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Understanding the structure-property relationships in hydrothermally reduced graphene oxide hydrogels

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ABSTRACT

Graphene hydrogel (GH) has attracted increasing attention in energy storage and conversion, pollutant adsorption, catalysis, sensors and tissue engineering applications. However, a good understanding of the structure-property relationship is essential to precisely tune their properties. In this work, a pH assisted hydrothermal process was used to synthesize reduced graphene oxide (rGO) hydrogels with different three-dimensional (3D) porous structures. We systematically investigated the structure-property relationships in the GH, with a focus on the effects of geometrical dimensions of the pore structure. We found that the best mechanical properties were achieved in a compact microstructure consisting of small pores but thick walls. Despite having a lower C/O ratio, the compact structure gave rise to the highest electrical conductivity, attributed to the highly interconnected 3D porous structure providing conductive pathways. On the other hand, the hydrogels prepared under basic conditions exhibited higher C/O ratio but lower mechanical and electrical properties due to the disordered pore structure with large pores and thin walls.

1. Introduction

Graphene consists of sp^2 hybridized carbon atoms in a hexagonal two-dimensional (2D) lattice and has extraordinary mechanical, thermal and electrical properties. However, one problem in practical applications is the aggregation and restacking between neighbouring graphene layers. In contrast, transforming 2D graphene sheets into graphene hydrogel (GH) consisting of a three-dimensional (3D) porous structure is a possible way to mitigate this problem. Recently, 3D GH has been widely investigated in energy storage and conversion [1–4], catalysis [5,6] and sensors [7,8]. Furthermore, its high accessible surface area provides large adsorption capacities for toxic gases and pollutants and can be conveniently recycled due to its good mechanical strength [9–11]. With its bio-compatibility, the potential application also includes cartilage and bone tissue engineering [12,13].

Various methods have been practised to produce GHs, but the sol-gel process is the commonly used approach, in which an aqueous graphene oxide (GO) dispersion is gelatinized via reduction of GO, followed by supercritical or freeze drying. Sol-gel process can be carried out across a range of temperatures either by utilizing small molecules [14,15] or polymers [16] acting as cross-linkers or simply using concentrated GO dispersions. Gelation of GO can be realized by hydrothermal reduction [12,17] or chemical reduction [18,19]. Compared with the chemical-assisted reduction process, hydrothermal reduction attracts increasing interest because it generates lower impurities caused by reduction agents. Xu et al. reported the synthesis of a mechanically strong and electrically conductive GH by the hydrothermal reduction process [17]. During the hydrothermal reduction, the interconnected 3D porous framework of GH is formed by overlapping and coalescing of rGO sheets due to strong π- π, hydrophobic and electrostatic interactions. Zhou et al. observed that rGO is much more dispersible in water when GO is hydrothermally reduced in basic pH compared to acidic pH [20]. Mungse et al. carried out the hydrothermal reduction over a wide range of temperature and pressure and proposed several deoxygenation mechanisms for the elimination of hydroxyl, epoxy, carboxyl and carbonyl groups [21]. Several efforts were made to optimize the synthesis process to generate GHs with controlled internal structure and properties by introducing molecules/ions and adjusting reaction parameters [14,18,22]. However, those methods introduce non-carbon impurities to the resulting GHs, and also proved less effective when it came to optimizing the properties.

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Understanding the self-assembly mechanism and the reduction of GO is extremely vital when determining the structure and the properties of the resulting GH. A fundamental understanding is required to manipulate the behaviour of GO sheets in aqueous dispersion to precisely tune the final properties of the GH. We hydrothermally reduce the GO dispersion at different pH values to obtain GHs with different pore structures. We characterized the porous structure of each GH by measuring the pore dimensions in terms of pore width, pore wall length and pore wall thickness, to systematically reveal the structure-property relationship. Our study demonstrates that the unique 3D macroporous architecture is the key factor that governs the properties and ultimately determines the practical applications of GHs.

2. Experimental

2.1. Materials

Graphite powder was purchased from Sigma Aldrich (Pvt.) Ltd. Sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2, 30 wt%) were purchased from Chem-Supply (Pvt.) Ltd. Sodium hydroxide (NaOH) pellets and *ortho*-phosphoric acid (H_3PO_4 85%) were purchased from Merck KGaA. Hydrochloric acid (HCl 32%) was purchased from Ajax Finechem (Pvt) Ltd.

2.2. Preparation of GO

GO was prepared by oxidation of graphite powder by improved Hummers' method [23]. In brief, a 9:1 mixture of H_2SO_4/H_3PO_4 was added to a mixture of graphite and $KMnO_4$ (1:6). The reaction was heated to 50 °C and stirred for 12 h. Then the reaction mixture was cooled down to room temperature and poured onto a mixture of ice (~400 mL) and H_2O_2 (3 mL). The final product was sieved through a metal US standard testing sieve (250 µm) and the filtrate was centrifuged at 4000 rpm for 30 min. The precipitate was washed with DI water, HCl and ethanol several times. The final precipitate was dissolved in DI water and freeze dried for 72 h.

