Magnetic defects in chemically converted graphene nanoribbons: electron spin resonance investigation

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Electronic spin transport properties of graphene nanoribbons (GNRs) are influenced by the presence of adatoms, adsorbates and edge functionalization. To improve the understanding of the factors that influence the spin properties of GNRs, local (element) spin-sensitive techniques such as electron spin resonance (ESR) spectroscopy are important for spintronics applications. Here, we present results of multi-frequency continuous wave (CW), pulse and hyperfine sublevel correlation (HYSCORE) ESR spectroscopy measurements performed on oxidatively unzipped graphene nanoribbons (GNRs), which were subsequently chemically converted (CCGNRs) with hydrazine. ESR spectra at 336 GHz reveal an isotropic ESR signal from the CCGNRs, of which the temperature dependence of its line width indicates the presence of localized unpaired electronic states. Upon functionalization of CCGNRs with 4-nitrobenzene diazonium tetrafluoroborate, the ESR signal is found to be 2 times narrower than that of pristine ribbons. NH3 adsorption/desorption on CCGNRs is shown to narrow the signal, while retaining the signal intensity and g value. The electron spin-spin relaxation process at 10 K is found to be characterized by slow (163 ns) and fast (39 ns) components. HYSCORE ESR data demonstrate the explicit presence of protons and 13C atoms. With the provided identification of intrinsic point magnetic defects such as proton and 13C has been reported, which are roadblocks to spin travel in graphene-based materials, this work could help in advancing the present fundamental understanding on the edge-spin (or magnetic)-based transport properties of CCGNRs. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4870942]

I. INTRODUCTION

Graphene-derived materials show remarkable spin transport properties originating from a very low intrinsic spin-orbit coupling \( \langle \Delta_{SO} \rangle \approx 1 \mu\text{eV} \) and small hyperfine (hf) interaction (due to a...
low abundance of the C\textsuperscript{13} isotope).\textsuperscript{1–3} Among all, graphene nano ribbons (GNRs) are expected to show superior semiconducting properties over pristine graphene due to a tunable band gap.\textsuperscript{4, 5} GNRs have been shown to exhibit novel properties upon functionalization. For instance, it has been reported that edge (spin) functionalization leads to non-linear edge magnetization.\textsuperscript{6} In particular, edge functionalization with oxygen-containing groups has been shown to significantly lower the electric field required to induce half metallicity in zigzag GNRs (ZGNRs).\textsuperscript{7} Boron substitutional doping, either on the edge or in the bulk, was reported to cause a metal-semiconductor transition in the ferromagnetic and nonmagnetic ZGNR states.\textsuperscript{8} Room temperature magnetic ordering has been reported in functionalized graphene,\textsuperscript{9} though the origin of magnetic properties of such materials has been intense experimental and theoretical interest. To better understand the magnetic and electronic properties of graphene-based materials, it is important to employ sophisticated spin-sensitive local probes such as electron spin resonance (ESR).

As indicated above, owing to their novel physical properties, graphene-based materials have been thought to be excellent candidates envisaging them for applications ranging from information storage to catalysis, which are controlled by native and foreign defects. It is of fundamental scientific and technological interest to identify and understand the nature of such defects. ESR spectroscopy provides an important wealth of information pertaining to the nature and environment of defects which contain the unpaired electrons through frequency- and temperature-dependent measurements. Important information regarding the nature of paramagnetic centers and their surroundings can be obtained from the analysis of the ESR spectra such as line shape, line width and g-factor.

