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Muons Probe Strong Hydrogen Interactions with Defective Graphene

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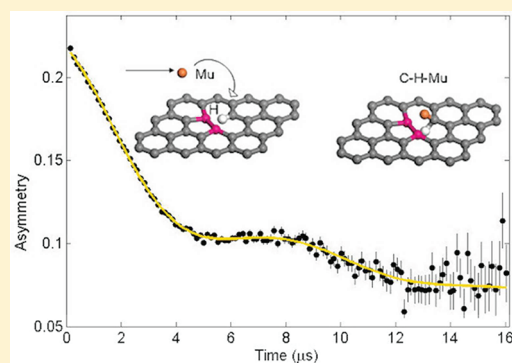
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S Supporting Information

ABSTRACT: Here, we present the first muon spectroscopy investigation of graphene, focused on chemically produced, gram-scale samples, appropriate to the large muon penetration depth. We have observed an evident muon spin precession, usually the fingerprint of magnetic order, but here demonstrated to originate from muon–hydrogen nuclear dipolar interactions. This is attributed to the formation of CHMu (analogous to CH₂) groups, stable up to 1250 K where the signal still persists. The relatively large signal amplitude demonstrates an extraordinary hydrogen capture cross section of CH units. These results also rule out the formation of ferromagnetic or anti-ferromagnetic order in chemically synthesized graphene samples.

KEYWORDS: Graphene, muon spectroscopy, defects in graphene, carbon magnetism, hydrogen storage



Graphene displays many features which are very promising for future attractive applications.^{1,2} Of particular interest in meeting the needs of the transportation industry is the possibility of developing graphene-based hydrogen storage systems.^{3,4} Indeed its single atom thickness and the consequent record surface/weight ratio of 2630 m²/g makes it an ideal system for gas adsorption. Other valuable industrial applications could come in the area of spintronics, if the theoretically anticipated development of long-range magnetic order, triggered by the presence of defects,⁵ can be experimentally confirmed.

Polarized muons have proved to be reliable and sensitive probes of local magnetic fields in matter and an important tool for the investigation of hydrogen reactions in low electron density materials such as carbon.⁶ In defective graphene, muon spectroscopy (μ SR) could thus help to address two open and well-debated questions: the possible onset of magnetism^{7,8} and the interaction with hydrogen.^{9,10} In a μ SR experiment the spin evolution of polarized positive muons, implanted in the sample, is detected courtesy of the parity violating decay of muons into positrons, which are emitted preferentially in the direction of the muon spin.¹¹ In particular, in systems with a relatively low electron density like graphene, the implanted muons, after being thermalized, capture an electron and form muonium (Mu), a light isotope of hydrogen having similar chemical behavior.⁶ In some materials, like clean semiconductors or in the presence of organic unsaturated molecules, the stopped muon still interacts

with a single electron. These paramagnetic states are thus very sensitive to even extremely small local magnetic fields. In other cases, Mu forms a covalent bond which provides two electrons around the positive muon. In this “diamagnetic state” the muon probes, now directly, the local magnetic field. Due to the typical range of muon stopping lengths (~ 0.5 mm), μ SR is suitable for studying bulk quantities of materials rather than single atomic layers. The recent development of various chemical methods for large scale production of graphene¹² has made μ SR investigation feasible. Chemically produced graphene is less “crystalline” than samples obtained by epitaxial growth or by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG). Indeed different concentrations of in plane defects, mainly vacancies, are known to be invariably produced by the chemical treatments.¹³ These defects are quite reactive and are known to induce a partial reoxidation if the defective graphene is exposed to air.¹⁴ For this reason, all investigated samples have been handled under strict oxygen- and moisture-free conditions.

In this Letter, we present the μ SR study of various chemically prepared graphene samples, possessing different concentrations of defects. In sp² carbon systems such as graphite, muonium attaches to the planar surface,¹⁵ similarly to hydrogen,¹⁶ as shown

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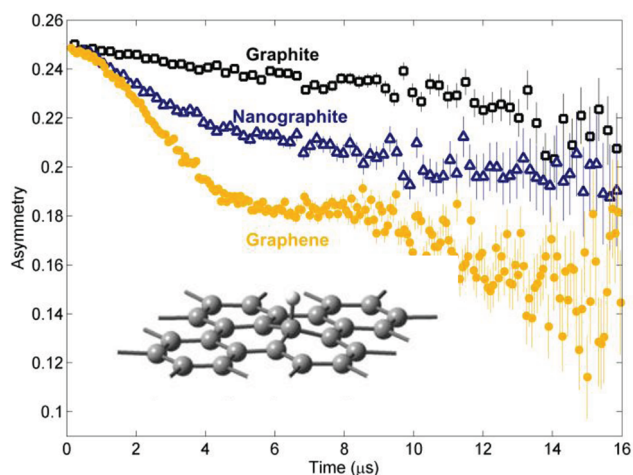


