



Research article

Electrochemical exfoliation of graphite using aqueous ammonium hydrogen carbonate solution and the ability of the exfoliated product as a hydrogen production electrocatalyst support

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ABSTRACT

Electrochemical exfoliation of graphite has attracted much attention as a practical mass production of two-dimensional graphene-like materials. There is an increasing desire to find new and improved methods to create unique exfoliated products with excellent functionality. We used aqueous ammonium hydrogen carbonate solution as a new electrolyte for anodic oxidative exfoliation of graphite. The exfoliated product has a porous two-dimensional structure, and it can be dispersed in water for over five years. The oxidized and defected porous surface serves as an ideal support for molecular metal complexes, effectively functioning as heterogeneous electrocatalysts for hydrogen production.

1. Introduction

Graphite consists of graphene layers stacked along the vertical direction by weak van der Waals forces; therefore, two-dimensional materials such as graphene and graphene oxide can be obtained by delamination of the graphite layers [1–5]. Top-down chemical process as represented by Hummers' method [6] is a promising mass production method of graphene oxide, one of the most attractive graphene analogues for industrial purposes due to its unique and tunable chemical properties derived from its surface functional groups [1–5]. However, the process consumes a large amount of oxidant and strong acid, and requires quite a long reaction time.

Recently, top-down electrochemical exfoliation of graphite has attracted much attention [7–22]. Exfoliation of graphite has generally been induced by electrochemical intercalation of large ions into the graphite anode or cathode, and subsequent delamination. For the anodic electrochemical exfoliation, graphene is obtained in an oxidized form, graphene oxide, for a very short reaction time using inexpensive and industrially available electrolytes such as sulfuric acid [9,10]. Therefore, the anodic electrochemical exfoliation is expected to be a candidate for the mass production process of graphene oxide.

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Previously, various electrolytes have been explored [11–22] based on the mechanism that electrochemical ion intercalation and gas generation for delamination. However, as long as exfoliation is based on the same mechanism, it is difficult to develop exfoliated products with a unique structure. Here we synthesized graphene oxide with numerous holes on its surface using ammonium hydrogen carbonate (NH_4HCO_3) aqueous solution as an electrolyte for the anodic exfoliation of graphite. According to our screening experiments with 30 different electrolytes (Table S1 and Fig. S1 in the Supplementary Materials), NH_4HCO_3 electrolyte, which gave a higher dispersible exfoliated products in *N,N*-dimethylformamide than other electrolytes, has been selected. The present attempt is challenging from the perspective that there are very few studies on anodic exfoliation using alkaline electrolytes [23]. In addition, a nanocomposite of obtained graphene oxide with a molecular metal complex was studied for its heterogeneous electrocatalytic hydrogen evolution activity.

2. Materials and methods

A highly oriented graphite sheet (HOGS: 40 μm in thick, Kaneka) and a SUS316L plate (0.1 mm in thick) were used as the anode and cathode, respectively. Constant voltages of 10–20 V and a constant current of 26.5 A g^{-1} were applied in $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$ electrolyte at initial temperature of 25 °C. After the process, the exfoliated product dispersed in the electrolyte were collected and washed several times with deionized water by centrifugation. Then, they were subjected to X-ray diffractometry (XRD, MiniFlex600, Rigaku), Raman spectroscopy (T64000, Horiba Jobin Yvon Inc.), X-ray photoelectron spectroscopy (XPS, JSP9030, JEOL), light microscopy (BX-53M, Olympus), scanning electron microscopy (SEM, JSM-6701 F, JEOL), transmission electron microscopy (TEM, JEM-2100, JEOL), and atomic force microscopy (AFM, SPM-9700HT, Shimadzu). The DC electrical conductivity of the thin film samples was evaluated by the two-terminal method. The bis-dithiolene nickel(II) complex, $[\text{Ni}\{\text{S}_2\text{C}_2(\text{Ph}-p\text{-OCH}_3)\}_2]$ (1), was prepared according to a procedure described in the literature [24], and was combined with exfoliated products. Voltammetry and controlled potential electrolysis of the composites were carried out using a CHI720E potentiostat (CHI Instruments, Inc., USA) in a three-electrode cell under a N_2 atmosphere at room temperature. The detailed experimental methods are described in the Supplementary Materials.

