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Paramagnetic centers in graphene nanoribbons prepared from longitudinal unzipping of carbon nanotubes

S S Rao¹,²,⁶, A Stesmans¹,², D V Kosynkin³, A Higginbotham³ and J M Tour³,⁴,⁵

¹ Department of Physics, University of Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium
² INPAC—Institute for Nanoscale Physics and Chemistry, Leuven, Belgium
³ Department of Chemistry, Rice University, MS-222, 6100 Main Street, Houston, TX 77005, USA
⁴ Department of Mechanical Engineering and Materials Science, Rice University, MS-222, 6100 Main Street, Houston, TX 77005, USA
⁵ Smalley Institute for Nanoscale Science and Technology, Rice University, MS-222, 6100 Main Street, Houston, TX 77005, USA

E-mail: srinivasasingamaneni@boisestate.edu

Abstract. Electron spin resonance (ESR) investigation of graphene nanoribbons (GNRs) prepared through longitudinal unzipping of multi-walled carbon nanotubes indicates the presence of C-related dangling bond centers, exhibiting paramagnetic features. ESR signal broadening from pristine or oxidized GNRs is explained in terms of unresolved hyperfine structure, and in the case of reduced GNRs, the broadening of the ESR signal can be due to enhancement of conductivity upon reduction. The spin dynamics observed from ESR line width-temperature data reflect a variable range hopping mechanism through localized states, consistent with resistance-temperature data.

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The recent interest in the physics and applications of graphene nanoribbons (GNRs), with tunable band gap over graphene and higher carrier mobilities over carbon nanotubes (CNTs) and Si, for future generations of nanoelectronic devices has evoked impressive research. Field-effect transistors (FETs) based on GNRs have already been demonstrated [1]. Several proposals have been made to apply GNRs in high-magneto-resistive [2] and high-frequency devices [3].

A noteworthy feature of GNRs is the appearance of ‘edge-spin’ polarization at the edges of the zigzag-edged GNRs (ZGNRs). Recently [4–8], it has been shown that such edge-spin polarization can be engineered by functionalization with transition metals [4], biasing the ribbons [5, 6], and by doping [7] to induce a half-metallic [9–12] band structure. For example, in a pioneering experimental study [10], the half-metallicity has been achieved by applying in-plane homogeneous electric fields across the zigzag-shaped edges of the GNRs. In another theoretical work [11], GNRs have been predicted to exhibit half-metallicity through patterned chemical modification. Therefore, heading towards the realization of GNR spintronic devices, it is important to understand the spin-dependent properties of ZGNRs. Theoretical work [13] has shown that ZGNRs are magnetic and can carry a spin current in the presence of a sufficiently large electric field.

Theoretical studies [14] showed the presence of σ- and π-defects at GNR edges, a property that was proposed for building spin filters. Using first-principle calculations [15], the effect of magnetic point defects (vacancies and adatoms) was investigated in ZGNRs. While pristine ribbons display anti-parallel spin states at their edges leading to anti-ferromagnetism, the defects are found to perturb this coupling. The introduction of a vacancy drastically reduces the energy difference between parallel and anti-parallel spin orientations, although the latter is still favored. Moreover, the local magnetic moment of the defect is screened by the edges so that the total magnetic moment is quite small. In contrast, when an adatom is introduced, the parallel spin orientation is preferred and the local magnetic moment of the defect adds up to the contributions of the edges.

Furthermore, a spin-polarized transmission is observed at the Fermi energy, suggesting the possible use of such GNRs in spin-valve devices. Recent theoretical calculations [16] have predicted that the total spin moment of a GNR should be zero as the local magnetic moments at the two edges are coupled anti-ferromagnetically. In the same study, it was also concluded that hydrogenated GNRs can have a finite total magnetic moment leading to a ferromagnetic ground state. Hence, it appears that investigating the role of defects is highly important in realizing GNRs in digital electronics and spintronics. Several research groups have demonstrated experimentally ferromagnetic-like features in graphite [17], proton-irradiated graphite [18], carbon films [19] and C_{60}-based polymers [20]. Experimental work probing the magnetic features in graphene, a building block of graphite, has been scarce [21]. The observed magnetism was shown to originate mainly from isolated vacancies, vacancy–hydrogen complexes, grain boundaries and planar and topological line defects, as these defects possess localized spin moments and thus may lead to magnetism.

