Supplementary Information:

A Free-standing, Hybrid TiO_2/K-OMS-2 Hierarchical Nanofibrous Membrane with High Photocatalytic Activity for Concurrent Membrane Filtration Applications

Tong Zhang, Yinjie Wang, Jiawei Ng, Darren D. Sun*

Nanyang Technological University, School of Civil & Environmental Engineering, Block N1, Nanyang Avenue, Singapore 639798

Experimental

Synthesis of hierarchical TiO_2/K-OMS-2 nanowires*:* Firstly, K-OMS-2 nanowires were synthesized via a hydrothermal method.[1] In a typical procedure, 12 mmol of K_2SO_4, 12 mmol of $K_2S_2O_8$, and 8 mmol of $MnSO_4 \cdot H_2O$ were dissolved in 70 ml of deionized water. The solution was then transferred to a 125 ml Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated in an oven at 250 ^oC for 4 days. The resulting black precipitate was suspended in 1000 ml deionized water, and stirred vigorously for 12 h. After thorough washing with deionized water to remove remaining ions present in the product, the sample was dried at 105 ^oC for 24 h. Thereafter, 50 mg of the synthesized K-OMS-2 nanowires, 400 mg titanous sulfate, and 0.4 ml concentrated H_2SO_4 (98%) were added into 70 ml deionized water. After homogenization by an ultrasonic homogenizer (Sonics and Materials, CT, USA) for 10 min, the solution was transferred to the 125 ml Teflon-lined autoclave again and heated at 105 ^oC for 20 h. In order to remove all soluble ions in the solution, the

product was washed several times before being separated using a centrifuge. Then, the resulting product was dried in vacuum for 48 h.

Assembly of TiO_2/K-OMS-2 membrane: Firstly, the suspension of the synthesized hierarchical TiO_2/K-OMS-2 nanowires was vigorously stirred for 10 min. Then, the suspension was filtered on a vacuum-filtration setup with a glass filter (ADVANTEC, GC-50, 0.45 μm), and the hierarchical nanowires will form a compact cake layer on the glass filter. After drying at 105 ^oC for 1 day, a free-standing membrane was formed after removal of the glass filter. The membrane was further pressurized under 5 bar at 120 ^oC on a customized hot press for 2 mins. Finally, the membrane was calcined at 550 ^oC for 1 h.

Synthesis of TiO_2: TiO_2 was also synthesized via a hydrothermal process identical to that of aforementioned hierarchical TiO_2/K-OMS-2 nanowires, except without the addition of K-OMS-2 nanowires.

Material Characterization: The XRD data was collected on a Bruker D8 Advance X-ray diffractometer (Cu Kα λ=1.5406 Å). Morphology of the membrane was studied using a field-eimission scanning electron microscope (FESEM) Jeol JSM-6340F (Japan) operated at 5 kV, and transmission electron microscopy (TEM) was carried out on a Jeol JEM-2100F (Japan) operated at 200 kV. Brunaur-Emmett-Teller (BET) surface area of the nanowires was measured by N_2 sorption using a Quantachrome Autosorb-1 instrument (USA). The pore size of the synthesized membrane was measured using standard polystyrene (PS) microspheres.[2] The PS microspheres of diameters 0.05, 0.1, 0.2, 0.5, 1, and 2 μm, were purchased from Alfa Aesar. The

concentration of PS microspheres solution was prepared to 0.033 wt. %, and a lab-scale dead-end filtration setup was used for filtration. The concentration of microspheres in the feed and filtrate were determined by a Shimadzu TOC-VCSH total organic carbon (TOC) analyzer. The retention rate (R) of the microspheres by the membrane were determined using the fomula below:

$$R = (1 - \frac{TOC_{filtrate}}{TOC_{feed}}) \times 100\% \quad (1)$$

Kinetics of acid orange 7 (AO 7) adsorption on the materials: Kinetic experiments were carried out in 250 ml glass bottles at room temperature (20 ± 1 ^{o}C). 0.1 g of the synthesized TiO_2 and TiO_2/K-OMS-2 were added into 100 ml of 20 ppm AO 7 solutions to obtain a 1 g/L suspension, respectively. The suspensions were mixed using a magnetic stirrer, and the pH was maintained at 5 with controlled addition of 0.01 mol/L HCl and 0.01 mol/L NaOH. Samples of 3 ml were withdrawn from glass bottle periodically. The samples were immediately filtered using glass syringe filter (0.45μm) to separate the material for subsequent analysis. Concentration of AO 7 was determined by a UV–visible spectrophotometer (Thermo Scientific Evolution 300) at a fixed wavelength of 484 nm.

