NANO LETTERS

Letter

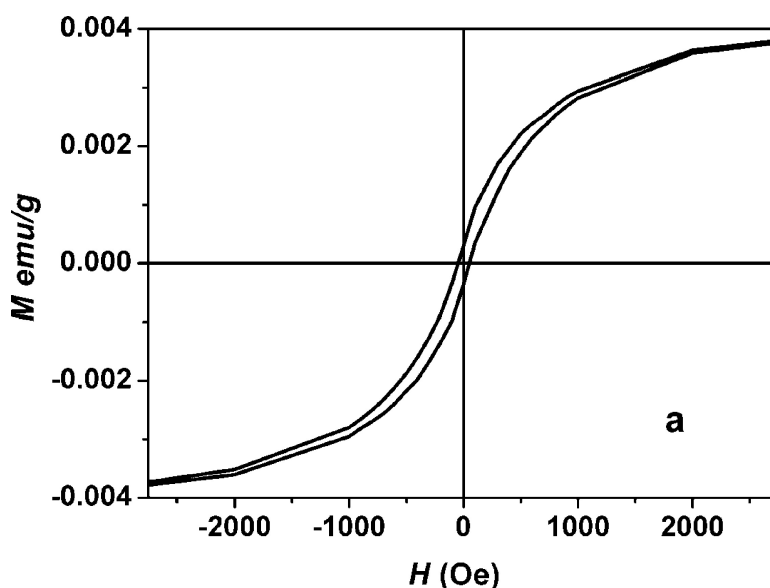## Room-Temperature Ferromagnetism of Graphene

Yan Wang, Yi Huang, You Song, Xiaoyan Zhang, Yanfeng Ma, Jiajie Liang, and Yongsheng Chen

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Room-Temperature Ferromagnetism of Graphene

Yan Wang,[†] Yi Huang,*[,†] You Song,[‡] Xiaoyan Zhang,[†] Yanfeng Ma,[†] Jiajie Liang,[†] and Yongsheng Chen*[,†]

Key Laboratory of Functional Polymer Materials and Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China, and State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ABSTRACT

Aiming at molecular-based magnets, ferromagnetism of pure carbon-based materials is fundamentally and technologically extremely important for many applications. While it is still not fully understood, many recent theoretical works have suggested that one-atom-thick two-dimensional graphene materials may show ferromagnetism due to the existence of various defects or topological structures as the spin units and the possible long-range ordered coupling among them. Here, we report the experimental results on the ferromagnetism of graphene-based materials at room temperature. The observed room-temperature ferromagnetism is believed to come from the defects on graphene.

Organic magnets are both fundamentally and technologically extremely important and have been sought for many years.[1] However, ferromagnetism in organic materials is usually observed only at very low temperatures,[2,3] and the reports about the existence of intrinsic magnetism of pure carbon-based materials,[4,5] which have only s/p electrons, have been much controversial due to trace amounts of Fe or other magnetic impurities. The scientific community became much more aware of the possible existence of room-temperature carbon-based and metal-free organic ferromagnets since the serendipitous discovery of strong signals in rhombohedral C_{60} was reported in 2001.[6] While it was retracted in 2006, the article did raise (again) the possibility and expectation of pure carbon-based materials with Curie temperature above room temperature. Several groups have reported the experimental ferromagnetism of highly oriented pyrolytic graphite (HOPG) materials.[4,5,7] A spongy, ultralightweight form of carbon with a strong but temporary ferromagnetism was also reported in 2004.[8] Esquinzai et al. have reported that HOPG samples bombarded with protons appeared ferro- or ferrimagnetism with a stable magnetic ordering at room temperature.[7] Their results have provided a possible answer to the origin of ferromagnetism in other carbon-based structures, which is not correlated with the magnetic impurities. This kind of magnetic behavior may be ascribed to itinerant electron magnetism rather than superexchange magnetic coupling interaction between spins like molecule-based magnets. Many theoretical studies[9,10] have also suggested the highly possible existence of ferromagnetism for pure carbon materials, even at room temperature. The recent discovery of graphene,[11] one-atom-thick two-dimensional (2D) layers of sp2-bonded carbon, and its many unusual properties have prompted intensive studies for this 2D nanoscale pure carbon material. In addition to their extraordinary mechanical[12] and electronic transport[13,14] properties, numerous reports have predicted ferromagnetic ordering could exist among various defects on graphene structures, such as vacancy, topological defects or frustration, and hydrogen chemisorption or perhaps the edge.[4,15−19] Interestingly, the proposed simplest building block[17,18] for these graphene fragments with nonzero net spin has a phenalenyl molecule structure unit and quite some of these stable radical organic molecules with this or similar structures have been synthesized and characterized elegantly by Haddon and other groups.[20−22] At solid state, these pure organic magnetic materials also show interesting semiconducting properties. The large π-conjugation in these radical organic molecules offers the required stability for the unpaired electrons in these structures as net spin units.[20−22] Also, the molecular structure of bulk graphene materials produced using wet chemistry[23−25] from graphite is similar (but much larger) with many large fused polyaromatic "graphene molecules" reported by Mullen and other

