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Supramolecular Assembly of DNA on Graphene Nanoribbons

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Abstract

Graphene's adhesive and charge delocalization properties offer the opportunity for the direct study of biological molecule in the nanoscale regime. The inherent charge on DNA base pairs and the associated phosphate backbone can be probed by non-covalent interactions with graphene, which is a useful platform for the creation of anisotropic nanopatterned biological assemblies. Here, we report the graphene nanoribbon (GNR) supported anisotropic supramolecular self-assembly of single stranded adenine (A), cytosine (C), guanine (G), thymine (T), AT, and GC 20mer oligonucleotides, as well as the unique ordering of double stranded plasmid (circular) and Herring sperm (linear) DNA. The GNRs serve as a double sided adhesive platform for attachment to the SiO₂ substrate, as well as DNA oligomers and polymers. The self-assembly is attributed to donor-acceptor interactions between DNA and graphene. These findings demonstrate that the DNA-GNR assembly yields a prospective route to novel bio-relevant nanostructures.

Graphene,^{1,2} an all-carbon honeycomb lattice, has emerged as an attractive substrate for the ordered attachment of deoxyribonucleic acid (DNA).^{3–5} Configuring graphene into ribbon structures presents a well-defined two-dimensional electronic environment useful for controlled non-covalent interaction in the nanoscale regime.⁶ GNR's planar structure with primarily zigzag edges has potential applications in biodiagnostics, DNA nanoelectronics, bio-sensor devices, spintronics and nanoelectronics.^{7–10} GNRs have been fabricated via metal particle-assisted,^{11–13} and lithographic methods,^{14–16} as well as by oxidative longitudinal unzipping of multiwall carbon nanotubes (MWCNTs).^{7,17,18} Oxidative chemical treatment of GNRs results in the oxygen species modification of the basal plane and edge with carboxylic acid, hydroxyl, epoxide, and carbonyl groups. These oxygen species significantly decrease GNR conductivity, which can be substantially recovered with hydrazine chemical treatment or annealing.^{17,18} GNRs deposited on SiO₂ surfaces present a well-defined electronic environment to self-assembly and are advantageous over other forms of graphene and graphene oxide, particularly in regards to straight edges and free from strain effects present in epitaxial graphene.

Recently, various self-assembled graphene-based materials have been fabricated.^{19–24} These bottom-up ensembles include co-assemblies of graphene nanosheets,¹⁸ organic monolayers,^{25,26} synthetic polymers,^{22,25,27} and proteins.²³ The intermolecular forces that drive the formation of the nanoscale assemblies arise from hydrogen bonding, π - π stacking, dipolar, van der Waals, electrostatic, or metal-ligand interactions.¹⁹ Charge-transfer between graphene and electron-donating or accepting molecules leads to n-type and p-type doping, respectively. Adduct charge transfer interactions yield perturbations to the electronic structure character of graphene. Raman spectroscopy has been effective in revealing graphene configuration and quality, as well as graphene doping effects due to charge

transfer.^{19,20} Electron donors and acceptors have been shown to change the characteristic Raman graphene band (G-band).²⁸ The charge-transfer effects of adsorbed bromine, iodine, and aromatic molecules with single or bilayer graphene are more pronounced in comparison to few-layer graphene.³² The effects on the characteristic G-band are blue (red) shifted for electron acceptor (donor) molecules, respectively.²⁷

A fundamental research goal in nanobiotechnology is the rapid determination of the nucleotide sequences consisting of A, C, G, and T in DNA.¹⁰ Characteristic nucleotide fingerprints have been determined using high-resolution microscopic,^{29–31} spectroscopic²⁵ and electrical^{35–41} techniques. Experimental and theoretical studies have revealed that positive charge can migrate over 200 Å in double strand DNA (dsDNA).^{32–34} Single base mismatches have been detected by electrochemical and photoinduced charge transfer in DNA films.³⁵ The incorporation of redox-active intercalations into mismatch sites in dsDNA films has allowed for the electrochemical differentiation between complementary versus mismatched DNA oligonucleotide duplexes.^{34,42} Differences in charge transfer across DNA films through interceding base-pair mismatches have sensitivity that makes it suitable to probe DNA sequences mutations. Nucleotide stacks in DNA are especially sensitive to base-pair mismatch, which can induce moderate structural changes like intervening bulges. Mismatches alter the electronic properties of the base-pair stack, which results in reduced electron-transfer efficiency.^{34,42} In particular, guanine-containing mismatches disrupt the efficiency of charge transfer in DNA.⁴³ The charge transfer may be due to phonon, polaron or long-range hopping mechanisms between guanine nucleotides.^{44,48,49}

