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Ferritin-mixed solution plasma system yielding low-dimensional carbon nanomaterials and their application to flexible conductive paper

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ABSTRACT

We demonstrate the production of low-dimensional carbon nanomaterials using a solution plasma system and their application to flexible conductive paper. The solution plasma system consists of two graphite electrodes and a beaker filled with ferritin-mixed deionized water. Ferritin molecules are used as the growth catalyst of the carbon nanomaterials. A high voltage of 15 kV at a frequency of 25 kHz is supplied to the electrodes using an alternating-current power source. The effects of the graphite rod diameters and the concentration of ferritin molecules are comparatively investigated. The produced carbon nanomaterials are characterized using Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy. We confirmed the synthesis of graphitic platelets, onion-like structures, and carbon nanotubes. Finally, we fabricated flexible conductive papers using the produced materials with a good electrical conductance.

1. Introduction

Low-dimensional carbon nanomaterials such as fullerenes, carbon nanotubes (CNTs), and graphene have attracted much attention owing to their unique and remarkable properties as well as their potential applications in many areas such as electronics, sensors, and composites [1–3]. The development of facile and reliable synthetic methods to obtain desirable nanostructured materials at an appropriate cost might be the first task to realize their potential applications. Several synthetic approaches for efficient production have been attempted including the arc discharge method [4,5], laser ablation [6], mechanical or chemical exfoliation [7], chemical vapor deposition (CVD) [8,9], and others [10,11]. To date, CVD has been prevailingly used as one of the most suitable methods for the structure-controlled synthesis of carbon nanomaterials with a high quality. However, some intrinsic characteristics hamper the cost-effective mass production of carbon nanomaterials; specifically, the CVD process is carried out at a high temperature in the range of 700–1000 °C, and the CVD chamber needs to be evacuated to prevent oxidation.

Recently, a plasma-assisted arc system under water has attracted significant attention as a novel production method because it can be operated at room temperature without a bulky chamber and evacuation system. After the first report by Sano et al., many works have focused on carbon nanomaterial production using a solution plasma system [12]. As metal nanoparticles (NPs) such as Fe, Co, Ni, and Au have generally been used as catalysts for CNT synthesis using CVD [13–15], the synthesis of CNTs in a solution plasma system was also previously reported using metal powders of Ni, Fe, Y, and Gd [16,17]. However, this approach requires a complex geometry of the graphite electrodes for insertion of the catalytic metal powder into the rods. The use of a solution that contains metal NPs such as metal sulfates or colloids would result in a more simple process and the continuous synthesis of carbon nanomaterials. Some attempts have already reported using metal sulfates as catalysts, including $NiSO_4$, $CoSO_4$, and $FeSO_4$, and alcohol or aromatic carbon solvents such as benzene have been employed for the liquid-phase carbon source [18–20].

Here, we present the construction of a laboratory-made simple solution plasma system that consists of rod-shaped graphite electrodes and a ferritin-mixed solution for cost-effective mass production of low-dimensional carbon nanomaterials. We especially focus on the effect of the diameter of the electrodes and the concentration of the ferritin molecules in the plasma system. Ferritin is

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a type of protein that consists of 24 subunits and contains iron compounds in its hollow inner space. Ferritin-induced iron-oxide NPs can be obtained through soft calcination and actively used as catalysts for single-walled CNT (SWNT) growth owing to their appropriate size, approximately 5 nm in diameter [13]. In addition, a high power, typically a few tens of volts (30–50 V) and amperes (30–80 A), was applied to the system using a direct-current power supply to ignite the arc discharge and produce nanomaterials under water [21–23]. Here, we adopt a high voltage of 15 kV at a frequency of 25 kHz using an alternating-current power source to reduce the power consumption of the solution plasma system. As a result, we confirmed the synthesis of graphitic platelets, onion-like structures, and carbon nanotubes. Furthermore, we demonstrate the fabrication of flexible conductive papers using the produced materials.

2. Experimental

The solution plasma system consists two graphite rod electrodes and a beaker filled with ferritin-mixed deionized (DI) water, as shown in Fig. 1. The ferritin-mixed solution was prepared by dilution of ferritin molecules (Sigma–Aldrich) in 1 L of DI water (18.2 MΩ), and the final concentration was adjusted to 1 and 5 μg/mL. We would expect that the ferritin-induced Fe nanoparticles may contribute to the production of material as a growth catalyst, as they were actively used in CNT growth [24,25]. The high-purity graphite rods (99.5%, Nilaco), which act as electrodes for plasma generation as well as a carbon source for carbon nanomaterial formation, were used with different diameters of 3 and 6 mm. The ends of the rods were prepared to have a conical shape with an angle of 28° for efficient plasma formation (Fig. 1). A high voltage of 15 kV at a frequency of 25 kHz was applied to the graphite electrodes to ignite the plasma in the solution. A relatively low power of 300 W, as compared with other reported solution plasma systems, was applied in this system [16–23]. For stable ignition of the plasma during synthesis, the gap between the graphite electrodes was constantly maintained at 1 mm by careful adjustment of the graphite rod through a micrometer. The synthesis time was varied from 1 to 5 h.

