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Size and Structural Effect of Crumpled Graphene Balls on the Electrochemical Properties for Supercapacitor Application

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ABSTRACT

Effect of size and structure of a three-dimensional (3D) crumpled graphene balls (CGBs) on the electrochemical performance was investigated for supercapacitor application. Different sized CGBs were firstly fabricated by one-step aerosol spray pyrolysis. Electrochemical performance of 3D CGBs for supercapacitor was then measured with respect to size and structural characteristics. The average size of CGBs was controlled in a range of 0.3 to 0.7 μm. CGBs were composed of a few tens of 2D graphene sheets, resulting in different porous structures. CGBs exhibited higher specific surface area and smaller pore volume, and they are composed of micro- and mesopores. The electrochemical performance of supercapacitors fabricated with the as-prepared CGBs, having a different morphology and pore structure, was then evaluated. The maximum specific capacitance of 156 F/g was obtained when 0.7 μm CGBs were employed. In that case, the highest specific energy density and power density were approximately 22 Wh/kg and 4 kW/kg, respectively.

1. Introduction

Supercapacitors, also known as electrochemical double layer capacitors (EDLCs), have been of great interest as one of the most attractive energy storage devices due to their high power density (>10 kW/kg), long cycle life (>10^5), and fast charge–discharge processes (within seconds) [1,2]. EDLCs store electrostatic charges accumulated at the electrode/electrolyte interface; therefore, these devices are strongly dependent on an abundant porous texture combined with suitable pore size distribution in an electrode material so that their surfaces are accessible to the electrolyte ions [3]. Carbon based porous materials, such as activated carbon [4,5], activated carbon fibers [6], carbon aerogels [7], carbon nanotubes [8,9], mesoporous carbon [10], carbide derived carbon [11], etc., have been widely investigated as electrode materials for EDLCs. A new class of carbon materials, graphene has received rapidly growing attention for use in EDLCs because of its high specific surface area, great mechanical strength, and high electrical conductivity [12–15]. In addition, graphene can be manufactured using cost-effective chemical methods with high yield, making graphene a potentially promising active material for commercial and industrial applications [16–18]. However, due to strong van der Waals attraction, the typically two-dimensional (2D) sheet-like graphene tends to aggregate and restack irreversibly during electrode fabrication. This major hurdle leads to the loss of actual surface area and of solution accessibility, both of which are detrimental to EDLC performance.

To solve this problem, the use of a three-dimensional (3D) graphene architecture has been demonstrated as one of the most effective strategies to inhibit the aggregation and stacking of 2D graphene sheets (GSs). Much effort has been devoted to the rational design and synthesis of 3D graphene materials using such methods as chemical vapor deposition (CVD) [19], the template-induced method [20], and ice-segregation induced assembly [21]. Recently, Luo et al. and Mao et al. have reported a novel strategy to prepare CGBs with aggregation-resistant properties via aerosol spray pyrolysis (ASP) process [22,23]. It has also been revealed that the ASP method has many advantages because it is facile, low cost, and easy to scale up for mass production of 3D CGBs. Luo et al. also demonstrated that CGBs maintained higher and more stable specific capacitance compared to that of flat and wrinkled GSs because of the aggregation-resistant properties of CGB [24]. Since a

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single CGB is composed of a few tens of 2D sheets, it has an interesting pore structure that influences its charge transport and the access of electrolyte ions. The pore structure varies for CGBs with different particle sizes, which can be synthesized at different graphene oxide (GO) concentrations. From this point of view, the size dependent property of CGBs, which can have different pore structures, is the characteristic parameter of CGBs that holds the most potential for achieving optimal performance of supercapacitors. This is because different sized CGBs should have different particle size distributions as well as different levels of electronic conductance; nevertheless, very few actual investigations have been focused on this area of research. Moreover, to the best of our knowledge, no clear relationship between the morphological structure of CGBs and the performance of EDLCs has ever been addressed systematically.

In this study, we present interesting results on the performance of supercapacitors fabricated with CGBs having different sizes and pore structures for the first time. The CGBs were prepared from GO colloidal solutions with different concentrations using a one-step ASP as shown in Fig. 1. We analyzed the morphology, diffraction pattern, degree of disorder, specific surface area and pore size distribution of the CGBs synthesized with different diameters. We then measured the electrochemical characteristics such as the specific capacitance, electrical conductivity, and long-term stability of the as-prepared CGB supercapacitor electrodes using two-electrode system.

