

## Superconductivity in Potassium-Doped Few-Layer Graphene

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## S Supporting Information

**ABSTRACT:** Here we report the successful synthesis of superconducting potassium-doped few-layer graphene (K-doped FLG) with a transition temperature of 4.5 K, which is 1 order of magnitude higher than that observed in the bulk potassium graphite intercalation compound (GIC)  $\text{KC}_8$  ( $T_c = 0.39$  K). The realization of superconductivity in K-doped FLG shows the potential for the development of new superconducting electronic devices using two-dimensional (2D) graphene as a basis material.

The recent discovery of proximity-induced superconductivity in graphene layers<sup>1,2</sup> has ignited tremendous interest in the intrinsic superconductivity of graphene and its derivatives. In fact, superconductivity has been extensively studied for several decades in some carbon allotropes with graphene as the basic structural element.<sup>3–7</sup> The graphite becomes superconducting after intercalation with alkali or alkaline-earth metals, with the transition temperature ( $T_c$ ) ranging from 0.39 K for  $\text{KC}_8$  up to 11.5 K for  $\text{CaC}_6$ .<sup>3,4</sup> These graphite intercalation compounds (GICs) can be viewed as a set of doped graphene layers in which the superconductivity originates in graphene sheets while the main role of the intercalants is to provide the charge to fill the graphene  $\pi^*$  states.<sup>8–11</sup> Amazingly, alkali-metal-doped  $\text{C}_{60}$  fullerene has produced a  $T_c$  as high as 38 K, the maximum  $T_c$  observed in carbon-based materials.<sup>5</sup> It is surprising that superconductivity above 10 K was reported for undoped single-walled<sup>6</sup> and multiwalled carbon nanotubes,<sup>7</sup> which can be viewed as rolled-up single or multiple graphene sheets, despite the theoretical expectation that producing superconductivity in such low-dimensional systems (quasi-1D) without any carrier doping should be difficult because of the low density of states and strong quantum fluctuations. Hence, in this sense, superconductivity in graphene has become of tremendous interest after the experimental realization of single-layer graphene (SLG) and few-layer graphene (FLG) in 2004;<sup>12</sup> although intrinsic superconductivity has been predicted for graphene using several theoretical models,<sup>13–15</sup> direct evidence for superconductivity in these materials is still missing.

There have been expectations that carrier doping would be an efficient method for modifying the electronic structure in SLG or FLG to bring out superconductivity. For instance, it has been suggested that Ca-doped graphene from monolayer to

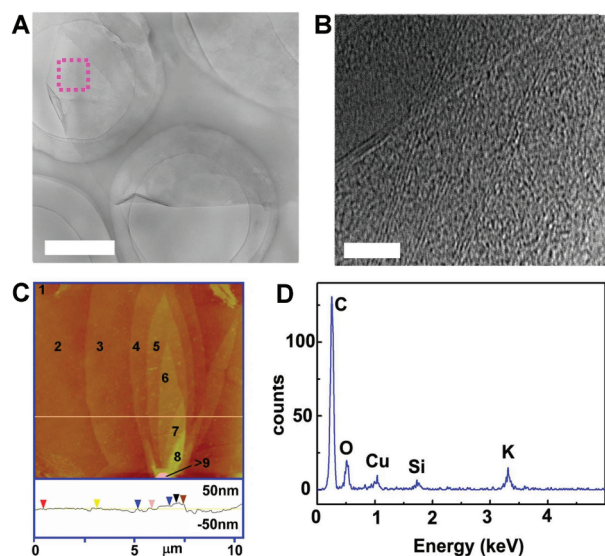
trilayer should show a substantial superconducting property similar to that of bulk  $\text{CaC}_6$ ,<sup>12</sup> while lithium-covered graphene has been proposed to be superconducting with a much higher temperature.<sup>16</sup> Recent reports show that it is possible to dope alkali metals (K, Li) or molecules ( $\text{FeCl}_3$ ,  $\text{Br}_2$ ) into SLG and FLG layers by the vapor transport method, and control of the electronic structure of SLG and FLG have also been demonstrated.<sup>17–19</sup> For the vapor transport method, SLG and FLG flakes prepared by mechanical cleavage are usually used as the starting material. However, our attempts to prepare a K-doped superconducting phase using the same route have proved unsuccessful because of the great difficulty of controlling the content of potassium in a few pieces of SLG or FLG flakes. To enable better control of the K-doping process, we took a wet chemistry approach that uses a binary Na/K alloy and 1,2-dimethoxyethane as the impregnant. A similar approach<sup>20,21</sup> that was recently developed for producing SLG or FLG has received dramatic attention due to the large-scale and high yield production.

