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Solution-assisted ultrafast transfer of graphene-based thin films for solar cells and humidity sensors

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Abstract
Vacuum filtration enables the fabrication of large-area graphene-based membranes (GBMs), possessing a smoother surface than that by spray, spin coating or drop casting. However, due to the strong interaction with substrates, the separation of thin GBMs from the filter is problematic. Conventional stamping separation/transfer of graphene oxide (GO) thin films requires another substrate and pressing for >10 h, which may damage the delicate structure of the transfer substrates. Other methods require GO to be reduced on filters before separation, thus limiting the reduction methods. Inspired by a coagulation bath that enables rapid formation of ultrastrong GO fibers, we present an ultrafast (<1 min) and solution-assisted strategy to fabricate smooth and freestanding GO films. The diverse interfacial energy of hydrogen bonds also demonstrates another reason for the successful separation. The film thickness ranges from 45 nm to several micrometers. When used as a composite of counter electrodes in dye sensitized solar cells, it showed higher (8.58\%) power conversion efficiency than its spin-(7.71\%) and spray-coated (8.07\%) counterparts. It also showed promising performance in capacitive humidity sensors. The capacitance varied by three orders of magnitude in the range of the relative humidity of 15\%–95\%. Therefore the strategy realizes an ultrafast and high-quality film production which is suitable for various applications.

Supplementary material for this article is available online

Keywords: graphene-based thin membranes, ultrafast transfer, solution-assisted, solar cells, humidity sensors

(Some figures may appear in colour only in the online journal)
GO is a layered material that carries plenty of oxygen functional groups. Thus, GO is also considered as a potential material in electronic and environmental applications. Several strategies, e.g. layer-by-layer (LbL) assembly, Langmuir–Blodgett (LB) assembly, spin coating, drop casting, dip coating, spraying, and dry/solution-based transfer technology were recently investigated for preparing ultrathin and paper-like GO films [4–10]. However, these strategies have limitations. LbL or LB assembly is highly laborious and leaves residual chemicals on the surface, and also requires complex operation conditions, while dip coating, spin coating, drop casting, spraying, and dry/solution-based transfer technologies suffer from inhomogeneity and an uncontrollable thickness of films.

Vacuum filtration is widely applied in depositing highly smooth GO films and can generate uniform membranes with controllable thickness [11–13]. Since the size of the GO membrane is determined by the wick size of the filtration device, it is convenient to fabricate the GO membrane, especially a large size membrane, by adjusting the area of the filtration wick. During the film production, drying the GO films before separation from the substrates entails at least several hours. As the thickness of the GO film decreases, the increasing Van der Waals force causes firmer adhesion between the GO layer and filter, which significantly increases the difficulty in separating the two parts [14]—thus, it is feasible for thick films (>3 μm) produced by vacuum filtration [15, 16]. Although obtaining freestanding and ultrathin GO films by substrate etching is possible, the process is chemically intensive and costly [17]. In recent research, ultrathin graphene filtration membranes (FM) that were reduced from GO FM were reported to be successfully exfoliated from the substrates [14, 18]; however, the reduction strategies are limited by the presence of substrates, and the GO FM still remain unavailable.

Here, we report a facile and repeatable strategy to prepare freestanding and ultrathin GO FM for the first time. Inspired by a coagulation bath that allows rapid formation of ultrastrong GO fibers [19], we come up with a strategy that realizes the ultrafast (<1 min) separation of GO film from the substrate as long as the filtration process is finished. The obtained GO FM are smooth and compact with significant optical characteristics (transparency >90%) and electrical properties (14.872 Ω sq⁻¹). GO FM can be reduced to graphene by various reduction methods, particularly by high-temperature (>800 °C) thermal treatment, which is recognized as the most thorough means of reduction. Resistance can be tuned by controlling film thickness. The GO films may maintain maximal purity and uniformity because the environment of the separation bath is comparatively favorable, which makes the films advantageous in versatile applications.

