Electronic Supplementary Material

Interlayer-confined two-dimensional manganese oxide-carbon nanotube catalytic ozonation membrane for efficient water purification

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Text S1 Preparation of modified support

Firstly, 25 g of Al_2O_3 was added to the deionized water and then the pH of the solution was adjusted to 2 with nitric acid. After stirring evenly, the above solution was ultrasonic dispersed for 30 min to ensure that there is no precipitation at the bottom. Secondly, 10 g of PVA was added to the mixed solution and the ultrasound was continued for 30 min to obtained the homogeneous coating suspension. Subsequently, the supports with both ends sealed by Teflon tape were immersed into the suspension for 5 s and and taken out carefully, followed by complete drying at 100 ℃ for 12 h. Finally, the modified supports were calcinated at 1100 °C with the rate of heating and cooling set at 2 ℃/min.

Text S2 Characterization analysis of original support and modified support

The pore size distribution and morphologies of the support and modified support were shown in Fig. S1. It could be seen that the support exhibited a large pore size of (~ 450)nm (Fig. S1(a)), which could also be verified by the outside surface SEM image of the CM (Fig. S1(b)). Several macro cavities and a rough surface could be observed clearly, which would make it hard to fabricate a dense and continuous MnO_2 layer on the surface of the support. Therefore, a Al_2O_3 interlayer was introduced to narrow the pore size and smoothen the surface. In the case of the modified support,

Al_2O_3 layer played a crucial role in narrowing the pore size and blocking the macro holes (Fig. S1(c)). In addition, the surface of the interlayer was relatively smooth (Fig. S1(d)). The prepared modified support exhibited a quite high pure water permeance of 287 L m^{-2} h^{-1} bar^{-1}, but the rejection of methylene blue is very low.

Text S3 Chemicals

Potassium permanganate ($KMnO_4$, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Sigma-Aldrich), concentrated sulfuric acid (H_2SO_4, Sigma-Aldrich), methylene blue (MB, Sigma-Aldrich), Potassium dihydrogen phosphate (KH_2PO_4, Sigma-Aldrich), Sodium phosphate dibasic (Na_2HPO_4, Sigma-Aldrich), Indigo Carmine ($C_{16}H_8N_2Na_2O_8S_2$, Aladin), Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, Sigma-Aldrich), aluminium oxide (Al_2O_3, average particle size is 300nm), vinylalcohol polymer (PVA, degree of polymerization: 1750 ±50, Sigma-Aldrich), multiwalled carbon nanotube (MWCNT, Jiangsu XFNANO Materials Tech Co., Ltd.), concentrated nitric acid (HNO_3, Sigma-Aldrich). tert-butanol (t-BA, Sigma-Aldrich), p-benzoquinone(p-BQ, Sigma-Aldrich), methanol (Sigma-Aldrich). 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO, Aladin).

Text S4 Synthesized of original MnO_2 nanosheets

32 mL of 0.1 M SDS solution was added into 283ml distilled water and the pH of the solution was adjusted to 3 with 0.1M H_2SO_4 solution. Then, the mixed solution was stirred evenly and heated at 95℃for 15 min. Next, 3.2ml of 0.05M $KMnO_4$ solution was quickly added to the above mixed solution and heated for 60 min to obtain a homogeneous dark brown solution. Finally, the obtained MnO_2 nanosheets was centrifuged and washed with deionized water and alcohol to remove some impurities.

Text S5 Oxidation treatment of CNT

1 g of CNTs was refluxed with constant stirring for 4 h at 60 ℃ in 160 mL of a H_2SO_4/HNO_3 (3:1 by volume) mixture. Then, the mixed solution ws repeatedly washed with deionized water and filtered until the filtrate reached neutral. Finally, the treated CNTs were dried for 6 h at 80 ℃.

Text S6 Preparation of 2D MnO_2-CNT-COM

First, a MnO_2 nanosheets aqueous solution with a high concentration(300mg/L) was prepared by dissolving MnO_2 nanosheets powder in deionized water with sonication for 1.0 h. Agglomerated powder and impurities in MnO_2 nanosheets solution were removed by centrifugation at 3000 r/min for 20 min. The prepared solution was then diluted 10 times to get a MnO_2 nanosheets aqueous solution with a low concentration (30 mg/L). Then, as shown in Fig. 2(a), the modified support was soaked into the MnO_2 nanosheets suspension with one end sealed and another end connected to a vacuum pump. Under the driving force of transmembrane pressure of -0.1MPa, MnO_2 nanosheets stacked on the outer surface of the modified support.

