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Formation of graphite zigzag edges by cathodic electrochemical etching in acidic solution

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Abstract

We examined the edge structure of graphite formed by a cathodic electrochemical reaction in acid solutions associated with water electrolysis. Pole figures of the x-ray diffraction show that the edge orientation is parallel to the zigzag edge direction on a macroscopic scale. The polarization dependence of the G-band and D-band of the Raman spectra is consistent with the zigzag edge formation on a microscopic scale. It was found that the etched carbon atoms are converted to CH_4 in the evolving gas and molecular species in the solution.

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1. Introduction

Edge structures of graphene and graphitic carbons are very important for their electronic structures and catalytic activities. The armchair edges are thermodynamically stable in pristine graphene[1], but do not have the useful properties of the zigzag edges[2]. Therefore, the research efforts were focused on the formation of zigzag edges. Various methods have been reported to control the edge structures; i.e., catalytic hydrogenation using Fe[3] or SiO_x[4] nanoparticles, heavy dose of electron beams under TEM observation[5], highly controlled CVD on Cu foil [6], hydrogen plasma irradiation[7], high temperature oxidation in the presence of ammonia[8] and controlled etching by Ar/H_2 gas[9]. They have a drawback of requiring high temperatures and/or harsh environment, thus an alternative method is desired.

We noted that these procedures for the zigzag edge formation are all involved with the reduction of carbon. It is expected that carbon can be etched in a cathode reaction based on the Pourvaix diagram[10].

$C + 4H^+ + 4e^- \rightarrow CH_4 \qquad E_0 = 0.132 + 0.0591pH$ V vs. NHE.

We reported the electrochemical etching of graphite under reducing conditions in aqueous acid solutions. AFM images indicated the appearance of straight lines crossing in the multiples of 60^o, which suggests the formation of low index crystallographic edges[11]. In this paper, we report the experimental determination of the edge orientation obtained by the electrochemical reduction. The carbon species in the evolving gas and

the solutions were also analyzed by gas chromatography and combustion analysis, respectively.

2. Experiment

We conducted the electrolysis of an acidic water solution using a graphite crystal as the cathode, Pt wire as the anode, and Ag/AgCl as the reference electrode. The sample was a Kish graphite (Covalent Materials, grade A, fused single crystals with a ~500 μm size, no Fe 2p signal was detected by X-ray photoelectron spectroscopy) or a natural graphite (Nippon Graphite Industries, a ~ 300 μm single crystal), both of which were thin plates with irregular shapes. Their crystal structure was the 2H-polytype as measured by x-ray diffraction. The solution was a 10 weight % H_2SO_4 aqueous solution. We applied -0.3 V vs Ag/AgCl (~-0.1V vs NHE) to the graphite sample. Gas was evolving from both the anode and the cathode. We observed a macroscopic change in the morphology of the surface and the periphery. The electrolysis was continued for 8 ~ 16 h. We measured the x-ray diffraction pole figures using a Brucker D8 diffractometer with a two-dimensional detector to determine the relationship between the crystallographic axes and the macroscopic edges. We used polarized Raman spectroscopy (Renishaw inVia, 532 nm excitation) to observe the microscopic orientation of the edges of the etched natural graphite, which was placed on a silicon wafer before and after the etching. We collected the gas evolved from the anode and analyzed it by calibrated gas chromatography (Shimadzu GC-8A, FID detection, 3 meters-long Porapak-Q column operated at 80 ^{o}C).

We analyzed the solution after the electrolysis experiment using a carbon analyzer (Horiba EMIA-110), which measures the infrared absorption of CO_2 gas formed by the combustion of the solution. In order to remove any possible graphitic powders formed during the etching, we ultra-centrifuged the solution at 3500 rpm for 15 min and used the supernatant liquid containing no particles optically visible by microscopy.

3. Results and Discussion

Figure 1 shows the laser optical microscopic images (Keyence VK-8710) taken before and after the electrolysis. The crystal was dry deposited on a silicon wafer and the electric contact for the electrolysis was made by pressing a coated Pt needle on a point of the surface which is not shown in the image. Clear straight edges are visible after the etching (b), whereas an irregular roughness was observed before the etching (a).