2. Results and discussion

The schematic of the fabrication process is illustrated in figure 1(a). GO nanosheets were obtained from graphite through the modified Hummers’ method [20], and then were dispersed in water to form the GO suspension (of 2 mg ml⁻¹). The TEM image is presented in figure S1 and is available at stacks.iop.org/NANO/28/134004/mmedia in the supporting information. Vacuum filtration was carried out by filtrating the GO suspension through a commercial filter with an average pore size of 400 nm. When the water ran out, the GO/filter composite was placed in a container and ethanol (or another specific organic solvent) was slowly poured in. The spontaneous separation of the GO film from the substrate was completed within 1 min. (See figure S2, movie S1 in the supporting information). The resultant GO film floated on the ethanol surface and could be immediately transferred to various substrates, such as a silicon wafer, glass plate, plastic, metal plate, and rubber sheet.

The reasons for the separation are further investigated. Firstly, a coagulation bath provides a rapid coagulation channel from a marginally good solvent to a poor solvent [21]. Specifically, after filtration, a great number of water molecules are still kept in the GO layers because of hydrophilicity. Ultrafast molecular exchange occurs after placing the GO layers in ethanol because of the excellent miscibility between water and ethanol. Water molecules run out while ethanol molecules fill the space. The GO nanosheets aggregate, interlink and a firmer film forms rapidly because the GO nanosheets cannot be well dispersed in ethanol [22]. Besides, compared with the formation of GO fibers, GO FM should take a solid-phase substrate into consideration. Figures 1(b) and (c) show the analysis of the substrate–GO–water/ethanol interface. The binding energy of the hydrogen bonds formed between water and GO is stronger because the electronegativity of oxygen in water is more negative than that in ethanol. The different hydrogen bond strengths cause different energies for electronic transitions, leading to a diverse ultraviolet absorption spectrum. Based on equation (1) [23]:

$$E_{\text{bond}} = N_A \hbar c \left( \frac{1}{\lambda_p} - \frac{1}{\lambda_n} \right)$$  \hspace{1cm} (1)

where $N_A$, $c$, $\lambda_p$, and $\lambda_n$ represent the Avogadro constant, Planck constant, light velocity, and wavelength of the absorption band in polar solvents and nonpolar solvents, respectively. We identify $E_{\text{H-bond1}}$ and $E_{\text{H-bond2}}$ as the intensity of the hydrogen bonds in water and ethanol. Through equation (1) we can get:

$$\nabla E = E_{\text{bond1}} - E_{\text{bond2}} = N_A \hbar c \left( \frac{1}{\lambda_p} - \frac{1}{\lambda_n} \right).$$  \hspace{1cm} (2)

According to the ultraviolet absorption spectrum test (see supporting information S4), $\lambda_{p1} = 228.1$ nm and $\lambda_{p2} = 229.3$ nm; thus, $\nabla E$ was calculated to be 2.75 kJ mol⁻¹, which was consistent with the theoretical assumption. Therefore, the binding energy between GO and water is stronger, and thus, the occurrence of separation is more difficult.

The pyrolysis characteristics of both the thermogravimetric (in wt %) and derivative thermogravimetric (in wt % °C⁻¹) curves of membranes (with 3 μm thickness) before and
after exfoliation are shown in Figure 1.

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Figure 1. Schematic of the reproducible transfer process and microcosmic explanation. (a) Fabrication and transfer of freestanding GO FM. (b)–(c) Stacked GO FM before and after separation. The insets show the atomic schematic diagram. The intensity of the hydrogen bonds between GO and water is stronger than between GO and ethanol. (d)–(e) Thermogravimetric analysis and derivative results of GO FM before and after exfoliation, which confirms that molecule exchange occurs.

exhibited smooth and uniform surfaces. (As for a typical GO FM of thickness ~1 μm, the surface roughness observed has been estimated at a sub-micrometer scale, which can be proven in the SEM images in figure S3 in the supporting information). It is worth noting that the thinnest GO FM obtained by this novel strategy was approximately 45 nm, which was difficult to obtain by conventional separation methods. For 20 samples with this thickness, the transmittance was roughly 90% at 550 nm (figure 2(b)). The high transparency of the ultrathin thickness of the GO FM indicated the potential usage in optical component applications.

After separation, the insulating GO can be reduced to graphene through various methods regardless of the substrates. Thermal annealing in an inert environment is one of the methods that can achieve maximum reduction [24]. Figure 2(c) indicates that as the thickness of the films increased, the resistance decreased from 150.6 Ω sq−1 to 14.9 Ω sq−1 at a reduction temperature of 800 °C, thereby exhibiting potential electrical conductivity. The electrical conductivity properties of the GO membranes can be adjusted by controlling the reduction temperature. The photographs of the GO FM after being reduced to graphene on ITO are displayed in figure S6 of the supporting information.

