



Article

Hydrophobic PTFE/rGO Aerogels with High Polymer Content as Water Sorbents

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Abstract

Composite aerogels based on polytetrafluoroethylene (PTFE) and graphene oxide (GO) with a high polymer content of 90, 95 and 98 wt.% were synthesized for the first time. It was found that GO performs a structure-forming function, allowing the production of monolithic three-dimensional frameworks stable under freeze-drying conditions even at a minimal concentration of 2 wt.%, whereas pure PTFE is destroyed under these conditions. Subsequent annealing of the composites at 370 °C, which is higher than the decomposition temperature of oxygen-containing groups of GO and the melting point of PTFE, leads to the formation of PTFE/reduced graphene oxide (rGO) aerogels. A direct dependence of shrinkage during annealing on the polymer content was observed: it sharply increases from 2.1% to 26.6% with an increasing proportion of PTFE. This effect is explained by the dominant role of capillary forces pulling together the rGO sheets in the molten polymer, while the rGO frame resists the shrinkage. The most significant result is the achievement of a record low water sorption capacity (Q_w) for an aerogel with 98% PTFE, amounting to only 0.001 g/g. This value is several orders of magnitude lower than that of pure rGO aerogel (~20 g/g), confirming that a high content of hydrophobic polymer combined with thermal treatment effectively shields the hydrophilic sites on the surface of the rGO sheets. The composites obtained in this work exhibit high hydrophobicity (contact angles up to 144°) and unique potential for the selective absorption of organic solvents from water.

Keywords: composite aerogel; polytetrafluoroethylene; graphene oxide; hydrophobicity; contact wetting angle



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1. Introduction

Polytetrafluoroethylene (PTFE) is a unique fluoropolymer that combines exceptional chemical inertness, thermal stability over a wide temperature range, and pronounced hydrophobicity. These properties have led to its widespread use in the chemical industry, electrical engineering, medicine, and membrane technologies [1]. However, the practical use of PTFE as a material for sorbents or catalyst supports is limited by its processing characteristics: a very high melting point (~327 °C) and an extremely high melt viscosity, which persists even when heated above the decomposition temperature, make it impossible to produce three-dimensional porous structures using conventional methods such

as foaming. Attempts to create low-density aerogels based on pure PTFE also encounter the problem of the absence of a structure-forming matrix. As shown in the present work, after freeze-drying, a frozen sample of a dispersion of pure PTFE completely disintegrates, failing to retain the desired shape.

One promising approach to solving this problem is the use of templates or structure-forming additives. In work [2], it was demonstrated that the introduction of graphene oxide (GO), which is capable of forming a three-dimensional network in aqueous dispersions at concentrations above 3 mg/L [3], makes it possible to obtain PTFE/GO composite aerogels. In such a system, GO sheets act as a reinforcing framework, distributing the polymer particles between themselves and preventing structural collapse during freeze-drying. The aerogels prepared in [2] with an equal mass ratio of PTFE to GO (50:50) exhibited superhydrophobic properties and high sorption capacity for organic solvents. However, with this composition, a significant portion of the surface consists of reduced graphene oxide (rGO), which retains a certain amount of oxygen-containing functional groups even after thermal treatment. This leads to the presence of hydrophilic regions and residual water sorption [4,5], which reduces the sorbent's selectivity in the separation of "organic–water" mixtures.

In this regard, a logical development of the approach is to increase the proportion of PTFE in the composite in order to block hydrophilic sites on the GO surface and form a continuous or semi-continuous polymer phase. However, increasing the polymer content is associated with a number of risks. First, reducing the proportion of GO may weaken the structure-forming framework. Second, during annealing at temperatures above the melting point of PTFE (370 °C), the polymer melts, and the resulting capillary forces begin to pull the flexible GO sheets together. The higher the content of molten PTFE, the stronger these forces and the greater the expected shrinkage of the material. Consequently, there is a trade-off between the desire to close hydrophilic pores and the need to maintain acceptable porosity and mechanical integrity.

Thus, the aim of this work was to obtain monolithic PTFE/GO aerogels with the highest possible polymer content (up to 98 wt.%), a systematic study of their structure, thermal behavior, electrophysical properties, and, most importantly, sorption characteristics with respect to water and organic solvents. We hypothesized that annealing at 370 °C, leading to melting of PTFE and reduction of GO, would allow not only the removal of surfactants but also the formation of a three-dimensional polymer network that effectively screens hydrophilic residual groups on rGO. This should ensure a sharp decrease in water sorption while maintaining practical capacity for organic liquids.

The conducted experiments fully confirmed this hypothesis. As will be shown below, the main result was the achievement of extremely low water sorption—only 0.001 g/g for a sample with 98% PTFE—which is significantly lower than the values reported in the literature [2,6]. At the same time, a clear correlation was found between composition, shrinkage during annealing, porosity, and sorption properties. In particular, the increase in shrinkage from 2.1% (90% PTFE) to 26.6% (98% PTFE) is accompanied by a decrease in porosity (from ~95% to ~73%) and a reduction in sorption capacity for organic solvents; however, even under these conditions, the sample containing 98% PTFE retains selectivity toward organic compounds (for example, 2.8 g/g for THF and acetone) with almost zero water uptake. Thus, this work demonstrates for the first time that a delicate balance between polymer content, shrinkage, and porosity allows for the targeted creation PTFE/rGO aerogels with record-high hydrophobicity and sorption selectivity, which opens prospects for their use in separating immiscible "organic–water" media.

2. Experimental Details

2.1. Materials

Graphite was purchased from LLC “NPP AVERS” (Chelyabinsk, Russia), sulfuric and nitric acids, and solvents were purchased from JSC “Base No. 1 of Chemical Reagents” (Staraya Kupavna, Russia).

An aqueous F-4D suspension (Kirovo-Chepetsk Chemical Company, TU 6-05-1246-81, Kirovo-Chepetsk, Russia) was selected as a source of PTFE. The suspension contains PTFE (molecular weight 140,000–500,000), surfactants (a mixture of ethoxylated alkylphenols) as a stabilizer, and water in a ratio of 6:1:3.

2.2. Production of Graphene Oxide

To obtain graphene oxide, we used a modified Hummers method [7]. Details of our method for producing graphene oxide are described elsewhere [8]. The lateral size of the graphene oxide particles ranged from 0.5–5 μm , and the particle thickness from 0.7 to 1.7 nm.