Text S7 Materials and membrane Characterization

Transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan) was performed to observe the morphology of the CNTs. Field-emission SEM (Hitachi S-4800) was used to observe the morphology of MnO_2 under different calcination temperatures, as well as the the surface morphology and thickness of the prepared membranes. Atomic force microscopy (AFM) (XE-100) measurements were executed to examine the morphology of the MnO_2 nanosheets. Fourier transform infrared (FTIR) spectroscopy was used to identify chemical bonds in the MnO_2 using a PerkinElmer Instrument Spectrum GX spectrometer with a KBr pellet operating in transmittance mode. X-ray photoelectron spectroscopy (XPS) (Kratos Axis Supra spectrophotometer, Shimadzu) with dual anode monochromatic Kα excitation source of 1486.7 eV was employed to detect the chemical composition and oxidation states of the MnO_2. A Zetasizer (ZS90, Malvern, England) was used to characterize the zeta potential of MnO_2 particals. UV−Vis spectrophotometer (UV-1800, Shimadzu) was employed to determinate the dye concentration. X-ray diffraction (XRD, Rigaku MiniFlex 600) using Cu Kα radiation was used to examine the crystalline phase of the prepared MnO_2 materials under different calcination temperatures, as well as the interlayer spacing of the MnO_2-CNT composite membranes.

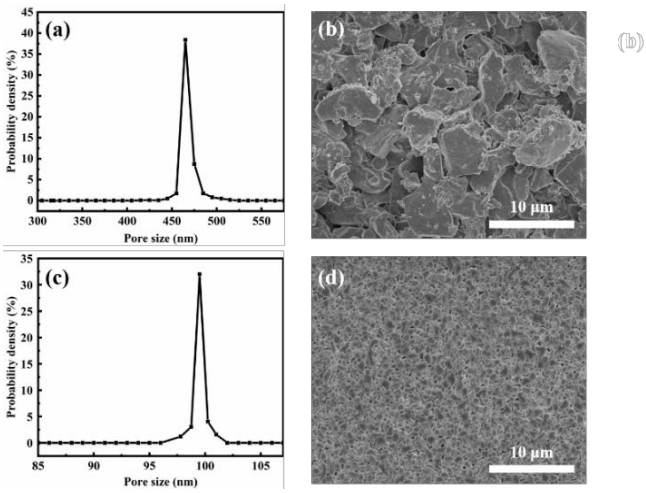


Fig. S1 (a) and (c) Pore size distribution of support and modified support, (b) and (d) Surface morphologies of support and modified support.

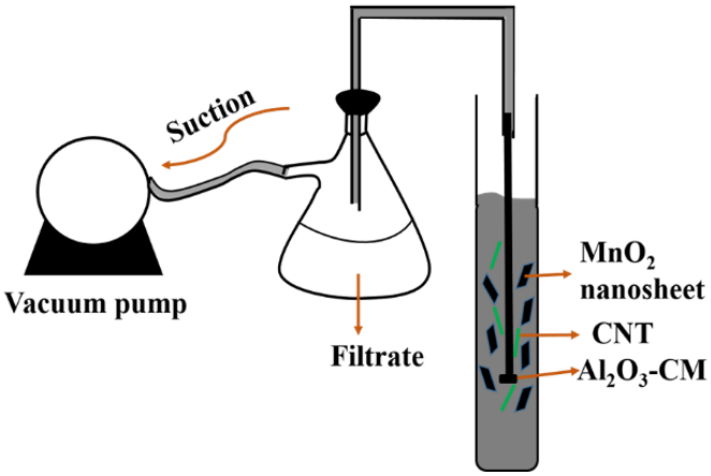


Fig. S2 The fabrication process of 2D MnO_2–CNT–COM.