Here, we briefly review the ESR investigations reported\textsuperscript{10–13} in the literature while probing for the spin properties of graphene-derived materials. For instance, an interesting work\textsuperscript{10} carried out on chemically-derived graphene oxide and reduced graphene oxide through ESR spectroscopy reported on the presence of localized paramagnetic defects and discussed how these defects influence the transport properties. In a detailed combined theoretical-experimental study,\textsuperscript{11} Arash and co-workers have investigated the paramagnetic centers detected from the assembly of chemically exfoliated graphene nanoribbons. This study has identified both localized and extended defects from the ribbons. In another systematic work,\textsuperscript{12} Su and co-authors have employed ESR spectroscopy in exploring the catalytic properties of graphene oxide and illustrated the role of defects, concluded that localized spins are created at the edge of pi-electron system. In another work,\textsuperscript{13} while exploring the spin magnetism of nano sized graphite particles, EPR spectroscopy has revealed the presence of strongly coupled localized and itinerant spins. A more recent ESR-NMR study\textsuperscript{14} carried out on graphene oxide derived from Hummers method revealed isolated extrinsic Mn\textsuperscript{2+} impurities and discussed how these impurities modify intrinsic spin relaxation times. Excellent reviews on the possible role of defects, doping and chemical modification in graphene sheets on the magnetic and electronic properties can be found in Refs. \textsuperscript{15 and 16}.

As outlined above, so far, the presence of localized spins originating from carbon-related defects present at the graphene edges was studied using only with the conventional single frequency X-band (\textasciitilde9.35 GHz) ESR spectroscopy. Importantly, further understanding on how these spins behave at higher microwave frequencies and how these spins respond in proximity with another spin species that might occur in the form of edge functionalization/doping and with the simple physical adsorption is apparently missing in the literature. More fundamentally, the previous spin transport studies\textsuperscript{8, 10, 15, 16} on graphene-derived materials have indicated the influence of native point defects such as carbon related dangling bond defects, \textsuperscript{1}H and \textsuperscript{13}C resulting inferior transport characteristics, though unraveling their explicit presence remains elusive, which has motivated to take up the present study.

In the present work, the nature and dynamics of paramagnetic native point defects present in chemically converted GNRs (CCGNRs) is reported as a function of microwave frequency and temperature. Furthermore, the current study investigates these defects when the ribbon edge atoms are functionalized with nitrogen-containing groups and up on NH\textsubscript{3} adsorption. More importantly, this study provides the explicit evidence for the presence of native point defects such as \textsuperscript{1}H and \textsuperscript{13}C in pristine ribbons, obtained using low temperature pulsed X-band (\textasciitilde9 GHz) ESR spectroscopy.
II. EXPERIMENTAL

Oxidatively unzipped GNRs were prepared by the longitudinal chemical unzipping of MWCNTs. Briefly, the method involves the treatment of MWCNTs, consisting of 15–20 concentric cylinders (diameter 40–80 nm), first with concentrated H₂SO₄ and subsequently by KMnO₄ (an oxidizing agent) at room temperature; after quenching in acid, the GNRs were further reduced by hydrazine (N₂H₄), forming chemically converted graphene nanoribbons (CCGNRs). This process forms CCGNRs up to 4 μm long, with widths of 100–500 nm and thicknesses of 1–5 graphene layers. Several techniques were used to fully characterize CCGNRs and to test their electronic properties as reported earlier. CCGNRs have been functionalized with 4-nitrobenzene diazonium tetrafluoroborate (4-NBDTFB), designated as functionalized-GNRs (FGNRs). The FGNRs are soluble in water and are free from most oxygen-containing groups other than on the nitrobenzene functionalities. High-resolution X-ray photoelectron spectroscopy (XPS), infra red (IR) spectroscopy and Raman spectroscopy were used to confirm the successful functionalization of FGNRs.

High frequency continuous wave (cw) ESR experiments were performed at 336 GHz using the quasioptical spectrometer that has been developed at the National High Magnetic Field Laboratory (NHMFL). This superheterodyne spectrometer employs a quasioptical submillimeter bridge and operates in the reflection mode without cavity, complemented with a sweepable 12.5 T superconducting magnet. The incident microwave power P₀ on the sample was about 500 μW. Conventional cw X (~9.1 GHz) and Q (~34 GHz) band measurements, generally detecting first derivative dP/dB spectra (where B is the applied magnetic field) were carried out using a commercial Jeol JES-FA 100 and a Bruker EMX spectrometer, respectively, driven in the adiabatic slow passage mode. Cw X-band (~8.9 GHz) and K-band (~20.5 GHz) measurement at liquid-He temperatures were made using locally constructed spectrometers, equipped with a bath cryostat.

