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Evidence for formation of multi-quantum dots in hydrogenated graphene

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Abstract

We report the experimental evidence for the formation of multi-quantum dots in a hydrogenated single-layer graphene flake. The existence of multi-quantum dots is supported by the low-temperature measurements on a field effect transistor structure device. The resulting Coulomb blockade diamonds shown in the color scale plot together with the number of Coulomb peaks exhibit the characteristics of the so-called 'stochastic Coulomb blockade'. A possible explanation for the formation of the multi-quantum dots, which is not observed in pristine graphene to date, was attributed to the impurities and defects unintentionally decorated on a single-layer graphene flake which was not treated with the thermal annealing process. Graphene multi-quantum dots developed around impurities and defect sites during the hydrogen plasma exposure process.

Keywords: Multi-quantum dots, Single-layer graphene flake, Coulomb peaks

Background

Graphene, a mono-layer of carbon atoms arranged in a honeycomb lattice, has extraordinary electrical properties, such as the gapless linear dispersion [1-4]. In order to realize graphene-based nanoelectronic device applications, many research groups tried to open the energy bandgap in the gapless linear dispersion in different ways, for instance, graphene nanoribbons [5,6] and bilayer graphene applied by the electric field [7-9]. Recently, hydrogenated graphene attracts a great deal of attention because of its bandgap behavior driven by the chemical functionalization [10-17]. The adsorbed atomic hydrogen atoms form three-dimensional C-H sp^3 covalent bonds with carbon atoms by interrupting C-C sp^2 bonds, thus, removing the conducting π bonds and opening a bandgap [11,18,19]. In 2010, Singh and co-workers proposed that graphene could form natural host for graphene multi-quantum dots, clusters of vacancies in hydrogen sublattice [20]. According to the surface dynamics, thermally energetic hydrogen atoms adsorbed on graphene could be desorbed from the graphene surface or migrate

to the proper bonding sites or nucleate randomly (due to short diffusion length) to form dense islands of coexisting two-dimensional phases, C-H and C-C [14,20,21]. On the other hand, some reports proposed that the multi-quantum dots were unintentionally formed by impurities or defects in single-wall carbon nanotubes, which belong to the same honeycomb lattice as single-layer graphene [22-24].

In this study, we propose a possible explanation based on the aforementioned mechanism for the formation of multi-quantum dots on our single-layer graphene flake and supported by the low-temperature electrical transport measurements.

Methods

A graphene field-effect transistor (FET) device was fabricated for the investigation described in this work. A single-layer graphene flake, mechanically exfoliated from natural graphite, was deposited onto a highly doped Si substrate capped with a 300-nm-thick SiO₂ layer, serving as a back gate [25]. Optical microscopy was used to locate graphene flakes and confirms that it was a single layer shown in the inset to Figure 1a [1,25]. Two Ti/Au contacts (5/50 nm) were patterned, using e-beam lithography and lift-off processing, into the source and drain contacts. To retain the defects and impurities in the