Despite a plethora of theoretical studies and numerical calculations which describe the exotic properties of graphene and GNRs, in particular with regard to the presence of defects and their magnetic properties, it appears that little experimental work has been carried out on the nature of defects in graphene [22, 23]. Progress [24] in producing substantial quantities of high-quality GNRs using a chemical route has enabled and motivated us to perform first electron
spin resonance (ESR) measurements to gain more detailed information and to test theoretical predictions. Even though electronic transport measurements carried out on monolayer GNR devices showed an ambipolar electric field effect typical for graphene, the conductivity of monolayer GNRs ($\sim 35$ S cm$^{-1}$) and mobility of charge carriers ($0.5$–$3$ cm$^2$ (V s)$^{-1}$) are found to be less than those of pristine graphene. The inferior values were explained [23] to be a result of harsh oxidative treatment during the unzipping of multi-walled carbon nanotubes (MWCNTs), which produces defects in the GNRs, thereby leading to a decrease in conductivity and mobility. Accordingly, the main goal of the present work is twofold: (i) to probe by ESR the charge trapping centers causing the lower conductivity (lower mobility) in comparison with graphene and graphite exfoliated ribbons; (ii) to investigate the magnetic nature and spin dynamics of these defects. On the basis of ESR probing, a suitable local probe for atomic identification of defects and their local surroundings, we suggest that the observed magnetism originates from C-related dangling bond defects that form localized states.

GNRs were prepared by chemical longitudinal unzipping of MWCNTs as reported by Kosynkin et al [24]. Briefly, this method involves the treatment of MWCNTs, consisting of 15–20 concentric cylinders, of 40–80 nm diameter with concentrated H$_2$SO$_4$ followed by KMnO$_4$ (an oxidizing agent) at room temperature. This process chemically unzips the nanotubes, forming nanoribbons up to 4 $\mu$m long, with widths of 100–500 nm and thicknesses of 1–20 graphene layers: these samples are labeled as oxidized GNRs (OGNRs). These were characterized by several techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA), attenuated total reflection infrared (ATR-IR) spectroscopy and x-ray photoelectron spectroscopy (XPS). Electronic properties of the thus obtained monolayer GNRs have also been measured [25], exhibiting FET characteristics, and the temperature-dependent electronic transport obeyed a variable range hopping (VRH) mechanism. It has been found that OGNRs (as prepared) are poor conductors due to the disruption of the $\pi$ conjugation. The conductivity could be improved significantly after reduction with N$_2$H$_4$, resulting in partial restoring of the disrupted conjugated $\pi$ network—samples labeled as reduced GNRs (RGNRs). More details of the formation mechanism of GNRs, characterization and physical properties can be found in [24, 25]. In the present work, to investigate the effect of H$_2$ on OGNRs and in an attempt to passivate C-related defects to enhance conductivity and mobility, OGNRs were treated with H$_2$ at 350 °C (1.1 atm) for 37 min; this sample is labeled as hydrogenated GNRs (HGNRs).

Conventional first-derivative CW ESR experiments were carried out on OGNRs, RGNRs and HGNRs in the temperature ($T$) range of 4.2–120 K using a home-built K-band (\(\approx 20.6\) GHz) [26] and Q-band (\(\approx 34\) GHz) Bruker EMX spectrometer. All were operated under conditions of adiabatic slow passage. Conventional low-power first-derivative absorption $\frac{dP_\mu}{dB}$ ($P_\mu$ being the reflected microwave power) spectra were detected by applying sinusoidal modulation (\(\approx 100\) kHz, amplitude $B_m \approx 0.5$ G) of the externally applied magnetic field $\vec{B}$, with incident microwave power $P_\mu$ as well as $B_m$ cautiously reduced to avoid signal distortion. The defect spin density was quantified by double numerical integration of the K-band derivative absorption spectra by making use of a co-mounted calibrated Si:P intensity marker, also serving as g marker: $g(4.2$ K) = 1.99869. The obtained relative and absolute accuracies on defect densities are estimated at $\sim 5$ and $12\%$, respectively.

Figure 1 shows representative low-power K-band ESR spectra measured on samples OGNRs (a), RGNRs (b) and HGNRs (c) at 4.2 K. As shown, in each case only one ESR
Figure 1. First-derivative CW K-band ESR spectra measured at 4.2 K on (a) OGNRs, (b) RGNRs and (c) HGNRs, where the latter two are obtained by subjecting OGNRs to different post-manufacturing treatments, using $B_m = 0.42$ G and $P_\mu = 2.5$ nW. The signal at $g \approx 1.99869$ stems from a co-mounted Si:P marker sample.

