation protection by graphene on Cu is on the order of 1 h at 185 °C, about an order of magnitude longer than similar systems at 250 °C. Hence, graphene appears to provide significant short-term thermal oxidation protection to Cu for temperatures between 185 and 250 °C. This result agrees with several recently published studies in which graphene-covered metals were mostly protected from oxidation when exposed to harsh conditions (thermal oxidation, immersion in corrosive solutions, driven electrochemical reactions) for a period of minutes or hours.[11−15]
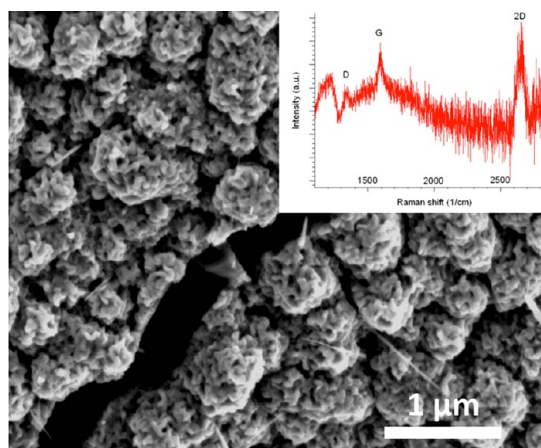
Figure 2. Complete surface oxidation (at 250 °C) of Cu foil covered with monolayer CVD graphene. Monolayer graphene fails as an oxidation barrier at temperatures below the onset of graphene oxidation (~300 °C). After 17 h in atmosphere at 250 °C, the surface of graphene-covered Cu foil turns a uniform matte black. EDAX reveals that the entire Cu surface is converted to CuO after treatment at 250 °C. In this SEM image, the CuO morphology is shown to be small flower-like balls. The thick surface oxide develops strain relative to the Cu substrate, leading to crack formation (seen in the middle of the image). Raman spectroscopy (514 nm excitation, shown in inset) confirms that monolayer graphene is still present at the surface, though the signal is likely diminished by the greatly increased surface roughness.

Before extending our study to lower temperatures and longer times, we examine the microscopic limits of graphene's high temperature oxidation protection. CVD-grown graphene on Cu is known to be polycrystalline with innumerable grain boundaries, folds, wrinkles, and microscopic tears.[16−19] It is reasonable to expect that any corrosion or thermal oxidation of graphene-coated Cu is initiated at defects in the graphene crystal structure. Indeed, our microscopic examination of graphene-covered Cu foils heated at 185 °C in air for 20 min (Figure S1 in the Supporting Information) reveals that oxidation of graphene-coated Cu initially occurs in the relatively sparse regions of graphene grain boundaries, cracks, and point defects.

Over longer time scales, the Cu surface is uniformly oxidized, even in regions below an intact graphene coating. This is seen in Figure 2, a scanning electron microscope (SEM) image of the surface of the fully oxidized, graphene-coated sample used for Figure 1f. EDAX performed in the SEM reveals a Cu:O stoichiometry of 47:53 atomic percent, suggesting a reasonably thick CuO surface phase. The thick surface oxide develops strain relative to the Cu substrate, leading to crack formation, as observed in the middle of the image. Raman spectroscopy (inset in Figure 2) confirms that graphene is still present at the surface.[20]

Many industrial processes requiring Cu corrosion or oxidation protection involve less extreme operation temperature but time scales of many months to years. Thus, a critical test of graphene's anticorrosion performance requires an extended-duration experiment. Although extrapolation of the above results predicts

that graphene could protect Cu surfaces from corrosion at ambient temperature over long-term conditions, we find exactly the opposite. In the long term at room temperature, graphene promotes Cu corrosion.

