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研究課題名（英文） Atomically precise oxidation and alkylation of graphene leading to nanopattern formation on the surface

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研究成果の概要（和文）：本研究ではほぼ単層のグラフェン上における完全な酸化及びアルキル化を達成する新手法を開発する。私はSi露出SiC基板上にエピタキシャル成長させたグラフェンを用いて、二種の液相酸化反応により、選択的に片面のみのグラフェンを広域に酸化する方法の開発を行った。その上、グラフェンを二段階の光化学的手法を用いた塩素化/アルキル化により、アリル/アルキル基をSiC上グラフェンへ結合することができた。他のハロゲン化したグラフェンをさらに化学修飾させることができるか確かめるため、SiC上グラフェンをハロゲンと反応させ、更にアリルグリニャール試薬と反応するか研究した。

研究成果の概要（英文）：The present research project is focused on the invention of new chemistry for atomically precise oxidation and alkylation of graphene, which can lead to entirely new classes of two-dimensional nanomaterials with vast tunability in chemical, electrical, and optical properties. I have investigated aqueous phase oxidation of epitaxial graphene (EG) on the Si-face of the SiC substrate using two different methods, which results oxidized EG with high concentration of chemisorbed O species. I have also developed a new chemical approaches for alkylation/arylation of EG through photochemical chlorination of graphene followed by reaction with Grignard’s reagent.
To see if the other halogenated graphene can be utilized for further modification, I have made detailed investigation of halogenations of EG on SiC and its reaction with aryl Grignard reagents.

研究分野： 総合理工

キーワード： ナノ表面・界面　グラフェン

１．研究開始当初の背景

Graphene has attracted substantial attention due to its extreme electronic, thermal, and physical properties (*Science* **2004**, *306*, 666; *Nature* **2005**, *438*, 197 ; *Nature Mat.* **2007**, *6*, 183 ; *Science* **2009**, *324*, 1530). A defect-free and highly ordered crystal of graphene is the thinnest and strongest material in nature. Graphene is optically transparent, chemically inert, and electrically and thermally highly conductive (*Science* **2004**, *306*, 666; *Science* **2009**, *324*, 1530). Such an unusual combination of extreme properties makes graphene attractive for a wide range of applications. It can be used in electronics devices such as high-frequency transistors, photonics and optoelectronics devices such as displays, touch screens, light-emitting diodes and solar cells, etc (*Science* **2009**, *324*, 1530 ; *Nature Photonics* **2010**, *4,* 611).

２．研究の目的

To make the graphene suitable for application in next generation electronics and other devices, one must alter its properties. One of the prominent ways to tune the materials electronic properties is through chemical modification of its surface. However, compared to the vast overall recent literature on graphene, relatively few studies have focused on strategies for chemically modifying graphene surfaces (*J. Mat. Chem.* **2010**, *20*, 2277; *J. Am. Chem. Soc.* **2010**, *132*, 15399). Hence, the present research project is focused on the invention of new chemistry for atomically precise oxidation and alkylation of graphene at nearly monolayer coverage, which can lead to entirely new classes of two-dimensional nanomaterials with vast tunability in chemical, electrical, and optical properties.

３．研究の方法

I have explored the various chemical methods for (i) atomically precise oxidation and (ii) alkylation of graphene up to monolayer coverage, which can be tailored to a new class of graphene-based nanomaterials. Epitaxial graphene (EG) grown on commercially available Si-face SiC substrate was used. EG was prepared by annealing 6H-SiC(0001) samples at 1350 ºC for 10-12 cycles of 30 s under UHV conditions (maximum pressure ~ 5.0 x 10^{-9} Torr). Thus prepared EG on the Si-face of SiC substrate usually contains 1-3 layers of graphene (*J. Am. Chem. Soc.* **2010**, *132*, 15399-15403; *J. Phys. D: Appl. Phys.* **2010**, *43*, 374009). The EG grown in UHV is stable in air, hence, is used ex-situ for oxidation and alkylation.

