Atomic-scale Observations of Reduced Graphene Oxide Nanosheets Dispersed on HOPG Substrates

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Reduced graphene oxide (rGO) is a promising catalyst as an electrode for fuel cells [1] and as a chemical tool for a semiconductor surface [2, 3]. To obtain a high catalytic performance, the structure of an rGO sheet should be controlled on the atomic scale. With this motivation, we performed atomically resolved scanning tunneling microscopy (STM) observations on a single-layer rGO sheet dispersed on highly oriented pyrolytic graphite (HOPG). The rGO sheets were obtained via the chemical reduction of graphene oxide (GO) sheets using hydrazine [2].

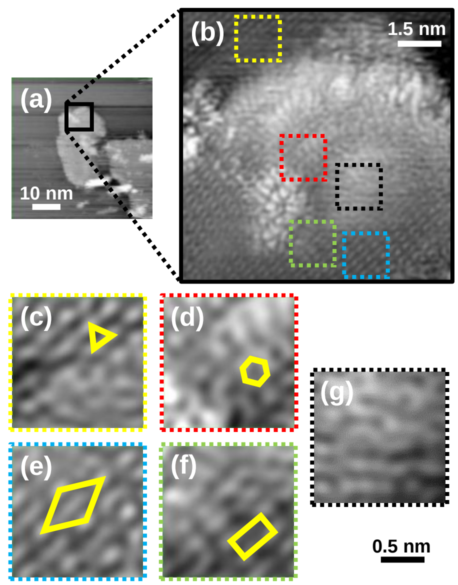

Figure 1. Atomically resolved STM images of a single rGO sheet on HOPG.

The observed rGO sheet is shown in Figs. 1(a) and 1(b). The triangle in Fig. 1(c), in which the distance between neighboring bright spots is approximately 0.25 nm, represents the HOPG substrate. The results in Figure 1(c) confirmed that the probe has atomic-scale resolution. More importantly, the STM images in Figs. 1(d)-1(g) reveal four distinct local structures on the rGO sheet. The first is a hexagonal pattern, as shown in Fig. 1(d), which indicates the single layer of the graphene network. The second is a $\sqrt{3} \times \sqrt{3}$ superlattice, as shown in Fig. 1(e), which has been observed near the edges of a graphene sheet [4, 5]. The third feature is a rectangular superstructure with dimensions of ~ 0.25×0.44 nm, as presented in Fig. 1(f); this structure is indicative of domains in the GO that were not reduced by hydrazine during the reduction process [6]. We also found localized regions within which dots are distributed irregularly. One such example is shown in Fig. 1(g), which likely represents defect sites of the rGO sheet. Furthermore, the bias-dependent STM images showed that both edge and defect sites of the rGO had high local density of states around the Fermi level.

[1] L. Lai, J. R. Potts, D. Zhan, L. Wang, C. K. Poh, C. Tang, et al., Energy Environ. Sci. **5**, 7936 (2012).
[2] **S. Li**, K. Nakade, T. Hirano, K. Kawai, K. Arima, Mat. Sci. Semicon. Proc. **87**, 32 (2018).
[3] T. Hirano, K. Nakade, **S. Li**, K. Kawai, K. Arima, Carbon **127**, 681 (2018).
[4] Y. Kobayashi, K. Fukui, T. Enoki, K. Kusakabe, Y. Kaburagi, Phys. Rev. B **71**, 193406 (2005).
[5] P. L. Giunta, S. P. Kelty, J. Chem. Phys. **114**, 1807 (2001).
[6] D. Pandey, R. Reifenberger, R. Piner, Surf. Sci. **602**, 1607 (2008).

