Effective preparation of graphite nanoparticles using mechanochemical solid-state reactions¹

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Abstract

The mechanochemical milling was utilized to control the nanostructures of plate-like graphite (Gp) microparticles in an argon atmosphere and at room temperature. The aggregated Gp nanoparticles were prepared by the simple solid-state process without organic solvent. Electron microscope observations, X-ray diffraction patterns and Raman spectra revealed the fractured plate-like Gp microparticles as well as the Gp microparticles agglomerated to each other through the dissociative edge surfaces by the milling process to finally generate the Gp nanoparticle aggregates. In the process, the ratio of the edge plane surfaces with the dangling bondings to layered internal surfaces clearly increased with the milling. Therefore, the low environmental burden process for preparing the Gp nanoparticle aggregation was achieved.

Keywords

A. Graphite; B. Mechanochemistry; C. Nanostructures; E. Electron microscopy

1. Introduction

Graphite (Gp) is widely used as an anode active material of lithium-ion batteries in most commercial products, and the nanoparticle aggregation (nanoporous solid) state is focused because of the conductivity as well as the specific surface area. Recently, the Gp nanoparticle-aggregated electrodes are functionalized by composting with other elements such as iron and copper in order to achieve high performance. The crystallographic structures, surface morphologies, and physicochemical parameters of Gp have a significant influence on the properties of such composites doped with other elements. Thus, the composite techniques for Gp have been widely investigated [1, 2]. The techniques involving an organic binder are mainly used for enhancing the interfacial interactions [3, 4]; however, it decreases mechanical properties and contaminates a furnace during the sintering process. Therefore, the preparation of nanoparticle aggregation as well as the development of a new Gp surface modification without an organic binder is desired.

Gp has plate-like morphology and layered structure with crystalline carbon networks [5], which are stabilized by the end C–H groups [6]. The terminal hydrogen atoms can be removed by thermal heating at 700–900 °C. The generated dangling bondings subsequently form the bondings among the end surfaces, resulting in nanographites with single/double-walled carbon nanotubes and graphene [7]. Thus, the dissociation of the Gp end groups will generate the activated Gp surfaces with dangling bondings [8], which would form the unique morphologies.

A new approach to control the Gp morphologies and nanostructures is termed a mechanochemical milling technique in this study. The force-induced defects and dangling bondings in the lattice will provide the composites doped with other materials. We have already

proposed that the control of surface structures with a mechanochemical methodology, which is a powerful tool to modify a solid state material and to obtain new defect states unachievable by other means, is an important *issue*. Such control is mainly stimulated by modern materials science, the needs of industry for new nanomaterials and green technologies [9–13]. The goal of the mechanochemical reactions is determining the major factors influencing the dynamics of the process for compositing heterogenetic atoms [10, 11], as well as revealing the possibilities to regulate the structure and properties of a product, that is, the traditional goal of solid state chemistry to adjust the reactions in time and space [13]. Therefore, these controllable defects and the formation of dangling bondings in the lattice structure will provide novel activation properties as well as nanomorphologies.

In this study, the mechanochemical milling control of the nanostructures of plate-like Gp microparticles in an argon atmosphere and at room temperature was conducted for the first time. The surface chemical states of the activated Gp were investigated to clarify the fracture and aggregation mechanism among the mechanochemically-activated Gp nanoparticle surfaces.

2. Experimental

2.1. Preparation of Gp Nanoparticles

The experimental set-up for the mechanochemical solid-state reaction and photographs during the milling are shown in the Supporting Information, Scheme S1. The milling vessel made of a stainless steel rod (SUS304) was used and was surrounded by a water jacket in order to suppress the heat generated and keep room temperature (20–25 °C) during the milling. Twenty SUJ2 steel

balls (AISI52100) with the diameter of 10 mm were used as the milling medium. The detailed experimental set-up was described in our previous reports [10, 11].