2.3. Synthesis of PTFE/GO Aerogels

The method used in this study to prepare PTFE/GO aerogels slightly differs from that described in [2]. The main difference is the high concentration of PTFE in the forming hydrogel. For freezing the hydrogels, we used a setup developed by our team. It consists of a glass Dewar vessel containing a solid copper cylinder with a diameter of 50 mm and a length of 250 mm. A copper plate measuring 150 $\times$ 150 $\times$ 15 mm was mounted atop the cylinder, and the hydrogels were frozen on this plate (Figure S1 of the Supporting Information). The setup was equipped with an electronic thermometer with a type K thermocouple to monitor the platform temperature. The setup operates by lowering the platform temperature using liquid nitrogen in the Dewar vessel. To produce shaped aerogels, rectangular or cylindrical molds made of ABS polymer were prefabricated by Fused Deposition Modeling (FDM) 3D printing. During freezing, the temperature of the copper plate was maintained between -80 and -90 $^{\circ}\text{C}$. After the plate temperature had stabilized, the mold was placed on it and filled with the PTFE-GO suspension. The freezing time depended on the suspension volume: for cylindrical samples ($r = 20$ mm, $h = 20$ mm) and for rectangular samples (100 $\times$ 100 $\times$ 12 mm) it was approximately 5 min and 10 min, respectively. The frozen hydrogel was removed from the plate and placed into the chamber of an IlShin BioBase FD5512 freeze dryer (Seoul, Republic of Korea). The drying parameters were as follows: pressure of 5 mTorr, condenser temperature from -45 $^{\circ}\text{C}$ to -55 $^{\circ}\text{C}$. The drying time for cylindrical aerogels was at least 72 h, and for rectangular aerogels it was increased to at least 120 h (shelf heating in the chamber was not used).

2.4. Annealing of PTFE/GO Aerogels

The obtained PTFE/rGO aerogel samples were annealed in order to remove surfactant, restore GO, and form a three-dimensional polymer network. Annealing conditions were 370 $^{\circ}\text{C}$, 2 h, in air.

2.5. Equipment

Thermogravimetric analysis (TGA) of the samples was performed using an STA 449 F3 Jupiter instrument (Selb, Bavaria, Germany). To calibrate the balance, the instrument chamber was evacuated (10^{-2} bar) and filled with high purity He gas (grade 6.0, 99.9999%). After that, two empty corundum (Al_2O_3) crucibles were placed on the sample holder in the working chamber and a baseline was recorded. Next, the sample was placed into one of the empty crucibles, the instrument chamber was again evacuated and filled with helium.

Measurements were carried out in the temperature range of 20–600 °C at a heating rate of 10 °C/min in a helium flow of 50 mL/min.

IR spectra (resolution 4 cm^{−1}, 32 scans) were recorded at room temperature in the range of 4000–450 cm^{−1} using a “Perkin Elmer Spectrum Two” FTIR spectrometer (Shelton, CT, USA) with an attenuated total reflection (ATR) accessory.

Raman spectra were obtained using a Comfotech NR500 Raman microscope (SOL Instruments, Augsburg, Germany). The excitation laser wavelength was 532 nm, the power at the measurement point was 0.1 mW, and the beam diameter was approximately ~2 µm.

To measure the contact angle (CA or θ) of a flat surface with water, the contour of a “sitting” drop was analyzed using an OCA 20 instrument (DataPhysics Instruments GmbH, Filderstadt, Germany) at room temperature. The results were processed using the Young–Laplace method, taking into account the physical properties of the sessile drop and the curved surface of the liquid interface, using the SCA 20 module software version 4.1.12 from DataPhysics Instruments GmbH (Filderstadt, Germany).

Electrical resistance was measured using a digital multimeter Agilent 34410A (Santa Clara, CA, USA). Measurement range: 0–100 MΩ (resolution 100 µΩ). The schematic of the cell for measuring the specific electrical resistance of cylindrical aerogels is shown in Figure 1.

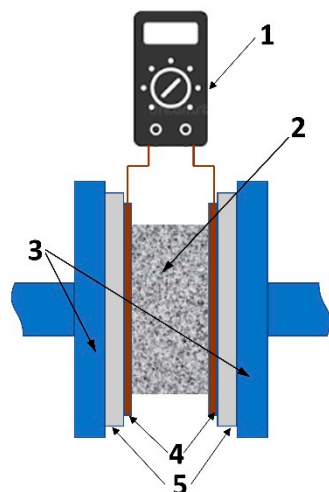


Figure 1. The scheme of a cell for measuring the specific electrical resistivity of cylindrical aerogels: 1—resistance meter (Agilent 34410A), 2—aerogel sample, 3—clamp with fixed clamping force, 4—copper plates, 5—ABS+ polymer plates.

To measure thermal conductivity, we used the ITP-MG-4 “100” thermal conductivity meter (SKB Stroipribor LLC, Chelyabinsk, Russia). This device is designed to measure the thermal conductivity coefficient λ of materials under steady-state thermal conditions. The measurement range of λ is from 0.02 to 1.50 W/(m·K). The device was calibrated using an organic glass sample ($\lambda = 0.167$ W/(m·K)). The limits of the permissible relative measurement error of thermal conductivity under steady-state thermal conditions were $\pm 5\%$. The samples for measurements using the ITP-MG-4 “100” are parallelepipeds with geometric dimensions of 100 mm $\times$ 100 mm $\times$ 16–30 mm. Other conditions for measuring the thermal conductivity of the studied samples are as follows: ambient air temperature from 19 °C to 22 °C, relative air humidity from 30% to 40%, refrigerator temperature 17.5 °C, and heater temperature 37.5 °C.

2.6. Study of Sorption Properties

The sorption capacity of aerogels with respect to solvents, water, and oil was studied under static conditions at room temperature. For this purpose, the test container was filled

with liquid so that the thickness of its layer was at least 2.5 cm. A pre-weighed aerogel sample with a mass of 17–76 g was placed in a mesh basket, which was then immersed in the container so that the basket with the aerogel was freely positioned inside the container. After 10 min, the basket with the aerogel was removed and allowed to drain of residual solvent for 1 min. After that, the basket content of was transferred to a tray of known weight. Then, the tray with the aerogel was weighed, and the result was recorded. The mesh basket was fabricated from stainless steel wire with a thickness of 200 μm and a mesh size of 5 mm. Such a basket design makes it possible to neglect the mass of the solvent wetting it due to the extremely small surface area. Most solvents used in sorption experiments completely evaporate from the mesh surface during the draining time (~ 1 min).

