

Fabrication and properties of three-dimensional nanoporous graphene foams with magnesium binder



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ABSTRACT

Three dimensional (3D) nanoporous graphene foams with magnesium as binder were fabricated by spark plasma sintering (SPS) technique. Their microstructures, adsorption properties of nitrogen and mechanical properties were investigated. Experimental results showed that the nanocomposite graphene foams can be fabricated with magnesium binder by the SPS at temperature of 650 °C. The resulting graphene foams exhibited average nanopore size of 5–6 nm and surface area up to $(304.4 \pm 8) \text{ m}^2/\text{g}$, and high compressive strength up to $(4.23 \pm 0.09) \text{ MPa}$. Our results demonstrate a facile strategy for the fabrication of 3D nanoporous graphene foams with tailored structure and properties by using the SPS.

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Graphene is a two-dimensional material and has attracted tremendous attention due to its extraordinary properties, such as excellent mechanical features, high conductivity and a large specific surface area [1]. Three-dimensional (3D) graphene foams with micro- or nano-pores may benefit from these properties to achieve outstanding performance. There are numerous reports showing remarkable features of graphene foams [2,3], such as low density, large specific surface area and satisfactory electrical conductivity and so on. Porous graphene foams have been extensively applied in various applications [4,5], such as electrodes, energy storage units in supercapacitors, bio and gas sensors, and efficient liquid or gas sorbents.

The fabrication of graphene foams can be divided into template-dependent and template free protocols. The template-dependent strategy can generate porosity with low densities and well-controlled porous structures [2,5]. For example, graphene foams have been prepared by chemical vapor deposition using nickel foam as a template, and the nickel template was etched away in some chemical solution finally [6,7]. The hydrophobic silica template has been used a template to produce nanoporous graphene foams by calcination and silica etching subsequently [8]. However, this template-dependent strategy suffers from problems of high cost, low yields and template residue after etching. Template free strategy is much cheaper and more suitable for massive production

[9,10]. For example, graphene sponge has been assembled with graphene oxide sheets by hydrothermal treatment with the assistance of thiourea [11]. Freeze casting is also a recently developed template-free strategy for graphene foam fabrication [10]. So far, the graphene foams prepared by both of these two strategies exhibited very low mechanical strength with compressive stress up to 204.4 kPa at temperature of -170 °C [2,10]. Therefore, this study will explore a new template free method to improve the mechanical properties of the graphene foams and at the same time to achieve nanoporous structures.

Spark plasma sintering (SPS), which is also called pulsed electric current sintering (PECS) or field assisted sintering technique (FAST), is an electric field assisted sintering process utilizing ON-OFF DC pulse energizing [12]. The SPS process is based on electrical spark discharge phenomenon. Due to the repeated application of an ON-OFF DC pulse voltage and current in powder materials, the spark discharge point and the Joule heating point (local high temperature-state) are transferred and dispersed to the overall specimen. During SPS treatment, powders contained in a die can be processed for diverse novel bulk material applications [13], for example nanostructured materials, fine ceramics, functional graded materials, hard alloys, biomaterials, porous materials, etc. The SPS has been used to prepare diverse advanced materials; nevertheless, it is still a relative new technique for the fabrication of nanoporous materials.

In this study, the SPS is employed to prepare the 3D graphene foams in order to improve their mechanical properties and to

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achieve nanoporous structures. The magnesium (Mg) and magnesium hydride (MgH_2) are used as binder and pore forming agent, respectively. The microstructures of the nanocomposite graphene foams are analyzed by using X-ray diffraction, scanning electron microscopy. Their adsorption properties of nitrogen (N_2) and mechanical properties of the foams are investigated.

The graphene nanoplatelets obtained from XG Sciences (USA) were unique nanoparticles consisting of stacks with less than 10 sheets having platelet shapes with surface areas of $750 \text{ m}^2/\text{g}$ (Grade C750). This led to particle thicknesses of less than 2 nm and diameters of less than $2 \mu\text{m}$. The concentration of N_2 was less than 2 at.%, and the concentration of oxygen was below 8 at.%. Mg powder and MgH_2 powders with high purity (99.0%) and particle size of $10 \mu\text{m}$ were used. The graphene nanoplatelet powders and Mg powders as well as MgH_2 powders were mixed by using a rotating cylinder ball mixing machine for 10 h. The weight ratio of graphene and Mg powder was 2:1. The MgH_2 powders was doped with 0 wt.%, 11 wt.%, 33 wt.%, 56 wt.% and 78 wt.% of total weights of graphene and Mg powders. SPS experiments were conducted in a spark plasma sintering furnace FCT-HP-D5 (FCT Systeme GmbH, Germany) installed at School of Materials Science and Engineering, Southeast University. The powder mixtures were pressed into a 10 mm diameter graphite die with a special design. A heating rate of $100 \text{ }^\circ\text{C}/\text{min}$ was adopted and the sintering holding time lasted typically for 5 min. The sintering temperatures were measured by thermal couple and tested at temperatures ranging from $550 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$. The sintering process was performed under Ar condition. The applied direct pulsed current for SPS was 1000–2000 A with pulse lengths of 12 ms on-pulses and 2 off-pulses. The final samples were cylinder-shaped samples with diameters of 10 mm and height of 10 mm.