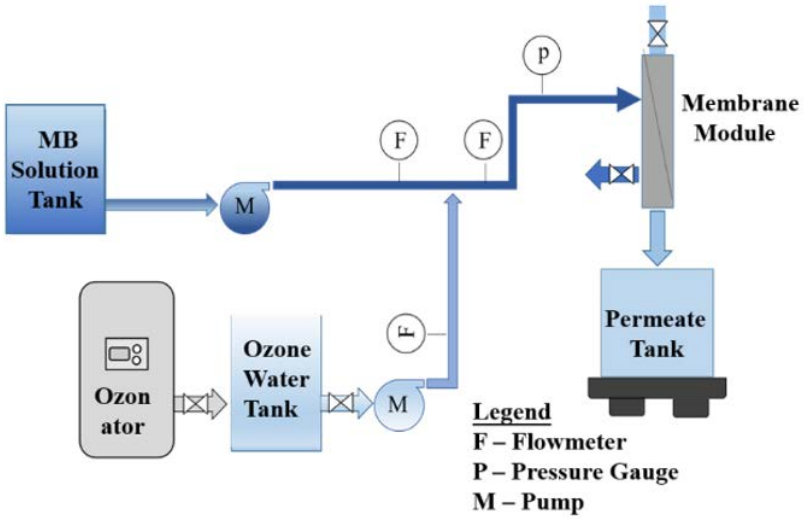


Fig. S3 Device for evaluating the performance of the COM reactor

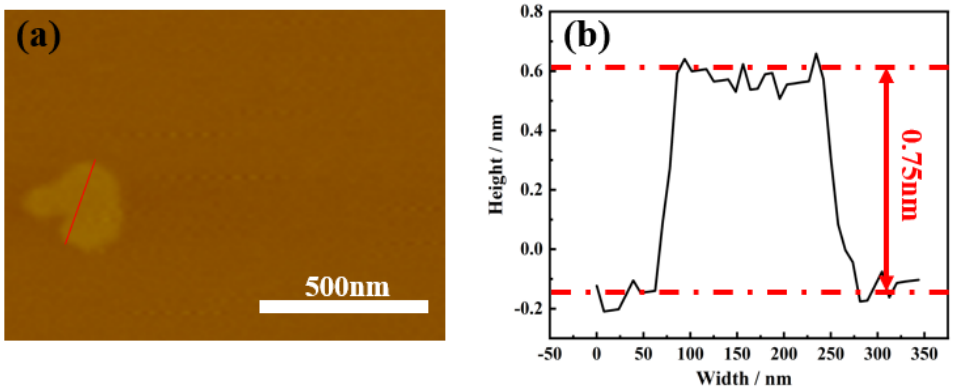


Fig. S4 (a) AFM image of the MnO_2 nanosheet on a mica substrate. (b) Longitudinal size of the MnO_2 nanosheet

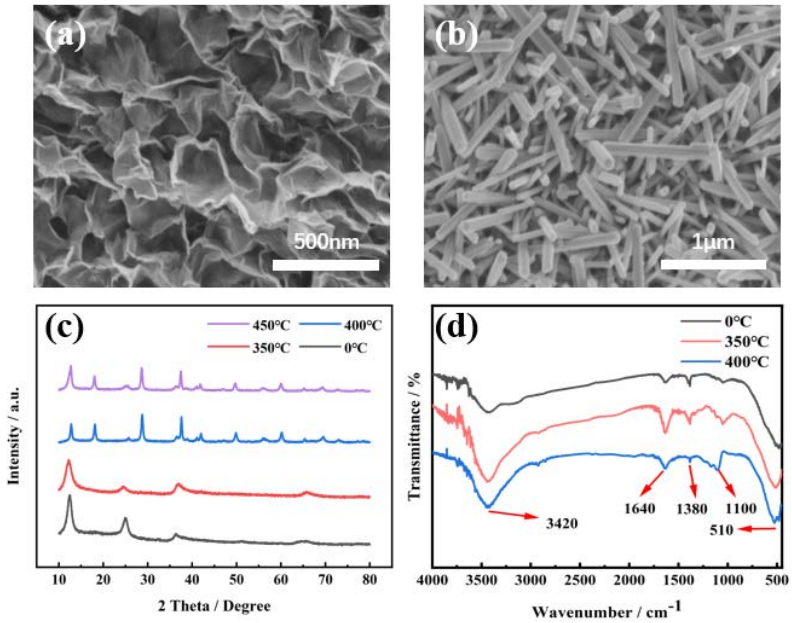


Fig. S5 SEM images of the α-MnO_2 nanosheet formed after calcination at (a) 400 and (b) 450 °C. (c) XRD patterns of the MnO_2 samples calcined at different temperatures. (d) FTIR spectra of the MnO_2 samples calcined at different temperatures