In this work, 0.23 g of precursor graphite flakes mixed with 0.46 g of potassium, 0.06 g of sodium, and 150 mL of 1,2-dimethoxyethane and stirred for 120 h at room temperature produced well-dispersed FLG nanosheets, as shown in Figure 1a–c. Reproducible superconductivity was achieved for the resulting FLG after the potassium content was adjusted with ethanol etching. A close look at the folded regions at the edges by high-resolution transmission electron microscopy (HRTEM) suggests that the as-prepared FLG sheets mainly contain four graphene layers (Figure 1b). An atomic force microscopy (AFM) image (Figure 1c) clearly shows the overlap of misoriented FLG sheets with a uniform thickness of  $\sim 1.5$  nm. Energy-dispersive X-ray spectroscopy (EDX) results (Figure 1d) confirm the successful intercalation of potassium into the graphene sheets. No tail of Na features was detected for any of the samples.

Figure 2a presents the magnetic susceptibility as a function of temperature from 2.5 to 6 K for K-doped FLG obtained from zero-field-cooling (ZFC) and field-cooling (FC) measurements at an applied field of 50 Oe. The ZFC susceptibility  $\chi$  shows a sharp drop at  $\sim 4.5$  K. Such diamagnetic behavior is characteristic of superconductivity. The distinct magnetic signatures of ZFC and FC below the superconducting critical

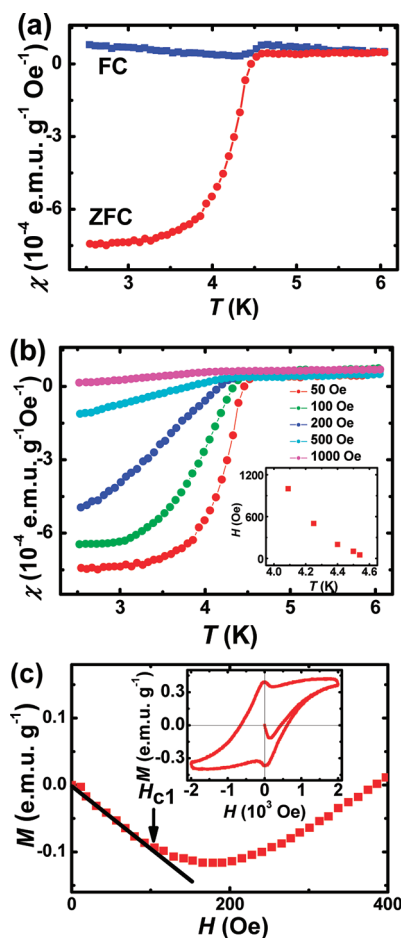
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**Figure 1.** Microstructural analyses of K-doped FLG. (a) Bright-field TEM image of typical FLG sheets. (b) HRTEM image showing the perfect layer structure. The number of dark lines indicates that the as-prepared FLG contains four graphene layers. (c) AFM image of the exfoliated FLG sheets. A slightly different color arises from the overlapping of misoriented graphene sheets with a uniform thickness of  $\sim 1.5$  nm. (d) EDX spectrum coming from the square-enclosed region in (a). A K peak was detected among the graphene layers. The Cu and Si peaks originated from the copper substrate mesh and the detector, and the O peak came from oxidation in the TEM sample preparation step. Scale bars: (a) 500 nm; (b) 5 nm.

