Magnetic moment manipulation in hydrogen-peroxide-doped grafoil, pyrolytic graphite and Fe$_3$C-filled multiwall carbon nanotubes

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Keywords: grafoil, hydrogen peroxide, HOPG, carbon nanotubes, defects induced ferromagnetism, electron correlation

Abstract
Observation of granular superconductivity and percolative ferromagnetism in hydrogen/oxygen doped graphite materials has motivated recent research because of the unexplored scenarios in the field of magnetic-devices and spintronics. Here we report a novel investigation of the effects of hydrogen-peroxide-doping on the magnetic properties of grafoil, highly oriented pyrolytic graphite (HOPG) and carbon nanotube (CNT) samples characterized by specific defective characteristics. ZFC and FC magnetic curves acquired on the undoped boundary-defect-rich grafoil samples from 2 K to 300 K, revealed a spin-glass-like behaviour, with magnetic irreversibilities indicating the existence of percolative ferromagnetism. An enhancement in such effect was found in the post-doped samples below ~70 K, together with a magnetic transition. This was evidenced further by ESR, with the appearance of a broad differential absorption peak at 77 K for $g\sim3.54$, compatible with antiferromagnetic ordering in presence of ferromagnetic multilayers. An analogous enhancement of ferromagnetic signals was found on sp$^3$-defect-rich HOPG, with the appearance of localized ESR differential absorption features at $g$ factors of $\sim2.14$, $\sim2.08$, $\sim2.02$, $\sim1.91$ and $\sim1.86$ at 77 K. Instead, comparisons performed in vacancy-rich doped CNTs revealed a significantly different trend, with an anomalous demagnetization of both the vacancy-rich graphitic CNT layers and encapsulated Fe$_3$C nanowires. These observations seem to highlight a possible role of specific defects towards modifications of magnetic correlation in presence of hydrogen/oxygen species.

Introduction
The recent observations of ferromagnetic correlation in carbon-based materials [1–16] has attracted significant attention towards possible applications of these systems into multi-layered devices and/or in spintronics systems [1, 2]. Applications in exchange bias devices and magnetic tunnel junctions have been suggested in presence of layered ferromagnetism [1, 2].

Magnetic correlation phenomena have been reported to occur intrinsically within the interfaces of multi-layered graphitic-based materials owing to the existence of certain type of defects [1, 5–15]. In particular, disclinations and topological disorder have been indicated as important parameters for the creation of magnetically active areas in the form of localized randomly oriented ferromagnetic clusters [11–15]. Experiments performed on glassy carbon have evidenced a significant role of the graphitization process in inducing such topological-defects-formation (in the form of pentagon/heptagons) and consequent appearance of ferromagnetic correlation effects [12]. Superconductive and ferromagnetic correlation phenomena have been reported also in twisted graphene bilayers (TGBs) [16–18], the latter being in the form of an exotic ferromagnetic phase, under certain conditions of layer rotations of $\sim1.8^\circ$ [18].
In addition to these observations, a recent work reported by Arnold et al has shown existence of a superconductive transition in grafoil below 14 K, highlighting the possible existence of an unknown type of crystal defect [19].

It is also important to mention about a different type of correlation effect which recently has been reported in highly oriented pyrolytic graphite (HOPG) materials when doped with certain type of liquids, such as water and/or alcoholic beverages [20–27]. These phenomena are of particular importance, since can offer new possibilities of magnetic moment modification involving doping with certain hydrogen or/oxygen-based species. This effect was evidenced in alcoholic beverages containing FeTe$_{1-x}$S$_x$; in these systems the tartaric acid was identified as a critical factor for the formation of superconductive ordering [23, 24].

Other works have shown that diffusion of hydrogen and/or oxygen species within graphitic interfaces could allow for the deliberate creation of superconductive ordering [20, 21]. Despite the important progress reported up to now, the critical factor at the origin of the superconductive ordering remains not well understood. Indeed, a recent work has evidenced the occurrence of a hydrogen-induced ferromagnetic transition in the $\pi$-electron signal of these systems [26].