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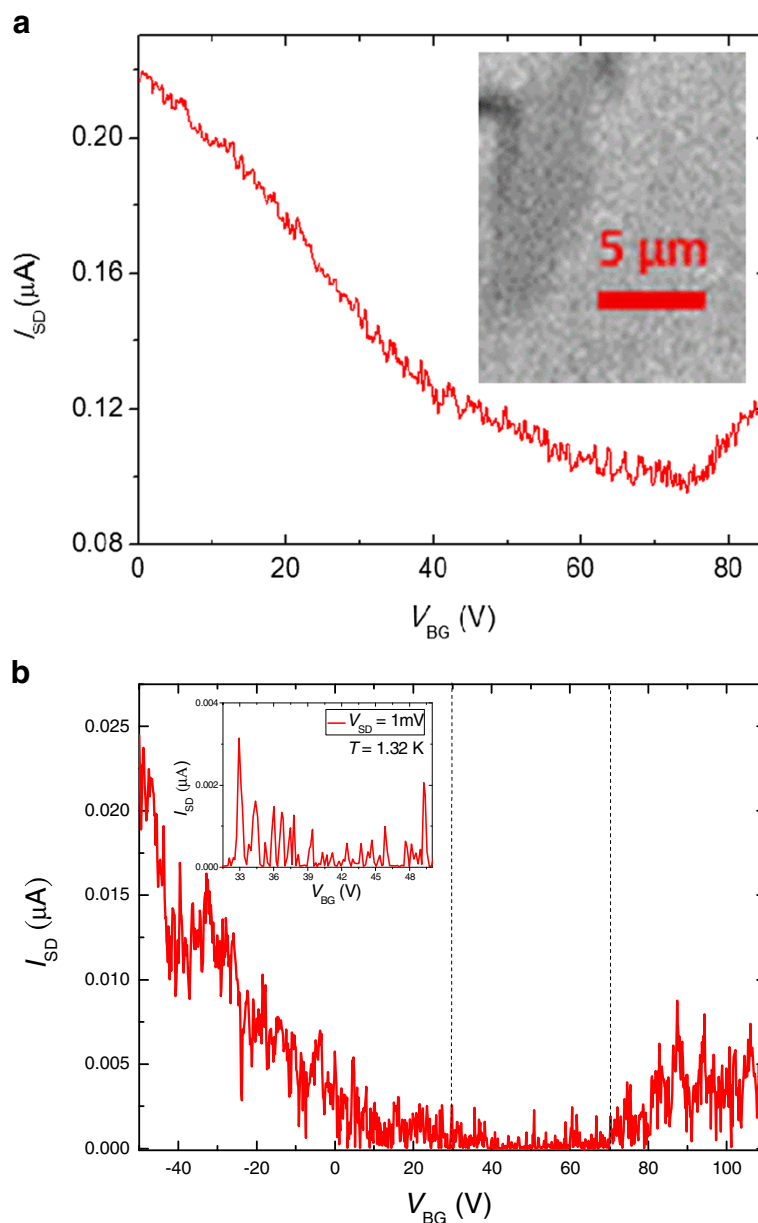