signal, of symmetric shape, is observed with corresponding zero-crossing $g$ value ($g_c$) = 2.0029, 2.0032 and 2.0031, respectively. This value falls within the reported [27] carbon ESR signal range ($g = 2.0022-2.0035$), indicating that the signal may be ascribed to C-related dangling bonds of spin $S = 1/2$. For all three samples, the 4.2 K signal can be fitted by a Lorentzian line shape (closely) peak-to-peak width of $\Delta B_{pp} = 2.8$, 6.4 and 4.3 G for OGNRs, RGNRs, and HGNRs, respectively. The corresponding inferred spin densities are $\approx 2.3 \times 10^{18}$, $1.5 \times 10^{17}$ and $2 \times 10^{17}$ spins g$^{-1}$. The ESR spectral parameters have been inferred at various $T$’s by means of computer simulations using Lorentzian line shapes with optimized fitting parameters. Despite intense signal averaging over broad field ranges under various extreme and optimized spectrometer parameter settings, no other signals could be observed over a broad magnetic field sweep range up to 9000 G. Although intensely searched for, neither any correlated additional signal structure could be traced nor any sign of hyperfine structure possibly ensuing from highly abundant $^1$H, $^{14}$N, $^{16}$S and $^{55}$Mn nuclei.

Figure 2 shows the temperature dependences of $\Delta B_{pp}$, $g$ and the integrated intensity (proportional to $\chi_{\text{ESR}}$) for OGNRs. We find that $\Delta B_{pp}$ decreases slowly with $T$ increasing from 4.2 K upward, while $g$ is found to be almost constant at $g_{av} = 2.0029 \pm 0.0001$; the ESR spin susceptibility ($\chi_{\text{ESR}}$) exhibits a Curie-like paramagnetic behavior. The C-based paramagnetic

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Figure 2. The temperature dependence of K-band ESR spectral parameters obtained on OGNRs using optimized computer simulations indicating an almost Lorentzian line shape. The solid line in panel (c) is a guide to the eyes.

center may arise from oxygen-containing functionalities such as carbonyl (C=O) and carboxyl groups residing at the edges and/or surface of the GNRs.

The inferred \( T \) dependences of \( \Delta B_{pp} \), \( g \) and \( \chi_{ESR} \) of RGNRs, shown in figure 3, are very similar to those of OGNRs (figure 2). This may indicate the ESR signal to originate from the carboxylic groups, which could not be reduced by \( \text{N}_2\text{H}_4 \), as the latter treatment would eliminate most of the carbonyl groups [24].

As indicated above, the defect densities remain almost unaltered after treatment of OGNRs with \( \text{H}_2 \). Yet, we noticed a substantial increase in the conductivity. Indeed, no ESR measurements could be carried out for \( T \gtrsim 20 \text{K} \) because of excessive loading of the cavity \( Q \)-factor (not shown) due to the developed semiconducting properties of GNRs as a result of the \( \text{H}_2 \) treatment. Besides, after this treatment, other ESR properties were left unaffected.

As is evident from figures 2 and 3 the \( g \) value and \( \Delta B_{pp} \) increase upon \( \text{N}_2\text{H}_4 \) treatment of OGNRs. \( \Delta B_{pp} \) increases by more than a factor of 2 (at 4.2 K). This could not have resulted from enhanced dipole–dipole (DD) interaction as the defect density is observed to decrease by an order of magnitude upon treatment with \( \text{N}_2\text{H}_4 \). The observed line width at 4.2 K \( \Delta B_{pp} \sim 2.8 \text{G} \) can be explained by invoking unresolved hyperfine broadening, which is temperature independent. Another possibility is that spin clustering has led to a local increase in the spin density and hence enhancement of the dipolar contribution to \( \Delta B_{pp} \).
Figure 3. The temperature dependence of K-band ESR spectral parameters obtained on RGNRs using optimized computer simulations indicating almost Lorentzian line shapes. The solid line in panel (c) is a guide to the eyes.

On reduction of GNRs by $N_2H_4$, the oxygen-containing functional groups decreased (although not removed completely), leading to enhancement of conductivity and thereby decreasing the ESR ‘visible’ spin density by an order of magnitude. The estimated DD contribution in RGNRs to $\Delta B_{pp}$ is 0.024 G, that is, negligibly small. According to previous suggestions [28], exchange narrowing cannot be a significant determining factor given that $\Delta B_{pp}$ increases as the spin concentration decreases. Hence, the enhancement of conductivity could be the main plausible candidate for the increase in $\Delta B_{pp}$ and also for the enhancement of the observed $g$ value. A cross-sectional TEM image of monolayer OGNR is shown in figure 4 of [25], illustrating the non-uniform disorder structure due to the presence of functional groups, which may lend support for the observation of localized states. The high density of ‘ESR-visible’ C-defects may arise from the sizeable disorder present in the GNRs. In light of the decrease in resistance upon reduction treatment as well as from earlier work suggesting ([29] and references therein) unpaired electrons to interact with conduction electrons (ESR ‘invisible’) to shorten spin relaxation times and therefore to increase $\Delta B_{pp}$, we suggest that enhancement of the conductivity upon reduction treatment of GNRs is the dominant $\Delta B_{pp}$ determining factor. Here, we should add that the effect of molecular paramagnetic oxygen in broadening the ESR signal cannot be ruled out either, which may form the subject of future work.
Figure 4. The $T$ dependence of the observed Q-band ($\sim 34$ GHz) ESR linewidth $\Delta B_{pp}$ of a freestanding ensemble of RGNRs (the left $Y$-axis), obtained through computer simulations of observed spectra using Lorentzian line shapes. The $T$ (35–120 K)-dependent resistance ($R$) measured on a monolayer of GNRs on a Si substrate is also shown (right $Y$-axis) [25]. The close parallelism between the $\Delta B_{pp} (T)$ and $R (T)$ dependences, expressed in log scale, suggests that the VRH mechanism, describing the $R (T)$ data, also applies to the $\Delta B_{pp} (T)$ results. This is further exemplified in the inset, exposing a linear $\ln(\Delta B_{pp})$ versus $T^{-1/3}$ relationship for the 2D system. The solid line is a guide to the eyes.

