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A flexible oxygenated carbographite nanofilamentous buckypaper as an amphiphilic membrane

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Abstract

Here, for the first time, oxygenated amorphous carbon /graphite (a-CO_x/G) hybrid nanofilaments are produced and used as the building blocks of a buckypaper membrane. The nanofilaments are in fact the innovatively chopped version of brittle, highly graphitized polyacrylonitrile (PAN) precursor nanofibers. The high temperature (1250 °C) graphitization and then fast cooling bring about biphasic nanofibers made of graphite and amorphous carbon, readily re-oxidized during cooling. The combination of polar and non-polar domains in the nanofilaments governs a desirable amphiphilicity, thus selectivity to a variety of polar/nonpolar water pollutants. Through electrostatic and π - π interactions, the membrane efficiently discriminates amphiphilic castor oil as well as cationic methylene blue dye from water. Moreover, the buckypaper-like structure of the membrane is 100% efficient in depth filtration of colloidal particles from water. The membrane's water flux is 16 times higher than that of commercial microfiltration membranes, promising an advanced energy/cost efficient filtration process. Thus, being multispectrally selective and highly water permeable, the a-CO_x/G nanofilamentous membrane is regarded potentially a next-generation, cost-effective, and sustainable alternative to the long-existing thin-film composite membranes for water treatment.

1. Introduction

As declared in the *Global Risks 2015 Report* of the World Economic Forum, the crisis of water shortage is the top 1 high-impact risk for our age.^[1, 2] As a global crisis, ~1.2 billion people across the world are influenced by water scarcity and its adverse impacts on health, food and energy.^[3, 4] According to the world water council reports, the number of influenced people will increase to 3.9 billion in the coming decades.^[5, 6]This dilemma stems from population growth, progressive industrialization and larger energy demands. Additionally, the global warming as shrinkage of glaciers, loss of snowmelt etc. will intensify this challenge in the years

ahead. Thus, extensive research activities have been and are being devoted to the water decontamination using advanced, efficient materials and technologies.

To purify water, the novel family of carbon nanomaterials including mono/few layer graphene oxide (GO) and reduced graphene oxide (rGO) has offered many interesting properties. These abilities include adsorption of metal and organic dyes, antimicrobial capability and photocatalytic degradation of organic molecules.^[7-12] Also, carbon nanotubes (CNTs) are able to supply a vast surface area whose chemistry can be tuned by functionalization strategies for the sake of adsorption of water pollutants.^[13] However, utilization of CNTs and graphene e.g. as sorbents in suspension form, due to the possibility of agglomeration, thus loss of reactive surface area, high risk of their release in water streams and their potential toxicity, is challenging. ^[14, 15]

Similar to graphene and CNT, carbon nanofibers offer amazing sorption properties mainly for hydrophobic (non-polar) pollutants.^[16] In contrast to the particulate carbon adsorbents, there is no need to recovery of the nanofibrous adsorbents after the adsorption process and with no agglomeration challenge, they can maintain their high surface area that can be functionalized for further reactions. However, for the sake of water treatment, they have been either synthesized in a complex (need to use of metal catalysts), costly manner,^[17] lowering the chance of upscaling, or functionalized by secondary elements such as CNTs to extend adsorptive property towards polar pollutants.^[16] In contrast to such studies, for the first time, we develop almost pure amphiphilic a-CO_x/G nanofilaments through a simple process comprising electrospinning and a thermal treatment of polyacrylonitrile (PAN) precursor nanofibers. The oxidized PAN nanofibers undergo a high temperature (1250 °C) annealing process leading to formation of an almost pure biphasic graphitic nanofibrous structure consisting of non-polar graphite and polar a-CO_x. We intentionally chose a very high graphitization temperature and a high cooling rate to endow the nanofibers with a pure biphasic graphitic structure. As Cho et al.^[18] have stated by a carbonization treatment at a high

temperature of 1200-1300 °C, carbon content reaches a remarkable level while impurities such as oxygen and nitrogen decline notably. The fast cooling rate (5 °C.min⁻¹) preserves the amorphous phase, though at a much lower fraction compared to the graphitic matrix. In a pure biphasic graphitic structure, it is well-known that the amorphous carbon phase is more susceptible to oxidation than the graphite one ^[19] and can be re-oxidized during the cooling process.

Such a biphasic graphitic nanostructure holds a great promise for concurrent discrimination of a wide range of polar/non-polar pollutants from water. The oxidized region bears oxygen containing functional groups such as carbonyl and hydroxyl groups and thus are negatively charged.^[20] Accordingly, specifically for water treatment, they can interact with the charged water pollutants and adsorb and repel the co- and counter charged pollutants, respectively. On the other hand, due to presence of a graphite matrix, possibility of π - π interaction with non-polar water pollutants is remarkable.

Despite the aforementioned merits, the high temperature thermal treatment can lead to brittleness and disintegration of a-CO_x/G nanofibers during a dynamic filtration process. Here, we took the risk of brittleness to exploit amazing features of a-CO_x/G nanofilaments. In fact, we employed the brittleness to maximize the surface area of a-CO_x/G nanofibers as chopped nanofilaments, thus their interactivity with water pollutants. For the first time, we synthesized a-CO_x/G nanofilaments and assembled them as a buckypaper like membrane for water treatment. In this membrane, the specific composition of a-CO_x/G can bring about suitable amphiphilicity thus selectivity to polar/non-polar pollutants of water. With respect to permeability, the mesh structure of the membrane is highly porous and thus water permeable. This feature is promising in relevance to energy/cost efficiency of the filtration process. To the best of our knowledge, an amphiphilic a-CO_x/G buckypaper has never been considered for water treatment and our membrane with its multifunctionality goes beyond the present state of the art.