---

* Corresponding authors, yschen99@nankai.edu.cn and yihuang@nankai,edu.cn.
† Key Laboratory of Functional Polymer Materials and Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University.
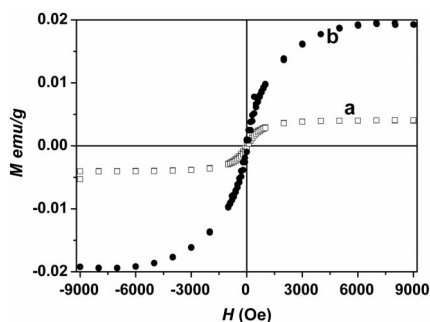‡ State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University.

Figure 1. Magnetization hysteresis loops at 300 K in the range of −10 kOe < H < +10 kOe. (a) Sample Graphene-400 (□), M_s = 0.004 emu/g. (b) Sample Graphene-600 (●), M_s = 0.020 emu/g.

groups.[26]And these materials, with 2D graphene molecular structures, are rather stable at ambient condition with many interesting electronic and optoelectronic properties. Furthermore, it has been shown theoretically that zigzag-edged graphene flakes with topological structures can have ferromagnetic order and linearly scaling net spin and these structures are stable at room temperature with an energy gap of 0.3−0.5 eV at their Fermi level.[17] Very recently, we have reported the results of transparent electrodes[13] and photovoltaic devices[27] using these bulk solution-processable functionalized graphene (SPFGraphene) materials. In this Letter, we report the room-temperature ferromagnetism of graphene based on these soluble graphene materials.

Perfect graphene does not exist naturally, but bulk and solution-processable functionalized graphene materials including graphene oxide (GO) can now be prepared.[13,23−25] The graphene material used in this study was prepared from GO, which was prepared by the modified Hummers method[28] from graphite as described elsewhere.[27] GO can be dispersed and processed at individual sheet level in water.[27,29] The graphene samples for magnetic studies in this work were prepared by two steps. GO was first reduced using hydrazine to get the partially reduced graphene oxide sample, and then it was annealed at different temperatures under an argon environment to generate the final products for the magnetization measurement. Three samples, Graphene-400, Graphene-600, and Graphene-800, were prepared at annealing temperature of 400, 600, and 800 °C, respectively. Details of the experimental procedure are described in Methods below. The magnetization measurements were performed with a SQUID XL-7 magnetometer from Quantum Design with the reciprocating sample option and a sensitivity of ≤10^{-7} emu.

Figure 1 shows the magnetization hysteresis loops measured at temperature of 300 K in the field range of −10 kOe < H < +10 kOe for the two samples of Graphene-400 and Graphene-600, where saturation of the magnetization is clearly seen at about M_s = 0.004 and 0.020 emu/g after subtracting the diamagnetic background. The magnetization was saturated at 1500 and 6000 Oe for samples Graphene-400 and Graphene-600, respectively. In a smaller field range as shown in Figure 2, an enlarged and clearer magnetization hysteresis loop was observed for both samples of Graphene-400 and Graphene-600.