Concurrent filtration, adsorption and photocatalytic oxidation (PCO) experiments: The concurrent filtration, adsorption and PCO process using the synthesized membrane was conducted in a dead-end filtration equipment as shown in Figure S2. AO 7 was chosen as the model organic pollutant, and a UVP lamp (Upland 3SC9, 254 nm) was employed as the UV light source. In a typical procedure, 500 ml of 20 mg/L

AO 7 solution was filtered in continuous mode over the synthesized membrane under UV irradiation. The AO 7 and TOC concentrations of the permeate were measured. Membrane flux was maintained at 30, 40, 50, 60, 70, 80 $L/m^2 \cdot h$, respectively.The membrane filtration without UV irradiation was also carried out as control.

Table S1. Rejection rates of the synthesized membrane for different diameter polystyrene microspheres

PS (μm)	Rejection rate (%)
0.05	85.8
0.1	93.9
0.2	97.3
0.5	97.9
1	98.1
2	98.3

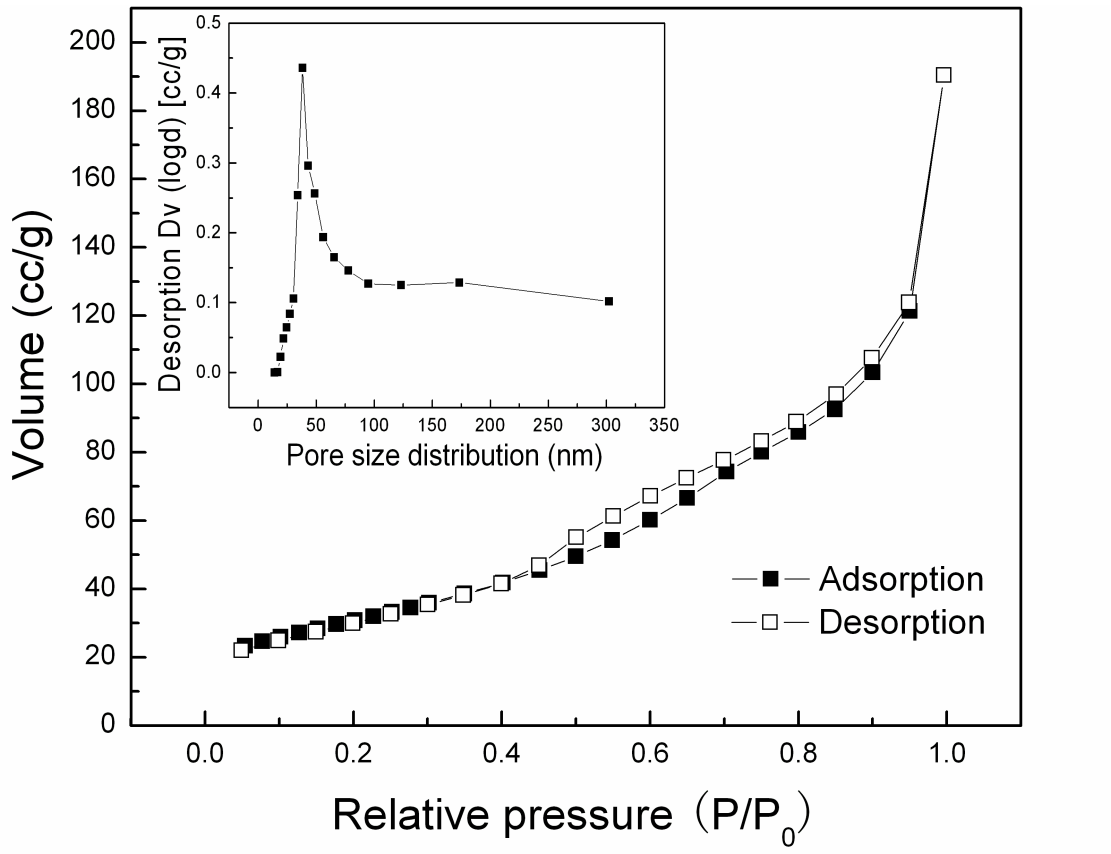

Figure S1. N_2 adsorption/desorption isotherm curve of hierarchical TiO_2/K-OMS-2 nanowires; Inset is the pore size distribution of hierarchical TiO_2/K-OMS-2 nanowires.