The deposition of the uniformly thin films enables facile fabrication of thin film technology (TFTs) on various substrates without using complicated lithography. A silicon wafer [25], polyethylene terephthalate (PET) panel [26], interdigital capacitor [27], and glass board [28] are four common substrates to fabricate various sensors, flexible devices, solar cells
and many other electronic products. Traditional GO TFTs, such as spin and spray coating and drop casting, are widely used, but unfortunately suffer the problems of uneven surface and inaccurate control of thickness. GO FM with controllable thickness can be transferred to those substrates and show good adhesion because of its smoothness, as shown in figures 3(a)–(d). Considering the importance of the practical applications of this material, two demonstrations were conducted by using the as-prepared GO FM with different thickness values. In the first example, ultrathin and reduced GO films (∼50 nm) served as a moisture-sensitive material in ultrasensitive humidity sensors.

Figure 4 and table S1 show the performance of FM graphene–CoS DSSCs. Many studies have investigated graphene–CoS DSSCs [29, 30]. GO deposition by spray coating is regarded as the fastest and most effective method by far [28]. However, the structure of the GO film fabricated by spray coating is loose and rugged, which causes the formation of relatively few active sites, as well as layers with poor conductivity. By comparison, the present protocol can completely fulfill the electrode requirement, unlike spray coating. Figure 4(a) depicts the schematics of a graphene–CoS composite CE. The photocurrent density–voltage (J–V) curves of the DSSCs with pure CoS, spray-coated graphene–CoS, spin-coated graphene–CoS, and graphene FM–CoS were attained and compared in figure 4(c) (light intensity: 100 mW cm$^{-2}$).

It is clear to see that the graphene FM layer induced the most concentrated CoS to grow according to the inset which exhibits the photographs of the four kinds of CE (SEM images are given in figure S7 of the supporting information). Table S1 shows the conclusion of the photovoltaic parameters of the different CEs. Among all the graphene films reduced by three kinds of GO films, FM GO obtained a PCE value of 8.58%, which was higher than that of the spin coated GO (7.71%) and spray coated GO (8.07%). Figure 4(b) shows that, compared with the other CEs, the FM graphene–CoS composite CE possesses the largest slope of the anodic or cathodic branches in the Tafel zone, which indicates that it had the highest exchange current density ($J_0$) on the electrode surfaces. $J_0$ is indicated in the following equation [31]:

$$J_0 = \frac{RT}{nFRC_s}$$

(3)

where $n$, $F$, $R$, and $T$ represent the number of electrons involved in the reduction of I$^{3-}$, Faraday’s constant, the gas constant, and absolute temperature. $R_c$ refers to the charge-
transfer resistance. In this way, the FM graphene–CoS composite CE yielded the highest $J_0$ because of the lowest $R_{ct}$.

In the other example, capacitive humidity sensors were fabricated based on the prototype of commercialized sensors. GO is known as a highly layered material which has a large specific area and presents abundant oxygen-containing functional groups (see figure S8 of the supporting information). Therefore the surface hydrophilicity is highly enhanced compared to pristine graphene or graphite; accordingly GO can be applied as a sensitive material in humidity sensors [32]. An as-obtained GO film (1 μm thick) was used as the dielectric layer and was stuck on top of the Al interdigital electrodes. Being smooth, no adhesive was needed to achieve a firm adhesion. The optical photograph of the humidity sensor with a Chinese coin 25 mm in diameter, as well as the complete structure diagram, are shown in figure 5(a). The SEM image of the bare interdigital electrodes is presented in figure 5(b). The performance of our humidity sensor was tested inside a well-controlled temperature humidity chamber, and the humidity inside changed from 15% RH to 95% RH. As the RH increased, GO absorbed more moisture, leading to a higher dielectric constant, and therefore the capacitance value increased. Figure 5(c) reports the sensitivity of the GO humidity sensor, showing significantly improved sensitivity than the previously reported sensor with the same structure and design, apart from the dielectric layer, which was composed of 1.7 μm thick polymide instead [33]. When the RH level changed from 15% RH to 95% RH, the capacitance increased from 3.85 pF to 2 505 pF, surpassing its drop casting counterpart. The sensitivity of the commercial counterparts may be defined as follows [34]:

$$\text{Sensitivity} = \frac{C_x - C_{15}}{C_{15}} \times 100\% \quad (4)$$

where $C_x$ and $C_{15}$ represent the capacitances at x% and 15% RH, respectively. The sensitivities of traditional capacitive humidity sensors usually range from 43%–37 800% [33–37].

