Self-Assembly of Adjustable Micropatterned Graphene Oxide and Reduced Graphene Oxide on Porous Polymeric Surfaces

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The breath figure (BF) method is a simple technique for fabricating micropatterned surfaces but has been rarely studied using graphene oxide (GO) or reduced GO (rGO). Additionally, fabrication of GO or rGO micropatterned (MPGO or MPrGO) by the BF method focuses on smooth and dense inorganic substrates, and the investigation of adjusting the MPGO morphology has been limited. This research systematically studies self-assembly of MPGO and MPrGO on the surface of two model porous polymers by the BF method and explores its potential applications for surface modification. It is found that the size range of the MPGO is 1–50 µm and that the structures can be adjusted by changing the process parameters. Specifically, under specific conditions, a uniform honeycomb MPGO is obtained. Surface characteristics demonstrate that the unique MPGO morphology alters the surface water contact-angle from ≈65° to ≈100° and that MPrGO decreases the surface resistivity to 1–5 kΩ cm−2. Additionally, MPGO coating on a microfiltration membrane gives it a much greater permeability than GO coating without micropatterned morphology and antibiofilm properties. Overall, this study shows that MPGO and MPrGO with adjustable morphologies are easily obtained on polymeric surfaces, thus altering the surface properties and giving the polymers various potential applications.

1. Introduction

Surface micropatterning is being investigated as a tool to tailor and modify the properties of materials or to add specific functionalities.[1] For example, in the field of filtration membrane research, the fabrication of uniform organic or inorganic thin layers with micropatterned morphologies can help prevent surface fouling and biofouling, control cell-surface interactions, adjust surface physicochemical properties, and increase specific surface area.[2,3] Much of the research on micropatterning is inspired by nature (i.e., biomimetic surfaces), with honeycomb morphology being one of the most interesting. This structure is ubiquitous, being found in bee and wasp nests, tripe, bone, compound eyes of insects, snowflakes, coral, pineapples, and the Giant’s Causeway, and has been studied for thousands of years. Many different materials with microhoneycomb morphologies have been investigated for their potential use in fields such as biological research, templates, electronics, catalysis, and optics.[4,5] Specifically, carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene oxide (GO), have been used to obtain microhoneycomb-patterned CNTs[6] and GO[7] surfaces due to their advanced electronic, mechanical, and thermal properties.[8]

Micropatterned surfaces are commonly fabricated by emulsion templating[9] (photo)lithography[10] and phase separation micromolding.[11] However, these technologies can be relatively complicated. For example, (photo)lithography uses much energy and complex instruments. Emulsions are thermodynamically unstable and short-lived. The templates for micromolding can be difficult to develop or remove.

The breath figure (BF) is a universal natural phenomenon that involves the condensation of water vapor that self-assembles into an array of water droplets on a cold surface. Inspired by this, the BF has been explored as a method to prepare micropatterned morphologies, including microhoneycomb...
morphologies,[12] due to its ease, rapid, and inexpensive characteristics.[4,5] The method employs an array of condensed water droplets that act as a template distributed on a water-immiscible solution surface. The solutes in the water-immiscible solvent stabilize the water droplets, and a micropatterned solute morphology is formed following complete evaporation of the solvent and condensed water droplets.[13] Manipulation of the composition of the solution (solvent, solutes, and additives), concentration, and volume, as well as relative humidity (RH), temperature, substrate, and external forces, can derive diverse micropatterned morphologies with multiple potential uses.[14] The BF method has been investigated in order to prepare micropatterned morphologies using solutes of polymers, ceramics, nanoparticles, small organic molecules, DNA, carbon materials, and living bacteria.[5] However, few studies have reported the BF fabrication of micropatterned carbon materials in general or GO and reduced GO (rGO) in particular. In addition, prior works formed micropatterned GO and rGO on inorganic surfaces such as glass or directly on the water. For example, Yin et al. (2013) fabricated a thin layer of microhoneycomb GO film by BF on water and transferred the film onto a glass slide. Titanium dioxide nanoparticles were added to the honeycomb scaffolds to obtain highly antibacterial properties[16] and enhance light-harvesting efficiency. The structure showed high stability during photoconversion. Furthermore, reducing the film achieved high conductivity. Nevertheless, to the best of our knowledge, fundamental research on controlling the micropatterned GO and rGO morphology on polymeric surfaces by the BF method has yet to be conducted. The present work, therefore, aimed to develop and comprehensively study the adjustable BF self-assembly of micropatterned GO and rGO (MPGO and MPrGO) on two polymeric surfaces (hydrophilic polytetrafluoroethylene [hPTFE] and nonwoven polypropylene [PP] membranes) and their potential applications.

2. Results and Discussion

2.1. Effects of Various Parameters on the Morphology of MPGO on Polymers

The MPGO structure was obtained by the BF method. As illustrated in Figure 1, the GO–organic solvent solution was obtained after 1 week of stirring the aqueous GO solution and dioctadecyldimethylammonium bromide (DODAB)–organic solvent solution. After casting the GO–solvent solution on polymer coupons, the rapid evaporation of organic solvents cools the surface of GO–solvent solutions. When the surface temperature reaches the dew point, the surrounding water vapor condenses, resulting in water droplet nucleation. The GO dispersed in the organic solvents aggregates around the condensed water droplets, preventing their coalescence.[17] The water droplets re-organize and pack in an ordered structure by Rayleigh or Marangoni convection induced by thermo-capillary force.[5,17,18] Consequently, a patterned array of water droplets with adjustable micrometer sizes is distributed across the surface of the cast GO–solvent solution.[19] The rapid evaporation of the highly volatile solvents and aggregation of GO around the water

![Figure 1. Schematic illustration of the formation of MPGO-coated polymer. 1) Mixing aqueous GO with DODAB–chloroform solution. 2) Obtaining GO–chloroform solution after transferring the GO from water to chloroform phase. 3) Coating polymeric surface with GO–chloroform solution. 4) Condensation of water vapor on the GO–chloroform solution surface. 5) Water droplets submerge, become stabilized by the dispersed GO in chloroform, and arrange by convection. 6) The obtained MPGO-coated polymer after complete evaporation.](image-url)
droplets secures the phase-separated geometry.\textsuperscript{[20]} Finally, the water evaporates, leaving GO films with a micropatterned morphology on the polymeric membrane surface.

