Property Control of Graphene by Employing "Semi-Ionic" Liquid Fluorination

Jong Hak Lee, Gavin Kok Wai Koon, Dong Wook Shin, V. E. Fedorov, Jae-Young Choi, Ji-Beom Yoo, and Barbaros Özyilmaz**

Semi-ionically fluorinated graphene (s-FG) is synthesized with a one step liquid fluorination treatment. The s-FG consists of two different types of bonds, namely a covalent C-F bond and an ionic C-F bond. Control is achieved over the properties of s-FG by selectively eliminating ionic C-F bonds from the as prepared s-FG film which is highly insulating (current $< 10^{-13}$ A at 1 V). After selective elimination of ionic C-F bonds by acetone treatment, s-FG recovers the highly conductive property of graphene. A 10^9 times increase in current from 10^{-13} to 10^{-4}A at 1 V is achieved, which indicates that s-FG recovers its conducting property. The properties of reduced s-FG vary according to the number of layers and the single layer reduced s-FG has mobility of more than 6000 cm^2 V^{-1} s^{-1}. The mobility drastically decreases with increasing number of layers. The bi-layered s-FG has a mobility of 141cm^2 V^{-1} s^{-1} and multi-layered s-FG film showed highly p-type doped electrical property without Dirac point. The reduction via acetone proceeds as $2C_2F_{(semi\text{-}ionic)} + CH_3C(O)CH_{3(l)} \rightarrow HF + 2C_{(s)} + C_2F_{(covalent)} + CH_3C(O)CH_{2(l)}$. The fluorination and reduction processes permit the safe and facile non-destructive property control of the s-FG film.

1. Introduction

Graphene has attracted enormous scientific attention on account of its extraordinary electronic and mechanical properties resulting from hexagonally arrayed sp2-hybridized one-atom-thick carbon structure.[1,2] Graphene's high electronic mobility has been introduced to applications such as transistors and flexible transparent electrodes.[2,3] Recently, one of the main graphene research directions is adatom engineering on graphene surface. The electronic state of graphene can be altered from insulator to semiconductor by decoration/re-decoration of the atoms and molecules on the surface. One of the interesting derivatives of graphene resulting from adatom engineering is "graphane", which has a compressed stoichiometric crystal lattice and the hydrogen atom is attached to every carbon atom of graphene. Graphane exhibits metal-insulator transition and mid-gap states as a function of 1/T.[4] Theoretical predictions show that not only hydrogen but also fluorine is a good candidate for creation of the (tunable) bandgap in graphene's energy spectrum.[5–7] Geim et al. reported that fluorographene is a high-quality insulator (resistivity $>10^{12}\Omega$) with an optical gap of 3 eV and is stable up to 400 °C under ambient conditions.[5] Other researchers have shown similar electrical insulating properties of fluorographene through atomic fluorine exposure. The conductivity of fluorographene was dramatically changed by fluorination and de-fluorination processes.[8,9] However, proposed methods require long process times for multi-layered graphene fluorination.[5,8,9] In addition, after the chemical or thermal de-fluorination process, reduced fluorographene showed poor conducting

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Dr. J. H. Lee, D. W. Shin, Prof. J.-B. Yoo
SKKU Advanced Institute of Nanotechnology (SAINT)
Sungkyunkwan University
Suwon 440-746, Republic of Korea
E-mail: jbyoo@skku.edu

Dr. J. H. Lee, G. K. W. Koon, Prof. B. Özyilmaz
Department of Physics
National University of Singapore
117542, Singapore
E-mail: barbaros@nus.edu.sg

Dr. J. H. Lee, Prof. B. Özyilmaz
Graphene Research Center
National University of Singapore
117542, Singapore

Prof. V. E. Fedorov
Nikolaev Institute of Inorganic Chemistry
Siberian Branch of Russian Academy of Sciences 3
Acad. Lavrentiev prospect, Novosibirsk, 630090, Russia

Dr. J.-Y. Choi
Samsung Advanced Institute of Technology
Yongin, Gyeonggi, 446-712, Republic of Korea

Prof. J.-B. Yoo
School of Advanced Materials Science & Engineering (BK21)
Sungkyunkwan University
Suwon 440-746, Republic of Korea

