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Selective preparation of polyhedral graphite particles and multi-wall carbon nanotubes by a transferred arc under atmospheric pressure

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ABSTRACT

High-purity polyhedral graphite particles (PGPs) and multi-wall carbon nanotubes (MWNTs) were selectively synthesized by a transferred arc discharge method under atmospheric pressure. PGPs and MWNTs were characterized by the field emission scanning electron microscope (FE-SEM), transition electron microscopy (TEM), and Raman spectroscopy. The products were successfully controlled by varying the arc current and the anode diameter. PGPs were the main products in the case of a relatively high arc current of 100 A or a large anode diameter of 30 mm, while MWNTs were the main products when the arc current was reduced to 80 A or the anode diameter was decreased to 15 and 10 mm. The ratio of carbon ions to carbon radicals near the cathode tip was employed to explain the mechanisms of PGP and MWNT formation. Relatively high ratio of carbon ions to carbon radicals contributed to the formation of PGPs. In contrast, relatively low ratio of carbon ions to carbon radicals led to the formation of MWNTs.

1. Introduction

Arc discharge method has been applied to prepare many kinds of carbon allotropes such as fullerene [1], multi-wall carbon nanotube (MWNT) [2], single-wall carbon nanotube (SWNT) [3], and graphene [4]. However, the mechanisms of carbon allotrope formation are unclear due to the complicated nature of the arc discharge. Especially, the formation process of MWNTs remains a controversial topic, although lots of work has been dedicated to establish the synthesis mechanism [5–9].

Polyhedral graphite particles (PGPs) are polyhedral shape nanoparticles consisting of concentric graphitic shells. They exhibit peculiar elasticity and stability under high pressure, which could be applied as solid lubricant [10]. Moreover, PGPs have the potential to be applied as an electron field emitter [11] and supercapacitor [12,13] because of their unique curvature. Therefore, the potential applications of PGPs attract much attention. However, the reports about the mechanism of PGP formation are limited up to now, because most of researchers paid more attention to the formation of MWNTs. In the past several years, the researchers provided lots of explanations about the mechanism of MWNT formation, neglecting that of PGP. Iijima et al. [5] proposed the open-ended growth at atomic level based on transition electron microscopy (TEM) observation, demonstrating an anisotropic growth of nanotubes. Guo et al. [6] suggested the lip–lip interaction model for the stabilization of open growing edge of multi-wall nanotubes. Louchev et al. [7] explained the growth of carbon nanotube from the kinetic point in detail.

Although few mechanisms about PGP formation have been proposed, the relationship between PGPs and MWNTs is still unclear. Ugarte [14] put forward that the bending of graphite basal planes is favorable to the formation of PGPs by eliminating the dangling band. Although the growing condition of MWNTs was also described in Ugarte's work, the relationship between PGPs and MWNTs was not explained. Moreover, Saito et al. [15] suggested a mechanism that carbon ions and C_n cluster are the precursors for the growth of PGPs and MWNTs from a similar initial seed. However, the conditions about the growth of PGPs and MWNTs were not explained in Saito's work. Although they introduced electric field to explain the growth of the nanotubes, many experiments and simulations confirmed that the electric field is in fact neither a necessary nor a sufficient condition for the growth of carbon nanotubes [16,17]. Moreover, Gamaly and Ebbesen [18] suggested that the carbon atoms contribute to the formation of spherical carbon particles, while carbon ions contribute to the formation of MWNTs. The discovery of MWNTs on the anode deposit confirmed that carbon ions are not the necessary condition for the growth of MWNTs by the arc discharge method [19,20]. Therefore, the mechanisms of PGP and MWNT involved remain rather poorly understood. The lack of detailed understanding of these mechanisms has been a serious impediment to apply the arc discharge method for the preparation of PGPs and MWNTs.

In the present work, a transferred arc discharge method was used to prepare PGPs and MWNTs controllably by changing the arc current and the anode diameter. The relative ratio of carbon ions to carbon radicals near the cathode tip was examined as an important parameter to

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control the growth of PGPs and MWNTs. Based on the different energies of the precursors, the mechanisms of PGP and MWNT formation by the arc discharge method are suggested.

2. Experimental methods

2.1. Experimental setup

The schematic illustration of an experimental apparatus for the preparation of PGPs and MWNTs is shown in Fig. 1. A graphite anode (99.99%, Toyo Tanso Co. Ltd) with an inclined top plane was put on the water-cooled anode holder of a cupper plate. A graphite cathode rod (99.99%, Toyo Tanso Co. Ltd) which has the fixed diameter of 6 mm, was placed at an oblique angle from the anode. The electrode gap distance was fixed at 1 mm, and the arc discharge was operated for 8 min in helium environment at atmospheric pressure for each experimental condition. The arc current was changed by 80, 100, and 150 A at the fixed anode diameter of 30 mm to investigate the effects of the arc current on the synthesis of PGPs and MWNTs. For the anode size effect, different diameters of 10, 15, and 30 mm were used at the fixed arc current of 100 A.

The anode was evaporated after igniting the plasma due to the high heat flux from the arc discharge. Then, evaporated carbon was deposited on the cathode surface forming the cathode deposit. The cathode deposit composed of a gray outer shell and a dark inner core was formed by the evaporated carbon from the anode. The inner core as the main region for the growth of carbon allotropes was investigated. In addition, the materials obtained from different regions of the experimental apparatus were analyzed to examine the effect of carbon species and temperature on the products. Additional sampling positions of carbon product were the inner surface of the chamber, top surface of the anode holder, side surface of the cathode, and the top surface of the anode.