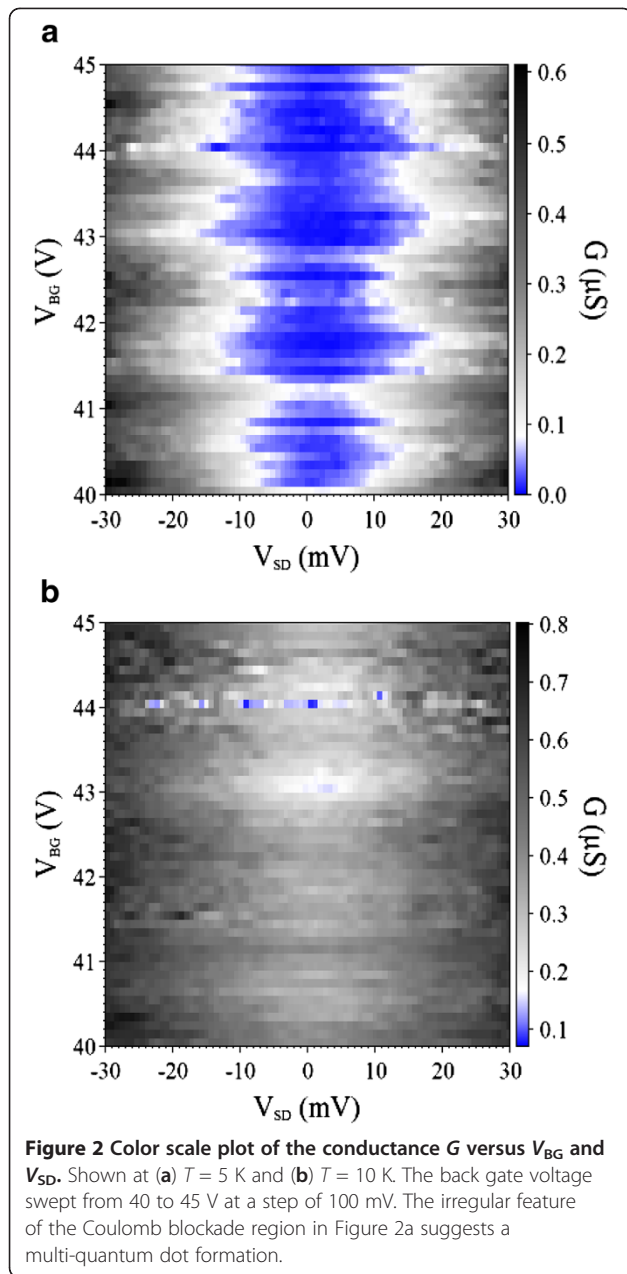
Figure 1 Source-drain current (I_{SD}) dependence. (a) I_{SD} measured at V_{BG} from $V_{BG} = 0$ to 85 V at 1.32 K with a fixed source and drain voltage, $V_{SD} = 0.1$ mV, before hydrogen plasma treatment. The neutrality point voltage V_{NP} is near 74 V. Inset: the optical image of a single-layer graphene flake in contrast (b) I_{SD} measured from $V_{BG} = -50$ to 110 V at $T = 1.41$ K with a fixed source and drain voltage $V_{SD} = 20$ mV after hydrogen plasma treatment. The Coulomb blockade oscillations occur between 30 and 50 V. Inset: the Coulomb peaks at $T = 1.32$ K with a fixed source and drain voltage $V_{SD} = 1$ mV.

graphene flakes to facilitate the formation of multi-quantum dots, the FET device was conditioned by the hydrogen plasma at conditions of power = 16 W and pressure = 0.2 Torr for 6 s without post-exfoliation annealing treatment [10,26].

