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Graphene Hydrogels

Ordered Gelation of Chemically Converted Graphene for Next-Generation Electroconductive Hydrogel Films**

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From a chemistry point of view, graphene is essentially a conducting polymer with a giant, two-dimensional (2D) molecular configuration. Research on this unique macromolecule has previously been centered on its physics.[1] Although the study on the chemistry of graphene can be traced back to over a century ago, graphene chemistry did not receive much interest until very recently.[2] Nevertheless, recent studies on the chemistry of graphene and its derivatives have been very fruitful, and a number of exciting chemical properties and chemistry-enabled applications have been reported.[3] We have been particularly interested in studying the colloidal chemistry of graphene because understanding the colloidal behavior is highly desirable for developing new methods for efficient and controllable assembly of graphene into new useful materials.[4] We previously demonstrated that chemically converted graphene (CCG) can form a stable aqueous dispersion without the need for any surfactants.[5] Herein, we reveal an unusual gelation behavior of CCG. We demonstrate that a combination of 2D configuration, ultra-large molecular size, and self-contained functional groups makes CCG sheets self-gel at the solid–liquid interface during filtration, leading to a new class of oriented, conductive hydrogel films with unprecedented mechanical, electrical, and anisotropic stimuli-responsive properties.

Hydrogels are polymeric or supramolecular cross-linked networks that absorb large quantities of water without dissolving and are traditionally formed by physical or chemical cross-linking of natural or synthetic polymers.[6] Besides being widely consumed in our everyday life (e.g. fruit jellies, contact lenses, and hair gel), hydrogels have been extensively explored as functional soft materials for use in tissue engineering, sensors, actuators, drug delivery, and smart separation membranes.[6a,7] By blending with electrically conductive additives, including graphene,[8] hydrogels can be made conductive for potential use in implantable electrochemical biosensors, electrostimulated drug release devices, and neural prosthetics.[9] We have previously observed that CCG can gel in water without the need for additional gelators if the concentration of its dispersion exceeds a certain value.[5] Shi and co-workers have recently demonstrated that graphene hydrogels can be readily formed when a high concentration of graphene oxide dispersion is hydrothermally reduced.[3c] The graphene hydrogels formed in the bulk solutions using both the methods are composed of a randomly cross-linked 3D graphene network,[3c] which is similar to the structure of many conventional polymer hydrogels.

Filtration is a routine technique widely used for separating suspended particles from liquids. It has been recently demonstrated that ultrastrong graphene paper can be formed simply by vacuum filtration of graphene dispersions, followed by drying.[10] However, the structural evolution mechanism of CCG sheets during the filtration process has remained unclear. Given that the concentration of the remaining CCG solution usually increases as water is being filtered out, we surmised that CCG could gel during the filtration process.

Our experiments have revealed that gelation does occur during filtration, but surprisingly not in the bulk solution. The concentration of the CCG dispersion does not increase as the water is drained out (Figure 1b). A uniform black film is immediately formed on the filter membrane once vacuum is applied. Its thickness increases linearly with the volume of CCG dispersion filtered. Of particular interest is that as-formed undried film (see the Experimental Section for details of preparation) is highly hydrated, containing about 92 wt% of water, indicating that the film obtained is indeed a hydrogel. These results suggest that CCG sheets are continuously deposited on the filter membrane, apparently in a

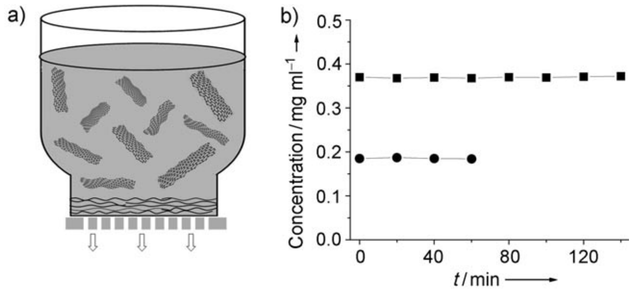

Figure 1. a) The formation process of an OGH film by vacuum filtration. b) The concentration of CCG versus filtration time for two samples. The filtration took about 150 min for 24 mL of 0.37 mg mL^{-1} CCG colloid (■) to completion and 60 min for 24 mL of 0.18 mg mL^{-1} (●). Concentrations of CCG colloids left in the filter container were monitored by UV/Vis spectroscopy.

