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# Reaction-mediated structuring of three-dimensional honeycomb-structured graphene scaffold

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## ABSTRACT

We demonstrated a facile approach for synthesizing three-dimensional (3D), honeycomb-structured graphene scaffold in the solid flame of a  $(0.5 + k) \text{Zn} + k\text{CuO} + (\text{CH}_2\text{-CHCl})_n$  reaction system. FESEM-based analyses of the acid purified porous graphene samples revealed that the synthesized graphene had a 3D, honeycomb-like structure with cell sizes of 20–100 nm and wall thicknesses of 1–3 nm. The specific surface area of the graphene sample prepared in the solid flame was about  $\sim 1043 \text{ m}^2/\text{g}$ .

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## 1. Introduction

Graphene, which comprises two-dimensional (2D) carbon sheets [1] has attracted great interest owing to its unique properties [2,3]. Numerous approaches have been developed for the synthesis of graphene, including mechanical cleavage [1], epitaxial growth [4], and chemical vapor deposition (CVD) [5]. In all these techniques, graphene sheets are fabricated on a substrate. In addition, the chemical exfoliation of graphite has been used for preparing graphene oxide solutions as well as graphene-based composite materials [6,7].

Of late, significant efforts are being dedicated to the design and development of methods for modulating the properties of graphene with different shapes [8–16]. Chen and co-workers synthesized graphene foam using porous Ni foam as a template for the CVD growth of graphene; the Ni skeleton was subsequently removed by etching [8]. Zhu et al. prepared porous graphene paper by the microwave-assisted exfoliation of graphene oxide, using KOH for activation [9]. Recently, Wu and co-workers reported the synthesis of three-dimensional (3D), hierarchical macro- and mesoporous graphene frameworks (GFs) from hydrothermally assembled 3D graphene aerogels and silica networks, respectively [10,11]. In addition, Yu et al. [12] and Hu et al. [13] have reported the fabrication of graphene tubes that could be selectively functionalized for use in a wide range of applications. Choi et al. synthesized macroporous graphene using

colloidal polystyrene particles in a graphene oxide suspension as sacrificial templates [14]. In this case, the pore sizes could be tempered simply by varying the size of the template particles [15]. These results suggest that it is possible to tune the properties of graphene sheets by controlling their shapes.

One of the facile and attractive methods for synthesizing graphene materials is self-propagating high temperature synthesis (also known as solid-state combustion synthesis) [16]. Graphene synthesis by solid-state combustion reaction between silicon carbide and polytetrafluoroethylene (PTFE) diluted by NaCl was recently reported by Manukyan et al. [17,18]. The graphene sheets synthesized by a described technique were consisted of single layer, bilayer and multilayer graphene sheets with 500–950  $\text{m}^2/\text{g}$  specific surface area. Gas-solid combustion reactions are also known to produce 2D graphene sheets. The known approaches includes the combustion of metals (Mg, Li, Ca, Ti, Al, Zr) in carbon dioxide, followed by the acid-purification of the solid product that was used to produce the multilayer graphene [19,20]. However, to the best of our knowledge, 3D, honeycomb-structured graphene scaffold has not been investigated widely. There has been only one report, by Wang et al., on the synthesis of carbon sheets with a 3D, honeycomb-like structure [21]. Wang and co-workers were able to fabricate the carbon sheets through a reaction between  $\text{Li}_2\text{O}$  and CO in a batch ceramic-tube reactor. The resultant black powder was identified as being carbon and had a specific surface area of 128–153  $\text{m}^2/\text{g}$  and pore size of 115–170 nm. However, the 3D, honeycomb-structured carbon powder obtained by this approach has a very low specific surface area and a relatively large honeycomb cell size (50–500 nm). Moreover, the method involves long processing times at 550 °C and cannot yield 3D, honeycomb-structured carbon scaffold.

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Herein, we introduce a simple, but efficient, approach for the 3D, honeycomb-structured graphene scaffold. In this method, graphene is synthesized in the solid flame of the exothermic mixture consisted of organic polymers (such as polyethylene, polystyrene, polyvinylchloride, polyvinyl alcohol, and polyvinyl acetate, among others), inorganic oxidant (such as  $\text{KClO}_3$ ,  $\text{CuO}$ , and  $\text{NH}_4\text{NO}_3$ ) and metal reductant (such as  $\text{Mg}$ ,  $\text{Al}$ , and  $\text{Zn}$ ) or both. The model system selected to test the process was formed by polyvinylchloride (PVC) with  $\text{Zn}$  powder and  $\text{CuO}$ ; this mixture was then subjected to burning process in an argon atmosphere. The process yielded a crude bulk sample consisting of a graphene scaffold along with reaction by-products. However, after chemical purification, 3D, honeycomb-structured graphene scaffold could be harvested.

