Photocatalytic Treatment of PFAS in Single-step Ultrafiltration Membrane Reactor

Supplementary Information

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Text S1. Chemicals and materials

Adsorptive catalysts were synthesized from titantium (IV) oxide (GPR Rectapur ≥99%, VWR Chemicals, Italy); powdered activated carbon, (20+40 mesh, Afla Aesar, Thermo Fischer, Germany); indium (II) nitrate hydrate (≥99.9%, Sigma Aldrich, USA); gallium nitrate hydrate (>99.9%, Acros Organics, Czech Republic); and iron (III) chloride hexahydrate (>99%, Thermo Scientific, India). A stock solution of 0.1 M sodium hydroxide was made by dissolving reagent grade beads (VWR Life Sciences, USA) in pure water. Hydrochloric acid (37 vol.%, EMSURE®, Supelco, Austria) was dilute to an 0.1 M solution with ultrapure water. Ultrapure water was generated by a Millipore Instrument (Molsheim, France) equipped with a Millipak® 0.22 μm filter and a Q-Guard® 1 purification cartridge (Merck Millipore). Prior to modifications, UF membranes were washed with ultrapure water and methanol (GPR Rectapur, VWR, France). Grafting solutions were made from acrylic acid (Sigma Aldrich, Germany), isopropanol (≥ 99.5%, Sigma Aldrich, Germany), dopamine hydrochloride (Sigma Aldrich, Merck, Germany) and potassium phosphate buffer solution (0.2 M, Thermo Fisher Scientific, Germany), adjusted to pH = 8 using 0.1 M NaOH solution.

Perfluorooctanoic acid (PFOA, >98%), nonafluoro-1-butanesulfonic acid (PFBS, >98%), and heptafluorobutyric acid (>98%, PFBA) were purchased from Tokyo Chemical Industry, Co. Ltd. (Japan); heptadecaoctonaesulphonic acid (H-PFOS, >97%) was purchased from abcr, GmbH (Germany). Powdered PFAS were dissolved in methanol, then diluted to the desired stock solution concentration with ultrapure water. PFAS standards were made regularly from dissolving pure contaminants in a 50:50 methanol-water solution and used for calibration. Fluoride Standard (Orion ionplus®, Thermo Scientific, USA) was used as the analytical standard for calibrating the IC. Dilutions of pure formic (≥99%, HiPerSolv Chromanorm®, VWR Chemicals, United Kingdom) and acetic acid (≥99%, ReagentPlus®, Sigma Aldrich,

USA) in ultrapure water, individually and combined with fluoride ion standards, were used to confirm observed acetate and formate peaks using the IC.

All samples were collected using polypropylene/polyethylene syringes (5 mL Luer, Chirana) and filtered through PES filters 0.45 μm (Captiva Econofilter, Agilent), before transferring to analysis vials, except for permeate samples, which were directly transferred analysis vials without additional filteration. For ion chromatography, 5 mL PP analysis vials and caps (PolyVials, Thermo Fisher Scientific) were used, while 2 mL PP vials and caps with silicon/PFTE septum were used for liquid chromatography (SureSTART^{TM}, Thermo Fisher Scientific).

Text S2. Photocatalyst synthesis

Iron-, indium-, and gallium-enhanced titanium nanotubes on activated carbon (TNT@AC) were synthesized using hydrothermal and doping methods, which have been documented in detail by others. Briefly, titanium dioxide and powdered activated carbon were stirred in a basic solution for 12 hours, then baked at 130 °C for 72 hours. Next, the suspension was washed to achieve a neutral pH, then centrifuged, decanted, and dried at 105 °C overnight. The TNT@AC particles were resuspended in ultrapure water, to which the respective 0.1 M metal salt solution were added to achieve the targeted amounts: 1 wt.% iron, 2 wt.% gallium, and 2 wt.% indium. After neutral pH adjustment, the suspension was stirred overnight. Then, the suspension was centrifuged, decanted, and dried before being calcinated at 550°C for 3 hours with nitrogen flow (approximately 200 mL/min). Finally, any organic residues were removed from the calcinated particles by washing in ultrapure water, then centrifuged, decanted, and dried at 105°C for 24 hours. Dried catalyst was stored in screw top PP tubes.