Prof. B. Özyilmaz
NanoCore, National University of Singapore
117576, Singapore

Prof. B. Özyilmaz
NUS Graduate School for Integrative Sciences and Engineering (NGS)
National University of Singapore
117456, Singapore

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property (at least more than 10^5 Ω/sq) similar to reduced graphene oxide[8–13] because functionalized carbon atoms consist of strong covalent C-F bond which can cause the defect during de-fluorination. In this study, we introduced the "semi-ionic" C-F bond to graphene which consists of strong covalent C-F bond and easily controllable ionic C-F bond. The semi-ionically fluorinated graphene (s-FG) film was synthesized by one-step functionalization process. The thin s-FG film device shows a diametrical property in electrical investigation through selective ionic C-F bonds elimination.

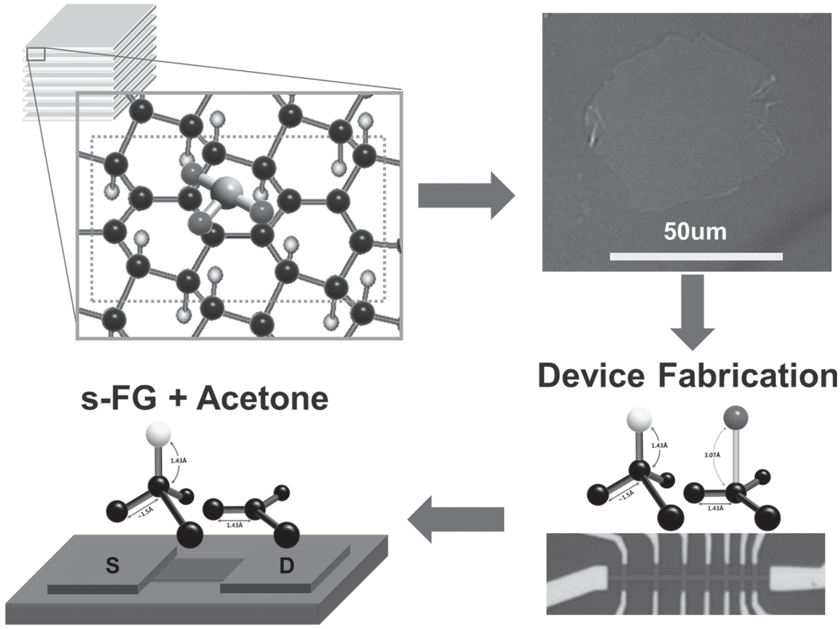

Figure 1. Schematic representation of the s-FG based device fabrication and reduction process; schematics of s-FG and reduced s-FG structures. Inset scale bar is 50 μm.

2. Results and Discussion

Figure 1 summarizes the experimental procedures used to fabricate the s-FG based device for transport measurements. The s-FG was synthesized using the single functionalization and intercalation process with ClF_3. The s-FG contains inorganic volatile intercalating agent ClF_3 with molecular formula $C_2F \cdot nClF_3$ as reported elsewhere.[14] Five grams of pure natural graphite was added to cold liquid ClF_3 in a Teflon reactor and kept for intercalation and fluorine functionalization for 5 h. Later, excess ClF_3 was removed, and the graphite compound with a composition of $C_2F \cdot 0.13ClF_3$ was obtained. The obtained s-FG is golden in color and the composition in mass% is C 44.22; F 44.79; Cl 12.49. Using the mechanical exfoliation method, we have succeeded in obtaining s-FG films of several tens of micrometers in size onto the p-type doped silicon substrates covered with a thermally grown 300 nm thick SiO_2 layer. After s-FG transfer, two junction devices or hall-bar geometry devices were fabricated followed by the reduction process with acetone at room-temperature.