First, a 0.2 g sample of plate-like Gp microparticles (average diameter: ca. 10 μm , purity: > 99 %, Nihonkokuenkogyo Co., Ltd.), which was determined by the optimum Gp volume to medium balls for efficient milling, was added into the milling vessel. The vessel was mounted on a centrifugal ball mill (NEV-MA-8, Nisshingiken Co., Ltd.) and stored under vacuum for 1 day in order to remove water molecules and other substances adsorbed on the surfaces. Then, dry argon gas (purity: > 99.999 %) was introduced into the milling vessel until the pressure increased to 203 kPa. This process was repeated three times by completely replacing the argon. The vessel was then immediately swung at the speed of 59.1 rad/s for 8 h under room temperature.

The kinetic energy transfer from the media to the Gp particles was calculated by the following equations. The medium moves in a circular path against the inside wall of the vessel to subsequently press against the wall by centrifugal force. As a result, the kinetic energy transfer from the media to the particle occurs when the balls compress the trapped particles between the balls and the wall. The compressed force (F) can be expressed by equation (1),

$$F = mr\omega^2 \quad (1)$$

where m is the mass of the ball, r is the orbit radius of the ball movement and ω is the milling rate. F can be regarded as the working force on the particle surfaces, and was calculated using m of 3.5×10^{-3} kg, r of 2.7×10^{-2} m and ω of 40 rad/s to be 1.5×10^{-1} N. Therefore, the kinetic energy transfer to the media can be expressed by equation (2),

$$E = \frac{1}{2}nmv^2 \quad (2)$$

where E is the kinetic energy, n is the number of balls, v is the circumferential velocity that can be obtained for the product of the orbit radius r and the milling rate ω . E was calculated using n of 20 and v of 1.1 m/s to be 4.1×10^{-2} J.

2.2 Characterization

The resultant Gp particles were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy.

The morphology of the Gp particles was observed using a FE-SEM (S4800, Hitachi Co., Ltd.) at an accelerating voltage of 15 kV. The detailed nanostructures based on bright-field and dark-field TEM and selected area electron diffraction (SAED) images were obtained and analyzed using a JEM-1400 (JEOL Co., Ltd.) at an accelerating voltage of 120 kV. DF-TEM images from Gp (002) diffraction were observed using an objective aperture. Selected DF-TEM images (from images covering 0–180° of the diffraction ring) were superimposed using software (DigitalMicrograph®; Gatan, Inc., Pleasanton, CA, USA) (for details, see Supporting Information, Fig. S2). The preparation of the samples before observation was done by dispersing a small amount of the Gp particles into ethanol, casting the suspension onto a carbon-coated copper grid, and then drying.

The XRD patterns were recorded by a Smartlab (Rigaku Co., Ltd.) using monochromatized CuK α radiation. The primary optics was equipped with a solar slit (5.0 °), a divergence slit (0.5 °)

1 and a scattering slit (0.5°). The secondary optics was equipped with a first receiving slit (0.08
2 mm), a Gp monochromator, a second receiving slit (0.13 mm) and a detector.

3 The Raman spectra were recorded by a NRS-7200 (JASCO Co., Ltd.) equipped with a
4 holographic grating (L400) and Nd:YVO₄ laser at the wavelength of 532 nm for the excitation.
5 The laser power was 3.56 mW to avoid any sample degradation. The exposure time, resolution,
6 scan times and measured wavenumber were 4 s, 6.8 cm^{-1} , 100 times and $100\text{--}1800\text{ cm}^{-1}$,
7 respectively. Based on the Gaussian function, the spectra were fitted to each of the characteristic
8 bands (*D*, *G*, and *D'*). In the deconvolution, the components, number of peaks, and peak
9 positions and widths were initially fixed according to previous reports [14, 15], and then were
10 refined only for the peak heights. During the final optimization, only the components and peak
11 widths were refined again to reduce the residual values up to less than 1.0×10^{-4} in order to
12 obtain the separated spectra. In the resulting spectra, the raw spectra, the deconvoluted spectra
13 and the summation were represented by black, green and red spectra color curves, respectively,
14 as shown in Fig. 3 (a). In the deconvoluted spectra, the integrated intensity ratios of the *D* band
15 to *G* band (I_D/I_G) and of the *D'* band to *G* band ($I_{D'}/I_G$) were calculated, leading to the
16 investigation of the lattice disorder as well as the formation of nanocrystalline Gp.