2. Experimental section

2.1. Preparation of crumpled graphene ball

GO was synthesized from graphite (99.9% purity, Alfa Aesar, USA) by modified Hummers and Offeman's method [16,17]. A schematic diagram of the synthesis of CGBs by the aerosol pyrolysis process is shown in Fig. 1. A colloidal solution as an aerosol precursor was prepared by dispersing the as-prepared GO in deionized water. The colloidal solution was sprayed using a nebulizer (Alfesa Pham Co. UN-511, Japan), which generated droplets with sizes of 1 ~ 10 μm. Using 1.0 L/min of Ar gas, the sprayed droplets were then carried into a heating zone of a furnace. Then, capillary compression generated by the evaporation of water in the sprayed droplets lead to form crumpled GO. At the same time, the GO sheets were thermally reduced in situ, producing the CGBs as indicated by the color change from brown to black [25,26]. The length and diameter of the heating zone were 40 and 2.5 cm, respectively. The residence time of the droplets in the furnace was 12 s at 400 °C. The different CGBs were prepared with GO solutions with concentrations ranging from 0.01 to 0.5 wt%, while keeping the operating temperature at 400 °C.

2.2. Analysis

The morphologies of the as-prepared CGBs were observed with a field emission scanning electron microscope (FE-SEM; Sirion, FEI). The crystallinities of the as-prepared CGBs were analyzed with X-ray diffractometry (XRD; SmartLab, Rigaku Co.). The molecular species of the particles were measured using Raman spectra (Lambda Ray, LSI Dimension P1) at wave numbers ranging from 1000 to 3000 cm^{-1} with excitation of a 532 nm laser. The specific surface area was characterized by analyzing the N_2 adsorption-desorption isotherms (BET; Tristar 3000, Micromeritics, USA) using the BET equation; the pore size distributions were analyzed from the desorption branches of the isotherms based on the Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical measurement

The electrochemical behavior of the CGB samples was characterized by constant current charge/discharge and impedance measurements with two symmetric electrodes in an HS FLAT CELL (HOHSEN Corp., Japan) using an electrochemical interface instrument (VSP, Bio-Logics, USA). Fabrication of the electrodes for the supercapacitors was conducted as follows. For each electrode, the CGBs were mixed with polyvinylidene difluoride (PVDF) binder (mass ratio, CGB: PVDF = 9:1), and then the correct amount of n-methyl-2-pyrrolidone (NMP) was added. After 20 min of mixing, a uniform suspension was obtained; this suspension was dried at 80 °C for 2 h in vacuum. The CGB electrodes were prepared by cutting out areas of ~2 cm^2 and then stacking them to achieve a mass loading of 5 mg per electrode. KOH solution (5 M) was used as the electrolyte; a piece of filter paper (Waterman, GF/C) was used as a separator.

3. Results and discussion

Fig. 2 shows FE-SEM images of the as-prepared CGBs with different concentrations of GO colloidal solutions prepared via an ASP process. The average size of the CGBs gradually increased from 0.3 to 0.7 μm along with the initial GO concentrations in the aerosol droplets (Fig. S1, see the ESI). The CGBs exhibited a quasi-spherical morphology composed of a few tens of 2D GSs. It was found that the size of the CGBs was effectively controlled by varying the concentration of GO in the aerosol droplets. Since the GO sheets in the sprayed droplets partially overlapped during crumpling as the droplet size decreased due to the evaporation of solvent in the droplet, a higher GO concentration resulted in thicker GO sheets and further led to less crumpled, larger particles with larger-sized pores, indicating that the size of the CGBs can be tuned by controlling the initial GO concentration. The porous structure of the CGBs can prevent severe face-to-face restacking as the CGBs are packed into an electrode. It was also seen that these CGBs, although they all exhibit similar 3D networks, present different pore size distributions, for example, plenty of larger meso/macropores appeared and micropores were barely produced in the CGBs with lager size.

The XRD patterns of the CGBs prepared at different concentrations of 0.01, 0.05, 0.1, and 0.5 wt% are shown in Fig. 3. The standard card of graphite (JCPDS No. 26-1079) shows seven well defined diffraction peaks that are characteristic of graphite, with the most intense (002) peak centered at 26.6°; on the other hand,

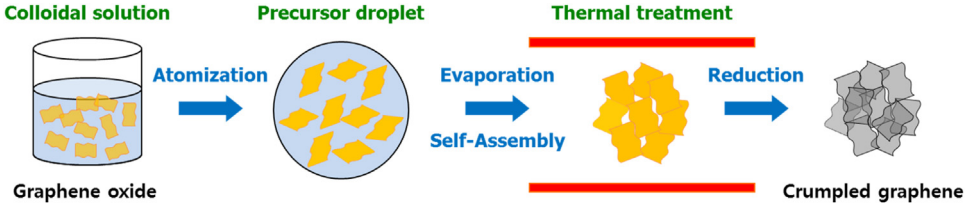

Fig. 1. Schematic illustration of the formation of CGB from GO colloidal solution via aerosol spray pyrolysis.