Text S3. Photocatalytic membrane grafting methods

Although polyvinylidene fluoride (PVDF) is considered the most robust polymeric membrane material, it could potentially contaminate tests as a fluorinated polymer. Therefore, polyethersulfone (PES), which has also good chemical stability and heat tolerance, was chosen as the basis for the UF membrane modifications. For the acrylic acid graft, the membrane surface was first cleaned and activated by generating plasma under anaerobic conditions for 300 seconds at power 50 W using an ENI model ACG-6B generator. Anaerobic conditions in the plasma reactor were ensured by purging the chamber with nitrogen gas three times and pumping a vacuum before the generator was switched on. The activated membranes were immediately immersed in an acrylic acid solution (15 vol.% in isopropanol) at 60 °C for two hours.

The polydopamine grafting method consisted of cleaning the membrane via sonication in methanol and ultrapure water (for 5 minutes each solution). Then, the cleaned membranes were immersed in a buffered dopamine hydrochloride solution (1 g/L of dopamine hydrochloride, pH = 8) under continuously stirring, where they were allowed to spontaneous polymerization under aerobic conditions for 2 to 5 hours.

After grafting, the photocatalyst was deposited onto the grafted membranes via vacuum filtration. This method allowed for better control of the catalyst loading, ranging from 2.5 mg to 25 mg per membrane. Coated membranes were rinsed with ultrapure water to remove any unadhered particles. The rinse water was filtered through a 2 μm glass fiber filter (Whatman, 47 mm diameter) and dried, before weighing dried residuals to determine final catalyst loading on the membrane. Coated membranes were stored refrigerated in ultrapure water to prevent cracking of the polydopamine coating when dried. A summary of the synthesized membranes is provided in the SI (Tables S1 and S2). For comparison, photocatalyst was also loosely loaded on an unmodified, commercial nanofiltration (NF) membrane (Alfa Laval NF, MWCO = 300

Da) by vacuum filtration of Fe/TNT@AC particles suspended in water, then placed directly in the reactor.

Table S1. Inventory of the photocatalytic membranes synthesized with acrylic acid grafting solution.

Membrane ID	Catalyst Coating	Catalyst Loading (mg)	Avg. Catalyst Loading (mg)	Catalyst Loading (wt.% of membrane)	Avg. Catalyst Loading (wt.% of membrane)
AAT_002	TNT@AC	0.6		0.28%	
AAT_003	TNT@AC	0.5		0.23%	
AAT_004	TNT@AC	1.0	0.7	0.46%	0.32%
AAI_004	In/TNT@AC	2.8		1.28%	
AAI_005	In/TNT@AC	2.7		1.24%	
AAI_006	In/TNT@AC	3.1	2.9	1.42%	1.31%
AAI_007	In/TNT@AC	13.4		9.02%	
AAI_008	In/TNT@AC	13.2		8.88%	
AAI_009	In/TNT@AC	14.1	13.6	9.49%	9.13%
AAG_004	Ga/TNT@AC	3.6		1.65%	
AAG_005	Ga/TNT@AC	2.7		1.24%	
AAG_006	Ga/TNT@AC	2.7	3.0	1.24%	1.38%
AAG_007	Ga/TNT@AC	11.0		7.40%	
AAG_008	Ga/TNT@AC	10.5		7.07%	
AAG_009	Ga/TNT@AC	10.5	10.7	7.07%	7.18%
AAF_004	Fe/TNT@AC	2.7		1.24%	
AAF_005	Fe/TNT@AC	1.5		0.69%	
AAF_006	Fe/TNT@AC	1.8	2.0	0.83%	0.92%
AAF_007	Fe/TNT@AC	13.8		9.29%	
AAF_008	Fe/TNT@AC	14.0	13.9	9.42%	9.35%

Table S2. Inventory of the photocatalytic membranes synthesized with polydopamine grafting solution.