However, in our case, the corresponding sensitivity was 64 965%, which could be classified as ‘ultrasensitive’. Another notable superiority was its outstanding subsection linearity (15%–60% and 60%–95% in this case), which is an important parameter to evaluate the quality of humidity sensors. This superiority could also be attributed to its superior surface flatness. To investigate the stability of the GO-based humidity sensor, we recorded the capacitance every 3 h at a constant RH, and ten successive samples were obtained at 25% RH and 95% RH, respectively (figure 5(d)). The variation was less than 1.2% at 25% RH and less than 3% at 95% RH.
RH. The negligible fluctuation with time guarantees the stability of the GO-based humidity sensors in the present study. Furthermore, we increased the humidity from 25% to 95% and decreased it to 25% for many cycles. The capacitance could maintain good consistency (see figure S9 in the supporting information).

3. Experimental sections

3.1. Preparation of ultrathin GO FM

GO was produced by oxidation of flake graphite powders according to the modified Hummers’ method. We obtained 2 mg ml⁻¹ GO dispersion by stirring and ultrasonication of GO sheets for 1 h. To further purify the GO dispersion, centrifugation was conducted under 8000 rpm for 10 min and then supernatant was collected. Fabricating GO films with a variable thickness, a series of GO dispersions with different amounts ranging from 40 μl–10 ml was diluted to 50 ml with deionized water. Subsequently, the prepared GO solution (50 ml) was filtrated to obtain smooth GO FM. After filtration, the GO/Filter membrane was placed in a beaker. Specific organic solvent (ethanol, methanol, acetone) was slowly added into the container until the membrane was fully immersed. The GO layer quickly became compact and was spontaneously separated from the filter.

3.2. Fabrication of graphene FM–CoS solar cells and capacitive humidity sensors

After separation, the GO films with a thickness of around 50 nm were cut into small pieces and stuck to an ITO substrate, instead of by a traditional method, such as spin or spray coating, to fabricate the counter electrodes in dye-sensitized solar cells. Meanwhile, GO FM (1 μm thick) was applied as the dielectric layer and was stuck on top of the Al interdigital electrodes. More details are shown in the supporting information.

3.3. Characterization of the films

The surface morphology and cross section of the products were characterized by scanning electron microscopy (JSM-7600F, JEOL, Japan). The transmittance test was characterized by ultraviolet visible spectrophotometry (UV-2450, Shimadzu, Japan), and the sheet resistance was measured by a digital four probe tester (ST2253, Jinge, China). As for the solar cells, a CHI-660D electrochemical workstation was used.
to deposit materials and take related tests. In terms of the sensitivity and stability of the FM GO humidity sensors, they were both tested in a climatic test chamber (C, 340, 270) with a precise control module (OMEG 205).

4. Conclusion

In conclusion, we have developed a facile and reproducible strategy to fabricate freestanding, super-flat, and papery GO films with a controllable thickness ranging from 45 nm to several micrometers using a transfer process onto various substrates with a simple organic solution. The process is environmentally friendly, and remarkably, the membrane can be achieved within 1 min directly in the wet state without requiring an additional drying process. Characterizations demonstrate that the as-obtained GO films exhibited an excellent optical property (approximately 90% transmittance corresponding to 45 nm film). Thermal reduction can be applied to acquire graphene films, which are unrelated to the substrates, thereby improving the electrical performance of graphene films (14.9 ± 20% for 3 μm film). Transferring the GO membrane to another smooth substrate is convenient because of its superior flatness. In the case studies, we innovatively transferred the ultrathin film to an ITO substrate as the main composite of high-efficiency counter electrodes in a DSSC, whereas thicker films were applied as moisture-sensitive material in the humidity sensor. The results demonstrate that the PCE value of DSSC using our method was higher than those of their counterparts by using spin-coated and spray-coated graphene films. With regards to the humidity sensor, it exhibited ultrahigh sensitivity, excellent stability, and superior subsection-linearity. Therefore, this present approach shed light on the broad range of graphene membrane materials in other technological applications, including flexible devices, optical components, energy conversion, and desalination of sea water.

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