Previous density functional theory (DFT) calculations show that graphite fluoride possesses a wide band gap of approximately 3 eV at the K point of its band structure which agrees with its highly electrical insulating properties.[9,15] Before investigating the electrical properties of s-FG devices, as a "control reference" we measured the current between two bare electrodes without s-FG channel which is shown in **Figure 2**a. As shown in Figure 2a, as prepared s-FG device has 10^{-13} A at $V_{DS} = \pm 1$ which is similar current level to SiO_2 channel device (control). The obtained 10^{-13} A level at $V_{DS} = \pm 1$ from the s-FG is comparable to the highest insulating property of high quality fluorographene which is synthesized by double-sided XeF_2 fluorination of suspended graphene.[5,8] The XeF_2 treatment is an effective way for high quality fluorination of suspended graphene, however it is insufficient for multi-layered fluorographene and even for bilayered fluorographene.[5] We synthesized several grams of s-FG with only one step fluorination process for 5 h which results not only in obtaining high quality fluorographene but also a way to mass produce s-FG for future industrial application.

A simple acetone treatment has been used for the safe recovery of the conducting property of fluorographene. After the acetone treatment for one week at room-temperature, the current level was dramatically increased by nine orders of magnitude (Figure 2a). This is the first observation of such a huge current increase in fluorographene and graphene oxide (GO) research.[8–10,16–19] GO is an electrical insulator and randomly decorated with hydroxyl and epoxy groups and obtained by reaction of graphite with liquid oxidizing agents. Reduced GO and fluorinated graphene resemble graphene but still exhibit poor conductivity compared to pristine graphene due to some residual oxygen and structural defects even after extensive chemical (hydrizine) or thermal (~1000 °C) reduction treatments.[8,16,17] Compared to reduced GO and fluorographene, our reduced s-FG shows much higher current increase after simple reduction process at room-temperature. However, the reduced s-FG device has highly p-type doped electrical characteristics as shown in Figure 2b. We couldn't obtain the Dirac point within ±100 V_G range and there is only hole majority carrier region and the measured hole mobility is about 100 $cm^2 V^{-1} s^{-1}$.

Generally, solid state fluorographene is prepared by two methods. First one is the direct reaction of graphite with a fluorine source such as $XeFe_2$ or F_2 gas. Second method is by liquid volatile fluoride treatment using chemicals such as HF, ClF_3, etc. for the graphite intercalation compounds (GIC) synthesis. The direct fluorine-carbon reaction usually induces the covalent C-F bond. The covalent C-F bonds increase the strain in graphene structure and cause some disorder in graphene structures such as interlayer carbon-carbon bonds[15] which can further disturb the fluorination process. Therefore, to achieve severe fluorination state, high temperature of at least 350 °C or longer process time is necessary (XeF_2 treatment for several days is insufficient even for bilayered graphene fluorination).[5,20] On

