Fluidic behaviours in a 2D folded-graphene aerogel monolith

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Abstract

Conduction of pressurized water through two-dimensional (2D) layers in monolithic folded-graphene aerogels (FGA) is investigated experimentally. The synthesized FGA has a regular layered structure with a uniform d-spacing around 20 nm. Compared with one-dimensional nanofluidics in carbon nanotube arrays that have a similar characteristic length scale, the conduction pressure of FGA is much lower by nearly 2/3. The reduction in pressure may be attributed to the more energetically favourable molecular configurations in the 2D nanoenvironment, associated with the relaxation of lateral constraints of water molecules. The water conduction pressure through FGA rises exponentially with the sample thickness, due to the interlayer resistance. This finding may find wide applications in nanotransportation, nanofiltration, and nanofluidic energy management.

Keywords: graphene aerogel, interlayer resistance, nanotransportation, nanofiltration, nanofluidic energy management

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanofluidics in nanopores, nanochannels, nanoribbons, and nanolayers [1–5] were investigated extensively in recent years, due to their unique molecular motions [6] and enhanced conduction rates [7, 8]. The discovered superior nanoconduction dramatically improved the fluid transport efficiency and reduced the driving energy, which has greatly promoted the applicability of these nanofluidic systems in a wide variety of areas, such as biosensors, microchips, nanoactuators, nanofiltration, and nanoscale energy management [9–17].

Previous researches on nanofluidics were mainly focused on one-dimensional (1D) structures, e.g. water transport through carbon nanotubes (CNTs). Although frictionless superconduction may be achieved, liquid molecules are constrained from the lateral directions, leading to a column resistance that raises the system free energy [18]. It is envisioned that, if an additional degree of freedom can be provided, more energetically favourable configurations would be obtained. One feasible approach is to conduct a liquid through a 2D nanoenvironment, e.g. graphene layers.

Graphene oxides (GO) and chemically modified graphene (CMG) sheets could be employed to form membranes with regular 2D nanostructures, by using facile evaporation-assisted or filtration-assisted self-assembly methods [19–22]. Water molecules can pass through these GO or CMG membranes as the d-spacing between the graphene layers is relatively large (≥0.78 nm); however, functional groups on graphene sheets, such as oxygen or organic groups, may induce ‘friction-like’ resistance [23, 24]. To avoid this, GO and CMG membranes
may be thermally or chemically reduced to eliminate the grafted surface groups, so that the permeability to water molecules is modified [25, 26]. However, the \( d \)-spacing of a so-reduced graphene membrane is only about 0.334 nm, smaller than the diameter of water molecule [27]. In order to promote water conduction, the \( d \)-spacing must be increased. Recently, gas or liquid permeation across neat graphene layers has been reported [28–30], however the superior conduction is mainly due to the fluid molecules going through the pores on the graphene sheets, not an absolute 2D nanoflow.

Three-dimensional (3D) graphene-based metamaterials, such as hydrogels, sponges, foams and aerogels [31–35], have recently attracted great attention due to their ultralight weight, high specific surface area, and excellent electrical conductivity. Among these graphene monoliths, graphene aerogel (GA) tends to have a much lower density [36], higher compressibility [37], and good electrical conductivity [38]. Due to its highly porous, well organized, easily scalable and oriented framework, GA may be a good potential candidate for gas and fluid conduction, which have received little attention, inspiring this study.

In the current study, the folded-graphene aerogel (FGA) was prepared by compressing 3D GA into a layered structure with a uniform \( d \)-spacing around 15–20 nm. Conduction of water molecules through pure carbon FGA was systematically investigated. The results shed light on nanotransportation, nanofiltration, and nanofluidic energy management.

2. Experimental methods

The preparation process of FGA is illustrated in figure 1. Large graphene oxides (LGO) (figure 1(a)) were firstly prepared via a modified Hummers method [39, 40]. Then, 540 \( \mu l \) ethylenediamine (EDA) were homogeneously dispersed into 45 ml LGO suspension (10 mg ml\(^{-1}\)) by mild ultrasonication for 30 min. Next, 3–15 ml of the suspensions were respectively sealed in teflon-lined autoclaves and maintained at 120 \(^\circ\)C for 6 h (figure 1(b)). After that, the autoclaves were naturally cooled to room temperature and the as-formed hydrogels was poured out and dialysed with 1 l solvent composed by distilled water and ethanol with the volume ratio of 5:1 for 24 h. Then the hydrogels were frozen at \(-80 \, ^\circ\)C for 24 h and freeze-dried into the aerogels. At last, the aerogels, heights from 10 to 50 mm, were reduced at 800 \( ^\circ\)C under argon protection for 1 h and axially compressed under 60 MPa for 30 min to form the FGA, as depicted in figure 1(c). It is noted that the compressed deformation can be recovered when the compressed force is small (about 1 kPa), as presented in our previous work [34]. However, the compressed stress in this work is much larger. Permanent deformation occurred under so large stress and the compressed pancake specimens are validated to be stable.