Membrane ID	Catalyst Coating	Grafting Solution	Catalyst Loading (mg)	Avg. Catalyst Loading (mg)	Catalyst Loading (wt.% of membrane)	Avg. Catalyst Loading (wt.% of membrane)	Polymerization Time (hours)
PDT_001	TNT@AC	PDA	3.2	3.2		2.09%	3 h
PDI_001	In/TNT@AC	PDA	10.1		6.59%		4 h
PDI_002	In/TNT@AC	PDA	14.6	12.4	9.52%	8.06%	5 h
PDG_001	Ga/TNT@AC	PDA	6.3		4.11%		3 h
PDG_002	Ga/TNT@AC	PDA	10.1	8.2	6.59%	5.35%	5 h
PDF_001	Fe/TNT@AC	PDA	15.6		10.18%		4 h
PDF_002	Fe/TNT@AC	PDA	15.5		7.1%		2
PDF_003	Fe/TNT@AC	PDA	3.9		1.8%		2.5
PDF_004	Fe/TNT@AC	PDA	10		4.6%		3
PDF_005	Fe/TNT@AC	PDA	20.2		9.3%		3
PDF_006	Fe/TNT@AC	PDA	15.9		7.3%		3
PDF_007	Fe/TNT@AC	PDA	17.04		7.8%		3
PDF_008	Fe/TNT@AC	PDA	5.25		2.4%		3.5
PDF_009	Fe/TNT@AC	PDA	13.37		6.1%		3
PDF_010	Fe/TNT@AC	PDA	24.76	14.2	11.4%	6.79%	3.25

Text S4. Batch slurry tests

Batch tests were conducted in slurry, where photocatalysts were suspended in lab-contaminated water, then irradiated. An aliquot of 40 mL 200 ppb PFOA in ultrapure water was allowed to adsorb to the photocatalyst for 30 minutes. Since investigating its defluorination ability was the focus of the experiment, a high dose of photocatalyst (1 g/L) was selected to ensure adsorption of PFOA prior to photodegradation. Then, the solution was centrifuged and decanted. The decanted solution was prepared for UPLC-MS/MS analysis. Meanwhile, the settled catalyst and 10 mL of solution were transferred to a quartz reactor, placed in the photoreactor and irradiated for 4 hours. After irradiation, the sample was filtered and transferred to vials for UPLC-MS/MS and IC analyses. For comparison, parallel experiments were run with the three UV chips (PureFize) as the light source.

Text S5. Photocatalytic membrane reactor (PMR) cleaning procedure

After running an experiment, all lines were drained of contaminated lab water. Then, ultrapure water was pumped through the system for 10 minutes. Next, the membrane was removed from the PMR and stored in a 0.1% sodium sulfide solution at 4°C. A methanol solution (10 vol. %) was then pumped through the system for 10 minutes, followed by another 10-minute rinse with ultrapure water. A sample was collected at the end of the cleaning cycle to verify there was no contamination of the system.

Text S6. Analysis and Characterization

Membrane Characterization

Topographical scans of the unmodified, grafted, and coated membranes were taken using a Solver AFM (NT-MDT Spectrum) fit with a microcantilever (AC 160 TS, Oxford Instruments); scans were processed using WSxM imaging software. SEM images were collected using a NOVA nano SEM 600 instrument with TLD detector. Prior to SEM scans,

membranes were sputtered with a 6-nm thick platinum coat using a high vacuum sputter system (Leica EM SCD 500). Data from SEM-EDX (TM3030plus, Hitachi High-Tech) were analyzed via the Cliff-Lorimer Ratio method.

An optical tensiometer (OneAttension Theta Lite, Biolin Scientific, Finland), fitted with a 200 μL tip, released a 4 μL drop of water onto the membrane surface while capturing 20 frames per second, from which the water contact angles were measured in ImageJ (NIH, public domain). The streaming surface potentials were measured at neutral pH using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria). Finally, the pore sizes of the membranes were verified by wet and dry analysis on a porometer (POROLUX™ 1000, Germany), after soaking samples in the manufacturer's Porefil™ solution; pressure was ramped up from 0 to 35 bar, while the instrument recorded nitrogen gas flow through the membrane.

Fluorine ion analysis

An ion chromatograph (Dionex™ Aquion AS-DV, Thermo Scientific) with a Dionex™ IonPac™ AS23 analytical column (2 × 250 mm) and guard column was used to measure F^- concentrations following batch experiments. The instrument was also equipped with a Dionex™ AERS 500 carbonate suppressor (2 mm) ahead of the conductivity cell, which was kept at 35 °C and had a collection rate of 5 Hz. A sodium carbonate/bicarbonate (Dionex™ AS23 Eluent, Thermo Scientific) eluent solution was used. Sample was injected and eluted through the column at 0.25 mL/min for 30 minutes.

