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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Organic modification of graphene through binding of transient radical directly from reaction mixture

研究課題名（英文）Organic modification of graphene through binding of transient radical directly from reaction mixture

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研究成果の概要（和文）：当初計画した通り、SiC上のエピタキシャルグラフェン(EG)にフッ素置換アリールおよびクロロアルキルラジカルの化学結合に成功した。これら(フッ素置換アリール，クロロアルキルラジカル)は2種類の典型的な有機ハロゲン化物（ブロモペンタフルオロベンゼンおよびブロモジクロロメタンを用いたグリニャール試薬の合成中に一時的に生み出される。-SHで官能化された表面は、ナノ粒子および生体分子に対するより高い親和性のために、技術的により重要であることが知られている。実際、私はグラフェン上への金ナノ粒子の固定化を成功させ、次に単純な生体分子を用いてさらなる反応を成功させた。

研究成果の学術的意義や社会的意義
The present result for binding the active functional group on graphene followed by immobilization of gold-nanoparticles could be exploited in high performance electronic devices such as chemical and biosensors, composite materials, drug delivery, display, touch screens, and solar cells, etc.

研究成果の概要（英文）：The present research project was focused on exploring a new chemical approach for functionalization of graphene with different active end groups through direct binding of transient radical species formed in a reaction mixture. As planned initially, I have succeeded in the chemical binding of fluoro substituted aryl and chloro alkyl radical on EG on SiC, which are transiently generated during the preparation of Grignard reagent using two different kinds of typical organic halides (bromopentafluorobenzene, C_6F_5Br and bromodichloromethane, $CHCl_2Br$). In addition, I have performed and succeeded in functionalization, for the first time, of graphene with -SH group. As we know that -SH functionalized surface is technologically important because of its higher affinity toward nano-particles and bio-moelcules. Indeed, I succeeded in the immobilization of gold nanoparticles (AuNPs) on graphene followed by further reaction with some simple bio molecules as planned initially.

研究分野：表面化学

キーワード：グラフェン　表面　ナノ材料

１．研究開始当初の背景

Graphene, one carbon atom thick planar sheet of sp^2 carbon atoms arranged in a honeycomb lattice, is considered as the most promising materials for the next generation technologies. Because of its chemical and geometrical structures, graphene is chemically inert, electrically and thermally highly conductive, optically transparent, highly flexible (*Science* **2004**, *306*, 666; *Science* **2009**, *324*, 1530). Based on the unique and extreme material properties, graphene is expected to be utilized in various applications such as ultra-sensitive sensor, 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). However, graphene in its pristine form cannot be utilized in many of those anticipated applications. For example, chemical inertness of graphene towards molecules limits its application in various types of sensor such as bio-sensor, where the graphene based electrode needs to be interacted with desired bio molecules. Because of the zero band-gap, the pristine graphene is not appropriate for digital circuitry that comprises majority of integrated circuit. Hence, to make the graphene suitable for many of those next generation electronics and other applications, one must modify its properties. One of the prominent ways to tune the materials chemical and electronic properties is through modification of its surface by attachments of atoms or molecules. However, compared to enormous studies on graphene, relatively few studies have focused on the chemical reaction of graphene with organic molecules leading to the development of new graphene derivatives and its second step reaction (*J. Mat. Chem.* **2010**, *20*, 2277; Hossain et al. *J. Am. Chem. Soc.* **2010**, *132*, 15399 and references therein).

２．研究の目的

Organic modification of graphene is expected to lead to an entirely new class of graphene derivatives with vast tunability in chemical, electrical, and optical properties. Because of the bonding nature of sp^2 C atoms, only reactive radical species undergo covalent bonding when exposed to graphene. As noted above, the covalent organic modification approaches are limited to few selected molecules such as aryl-diazonium salt (Hossain et al. *J. Am. Chem. Soc.* **2010**, *132*, 15399 and references therein), benzoyl peroxide (*J. Am. Chem. Soc.* **2009**, *131*, 17099) and *di-tert*-butyl peroxide (*Small* **2013**, *9*, 1348). In addition, our recently developed two-step chlorination-alkylation reaction (Hossain et al. *J. Phys. Chem. C* **2014**, *118*, 22096) is also limited to the availability of stable Grignard reagent. In the case of benzoyl peroxide and *di-tert*-butyl peroxide, photochemical dissociation generates the gas phase CH_3 radical, whereas spontaneous reduction of aryl-diazonium salt generates the Ar (aryl) radical, which ultimately chemisorbed onto graphene surface. To date, there is no report to our knowledge, which deals with capturing the transient radical species formed during the muti-step reaction desiring a particular product such as Grignard reagent. The present research plan is focused on binding the transient radical species formed during the synthesis of different Grignard reagents from variety of alkyl/aryl halides and Mg as well as the synthesis of diazonium salts, which can be tailored to develop a graphene based biosensor.