The density was evaluated from the weight and the apparent volume of the specimens. The relative density calculation was made by dividing the density of the cellular specimen by density of the parent one. X-ray diffraction (XRD, D8-Discover, Bruker) was used to characterize the phase composition of the powders and the sintered foams. The morphologies of the graphene foams were investigated by using field-emission scanning electron microscope (SEM, Sirion, FEI). Nitrogen adsorption on the graphene foams were measured by the Micromeritics Accelerated Surface Area and Porosimetry System 2020 (ASAP 2020, America) Analyzer. The materials in the form of solid foams (with sample mass of at least 200 mg) were degassed within two stages. In the first stage, samples were degassed under an evacuation phase for 2 h and later in a heating phase for 10 h at $300 \text{ }^\circ\text{C}$. After cleaning, the samples were plugged into the Analyzer. Incrementally dosing of N_2 into sorbent tubes was applied to analyze at different pressures. The specific surface areas were calculated by using the Brunauer Emmett and Teller (BET) equation through N_2 adsorption isotherms collected at $-196 \text{ }^\circ\text{C}$. The pore size distributions in the materials were measured using Barrett-Joyner-Halenda (BJH) analysis following the adsorption of N_2 on the foams. The mechanical properties of the fabricated foams were evaluated by compression tests, each with five specimens per unit cell size. The stress measurements were carried out on an electronic universal testing machine (CMT4503, SANS), equipped with a 5.0 kN load cell at $0.5 \text{ mm}/\text{min}$ with loading direction parallel to the building direction. The compressive stresses were determined from stress–strain curves. The elastic modulus of the foams was calculated from the linear regime of the loading curve by dividing the compressive stress by the strain.

The fabrication process of the 3D graphene foams by using the SPS is schematically elucidated in Fig. 1. The Mg and MgH_2 powders were sieved to particle size of around $10 \mu\text{m}$. These two kinds of powders with graphene nano-particles were weighted to the required fractions (Fig. 1a). Then, the powders with different

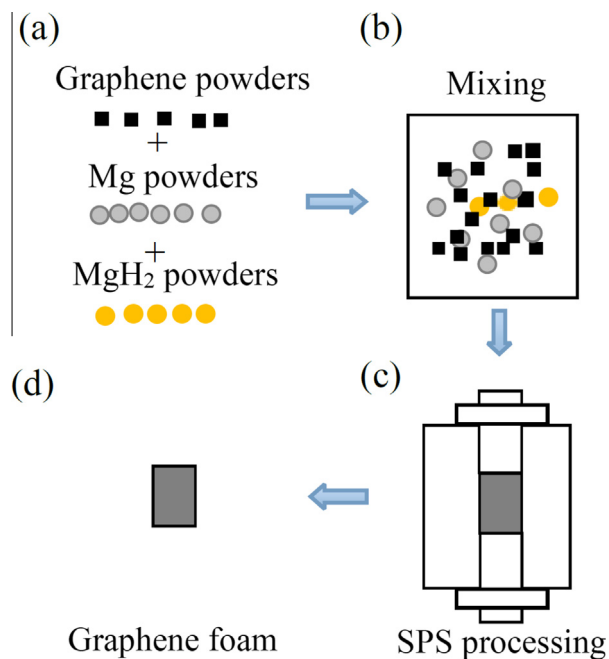


Fig. 1. Schematic illustration of the pore forming process by using the SPS: preparation of the graphene, Mg and MgH_2 powders (a), mixing of the graphene, Mg and MgH_2 powders (b), processing by the SPS with a special mold design (c), obtaining of the graphene foams (d).

weight ratios were mixed thoroughly (Fig. 1b). Additionally, the apparent density of the graphene/Mg/ MgH_2 powder mixtures was measured. The powders were weighted with two times of the apparent density multiplied by the volume ($\Phi 10 \times 10$), and then were subjected to spark plasma sintering at various parameters (Fig. 1c). The force applied during the SPS was controlled by a special design of the graphite die. At the beginning of sintering, the up-punch of the die got in touch with the powders at the minimum pressure of SPS (3 kN). Hence, the electric current can flow through the graphene sample. The travelling of the up-punch stopped when the graphite hoop contacted with the form. The final internal height of the graphite form chamber is 10 mm. After sintering, the graphene foams with a cylinder shape were obtained.

Fig. 2(a) shows a digital photo of the spark plasma sintered graphene foams using magnesium binder. The final sintering parameter for these foams is $650 \text{ }^\circ\text{C}$ for holding time of 5 min in the SPS. The diameter of the graphene foams is 10 mm with height of 10 mm. It shows that the porous graphene are free-standing foams. Fig. 2(b) demonstrates the X-ray diffraction patterns of the raw graphene and spark plasma sintered graphene foams. The graphene nanoplatelet powders show a main diffraction peak at 2θ of 26.38° corresponding to the graphite-2H (002) plane, and weak peaks at 2θ of 42.2 and 54.5° corresponding to the graphite-2H (100) and (004) planes, respectively. After the SPS processing, it is shown that the foams consisted composition of mainly graphene and magnesium phase, which are nanocomposite foams. There are a small amount of MgC_2 phases, which are due to the chemical reaction between the graphene and magnesium during the sintering. The MgH_2 was decomposed into Mg and H_2 with heating in argon. The reaction between the H_2 and the graphene was not detected by the XRD. The microstructures of the graphene foams were inspected by the SEM. Fig. 2(c and d) shows the SEM micrographs of the fracture surfaces of the sintered graphene foams at various magnifications. The low magnification micrograph in Fig. 2(c) shows that the fracture surfaces contain few sub-micrometer pores less than 500 nm. The higher magnification

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