Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary information

Massive-Exfoliation of Magnetic Graphene from Acceptor–Type GIC by Long-Chain Alkyl Amine

Masaki Ujihara[a,]*, Mahmoud Mohamed Mahmoud Ahmed[a], Toyoko Imae[a,b]* and Yusuke Yamauchi[c]

[a]Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan
E-mail: masaki.ujihara@mail.ntust.edu.tw

[b]Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan
E-mail: imae@mail.ntust.edu.tw

[c]World Premier International Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

1. Time dependency of the expansion of $FeCl_3$-GIC

The Raman spectra of HA- and DA-treated products (Fig. s1) indicated that the HA could not accomplish the reaction within 6 h; the trace of GIC was detected as the G-band at 1606 cm^{-1}.

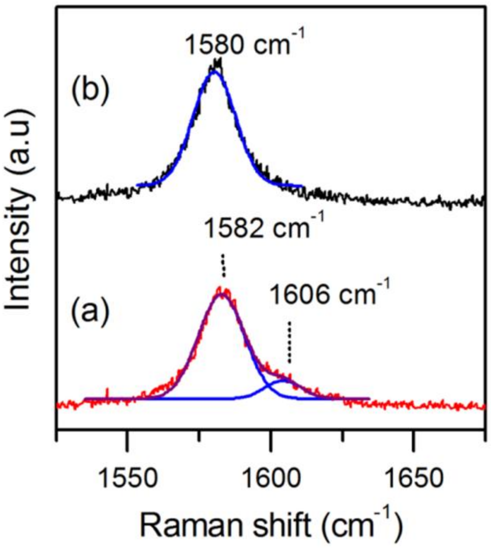

Fig. s1 Raman spectra of $FeCl_3$-GIC after treated with (a) HA and (b) DA. The blue curves are Gaussian fitting curves of band deconvolution.

For the DA-treated product, the expansion process was traced by Raman scattering (Fig s2A) and XRD (Fig. s2B). The Raman spectra indicated that the stage-2 GIC (G-band at 1614 cm^{-1}) appeared after 2 h, and the GIC of higher stage (less intercalation) ~ graphene structures were suggested. Although the reaction was almost finished after 4 h, the GIC structure was found as the broadening of G- band. XRD results showed that the $FeCl_3$-GIC had clear periodical structures, which were assigned to the (002), (004), and (006) planes. The amine treatment weakened the XRD patterns, that is, the layered structures were disordered as the result of expansion. The layer distance was slightly expanded in the early stage, which could be attributed to the penetration of amine molecules. The expansion was almost completed within 6 h.