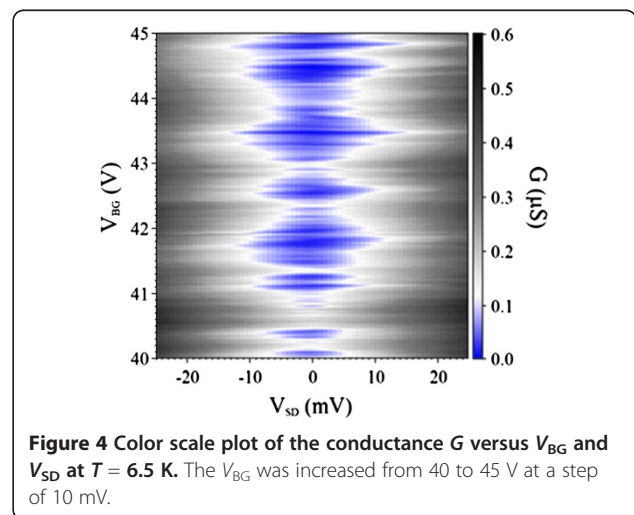
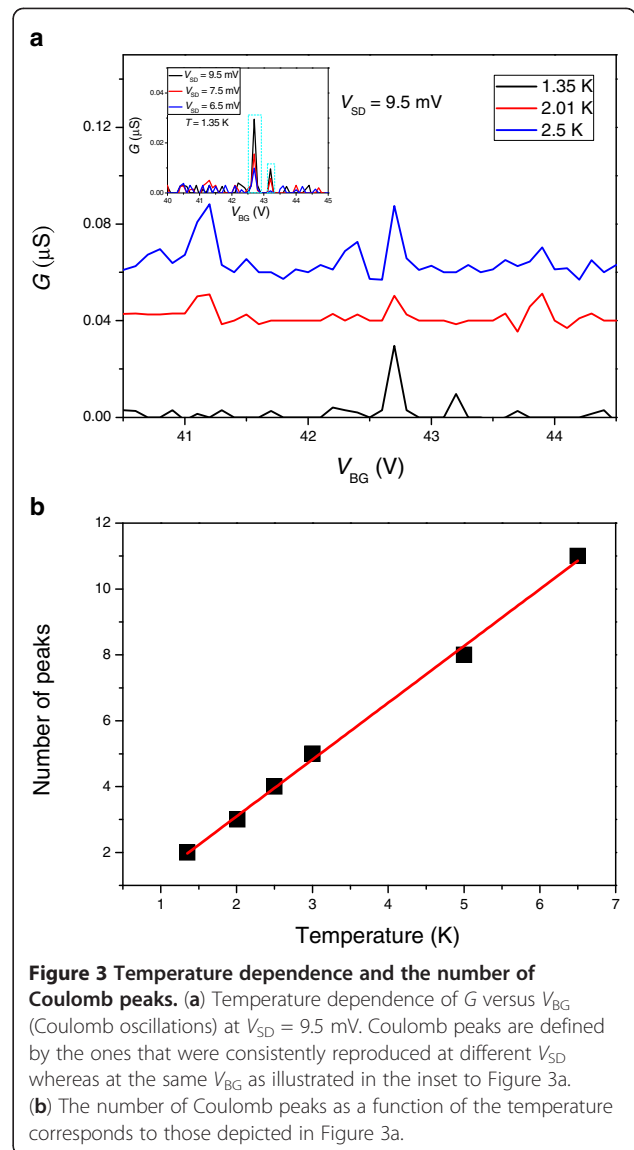
An Oxford top-loading He⁴ cryostat was used to carry out the two-terminal conductance measurements using standard AC lock-in technique at 77 Hz with a DC bias at the temperature range between 1.3 and 40 K.

Results and discussion

Figure 1a shows the source-drain current (I_{SD}) dependence on the back gate voltage (V_{BG}) measured at the charge neutrality point, $V_{NP} = 74$ V, with a fixed source-drain voltage $V_{SD} = 0.1$ mV at $T = 1.32$ K before the hydrogen plasma treatment. The charge neutrality point, which is far from the zero voltage, can be attributed to the hole-doping impurities left on the graphene flake [27,28]. Figure 1b shows the I_{SD} - V_{BG} measurement after



hydrogen plasma treatment. Strong suppression of the source-drain current in the Coulomb blockade oscillation region (between the dashed lines) with a fixed source-drain voltage $V_{SD} = 20$ mV at $T = 1.41$ K is observed. To assure the Coulomb peaks in the Coulomb blockade oscillation region, we examined the Coulomb peaks with a fixed $V_{SD} = 1$ mV at $T = 1.32$ K shown in the inset to Figure 1b [29]. To further investigate the Coulomb blockade effect, the Coulomb blockade color scale plot of the conductance G in a V_{BG} - V_{SD} plane was adopted for a better illustration of the existence of multi-quantum dots in our graphene flake sample; overlapped diamond-shape pattern was expected.