３．研究の方法

EG on SiC was prepared by direct heating of a SiC sample (~ 8 mm x 20 mm) cut from a 6H-SiC(0001) wafer at 1350 ^{o}C for 5-7 cycles of 1 min in UHV (maximum pressure ~ 5.0 x 10^{-9} Torr) chamber.

For binding the radical species onto epitaxial graphene (EG) on SiC during the preparation of Grignard reagent from the bromopentaflurobenzene (C_6F_5Br) or bromodichlomethane ($CHCl_2Br$) and magnesium. A magnesium rod was cut into pieces (~1.00 g) and put into a three-necked bottomed flask. Then, a SiC sample was put on Mg turnings with graphene face up and added ~20 ml of tetrahydrofuran (THF) or diethyl ether. After 5 min Ar flow, ~5 ml of C_6F_5Br (or $CHCl_2Br$) was added into the flask. The reaction was allowed for ~2 h at 60 degree (room temperature in case of diethyl ether) keeping the Ar flow very slow (one bubble per 2 s). In case of C_6F_5Br, a slow reaction is discernible as the color of the reaction mixture gradually turned into brown around Mg turnings. In the case of $CHCl_2Br$, a vigorous reaction occurs, and the reaction mixture turned to brown in just few seconds. The reaction was done in Ar atmosphere. After the completion of the reaction, the SiC sample was taken out of the three-necked bottomed flask and rinsed with tetrahydrofuran (THF), methanol, acetonitrile and a mixture of methanol and acetic acid with ratio of 10:1 consecutively.

Surface modification of EG on SiC through diazotization procedure is done in borosilicate glass test tube to avoid any contact of the graphene surface with the wall of the reaction vessel. In a typical set up, a 15 ml test tube is loaded with 5 mmol of desired amine in 5 ml water followed by addition of 10 mmol of conc. HCl, and shaked well for completely dissolving the amine. The aqueous solutions of those amines are colourless. Then the EG on SiC sample is immerged vertically into the tube containing the clear amine solution. The tube is then cooled to below 5 ^{o}C in ice bath and slowly added the 5 mmol of solid $NaNO_2$. The solution immediately turned into orange red (for $HS\text{-}C_2H_4\text{-}NH_2$) and light blue (for $F_2C_6H_3\text{-}NH_2$) indicating the formation of diazonium salt. The *in-situ* reduction of freshly formed diazonium salt in solution is visualized by the bubble formation onto the EG on SiC substrate, which gradually lifts the SiC sample to float and re-sink after breaking the bubbles. After ~30 min reaction of the diazonium salt with the EG on SiC below 5 °C, almost 90% of diazonium salt solution is decanted from the tube and immediately added ultra-pure water to the tube containing SiC sample. After few cycles of decanting and dilution processes, the EG on SiC is taken out of the tube and immerged into pure water in a beaker, and gently rinsed the sample. Thus a microscopically clean EG on SiC is obtained.

For binding AuNPs on the –SH functionalized graphene, the EG/ SiC sample was directly immersed into the as-prepared AuNPs solution during the AuNP synthesis. The AuNPs were prepared by the reduction of 1 mM $HAuCl_4$ solution by sodium borohydrade ($NaBH_4$) (slow addition) at room temperature and ~ 80 °C.

The clean and chemically modified EG on SiC is characterized by x-ray photoelectron spectroscopy (XPS), Raman and scanning tunneling microscopy and spectroscopy (STM/STS).

４．研究成果

Organic functionalization through direct binding of transient radical from Grignard reaction mixture：

We succeeded in developing a common and versatile chemical method for organic functionalization of graphene using a well-known reaction mixture. The established reaction mechanism suggests that the reaction steps for preparation of Grignard reagent from organic halides and metallic magnesium in organic solvent involves the generation of a transient radical in the reaction mixture. Using two different kinds of typical organic halides (bromopentafluorobenzene, C_6F_5Br and bromodichloromethane, $CHCl_2Br$), we have found that such transient substituted aryl or alkyl radical generated during the preparation of Grignard reagent can be bind onto a graphene sample preloaded into the reaction vessel, though the corresponding aryl or alkyl bromide and Grignard reagent itself do not react with pristine graphene (*Chem. Commun. 2016, 52, 14380*). The modified surface was characterized by XPS, STM and Raman spectroscopy. Chemisorbed states of C_6F_5Br are confirmed by XPS spectra as shown in figure 1.