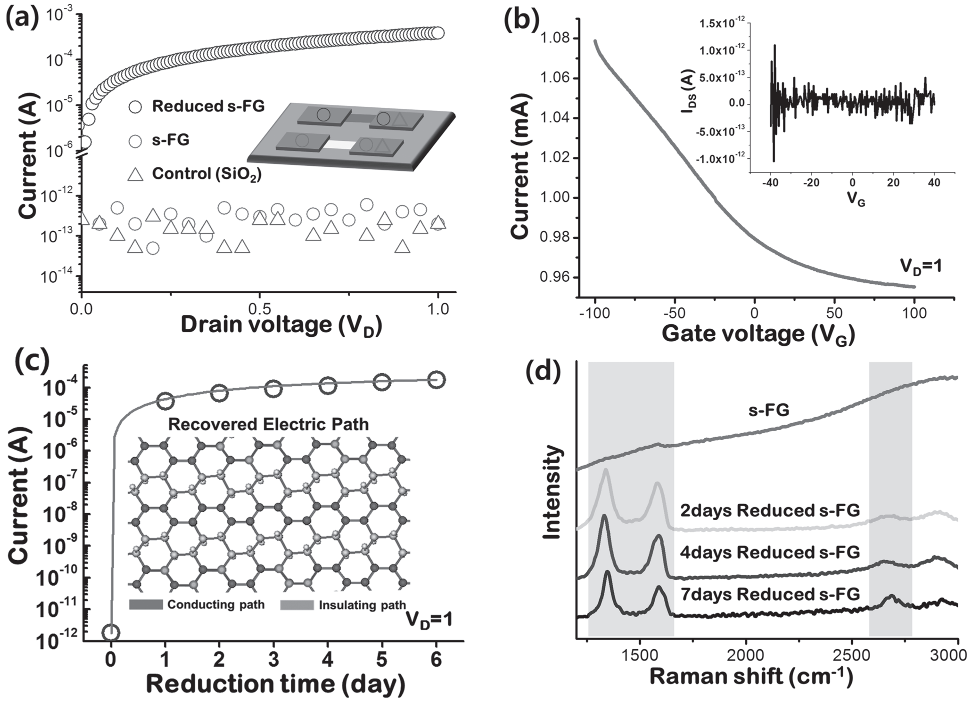

Figure 2. a) *I–V* characteristics of prepared multi-layered s-FG and reduced s-FG films, b) *I–V*$_g$ characteristics of multi-layered s-FG FET before (inset) and after reduction process. c) Current variation depends on the reduction time; schematic of conducting path in reduced s-FG structure. d) Raman spectroscopy results according to the reduction time.

the other hand, in GIC case, the presence of intercalant allows penetration of the fluorine molecules between the graphene layers. Instead of reacting immediately with the graphene sheets to form CxF, the fluorine atoms diffuse and spread all over the available graphite material. As the intercalation proceeds, the fluorine concentration increases all over the sample. When the fluorine concentration becomes high enough, transformation from covalent bonding to ionic bonding occurs (thus the name “semi-ionic” bond).[21] This process can help not only in producing high quality fluorinated graphene but also maintains its planar structure. The semi-ionic character of the bond which is considered to be intermediate between ionic and covalent, has been suggested by some physicochemical measurements.[22] For example, ^{13}C-NMR spectroscopy has proven that there are two carbon types: carbon atoms close to sp2 type with weak C-F interaction (ionic) and carbon atoms with stronger C-F interaction (covalent).[22] The ionic C-F bond has charge transfer of 1/6 of a hole per fluorine atom from graphene.[21] The bond dissociation energy (BDE) is related to the strength of C-F. The BDE of covalent C-F is < 460 kJ/mol and that of ionic C-F is about 54 kJ/mol.[22] In addition, some studies suggest the reaction of F with $CH_3C(O)CH_3$ through H-atom abstraction reaction such as $F + CH_3C(O)CH_3 \rightarrow HF + CH_3C(O)CH_2$ and CH_3 displacement reaction such as $F + CH_3C(O)CH_3 \rightarrow CH_3 + CH_3C(O)F$ mechanisms.[23,24] The abstraction mechanism is the major channel, but both abstraction (-38.3 kcal/mol) and displacement (–0.39 kcal/mol) steps are essentially barrier less and it is well-known that fluorine gas ignites in contact with acetone. Therefore, we infer that the reaction of s-FG with acetone is related with ionic C-F bond due to its low BDE and the process is likely to proceed through this reaction mechanism $2C_2F_{(semi\text{-}ionic)} + CH_3C(O)CH_{3(l)} \rightarrow HF + 2C_{(s)} + C_2F_{(covalent)} + CH_3C(O)CH_{2(l)}$. Furthermore, it was checked whether s-FG can be reduced by methanol and water but there was no electric current or color change.

The reduction of multi-layered s-FG film using acetone is well proven by Raman and transport measurement analysis. Our multi-layered s-FG film has no characteristic peaks of graphene. The disappearance of all the characteristic peaks, also clearly proven by other reports, it is assumed that the film is completely fluorinated.[5,8] As the reduction time increases, the D and G peaks of respective carbon sp3 and sp2 bonds are appeared. After a week, the 2D peak (2700 cm^{-1}) was recovered too. The significant change of Raman spectra was in the first two days which agrees well with the current variation results. The increase in the current was steep in the initial stages followed by a gradual increase after two days.

