

Reduction and functionalization of composite Graphene Oxide/PVA/PEG freestanding paper via atmospheric pressure plasma for use in filtration membranes

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Abstract

Graphene oxide (GO) and reduced Graphene oxide (rGO) are extensively researched for their use in water filtration membranes. However, the lack of scalable, economically viable manufacturing methods hinders their widespread application. Particularly, due to incompatibility with roll-to-roll production. Herein, we present a simple and scalable method for preparation of composite GO/PVA/PEG freestanding paper via spraying deposition, followed by fast (<2 s) reduction using Diffuse Coplanar Surface Barrier Discharge (DCSBD). This approach does not require any toxic chemicals, operates at atmospheric pressure and room temperature, and requires only electric power and technical nitrogen as working gas, making the process simple and compatible with in-line production. During the reduction, a quick release of gaseous products such as CO₂, CO and water vapor exfoliates the composite paper leading to an expanded, highly porous (>400 m²/g) rGO/PVA/PEG structure. Such rGO/PVA/PEG composite paper can further be functionalized with a modified DCSBD set-up called DCSBD linear jet. Instead of standard treatment, this set-up generates a stream of ionized gas in the form of a plasma curtain suitable for functionalization of the porous rGO/PVA/PEG structure. Using various working gases (Nitrogen, Air, Forming gas) we can selectively tune oxygen or nitrogen functional groups, thus changing the performance of the rGO/PVA/PEG paper for later use in the water filtration membranes. The presentation will focus on the effect of plasma working gas on the functionalization of composite rGO/PVA/PEG structures studied primarily with XPS, FTIR and SEM methods. Such material was subsequently incorporated as active material in assembled water filtration membranes and filtration performance was tested on model organic dyes pollutants.

Keywords

Reduced graphene oxide, rGO membrane, Atmospheric pressure plasma, Plasma reduction, Plasma functionalization, Water filtration, Organic dyes separation

1. Introduction

Since its discovery, graphene and its derivatives graphene oxide (GO) and reduced graphene oxide (rGO) have been widely demonstrated to enhance the performance of materials across a broad range of industrial applications [1], [2], [3]. The selection of specific graphene-based material is strongly dependent on the intended application. Pristine, defect-free graphene produced via graphite exfoliation is chemically inert, poorly dispersible in polar solvents, and prone to restacking due to strong π - π interactions, which complicates its processing, particularly at larger scales [4]. In contrast, oxidation of graphite prior to exfoliation introduces oxygen-containing functional groups, yielding GO with a highly polar character. This modification enables excellent dispersibility in polar solvents such as water and facilitates large-scale production [5]. GO dispersions can be readily cast onto flat substrates and dried to form thin films composed of parallelly stacked GO flakes held together by weak van der Waals interactions. The interlayer spacing between these flakes forms nanoscale capillaries, which promote the transport of small molecules (e.g., water) along the plane of the flakes. By tuning this interlayer spacing, GO films can function as size-selective membranes [6]. However, pristine GO films lack structural integrity in aqueous environments due to the absence of covalent bonding between flakes, leading to dissolution upon contact with water. To address this limitation, the incorporation of polymeric matrices and covalent crosslinking strategies is widely employed to enhance mechanical integrity and stability. Hydrophilic polymers such as poly(vinyl alcohol) (PVA) and polyethylene glycol (PEG) are particularly attractive due to their high density of hydroxyl groups, which enables strong intermolecular hydrogen bonding with oxygen-containing functional groups on GO [7]. These interactions improve interlayer adhesion, suppress excessive swelling, and mitigate delamination. Beyond physical interactions, covalent crosslinking provides a more robust stabilization mechanism. This results in a three-dimensional network that bridges adjacent GO flakes and polymer chains, significantly improving mechanical strength, water stability, and long-term durability. The crosslinking density can be tuned via processing parameters, allowing control over membrane properties such as permeability and selectivity. An alternative approach to membrane design involves rGO, where transport occurs perpendicular to the plane of the flakes. The reduction of GO partially restores the sp^2 carbon network while introducing structural defects. These defects generate nanopores suitable for size-exclusion-based filtration of larger species such as heavy metal ions. Additionally, reduction increases the specific surface area, enhancing adsorption capacity, while residual functional groups enable specific interactions with target pollutants [8].

Residual oxygen-containing functional groups in rGO, such as hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), carbonyl ($\text{C}=\text{O}$), and epoxy ($\text{C}-\text{O}-\text{C}$) groups, impart a negative surface charge, particularly under neutral to alkaline pH conditions [9], promoting electrostatic attraction toward cationic species. As a result, rGO exhibits strong adsorption affinity toward positively charged organic pollutants such as Rhodamine B, commonly used as a model contaminant due to its well-defined structure and optical properties [10]. The adsorption mechanism is governed by multiple synergistic interactions. Electrostatic attraction occurs between negatively charged rGO surfaces and cationic dye molecules. Simultaneously, π - π stacking interactions between the aromatic structure of the pollutant and the sp^2 domains of rGO significantly enhance adsorption capacity [11]. Hydrogen bonding between functional groups on both the adsorbent and adsorbate further stabilizes the interaction. To further enhance adsorption performance, nitrogen functionalization of rGO has been extensively studied. Nitrogen doping can be achieved through thermal, chemical, and plasma-based approaches [12], [13], [14]. Thermal treatments with nitrogen-rich precursors such as ammonia, urea, or melamine introduce nitrogen into the carbon lattice, forming pyridinic, pyrrolic, and graphitic nitrogen configurations. Chemical methods, including hydrothermal treatments with ethylenediamine or ammonia, enable both lattice doping and surface functionalization, introducing amine ($-\text{NH}_2$), amide ($-\text{CONH}-$), and imine ($-\text{C}=\text{N}-$) groups. Amination reactions, in particular, graft amine functionalities onto defect sites or residual oxygen groups, enhancing adsorption via hydrogen bonding and acid-base interactions. Plasma-based methods provide a versatile and solvent-free alternative for nitrogen incorporation. Plasma treatments can be conducted under either low-pressure or atmospheric-pressure conditions. Low-pressure plasma systems, such as radio-frequency (RF) or microwave plasmas, offer precise control and uniform functionalization but require costly vacuum infrastructure and are limited to batch processing. In contrast, atmospheric-pressure plasmas, including dielectric barrier discharge (DBD), corona discharge, plasma jets, and Diffuse Coplanar Surface Barrier Discharge (DCSBD), operate under ambient conditions and enable scalable, continuous processing. These systems generate a wide range of reactive species (e.g., N_2^* , NH , N radicals, NO_x), facilitating the incorporation of diverse nitrogen functionalities such as pyridinic-N, pyrrolic-N, graphitic-N, as well as amine and amide groups. In this work, we employ an atmospheric-pressure plasma system called Diffuse Coplanar Surface Barrier Discharge [15], [16], [17]. Firstly, to reduce free-standing GO or GO/PVA/PEG film, followed by functionalization using DCSBD jet with either N_2 , air or forming gas. Prepared samples were studied via XPS, SEM, FTIR and BET.

