Supporting Information

Organic functionalization of epitaxial graphene on SiC through direct binding of transient radical from reaction mixture

M. Z. Hossain*, H. Yoko, M. A. M. Jusoh

International Research and Education Center for Element Science, Graduate School of Science and Engineering, Gunma University, Japan

SI-1. **Experimtantal details:** Figure S1 shows the experimental set-up 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.

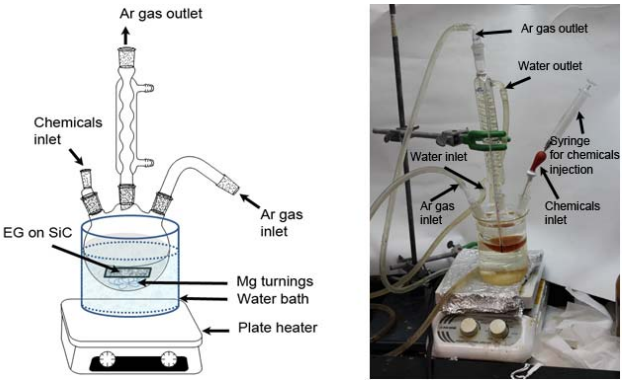

Figure S1. Schematic for experimental set-up for reaction of C_6F_5Br and $CHCl_2Br$ with EG on SiC in presence of Mg in THF solvent. Right panel is a photograph of the experimental setup.

The XPS data were obtained with an AXIS-NOVA XPS system using an AlKα x-ray source. For XPS measurements, the incident and emission angles were 60 and 0 degree to the surface normal. The analyzer pass energies for wide range and high-resolution measurements were set at 160 and 20 meV, respectively.

Ambient STM measurements were performed using a Nanosurf easyScan 2 STM system. The Pt-Ir tip is used for scanning. The clean and modified EG on SiC were mounted on the magnetic steel disc using silver paste, which was then

attached to the sample holder for STM measurement. In Nanosurf easyScan 2 STM system, bias was applied to the tip during STS and constant current STM measurement. STS data were obtained by sweeping the tip bias from negative to positive values with constant tip-surface distance defined by the set-point (i.e. V_{tip} = 0.5 V and I_{tunnel} = 1 nA). Each STS spectrum is the average of 128 measurements on 128 points. Raman measurements were performed by Nicolet Almega XR Raman with a 532 nm laser. Raman spectra were acquired with 100X objective, which results in spatial resolution down to 1 μm. Both STS and Raman measurements were acquired on microscopically clean area as seen in STM image shown in the article.

SI-2. **Reaction mechanism:** Reaction steps involving the preparation of Grignard reagent from C_6F_5Br and magnesium. The transient radical (shown as red) chemisorbs onto EG on SiC.

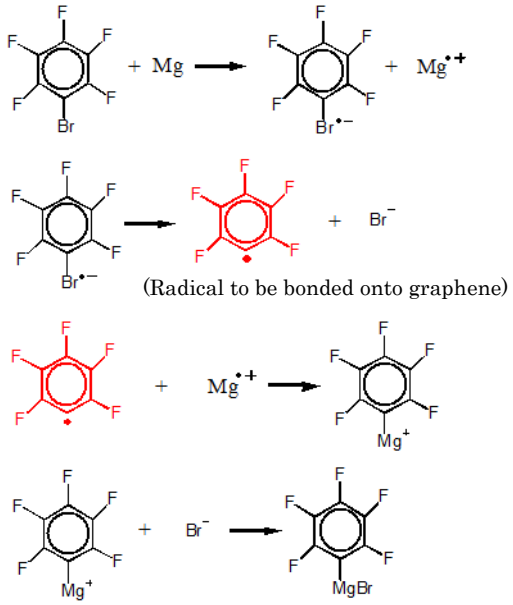

Figure S2. Reaction mechanism for formation of Grignard reagent by reaction between C_6F_5Br and Mg.

SI-3. **XPS data for controlled experiments:** Wide range and high resolution C 1s XPS spectra of clean EG on SiC and the same surface after treatment with as prepared Grignard reagent (C_6F_5MgBr) and bromopentafluorobenzene (C_6F_5Br) under similar condition but in absence of Mg turnings. The XPS spectra after the treatment with C_6F_5MgBr [figure S3a(ii)] and C_6F_5Br [figure S3a(iii)] are identical to that of clean EG on SiC [figure S3a(i)], i.e., no addition peak is observed. High-resolution C1s spectra

(figure S3b) are also identical. These controlled experiments clearly suggest that both C_6F_5MgBr and C_6F_5Br molecule alone do not undergo any reaction with EG on SiC.