3. Results and discussion

Fig. 1 shows the electrolytic behavior, photographs of the graphite anode, and dispersed samples. In constant voltage electrolysis, the current increased sharply at the beginning and then decreased gradually. The part immersed in the electrolyte disappeared in 140, 60, and 40 min at 10, 15, and 20 V, respectively. In constant current electrolysis, the voltage increased rapidly and the part immersed in the electrolyte disappeared in 15 min. During the electrolysis, bubbles were generated on the anode surface and the fine exfoliated materials were dispersed in the electrolyte. When the anode was pulled up during electrolysis to confirm its appearance, no expansion

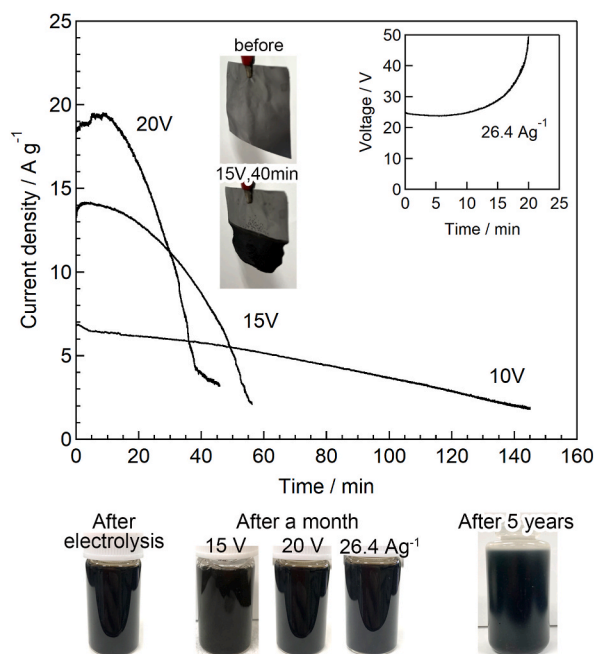


Fig. 1. Current-time curves for the constant voltage electrolysis at 10–25 V and the voltage-time curve (right upper inset) for the constant current electrolysis at 26.4 A g^{-1} using $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$. A photograph after constant voltage electrolysis at 15 V for 40 min (inset figure). Photographs of dispersed samples in *N,N*-dimethylformamide just after electrolysis and after a month (bottom left 4 photographs). A photograph of the water dispersed sample after 5 years (bottom right photograph).

was observed (inset to Fig. 1). This was similar to the case of using alkaline electrolyte such as KOH aqueous solution because the hydrated OH^- intercalants have a very small size than the interlayer distance between graphene layers [23]. In addition, the anode seemed to be scraped off from the edge and surface (inset to Fig. 1), suggesting that exfoliation occurs by a mechanism in addition to the usual ion insertion and gas generation. The most likely additional mechanism is an in-plane attack reaction into the graphite surface, which is inferred from the electron microscopy results in Fig. 3, as discussed below. The suspension of exfoliated materials in *N,N*-dimethylformamide showed good dispersibility and well dispersed even after a month in all electrolytic conditions (bottom left 4 images of Fig. 1). In our preliminary study ~ 5 years ago, a constant current electrolysis of 22 A g^{-1} using $0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$ was applied to a graphite sheet to obtain the exfoliated product. The sample, which was dispersed in neutral water at that time has remained well dispersed to this day (bottom right image in Fig. 1), indicating that the fine and hydrophilic exfoliated particles could be obtained.