temperature originate from the screening supercurrents (ZFC regime) and the Meissner–Ochsenfeld effect of magnetic flux expulsion. The critical temperature  $T_c$  is usually identified with the temperature of the sharp decrease in the ZFC curve. Therefore,  $T_c$  was defined to be 4.5 K, as seen from Figure 2a. Figure 2b shows the temperature dependence of  $\chi$  at various applied fields  $H$  obtained from ZFC measurements. There is an obvious drop in  $\chi$  at 4 K even at 1000 Oe, indicating that the superconducting phase is not completely destroyed at weak applied fields. The fact that  $T_c$  is suppressed slowly by the application of a magnetic field indicates that the observed superconductivity in this material is intrinsic. The corresponding upper critical field ( $H_{c2}$ ) is plotted versus  $T$  in the Figure 2b inset. At the present stage, it is difficult to determine  $H_{c2}$  from the  $H$ – $T_c$  curve. On the basis of the ZFC data, the superconducting shielding fraction was estimated to be  $\sim 2\%$  at  $H = 50$  Oe (assuming a density of  $2 \text{ g/cm}^3$ , the same as for  $\text{KC}_8$ ). This value is comparable to that of recently discovered K-doped polycyclic aromatic hydrocarbons (PAHs, which can be viewed as well-defined cutouts of graphene; larger PAHs are therefore sometimes called nanographenes).<sup>22,23</sup> This value is also about the same as that of initially reported K-doped  $\text{C}_{60}$  and Rb-doped  $\text{C}_{60}$ ,<sup>24,25</sup> although following works have dramatically increased the superconducting fraction for alkali-metal-doped  $\text{C}_{60}$ .<sup>26</sup> Here the small shielding fraction might result from the fact that the size of small superconducting grains (islands) is comparable to (or smaller than) the London penetration depth (estimated to be a few thousand angstroms). It seems probable that only a very small portion of potassium survived in the center of the FLG nanosheets after the etching process with ethanol because of the highly reactive behavior of potassium. Thus, it is reasonable to expect that a higher volume

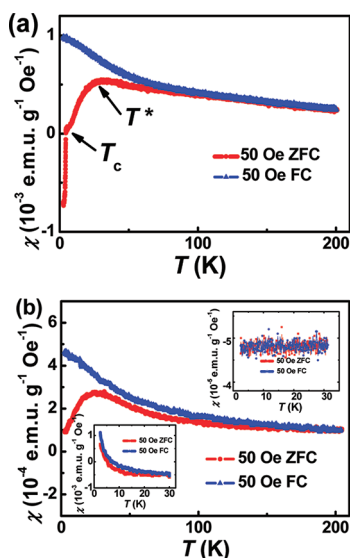


**Figure 2.** Temperature dependence of magnetization for the K-doped FLG. (a)  $\chi$  vs  $T$  plots with  $T_c = 4.5$  K obtained from ZFC (red) and FC (blue) measurements at  $H = 50$  Oe. (b)  $\chi$  vs  $T$  plots obtained from zero-field cooling (ZFC) measurements at magnetic fields ( $H$ ) of 50, 100, 200, 500, and 1000 Oe. The  $H$  vs  $T_c$  plot is shown in the inset. (c)  $M$  vs  $H$  plots at 2.5 K at low magnetic fields. Inset: magnetization hysteresis loop obtained at 2.5 K.

fraction might be achieved if in future studies we can develop a new approach to control the doping of potassium well.

The  $M$  versus  $H$  plot measured at 2.5 K (Figure 2c) indicates that K-doped FLG is a type-II superconductor with strong vortex pinning. One can see that the diamagnetic signal starts to decrease above applied fields of 200 Oe and reaches zero at  $\sim 400$  Oe. The value of the lower critical field  $H_{c1}$  seems to be reasonable, on the order of 100 Oe at 2.5 K. This small value suggests that the Meissner signal appears only under very low magnetic field or even no signal, which is consistent with our observations of the FC susceptibility. Here the  $H_{c1}$  is slightly lower than that of K-doped picene ( $\sim 300$  Oe,  $T_c = 18$  K)<sup>22</sup> but similar to that of K-doped phenanthrene ( $\sim 150$  Oe,  $T_c = 5$  K).<sup>23</sup> Interestingly, as shown in the inset of Figure 2c, the  $M$ – $H$  loop does not appear to be standard but rather exhibits a superposition of a diamagnetic response and a ferromagnetic-like component.

To clarify further the unconventional magnetism, we performed the ZFC and FC susceptibility measurements at temperatures ranging from 2.5 to 200 K (Figure 3a). At high temperatures, the ZFC and FC susceptibilities follow the Curie–Weiss temperature dependence. However, in the low-temperature region, the ZFC curve always lies below the FC



**Figure 3.** High-temperature magnetic behavior of K-doped FLG. (a)  $\chi$  vs  $T$  plots for superconducting K-doped FLG at temperatures ranging from 2.5 to 200 K. (b)  $\chi$  vs  $T$  plots for the sample after total ethanol etching. Upper inset:  $\chi$  vs  $T$  plots for precursor graphite. Lower inset:  $\chi$  vs  $T$  plots for the as-doped sample before etching.