PFAS extraction and analysis

To extract adsorbed PFAS for quantification, photocatalyst particles were removed from slurry and placed in methanol and heated for 4 hours at 80 °C. After PMR testing, the photocatalytic membrane was removed and placed directly in a solution of 100 mmol/L

ammonium acetate in methanol, and sonicated for 30 minutes. After extraction, the supernatants were filtered, then analyzed by UPLC-MS/MS.

Ultra-high performance liquid chromatography with mass spectroscopy (UPLC-MS/MS) was used for the identification and quantification of PFAS and its degradation byproducts in aqueous and extraction samples. The UPLC instrument used was a Thermo Scientific Dionex™ UltiMate 3000 series. The UPLC was equipped with an analytical column (Waters™ ACQUITY UPLC® HSS T3, 1.8 µm, 2.1 x 100 mm) with a guard column (Waters™ ACQUITY UPLC® HSS T3 VanGuard Pre-column, 1.8 µm, 2.1 × 5 mm), and the same chromatographic method was used. An aliquot of 5 µL of sample was injected to the analytical column, which was maintained at 35 °C. Then, the organics were eluted from the column using a mobile phase gradient program at 0.25 mL/minute (see SI). The main components of the mobile phase were ultrapure water, methanol, and ammonium formate (2 mM). The mobile phase gradient program was:

- Two minutes with a mobile phase of 12.5% Solution B.
- Increase to 75% Solution B over 5 minutes.
- Increase to 97.5% Solution B over 11 minutes.
- Hold for 4 minutes with 97.5% Solution B.
- Decreased to 12.5% Solution B and maintained for 3 minutes to re-equilibrate the column.

Solution A was a mixture of demineralized water:methanol (20:80, v/v) with 2 mM of ammonium formate. Solution B was 2 mM of ammonium formate in methanol.

Eluted samples were analyzed on a mass spectrometer (MS) with electrospray ionization (ESI). Either a Bruker compact quadruple time-of-flight (QToF) MS or a TSQ Fortis Plus Triple Quadrupole MS was used for detection. The detection methods varied slightly for each

166 instrument. The Bruker compact QToF MS was set up in the negative ion mode, at a dry
167 temperature of 300 °C, a dry gas flow of 5.0 L/minute, cone voltage of 500 V, and the nebulizer
168 setting at 2.0 bar. The TSQ Fortis Plus Triple Quadrupole MS was set up in the negative ion
169 mode (2500 V) with a vaporizer temperature of 300 °C and ion transfer tube temperature of
170 325 °C. Different SRM parameters were set for each compound and are provided in the
171 following table.

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Table S3: SRM parameters for TSQ Fortis Plus Triple Quadrupole Mass Spectrometer.

Compound	Start time (min)	End time (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Minimum Dwell Time (ms)
TFAA	0.9	1.8	112.873	68.967	10	299.271
PFPrA	1.8	4	162.853	119.05	8.94	299.271
PFBA	4	6	212.853	169.05	7	40.513
PFBS	5	7	298.91	79.967	31.78	40.513
PFHxA	5	8	312.856	269.05	7.43	40.513
PFHxS	5	10	398.91	79.883	38.73	40.513
PFOA	5	11	412.933	369.05	7.86	40.513
PFOS	5	11	498.813	79.967	47.11	40.513

Quality control and data analysis

Calibrations using analytical standards were performed on all instruments for the selected compounds. Blanks were run at the beginning and end of each analysis group to validate the baseline and verify there was no contamination. Additionally, standards were run with each analysis group. In all instances, >90% recovery of standards was observed on the IC. The detection limits were 0.05 ppm fluorine ion for the IC, and 0.001 μM for PFAS analyzed by UPLC-MS/MS. Samples were analyzed using double and triple injections on the IC and UPLC-MS/MS, respectively; results are reported as an average of the injections, unless there was an outlier, in which case the outlier was removed.

