Graphene surface induced specific self-assembly of poly(3-hexylthiophene) for nanohybrid optoelectronics: from first-principles calculation to experimental characterizations†

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We demonstrate a specific chain alignment of π-conjugated polythiophenes on the graphene monolayer via first-principles calculation and experimental characterizations. The effects of alkyl chain and thiophene backbone in poly(3-hexylthiophene) (P3HT) on the specific binding energy and molecular configuration on the graphene monolayer are independently investigated. Due to specific π–π interaction and van der Waals interaction between P3HT and graphene monolayer, two different configurations (edge-on and face-on) of P3HT are formed on the graphene, while only edge-on configuration of P3HT is found on the indium tin oxide (ITO). These behaviors are verified by using atomic force microscopy (AFM) and transmission electron microscopy (TEM). We also explore the molecular orientation of P3HT chains on the graphene using 2D grazing incidence X-ray diffraction (GIXD) to obtain molecular orientation features over a large area. Our results will provide a strategy to create next-generation polymer–graphene nanohybrid optoelectronic devices.

1 Introduction

Graphene is a two-dimensional (2D) gapless semiconductor with a large π-conjugation, and has shown extraordinary electrical, thermal, and mechanical properties due to its unique structure.1–3 The high electron mobility (∼10 000 cm2 V−1 s−1) of graphene at room temperature and ease of incorporation into the polymers have also opened up the possibility of their use as promising transparent conductors4–9 and hybrid-type semiconductors10–13 in future printable and flexible optoelectronic devices. Furthermore, the one-atom thickness and large 2D plane of graphene can expect a large specific surface area in the polymer matrix, and thus very large functional interfaces can be formed. Graphene hybridized with polymer semiconductors is expected to be a good candidate for an acceptor material because large donor–acceptor interfaces for charge generation and a continuous pathway for efficient electron transfer can be built by the graphene component.14–16 Based on the fundamental electronic and structural properties, graphene could be employed to fabricate printable organic electronics, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs).17–19

Interfacial interactions between the chemically inert graphene surface and the organic semiconductor are dominated by π–π interactions, i.e., dispersion and electrostatic forces.20 Hence, molecular adsorption of organic semiconductors on the graphene surface is an ideal model system to study the effects of intermolecular π–π interactions on the self-assembly and molecular orientation on the graphene surface. Recently, some groups have reported epitaxial growth of conjugated small molecules, such as perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and pentacene, on the graphene surfaces via vacuum processing and demonstrated the effect of epitaxial growth of π-conjugated organic molecules on OFET performances.21–23 Furthermore, two-dimensional molecular assembly of π-conjugated polymers on highly oriented pyrolytic graphite (HOPG) surfaces has been studied by scanning tunneling microscopy (STM).24–28 Most of the studies, however, have focused on a vacuum process via layer-by-layer deposition on the graphene surface, and the epitaxial growth of π-conjugated polymers on a HOPG surface is a good model to confirm
polymer–carbon interface, but not easy to be applicable for real nanohybrid structures because HOPG is so bulky. To realize future printable electronics such as bulk heterojunction OPVs and hybrid OFETs, it would be desirable to prepare solution-processable layers via a spin-coating or printing process of π-conjugated polymers with graphene, in which functional nanohybrid interfaces incorporated with graphene can be formed. Promising performances have been reported in the previous studies of graphene-based printable organic electronics,\textsuperscript{1,6,11,12,13} however, knowledge regarding interfacial self-assembly characteristics of π-conjugated polymers on a graphene surface has not been reported, which is critical in designing and developing next generation printable optoelectronics integrated with graphene.