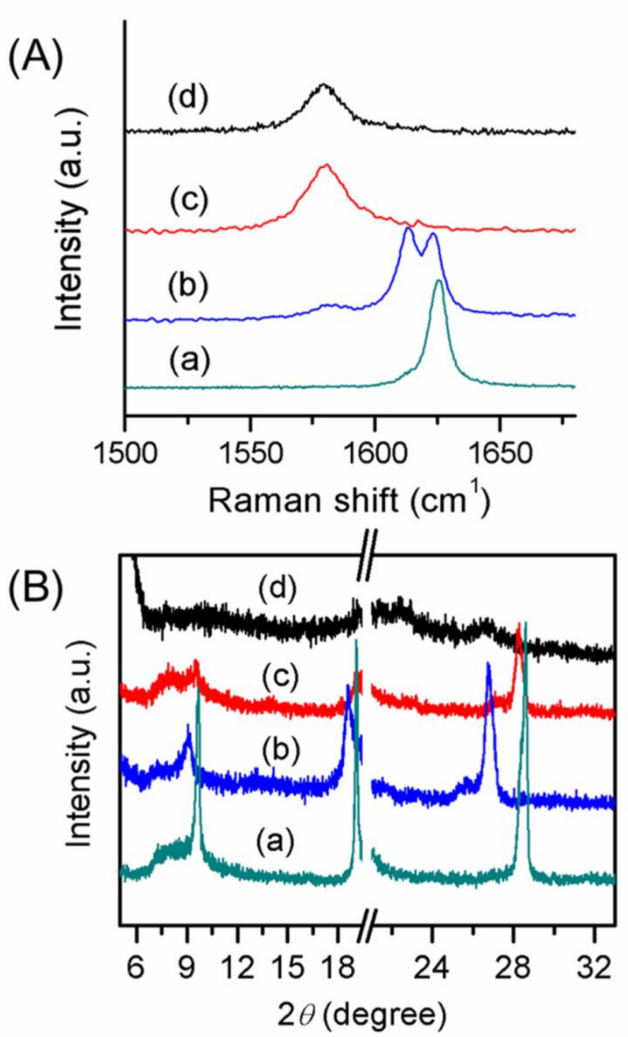

Fig. s2 (A) Raman spectra and (B) XRD analyses of (a) $FeCl_3$-GIC, and after treated with DA for (b) 2 h, (c) 4 h, and (d) 6 h at 90 °C.

The TGA analysis also revealed the process of penetration (Fig. s3A). The residual at 900 °C largely decreased after 2 h, and the weight loss at 400 °C increased. After 4 h, the weight loss at 400 °C became larger, and the residual was less than those at 2 h; however, the reaction was in the process. The reaction for 6 h indicated more weight loss at 400 °C and less residual than the reaction for 4 h. Even after 24 h, the TGA curve did not significantly changed from 6 h, that is, the reaction was already accomplished at 6 h. The reaction was also examined at stronger condition at 250 °C for 6 h, but the result was almost the same with that at 90 °C (Fig. s3B). The octadecylamine (ODA) could slightly decrease the residual but not radically improved.

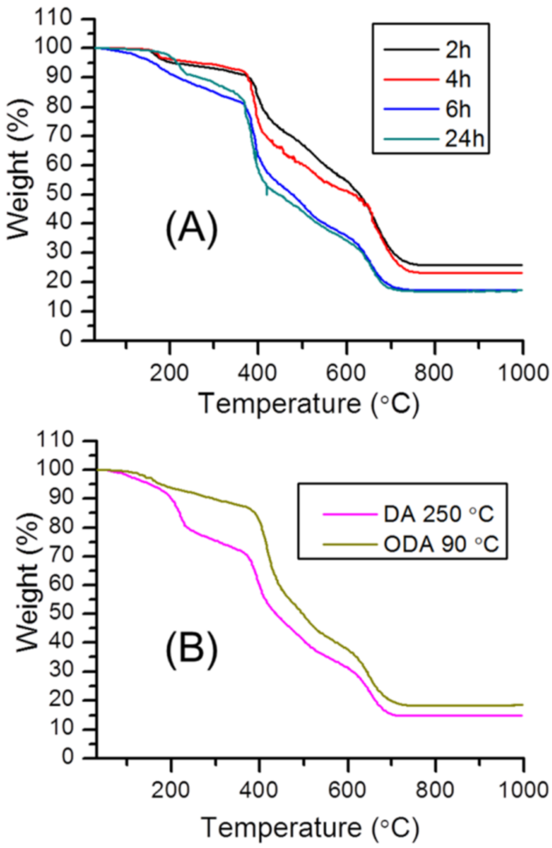

Fig. s3 TGA diagrams of (A) $FeCl_3$-GIC and products after treated with DA for 2 h, 4 h, 6 h, and 24 h at 90 °C, (B) products after treated for 6 h with DA at 250 °C and with ODA at 90 °C.

2. Characterization of the residual in the expansion process

The residual at high temperature was considered iron compounds, which were formed from $FeCl_3$. Then, the residual in the expansion process (the amine treatment) was characterized by X-ray photoelectron spectroscopy (XPS). After the amine treatment, the product was washed by pyridine to remove the remaining amine, and it was used for XPS analysis (Figure s4). The relative intensity of XPS signals of Cl and Fe (Cl/Fe) decreased to the half of the $FeCl_3$-GIC, and the signal of Cl was shifted from 198.5 eV (GIC) to 197.5 eV (after washing). Then, it was confirmed that the $FeCl_3$ was decomposed by the amine treatment, and the Cl^- ion was partially removed in the washing process. The magnetic property of residual suggested that the residual contained the magnetic iron compounds (typically, Fe_3O_4 and γ-Fe_2O_3), and the both were possible because the Fe^{2+} could be generated by the disproportionation reaction of $2FeCl_3$ toward $FeCl_2$ and $2Cl_2$. The XPS data showed that the main species resembled those in the GIC: The main signals at 710 and 711 eV corresponded to Fe^{3+}, and Fe^{2+} at ~709 eV was minor. Then, it was concluded that the magnetic property was due to the γ-Fe_2O_3, which was consistent with the XPS signals from oxygen (531 eV).

