**Supporting information**

**A spiral-windable, free-standing, durable membrane constructed with ultralong hydrogel@MnO2 nanowires for oil/water separation under harsh environment**

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Fig. S1. Droplet size distribution of emulsified oil.

Fig. S1. shows the droplet size distribution of emulsified oil-in-water feed used in this research. Statistical analyses of this distribution showed the mean diameter of oil droplets was around 3.61 μm with a d50 and d90 of 2.89 μm and 5.96 μm.

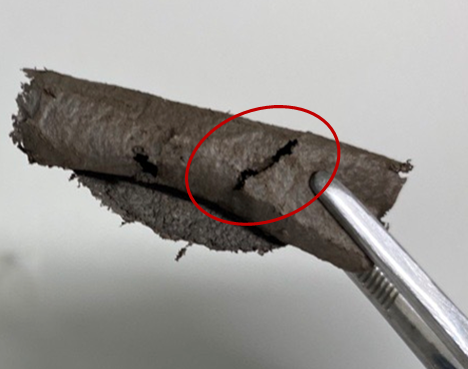


Fig. S2. Optical image of pristine MnO2 nanowire membrane when folded, showing the crack (red circle) on the membrane. This highlights its fragility and reduced flexibility when compared with a PVA- functionalized MnO2 nanowire membrane.



Fig. S3. The pore size distributions of pristine MnO2 and PVA-coated MnO2 nanowire membranes were analyzed using a pore size analyzer (porometer 3Gzh, Quantachrome). The results indicate that the average pore sizes of the membranes decreased from 0.09 µm to 0.07 µm following 1 w/w % PVA hydrogel coating on MnO2 nanowire membranes.

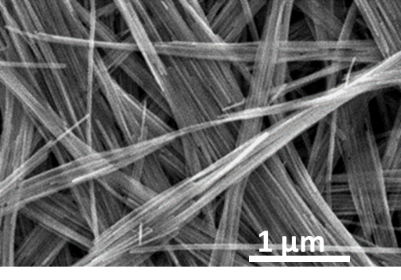


Fig. S4. The SEM image of the nanowire membrane coated with 2 w/w % PVA hydrogel, showing the pores of the nanowire membranes becoming partially blocked.

Excessive addition of PVA caused a reduction in the porosity and pore size of the membrane, which reduced the permeation rate of the nanowire membrane. This is primarily due to the blockage in porous structure of MnO2 membranes when the PVA concentration was increased from 1% to 2%. For all the filtration performance tests, the membranes were fabricated using the adjusted PVA concentration of 1%.

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Description automatically generated

Fig. S5. The deconvolution of the Mn2p, C1s and O1s for the 3 different samples: raw MnO2(1st row), the PVA1% coating (2nd row) and PVA 2% coating (3rd row). A Voigt type profile (GL(30)) is utilized after a proper Shirley background subtraction.

For the raw MnO2, a typical MnO2 shape is given. The deconvolution of the Mn2p gives 3 major signal corresponding to Mn2+, Mn3+ and Nn4+ at 640.8eV, 641.9eV and 642.9V, respectively. A blue peak at 644.0eV relates to a shake-up satellite. All component present similar relative content for the 3 samples. In the C1s case, the raw MnO2 sample1 present the typical adventitious carbon contamination. While the PVA coating brings the signal of C-O at 286.2eV. Similarly, the O1s also presents the Mn-O bond, the Mn-OH bond at 529.6eV, 530.9eV, the C-O bond at 532.4eV and the H2O at 533.0eV. The C-O bond was enhanced significantly with the PVA coating.



Fig. S6. The membrane’s performance in water flux and oil rejection rate was evaluated as a function of the times of membrane folding. The consistent performance observed under these conditions indicates the durability of the membrane, attributed to the robust cross-linked PVA coating.

Table S1. Water contact angle (WCA) and underwater oil contact angle (UWOCA) of the PVA-coated MnO2 membrane after exposure to various pH solutions.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| pH values | 2 | 4 | 6 | 8 | 10 | 12 |
| WCA | 0° | 0° | 0° | 0° | 0° | 0° |
| UWOCA | 152 ± 1.3° | 153 ± 1.5° | 151 ± 1.4° | 153 ± 1.5° | 151 ± 1.4° | 151 ± 1.3° |

The water contact angle (WCA) and underwater oil contact angle (UWOCA) of the PVA-coated MnO2 nanowire membranes following exposure to different pH solutions were presented in Table S1. The results indicate consistent WCA and UWOCA values even after immersion in various pH solutions. This underscores the stability of the membrane surface properties against pH variations, attributed to the presence of cross-linked PVA coating on the membrane surfaces.

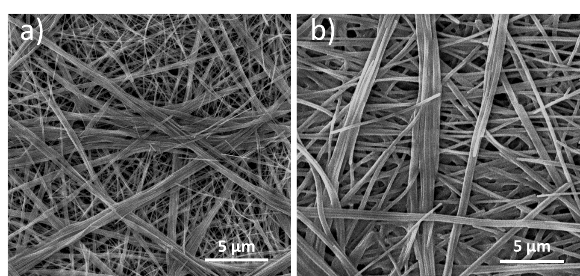


Fig. S7. Typical SEM images depicting the hydrogel-functionalized MnO2 nanowire membranes before (a) and after (b) immersion in solutions of varying pH values. No visible changes in membrane morphology were observed between pre- and post-tests, indicating the resilience of the PVA hydrogel-functionalized MnO2 nanowire membranes under challenging environmental conditions.

To investigate the possible leaching of manganese metal ions from the membrane into the effluent, we utilized the periodate oxidation method (Hach Method 8034). This method is suitable for determining manganese concentrations ranging from 0.1 to 20.0 mg/L in wastewater. Our findings revealed that the manganese concentration in the effluent treated by the PVA-coated MnO2 nanowire membrane consistently remained below 0.1 mg/L. This outcome suggests that our membrane effectively prevents manganese ion leaching, attributed to the robust protection provided by the cross-linked PVA coating on the surface of the MnO2 nanowires.



Fig. S8. SEM images of (a) top view and (b) side view of the as-prepared nanowire membranes. In both images, the interconnected porous structure of the membranes was revealed, forming a three-dimensional network with interconnected channels. This structure minimizes the resistance to water permeation, leading to high water flux.

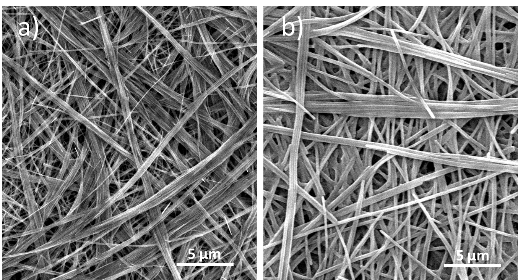
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Fig. S9. Typical SEM images of the hydrogel-functionalized MnO2 nanowire membranes (a) before and (b) after treatment. No visible change in surface topography was observed pre- and post-treatment, indicating the high stability of the hydrogel-functionalized MnO2 nanowire membranes under the treatment condition.



Fig. S10. XPS characterization was utilized to provide the comparison of surface chemical composition, Mn2p, O1s and C1s, on the membranes before and after the treatment.

XPS characterization was employed to unveil the chemical composition of the PVA hydrogel-functionalized MnO2 nanowire membranes, assessing their stability pre- and post-treatment. Despite intensity variations, Fig. S10 illustrates that Mn2p, C1s, and O1s components remained consistent in type (same binding energy position), with no emergence of new chemical states. This strongly suggests the chemical stability of the as-prepared membranes.