The sorption capacity Q_m (g/g) was calculated using the formula:

$$Q_m = m_s / m_a \quad (1)$$

where m_s is the mass of sorbed solvent, water, or oil in g; m_a is the mass of dry aerogel in g.

3. Results and Discussion

3.1. Appearance, Bulk Density, and Porosity of Aerogels

Figure 2 shows a monolithic square-shaped piece made of freeze-dried PTFE/GO aerogel with a polymer content of 98% (Aerogel 98 or A98). Next to it in a Petri dish is an aerogel without GO (Aerogel A100), which was obtained using the same procedure as aerogel 98. It can be seen that aerogel 100 disintegrates after freeze-drying (it does not retain its intended shape). This experiment demonstrates that GO is the shape-forming component in the PTFE–GO system even at low concentrations.



Figure 2. Photographs of aerogels 100 and 98 after freeze-drying.

After annealing in air at a temperature of 370 $^{\circ}\text{C}$, the monolithic samples retain their shape but undergo slight shrinkage (Table 1) and change color from light yellow to dark (Figure 3).

As is well known, GO sheets with lateral dimensions of several micrometers are capable of contacting one another, forming a loose network in solution if their concentration exceeds 3 mg/L [3]. From the data presented in Table 1, one can calculate that the specific density of GO in aerogels 90, 95, and 98 is within the range of 9–11 mg/cm³, which significantly exceeds the lower gelation threshold of GO in water. The color of aerogel 100 annealed under the same conditions is found to be non-uniform (Figure S2 of the

Supporting Information). This suggests that the conditions for oxidative degradation of the surfactant present in aerogel 100 may differ in different parts of the bulk material.

Table 1. Volumetric shrinkage during annealing (transition from PTFE/GO to PTFE/rGO), bulk density (d), bulk porosity (P), specific resistance (ρ), and thermal conductivity (λ) of PTFE/rGO aerogels.

Parameter	90/10 PTFE/rGO	95/5 PTFE/rGO	98/2 PTFE/rGO
shrinkage, %	2.1	14.4	26.59
d , g/cm ³	0.0907	0.2134	0.5378
P , %	95.3–95.6	89.0–89.8	72.2–74.3
ρ , Ohm·m	$(1.49 \pm 0.12) \cdot 10^3$	$(6.77 \pm 0.98) \cdot 10^3$	$(1.80 \pm 0.22) \cdot 10^4$
λ , W/m·K	0.04 ± 0.01	0.06 ± 0.02	0.09 ± 0.04

Therefore, 2 h at 370 °C is clearly insufficient for the complete removal of surfactant degradation products from thick pieces of dried F-4D suspension (or, formally, aerogel 100). We believe that the situation may be similar for aerogels containing graphene oxide. However, for PTFE/GO aerogels, it is impossible to visually observe different levels of removal of the surfactant degradation products, because graphene oxide also becomes dark after thermal treatment.

An optical microscope examination of the aerogel surfaces revealed that the surface topography of the aerogel monolith in contact with the copper plate (bottom) differs from that of the surface in contact with air (Figure S3 of the Supporting Information). At the magnification used, the bottom surface appears smoother. These differences persist after heating at 370 °C. At higher magnification, pores are clearly visible on the lower surface of the PTFE/rGO aerogels (Figure 4). Such large pores were not observed on the upper surface.

It was found that the surface density of optically visible pores is 32%, 23%, and 25% on the lower surface of aerogels 90, 95, and 98, respectively. If small pores are disregarded, it can be stated (taking into account the data reported in [9]) that the near-surface region of the obtained aerogels is denser compared to the bulk. From Table 1 it follows that the bulk porosity of the aerogels decreases with increasing polymer content.

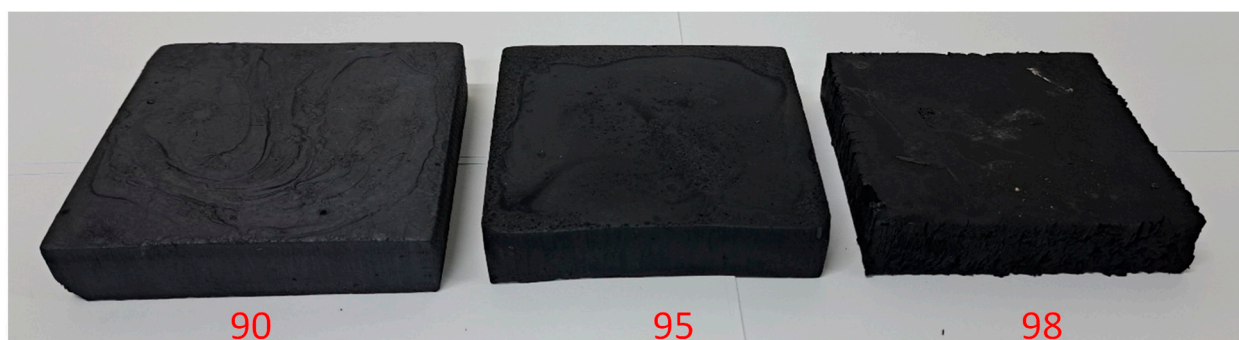


Figure 3. Photographs of aerogels 90, 95, and 98 after annealing in air at 370 °C.

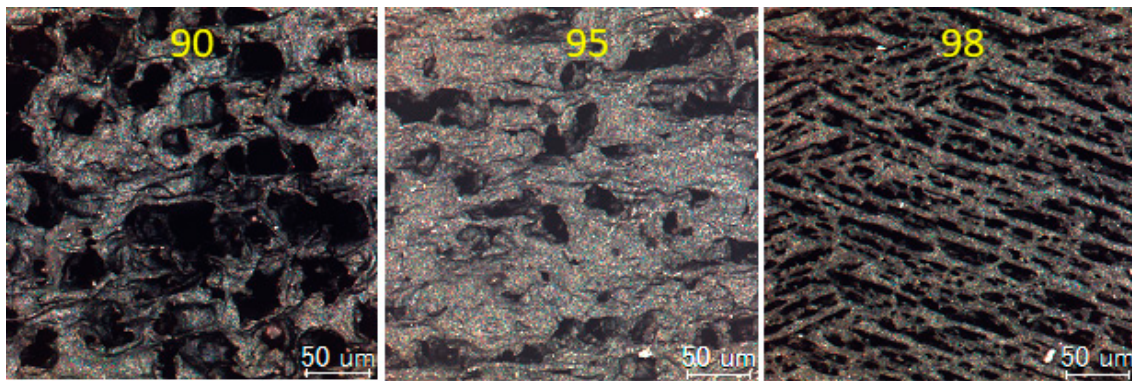


Figure 4. Topography of the bottom surface of aerogels 90, 95, and 98.

