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Change in the Morphology of the Terrace Edges on Graphite Surfaces by Electrochemical Reduction

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We found that graphite surfaces can be etched by electrochemical reduction in sulfuric acid. Terraces with straight edges crossing with 60°-multiple angles were found on surfaces by AFM observation. It suggests that crystallographic edges can be formed at room temperature in a controlled manner. Layer-by-layer etching of graphene sheets was possible by tuning the etching condition.

After the success in separation of single layer graphene,[1] graphene-related materials have been studied extensively. Some of the characteristic properties of graphene come from its unique edge states.[2] In order to make use of the full-potential of graphene-related materials in electronic devices, edge-defined processing is extremely important. There are two types of edges with low crystallographic indices, i.e., an armchair edge and a zigzag edge. Electronic degeneracy is expected only in zigzag edges, which will lead to unique properties such as characteristic magnetism, ferromagnetism, and halfmetallicity,[3–6] while armchair edges will show normal electronic dispersion. Thus chemical or physical processes controlling the edge structure as designed are awaited but have not been established so far.

It is predicted that armchair edges are thermodynamically stable.[7] Zigzag edges are only obtained by etching in reductive environment (H_2) with Fe clusters at 900 °C.[8,9] This technique has a great advantage in making nanoribbons with well-defined edges, but it requires hydrogen environment and high temperature.

In this letter, we explored the possibility of reductive etching in electrochemical environment for the edge-defined processing of graphene. If electrochemical etching is feasible, it does not require high temperature or dangerous hydrogen environment. Although it is reported that AFM oxidization in tip adsorbed water can be used for patterning of graphene,[10] formed edges were not characterized.

It has long been suggested in Pourbaix diagram that the following reaction is possible in aqueous solution.[11]

$$C + 4H^+ + 4e^- \rightarrow CH_4 \qquad (1)$$

It is expected from this reaction that carbon solids can be etched by electrochemical reduction, but this possibility has not been applied to graphene or graphite.

We used highly oriented pyrolytic graphite (HOPG) for the attempt of electrochemical reduction. The specimen size was typically 8 mm × 3 mm × 2 mm, and the surface was cleaved in air by adhesive tape. The HOPG specimen was used as a working electrode, and a Pt wire and Ag/AgCl were used as a counter and a reference electrode, respectively. These electrodes were immersed in a 10 vol % aqueous H_2SO_4 solution for cyclic voltammetry using an HSV-100 (Hokuto Denko) voltammeter. For the reductive etching experiments, concd H_2SO_4 was used in addition to the 10 vol % H_2SO_4. Surface morphologies before and after electrochemical treatment were inspected by AFM (SII SPI 3800N).

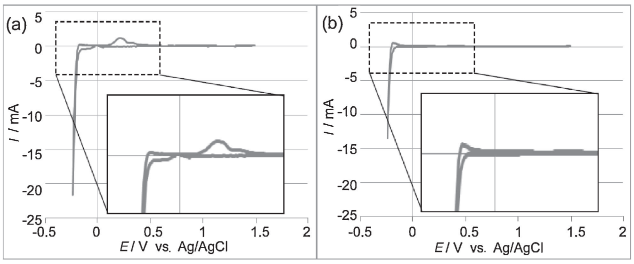

Figure 1. Cyclic voltammogram of HOPG with Pt wire (a) and Pt wire only (b) in 10 vol % H_2SO_4.

Figure 1a shows cyclic voltammetry (CV) using HOPG working electrode in 10 vol % H_2SO_4. CV without HOPG (Pt wire only) is shown in Figure 1b for comparison. When the potential (E) was higher than ca. +1.8 V vs. Ag/AgCl, HOPG turned black and swelled by intercalation of H_2SO_4-derived species and oxidization as reported in ref 12. Between +1.5 and 0 V vs. Ag/AgCl, no drastic change was observed visually. When the potential was lower than −0.11 V vs. Ag/AgCl, the current was drastically increased and hydrogen bubbles were observed. As shown in the inset of Figure 1, a shoulder was observed at −0.1 V vs. Ag/AgCl when the potential was lowered, and a hump was observed at around +0.2 V vs. Ag/AgCl when the potential was increased. The nature of these small structures is unknown because no measurements have been reported in the reduction side of graphite to the authors' knowledge. We speculate that the shoulder and the hump correspond to the reductive etching of carbon, or protonation of edges, and deprotonation of edge hydrogen, respectively. We note that the former potential is similar to the value suggested from Pourbaix diagram (−0.082 V vs. Ag/AgCl).

Figure 2 shows the AFM images before (a) and after (b) electrochemical processing. We applied −0.20 V vs. Ag/AgCl to HOPG working electrode in 10 vol % H_2SO_4 for 20 min. The images were taken from the same sample. We obtained many images in a wide area of the sample at almost identical positions, and we have confirmed that the images shown in Figure 2 are representative ones before and after the electrochemical reduction. HOPG surfaces after cleavage show no characteristic morphology (Figure 2a), and the height difference in 10 µm × 10 µm area was about 30 nm.

