ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 10978–10980

www.rsc.org/chemcomm

COMMUNICATION

Optical switching of the Dirac point in graphene multilayer field-effect transistors functionalized with spiropyran†

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Received 16th August 2012, Accepted 20th September 2012
DOI: 10.1039/c2cc35933b

A facile method for achieving optical switching of the Dirac point and conductance in reduced graphene oxide multilayer FETs that are non-covalently functionalized with a photoresponsive spiropyran derivative is presented. The photoresponsive transition from spiropyran to merocyanine induces the reversible optical switching in graphene based FETs.

Since its first isolation by mechanical exfoliation in 2004, graphene, a monolayer with a two-dimensional aromatic carbon lattice, has attracted tremendous attention as a promising nanomaterial in various fields of science and engineering.[1–5] Among many unique superlatives graphene possesses, its superior electronic properties with excellent chemical and mechanical stability make graphene an ideal candidate for future electronic devices and sensor applications.

To further exploit the superior characteristics of graphene in electronic applications, particularly for field-effect transistors (FETs), achieving precise control over transport behavior is still challenging. Toward this end, recent progress has been reported to access unipolar conduction in graphene including tuning the band gap *via* downsizing to nanoribbons or nanomeshes, introducing impurities or chemical doping, controlling the interface polarization *via* a self-assembled monolayer, and controlling the charge-density pinning effect at metal contacts.[6–12] Among these efforts, the chemical doping method is one of the most popular approaches for controlling the electric properties of graphene; however, it often introduces defects that suppress the carrier mobility and reduce the electronic conductivity of graphene.[13] Non-covalent functionalization of graphene, on the other hand, has been known to be a versatile protocol for introducing other functional molecules and biomolecules on the surface of graphene, while still preserving the innate structure of graphene.[14,15] From a practical perspective, fabricating graphene FETs onto various substrates by a solution process provides versatile opportunities to employ graphene in low-cost and flexible electronic applications, despite its intrinsically low electronic properties due to the presence of defect sites.

Molecular transformation triggered by light has long been a source of inspiration in designing molecular machines that mimic natural photoconduction processes.[16,17] Among a class of synthetic photoresponsive molecules, spiropyran is a well-known photochromic molecule due to its interesting tunability, stability, and fast response time.[18] For example, spiropyran undergoes a reversible transformation from colorless spiropyran to purple-colored merocyanine upon UV irradiation with a marked dipole moment increase associated with the structural conversion from a neutral to a charge separated zwitterion. With this interesting photoresponsive feature, spiropyran has been employed in optical sensors and memory devices.[18] In a representative example, Nuckolls and co-workers reported a reversible modulation of transport behavior of single walled carbon nanotube (SWNT) FETs that were modified with spiropyran-based molecular switches.[19] However, the approach for integrating photoresponsive spiropyran with graphene-based FETs and investigating its optical switching has not been reported to date.

In this communication, we report a facile solution-processable fabrication of graphene FETs that are functionalized with spiropyran derivatives and demonstrate their unique photoresponsive charge transport properties. Specifically, here we have employed the layer-by-layer (LbL) assembly of two oppositely charged graphene oxide (GO) nanosheets to access the graphene-based transistor by a solution-based protocol followed by a subsequent chemical reduction process (Fig. 1). As a true nanoscale blending method, the LbL assembly offers a unique opportunity to prepare graphene multilayers of desired composition with a precise nanoscale control over the thickness,

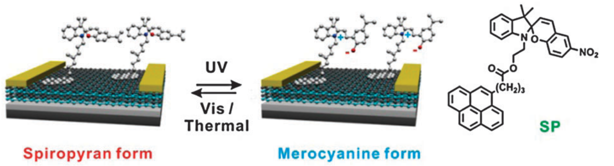

Fig. 1 Schematic representation of the photoresponsive spiropyran functionalized layer-by-layer (LbL) assembled graphene multilayer FET structures with a chemical structure of pyrene-functionalized spiropyran (SP) used in this study.

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† Electronic supplementary information (ESI) available: Details of experimental procedures and additional data. See DOI: 10.1039/c2cc35933b

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transparency, and conductivity.[20–23] LbL-assembled graphene multilayer transistors can be functionalized with photoresponsive spiropyran that is modified with a pyrene moiety through non-covalent interaction. We found that the resulting graphene multilayer transistor exhibited an n-type doping effect with a significant Dirac point shift of −5.4 V. Furthermore, we observed the reversible switching of the Dirac point as well as the changes in conductance induced by the photoswitchable property of the spiropyran group upon exposure to UV and visible light.