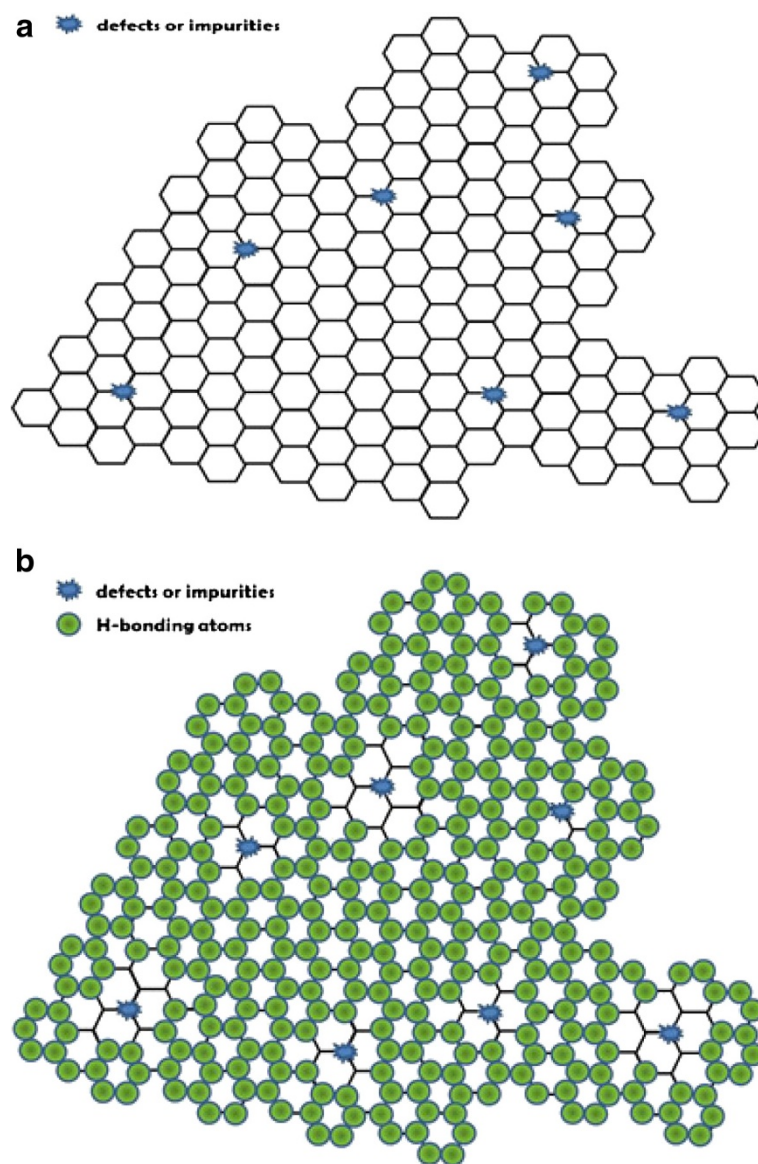


Figure 5 Schematics of defects and impurities and the formation of multi-quantum dots. (a) Schematic of defects and impurities on a single-layer graphene flake before hydrogen plasma treatment. **(b)** Schematic of the formation of multi-quantum dots on hydrogen graphene. The white regions, containing the defects and impurities, enclosed by the hydrogen atoms (the green dots) represent graphene multi-quantum dots.

Figure 2 shows a color scale plot of the differential conductance G versus V_{BG} and V_{SD} at $T = 5$ K. The overlap of Coulomb diamonds, so-called 'Coulomb shards', was observed [30]. The Coulomb shards, which is also called stochastic Coulomb blockade, occurred due to the multi-quantum dots coupling in series during the carrier transport tunneling process [30-33]. Results of the measurements indicated that the multi-quantum dots formed in a two-dimensional manner. In other words, carriers could tunnel through the potential barriers of the quantum dots dispersed randomly. Coulomb shards disappeared while the temperature was increased

to $T = 10$ K as shown in Figure 2b, whereby it implied that thermal energy dominated the carrier transport behavior rather than the multi-quantum dot Coulomb blockade tunneling [31-33].

The stochastic Coulomb blockade in the multi-quantum dot system is further supported by investigating the temperature dependence of the number of the Coulomb peaks. Figure 3a shows the differential conductance as a function of V_{BG} between 40.5 and 44.5 V at different temperatures with a fixed $V_{SD} = 9.5$ mV. To distinguish the real Coulomb blockade peaks from the background noise, only reproducible peaks observed at

the same V_{BG} with varying V_{SD} ($V_{SD} = 6.5, 7.5,$ and 9.5 mV) are considered, shown in the inset to Figure 3a. The oscillations in Figure 3a are non-periodic, and the number of Coulomb peaks increases monotonically as the temperature is increased as shown in Figure 3b [22,30,31]. Both the aforementioned are the typical characteristics of the stochastic Coulomb blockade which suggests a formation of multi-quantum dots [31-34].