For the cw ESR (X-band) experiments on FGNRs, use was made of a co-mounted LiF:Li marker (S = 1/2, g = 2.002 29 ± 0.000 02) for g value and intensity calibration purposes. For ESR (X-band) NH₃ gas adsorption studies of CCGNRs, we used a MgO:Mn²⁺ marker, with details as described below: The MgO:Mn²⁺ marker (electron spin S = 5/2; ⁵⁵Mn: 100 % natural abundance; nuclear spin I = 5/2) was supplied together with the Jeol X-band spectrometer in the shape of a small rod that can be electromechanically inserted from outside into the microwave cavity. The Mn²⁺ in MgO matrix gives a spectrum of 6 clear (sharp) hyperfine (hf) split lines (Lorentzians in X-band measurements) with adjacent peak separation of ~ 85 × 10⁻⁴ T. For g value calibration, use was made of only the Mn²⁺ line closest in g factor to the signal of interest, i.e., the fourth line of the Mn²⁺ sextet with g (X-band) calibrated as 1.9807 ± 0.0001. The ESR spectra were measured in situ: a quartz tube containing the sample at one end was inserted in the ESR cavity, with the other end connected to the gas-adsorption facility, composed of high purity (≥ 99.9995 %) gas reservoir of NH₃, a pressure gauge and a liquid-N₂ baffled vacuum diffusion pump (10⁻⁴–10⁻⁵ Torr range).

The pulse ESR experiments were performed using a Bruker Elexsys-580 X-band pulse ESR spectrometer, which was equipped with an CF935 flow cryostat. To record field-swept echo (FSE) ESR spectra and to measure the spin-spin relaxation time T₂ or phase memory time (TₐM) at 10 K, the two-pulse-echo sequence was used. The lengths of the microwave π/2 and π pulses were 12 and 16 ns, respectively, and the entire echo was integrated.

X-band (~9.64 GHz) HYSCORE spectroscopy was carried out at temperature = 10 K with a repetition time of 1 ms using the four-pulse sequence π/2-τ-π/2-τ₁-π₁-τ₂-π-π/2-τ-echo (τ is the time between two pulses). The microwave (mw) pulse lengths applied were τ₁/2 = 12 ns and τ₂ = 24 ns, starting times τ₀ = τ₂₀ = 260 ns, a τ = 164 ns and a time increment of Δτ = 8 ns (data matrix 512 × 512). Special attention has been paid to make sure that no external impurity was introduced while handling samples during the measurements. All the ESR measurements were done on the ensemble of ribbons in solid form.

III. RESULTS AND DISCUSSION

In our previous X-band ESR work on CCGNRs (then, the ribbons were labeled as GNRs), we have shown the presence of a specific carbon defect-related paramagnetic center (GC) at g = 2.0032
and peak to peak line width ($\Delta B_{PP}$) $\sim$ 3–4 (10$^{-4}$T). Our previous work$^{20}$ also suggested that C edge defects at the periphery of graphene ribbons are at the origin of the observed ESR signal. The defect is observed to be readily quenched upon O$_2$ adsorption, strongly dependent on O$_2$ partial pressure and temperature, this process is found to be fully reversible upon oxygen desorption. The $\Delta B_{PP}$ and $g$-values were found to be independent of O$_2$ partial pressure. Other gases like H$_2$, He, N$_2$, and Ar are found to have no impact on the ESR spectral properties, pointing to a unique and specific GC$-$O$_2$ interaction, indicating the GC center may serve as a high sensitive, reversible O$_2$ sensor. The spin density in CCGNRs is estimated at $\sim$1.5 $\times$ 10$^{17}$ g$^{-1}$.