17 X-ray photoelectron spectroscopy (XPS) spectra of the particle surfaces were measured by a
18 PHI5000 Versa Probe (ULVAC-PHI, Inc.) using a monochromatized Al X-ray source (Al
19 $K\alpha$ line at 1.4866 keV) at 15 kV and 25 mW. The C 1s spectra were measured in the ranges
20 between 282–287 eV and the detailed characterization procedure is described in the **Electronic**
21 **Supplementary Materials, XPS Characterization Procedure.**

3. Results and discussion

Fig. 1 shows the representative FE-SEM and TEM images of the Gp microparticles **without milling and milled for 1 and 8 h**. The Gp microparticles **without milling** exhibit a plate-like shape with the particle size of 2–10 μm which circumferentially consists of flake-shaped crystals (Fig. 1 (a–c)). Here, the Gp crystalline structure is one in which the carbon atoms lie in the six-membered ring honeycomb network structure sheets with extremely strong covalent bonds between the atoms inner each sheet. One layer of the sheet is well-known as graphene. The plane corresponds to (001) in the Miller index called the basal plane [16]. The end of the six-membered ring structure is called the edge plane, exhibiting the active surfaces such as $-\text{COOH}$, $=\text{C}=\text{O}$, and so on. Therefore, the larger plate-like morphologies at the initial milling stage indicates that the inactive layered graphene sheets were dominant as compared with the active edge surfaces.

During the mechanochemical milling for 1 h, cracks were newly formed parallel to the plate plane (i.e., c-plane) as shown in Fig. 1 (d and e). The partially-fragmented plates were aggregated and stacked as shown in Fig. 1 (f). In appearance, the plate-like shaped particles are preserved after the milling for 1 h. However, as shown in Supporting Information Fig. S2 (BF-TEM and DF-TEM images with SAED), the arbitrary SAED spots in the Debye rings based on the (002) diffraction patterns indicate the polycrystalline structures with different orientations. **The size of crystallites** is on a nanometer scale (ca. 100 nm), which corresponds to the domain sizes formed by the cracking in the TEM image (Fig. 1 (f)).

During the milling for 8 h, the plate-like shapes completely changed to nanoparticulate structures with the average size of ca. 50 nm, and the nanoparticles were aggregated as shown in Fig. 1 (g–i). Gp nanoparticles were formed by the mechanochemical milling process, while

1 preserving the aggregation state. Generally, it is known that the milling in an inert atmosphere
2 induces an effective milling which can form smaller size particles as compared to those form in
3 reactive atmospheres (e.g., O₂, H₂) [16]. In fact, we also conducted the milling in dried O₂ and
4 air. As a result, the plate-like particle morphology and size did not change, indicating no
5 aggregation and fragmentation among the particles in the atmospheres because of the smaller
6 friction coefficient by the adsorbed oxygen gas at the interfaces. This suggests the importance of
7 the milling in an inert atmosphere. The inert atmosphere enhances the aggregation among the
8 newly-generated active surfaces with the dangling bondings by the milling, enabling an effective
9 milling [10, 11, 17]. On the other hand, the active atmosphere reacts with the newly-generated
10 surfaces to immediately reach an equilibrium milling state without aggregation [17]. That is
11 because the dispersion state significantly provides a lubrication effect due to the slipping of basal
12 plane during the milling, forming the larger size particles [18]. Therefore, it was suggested that
13 the present simple milling process in nitrogen atmosphere induces the aggregation state among
14 the newly-generated Gp edge surfaces with dangling bondings.