Non-detect or results below the detection limits (BDL) of the instrument were treated as zero value when analyzing the data. The PFAS removal efficiency was calculated by

subtracting the final concentration from the initial concentration, dividing by the initial concentration, and converting to a percentage. The maximum theoretical F^- concentration was calculated based on the initial PFOA concentration, its molecular weight, and the number of fluorine atoms in the molecule (Equation S1). Then, the defluorination rate (deF%) of PFOA was calculated by dividing the fluoride anion (F^-) concentration by the theoretical maximum concentration and converting to a percentage (Equation S2):

$$[F^-]_{theoretical} = [PFOA]_0 \times \frac{MW_F \times 15}{MW_{PFOA}} \quad \text{(S1)}$$

$$deF\% = \frac{[F^-]_{released}}{[F^-]_{theoretical}} \times 100\% \quad \text{(S2)}$$

where $[F^-]_{theoretical}$ is the theoretical concentration of fluorine ions, if all the initial PFOA, $[PFOA]_0$, is mineralized; MW_F and MW_{PFOA} are the molecular weights of fluorine ion and PFOA, respectively; and $[F^-]_{released}$ is the measured fluorine ion concentration after treatment.

Table S4: PFAS compounds observed in samples following the batch photodegradation tests

Sample	Catalyst	PFOA, ppb average (range)	PFHxA, ppb average (range)	PFBA, ppb average (range)	PFPrA, ppb average (range)	Average percent removal of PFOA
November 2022 Trials						
Initial	n/a	351 (348 - 352)	0 (ND - 0)	ND	ND	n/a
After adsorption	TNT@AC	137 (ND – 145)	ND	ND	ND	73.7%
	In/TNT@AC	14 (ND – 29)	ND	ND	ND	95.9%
	Ga/TNT@AC	31 (ND – 63)	ND	ND	ND	91.0%
	Fe/TNT@AC	13 (ND – 26)	ND	ND	ND	96.3%
After irradiation	TNT@AC	1 (ND – 2)	ND	ND	0.1 (ND – 0.2)	99.3%
	In/TNT@AC	0.5 (ND – 2)	ND	ND	0 (ND – 0.5)	99.8%
	Ga/TNT@AC	1 (ND – 3)	ND	ND	ND	99.6%
	Fe/TNT@AC	0.6 (ND – 1)	ND	ND	ND	99.8%
Extracted after irradiation	TNT@AC	313 (284 – 341)	2	0.4	ND	89.3%
	In/TNT@AC	459 (446 – 471)	2 (2-3)	ND	ND	131%
	Ga/TNT@AC	548 (541 – 555)	1 (1 – 2)	ND	ND	156%
	Fe/TNT@AC	501 (478 – 524)	3 (2 – 5)	ND	ND	143%
Control – 4h UVC	n/a	389 (356 – 421)	1	ND	ND	-11%
February 2023 Trials						
Initial	n/a	135 (125 – 142)	0 (ND – 0.3)	ND	ND	n/a

After adsorption and irradiation	TNT@AC	ND	ND	ND	ND	100%
	In/TNT@AC	ND	ND	ND	ND	100%
	Ga/TNT@AC	0.2 (ND – 0.4)	ND	ND	ND	99.8%
	Fe/TNT@AC	ND	ND	ND	ND	100%
Control – 4h dark	Fe/TNT@AC	2	ND	ND	ND	98.5%
Control – 4h UVC	n/a	120	ND	ND	ND	10.7%