2. Sample preparation

Firstly, 200 g of a highly concentrated graphene oxide (GO) paste (2 wt%, Graphenea, Spain) was diluted with deionized water to obtain a total volume of 500 mL and stirred for 4 h to ensure homogeneous dispersion. In parallel, 0.8 g of poly(vinyl alcohol) (PVA, corresponding to 20 wt% relative to GO) was dissolved in 400 mL of deionized water at 80 °C under continuous stirring. After 2 h, the heating was discontinued, and the solution was allowed to cool to room temperature while stirring. Subsequently, the GO and PVA suspensions were combined and stirred overnight. The following day, 0.6 g of polyethylene glycol (PEG 400, 15 wt% relative to GO) was dissolved in 100 mL of deionized water under stirring for 1 h and then added to the GO/PVA mixture. The resulting GO/PVA/PEG suspension was further stirred overnight to ensure complete homogenization. For film preparation, 200 mL of the final suspension was cast onto a polytetrafluoroethylene (PTFE) foil (approximately A4 size) placed on a hot plate maintained at 60 °C. After 5 h of drying, a self-standing GO/PVA/PEG composite film was obtained and carefully peeled from the substrate. Additional samples with varying compositions were prepared following the same procedure. The prepared composite films were cut into 5 × 5 cm samples and reduced in a nitrogen atmosphere using Diffuse Coplanar Surface Barrier Discharge (DCSBD) plasma (**Fig.1a-b**, **Fig.1f**). Detailed parameters of the reduction process are reported elsewhere [16]. Following the reduction, the rGO/PVA/PEG samples were further treated using a DCSBD linear plasma jet system (schematics shown in **Fig.1c**) [18], mounted on a 6-axis robotic arm and operated in an enclosed, ventilated chamber. The working gas flow rate was set to 30 L·min⁻¹, and the samples were positioned 5 mm from the plasma jet. Treatment times ranged from 10 to 100 s. For treatments in forming gas, a custom-built chamber (45 × 25 × 25 cm) equipped with a 1-axis actuator sample holder was used. The chamber was initially purged with nitrogen (28.5 L·min⁻¹) delivered through the DCSBD jet for 10 min. Subsequently, hydrogen (1.5 L·min⁻¹) was introduced to create a forming gas mixture. The exhaust gas was safely combusted using a Bunsen burner. Samples were plasma treated from both sides. Finally, the treated rGO composite films were mechanically compressed between 2 polyethersulfone (PES) nonwoven textile substrate using a metallic rolling pin (**Fig.2**).

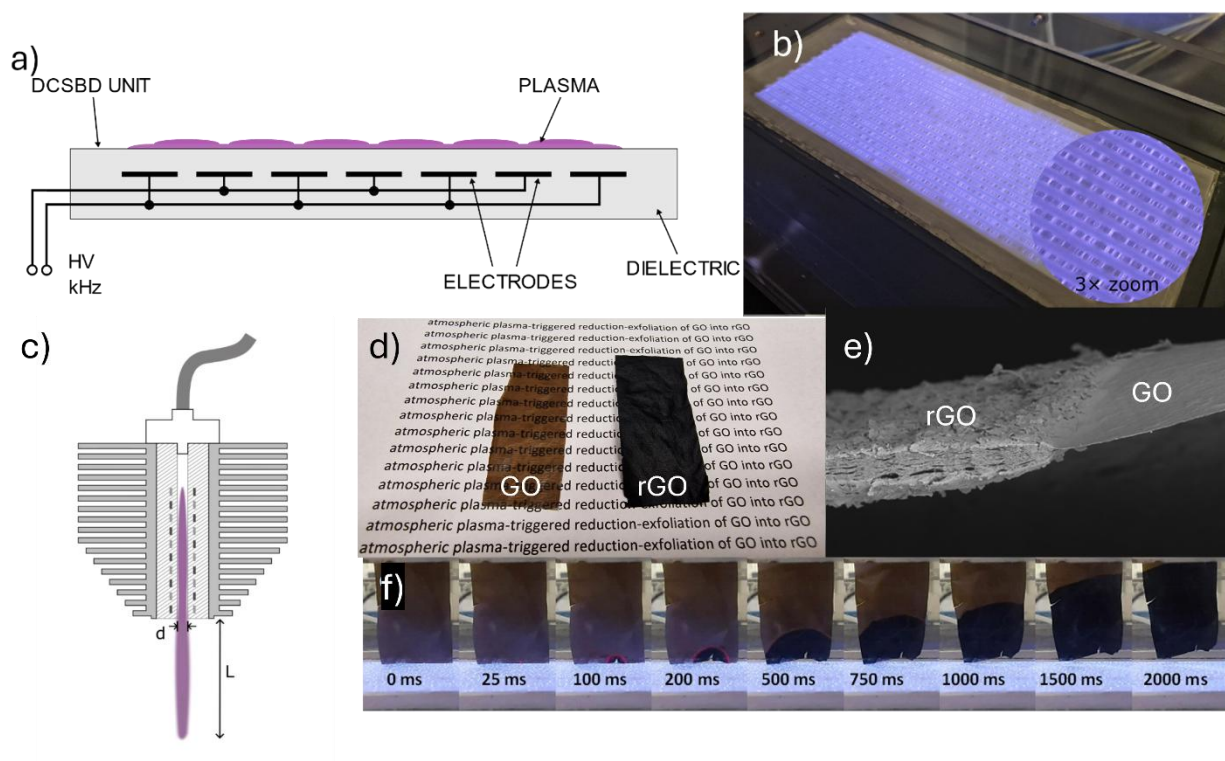


Figure 1: DCSBD plasma system schematic (a); DCSBD plasma unit photograph (b); DCSBD linear jet schematic (c); GO and rGO photograph (d); SEM cross-section of rGO/GO interface (e); GO reduction collage (f).

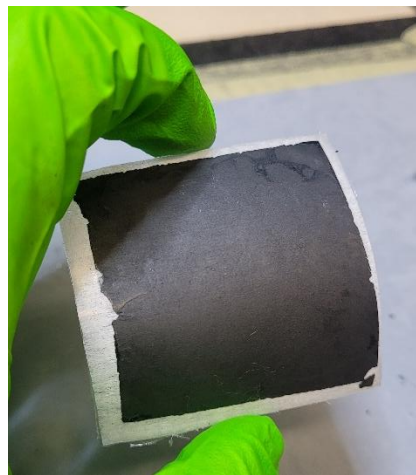


Figure 2: Photo of rGO-based membrane compressed on PES textile.