To investigate long-term behavior, samples of bare and CVD graphene-coated Cu are stored under ambient conditions (~25 °C, variable but low humidity) for up to 2 years and examined optically over time. Selected data are displayed in Figure 3. Figure 3a and b show bare Cu at time $t = 0$ (immediately after H_2 reduction of the native oxide) and at $t > 2$ years, respectively. The slight color change reflects the well-known natural and relatively slow room-temperature oxidation of Cu.[21] Figure 3c−f show the temporal evolution of graphene-coated Cu from $t = 0$ to $t = 18$ months. In the first 1−2 weeks after graphene growth the graphene-coated Cu appears shiny and free of oxide (Figure 3d). Within a month the graphene-coated Cu surface starts to tarnish nonuniformly with small patches (several hundred micrometers in size) of oxide. Within a few months most regions of the graphene-covered Cu appear highly oxidized, with an oxide tens or hundreds of nanometers thick, as seen in Figure 3e. Variations in oxide thickness, and corresponding color variations, appear to correlate with crystal domains of the underlying Cu substrate.

Apparently, the alignment between the Cu substrate and graphene grains influences the ability of O_2 or H_2O to move along the surface and interact with the substrate. Some Cu grains remain largely protected after many months, as shown in the center of Figure 3e. EDAX analysis of these unique protected regions reveals oxygen content comparable to or lower than a native oxide on foils 3−12 months after graphene growth. After 18 months (Figure 3f) virtually all of the Cu substrate is heavily oxidized, even those areas that initially resisted oxidation. EDAX analysis reveals that the oxide phase is predominantly Cu_2O (with a Cu:O ratio of 67:33 atomic percent). Thus, at room temperature and on time scales of 1 month to 2 years, graphene is a worse choice for an anticorrosion barrier on Cu than no coating at all.

We propose mechanisms for both the short- and long-term behavior of CVD graphene anticorrosion and antioxidation coatings grown on Cu. Graphite (many-layer graphene) is cathodic to Cu and will drive galvanic corrosion of Cu.[14,22] However, this process is slowed considerably due to the impermeability of pristine graphene to gases and due to the close graphene−Cu bonding[23] that suppresses the diffusion of O_2 and H_2O between the graphene and Cu surface. Over several months at room temperature O_2 and H_2O bleed through graphene defects and diffuse between the graphene and Cu, corroding the entire Cu surface. Furthermore, whereas a uniform native oxide on bare Cu would eventually block the half-reactions needed for wet corrosion,[24] a graphene coating maintains electrical contact across the surface of the Cu and to sparse protected regions of Cu, maintaining charge transfer to the bulk of the Cu and
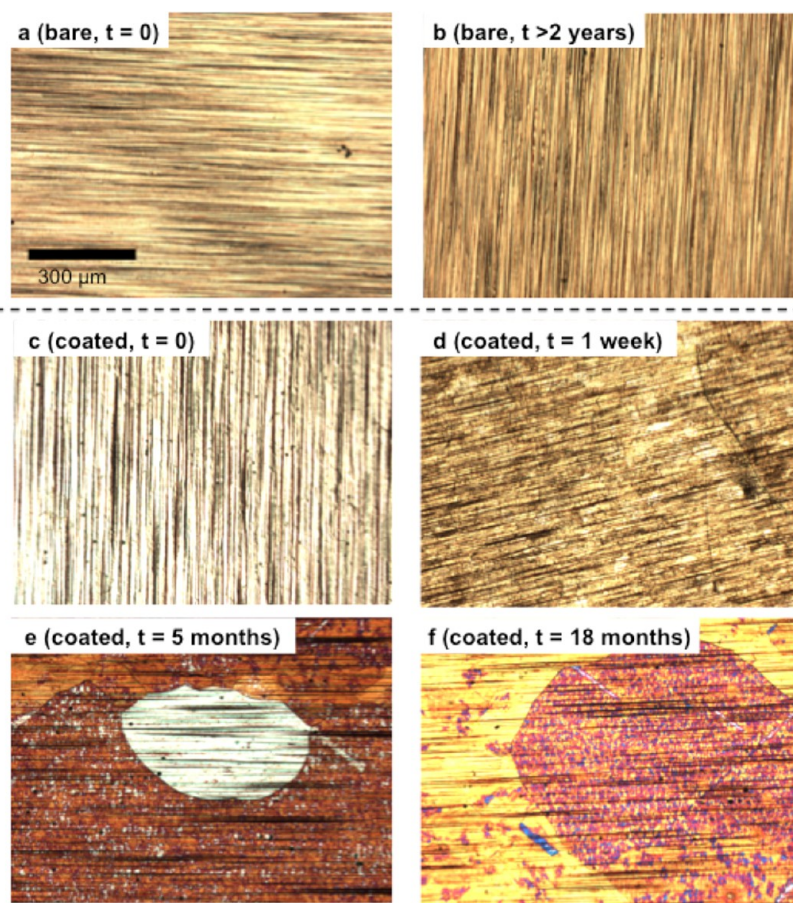
Figure 3. "Aging" of graphene-covered Cu in ambient conditions. Optical micrographs of "aged" bare and graphene-covered Cu foils, captured with the same lighting conditions and at the same magnification (scale bar in part a applies to all photos). (a) Bare Cu immediately after a H_2 anneal to remove all oxide from the surface. (b) Bare Cu with a native oxide accumulated over many years in ambient conditions. (c) Graphene-coated Cu immediately after growth. The surface is reduced by a H_2 anneal prior to growth to remove native oxide. (d) Graphene-covered Cu shown 1 week after graphene growth. The surface appears well protected from oxidation or corrosion and remains a pale orange color. (e) Graphene-covered Cu shown 5 months after graphene growth. Most Cu grains have been heavily corroded, but certain Cu grains (like the oval in the center) appear to resist oxidation longer than others, perhaps due to a stronger graphene—Cu interaction based on the local Cu faceting. (f) Graphene-covered Cu shown 18 months after graphene growth. The entire Cu surface now appears corroded (including previously protected regions), though the thickness and microstructure (see Supporting Information Figure S3b) of the oxide varies significantly among Cu grains.