2. Results and Discussion

2.1. Synthesis of the a-CO_x/G nanofilamentous buckypaper

Graphite nanofibers can be produced through different approaches including vapor growth method ^[21] and plasma enhanced chemical vapor deposition.^[22] However, these techniques are very complicated and costly.^[23] In contrast, graphite nanofibers can be made through electrospinning of a polymer precursor such as PAN and its subsequent stabilization and carbonization in a simpler and cheaper manner.^[23-25] In our study, to fabricate the a-CO_x/G nanofilaments, PAN nanofibers as the precursor were made through electrospinning. The electrospun nanofibers were subsequently oxidized and graphitized at a high temperature of 1250 °C (the maximum operating temperature of our lab furnace) under Argon atmosphere. In addition, a fast cooling rate (5 °C.min⁻¹) enabled preservation of the amorphous carbon phase that was readily re-oxidized by the removed oxygen. As will be shown later, this high temperature annealing process was completely efficient in removal of residue impurities and formation of an almost pure a-CO_x/G composite. However, as mentioned earlier, this sort of annealing made the obtained a-CO_x/G nanofibers drastically brittle and difficult to handle. ^{[26-} ^{29]} To address the latter challenge, the brittleness of the nanofibers was utilized to make a buckypaper membrane comprising a-CO_x/G nanofilaments and also to raise the reactive surface area for interaction with water pollutants (Figure S1). To do so, the a-CO_x/G nanofibers were chopped through an ultrasonication process of their dispersed aqueous suspension and subsequently vacuum filtered on a technical non-woven of polyphenylene sulfide (PPS). Additional details of the sample preparation and characterization are provided in the Experimental Section. The schematic of the fabrication process is illustrated in Figure 1a. As shown in this Figure, the fabricated a-CO_x/G nanofilaments were hydrophilic and remained suspended in water even after one year without any sign of aggregation or deposition. The oxygen rich functional groups of a-CO_x domains endow the graphite nanofilaments with good dispersibility and processability in water.^[30] After vacuum filtration, the nanofilaments are

stuck to each other via physical attachment caused by the filtration process and hydrogen bonds between the oxygen containing functional groups of a-CO_x domains.^[31] In addition, van der Waals forces lead to firm adhesion between the graphite domain of the nanofilaments and substrate (PPS), which significantly increases the difficulty of their separation.^[31] As depicted in Figure 1a, the membrane seems totally flexible. This filtration based fabrication method not only is simple and highly reproducible but also allows precise control of the thickness of the membrane.

2.2. Characterization of the a-CO_x/G nanofilaments

Figure 1b exemplifies TEM images of the a-CO_x/G nanofilaments. The image indicates the a-CO_x domain with no crystalline structure (i.e. without long-range ordering inside graphitic planes as further proven by electron diffraction experiments (not shown)) and a brittle fracture owing to the high temperature annealing process. In this regard, the high resolution TEM images, Figure S2, illustrate fromation of the major, packed graphitic regions comprising stacked graphitic sheets along with the sparse, haphazard amorphous carbon regions. As shown in the AFM pictures (Figure S3a), the nanofilaments are several μ m in length and ~260 nm in breadth. Figure S3b also demonstrates the size histogram obtained based on SEM images, implying that the nanofilaments are mostly as large as 260-300 nm in diameter.

Conversion process of PAN to a-CO_x/G nanofibers is done through stabilization followed by graphitization. The oxidative stabilization leads to orientation of the polymer chains, cyclization of the nitrile groups (C=N), cross-linking of the chain molecules, dehydrogenation and subsequent oxidation, giving rise to a thermally stable structure in ladder form. In the next step, the non-carbon elements are mostly removed during a graphitization process performed at a high temperature (1250 °C in our study) under an inert atmosphere.^[32] Thus, the previously formed oxidized polymer phase is converted to graphite. The chemical composition changes during the conversion process of PAN to a-CO_x/G nanofilaments could

be tracked via Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR) as shown in Figure 1c. The characteristic vibrations for the chemical groups in PAN are observed at 2241–2243 cm⁻¹ due to CN nitrile group, at 2870–2931 cm⁻¹, 1450–1460 cm⁻¹, 1350–1380 cm⁻¹ and 1220–1270 cm⁻¹ because of the aliphatic CH groups (CH, CH₂ and CH₃). The other strong band visible at 1671 cm⁻¹ is related to carbonyl vibration of N-C=O group caused by the remaining solvent DMF.^[29, 33]

Upon graphitization and thermal annealing, the above mentioned groups are eliminated while some new groups emerge. The strong peak which appears at 1589 cm⁻¹ is attributed to the unoxidized sp^2 C=C groups formed by aromatization process that occurred during the thermostabilization of PAN nanofibers.^[8, 33] The other emerging groups appearing at 1000-1300 (2 bands) and 3800 cm⁻¹ are corresponding to C-OH bond. The last remaining peak at 2350 cm⁻¹ is attributed to the presence of CO₂ during the measurement.^[34] The C-OH and C=C groups imply co-existence of polar and non-polar domains in the nanofilaments induced by oxidative stabilization and subsequent thermal annealing. This point i.e. amphiphilicity of the a-CO_x/G nanofilaments was further confirmed by X-ray photoelectron spectroscopy (XPS).