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Supplementary Information

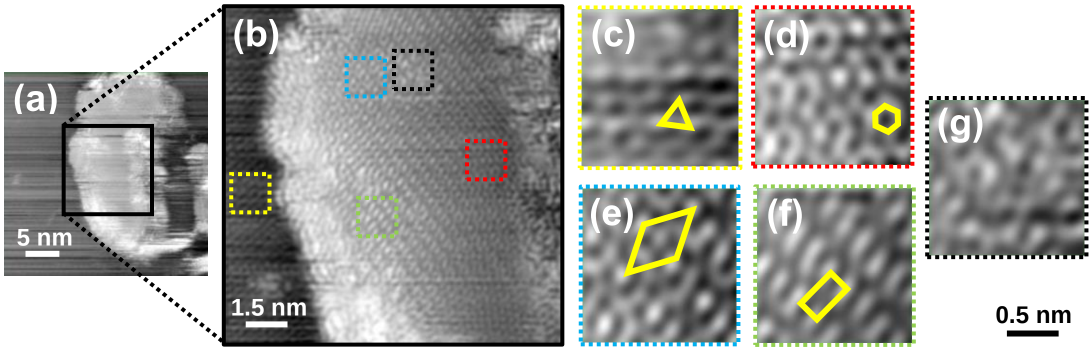

Figure S1. Other STM images showing the four distinct features of the rGO sheet on HOPG. (a) The rGO sheet on HOPG. (b) An enlarged area of (a). (c) Triangular pattern of HOPG. (d) Hexagonal pattern of rGO. (e) $\sqrt{3} \times \sqrt{3}$ superlattice of rGO. (f) Rectangular superstructure of rGO. (g) Defective area of rGO.

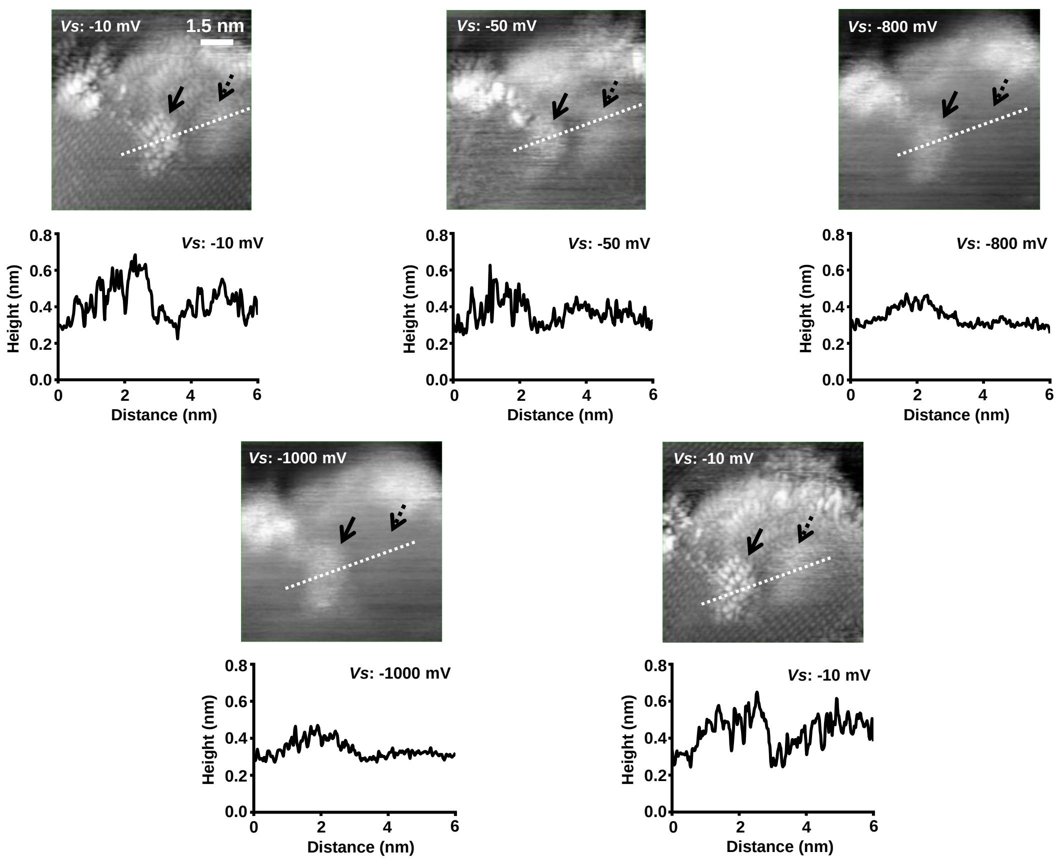

Figure S2. STM images of a defective area (marked by arrows) of an rGO sheet. Images were taken with different sample biases from -10 mV to -1000 mV. One image was taken with a -10 mV sample bias again. The cross-sectional profiles corresponding to the white dotted lines are shown directly below each STM image.