

Supporting Information

Beads-on-String Structured Nanofibers for Smart and Reversible Oil/Water Separation with Outstanding Antifouling Property

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Exact procedure for contact angle measurements.

The sample for contact angle measurement of the PVDF or T-P nanofiber membrane was prepared by attaching one piece of the as-spun membrane (with size $1 \times 2 \text{ cm}^2$) on a cleaned glass slide by double sided adhesive tape. The spin-coated T-P membrane was fabricated on a cleaned glass slide with rotate speed of 1600 rpm for 15 s followed by 3000 rpm for 5 s. The droplet volume of the testing liquid (DI water or chloroform) for contact angle measurements was $2 \text{ }\mu\text{L}$. For the measurement of oil-in-water contact angle, the as-spun T-P nanofiber membrane was attached on the bottom of a quartz cuvette containing DI water, then $2 \text{ }\mu\text{L}$ of chloroform droplet was dragged by the needle tip to contact the surface of the T-P nanofiber membrane under water. Each value of the contact angle was averagely calculated from 5 repeated measurements.

Investigation of self-cleaning property.

A piece of the prepared T-P nanofiber membrane with size of $2 \times 2 \text{ cm}^2$ was stained by 0.1 ml of the ethanol solution (to ensure the even distribution and spreading on the membrane surface) of oleic acid (with concentration of 10 vol.%). The stained membrane was then dried in an oven at $80 \text{ }^\circ\text{C}$. The UV or sunlight irradiation was performed in a dry state in air. No rinse step was carried out by any solvent. The samples after UV or sunlight irradiation were directly used in the following observation.

Durability study.

The durability of the prepared T-P nanofiber membrane was studied by applying repeated UV and heating treatment on it. The gradual change of membrane morphology, hydrophobicity and Ti content after each light-heat cycle were recorded through SEM, WCA and EDX tests, respectively. The average diameter of the beads on the nanofibers were calculated from 20 measurements using the software ImageJ. The Ti content on the surface of the T-P membrane after each cycle of light-heat treatment were averagely calculated from 3 measurements in different areas.