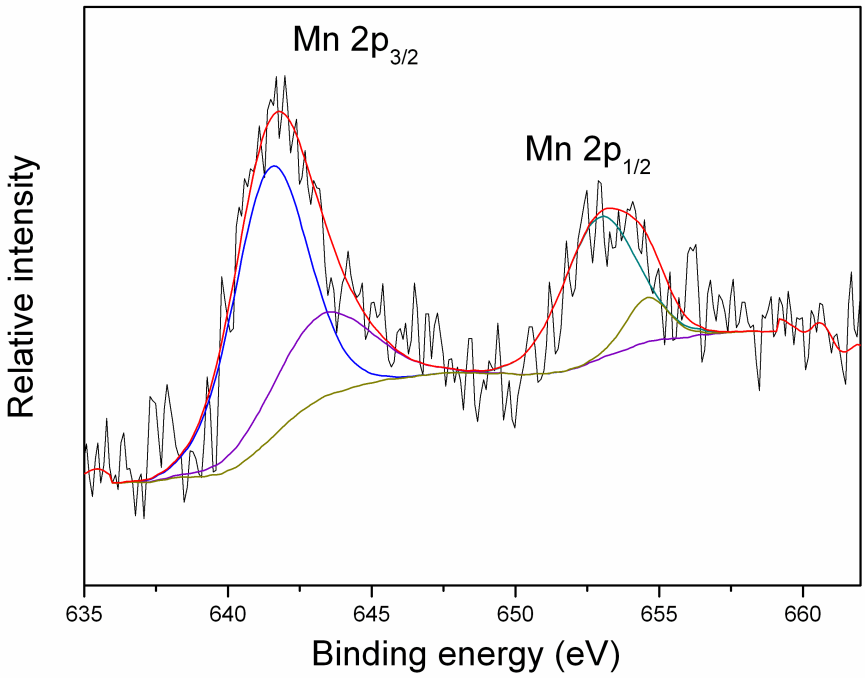

Figure S2. High-resolution XPS spectra of the Mn 2p taken on the TiO_2/K-OMS-2 nanowires.

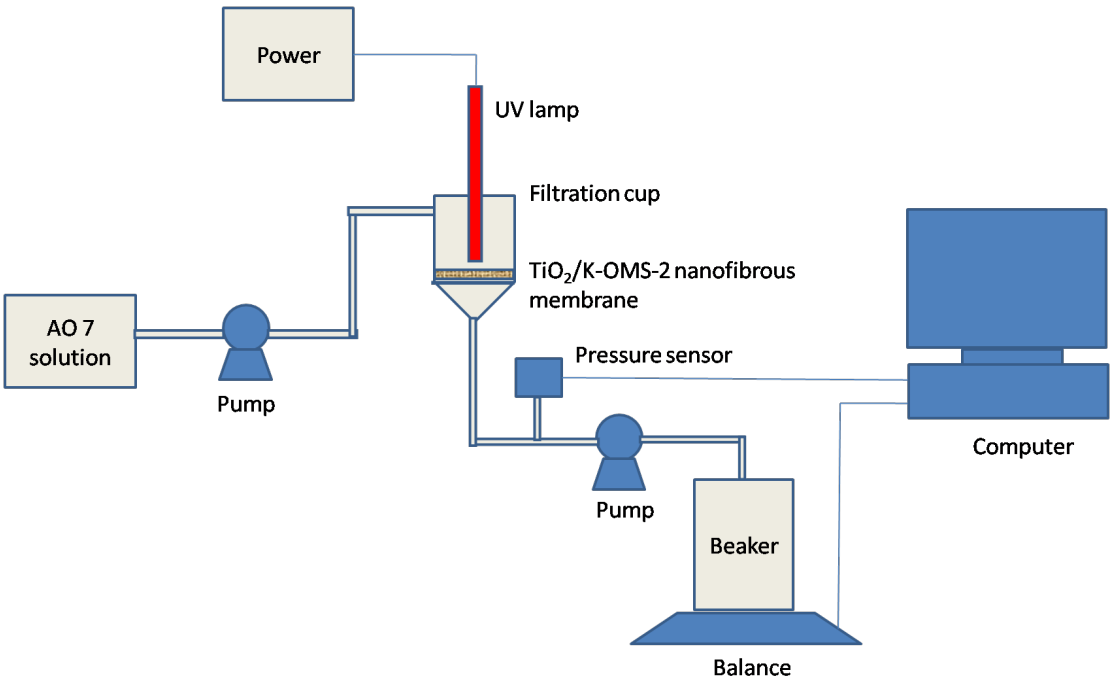

Figure S3. The setup of concurrent filtration, adsorption and photocatalytic oxidation.