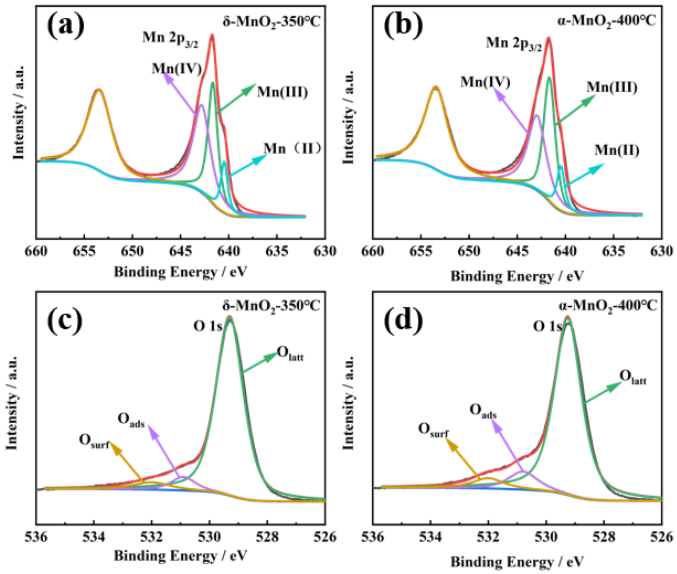


Fig. S6 Mn 2p and O 1s XPS spectra of the (a and c) δ-MnO_2 and (b and d) α-MnO_2 nanosheets

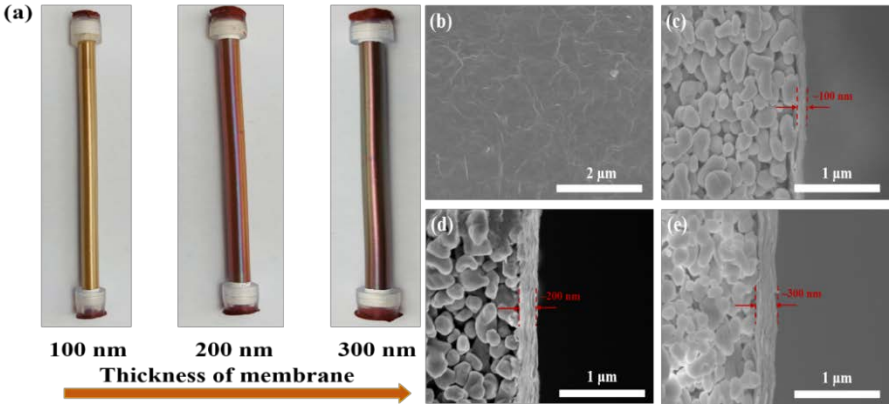


Fig. S7 (a) Photographs of the 2D MnO_2 membrane with different thicknesses. (b–e) Surface and cross-sectional morphologies of the membrane

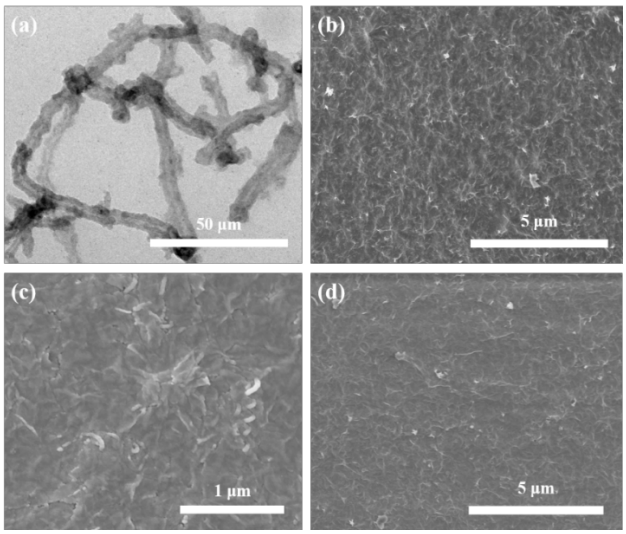


Fig. S8 SEM images of (a) CNTs, (b and c) the surface of 2D MnO_2–CNT–COM, and (d) 2D MnO_2 membrane