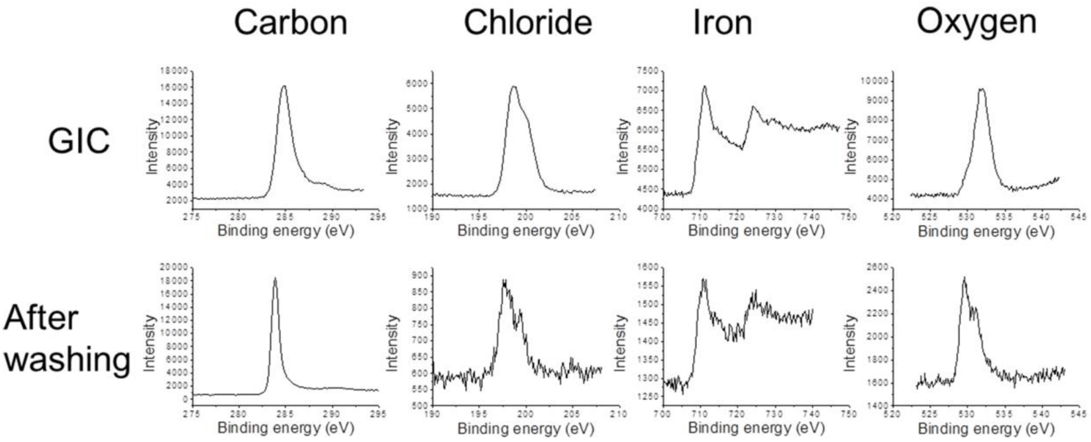

Fig. s4 XPS data of $FeCl_3$-GIC and the product after DA treatment and washing in pyridine.

The TGA analysis indicated that the iron compounds remained even after treatment with concentrated HNO_3 (Fig. s5). The product was first washed by the HCl/ethanol before HNO_3 treatment, and then it was suggested that the iron compounds were protected from the acid by the graphene layers.

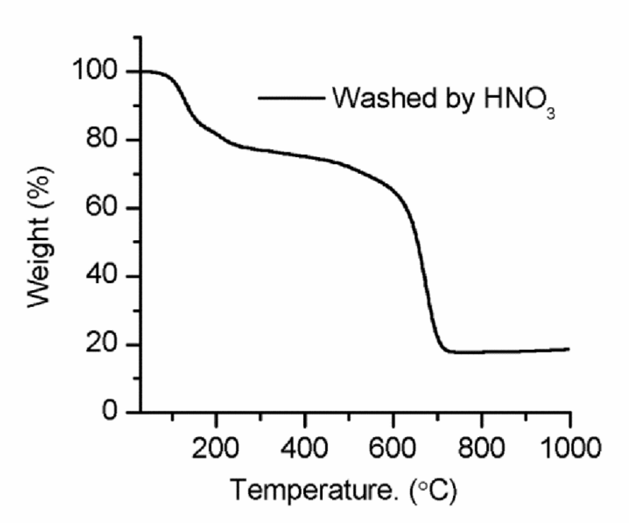

Fig. s5 TGA diagrams of the DA-treated product washed by HNO_3.

The residual was observed with a transmission electron microscope (TEM, Hitachi H-7000, accelerating voltage was 100 kV.) The product was sonicated in pyridine, and a drop of the dispersion was taken on a carbon-coated copper grid and air-dried. Then the specimen was used for the observation.