Being interested in gaining a better understanding of the magnetic ordering resulting from the doping process, we investigated the existence of magnetic correlation phenomena in hydrogen-peroxide-doped grafoil, HOPG and multiwall carbon nanotubes (MWCNTs) filled with Fe$_3$C nanowires. Zero field cooled (ZFC) and field cooled (FC) magnetic curves acquired from 2 K to 300 K from as purchased grafoil samples (by employing superconducting quantum interference device, SQUID), revealed the occurrence of a spin–glass-like behaviour. Magnetic irreversibilities, indicating the existence of percolative ferromagnetism were detected. An enhancement in such a spin–glass-like effect was found in the doped grafoil samples. Below ~ 70 K, a possible antiferromagnetic transition could be probed on the basis of the negative difference between the magnetic moments of FC and ZFC ($m_{FC} - m_{ZFC}$). This phenomenon was evidenced further by electron spin resonance (ESR), with the observation of a magnetic transition at 77 K for $g$ ~ 3.54, in agreement with [28]. This technique highlighted also significant differences in the localized paramagnetic features at 77 K for $g$ factor of ~ 2.0 in doped grafoil and HOPG. Particularly, multiple differential absorption features were found at $g$ ~ 2.14, ~2.08, ~2.02, ~1.91 and ~ 1.86, in analogy with the results reported by Gao S et al [26].

Further comparisons performed in doped (vacancy-rich) multiwalled carbon nanotubes (MWCNTs) filled with Fe$_3$C nanowires, revealed instead an different-trend, with a deactivation of the magnetic moment in both the CNT layers and encapsulated Fe$_3$C nanowires.
Experimental

Grafoil was purchased from Suzhou Dasen Electronics Material Co., Ltd. HOPG samples with dimensions of 5 × 5 × 1 mm were purchased from XFNANO, INC (mosaic angle 0.5°). Fe₃C-filled CNTs were produced through a Cl-assisted CVD approach following the method reported in [29].

The doping process was achieved by using commercially available hydrogen-peroxide (30–32 g l⁻¹) as doping agent at ambient pressure. Infiltration was done by dipping the grafoil, HOPG and CNT samples inside hydrogen-peroxide for 24 h. EPR measurements were performed with a JEOL JES-FA200 at 77 K, 150 K and 300 K in order to detect possible presence of paramagnetic-defective centers in the samples. Magnetic characterization was performed with a superconducting quantum interference device system (SQUID, Quantum Design) with controlled sample-orientation with respect to the applied field. The controlled sample orientation was achieved by position the grafoil sample with the graphitic layers perpendicular or parallel to the applied field. Instead due to the sample-dimensions, only measurements with layers orientation parallel to the field could be performed in the case of HOPG.

Raman Spectra were collected in a custom-built Raman system using a triple grating monochromator (Andor Shamrock SR-303i-B, EU) with an attached EMCCD (ANDOR Newton DU970P-UVB, EU), excitation by a solid-state laser at 532 nm (RGB lasersystem, NovaPro 300 mW, Germany) and collection by a 20×, 0.28 NA objective (Mitutoyo, Japan). These measurements allowed to identify the defective areas of the samples. XRD structural measurements were also performed on a PANalytical Empyrean powder x-ray diffractometer (Cu K-α1, λ = 0.15406 nm) at room temperature. Morphological and compositional analyses were performed with an JSM-7500 F scanning electron microscope (SEM) at 10–20 kV. See ESI for energy dispersive x-ray analyses.

Figure 2. In A–B, ZFC and FC magnetic curves acquired on the as purchased grafoil sample with orientation parallel (a) and perpendicular (b) to the applied magnetic field. Note the presence of magnetic irreversibilities observable at ~ 70 K for both sample orientations, which indicate the existence of percolative ferromagnetism in the form of randomly oriented uncorrelated and correlated ferromagnetic-clusters [1, 13–15]. In C, D magnetization versus field measurements revealing the presence of a ferromagnetic hysteresis with a coercivity parameter that increases with the decrease of the temperature.
Results and discussion

The superficial properties of the as purchased grafoil sample were firstly revealed by SEM (see also ESI figures S1–3 for compositional analyses). As shown in figures 1(a)–(d), an unusual morphology characterized by defective faceted-like features and disclinations was found. The layered structure of the films was highlighted by x-ray diffraction (XRD) in figures 1(e), (f) with the appearance of intense 002 and weak 004 reflections. It is also noticeable the presence of two unknown peak features at approximately $\sim 23^\circ$ and $30^\circ$ 2$\theta$.