3.2. Specific Resistance and Thermal Conductivity of Aerogels

Table 1 shows that the electrical resistivity and thermal conductivity of the studied aerogels increase with increasing PTFE content. Obviously, the contribution of the electronic system to the overall thermal conductivity can be neglected for the presented values of ρ . We attribute the measured low values of λ (for dense PTFE samples, $\lambda = 0.25 \text{ W/m}\cdot\text{K}$) to phonon scattering by three-dimensional defects such as pores and to the increased heat-transfer path length.

3.3. Mechanical Properties of PTFE/GO and PTFE/rGO Aerogels

After annealing in air at 370°C , the aerogels became mechanically stronger. For cylindrical A95 samples, a load of 4.5 kg was selected, which destroyed the PTFE/GO samples but did not destroy the PTFE/rGO samples, as shown in Figure 5. Surprisingly, the original PTFE/GO samples withstood a load of 4 kg. From the presented data, it is easy to calculate that for the PTFE/GO sample, the compressive strength is in the range of 0.31 MPa to 0.35 MPa, whereas for the PTFE/rGO sample it exceeds 0.35 MPa. For comparison, the compressive strength of polystyrene foam is 0.15–0.30 MPa.

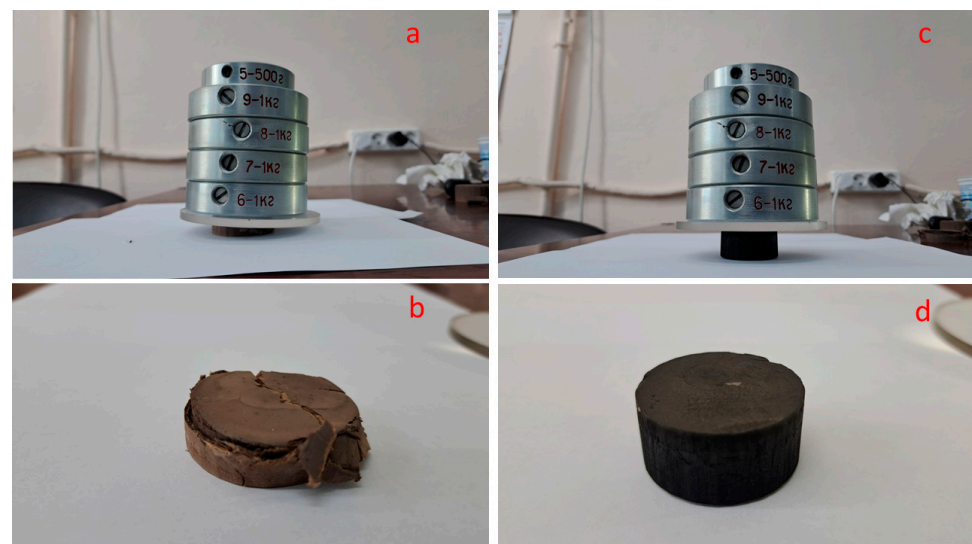


Figure 5. Photographs of cylindrical samples of aerogel 95 under a load of 4.5 kg: (a)—after freeze-drying and (c)—after annealing at 370°C ; and after removing the load (b)—after freeze-drying and (d)—after annealing at 370°C .

3.4. IR Spectra of Aerogels

Figure 6 shows the IR spectra of PTFE/GO aerogels annealed at 370 °C with PTFE contents of 90, 95, and 98 wt.%. For comparison, the spectrum of the initial suspension, from which water was removed by freeze-drying, is also presented. The most intense absorption bands in the spectra of all aerogels are those at 1203 and 1147 cm^{-1} , associated with the stretching vibrations of CF_2 fragments in PTFE [10,11]. The absorption bands at 638.2, 625.4, 533.8, and 500.2 cm^{-1} (not marked in the figure) correspond to the wagging, deformation, and rocking vibrations of CF_2 groups. The absorption band at 1726 cm^{-1} is attributed to the stretching vibration of the $-\text{C}=\text{O}$ fragment in reduced graphene oxide [12].

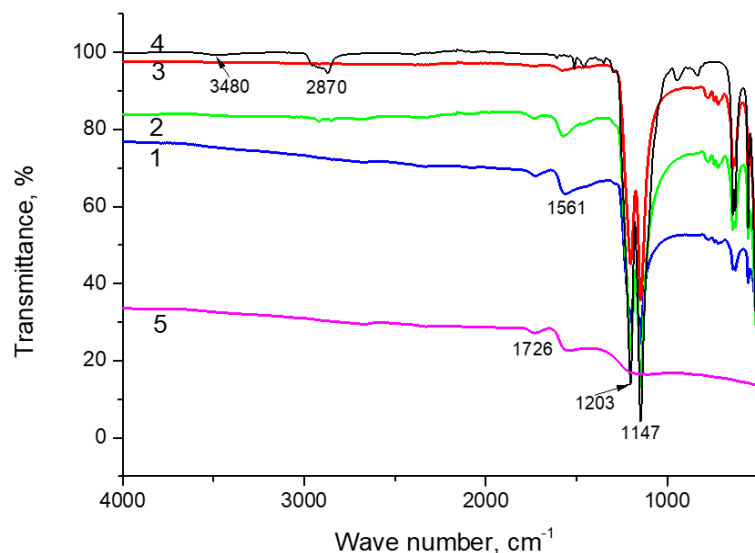


Figure 6. IR spectra of aerogels 90, 95, and 98 after annealing at 370 °C (curves 1, 2, and 3, respectively). For comparison, the figure shows the spectrum of the F-4D suspension after freeze-drying (curve 4) and the spectrum of GO after annealing at 370 °C (curve 5).