2.3. Preparation of GHs

A 30 mL homogenous dispersion of GO in DI water (3 mg/mL) was obtained by employing an ultrasonicator for 30 min. The pH value of the GO dispersion was adjusted to 2.04, 4.46, 6.97, 9.52 and 12.03 by adding either HCl or NaOH. Then the resulting GO dispersion was sealed in a Teflon-lined autoclave and was hydrothermally treated at 180 °C for 12 h. Finally, the as-prepared GHs hereafter referred to as GH-2.04, GH-4.46, GH-6.97, GH-9.52 and GH-12.03, respectively were immersed in deionized water for at least 72 h, while filtering the water every 6 h in order to wash out excessive HCl and NaOH which were added to the GO dispersion prior to hydrothermal reduction.

2.4. Characterization

The “freeze dried GHs” (graphene aerogel, GAs) were used to study the microstructure, degree of reduction and electrical conductivity. The microstructure of the GAs was investigated by Zeiss Sigma VP field emission scanning electron microscope (FESEM). Pore size distribution was measured by N_2 adsorption isotherms at 77K using Micrometrics Tristar II 3020 system. Before measurements, samples were degassed in vacuum at 150 °C for 12 h. Raman spectra were recorded by Renishaw inVia Raman microscope using a 523 nm edge filter laser beam. FTIR spectra were obtained from FTIR 5700 Nicolet Diamond ATR spectrometer. X-ray photoelectron spectroscopy was carried out by Kratos AXIS Supra photoelectron spectrometer. X-ray diffraction (XRD) spectra were obtained by Rigaku Smart Lab X-ray diffraction system using Cu Kα radiation with a wavelength of 1.541 Å. Compressive stress-strain measurements of freshly prepared GHs were performed by Instron 5944 single column tensile and compression tester with a 100 N load cell. Rheological behaviour of as prepared GHs was investigated by Anton Parr M302 Rheometer using a 25 mm parallel-plate geometry at 25 °C. A 2 mm gap between two plates was maintained. The frequency sweep of GHs was measured in the range of 1–100 rad/s at 0.2% oscillatory strain. Oscillatory strain sweep was carried out to measure the oscillatory stress. The electrical conductivities of GAs were measured by two probe method according to the procedure reported by Xu et al. [17]. In brief, GA was sandwiched between two platinum foils and connected to a potentiostat. A thin layer of silver paste was used to improve the contact between the sample and the electrodes. The applied voltage was increased from −0.5 V to 0.5 V and the I-V curve was drawn accordingly. Electrical resistance (R) was obtained from the gradient of the curve. Electrical resistivity (ρ) was calculated according to, $\rho = R\frac{l}{A}$ where l and A are the length and the cross sectional area of the GA. Electrical conductivity (σ) was calculated according from the equation, $\sigma = \frac{1}{\rho}$.

3. Results and discussion

3.1. Tailoring the microstructure of the GH

A series of cylindrical graphene hydrogels was prepared by hydrothermally treating a pH adjusted GO dispersion in an autoclave (Fig. 1). Although the same volume and the same concentration of GO dispersion were used to prepare each GH, the volume of GHs increased significantly with the increase of the pH value. From the macroscopic observation, GHs prepared at low pH values, exhibited a large volume shrinkage compared with the GHs prepared at high pH values. Therefore, the diameter and the water content of GHs were measured and the results are presented in Table 1.

The water content of the GH was calculated by the following equation,

$$\text{Water Content } (\%) = ((M_{GH}\text{-}M_{GA})/M_{GH}) \text{ x } 100$$

where, M_{GH} is the mass of the graphene hydrogel and M_{GA} is the mass of the freeze dried GHs (GAs). According to the results, both the diameter and water content of GHs increased as the pH value was increased. The diameter of the GH increased from 8.04 mm to 10.87 mm and the water content increased from 97.6% to 98.6 when the pH value of the GO dispersion was increased from 2.04 to 12.03.

To investigate the influence of the electrostatic repulsion force towards the formation of 3D porous structure, we measured the zeta potential (surface charge) of GO by varying the pH value of the dispersion (Fig. 2a). The dispersibility of GO is mainly attributed to the hydrophilic oxygen functional groups present at both the edges and basal plane, and the electrostatic repulsion force between GO sheets. Due to the ionization of carboxylic and hydroxyl groups, GO sheets are negatively charged when dispersed in water [24,25]. By changing the pH value of the GO dispersion, the ionization degree of the carboxyl and hydroxyl groups can be altered (Fig. 2b). In a basic medium, the deprotonation of the carboxyl and hydroxyl groups is favoured and it increases the negative charge of GO significantly. Therefore according to Fig. 2a, when the pH value increases from 2 to 12, the zeta potential of the GO dispersion decreases from −26.0 to −52.3 mV, which simultaneously increases the electrostatic repulsion force between GO sheets. The increased electrostatic repulsion reduces the tendency of the GO sheets to agglomerate [20,26]. Upon reduction, reduced graphene oxide