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Defects induced ferromagnetism in plasma-enabled graphene nanopetals

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Abstract

Ferromagnetism in graphene is fascinating, but it is still a big challenge for practical applications due to the weak magnetization. In order to enhance the magnetization, here, we design plasma-enabled graphene nanopetals with ultra-long defective edges of up to 105 m/g, ultra-dense lattice vacancies, and hydrogen chemisorptions. The designed graphene nanopetals display robust ferromagnetism with large saturation magnetization of up to 2 emu/g at 5 K and 1.2 emu/g at room temperatures. This work identifies the plasma-enabled graphene nanopetals as a promising candidate for graphene-based magnetic devices. 2014 AIP Publishing LLC.

Keywords

defects, graphene, induced, nanopetals, ferromagnetism, plasma, enabled

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Defects induced ferromagnetism in plasma-enabled graphene nanopetals

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Ferromagnetism in graphene is fascinating, but it is still a big challenge for practical applications due to the weak magnetization. In order to enhance the magnetization, here, we design plasma-enabled graphene nanopetals with ultra-long defective edges of up to 10^5 m/g, ultra-dense lattice vacancies, and hydrogen chemisorptions. The designed graphene nanopetals display robust ferromagnetism with large saturation magnetization of up to 2 emu/g at 5 K and 1.2 emu/g at room temperatures. This work identifies the plasma-enabled graphene nanopetals as a promising candidate for graphene-based magnetic devices. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867891>]

Magnetic ordering in carbon-based materials has attracted widespread attention as variable light-element alternative to conventional transition metals like Fe, Co, Ni, etc.^{1–4} Carbon-based magnetic materials possess a lot of attractive properties, such as low density, biocompatibility, and plasticity, which are practical significance for next generation magnetic devices.^{5,6} Graphene, a two dimensional single sheet of carbon, shows extraordinarily high electron mobility, thermal conductivity, and mechanical strength, and is promising for many applications such as nanoelectronics, spintronics, and optoelectronics.^{7,8} Magnetic ordering in graphenes may be used in the design of future magnetic nanoelectronic and spintronic devices. Ferromagnetism has been predicted and observed in graphite and graphene and is attributed to localized unpaired spins induced by defects.^{9–13} The induced magnetic moments interact ferromagnetically if defects are present at different hexagonal sublattices of graphene.¹⁴

Many approaches have been used to produce ferromagnetism in graphene, including introduction of hydrogen (H) chemisorptions defects, vacancy defects, and edge defects as well as proximity effects.^{13,15–18} To date, however, the observed maximum magnetization in either polycrystalline or single-crystal graphene synthesized by Chemical Vapor Deposition (CVD) or mechanical cleavage is weak.^{5,11} This is because only a tiny fraction of the carbon atoms in graphene contribute to the magnetism.³ The lack of large magnetization hinders the applications of graphene in practical magnetic devices. In order to achieve large magnetization and realize practical applications, it is essential to employ new techniques to enhance intrinsic magnetization of graphenes.

Here, to achieve robust ferromagnetism and large saturation magnetization, we design plasma-enabled graphene nanopetals (PEGN) with ultra-long defective edges, ultra-dense vacancies, and H chemisorptions on edges and

vacancies. Indeed, the PEGNs display robust ferromagnetism with enhanced saturation magnetization of up to 2 emu/g at low temperatures and 1.2 emu/g at room temperatures. The observed ferromagnetism is an intrinsic magnetic behavior of nanopetals and can be attributed to the ultra-long defective edges, plasma-induced vacancy defects, and H adatoms during growth process. Our results indicate that the plasma aided synthesis is a new way to enhance the ferromagnetism in graphenes for practical applications.

Plasma aided growth has been found widely used for the controlled synthesis of nanostructures.^{19,20} For example, vertical graphene networks can be grown directly with self-organized patterns by the plasma-enhanced CVD (PECVD) without any catalyst and substrate heating.^{21,22} The growth of PEGNs was carried out in an inductively coupled plasma (ICP-CVD, 13.56 MHz, 1.0 kW) reactor. First, Ar gas was fed into the chamber where the plasma was generated at 3.0 Pa with RF power 800 W. Likewise –50 V of substrate bias was used to enhance the plasma interaction with Si substrate. After 3 min of the plasma treatment, a gas mixture of 30% CH₄, 20% H₂, and 50% Ar was fed into the chamber and the rf power was increased up to 800 W for the deposition. Here, H atoms can be adsorbed on graphene surface when H plasma is exposed to the sample at high temperatures. Hence, the plasma serves as a main H source and produces hydrogen absorption defects in graphene.²³ The deposition time was kept for 8 min.

Figure 1(a) shows the scanning electron microscope (SEM) images of PEGNs on Si, in which the graphene nanosheets are all nearly perpendicular to their substrates, with the height ranging from 300 to 500 nm. Based on the scale of SEM images, the estimated edge length is up to 10^5 m/g. To ensure the magnetic signal originating from the graphene nanosheets, we have analyzed the graphene nanopetals with X-ray Photoelectron Spectroscopy (XPS) and Energy-dispersive X-ray Spectroscopy (EDX). As shown in Figs. 1(c) and 1(d), only carbon elements have been detected, which proves that our PEGNs have high purity.

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FIG. 1. (a) and (b) SEM images, (c) XPS spectra, and (d) EDX spectra for the PEGNs.