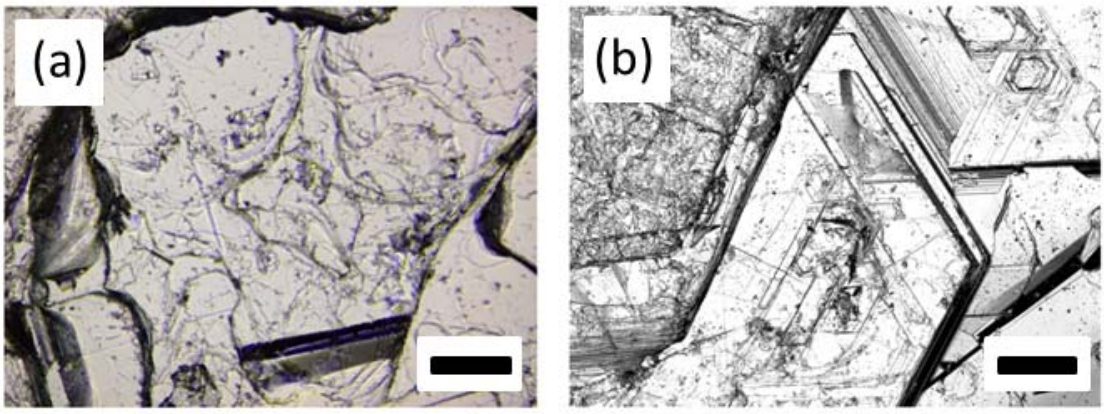

Fig. 1: Laser optical microscope images of a Kish graphite before (a) and after (b) the electrochemical cathodic etching. Scale bar is 200 μm.

In order to analyze the edge orientation with respect to the crystal axes, we measured the X-ray diffraction pole figure. Since the Kish graphite is fused polycrystals as seen from the edge orientation in Fig. 1(b), we chose large domains with hexagonally aligned edges and etch pits from the Kish graphite pieces after the etching. We cut out the domains using a scalpel under a microscope and obtained samples with hexagonal edges formed by the electrochemical etching. We glued the sample on a flat quartz glass and placed it on the goniometer stage of the 4-axis diffractometer. The notation of the instrument angles is shown in Fig. 2(a). The in-plane rotation angle ϕ was defined so that the sample orientation in Fig. 2(b) corresponds to $\phi = 0^{o}$. The pole figure was taken with $\omega = 22.5^{o}$ and the diffraction spot appeared at $\chi \simeq 33^{o}$, $2\theta \simeq 50^{o}$, and $\phi \simeq 30^{o} + 60^{o}\, n$ with integer n (Fig.2(c)).

The coordinate of the reciprocal lattice point ${}^{t}(r_x, r_y, r_z)$ in the axis system fixed with the sample rotation stage (ϕ axis system in Ref [12]) corresponding to the diffraction detected at 2θ, ω, χ, ϕ is expressed as follows [12, 13]:

$$\begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix} = \frac{2\sin\theta}{\lambda} \begin{pmatrix} \cos(\omega-\theta)\cos\chi\cos\phi - \sin(\omega-\theta)\sin\phi \\ \cos(\omega-\theta)\cos\chi\sin\phi + \sin(\omega-\theta)\cos\phi \\ \cos(\omega-\theta)\sin\chi \end{pmatrix} \qquad \text{(Eq. 1)}$$

where $\lambda = 1.54$ A (Cu Kα).

From Eq. 1, it was found that the diffraction spots observed in the pole figure (Fig. 2(c)) is the 102 diffraction of the 2H-graphite within a 5 % error. The error, readily seen as a distortion of the hexagon pattern in the pole

figure (Fig. 2(c)), comes from the curl of the graphite crystal. Since the reciprocal lattice shown Fig. 2(d) is converted to the real lattice shown in Fig. 2(e), the obtained pole figure (Fig. 2(c)), which agrees with the orientation shown in Fig. 2(d), means that the orientation of the real lattice is as shown in Fig. 2(e). It follows that the edges observed in Fig. 2(b) are zigzag edges. It is concluded that the macroscopic orientation of the edges formed by electrochemical reduction is along the zigzag edge.