allowing the full electrochemical reaction to continue unimpeded. Additionally, mechanical stress may build in the thick and nonuniform oxide layer on graphene-covered Cu, leading to cracking of the oxide layer, which opens up new avenues for corrosion. The proposed long-term oxidation of bare and graphene-covered Cu foils is shown in a schematic in Figure 4.

We also investigate graphene's performance as an antioxidation coating for another industrially important material, Si. Bare Si forms a native oxide at room temperature on the time scale of minutes to days,[25] and the graphene—Si interface is itself an interesting system, as graphene is a promising transparent conducting heterojunction material for various devices including Si solar cells.[26−28] In contrast to Cu, Si does not easily catalyze graphene growth. Therefore in these experiments we transfer graphene onto the Si using a poly(methyl methacrylate) (PMMA) scaffold and perform a post-transfer reduction step (annealing in H_2 as described in the Methods) to create the initial graphene—Si interface. To monitor the ambient temperature surface oxidation of Si, X-ray photoelectron spectroscopy (XPS) was performed on bare (HF-etched and unprotected) and graphene-covered Si. As seen in Figure 5, both the bare and graphene-covered samples exhibit similar oxygen and Si^{4+} peaks after one week in atmospheric conditions, indicating that the graphene fails to prevent long-term Si oxidation. This failure could present potential stability problems for graphene—Si solar cells. Indeed, additional oxidation experiments on graphene Schottky solar cells with n-type Si (see Supporting Information) provide consistent evidence of the short-term failure of graphene oxidation barriers. The performance of monolayer graphene n-type Si cells is observed to decrease for weeks after preparation, suggestive of the formation of a resistive SiO_2 layer since other possible effects (the initial H_2 treatment[29] and atmospheric doping,[30] which tend to p-dope graphene on SiO_2) should improve device performance over time.

CONCLUSION

We show that CVD-grown graphene is effective at limiting Cu and Si oxidation and corrosion only over short time scales, likely due to the impermeability of graphene to gases and slowed diffusion of O_2 and H_2O between graphene and the substrate. Over long time scales O_2 and H_2O infiltrate defects in the graphene and oxidize or corrode the surface of the underlying substrate. Graphene-catalyzed corrosion proceeds nonuniformly, building stress, which leads to cracks in the resulting oxide and further corrosion. Conducting graphene coatings can further promote corrosion by facilitating electrochemical reactions both across the surface and through the bulk of the substrate, whereas typical native oxides passivate the surface and terminate the electron transfer needed for continued corrosion. Graphene protective layers intended for anything but short-term (minutes to hours) industrial processes must avoid these potential pitfalls.