We report here the graphene surface driven specific self-assembly of π-conjugated polymers based on the intermolecular interactions via first-principles calculations and experimental analyses. Regioregular poly(3-hexylthiophene) (P3HT) was chosen as a π-conjugated polymer because it has been extensively studied in the field of organic electronics, such as OFETs and OPVs. Since P3HT consists of 2D sheets of π-stacked backbones separated by alkyl side-chains,\textsuperscript{29} it may lead to specific self-assembly on a graphene surface. Therefore, we first investigate the alignment mechanisms of P3HT on a graphene surface through first-principles calculation. Particularly, the effect of a thiophene backbone and alkyl chain in P3HT on the molecular orientation with graphene is investigated for the first time in this study. To experimentally confirm the structural characteristics of P3HT films self-assembled on a graphene monolayer, we examined the surface/ cross-sectional morphological features using atomic force microscopy (AFM) and transmission electron microscopy (TEM). We also explored the molecular orientation of P3HT chains on the graphene using 2D grazing incidence X-ray diffraction (GIXD) to obtain molecular orientation features over a large area.

2 Experimental

Graphene films were synthesized on the Cu foil (wacopa, purity 99.9%) by a chemical vapor deposition (CVD) method.\textsuperscript{30} In brief, hydrogen gas at 4 sccm was fed into the chamber to approximately 250 mTorr. The temperature of the chamber was elevated to 1000 °C and annealed for an hour. For growth, methane (CH\textsubscript{4}) gas was then injected for 20 min at a flow rate of 20 sccm. Finally, the temperature was cooled to 180 °C while maintaining hydrogen gas without CH\textsubscript{4} for 2 hours. After synthesis, poly(methyl methacrylate) (PMMA) was coated onto the synthesized graphene films, followed by dipping in a Cu etchant (FeCl\textsubscript{3}, Transene, Co., Inc. type I) solution. When the Cu foil was completely etched away, the resulting graphene sheets coated with PMMA were rinsed several times in deionized water to remove any etchant residue. Then, the PMMA-coated graphene sheets were transferred to the SiO\textsubscript{2}/Si substrate. PMMA was removed by acetone after the graphene was completely adhered to the substrate, and then thermal treatment of the sample was conducted to remove residual PMMA at 350 °C under H\textsubscript{2} (50 sccm) and Ar (50 sccm) for 1 h. Graphene was analyzed by TEM (JEM 2100F, JEOL) and Raman spectroscopy (Renishaw RM1000-Invia) at an excitation energy of 2.41 eV (514 nm, Ar\textsuperscript{+} ion laser).

To confirm the nano-morphology and crystalline microstructure, P3HT was characterized by using an AFM (Dimension V, Veeco Co.) operated in the tapping mode with a carbon nanotube cantilever, which was used to characterize the surface morphologies of the samples. High-resolution TEM (JEM 2100F, JEOL) with a 120 kV accelerating voltage was used to characterize the cross-sectional features of P3HT films. 2D GIXD measurements were performed at a 4C2 beam-line (wavelength: ~1.54 Å) in the Pohang Accelerator Laboratory.

3 Results and discussion

First-principles calculations based on the density functional theory (DFT) were performed using the VASP code to compute the binding energies of the π-conjugated polymer (here, P3HT) on graphene.\textsuperscript{31–33} Two models (see Fig. S1†) were designed to clearly understand the roles of an aromatic component (i.e. a thiophene backbone) and alkyl chains for the arrangement of P3HT on a graphene surface. In Model I (Fig. 1a and b), P3HT was designed to be a thiophene trimer (S\textsubscript{3}C\textsubscript{12}H\textsubscript{24}) with alkyl chains (R = C\textsubscript{6}H\textsubscript{13} and terminated with CH\textsubscript{3}). Model II (Fig. 1c and d) was designed for P3HT to be a thiophene trimer (S\textsubscript{3}C\textsubscript{6}H\textsubscript{6}) without alkyl chains (R = H and terminated with H). In Fig. S2(a),† the detailed side view of Fig. 1b is shown. The plane-wave cut-off energy was 400 eV and gamma point calculations were performed. The exchange–correlation interactions between electrons were described by the generalized gradient approximation (GGA), and projector-augmented wave (PAW) potentials were used for the description of ion–electron correlations.