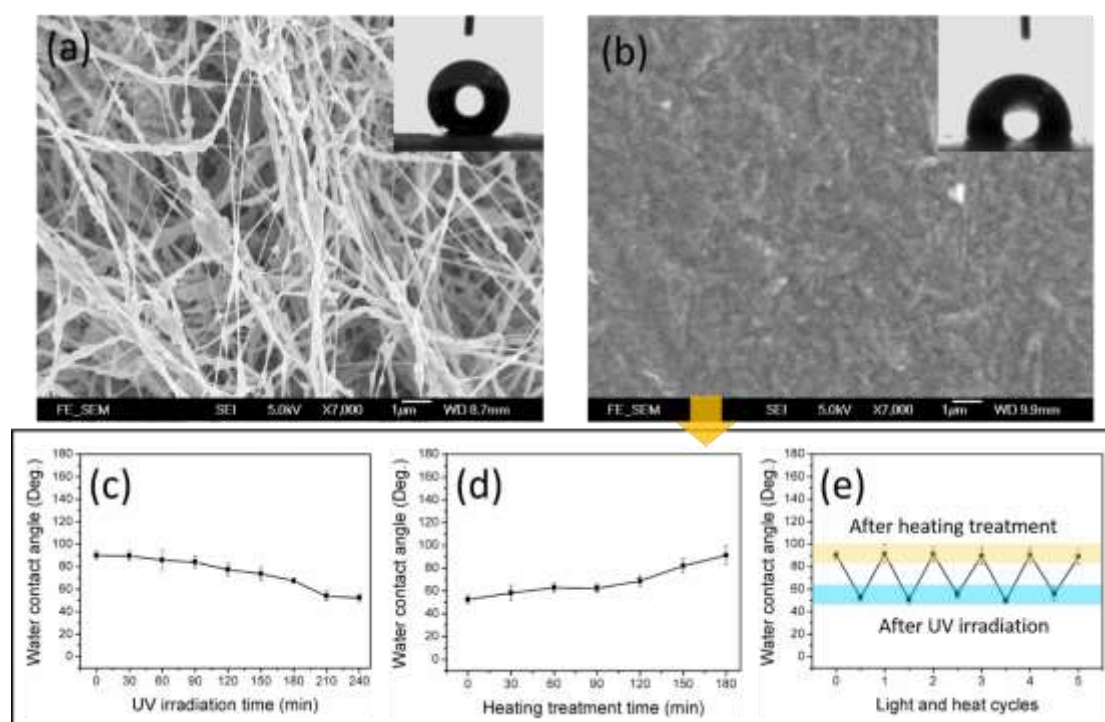


Figure S1. The morphology and WCA comparison between TiO_2/PVDF membranes produced by electrospinning (a) and spin-coating (b); (c) WCA changes on the spin-coated T-P membrane with increasing time of UV irradiation; (d) hydrophobicity recovery indicated by WCAs of the spin-coated T-P membrane along with increasing time of heating treatment at 110°C ; (e) reversible WCA changes of spin-coated T-P membrane along with repeated light and heat cycles. Compared to electrospun T-P nanofiber membrane, the spin-coated one exhibited a narrower range of WCA switch

(only between $\sim 50^\circ$ and $\sim 90^\circ$) and longer duration needed until it can be restored to hydrophobicity or hydrophilicity upon heating or UV treatment. The smoother morphology (or lower roughness) of the spin-coated T-P membrane compared to the electrospun one might be responsible for its narrower range of wetting state switch. Similarly, the lower sensibility of it towards UV and heating treatment might also be attributed to the less reception and internal reflection of the applied light and heat due to its lower exposed surface area and smoother morphology compared to the 3D porous structure formed on the electrospun T-P membrane.

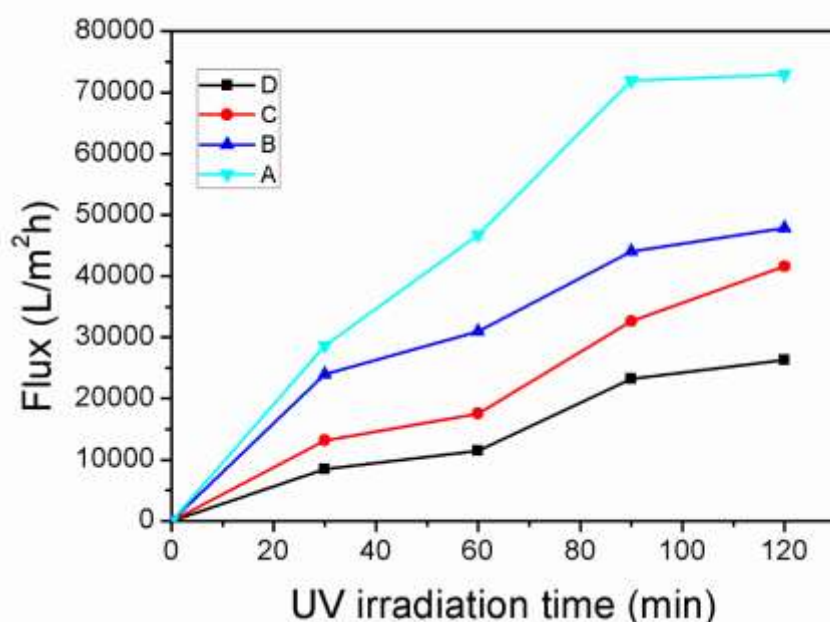


Figure S2. Water fluxes passing through the T-P membranes with different thicknesses along with increasing UV irradiation time. The membrane thicknesses are: A $\sim 5.6\ \mu\text{m}$, B $\sim 9.7\ \mu\text{m}$, C $\sim 17.6\ \mu\text{m}$, D $\sim 32.1\ \mu\text{m}$.