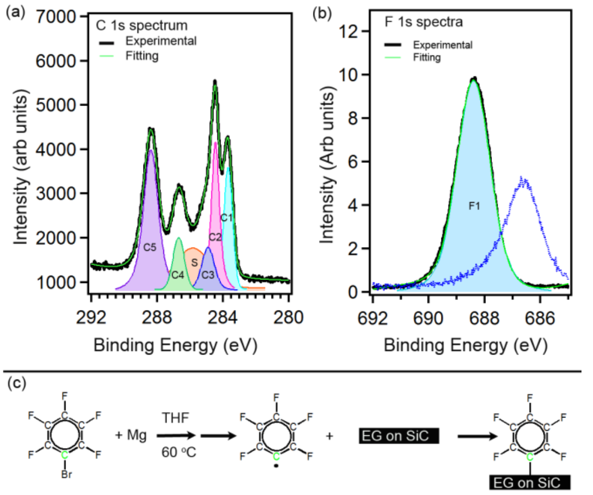

Figure 1. High-resolution (a) C 1s and (b) F 1s spectra of C_6F_5Br treated EG on SiC. Experimental results and computational Voigt fitting to the experimental results are shown. Different components resolve by the fitting are indicated. For comparison, F 1s peak for F atoms directly chemisorbed onto the EG on SiC is also included as dotted line in (b). (c) The schematic of chemical process involving the formation of C_6F_5radical and it's binding on EG on SiC (reproduced from *Chem. Commun*. **2016**, *52*, 14380)

Functionalization with reactive end group through amine diazotization:

One of the prominent and well-studied chemical methods for modification of graphene and other carbon materials is the reduction of diazonium compounds onto the materials surfaces (*J. Am. Chem. Soc.* **2010**, *132,* 15399.). Binding of molecules onto the material surface using diazonium salts is usually done through electrochemical process or simply dipping the sample into the diazonium salt solution in organic solvents (*J. Am. Chem. Soc.* **2010**, *132*, 15399; *J. Am. Chem. Soc.* **2009**, *131*, 1336; *J. Am. Chem. Soc.* **1992**, *114*, 5883; *Chem. Commun*. **2013**, *49*, 6289). Indeed, the surface reduction process of diazonium salt also involves the creation of radical species that ultimately bind onto the surface. In previous studies, either commercially available or freshly synthesized and purified diazonium salts are used. Usually diazonium salts are synthesized through well-known diazotization of primary amine. However, commercially available diazonium salts are limited because diazonium salts freshly synthesized specially from apliphatic amines are not always stable enough to isolate from the reaction mixture. Hence, in spite of number of studies attempting to functionalize graphene, the functionalization of well-defined pristine graphene with active functional

group (such as –SH and COOH) that can be tailored to bioactive surface through further modification could not achieved yet. Hence the graphene functionalized with active functional group holds the great promise for development of ultra-sensitive biosensors.
A large numbers of different amines are commercially available that do not result stable diazonium salts through diazotization reaction. In this study, we focus on the functionalization of epitaxial graphene (EG) on SiC with reactive end group such as –SH through *in-situ* reduction of amine derived diazonium salts instead of using pre-synthesized salts. Using two different molecules, 2-aminoethanetiol ($HS-C_2H_4-NH_2$) and 3,5-difluorophenylamine ($F_2C_6H_3-NH_2$), we found that graphene can be functionalized during diazotization of amines simply by dipping the graphene sample into the reaction mixture (*J. Phys. Chem. C* **2017**, *217*, 25223).