As shown in Figure 1d, the XPS spectra of the nanofilaments prove the presence of carbon (C), oxygen (O), and nitrogen (N) at varying concentrations. Interestingly, nitrogen concentration is almost negligible and the nanofilaments are mainly composed of carbon and oxygen. This means that the a-CO_x/G nanofilaments are highly pure. As presented in Table S1, expulsion of O by the annealing process increases the concentration of C to over 95% versus other elements such as O (3 %) and N (less than 2%). The optimum purity of the nanofilaments is caused by the high graphitization temperature, while the fast cooling rate preserves the amorphous carbon phase that can readily be re-oxidized. The success of our thermal treatment cycle is stressed when comparing the atomic percentage of N, C and O of the a-CO_x/G nanofilaments with that of the carbon nanofibers carbonized at a much lower temperature (1000 °C) but for a larger holding (annealing) time and cooled down normally.^[16] Peter et al. ^[16] report

the presence of less than 1.5% O in their carbon nanofibers carbonized at a temperature of 1000 °C that is 250 °C lower compared to our carbonization temperature. The important influence of cooling rate was also verified using X-ray Diffractometry (XRD). Figure S4 shows that despite a lower carbonization temperature (1050 °C), the sample cooled down normally exhibits a larger graphitic content, as represented by a sharper, stronger peak related to graphite, compared to the sample carbonized at a higher temperature (1250 °C) but cooled down fast. The former sample possesses larger graphitic crystallite as well, implying possibility of growth of the crystallites during the normal cooling process.

The C1s XPS spectrum, shown in Figure 1e, contains several main peaks at ≈ 284.6 , 286.8, 288.1 and 291 eV corresponding to sp^2 and sp^3 C, single-bonded carbon–oxygen (C-O), double-bonded carbon–oxygen (C=O) and $\pi \rightarrow \pi^*$ (HOMO-LUMO) transition of conjugated C=C. The latter peak and behavior of a-CO_x/G structure in our study has not been observed in the graphite film counterparts. ^[35] This could be attributed to the large surface area of the a-CO_x/G nanofilaments and/or their high purity. Such a transition could lead to an optimized electrical conductivity in our a-CO_x/G nanofilaments, beneficial for other advanced applications relevant to energy and sensing. One important observation with respect to C1s XPS is the asymmetric peak of C1s that once more stresses on the biphasic graphitic structure of a-CO_x/G nanofilaments.

The degree of sp^2 bonding is a main characteristic of the graphite structures and can be identified by using near-edge X-ray absorption fine structure spectroscopy (NEXAFS). As shown in Figure 1f, the carbon K near-edge structure for a-CO_x/G nanofilaments and a graphite reference sample (HOPG) of equivalent thickness is compared. In this Figure, a pre-edge resonance is seen at 285.3 eV, that is attributed to the transitions from C1s $\rightarrow \pi^*$ originating from sp^2 (C=C) sites. In addition, the broad band appearing in the range of 288–310 eV is attributed to the overlapping C1s $\rightarrow \sigma^*$ transitions at the sp^3 , sp^2 , and sp^1 sites of the *a*-CO_x/G nanofilaments.^[36-39] By normalizing the area of the C1s $\rightarrow \pi^*$ resonance with that of C1s $\rightarrow \sigma^*$

(i.e. $sp^2/(sp^2+sp^3)$), the amount of sp^2 bonded carbon atoms can be estimated. The obtained sp^2 value can be compared with that calculated similarly for a reference material (highly oriented pyrolytic graphite (HOPG) in our study), to determine the relative sp^2 content. ^[38] Accordingly, the $sp^2/(sp^2+sp^3)$ of the *a*-CO_x/G nanofilaments and HOPG were 0.07 and 0.08, respectively and the relative sp^2 content of the *a*-CO_x/G nanofilaments was 87.5%.

While the NEXAFS technique (in total electron yield (TEY) mode, we employed here) is in fact a surface sensitive analysis method, ^[40] to further investigate the graphitic structure of the *a*-CO_x/G nanofilaments, particularly in the bulk state, electron energy loss spectroscopy (EELS) was carried out. The appearance, position and intensity of various features within the EEL spectra help to characterize the *sp*² bonding level, thus to define the chemical state and elemental concentrations of the *a*-CO_x/G nanofilaments. ^[41] As shown in Figure 1g, the carbon *K* near-edge structure for the *a*-CO_x/G nanofilaments and a graphite as well as an amorphous carbon reference sample is compared. In the edge obtained from the *a*-CO_x/G nanofilament, the π^* feature at 285 eV energy loss is sharp and readily distinguished. In contrast, over the following 20 eV, the spectrum is smooth and featureless, resembling that of the amorphous carbon reference. The first feature at 285 eV represents a transition of a 1*s* electron to the π^* antibonding orbital, while the feature appearing at next ~20 eV is due to excitations to σ^* states. As Daniels et al.^[41] state the variation of interatomic distances and co-ordinations within the material implies that all features are almost 'smeared' out. Under this circumstance, the *a*-CO_x/G nanofilaments are an isotropic mixture of polynuclear aromatic molecules.

Since a delocalized π -type bond originates only from the occurrence of a sp^2 hybridized C atom, the relative intensity of features within the EEL spectrum, due to excitations of electrons to higher energy levels, i.e. π -type antibonding orbitals, represents the sp^2 amount of the *a*-CO_x/G nanofilaments, analogous to the sp^2 content calculated from XPS spectra. ^[41] The low energy resolution of the acquired EEL spectra prohibits an exact sp^2 quantification, however, comparing the intensities of the π^* and σ^* features of *a*-CO_x/G and the graphite

reference yields an intensity difference of about 13%. Given that graphite only contains sp^2 hybridized carbon this semi-quantitative approach yields almost exactly the same result as the XPS analysis above.