In the current work, with the aim of gaining additional information on the spin dynamics from CCGNRs, we measured the ESR response from CCGNRs at high microwave frequency (336 GHz) as a function of temperature. As clearly illustrated in the inset of Fig. 1, a symmetric, isotropic behaving, ESR signal is observed at zero-crossing $g$ value $g_c$ = 2.0032, which falls within the carbon ESR signal range ($g$ = 2.0022 – 2.0035), and may be ascribed$^{20}$ to C-related dangling bonds with spin $S$ = 1/2. At all temperatures the signal can be fitted with a single Lorentzian. No other ESR signals could be observed over a broad magnetic field sweep range. Neither any correlated additional signal structure was detected nor any sign of a hf structure ensue from $^1$H, $^{14}$N, $^{16}$S and $^{55}$Mn nuclei. As shown in Fig. 1, we find that $\Delta B_{PP}$ measured at 336 GHz gradually decreases with increasing temperature, while $g$ is found to remain almost constant at $g$ = 2.0032 ± 0.0001. As reported in our earlier work$^{21}$ (see Fig 3a in ref 21), the temperature dependence of ESR spin susceptibility measured at K-band ($\sim$20.6 GHz) on the CCGNRs (then, the sample was labeled as RGNRs) exhibits a Curie-type paramagnetic behavior, with the temperature independent $g$-value of 2.0032.
To better understand the nature of spins and to get deeper insight, now, we analyze the temperature dependence of line width ($\Delta B_{pp}$). According to the variable range hopping (VRH) mechanism, in the paramagnetic phase, the $T$ dependence of $\Delta B_{pp}$ can be described by

$$\Delta B_{pp} = K \exp\left(\frac{T_0}{T}\right)^{1/n}$$

where $n-1$ is the dimensionality of the system and $T_0$ (determined by the characteristics of localized states) and $K$ are constants. It appears that this dependence from 20 K – 70 K follows VRH mechanism which exhibits linear relationship expressed $\ln(\Delta B_{pp})$ versus $T^{-1/3}$ coordinates for a two-dimensional (2D) system as shown in Fig. 2, thus further supporting the existence of localized states, created by atomic defects at the graphene edges in GNRs. Hence, from these measurements, it is inferred that the charge transport is dominated by hoping through localized states. As reported in our earlier work, the resistance/temperature data is consistent with the 2-dimensional VRH mechanism, typically applicable for materials containing large number of defects. In addition, as we reported earlier, in monolayer CCGNR, the conductivity (∼35 S/cm) and mobility (0.5–3 cm²/Vs) of charge carriers are less than the conductivity and mobility of pristine graphene, which was explained by oxidative damage caused by the harsh H₂SO₄/KMnO₄ used to make CCGNRs. The resistance of ribbon devices increases by about three orders ($10^6–10^9$ ohms) of magnitude upon cooling from 300 to 20 K. The edge defects and residual oxygen containing functional groups were believed to be responsible for the inferior conductivity and mobility values when compared to pristine graphene. Also, our transmission electron microscopic images suggest that the ribbons have a nonuniform structure. The VRH-type electron transport mechanism has also been reported in several other graphene-derived materials such as reduced graphene oxide and patterned GNR.
FIG. 3. The microwave frequency dependence of $\Delta B_{PP}$ of CCGNRs at 4 K. A linear frequency dependence was observed, suggesting a strain-induced spread in $g$ as major line broadening ($\sim 0.179 f (\text{GHz}) \times 10^{-4} T$) mechanism, with a $f$-independent part of $2.73 \times 10^{-4} T$). The solid lines represent a least-square linear fit, described by $\Delta B_{PP} (10^{-4}T) = 2.73 + 0.179 f$ (GHz).

From the slope of the VRH-fitting, the characteristic temperature ($T_o$) is estimated at $\sim 784$ K. Previous studies have reported the characteristic temperature as high as 1800 K in highly reduced graphene oxide materials. From $T_o$, the localization length $\xi$, an indication of edge disorder, is estimated by,

$$T_o = \left(\frac{(2.8 e^2)}{4\pi \varepsilon \varepsilon_o k_B \xi}\right)$$

Where, $\varepsilon_0$ and $\varepsilon$ are the value for permittivity of vacuum and the dielectric constant of the material. We used an effective dielectric constant of $\varepsilon = 3.5$ for graphene nanoribbons. The derived localization length ($\xi$) is of $\sim 18$ nm. The localization length derived here is in good agreement with those of literature values ranging from 7 nm to 7 $\mu m$. The $\xi$ values obtained in VRH allowed us to estimate the bandgap ($E_g$) by

$$E_g = \frac{h V_F}{2\pi \xi}$$

Where, $V_F$ is the Fermi velocity of graphene. The derived band gap ($E_g$) is $\sim 30$ meV, is in close agreement with the band gap ($\sim 50$ meV) reported by some of us on the similar high temperature hydrogen-annealed graphene nanoribbons using transport measurements and also reported in lithographically patterned graphene nanoribbons (10–100 meV).

