Electrochemistry: An Efficient Way to Chemically Modify Individual Monolayers of Graphene

Lin Gan, Dayong Zhang, and Xuefeng Guo*

Considerable interest has been recently given to the incorporation of the emergent nanomaterial graphene as fundamental building nanoblocks in both science and technology communities,^[1] particularly in the electronic-device community.^[2] However, many important issues still need to be addressed to fully utilize this material. These include bandgap engineering and the controllable doping of semimetal graphene. Because graphene is 2D and composed of a single layer of carbon atoms that are entirely exposed to the environment, surface chemistry plays an important role in controlling its electronic properties.^[3] However, due to the inert reactivity of its surface, there remains a dearth of efficient approaches to covalently modify graphene; only a few chemical reactions,^[4] such as hydrogenation,^[5] diazonium chemistry,^[6] cycloaddition,^[7] photochemistry,^[8] and fluorination,^[9] have been reported.

Here we report an easy and efficient way of electrografting graphene surfaces by the electrochemical formation of aryl radicals from diazonium salts under mild conditions (**Scheme 1**). The chemical bond between the graphene surface and the organic layer originates from the attack of the aryl radical, which was obtained from the reduction of the diazonium salt.^[10] According to diazonium chemistry, aryl radicals can also be produced from diazonium salts through a thermal process, by which the diazonium compounds, from strong π -electron donors to strong π -electron acceptors, have been used to tune the transport properties of silicon semiconductors after grafting the aryls onto device surfaces, similarly to adding n- and p-dopants.^[11] Recently, similar results have been reported on diazonium grafting of graphenes,^[6] which proves that diazonium chemistry might be a promising

L. Gan, D. Zhang, Prof. X. Guo Center for Nanochemistry Beijing National Laboratory for Molecular Sciences State Key Laboratory for Structural Chemistry of Unstable and Stable Species College of Chemistry and Molecular Engineering Peking University Beijing 100871, P. R. China Fax: (+86) 10-62757789 E-mail: guoxf@pku.edu.cn Prof. X. Guo Department of Advanced Materials and Nanotechnology College of Engineering Peking University Beijing 100871, P. R. China

DOI: 10.1002/smll.201102302

s a la construction de la constr

Graphene

pathway toward graphene circuits with tunable electrical properties.^[6c,e] However, this thermally initiated process is time-consuming, for example, up to ~20 h^[6]b] or ~7 h.^[6]d] In our study, we found that electrografting graphene surfaces with (4-nitrophenyl) diazonium tetrafluoroborate (NDTB) can be finished within a few seconds. More interestingly, by selectively setting the potential bias, the ratio of electron-withdrawing nitro groups to electron-donating amino groups can be controlled, thus realizing the successful modification of the electronic properties of graphene.

Large-area high-quality single-layer graphenes (SLGs) were grown on Cu foils through a chemical vapor deposition (CVD) process and then transferred onto silicon substrates with 300 nm layer of thermally grown SiO₂ using a nonde-structive polymer-mediated transfer technique developed elsewhere.^[12] By using SLGs as the working electrode with the aid of Au metal, cyclic voltammetry (CV) experiments were performed in an electrolytic cell as shown in Scheme 1a



Scheme 1. a) Structural representation of the electrolytic cell used for diazonium electrografting of graphenes. WE (working electrode): graphene; CE (counter electrode): Pt; RE (reference electrode): Ag/AgCl (3 μ KCl). b) Schematic of electrochemical reduction of diazonium salts and nitro groups.



Figure 1. a,b) Cyclic voltammograms of NDTB (2 mm) on SLGs in 0.1 M H₂SO₄. Scan rate: 0.2 V/s, T = 298 K. c) An AFM image of a modified SLG. d) The height profiles across the reaction boundary as labeled in Figure 1c.

in an aqueous solution of sulfuric acid (~0.1 M) containing NDTB (~2 mM, from Sigma Aldrich). Before the experiments, we purged the system by a stream of pure Ar gas to remove any trace of air or oxygen in the cell. After electrochemical reactions, the graphenes were prepared for characterization by sequentially rinsing with copious amounts of de-ionized (DI) water and acetone under ultrasonic treatments three times to completely remove diazonium salts that had been physically absorbed onto the graphene surface.