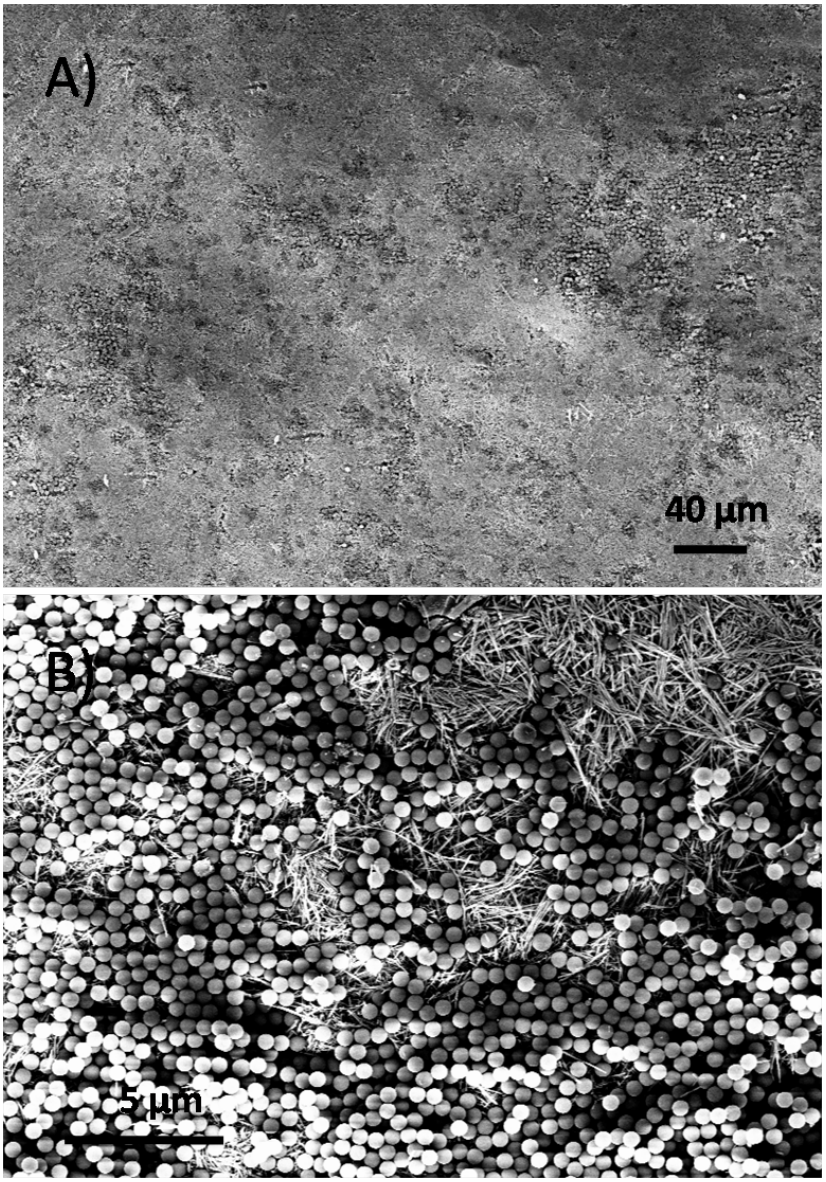

Figure S4. The upper-surface SEM image of the TiO_2/K-OMS-2 membrane after the filtration of 0.5 μm PS microspheres solution: A) Low magnification image, B) High magnification image.

References

1 J. Yuan, K. Laubernds, J. Villegas, S. Gomez and S. L. Suib, *Advanced Materials*, 2004, **16**, 1729-1732.
2 S. Nakao, *J. Membrane Sci.*, 1994, **96**, 131-165.