On the other hand, terraces with straight edges were observed after the reduction (Figure 2b). The terrace height was 70 nm at the maximum. The terrace edges cross each other with characteristic angles that are multiples of 60°. Observation of these characteristic angles strongly suggests that terrace edges correspond to low-

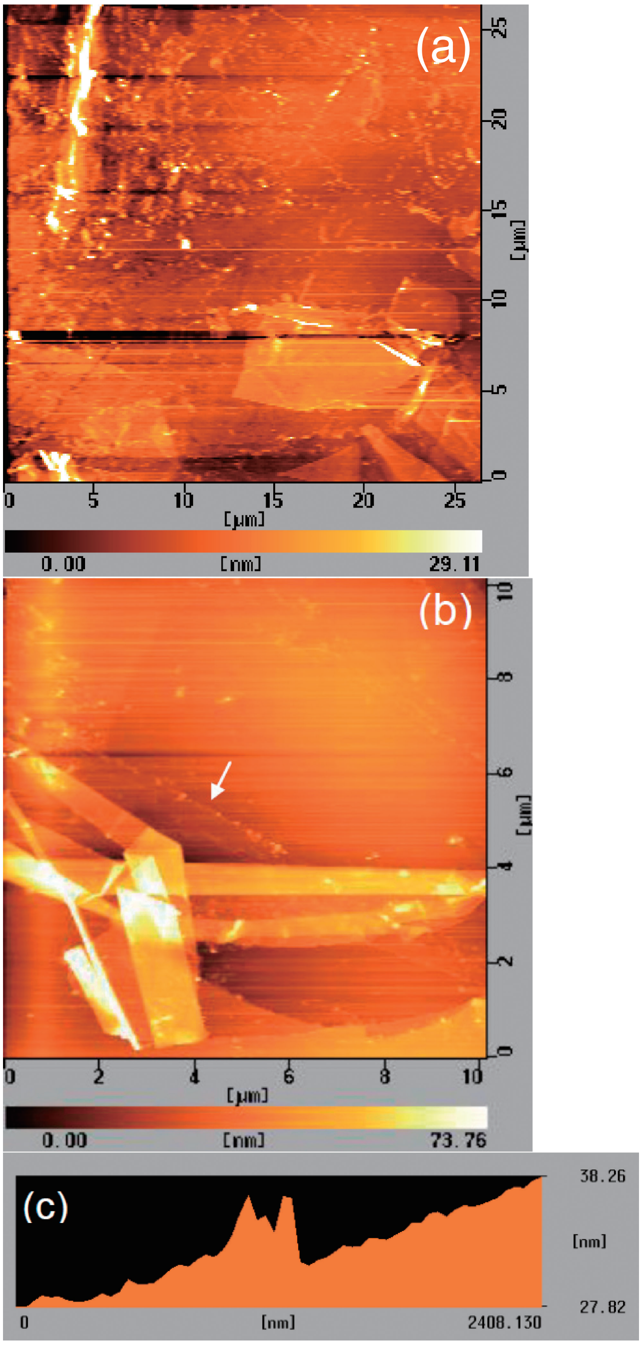

Figure 2. AFM images of (a) cleaved HOPG and (b) HOPG after electrochemical reductive etching. (c) is the cross section plot of the line protrusion indicated by the arrow in (b).

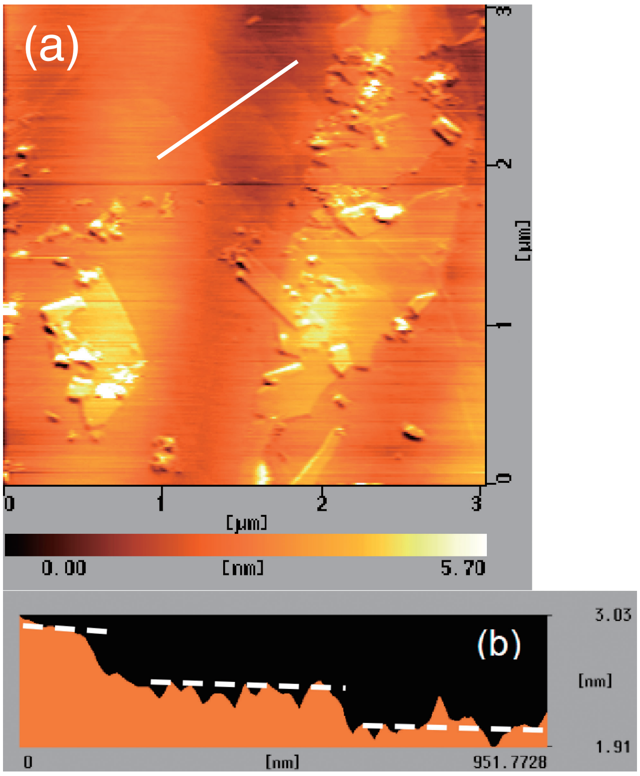

Figure 3. (a) AFM image of HOPG after electrochemical reductive etching in concd H_2SO_4. (b) Cross-sectional view along the line in Figure 3a. White dotted lines are guide to eyes indicating layers.

index crystallographic orientation. A line protrusion was observed in Figure 2b, which is marked with an arrow. This is probably the rolling of graphene sheets during the etching.

Next we examined the effect of using concentrated H_2SO_4 as the electrolyte. By electrochemical reduction under the same conditions as Figure 2b, similar characteristic morphology was observed (Figure 3a). It is noted that the height difference is far smaller (5.7 nm) than 10 vol % H_2SO_4 (74 nm). The cross-sectional view shown in Figure 3b indicates the existence of monographene steps (0.335 nm). It shows that the reaction speed can be controlled by the concentration, which is beneficial to the practical processing of graphene and related materials.

In conclusion, we found that surface morphology of HOPG is drastically changed by electrochemical reduction in H_2SO_4. Observation of terraces with straight edges and line protrusion strongly suggests that crystallographic low-index edges were prepared by this technique. Single graphene steps were observed by the electrochemical reductive etching in concd H_2SO_4.

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