Figure 1. Muon decay asymmetry (evolution of the spin polarization) in different sp^2 carbon systems at room temperature. In graphite (squares) a slow Korringa relaxation is observed. If crystallites dimension is reduced by mechanical milling, the influence of the paramagnetic edges induces a further spin depolarization (triangles). If the graphite gets exfoliated into single layers, a clear spin precession appears (full circles, graphene sample TTSG, see Supporting Information). Like a hydrogen atom, on an ideal graphene layer muonium gets chemisorbed, as shown in the inset.

in the inset of Figure 1, and creates a “diamagnetic state”. The time dependence of the muon polarization asymmetry $A(t)$, in absence of an external field, shows a slow depolarization (Figure 1, squares) ascribed to the muon spin interaction with the π conduction electrons (Korringa).^{6,15} The relaxation rate is further increased in nanographite (Figure 1, triangles), obtained by mechanical ball milling,¹⁷ due to the interaction of the muon spin with the localized paramagnetic centers (dangling bonds). A similar behavior is also observed in graphite oxide, commonly used as a graphene precursor, where the presence of defects leads to an increase in the observed relaxing amplitude (relaxation rate consistent to that of ball milled graphite).

Unlike all these cases, a qualitatively different behavior is observed whenever graphite is exfoliated into single layers: a clear oscillation appears on top of the decaying signal (Figure 1, solid circles). This μ SR precession originates from a uniform quasi-static local magnetic field at the muon stopping sites (of the order of 5 Oe in our case). Such a coherent precession is usually the signature of long-range magnetic order, although in a few cases it may be due to the dipolar interaction of the muon with an isolated magnetic nucleus like ^{19}F or ^1H .¹⁸ The latter case is properly indicated as a μ -F (μ -H) entangled state.¹⁹

The presence of magnetism in defective graphene has been theoretically anticipated:^{16,20} both vacancies and chemisorbed hydrogen bear a magnetic moment and, when present in sufficient amounts, these defects can trigger the onset of magnetic ordering. In particular an antiferromagnetic order is predicted in the case of a fully disordered graphene system.²¹ Furthermore, transition temperatures above room temperature are expected, as reported in proton irradiated graphite.²² We first verified that the corresponding mathematical model adequately fit the experimental data for as-prepared graphene samples (see Supporting Information for details). Then to further test this hypothesis, the investigation was focused on the dependence of the precession signal upon defects concentration. As described in the

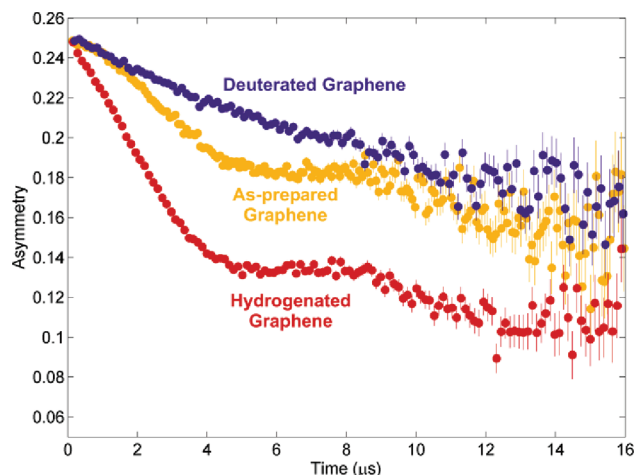


Figure 2. Muon decay asymmetry in different graphene samples at room temperature. As-prepared graphene (yellow circles, sample TTSG, see Supporting Information), after treatment with H_2 at 1073 K (red circles, sample HTG, see Supporting Information) and after treatment with D_2 at 1073 K (blue circles, sample DTG see Supporting Information). While after hydrogenation the precession signal amplitude increases from 12% to 40% of the implanted muons, the deuteration inhibits the precession and only the decaying fraction of the signal is left.

Supporting Information the preparation procedures were modified to produce graphenes with different concentrations of defects that were estimated by Raman and SQUID magnetometry. An evident correlation between the observed oscillation amplitude and the defects concentration was found (see Figure S8 in the Supporting Information). The magnetic hypothesis, however, began to weaken when the investigation of the temperature dependence of the precession signal showed that it persists up to 1250 K (Figure 4). Such a high critical temperature far exceeds the highest transition temperature ever reported in carbon materials and is hardly conceivable. A clearer picture could only be obtained upon the investigation of hydrogen treated samples.