![Fig. 1 Molecular configuration of P3HT on graphene for first-principles calculation. Model I: thiophene trimer with hexyl for (a) face-on and (b) edge-on orientations, and Model II: thiophene trimer without alkyl chains for (c) face-on and (d) edge-on orientations.](image-url)
interactions. The conjugated gradient method was used for geometric optimizations, and the optimization procedure was truncated when the residual forces of the relaxed atoms were less than 0.03 eV Å⁻¹. The binding energies \( E_{\text{binding}} = E_{\text{graphene/P3HT}} - E_{\text{graphene}} - E_{\text{P3HT}} \) between graphene and P3HT were calculated using the total energy difference between the binding systems \( (E_{\text{graphene/P3HT}}) \) and the separated systems \( (E_{\text{graphene}}, E_{\text{P3HT}}) \). The van der Waals force is the main interaction between graphene and P3HT. The conventional DFT method has limitations for describing the van der Waals interaction. Therefore, the DFT-D2 method with semi-empirical corrections was used.

The calculated binding energies for Model I and II are shown in Fig. 2, in which the binding energy was normalized to the energy per thiophene monomer. In both Model I and II, face-on configuration of P3HT on the graphene surface was more stable than the edge-on configuration since a much larger binding energy was determined for the face-on configuration. This might be attributed to the strong π–π interaction between the thiophene backbone and the graphene monolayer. The primary difference between Model I and II was the variation in binding energy from the edge-on to face-on configurations. The binding energy increase from edge-on (0.75 eV) to face-on configuration (1.94 eV) was 2.6-fold for Model I and 4.3-fold (from 0.2 eV to 0.86 eV) for Model II, which implies that the alkyl chains can have a critical effect on the configuration of P3HT on a graphene monolayer. Therefore, the design of alkyl chains on the thiophene backbone is greatly important for self-assembly of thiophene-based conjugated polymers on the graphene surface. Of course, the edge-on configuration for the trimer with alkyl chains was represented as shown in Fig. 1b, but such an orientation becomes unstable as thiophene units increase. Thus, we calculated the model similar to the real polymer system as shown in Fig. S2(b), in which the long-axis of a trimer with alkyl chains is further oriented parallel to the graphene substrate (see the schematic diagram in Fig. S3†). The result (i.e. the binding energy) from the model of Fig. S2(b)† was still less than that from the trimer with face-on orientation (Fig. 1a).

To experimentally characterize the surface-mediated self-assembly of P3HT on graphene, we used a grown graphene by chemical vapour deposition (CVD) on Cu foil. The TEM plane view of graphene as shown in Fig. 3a shows no appreciable contrast, indicating the uniformity of a graphene monolayer. The electron diffraction pattern clearly shows well-defined hexagonal spots (Fig. 3b), which indicate that our graphene layer was highly ordered. Fig. 3c shows a surface roughness of graphene by a tapping mode of AFM. The surface roughness of graphene (root-mean-square \( R_q = 2.0 \text{ nm} \)) was similar to that of ITO \( (R_q = 2.2 \text{ nm}, \text{see Fig. S4}^\ddagger) \) in the larger area \((3 \mu \text{m} \times 3 \mu \text{m})\) due to the ripple of graphene during the transfer process; however, the ripples were only line patterns in a local region, and a smooth area \( (R_q = 0.6 \text{ nm}) \) of graphene was distributed on most of the surface. Raman peaks of our graphene, \( G \) and \( G' \) bands, were observed at 1591 cm⁻¹ and 2686 cm⁻¹, respectively (Fig. 3d). The graphene layer can be characterized using the \( G'/G \) intensity ratio and the full width at half-maximum (FWHM) value of the \( G' \) peak in the Raman spectra, as shown in Fig. 3c. The \( G'/G \) intensity ratio of 2.27 and the FWHM of 36 cm⁻¹ reflect the monolayer character. This result indicates that our graphene layer is well ordered with high crystallinity.

