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

Toshihiro Shimada [a,b,*], Shosei Kubota [a], Takashi Yanase [a,c], Taro Nagahama [a]

[a] Division of Materials Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[b] JST-CREST, Goban-cho, Chiyoda-ku, Tokyo 102-0076, Japan
[c] Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

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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.

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].

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

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°, 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 wt.% H_2SO_4 aqueous solution. We applied −0.3 V vs Ag/AgCl (~ −0.1 V vs. NHE) to the graphite sample.

* *Corresponding author at:* Division of Materials Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan. Fax: +81 11 706 6576.
E-mail address: shimadat@eng.hokudai.ac.jp (T. Shimada).

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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 °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

Fig. 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).

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 hex-

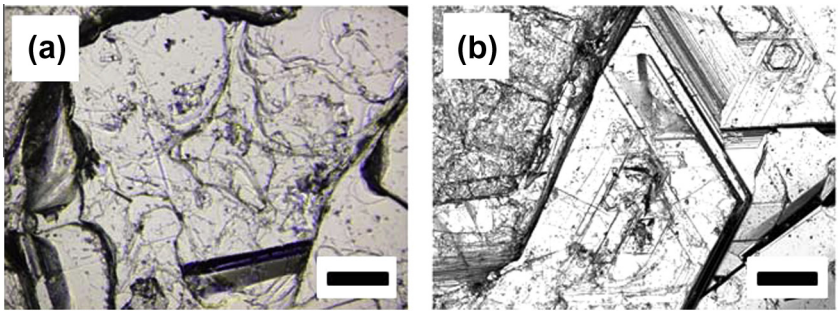

Fig. 1 – Laser optical microscope images of a Kish graphite before (a) and after (b) the electrochemical cathodic etching. Scale bar is 200 μm. (A colour version of this figure can be viewed online)

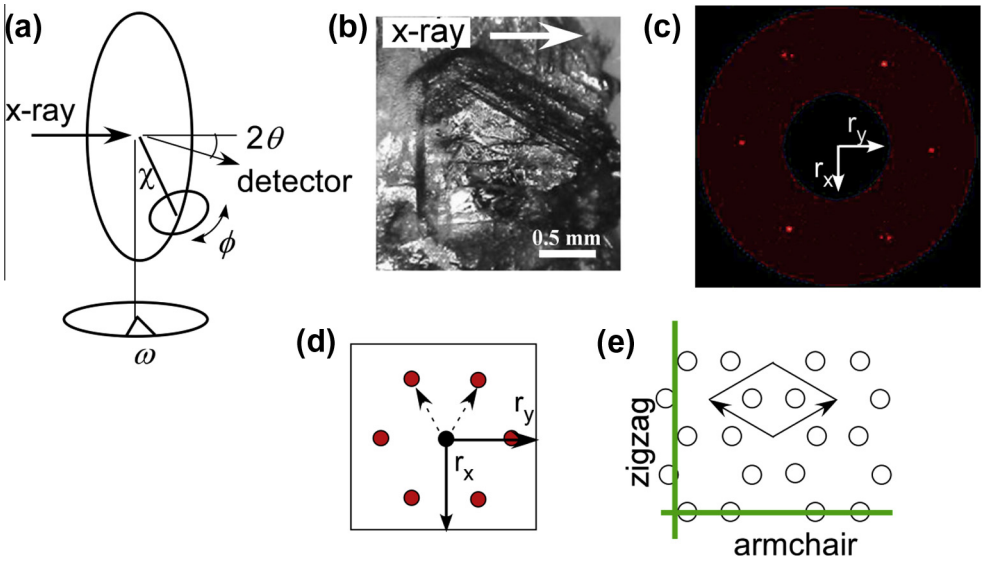

Fig. 2 – Pole figure measurement of the electrochemically etched graphite. (a) The definition of the diffractometer angles and the laboratory axis system coordinates. (b) Sample orientation at $\phi = 0°$, $\omega = 0°$, and $\chi = 0°$. (c) Pole figure showing graphite 102 diffraction as hexagonal spots. 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. (A colour version of this figure can be viewed online)