3. Results and discussion

3.1. Elemental composition and nanostructure of FGA

Elemental composition of FGA is revealed by x-ray diffractometer (XRD), Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS). Figure 2(a) shows the XRD patterns of LGO, graphene aerogel (GA), reduced graphene aerogel (RGA) and FGA. For LGO, the peak at 7.5\(^\circ\) corresponds to the typical diffraction peak with the \( d \)-spacing of 1.18 nm. However, for GA, a wide diffraction peak appears at about 22\(^\circ\), indicating a restoration of the conjugation of \( sp^2 \) regions and \( \pi-\pi \) stacking interactions between graphene sheets during their self-assembling process. After thermal
reduction, a graphite (0 0 2) diffraction peak (26.5°) can be observed in RGA, demonstrating a further reduction of graphene sheets with additional restoration of π–π stacking interactions. For FGA, only a sharp graphite (0 0 2) diffraction peak can be found in the spectra, which can be attributed to the physically-assisted restoration of π–π stacking interactions between the graphene layers. Figure 2(b) shows the Raman spectra of LGO, GA, RGA and FGA. Compared with LGO, the intensity ratio of graphene D band and G band in GA, RGA and FGA was enhanced after reduction. The intensities of 2D bands at 2680 cm⁻¹ in FGA are larger than those of GA and RGA, indicating additional restoration of conjugated sp² regions in 2D folded aerogels than their 3D original states [41].

Figure 2(c) shows the wide-scan XPS profiles of LGO, GA, RGA and FGA. Only C1s (284.6 eV) and O1s (532 eV) peaks can be observed from LGO while additional N1s (400 eV) peak can be observed from GA, RGA and FGA, which is attributed to the grafted amine groups after EDA-mediated hydrothermal reduction. From the C1s spectra (figure 2(d)), regular peaks of oxygen groups on LGO can be clearly observed. After the EDA-mediated hydrothermal treatment, a considerable portion of the oxygen groups (hydroxyl C–OH at 285.7 eV, epoxy C–O at 286.7 eV and carbonyl C = O at 288.4 eV) are eliminated while most of the oxygen and amine groups can be removed after the thermal reduction, as shown in RGA and FGA.

The structure of FGA was investigated by transmission electron microscope (TEM) and scanning electron microscopy (SEM). From figure 3(a), the as-fabricated LGO are in regular monolayer form with typical hexagon diffraction spots. While after graphene self-assembling process and thermal reduction, RGA show honeycomb-like 3D porous architectures (figure 3(b)) with average pore size about 30 μm. The cell pores are shaped with the formation of ice crystals during the freeze-drying process and the pore walls are assembled via the graphene π–π stacking interactions [37].

Figure 3(c) shows the structure changes as 3D RGA are gradually compressed into FGA. It can be clearly observed that with the increase of the external pressure (from 0 to 60 MPa), the micro-sized pores of RGA can be compacted into nano-sized slits. When the external pressure is removed, the as-formed FGA, as shown in figures 3(d) and (e), exhibit a ‘pancake’ shape with well-layered inner structures, which can be attributed to the physically-assisted restoration of π–π stacking interactions between pore walls. From figures 3(d) and (e), no other fluidic pathways, such as pores or channels can be observed in FGA. Furthermore, these well-layered nanoslits of FGA show a uniform d-spacing (15–20 nm), which can be directly measured from the SEM images (figures 3(f) and (g)). The SEM measurement accuracy is verified by the Brunauer–Emmet–Teller (BET) method, as shown in figures 3(h) and (i). The BET d-spacing of FGA is around 20 nm, which is in accordance with the SEM measured...
$d$-spacings. Larger external pressure (over 60 MPa) on RGA will induce even smaller $d$-spacing nanoslits in FGA, but this trend is becoming less obvious as RGA is gradually compacted, which will be studied in the future.

The as-prepared FGA was immersed in water to form a 2D nanofluidic system, as depicted in figure 4(a). The samples were mounted at the centre of the right chamber by two steel sieve holders and a stainless steel piston was installed in the left chamber. By moving the stainless steel piston back and forth, the liquid phase was forced to flow across the FGA sample repeatedly. Before loading test, the setup was filled with water and the trapped air was pumped out via venting valves. Quasi-static (2 mm min$^{-1}$) loading tests were carried out and the load was applied and measured by a type MTS-810 machine in a step-wave displacement control mode.