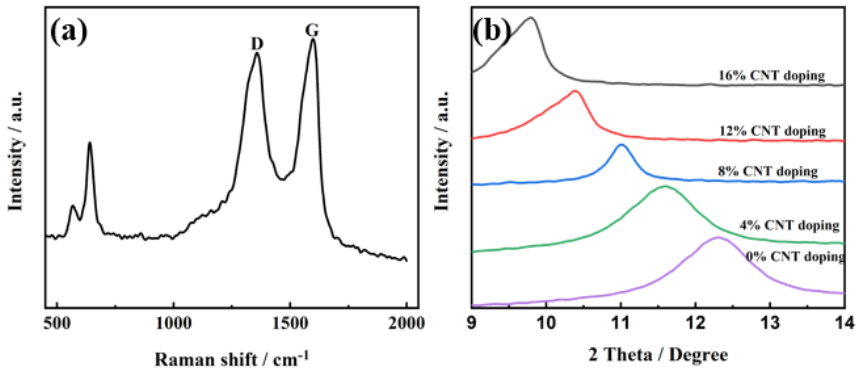
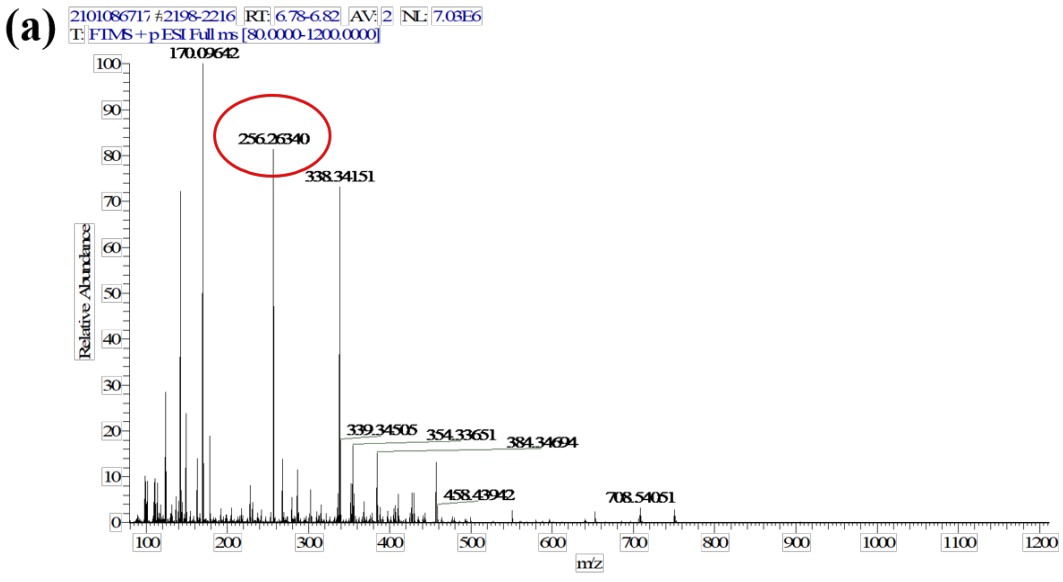
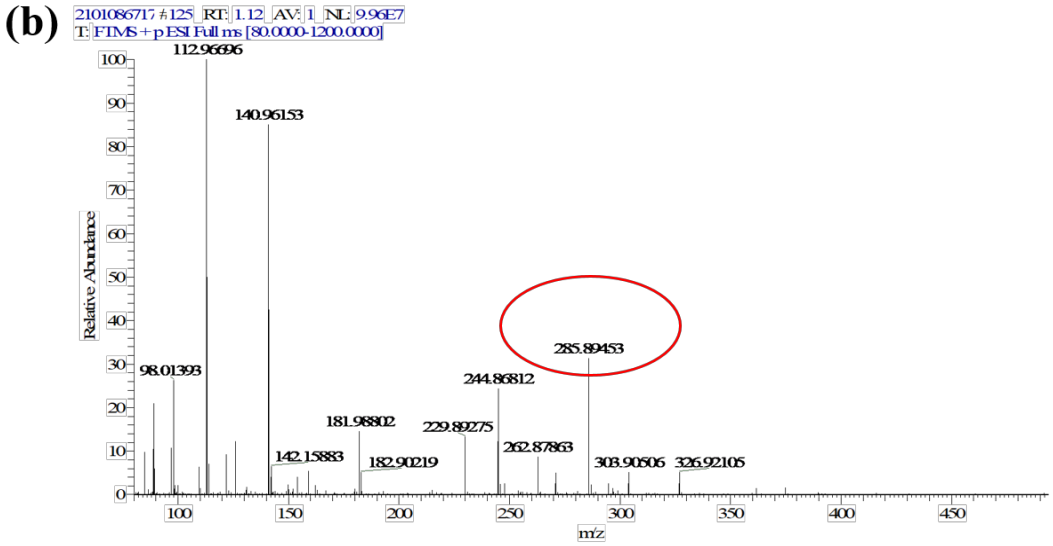