The broad absorption band with a maximum at 1561 cm^{-1} is also associated with reduced graphene oxide (Figure 6), but its intensity is contributed to by both the stretching vibrations of $-\text{C}=\text{C}-$ bonds and the deformation vibrations of $\text{O}-\text{H}$ groups in $\text{C}-\text{O}-\text{H}$ [13]. The remaining absorption bands are attributed to products of surfactant decomposition at 370 °C in air. Comparison of the spectra shows that during annealing of the PTFE/surfactant/GO aerogels, fragments such as $\text{O}-\text{H}$ and $\text{C}-\text{H}$ are removed and/or destroyed first (absorption bands with maxima at 3480 and 2870 cm^{-1} , respectively). Only in the spectrum of aerogel 95 can small peaks be observed in the region corresponding to $\text{C}-\text{H}$ stretching vibrations. It should also be noted that the spectra shown in Figure 5 were not subjected to any processing. The change in the background of the aerogel spectra is attributed to the presence of reduced graphene oxide in their composition, which possesses electronic conductivity.

A comparison of the spectra shows that during annealing, fragments such as $\text{O}-\text{H}$ and $\text{C}-\text{H}$ (peaks at 3480 and 2870 cm^{-1} , respectively) are primarily removed and/or destroyed from PTFE/surfactant/OG aerogels. Only in the spectrum of aerogel 95 can small peaks be seen in the region of $\text{C}-\text{H}$ valence vibrations. We also note that the spectra shown in Figure 5 have not been subjected to any processing. We attribute the change in the background of the aerogel spectra to the presence of reduced graphene oxide in their composition, which possesses electronic conductivity.

3.5. Raman Spectra of Aerogels

The Raman spectra of aerogels 90, 95, and 98 after heat treatment are shown in Figure 7. Only one low-intensity peak in the spectrum of aerogel 90 at $\sim 730\text{ cm}^{-1}$ can be attributed to PTFE [14,15]. The two most intense peaks in the spectra of all aerogels correspond to the G and D bands of the sp^2 phase of graphene-like materials [16–21].

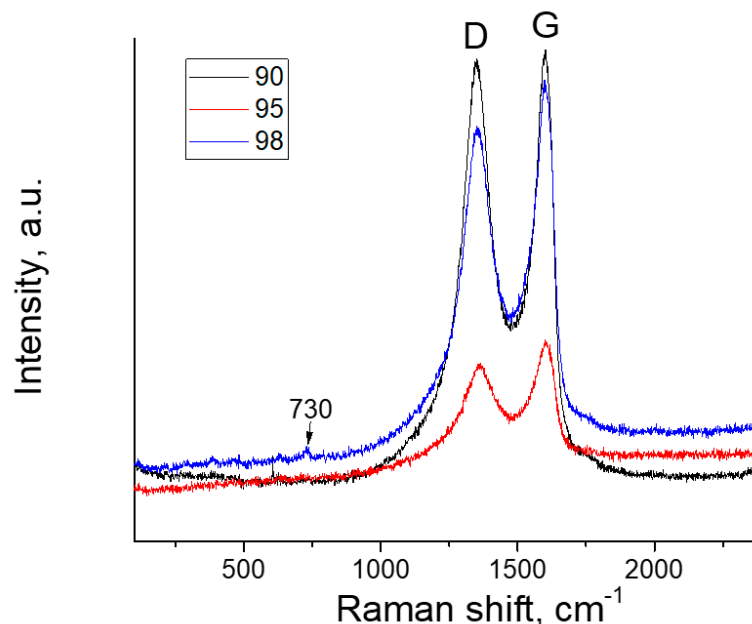


Figure 7. Raman spectra of the samples under study.

Figure 8 presents an example of approximating the Raman spectrum of an aerogel in the range of $750\text{--}2000\text{ cm}^{-1}$ using five functions, whose parameters for the aerogels studied are given in Table 2. The approximation was carried out using the method proposed in [18]. Since in our work and in [18], a laser with the same wavelength (532 nm) was used to excite the Raman spectra, we can use the correlations proposed in [18] to determine the oxygen content in graphene oxide present in the aerogels under study. According to the correlation between the position of the D^* peak and oxygen content reported in [18], the oxygen content in rGO present in aerogels 90 and 98 is in the range of 25 to 40 wt.%, while in aerogel 95 it is about 50%.

Table 2. Fitting parameters calculated for Raman spectra of PTFE/GO aerogels (x_c is the peak center position in cm^{-1} , I is the peak intensity in %, w is the half-width of the peak in cm^{-1}). The peak designations are shown in Figure 8.

Sample	D* (Gauss)			D (Ps-Voigt)			D'' (Gauss)			G (Ps-Voigt)			D' (Ps-Voigt)		
	x_c (cm^{-1})	I (%)	w (cm^{-1})	x_c (cm^{-1})	I (%)	w (cm^{-1})	x_c (cm^{-1})	I (%)	w (cm^{-1})	x_c (cm^{-1})	I (%)	w (cm^{-1})	x_c (cm^{-1})	I (%)	w (cm^{-1})
90	1130	2.15	164	1348	62.96	130	1520	8.46	139	1596	23.94	49	1616	2.49	50
95	1122	1.06	132	1355	69.86	181	1525	6.23	122	1585	20.76	66	1616	2.08	50
98	1130	1.87	169	1351	62.14	148	1522	8.49	122	1585	25.01	55	1613	2.50	50

However, if the position of the D'' peak is used to determine oxygen content, then this value is approximately 25 wt.% for all three samples. The low accuracy in estimating oxygen content obtained using the positions of the D^* and D'' peaks is due to the scatter of data points on the correlation plots in [18]. It is also possible that at a higher signal-to-noise ratio in the experimental spectra (Figure 3), the positions of the fitted peaks would also change slightly. Nevertheless, the presented data indicate that the oxygen content in rGO is most likely in aerogel 95 is higher than in aerogels 90 and 98.

The intensity ratio of the D and G bands (I_D/I_G) can serve as a measure of disorder in the carbon lattice (Table 3). It can be seen that the carbon lattice of aerogel 95 is the most disordered. In addition, the I_D/I_G value can be used to estimate the size of sp^2 domains L_a [22] as follows:

$$L_a = (2.4 \times 10^{-10}) \lambda_L^4 (I_D/I_G)^{-1}$$

where λ_L is the wavelength (in nm) of the excitation laser. The L_a values calculated using the equation are presented in Table 3.

