

Supplementary Information

Tunable doping of graphene nanoribbon arrays by chemical functionalization

Pablo Solís-Fernández,^a Mark A. Bissett,^{a,†} Masaharu Tsuji^a and Hiroki Ago^{a,b,*}

^a*Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, Kasuga, Fukuoka 816-8580, Japan.*

^b*PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 243-0198, Japan.*

[†]*Current address: Faculty of Engineering and Physical Sciences, School of Chemistry, University of Manchester, Manchester M13 9PL, UK*

XPS C1s peak of the GNRs before and after functionalization:

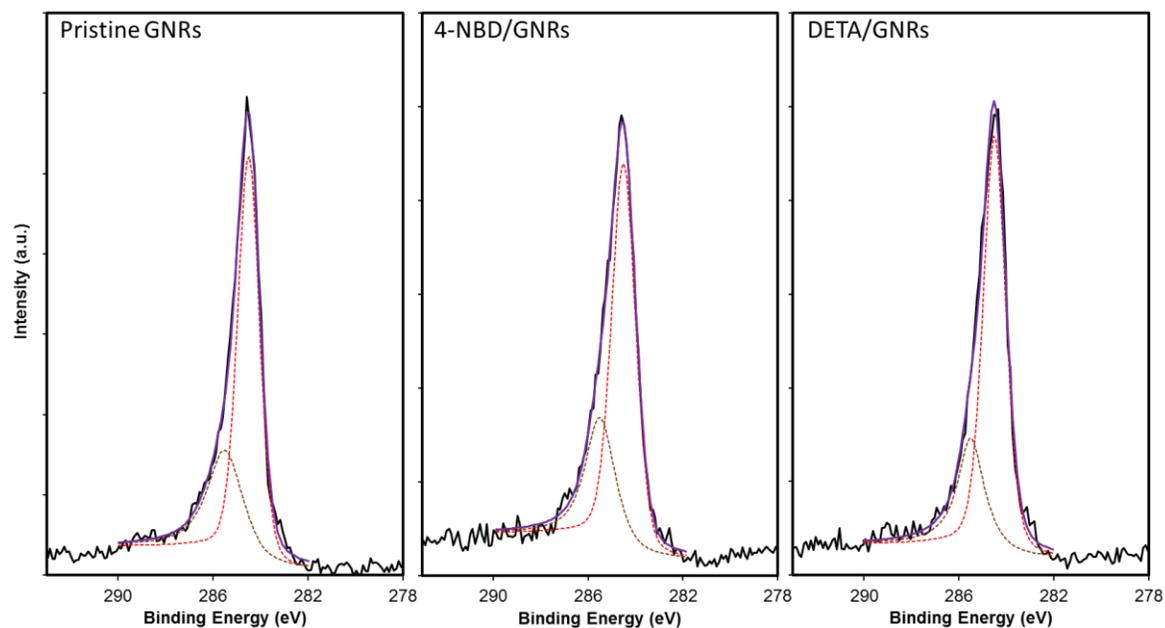


Fig. S1 XPS C1s peak of the pristine GNRs, and after functionalization with 4-NBD and DETA (continuous black curves). Peaks were fitted with two components, one corresponding with sp^2 bonded carbon at 284.eV (red dotted curves) and the second located at 285.5 eV (dotted brown curves) and assigned to sp^3 hybridized bonds, C-N bonds and contamination from exposure to ambient. The purple curves are the sum of the fitted components.

Effect of 4-NBD on residual PMMA on the sample:

After transfer of the GNRs, some PMMA residue can usually be observed on the borders of the samples, which remains even after prolonged rising in acetone (yellow features of Figure S1a). After just 2 seconds of functionalization with 4-NBD, optical microscopy show that all the residue visible on the edges completely disappear (Figure S1b). In the center of the samples, where data was collected for the present work, neither optical microscopy nor Raman show evidences of the presence of PMMA polymer residue after the transfer. Recently it was shown that residual polymer can be difficult to detect and to remove just by conventional washing in acetone.¹ Thus, the presence of a marginal quantity of PMMA in the samples cannot be excluded, which would explain both the initial doping observed by FET, and the sudden changes observed after short treatments with 4-NBD (see Figure 2e, f).