Fig. S9 (a) Raman spectrum of 2D MnO_2–CNT–COM. (b) XRD patterns of 2D MnO_2–CNT–COM with different CNT dopings





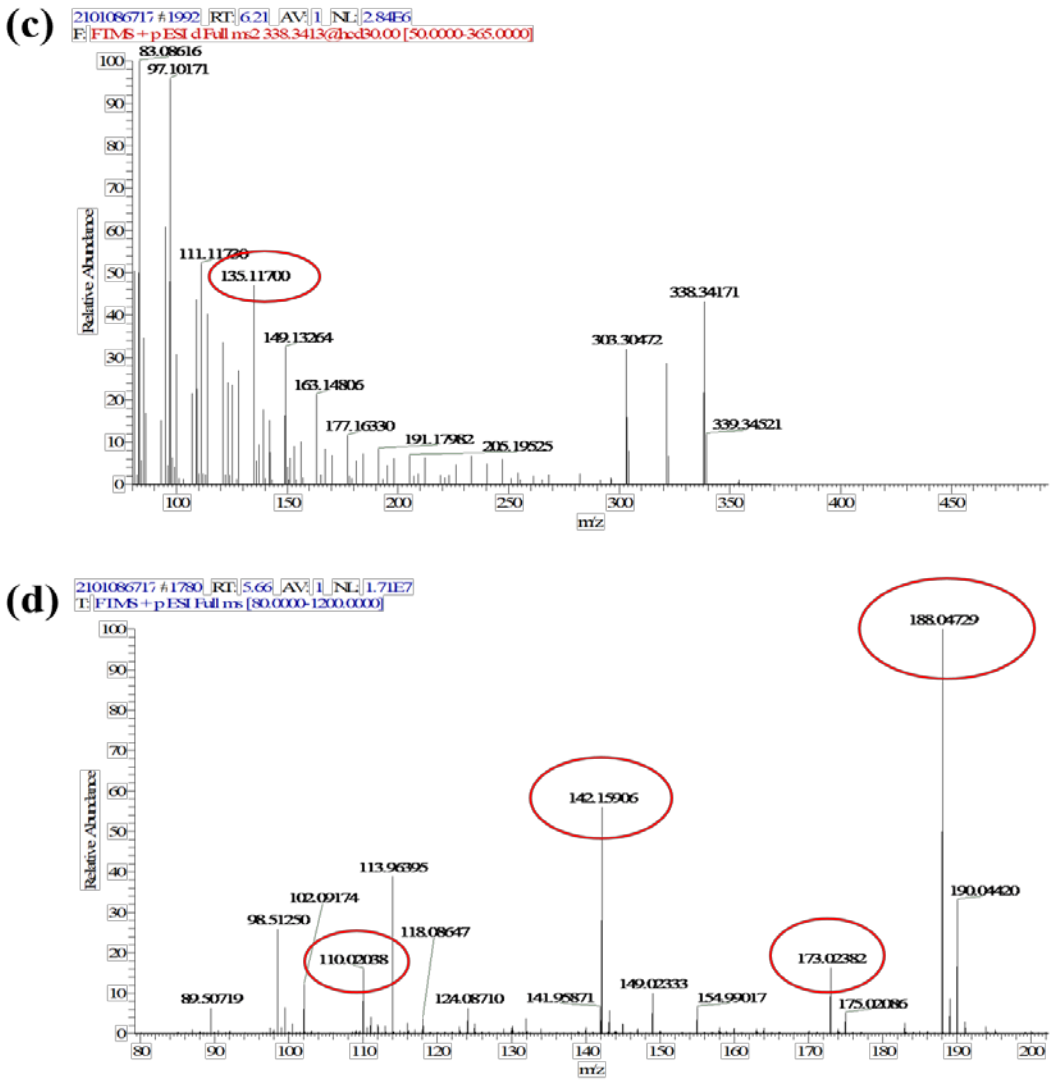


Fig. S10 Ion fragment mass spectra of intermediates with different retention times