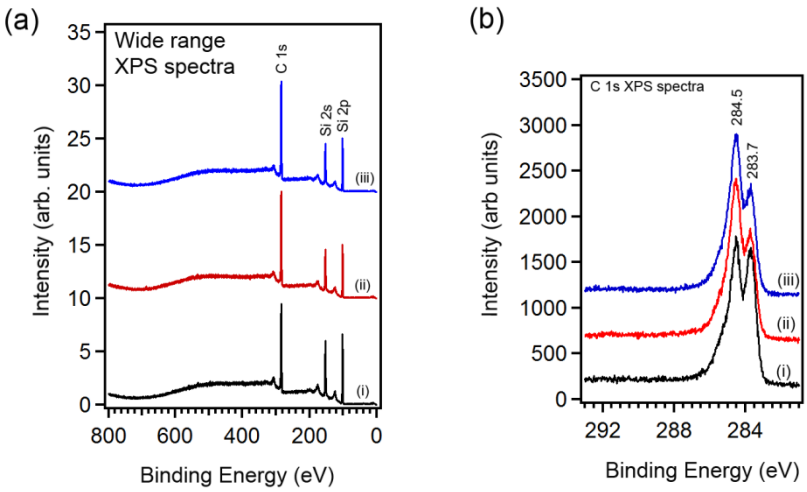

Figure S3. (a) Wide range and (b) high-resolution C 1s XPS spectra for (i) clean EG on SiC and clean EG on SiC after treatment with (ii) as prepared Grignard reagent (C_6F_5MgBr) and (iii) bromopentafluorobenzene (C_6F_5Br) under similar condition to that of functionalization procedures but in absence of Mg turnings. The C 1s, Si 2p and Si 2s peaks are indicated in (a). The wide background intensity (400 – 600 eV) arises from the instrumental trouble. The C 1s peaks for graphene and SiC substrate are located at 284.5 and 283.7 eV, respectively.

SI-4. **Large area STM data**: Large area ambient STM images of chemically modified and clean EG on SiC is shown in figure S4. Large terrace with atomically resolved surface steps ensure that cleanliness of the surfaces is similar, i.e., no major contamination is found after the reaction of EG on SiC with C_6F_5Br in presence of Mg in THF. Those irregular shaped white features are always observed in the case of EG on SiC, which are ascribed to

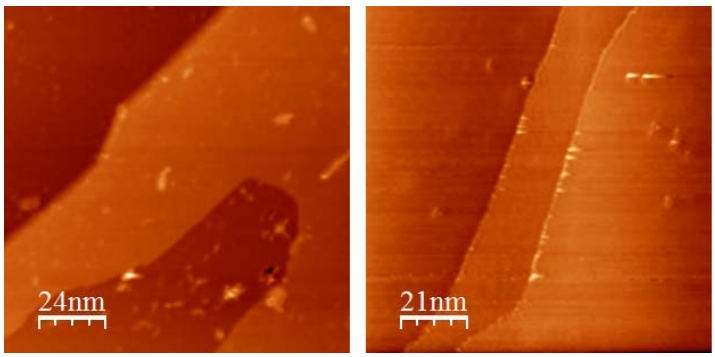

Figure S4. Large area STM image of chemically EG on SiC (left panel) and clean EG on SiC (right panel) in ambient condition. V_{tip} = 0.5 V and I_{tunnel} = 1 nA.

different surface and sub-surface graphitic carbon defects (*Nat. Chem.* **2009**, *1*, 206). Indeed those features does not results any additional peaks in XPS measurement (as indicated by XPS spectrum of clean EG on SiC).

SI-5. **Scanning tunneling spectroscopy (STS) I-V data**: STS I-V curves for clean and modified EG on SiC is shown in figure S5. Noticeable change between the curves for clean EG and after modification indicates a significant change in local electronic states near Fermi level following the treatment of EG on SiC with C_6F_5Br in presence of magnesium in THF.

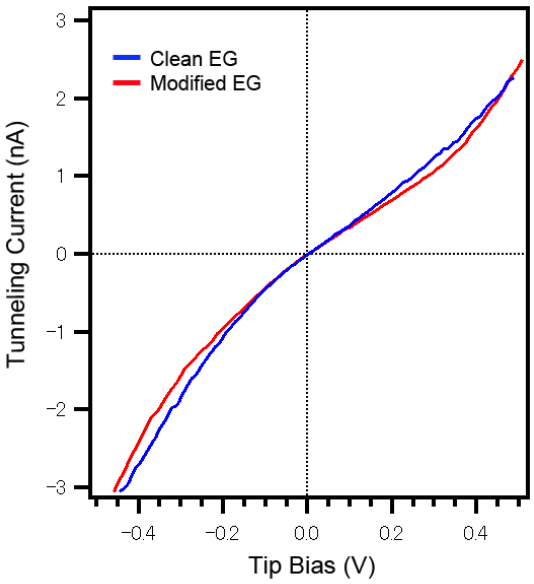

Figure S5. STS I-V curves for clean EG on SiC and after the treatment with C_6F_5Br in presence of magnesium in THF. The initial set point for STS I-V measurement is V_{tip} = 0.5 V and I_{tunnel} = 1 nA.