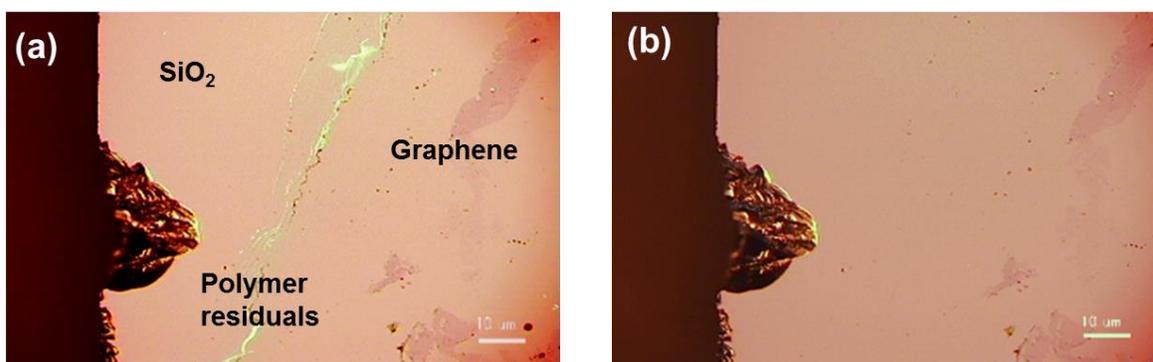


Fig. S2 Optical microscope images of the border of a SiO₂/Si piece with graphene (dark contrast areas) before (a) and after (b) 2 seconds of treatment with 4-NBD. PMMA residue (yellow features) are almost completely removed after the treatment in diazonium, while graphene remains unaltered.

Functionalization of the GNRs with 4-MBD

4-NBD was found to cause p-type doping in the GNRs due to the electron withdrawing nitro group. By changing the diazonium salt for one with an electron donating group in principle it should be possible to produce n-type (electron) doping.^{2,3} Thus, we tried to induce n-type doping to the GNRs by changing the diazonium compound to 4-methoxybenzenediazonium (4-MBD, Tokyo Chemical Industry, Japan). The methoxy group present in the 4-MBD (Fig. S2a) is known to be an electron donating group that is expected to induce n-type doping when it is covalently attached to the graphene, but given its higher redox potential, reaction rate of the 4-MBD is much lower than that of the 4-NBD (see Fig.

S2b for a comparison of the I_D/I_G ratio variation for a graphene sheet after functionalization with 4-NBD and 4-MBD).^{2,4}

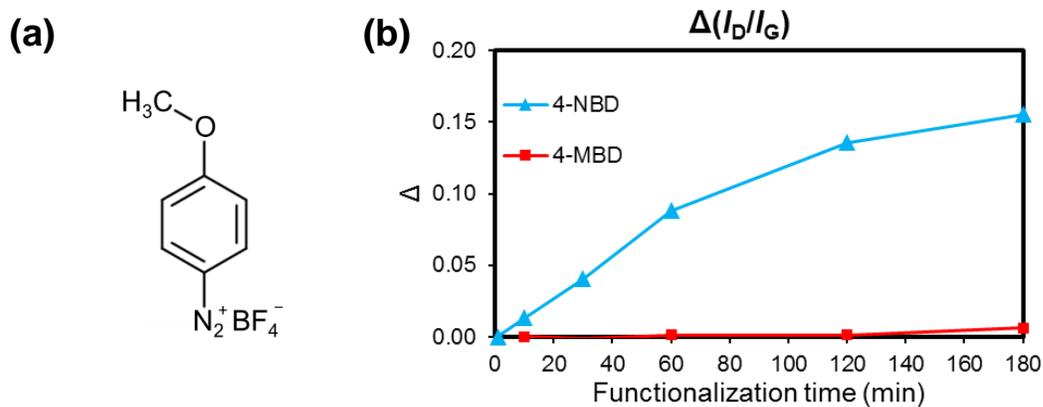


Fig. S3 (a) 4-MBD molecule. (b) Comparison of the variations in I_D/I_G for a single-layer graphene sheet after functionalization with 4-NBD (blue triangles) and 4-MBD (red squares).

