

Electronic Supplementary Information

Fabrication of Visible-light Response Mesoporous TiO₂ Membrane with Superior Water Permeability via Weak Alkaline Sol-gel Process

Xueping Cao, ^a Wenheng Jing, ^{*a} Weihong Xing, ^a Yiqun Fan, ^a
Yan Kong ^a and Junhang Dong ^b

^a State Key Laboratory of Material-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Road, Nanjing 210009, P. R. China.

^b Department of Chemical and Materials Engineering
The University of Cincinnati
Cincinnati, OH 45221-0012, USA

* E-mail: jingwh@njut.edu.cn

1. Experimental

Titanium dioxide polymeric sol was obtained via hydrolysis of tetrabutyl titanium ($\text{Ti}(\text{OC}_4\text{H}_9)_4$). An aqueous solution of DMF was added drop wise to a solution of tetrabutyl titanium in acetylacetone (AcAc) under vigorous stirring. The stirring was kept for two hours after the hydrolysis is completed, and then different amounts of P123 were added to the sol under continued stirring until the final sol was clear. The molar ratio of $\text{Ti}(\text{OC}_4\text{H}_9)_4$: AcAc: DMF: H_2O was 1:1:6:3 and the P123 content in the final sol was varied from 0 to 20wt%. The samples with 0wt%, 5wt%, 10wt%, and 20wt% of P123 were denoted as TP-0, TP-1, TP-2 and TP-3, respectively.

Membranes were prepared on tubular asymmetric $\alpha\text{-Al}_2\text{O}_3$ microfiltration membranes with a wall thickness of 3mm, an outer diameter of 12.5 mm, a length of 110 mm and an average pore size of 0.21 μm (Membrane Sci. & Tech. Research Center, Nanjing, China). The porous $\alpha\text{-Al}_2\text{O}_3$ tubular supports were pretreated with poly (vinyl alcohol) (PVA) as pore-filling substance¹ to prevent nanoparticle penetration during dip-coating. The dip-coating, aging/drying, and calcining cycle was repeated four times to obtain mesoporous membranes free of pinholes and cracks. Unsupported gel films were also prepared by drying the sol in Petri-dishes. For both the supported membranes and unsupported films, identical thermal treatments were applied, including drying at 70°C for 12 h followed by 200-min calcination at 400°C for 2h in air atmosphere, with a heating rate of 0.5°C/min.

An environmental scanning electron microscope (Quanta 200) was used to measure the thickness of the membrane and observe the surface morphology of the TiO₂ membrane. The pure water flux of the supported titania membrane were measured at 293K under a transmembrane pressure of 0.1MPa.

The photocatalytic activities tests were measured by the degradation of methyl orange in an aqueous solution. A 500W xenon lamp (CHF-XM 500, Beijing, China) was used as a visible-light source (700 nm λ > 420 nm). 0.5g photocatalyst was put in 100 mL aqueous solution of 5 $\times$ 10⁻⁴g L⁻¹ methyl orange. The concentration of the methyl orange solution was monitored every 30min by measuring the maximum absorbance of methyl orange at 465nm² using the UV spectrophotometer.

2. Characterization

2.1 Dextran retention curves of supported membranes

The dextran retention of the supported titania membrane were measured at 293 K under a transmembrane pressure of 0.1MP following the ASTM E 1343-90 method. The concentrations and molecular weights of dextrans in the feed and permeate solutions were analyzed by a gel permeation chromatographer (Waters Corp.).

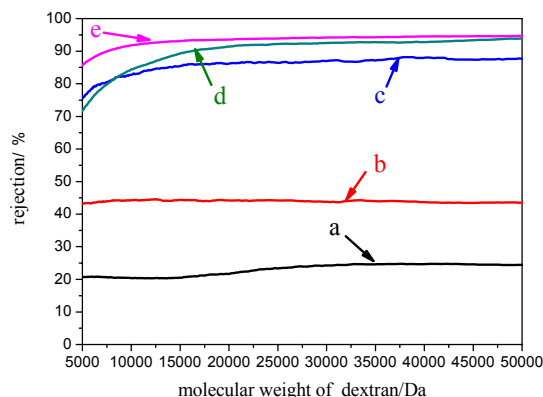


Figure S1. Dextran retention of membrane under different coating times a: support, b: first coating, c: second coating, d: third coating, e: fourth coating

2.2 Nitrogen adsorption-desorption isotherms and BJH pore-size distribution curves

The BET specific surface area, pore size distribution and pore volume of the catalyst was characterized by N₂ adsorption at liquid nitrogen temperature using BELSORP II.

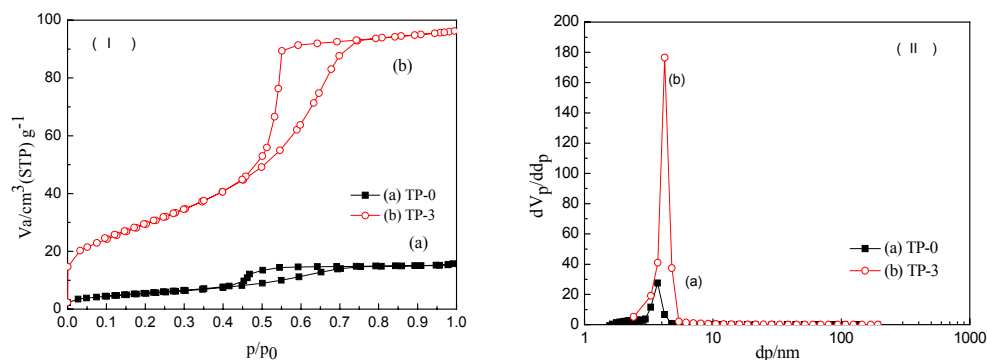


Figure S2. N₂ adsorption-desorption isotherms (I) and BJH pore size distribution curves (II) of the TiO₂ film (a) TP-0, (b) TP-3

2.3 X-ray photoelectron spectroscopy studies

The XPS data were measured by using VG ESCALAB MKII spectrometer (Al K α 1486.6 eV photons). All binding energies were referenced by C 1s neutral carbon peak at 284.6 eV of the surface adventitious carbon.