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sheet-by-sheet fashion. The sol-gel transition occurs only at the interface, which is sharply different from the gelation process in a bulk solution.[3c]

Scanning electron microscopy (SEM) analysis further confirms that the gelation of CCG only occurs at the liquid–solid interface during filtration. When the resultant gel film is freeze-dried, its thickness is reduced by a factor of about 20, whilst little shrinkage is observed in the lateral dimension. As shown in Figure 2b, the freeze-dried gel film shows a uniform layered structure across the entire cross-section, in contrast to the 3D porous structure of the dried gel formed in bulk solution. If the assembly had happened in the bulk solution, at least the top layer of the film would show a randomly cross-linked 3D structure.[3c] These results further indicate that CCG gels at the interface in a highly ordered manner during the filtration process.

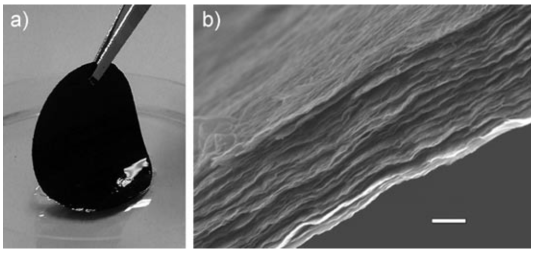

Figure 2. a) Photograph of the as-formed OGH films peeled off from the filter membrane; b) SEM image of the cross-section of a freeze-dried graphene hydrogel film. Scale bar: 1 μm.

We have found that the water can be stably trapped within the film and the gel structure will not collapse with time so long as it is kept wet. The formation of such an unusual structure is ascribed to the unique chemical structure of CCG sheets and their corrugated configuration in water. Unlike pristine graphene, there are a considerable amount of oxygen-containing groups remaining on CCG sheets. Thus, CCG sheets are essentially amphiphilic. Furthermore, our recent experiments[11] have suggested that CCG sheets suspended in water are microscopically corrugated owing to the presence of sp^3 hybridization of some carbon atoms in CCG and thermal fluctuation. As shown in Figure 1a, the 2D CCG sheets are prone to lie down on the filter membrane plane under a directional flow caused by vacuum suction.[12] CCG sheets are deposited on the filter membrane in a nearly parallel manner. These sheets are held together by intersheet hydrophobic attractions and hydrogen bonding of oxygen-containing groups. However, because of corrugated configuration of CCG sheets as well as various repulsive forces between hydrated CCG,[13] the face-to-face stacked CCG sheets cannot be packed as tightly as their counterparts in graphite.

Water or hydration of CCG plays an important role in the formation of the oriented graphene hydrogel (OGH).[13] Owing to the presence of hydrophilic oxygen-containing groups on the CCG surface, a layer of water molecules can be adsorbed rather tightly to enable strong repulsive hydration forces[14] between CCG sheets. The hydration forces, together with the electrostatic repulsions between hydrated CCG sheets, prevent the CCG sheets from being fully compacted.[13] In other words, CCG sheets in the film are linked with each other by partial π–π stacking but remain largely separated owing to the hydration-induced repulsive forces (See Figure 1a for a representation of the gel film formed on the filter membrane). As a result, a significant amount of water is stably trapped between CCG sheets to allow the formation of the oriented hydrogel structure. Because the CCG sheets are largely separated, the OGH film does not give a prominent XRD peak at the diffraction angle that corresponds to the *d* spacing of tightly stacked graphene sheets or graphite.[13] Upon freeze-drying, these intersheet repulsive forces disappear, leading to a significant shrinkage along the thickness direction. As for many other hydrogels, dried CCG films are almost unswellable in water.

As will be discussed below, the self-orientation of individual sheets offers the resultant gel exceptional mechanical, electrical, and stimuli-responsive properties. Despite containing a high content of water, the OGH gel exhibits high mechanical strength. If the OGH film is thicker than about 65 μm, the OGH gel can be peeled off from the filter membrane to obtain a self-supported flexible film (Figure 2a). In contrast to graphene oxide paper,[12] the resultant OGH film can retain its structural integrity in both acidic and basic solutions. It can also survive in boiling water and can withstand bending and vigorous mechanical agitation (see video in the Supporting Information).

The thin film form allows us to perform the tensile test directly on the sample. The tensile measurement (Figure 3) reveals that the OGH films display an average tensile modulus of (76 ± 5) MPa, which is comparable to that of conventional rubbers and several orders of magnitude higher than those of conventional polymer hydrogels with similar water content (usually reported in the range of 0.01 to 10 kPa[6a]). To our knowledge, the OGH film is the stiffest hydrogel ever reported. The ultimate tensile stress is (1.1 ± 0.2) MPa, which is comparable to that of the polymer hydrogels containing a high content of clay.[15] The ultimate tensile strain is around 1.5 %, which is greater than the dried graphene films[10a] but is much smaller than that of conventional polymer hydrogels. Similar to the mechanical behaviors of graphene oxide paper,[12] the stress–strain curves of the OGH films also display a "washboard" pattern (Figure 3b) that is indicative of a slide-and-lock tensile mechanism. Because the corrugated CCG sheets are interlocked together in a highly ordered manner, when progressively stressed, the corrugated graphene sheets can slide and then click into place. This structure, together with the trapped water, allows for a