The microstructure depends on parameters such as the DODAB and GO concentrations, temperature, RH, stirring speed, solution aging, substrates, and solvents. Thus, the effects of these parameters on the micropatterned morphology were systematically studied.

2.1.1. Effect of Surfactant Concentration

DODAB is a hydrophobic cationic surfactant that can strongly adsorb to GO\textsuperscript{[21]} and is highly soluble in chloroform. Thus, it was used to transfer GO from water to the organic solvent phase. The effects of DODAB concentration were studied using 1 mg mL\textsuperscript{-1} aqueous GO solution and different concentrations of DODAB in the chloroform (0.2, 1, 6, and 12 mg mL\textsuperscript{-1}). Transfer ratios were evaluated by measuring the residual aqueous GO concentration using UV absorbance at 230 nm at the end of the transfer period (after 1 week). A linear relationship was obtained between the aqueous GO concentration and the optical density at that wavelength (Figure S1, Supporting Information). Therefore, the transfer efficiency of 1 mg mL\textsuperscript{-1} GO from water to chloroform when using 0.2, 1, 6, and 12 mg mL\textsuperscript{-1} DODAB in chloroform was 59%, 76%, 80%, and 99.9%, respectively; increasing the DODAB concentration improved the GO transfer.

Moreover, altering the surfactant concentration also affected the GO dispersion in chloroform. At the two lowest DODAB concentrations, GO transferred to chloroform, aggregated, and formed floccules, with larger floccules at the lowest DODAB concentration. In contrast, the two higher DODAB concentrations gave relatively homogenous GO–chloroform solutions. The GO–chloroform solution color also reflected these differences. Increasing the DODAB concentration made the GO–chloroform solution less dark and more transparent: it was black and opaque with 0.2 mg mL\textsuperscript{-1} DODAB, but almost transparent reddish-brown (similar to the 1 mg mL\textsuperscript{-1} adsorb to GO) and is highly soluble in chloroform. Thus, raising the DODAB/GO ratio increased the GO dispersion and solution concentration and thus limited the motion of GO inside the solution droplet, giving a more-uniform and almost complete coverage of the GO film on the PDA/hPTFE surface (Figure S2e,f, Supporting Information). The white stains at the periphery that emerged using the highest DODAB concentration (Figure S2f, Supporting Information) were due to residual dry DODAB, as confirmed by dispersing 12 mg mL\textsuperscript{-1} DODAB without GO on hPTFE.

The effect of DODAB concentration on the MPGO morphology on the PDA/hPTFE surface was studied using SEM. The MPGO morphology formed using the BF method under all conditions (Figure 2) varied with increasing DODAB concentration. Specifically, using 0.2 mg mL\textsuperscript{-1} DODAB (Figure 2a) gave an MPGO film with micropatterned holes of ≈10–15 µm, though with some defects (breakage of the bridges among the micropatterned cells, marked with red triangles in the figure). At 1 mg mL\textsuperscript{-1} DODAB (Figure 2b), a microstructure morphology with a columnar cell shape formed. The micropatterns consisted of two size ranges: the larger were ≈6–10 µm, and the smaller were ≈1–2 µm on the bridges connecting the micropatterned cells (marked with red triangles in the figure). A microhoneycomb patterned GO (MhPGO) with hexagonal cells of 1–5 µm was formed using 6 mg mL\textsuperscript{-1} DODAB (Figure 2c). This morphology seemed to collapse when using 12 mg mL\textsuperscript{-1} DODAB (Figure 2d). Side-view SEM images were also taken by tilting the samples ≈30° away from the cross-sectional orientation to better analyze the MPGO morphology.\textsuperscript{[26]} These images (Figure 2e–h) show that the MPGO had three parts: a GO bottom layer, partially interconnected GO vertical “walls” (of 5–6 µm in height as seen in Figure 2e), and a thin micropore surface morphology located on top of the walls. Other works have reported similar polymer structures emerging from BF fabrication.\textsuperscript{[27]}

Micropatterned BF coating was also applied to nonwoven PP with a fibrous network. SEM images of samples prepared with 1 mg mL\textsuperscript{-1} aqueous GO and 6 mg mL\textsuperscript{-1} DODAB–chloroform (Figure 2i,j) showed relatively uniform MhPGO on the 3D PP fibrous structure, demonstrating the method’s efficiency to coat various surfaces with micropatterned morphologies.

Surfactant DODAB likely affects the MPGO morphology by changing the water–chloroform interfacial tension\textsuperscript{[28]} and the dispersion of GO in chloroform. In general, this occurs by reducing the former and, as discussed above, increasing the latter (along with the GO concentration in chloroform). The relatively high interfacial tension at low DODAB concentration (0.2 mg mL\textsuperscript{-1}) hindered the early submerging of condensed water droplets into the chloroform. In addition, the low GO concentration in the chloroform could not well stabilize the condensed water droplets. As a result, the condensed water droplets grew continuously by coalescing and formed a large micropattern morphology after the chloroform evaporated. Increasing the concentration of DODAB to 1 mg mL\textsuperscript{-1} decreased the water–chloroform interfacial tension and increased the transferal of GO from the water to the
Consequently, the condensed water droplets could submerge into the chloroform more easily, and the increased GO concentration in the chloroform inhibited water droplet growth. A micropatterned morphology with smaller holes was thus created. Using DODAB at 6 mg mL$^{-1}$ gave uniform MhPGO with much smaller holes. Hexagonal cells may have formed because, at that concentration, the condensed water droplets were preferably arranged (packed) in a honeycomb pattern.[16] Using 12 mg mL$^{-1}$ DODAB led to MhPGO with a similar size and shape as that formed with 6 mg mL$^{-1}$ DODAB, but the morphology almost completely collapsed. The collapse was probably due to the high dispersivity of the transferred GO in chloroform resulting in many interconnected pores on the GO vertical walls (as seen in Figure 2e−g). This led to the collapse of the walls of the MhPGO morphology.[19]