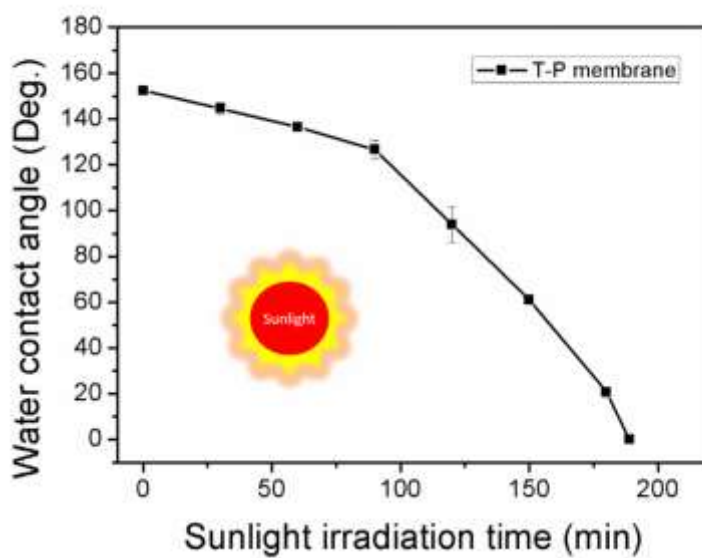


Figure S3. Sunlight-induced WCA change of T-P nanofibrous membrane (with TiO_2 of 8%) after different sunlight irradiation time.

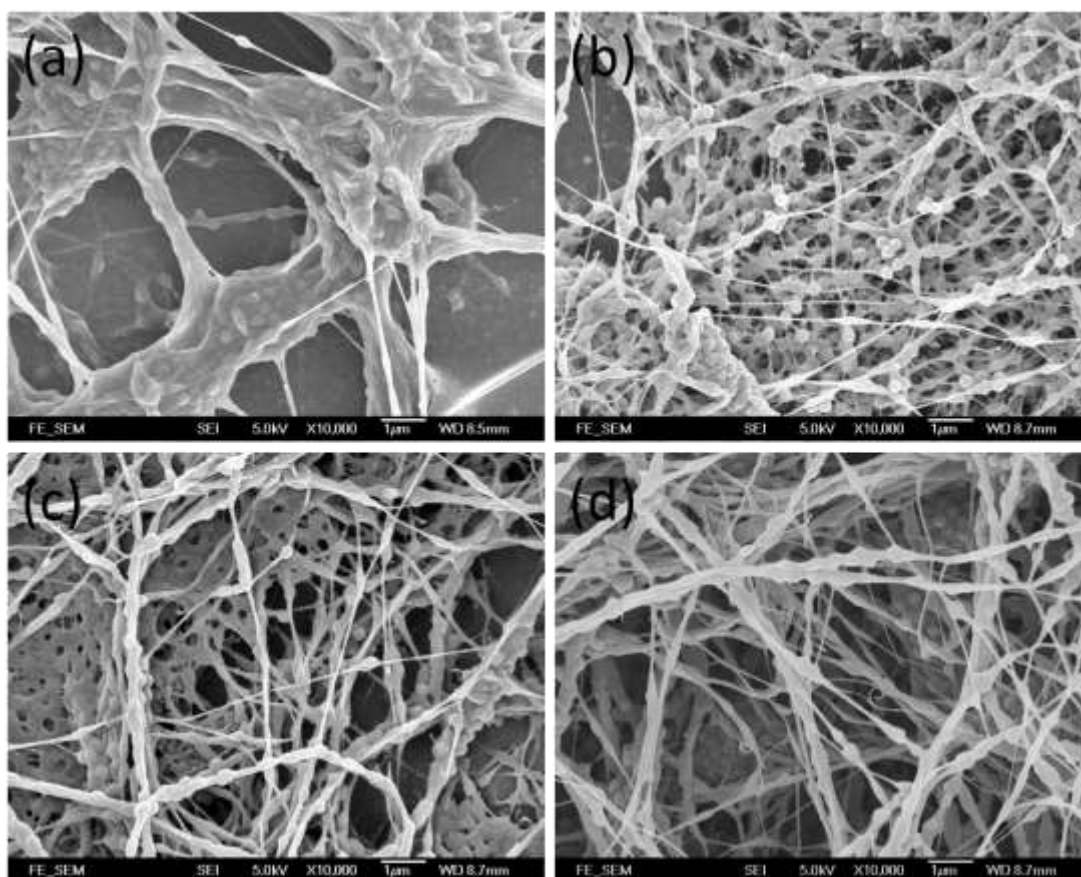


Figure S4. FE-SEM images showing the morphologies of T-P nanofiber membranes with TiO_2 /PVDF weight ratio of 2% (a), 4% (b), 6% (c), 8% (d).