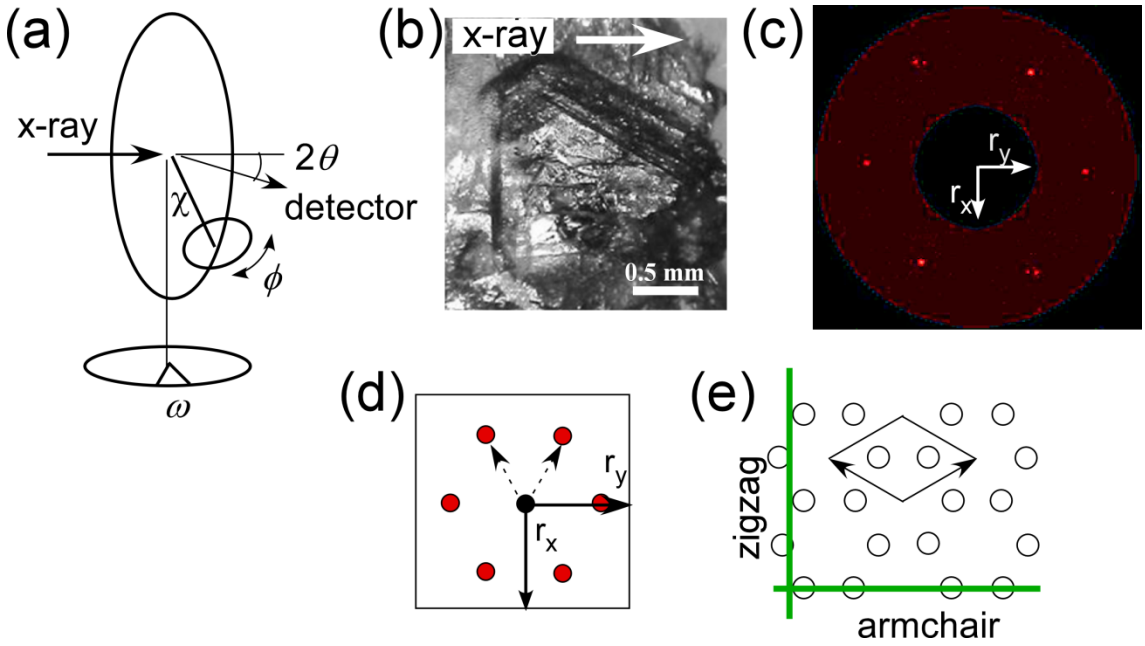

Fig. 2: Pole figure measurement of the electrochemically etched graphite. (a) The definition of the diffractometer angles and the laboratory axis system coordinates. (b) Sample orientation at $\phi = 0^{o}$, $\omega = 0^{o}$ and $\chi = 0^{o}$. (c) Pole figure showing graphite 102 diffraction as hexagonal spots. r_x and r_y are coordinate axes in the reciprocal space. (d) Reciprocal lattice with their primitive vectors indicated as dotted arrows. (e) Real lattice of graphite corresponding

to (d). Primitive vectors are indicated by arrows.

In order to observe the microscopic orientation of the edge formed by the electrochemical cathodic etching, we measured the polarized Raman spectra by changing the sample orientation. A polarized laser (532 nm) was irradiated through the objective lens (x 20) and the Raman scattering coming through the same objective lens was measured without analyzing the polarization. The sample was a natural graphite single crystal placed on a silicon wafer. We carefully manipulated the sample to measure the same location of the edge by rotating the sample with respect to the incident laser polarization. It is reported that with this measurement configuration, the edge orientation can be analyzed[14]. The result is shown in Fig. 3, before (a) and after (b) the etching.