15 After the milling, we took out the samples from the chamber to air and then measured XPS
16 spectra. The C 1s XPS spectra after the milling were divided into two peaks attributed to the
17 C–C (284.8 eV) as well as C–O (286.1 eV). The peak positions and intensities are almost the
18 same irrespective of the time (data not shown). In this case, the C–C bonding is attributed to the
19 Gp framework structures. Given that a reaction occurred in air, the C–O bonding might be
20 similar to the oxidized layer of Gp, indicating the formation of dangling bonds on the end of Gp.
21 An NMR study has revealed that Gp oxides contain aromatic regions randomly interspersed with
22 oxidized aliphatic six-membered rings, and the oxidized rings contain C–O–C (epoxide) and
23 C–OH groups, while the sheets terminate with C–OH and –COOH groups [30]. In this study, the

1 oxidation groups formed in air imply the formation of dangling bondings at the Gp edge
2 surfaces.

3 Fig. 2 shows the XRD patterns of the Gp microparticles without milling and milled for 0.5 h, 1
4 h, 2 h and 8 h. All the diffraction patterns exhibit the Gp hexagonal and rhombohedral phases.
5 Here, the interlayer bondings among the graphene sheets mutually work with the weak
6 interactions. The *AB AB...* stacking sequence results in the hexagonal crystal symmetry, *D6h*
7 [19]. Furthermore, an alternative *ABC ABC...* stacking sequence based on the rhombohedral
8 symmetry is known to be in the present defective Gp, always as a mixture with the hexagonal
9 phase [20]. In Fig. 2 (a), peaks at 26.6 ° and 54.7 ° attributed to the hexagonal interlayer spacing
10 (001) ((002) and (004)) were clearly observed [20]. The peak shapes were broaden with
11 increasing reaction time. In Fig. 2 (b), peaks at 42.4 °, 43.4 °, 44.6 °, 46.2 °, 50.7 °, 59.9 °, 72.6 °,
12 77.5 °, 82.6 ° and 87.1 ° due to the hexagonal (100), rhombohedral (101), hexagonal (101),
13 rhombohedral (012), hexagonal (102), hexagonal (103), hexagonal (104), hexagonal (112),
14 hexagonal (105) and hexagonal (106), respectively, were also observed [20].

15 In the peaks between $2\theta = 42\text{--}47^\circ$, the studies on non-graphitic carbons have determined the
16 (100) reflections of randomly stacked graphene sheets [25], suggesting that the milled Gp
17 particles in the present study partially consist of randomly stacked graphene sheets at the final
18 milling stage. During the milling, the 2D arrangement in the graphene planes was preserved,
19 whereas the 3D arrangement was gradually destroyed. It can be explained by the different
20 interactions based on the strong sp^2 C–C covalent bondings. These bondings make up the
21 graphene planes with the weak van der Waals forces that stack these planes together [16, 25]. In
22 other words, the preferential cleavages along the weak interlayer bondings disrupt the layered

structures as well as the C–C networks in the plane by the milling. Based on these viewpoints, the (002) diffraction peak position slightly changes from 26.6 ° to 26.5 ° after the milling for 8 h, indicating that the weak van der Waals forces that stack the planes slightly changed (this has also been reported in the other reports) [16, 22, 23]. Furthermore, the peak positions attributed to the Gp edge planes (e.g., hexagonal (101), (102), (103), (104) and (105)) preferentially broadened and then disappeared with increasing milling time. It indicates the decrease in the crystalline sizes as well as the effective increase in the reactive fine edge surfaces [17, 21]. Therefore, these changes in diffraction width would be the result of the structural disordering [24]. The dangling bondings at the edges would also be effectively generated along with preserving the layered structures by the milling.