These results clearly show that the graphene samples have a weak ferromagnetic ordering at room temperature. So we further measured the magnetization of the same samples at 2 K (Figures 3 and 4). As Figure 3 shows, the saturation magnetization M_s reaches 0.25 and 0.90 emu/g for Graphene-400 and Graphene-600, respectively, significantly increased compared with that at room temperature. We have also measured the sample Graphene-800 prepared at 800 °C from the same precursor sample as for Graphene-400 and Graphene-600. However, the Graphene-800 sample did not show clear ferromagnetism. The reason for this is yet to be understood.

The reports about the existence of intrinsic magnetism of pure organic materials have been very controversial, and the purity of the material is critical. We took great care to eliminate any possible ferromagnetic impurities. Since all the three samples (Graphene-400, Graphene-600, and Graphene-800) came from the same source, e.g., the partially reduced graphene oxide, the magnetic contribution from the possible metallic impurity should be similar for all these three samples. So the negative result for ferromagnetism of Graphene-800 suggests that metallic impurity should not be the reason (or at least the major one) of the observed ferromagnetism of Graphene-400 and Graphene-600. The expected M_s value would be 502 emu/g,[30] assuming all the carbon atoms have a ferromagnetic unpaired electron. Thus, the observed M_s (0.9 emu/g) value at 2 K for sample Graphene-600 corresponds to ~0.2% carbon atoms.

To further check the contribution from magnetic impurities, magnetic measurements were also carried out for the GO samples and those after only hydrazine reduction or annealing and no ferromagnetism was observed for these three samples. The total amount of magnetic (Fe, Ni, Co) impurities by atomic absorption spectrometry (AAS) analysis was 48.6 ppm for the partially reduced graphene oxide samples before annealing. More importantly, the total amount of magnetic impurities by AAS was 86 ppm for Graphene-600 after annealing. The increase of magnetic impurity may be ascribed to the weight loss for the functional groups. The observed M_s (0.9 emu/g) value for sample Graphene-600 at 2 K is equivalent to ~4700 ppm Fe, 2 orders greater than the AAS analysis result. Furthermore, we have carried out the magnetic measurements for five batches of samples on three different SQUID instruments, and the results are quite repeatable. All these results indicate it is very likely that the room-temperature ferromagnetism comes from the intrinsic properties of graphene-based materials.

As mentioned above, many theoretical works have been published about the possible ferromagnetism and its origin for graphene. But while all the theoretical works so far show that it is quite easy to nucleate magnetic moments in the defective sp^2 carbon samples, the fact that they order ferromagnetically is yet to be fully understood. The structure of GO contains many C−O−C (epoxide), C−OH, −COOH, and C=O groups on the main graphene skeleton.[13,29] Initial reduction of GO with hydrazine would remove some of these groups and restore some of the damaged sp^2 carbon conjugation during the GO preparation process and, thus, increase its electrical conductivity.[31] During further annealing process
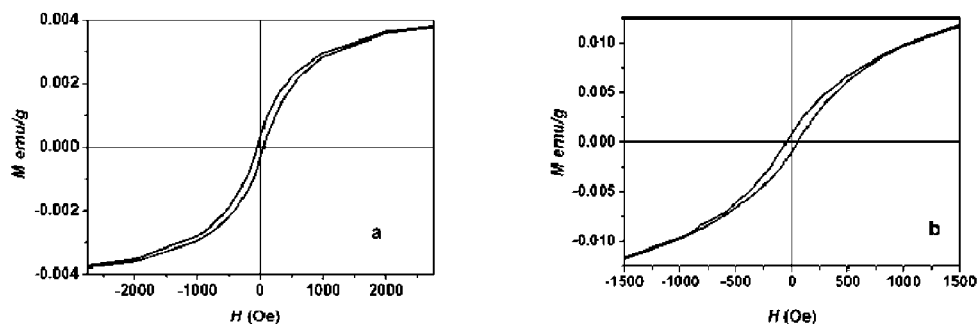
Figure 2. An enlarged M vs H loop at $T = 300$ K. (a) Sample Graphene-400, hysteresis was observed in the field range -2500 Oe $< H < 2500$ Oe, $H_c = 46$ Oe. (b) Sample Graphene-600, hysteresis was observed in the field range -1500 Oe $< H < 1500$ Oe, $H_c = 40$ Oe.