curve, and it shows a broad peak at  $\sim 30$  K ( $T^*$  in Figure 3a). This feature is similar to that observed in the C–S system,<sup>27</sup> where possible superconductivity with  $T_c = 30$  K was claimed. To exclude the possibility of superconductivity, we etched the sample with ethanol for a long time and measured its magnetic susceptibility. No obvious difference was found except for the disappearance of superconductivity at 4.5 K (Figure 3b). Preliminary studies<sup>28–30</sup> on the magnetic properties of FLG prepared by other methods also showed similar magnetic behaviors as well as divergence between the ZFC and FC processes, and the behaviors were found to be very sample-dependent and very sensitive to heat treatment and aging. Numerous reports have predicted that the local spins come from various defects on graphene structures (e.g., vacancies, topological defects or frustration, and hydrogen chemisorption) or perhaps the edge.<sup>31–33</sup> In our experiment, vacancies and/or other defects with unpaired electrons would be introduced on the graphene sheets during this process of washing. Here the superparamagnetic-like or spin-glass-like behavior and superconductivity appear to be intrinsic properties of the samples, although it is not clear whether the local spins have any direct relation to the superconductivity. It should be noted that such magnetism also obstructs the appearance of magnetization drops in the FC and ZFC regimes.

For comparison, the ZFC and FC magnetizations of precursor graphite and of the as-synthesized sample (not etched with ethanol) are shown in the upper and lower insets of Figure 3b, respectively. The former is diamagnetic over the entire temperature range because of the strong orbital diamagnetism of graphite,<sup>34</sup> while the latter shows Pauli- or Curie-like behavior at low temperature, indicating that local spins exist in this as-doped FLG specimen. In both cases, the ZFC and FC curves coincide with each other, and there is no detectable difference greater than the experimental error of  $0.5 \times 10^{-6}$  emu. Therefore, these data further support the conclusion that the observed diamagnetic signal for the K-doped FLG comes from the occurrence of superconductivity near the optimal doping.

Overall, we have succeeded in synthesizing K-doped FLG through a wet chemistry approach. Superconductivity can be achieved in this material after optimization of the potassium concentration by ethanol etching. The successful realization of superconductivity in FLG suggests that it should be possible to achieve superconductivity in monolayer graphene with optimal doping, thus inspiring us to make greater efforts to explore the superconductivity by developing new approaches. We believe that such results will be an interesting subject for future research for the practical applications of graphene in superconducting electronics and devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Shailos, A.; Nativel, W.; Kasumov, A.; Collet, C.; Ferrier, M.; Guéron, S.; Deblock, R.; Bouchiat, H. *Europhys. Lett.* **2007**, *79*, No. 57008.
- (2) Heersche, H. B.; Jarillo-Herrero, P.; Oostinga, J. B.; Vandersypen, L. M. K.; Morpurgo, A. F. *Nature* **2007**, *446*, 56–59.
- (3) Hannay, N. B.; Geballe, T. H.; Matthias, B. T.; Andres, K.; Schmidt, P.; MacNair, D. *Phys. Rev. Lett.* **1965**, *14*, 225–226.
- (4) Weller, T. E.; Ellerby, M.; Saxena, S. S.; Smith, R. P.; Skipper, N. T. *Nat. Phys.* **2005**, *1*, 39–41.
- (5) Ganin, A. Y.; Takabayashi, Y.; Khimyak, Y. Z.; Margadonna, S.; Tamai, A.; Rosseinsky, M. J.; Prassides, K. *Nat. Mater.* **2008**, *7*, 367–371.
- (6) Tang, Z. K.; Zhang, L.; Wang, N.; Zhang, X. X.; Wen, G. H.; Li, G. D.; Wang, J. N.; Chan, C. T.; Sheng, P. *Science* **2001**, *292*, 2462–2465.
- (7) Takesue, I.; Haruyama, J.; Kobayashi, N.; Chiashi, S.; Maruyama, S.; Sugai, T.; Shinohara, H. *Phys. Rev. Lett.* **2006**, *96*, No. 057001.
- (8) Csányi, G.; Littlewood, P. B.; Nevidomskyy, A. H.; Pickard, C. J.; Simons, B. D. *Nat. Phys.* **2005**, *1*, 42–45.
- (9) Calandra, M.; Mauri, F. *Phys. Rev. B* **2007**, *76*, No. 161406(R).
- (10) Pan, Z.-H.; Camacho, J.; Upton, M. H.; Fedorov, A. V.; Howard, C. A.; Ellerby, M.; Valla, T. *Phys. Rev. Lett.* **2011**, *106*, No. 187002.
- (11) McChesney, J. L.; Bostwick, A.; Ohta, T.; Seyller, T.; Horn, K.; González, J.; Rotenberg, E. *Phys. Rev. Lett.* **2010**, *104*, No. 136803.
- (12) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666–669.
- (13) Jishi, R.; Guzman, D.; Alyahyaei, H. Theoretical Investigation of Two-Dimensional Superconductivity in Intercalated Graphene Layers. 2011, arXiv:1107.1845. arXiv.org e-Print archive. <http://arxiv.org/abs/1107.1845> (accessed Jan 23, 2012).
- (14) Uchoa, B.; Castro Neto, A. H. *Phys. Rev. Lett.* **2007**, *98*, No. 146801.