For a better visualization of the individual Coulomb diamond in the blockade region, the Coulomb diamond color scale plot of the conductance G with a better resolution $\Delta V_{BG} = 10$ mV at $T = 6.5$ K was shown in Figure 4. The clear Coulomb diamonds indicated that the charging effect existed in our hydrogenated graphene system [35-37].

To justify the revealed overlapped Coulomb diamonds in our hydrogenated graphene system, a possible explanation for the formation of the multi-quantum dots is depicted in Figure 5. Without the post-exfoliation annealing process, the impurities or/and as-grown defects, shown as dots in Figure 5a, existed on the single-layer graphene flake [38-40]. In the vicinity of defects (mostly vacancies) or impurities, hydrogen passivated the edge carbon atoms on the vacancy sites or substituted impurities by keeping the C-C sp^2 bonding structure. In the defect/impurity-free regions, the C-H bonding transformed the C-C bonding from sp^2 into sp^3 structure [10,26]. After hydrogen plasma exposure, graphene multi-quantum dots were formed in the proximity of defects/impurities, depicted in Figure 5b. The asymmetric hydrogenated graphene quantum dot array could be treated as the sequential tunneling of charges through the two-dimensional (2D) array of single-layer graphene quantum dots [41]. The experimental results indicated that 2D multi-quantum dot array can be achieved by the hydrogenation of exfoliated graphene flakes experiencing no annealing process. More detailed fundamental understanding of the origin of multi-quantum dots formed on the non-annealed hydrogenated graphene flakes can greatly promote the development of graphene-based multi-quantum dot devices for quantum computation [42,43].

Conclusions

Two-dimensional multi-quantum dots can be realized on a mechanically exfoliated graphene flake followed by the hydrogen plasma treatment without executing post-exfoliation thermal annealing. The overlapped Coulomb blockade diamonds observed from the electrical measurements, as well as the monotonic increase of the number of Coulomb peaks with the ascending temperature, suggest the formation of two-dimensional multi-quantum dots that is unprecedented on the annealed graphene flakes with similar hydrogenation processes. Therefore, we suggest a defect (or vacancy) and impurity-related mechanism to

account for the formation of the multi-quantum dots discovered on our device. Further characterizations, such as AFM or SEM, on the atomic structure of un-annealed graphene layers might shed light on the origin of the quantum dot formation, whereas the degree of post-growth annealing could be utilized to engineer the quantum dots in terms of its size, density, shape, or charging states in a cost-effective way for quantum chip device applications.

Abbreviations

FET: field-effect transistor; 2D: two-dimensional.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

CC and RKP fabricated the samples. CC, RKP, and MRC performed the measurements. CC and HDL drafted the paper. TMC and STL provided models, interpretation, and possible explanations for the results. CGS and CTL coordinated the project. All authors read and approved the final manuscript.

Authors' information

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References

1. Geim AK, Novoselov KS: **The rise of graphene.** *Nat Mater* 2007, **6**:183.
2. Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, Geim AK: **The electronic properties of graphene.** *Rev Mod Phys* 2009, **81**:109.
3. Zhao S, Lv Y, Yang X: **Layer-dependent nanoscale electrical properties of graphene studied by conductive scanning probe microscopy.** *Nano Res Letts* 2011, **6**:498.

