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Fabricating graphene hydrogels with controllable pore structure via one-step chemical reduction process

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A B S T R A C T

The porous graphene hydrogels (GHs) are of particular interest in various applications, such as energy-storage devices, catalyst and sensors. In this paper, GHs with controllable pore structure are prepared from graphene oxide (GO) aqueous dispersion by a facile chemical reduction method. The pore size distribution (PSD) and specific surface area (SSA) of GHs can be regulated by adjusting the pH value of GO dispersion. It is found that both the pore size and SSA of GHs gradually increase with the pH value of GO dispersion. For the GH prepared at pH = 1.65, the PSD has one peak at 1.83 nm with a SSA of 723.35 m^2/g. As the pH value increases to 11.73, the peak moves to 3.2 nm and the SSA keeps rising to 1107.24 m^2/g. Rheological measurements show that both the storage modulus and yield stress of the GHs decrease with the increasing pH value. Electrochemical evaluation of GHs as the electrodes of supercapacitors reveals that the specific capacitance reaches the highest value for GH prepared at pH = 5.25, which has a specific pore structure, showing the coexistence of large (3.2 nm) and small pores (1.89 nm).

1. Introduction

During the last decades, graphene has aroused increasing interest considering its extraordinarily electrical, thermal and mechanical properties [1–3]. But the severe agglomeration and restacking of graphene sheets, as a result of the π-π interactions between neighbouring graphene sheets, hinders its practical application [4,5]. Fabricating 2D graphene nano-sheets into 3D macroscopic materials with porous network, can partly preserve the inherent structure and properties of graphene sheets, thus has attracted considerable interest. Due to the synergistic combination of the graphene characteristics and the unique micro-structure, 3D macroscopic graphene materials display super performance in versatile applications such as: energy storage [6–8], environmental systems [9–11], catalysis [12,13] and sensors [14,15]. For these applications, the pore characteristics, such as specific surface area (SSA), pore structure and pore size distribution (PSD) of these graphene materials have great influence on the performance [16,17]. In supercapacitors, it is widely accepted that larger pores are better for the penetration/distribution of electrolyte and thus preferable for enhanced performance [18–20]. But some other reports revealed that the performance could be significantly improved when the 3D micro-structure presented appropriate PSD [21–23]. Mechanical strength is another property that affects the application of 3D graphene materials. Recently, a kind of 3D macroporous graphene materials with different morphology were prepared using hexane droplet as the template [24]. The morphology of these materials could be modulated by adjusting the concentration of graphene oxide (GO) dispersion and then greatly influenced the mechanical properties.

Apart from numerous methods that have been developed to prepare graphene hydrogels (GHs), self-assembling technique, especially using GO dispersion as the precursor, attracts particular interest because it is low cost, controllable and large scalable [6,25,26]. GO, containing a large number of oxygenated functional groups, can be easily dispersed in water and interact with each other to construct GHs [27,28]. Xu et al. first reported that GO dispersed in aqueous could be hydrothermally reduced and then self-assembled into GHs, which were mechanical strong, electrical conductive and thermal stable [29]. After that, many reducing agents have been applied to assist the preparation of GHs in milder condition, such as vitamin C [26,30], $FeSO_4$ [31], HI [32] and hydroquinone [20]. The pore size of the as-prepared GHs was always randomly distributed, ranging from submicrometer to several micrometers. Many efforts have been paid to optimize the synthesis method to prepare GHs with preferable internal structure [17,19,33]. Incorporating metal oxides into GHs, for example, not only brings GHs with novel properties but also weakens the

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interactions between graphene sheets and enlarges the pore size [7,34]. There also has been reported that the self-assembling process could be optimized by changing the fraction of $KMnO_4$ and concentration of GO, allowing to the formation of GHs with different pore size and pore wall structure [25]. Another interesting work is that combined pre-reduction process with hydrothermal reduction can suppress the shell formation and thus prepared GHs with different architecture [35]. However, the reported methods of manipulating the pore structure of GHs are of multi-step and complicated with limited regulating capability.

Herein, we describe a facile one-step method in which GHs with continuous changing pore characteristics can be fabricated from GO dispersion via a modified chemical reduction process. Prior to chemical reduction, different mass of H_2SO_4 or NaOH solution is added into GO dispersion to regulate the pH, achieving the formation of GHs with tunable pore structure. As the pH value of GO dispersion increases, both the size and the pore diameter of the GHs gradually increase, while the thickness of pore wall decreases. The changing behaviour of the resulting GHs is systematically investigated and a possible mechanism is proposed. Based on these GHs with various pore structure, the rheological and electrochemical measurements are conducted to investigate the relationship between pore structure and properties of GHs. The GHs prepared at lower pH range have higher mechanical strength as a result of the thicker pore walls. While the best capacitance performance is obtained at the middle pH value, i.e. pH = 5.25, where the pore structure of the hydrogel demonstrates an appropriate PSD with the coexistence of large and small pores.