Functionalization of the GNRs with 4-MBD showed some differences from the case of 4-NBD, with the I_D/I_G ratio undergoing a small increase with reaction time (Fig. S3a and S3c), and a lower effect on the doping level (as measured by the change in the ratio I_{2D}/I_G (Fig. S3b and S3d) and by the shifts of the G band (Fig. S3e) and of the 2D band (Fig. S3f)). In contrast to the case of the functionalization with 4-NBD, the small degree of doping now is not enough to account for the effects of attaching new functional groups, thus producing a net small increase of the I_D/I_G ratio. It seems that the doping effects of the 4-MBD saturates within the first 30 minutes of the treatment. In FET measurements, the CNP shifted towards higher values (Fig. S3g) indicating that the functionalization of the GNRs with 4-MBD induces p-type doping, instead of the expected n-doping. The p-type doping is also evidenced in the upshift produced in both the G and 2D bands in the Raman spectra. This unexpected p-type doping has been already reported to occur for different diazonium salts with electron donating radicals,⁵ and was attributed to a decrease in the electron density due the grafting process of the aryl groups.

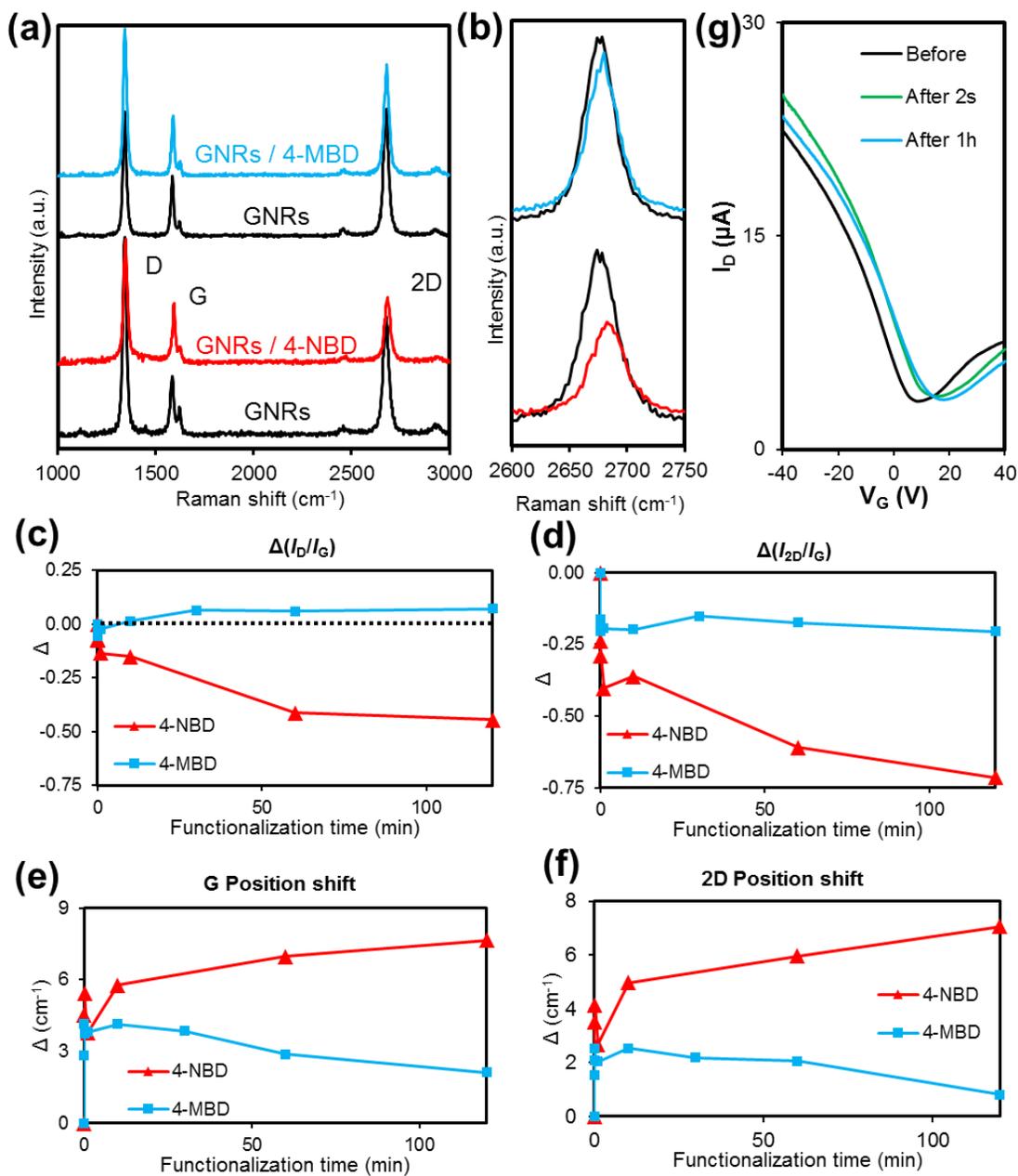


Fig. S4 (a, b) Raman spectra of GNRs both before (black) and after (red, blue) functionalization with 4-NBD (bottom) and 4-MBD (top). Spectra are normalized to the G band intensity and are vertically shifted for clarity. (a) General spectra, (b) 2D band region. Comparison of evolution