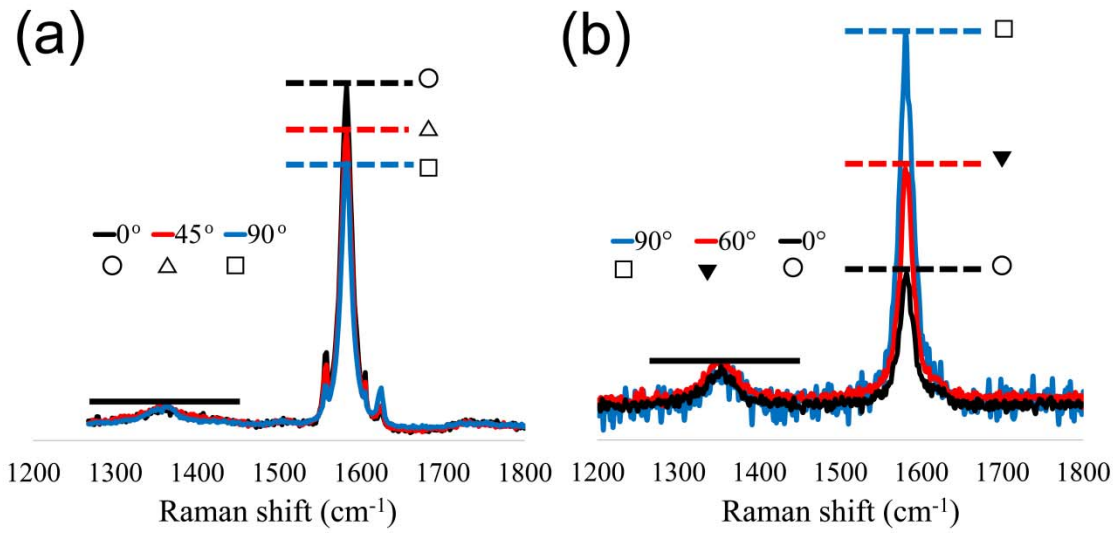

Fig. 3: Polarized Raman spectra of natural graphite periphery before (a) and

after (b) the electrochemical cathodic etching. Shown after normalization at D peak (~ 1370 cm^{-1}). The polarization angles are indicated with respect to the sample edges.

Since the periphery of the natural graphite before the etching was irregular under the microscope, the polarization angle was measured from the macroscopic envelope. After the etching, the edges formed straight lines and a clear difference in the G/D peak ratio was observed as shown in Fig. 3(b). The observed dependence on the polarization is in agreement with the reported behavior of the zigzag edges. We concluded that the edges formed by the electrochemical reduction are zigzag edges.

Graphene edges are now gaining much attention regarding the electrocatalysis in a cathodic environment (carbon-alloy catalysis [15-21]). It is often assumed that zigzag edges with some heteroatoms are responsible for the catalytic activities[15]. The present finding of the formation of zigzag edges in a cathodic environment is consistent with that assumption.

In order to study the reaction occurring during the etching, we analyzed the gas evolving from the graphite. The gas was collected by displacement of the solution in a thin glass tube. It was postulated that the main component of the cathodic gas was hydrogen and we used the detection blind to the hydrogen (FID). Figure 4 shows the gas chromatography result. The apparatus was calibrated with CH_4, CO and CO_2.

The result clearly shows that the main component is CH_4, while a small amount of CO was detected. The concentration of CH_4 in the gas was 700 $\pm$

50ppm (in H_2).

The reaction assumed from the Pourbaix diagam

$$C + 4H^+ + 4e^- \rightarrow CH_4$$

was confirmed by the detection of CH_4.

The small amount of CO is probably due to the anodic gas, which was mixed in with the collected gas in a small ratio. Since we used a Pt anode, the CO must come from the oxidation of the carbon spiecies in the solution. In order to see the carbon species in the solution, we performed a combustion analysis of the solution after the etching. The result was a carbon concentration in the solution of 21mg / 1kg. It is understood that the carbon from the etched graphite, probably solvated as some aromatic molecules, was oxidized at the anode to form CO, which was detected in the collected gas.

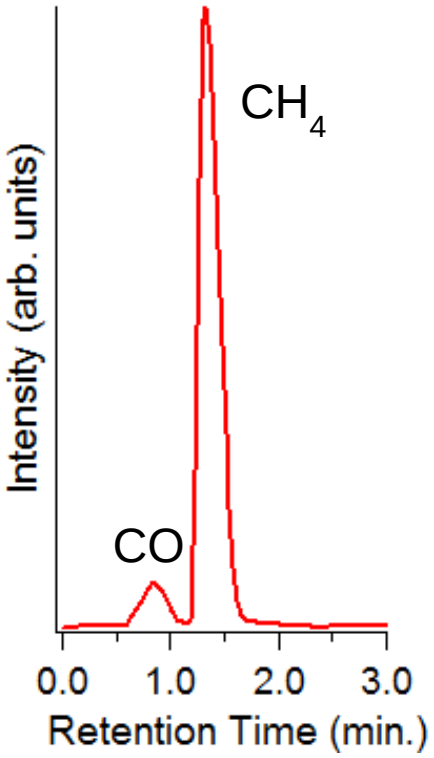

Fig.4: Gas chromatography of the gas evolving during the etching (mainly cathodic).

4. Conclusion

We studied the etching process of graphite used as a cathode in the electrolysis of acidic solutions. We examined the edge structure by x-ray diffraction and Raman spectroscopy. Pole figures of the x-ray diffraction showed that the edge orientation is parallel to the zigzag edges on a macroscopic scale. The polarization dependence of the G-band and D-band of the Raman spectra is consistent with the zigzag edge formation on a microscopic scale. The etched carbon atoms are converted to CH_4 in the evolving gas and molecular species in the solution. We speculate that the mechanism behind this selective etching might be the stability of an edge carbon atom temporarily connected with two hydrogen atoms. The present finding opens a way to mass produce the graphene zigzag edges for carbon-based catalysis and for the nanoscale processing of graphene devices.

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