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Effective preparation of graphite nanoparticles using mechanochemical solid-state reactions

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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.

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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 on 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 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 mechanochamical 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

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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 mechanochemicaly-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 Eq. (1),

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

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 Eq. (2),

$$E = (1/2)nmv^2 \qquad (2)$$

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

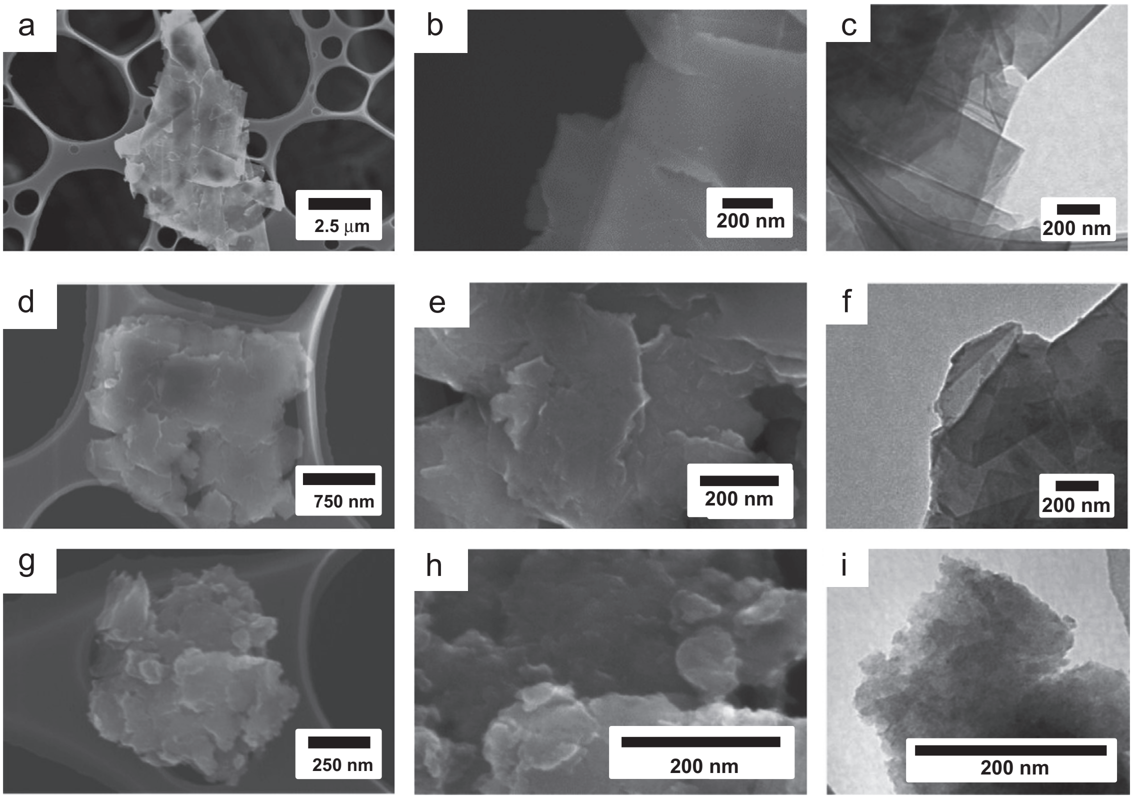

Fig. 1. Representative (a, b, d, e, g, h) FE–SEM and (c, f, i) TEM images of the GP microparticles (a–c) without milling and milled for (d–f) 1 h and (g–i) 8 h. The magnifications are (a) × 8k, (b) × 50k, (c) × 50k, (d) × 30k, (e) × 120k, (f) × 5k, (g) × 60k, (h) × 200k and (i) × 250k.

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