METHODS

Graphene is grown *via* CVD on Cu foil at ∼1000−1020 °C using methane as a precursor gas.[2] Transfer of graphene layers (when performed) is accomplished using PMMA cured at 165 °C
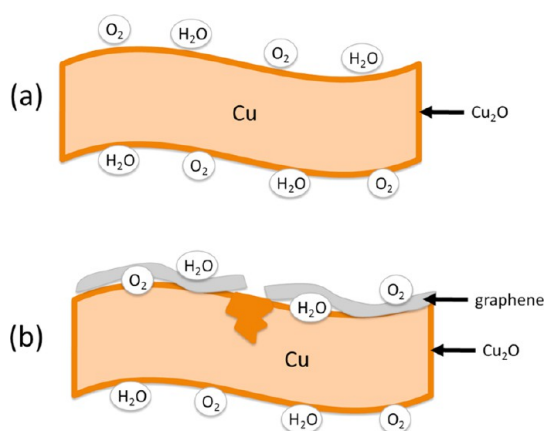

Figure 4. Schematic of native Cu oxide formation as compared with graphene-assisted Cu corrosion. (a) Bare Cu forms a passivating native oxide, which limits further corrosion by blocking the half-reactions needed to continue oxidation. (b) A graphene coating on Cu slows diffusion of O_2/H_2O but assists long-term Cu corrosion in a number of ways: maintaining a conductive pathway across the Cu surface and to selected regions of the Cu, where it maintains intimate contact; causing nonuniform oxidation, beginning in locations of graphene defects, which leads to stress and cracking of the oxide; and providing an electrochemical driving force (graphitic materials are cathodic to many corrosion-prone metals).

to mechanically stabilize the graphene while etching the Cu growth substrate with aqueous $FeCl_3$. For the experiment on oxidation and reduction of Cu with monolayer and bilayer graphene coatings (Figure S2), anneals are conducted in a tube furnace at 225 °C for 60 min and 450 °C for 90 min under O_2 and H_2 flow, respectively. A FEI Sirion XL30 scanning electron microscope is used for imaging, lithography, and EDAX (2 kV, 50 kX).

For the Si oxidation experiment, graphene−Si junctions are fabricated on commercially available phosphorus-doped (n-type) Si wafers with 300 nm of SiO_2 grown by the manufacturer. A window is etched in the SiO_2 to access bare Si *via* buffered hydrofluoric acid (BHF) immediately before graphene transfer, and a reduction anneal is conducted immediately before the initial measurement for monolayer devices (and immediately before the second graphene deposition transfer for bilayer devices discussed in the Supporting Information). XPS data are collected using Cu Kα radiation in a home-built system.
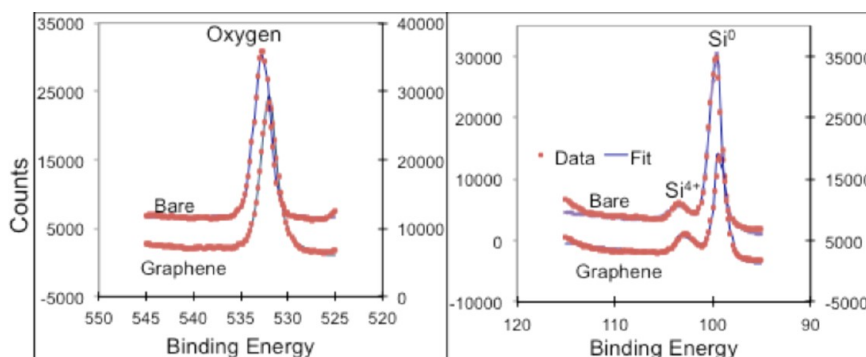
Figure 5. X-ray photoelectron spectroscopy data for bare and graphene-covered Si. These XPS data correspond to monolayer-graphene-covered and bare n-cSi wafers. Both the bare and graphene-covered wafers are initially etched with BHF to remove any initial silicon oxide. After one week of atmospheric exposure, the Si^{4+} and oxygen peaks for both bare and graphene-covered Si have a similar magnitude, indicating that the graphene fails to protect the Si surface from oxidation. Additional information on this data is found in Table S1 in the Supporting Information.