of the variations of (c) I_D/I_G , (d) I_{2D}/I_G and the G (e) and 2D (f) band positions for GNRs during functionalization with 4-NBD (red triangles) and 4-MBD (blue squares). (g) Transfer characteristics of the GNRs before (black) and after functionalization in 4-MBD for 2s (green) and 1h (blue).

Functionalization of graphene with DETA

For the sake of comparison, functionalization of graphene sheets with DETA was also conducted. As evidenced by Raman, the effects of DETA on graphene were smaller than those produced in the GNRs under the same conditions (see Fig. S4). Decrease of the I_{2D}/I_G ratio was significantly smaller for the graphene (~ 0.2 and ~ 0.9 for graphene and GNRs respectively), and the same happened with the upshift of the G band ($\sim 1.5 \text{ cm}^{-1}$ and $\sim 2.9 \text{ cm}^{-1}$ for graphene and GNRs respectively). This indicates that the degree of functionalization attained for the GNRs is significantly higher than that of graphene. Pristine graphene showed a negligible D band, except for wrinkles produced during the transfer. After exposure to DETA, the relative intensity of the D band slightly decreased in those areas, as evidenced in the mapping of I_D/I_G (Fig. S4).

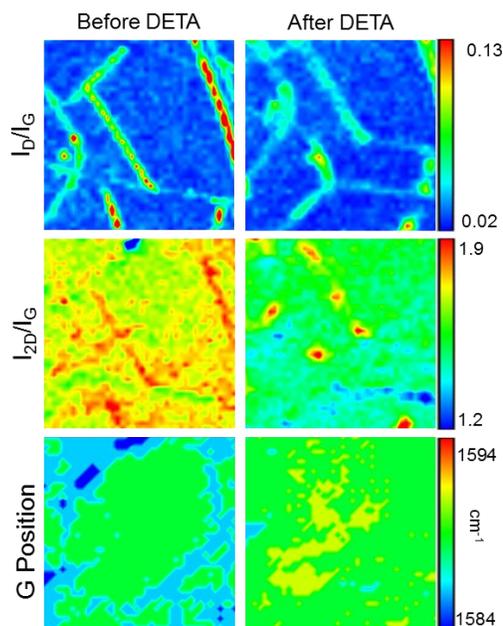


Fig. S5 Raman mappings of approximately the same area ($20 \times 20 \mu\text{m}^2$) of graphene before (left column) and after functionalization with DETA (right column). For direct comparison, vertical scales are same as those of figure 3b (except that of I_D/I_G mappings).