### 2.1.2. Effect of GO Concentration

The effects of different aqueous GO concentrations (0.05, 0.1, 0.5, 1, and 3 mg mL$^{-1}$) on the micropatterned morphology were investigated next. In each case, GO was transferred to chloroform using 6 mg mL$^{-1}$ DODAB. An aqueous GO concentration of 0.01 mg mL$^{-1}$ was also used, but the GO aggregated in the water phase and did not transfer to the chloroform. It was therefore not studied.

The transfer efficiencies of the five GO concentrations (from low to high) were ≈100%, ≈100%, ≈100%, ≈80%, and ≈44%. This means that the actual GO concentrations in the chloroform were 0.05, 0.1, 0.5, 0.8, and 1.3 mg mL$^{-1}$. Using 3 mg mL$^{-1}$ GO also resulted in GO floccules, and the obtained GO film did not completely cover the hPTFE, as was seen when 1 mg mL$^{-1}$ aqueous GO with low DODAB concentrations were used (Section 2.1.1).

SEM imaging of the samples after using different concentrations of aqueous GO showed that MhPGO formed at all five GO concentrations (Figure 3 and Figure S3, Supporting Information). However, 0.05 mg mL$^{-1}$ aqueous GO gave a very low GO concentration in the chloroform, resulting in a discontinuous honeycomb structure (Figure S3a, Supporting Information) and very low (≈7%) GO film coverage on the substrate surface. The SEM images in Figure 3 also show that the cell size and order of the MhPGO morphology slightly decreased with increasing GO concentration, and were ≈4, ≈2−4, and ≈1−3 µm for 0.1, 0.5, and 1 mg mL$^{-1}$ aqueous GO, respectively. Using aqueous GO at 3 mg mL$^{-1}$ (Figure S3b, Supporting Information) gave a similar cell size as seen at 1 mg mL$^{-1}$ aqueous GO. However, the obtained MhPGO was more disordered and comprised various morphologies. In general, the reduction of the microhoneycomb size and order may be explained by the increased GO concentration in the chloroform. A higher GO concentration improves the stability and confinement of water droplets, thus limiting their growth and mobility leading to smaller microhoneycomb sizes and less ordered morphology. A high concentration of the GO in the aqueous solution also resulted in various GO stabilities in the chloroform with different aggregating degrees and dispersal.

### 2.1.3. Effect of GO−Chloroform Solution Temperature

The effect of GO−chloroform solution temperature (≈0, ≈22, and ≈40 °C) on the morphology of the MhPGO-coated PDA/hPTFE polymer was studied using GO−chloroform solution prepared from 1 mg mL$^{-1}$ aqueous GO and 6 mg mL$^{-1}$ DODAB−chloroform and the BF was conducted at room temperature (≈22 °C) with ≈75% RH. SEM images of the resulting structures (Figure 4) suggest that similar uniform MhPGO morphologies were obtained using GO−chloroform solution precooled to 0 °C (ice bath) and GO−chloroform at 22 °C, while a less uniform MhPGO morphology with smaller-opening cells was produced when the GO−chloroform solution was preheated to ≈40 °C (water bath).

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**Figure 3.** SEM images of MhPGO-coated PDA/hPTFE obtained from a) 0.1, b) 0.5, and c) 1 mg mL$^{-1}$ aqueous GO with 6 mg mL$^{-1}$ DODAB−chloroform. Magnification: ×1000.

**Figure 2.** SEM images of MhPGO-coated PDA/hPTFE obtained from 1 mg mL$^{-1}$ aqueous GO with different concentrations of DODAB−chloroform: a,e) 0.2 mg mL$^{-1}$ DODAB; b,f) 1 mg mL$^{-1}$ DODAB; c,g) 6 mg mL$^{-1}$ DODAB; d,h) 12 mg mL$^{-1}$ DODAB. (a)–(d) are surface images, and (e)–(h) are side-view SEM images taken 30° tilted from the cross-sectional orientation. Yellow arrows represent the vertical GO walls of the MhPGO morphology; red arrows represent the interconnected pores on the GO walls; blue arrows represent surface micropores; green arrows represent the bottom GO layer of the MhPGO morphology. i,j) SEM images from nonwoven PP and 1 mg mL$^{-1}$ MhPGO-coated PDA/PP, respectively. a–d) Magnification: ×1000, e–h) magnification: ×2000, and i,j) magnification: ×100 (main images) and ×1000 (insets).
The GO–chloroform temperature influences three BF parameters: the interfacial tension, the solvent evaporation rate, and the temperature difference between the dew point (i.e., the onset water droplets start condensation) and the GO–chloroform solution surface. At RH of ≈75%, the dew point was ≈17.4 °C. When the GO–chloroform solution was precooled to ≈0 °C, the surface was already below the dew point, so water vapor condensed immediately. When the GO–chloroform solution was ≈22 °C, the chloroform evaporated more quickly than at 0 °C, but water vapor condensation began only when the surface temperature reached the dew point (i.e., there was a lag between GO–chloroform dispersion and water condensation). At ≈22 °C, the lag time was very short, and therefore the MhPGO had a similar morphology to that at ≈0 °C. In contrast, chloroform evaporated quickly when the GO–chloroform solution was ≈40 °C, and the lag-time was long. Consequently, much of the chloroform had evaporated before the water condensed, thus enriching the GO content in the chloroform solution before water condensation occurred. The delayed condensation led to fewer water droplets on the GO–chloroform solution surface, while the more-concentrated GO enhanced the confinement of the water droplets. Moreover, interfacial tension is known to decrease with increasing temperature.[30] At ≈40 °C, the interfacial tension was the lowest among the three studied examples in the GO–chloroform solution. This slightly enhanced the submersion of water droplets into the chloroform. Together, these effects resulted in the MhPGO film from a GO–chloroform solution temperature of ≈40 °C having a less uniform morphology and smaller microhoneycomb than those prepared from other solution temperatures.