Figure 1a shows the cyclic voltammogram of NDTB by simply dipping a SLG sheet into the aqueous solution of sulfuric acid. A broad monoelectronic irreversible wave located at a very positive potential ($E_p = -0.05$ V vs. Ag/AgCl) was observed at a scan rate of 0.2 V/s. The potential of this wave corresponds to the reduction of NDTB to its radical anion, as already observed in aqueous media.^[10h] Upon the second scan, this irreversible wave disappeared and could not be restored upon further scans as shown by CV (Figure 1a), indicating the completion of the diazonium electrografting. These results on our CVD-grown SLGs are similar to those obtained on other carbon materials in various forms^[10] and clearly indicate that nitrophenyl groups have been grafted to the surface of SLGs within 5 s (Scheme 1b). Examination of modified SLGs by atomic force microscopy (AFM) proves the formation of a compact nitrophenyl layer. After electrodeposition followed by careful ultrasonic rinsing with both copious amounts of DI water and acetone, the AFM image obtained in tapping mode reveals an obvious boundary between pristine and modified SLGs (Figure 1c), and an average thickness value of ~1.60 nm was estimated (Figure 1d). This indicates the formation of a thin film corresponding to about 2-3 layers, considering a value of 0.66 nm for the height of a monolayer.^[14b] This is because the same radical can attack the first grafted aryl groups to give a polyaryl layer with a nanometer thickness.^[10a] By integration of the electrochemical current from data in Figure 1a, we derived a surface concentration, Γ , of grafted nitrophenyl groups of $\sim 1.4-2.2 \times 10^{-10}$ mol/cm² (see the Supporting Information (SI) for more details). This value is consistent with values obtained for highly ordered pyrolytic graphite (HOPG) produced electrochemically,^[13,10a] but lower than those obtained for epitaxial graphene produced through a thermal process.^[6b] Based on this value, we can estimate the nitrophenyl group coverage on graphene surfaces to be ~12.7–20.0%, assuming that nitrophenyl groups are spheres with a diameter of 4.34 Å and vertically close-packed on the graphene surfaces (see SI). Realization of monolayer formation using rational strategies of diazonium electrografting, for example by incorporating the protecting groups into diazonium substrates for controlling film growth,^[14] is the challenge for future studies to overcome.



Figure 2. a) Raman spectra of the same graphene sheet before and after diazonium electrografting. b,c) The spatial maps of the I_D/I_G ratios over the same large area of an SLG before and after diazonium electrografting. Inset shows the optical microscopy image of the graphene sheet used. The scale bar is 2 μ m.

To further demonstrate the successful diazonium electrografting of graphenes, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) studies were used to characterize the modified graphene surfaces. Figure 2a shows the comparison of the Raman spectra before and after nitrophenyl grafting. Before the reaction, a single symmetric 2D peak (full width at half-maximum, ca. 34 cm⁻¹), a small G:2D ratio, and a negligible D peak were observed, which indicates that our graphene is a single layer with high quality. As clearly shown in Figure 2a, however, the intensity of the D peak at 1340 cm⁻¹, which is indicative of the presence of defects,^[15] was sharply enhanced after the reaction. This should be ascribed to the breaking of the translational symmetry of the C=C sp² bonds and the formation of C-C sp³ bonds by nitrophenyl grafting. To probe the reaction uniformity, we screened the spatial maps of the intensity ratios of D peaks to G peaks, I_D/I_G , over the same large area of a SLG before and after reaction. As shown in Figure 2b.c. the whole region exhibits uniformity, but a greater degree of disorder is observed after the reaction than before. The large-area uniformity of the reaction proves that diazonium electrografting of graphenes happens at both the edges and the basal plane. Interestingly, we found that bi- or multilayers of graphene in the center (Figure S2, SI) exhibited similar $I_{\rm D}/I_{\rm C}$ ratio before and after electrochemical treatment even after a dozen CV cycles. This proves that single-layer graphenes are more reactive than bi- or multilayers of graphenes (by at least 10 times), which is consistent with previous reports based on thermally or photo-induced radical reactions.^[6d,8] We speculate that the increased reactivity of SLGs results from the surface-induced corrugation, the lack of interlayer π -stacking, and/or the ionized impurities on the substrate.^[6d,8] Note that the intensity of the D peak did not decrease upon ultrasonic rinsing of modified SLGs in both DI water and acetone, indicating a strong covalent bonding of the nitrophenyl groups to the graphene surfaces. The bonding of nitrophenyl groups can be confirmed by XPS. A clean SLG only presented a negligible signal at 406 eV (corresponding to the nitro group); after CV treatments, a remarkable signal was observed at this position (Figure 3). Consequently, these results based on Raman and XPS measurements strongly prove that nitrophenyl groups were covalently attached to the surface of SLGs, in agreement with the CV and AFM characterizations analyzed above.

