Electrically conductive, mechanically robust, pH-sensitive graphene/polymer composite hydrogels

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ABSTRACT

Electrically conductive yet mechanically strong composite hydrogels are highly desired in many applications, and graphene would be the most promising candidate for these hydrogels. While previous research utilized either as-prepared or reduced graphene oxide, we herein prepared high structural integrity yet solution-processable graphene sheets for the development of graphene/polymer composite hydrogels. A percolation threshold of electrical conductivity was found at 0.4 vol% graphene for these hydrogels. At 1.0 vol%, Young's modulus and compressive strength were respectively enhanced from 1.64 to 19.03 MPa and from 0.37 to 6.90 MPa, corresponding to 1060% and 1765% improvements. These improvements were explained from the perspectives of the graphene sheets' dispersion and their interaction with the polymer and water molecules. It is worth noting that the addition of graphene improved the hydrogel pH sensitivity.

1. Introduction

Hydrogels are the network of hydrophilic polymer chains containing a large amount of water; they are physically or chemically cross-linked, and have good flexibility, high water absorptivity and biocompatibility. Hydrogels have received considerable attention over the past 50 years, as they are extensively used in many fields, such as biocompatibility studies [1], tissue scaffold [2], smart devices [3] and drug release [4]. But their wider practical applications are limited due to lack of electrical conductivity and sufficient mechanical robustness [5].

Electrically conducting and mechanically robust hydrogels are an emerging class of hydrogels, which can be prepared by either adding conductive particles to gel matrices [6] or synthesizing directly from conjugated polymers [7]. Since the latter method is limited by the inherent rigidity of the conjugated macromolecular chains, conductive particle adding method appears more promising. Carbon nanotubes (CNTs) have potential to address these limitations, since CNTs have already been used to reinforce or toughen polymers [8–12] and to develop composite hydrogels [13]; these achievements are respectable but limited by high cost, complex processing, debundling and dissolution issues.

Compared with CNTs, graphene — a single layer of graphite — is a monolayer of sp^2 hybridised carbon atoms patterned in a honeycomb lattice form. It has received attention owing to exceptional Young's modulus (1 TPa), ultimate strength (130 GPa), electrical conductivity (6000 S cm^{-1}) and surface area (2630 m^2 g^{-1}) [14]. Pristine graphene is usually fabricated by chemical vapour deposition and epitaxial growth processes, both of which are not suitable for polymer composites as they produce inert surfaces, large lateral dimensions and low yields. Consequently, functional groups-rich graphene oxide (GO) has been developed from graphite oxide by heavy oxidation for imparting compatibility of nanomaterials with hydrophilic polymer matrices; these sheets have many sites of disorder (sp^2 to sp^3 of the carbon framework due to over oxidation) resulting in little or no conductivity; on the other

hand, these defects were used to attached nanoparticles for energy storage and other applications [15,16]. Subsequent chemical reduction or thermal treatment recovered partial conductivity though sacrificing ~75% stiffness [17].

A lot studies have been conducted on graphene/polyacrylamide hydrogel composites [18–21], but few has been done on graphene/polyacrylic acid (PAA) composites [6,22,23], because graphene sheets suspend well in alkaline solution but not in acidic environment. Shen et al. [6] reported GO/PAA composite hydrogels prepared by using N,N-methylenebisacrylamide (BIS) as the cross-linker; these composite hydrogels showed fairly good strength but fractured easily upon a low strain 300%, similar to the gels made by conventional organic cross-linkers. In another study the compressive modulus of GO/PAA hydrogel was found three times higher than that of neat gel due to the good compatibility between GO sheets and PAA [23]. To add electrical conductivity to hydrogels, a reported strategy is to reduce graphene oxide during the gel synthesis, but this unfortunately increases cost and complicates the processes. Thus it remains a formidable challenge to develop strong and electrically conductive graphene/PAA composite hydrogels. Accordingly, a hypothesis made in this study was that using high structural integrity yet solution-processable graphene would lead to electrically conductivity composite hydrogels; by tuning synthesis condition, the gels can be mechanically robust.

Herein, we report novel graphene/polyacrylic acid composite hydrogels made by *in situ* polymerisation. Graphene is synthesised by simultaneously oxidizing and ultrasonicating graphite within 1 h where no reduction is involved. Then the graphene sheets are mixed with acrylic acid in the presence of a cross-linker and an initiator. The composite hydrogels demonstrate not only a low percolation threshold of electrical conductivity at 0.4 vol% but high mechanical performance. These gels are found pH-sensitive, and so can be used as smart devices in future. The impressive properties are explained from the perspectives of composite fabrication and structure.