2.1.4. Effect of RH

Next, the effect of RH on the morphology of the MPGO-coated PDA/hPTFE surface was considered. Samples were made up of 1 mg mL⁻¹ aqueous GO and 6 mg mL⁻¹ DODAB–chloroform and spin-coated on the polymer coupon at ≈22 °C (i.e., surface temperature). An RH of ≈45% was obtained at room (air) temperature ≈22 °C in a fume hood. RHs of ≈75% and ≈90% were achieved at the same temperatures but in a half-closed and completely closed water bath (Julabo SW22), respectively. For the ≈90% RH, the sample was placed in the bath through a small opening on the bath cover to avoid changing in the RH.

The BF at ≈90% RH was also studied at a surface temperature of ≈22 °C and an air temperature of ≈34 °C (water bath temperature of 40 °C).

SEM characterized the resulting MPGO morphologies (Figure 5). Fabrication at ≈45% RH gave a GO coating with no micropatterning (Figure 5a, GO-coated PDA/hPTFE). Similar findings on preparing micropatterned polymer by the BF method have also been reported.[31] As discussed above, a uniform MhPGO coating (with ≈1–3 µm micromicrohoneycomb cells) was produced at ≈75% (Figure 5b). However, disordered MPGO with various morphologies was produced at 90% RH with uneven microholes (≈1–10 µm marked with blue arrow; ≤1 µm marked with a purple arrow; and dense areas, marked with green arrow) and collapsed areas (marked with a red arrow) (Figure 5c). Moreover, at ≈90% RH and ≈34 °C air temperature (Figure 5d), the MPGO morphology was similar to the morphology obtained at ≈22 °C but with a much more disordered structure.

The morphological differences reported occurred owing to the changing dew point with RH. No condensation will occur if the GO–chloroform solution surface temperature is similar to or higher than the dew point. At an environmental temperature of ≈22 °C, the dew point is ≈9.5 °C at ≈45% RH, ≈17.4 °C at ≈75% RH, and ≈20.3 °C at ≈90% RH. In contrast, the dew point is ≈32.1 °C at ≈90% RH and air temperature of ≈34 °C. Therefore, the absence of microholes at ≈45% RH was probably due to the absence of water condensation (GO–chloroform solution surface temperature was higher than ≈9.5 °C during the process) needed to create microhole templates.[32] With an RH of ≈75%, the GO–chloroform solution surface temperature was easily decreased from ≈22 to ≈17.4 °C, and the MhPGO coating had an evenly distributed honeycomb morphology. However, the honeycomb morphology changed to a disordered MPGO at RH ≈90% when the surface temperature decreased from ≈22 to ≈20.3 °C. The smaller temperature gap (solution surface temperature and dew point) at RH ≈90% compared with at RH ≈75% resulted in a faster water vapor condensation that easily accumulated more water droplets on the GO–chloroform surface. These water droplets coalesced, disrupting their ordered distribution on the GO–chloroform solution surface. When the air temperature was ≈34 °C and ≈90% RH, the water vapor condensed when the GO–chloroform solution was exposed to the water vapor, as the initial surface temperature of the GO–chloroform solution was ≈22 °C, much
lower than the dew point (≈32.1 °C). As a result, the water vapor in the water bath condensed massively and accumulated on the GO–chloroform solution surface, thus resulting in a much more disordered morphology surface, thus resulting in a more disordered morphology than the one obtained at ≈22 °C surface temperature and 90% RH. These results indicate that the dew points (determined by humidity and air temperature) and the gap between the dew point and the surface temperature control the micropatterned morphology.

2.1.5. Effect of GO–Chloroform Solution Aging

The effect of the GO–chloroform solution aging (stored for 1 month after the GO transfer) as is or following 1-h sonication was studied under similar conditions of the freshly prepared solution. The GO–chloroform solution was prepared from 1 mg mL$^{-1}$ aqueous GO with 1 mg mL$^{-1}$ DODAB–chloroform. The GO dispersed well in chloroform when freshly prepared. However, it phase-separated after 1 month, with the GO floating and aggregating at the aqueous–organic interface and a white DODAB layer emerging on top of the chloroform. Additional DODAB precipitated occurred on top of the chloroform phase after ultrasonication of the aged solution.

The SEM images in Figure S4, Supporting Information, show micropatterned morphology with decreasing size in the fresh (≈8 µm), 1-month-old (≈4 µm), and further ultrasonicated 1-month-old (≈3 µm) GO–chloroform solutions. They also show that a more uniform MhPGO morphology formed using the aged solution. The decrease in MPGO hole size indicates increased stability of the condensed water droplets. This stabilization could have been, as discussed above, caused by decreased GO dispersity in the chloroform. This poor dispersity resulted from a reduced DODAB concentration due to its visible precipitation with aging in the GO–chloroform solution. Ultrasonication further increased DODAB precipitation and lowered the GO dispersity, which further stabilized the water droplets, ultimately forming smaller microholes.