For oxidation of EG, I have employed aqueous phase oxidation procedures under different experimental conditions. The EG is oxidized *ex situ* using Hummers oxidizing agents in two different reaction procedures termed as the ‘dipped-in’ and ‘drop-casting’ procedures. In the case of the ‘dipped-in’ procedure, the EG on SiC is placed into a conical flask followed by addition of 20 ml concentrated H_2SO_4 and 0.1 g of $NaNO_3$. Then, 0.6 g of $KMnO_4$ is slowly added into the flask with constant stirring in an ice bath. In the case of the ‘drop-cast’ procedure, a few drops of Hummer solution are carefully placed onto the surface so that the meniscus of the droplet does not touch the edge of the sample. The sample is then heated to the desired temperature by placing the sample on a hot plate. After oxidation, the sample is cleaned by DI water and H_2O_2 repeatedly.

As planned initially, I have employed two strategies in order to modify the epitaxial graphene with alkyl/aryl groups. (i) Dipping the EG on SiC sample in the reaction flask where alkyl diazonium ion is synthesized and (ii) photochemical chlorination of graphene followed by reaction with Grignard’s reagent. Though the first method was not successful, the second two-step chlorination-alkylation procedure is found very effective for alkylation of EG on SiC. Chlorination of EG is done by exposing the surface to Cl_2 under UV light (300 mW; 365 nm.) in N_2 atmosphere. The Cl_2 is produced by the reaction of 98 % HCl acid and trichlorocyanouric acid ($C_3Cl_3N_3O_3$) as well as potassium permanganate ($KMnO_4$). The Cl_2 is passed through concentrated H_2SO_4 for drying before reaching to the EG. For methylation process, the EG on the SiC(0001) wafer is placed into a Schlenk tube fitted with a water cooled condenser, pure Ar purge line, inlet for the Grignard reagent (*Langmuir* **1999**, *15*, 3831-3835). The Schlenk tube placed into an oil bath is purged with pure Ar for 5 min before introducing the Grignard reagent in THF. The temperature around the tube is raised to 65 ^{o}C and maintained for about 2 h while keeping the Ar flow very slow. For terminating the reaction, the EG sample is taken out of the tube and dipped into pure THF in a beaker. Finally the surface is cleaned by THF, pure water and 1,1,2-trichloroethane as reported earlier (*Langmuir* **1999**, *15*, 3831-3835).

The pristine and chemically modified surface was characterized by different surface probe techniques such as scanning tunneling microscope (STM), Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS), etc.

4． 研究成果

(i) **Atomically precise oxidation:**

The Raman spectrum of epitaxial graphene on SiC shows the characteristic 2D and G bands at 2748 and 1605 cm^{-1} as shown in figure 1 (*Appl. Phys. Lett.* **2008**, *92*, 201918). The G band is ascribed to the in-plane vibration of sp^2 carbon atoms, which is a doubly degenerate phonon mode (E$_{2g}$ symmetry) at the Brillouin zone center (*Phys. Rev. B*, **2011**, *84*, 035433). The 2D band is a two-phonon process, which is allowed only for a perfect lattice of graphene (*Phys. Rev. B*, **2011**, *84*, 035433). The small D peak at 1380 cm^{-1} is a defect induced band, which appears in the case of clean graphene on SiC due to the interaction of graphene with the substrate (*Appl. Phys. Lett.* **2008**, *92*, 201918). Note that no such bands are observed in the Raman spectrum of bulk SiC. Following oxidation by both the 'dipped-in' and 'drop-cast' procedures, the 2D band of the Raman spectra almost disappears and the D band is significantly enhanced because of the creation of defect sites by chemisorption of oxygen. The increased intensity of the G band in the case of oxidized graphene is perhaps related to Raman enhancement due to increased roughness of the surface caused by the chemisorption of oxygen. The D/2D ratio of the Raman spectra suggests that the extent of oxidation by these two methods are almost equal (i.e., the 'drop-cast' procedure is equally effective at oxidizing the surface as the 'dipped-in' procedure). The extent of oxidation is further confirmed by both XPS and high resolution XPS measurements on different samples. Taking into consideration of the photoemission cross-section of C 1s and O 1s electrons, the O/C ratio is estimated by both area intensities of the graphene C 1s and O 1s peaks in the narrow scan spectra, and the corresponding peak heights in the survey spectrum obtained by low energy X-rays. The estimated values are found to be 0.30-0.35 and 0.36-0.38 for the 'drop-cast' and 'dipped-in' oxidized samples, respectively.

