Here we report on the “scrolling” of planar graphene induced by water as a result of the interplay between water capillarity and graphene elasticity. This scrolling leads to the formation of stable nanochannels that encapsulate water and nanoscale objects. We demonstrate that these graphene nanochannels can be used as nanofluidic platforms for dynamic imaging of nanoscale processes in liquids with Transmission Electron Microscopes (TEMs). These water-impermeable graphene nanochannels have practical application in the design of nanofluidic devices used in biosensors and many analytical separation devices.

Calculations by Patra et al. predicted that nanodroplets of water would fold planar graphene sheets into scrolls. Previous experimental work has shown that carbon nanoscrolls can be formed from graphene in the presence of stress induced by an electric field, by mechanical stress during graphene detachment from the surface or by controlling conditions during the graphene synthesis. These scrolls resemble tubular channels that may hold the potential for nanofluidic applications. Several attributes of graphene, that make it a highly coveted material for nanofluidic platforms are its mechanical strength, transparency, flexibility, and ease of production at large scales. Graphene-based fluidic platforms are promising candidates for some key technological applications, such as biosensing and water filtration, where size-based separation and sieving is accomplished by passing biomolecules and water through graphene nanopores and nanochannels. One intriguing application of graphene-based nanofluidics is in situ transmission electron microscopy (TEM) in a liquid environment due to its ability to entrap water. Imaging the dynamics of processes in liquids at the nanoscale is important in understanding the growth pathways of new materials, but until recently the dynamics were imaged through fragile electron-translucent silicon nitride windows. However, thin liquids encapsulated by graphene offer lattice-scale imaging by enhancing both contrast and resolution.

Here, we report on the formation and entrapment of water in tubular graphene nanoscrolls for observing dynamic nanoscale processes – a step towards a nanofluidic platform. As described by Patra et al. and Xia et al., scrolling of graphene results from the interplay between capillarity and elasticity.

The formation process of graphene nanoscrolls was as follows. A single-layer graphene was grown by chemical vapor deposition on a copper foil, which was then etched away with 0.7% aqueous ammonium persulfate solution, which results in the transfer of the monolayer of graphene on to the carbon mesh of the gold TEM grid. The graphene is rinsed by floating the grid on water (Fig. 1, steps I–III). Raman spectra with a 532 nm laser of a single graphene layer (step III, Fig. 1) shows the G and 2D peaks at 1580 cm$^{-1}$ and 2680 cm$^{-1}$, respectively, as expected for graphene. The $I_{2D}/I_{G} \sim 3$ in the spectrum which confirms the presence of single layer graphene.

The very low intensity of the defect (D) peak implies that the transferred single layer graphene is of high quality with minimum impurities and defects. Separately, a second “graphene on copper” foil was placed in ammonium persulfate solution with the graphene side facing up and free from any contact to the etchant. A drop of deionized water was placed gently on the graphene side of the foil surface and then overlaid with the TEM grid with graphene film prepared earlier (step IV, Fig. 1). The existing graphene film on the grid helps to retain water by preventing it from leaving through the mesh. After copper was completely etched away, the grid was rinsed with water and dried at 60 °C for 5 min prior to loading into the column of the TEM (step V, Fig. 1). Samples are examined at a low magnification by TEM (Tecnai T12; FEI) with an electron accelerating voltage of 120...
kV, with an electron dose of 10–50 e/(Å s) or at a higher magnification at 200 kV with JEOL 2010FEG TEM.