2.1.6. Effect of Solvent

Various organic solvents replacing chloroform were next considered for the formation of MPGO coatings on PDA/hPTFE surfaces, as described in Section 4. Methyl tert-butyl ether (MTBE) and diethyl ether achieved almost complete GO transfer (the aqueous phase appeared almost transparent), while cyclohexane left some GO in the aqueous phase. The transferred GO remained stable in the first two organic solvents, but the GO settled after 30 min in cyclohexane. In addition, the color of the obtained dry MPGO coatings on the PDA/hPTFE surface gradually changed from brownish when using cyclohexane to dark brown when using MTBE to black with diethyl ether.

The SEM images (Figure 6) show the various morphologies of MPGO obtained on PDA/hPTFE with these solvents. Generally, none of them gave a honeycomb structure. MPGO holes of 1–3, 2.5–20, and 5–50 µm were formed using cyclohexane, MTBE, and diethyl ether, respectively.

As the different GO–solvent solutions were prepared under similar conditions, the morphological differences were
attributed to the properties of the solvents (Table 1). Generally, water vapor was condensed when using all three solvents. However, the quick mixing applied during GO transfer resulted in larger GO aggregation in these three solvents (relative to that in chloroform), leading to less-ordered microstructures. Specifically, cyclohexane gave the smallest cells (Figure 6a) as it had the slowest evaporation (i.e., the least water vapor condensation) and very low water solubility. [31] Using MTBE (Figure 6b) gave MPGO the structure closest to the morphology obtained using chloroform (Figure 2); that is, the morphology consisted of a bottom layer of GO, GO walls, and surface micropores. Nevertheless, the higher vapor pressure, higher water solubility, and lower density than chloroform led to a micropatterned morphology with various cell sizes when using MTBE. Microhole morphologies were also observed at the bottom GO layer (marked by red arrows). The cells of the MPGO structures formed using diethyl ether (Figure 6c) were the largest among the four studied solvents, probably due to the solvent having the highest vapor pressure and water solubility, which enhanced the drop size and led to in situ growth of water droplets in the solvent.

2.1.7. Effect of rGO Solution

As rGO is more hydrophobic than GO and can transfer much faster (in 2 days) to the DODAB–chloroform solution, its ability to form microstructures was studied. 1 mg mL⁻¹ aqueous GO was reduced by ascorbic acid. The obtained rGO–chloroform solution was used to produce directly MPrGO-coated PDA/hPTFE by the BF method. The resulting morphology was disordered, with a random distribution of various microholes (Figure S5, Supporting Information). The hydrophobic rGO has an affinity to DODAB but less than GO. [21] Therefore, the DODAB-modified rGO was likely more crumpled than the DODAB-modified GO in chloroform. [21] In addition, rGO usually aggregates more than GO. [13] even at high pH. [34] Overall, aggregated hydrophobic rGO in chloroform hindered the submergence of water droplets; it was also unstable in chloroform, and the water droplets were not stabilized, resulting in morphology with randomly distributed small microholes.

2.1.8. Stability of MhPGO-Coated Polymers in Water and Ethanol

The stability of MhPGO coatings (prepared using 1 mg mL⁻¹ aqueous GO and 6 mg mL⁻¹ DODAB–chloroform at regular conditions) was evaluated by placing MhPGO-coated PDA/hPTFE in Petri dishes with water for 1 month under gentle shaking (≈50 rpm). The SEM (Figure 7) showed that the 3D microhole structure disappeared after 31 days, but an almost 2D microhole structure remained visible. The elimination of the 3D microhole structure can be attributed to the mechanical fragility of the vertical MhPGO structure to the shear force induced by shaking. [35] Besides, neat GO films did disintegrate in water in 1 day unless cross-linked by multivalent metal cationic ions. [36] The finding in the present research showed that the obtained MhPGO coating indeed showed extended stability of the GO films in water to 1 month. Additionally, since surfactant DODAB can dissolve in absolute ethanol, the stability of MPGO coating on polymers was also tested with absolute ethanol soaking. Not surprisingly, patterned MhPGO morphology was completely removed (as observed by SEM) within 5 h of soaking (data not shown).

2.2. Potential Applications of MPGO- and MPrGO-Coated Polymers

2.2.1. Wettability

The micropatterned structures studied here were formed using 0.1, 0.5, and 1 mg mL⁻¹ aqueous GO with 6 mg mL⁻¹ DODAB–chloroform, and the obtained GO–chloroform solution at 22 °C by the BF at ≈75% RH. Morphological effects were also assessed for GO-coated polymers with no micropatterning, that is, prepared under identical conditions but at an RH of ≈45%.

Table 1. The physical properties of the four solvents used in this study (at 20 °C).

| Solvent    | Boiling point [°C] | Water solubility [g/100 mL] | Vapor pressure [torr] | Density [g cm⁻³] |
|------------|--------------------|------------------------------|-----------------------|------------------|
| C6H12      | 80.7               | 0.005                        | 77.5                  | 0.779            |
| CHCl3      | 61.2               | 0.81                         | 158.4                 | 1.49             |
| (CH3)3COCH3| 55.2               | 4.8                          | 240                   | 0.740            |
| (C2H5)2O   | 34.6               | 7.5                          | 442                   | 0.713            |

Figure 6. SEM images of MPGO morphologies on PDA/hPTFE formed using a) cyclohexane, b) MTBE, and c) diethyl ether. Magnification: ×1000 (main image, a,b), ×3000 (inset, a), ×3000 (inset, b), and ×500 (c).
Figure 8 presents water contact angles from sessile drop measurements. The average water contact angle for hPTFE was ≈62°. The contact angles slightly increased to ≈74° for GO-coated polymers (no micropatterning), irrespective of the GO concentration, probably owing to the hydrophobic DODAB that modified the GO. The water contact angles for MhPGO-coated polymers increased from 83° to 97° as the aqueous GO concentration increased from 0.1 to 0.5 mg mL\(^{-1}\) but did not change much for 1 mg mL\(^{-1}\) aqueous GO. As the BF process was conducted under the same conditions, the greater contact angle seen with MhPGO than with GO coating was attributed to the micropatterning; the wetting of the MhPGO coatings was probably in the Cassie state.[37]