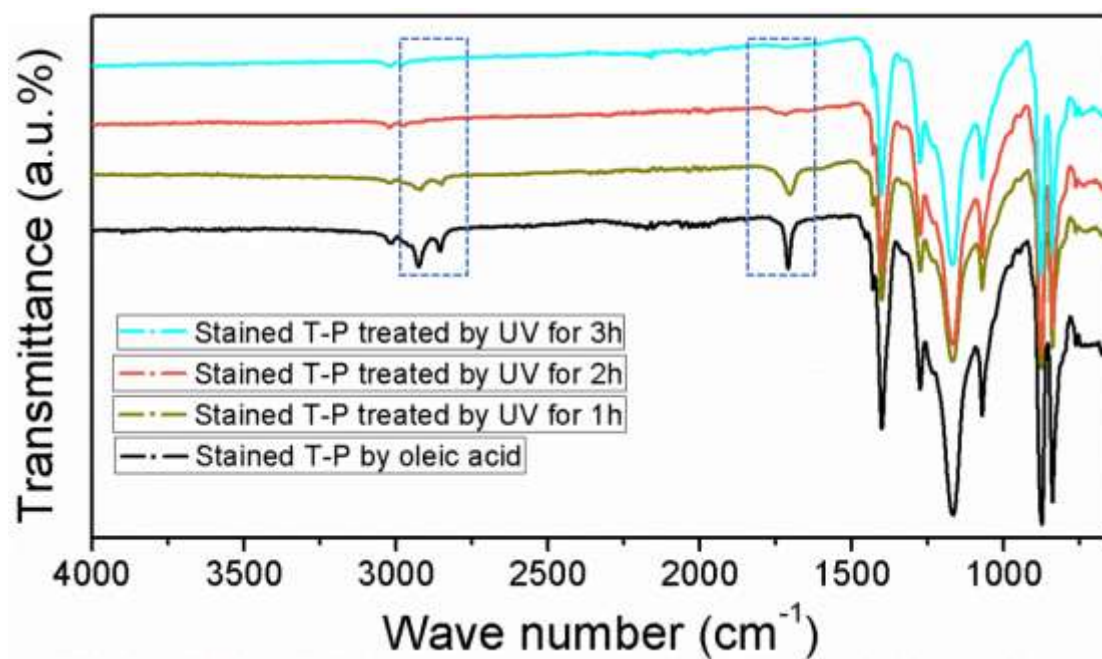


Figure S5. FTIR spectrums of the stained T-P nanofibers with subsequent UV irradiation for 0-3 hours.