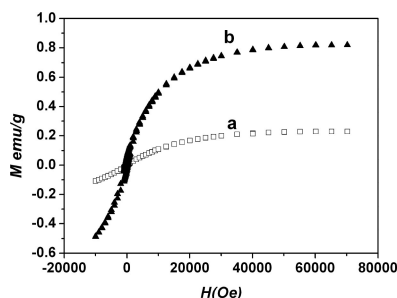**Figure 3.** Magnetization hysteresis loops at 2 K. (a) Sample Graphene-400 (□), $M_s = 0.25$ emu/g. (b) Sample Graphene-600 (▲), $M_s = 0.90$ emu/g.

under argon, most if not all of the functional groups would be removed from the graphene sheets. Thus, the isolated π-conjugation area on the pristine graphene sheet should be restored (or partially) again, resulting in improved electrical conductivity (10^2-10^3 Ω/square[13,32]) of these graphene sheets, with structure more or less like those "graphene molecules".[26] And more importantly for its magnetic properties, vacancies and topological defects with unpaired electrons would be introduced on the graphene sheets during this process of annealing, due to the removal of the functional groups, such as carbon dioxide, OH, etc.[18,32] The removal of these groups under certain conditions would introduce various edge and defect sites with spin units on sp[2] carbon materials, and this has been studied thoroughly and elegantly by Radovic.[18] These defects could include carbene, benzye,[18] phenylene units,[17] topological defects,[16,18,32] or a more complicated zigzag edge.[18] It should be pointed out that both theoretical[4,7,8,18] and experimental[4,7] works have proved that

most if not all the above unit structures with net spin are stable within a large conjugation system such as in graphene at room temperature. We want further to emphasize that many stable molecules with structures the same or similar as those proposed spin units[15−18,32] in graphene have been isolated and characterized fully mainly by Haddon's group,[20−22] and the reason for their stability is due to the huge π-conjugation in these molecules. Then, if indeed the long-range orderly magnetically coupling of these spins exists, for example with the PKKY mechanism[15] via either intramolecular interaction in individual graphene sheets or/ and intermolecular/lattice interaction between neighboring graphene sheets,[9,15−19,21,33] the ferromagnetism could then arise. While results are based on current theoretical work and experimental results, we believe that the room-temperature ferromagnetism is an intrinsic property of graphene-based materials, and we are looking for direct and conclusive evidence, such as some topographic/structural data. Furthermore, the confirmation and understanding for this pure organic material room-temperature ferromagnetism, as one of the most difficult topics in physics and material science, certainly deserve much more through study, and the results could be very rewarding with far and wide implications.

In summary, we have observed the room-temperature ferromagnetism of bulk graphene materials prepared from soluble functionalized graphene sheets. The possible origin of the ferromagnetism may come from the long-range coupling of spin units existing as defects in graphene sheets, which are generated in the annealing process. But more direct evidence is needed for a conclusion. The likely intrinsic room-temperature ferromagnetism, combined with its semi-
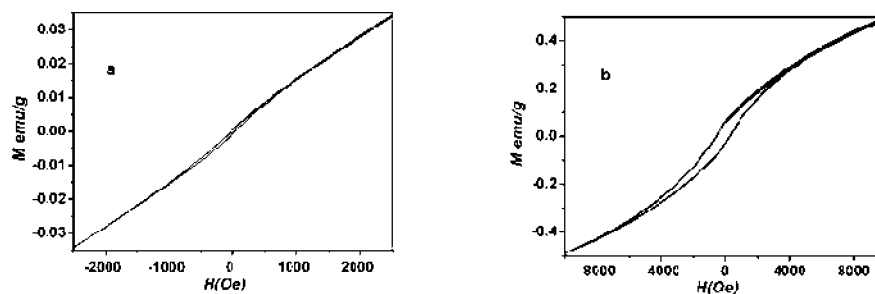

Figure 4. An enlarged M vs H loop at $T = 2$ K. (a) Sample Graphene-400, hysteresis observed in the field range -2500 Oe $< H < 2500$ Oe, $H_c = 33$ Oe. (b) Sample Graphene-600, hysteresis observed in the field range -6000 Oe $< H < 6000$ Oe, $H_c = 596$ Oe.

conductivity and solution-processing capability, should have wide-reaching implications in material science, and these collective properties could make graphene-based materials a competent choice for many important device applications, including spintronic, magnetoresistance, magnetic memory devices, and so on. Our results may also prompt more thorough and carefully studies for the room-temperature ferromagnetism of pure carbon-based materials, including C_{60} and carbon nanotubes.