Information related to spin dynamics might come from the functional dependence of $\Delta B_{pp}$ on $T$. According to the variable range hopping (VRH) mechanism [30], in the paramagnetic phase, the $T$ dependence of $\Delta B_{pp}$ can be described by $\Delta B_{pp} = K \exp(T_0/T)^{1/n}$, where $n - 1$ is the dimensionality of the system, $T_0$ and $K$ are constants and in analogy with the $T$ dependence of the resistance ($R$) [25]. Figure 4 describes the parallelism between the $T$ (10–120 K) dependence of the Q-band ESR $\Delta B_{pp}$ (the left $Y$-axis) as observed from an ensemble of freestanding RGNRs and the $T$ (35–120 K) dependence of $R$ (the right $Y$-axis) extracted from a monolayer GNR held by a Si substrate. It appears that this dependence qualitatively follows the VRH mechanism, which exhibits a linear relationship in $\ln(\Delta B_{pp})$ versus $T^{-1/3}$ coordinates for a two-dimensional (2D) system as shown in the inset of figure 4. This further supports 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 hopping through localized states. The VRH-type electron transport mechanism has also been reported [31] in lithographically patterned disordered GNR.
Another interesting observation is the increase in $g$ value from the oxidized state (OGNRs) to the reduced state (RGNRs). In the oxidation procedure, $\text{H}_2\text{SO}_4$ was used to obtain the GNRs. During that procedure, there may be entrapment of $\text{HSO}_4^-$ acceptors between the graphite layers that may be responsible for the reduction of $g$ value. Elimination of such acceptors upon reduction, which also leads to enhancement of conductivity, could cause an increase in $g$ value. As for the current first ESR investigation performed on GNRs, the obvious quest concerns the atomic nature of the defect at the origin of the observed ESR signal. The chemically bonded groups such as –OH, –O, –CO and –C═O can form ESR radicals. The $g$-factor $\sim 2.003$ of the benzoin radical [32] (–(CO)O) is close to the observed $g$-factor of the RGNRs.

Recently [23] reported temperature-dependent ESR data on mechanically exfoliated graphene indicated a conical band dispersion (linear $\chi(T)$) as expected for graphene, which appears to be absent in the current GNRs likely due to the presence of non-conducting oxygen-containing functional moieties. In the same study, a very weak $T$ dependence of $\Delta B_{pp}$ is also reported at high $T$ ($>50$ K), along with an increase in line width at low $T$ ($<50$ K) due to defects. However, both $\Delta B_{pp}$ (9 G) and the $g$-value (2.004) measured at 4 K are found to be higher than those observed here. Even though, in the current sample, a strong $T$ dependence of resistance ($R$) is observed for a monolayer of GNRs, the $T$ dependence of $\Delta B_{pp}$, indicative of spin dynamics, is much weaker; this is partially due to the cumulative effect of grouped GNRs.

To compare ESR spectral parameters with those of GNRs, we have also measured ESR on highly oriented pyrolytic graphite (HOPG) and MWCNT samples. We find a highly anisotropic Dysonian-shaped ESR signal and an isotropic Lorentzian-shaped itinerant ESR signal as expected from HOPG and MWCNTs, respectively. The electronic properties of GNRs are found to be distinctly different from those of MWCNTs and HOPG.

To summarize, the current ESR results demonstrate that GNRs, produced from longitudinal unzipping of MWCNTs, suffer from C-related localized states, exhibiting paramagnetic features. These are believed to be potential charge trapping centers, leading to a decrease in conductivity and mobility of GNRs, making them inferior to pristine graphene. The spin dynamics of GNRs appear to follow a VRH mechanism through localized states, supporting the electronic transport data.

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