ND = non-detect

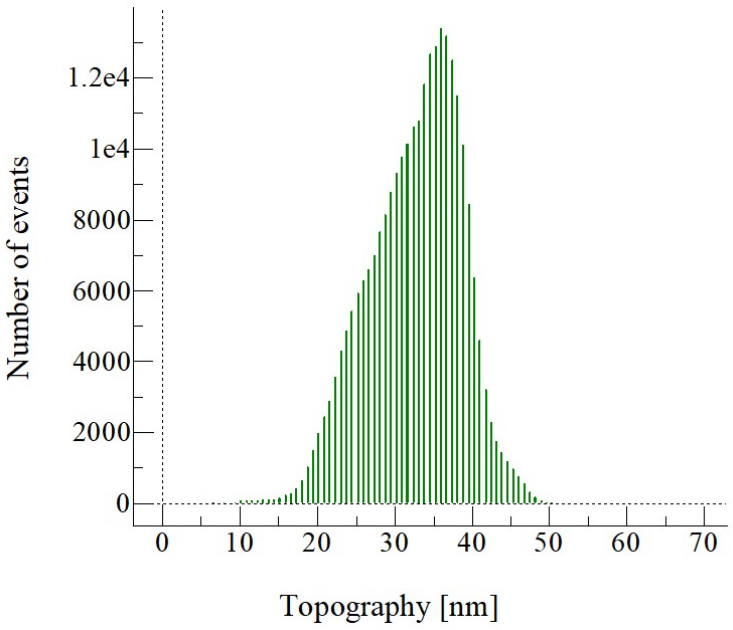

Figure S1. Height histogram of the pristine membrane, showing the number of times each height was recorded during the topographical AFM scan.

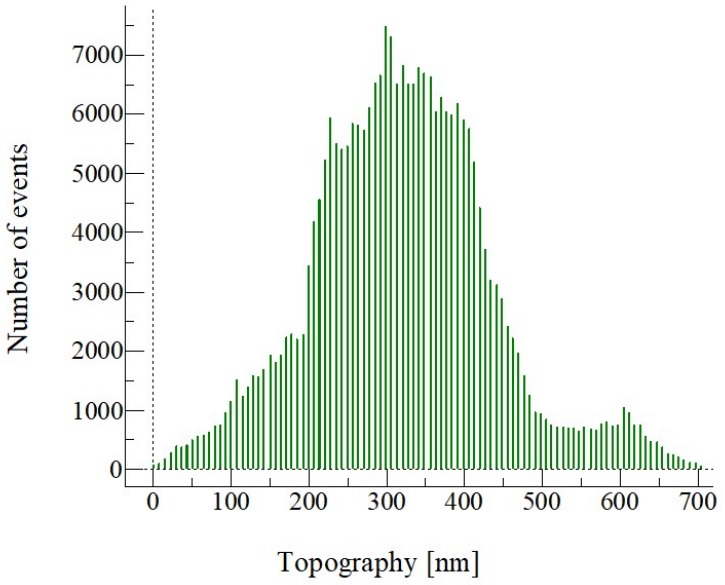

Figure S2. Height histogram of the polydopamine-grafted membrane, showing the number of times each height was recorded during the topographical AFM scan.

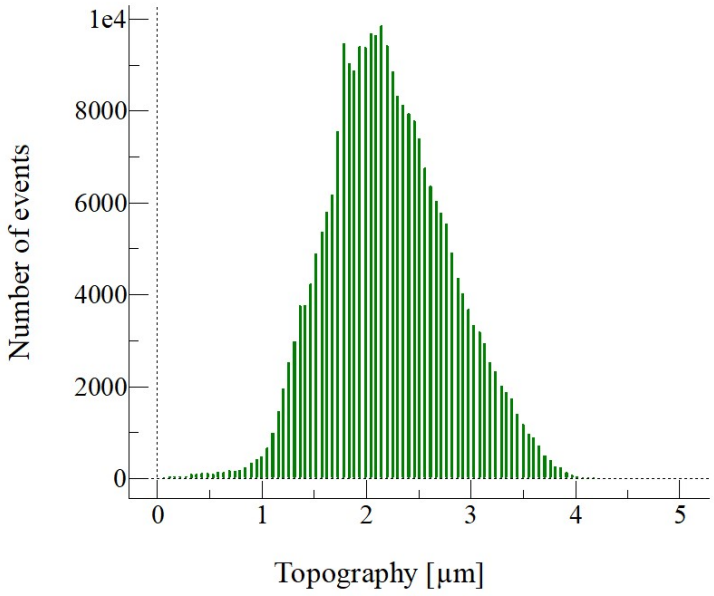

Figure S3. Height histogram of the Fe/TNT@AC coated membrane, showing the number of times each height was recorded during the topographical AFM scan.