3. Characterization

Structure and morphology were characterized by Clara SEM (Tescan, Czech Republic) using SE and quadrupole BSE detectors. Accelerating voltage was set to 15 kV, current to 100 pA and distance was kept at 10 mm. Brunauer–Emmett–Teller (BET) analyses were performed on a Quantachrome Autosorb iQ3 gas porosimeter. All samples were degassed at 80 °C, after reaching a pressure rise of 20 mtorr.min⁻¹ the temperature was

reduced to 40 °C and the samples were kept under vacuum until measurement. FTIR spectra were obtained by VERTEX™ 80v FTIR spectrometer (Bruker, USA) at 2.5 hPa equipped with Praying Mantis™ diffuse reflectance attachment (Harrick Scientific Products, USA). The XPS measurements were done on the ESCALAB 250Xi (ThermoFisher Scientific). System is equipped with 500 mm Rowland circle monochromator with microfocused Al K α X-Ray source. An X-ray beam with 200 W power (650 microns spot size) was used. The survey spectra were acquired with pass energy of 50 eV and a step size of 1 eV. High-resolution scans were acquired with pass energy of 20 eV and a step size of 0.1 eV. In order to compensate the charges on the surface electron flood gun was used. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.5 eV. The spectra calibration, processing and fitting routines were done using Avantage software. Filtration performance of prepared membranes was tested in a custom-made filtration cell, illustrated in **Fig.3**. Peristaltic pump was used to pump 10 mg/L Rhodamine B solution concentration out of 100 mL reservoir through the membrane, from which the filtered solution returned to the reservoir, creating loop filtration system. Pressure gauge with 0-1 bar range was used to measure pressure during filtration. Filtrations were done for 30 minutes. Every 5 minutes an aliquot was taken for UV VIS measurements using LAMBDA 1050+ (Perkin Elmer, USA). Measurements were done in 400-600 nm range using 3 nm integration window. Plastic cuvettes of standard dimension were used. Calibration set (0-10 mg/L) was measured to calculate concentrations of filtered aliquots.

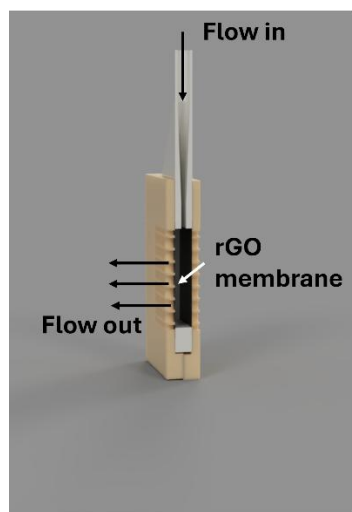


Figure 3: 3D illustration of the filtration cell cross-section.

4. Results and discussion

Firstly, the effect of PVA incorporation on the morphology of the samples was investigated using scanning electron microscopy (SEM). Surfaces of samples containing 0–20 wt% PVA were analyzed. **Fig. 4-6** presents representative SEM images of rGO, rGO/PVA10,

and rGO/PVA20 acquired in secondary electron (SE) mode, along with a compositional image constructed from four backscattered electron (BSE) quadrants. This composite image enhances the contrast of surface features and is particularly effective in revealing cracks within the rGO structure. The SEM micrographs show a clear evolution in surface morphology with increasing PVA content. The pristine rGO sample exhibits a highly disrupted structure, characterized by wrinkled sheets and the presence of large-scale cracks. Upon incorporation of PVA, morphology becomes progressively more homogeneous. At 10 wt% PVA, the rGO sheets appear more interconnected, with the formation of larger continuous domains and a reduced density of cracks. This behavior suggests that PVA intercalates between rGO layers and acts as a binder, improving interlayer cohesion [7]. At higher PVA content (20 wt%), this effect is further enhanced. The structure consists of larger, more compact rGO domains with only minor cracks or voids. Correspondingly, the mechanical handling of rGO/PVA samples is significantly improved compared to pristine rGO, which tends to be fragile and prone to disintegration. The reduced crack formation is therefore consistent with the observed enhancement in mechanical stability. However, prior to reduction, GO/PVA films exhibit increasing brittleness with higher PVA content. To address this limitation, polyethylene glycol (PEG 400) was introduced as a plasticizing agent. The effect of 15 wt% PEG 400 on morphology is evident in **Fig. 7**, where a more compact structure with significantly reduced visible cracking is observed. This indicates that PEG effectively improves film flexibility and mitigates brittleness while maintaining structural integrity.

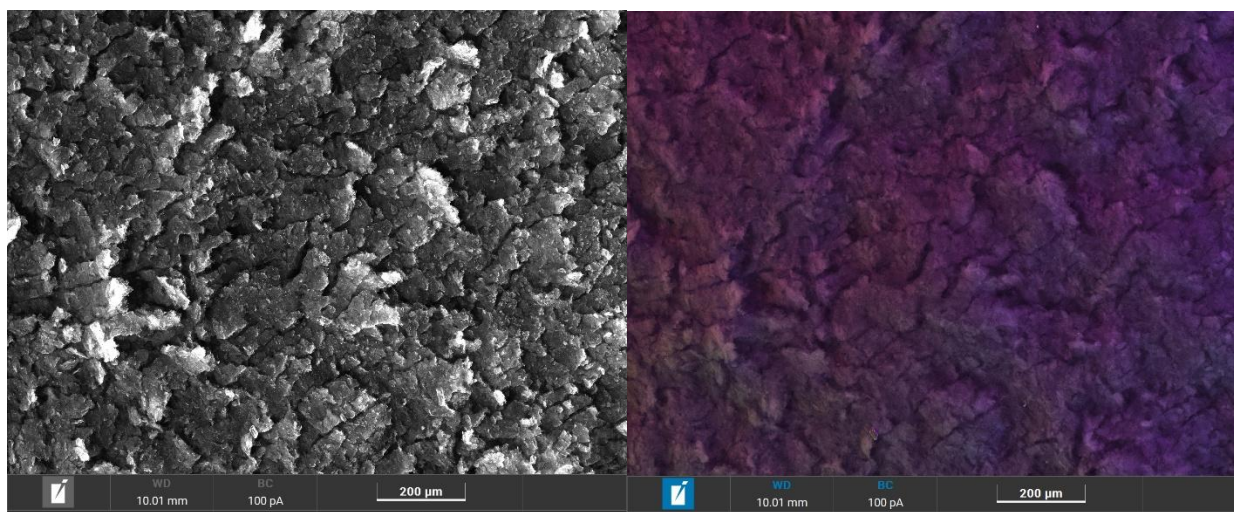


Figure 4: SEM micrographs of rGO, SE image (left) and BSE image (right).