2.2.2. Membrane Coating

As the hPTFE is also an MF membrane, its pure water permeability \((L_p)\) following coating was considered next. Various MhPGO- and GO-coated PDA/hPTFE samples (prepared from 0.1, 0.5, and 1 mg mL\(^{-1}\) aqueous GO and 6 mg mL\(^{-1}\) and at DODAB–chloroform GO–chloroform solution of 22 °C and at ≈75% RH) were tested for water permeability \((L_p)\) after 2–3 h compaction until the flux was stable. The permeability was calculated as

\[
L_p = \frac{\Delta V}{A \cdot \Delta t \cdot \Delta P}
\]

where \(V (L)\) is the volume of the permeate, \(\Delta t (h)\) is the time, \(A (m^2)\) is the membrane area, and \(\Delta P\) is the applied pressure.

The permeability of the pristine membrane was 4641 LMH/bar, while GO-coated PDA/hPTFE membranes were almost impermeable to pure water, in agreement with previous works.[38] The permeability of MhPGO-coated PDA/hPTFE was 678, 106, and 92 LMH/bar for the increasing aqueous GO concentrations used. The decreased permeability can be
attributed to the hydrophobicity of these samples. As discussed in Section 2.1.1, the bottom stacked GO layer of the MhPGO morphology probably also significantly decreased permeability. Nevertheless, these results suggest that the BF is a promising method for developing GO or rGO micropatterned membranes. However, for membranes to be practically useful requires improved MhPGO stability and, in the case of pressure-driven membranes, the attenuation of the bottom structure of the MhPGO.

2.2.3. Antibacterial Potential of MhPGO-Coated Polymers

The applicability of MhPGO as an antibacterial coating was also investigated. Biofilm formation under static conditions on pristine PP and MhPGO-coated PDA/PP was evaluated using *Pseudomonas aeruginosa* (*P. aeruginosa*) (PAO1) based on previous studies.[39] The biofilm was imaged using confocal laser scanning microscopy (CLSM), and the biovolume was analyzed using IMARIS software.[40] The MhPGO-coated PDA/PP used here was prepared using 1 mg mL$^{-1}$ aqueous GO with 6 mg mL$^{-1}$ DODAB–chloroform. Representative biofilm images and biovolume results (Figure 9) show a significantly lower (approximately half) live biovolume on the MhPGO-coated coupon than on the control. The MhPGO-coated PP coupon was also more bactericidal, as seen from its much higher dead cell fraction than that of the control membrane. These results illustrate the antibacterial activity of MhPGO coating and its potential to reduce biofilm growth on polymeric surfaces in different applications.[41]

2.2.4. Conductive MPrGO-Coated Polymers

The reduced MPrGO coating (MPrGO) as a conductive micropattern surface was then investigated. To avoid the presence of iodine and maintain the integrality of the micropatterned coating, MPrGO-coated polymers were obtained from the reduction of MPrGO-coated polymers (prepared using 0.5 and 1 mg mL$^{-1}$ aqueous GO and 6 mg mL$^{-1}$ DODAB–chloroform) by hydrobromic acid (HBr), instead of hydroiodic acid[42] and hydrazine hydrate. The resulting micropattern morphology seemed to delaminate to some degree (Figure S6, Supporting Information), especially in MhPrGO-coated PDA/PP (Figure S6c,d, Supporting Information). The reduction was estimated using Raman spectroscopy (Figure 10). The blueshift of the G band (7.9 cm$^{-1}$ at 0.5 mg mL$^{-1}$ aqueous GO, and 4.8 cm$^{-1}$ at 1 mg mL$^{-1}$ aqueous GO) and the redshift of the D band (13.9 cm$^{-1}$ at 0.5 mg mL$^{-1}$ aqueous GO and 6.2 cm$^{-1}$ at 1 mg mL$^{-1}$ aqueous GO) indicate the reduction of GO by 0.5 and 1 mg mL$^{-1}$ aqueous GO and 6 mg mL$^{-1}$ DODAB–chloroform.

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**Figure 9.** *P. aeruginosa* (PAO1) static biofilm growth on PP and MhPGO-coated PDA/PP prepared from 1 mg mL$^{-1}$ aqueous GO with 6 mg mL$^{-1}$ DODAB–chloroform. CLSM images of biofilm after 24 h growth showing viable (green) and dead (red) cells with the BacLight Dead/Live Kit. Graph showing the mean biovolume. Error bars indicate standard deviations, $n \geq 4$. The dead and alive biovolumes on the coated coupon are statistically significantly different from those on the control ($p < 0.05$).

**Figure 10.** Raman spectra of the MhPGO-coated PDA/hPTFE and MhPrGO-coated PDA/hPTFE from a) 0.5 and b) 1 mg mL$^{-1}$ aqueous GO with 6 mg mL$^{-1}$ DODAB–chloroform. D and G indicate the corresponding bands.
HBr. Moreover, the $I_D/I_G$ ratio (i.e., the $sp^3/sp^2$ ratio) can quantify defects present in a sample and the reduction efficiency.$^{[44]}$

At 0.5 mg mL$^{-1}$ aqueous GO, HBr treatment increased the initial $I_D/I_G$ ratio of MhPGO-coated PDA/hPTFE from 1 to 1.3 (MhPrGO-coated PDA/hPTFE), and for 1 mg mL$^{-1}$ aqueous GO, the initial ratio of MhPGO-coated PDA/hPTFE increased from 1.1 to 1.2 (MhPrGO-coated PDA/hPTFE). The higher initial ratio for the 1 mg mL$^{-1}$ MhPGO coating might have resulted from larger aggregates of GO that transferred to the GO, the initial ratio of MhPGO-coated PDA/hPTFE increased to 1–5 kΩ cm$^{-1}$. The increase following HBr treatment can be attributed to increased fragmentation, that is, the production of more-isolated and smaller $sp^2$ domains upon reduction (restoration of $sp^2$ bonding)$^{[46]}$ owing to the removal of oxygen-containing functional groups from the GO. The smaller increase of $I_D/I_G$ ratio at 1 mg mL$^{-1}$ than for the 0.5 mg mL$^{-1}$ aqueous GO indicates a lower degree of reduction in the former.