The properties of the undoped samples were further investigated by Raman spectroscopy. As shown in ESI figure S4 weak D and D’ bands were found in multiple areas of the sample, together with an intense G band. The deconvolution analyses in ESI figure S4(b) evidenced an $AD/AD' \sim 3.5$ attributable to the existence of boundary defects in the as purchased grafoil sample [30].

Comparative measurements performed in HOPG, revealed the presence of a larger D band in ESI figure S4(h) only in proximity of the sample edges. The ratio of $AD/AD' \sim 13$ allowed in this case the identification of $sp^3$-type defects [30].

The magnetic characteristics of the as purchased grafoil samples were investigated further by SQUID magnetometry. As shown in figures 2(a), (b) and ESI figure S5, ZFC and FC magnetic curves acquired on the as purchased grafoil sample with orientation parallel and perpendicular to the applied magnetic field revealed the presence of magnetic correlation effects in the form of magnetic irreversibilities, observable at $\sim 70$ K for both sample orientations. These observations indicate the existence of percolative ferromagnetic signals in the form of randomly oriented uncorrelated and correlated ferromagnetic-clusters in analogy with the work reported by Taallah et al in HOPG [1]. In figures 2(c), (d) magnetization versus field measurements revealed ferromagnetic hysteresis below 300 K with a progressively increasing coercivity as the temperature was decreased from 300 K to 2 K. Additional ESR measurements shown in ESI figure S6 acquired from 300 K to 77 K confirmed the presence...
of temperature induced ferromagnetic correlation, with a significant shift in the position of the $\pi$-electron differential absorption feature from $g \sim 1.92$ at 300 K, 150 K and 77 K. Another significantly intense differential absorption peak was identified at 77 K for $g \sim 3.54$ indicating the presence of a magnetic transition of possible antiferromagnetic origin (A). A weak feature could be also found at $g \sim 2.07$ (B). In C, D ESR measurements performed on the hydrogen-peroxide doped HOPG sample (see ESI for measurements performed at 300 K, 150 K and 77 K). Note at 77 K the presence of a significant broadening in the $\pi$-electron differential absorption signal for $g \sim 1.98$, with appearance of additional paramagnetic differential absorption peaks at $g$ factors of $\sim 2.14$, $\sim 2.08$, $\sim 2.02$, $\sim 1.91$ and $\sim 1.86$ in its proximity.

ZFC and FC magnetic curves were then acquired from hydrogen-peroxide doped grafoil and hydrogen peroxide doped HOPG, for comparison. As shown in figure 3(a) for grafoil, a significant change in the shape of the slope of the ZFC magnetic curve was found, with an enhanced spin-glass-like behaviour observable at $\sim 70$ K. Measurements performed in doped HOPG revealed an apparently comparable trend, with a magnetic irreversibility at $\sim 50$ K in figure 3(b).

By applying the $m_{\text{FC}-\text{ZFC}}$ ($\Delta m_{\text{FC}-\text{ZFC}}$) analytical subtraction method ($m$ being the magnetic moment in emu, see figures 3(c) and (d)) additional information could be extracted from the acquired ZFC and FC curves. An increase in the value of $\Delta m_{\text{FC}-\text{ZFC}}$ with the decrease of the temperature was found in both cases as shown in figures 3(c) and (d). This observation evidences the presence of an enhanced ferromagnetic component in both the doped samples, possibly resulting from hydrogen doping [28].