REFERENCES AND NOTES

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

2. Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; *et al.* Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.

3. Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Impermeable Atomic Membranes from Graphene Sheets. *Nano Lett.* **2008**, *8*, 2458–2462.

4. Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. Unimpeded Permeation of Water through Helium-Leak-Tight Graphene-Based Membranes. *Science* **2012**, *335*, 442–444.

5. Leenaerts, O.; Partoens, B.; Peeters, F. M. Graphene: A Perfect Nanoballoon. *Appl. Phys. Lett.* **2008**, *93*, 193107.

6. Liu, L.; Ryu, S. M.; Tomasik, M. R.; Stolyarova, E.; Jung, N.; Hybertsen, M. S.; Steigerwald, M. L.; Brus, L. E.; Flynn, G. W. Graphene Oxidation: Thickness-Dependent Etching and Strong Chemical Doping. *Nano Lett.* **2008**, *8*, 1965–1970.

7. Surwade, S. P.; Li, Z. T.; Liu, H. T. Thermal Oxidation and Unwrinkling of Chemical Vapor Deposition-Grown Graphene. *J. Phys. Chem. C* **2012**, *116*, 20600–20606.

8. Reina, A.; Jia, X. T.; Ho, J.; Nezich, D.; Son, H. B.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.* **2009**, *9*, 30–35.

9. Coraux, J.; N'Diaye, A. T.; Engler, M.; Busse, C.; Wall, D.; Buckanie, N.; Heringdorf, F.; van Gastel, R.; Poelsema, B.; Michely, T. Growth of Graphene on Ir(111). *New J. Phys.* **2009**, *11*, 1–22.

10. Xue, Y. Z.; Wu, B.; Guo, Y. L.; Huang, L. P.; Jiang, L.; Chen, J. Y.; Geng, D. C.; Liu, Y. Q.; Hu, W. P.; Yu, G. Synthesis of Large-Area, Few-Layer Graphene on Iron Foil by Chemical Vapor Deposition. *Nano Res.* **2011**, *4*, 1208–1214.

11. Chen, S. S.; Brown, L.; Levendorf, M.; Cai, W. W.; Ju, S. Y.; Edgeworth, J.; Li, X. S.; Magnuson, C. W.; Velamakanni, A.; Piner, R. D.; *et al.* Oxidation Resistance of Graphene-Coated Cu and Cu/Ni Alloy. *ACS Nano* **2011**, *5*, 1321–1327.

12. Prasai, D.; Tuberquia, J. C.; Harl, R. R.; Jennings, G. K.; Bolotin, K. I. Graphene: Corrosion-Inhibiting Coating. *ACS Nano* **2012**, *6*, 1102–1108.

13. Topsakal, M.; Sahin, H.; Ciraci, S. Graphene Coatings: An Efficient Protection from Oxidation. *Phys. Rev. B* **2012**, *85*, 155445.

14. Raman, R. K. S.; Banerjee, P. C.; Lobo, D. E.; Gullapalli, H.; Sumandasa, M.; Kumar, A.; Choudhary, L.; Tkacz, R.; Ajayan, P. M.; Majumder, M. Protecting Copper from Electrochemical Degradation by Graphene Coating. *Carbon* **2012**, *50*, 4040–4045.

15. Kirkland, N. T.; Schiller, T.; Medhekar, N.; Birbilis, N. Exploring Graphene as a Corrosion Protection Barrier. *Corros. Sci.* **2012**, *56*, 1–4.

16. Kim, K.; Lee, Z.; Malone, B. D.; Chan, K. T.; Aleman, B.; Regan, W.; Gannett, W.; Crommie, M. F.; Cohen, M. L.; Zettl, A. Multiply Folded Graphene. *Phys. Rev. B* **2011**, *83*, 245433.