2.3. The a-COx/G nanofilamentous buckypaper for water treatment

Based on ATR-FTIR and XPS results, it is proved that the nanofilaments contain oxygen functional groups and non-polar carbon based domains. Thus, it could be interpreted that they are amphiphilic. To ascertain this feature, a water contact angle test was also performed. Interestingly, different regions of the buckypaper showed a different behavior in terms of hydrophilicity. Deposition of a 5 μ l water droplet on the buckypaper's surface implied the presence of some highly hydrophobic regions with a contact angle of 130° along with some superhydrophilic ones wherein the water droplet instantly disappeared. This bizzare behavior is attributed to self-organization of the nanofilaments via hydrophobic-hydrophobic interactions and hydrogen bondings.

Proving the amphiphilicity of the buckypaper membrane, it can be employed in discrimination of polar/non-polar water pollutants through hydrophilic and hydrophobic interactions.

The *a*-CO_x/G buckypapers possess an optimum porosity, as could be seen in Figure S5. Such a high porosity is assumed to offer an extraordinary permeability to the water streams to be filtered. As we measured, the *a*-CO_x/G buckypaper showed a pure water flux of ~19 kl.h⁻¹.m⁻² which is incredibly high compared to the conventional microfiltration (MF) membranes (e.g. at most 1.2 kl.h⁻¹.m⁻².bar⁻¹ for a PAN commercial MF membrane ^[42]). It is worthy to note that no significant feed pressure was applied. Such a high permeability is interpreted as very low energy consumption for a water filtration process.

In terms of selectivity, amphiphilicity of the buckypaper membrane can be beneficial in removal of amphiphilic pollutants from water. To prove this hypothesis, we employed

castor oil, i.e. an amphiphilic oil as a water pollutant model. Oils including vegetable and petroleum oils are not quickly and easily broken down by bacteria and can lead to permanent pollution in water environments. Moreover, when oils in a large amount are discharged to receiving waters from community systems, due to a lower density they may float to the surface and harden, causing aesthetically unpleasing conditions and inhibit the oxygen transfer efficiency of water causing septic condition. Therefore, removal of oils from wastewaters is an important task in water filtration processes.

In the current study, the a-CO_x/G buckypaper was utilized in removal of Castor oil (a vegetable oil model) from water. In this regard, the oil sorption efficiency was assessed by weight gain, defined as wt% = (weight after saturated sorption - initial weight)/initial*weight*.^[43] As seen in Figure 2a, the membrane separated $900 \pm 210 \text{ mg.g}_{nanofiber}^{-1}$ oil of the respective feed emulsion. Camera images of the feed and permeate samples (inset of Figure 2a) clearly show the oil removal efficiency of the membrane. As shown in Figure 2b, possessing hydroxyl (1167 and 3400 cm⁻¹) and carbonyl (1742 cm⁻¹) groups, Castor oil is a negatively charged organic matter. Hence, it can be repelled by the negatively charged oxygen containing functional groups of the a-CO_x part of the nanofilaments. Moreover, induced by presence of the non-polar graphitic domains, the amphiphilic oil molecules (Figure 2c) are also captured via hydrophobic interactions. As stated by Xu et al. ^[44], even for the hydrophilic pollutants, if they contain hydrophobic parts (forming an amphiphilic structure), the hydrophobic interaction occurs between the hydrophobic parts and graphene structure, contributing to the whole adsorption interaction. The non-polar domain of the nanofilaments can stimulate stronger binding affinity for organic liquids.^[45, 46] A π - π interaction between the graphite and castor oil's organic part is imaginable and leads to removal of oil. Thus, from one hand, an electrostatic repulsion is present between polar domains of the a-CO_x/G nanofilaments and the oil molecules. On the other hand, hydrophobic attraction keeps the oil molecules adsorbed to the non-polar domains of the nanofilaments. Combination of these effects leads to an optimum removal

efficiency of oil from water. But, since hydrophobic bonding is not so stable and the oil molecules carrying a negative charge prefer to be away from the negatively charged domains of the nanofilaments, in long term filtration processes and under harsh dynamic conditions, oil molecules can be released. This hypothesis was verified through flushing the membrane after filtration. This process was done via passing water through the oil contaminated membranes by using a pump with a feed rate of 83 kl.h⁻¹.m⁻². Figure 2a shows the amount of the adsorbed oil before and after flushing. It is seen that after the flushing the amount of the oil captured by the membrane declines. The high hydrodynamic pressure supplied by the pump can lead to release of the previously bound oil from the nanofilaments.

Thanks to presence of the negatively charged functional groups, oxidized carbon nanomaterials such as GO are known as very strong adsorbents for many organic substances, including most organic dyes (e.g. MB).^[10, 30] Such an ability was tracked in our *a*-CO_x/G system (possessing oxygen functional groups), as well. Since, the wastewater streams of industrial dyeing processes are usually highly alkaline, ^[47, 48, 49] we investigated MB removal ability of our membrane under such a condition. As observed in Figure 3a, the *a*-CO_x/G buckypaper is able to remove 95% of the MB dye from water for 10 ml solution at an alkaline condition (pH9). The $\pi=\pi$ interaction between benzene rings of the graphite moiety and MB can contribute to the high dye removal efficiency. On the other hand, the negatively charged a-CO_x domains due to presence of carboxyl groups facilitate the sorption and removal of low weight and cationic compounds like MB from water.^[17, 50, 51] Due to de-protonation of functional groups at high pH values, negative charge of the membrane, and thereby interaction tendency towards the positively charged dye molecules is intensified.