The reproducibility and efficacy of DNA film assays are sensitive to the close ordering of the films. Questions remain as to whether intercalators diffuse through the DNA monolayer to the underlying electrode in biased electrochemical studies. Thus, the controlled packing order in DNA films continues to be an area of interest in DNA biosensor assays.^{37–46} Here, we provide a fundamental structural and spectroscopic analysis of single and double stranded DNAs on GNRs. Our results show that GNRs induce anisotropic super-assembly of single stranded DNA (ssDNA) into ribbon structures. These directionally dependent morphologies are not observed on other forms of graphene and graphene oxide. GNRs were also found to induce pComb-5 plasmid—a covalently closed circular double stranded DNA—to form hexagonal ordered films. The electronic structure calculations of the DNA assembly on GNRs reveal doping of GNRs by specific DNA sequences. These results demonstrate the suitability of GNRs as nucleation sites for the multi-micron formation of DNA films. Although there are a few experimental investigations of DNA self-assembly on exfoliated and epitaxial graphene, the use of GNRs as the self-assembly substrate is advantageous in that the solution-casted GNRs are free from the strain effects inherent in epitaxial graphene. The DNA films described herein are of interest from the perspective of better understanding bio-functionalized DNA/graphene nanoscale topography.

We prepared GNRs from unzipped MWCNTs using previously described oxidative chemistry techniques developed by Tour and co-workers.^{17,18} The unzipped GNRs have an approximate height of 0.50–0.75 nm and a width of 400–500 nm. We show in Fig. 1 typical atomic force microscopy (AFM) images of single-stranded, 20-base oligo adenine (A), guanine (G), thymine (T), cytosine (C), AT, and GC DNA (at 30 µM-strand concentrations), respectively. Oligo A, G, T, and C are expected to exist in solution as disordered single strands.⁵⁰ Annealed oligo AT can form a right handed B-DNA helix (as self-annealed duplexes, hairpins, or concatenates), about 2 nm in diameter with a helix pitch of 3.4 nm. In contrast, oligo GC has a propensity to form a left-handed Z-DNA helix at high salt concentrations, with a diameter of 1.8 nm and a helix pitch of 4.4 nm.

The 20 base oligo ssDNA was suspended in aqueous media and annealed in the presence of SiO₂ chips with adsorbed GNRs. AFM studies reveal that the oligo A, G, T, C, and AT ssDNAs spontaneously self-assemble along the entire graphene ribbon as axially aligned nano-ropes (Fig. 1a–e), whereas oligo GC ssDNA assembles into lamellar nano-platelet configuration (Fig. 1f). The ssDNA/GNR composite structures generally retain the approximate width of the underlying GNR. The rope structures have a periodicity of 65 ± 10 nm, and an overall height of 15–145 nm. The mean corrugation height along the cross section of the hybrid ribbon is 10 ± 5 nm (Fig. 1e). The lamellar nano-platelet structure of GC ssDNA has a periodicity of 65 ± 10 nm, and an overall height of 135–145 nm. The mean corrugation height along the cross section of the hybrid ribbon is 7 ± 5 nm (Fig. 1f). The self-assembled patterns on GNRs are in stark contrast to the lack of distinguishable ordered ssDNA structures on the amorphous SiO₂ surface.

Typical random aggregates of DNAs in the absence of GNRs are well extended on the surface. By contrast, the GNRs serve as attracting source for the self-assembly. The smooth edges of the DNA on GNRs strongly suggest that the assembly is predominantly along the GNR. Branches at the end of the assembled patterns can be observed, which are attributed to the lack of underlying GNR “support”. As seen from Fig. 1, the height profile is largely determined by the DNA sequence. However, there seems no apparent ordering within the GNR region.