Fig. 2 shows (a) XRD patterns, (b) Raman spectra, and (c) XPS spectra of the exfoliated products. Based on the XRD results (Fig. 2a), although a small peak assigned to (002) plane of graphite remained, most of the graphite changed to an amorphous-like pattern, showing the exfoliation of graphite layer progressed. The peak intensity of (002) plane decreased with increasing voltage/current. In the Raman spectra (Fig. 2b), in addition to the broad G band (1581 cm^{-1}), D band (1360 cm^{-1}) and D' band (1620 cm^{-1}) were detected, indicating the introduction of in-plane defects [25]. Although the $I_{\text{D}}/I_{\text{G}}$ ratio of the two different preparation conditions showed almost the same value of ~ 1.9 , the spectra broadened with increasing voltage/current, presumably indicating the increasing defects at higher voltage/current conditions. In XPS C 1s spectra (Fig. 2c), in addition to C=C bond (284 eV), C-O (286 eV), C=O and -COO- (288 eV) groups [26,27] were detected, indicating the oxidation by electrolytic reaction. The oxidation degree increased with increasing voltage/current: C/O ratio decreased from 4.6 to 4.0 for the samples prepared at 15 V and 26.4 A g^{-1} , respectively. O 1s spectra strongly support the C 1s result. In addition, N 1s spectra were detected, although the peak intensities were quite weak with the nitrogen contents of 1.9 and 1.3 at% for the samples prepared at 15 V and 26.4 A g^{-1} , respectively, suggesting a partial introduction of nitrogen as a result of the reaction of ammonium ions with oxygen functional groups to form salts and/or amino groups [28,29]. In addition, the DC electrical conductivity of the thin film sample prepared at 15 V showed higher value ($8.7 \times 10^{-4} \text{ S cm}^{-1}$) than that ($4.8 \times 10^{-4} \text{ S cm}^{-1}$) of the sample prepared at 26.4 A g^{-1} , which is consistent with the results of XRD, Raman, and XPS.

Fig. 3 shows micrographs of exfoliated products. In the light microscope observation (for 15 V sample), there are many two-dimensional small particles with white contrast, while thick and insufficiently exfoliated particles were also observed as brown contrast. The extremely fine particles smaller than $1 \mu\text{m}$ were confirmed in the high magnification image. At a high voltage/current condition (26.5 A g^{-1}), the number of insufficiently exfoliated thick particles decreased, and the overall particle size reduced. At high magnification, fine particles smaller than $1 \mu\text{m}$ were mainly observed. In the SEM observation (for 15 V sample), in addition to the fine particles identified by light microscopy, extremely thin and large sheets were observed. As the voltage/current increased (26.5 A g^{-1}), the particle size of the former became smaller, and numerous pores were formed in the latter thin sheet. The nanostructure was observed in detail using TEM measurements. At 15 V, many steps were present on the surface of the exfoliated thin sheets and the surface was rough. In high magnification observation, many holes with sizes ranging from a few nm to 40 nm were observed on the surface of the exfoliated thin sheets. In addition, very careful observation of particularly thin areas revealed that some of the exfoliated thin layers were close to a single layer or several layers. However, 3–5 nm thick particles were often observed in AFM measurements (Fig. S2 in the Supplementary Materials). The prepared samples could have a very broad thickness distribution ranging from the angstrom to the micrometer scale. As the voltage/current increased, the surface became rougher and numerous holes were also observed as at 15 V. These microscopic observations suggest that NH_4HCO_3 electrolyte specifically induces, in-plane reaction as well as the usual ion intercalation and gas generation, resulting in mixtures of small two-dimensional particles and large thin sheets with rough surface and numerous holes. In addition, we confirmed that the pH value of the electrolyte increased from 8.1 before electrolysis to 8.8 after electrolysis, indicating the partial consumption of carbonate ions in the electrolyte. This result supports the above-mentioned in-plane reaction of graphite with carbonate ions. Other carbonate-containing electrolyte such as potassium hydrogen carbonate (KHCO_3) yielded similar results (Fig. S3 for appearance and Fig. S4 for microscope images in the Supplementary Materials), suggesting that carbonate ions could be a main factor for producing such unique porous structure. It has been reported that exfoliation of graphite occurs when heat-treated highly oriented pyrolytic graphite is quenched in an aqueous ammonium hydrogen carbonate solution [30]. Because there are no pores in the exfoliated material obtained by this method, carbonate ions and electrolysis should be