More insight on the line broadening mechanisms may be obtained from measurements performed at different microwave frequencies ($f$’s). As plotted in Fig. 3, for data taken at 4 K, the ESR line width $\Delta B_{PP}$ is found to be linearly dependent on microwave frequency ($f$). Upon least squares computer fitting of the experimental data, the $f$-dependent part is obtained as $\Delta B_{PP}^{f} = 0.179 \times 10^{-4}$ T/GHz, a Gaussian broadening, and a $f$-independent part of $2.73 \times 10^{-4} T$. A similar linear frequency
FIG. 4. First derivative X-band ESR spectra measured at 300 K on FGNRs using $B_m = 0.4 \times 10^{-4}$ T (as amplitude of the applied $\sim 100$ kHz magnetic field modulation) and $P_\mu = 1.8$ nW. The signal at $g \approx 2.00229$ stems from a co-mounted LiF:Li marker sample; The experimental curve can be simulated using a Lorentzian line shape (in red). In the inset is shown a broad magnetic field range ($0.6$ T) X-band ESR spectrum (using $B_m = 0.5 \times 10^{-4}$ T, $P_\mu = 1.8$ nW).

The dependence of $\Delta B_{pp}$ behavior has been reported$^{21}$ in our earlier work on different (from current samples) type of graphene nano ribbons prepared$^{27}$ through potassium-split of carbon nanotubes. The residual Gaussian part can be attributed to a $g$-distribution effect resulting from different local environments of paramagnetic centers in CCGNRs. The remaining large $f$-independent part can be due to dipolar interaction, unresolved hyperfine (hf) interaction —perhaps, arising from hydrogen nuclei— resulting in inhomogeneous Gaussian broadening and also the contribution from molecular oxygen. However, in our recent work$^{20}$ on CCGNRs (then, the ribbons were labeled as GNRs), we found that molecular oxygen does not broaden the ESR signal width. Then, the main contribution might arise from the unresolved hf coupling (hfc) coming from protons. The explicit evidence for the presence of protons in CCGNRs is demonstrated by the HYSCORE measurements, as will be discussed below.

Results of room temperature (300 K) X-band ($\sim 9.169$ GHz) cw ESR experiments have been performed on FGNRs are shown in Fig. 4, where we plot the observed as well as simulated ESR spectrum of FGNRs. Interestingly, we notice that upon functionalization with 4-NBDTFB, $\Delta B_{pp} \approx (1.6 \pm 0.1) \times 10^{-4}$ T decreases more than two times compared to that ($\approx 3.75 \pm 0.10$) $\times 10^{-4}$ T of pristine ribbons measured under similar experimental conditions.$^{20}$ The corresponding electron spin-spin relaxation times $T_2 = 1/(\gamma_e \Delta B_{pp})$ before and after functionalization are estimated as $\sim 15$ ns and 35 ns, respectively, where $\gamma_e$ is the gyromagnetic ratio for electrons, with a value of $1.760 \times 10^{11}$ s/T. While transferring the line width to spin-spin relaxation time ($T_2$), other broadening mechanisms such as instantaneous diffusion (ID) can be operative, particularly at low temperatures.

In the present case, we assumed that contribution is smaller as the signal shape is Lorentzian and homogenously broadened, hence, we did not take this into account. However, the $g$ value ($g = 2.0032$) and the Lorentzian character of the signal remain practically the same as that of pristine ($g = 2.0032$)
FIG. 5. First derivative X-band (∼9.18 GHz) ESR spectra (typically, 5–10 scans each) measured at 300 K on CCGNRs under exhaustive evacuation (diffusion pumped), NH₃ passivation at P_{NH₃} = 1210 Torr, and after re-evacuation using B_m = 0.25 × 10⁻⁴ T and P_e = 2 mW. The CCGNRs defect center (G_C) appears at g_C = 2.0032. The spectrum has been normalized relative to the signal of a co-mounted Mn marker. The inset represents the enlarged version of G_C signal recorded under various conditions.