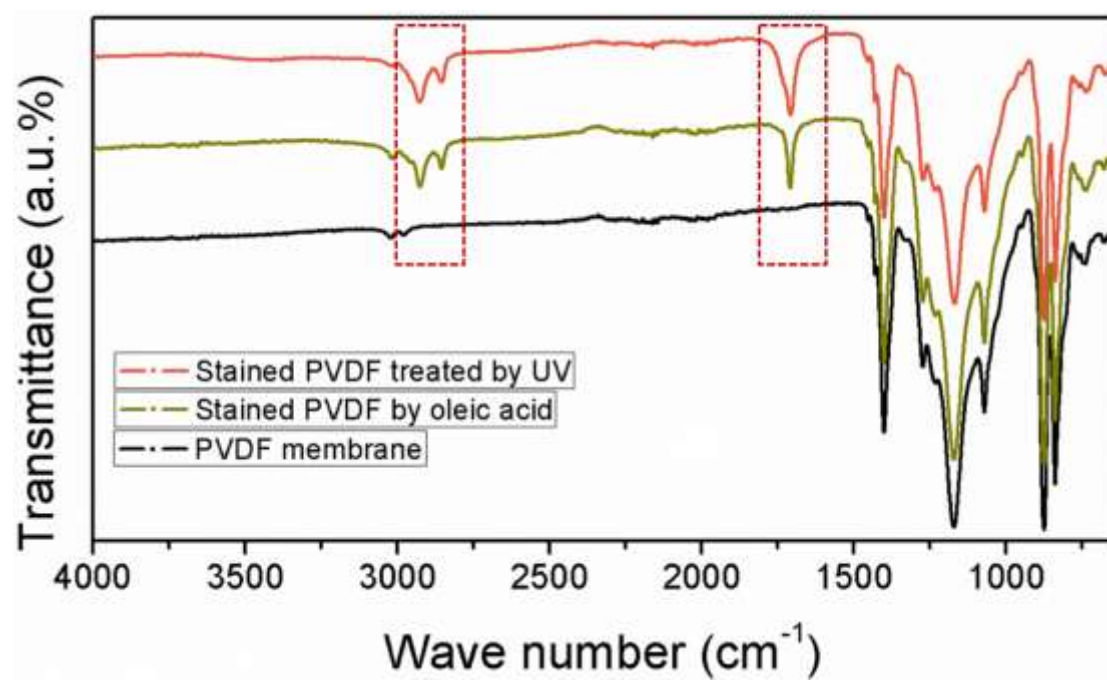


Figure S6. FTIR spectrums of PVDF nanofiber membrane, oleic acid stained PVDF nanofiber membrane, and oleic acid stained PVDF nanofiber membrane with subsequent UV irradiation for 3 hours.

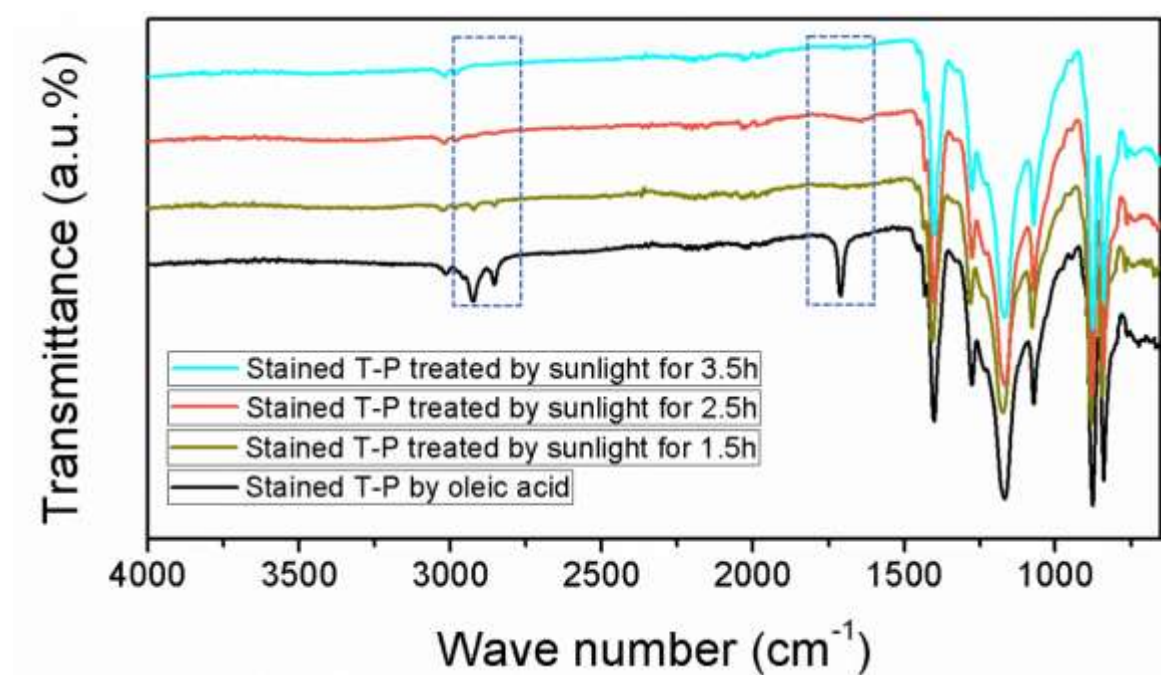


Figure S7. FTIR spectrums of the stained T-P nanofibers with subsequent sunlight irradiation for 0-3.5 hours.