2. Experimental

2.1. Materials

Graphite powder (325 mesh, 99.95%) and sodium ascorbate (99%) were supplied by Aladdin (Shanghai, China) and used as received. Concentrate sulfide acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30 wt%) and hydrochloric acid were obtained from Kaixin Chemical Reagent Co., Ltd. (China). Sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) were all of analytic grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China). All chemicals were used without further purification.

2.2. Preparation of GO

GO was prepared from graphite powder by modified Hummers' method [36,37]. In brief, 5 g graphite powder was first mixed with 2.5 g $NaNO_3$ in a 2000 mL round flask, 115 mL concentrate sulfide acid was then poured into the flask in an ice bath with vigorous agitation for 2 h. After that, 25 g potassium permanganate was slowly added into the flask in 30 min while the system was kept in ice bath to maintain the temperature under 20 °C. The ice bath was then removed, followed by heating the suspension to 35 °C for another 1 h reaction, forming a thick paste. At the end of the reaction, 230 mL water was slowly added into the flask with an increasing temperature to 95 °C, and the suspension stayed at this temperature for another 15 min. Next, the suspension was further diluted by 700 mL hot water together with 20 mL H_2O_2 (30%). The mixture was then filtered and washed by 1:10 HCl solution followed by washing with hot water and centrifugation for three times. Later the resulting solid was dispersed in 700 mL water with the help of ultrasonication for 1 h and then submitted to centrifugation at 8000 rpm for 10 min to remove the undissolvable particles. Finally, the GO aqueous dispersion (about 7 mg/mL) was obtained as a result of further purification by dialysis for 1 week.

2.3. Preparation of GHs

The GHs were prepared by a modified chemical reduction method [29,38]. Typically, 10 mL GO dispersion (3 mg/mL) was firstly submitted to ultrasonication for 20 min to further exfoliate the GO sheets followed by adding 66 mg sodium ascorbate under ultrasonication to form homogeneous dispersion. And then the pH of the GO dispersion was adjusted by adding NaOH or H_2SO_4 solution. Successfully, the mixture was sealed in a glass vial and heated at 90 °C for 3 h to form the GHs. Finally, the GHs were purified by dialysis for following experiments.

2.4. Characterization

The micromorphology of the freeze-dried GHs was investigated by scanning electron microscopy (SEM) using a Zeiss Merlin SEM. The zeta potential of graphene oxide dispersion was measured by Zetasizer Nano-ZS instrument (Malvern Instruments). Powder X-ray diffraction (XRD) analysis of freeze-dried GHs was carried out on Bruker D8 ADVANCE diffractometer with Cu Kα radiation generator. The surface chemistry of the GHs was studied on Thermo Scientific Escalab 250Xi with an exciting source of Al. Fourier transform infrared spectra (FTIR) of GO and GHs was obtained using a VERTEX 33 instrument, Bruker, German. Raman spectra were taken by a LabRAM Aramis (HORIBAJobinYvon, France) with $\lambda_{exc} = 532$ nm. Pore size distribution was measured from N_2 absorption at 77 k using the TriStar II 3020 (Micromeritics Inc.) system and calculated according to the Barret–Joyner–Halenda (BJH) equation. The samples were applied to degas at 150 °C for 12 h before the analysis.

The water content of the GHs (C_w) was measured according to $C_w = (M_{GH} - M_D)/M_{GH} \times 100\%$ [29], where M_{GH} is the original weight of GHs and M_D is the weight of the freeze-dried GHs.

The rheological investigation of GHs was performed on MCR 300 (Paar Physica) Rheometer at 25 °C. A 25 mm parallel-plates geometry was chosen with the fixed gape distance of 2 mm. The dynamic frequency sweep experiments were measured from 1 to 100 rad/s and the oscillatory strain was set to be 0.2% followed by the oscillatory strain sweep measurements.

The electrochemical properties of the hydrogels were measured by a conventional three-electrode system using 1 mol/L H_2SO_4 aqueous solution as the electrolyte. In a typical procedure, GHs were first cut into slices with the thickness of 2 mm, and then immersed in 1 mol/L H_2SO_4 aqueous solution for 12 h to ensure the complete penetration of electrolyte. After that, the as-prepared slices of GHs were fixed by a platinum clip to make the working electrode. The saturated calomel electrode (SCE) and platinum plate were used as the reference and counter electrode, respectively. Both electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were carried out on the electrochemical workstation (PGSTAT 302N, Metrohm AG, Switzerland). CV measurements with different scan rates were performed in the potential window of 0–0.8 V. The specific capacitance values were calculated from the CV curves according to the formulation, $C = A/2ms\Delta V$, where A is the integration of CV curve, m is the mass of electrode, s is the scan rate and ΔV is the potential window.

3. Results and discussion

3.1. Structure of GHs

The preparation procedure of GHs with different pore structure is illustrated in Fig. 1a. A series of GO/sodium ascorbate suspensions are first mixed with NaOH or H_2SO_4 solution to adjust the pH to be