Effects of washing of the DETA functionalized GNRs

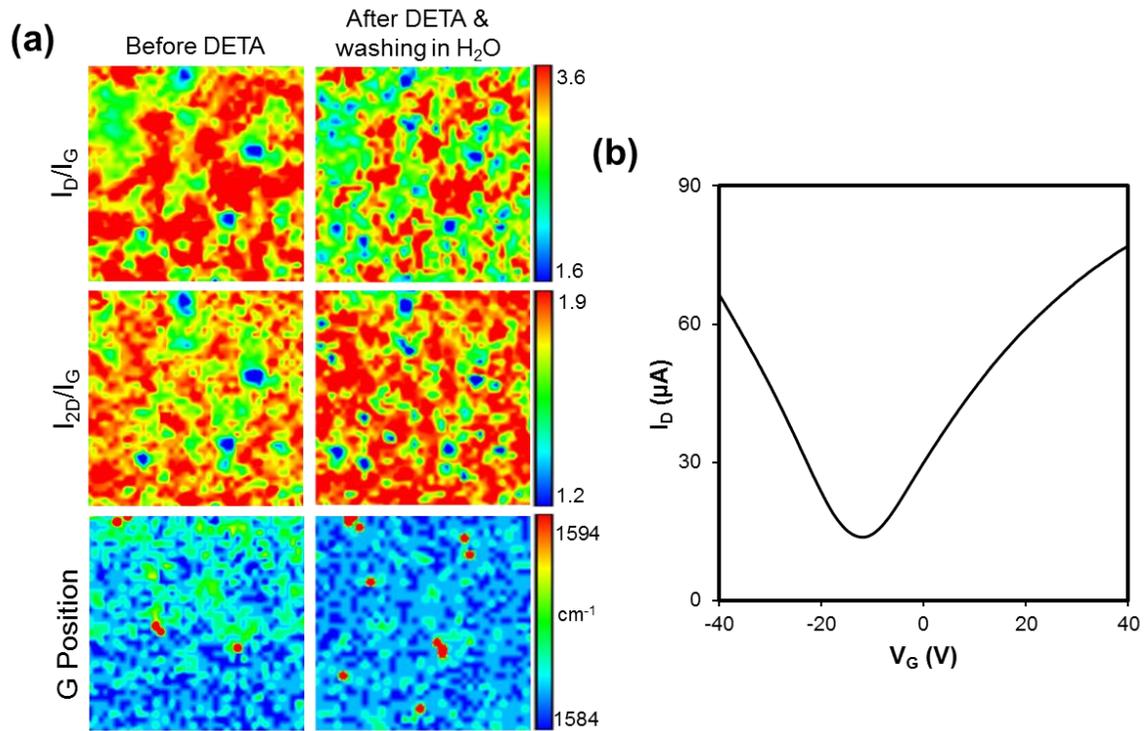


Fig. S6 (a) Raman mappings of the pristine GNRs (left) and after exposure to DETA and subsequent washing in H₂O and isopropanol (right). (b) FET transfer characteristics of GNRs after exposure to DETA and washing in H₂O and isopropanol.

References:

- 1 J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande and R. S. Ruoff, *Nano Lett.*, 2013, **13**, 1462.
- 2 M. A. Bissett, S. Konabe, S. Okada, M. Tsuji and H. Ago, *ACS Nano*, 2013, **7**, 10335.
- 3 Y.-J. Do, J.-H. Lee, H. Choi, J.-H. Han, C.-H. Chung, M.-G. Jeong, M. S. Strano and W.-J. Kim, *Chem. Mater.*, 2012, **24**, 4146.
- 4 G. L. C. Paulus, Q. H. Wang and M. S. Strano, *Acc. Chem. Res.*, 2013, **46**, 160.
- 5 E. Pembroke, G. Ruan, A. Sinitskii, D. A. Corley, Z. Yan, Z. Sun and J. M. Tour, *Nano Res.*, 2013, **6**, 138.