## 2. Experimental

Copper oxide powder with an average particle size of  $10\ \mu\text{m}$  (purity 98%, Acros Chemical, USA) and polyvinylchloride powder with an average size of  $50\text{--}300\ \mu\text{m}$  (Junsei Chemical Co., Japan) were used as feedstock powder. Zinc powder (purity 99%, Samchun Chemical Co., Korea) was used as a reductive agent. The reaction mixture was  $k\text{CuO} + (0.5+k)\text{Zn} + \text{PVC}$  ( $k$  denotes the number of moles of  $\text{CuO}$ ). The  $k$  value of  $\text{CuO}$  was varied from 0–0.4 mol. The initial mixing of powders was carried out using a mortar and pestle for 15–20 min, and the as-prepared powder mixture was then loosely packed into a cylindrical paper cup ( $3.5 \times 7.0\ \text{cm}$ ). The cup was then placed at the center of a high-pressure reactor under a nickel-chromium wire. Vacuum was applied to remove air from the combustion vessel, which was then filled with argon gas at a pressure of 2.0 MPa. After the local ignition of the sample using a resistivity-heated nickel-chromium wire, a combustion wave formed and propagated throughout the reaction mixture. During the combustion process, a data acquisition system (GL200A, Graphtec Co., Japan) continuously recorded the time profile of two tungsten-rhenium thermocouples (W/Re-5 versus W/Re-26; diameter:  $100\ \mu\text{m}$ ) that had been inserted into the reaction pellet for temperature measurements. After the reaction mass was cooled to room temperature, a black solid was obtained. The combusted sample was leached by  $\text{HCl}/\text{H}_2\text{O}$  (1:2 v/v) and  $\text{HNO}_3/\text{H}_2\text{O}$  (1:2 v/v) solutions and rinsed with water to eliminate  $\text{ZnO}$  and  $\text{ZnCl}_2$  and  $\text{Cu}$  phases formed during the combustion process.

The crystal structures and morphologies of the final powders were characterized using an X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (Siemens D5000, Germany), field-emission scanning electron microscopy (FESEM) (JSM 6330 F) and transmission electron microscopies (FE-SEM TEM, JEOL JEM-1400, Japan). Specific surface area was determined using SA-9600 BET Surface Area Analyzer (Horiba). Raman scattering spectra were obtained at room temperature using a Horiba Jobin Yvon LABRAM-HR800 laser micro-Raman spectrometer with a 633 nm laser.

## 3. Results and discussion

The temperature-time profiles in the solid flame for the  $(0.5+k)\text{Zn} + k\text{CuO} + (\text{CH}_2\text{-CHCl})_n$  system for different  $k$  values (0, 0.1, 0.2, and 0.4) are shown in Fig. 1. The maximum temperature observed in the  $(\text{CH}_2\text{-CHCl})_n + 0.5\text{Zn}$  binary mixture ( $k=0$ ) was  $360\ ^\circ\text{C}$  (plot 1); this value is unusually low for a self-sustaining solid flame process. The temperature-time plot exhibits multiple stages, with quasi-isothermal fields being present at temperatures of  $180\text{--}220\ ^\circ\text{C}$  and  $300\ ^\circ\text{C}$ ; it is likely that these are related to the thermal degradation of PVC. Meanwhile, the plots corresponding to  $k=0.1\text{--}0.4$  were smooth and consisted of a single stage. The temperature increased continuously until a maximum was