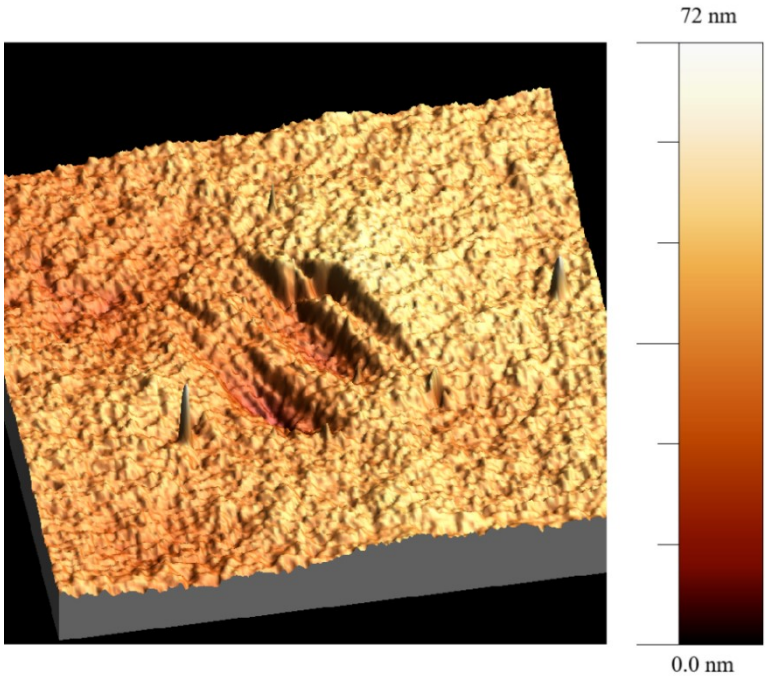

Figure S4. 3D image generated from the topographical AFM scan of the pristine membrane.

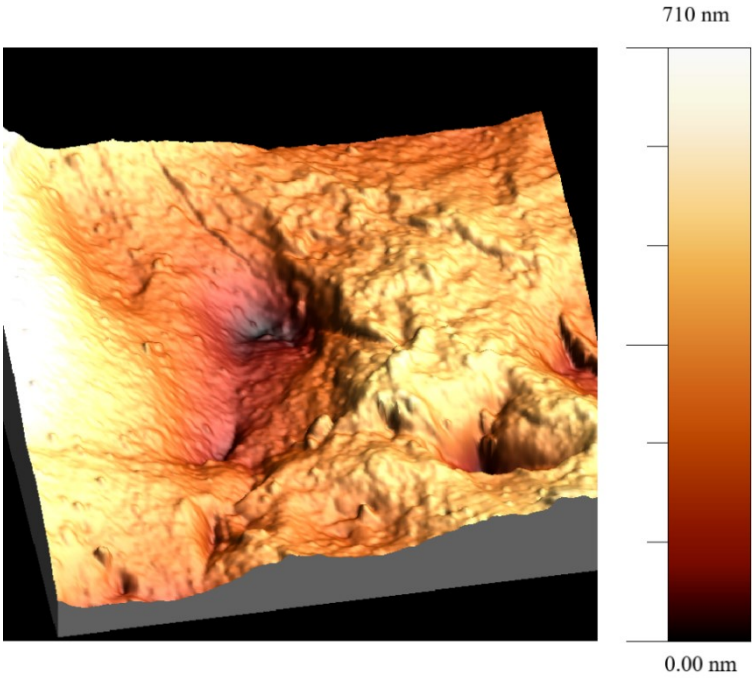

Figure S5. 3D image generated from the topographical AFM scan of the polydopamine-grafted membrane.