As demonstrated in our recent reports, we have assembled reduced graphene oxide multilayers *via* LbL assembly based on the electrostatic interactions.[23] With the two stable negatively charged GO (GO$^-$)[24] and positively charged GO (GO$^+$) suspensions (lateral dimension of 0.7–1.5 μm), we have fabricated multilayer films by repeatedly spin-coating onto a planar SiO_2/Si substrate to afford the multilayer with a composition of $(GO^+/GO^-)_n$ (n = number of bilayers). The GO multilayers were then subjected to a chemical reduction process to yield the reduced graphene oxide multilayer films (hydrazine vapor followed by 300 °C treatment). The fabrication of graphene multilayers was confirmed by UV/vis spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy (ESI†), and ellipsometry, showing a linear growth of homogeneous graphene films with an average bilayer thickness of 1.0 nm, which is consistent with our previous data.[23] For the functionalization of graphene multilayer films, non-covalent π–π interaction based on pyrene moieties was employed as it has been traditionally used for the functionalization of graphitic layers. Thus, the spiropyran modified with pyrene (SP) was synthesized using a modification of the published protocol (ESI†).[25] The synthesized SP displayed a photoresponsive property in solution upon UV irradiation (365 nm, hand-held UV lamp of 5 W); for example, the as-synthesized colorless SP transforms into a purple-colored isomeric merocyanine form (MC) within a couple of seconds and continues to change with an increase in absorbance at around 580 nm as measured by the UV/vis spectroscopy (ESI†). Interestingly, the visible white light exposure can also reverse the process from MC to SP. The characteristic absorption bands of the pyrene anchoring group remain unchanged during the conversion, confirming that the photoresponsive reaction occurred in the spiropyran moiety. After confirming the photoresponsive nature, the SP solution was deposited onto the prepared LbL-assembled graphene films for 24 h and the residual SP molecules were thoroughly washed with ethyl acetate, followed by gentle N_2 drying.

The photoresponsive charge transport of the LbL-assembled graphene films was further investigated by employing graphene FET devices. The LbL-assembled graphene multilayer was built on a heavily doped Si wafer with a 300 nm thick SiO_2 layer. The Si wafer itself and the SiO_2 layer worked as the gate electrode and dielectric, respectively. Finally, Au source and drain electrodes were deposited on the graphene multilayer films with a channel length and width of 100 and 800 μm, respectively.

Fig. 2 shows the drain current (I_D) as a function of gate voltage (V_G), which is characteristic of SP functionalized 2-bilayer graphene multilayer FETs upon UV and white light illumination. The LbL-assembled graphene FETs without SP molecules showed a slight p-type behavior with a Dirac point of 3.6 V. Interestingly, however, the devices displayed a weak n-type doping behavior with a Dirac point of −1.7 V upon the deposition of SP molecules. This is due to the net negative charge transfer from assembled SP to the graphene multilayer, which is consistent with the previous result based on SP-functionalized SWNTs.[19] This observation is, however, in clear contrast to typical p-type doping that is commonly induced by physical adsorbates such as oxygen and water during the preparation of graphene FETs.[26]

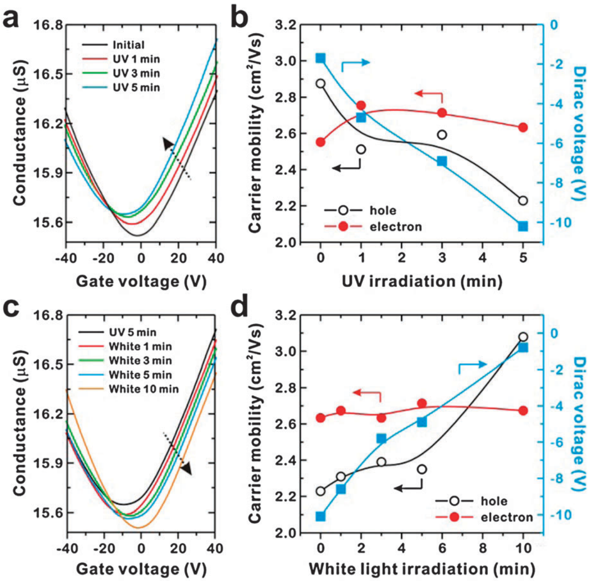

Fig. 2 Transfer characteristics of the SP functionalized 2-bilayer graphene FETs (V_D = −0.1 V) upon (a, b) UV and (c, d) white light irradiation. (b, d) The right panels show the corresponding changes of the carrier mobilities and Dirac voltage as a function of UV and white light irradiation time.