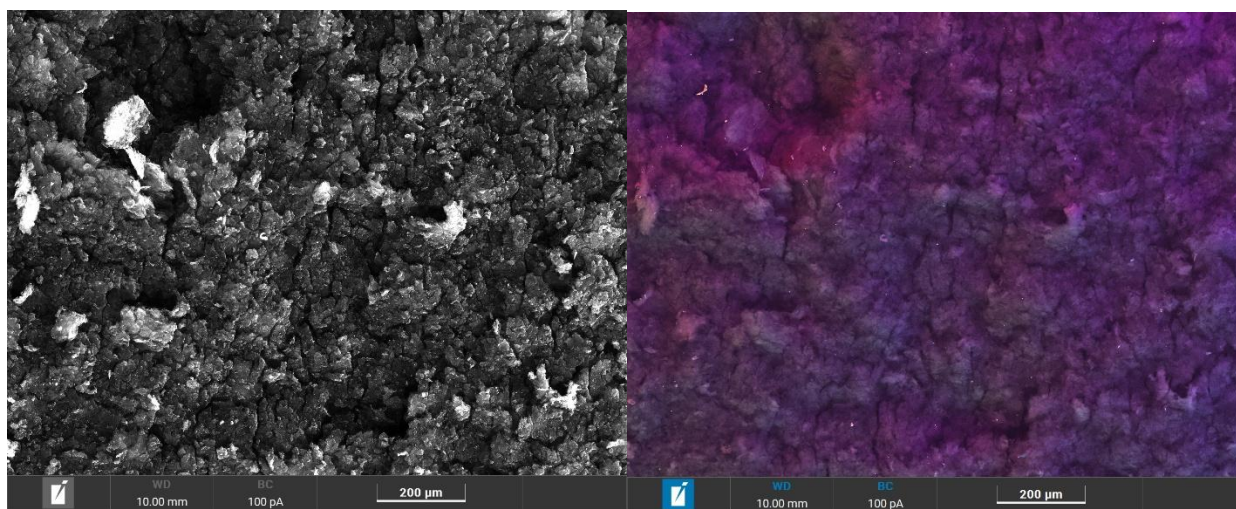


Figure 5: SEM micrographs of rGO/PVA 10. SE image (left) and BSE image (right).

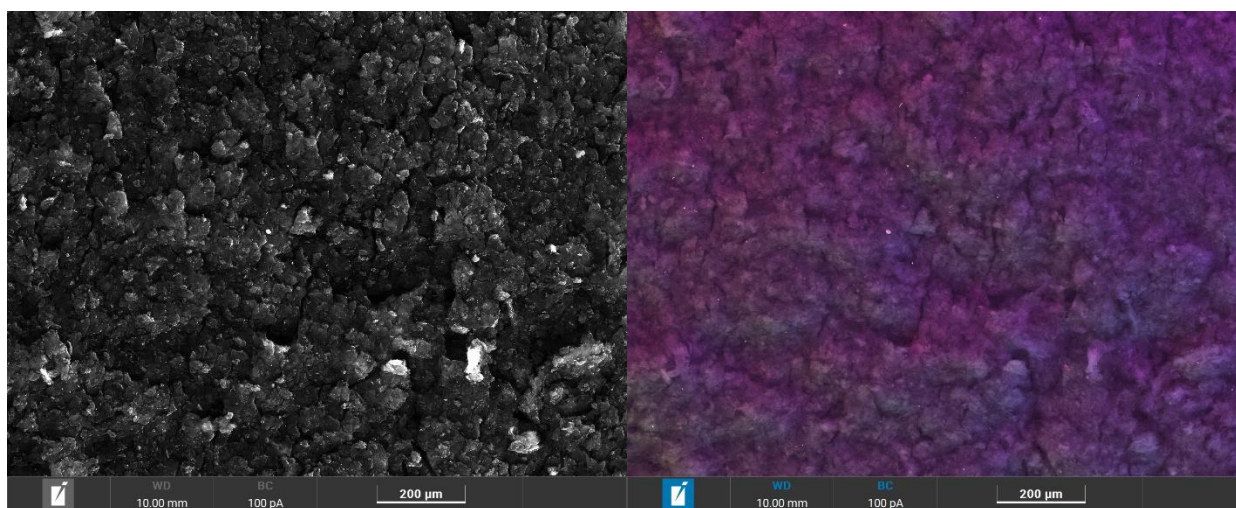


Figure 6: SEM micrographs of rGO/PVA 20. SE image (left) and BSE image (right).

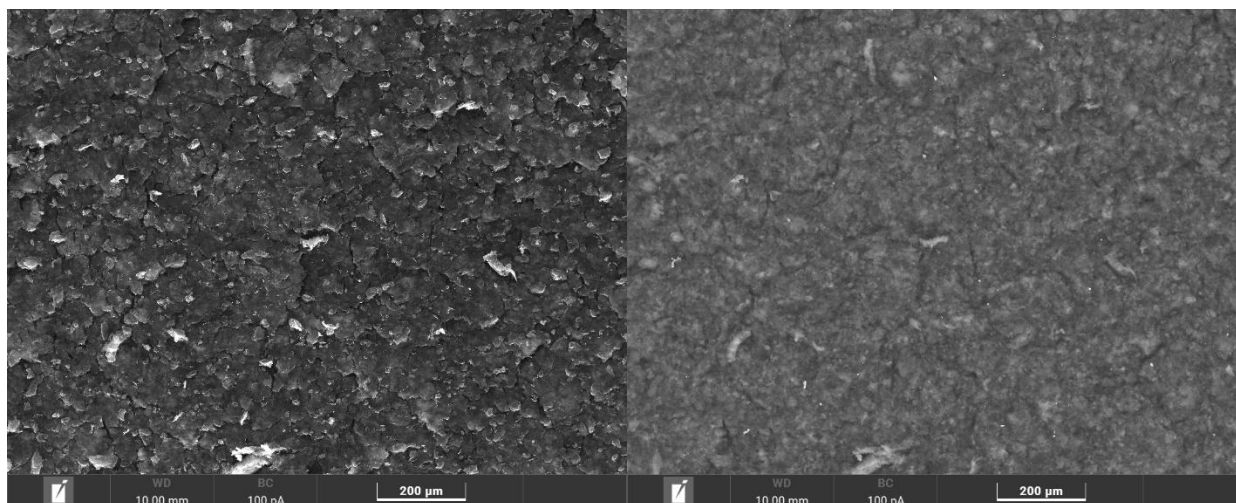


Figure 7: SEM micrographs of rGO/PVA 20/ PEG 15. SE image (left) and BSE image (right).

The increased compactness of the composite samples is expected to be reflected in BET analysis as a decrease in specific surface area. **Fig. 8a** shows the pore size distribution of pure rGO and rGO/PVA 20/PEG 15 composites prepared according to the described procedure, where either 200 mL or 100 mL of the suspension was cast, resulting in thicker and thinner films, respectively. As anticipated, pristine rGO paper exhibits the highest specific surface area ($393.8 \pm 2.7 \text{ m}^2\cdot\text{g}^{-1}$). In contrast, the composite samples show a reduction in surface area to $333.0 \pm 3.5 \text{ m}^2\cdot\text{g}^{-1}$ (100 mL sample) and $290.9 \pm 1.3 \text{ m}^2\cdot\text{g}^{-1}$ (200 mL sample), consistent with the formation of a more compact structure due to polymer incorporation. The decrease is more pronounced for the thicker sample, indicating a stronger limitation of accessible surface area with increasing film thickness. The rGO/PVA 20/PEG 15 composites were subsequently treated using a DCSBD plasma jet with N_2 as the working gas. **Fig.8b** and **Fig.8c** illustrate the changes in surface area after plasma exposure for 50 s (100 mL sample) and 100 s (200 mL sample), respectively. Plasma treatment leads to an increase in specific surface area in both cases. However, the effect is significantly more pronounced for the thinner sample. After 50 s of treatment, the surface area of the thinner sample increases to $510.6 \pm 9.4 \text{ m}^2\cdot\text{g}^{-1}$, whereas the thicker sample shows only a slight increase to $297.5 \pm 2.8 \text{ m}^2\cdot\text{g}^{-1}$ after 100 s. This behavior can be attributed to the combined influence of sample thickness and initial porosity. The higher initial surface area and reduced thickness of the thinner film likely facilitate deeper penetration of reactive plasma species, enabling more effective etching and activation of internal surfaces. In contrast, the thicker sample presents a diffusion barrier that limits plasma interaction primarily to the surface layers. These results highlight

that plasma treatment efficiency is strongly dependent on both the structural accessibility and thickness of the material.