The surface resistance of PDA/hPTFE and MhPGO-coated PDA/hPTFE (using 1 mg mL$^{-1}$ aqueous GO with 6 mg mL$^{-1}$ DODAB–chloroform) was, as expected, very high ($>2 \times 10^8 \Omega \text{ cm}^{-2}$). After the HBr treatment, the surface resistance of the obtained MhPrGO-coated PDA/hPTFE decreased to $\approx 1-5 \Omega \text{ cm}^{-2}$. The small defects in the MhPrGO seen in the SEM images were probably the reason the surface conductivity was not as high as expected. Nevertheless, the reduction of the MPGO to MPrGO on the hPTFE polymer shows its potential application as a conductive surface, for example, for conductive membranes or electrocatalysis,$^{[47]}$ however, the surface resistivity should be further decreased.

3. Conclusions

MPGO films with adjustable morphology controlled by various parameters were self-assembled on porous polymeric surfaces by the BF method. The concentrations of GO and DODAB, GO–solvent solution temperature, RH value, stirring speed, GO–solvent solution aging, and solvent property altered the micropattern morphology. The differences were related to the GO conformation in the solvent, that is, its degree of aggregation during the preparation of GO–solvent solutions; GO stability around water droplets in the organic solvent, which depended on GO concentration in the solvent, aggregation degree, and water–solvent interfacial tension; the evaporation rate of the organic solvent, which also depended on the temperature difference compared to the environment; the amount of water vapor condensation; and the water drop stability on the GO–solvent surface. The MPGO morphology consisted of bottom-stacked GO, middle vertical GO walls with interconnected pores, and surface GO micropores. Specifically, a uniform GO honeycomb micropattern with hexagonal cells was obtained on polymeric surfaces using 6 mg mL$^{-1}$ DODAB 75% RH at room temperature.

The MPGO coatings modified the polymers’ surface wettability and introduced antibacterial properties. The BF also represented a promising method for developing MPGO- and MPrGO-coated membranes. Reduction of the MPGO formed a conductive surface. However, further research is required to enhance the MPGO’s stability and minimize the GO film at the bottom of the microstructure. Future related research could also include investigating additional parameters affecting the micropatterned morphology (such as heating, pH, substrates, ion strength, and the GO dimensions), enhancing the conductivity of MPrGO coatings, and further studying the potential of the MPGO and MPrGO coatings for different applications.$^{[48]}$

4. Experimental Section

Materials: Graphite (325 mesh), 98% sulfuric acid, potassium persulfate, phosphorus pentoxide, potassium permanganate, dopamine, 48% HBr, and MTBE were purchased from Sigma (Israel). Tris-aminomethane (tris) was purchased from Merck. Absolute ethanol, 30% hydrogen peroxide, and DODAB were purchased from TCI (Japan). Chlorofur, cyclohexane, and diethyl ether were purchased from Bio-Lab (Israel). hPTFE was purchased from Tisch Environment, Inc., (USA), and nonwoven PP fabric (Novatexx 2471) was obtained from Freudenberg (Germany).

Preparation of GO–Solvent Solutions: The GO was prepared from graphite based on the Hummers and Offeman method.$^{[44]}$ Then, the obtained GO was dispersed in DDW, ultrasonicated for 2 h (Sonics Vibra-Cell VCX130, 130 W, 20 kHz), centrifuged at 10 000 rpm min$^{-1}$ for 10 min, and was adjusted to pH 9 using NaOH to stabilize the dispersion of the GO$^{[50]}$ and the (remained precipitate was discarded). The experiments were performed using chloroform as the solvent unless stated otherwise.

First, 20 mL chloroform with dissolved DODAB (DODAB–chloroform solution) was slowly added to 20 mL of the aqueous GO solution in a 50 mL conical flask. The flask was sealed with a Septum Stopper (sleeve type, Fisher Scientific) and stirred slowly ($\approx 150$ rpm) for around 1 week at room temperature ($\approx 22^\circ \text{C}$) in a fume hood. After 1 week, the upper water phase was discarded and replaced with the same amount of DDW for storage, and the bottom GO–chloroform solution was used for the experiments. Different concentrations of GO–chloroform solutions were prepared using different concentrations of aqueous GO (0.05, 0.1, 0.5, 1, and 3 mg mL$^{-1}$) and DODAB–chloroform (0.2, 1, 6, and 12 mg mL$^{-1}$) to investigate the effect of the GO and DODAB concentration on the micropattern morphology. To study the effect of the stirring rate, the aqueous-chloroform solution was also stirred at 300 rpm; however, this stirring speed yielded an MhPGO morphology with many defects (See Supporting Information and Figures S7 and S8, Supporting Information) and thus was not explored in detail. To study the effect of the GO–chloroform solution aging, the flask was also stored in a fume hood at $\approx 22^\circ \text{C}$ for 1 month. Then, the aged bottom GO–chloroform solution was used as is or following 1-h sonication. Three additional solvents, namely, cyclohexane, MTBE, and diethyl ether, were also used to prepare a GO–solvent solution to investigate the solvent effect on the micropatterned morphology. Here, 6 mg mL$^{-1}$ DODAB was first dissolved in 10 mL of one solvent and then mixed with 10 mL of 1 mg mL$^{-1}$ aqueous GO in 20 mL scintillation vials. Dissolution of the DODAB in all three solvents required heating. As the DODAB precipitated from these solvents when the temperature subsequently decreased, the aqueous GO and DODAB–solvent phases were mixed while heated (close to each solvent’s boiling point). Then, fast shaking to the vials was applied to facilitate the GO transfer from water to the solvent, and the freshly prepared solution was used for the experiments.