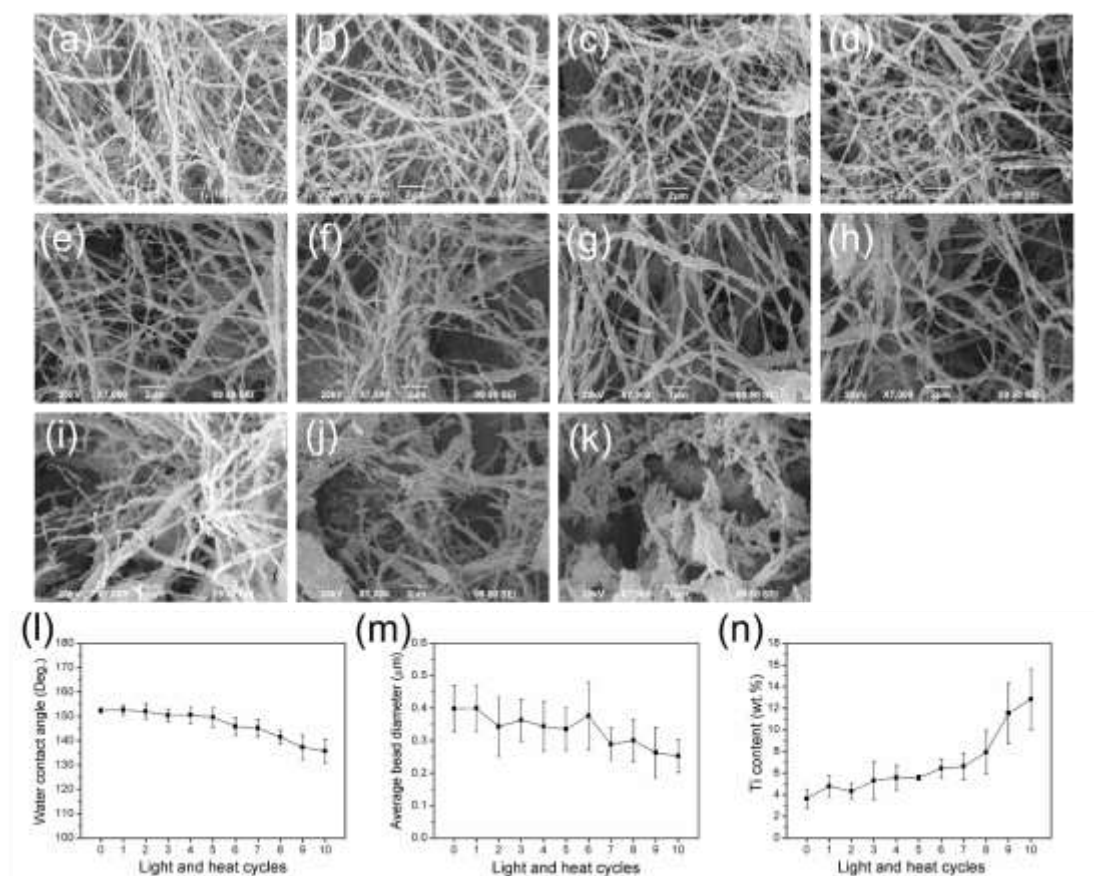


Figure S8. SEM images showing the UV-induced TiO_2 -catalyzed photochemical oxidation (or aging) of the T-P nanofiber membrane after 0-10 cycles (a-k, respectively) of UV-heat cyclic treatments, and (l-n) shows the corresponding changes of WCA, average bead diameter, and Ti content on the surface of the T-P nanofiber membrane. The fracture of the T-P nanofibers caused by UV-induced photochemical oxidation occurs from thinner nanofibers to thicker ones. After 5 cycles of UV-heat treatment, the overall morphology (with only a few of thin nanofibers fractured) and superhydrophobicity (with WCA of $\sim 150.3^\circ$) of the T-P nanofiber membrane can be well retained. However, apparent damage can be observed on the morphology (with the fracture of thick nanofibers shown in i-k) after 8-10 cycles of UV-heat treatments. The decrease of WCA and bead diameter along with increased UV-heat cycles (l-m) can indirectly indicate the damage of T-P nanofibers. The increasing Ti content obtained from EDX test indicates the increasing exposure of TiO_2 NPs on the nanofiber surface caused by TiO_2 -catalyzed photochemical oxidation induced by UV. In practical use, nevertheless, frequent UV

or heat treatments are hardly needed because each of the wetting status (water-wetting or water-resisting) can last for a long time once triggered.