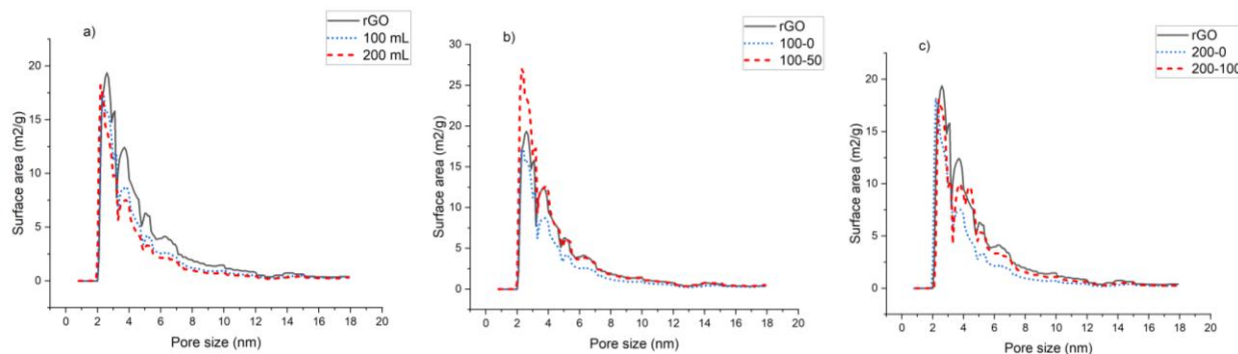


Figure 8: BET pore size distributions; a) rGO, thinner and thicker rGO/PVA20/PEG15; b) thinner 100 mL sample; c) Thicker 200 mL sample.

The FTIR spectra presented in **Fig.9a–d** provide an overview of the chemical and structural evolution of GO subjected to plasma reduction and post-treatment, modified with varying amounts of PVA and PEG. The spectra consistently reflect the interplay between removal of oxygen-containing functional groups, incorporation of polymeric components, and structural reorganization toward a graphitic network. In **Fig.9a**, the transition from GO to rGO is clearly evidenced by the disappearance of characteristic oxygen-related bands. Upon GO reduction using a DCSBD N_2 plasma, a propagating thermal reduction front accompanied by visible emission (indicative of local temperatures exceeding $\sim 600^\circ C$, **Fig.1f**) removes the majority of labile oxygen functionalities, including epoxy, alkoxy, and hydroxyl groups, as evidenced by the disappearance of bands at $\sim 800\text{--}1150\text{ cm}^{-1}$, associated with C–O stretching of alkoxy group. Notably, a residual band remains at $\sim 1300\text{ cm}^{-1}$, suggesting that the reduction is not complete and that some oxygen-containing functionalities persist. This band is most commonly attributed to C–O stretching vibrations of phenolic or hydroxyl-related groups located at defect sites or sheet edges, indicating the presence of more thermally stable oxygen functionalities that are not fully removed during plasma treatment. The band near $\sim 1760\text{ cm}^{-1}$, attributed to carbonyl groups, is also diminished. Concurrently, the band near $\sim 1610\text{ cm}^{-1}$ becomes relatively more pronounced, indicating restoration of sp^2 carbon domains. The addition of PVA to GO results in increased intensity in the $\sim 1450\text{ cm}^{-1}$ region, corresponding to C–O and CH_2 vibrations of the polymer. These features confirm successful incorporation of PVA but also highlight that polymer signals overlap with GO oxygen functionalities. **Fig.9b** demonstrates the effect of increasing PVA content prior to reduction in rGO/PVA composites. A subtle increase in the intensity of band near $\sim 1450\text{ cm}^{-1}$ (CH_2 deformation) is observed with increasing polymer fraction, suggesting fraction of the polymer survived the high temperature reduction front. The relative intensity of the $\sim 1600\text{ cm}^{-1}$ band decreases with increasing PVA content, not due to loss of graphitic structure, but rather due to dilution of the rGO signal by the polymer matrix. The most reliable trend observed

in **Fig.9c** is a gradual decrease in the relative intensity of the broad O–H stretching band ($\sim 3500\text{--}4000\text{ cm}^{-1}$) with increasing plasma treatment time. This decrease indicates a progressive reduction in the concentration of hydroxyl-containing species within the system, including PVA hydroxyl groups, residual oxygen functionalities on rGO, and adsorbed water. **Fig.9d** illustrates the effect of PEG addition to rGO/PVA 20 composites. The $\sim 1450\text{ cm}^{-1}$ band increases due to CH_2 deformation modes from PEG chains. The O–H stretching region becomes broader and more intense, reflecting enhanced hydrogen bonding involving PVA, PEG, and residual rGO oxygen groups.