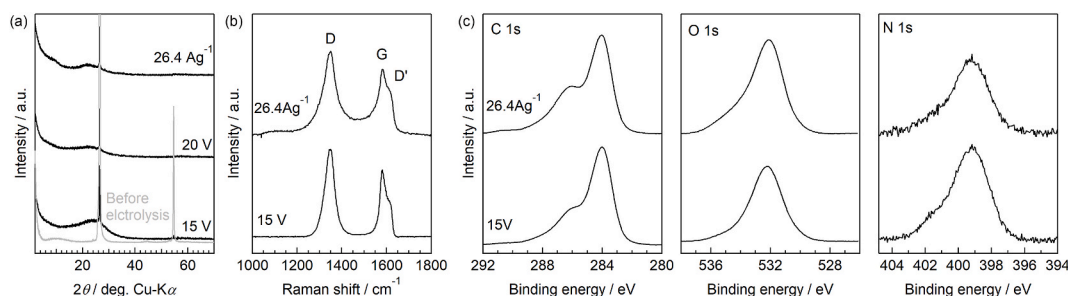


Fig. 2. (a) XRD patterns, (b) Raman spectra, and (c) XPS spectra of the exfoliated samples prepared using $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$ under constant voltage electrolysis at 15–20 V and constant current electrolysis at 26.4 A g^{-1} .

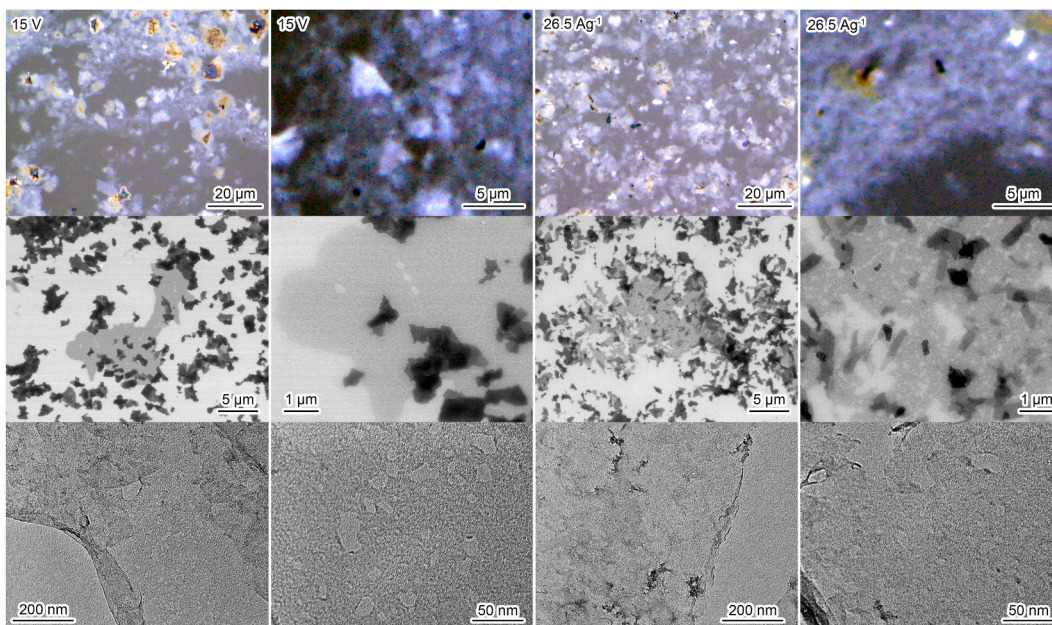


Fig. 3. Light microscope (top), SEM (middle), and TEM (bottom) images for the exfoliated samples prepared using $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$ under constant voltage electrolysis at 15 V and constant current electrolysis at 26.4 A g^{-1} . In the same preparation condition, the left and right images show low and high magnification images, respectively.

key factors to form the unique porous structure. Further elucidation of the exfoliation mechanism will be done in our future work. Since these structures cannot be achieved using conventional electrolytes such as sulfuric acid and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) electrolytes [9,10,31,32] (Fig. S5 in the Supplementary Materials), the exfoliated products are considered to possess characteristics that are distinct from traditional graphene oxide. We tested the possibility for a highly effective scaffold for catalysts.