Figure 2 (red circles) reports the muon spin asymmetry after the sample has been treated with H_2 at 1073 K. When compared with the untreated graphene (yellow circles), a dramatic increase in the signal amplitude (from 12% to 40% of the implanted muons) is observed. Although this indicates that hydrogen is directly involved in the creation of the local magnetic field at the muon site, it cannot dispute the magnetic hypothesis, as chemisorbed hydrogen is known to produce local magnetic moments on graphene.¹⁶ A definitive interpretation was obtained by treating the graphene samples with deuterium. Of course the isotopic substitution would lead to no differences in the case of magnetic order, while after deuterium treatment the precession completely disappears (Figure 2, blue circles). This proves that the origin of this signal is the nuclear dipolar interaction of the muons with the spins of absorbed hydrogen. Although deuterium also possesses a nuclear moment, it is 7 times smaller than that of protons, implying an equivalent reduction in muon precession frequency. The expected oscillations are consequently not appreciable within the accessible experimental time scale.

Figure 3 shows the fit of the observed muon spin evolution in a hydrogenated sample, under the hypothesis of the formation of a μ -H entangled state. The high statistics acquired in this experiment (150 million events) allowed for the comparison of the magnetic model fit (just one frequency) with the dipolar one,

having the beat of three frequencies involved (see details of μ SR data analysis in the Supporting Information). This showed that the latter model provided a better fit to the data especially at longer time scales. The fit gives a Mu–H internuclear distance of 1.70 ± 0.02 Å. This value matches the typical interhydrogen separation in CH_2 groups with the carbon atom in the sp^3 hybridization. Thus the precession signal originates from an isolated CHMu group, whose formation at a vacancy site, edge, or a related defect can be easily explained and is represented in Figure S9 in the Supporting Information. It is known that the vacancies formed after the detachment of hydroxyl groups from the graphite oxide precursor, partially reconstruct by connecting two out of three sigma dangling bonds.^{16,20} The third dangling bond tends to react with the residual hydrogen generated, for example, during the exfoliation process. This monohydrated vacancy containing a

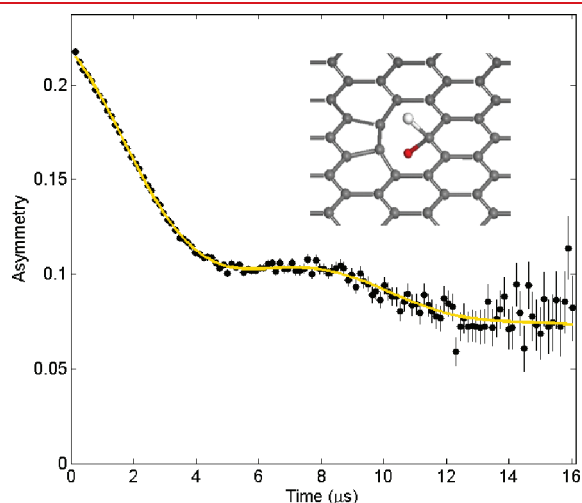


Figure 3. Fit of the muon decay asymmetry for an hydrogenated sample in the μ -H hypothesis (sample HTG see Supporting Information for preparation methods). The large amplitude of the signal and the high statistics of the measurement allowed to attribute the precession signal to the dipolar interaction with a nearby hydrogen atom. The fit for the hypothesis of long-range magnetism is less satisfactory in the long times region (see Supporting Information). The fitted Mu–H distance (1.70 Å) matches the interproton distance in a CH_2 group, with the carbon atom in sp^3 hybridization. The formation of this group at a graphene vacancy is depicted in the inset.

H-terminated sp^2 carbon atom traps the muonium and forms the CHMu group by changing the hybridization state of this carbon atom into the sp^3 state (shown in the inset of Figure 3). This isolated, dipolar coupled, μ -H entangled state generates the observed muon precession signal.

Hydrogen annealing further increases the number of H-containing trapping centers, inducing the observed increase of precession amplitude. The order of magnitude difference between the estimated defects concentration ($(0.5\text{--}2.5) \times 10^{-3}$ molar ratio as estimated by SQUID magnetometry) and the number of muons trapped by them (10–40%) indicates an exceptional hydrogen (muonium) capture efficiency of bare and monohydrogenated vacancies. In order to account for this behavior, we performed first-principles calculations. We found that the binding energy of muonium to the hydrogenated vacancy (Figure 3, inset) was 1.74 eV larger than the binding energy to pristine graphene, leading to the configuration shown in the inset of Figure 1. Similarly, we observe thermodynamic preference toward the binding of muonium to hydrogen-terminated graphene edges with edge carbon atoms in sp^2 hybridization. The results of our calculations point out that the high efficiency in trapping muonium or hydrogen is a general feature of sp^2 carbon atoms at defects in graphene.