However, it is of particular importance the transition observed at $\sim 70$ K in figure 3(c) (only for the doped grafoil sample). The observed negative $\Delta m_{\text{FC}-\text{ZFC}}$ at $\sim 70$ K and the subsequent sharp increase in $\Delta m_{\text{FC}-\text{ZFC}}$ are attributable to possible antiferromagnetic interactions arising between two ferromagnetic components [2].

Also, the absence of such an antiferromagnetic transition in the doped HOPG sample, implies that the interfaces and localized defective areas present in the two samples can react differently to the hydrogen peroxide doping.

The origin of the observed magnetic signals and the effect of hydrogen peroxide doping on the $\pi$-electron magnetism were further investigated by ESR. The signals acquired at 77 K, 150 K and 300 K in hydrogen-peroxide-doped grafoil and HOPG are shown in figure 4 and in ESI figures 7, 8.

As shown in figures 4(a), (b), an intense differential absorption feature could be identified in the doped grafoil sample at 150 K and 77 K for $g \sim 1.98$ and attributed to the $\pi$-electron signal. A magnetic transition at 77 K
The AD/AD’ ratio extracted by deconvolution analyses highlight presence of vacancies in the graphitic CNTs layers. This interpretation was corroborated by ESR analyses. A shift in the $\pi$-electron feature, possibly indicating a ferromagnetic transition was found below 300 K in the undoped sample, as shown in C-D. Deactivation of the magnetic correlation effect was then found in the doped sample, as shown in E (from 0 to $\sim$ 300 mT) and in F (from 320 to 350 mT). These results highlight a complete annihilation of the magnetically active defective areas (detected in B). In G,H ZFC and FC magnetic curves acquired before (G) and after (H) doping. The acquired signals confirm the ESR trend and highlight a demagnetization effect (after doping) possibly attributable to sample oxidation.
for $g \sim 3.54$ was further found (figure 4(a)). The latter observation seem in agreement with the ZFC and FC magnetic curves presented above and highlight the existence of a possible antiferromagnetic interaction between ferromagnetic components [2]. Note also the presence of an additional peak feature observable for $g \sim 2.07$ at 77 K.

Comparable investigations were then considered in hydrogen-peroxide-doped HOPG; the signals acquired at 300 K, 150 K and 77 K are shown in figures 4(c), (d) and in ESI figure 8. Interestingly, in this case a different result was found; note the significant broadening of the $\pi$-electron signal, together with the appearance of other additional differential absorption features for g-factors of ~ 2.14, ~ 2.08 and ~2.02; Observation of these features has analogy to those reported by Gao et al in water doped HOPG [26] and can be attributed to hydrogen-induced ferromagnetism. Together with these features, other additional differential absorption peaks could be noticed for $g \sim 1.91$ and $g \sim 1.86$.

The observed significant differences in the doping outcomes observed in grafoil and HOPG may indicate the existence of a specific role of defects in the interaction process with hydrogen peroxide.

In the attempt to verify this hypothesis, additional characterization was performed in a different type of sample, consisting of vacancy-rich MWCNTs filled with $Fe_3C$ nanowires. A typical TEM micrograph revealing the interface between the multiwall CNT layers and the encapsulated nanowire is shown in figure 5(a) while the typical Raman spectra acquired from an as grown sample is shown in figure 5(b). By carefully analysing the variation in the ESR signal (acquired from 0 to 500 mT) of the $\pi$-electrons of undoped (figure 5(c)) from 0 to ~ 200 mT and figure 5(d) from ~ 200 to 450 mT and hydrogen peroxide doped (figure 5(e) from 0 to ~ 300 mT and figure 5(f) from ~ 320 to 350 mT) samples it is evident the presence of an unusual demagnetization effect in post-doping conditions, not only in the vacancy-rich graphitic CNT layers but also in the encapsulated $Fe_3C$ nanowires, as shown in figures 5(g), (h); particularly note (in figures 5(g), (h)) the significant drop in magnetic moment values as a result of the doping process. These observations evidence a significantly different doping effect in this latter type of nanostructures.