For systematic charge transport studies, we fabricated hall bar geometry devices of single and bi-layered s-FG using electron beam lithography (EBL) technique. The mobility of single layered s-FG depended on its fluorination state. The mobility increases with increasing ratio of 2D/D intensity peaks in Raman spectra (**Figure 3**a–c). Single layer s-FG samples with one week reduction treatment showed mobility as high as 6300 cm^2 V^{-1} s^{-1}.However with bi layer s-FG samples, the mobility dramatically decreased down to 141 cm^2 V^{-1} s^{-1} (Figure 3d). This change is due to the structural hindrance of covalent C-F bonds of graphene layers which can prevent further de-fluorination process. The differences between single and multi-layered s-FG reduced states are well proven by

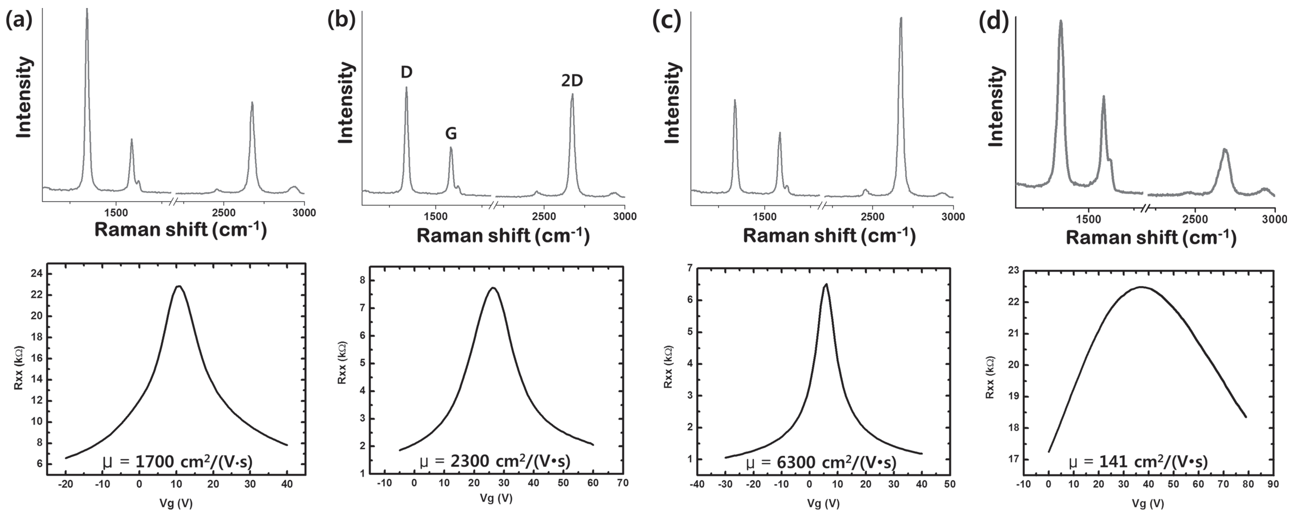

Figure 3. Raman characteristics and resistance vs V_{bg} of reduced single and bi-layered s-FG devices: a) as prepared, b) intermediate, and c) 1 week reduced. The mobility of single layered s-FG was related with the 2D/D ratio of its Raman results. d) Even after reduction treatment for 1 week, bi-layered s-FG has high D peak and a mobility of 141 cm^2 V^{-1} s^{-1}.

fluorescence microscopy. As shown in Supporting Information Figure S3 and S4, a big flake has a uniform fluorescence for the entire area before the reduction treatment. However after acetone treatment, we could clearly distinguish the differences between various layers using the fluorescence microscopy image. The single layered s-FG easily loses its fluorescent characteristics but multi-layered s-FG area maintains its fluorescence signal. From the fluorescence results, we can confirm that the reduction process occurred mainly in the top surface which is in contact with acetone while the area between the multi-layered s-FG is still insulating.

The color and electrical properties of fluorinated graphene are related to the content of fluorine atom. Recently, there are a few reports on theoretical electronic structure of fluorinated graphene.[8–10,15] As the F atom content increases in graphite compound, the band gap increases as well. The fully fluorinated graphene with its new crystalline structure is an insulator with a band gap of 3 eV resulting in different electronic properties from graphene and the absence of G and D features in the Raman spectra. However, there are still a lot of controversies concerning relationship between the electrical, optical properties and F contents due to the difficulty in the synthesis of stoichiometric fluorographene.