ribbons. In addition, we did not observe noticeable change in the spin density (∼2.2 × 10¹⁷ g⁻¹) estimated from these ribbons after functionalization, and hence could not be ascribed line narrowing to a simple dipole-dipole interaction. The decrease in ESR signal width after functionalization could be due to exchange narrowing mechanism as we observed homogeneously narrowed Lorentzian ESR signal. Furthermore, the narrowing of the ESR signal upon functionalization of CCGNRs might be related to the observed decreases in electrical conductivity. This particular observation has been explained by the covalent attachment of 4-nitrophenyl groups to the CCGNRs, resulting in the transition of the graphene carbon atoms from sp² to sp³ hybridization. Such line narrowing and increase in spin-spin relaxation times are reported in previous studies on graphene-like nanocarbon sheets doped with nitrogen. Also, in another work on carbon films, it was reported that the ESR signal width and conductivity decreases as a function of nitrogen doping, attributed to exchange narrowing mechanism. Our results infer that there could be weak nitrogen doping during the process of functionalization with 4-NBDTFB as nitrogen is well-known donor.

Room temperature (300 K) X-band (∼9.180 GHz) cw ESR experiments have been carried out on CCGNRs upon NH₃ adsorption and desorption using a Jeol X-band ESR spectrometer. Figure 5 shows a selection of ESR spectra measured under, consecutively, evacuation (∼10⁻⁴ Torr) (black), adsorption of NH₃ with the partial pressure of P_{NH₃} = 1210 Torr (red), and re-evacuation (∼10⁻⁴ Torr) (blue). The right narrow signal in each trace stems from the MgO:Mn²⁺ marker placed inside the cavity. As shown by the spectrum in black, a symmetric and isotropic Lorentzian ESR signal is revealed at g_C = 2.0032 with ΔBPP ≈ 3.7 ± 0.15 × 10⁻⁴ T, showing the signature of a C-related spin S = 1/2 defect, named as G_C. The fits of each observed ESR signal with the Lorentzian line shape are shown in the supplemental information (see, Fig. S1), which are in close agreement.
with the observed signal, though with the residual difference. As evidenced by the trace represented in red shown in Fig. 5, upon immersion in NH₃ (P NH₃ = 1210 Torr), the GC signal seems not to change. However, upon NH₃ adsorption, we observed a clear signal narrowing (by ∼0.5 ± 0.16 × 10⁻⁴ T) with attendant small increase in the peak-to-peak signal height; Yet, double numerical integration of the signals indicates that the total spin density (∼2 × 10¹³ g⁻¹) remains unchanged. Interestingly, upon desorption (re-evacuation) of NH₃, the ESR signal width did not fully recover as demonstrated by trace displayed in blue in Fig. 5 (see the zoomed in spectra in the inset for more clarity). In analogy to the case of MWCNTs, electron-donating ammonia seems to effect the interlayer interaction in CCGNRs thereby narrowing the ESR signal. Noteworthy also is that, even after the functionalization and NH₃ gas adsorption, we observe that neither GC sites are ‘lost’ nor are additionally ones created – one is dealing with an inherent (robust) set of edge defects. We did not see any indication of a characteristic hf triplet typically expected for interaction of the unpaired electron with the ¹⁴N nucleus (¹⁴N; I = 1; 99.63 natural abundance) as might arise from the process of functionalization with 4-NBDTTFB and NH₃ adsorption. In other words, besides GC, no other ESR signal could be traced over a sweep range up to 0.55 T as shown in the inset of Fig. 4.

Pulsed ESR methods use the electron spin echo (ESE) signal for studying the dynamical behavior of a spin system through observation of spin system magnetization behavior after a short (ns) microwave pulse excitation. In contrast to classical cw ESR, which operates on resolved spectral lines, the ESE methods can resolve the linewidth of the constituent unresolved homogeneous spin packets. The hyperfine interactions (HFIs) of unpaired electrons with surrounding nuclei lead to the appearance of quantum beats in the system response to microwave pulses. These beats are called electron spin echo envelope modulation (ESEEM). The frequency spectrum of such modulations contains information about the hyperfine coupling parameters and can be used to draw valid conclusions about the structure of the studied paramagnetic centers.