- (15) Kopnin, N. B.; Sonin, E. B. *Phys. Rev. Lett.* **2008**, *100*, No. 246808.
- (16) Profeta, G.; Calandra, M.; Mauri, F. *Nat. Phys.* **2012**, *8*, 131–134.
- (17) Jung, N.; Kim, N.; Jockusch, S.; Turro, N. J.; Kim, P.; Brus, L. *Nano Lett.* **2009**, *9*, 4133–4137.
- (18) Zhao, W.; Tan, P. H.; Liu, J.; Ferrari, A. C. J. *Am. Chem. Soc.* **2011**, *133*, 5941–5946.
- (19) Ohta, T.; Bostwick, A.; Seyller, T.; Horn, K.; Rotenberg, E. *Science* **2006**, *313*, 951–954.
- (20) Vallés, C.; Drummond, C.; Saadaoui, H.; Furtado, C. A.; He, M.; Roubeau, O.; Ortolani, L.; Monthieux, M.; Pénicaud, A. *J. Am. Chem. Soc.* **2008**, *130*, 15802–15804.
- (21) Englert, J. M.; Dotzer, C.; Yang, G.; Schmid, M.; Papp, C.; Gottfried, J. M.; Steinrück, H.-P.; Spiecker, E.; Hauke, F.; Hirsch, A. *Nat. Chem.* **2011**, *3*, 279–286.
- (22) Mitsuhashi, R.; Suzuki, Y.; Yamanari, Y.; Mitamura, H.; Kambe, T.; Ikeda, N.; Okamoto, H.; Fujiwara, A.; Yamaji, M.; Kawasaki, N.; Maniwa, Y.; Kubozono, Y. *Nature* **2010**, *464*, 76–79.
- (23) Wang, X. F.; Liu, R. H.; Gui, Z.; Xie, Y. L.; Yan, Y. J.; Ying, J. J.; Luo, X. G.; Chen, X. H. *Nat. Commun.* **2011**, *2*, 507.
- (24) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R. B.; Deiderich, F.; Holczer, K. *Nature* **1991**, *351*, 632–634.
- (25) Rosseinsky, M. J.; Ramirez, A. P.; Glarum, S. H.; Murphy, D. W.; Haddon, R. C.; Hebard, A. F.; Palstra, T. T. M.; Kortan, A. R.; Zahurak, S. M.; Makhija, A. V. *Phys. Rev. Lett.* **1991**, *66*, 2830–2832.
- (26) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154–1157.
- (27) Ricardo da Silva, R.; Torres, J. H. S.; Kopelevich, Y. *Phys. Rev. Lett.* **2001**, *87*, No. 147001.
- (28) Ramakrishna Matte, H. S. S.; Subrahmanyam, K. S.; Rao, C. N. R. *J. Phys. Chem. C* **2009**, *113*, 9982–9985.
- (29) Rao, C. N. R.; Sood, A. K.; Voggu, R.; Subrahmanyam, K. S. *J. Phys. Chem. Lett.* **2010**, *1*, 572–580.
- (30) Saha, S. K.; Baskey, M.; Majumdar, D. *Adv. Mater.* **2010**, *22*, 5531–5536.
- (31) Yazyev, O. V. *Phys. Rev. Lett.* **2008**, *101*, No. 037203.
- (32) Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Boukhvalov, D. W.; Katsnelson, M. I.; Geim, A. K.; Novoselov, K. S. *Science* **2009**, *323*, 610–613.
- (33) Abergel, D. S. L.; Apalkov, V.; Berashevich, J.; Ziegler, K.; Chakrabortya, T. *Adv. Phys.* **2010**, *59*, 261–482.
- (34) Kelly, B. T. *Physics of Graphite*; Applied Science Publishers: London, 1981.