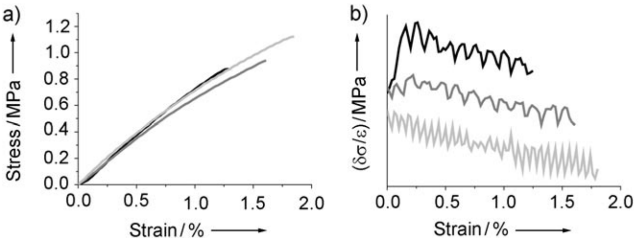

Figure 3. a) Typical stress–strain curves of the OGH films with different thicknesses. (Black line 65 μm, gray 128 μm, light gray 198 μm). b) The derivatives of the corresponding stress-strain curves.

highly effective load distribution across the entire sample when stressed, resulting in a high mechanical strength. Note that the OGH films with different thicknesses exhibit a similar mechanical strength (Figure 3). This result further indicates that the OGH film has a uniform structure along the normal direction.

As for conventional ionic polymer hydrogels,[6a] the volume of the CCG-based hydrogel film is responsive to pH and ionic concentration. As shown in Figure 4a, the thickness of the gel film increases with pH, which is consistent with the fact that the carboxylic groups become more ionized with increasing pH, resulting in greater intersheet electrostatic repulsions. The addition of electrolytes is known to suppress the electrostatic repulsion by screening the electrical double layer.[5,6] The OGH film indeed shrinks upon exposure to more concentrated NaCl solutions (Figure 4b). These results are in agreement with our previous study on the effect of pH/salt on the stability of the CCG colloids.[5] Our electrical impedance analysis also indicates that the electrical conductivity of the film is also sensitive to environmental change, allowing the response to be electrically detected (See the Supporting Information for more detailed discussion).

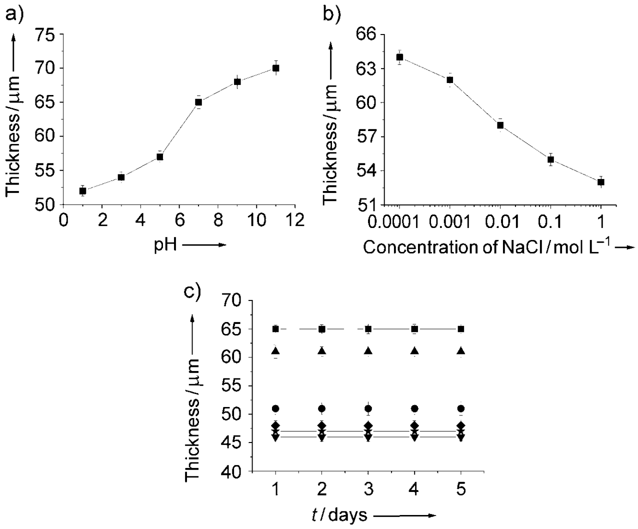

Figure 4. The response of the thickness of OGH films to pH and the concentration of NaCl: a) pH value; b) NaCl concentration; c) solvents used (■ H_2O, ▲ 1 M NaOH, ● 1 M H_2SO_4, ◆ DMF, ⋆ toluene, ▼ ethanol).

Of particular interest is that unlike most of conventional 3D hydrogels, the volumetric response to pH and electrolyte solutions is found to occur in the thickness direction only, with little response in the lateral direction. This result, together with the fact that the OGH film shrinks only in the thickness direction when freeze-dried, further confirms that the CCG sheets are preferentially oriented in the plane. This unique anisotropic responsive behavior provides several advantages over the conventional 3D randomly cross-linked gels. The 2D gel can offer a larger magnitude of stimulus response. For example, the OGH film gives rise to a volume change of 35 % when pH is changed from 1 to 11. In contrast, the 3D gel formed in the bulk phase gives little volumetric response to pH. In particular, this anisotropic response allows the film to form a reliable electrode contact with external circuits, offering a key advantage over conventional isotropic conductive hydrogels which have problems in forming good electrical contacts owing to their propensity to shrink/swell in all dimensions.[9]

The parallel orientation of individual graphene sheets also makes the OGH film highly conductive in the film plane. The electrical conductivity of the resultant OGH film is found to be 0.58 $\mathrm{S\,cm^{-1}}$. This value is comparable to that of dried 3D graphene aerogels with individual sheets chemically cross-linked (ca. 0.87 $\mathrm{S\,cm^{-1}}$).[16] To our knowledge, this is the most conductive hydrogel film ever reported (containing about 90 wt % water).