As outlined, we have performed x-band pulsed ESR experiments. Though we did not see two ESR signals even at high frequency of 336 GHz in the cw ESR experiments (see inset of Fig. 1), in pulsed ESR experiments we found that the ESE signal could be deconvoluted into two components, a slower (163 ns) and a faster (39 ns) decaying one, as discussed below. Figure 6 presents the Hahn-echo decay trace (shown in black) for CCGNRs measured at 10 K and field position Bo ≈ 331 × 10⁻³ T. The red curve represents an optimized least-squares double exponential fit, involving two spin-spin relaxation time (T₂) values with an R² value of 0.9888, using the equation,

\[ y = y_0 + A \exp\left(-2\tau/T_2\right) \]

where \( y_0 \) is the off-set in ESE amplitude and \( A \) is the pre-exponential factor. The slower and faster relaxation components are characterized by \( T_2 = 163 ± 0 \) ns and \( 39 ± \) ns, respectively. We have tested also the validity of single exponential fit as shown in the supplementary information (see, Fig S2), however, yielding a reduced R² value of 0.9706. Therefore, we believe that the observed ESE signal could be well described by double exponential fit. These relaxation times are much smaller than those (∼600 ns and 200 ns for slow and faster components, respectively) obtained on K-split GNRs, as reported by us earlier. This might be partially explained by the presence of adatoms/adsorbates such as oxygen and hydrogen which are expected to substantially modify the spin relaxation times through modifying the spin-orbit interaction. It should be noted, however, that while a two-component decay may well describe the experimental data, it is possible that we have a superposition of more than 2 components, and is due to a distribution of T₂ values. In a recent interesting ESR work on graphene-based materials, T₂ values of 0.2–0.6 μs have been reported. A two-component spin relaxation process has been observed previously in the case of hydrogenated amorphous carbon. To probe the spin dynamics, Clewett and co-authors have conducted power saturation ESR studies on MWCNTs to extract temperature-dependent relaxation data. Similar to our observations, they also have reported higher T₂ of the order of ∼500 to 600 ns at all temperatures measured. In a recent systematic study of spin transport in bi-layer graphene (BLG), long spin relaxation times of as long as 2 ns have been observed at room temperature, and is reported to be longer than those of single layer graphene (SLG), attributed to the dominance of D’yakonov-Perel’ spin scattering in BLG.
FIG. 6. An X-band ESR pulse inversion-recovery trace (black) for CCGNRs measured at 10 K at the field position $B_0 = 3310 \times 10^{-4}$ T for the spin-spin relaxation time ($T_2$)/phase memory time ($T_M$). The red curve represents an optimized least square fitting result of the sum of two exponentials (cf. Eq. (4)) with the involved spin-spin relaxation times $T_2$ inferred as $\sim 39$ ns and 163 ns. Least-squares double exponential fit is indicated by red trace with an $R^2$ value of 0.9888. For further details, see the text.

When the paramagnetic center is surrounded by several nuclei, it is often difficult to interpret the 1-dimensional (1D) ESEEM spectra if there is a broad distribution of hyperfine coupling values. To circumvent this issue, and to shed additional light, one fruitful way of simplifying the analysis of complex 1D ESEEM spectra is the use of two dimensional (2D) techniques such as HYSCORE (HYperfine Sublevel COrRElation) spectroscopy in orientationally disordered samples such as CCGNRs. HYSCORE is a high-resolution 2-dimensional pulsed ESR technique used here to measure small hfc’s not resolved in the CW ESR spectrum.