Images of the grid reveal an extensive network of structures (Fig. 2A), some of which at a higher resolution are μm-long tubular channels with an inner diameter varying between 20–60 nm. The walls of the channel (Fig. 2B–C) appear as closely-spaced lines with a center-to-center distance of 3.46 ± 0.06 Å. The spacing is consistent with the interplanar spacing of graphene layers in graphite (Fig. 2C) and indicates that the tube is formed from a graphene sheet rolling onto itself several times into a scroll. We observe water and bubbles trapped within these scrolls. When irradiated with a high flux of electrons, the bubbles and droplets move by sliding along the channel (Fig. 2D). Because water can persist inside some of the channels for over three months, we infer that the ends of the tubes are sealed during the nanochannel formation. We speculate that the nanoscroll networks may form at the last stage of drying. As water between the two graphene layers is removed (evaporation), surface tension tears and scrolls the graphene pieces sealing nanometer-size droplets. In addition to the nanochannels, graphene may fold into other structures (Fig. S1, ESI†). In the absence of water between two graphene layers we rarely observe nanochannels, which indicates that the presence of the water between two graphene layers is needed for scrolling the graphene.

The driving force of graphene scrolling is due to the energy difference between the total surface energy of the system and the elastic energy associated with graphene bending.1,23 The fact that scroll-shaped nanochannels are formed in the presence of the water layer between two graphene films suggests that water initiates scrolling of detached fragments of graphene from the etched copper substrate. We propose that a nanochannel is produced in two stages: first a flat graphene sheet bends around the water to minimize the total surface energy of the water–graphene system by reducing the exposed surfaces of both graphene and water. Second, after water is enwrapped by a single layer of graphene, subsequent rolling of graphene is driven by the reduction of the total area of the exposed graphene surface, and, consequently, the total surface energy of the system is minimized by tightly wrapping adjacent layers of the scroll together. In both cases the elastic energy associated with bending increases.

To assess whether water can wrap itself within a layer of graphene we consider a cylinder of water sitting on top of a graphene sheet (Fig. 2E). The change in Gibbs free energy when water fully wraps itself within a tube once is then:

\[
\Delta G = 2\pi R h (\gamma_{g-w} - \gamma_g - \gamma_w) + 2\pi RhDk^2/2
\]

\[
= 2\pi R h (Dk^2/2 - \gamma_w (1 + \cos \theta))
\]

(1)

The first term of this equation is the change in the surface energy of the graphene–water system when it rolls around the tube and completely encloses the water. The second term is the bending energy associated for a graphene roll of a curvature \( \kappa = 1/R \).24 The surface energy term is expressed in terms of the contact angle through Young’s equation:29 \( \gamma_w \cos \theta = \gamma_g - \gamma_{g-w} \) where \( \gamma_w = 0.072 \text{ N m}^{-1}, \gamma_w \gamma_g \) and \( \gamma_{g-w} \) are the surface energy of water, graphene and the graphene–water interface, and \( \theta \) is the contact angle of water on the graphite surface, which is measured to be \( \sim 85^\circ \). Using the following values: \( R \sim 20 \text{ nm for tube radius}, h \sim 500 \text{ nm for tube width}, D = 0.225 \times 10^{-18} \text{ N m}^{30} \) for the bending modulus of a single graphene layer we get:\( \Delta G \approx -4.9 \times 10^{-15} \text{ J} \). The negative value of the Gibbs free energy suggests that the energy of the system is lowered by rolling a graphene layer around the water tube, thus this rolling process is energetically favored. Next, we consider the possibility of subsequent rolling of graphene to produce a second layer of a scroll and so on. The energy associated with each subsequent rolling can be expressed as:

\[
\Delta G = -4\pi Rh_2 + 2\pi RhDk^2/2 = 2\pi Rh (Dk^2/2 - 2\gamma_g)
\]

(2)

Using the same values as before and \( \gamma_g = 0.047 \text{ N m}^{-1} \) we find:\( \Delta G \approx -5.9 \times 10^{-15} \text{ J} \). Thus, again we find that formation of a multiwall channel configuration is preferred. Gibbs free
energy becomes positive in eqn (1) and (2) when the channel radius is smaller than 1.2 nm and 1.1 nm, respectively. Therefore, theoretically channels 2.4 nm or greater in diameter could be formed. We have not observed any channels larger than ~80 nm in diameter, probably because graphene cannot seal larger amounts of water against evaporation.