Preparation of MPGO-Coated Polymers: hPTFE and PP, two common polymers used in many applications, and were also resistant to chloroform, were chosen as model polymeric surfaces. The hPTFE was a 0.45 $\mu \text{m}$ membrane, and the micropatterned formed on its surface, whereas the nonwoven PP had a fabric-like structure, and the micropattern coated the fibrous. The hPTFE and nonwoven PP were coated with polydopamine by immersion in 2 g L$^{-1}$ dopamine Tris-solution (10 mm, pH 8.5) for 2 h$^{[46]}$ to enhance the adhesion of GO to the polymeric surface. The residual polydopamine solution was washed off the surface with DDW, and the polydopamine-modified hPTFE and PP (PDA/hPTFE, PDA/PP) were kept in water until use. The preparation of MPGO-coated polymers was conducted in a fume hood. MPGO-coated
PDA/hPTFE was obtained by the BF method, as illustrated in Figure 1. Before the experiments, the GO–solvent solution at ≈22 °C was gently shaken to redisperse the GO before casting it on the polymer surface. The shaking step was especially important for GO–solvent solutions with relatively high GO and low DODAB concentrations or aging experiments. The polymer coupons (diameter 3 cm) were fixed on a glass cover, and 300 µL GO–the solvent solution was spin-coated on their surface (using Laurell Technologies WS-408BZ.6NP/LTIE spin-coater at 30 rpm for ≈30 s) in two steps: first, 50–100 µL GO–the solvent solution at ≈22 °C was spread over the surface, then the rest of the volume was placed at the middle of the polymer coupons. This procedure produced the most homogeneous GO–solvent solution coverage on the surface of the coupons. To initiate the BF process, the GO–solvent cast coupons were quickly and carefully transferred to a closed water bath (Julabo SW22) at ≈22 °C and RH =75% (unless stated otherwise) and a water level 2 cm lower than the coupons. MPrGO-coated PDA/hPTFE and MPrGO-coated PDA/PP were obtained after complete evaporation of the solvent (typically ≈5 min). To study the effect of the RH, the experiments were conducted at RH =45% by placing the coated coupon outside the water bath (in the hood) and RH =90% by keeping the water bath cover closed and positioning the sample through a small opening. The authors also studied the BF process for the case where the dew point was much higher than the surface temperature. This was done by increasing the bath temperature to ≈40 °C, which translated to ≈34 °C air temperature and keeping the RH at ≈90%. To study the effect of the GO–chloroform solution temperature (i.e., surface temperature), the GO–chloroform solution was precooled to 0 °C in an ice bath or preheated to 40 °C in a water bath before spin coating on the polymer coupon. The stability of the obtained MPG coating on the polymer was evaluated by soaking samples in ethanol and DDW with gentle shaking (≈30 rpm).

Preparation of MPrGO-Coated Polymers: MPrGO-coated polymers were obtained by reducing the MPG-coated polymers using HBr in a fume hood. The reduction was achieved through soaking MPrGO-coated polymers in 10 mL conical flasks containing 5 mL 48% HBr at 50 °C oil bath for 3 days.[12] Then, the coated polymers were washed with DDW times until pH >7. To investigate whether the MPrGO coating could be prepared directly from rGO solution by the BF method (d-MPrGO-coated PDA/hPTFE), aqueous GO (1 mg mL⁻¹) was first reduced by 2 mL ascorbic acid at 95 °C for 24 h.[13] Then, the aqueous rGO was sonicated for 1 h and then mixed slowly (≈150 rpm) with 6 mg mL⁻¹ DODAB–chloroform without adjusting the pH. All of the rGO was transferred to the chloroform phase within 2 days. Next, the rGO–chloroform solution was applied to the PDA/hPTFE through the abovementioned steps.

Surface Characterization: Surface morphology was characterized using SEM (JSM-IT200). Before imaging, samples were vacuum dried at 50 °C overnight and spattered with 4 nm gold and palladium layers. Water contact angles were measured using the sessile drop method with an automatic system (OCA 20 Plus, Dataphysics GmbH, Germany). Raman spectroscopy was measured using 785 nm laser wavelengths and an automatic system (OCA 20 Plus, Dataphysics GmbH, Germany). Image processing was done by IMARIS (LSM880, Zena, Germany).

Biofilm Experiment: P. aeruginosa PAO1 strain was incubated for 24 h in LB broth medium at 37 °C. The bacterial suspension was diluted at 1:100 and incubated for ≈3 h until the mid-log growth phase. An optical 96-well plate (catalog number 165305, Thermo Scientific, USA) was filled with 200 µL LB, and a square polymer coupon (PP or MPrGO-coated PDA/PP) was placed at the bottom of each well. 2 µL mid-log growth suspension was placed in each well and incubated overnight (16 h). Following incubation, the membranes were washed twice with 200 µL PBS buffer and stained with BacLight Dead/Live Kit (catalog number L7007, Thermo Scientific, USA). The biofilm was imaged by CLSM (Zeiss LSM880, Zena, Germany). Image processing was done by IMARIS software (Bitplane, Zurich, Switzerland) to obtain the 3D images.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

antibiofilms, breath figure, graphene oxide, honeycomb structures, micropatterns

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