Diazonium electrografting successfully anchors electron-deficient nitro groups, which can be electrochemically transformed into electron-rich amino groups, on graphene surfaces, thus offering the chance to study the charge transfer effect of these groups on graphene. Firstly, to investigate the electrochemical behavior of nitro groups, we broadened the scanning ranges in CV experiments to the same conditions as shown in Figure 1b. The first monoelectronic wave was immediately followed by a second irreversible six-electron wave located at $E_p = -0.5$ V vs. Ag/AgCl (Figure 1b), which corresponds to the reduction of nitro groups to amino groups (Scheme 1b).^[16] On the second cycle, the reversible redox couple hydroxylamine/nitroso (Figure S1, SI) was observed at $E_{\rm P} = 0.28$ and 0.36 V vs. Ag/AgCl (Figure 1b).^[16] It should be mentioned that the reversible redox behavior of nitro groups was also observed when transferring CV-treated SLGs after thorough ultrasonic rinsing in an aqueous sulfuric acid (0.1 M) solution without NDTB. Again, the rich electrochemical information of nitro groups proves the successful attachment of nitrophenyl groups on graphene surfaces. To further prove the transformation of nitro groups to amino groups, XPS measurements were performed. Figure 4a shows the N1s core level spectra for an as-grafted SLG after



Figure 3. X-ray photoelectron spectroscopic studies of the same SLG sample before and after diazonium electrografting. Inset shows the enlarged the N 1s core-level spectra.



Figure 4. a) The N 1s XPS spectra of the same SLG at different potential biases for 120 s. Inset shows the optical image of a device used. The scale bar is 100 µm. b) Statistical time trace of the drain current, I_d , at the potential bias of -0.6 V (gate potential, $V_g = -40$ V). Inset shows the transistor characteristics of representative devices fabricated from graphene sheets in the same CV bath at different time stages; drain potential, $V_d = 1$ mV.

setting the potential biases from -0.1 V to -0.4 and -0.6 V vs. Ag/AgCl for 120 s. The N 1s spectrum reveals two peaks centered at 400 and 406 eV. The peak with a binding energy of 406 eV should be assigned to the nitrogen of the nitro group, and the signal at 400 eV could correspond to a contribution of the nitrogen in the various forms reduced from the nitro group such as NH₂ (399.4 eV), NHOH (400.3 eV), and azoxy (399.98 eV) groups (Figure S1, SI).^[17] Considering the strong and irreversible CV wave at $E_{\rm P} = -0.5$ V in a protic solution in the current case, we speculate that the classic reduction of nitro groups to amino groups occurs here, and amino groups dominate the contribution to the N 1s peak at 400 eV.^[10c,13,18] The ratios of the two different N 1s peaks, N 1s (400 eV): N 1s (406 eV), for the as-grafted 4-nitrophenyl layer were estimated from the data in Figure 2a to be approximately 0.7, 1.2, and 2.0, which correspond to the increasing potential biases from -0.1 V to -0.4 and -0.6 V, respectively. The increase of the ratios indicates that the polarization of modified SLGs at a more negative potential leads to a loss of nitro groups and an increase of amino moieties. It is remarkable that exploiting rational electrolytic potentials enables us to control the conversion of nitro groups into amino groups,

thus setting the foundation for the following device investigation. We noticed that the actual intensity loss for the 406 eV peak is not counterbalanced by a similar increase of the peak at 400 eV, which suggests that a fraction of the phenyl groups is cleaved from the graphene surface. Further optimization of the electrochemical condition needs to be done for improving the conversion of nitro groups into amino groups.