4. Ishikawa R, Bando M, Morimoto Y, Sandhu A: **Doping graphene films via chemically mediated charge transfer.** *Nano Res Letts* 2011, **6**:111.
5. Han MY, Özyilmaz B, Zhang Y, Kim P: **Energy band-gap engineering of graphene nanoribbons.** *Phys Rev Lett* 2007, **98**:206805.
6. Son Y-W, Cohen ML, Louie SG: **Energy gaps in graphene nanoribbons.** *Phys Rev Lett* 2006, **97**:216803.
7. Castro EV, Novoselov KS, Morozov SV, Peres NMR, Santos JMB L, Nilsson J, Guinea F, Geim AK, Castro Neto AH: **Biased bilayer graphene: semiconductor with a gap tunable by the electric field effect.** *Phys Rev Lett* 2007, **99**:216802.
8. Ohta T, Bostwick A, Seyller T, Horn K, Rotenberg E: **Controlling the electronic structure of bilayer graphene.** *Science* 2006, **313**:951.
9. Oostinga JB, Heersche HB, Liu X, Morpurgo AF, Vandersypen LMK: **Gate-induced insulating state in bilayer graphene devices.** *Nature* 2008, **7**:151.
10. Elias DC, Nair RR, Mohiuddin TMG, Morozov SV, Blake P, Halsall MP, Ferrari AC, Boukhvalov DW, Katsnelson MI, Geim AK, Novoselov KS: **Control of graphene's properties by reversible hydrogenation: evidence for graphene.** *Science* 2009, **323**:610.
11. Sofo JO, Chaudhari AS, Barber GD: **Graphene: a two-dimensional hydrocarbon.** *Phys Rev B* 2007, **75**:153401.
12. Boukhvalov DW, Katsnelson MI: **Chemical functionalization of graphene.** *J Phys Condens Matter* 2009, **21**:344205.
13. Ryu S, Han YM, Maultzsch J, Heninz TF, Kim P, Steigerwald ML, Brus LE: **Reversible basal plane hydrogenation of graphene.** *Nano Lett* 2008, **8**:4597.
14. Balog R, JØrgensen B, Nilsson L, Andersen M, Rienks E, Bianchi M, Fanetti M, Lægsgaard E, Baraldi A, Lizzit S, Slijvancanin Z, Besenbacher F, Hammer B, Pedersen TG, Hofmann P, Hornekær L: **Bandgap opening in graphene induced by patterned hydrogen adsorption.** *Nat Mater* 2010, **9**:315.
15. Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommett GHB, Evmenenko G, Nguyen ST, Ruoff RS: **Preparation and characterization of graphene oxide paper.** *Nature* 2007, **448**:457.
16. Park S, Ruoff RS: **Chemical methods for the production of graphenes.** *Nat Nanotechnol* 2009, **4**:217.
17. Chuang C, Puddy RK, Lin H-D, Lo S-T, Chen T-M, Smith CG, Liang C-T: **Experimental evidence for efros-shklovskii variable range hopping in hydrogenated graphene.** *Solid State Commun* 2012, **152**:905.
18. Boukhvalov DW, Katsnelson MI, Lichtenstein AI: **Hydrogen on graphene: electronic structure, total energy, structural distortions and magnetism from first-principles calculations.** *Phys Rev B* 2008, **77**:035427.
19. Withers F, Russo S, Dubois M, Craciun MF: **Tuning the electronic transport properties of graphene through functionalisation with fluorine.** *Nano Res Letts* 2011, **6**:526.
20. Singh AK, Penev ES, Yakobson BI: **Vacancy clusters in graphene as quantum dots.** *ACS Nano* 2010, **4**:3510.
21. Luth H: *Surface and Interfaces of Solid Materials.* New York: Springer Press; 1995.
22. Suzuki M, Ishibashi M, Ida T, Aoyagi Y: **Quantum dot formation in single-wall carbon nanotubes.** *Jpn J Appl Phys* 1915, **2001**:40.
23. McEuen PL, Bockrath M, Cobden DH, Yoon Y-G, Louie SG: **Disorder, pseudospins, and backscattering in carbon nanotubes.** *Phys Rev Lett* 1999, **83**:5098.