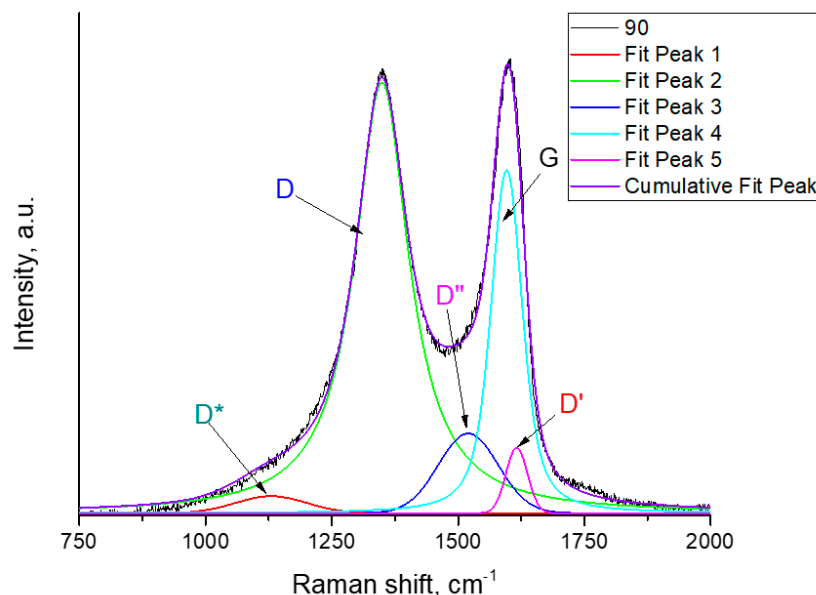


Figure 8. Raman spectrum of sample 90 in the range of 750–2000 cm^{-1} , along with its description by two Gaussians (peaks D* and D'') and three pseudo-Voigt functions (peaks D, G, and D').

Table 3. The ratio of peak intensities and L_a values (in nm) for the studied PTFE/GO aerogels.

Sample	I_D/I_G	L_a
90	2.63	7.31
95	3.36	5.72
98	2.48	7.75

The boundaries of such domains are presented by defects of the sp^2 lattice, which may include, in particular adjacent sp^3 -hybridized carbon atoms. In the literature, different authors use various methods to estimate the concentration of sp^3 -hybridized carbon from Raman spectra. For example, it was noted [23] that the presence of 20% sp^3 carbon atoms leads to a decrease in the shift of the G peak from 1600 cm^{-1} to 1510 cm^{-1} in carbon films with a low content of hydrogen and nitrogen. In our case, the position of the G peak (Table 2) indicates a noticeable, but not very high, fraction of sp^3 carbon atoms.

3.6. TGA

For the aerogel made of pure GO (sample 0), a mass loss (~11%) due to the removal of adsorbed water (Figure 9) was observed in the range from room temperature to 140 °C. The main mass loss (~35%) in GO occurs in the range from 140 to 250 °C and is explained by the decomposition of labile oxygen-containing functional groups. Across the entire temperature range above 300 °C, a slower, monotonic mass loss (~12%) occurs, which may be associated with the removal of more stable oxygen-containing functional groups. These results are in good agreement with previous studies of graphite oxide [10,24–29].

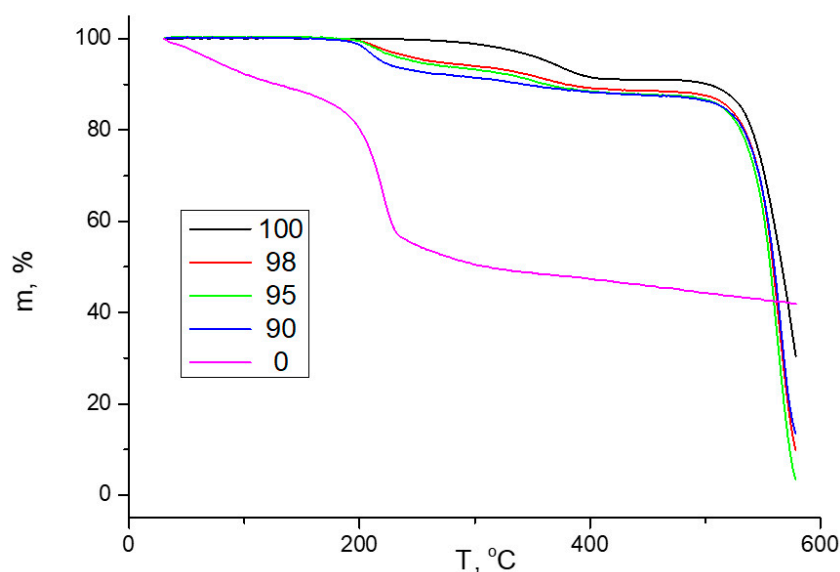


Figure 9. TG curves of the samples studied.

The behavior of TG curves for PTFE is well known. Degradation of PTFE in air begins at $T > 460$ °C (see, for example, [30]). In an inert atmosphere, weight loss begins at an even higher temperature [11]. In our case, weight loss ($\sim 9\%$) was observed in the range 150–430 °C for sample 100. We attribute this loss to the decomposition of surfactants used to stabilize the F-4D suspension. As expected, polymer degradation (T_d) begins at approximately 500 °C. If T_d is defined as the point at which PTFE mass loss is 5%, then $T_d = 526$ °C for sample 100.

In the case of composite aerogels, it is practically impossible to isolate on the TGA curve the weight loss associated with the removal of adsorbed water from graphene oxide (Figure 9). It is masked by losses caused by the decomposition of labile oxygen-containing functional groups of GO and the breakdown of surfactants that enter the aerogel together with the polymer-containing suspension. This is explained by the low content of GO in the composite aerogel. Interestingly, the weight losses at 250 °C for samples 95 and 98 are 5.10% and 4.33%, respectively, which exceed the GO content in these samples. This means that the main contribution to the weight loss of these samples at 250 °C is due to the decomposition of surfactants. The estimated T_d value for the composite aerogels is 524–525 °C, which is not much different from this value for sample 100.

3.7. DSC

According to the TG analysis, heating the aerogel made of pure GO in an inert atmosphere is accompanied by evaporation of adsorbed water and decomposition of oxygen-containing groups. However, the experimental DSC curve primarily shows a giant exothermic peak with a maximum at ~ 220 °C and a decomposition enthalpy ΔH of approximately 1480 J/g (Figure 10). The onset temperature of the exothermic transition was about 150 °C. It should be noted that heating a large sample of dense graphene oxide at the standard rate of 10 K/min may lead to micro-explosions and damage to the measuring equipment. In the case of graphene oxide aerogels, we did not observe micro-explosions even when heating at a higher rate, possibly due to the low density and high open porosity of the aerogels. Water evaporation superimposed on the large exothermic peak appears as a small, barely noticeable endothermic peak with a maximum at ~ 80 °C.