Now, let us examine the HYSCORE spectrum collected on CCGNRs displayed in Fig. 7 that reveals two nuclear isotopes coupled to the electron spins. There is a strong peak located at 14 MHz which is the NMR frequency of protons ($S = 1/2, I = 1/2$), which corresponds to weakly coupled protons, and a weaker peak appears at around 3.7 MHz, corresponding to the NMR frequency of $^{13}$C. Figure 6 displays ridges along the proton diagonal line with proton hfc’s in the range of 20–29 MHz ($\sim 0.892$ mT), implying that some radicals are more strongly coupled to protons. It should be mentioned that a similar HYSCORE spectrum collected at 9.7 GHz, 12 K has been reported in our earlier work on different type of graphene nano ribbons (then labeled as GNRs) prepared through potassium-split of carbon nanotubes. The isotropic component of the hfc results from a Fermi contact interaction, which indicates an electronic orbital overlap interaction between the unpaired electron and the proton(s), rather than a pure through space dipole-dipole interaction. A single carbon centered radical with bonded hydrogen atoms like a methyl radical can be ruled out since in this case typically $A(1H) \sim 67$ MHz (2.4 mT), a hfc much bigger than observed in the HYSCORE spectrum and would result in an observable splitting in the CCGNRs CW ESR spectra (line width of 0.35 mT), contrary to the present observation. The HYSCORE data from
Fig. 7 reveal proton hfc’s around 25 MHz, a value comparable to those found for conjugated aliphatic radicals. The detailed analysis of the cross-peak line shape and intensity is beyond the scope of this article, and will be presented elsewhere.

Similar to the analysis reported on hydrogen absorption in ball milled graphite, if we assume the ESR signals to result from $\pi$ radicals, then we can use the proton hfc’s to estimate the electron spin density $\rho$ at the adjacent carbon atoms by means of the McConnell equation, $a_H(\alpha) = Q_H \rho^7$, where $Q_H \sim 2.7$ mT is an intrinsic coupling value for unit density and $a_H(\alpha)$ is the proton hyperfine coupling in mT. The hfc of $\sim 0.89$ mT from the HYSCORE, thus corresponds to a carbon electron spin density about 33%. The presence of hydrogen is also supported by the recent muon spectroscopy measurements on graphene.

In analogy to our earlier HYSCORE work on other GNRs, in addition to the proton hf interactions, the HYSCORE $^{13}$C signals (in natural abundance) at low frequencies in Fig. 6 indicate $^{13}$C hfc’s are in the range $|A(^{13}C)| < 4$ MHz ($\approx 0.14$ mT). The observed $^{13}$C hyperfine splitting can arise from $^{13}$C nuclei closer to the center of the nanoribbons with significantly lower spin density. Hence the hfc’s derived from the HYSCORE data indicate that the (unpaired) spin density, and thus wave function of the radical is spread over small graphitic moieties. Most likely the magnetic states are created from the cleavage of graphene sheets of MWCNTs during the splitting process, resulting in so-called zigzag and armchair edges. There could also be a population of radicals associated with aliphatic structures. These structural types are thought to create nonbonding $\pi$-electron states, which accommodate a high unpaired spin concentration.

IV. CONCLUSIONS

We have presented the results pertaining to multi-frequency continuous wave (CW), pulse and hyperfine sublevel correlation (HYSCORE) electron spin resonance (ESR) spectroscopic measurements performed on oxidatively unzipped graphene nanoribbons, followed by chemical conversion (CCGNRs) with hydrazine. The temperature dependent multi-frequency ESR data infer the presence of localized electronic states in CCGNRs. Upon functionalization of CCGNRs with 4-nitrobenzene diazonium tetrafluoroborate, the ESR signal width is found to be 2 times narrower compared to that of pristine ribbons. NH$_3$ adsorption/desorption on CCGNRs is shown to narrow the signal, while retaining the signal intensity and g value. The electron spin-spin relaxation process at 10 K is found to be characterized by slow (163 ns) and fast components (39 ns). HYSCORE ESR data point to the presence of protons and $^{13}$C atoms that could not be detected by cw ESR and conventional spin
transport measurements. The present work provides useful information relevant to the effects of intrinsic magnetic scattering centers to the spin relaxation behavior in graphene-based materials, an item under much current attention.

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30. See Supplementary Material Document at http://dx.doi.org/10.1063/1.4870942 for Lorentzian line shape fits along with the observed and difference spectra for all the experimental ESR signals resulted from evacuation, NH3 adsorption and re-evacuation recorded; also for demonstration of the non-applicability of single exponential fit to the ESE signal.