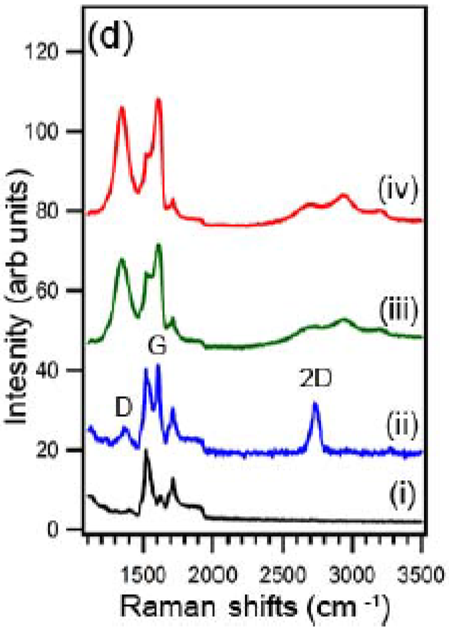

Figure 1. Raman spectra of (i) SiC substrate, (ii) clean EG on SiC, (iii) after oxidation of EG on SiC by 'drop-casting' method and (iv) after oxidation of EG on SiC by 'dipped-in' method. Hossain et al. *J. Phys. Chem. C 2014, 118, 1014.*

Aqueous phase oxidation of epitaxial graphene on SiC induces significant electronic property changes. The typical STS dI-dV curves extracted from the I-V curves measured on oxidized and non-oxidized areas of epitaxial graphene on SiC is shown as inset in Figure 2. The oxidized surface produced by the 'drop-cast' and 'dipped-in' procedures show almost identical STS I-V characteristics, which suggest similar levels of oxidation as previously deduced from Raman and XPS measurements. The STS dI-dV curve for the oxidized surface shows almost zero current around zero-tip bias (i.e., no density of states near the Fermi level) (*Annu. Rev. Anal. Chem.* **2009**, *2*, 37-55). For the oxidized surface, the differential tunneling conductance is nearly zero between +0.1 V and –0.3 V, suggesting a local band gap of ~0.4 eV is opened when epitaxial graphene

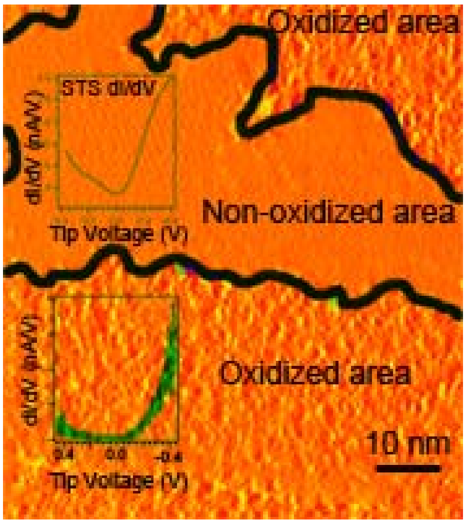

Figure 2. STM image showing the oxidized and non-oxidized areas of EG on SiC. Insets shows the extracted STS dI/dV curves acquired from the I-V measurements on the respective areas indicated. V$_{sample}$ = -0.5 V and I$_{tunnel}$ = 0.2 nA. Hossain et al. *J. Phys. Chem. C 2014, 118, 1014.*

is oxidized by the Hummers reagents. The curve for clean graphene indicates zero band gap and the Dirac point at ~ 0.3 V, which is characteristic of clean epitaxial graphene on SiC (*J. Am. Chem. Soc.* **2010**, *132*, 15399-15403). Furthermore, the asymmetry of the STS I-V curve suggests that the oxidized surface is p-type doped.

(ii) **Alkylation/Arylation of EG on SiC:**

One of the most prominent and general synthetic route for binding an alkyl, vinyl or aryl group to another C atom is the reaction between a Grignard reagent (RMgX, where R = alkyl, vinyl or aryl and X = Cl or Br) and R-X compound. The technique is successfully employed in the case of chlorinated Si surface and carbon nanotube for making alkyl-terminated surfaces (*Langmuir* **1999**, *15*, 3831; *Acc. Chem. Res.* 2002, *35*, 1087). We have invented the covalent binding of methyl group on the basal plane of epitaxial graphene on SiC(0001) through the two-step chlorination-alkylation processes using Grignard reagent (CH_3MgBr) as shown in figure 3.