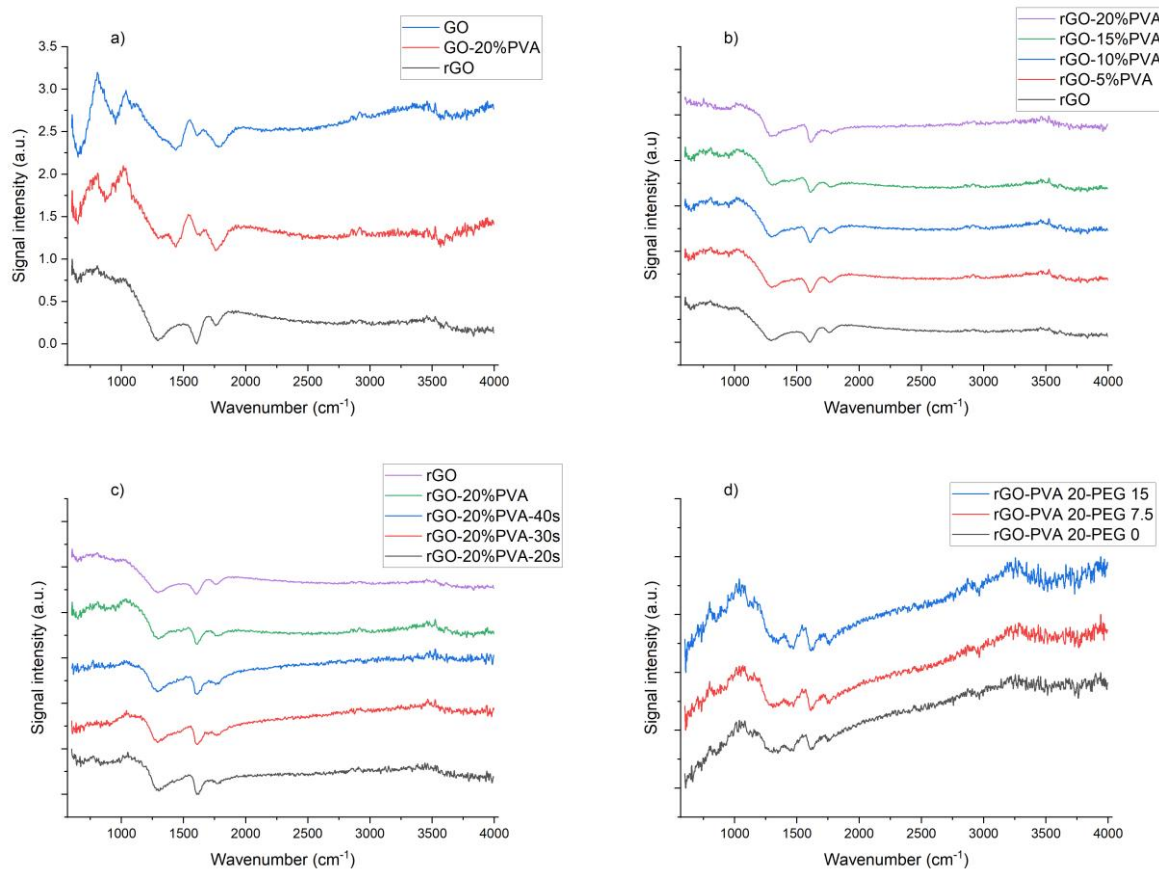
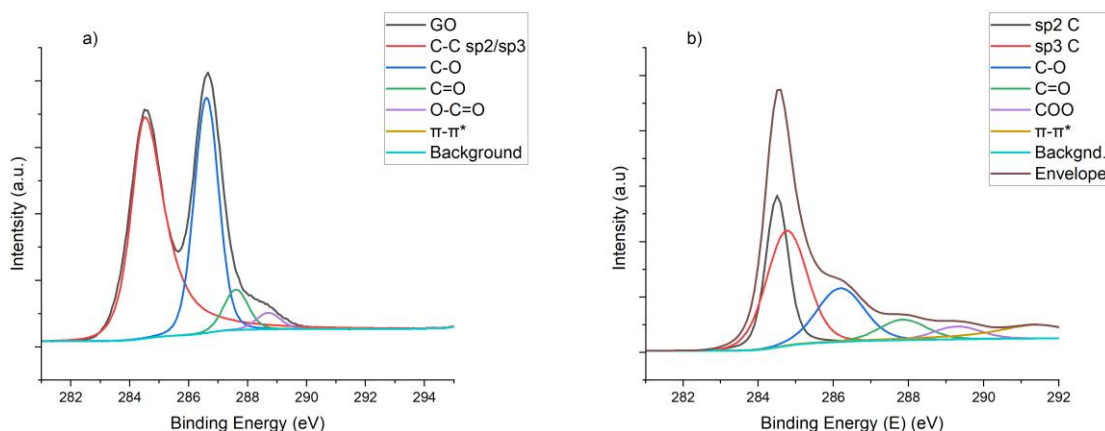


Figure 9: FTIR spectra of prepared samples. a) FTIR spectra of GO, rGO and GO with 20 wt% PVA. b) FTIR spectra of rGO with different amounts of PVA. c) FTIR spectra of rGO samples with 20% PVA post-treated for 20–40s with DCSBD jet using N_2 as working gas. d) FTIR spectra of rGO/PVA20 composites with various amount of PEG 400.

The X-ray photoelectron spectroscopy (XPS) $\text{C}1\text{s}$ spectra provides clear insight into the evolution of surface chemistry and bonding configurations from GO to rGO, and further under different plasma post-treatments. The deconvolution of the $\text{C}1\text{s}$ envelope into characteristic components— $\text{sp}^2\text{ C}=\text{C}$ (284.4), $\text{sp}^3\text{ C}-\text{C}$ (284.8 eV), $\text{C}-\text{O}$ (286.0 eV), $\text{C}=\text{O}$ (287.0 eV), $\text{O}-\text{C}=\text{O}$ ($\sim 288.5\text{--}289.0\text{ eV}$), and the $\pi-\pi^*$ shake-up (290–291 eV) enables a detailed assessment of the degree of oxidation, reduction, and heteroatom incorporation.

In the pristine GO sample (**Fig.10a**), the spectrum is dominated by oxygen-containing functional groups, with pronounced contributions from C–O, C=O, and O–C=O species. The presence of epoxy, hydroxyl, carbonyl, and carboxyl groups is consistent with the typical structure of GO [19]. The weak π – π^* satellite further confirms the loss of long-range aromatic order. Upon reduction to rGO (**Fig.10b**), a substantial restoration of the graphitic network is observed. The sp^2 C=C peak becomes the dominant feature, accompanied by a decrease in the intensity of oxygen-related components. This indicates effective removal of oxygen functionalities and partial re-establishment of conjugated π -electron systems [19]. However, residual C–O and C=O contributions suggest that the reduction is incomplete, and some defects and functional groups persist. The reappearance of π – π^* shake-up feature further supports the recovery of aromatic domains. Plasma post-treatment with N_2 (**Fig.10c**) introduces additional complexity into the C 1s spectrum. Alongside the retained sp^2 carbon peak, a new component attributable to C–N bonding emerges in the ~ 285.5 – 286.0 eV region. This indicates successful nitrogen incorporation into the carbon lattice, likely in the form of pyridinic, pyrrolic, or graphitic nitrogen species [20]. The coexistence of C–O and C=O peaks suggests that the N_2 plasma does not significantly enhance reduction compared to rGO but rather promotes functionalization and defect generation. The broadened spectral envelope and increased relative intensity of non- sp^2 components reflect a higher degree of structural disorder induced by plasma exposure. In contrast, treatment with forming gas plasma (**Fig.10d**) results in a more pronounced reduction effect. The sp^2 C=C peak is further intensified relative to the oxygenated components, indicating enhanced removal of oxygen functionalities due to the reductive role of hydrogen species. The overall spectral profile points to a more effective restoration of the graphitic structure, with fewer residual oxygen groups and moderate heteroatom doping. Finally, air plasma treatment (**Fig.10e**) leads to a re-oxidation of the rGO surface. The C 1s spectrum shows an increase in the intensity of C–O, C=O, and O–C=O components, accompanied by a relative decrease in the sp^2 C=C contribution. This indicates the introduction of new oxygen-containing functional groups, likely through interactions with reactive oxygen species in the plasma.