Conclusion

In conclusion, in this work we reported the novel observation of enhanced spin-glass-like effects in hydrogen-peroxide-doped grafoil. Raman spectroscopy evidenced existence of boundary defects in the as purchased sample. ZFC and FC magnetic curves acquired on undoped grafoil from 2 K to 300 K revealed the occurrence of a spin-glass-like behaviour, with magnetic irreversibilities indicating the existence of percolative ferromagnetism. An enhancement in such a spin-glass-like effect was found upon hydrogen peroxide doping, with an antiferromagnetic transition highlighted by negative $m_{ZFC} – m_{FC}$ values below ~ 70 K. This phenomenon was evidenced further by ESR at 77 K for $g \sim 3.54$. Comparative measurements performed in $sp^3$-defect-rich HOPG revealed a different doping effect, with absence of negative $m_{ZFC} – m_{FC}$ difference values in the whole temperature range. ESR spectroscopy acquired in doped HOPG highlighted further the presence of a different transition in the $\pi$-electrons, with a significant signal broadening below 150 K and appearance of localized differential absorption features at 77 K for g factors of ~ 2.14, ~2.08 and ~2.02, ~1.91 and ~1.86. The latter were analogue to those reported in [26]. Instead, comparisons performed in vacancy-rich multiwalled carbon nanotubes (MWCNTs) filled with $Fe_3C$ nanowires, revealed a post-doping deactivation of the magnetic moment in both CNT layers and encapsulated $Fe_3C$ nanowires.

Acknowledgments

Prof. Filippo Boi acknowledges research support from NSFC funds 11750110413 and 11950410752 and Sichuan Province fund 2019YFH0080.

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References

[1] Taallah A, Wen J, Wang S, Grasso S, He Y, Xia J, Gao S, Odunmbaku O, Corrias A and Boi F S 2020 Unusual butterfly-shaped magnetization signals and spin-glass-like behaviour in highly oriented pyrolytic graphite Carbon 167 85–91
[2] Hellwig O, Kirk T L, Kortright J B, Berger A and Fullerton E E 2003 A new phase diagram for layered antiferromagnetic films Nat. Mater. 2 112–6
[3] Mizogami S, Mizutani M, Fukuda M and Kawabata K 1991 Abnormal ferromagnetic behavior for pyrolytic carbon under low temperature growth by CVD method Synth. Met. 43 3271–4

[4] Kopelevich Y, Esquinazi P, Torres J H S and Moehlecke S 2000 Ferromagnetic- and superconducting-like behavior of graphite J. Low Temp. Phys. 119 691–702

[5] Esquinazi P, Setzer A, Höhne R, Semmelhack C, Kopelevich Y, Spemann D, Butz T, Kohlstrunk B and Lösche M 2002 Ferromagnetism in oriented graphite samples Phys. Rev. B 66 024429

[6] Fayazi M, Liu B, Li L, Gao S, Odummbaku O, Wang S, He Y and Boi F S 2019 Ferromagnetic hysteresis and structural recrystallization in turbostratic graphite Mater. Res. Express 6 105612

[7] Bhownik B N 2012 Ferromagnetism in lead graphite-pencils and magnetic composite with CoFe$_2$O$_4$ particles Composites Part B: Engineering 43 503–9

[8] Murata K, Ushijima H, Ueda H and Kawaguchi K 1992 A stable carbon-based organic magnet J. Chem. Soc., Chem. Commun. 7 567–9

[9] Ishii C, Matsumura Y and Kaneko K 1995 Ferromagnetic behavior of superhigh surface area carbon J. Phys. Chem. 99 5743–5

[10] Ishii C, Shindo N and Kaneko K 1995 Random magnetism of superhigh surface area carbon having minute graphitic structures Chem. Phys. Lett. 242 196–201

[11] Boi F S, Li J, Odummbaku O, Liu M, Medranda D, Taallah A, Lei L and Wang S 2020 Temperature-dependent c-axis lattice-spacing reduction and novel structural recrystallization in carbon nano-onions filled with Fe$_3$C/Fe nanocrystals Nano Express 1 020016