After having understood the electrochemistry of modified SLGs, we then turned our attention to examine the effect of the electrochemical reaction on the electronic properties of graphene. To rule out the possibility of diazonium grafting that happens on Au surfaces,^[10a] graphene sheets were fabricated according to our previous procedure^[12] and after CV treatments Au/Cr (40 nm/5 nm) electrodes were then directly deposited through a shadow mask to mass-produce graphene transistors (Figure 4a inset).^[19] Figure 4b shows the statistical time evolution of the drain current (I_d) from at least 10 devices obtained from the same sheet for each point at the potential bias of -0.6 V. Noticeably, at the beginning of the electrochemical reaction, the drain current (I_d) showed the dramatic decrease and then reached ~60% of the maximum change in less than 35 s, faster than the case of the reaction of graphene nanoribbons with NDTB (5 min) reported in the literature.^[6a] Interestingly, in addition to observing the same tendency of the changes in I_d from the transistor characteristics of representative devices fabricated from graphene sheets in the same CV bath at the different time stages (Figure 4a inset), another two significant features should be emphasized: i) the gradual shift of the neutrality point $(V_{\rm NP})$ to more negative values and 2) the gradual increase of the on:off ratio. Control experiments in which we treated graphene devices in the same CV conditions but without NDTB showed that exposure of SLGs to the environments used for CV experiments has a very small effect on device characteristics (Figure S4, SI). Previous studies have proven that electron-donating amino groups can behave as n-type dopants, resulting in the negative shift of $V_{\rm NP}$ and the change of the carrier density in graphene.^[3a,20] In the current case, we deduce that the synergistic effect of the breaking of the translational symmetry of the C=C sp² bonds by forming C-C sp³ bonds through nitrophenyl grafting and the n-type doping induced by amino groups through electrochemical reduction of nitro groups results in covalent surface functionalization of graphene and induces doping-like effects, thus tailoring its conductivity, shifting its $V_{\rm NP}$ and modulating its carrier mobility. Realization of the reversible conversion of surface-bounded functional groups and control of their effects on the transport behavior of graphene are challenges for future studies to overcome.

In conclusion, we demonstrated that electrochemistry appears to be an efficient and reliable approach for chemically decorating individual monolayer graphenes. Electrochemical reduction of aryl diazonium salts generates active aromatic radicals that attack graphene surfaces in a mild condition and then form large-area uniform thin films within a few seconds. It is remarkable that tuning the electrolytic potentials realizes the precise control of the conversion of nitro groups into amino groups. Our preliminary electronic experiments suggest that the synergistic effect of covalent C–C sp³ bond formation and the n-type doping of amino groups might induce a bandgap opening

communications

in graphene and modulate their transport properties in a simple and controllable way. The proven simplicity and efficiency of surface electrografting of graphenes and the flexibility to integrate functionalities into electronic devices suggests promising potential of this technique for a wide variety of device applications in both the industrial and scientific communities.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We are grateful to Zhongfan Liu and Zhenxing Wang from Peking University for their help and enlightening discussions. We acknowledge primary financial support from (2009CB623703 and 2012CB921404), NSFC (20833001, 50821061, 2112016, and 21003002).