Figure 4 shows the thermal evolution of the local field and precession amplitude. The signal amplitude was found to increase during heating to 1220 K while at 1320 K only a 15% reduction was observed. This indicates an exceptional stability of the CH–Mu (and more generally CH_2) fragments. The amplitude increase as a function of temperature shown in Figure 4b gives suggestions on the trapping mechanism. After the muon thermalization and electron capture, a thermally activated motion like the Mu diffusion on the graphene layer could account for the observed increase of amplitude. Further investigations are however required to identify a precise trapping model.

With respect to the magnetic hypothesis, these μ SR results rule out the existence of magnetic phases in the defective graphenes investigated. Muons are very sensitive to local internal fields and in this instance do not show the presence of any magnetization. In addition, our study also rules out the presence of antiferromagnetic order, not easily detectable with ordinary magnetometric techniques. This resolves the recent controversy raised by the recent reports of both existence²³ and absence⁷ of magnetic ordering in bulk graphene samples. We would like to note, that

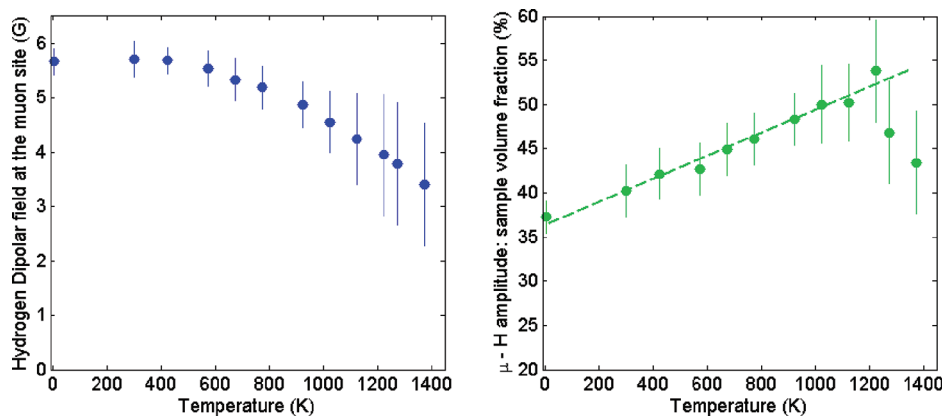


Figure 4. Temperature evolution of the muon precession frequency (a) and amplitude (b). The observed decrease in frequency is attributed to the thermally induced increase of H–Mu distance while the increase in amplitude suggests a thermally activated capture mechanism most likely associated with diffusion dynamics. The slight drop in amplitude observed above 1200 K shows the exceptional thermal stability of the CH–Mu group.

our conclusion regarding the absence of magnetic ordering in chemically synthesized graphenes does not concern other unambiguously proven cases, e.g., ferromagnetism in proton-irradiated graphite,²² small synthesized graphene fragments,²⁴ or the recently reported indication of edge-state magnetism in graphene nanoribbons.²⁵

In summary, we have shown that ZF- μ SR displays a muon precession whenever graphite is exfoliated into single layers. The muon precession was found to result from the nuclear dipolar interaction with a single proton located at a distance of 1.7 Å from the muon. The amplitude of the observed precession (related to the muons fraction involved) correlates with the density of defects and dramatically increases after hydrogenation of the samples. This observation is consistent with the formation of a CH–Mu group stable up to 1200 K. These results highlight the absence of magnetic ordering in the chemically derived defective graphenes. Muon spectroscopy has allowed a fundamental understanding of the atomic interactions between hydrogen and graphene, providing new insights for the engineering of platform graphene technologies for the storage of hydrogen.

■ ASSOCIATED CONTENT

S Supporting Information. Additional details on sample preparation, electron microscopy characterization, muon spin rotation/relaxation, μ SR data analysis, and first principles calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

M.R., M.M., and D.P. performed the μ SR experiments and data analyses, interpreted the results, prepared part of the samples, and performed the SQUID characterization. J.A.S. and M.C. synthesized part of the samples, performed elemental analysis and the Raman and microscopy investigations. O.V.Y. developed the theoretical model and performed first-principles calculations.

■ ACKNOWLEDGMENT

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