After synthesis, we prepared samples for characterization by dropping the solution from the upper part in the beaker. The characterization of the produced materials was performed using Raman scattering spectroscopy (Horiba, Aramis), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEM 2100F). For the Raman analysis, a laser with a wavelength of 532 nm and an output power of 3 mW was used as an excitation light source. The laser spot size was 1 μm, and the average profile of three random spectra was used as data. In order to prepare a flexible conducting film using the produced materials, vacuum filtration was performed using the solution, except for sediment. The sheet resistance of the prepared film was measured using a four-point probe (AIT, CMT-SR1000N).

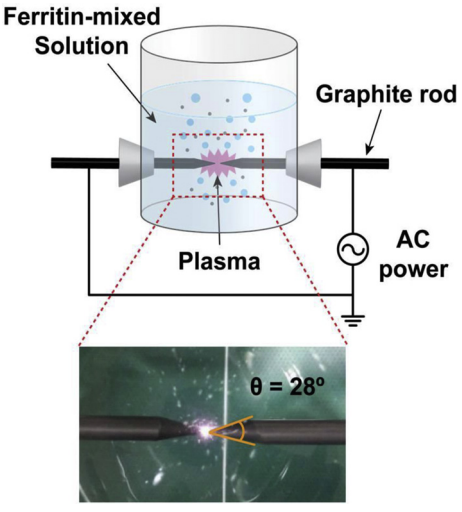

Fig. 1. Schematic of the solution plasma system. The photograph shows the conical shape of the graphite electrodes.

3. Results and discussion

Fig. 2(a) and (b) show SEM images of an as-prepared graphite rod and the planar surfaces of the rod. In order to investigate the effect of the ferritin molecules, we first ignited arc discharge using the solution without the addition of ferritin. Fig. 2(c) shows an SEM image of the plate-structured materials produced using rods with a diameter of 3 mm. The inset shows the same morphology of the products, and a more detailed nanostructure can be revealed by the TEM image in Fig. 2(d). The plate structures are greater than 100 nm in size. For rods with a diameter of 6 mm, the products also have a platelet morphology as shown in Fig. 2(e). According to the TEM observation results, the platelets exhibit graphitic structures with several layers, as representatively shown in Fig. 2(f).

Because there is a possibility that the observed products simply result from the delamination of the graphite rods during synthesis, we performed Raman spectroscopy to investigate the structural quality difference as shown in Fig. 2(g). Raman spectroscopy is a powerful tool for determining the structural integrity of carbon nanomaterials. There are three characteristic peaks around 1330 cm^{-1}, 1580 cm^{-1}, and 2700 cm^{-1}, which called D, G, and 2D bands, respectively. The structural disorder in carbon materials can be qualitatively confirmed from the intensity ratio of the D and G bands (I_D/I_G) as well as the full width at half maximum of the 2D band ($FWHM_{2D}$) [26]. The D′ band at 1625 cm^{-1} is also related to a disordered structure of the hexagonal network of sp^2 carbon and can be seen by peak splitting of G and D′ band. In addition, we can estimate the thickness of the synthesized graphite plates and multilayered graphene with the value of I_G/I_{2D} because the intensity ratio of the G and 2D bands (I_G/I_{2D}) is considered to be related to the number of layers in graphene films [27]. Here, the values of I_D/I_G, $I_{D'}/I_G$, I_G/I_{2D}, and $FWHM_{2D}$ of the as-purchased graphite rod are 0.96, 0.21, 1.98, and 71.3 cm^{-1}, respectively. The above values indicate the typical disordered structure of graphite due to the existence of edge structures. On the other hand, the corresponding values for the products after solution plasma synthesis in DI water are 0.48, 0.14, 1.87, and 68.2 cm^{-1} for 3-mm diameter rods, and 0.61, 0.20, 1.61, and 63.3 cm^{-1} for 6-mm diameter rods. Because lower values are obtained for the plasma-treated electrodes compared to those of the as-purchased rods, we can potentially expect that thinner and highly ordered graphitic plates are synthesized owing to the solution plasma process using DI water.

Next, we adopt ferritin molecules as a catalyst for the efficient synthesis of low-dimensional carbon nanomaterials. Fig. 3(a) and (b) show SEM images of the similar fibrous structures obtained after the solution plasma treatment using 1- and 5-μg/mL ferritin-mixed solutions with 3-mm electrodes, respectively. From the diameters of the fibers, which are significantly thicker than the ferritin protein, it is assumed that the fibers are not SWNTs but carbon-based materials because we only used ferritin and graphite rods in the plasma system. Additional investigation is needed to reveal the detailed structure.

Fig. 3(c) shows the typical Raman spectra from the products of the 1- and 5-μg/mL ferritin-mixed solutions. For the 1-μg/mL ferritin-mixed solution, the values of I_D/I_G, $I_{D'}/I_G$, I_G/I_{2D}, and