Previously, a graphene oxide was demonstrated as a good electrocatalyst support to enhance the hydrogen evolution electrocatalytic activity in the combination with a molecular nickel complex [32]. To study the potential of the present graphene oxide as an electrocatalyst support, the nanocomposite of the graphene oxide and molecular nickel complex was prepared and examined by voltammetry. As the molecular catalyst, the bis-dithiolene nickel(II) complex, $[\text{Ni}\{\text{S}_2\text{C}_2(\text{Ph-}p\text{-OCH}_3)\}_2]$ (**1**), was used, which has been reported as a molecular electrocatalyst for H_2 production (see Fig. S5 in the reference [32] for proposed H_2 production mechanism) [32–35]. Although this complex is known as a good electrochemical H_2 evolution catalyst in homogeneous condition (in solution), it is very less in activity when it was used under heterogeneous conditions because **1** has a low conductivity. In sharp contrast, the use of graphene oxide showed the higher catalytic current in voltammograms (Fig. 4a), probably due to the improved conductivity, on the onset potential of -1.3 V (vs Ag/AgCl) with the Tafel slope of 310 mV/degree (Fig. S6 in the Supplementary Materials), although the overlapped catalytic current derived from graphene oxide was also observed (670 mA/degree) (Figs. S6 and S7 in the Supplementary Materials). The higher current density is required for practical use in industry [36], however, the current density was limited as shown in Fig. 4 due to the presence of background reduction current at the more negative potential. The stability of catalyst was confirmed by

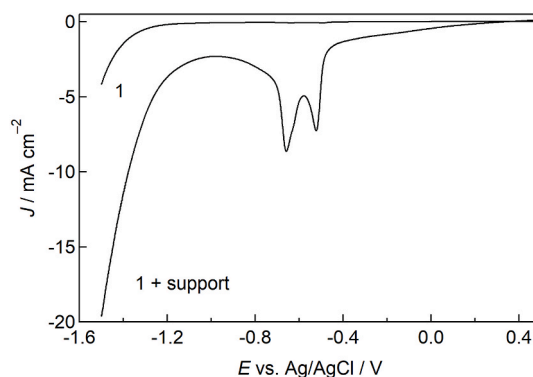


Fig. 4. Linear sweep voltammogram of **1** with the carbon support prepared at 15 V constant voltage electrolysis. The result of **1** alone was also shown for comparison.

the potential-controlled electrolysis experiments, which revealed the constant charge accumulation with the constant potential of -1.5 V for 15 min, indicating that the catalyst works without degradation at least 15 min (Fig. S8). Thus, the graphene oxide developed in this work demonstrated its good ability as an electrocatalyst support.

The electrochemical process can be used as an effective exfoliation method for hexagonal boron nitride, transition metal dichalcogenides, MXene, post-transition metal chalcogenides, and metal phosphorous trichalcogenides, etc. to obtain a variety of two-dimensional materials [37]. We hope that the electrolyte solution discovered in this study will be used to create novel two-dimensional materials with unique pore structures other than graphene and graphene oxide.

4. Conclusions

To prepare a new graphite-induced two-dimensional sheet material by anodic electrochemical exfoliation, aqueous NH_4HCO_3 solution was applied to an electrolyte, and the potential application of the exfoliated product as an electrocatalyst support for hydrogen production was investigated. The exfoliated products had a highly defective oxidized sheet structure with numerous nano-sized holes, which were enhanced by the increasing voltage/current conditions. The sheet material showed high dispersibility, for example, one of the materials maintained its excellent dispersibility in neutral pH water for more than five years. The composite electrode material of the exfoliated product and the molecular catalyst, the bis-dithiolen nickel(II) complex, was prepared by simply mixing the two materials in alcoholic solution. Although the molecular catalyst itself does not work as a heterogeneous catalyst because of its poor electrical conductivity, the composite electrode material showed higher catalytic current, showing that the electrochemical exfoliated product using aqueous NH_4HCO_3 solution have a high potential as an electrocatalyst support.

CRedit authorship contribution statement

Ryuichi Maekawa: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Hirooki Kajiwara:** Formal analysis, Investigation. **Yuto Washiyama:** Formal analysis, Investigation. **Yasushi Nishikawa:** Resources, Formal analysis, Investigation. **Naoto Kuwamura:** Writing – review & editing, Formal analysis, Data curation. **Toshinori Okura:** Writing – review & editing, Resources, Investigation, Funding acquisition. **Yuta Nishina:** Writing – review & editing, Resources, Investigation, Formal analysis, Data curation, Funding acquisition, Conceptualization. **Hideki Hashimoto:** Writing – review & editing, Visualization, Supervision, Resources, Formal analysis, Data curation, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e40751>.

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