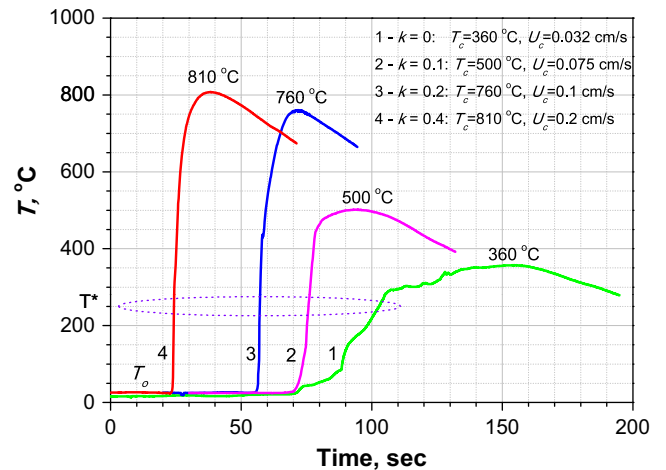


Fig. 1. Temperature-time profiles for the  $(\text{CH}_2\text{-CHCl})_n + (0.5+k)\text{Zn} + k\text{CuO}$  system for different  $k$  values: (combustion parameters (temperature,  $T_c$ , and wave velocity,  $U_c$ ) as functions of the  $k$  value are shown inset of Fig. 1).

reached; this temperature signifies the beginning of a localized reaction zone. Thereafter, a cooling process was initiated. Depending on the concentration of  $\text{CuO}$ , the period over which the temperature increased from the point of ignition ( $T^*$ ) to the maximum varied from a few tens of seconds to several seconds. Furthermore, the value of the maximum temperature increased with an increase in  $k$ , reaching  $810\ ^\circ\text{C}$  at  $k=0.4$  (plot 4).

The combustion parameters (i.e., the combustion temperature,  $T_c$ , and the wave velocity,  $U_c$ ) are shown as functions of the  $\text{CuO}$  concentration in the inset of Fig. 1. Both parameters exhibited an increase with an increase in  $k$ .

Fig. 2a shows the post-water-washing and post-HCl-leaching XRD patterns of the powder produced at  $k=0.2$ . After the powder had been washed with water, its XRD pattern contained peaks corresponding to three solid phases:  $\text{ZnO}$ ,  $\text{Cu}$ , and  $\text{Cu}_5\text{Zn}_8$  (carbon peaks intensity is low and hence cannot be clearly seen here) (Fig. 2a, plot 1). After the powder had been leached with  $\text{HCl}$ , peaks corresponding to crystalline  $\text{Cu}$  and  $\text{Cu}_5\text{Zn}_8$  were noticed (Fig. 3a, plot 2). Eventually, after the  $\text{Cu}$  and  $\text{Cu}_5\text{Zn}_8$  phases had been dissolved in a dilute  $\text{HNO}_3$  solution, the graphene peaks (0 0 2) and (1 0 0) could be seen clearly (Fig. 2b).

Fig. 3a shows the graphene scaffold synthesized from the  $(\text{CH}_2\text{-CHCl})_n + 0.7\text{Zn} + 0.2\text{CuO}$  mixture. The size of the species ranged from several millimeters to several centimeters, depending of the diameter of the particles of the initial sample and the leaching conditions. The microstructures of the synthesized graphene sample, after it had been leached with acids, are shown in Fig. 3b and c. As can be seen from the images, after leaching with  $\text{HCl}$  and washing with deionized water, which resulted in the removal of  $\text{ZnO}$  and  $\text{ZnCl}_2$ , 3D, honeycomb-like carbon with a few spherical submicrometer-sized particles of  $\text{Cu}$  and  $\text{Cu}_5\text{Zn}_8$  was obtained (Fig. 3b). Further leaching with  $\text{HNO}_3$  produced phase-pure porous graphene, which also exhibited a 3D, honeycomb-like structure and had a cell size of  $20\text{--}100\ \text{nm}$ . The thickness of the honeycomb walls (i.e., the graphene sheets) was approximately  $1\text{--}3\ \text{nm}$ , as estimated from Fig. 3c. Fig. 3d shows a high-resolution transmission electron microscopy (HRTEM) cross-sectional image of the stacked cells of the synthesized graphene sample. The interplanar distance,  $d_{002}$  (i.e., the spacing of the (0 0 2) planes) was determined to be  $0.37\ \text{nm}$ ; this value is larger than that of graphite ( $d_{002}=0.34\ \text{nm}$ ).

The Raman spectra of graphene synthesized by combustion method are shown in Fig. 4a. The spectra exhibit a structure characterized by three principle bands designated as the D, G and 2D bands. The D band usually appears when defects within the carbon lattice are present. The G band at  $1586.41\ \text{cm}^{-1}$  is an in-plane

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