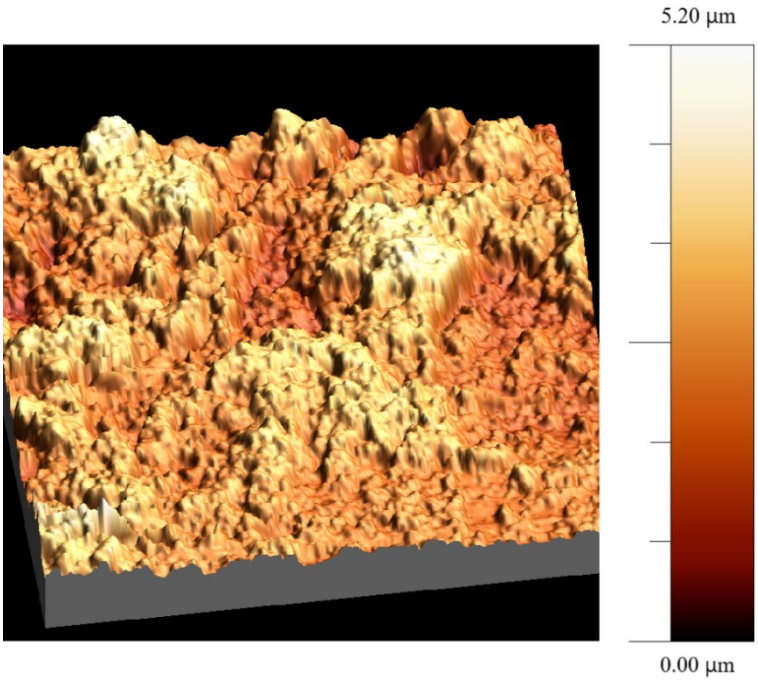

Figure S6. 3D image generated from the topographical AFM scan of the Fe/TNT@AC coated membrane.

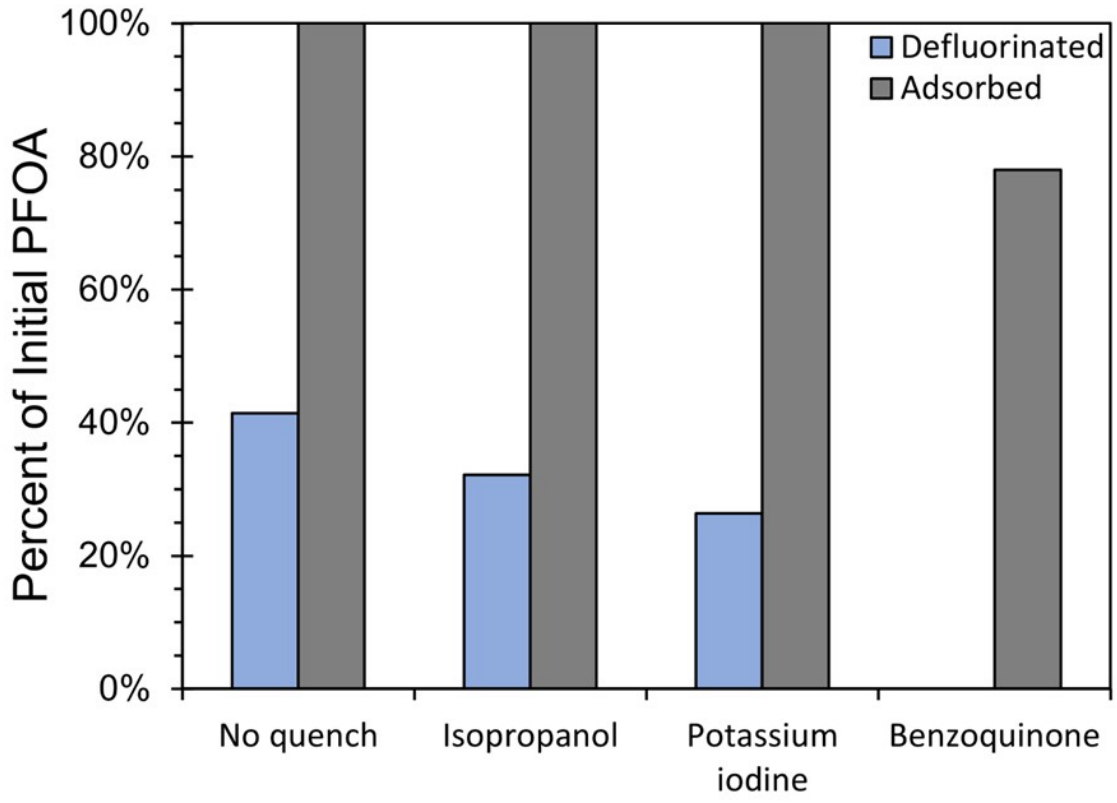

Figure S7: Quenching experiment with isopropanol (5 mM), potassium iodine (1 mM), and benzoquinone (1 mM) for 200 ppb PFOA solution treated with Fe/TNT@AC (1 g/L) under 4-hours UV irradiation in photoreactor.