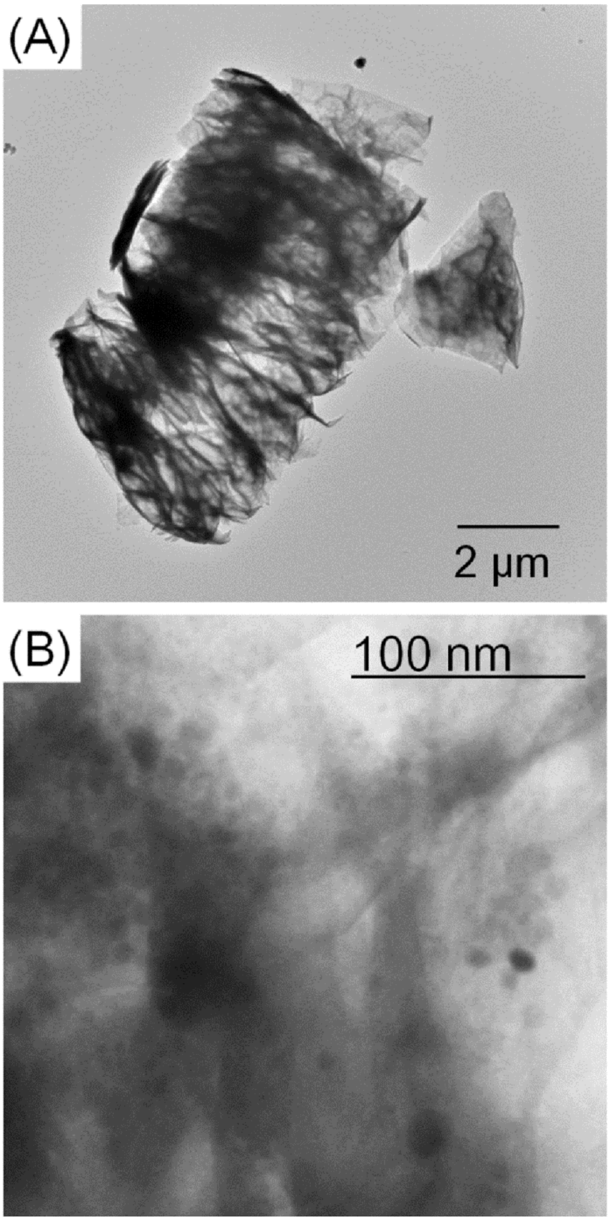

Fig. s6 TEM images of DA-treated GICs. (A) Low magnification and (B) high magnification.

After the expansion process, amine molecules remained in the product (see Fig. 4). To characterize the remaining amine, the SAXS data in Figure 3B was compared with the crystallographic data (reference 1). According to the crystallographic data, the crystal of DA-HCl salt has a dimension of 1.77385 nm in c-axis. Then, the double of the c-axis in

DA-HCl salt is ~3.55 nm. On the other hand, the observed d-space in the product was 3.46 nm. The difference between the d-space of 3.55 nm (2.49 °) and 3.46 nm (2.55 °) is recognizable in the SAXS chart (Fig. s7). Therefore, the remaining DA exists as an amine monomer but not as DA-HCl salt.

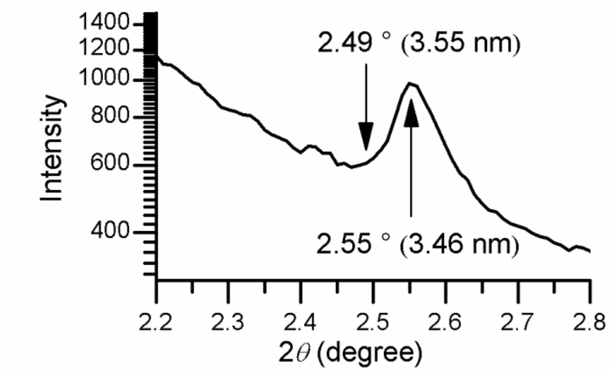

Fig. s7 SAXS analysis of the DA-treated product and DA-HCl salt. The arrow at 2.49 ° corresponds to the DA-HCl salt, and the arrow at 2.55 ° is for the product.

Reference

1: Yu-Xia Kong, You-Ying Di, Ya-Qian Zhang,Wei-Wei Yang and Zhi-Cheng Tan, *Thermochimica Acta*, 2009, **495**, 33–37.