A 0.3 wt% P3HT solution in chlorobenzene was spin-coated at 2000 rpm for 1 min on graphene and ITO substrates, and then annealed at 220 °C for 1 h under N₂ to enable P3HT chains to self-organize on each surface. The surface roughness of the P3HT-coated substrates was also measured. The surface \( (R_q = 0.9 \text{ nm}) \) of the P3HT-coated ITO was much smoother (Fig. S5a†). However, the surface of P3HT-coated graphene became much rougher \((R_q = 1.7 \text{ nm}) \) (Fig. 4a). Furthermore,
a FE-TEM was used to investigate the cross-sectional morphology and the film thickness of a P3HT/graphene and a P3HT/ITO bilayer, as shown in Fig. 4b and Fig. S5b.† The P3HT thin film on ITO approximately shows 7–8 nm thickness and much more uniform. On the other hand, the P3HT thin film on a graphene monolayer displays 5–10 nm thickness and slightly rough compared to that on ITO. Even though thin films were fabricated at identical P3HT concentration, P3HT films on graphene presented a thinner and rougher morphology. This may be attributed to the low surface energy (i.e., more hydrophobicity) of graphene and the mixed (face-on and edge-on) molecular configurations of P3HT chains on a graphene monolayer. Furthermore, this roughness in the graphene system could be due to PMMA residues, but we believe that 0.8 nm difference in the roughness originates from two kinds of orientation in P3HT chains onto the graphene surface. 2D GIXD measurements were conducted to more finely demonstrate the molecular packing and orientation of P3HT chains on ITO and graphene surfaces. As shown in Fig. 4c, strong (010) reflection at q = 1.65 Å⁻¹ and intense (h00) crystal reflections with higher-order peaks ((100) at q = 0.39 Å⁻¹, (200) at q = 0.77 Å⁻¹, (300) at q = 1.15 Å⁻¹, and (400) at q = 1.53 Å⁻¹) were observed with Debye rings in the q_z (out-of-plane) positions for P3HT films on graphene. In addition, unlike the P3HT films self-assembled on ITO (Fig. S6†), intense in-plane reflections appeared at a specific qx (≠0), which could be indexed to (100). These results indicate that P3HT films on the graphene surface consisted of multi-stacked layers that were oriented parallel and perpendicular to the substrate (Fig. 4d), which is different from the P3HT film on ITO with only an edge-on orientation (Fig. S7†). Note that this orientation of P3HT chains on the graphene surface is due to van der Waals interactions between alkyl side chains of P3HT and graphene, as well as π–π interactions between the thiophene backbone of P3HT and graphene, which corroborates the simulation results. This implies that the addition of alkyl side groups into the π-conjugated backbone for a printable system has a strong influence on molecular packing and orientation on the graphene surface compared to evaporated π-conjugated organic molecules, such as pentacene and PTCDI.
A point to be considered in our experiment is that a sub-monolayer of PMMA residue might be left on the graphene surface because we used a graphene monolayer transferred from Cu to SiO$_2$ using a PMMA-assisted step.$^{41,42}$ However, we think that the PMMA residue exists locally on graphene. If a sub-monolayer of PMMA residue totally covers the graphene surface, we should obtain a perfect one-phase orientation of P3HT chains from our GIXD results. However, as shown in Fig. 4c, we obviously confirmed two kinds of distinct molecular assembly such as edge-on and face-on orientation. This experimental result demonstrates that a sub-monolayer of PMMA residue might be locally left on graphene, which can lead to an edge-on orientation of P3HT chains on the graphene surface. Furthermore, the same GIXD experiment for P3HT film deposited graphene/Cu foil could provide more certain proof of the effect of graphene surface on the molecular orientation of P3HT. However, normally, to get a GIXD pattern, the substrate surface must be smooth to allow grazing-incidence angle mode diffraction. We tried to make smooth P3HT films onto the graphene/Cu foil substrate and measure the GIXD pattern by changing the grazing incidence angle, but unfortunately we could not get any pattern from this sample because of the rough structure of Cu foil.

4 Conclusions

In summary, we have demonstrated the surface-mediated, self-assembly of P3HT on a graphene monolayer via first-principles calculations and experimental characterizations. Due to the $\pi-\pi$ interactions between the thiophene backbone of P3HT and graphene, face-on configuration of P3HT on graphene was favourable. Furthermore, it was demonstrated that alkyl chains as well as thiophene backbones in P3HT are very important to determine the molecular configuration of P3HT on the graphene surface. These findings will enable nanohybrid structures with a $\pi$-conjugated polymer and graphene to be utilized in a variety of practical optoelectronic devices.

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Notes and references