The optimized adsorption in basic pH is described through the following mechanism: MB molecules are dissociated in aqueous media as:

$$C_{16}H_{18}N_3SCl \to C_{16}H_{18}N_3S^+ + Cl^-$$
 (1)

In basic condition, the surface hydroxyl groups of polar $(a-CO_x)$ domains are deprotonated as:

$$a - CO_x - OH + OH^- \rightarrow a - CO_x - O^- + H_2O$$
(2)

Accordingly, through the electrostatic attraction between the negatively charged oxygen atom and the dye cation, the adsorption process occurs.

$$a-CO_x-O^- + C_{16}H_{18}N_3S^+ \rightarrow a-CO_x-O^- S + N_3H_{18}C_{16}$$
 (3)

The higher degree of de-protonation for hydroxyl groups under basic condition will likely result in an enhanced chemisorption between the dye and polar domains of the nanofilaments.

Increase of the permeate volume leads to a lower sorption efficiency of 40% and 30% for 50 and 100 ml, respectively. Such a trend is also seen for the permeate flux (Figure 3b), that is, the permeate flux is decreasing with increase of the permeate volume but still very high (from 23 kl.h⁻¹.m⁻² at 10 ml permeate to 2.5 kl.h⁻¹.m⁻² at 100 ml permeate).

The reason for a very high sorption efficiency at the 10 ml permeate volume could be due to a high density of free adsorption sites at the beginning of the experiment. As much as the filtration goes on, the available adsorption sites are occupied and due to a steric hindrance effect, where those MB molecules already adsorbed at the earlier adsorption stage hinder further adsorption, the sorption efficiency decreases.^[17] The reason for the flux decline could also be attributed to shrinkage of the pores and porosity loss by accumulation of the dye separated. In general, in our study, dynamic nature of the filtration process as well as high permeability and large pore size of the membrane can lower the dye removal efficiency at large permeate volumes.

Other than π - π and electrostatic interactions, the buckypaper membrane could exclude coarse pollutants physically. According to a bubble point test, the *a*-CO_x/G buckypaper possesses a bubble point (i.e., the largest pore size) and mean flow pore diameter (the mean flow pore diameter is such that 50% of flow is through pores larger than the mean flow pore

diameter and 50% of flow is through pores smaller than the mean flow pore diameter) in the range of microfiltration (0.1-10 μ m) i.e. 3 μ m and 500 nm, respectively (Figure 4a).^[52] Thus, in terms of size exclusion property, the *a*-CO_x/G buckypaper can act as a microfiltration membrane. This hypothesis was verified through a particle challenge test to separate inorganic (TiO₂) nanoparticles from an aqueous suspension in a cross-flow mode and by designing a custom-built filtration set-up (Figure S6). This feed actually simulates real feed aqueous suspensions containing heterodisperse sub-micron inorganic particles. TiO₂ nanoparticles are the most extensively used nanoparticles in different commercial products e.g. for cosmetics, sunscreens, paints, coatings, and as catalysts for clean-up of pollutants. Here, titania is considered as the general representative of a broad range of oxides and silicate minerals which can form as a result of chemical weathering or spread into the environment from manufacturing sources (e.g., uranium oxide, zinc oxide, aluminum oxide, iron oxide etc.).^[53]

The *a*-CO_x/G buckypaper as shown in Figure 4b was completely successful in rejection of all the TiO₂ nanoparticles (100% efficiency) from the aqueous suspensions (with a concentration of 0.04 and 0.06 g.l⁻¹). As observed in Figure 4c, the permeate flux declines throughout the experiments till reaching to a plateau most likely due to gradual formation of a cake layer on the surface of the membranes clogging the pores. The rate of flux decline is higher for the suspension containing more nanoparticles i.e. 0.06 g.l⁻¹. The SEM image shown in Figure 4d represents the cake layer formed lowering the permeate flux. However, the final permeate flux (~ 1700 and 3400 l.h⁻¹.m⁻² for the feed concentrations of 0.06 and 0.04 g.l⁻¹, respectively) is still high compared to that of the conventional microfiltration membranes.^[54] Noteworthy, no significant feed pressure was applied for filtration i.e. an efficient low energy consuming MF process.

Permeability behavior of the *a*-CO_x/G buckypaper as presented in Figure 4c at a steady feed pressure (ΔP) and viscosity (μ) depends strongly upon the cake layer resistance and can be explained in a quantitative manner by the Darcy's law (equation (4)):^[55]

$$J = \frac{\Delta P}{R_{tot}\mu} \tag{4}$$

Where R_{tot} is the total hydraulic resistance and μ the viscosity of the permeate. R_{tot} can be defined as the sum of two contributions caused by the membrane (R_{mem}) and cake layer (R_{cake}).

The Kozeny-Carman equation (5) can be used for calculation of the cake layer resistance: ^[55, 56]

$$R_{cake} = \frac{180(1-\varepsilon)^2}{d_p^2 \varepsilon^3} \delta_c \tag{5}$$

where ε is the cake's void fraction, δ_c the cake layer thickness and d_p the particle diameter.

The isoelectric point of TiO₂ nanoparticles occurs at pH of ~6.4.^[57] The prepared TiO₂ suspensions show a pH value of 5.3 for both the suspensions of 0.04 and 0.06 g.l⁻¹. Hence, within the nanosuspensions the inorganic nanoparticles should be positively charged and repel each other. This means that through repulsion of the nanoparticles, the resultant cake layer should be porous and possess a higher void fraction (ε) i.e. a lower cake resistance (*R_{cake}*) thereby a higher permeability (*J*).