The oriented OGH conductive gel is in the form of thin film that is ready for integration into various devices. It is flexible and bendable, making it more suited for use in flexible electronics and biomedical devices compared to 3D rigid hydrogels. We have also found that the gel structure can be retained when water is exchanged with other solvents (Figure 4c). Thus the graphene gel film can be readily extended to other organic solvent systems if needed. Furthermore, the thickness of the OGH gel film can be readily controlled by varying the volume of CCG dispersion to be filtered.

As an emerging class of biomimetic functional soft materials, hydrogels have received a great deal of attention in a wide range of technological areas in the past decades.[6b] Among different types of hydrogels, electroconductive hydrogels, which allow electrically manipulating the functions of hydrogels, have been of particular interest.[9] They have been explored for use in neural prosthetic and devices and implantable electrochemical devices.[9] However, the electroconductive hydrogels that have been studied generally involved the use of traditional nonconductive polymer hydrogels blended with synthetic conductive polymers, such as polypyrrole and polyaniline. Their limited electrical conductivity, chemical stability, and mechanical strength have hindered the development of electroconductive hydrogel-based devices. Given that our OGH film can combine ease of fabrication, exceptional chemical and structural stability, high electrical conductivity, mechanical flexibility, and anisotropic responsive behaviors together and the residual oxygen-containing groups on CCG sheets provide reactive sites for further functionalization, we expect that the discovery of this new class of self-oriented highly conductive hydrogel will significantly boost the development of this emerging research field and open up many application opportunities. For example, we have observed that when used as electrodes for supercapacitors, the CCG gel film exhibits much superior performance than dried CCG paper and conventional porous carbon materials.[13]

In conclusion, we have demonstrated that owing to its unique chemical structure, chemically converted graphene can self-gel at the solution–filter membrane interface in an ordered manner during filtration. This unusual gelation behavior provides an amazingly simple strategy to create a new class of mechanically strong, highly conductive and anisotropic hydrogel films. This new graphene bulk nano-structure provides a unique platform for the study of many fundamental nanoscale phenomena and creation of new functional nanomaterials. This work also suggests that along with a range of unique physical properties, the chemical properties of graphene and its derivatives are also extraordinary. Further investigation on the fundamental chemical behavior of graphene is expected to lead to more new exciting materials.

Experimental Section

Preparation of OGH films: The chemically converted graphene (CCG) dispersion was prepared by chemical reduction of a graphene oxide solution. Details of the synthetic procedure and structural characterization were reported previously.[5] To prepare the OGH film, a certain amount of CCG dispersion (0.37 mg mL^{-1}) was filtered through a mixed cellulose esters filter membrane (47 mm in diameter, 0.05 μm pore size, Millipore) by vacuum filtration. The vacuum was disconnected once no free CCG dispersion was left on the filtrate cake (See the Supporting Information, Figure S1 for images). The resultant OGH film was then immediately transferred to a Petri dish and immersed in water overnight to remove the remaining ammonia and unreacted hydrazine. Relatively thick films were carefully peeled off from the filter membrane using tweezers and were used for most measurements. All of the OGH films were stored in water prior to use to prevent the water evaporation. The films were cut into certain sizes using a razor blade for various tests. The content of CCG in the OGH films was determined by weighing the samples dried in air at 100 °C for 12 h. The thickness of the OGH film can be controlled simply by adjusting the concentration and/or volume of the CCG dispersion. Note that, like graphene oxide[14], the filtration of CCG dispersion is a rather slow process. It is thus recommended that the thickness of the gel film be controlled to not exceed 300 μm. Otherwise, the top layer of CCG dispersion could coagulate owing to excessive evaporation, resulting in uneven films.

Stimulus response experiments: A piece of OGH film (0.45 mg cm^{-2}) was alternatively soaked in aqueous solutions of different pH values for 1 min prior to the thickness measurement, followed by soaking in distilled water. The pH was adjusted by H_2SO_4 (pH 1–6) and NaOH (pH 8–11), respectively. The thickness of the thick films was tested using a digital micrometer caliper. At least five different spots were measured and the averaged values were presented.

Stress-strain curves were obtained on a dynamic mechanical thermal analyzer (Rheometrics Mark IV DMTA). The samples were cut by scissors into 5×15 mm^2 rectangular strips. The OGH strips were then gripped through a film tension clamp. A controlled strain rate mode was used to test the mechanical properties of OGH films. The strain ramp rate was 0.01 % s^{-1} and the preload was 0.02 N.

SEM images were obtained using JEOL JSM 7001F scanning electron microscope. The electrical conductivity measurements for the hybrid films was carried out on a Jandel 4-point conductivity probe by using a linear arrayed four-point head.

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