24. Zhou C, Kong J, Yenilmez E, Dai H: **Modulated chemical doping of individual carbon nanotubes.** *Science* 2000, **290**:1552.
25. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA: **Electric field effect in atomically thin carbon films.** *Science* 2004, **306**:666.
26. Luo Z, Yu T, Kim K-J, Ni Z, You Y, Lim S, Shen Z, Wang S, Lin J: **Thickness-dependent reversible hydrogenation of graphene layers.** *ACS Nano* 2009, **3**:1781.
27. Ponomarenko LA, Yang R, Mohiuddin TM, Katsnelson MI, Novoselov KS, Morozov SV, Zhukov AA, Schedin F, Hill EW, Geim AK: **Effect of a high-k environment on charge carrier mobility in graphene.** *Phys Rev Lett* 2009, **102**:206603.
28. Connolly MR, Chiou KL, Smith CG, Anderson D, Jones GAC, Lombardo A, Fasoli A, Ferrari AC: **Scanning gate microscopy of current-annealed single layer graphene.** *Appl Phys Lett* 2010, **96**:113501.
29. Ponomarenko LA, Schedin F, Katsnelson MI, Yang R, Hill EW, Novoselov KS, Geim AK: **Chaotic dirac billiard in graphene quantum dots.** *Science* 2008, **320**:356.
30. Nazarov YV, Blanter YM: *Quantum Transport Introduction to Nanoscience.* Cambridge: Cambridge University Press; 2009.
31. Ruzin IM, Chandrasekhar V, Levin EI, Glazman LI: **Stochastic Coulomb blockade in a double-dot system.** *Phys Rev B* 1992, **45**:13469.
32. Kemerink M, Molenkamp LW: **Stochastic Coulomb blockade in a double quantum dot.** *Appl Phys Lett* 1994, **65**:1012.
33. Ishibashi K, Suzuki M, Ida T, Aoyagi Y: **Formation of coupled quantum dots in single-wall carbon nanotubes.** *Appl Phys Lett* 1864, **2001**:79.
34. Notargiacomo A, Gaspare LD, Scappucci G, Mariottini G, Evangelisti F, Giovine E, Leoni R: **Single-electron transistor based on modulation-doped SiGe heterostructures.** *Appl Phys Lett* 2003, **83**:302.
35. Guttinger J, Stampfer C, Fery T, Ihn T, Ensslin K: **Transport through a strongly coupled graphene quantum dot in perpendicular magnetic field.** *Nano Res Letts* 2011, **6**:253.
36. Liu XL, Hug D, Vandersypen MK: **Gate-defined graphene double quantum dot and excited state spectroscopy.** *Nano Letts* 2010, **10**:1623.
37. Molitor F, Dröscher S, Güttinger J, Jacobsen A, Stamper C, Ihn T, Ensslin K: **Transport through graphene double dots.** *Appl Phys Letts* 2009, **94**:222107.
38. Ishigami M, Chen JH, Cullen WG, Fuhrer MS, Williams EW: **Atomic structure of graphene on SiO₂.** *Nano Lett* 2007, **7**:1643.
39. Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, Novoselov KS: **Detection of individual gas molecules adsorbed on graphene.** *Nat Mater* 2007, **6**:652.
40. Hashimoto A, Suenage K, Gloter A, Urita K, Iijima S: **Direct evidence for atomic defects in graphene layers.** *Nature* 2004, **430**:870.
41. Joung D, Zhai L, Khondaker SI: **Coulomb blockade and hopping conduction in graphene quantum dots array.** *Phys Rev B* 2011, **83**:115323.
42. Nielsen MA, Chuang IL: *Quantum Computation and Quantum Information.* Cambridge: Cambridge University Press; 2000.
43. Loss D, DiVincenzo DP: **Quantum computation with quantum dots.** *Phys Rev A* 1998, **57**:120.

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