In order to demonstrate the potential of GNRs to serve as an adhesive platform and biological interface for high molecular weight DNA, supercoiled pComb-5 plasmid⁵¹ and Herring sperm DNA were drop cast onto a GNR-coated SiO₂. The DNA/GNR hybrids were incubated at room temperature for a period of 48 hrs. 3D confocal laser scanning microscopy (CLSM) shows GNR induced formation of closed circular double stranded plasmid DNA into geometrically hexagonal patterns (Fig. 2a). The dsDNA forms approximately 5 μ m hexagonal features that extend far beyond the underlying GNR footprint (Fig. 2a,b). Laser imaging reveals that the well-ordered DNA features are composed of laminar sheets. CLMS images indicate that darker regions within the hexagonal feature correspond to greater thickness in comparison to the edges. Atomic force microscopy (AFM) imaging (Fig. 2c) reveals that the well-ordered DNA features are composed of laminar sheets of about 14 nm heights.

In contrast, CLSM and optical imaging reveal that Herring DNA self-assembles on GNRs, forming aggregates on top of GNRs (Fig. 2d,e). The color variation present in optical images is representative of nanocomposite thickness. As the aggregates are larger than the typical size of the GNRs, there are no apparent ordered patterns of the Herring DNA/GNR nanocomposites. AFM imaging shows that the Herring DNA on GNR has a typical height of 13 nm (Fig. 2f), which is similar to the one-layer height of 14 nm for pComb-5 on GNRs. The lack of interconnection among the features suggests that GNR induces charge ordering over relatively few Herring DNA chains. Unlike synthetic oligonucleotides, DNA from eukaryotic cells may be modified by methylation on N6 of adenine and N4 or C5 of cytosine. Sperm DNA is relatively hypermethylated⁴⁸ and the distinctive chemical structure is attributed to the behavior of Herring sperm DNA. In addition, Herring sperm DNA is composed of chain fragments of varying lengths that can form highly stable aggregates.⁴⁹ It appears that Herring DNA aggregates do not efficiently transfer charge, leading to the loss of long-range interactions. This is contrasted to the constant length of synthetic ssDNA and closed-circular dsDNA. In the case of pComb-5 DNA, the GNRs induce charge ordering that extends over a few plasmid DNA chains. The long range hexagonal ordering of pComb-5 DNA is attributed to its well-defined architecture. The super coiled closed-circular double-stranded plasmid DNA self-assembles into an approximately spherical structure, which is able to efficiently redistribute charge across the nanostructure. GNRs induce the

ordered alignment of plasmid spheres' dipole, leading to long-range electric dipolar coupling.

We have employed Raman spectroscopy in order to investigate the charge transfer effects of inherent base charge on GNR electronic properties. Raman spectroscopy allowed us to monitor the degree of DNA interaction via shifts in characteristic Raman peaks. A typical Raman spectroscopy for the GNR polymer hybrid displays a graphene band (G-band, 1603 cm^{-1}) and a graphene defect (D) band (1354 cm^{-1}) of roughly equal intensity. Four bands (2D-band) observed from 2600 to 3200 cm^{-1} are typical of chemically prepared GNRs.¹⁸ Fig. 3 shows the extracted Raman G-band of GNRs and DNA/GNR composites. The G-band gradually red shifts about 14 cm^{-1} with ssDNA interaction, in the order of charge donating, oligo A, G, AT, T, C, and GC, respectively. There is no significant variation in the 2D-band and the $I(D)/I(G)$ intensity ratio with respect to varying ssDNA types. The Raman shifts are directly correlated to the charge transfer from electron-donating ssDNA to charge delocalizing GNRs. The charge of ssDNA sugar-phosphate backbone imparts a negative charge to graphene as a donor,⁵⁰ which corresponds to blue Raman shift to graphene or a red shift to oxidized GNRs.⁵¹ Consequently, graphene surface induces the stacking of nucleosides resulting in the hybridization with DNA.⁵²

Nucleic acids have been shown to assume a planar orientation on graphene due to the π - π interactions.⁵³ The phosphate-sugar backbone attached to the nucleotide bases are charged and highly polar and can perturb the structural attachment of ssDNA and dsDNA to graphene. In order to gain a fundamental understanding of DNA adsorption behavior on graphene, the charge transfer and binding energies of A, G, T, and C nucleotide monophosphates were calculated using dispersion-corrected density-functional theory (DFT) approach (Table 1). Illustrated in Fig. 4 are geometry optimized ball-and-stick models of A, G, T, C nucleotide bases and nucleotide monophosphate backbone orientations interacting with graphene. The calculated electron charge transfer of associated nucleotide bases and backbone confirmations on graphene is shown in bottom insets in Fig. 4. The explicit inclusion of sugar-monophosphate backbone is important to account for realistic doping effects.⁵³⁻⁵⁵ Dispersion-corrected DFT calculations demonstrate that nucleotide base-oriented conformations transfer more charge and more tightly bind to graphene, in comparison to the phosphate oriented end. Specifically, the results extracted from the Mulliken charge analysis indicate a descending order of A, G, C, and T in charge transfer (Fig. 4), which is consistent with the nucleotide charge transfer pattern observed in Raman spectroscopy (see Fig. 3). Due to the size of the GNRs (i.e., 500 nm in width), the edge effect of the GNRs was neglected in the calculations.