To confirm that the substance inside the tube is water and not a carbon contaminant, we analyzed the liquid-filled nanochannel by electron energy loss spectroscopy (EELS). EELS spectra were acquired with a Gatan Tridiem ER EELS detector on a FEI Titan TEM operating in scanning TEM mode at 200 keV, using a 0.5 nm electron probe and a dwell time of 40 s per spectrum. During the acquisition of each spectrum, the probe was manually moved along the center of the channel. EELS mapping was performed in TEM mode with the standard three-window method to form an oxygen map with electrons filtered to cover only the range 540–565 eV, where the oxygen K-edge is situated. The oxygen map (Fig. 3B) of the liquid and a bubble in a nanochannel (Fig. 3A) shows considerable oxygen in the liquid-filled region and detectable oxygen in the bubble. The oxygen signal in the bubble could originate from water vapor in the bubble and/or liquid water on the channel wall. EELS spectra from the filled and bubble locations can be used for fingerprinting the oxygen chemistry in more detail (Fig. 3C). The 535 eV peak in the oxygen K-edge EELS spectrum and the broad peak around 540 eV indicates the presence of liquid water. The peak at 532 eV suggests that some H₂O₂ was also formed, likely the result of electron beam-induced radiolysis that could not be avoided. The EELS results combined with the fluidity of the liquid in the channels is strongly indicative of the presence of liquid water.

The self-assembled graphene nanoscrolls allow for wrapping of an aqueous solution containing nanoparticles, which helps to elucidate the dynamic properties of the liquids in nanoscale confinement. Water, a nanobubble, and a nanoparticle trapped in a nanochannel serve as a good system to probe the interactions of the liquid with the nanoparticle, and a liquid–gas interface with the nanoparticle. The sliding movement of the bubble trapped in a channel is initiated by the electron beam and a particle can be dislodged when it comes in contact with this moving and expanding bubble (Fig. 4A) (ESI Video 1). The gas–liquid interface and the nanoparticle position along the nanochannel that is plotted in Fig. 4B–C shows that once the interface makes contact with the nanoparticle, the particle is locked to the interface and moves with the interface similar to a macroscopic situation. This motion gives an insight into the relative forces experienced by the particle, both by liquid flow and the surface tension force at the gas–liquid interface. As a column of liquid flows around a ~10 nm particle with the velocity of ~5 nm s⁻¹ the particle experiences a drag force of $F = 6\pi r n V \approx 4.3 \times 10^{-19}$ N, which can be compared to a much larger surface tension force of $F = \gamma n R \approx 3.6 \times 10^{-10}$ N that can be generated at a liquid–gas interface (η = 9 × 10⁻³ Pa s – the dynamic viscosity of water). The nine orders of magnitude larger surface tension force explains the movement of the particle when it contacts the gas–liquid interface,
while remaining stationary prior to contact. Therefore, to achieve a Stokes force on a particle comparable to the surface tension force the flow velocities must be larger than $1 \text{ m s}^{-1}$. This ability to lock particulates to the gas–liquid interface suggests a strategy for manipulating nanoparticles near surfaces or removing and cleaning surfaces from nano-contaminants with bubbles during nanofabrication.

In summary, the ability of graphene to wrap around water points to the more general property that graphene favors water, and the wrapping of water with graphene minimizes the surface energy of the sheet by increasing the area exposed to water. These nanochannels are ideally suited to study nanoscale processes in liquids using TEM. For example, now it is possible to image liquid interfaces, which may aid in furthering our understanding on how the first few layers of liquids interact with solid substrates. The interactions between graphene and water aid the sculpting of a nanochannel and may develop into new nanofluidic technologies that can be sculpted from a broad range of two-dimensional materials. Thus, in addition to electronic applications, electron-transparent graphene nanochannels may serve as a transition point from widely accepted microfluidic-based optical imaging to emerging nanofluidic-based high resolution dynamic imaging in TEMs.

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**References**

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