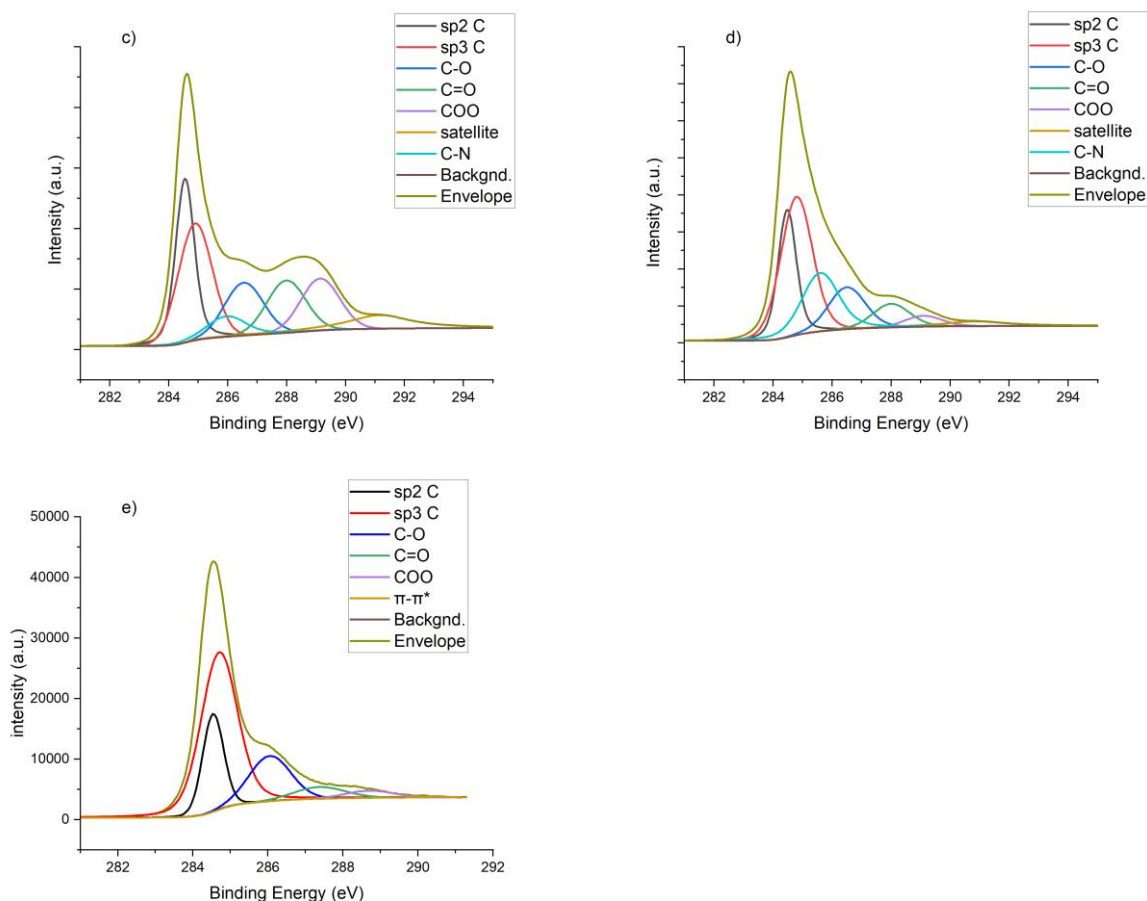


Figure 10: Deconvoluted XPS C1s spectra of GO (a); rGO (b); rGO + 20 s N₂ post-treatment (c); rGO + 20s forming gas treatment (d); rGO + 20 s air post-treatment (e).

The XPS-derived atomic composition clearly demonstrates that the plasma working gas strongly influences the surface chemistry evolution of rGO, with distinct trends observed for N₂, forming gas, and air as working gases. In the case of N₂ plasma (**Fig.11a**), depending on the applied power, a pronounced nitrogen incorporation is observed, increasing from approximately 2.1 at% at 5s treatment time to 7.5 at% and 4.7 at% after 30s treatment time at 40 W and 30 W, respectively. Simultaneously, the oxygen content doubles from 14.3 at% to 29.4 at%, while carbon correspondingly drops from 84.5 at% to 63.1 at%. This indicates that N₂ plasma induces both nitrogen functionalization and partial oxidation of the rGO surface. The effect is more pronounced at higher plasma powers (50 W), where the highest nitrogen concentrations and highest oxygen contents are achieved, suggesting enhanced activation of the surface and creation of highly reactive defect sites that promote both nitrogen incorporation and subsequent oxygen uptake, either from residual adsorbed water present during post-treatment on rGO, or from post-treatment exposure to air. In contrast, forming gas plasma (5% H₂ / 95% N₂, **Fig.11b**) results in different compositional changes. After 15 s, nitrogen content increased to 7.7 at%, indicating faster nitrogen incorporation compared to N₂ plasma post-treatment.

However, no significant change in oxygen content is evident. These trends suggest that forming gas hinders creation of highly reactive defect sites while promoting nitrogen functionalization. A markedly different behavior is observed for air plasma (**Fig.11c**), where no nitrogen incorporation is detected. Instead, an increase in oxygen content is observed, rising from approximately 14.3 at% up to 24.5 at% after 20s at 40W. Correspondingly, the carbon content decreases from 84.5 at% to 74.5 at%. This clearly indicates oxidative functionalization of the rGO surface, with the introduction of oxygen-containing groups and possible oxidative etching effects. The choice of plasma gas enables controlled tuning of the rGO surface chemistry from nitrogen-functionalized to reduced or oxidized states.

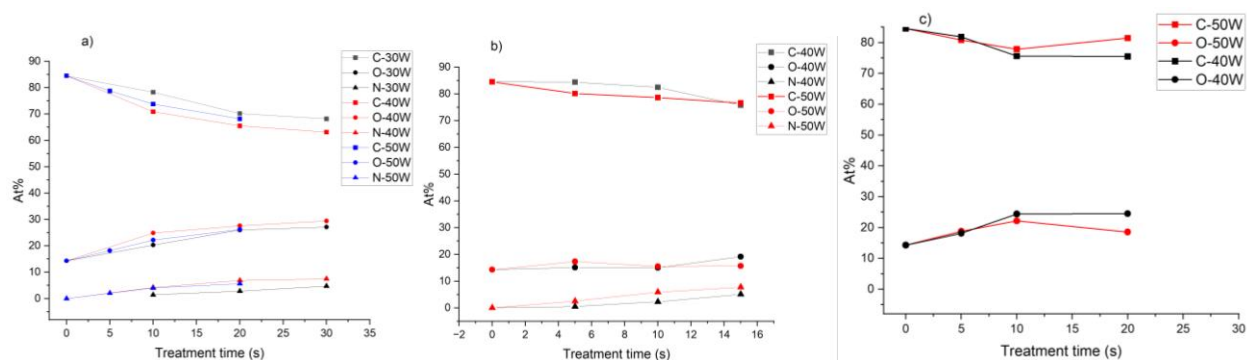


Figure 11: Elemental composition evolution of rGO after plasma post-treatment at increasing treatment time with Nitrogen (a), Forming gas (b) and Air (c).

Assembled filters made out of 2 layers of rGO + 20s N₂ plasma post-treatment and rGO/PVA20/PEG15 + 20s N₂ were tested in 3D printed filtration cell (**Fig.3**). Peristaltic pump voltage was varied between 3-8 V, pressure and time to let 100 mL of ultrapure water was measured to calculate permeability and hydraulic permeability (**Fig.12**). With the same peristaltic pump settings, membrane made from pure rGO (**Fig.12a**) exhibits much larger permeability at lower pressures (3430 L/m².h at 0.1 bar), compared to composite membrane (**Fig.12b**) (2570 L.h at 0.6 bar). This is in accordance with larger rGO surface area measured by BET compared to composite rGO/PVA20/PEG15.