17. Liu, N.; Pan, Z. H.; Fu, L.; Zhang, C. H.; Dai, B. Y.; Liu, Z. F. The Origin of Wrinkles on Transferred Graphene. *Nano Res.* **2011**, *4*, 996–1004.

18. Chae, S. J.; Gunes, F.; Kim, K. K.; Kim, E. S.; Han, G. H.; Kim, S. M.; Shin, H. J.; Yoon, S. M.; Choi, J. Y.; Park, M. H.; *et al.* Synthesis of Large-Area Graphene Layers on Poly-Nickel Substrate by Chemical Vapor Deposition: Wrinkle Formation. *Adv. Mater.* **2009**, *21*, 2328–2333.

19. Kim, K.; Lee, Z.; Regan, W.; Kisielowski, C.; Crommie, M. F.; Zettl, A. Grain Boundary Mapping in Polycrystalline Graphene. *ACS Nano* **2011**, *5*, 2142–2146.

20. Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; *et al.* Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 187401.

21. Iijima, J.; Lim, J. W.; Hong, S. H.; Suzuki, S.; Mimura, K.; Isshiki, A. Native Oxidation of Ultra High Purity Cu Bulk and Thin Films. *Appl. Surf. Sci.* **2006**, *253*, 2825–2829.

22. Zahran, R. R.; Ibrahim, I. H. M.; Sedahmed, G. H. The Corrosion of Graphite/Copper Composites in Different Aqueous Environments. *Mater. Lett.* **1996**, *28*, 237–244.

23. Yoon, T.; Shin, W. C.; Kim, T. Y.; Mun, J. H.; Kim, T. S.; Cho, B. J. Direct Measurement of Adhesion Energy of Monolayer Graphene As-Grown on Copper and Its Application to Renewable Transfer Process. *Nano Lett.* **2012**, *12*, 1448–1452.

24. Keil, P.; Frahm, R.; Lutzenkirchen-Hecht, D. Native Oxidation of Sputter Deposited Polycrystalline Copper Thin Films During Short and Long Exposure Times: Comparative Investigation by Specular and Non-Specular Grazing Incidence X-ray Absorption Spectroscopy. *Corros. Sci.* **2010**, *52*, 1305–1316.

25. Morita, M.; Ohmi, T.; Hasegawa, E.; Kawakami, M.; Suma, K. Control Factor of Native Oxide-Growth on Silicon in Air or in Ultrapure Water. *Appl. Phys. Lett.* **1989**, *55*, 562–567.

26. Schriver, M.; Regan, W.; Loster, M.; Zettl, A. Carbon Nanostructure-aSi:H Photovoltaic Cells with High Open-Circuit Voltage Fabricated without Dopants. *Solid State Commun.* **2010**, *150*, 561–563.

27. Li, X. M.; Zhu, H. W.; Wang, K. L.; Cao, A. Y.; Wei, J. Q.; Li, C. Y.; Jia, Y.; Li, Z.; Li, X.; Wu, D. H. Graphene-On-Silicon Schottky Junction Solar Cells. *Adv. Mater.* **2010**, *22*, 2743–2748.

28. Regan, W.; Byrnes, S.; Gannett, W.; Ergen, O.; Vazquez-Mena, O.; Wang, F.; Zettl, A. Screening-Engineered Field-Effect Solar Cells. *Nano Lett.* **2012**, *12*, 4300–4304.

29. Gannett, W.; Regan, W.; Watanabe, K.; Taniguchi, T.; Crommie, M. F.; Zettl, A. Boron Nitride Substrates for High Mobility Chemical Vapor Deposited Graphene. *Appl. Phys. Lett.* **2011**, *98*, 242105.

30. Ni, Z. H.; Wang, H. M.; Luo, Z. Q.; Wang, Y. Y.; Yu, T.; Wu, Y. H.; Shen, Z. X. The Effect of Vacuum Annealing on Graphene. *J. Raman Spectrosc.* **2010**, *41*, 479–483.