Figure 4a shows the basic optical properties of s-FG. After mild sonication in methanol with cold water circulation for few hours and vacuum filtration processes, we obtained s-FG paper which is about 3 cm with a thickness of 220 μm as shown in the inset of Figure 4a. The s-FG paper has an absorption edge at about 400 nm wavelength from the reflectance analysis. The yellowish color corresponds to the absorption of violet color. The combination of yellowish color and F content matches well with previous report.[25] In addition, there are no D and G peaks observation from the Raman spectra. Based on the observed bandgap and Raman spectra, we can infer that all graphene layers were highly fluorinated and s-FG paper has 3eV bandgap. The disappearance of D and G peaks of Raman spectroscopy was due to both the fluorination level and its stoichiometry. Even highly insulating fluorinated graphene could have graphene Raman signal at times due to its structural disorder.[20] The s-FG synthesized by graphite with liquid ClF_3 treatment is well known for stoichiometric compound.[25–27] We couldn't find the C-C bond from the XPS analysis as shown in Figure 4c. Figure 4b shows the XRD data of the synthesized s-FG and TEM image of a thin s-FG sheet suspended on a grid. From the inset XRD data, we can know the intensive fluorination and intercalation states. The data shows expanded interlayer distance signals instead of characteristic interlayer spacing of graphite (d_{001}; approximately 3.4 Å). This larger interlayer distance agrees well with AFM analysis (Supporting Information Figure S2c,d). In addition, the in-plane lattice distance (d_{100}) also showed an increase which is well expected because the covalent C-F bonds leads to larger interatomic distance sp3-type bonds.[5,9] The observed increase in the electron diffraction pattern is ≈2.1–4.2% larger compared to that of graphite. We measured the sample using AFM after 7-day reduction to investigate whether the reduction occurred only on the top surface or in the entire multi-layered fluorographene. There were no significant changes in the height and surface RMS value (Supporting Information Figure S1) unlike electron beam reduction.[28]

The fluorination states before and after reduction process were well proven by XPS analysis. As prepared, s-FG has the C-F (ionic) and C-F (covalent) bonds as main peaks and there is no C-C bond (Figure 4c). However, after reduction process, C-C bond was recovered and only the ionic bond peak area was reduced as shown in Figure 4d. The reduced s-FG paper has an absorption edge at about 460 nm from the reflectance analysis (Figure 4e) which indicates that there is still optical bandgap due to locally remained covalent C-F and ionic C-F bonds. Therefore, the reduced multi-layered s-FG device has highly p-type doped electrical characteristics which consists of only hole majority carriers and there is no Dirac point as shown in Figure 2b.