Low cake resistance along with the high porosity and interconnectivity of the pores of the a-CO_x/G buckypaper as its inherent structural features lead to an optimum permeability during the retention test.

Among the two feed suspensions, as shown in Figure 4e, the one containing 0.06 g.l⁻¹ possesses smaller particles (d_p) and due to a higher concentration it can make a thicker cake layer (δ_c) thereby a higher cake resistance compared to the suspension of 0.04 g.l⁻¹. Hence, as already shown in Figure 4c, loss of flux shows a higher rate for the suspension of 0.06 g.l⁻¹.

As shown in Figure 4e, particle size analysis of the feed suspensions reveals that the nanoparticles mostly possess a size smaller than the mean flow pore diameter of the membrane i.e. a good chance for passing through the membranes. In contrast to this expectation, complete rejection of the nanoparticles is obtained. There are two mechanisms involved in this perfect

efficiency. First, as mentioned earlier, the TiO₂ nanoparticles are positively charged and thus able to stick to negatively charged polar domains along the nanofilaments. Second, when the particle size is in submicron range, the velocity of migration of the particles away from the surface of fibrous membranes is at its minimum. The particles are adsorbed to the nanofilaments through direct interception, inertial impaction and diffusion (i.e. Brownian motion).^[58-60] Complete rejection of all the nanoparticles along with an optimum permeate flux implies a suitable filtration ability for the *a*-CO_x/G buckypaper acting as a MF membrane.

3. Conclusion

Here, we fabricated a selective permeable a-CO_x/G buckypaper membrane for water purification via a simple, fast and relatively low cost electrospinning approach. By a proper thermal treatment including high temperature graphitization and fast cooling, we ended up with amphiphilic nanofilaments composed of non-polar graphite and polar, functional oxygenated amorphous carbon. While the former step guaranteed a large graphitic fraction in the nanofilaments, the latter one brought about a minor fraction of amorphous carbon that could readily be re-oxidized during the cooling and keep polarity and functionality for interaction with water pollutants.

The *a*-CO_x/G membrane has exhibited a number of fascinating advantages over its currently available counterparts. First, it benefits from PAN as an inexpensive raw material, significantly lowering the membrane fabrication cost. Second, the fabrication procedure for the *a*-CO_x/G membrane is simple and scalable, providing technical readiness for upscaling of the membrane production. Thanks to a proper amphiphilicity, the synthesized *a*-CO_x/G membrane showed very high rejection of oil as well as an organic dye. In addition, it was able to discriminate micro/nanoparticles (100%) from water. The water flux of the membrane was about 16 times higher than that of most currently commercially available MF membranes. This optimum permeability can be interpreted as very low energy consumption thus cost efficiency.

4. Experimental Section

Materials: As the *a*-CO_x/G nanofiber precursor, PAN with the molar mass of 200,000 g.mol⁻¹ was purchased from Dolan GmbH (Germany). The solvent *N*,*N*-dimethylformamide (DMF) was obtained from Merck (Germany). To investigate the retention ability of the membrane, as the suspended solids and solutes in water, titania nanoparticles, MB and Castor Oil were also purchased from Degussa (Japan) and Sigma (USA), respectively. All the materials were used as received.

Synthesis of the a- CO_x/G *buckypaper*: PAN nanofibrous mats as the precursor of the *a*- CO_x/G nanofibrous membranes were produced by an electrospinning method. Briefly, a prepared PAN solution was fed with a constant rate into a needle by using a syringe pump (Harvard Apparatus, USA). By applying a given voltage (Heinzinger Electronic GmbH, Germany), PAN was electrospun on an aluminium foil. The conditions of electrospinning are tabulated in Table S2.

After peeling off from the aluminium foil, as the oxidative stabilization step, the electrospun nanofibrous mats were put in a furnace (Linn Elektro Therm, max T=1250°C) and heated in air at 250°C for 2 h. Subsequently, the air oxidized membranes were graphitized in argon atmosphere at the temperature of 1250 °C for 30 min and then cooled to the ambient temperature. The heating and cooling rates were 5 °C.min⁻¹.

The obtained graphite nanofibrous membrane was immersed in 10 ml distilled water and ultrasonicated for 2 min at a power of 20%. The ultrasonication process chops the a-CO_x/G nanofibers leading to a homogenous aqueous suspension of the a-CO_x/G nanofilaments which was cast over a circular poly(*p*-phenylene sulfide)(PPS) technical non-woven (diameter= 3.5 cm). The membrane was left to be dried in air overnight.

Structural and Chemical Characterization of the $a-CO_x/G$ nanofilaments: The morphology of the $a-CO_x/G$ nanofibers (before and after the chopping process) was characterized using a scanning electron microscope (SEM) (LEO 1550VP Gemini from Carl

ZEISS) and an atomic force microscope (AFM)(MultiModeTM Atomic Force Microscope from Bruker AXS). Moreover, the size histogram of the nanofilaments was determined from 60 random nanofilaments in an arbitrarily chosen area in the SEM images. Analysis by transmission electron microscopy was conducted on a FEI Tecnai F30 G2 STwin operated at 300 kV (field emission gun, Cs = 1.2 mm) and a GIF Tridiem 863 energy analyzer. The samples were prepared by gently grinding the hybrid carbon samples and placing the resulting powder on lacey carbon films or silicon nitride membranes. In case of lacey carbon films, only samples areas were analyzed that were not lying over the carbon film as to not obscure measurements with signal from the underlying carbon film. Spectra were taken with dispersions of 0.1 and 0.2 eV per channel. The data were background corrected and deconvolved in Gatan's DigitalMicrograph EELS Plugin. Diffraction patterns were taken with an aperture limiting the area of acquisition to 280 nm in diameter.