- [1] a) A. K. Geim, K. S. Novoselov, *Nat. Mater.* 2007, *6*, 183–191;
 b) A. K. Geim, *Science* 2009, *324*, 1530–1534; c) A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* 2009, *81*, 109–162.
- [2] a) The International Technology Roadmap for Semiconductors: http://www.itrs.net/Links/2009ITRS/Home2009.htm (Semiconductor Industry Association, 2009); b) F. Schwierz, Nat. Nanotechnol. 2010, 5, 487–96; c) C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, Angew. Chem. 2009, 121, 7890–7916; Angew. Chem. Int. Ed. 2009, 48, 7752–7777; d) W. R. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding, F. Braet, Angew. Chem. 2010, 122, 2160–2185; Angew. Chem. Int. Ed. 2010, 49, 2114–2138.
- [3] a) F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* 2007, *6*, 652–655;
 b) T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, A. I. Lichtenstein, *Nano Lett.* 2008, *8*, 173–177; c) J. H. Chen, C. Jang, S. Adam, M. S. Fuhrer, E. D. Williams, M. Ishigami, *Nat. Phys.* 2008, *4*, 377–381;
 d) F. Cervantes-Sodi, G. Csanyi, S. Piscanec, A. C. Ferrari, *Phys. Rev. B* 2008, *77*, 165427; e) D. W. Boukhvalov, *Phys. Rev. B* 2008, *77*, 035427; f) D. W. Boukhvalov, M. I. Katsnelson, *Phys. Rev. B* 2008, *78*, 085413; g) J. O. Sofo, A. S. Chaudhari, G. D. Barber, *Phys. Rev. B* 2007, *75*, 153401; h) Q. Wang, X. F. Guo, L. C. Cai, Y. Cao, L. Gan, S. Liu, Z. X. Wang, H. T. Zhang, L. D. Li, *Chem. Sci.* 2011, *2*, 1860–1864.
- [4] a) P. Loh, Q. L. Bao, P. K. Ang, J. X. Yang, J. Mater. Chem. 2010, 20, 2277–2289; b) J. R. Potts, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, Polymer 2011, 52, 5–25; c) S. H. Lee, D. R. Dreyer, J. An, A. Velamakanni, R. D. Piner, S. Park, Y. Zhu, S. O. Kim, C. W. Bielawski, R. S. Ruoff, Macromol. Rapid Commun. 2010, 31, 281–288; d) D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, Chem. Soc. Rev. 2010, 39, 228–240; e) S. H. Lee, H. W. Kim, J. O. Hwang, W. J. Lee, J. Kwon, C. W. Bielawski, R. S. Ruoff, S. O. Kim, Angew. Chem. Int. Ed. 2010, 49, 10084–10088; f) D. R. Dreyer, R. S. Ruoff, C. W. Bielawski, Angew. Chem. Int. Ed. 2010, 49, 9336–9344.
- [5] a) D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A.K.Geim, K.S. Novoselov, *Science* 2009, *323*, 610–613; b) R. Balog, B. Jorgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi,

M. Fanetti, E. Laegsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, L. Hornekaer, *Nat. Mater.* **2010**, *9*, 315–319.