2.2. Sample characterization

The morphological and structural characterization of as prepared products were examined by the field emission scanning electron microscopy (FE-SEM: S-5200, Hitachi), scanning electron microscopy (SEM: JSM-6610LA, JEOL), transmission electron microscopy (TEM: JEM-2010F, JEOL), and Raman spectroscopy (NRS-2100, JASCO) with 514.5 nm Ar^+ laser excitation. In the analysis of Raman spectrum, three positions for each sample were measured, and the average relative intensity was calculated for comparison. An optical spectrometer (iHR-550, HORIBA Jobin Yvon) with a CCD detector (Synapse, HORIBA Jobin Yvon) was used to collect the information of excited species in the plasma. An optical fiber was placed at the window of the arc chamber to measure the plasma emission near the cathode tip. Based on the database of the National Institute of Standards and Technology (NIST), the emission species were identified.

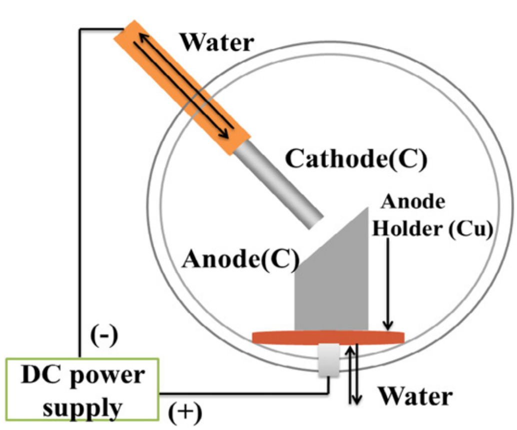

Fig. 1. Schematic diagram of experimental apparatus for the preparation of PGPs and MWNTs.

3. Experimental results

3.1. Arc current effect

Fig. 2 indicates FE-SEM images of the inner core of cathode deposit with different arc currents from 80 to 150 A at the fixed anode diameter of 30 mm. As shown in Fig. 2(a), the cathode deposit is composed

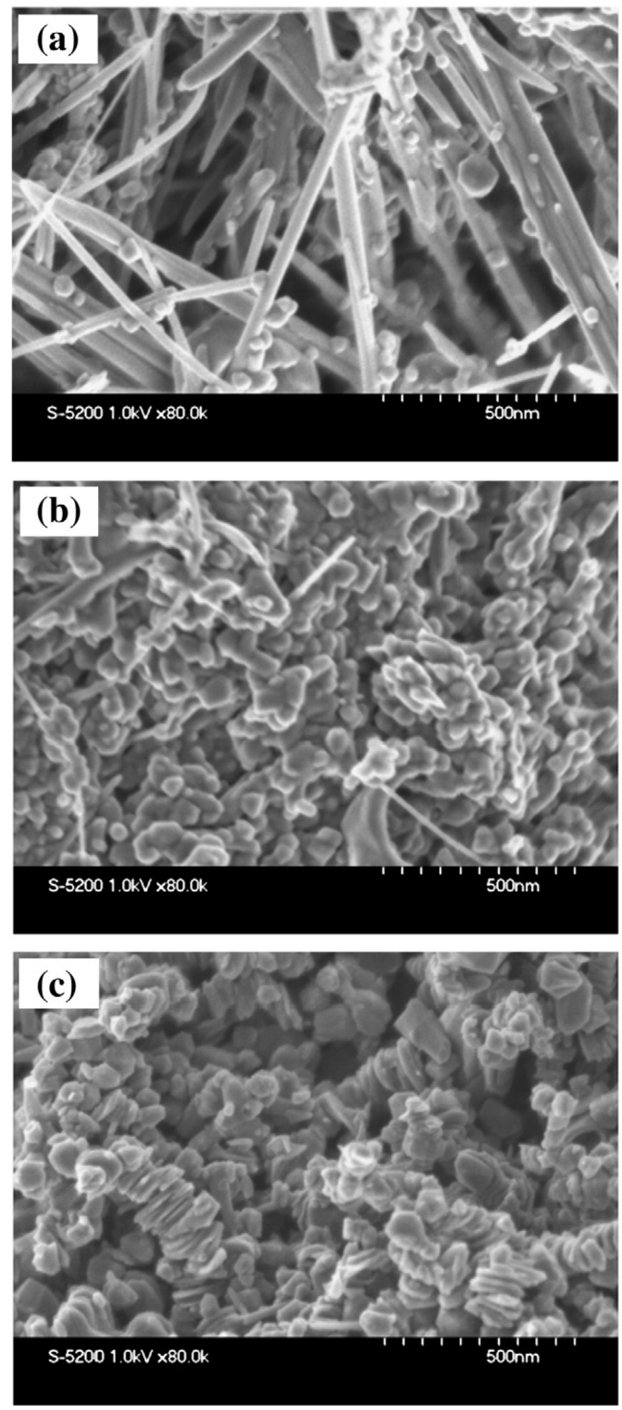

Fig. 2. FE-SEM images of the cathode deposit in different arc currents of (a) 80 A, (b) 100 A and (c) 150 A at the fixed anode diameter of 30 mm.