The magnetization analysis of the graphene nanopetal films has been performed with vibrating sample magnetometry (VSM) in Physical Property Measurement System (PPMS). To exclude the influences of SO_2/Si , the PEGNs were cleaved from the substrate before the VSM measurements. First, the sample holder and plastic tapes which were used to carry samples were measured and displayed absolute diamagnetism, as shown in Fig. 2(a). Fig. 2(b) displays the magnetic hysteresis loops of the PEGN powders (milled from PEGNs) measured at temperatures 5, 50, and 200 K, which show weak ferromagnetism at 5 K and paramagnetism at higher temperatures. The saturation magnetization M_s is about 0.6 emu/g at 200 K. Figures 2(c) and 2(d) exhibit the magnetization hysteresis loops for the PEGNs at 5, 10, 50, 100, 200, and 300 K. The saturation magnetic moment

reaches up to 2 emu/g at 5 K and 1.2 emu/g at 300 K. The ferromagnetism can be seen clearly in the enlarged hysteresis loops near zero field in Fig. 2(d).

Figure 3(a) shows the magnetic behavior of PEGNs as a function of temperatures [zero field cooled (ZFC) and field cooled (FC) measurements for $H = 1$ kOe]. A clear magnetic transition was observed at $T_c = 365$ K. The extracted temperature dependence of the saturation magnetization and coercivity are plotted in Figs. 3(b) and 3(c). Compared with the magnetization in PEGN powder, the saturation magnetization is significantly enhanced. This shows that the morphology and structure of PEGNs play a significant role in the generation of robust ferromagnetism and giant saturation magnetization.

Raman spectrum of PEGNs is shown in Fig. 4(a). D peak is located at 1350 cm^{-1} , G peak is located at 1580 cm^{-1} , D' peak is located at 1620 cm^{-1} , and 2D peak is located at 2700 cm^{-1} . Raman spectrum contains important information about the graphitic structure of our PEGNs. First, high I_D/I_G ratio of 2.0 reveals that our PEGNs contain a certain degree of defects in the structure. The presence of D' peak suggests the high possibility of our PEGN is hydrogenated.²³ The $I_D/I_{D'}$ peak ratio of 4.0 suggests that our graphene nanopetals also contain edge defects.²⁴

As shown in Fig. 4(b), in our PEGNs, the H adatoms are not only adsorbed on the graphene surfaces but also at interlayers during the plasma-growth process.²⁵ H adatoms in graphene nanopetals can generate spontaneous magnetism in graphene through forming C-H bonds and unpaired electrons.^{26–29} The H chemisorption defects give rise to strong Stoner ferromagnetism with a magnetic moment of $1\mu_B$ per defect when the defects are located at the same sublattice.³⁰ Hydrogen adatoms induce the formation of unpaired electrons which lead to the observed magnetization

FIG. 2. Magnetization hysteresis loops for (a) sample holder (plastic tube), (b) PEGN powders, (c) and (d) PEGNs at different temperatures.

FIG. 3. (a) ZFC and FC magnetization as a function of temperature, ranging from 5 K to 380 K. The arrow shows the magnetic transition temperatures, $T_c = 365$ K. (b) Saturation magnetization and (c) coercivity as a function of temperatures.

in graphene nanopetals.³¹ The stability of the magnetic configurations depends on the distance between H adatoms and the strength of exchange couplings between the defect-induced magnetic moments.³⁰ Additionally, strong long-range coupling between local magnetic moments at the same sublattice of PEGNs can maintain room-temperature ferromagnetic ordering against thermal fluctuations.

The PEGNs have one side with open defective edges and another side attached to the substrate. The zigzag and armchair edges coexist in PEGNs. The zigzag edges can be magnetic due to spin-polarized edge states.²⁸ The net spin moment in zigzag-edged nanosheets results from topological frustration of the π -bonds.³² Moreover, the absorption of H at the edges of PEGNs leads to the formation of a spin-polarized band at the Fermi level. The π electrons on hydrogenated zigzag edges of PEGNs may create a ferromagnetic spin structure on the edge due to edge localized states. In addition, H adatoms at zigzag edges of PEGNs can passivate the σ dangling bonds and leave all the π orbitals unsaturated and carrying the magnetic moments. The magnitude of the ferromagnetism strongly depends on the position of the H atoms relative to the edges.³³ As mentioned above, in the PEGNs, there are ultra-long edges of up to 10^5 m/g, which might contribute to the giant saturation magnetization.

Plasma-aided growth of the PEGNs leads to the formation of large amount of atomic vacancies in the graphene nanosheets (Figure 4(b)). These lattice vacancies in PEGNs can generate localized electronic states and magnetic moments due to the hybridization of p_z orbitals in the π -band. Moreover, vacancy defects in the same sublattice of PEGNs can induce ferromagnetic ordering and states in situations of sublattice symmetry breaking.²⁸ On the other hand, H adatoms can easily adsorb on vacancy dangling bonds and form vacancy-H complexes in PEGNs, which might provide larger magnetic moments and the observable macroscopic magnetic signals.³⁴

In conclusion, the plasma produced PEGNs exhibit robust ferromagnetic ordering with giant enhanced saturation magnetization. The observed ferromagnetism is much higher than the obtained magnetization in the case of flat few-layer graphene. The PEGNs can be particularly useful to explore magnetic ordering in graphene through introducing controllable edge, lattice vacancy, and hydrogen related defects. By manipulating the plasma conditions, it may be possible to tune the magnetism of graphene. Finally, the PEGNs are very promising candidates for the graphene based magnetic nanodevices.

FIG. 4. (a) The Raman spectra of PEGNs that display a relatively high density of defects. (b) Atomic structures of the PEGNs with hydrogen chemisorption defects, edge defects, and lattice vacancy defects.

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