Chemical surface analysis of the PAN and *a*-CO_x/G nanofibers was performed by Fourier Transform Infra Red Spectrometry (FTIR)(ALPHA (ATR-Ge, ATR-Di) from BRUKER Optik GmbH). X-ray photoelectron spectroscopy (XPS, Omicron Nano-Technology GmbH) was applied to determine the chemical composition of the *a*-CO_x/G nanofilaments. The setup was operating with an Al-anode at a power of 240 W. CasaXPS (version 2.3.16) was used to charge-reference the spectra by using aliphatic carbon C1s at 285.0 eV and quantify C, O and N.

The NEXAFS measurement was carried out at the HE-SGM beamline at the synchrotron radiation facility BESSY II, Berlin using the PREVAC end-station. Data were acquired in total electron yield (TEY) mode and spectra were corrected for the photon flux by division through a spectrum measured for a clean gold sample and spectra have been normalized to an edge-jump of 1.

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Structural analyses of the *a*-CO_x/G nanofilaments were carried out at room temperature using a X-ray diffractometer (XRD3000TT, RICH. SEIFERT & Co GmbH) with Cu- K α radiation (λ =0.1541 nm).

Membrane characteristics of the a- CO_x/G *buckypaper:* The static water contact angle of the *a*- CO_x/G buckypaper was measured using a contact angle analysis system (Kruess DSA 100, Germany). A 5 µl droplet was dispensed on the membrane and the resultant angle was measured.

The approximate pore size of the *a*-CO_x/G buckypaper in terms of bubble point and mean flow pore diameter was measured using an automated capillary flow porometer from Porous Materials Inc.(PMI,USA).

The membrane permeability was characterized through a pure water cross-flow filtration. The dried *a*-CO_x/G membrane (active filtration area ~ 7 cm²) was placed in the membrane module and the water in the reservoir (400 ml) was passed through by a pump (KNF LIQUIPORT) (feed rate = 62500 $1.h^{-1}.m^{-2}$). The time required for permeation of the water through the membranes was recorded and the flux according to the equation (6) was calculated:

$$J = \frac{Q}{A \Delta t} \tag{6}$$

where *J* is the water flux (l.h⁻¹.m⁻²), *Q* is the permeated volume (l) of water, *A* is the effective area of the membranes (m²), and Δt is the sampling time (h). The flux measurement tests were repeated three times.

To investigate the oil removal capacity of the *a*-CO_x/G buckypaper, an oil-water emulsion was passed through the membranes cyclically (3 successive cycles). Previously, the oil-water emulsion (3 wt%) was prepared by adding a given amount of castor oil to water and subsequent mixing via stirring for 20 min by a mechanical stirrer at 1800 rpm. To do the filtration experiment, the dried membranes were put in a membrane module and by a very low negative feed pressure supplied by a suction system, 50 ml oil-water emulsion was passed

through the membrane. This process was repeated three successive cycles in which the permeates were used as the new feeds for the new cycles. After an overnight drying of the samples, the weight was measured. The difference in weight of the membranes before and after filtration represents the oil removed from water. The experiment was repeated three times using new samples.

The retention capability of the membranes for organic dyes was determined using MB aqueous solutions in a dead-end mode. The dried membranes were placed in the membrane module of a custom-built set-up (shown in ^[61]). The reservoir of the set-up was filled with 100 ml MB solution (0.02 g.l^{-1}) to be passed through the membranes by a feed pressure of 0.5 bar. The pH of the solution was adjusted to be 9 by addition of 0.1 M NaOH.

Already constructed the standard MB calibration curve, the concentration of MB in the original feed and permeates was specified by UV-vis spectroscopy (HITACHI U3000, HITACHI).

The MB removal efficiency (*RE*) was determined according to the equation (7):

$$RE = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \tag{7}$$

where C_p and C_f are the concentration of MB in the permeate and feed, respectively.

The retention capability of the *a*-CO_x/G buckypaper for colloidal particles was determined using TiO₂ aqueous suspensions in a cross-flow mode. The dried hybrid membranes were placed in the membrane module of the custom-built set-up (Figure S6). The reservoir of the set-up was filled with a TiO₂ heterodisperse suspension (0.04 and 0.06 g.l⁻¹) to be passed through the membranes by a pump. The retention ability was probed by the presence and size of the remaining nanoparticles in the permeate suspension. The average particle size of the feeds and permeates (100 ml) was determined by using a particle size analyzer (Delsa C TM Nano particle size analyzer, Beckman Coulter, USA). Moreover, to calculate the permeate flux

according to the equation (6), the permeation time was also recorded. The measurements were repeated three times.

Supporting Information

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

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Figures







Figure 1. Schematic illustration of the formation cycle of the a-CO_x/G buckypaper and its chemical and morphological characteristics. a) fabrication process of the a-CO_x/G membrane (the homogenous dispersion of a-CO_x/G nanofilaments in water even after one year implies their hydrophilicity and water processability. In addition, the membrane pressurized by a tweezer shows an optimum flexibility) (the scale bars for two first SEM images is 2 µm while the last SEM image has a 1 µm scale bar); b) TEM bright-field micrograph showing the amorphous structure and a brittle fracture surface for the a-CO_x/G nanofilaments. ; c) ATR-FTIR representing the chemical conversion of PAN to a-CO_x/G; d) XPS spectra of the a-CO_x/G nanofilaments; e) C1s XPS data of the a-CO_x/G nanofilaments thermally treated to 1250 °C. The main peaks observed at ≈284.6 (red line), 286.8 (yellow line), 288.1 eV (green line) and 291 eV (blue line) correspond to sp^2 and sp^3 C, single-bonded carbon–oxygen (C-O), double-bonded carbon–oxygen (C=O) and $\pi \rightarrow \pi^*$ transition of aromatic sp^2 domains, respectively; f) The carbon *k*-edge NEXAFS spectrum of the a-CO_x/G nanofilaments (red line) versus that of highly oriented pyrolytic graphite (HOPG; black line)(note that the resonances for the a-CO_x/G nanofilaments are much smaller than those of HOPG and have been enlarged (x100) for the

sake of a better comparison); g) EEL spectra from a-CO_x/G nanofilaments (red line) versus an amorphous carbon (grey line) and a graphite (green line) reference.