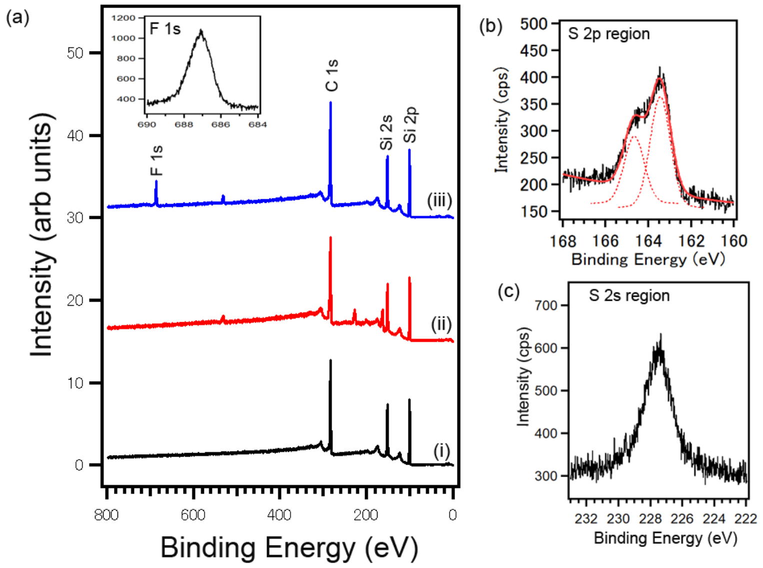

Figure 2. (a) Wide range XPS spectra of (i) clean EG on SiC, and EG on SiC after treatment with *in-situ* prepared diazonium salts of (ii) 2-aminoethanethiol ($HS-C_2H_4-NH_2$) and (iii) 3,5-difluoroaniline ($F_2C_6H_3-NH_2$). The zoomed-in F 1s region is shown in the inset. (b) High resolution XPS spectrum of S 2p region. Computational Voigt fitting to the experimental results are shown. (c) High-resolution XPS spectrum of S 2s region (reproduced from *J. Phys. Chem. C* **2017**, *217*, 25223).

It is well known that diazonium salts undergo spontaneous reduction on graphene surface (*J. Am. Chem. Soc.* **2010**, *132*, 15399). In present study, the *in-situ* prepared diazonium salts $HS-C_2H_4NN^+Cl^-$ and $F_2C_6H_3NN^+Cl^-$ are expected to undergo reduction on the preloaded EG on SiC resulting into $HS-C_2H_4$- and $F_2C_6H_3$- functionalized EG on SiC. The –SH functionalized graphene has high technological significance as it can be utilize for further attachment of metal cluster or bioactive molecules leading to the development of graphene based sensors. For chemical characterization of functionalized EG on SiC, detailed XPS investigation was done before and after the functionalization procedure. Figure 2a shows the wide range XPS spectra of (i) the clean EG on SiC and following the treatment with *in-situ* prepared diazonium salts, (ii) $HS-C_2H_4NN^+Cl^-$ and (iii) $F_2C_6H_3NN^+Cl^-$ in aqueous medium. For the clean EG on SiC [figure 2a(i)], only the C 1s, Si 2p and Si 2s peaks resulting from the epitaxial graphene and SiC substrate are observed (*J. Phys. Chem. C* **2014**, *118*, 22096; *New J. Chem.* **2016**, *40*, 1671; *Phys. Rev. B* **2008**, *77*, 155303.). The associated small peaks at higher binding energy side are due to the respective plasmon losses. Absence of any other peaks such as O 1s indicates that EG on SiC is free from any contamination.

In the XPS spectrum of $HS-C_2H_4NN^+Cl^-$ treated EG on SiC [figure 2a(ii)], the S 2p and S 2s peaks at ~164 and 227.5 eV are observed in addition to C 1s and Si 2p peaks (*Langmuir* **1999**, *15*, 6799; *ACS Nano* **2015**, *9*, 4193). High resolution XPS spectra of S 2p region reveals spin-orbit coupling for S 2p peak and single component for S 2s peak as shown in figures 2b and 2c. The S 2p components at 163.5 and 164.7 eV and the S 2s single peak at 227.5 eV suggest the presence of –SH group bonded to C atom as expected. Small O 1s peak (~530 eV), as seen in figure 2a(ii), always appears when EG on SiC is functionalized in liquid phase and exposed to air before the XPS measurement. We ascribe this small O 1s peak to the air oxidation of graphene C atoms next to bonding site of $HS-C_2H_4$ group. In the case of $F_2C_6H_3NN^+Cl^-$ treated surface [figure 2a(iii)], the F 1s peak at 687 eV is observed in addition to the C and Si related peaks, which indicates the presence of F containing functional group on graphene surface. It should be noted that no Na and Cl related peaks are observed which were present in the reaction mixture as Na^+ and Cl^- ions, i.e., no chemisorption of Na and Cl onto the graphene surface.