The electronic properties of the ssDNA/GNR hybrids were investigated by calculating band structures of the composites (Fig. 5). The calculated band structure of electron donating nucleotides on graphene shows discrete molecular levels or flat bands around the Fermi level, along with dispersed bands that arise from the contributions from graphene. The nucleotide flat bands refer to HOMO-derived or LUMO-derived bands of ssDNA, which are primarily present below and above the Fermi level, respectively. A, G, C, and T nucleotide bases deplete the electron cloud and have significant orbital hybridization with the graphene bands. The level hybridization is manifested by the mixing of the graphene dispersed bands and the discrete nucleotide molecular levels. In the case of the nucleotide bases' orientations, the electronic hybridization results in the downward shift of the Dirac cone.

In the case of the backbone orientations, there exists further symmetry breaking around the Dirac cone crossing point for the valence bands. Specifically, A, G and C nucleotide bases and backbone conformations significantly shift graphene Dirac cone below the Fermi level, which implies that A, G, and C bases act as charge donors, resulting in the n-doping of

graphene. In the case of T, the nucleotide bases on graphene are charge donating, while the backbone orientation is charge-accepting. Interestingly, in the case of backbone orientation of thymine-adsorbed graphene, a band gap at the Dirac cone crossing emerges as the result of the profound interactions.

Nanoribbon Formation

The MWCNTs were unzipped and reduced using an optimized method developed by Tour and co-workers.¹⁸ A modified GNR purification procedure was utilized, in which the product was isolated by repeated mixing and centrifugation steps, for the separation of exfoliated graphene ribbons from unzipped MWCNT. The resultant single and bilayer GNRs were spin cast from an ethanol/water (50:50) solution onto 300 nm SiO₂ wafers. This was followed by the drop casting of the Herring sperm or pComb-5 DNA.

30 mg of 110–170 nm diameter MWCNTs were suspended in 7.2 mL of H₂SO₄ by stirring the mixture for a period of 1hr. Phosphoric acid (85%, 0.8 mL) was then added, and the mixture was allowed to stir another 15 min before the addition of potassium permanganate (150 mg). The reaction mixture was then heated to 65 °C for 2 h, and allowed to cool to room temperature before product isolation. The product from the oxidation reaction was poured into a liquid nitrogen cooled 30% hydrogen peroxide (5 ml), which prevented the precipitation of potassium permanganate.

DNA Preparation

Single stranded deoxyoligonucleotides, 20-mers containing Adenine (A), Thymidine (T), Cytosine (C), and Guanine (G) bases, with combinations (AT and GC) were obtained from Integrated DNA Technologies (IDT, Skokie, IL). The oligos were re-suspended in nuclease free water in a 100 μmol concentration. The annealing was performed with GNR coated SiO₂ wafer in a 200 μl PCR tube containing with either a single oligo or a combination of two oligos at a 50 μmol concentration and 50 μl reaction volume on an Eppendorf Mastercycler (Eppendorf North America, NY USA) using the following cycling condition: 90°C for 2 minutes and 50 seconds, 70°C for 90 minutes, 60°C for 90 minutes, 50°C for 90 minutes, 45°C for 90 minutes, 37°C for 90 minutes and held at 16°C. Plasmid DNA was extracted from E. coli XL1Blue using a Qiagen Midiprep kit and DNA dissolved in TE buffer (10 mM Tris pH 8.0, 1 mM EDTA). Herring sperm DNA from Sigma-Aldrich (St. Louis, MO) was dissolved in TE buffer.

Density-Functional-Theory Calculations

Our first-principles calculations are based on general gradient approximation (GGA) with the exchange correlation of Perdew–Burke–Ernzerhof (PBE) parametrization.⁵⁶ We employed the dispersion correction using the Tkatchenko-Scheffler (TS) scheme, which exploits the relationship between polarizability and volume.⁵⁷ The TS dispersion correction takes into account the relative variation in dispersion coefficients of various atomic bonding by weighting values extracted from the high-quality *ab initio* database with atomic volumes derived from partitioning of the self-consistent electronic density. A 7×7 cell in the plane direction with a vacuum space of 17.6 Å normal to the graphene plane was used. A kinetic energy change of 3×10^{-4} eV in the double numerical orbital basis was sufficient to converge with the integration of the charge density. The optimization of the atomic positions proceeds until the change in energy is less than 1×10^{-5} eV per cell.