[12] Wang X, Liu Z X, Zhang Y L, Li F Y and Jin C Q 2002 Evolution of magnetic behaviour in the graphitization process of glassy carbon J. Phys.: Condens. Matter 14 101265

[13] González J, Guinea F and Vozmediano M A H 2001 Electron–electron interactions in graphene sheets Phys. Rev. B 63 134421

[14] Kopelevich Y, da Silva R R, Torres J H S, Penicaud A and Kyotani T 2003 Local ferromagnetism in microporous carbon with the structural regularity of zeolite Y Phys. Rev. B 68 092408

[15] Theodoropoulou N, Hebard A F, Overberg M E, Abernathy S J, Chu S N G and Wilson R G 2002 Unconventional carrier-mediated ferromagnetism above room temperature in ion-implanted (Ga, Mn)$_2$PC Phys. Rev. Lett. 89 107205

[16] Cao Y, Fatemi Y, Fang S, Watanabe K, Taniguchi T, Kaxiras E and Jarillo-Herrero P 2018 Unconventional superconductivity in magic-angle graphene superlattices Nature 556 43–50

[17] Arora HS et al 2020 Superconductivity in metallic twisted bilayer graphene stabilized by WS$_2$ Nature 583 379–84

[18] Seo K, Kotov V N and Uchoa B 2019 Ferromagnetic Mott state in twisted graphene bilayers at the magic angle Phys. Rev. Lett. 122 246402

[19] Arnold F, Nyéki J and Saunders J 2018 Superconducting sweet-spot in microcrystalline graphite revealed by point-contact spectroscopy JETP Lett. 107 577–8

[20] Scheike T, Esquinazi P, Setzer A and Böhlmann W 2013 Granular superconductivity at room temperature in bulk highly oriented pyrolytic graphite samples Carbon 59 140–9

[21] Scheike T, Böhlmann W, Esquinazi P, Barzola-Quiquia J, Ballestar A and Setzer A 2012 Can doping graphite trigger room temperature superconductivity? Evidence for granular high-temperature superconductivity in water-treated graphite powder Adv. Mater. 24 5826

[22] Esquinazi P (ed) 2016 Basic physics of functionalized graphene Springer Ser. Mater. Sci. 244 ISBN 978-3-319-39353-7 (Switzerland: Springer International Publishing)

[23] Deguchi K, Mizuguchi Y, Kawasaki Y, Ozaki T, Tsuda S, Yamaguchi T and Takano Y 2011 Alcoholic beverages induce superconductivity in FeTe$_{1-x}$S$_x$ Supercond. Sci. Technol. 24 055008

[24] Deguchi K et al 2013 Tartaric acid in red wine as one of the key factors to induce superconductivity in FeTe$_{1-x}$S$_x$ Physica C 487 16–8

[25] Gao S, Xia J, Taallah A, Shang H and Boi F S 2019 Anomalous T-induced second order diffraction loss and magnetic transition in red-wine-doped highly oriented pyrolytic graphite at the magic angle Mater. Res. Express 6 115608

[26] Gao S et al 2020 Ferromagnetic correlation in hydrogen doped highly oriented pyrolytic graphite Diamond Relat. Mater. 109 108030

[27] Qadir A, Sun Y W, Liu W, Oppenheimer P G, Xu Y, Humphreys C J and Dunstan D J 2019 Effect of humidity on the interlayer interaction of bilayer graphene Physical Review B 99 045402

[28] Moazed M, Alvarez J V and Palacios J J 2014 Hydrogenation-induced ferromagnetism on graphite surfaces Physical Review B 90 115441

[29] Guo J, Lan M, Wang S, He Y, Zhang S and Boi F S 2015 Enhanced saturation magnetization in buckypaper-films of thin walled carbon nanostructures filled with Fe$_3$C, FeCo, FeNi, CoNi, Co and Ni crystals: the key role of Cr Phys. Chem. Chem. Phys. 17 18159

[30] Eckmann A, Felten A, Mishchenko A, Britnell L, Krupke R, Novoselov K S and Casiraghi C 2012 Probing the nature of defects in graphene by raman spectroscopy Nano Lett. 12 3925–30