- [6] a) A. Sinitskii, A. Dimiev, D. A. Corley, A. A. Fursina, D. V. Kosynkin, J. M. Tour, ACS Nano 2010, 4, 1949–1954; b) E. Bekyarova, M. E. Itkis, P. Ramesh, C. Berger, M. Sprinkle, W. A. de Heer, R. C. Haddon, J. Am. Chem. Soc. 2009, 131, 1336–1337; c) D. B. Farmer, R. Golizadeh-Mojarad, V. Perebeinos, Y. M. Lin, G. S. Tulevski, J. C. Tsang, P. Avouris, Nano Lett. 2009, 9, 388–392; d) R. Sharma, J. H. Baik, C. J. Perera, M. S. Strano, Nano Lett. 2010, 10, 398–405; e) D. B. Farmer, Y. M. Lin, A. Afzali-Ardakani, P. Avouris, Appl. Phys. Lett. 2009, 94, 213106.
- [7] V. Georgakilas, A. B. Bourlinos, R. Zboril, T. A. Steriotis, P. Dallas, A. K. Stubos, C. Trapalis, *Chem. Commun.* 2010, 46, 1766–1768.
- [8] H. T. Liu, S. M. Ryu, Z. Y. Chen, M. L. Steigerwald, C. Nuckolls, L. E. Brus, J. Am. Chem. Soc. 2009, 131, 17099–17101.
- [9] a) J. T. Robinson, J. S. Burgess, C. E. Junkermeier, S. C. Badescu, T. L. Reinecke, F. K. Perkins, M. K. Zalalutdniov, J. W. Baldwin, J. C. Culbertson, P. E. Sheehan, E. S. Snow, *Nano Lett.* **2010**, *10*, 3001–3005; b) H. Sahin, M. Topsakai, S. Ciraci, *Phys. Rew. B* **2011**, *83*, 115432.
- [10] a) J. Pinson, F. Podvorica, *Chem. Soc. Rev.* 2005, *34*, 429-439; b) J. J. Gooding, *Electroanalysis* 2008, *20*, 573-582; c) P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J. M. Saveant, *J. Am. Chem. Soc.* 1997, *119*, 201-207; d) C. A. Dyke, J. M. Tour, *J. Am. Chem. Soc.* 2003, *125*, 1156-1157; e) H. Uetsuka, D. Shin, N. Tokuda, K. Saeki, C. E. Nebel, *Langmuir* 2007, *23*, 3466-3472; f) D. E. Jiang, B. G. Sumpter, S. J. Dai, *Phys. Chem. B* 2006, *110*, 23628-23632; g) T. Itoh, R. L. McCreery, *Anal. Bioanal. Chem.* 2007, *388*, 131-134; h) M. Delamar, G. Désarmot, O. Fagebaume, R. Hitmi, J. Pinson, J. M. Savéant, *Carbon* 1997, *35*, 801-807.
- [11] a) T. He, D. A. Corley, M. Lu, N. H. Di Spigna, J. L. He, D. P. Nackashi,
 P. D. Franzon, J. M. Tour, J. Am. Chem. Soc. 2009, 131, 10023– 10030; b) T. He, H. J. Ding, N. Peor, M. Lu, D. A. Corley, B. Chen,
 Y. Ofir, Y. L. Gao, S. Yitzchaik, J. M. Tour, J. Am. Chem. Soc. 2008, 130, 1699–1710; c) T. He, J. L. He, M. Lu, B. Chen, H. Pang,
 W. F. Reus, W. M. Nolte, D. P. Nackashi, P. D. Franzon, J. M. Tour, J. Am. Chem. Soc. 2006, 128, 14537–14541.
- [12] L. Gan, S. Liu, D. N. Li, H. Gu, Y. Cao, Q. Shen, Z. X. Wang, Q. Wang, X. F. Guo, Acta Phys-Chim. Sin. 2010, 26, 1151–1156.
- [13] Y. C. Liu, R. L. McCreery, J. Am. Chem. Soc. 1995, 117, 11254–11259.
- [14] a) C. Combellas, F. Kanoufi, J. Pinson, F. I. Podvorica, J. Am. Chem. Soc. 2008, 130, 8576–8577; b) Y. R. Leroux, H. Fei, J.-M. Noel, C. Roux, P. Hapiot, J. Am. Chem. Soc. 2010, 132, 14039–14041.
- [15] a) C. Thomsen, S. Reich, *Phys. Rev. Lett.* 2000, *85*, 5214; b) L. M. Malard, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rep.* 2009, 473, 51–87.
- [16] J. P. Stradins, V. T. Glezer, in*Encyclopedia of the Elements*, Vol. 13 (Eds: A. J. Bard, H. Lund), Marcel Dekker, New York, **1973**, pp. 97–202.
- [17] J. Moulder, W. Stickle, P. Sobol, K. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer Corp, Eden Prairie, MN 1992.
- [18] B. Ortiz, C. Saby, G. Y. Champagne, D. J. Bélanger, *Electroanal. Chem.* **1998**, 455, 75–81.
- [19] Due to chemical doping and/or charge transfer induced by etching agents and polymer resists (iron nitrate and polymethyl methracrylate), the newly made graphenes behave as p-type semiconductors. See references 3h and 12. Graphene transistors made by our previous procedure^[12] show the statistically uniform electronic properties (see Figure S3 in the Supporting Information).
- [20] T. Lohmann, K. von Klitzing, J. H. Smet, Nano Lett. 2009, 9, 1973–1979.

Received: October 31, 2011 Revised: December 12, 2011 Published online: February 22, 2012