Methods. *Materials.* Graphene oxide (GO) was synthesized by the modification of Hummer's method[13,25] and described elsewhere.[13] GO was placed in a vacuum desiccator, where a piece of filter paper saturated with the chemical reducing agent hydrazine (80% water solution) was placed for the first step of reduction. The reducing reaction time was controlled for 24 h to generate the partially reduced graphene oxide. The same partially reduced graphene oxide sample was then separated into batches of 100 mg and then annealed in argon atmosphere at 400, 600, and 800 °C to get the samples of Graphene-400, Graphene-600, and Graphene-800, respectively. The heating rate from room temperature to the desired temperature was 3 °C/min, and then the temperature was kept at the desired temperature for 3 h and finally cooled down to room temperature. The annealing and cooling processes were strictly applied under argon atmosphere.

Instruments. Magnetization measurements were performed using a Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer. The powder sample of graphene was packed in a bit of diamagnetic plastic film, and then the packed sample was put in a diamagnetic plastic straw and impacted into a minimal volume for magnetic measurements. Background magnetic measurements were checked for the packing material. At 2 or 300 K, the sample was installed in the SQUID chamber and the field dependence of magnetization was measured. The magnetic properties of the pristine partially reduced graphene oxide sample before annealing were also measured with the samples of Graphene-400, Graphene-600, and Graphene-800 for comparison. Electric properties were measured at 300 K using a QUANTUM DESIGN PPMS-9. Aqueous solutions of graphene oxide (10 mg/mL) were spin-coated onto a glass slide (500 revolutions/min, 12 s; 1000 revolutions/min, 30 s), and subsequently the film was carried out with the hydrazine reduction and annealing procedure strictly according to the same procedures for the preparation of Graphene-400/600/800 samples. Au electrodes were then vacuum deposited on the film, and then its conductivity was measured using a standard four-probe method. Impurity elements (Fe, Co, and Ni) of the pristine partially reduced graphene oxide were determined by atomic absorption spectrophotometer (Hitachi 180−80). The AAS analysis samples were prepared by dissolving samples completely using concentrated nitric acid at 100 °C.

References

(1) Miller, J. S. Organometallic- and organic-based magnets: New chemistry and new materials for the new millennium. *Inorg. Chem.* **2000**, *39*, 4392–4408.

(2) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. Bulk ferromagnetism in the β-phase crystal of the *p*-nitrophenyl nitronyl nitroxide radical. *Chem. Phys. Lett.* **1991**, *186*, 401–404.

(3) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. Organic molecular soft ferromagnetism in a fullerene C_{60}. *Science* **1991**, *253*, 301–303.

(4) Han, K. H.; Spemann, D.; Esquinazi, P.; Höhne, R.; Riede, V.; Butz, T. Ferromagnetic spots in graphite produced by proton irradiation. *Adv. Mater.* **2003**, *15*, 1719–1722.

(5) Makarova, T. Magnetism of carbon-based materials: Studies of high-Tc superconductivity; NOVA Science Publishers, Inc.: New York, 2003; Vol. 44.

(6) Makarova, T. L.; Sundqvist, B.; Höhne, R.; Esquinazi, P.; Kopelevichk, Y.; Scharff, P.; Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V. Magnetic carbon. *Nature* **2001**, *413*, 716–718.

(7) Esquinazi, P.; Spemann, D.; Höhne, R.; Setzer, A.; Han, K.-H.; Butz, T. Induced magnetic ordering by proton irradiation in graphite. *Phys. Rev. Lett.* **2003**, *91*, 227201.

(8) Service, R. F. American physical Society meeting: A positive spin on semiconductors. *Science* **2004**, *304*, 42–43.

(9) Harigaya, K. The mechanism of magnetism in stacked nanographite: theoretical study. *J. Phys.: Condens. Matter* **2001**, *13*, 1295–1302.