Covalent immobilization of gold nanoparticles on graphene: Following the –SH functionalization of graphene, AuNPs was immobilized on the graphene through the method described above (*J. Phys. Chem. C* **2019**, *123*, 3512). To analyze the size and distribution of the

AuNPs on the surface of –SH-functionalized EG, we carried out AFM measurements after the deposition of the AuNPs for 2 and 6 s at 80 °C. Figure 3 shows the AFM images of the –SH-functionalized EG/SiC sample (3a) after the AuNP deposition for 2 s (3b) and 6 s (3c). Figure 3d shows the magnified image of the selected area shown in Figure 3c. The clean –SH-functionalized surface showed clear surface terraces and steps. After immersing the –SH-functionalized EG/SiC sample in $HAuCl_4$ solution during the AuNP synthesis at 80 °C, small protrusions of different sizes were observed all over the surface. On the basis of the observation that the concentration of these small protrusions increased with an increase in the immersion duration and the XPS results (presence of only Au atoms on the surface), these small protrusions were ascribed to the AuNPs immobilized on the surface of the –SH-functionalized EG/SiC sample through Au-S covalent bonding. The immobilized AuNPs were found to be stable against ultrasonication with different solvents such as water, ethanol, methanol, and acetonitrile. However, they could be removed by aqua-regia. The high concentration of the AuNPs on the surface of the –SH-functionalized EG sample is in agreement with the XPS observation that the intensity of the S 2p peaks reduced drastically after the AuNP deposition.

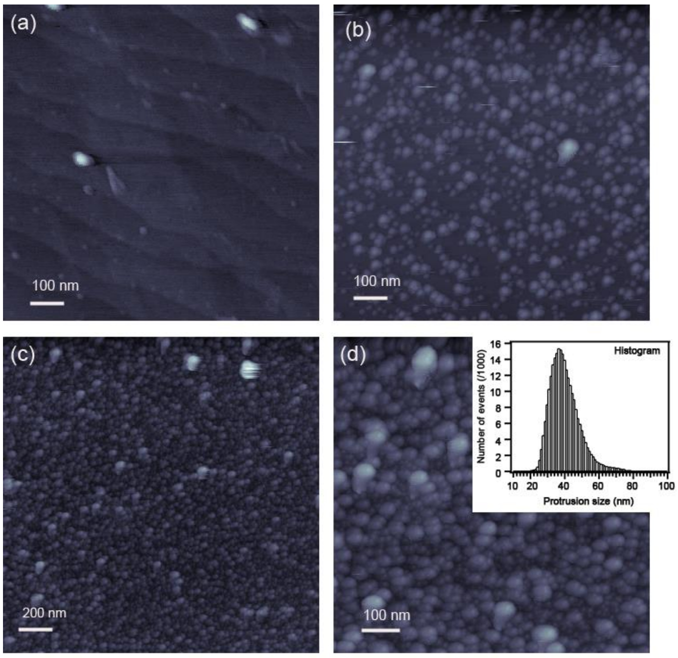

Figure 3. AFM images of (a) –SH-functionalized EG/SiC, (b) and (c) –SH-functionalized EG treated with the $HAuCl_4$ solution during the preparation of the AuNPs by $NaBH_4$ reduction for 2 and 6 s, respectively. (d) Zoomed-in image of the selected area shown in (c). The size distribution histogram for the AuNPs is shown as the inset of (d). (reproduced from *J. Phys. Chem. C* **2019**, *123,* 3512).

As can be seen from the AFM images, the size of the immobilized AuNPs was not uniform and seemed relatively larger than the standard size of AuNPs in the solution phase (5–30 nm). This can be attributed to the fact that unlike solution phase AuNPs, surface-deposited AuNPs are not stabilized by the surrounding borohydrate ions. Indeed, the –SH-functionalized EG surface treated with the AuNPs showed no XPS peaks corresponding to Na or B. The size of the AuNPs deposited on the EG surface was estimated to be 25–70 nm (*Chem. Rev.* **2012**, *112*, 2739.). The size distribution histogram of the AuNPs is shown as the inset of Figure 5d. The XPS spectra of the AuNPs-decorated surface suggest that these AuNPs were stable against air as the intensity of their O 1s peak was similar to that of the –SH-functionalized surface. Since such a covalent immobilization of AuNPs on graphene is considered to be desirable for graphene-based sensors, it was necessary to evaluate the reactivity of these AuNPs with other molecules of interest. We evaluated the reactivity of these immobilized AuNPs with hexanedithiol ($HSC_6H_{12}SH$) and pentachlorobenzenethiol ($C_{15}C_6SH$).

５．主な発表論文等

〔雑誌論文〕（計　3　件）

〔学会発表〕（計　7　件）

〔図書〕（計　0　件）

〔産業財産権〕
○出願状況（計　0　件）

名称：

発明者：
権利者：
種類：
番号：
出願年：
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：
国内外の別：

〔その他〕
ホームページ等

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