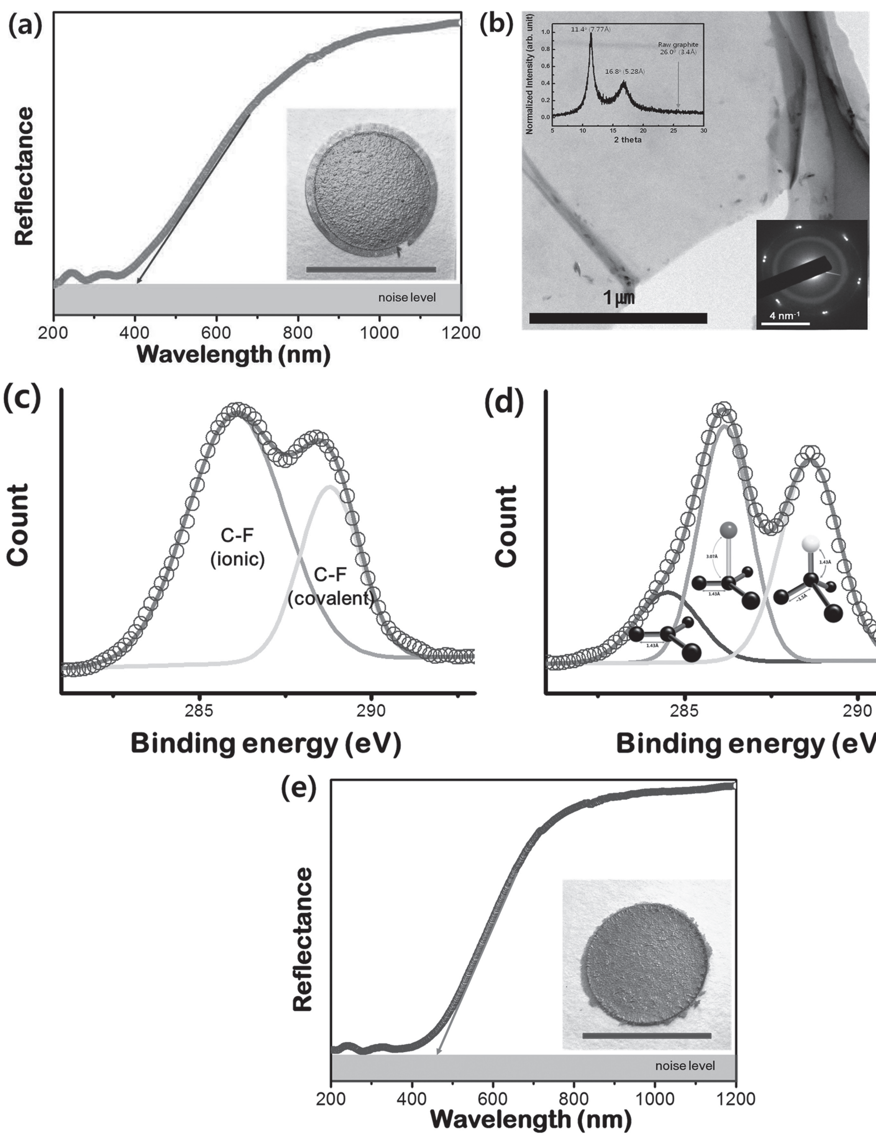

Figure 4. a) Reflectance result of s-FG paper. The absorption edge is about 400´nm. The inset scale bar is 3 cm. b) TEM image of s-FG film on grid, upper inset is the XRD result of s-FG powder and lower inset is electron diffraction (ED) pattern of s-FG film, c) XPS data of s-FG and d) reduced s-FG. e) Reflectance result of 1 week reduced s-FG paper. The absorption edge is about 460 nm and the scale bar of the inset is 3 cm.

3. Conclusions

We synthesized the semi-ionically fluorinated graphene (s-FG) with only one step liquid ClF_3 treatment within 5 h. The prepared s-FG film has high insulating properties. After reduction process, we observed that there is a 10^9 times increase in the current from 10^{-13} to 10^{-4}A which indicates the transition of insulator to graphene. The reduced multi-layered C_2F film shows highly p-type doped electrical properties. The reduction via acetone likely proceeds as $2C_2F_{(semi\text{-}ionic)} + CH_3C(O)CH_{3(l)} \rightarrow HF + 2C_{(s)} + C_2F_{(covalent)} + CH_3C(O)CH_{2(l)}$ at low temperature. This safe chemical reduction process produces high-quality graphene (fluorographene) and apart from this provides a non-destructive recovery. This fluorination and reduction processes could be useful not only for manufacturing high quality insulators such as in flexible insulator applications but also for adatom engineering studies.

4. Experimental Section

Synthesis of Semi-Ionically Fluorinated Graphene (s-FG): A teflon reactor was filled with 30 g of liquid ClF_3 and cooled with liquid nitrogen. Five grams of pure natural graphite (ash content < 0.05 mass%, particle size = 200–300 µm, Zaval'evsk coal field, Ukraine) was added to the cold ClF_3. The reactor was then sealed hermetically. The temperature was increased slowly to 22 °C and kept at that temperature for 5 h. Excess ClF_3 was removed using a nickel vessel cooled with liquid nitrogen until a constant mass was measured. The intercalation product (approximately 11 g) had an approximate composition of $C_2F{\cdot}0.13ClF_3$. Elemental analysis data (mass%): C 44.22; F 44.79; Cl 12.49.

Fabrication of Devices and Non-Destructive Reduction: Using the mechanical exfoliation method, s-FG films of several tens of micrometers in size were deposited on p-type doped silicon substrates coated with a thermally grown 300-nm-thick SiO_2 layer. To prove the acetone effect on s-FG, we deposited two contact metal electrodes (Cr:5nm/Au:70nm) on the large sized multi-layer s-FG using the shadow mask after s-FG transfer. For the hall bar geometry device fabrication, metal electrodes (Cr:5nm/Au:55nm) were deposited using electron beam evaporation for multi-layered s-FG. For the single and bi-layered s-FG devices, we used the electron beam lithography technique followed by the reduction process with acetone at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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