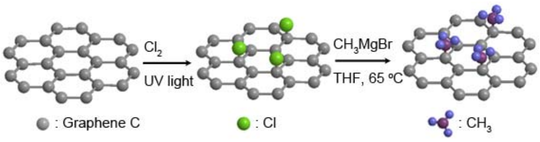

Figure 3. Schematic reaction steps for alkylation process. *Hossain et al. J. Phys. Chem. C 2014, 118, 22096.*

Chlorination of EG on SiC is done by exposing the sample to Cl_2 molecules under UV light. The CH_3-terminated graphene is achieved through refluxing the Cl-terminated graphene sample in CH_3MgBr solution in THF (tetrahydrofuran) at 65 °C. STM investigations reveal that the photo-chlorination and subsequent methylation reaction occur selectively on the monolayer graphene region. The covalently bonded Cl atoms are almost completely replaced by the CH_3 groups as revealed by the XPS data. The CH_3-terminated graphene is thermally more stable than that of the Cl-terminated surface. The changes in electronic states of graphene are also observed following chlorination and methylation.

To see if other halogenated surface can also undergo facile reaction with Grignard reagents, we have made a detailed investigation of halogenations of EG on SiC and it futher reactions with selected Grignard reagents. In this study we have focused on the reaction of fluorine, chlorine, bromine and iodine with the EG on SiC(0001). We have observed that irrespective of the layer thickness, EG grown on SiC can be fully fluorinated by exposing to XeF_2, as indicated by XPS spectra shown in figure 4.

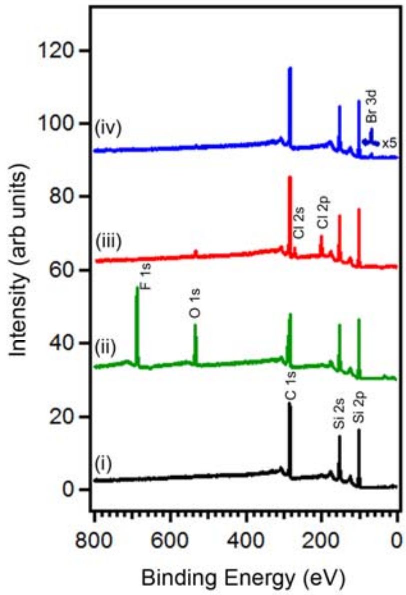

Figure 4. Typical wide range XPS spectra of (i) clean epitaxial graphene (EG) on SiC and EG exposed to (ii) XeF_2 vapor, (iii) Cl_2 and (iv) Br_2 under UV light. Ascription to the major peaks observed for different surfaces are indicated. hν = 1486 eV. *Hossain et al. New. J. Chem. 2016, 40, 1671.*

The XPS spectrum for clean EG on SiC [figure 4(i)] exhibit only C 1s, Si 2p and Si 1s peaks accompanied by the respective satellite features at higher binding energy side. The chemisorbed F is indicated by F 1s peak at ~ 687 eV. The high intensity F 1s peak indicates the effective fluorination of EG on SiC, which is further confirmed by Raman measurements. The chemisorbed F reaches to saturation coverage in ~16 h under XeF_2 vapor at room temperature. Compared to the F, the peak intensity is relatively small for Cl. As mentioned above, unlike fluorination, chlorination process undergoes very selectively onto the monolayer graphene regions. Very small concentration of bromine can be detected on EG on SiC following reaction with Br_2 under UV light. Iodine does not react with EG on SiC at room temperature.

While the chemisorbed Cl can be readily replaced by alkyl groups when treated with alkyl Grignard reagent, the fluorinated EG on SiC seems robust towards Grignard reagent. We also found that not only the alkyl group, the chlorinated EG on SiC can also be functionalized with fluoro substituted aryl groups by reaction with appropriate Grignard reagent.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　３　件）

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〔図書〕（計　０　件）

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○出願状況（計　０　件）

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況（計　０　件）

名称：
発明者：
権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕

ホームページ等

６．研究組織

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