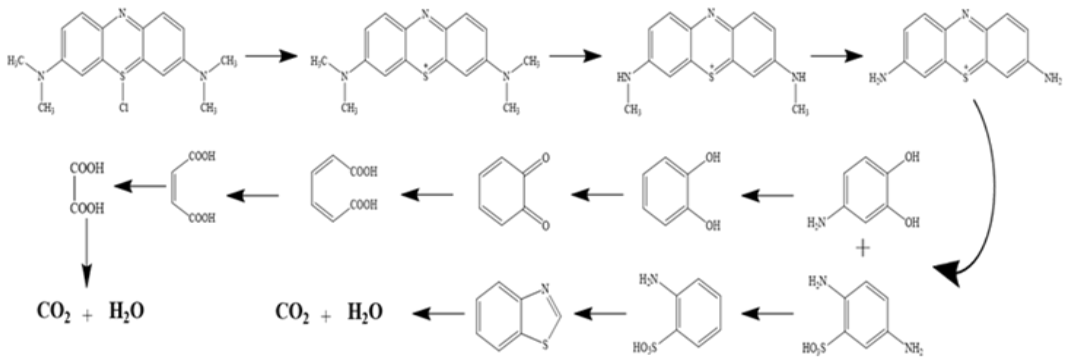


Fig. S11 Possible degradation pathway of MB by catalytic ozonation with 2D MnO_2-CNT-COM.

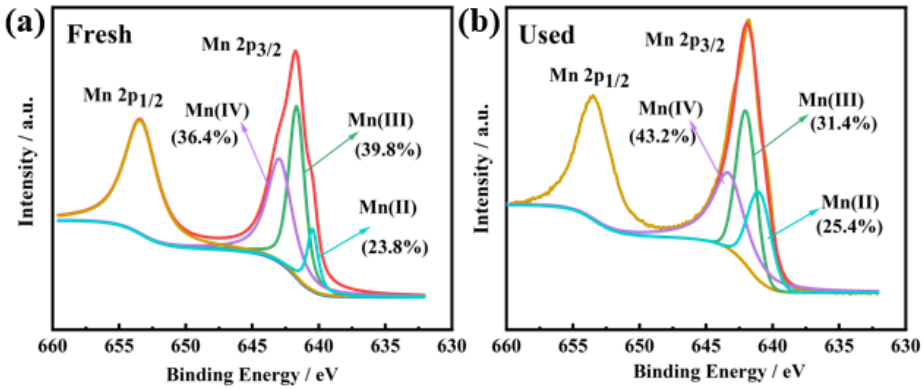


Fig. S12 High resolution XPS spectrum of (a) fresh α-MnO_2-400℃ nanosheet, (b) used α-MnO_2-400℃ nanosheet

Table S1. Specific $O_{3(aq)}$ consumption and comparison of various ozonation processes

Ref	Catalytic Membrane	Target Pollutant	TOC Removal	Specific $O_{3(aq)}$ Consumption for TOC Removal (mg $O_{3(aq)}$ mg^{-1} TOC removed)
[1]	Ce-CCM	BPA、BTZ、CA	29%	2.1
[2]	CeTi-CeCCM	DEET	35%	1.4
[3]	CoCM	SMX	15.3	-
This study	2D MnO_2-CNT-COM	MB	71.5%	1.2

References

1. Lee W J, Bao Y, Hu X, Lim T. Hybrid catalytic ozonation-membrane filtration process with CeOx and MnOx impregnated catalytic ceramic membranes for micropollutants degradation. Chemical Engineering Journal, 2019, 378: 121670
2. Lee W J, Bao Y, Guan C, Hu X, Lim T. Ce/TiO_x-functionalized catalytic ceramic membrane for hybrid catalytic ozonation-membrane filtration process: fabrication, characterization and performance evaluation. Chemical Engineering Journal, 2021, 410: 128307
3. Bao Y P, Lee W J, Lim T T, Wang R, Hu X, Pore-functionalized ceramic membrane with isotropically impregnated cobalt oxide for sulfamethoxazole degradation and membrane fouling elimination: Synergistic effect between catalytic oxidation and membrane separation. Applied Catalysis B: Environmental, 2019, 254: 37-46