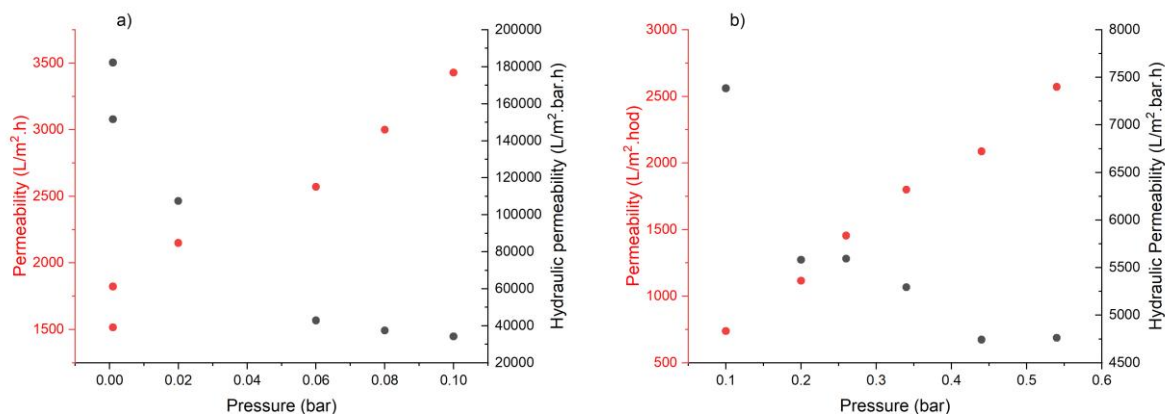


Figure 12: Permeability and hydraulic permeability of 2 layer rGO membrane (a) and 2 layer rGO/PVA20/PEG15 membrane (b).

For next testing, 1-3 layered rGO membranes were fabricated and their filtration efficiency tested with 100 mL of 10 mg/L rhodamine B solution over 30 minutes of continuous filtration with peristaltic pump set to 4 V. As expected, increasing the number of layers leads to better dye retention as shown in **Fig.13a**. Most significant difference is observed just after 5 mins where 1,2 and 3 layered rGO membrane retained 91.8 %,93.8 % and 98.5 %, respectively. After 20 minutes, all membranes retained over 99 % of the dye, while 3 layered rGO reached this limit after 15 minutes. Finally, 2 layered, 20 s plasma post-treated rGO and rGO/PVA20/PEG15 membranes were assembled to assess the effect of plasma post-treatment. Interestingly, nitrogen plasma post-treatment leads to a decrease in retention efficiency of both membranes as shown in **Fig.13b-c**. Incorporation of nitrogen functional groups tends to lead to more positive net charge on the rGO surface, thus worsening the interactions with positively charged rhodamine B ions. On the other hand, air plasma post-treatment increases the retention efficiency in both cases. Oxygen containing air plasma creates more reactive species and aggressive environment, that is probably more efficient in creation of defects containing oxygen functional groups. This should change the surface net charge to a more negative value, attracting rhodamine ions more effectively, and introducing more sites, where rhodamine ions can create intermolecular bonds with the rGO.

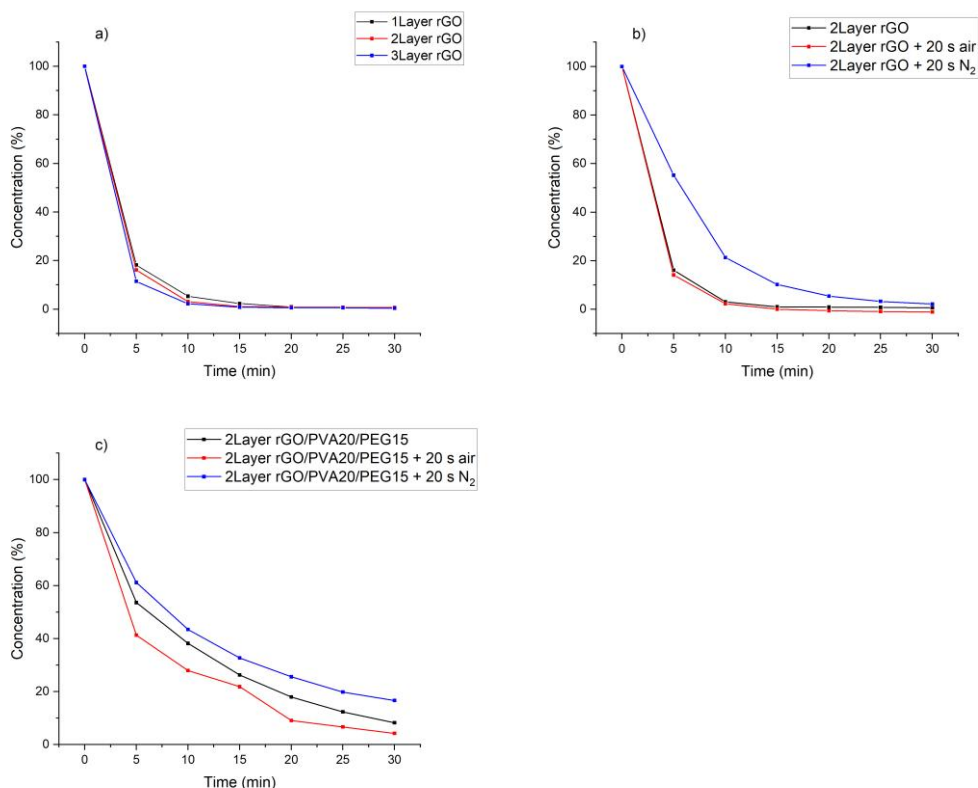


Figure 13: Rhodamine B retention of: 1-3 layered rGO membranes (a); N₂ and air post-treated 2 layer rGO membrane (b); N₂ and air post-treated 2 layer rGO/PVA20/PEG15 membrane (c).

5. Conclusion

Atmospheric pressure plasma is the most suitable technology for industrial-scale production of rGO-based membranes. We proved that DCSBD plasma system can be used to reduce large area GO films within seconds and then further functionalize the rGO surface by using industrially relevant working gases to modify its chemical properties. Whole process is compatible with in-line manufacturing processes thanks to the short treatment times. Using air as working gas, large number of oxygen-based functional groups are incorporated into the rGO structure, improving Rhodamine B retention. Using nitrogen as working gas, the concentration of both nitrogen and oxygen functional groups increases. This however negatively impacts the rhodamine B retention. Lastly, using forming gas leads to incorporation of just nitrogen functional groups. Addition of binding polymers like PVA or PEG can be used to modify the mechanical properties. However, as was demonstrated in this paper, large amounts of copolymers decrease the surface area and retention capabilities of the membrane. Therefore, further testing and optimization is required to understand the effect of functionalization and membrane composition on pollutants retention. Huge potential lies in electrical conductivity of rGO, which could be utilized for electrochemical reactions on the rGO surface, thus potentially further improving the efficiency and selectivity of rGO-based membranes.

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Conflict of interest

We declare no conflict of interest.

Use of AI tools

Portions of this text were revised with the assistance of ChatGPT (OpenAI, GPT-5.3), accessed through a paid subscription plan, to enhance clarity and readability. All final content was reviewed and approved by the main author.

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