(10) Lee, H.; Son, Y. W.; Park, N.; Han, S. W.; Yu, J. J. Magnetic ordering at the edges of graphitic fragments: Magnetic tail interactions between the edge-localized states. *Phys. Rev. B* **2005**, *72*, 174431.

(11) 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.

(12) Gomez-Navarro, C.; Burghard, M.; Kern, K. Elastic properties of chemically derived single graphene sheets. *Nano Lett.* **2008**, *8*, 2045–2049.

(13) Becerril, H. A.; Mao, J.; Liu, Z. F.; Stoltenberg, R. M.; Bao, Z. N.; Chen, Y. S. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *Acs Nano* **2008**, *2*, 463–470.

(14) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438*, 197–200.

(15) Vozmediano, M. A. H.; Lopez-Sancho, M. P.; Stauber, T.; Guinea, F. Local defects and ferromagnetism in graphene layers. *Phys. Rev. B* **2005**, *72*, 155121.

(16) Yazyev, O. V.; Helm, L. Defect-induced magnetism in graphene. *Phys. Rev. B* **2007**, *75*, 125408.

(17) Wang, W. L.; Meng, S.; Kaxiras, E. Graphene nanoflakes with large spin. *Nano Lett.* **2008**, *8*, 241–245.

(18) Radovic, L. R.; Bockrath, B. On the chemical nature of graphene edges: Origin of stability and potential for magnetism in carbon materials. *J. Am. Chem. Soc.* **2005**, *127*, 5917–5927.

(19) Fernandez-Rossier, J.; Palacios, J. J. Magnetism in graphene nanoislands. *Phys. Rev. Lett.* **2007**, *99*, 177204.

(20) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. Magneto-opto-electronic bistability in a phenalenyl-based neutral radical. *Science* **2002**, *296*, 1443–1445.

(21) Haddon, R. Design of organic metals and superconductors. *Nature* **1975**, *256*, 394–396.

(22) Beer, L.; Mandal, S. K.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. The First Electronically stabilized phenalenyl radical: effect of substituents on solution chemistry and solid-state structure. *Cryst. Growth Des.* **2007**, *7*, 802–809.

(23) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y. Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **2007**, *45*, 1558–1565.

(24) Si, Y.; Samulski, E. T. Synthesis of water soluble graphene. *Nano Lett.* **2008**, *8*, 1679–1682.

(25) Niyogi, S.; Bekyarova, E.; Itkis, M. E.; McWilliams, J. L.; Hamon, M. A.; Haddon, R. C. Solution properties of graphite and graphene. *J. Am. Chem. Soc.* **2006**, *128*, 7720–7721.

(26) Wu, J.; Pisula, W.; Mullen, K. Graphenes as potential material for electronics. *Chem. Rev.* **2007**, *107*, 718–747.

(27) Liu, Z.; Liu, Q.; Huang, Y.; Ma, Y. F.; Yin, S. G.; Zhang, X. Y.; Sun, W.; Chen, Y. S. Organic Photovoltaic devices based on a novel acceptor material: Graphene. *Adv. Mater.* **2008**, *20*, 3924−3930.

(28) Hummers, W.; Offeman, R. Preparation of graphite oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

(29) Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotechnol.* **2008**, *3*, 101–105.

(30) Murata, K.; Ueda, H.; Kawaguchi, K. Preparation of carbon powders by pyrolysis of cyclododecane under vacuum and their magnetic properties. *Synth. Met.* **1991**, *44*, 357–362.

(31) Gómez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K. Electronic transport properties of individual chemically reduced graphene oxide sheets. *Nano Lett.* **2007**, *7*, 3499–3503.

(32) Schniepp, H. C.; Li, J. L.; McAllister, M. J.; Sai, H.; Herrera-Alonso, M.; Adamson, D. H.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A. Functionalized single graphene sheets derived from splitting graphite oxide. *J. Phys. Chem. B* **2006**, *110*, 8535–8539.

(33) Rajca, A.; Wongsriratanakul, J.; Rajca, S. Magnetic ordering in an organic polymer. *Science* **2001**, *294*, 1503–1505.

NL802810G