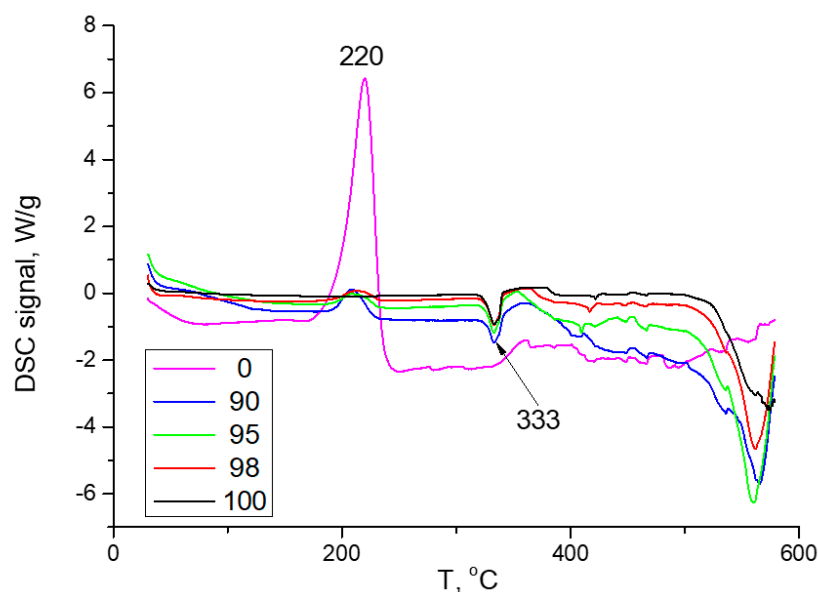


Figure 10. DSC curves of the samples under study.

Due to the high intensity, a peak at 220 °C can be observed for all samples containing graphene oxide. Moreover, its intensity correlates with the content of GO in the sample (Table 4). The endothermic peak with a maximum at 333 °C is attributed to the melting of PTFE. However, the ΔH value of this process cannot be used to determine the polymer concentration in the sample. One of the reasons for this may be the difficulty in determining the baseline when calculating the ΔH value in the case of samples 95 and 90 (see Figure 10).

Table 4. Positions of the peak maxima marked in Figure 9 and their corresponding thermal effects.

Sample	Peak 220		Peak 333	
	$T_{\max}$, °C	ΔH , J/g	$T_{\max}$, °C	ΔH , J/g
00	220.1	1480	-	-
90	208.4	109	333.2	79
95	208.0	64.9	332.6	69
98	214.0	61.6	333.1	55
100	-	-	333.5	70

3.8. Shrinkage of Samples During Annealing (Transition from PTFE/GO to PTFE/rGO)

After discussing the results of thermal studies, we can return to the discussion of sample shrinkage during annealing. The observed relationship, “the more PTFE, the greater the shrinkage”, seems puzzling at first glance. Let us examine why this happens, based on our data above and general principles of materials science.

Graphene oxide forms a three-dimensional network within the aerogel. Its sheets are capable of contacting each other, creating a relatively rigid and heat-resistant framework. This framework has its own structure and is able to withstand compression. PTFE is a “fusible filler”: in its initial state, PTFE consists of polymer particles distributed across the surface of the GO sheets. When heated to 370 °C (which is above the melting temperature of PTFE, as confirmed by the DSC peak at ~333 °C in Figure 8), the polymer melts and transitions into a viscous-flow state.

During annealing, PTFE particles begin to break down. From solid inclusions, they turn into a viscous liquid that tends to minimize its surface area. The molten polymer wets the surface of the GO sheets. Due to the curvature of the liquid menisci in the pores,

powerful capillary forces arise. These forces pull the flexible EG sheets toward each other. The more PTFE melt there is in the pores, the stronger the capillary contraction. It acts across the entire surface of the GO sheets, causing the framework to compress.

In samples with a high PTFE content, there is so little graphene oxide that the framework it forms becomes less robust. When the GO content drops to 2%, there are simply not enough of its sheets to form a rigid skeleton capable of withstanding the enormous capillary forces of the melt. As noted above, the GO density in the aerogels is above the gelation threshold, but this amount may be insufficient to create a strong reinforcing skeleton. As a result, the weak carbon framework “collapses” under the contracting forces of the molten polymer. This is precisely what leads to the maximum shrinkage of 26.6% for sample 98.

The destruction of the sample without GO (100% PTFE) during freeze-drying is direct proof that there is nothing to maintain the structure without GO. The data in Table 1 shows that the density increases from 0.09 to 0.54 g/cm³, while the porosity decreases from ~95% to ~73% as the PTFE fraction increases. This is a direct consequence of greater shrinkage and pore “collapse.” Thus, shrinkage is the result of molten PTFE, which contracts the structure through capillary forces. Graphene oxide, in contrast, acts as a reinforcing framework that resists this contraction. The less reinforcement (i.e., GO) present, the weaker the framework and the more the sample sags under its own “polymeric” tension.

3.9. Measurements of Contact Wetting Angle

The water contact angles (WCA) for the upper and lower surfaces of the PTFE/rGO aerogel samples are presented in Table 5. As could be seen, the WCA values for our samples exceed the known WCA value for a flat PTFE surface (106–108° [31]). This means that the surface morphology of the aerogels contributes to the altered values. It was not possible to establish any dependence of the WCA on composition. It should be noted that a superhydrophobic graphene aerogel with a WCA of 151.1–153.9° was previously obtained using chemical reduction of the surface [32]. For the PTFE/rGO aerogel (50:50) that we obtained, the water contact angle value is in the range of 161.9–163.7° [2]. In this respect, the aerogel samples obtained in this study are not outstanding.

Table 5. Contact angles of the upper and lower surfaces of PTFE/rGO aerogels (the lower surface was in contact with the smooth surface of a copper plate during hydrogel freezing).