Fig. 3 show the Raman spectra of the Gp microparticles without milling and milled for 0.5 h, 1 h, 2 h and 8 h. The changes in the structural order parameters of I_D/I_G and $I_{D'}/I_G$ with the reaction time are also shown in Fig. 3. The spectra clearly exhibit the *G*, *D* and *D'* bands at around 1350 cm⁻¹, 1580 cm⁻¹ and 1600 cm⁻¹, respectively. The *G* band is attributed to the E_{2g} mode of the six-membered ring structures [26], and the band intensity corresponds to the expansion between the C–C bonding in-plane direction of the (002) plane. The *D* and *D'* bands, which are thought to be due to the structural disorder, are attributed to the strained lattice disordering by surface modification and substituted impurity atoms along the planes, respectively [27–29]. Thus, the *G* band intensity decreased in this study (Fig. 3 (a)), indicating the breaking of the six-membered ring structures. In contrast, the *D* and *D'* band intensities increased, suggesting lattice disordering caused by the atomic reactions during the milling. Furthermore, both the I_D/I_G and $I_{D'}/I_G$ values increased with increasing milling time (Fig. 3 (b)). Therefore, the increase in the I_D/I_G and $I_{D'}/I_G$ values indicates the formation of defective surfaces in the six-membered ring structures that

1 increase the fine fragmented edge parts. These results correspond to the SEM images and XRD
2 patterns. It was found that the nanoparticles intriguingly consisting of the layered nanostructures
3 as well as reactive fine edge surfaces can be obtained by changing the milling time. According to
4 the previous report [31], the mechanochemical reactions of the Gp with iron oxides have been
5 reported to result in the reduction of the Gp (002) peak and the production of CO₂. In this study,
6 the production of CO₂ was not detected by the gas chromatography analysis, only a small amount
7 of hydrogen was produced. This new finding suggests that the C–H end groups of Gp effectively
8 reacted each other, thereby causing dissociation of C–H. This reaction mechanism is now under
9 investigation. The surface reactivity of the Gp nanoparticles with rich dangling bondings and the
10 reaction mechanism will be reported by our group soon.

12 4. Conclusions

13 The mechanochemical solid-state control of the nanostructures of plate-like Gp microparticles
14 was achieved in an argon atmosphere. The simple milling process led to the formation of Gp
15 nanoparticles with an aggregated state. The nanostructural analyses by FE-SEM, TEM and XRD
16 suggested that the Gp nanoparticles agglomerated each other to form the aggregation through the
17 dangling bondings on the fine edge surfaces newly formed by the milling. Furthermore, the
18 Raman spectra demonstrated that the ratio of the fine edges to layered inner planes in the Gp
19 significantly increased with the milling. The Gp nanoparticle aggregation, which was
20 successfully prepared by the low environmental burden process without organic solvent, will
21 provide a platform for carbon material functionalization.

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6 spectroscopy.

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Figure captions

Fig. 1 Representative (a, b, d, e, g, h) FE–SEM and (c, f, i) TEM images of the GP microparticles (a–c) without milling and milled for (d–f) 1 h and (g–i) 8 h. The magnifications are (a) ×8 k, (b) ×50 k, (c) ×50 k, (d)×30 k, (e) ×120 k, (f) ×50 k, (g) ×60 k, (h) ×200 k and (i) ×250 k), respectively.

Fig. 2 XRD patterns of the GP particles without milling and milled for 0.5 h, 1 h, 2 h and 8 h. (b) is magnified by 100 times from (a).

Fig. 3 (a) Raman spectra of the GP particles without milling and milled for 0 h, 0.5 h, 1 h, 2 h and 8 h, and (b) the changes in the structural order parameters of I_D/I_G and $I_{D'}/I_G$ during the reaction time.

2 **Fig. 1**

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1 **Fig. 2**

1 **Fig. 3**

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Graphical Abstract

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