Conclusions

In summary, our results demonstrate that ssDNA has high affinity to GNRs. Raman and DFT studies evidently show that electron donating ssDNA leads to marked changes in the electronic properties of GNRs. There exists anisotropic nanopatterning of ssDNA and pComb-5 dsDNA on GNRs. AFM and CLMS images reveal hierarchical structure of nanoropes and lamella platelets that are further ordered into features with the approximate lateral dimension of the GNRs. Notable GNR induced hexagonal ordering of pComb-5 plasmid DNA with regular layering has been observed. The self-assembly of ssDNA, natural DNA on GNRs is attributed to van der Waals and charge transfer interactions at the GNR basal plane. The present investigation provides a quantum level understanding of the non-covalent interaction between GNRs and ssDNA or high molecular weight dsDNA, which shed lights on the resultant bio-relevant nanostructures. The assembled plasmid spheres are formed by electric dipolar and weak van der Waals coupling mechanism. This work opens the opportunity for the fabrication of self-assembly of DNA on GNRs, which can be further analyzed by predictive experiments to yield refined and sequence-specific diagnostic Raman signals. These signals provide a novel method of characterizing variations in gene or whole genome DNA structures or sequences..

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Figure 1.

Supramolecular organization of DNA segments on GNR. 3D rendering of AFM topography data of supramolecular ordered 20 base ssDNA oligomers A (a), G (b), AT (c), T (d), C (e), and GC (f) on the GNR. Bottom insets: cross sections of ssDNA/GNR nanocomposites of A, G, AT, T, and C GNR composite revealing profiles of axially aligned bundled rope like structures, along with overlapping lamella architecture of GC/GNR composite.

Figure 2.

Multi-micron DNA ordering mediated by GNR. (a) CLSM image of 2D hexagonal ordering of pComb-5-DNA mediated by GNR, propagated on SiO₂. Inset: 3D CLSM and optical image of pComb-5 DNA/GNR composite feature. (b) CLSM and optical image (inset) of pComb-5 DNA/GNR composite features. (d) CLSM, and (e) confocal microscopy images of Herring DNA/GNR composites. (c, f) AFM images showing the supramolecular organization of pComb-5 and Herring DNA on GNRs, respectively.

Figure 3.

Raman spectrographs of ssDNA and natural DNA graphene composites. Shifts in the Raman G-band (observed at an excitation wavelength of 488 nm) of GNRs listed from top to bottom A, G, AT, T, C, GC, pComb-5, and Herring-DNA on GNRs, respectively.

Figure 4. Nucleotide conformations of nucleotide conformations on graphene. Ball-and-stick representation of optimized orientations of A, G, T, C nucleotide bases (NB) and nucleotide sugar-monophosphate backbone (BB) interacting with graphene. Bottom insets show the associated NB and BB orientation electron charge transfer values.

Figure 5.

Band Structure calculations of nucleotide conformations on graphene. Calculated band structures of A, G, T and C NB and BB orientations interacting with graphene. $\Gamma = (0,0)$, $K = (\pi/3a, 2\pi/3a)$, $M = (0,\pi/2a)$, where $a = 17.22 \text{ \AA}$ for a 7×7 rhombus unit cell. The Fermi level is shifted to 0 eV (dotted blue line).

Table 1

DFT calculations of base-pair conformations on graphene. A, G, T, C nucleotide bases (NB) and nucleotide sugar-monophosphate back bone (BB) interacting with graphene.

	A (NB)	C (NB)	G (NB)	T (NB)
Energy (eV)	-539.254	-531.506	-548.302	-541.845
Graphene (e)	-0.469	-0.912	-0.482	-0.494
DNA (e)	-1.528	-1.089	-1.518	-1.505
	A (BB)	C (BB)	G (BB)	T (BB)
Energy (eV)	-538.587	-530.920	-548.135	-543.876
Graphene (e)	-0.355	-0.307	-0.276	-0.375
DNA (e)	-1.644	-1.685	-1.726	-1.998