2. Experimental

2.1. Materials

Raw graphite powder (Micro 0850, ~5 μm in diameter) was provided by Asbury Graphite Mills Inc. Potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4) (95–98 wt%), hydrochloric acid (37 wt%), acrylic acid (AA), Sodium hydroxide (NaOH), N,N-methylenebisacrylamide (BIS), and potassium persulfate ($K_2S_2O_8$) were purchased from Sigma-Aldrich. Phosphoric acid (H_3PO_4) (85 wt%) and hydrogen peroxide (30 wt%) were bought from Chem-Supply. These were used to prepare hydrogels without further purification.

2.2. Graphene synthesis

Graphene sheets were synthesised from the commercial raw graphite powder. Typically, 0.1 g graphite was added to a mixture of 26 ml concentrated sulphuric acid and 26 ml phosphoric acid in a flask sitting in an ice bath, followed by stirring for 1 min. 0.4 g potassium permanganate was slowly added to keep the temperature below 20 °C. The mixture was then transferred to an ultrasonic bath (200 W and 42 kHz) for a treatment of 1 h below 20 °C, where oxidation and ultrasonication were simultaneously applied; a cooler was connected with the bath to prevent heat build-up. After the treatment, the mixture was move out of the bath and stored for another 1 h. Then 120 ml water and 5 ml H_2O_2 (30%) were slowly added into the mixture, and stirred for 1 min. The mixture was filtered and washed with HCl and de-ionised water to neutral. The resultant graphene sheets were purified by repeating similar processes. Finally, the prepared sheets

were stored in solvents such as water for the following fabrication. For characterisation in need of powder samples, the sheets were dried in an air-ventilated oven at 60 °C and then in a vacuum oven at 100 °C for 4 h to remove crystalline water.

2.3. Fabrication of graphene/polyacrylic acid composite hydrogels

All the hydrogels were prepared by free radical polymerisation at 70 °C for 4 h, with N,N-methylenebisacrylamide (BIS) as the cross-linker and potassium persulfate ($K_2S_2O_8$) as the initiator. In specific, we mixed 1 g acrylic acid, 0.01 g cross-linker, 0.01 g initiator and 10 g double distilled water in a polypropylene vial. The vial was purged with nitrogen gas for 30 min before sealed for polymerisation. The product composite hydrogel was washed three times using a large amount of deionized water to remove any unreacted monomer and initiator; filtration paper was used to remove water from the product surface. Graphene fractions were calculated according to the monomer mass. A neat polyacrylic acid hydrogel was synthesised following the same procedure. The gels were stored in an aqueous environment at room temperature. Table S1 in Supporting Information shows the composition of the neat and composite hydrogels.

Since weight fractions were used in the experiments, Eq. (1) was adopted to convert to volume fractions.

$$V_f = \frac{\rho_m W_f}{\rho_f \left(1 - W_f\right) + \rho_m W_f} \quad (1)$$

where ρ and W are density and weight fraction, respectively. Subscripts m and f refer to matrix and filler. Density values of acrylic acid and graphene were taken as 1.15 and 2.20 g cm^{-3}.

3. Characterisation

Micrographs of transmission electron microscopy (TEM) were obtained with a Philips CM200 at an accelerating voltage of 200 kV. The samples were prepared by suspending graphene sheets in THF at 0.0004 wt% by 0.5 h sonication and then dropping the solution on 200-mesh copper grids, followed by drying. The bright-field high-magnification TEM images were taken from a JEOL 2100F microscope operated at 120 kV.

Raman spectra were recorded at room temperature by a Renishaw in Via Raman micro spectrometer with 633 nm laser excitation and notch filters cutting at ~100 cm^{-1}. Extreme care was taken to avoid sample damage or laser-induced heating. Measurements were performed at 4–0.04 mW incident power.

XPS was utilized to evaluate the surface oxidation level and determine the surface composition of the as-prepared samples. C/O ratio is often used as a convenient measure of oxidation degree. High-resolution XPS measurements were carried out using a SPECS SAGE XPS system with a Phoibos 150 analyser and an MCD-9 detector, which used non-monochromated Mg Kα radiation at 10 kV and 20 mA (200 W). The analysis spot size was circular with a diameter of 3 mm.

The materials crystal structure was characterized by powder X-ray diffraction. X-ray diffraction (XRD) was used to investigate the layered structure of raw graphite and graphene sheets. The measurements were operated at room temperature using a Mini-Materials Analyser (MMA). The x-ray diffractometer was tuned to Cu $_{K\alpha}$ radiation at 35 kV and 12 kW ($\lambda = 0.15406$ nm). Spectra were collected under a reflection mode at 1° min^{-1} between $2\theta = 0$–40°.

The morphology and microstructure were examined by scanning electron microscopy (SEM). The freeze-dried hydrogels were fractured at room temperature by a pair of tweezers to expose their