### 3.2. Fluidic behaviours in FGA

In order to study 2D nanofluidic behaviours, water conduction in 1D carbon nanotubes (CNTs) array in our previous work is employed here for comparative analysis (figure 4(a)) [42]. The CNTs diameter and length are the same as the FGA $d$-spacings and thickness. From the 2D conduction isotherm (the red dash line in figure 4(b)), the curve is quite linear when the load is small, which can be attributed to the compression of liquid phase as well as the machine compliance. As the pressure increases and reaches about 0.1 MPa, water begins to enter and pass through the nanoslits in FGA continuously. As a result, a flat conduction plateau is formed rapidly. However, in 1D nanotubes (the blue solid line), the driving pressure is relatively high (~0.3 MPa) and the conduction plateau is not flat: as more and more liquid molecules enter the 1D nanotubes, the resistance of the tube walls becomes significantly pronounced, and, thus, the effective capillary force rises considerably [18, 43]. In the experiments on the 2D nanoslits, the driving pressure is only one third of that in 1D nanotubes and the conduction plateau becomes flat fast. Compared with the axial constraints of 1D nanotubes, 2D nanoslits or nanoribbons [44] relaxed the constraints from the lateral directions on the confined water molecules, and the additional
degree of freedom allowed the confined water molecules to reach a lower system free energy, promoting the formation of more energetically favourable molecular configurations with little interlayer resistance in 2D nanoenvironments.

The influence of the FGA thickness on water conduction is examined (figures 4(c) and (d)). By using different height of RGA (10–50 mm), the thickness of the as-formed FGA can be varied from 0.22 mm to 1.19 mm correspondingly with nearly the same \( d \)-spacing. From figure 4(c), it can be clearly observed that with the increase of the sample thickness, the driving pressures for water permeation go up rapidly, indicating a nonlinear growth pattern. Furthermore, all of the conduction plateaus remain flat, which demonstrate the more energetically favourable flow of water molecules in 2D nanoslits. Similar conduction behaviours can also be obtained when water is forced to go back, as the piston is moved backwards. Figure 4(d) shows the water conduction pressures as a function of the sample thicknesses. When the thickness is small (~0.22 mm), the driving pressure for water conduction is relatively low (~0.13 MPa), which may provide a promising application in 2D nanotransportation and nanofiltration areas. With the gradual increase of the sample thickness, water conduction pressures exhibit an exponential growth pattern, which can be attributed to the interlayer resistance enhanced by the lengthened effective transporting paths in the nanoslits. According to the water conduction mechanism in graphene layers [14, 26], increasing the sample thickness may lead to more inter-layer flow rather than cross-layer conduction, which eventually induced the exponential growth of the conduction pressure. Similar phenomenon can also be observed in graphene membranes [26]. Based on the high water conduction pressure, the thick FGA may explore a potential application in 2D nanofluidic damping devices.

4. Conclusions

In summary, water conduction through 2D nanoenvironment was investigated through a set of experiments on FGA. Compared with 1D nanofluidics in CNT array, the driving pressure in graphene nanoslits is much lower and the conduction plateau becomes flat faster, suggesting that the relaxation of the constraints from the lateral directions on the confined water molecules significantly reduces the system free energy. The interlayer resistance between graphene sheets may be enhanced by the increase of the FGA thickness, leading to the exponential growth of the driving pressure. Based on the energetically favourable conduction in thin nanoslits and enhanced interlayer resistance in thick ones, FGA can find their applications in nanotransportation, nanofiltration and nanofluidic energy management.
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References

[1] Nardecchia S, Carriazo D, Ferrer M L, Gutierrez M C and del Monte F 2013 Chem. Soc. Rev. 42 794
[2] Abgrall P and Nguyen N T 2008 Anal Chem. 807 2326–41
[3] Prakash S, Pinti M and Bhushan B 2012 Phil. Trans. R. Soc. A 370 2269–303
[4] Pirnusa A, Gong M, Sweekler J V and Bohn P W 2010 Chem. Soc. Rev. 39 1060–72
[5] Gregory M D 2010 Prog Mater Sci. 55 629–74
[6] Hummer G, Rasahat J C and Noworyta J P 2001 Nature 414 188
[7] Majumder M, Chopra N, Andrews R and Hinds B J 2005 Nature 438 44
[8] Holt J K et al 2006 Science 312 1034–7
[9] Das S, Dubsky P, Berg A and Eijkel J C T 2012 Phys. Rev. Lett. 108 138101
[10] Waggoner P S and Craighend H G 2007 Lab Chip 7 1238–55
[11] Ng J H and Ilag L L 2003 Biotechnol. Annu. Rev. 9 1–149
[12] Joshi R K, Carbone P, Wang F C, Kravets V G, Su Y, Ng J H and Ilag L L 2003 Biotechnol. Annu. Rev. 9 1–149
[13] Xiong W, Liu J Z, Ma M, Xu Z, Sheridan J and Zheng Q 2011 J. Phys. D: Appl. Phys. 44 2220–4
[14] Majumder M, Chopra N, Andrews R and Hinds B J 2005 Nature 438 44
[15] Holt J K et al 2006 Science 312 1034–7
[16] Das S, Dubsky P, Berg A and Eijkel J C T 2012 Phys. Rev. Lett. 108 138101
[17] Waggoner P S and Craighend H G 2007 Lab Chip 7 1238–55
[18] Ng J H and Ilag L L 2003 Biotechnol. Annu. Rev. 9 1–149