Sample	Wetting Contact Angle, Degrees	
	Lower Surface	Upper Surface
98	139.6	127.6
	136.0	129.2
	137.8	128.4
95	127.2	143.6
	124.3	138.8
	125.8	141.2
90	135.0	134.6
	137.3	138.2
	136.2	136.4

3.10. Adsorption Properties

The sorption capacity of aerogels 90, 95, and 98 was investigated with respect to a set of solvents of different chemical structures, including water, as well as oils (Table 6). It can be seen that, in terms of sorption capacity, aerogel 90 outperforms aerogels 95 and

98. Comparing the Q_w values of aerogels 90, 95, and 98 with those reported in [2] for a PTFE/rGO aerogel with a 50:50 composition, it can be concluded that the aerogels obtained in the present work are poorer sorbents.

Table 6. Sorption capacity Q_w of aerogels 50, 90, 95, and 98.

	Sorbate	Q_w , g/g			
		50	90	95	98
1	THF	23.23 ^a	4.145 ± 0.144	1.671 ± 0.032	2.784 ± 0.041
2	Toluene	15.52 ^a	3.055 ± 0.035	0.606 ± 0.101	0.899 ± 0.094
3	Acetone	23.15 ^a	4.738 ± 0.095	2.759 ± 0.056	2.817 ± 0.106
4	<i>n</i> -Hexane	18.97 ^a	4.553 ± 0.137	2.707 ± 0.125	2.296 ± 0.075
5	Methylpyrrolidone	-	0.079 ± 0.038	0.041 ± 0.022	0.042 ± 0.018
6	Isopropanol	18.97 ^a	4.340 ± 0.149	3.230 ± 0.079	1.198 ± 0.087
7	BR-2	-	3.434 ± 0.092	2.808 ± 0.114	1.923 ± 0.053
8	Oil	-	0.713 ± 0.235	0.385 ± 0.123	0.228 ± 0.098
9	Water	0.08 ^b	0.022 ± 0.09	0.008 ± 0.03	0.001 ± 0.001

^a data from Ref. [2]. ^b data from Ref. [6].

It is difficult to distinguish between aerogels 95 and 98 based on the Q_w values. However, aerogel 98 stands out with the lowest Q_w value for water, not only among the aerogels studied in the present work but also among a number of other aerogels obtained earlier [6]. Note that for aerogel 00 (a graphene oxide aerogel reduced at 370 °C), we obtained a Q_w value for water of approximately 20 g/g!

To test the feasibility of reusing our aerogels as sorbents, sorption–desorption cycling using hexane was carried out for the PTFE/rGO A98 sample, and the testing results are shown in Figure 11. As can be seen, the sorption capacity of the aerogel is well preserved during repeated testing.

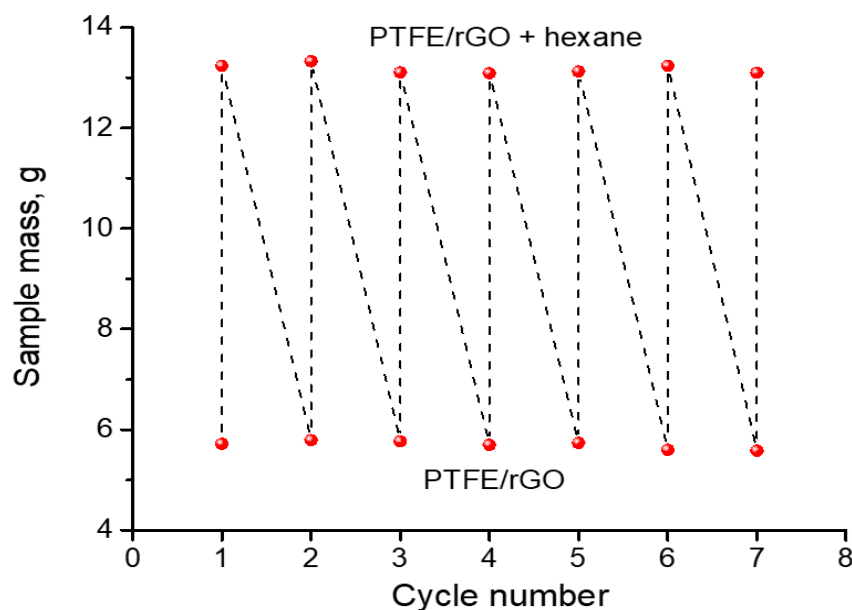


Figure 11. Sorption recyclability of the aerogel 98 for hexane.

4. Conclusions

For the first time, monolithic aerogels based on polytetrafluoroethylene (PTFE) and graphene oxide (GO) with polymer contents of up to 98 wt.% are obtained. It is shown that even at a minimal content (2%), graphene oxide plays a key role in structure formation, enabling the formation of a three-dimensional framework, whereas a sample of pure PTFE (aerogel 100) disintegrates during the freeze-drying process.

It has been established that increasing the PTFE content in the composite from 90% to 98% consistently leads to an increase in volumetric shrinkage during annealing (from 2.1% to 26.6%), an increase in density (from 0.09 to 0.54 g/cm³), and a decrease in porosity (from ~95% to ~73%). This is accompanied by an increase in specific electrical resistance and thermal conductivity.

Infrared spectroscopy and TG/DSC analysis confirmed that annealing at 370 °C leads to the effective removal of surfactants from the PTFE suspension, thermal reduction of graphene oxide, and melting of the polymer phase. This ensures the formation of an integral composite structure and improves the mechanical properties of the material. A key result of this work is the achievement of an extremely low water sorption capacity for the aerogel with the highest PTFE content (sample 98). The water sorption for this sample was only 0.001 g/g, which is significantly lower than that of previously studied aerogels. This confirms the hypothesis that a high polymer content and subsequent annealing effectively block hydrophilic sites on the surface of reduced graphene oxide.

Despite the decrease in the absolute values of sorption capacity for organic solvents compared to aerogels with lower polymer content, the obtained materials (especially sample 90) retain the ability to absorb organic liquids (THF, acetone, propanol) at a level of up to 4.7 g/g. Combined with exceptionally low moisture absorption, this makes the PTFE/GO (98/2) aerogel a promising material for the selective separation of immiscible organic–water media.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs10080407/s1>, Figure S1: Photo of the setup to freeze the hydrogels; Figure S2: Photo of aerogels 100 after annealing in air at 370 °C; Figure S3: Photographs of the bottom (a) and top (b) surfaces of aerogel 95 before annealing and photographs of the bottom (c) and top (d) surfaces of aerogel 95 after annealing in air at 370 °C. The scale bar is the same for all photographs. Details of our method for producing graphene oxide; Calculation of bulk porosity P (%); and three figures with photographs of the experimental setup, aerogel 100 after annealing, and aerogel surfaces.

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