Upon UV irradiation, ring opening of spiropyran proceeds to zwitterionic merocyanine with a significant dipole moment increase (from *ca.* 4 to 20 D) that induces the development of localized dipole field on the surface of graphene FETs. This localized dipole field strongly influences the shift of the Dirac point. Moreover, the phenoxide ion created in the open merocyanine form can possibly enhance the development of negative charges near the graphene multilayers.[27] UV-induced n-doping of graphene FETs is further evidenced by the fact that the hole mobility is suppressed from 2.9 to 2.2 $cm^2 V^{-1} s^{-1}$ while the electron mobility remains almost constant at 2.6 $cm^2 V^{-1} s^{-1}$ (Fig. 2b and d).[28] As proposed in recent reports, the small molecules and self-assembled monolayers at the interface of the graphene channel can play an important role in controlling the electronic properties of graphene FETs.[12,28]

The Dirac voltage shift was also dependent on the irradiation time; for example, the initial Dirac voltage of −1.7 V became −4.7 V after 1 min and −10.2 V after 5 min. This shift is fully reversible upon irradiation with white light, which converts the merocyanine back to spiropyran with a subsequent recovery of the Dirac voltage. In contrast, the control experiment of unmodified graphene multilayer FETs did not show any sign of photoresponsive behavior. Thus, we highlight here that the functionalization of SP can effectively introduce the means of fine tuning the Dirac point of graphene multilayers with light. We then turn to the increase in minimum conductance upon UV irradiation. It is possible that the conjugation length of

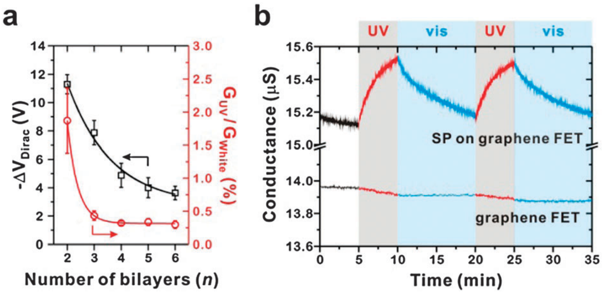

Fig. 3 (a) Dirac voltage shift ($-\Delta V_{\mathrm{Dirac}}$) and minimum conductance ratio ($G_{\mathrm{UV}}/G_{\mathrm{white}}$) between UV and white light irradiation as a function of the number of bilayers. (b) Time-course measurements of drain current of (top) SP-functionalized and (bottom) unmodified 2-bilayer graphene multilayer FETs (V_D = −0.1 V and V_G = −5 V).

graphene multilayers containing many defect sites increased owing to ring opening of spiropyran to fully conjugated merocyanine, thus increasing the density of charge carriers in the graphene channel.[27] In addition, the increased dipole moment of the merocyanine form leads to dielectric screening for an enhanced carrier mobility in graphene FETs as similarly observed by Tao and co-workers.[29]

By taking advantage of the LbL assembly, we also observed that the degree of Dirac voltage shift ($\Delta V_{\mathrm{Dirac}}$) under UV illumination could be precisely tunable by the number of bilayers in graphene multilayers. As shown in Fig. 3a, interestingly, the shift in Dirac voltage was most pronounced in the 2-bilayer film, which then gradually decreased with an increased number of bilayers. For example, the Dirac voltage shifts of 11.3 and 4.1 V were observed for 2- and 5-bilayer graphene FETs upon UV radiation for 5 min, respectively. This result stems from the reduced influence of SP molecules on the interfacial graphene channel as the number of bilayers increases (as the film becomes thicker), which eventually becomes saturated after 6-bilayer of graphene multilayers. In accord with the Dirac voltage shift, the conductance change ratio of UV *vs.* white light illumination ($G_{\mathrm{UV}}/G_{\mathrm{white}}$) diminishes as the film continues to become thicker (Fig. 3a). Taken together, this observation supports the argument that the observed photoresponsive effect originates from the interaction between SP molecules and graphene surfaces. Moreover, it should be noted that the number of bilayers of graphene films is the key factor in tuning both the degree of doping and electrical conductance of graphene films. These interesting features highlight the advantages of LbL assembly as a nanoscale bottom-up assembly that would have otherwise been hard to achieve with other techniques. Finally, in order to investigate the kinetics of the photoswitching process of SP-functionalized graphene multilayer FETs, I_D was monitored as a function of time (Fig. 3b). The channel conductance increased gradually with UV irradiation but decreased with white light irradiation (see ESI† for more description).

In conclusion, we present a facile method for achieving optical switching of the Dirac point in reduced graphene oxide multilayer FETs that are non-covalently functionalized with a photoresponsive spiropyran derivative. LbL assembly afforded a facile solution-based protocol for controlled assembly of graphene nanosheets. We found that the photoresponsive transition from spiropyran to merocyanine induced the observed optical switching of the Dirac point and modulation of conductivity. Further studies are underway to elucidate the detailed charge transport mechanisms of spiropyran on pristine graphene FETs and will be reported in due course. The versatile nature of LbL assembly integrated with the smart photoresponsive molecules as a means of controlling the device performance can be of potential interest in the design of new graphene based optical electronic devices and sensors.

This research is supported by WCU Program through the Korea Science and Engineering Foundation funded by the MEST (R31-2008-000-20012-0), the NRF (2010-0003219 and 2009-0083540), the Principal Research Program in the KIMS, and a grant (Code No. 2011-0031639) from the Center for Advanced Soft Electronics under the Global Frontier Research Program of the MEST, Republic of Korea.

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