Figure 2. Oil removal capacity of the *a*-CO_x/G buckypaper. a) oil adsorption capacity of the buckypaper before and after the flushing process (the bottles contain feed and permeate samples, respectively); b) ATR-FTIR graph demonstrates chemical structure of the oil as free and bound to the nanofilaments; c) the chemical structure of Castor oil.



Figure 3. Dye rejection efficiency of the *a*- CO_x/G buckypaper. a) MB retention ability (the bottles contain feed and permeate samples, respectively) and b) permeability of the *a*- CO_x/G buckypaper at the alkaline pH of 9.



Figure 4. The *a*-CO_x/G buckypaper's particle filtration performance. a) Bubble point test results implying that the buckypaper can be regarded as a MF membrane; b) particle rejection efficiency of the membrane at two feed concentrations (the bottles contain feed and permeate samples, respectively); c) permeate flux of the membrane at two feed concentrations; d) the cake layer formed on/into the surface layer of the membrane; e) particle size distribution of TiO₂ particles present in the feeds versus the mean flow pore diameter of the membrane.

The table of contents

Graphite nanomaterials are superhydrophobic and selectively adsorb non-polar water pollutants. Yet, this feature hinders their applicability in dynamic membrane processes due to fouling and presence of polar pollutants, unless they are hydrophilized. Here, graphite nanofilaments as the building blocks of a buckypaper membrane are oxidized (hydrophilized) through a customized thermal treatment to be able to remove polar and non-polar pollutants.

Keywords: ((graphite, amorphous carbon, nanofilaments, buckypaper, water treatment))

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A flexible oxygenated carbographite nanofilamentous buckypaper as an amphiphilic membrane



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Supporting Information

A flexible oxygenated carbographite nanofilamentous buckypaper as an amphiphilic membrane

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a- CO_x/G nanofibrous membrane a- CO_x/G nanofilamentous buckypaper membrane Supplementary Fig. 1. Schematic illustration of the structure of the a- CO_x/G membrane as nanofibrous and nanofilamentous.



Supplementary Fig. 2. HR-TEM images show arrangement of graphitic (dark) and amorphous carbon (grey) regions along an a-CO_x/G nanofilament as dense and aligned versus sparse and haphazard, respectively.



Supplementary Fig. 3. a) AFM images demonstrate dimensional features and morphology of the a-CO_x/G nanofilaments; b) Size histogram of the a-CO_x/G nanofilaments.

Supplementary Table 1. XPS results for the a-CO_x/G nanofilaments

	Pos.	Area	atomic %
C1s	285.03	29235.93	95.24
O1s	533.08	2654.84	2.95
N1s	400.53	1002.03	1.81

As shown in Supplementary Fig. 4, in the spectra related to the nanofillaments graphitized at two temperatures of 1050 °C and 1250 °C cooled down slowly and fast, respectively, a diffraction peak appears at 2θ = 24.5° that is attributed to (002) crystallographic plane of graphite. ^[62] The larger intensity of the peak for the sample graphitized at 1050 °C then cooled down normally implies its higher graphite content compared to the other sample. The Bragg and Scherrer equations (Eqs. 1 and 2) were implemented to calculate the average interplanar spacing "*d*(002)" and crystallite size parameter "*Lc*" as follows:^[62]

$$d_{(002)} = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$L_c = \frac{0.5\pi}{\beta \cos \theta} \tag{2}$$

Where λ is the wavelength of the X-ray, θ the diffraction angle, and β the width of the diffraction peak measured at half its height in radian. The interplanar spacing in the samples graphitized at 1050 °C (normal cooling) and at 1250 °C (fast cooling) equals to 3.62 and 3.65 Å, respectively. In addition, the sample graphitized at 1050 °C then cooled down normally possesses larger L_c (~ 1 nm) than the sample graphitized at 1250 °C then cooled down fast ($L_c = 0.6$ nm). Such discrepancies imply that normal cooling process consolidates the sheets of carbon atoms and allows the graphite crystallites grow. Thus, the interplanar spacing declines while the crystallite size rises. In contrast, the fast cooling process stops graphitization and preserves the amorphous phase.



Supplementary Fig. 4. XRD spectra implies that the thermal treatment including a lower graphitization temperature (GT) and a normal cooling rate leads to a larger graphitic content compared to that with a higher graphitization temperature and a fast cooling rate.



Supplementary Fig. 5. Optimum porosity of the a-CO_x/G buckypaper



Supplementary Fig. 6. The set-up designed for cross-flow filtration of particles

Supplementary Table 2. Electrospinning conditions of PAN nanofibers				
PAN concentration	8 wt%	Voltage	15kV	
Solvent	<i>N,N</i> -	Spinning distance	25 cm	
	dimethylformamide			
	(DMF)			
Feed rate	0.8 ml.h ⁻¹	Electrospinning	8 hours	
		duration		

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