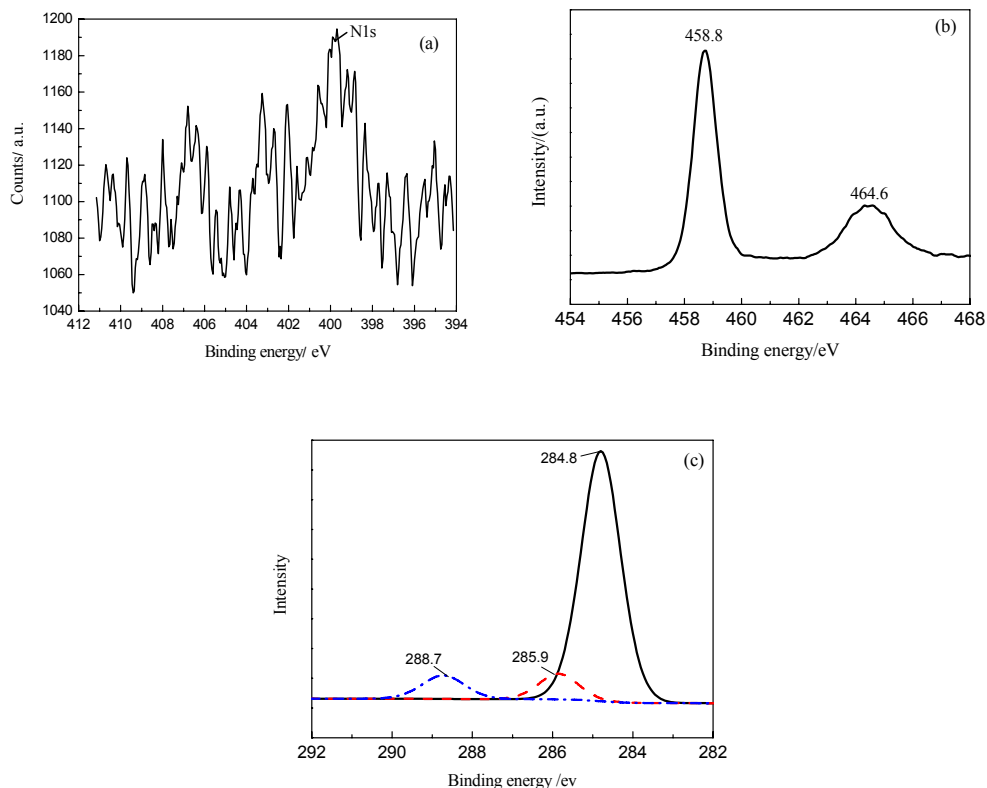


Figure S3. XPS spectra of (a) N 1s, (b) Ti 2p (c) C 1s for the TiO₂ membrane of TP-3: Figure 4S (a) confirms the states of the doped N atom, N 1s XPS spectrum of the sample, there is only one strong peak observed at 399.7 eV, which indicates that the N species existed in the form of nitrides, for instance as O-Ti-N linkage in the surface.³⁻⁵ XPS signals of Ti 2p in figure 4S (b) were observed at binding energies at around 458.8 eV (Ti 2p_{3/2}) and 464.6 eV (Ti 2p_{1/2}). The Ti 2p peaks were in good agreement with pure TiO₂, which indicates the titanium atom is bond with oxygen but not carbon. Figure 4(c) compares the XPS profiles in the region of C 1s binding energy (BE). Primary C 1s relevant peaks were found mainly at 284.8 eV, 285.9 eV, 288.7 eV. The first peak at 284.8 eV can be ascribed to adventitious hydrocarbon from the XPS instrument itself. The other two are assigned to the presence of single C-O bonds (hydroxyl group) and carboxylate impurities.⁶⁻⁸

2.4 X-ray diffraction patterns

Wide-angle X-ray diffraction (WAXRD) patterns were obtained by a Bruker D8

Advance X-ray diffractometer with Cu K α radiation ($\lambda=0.154$ nm) at 40 kV and 30 mA.

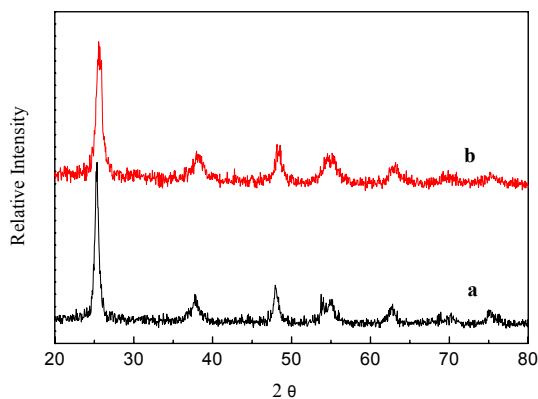


Figure S4. XRD patterns of TiO₂ film (a) TP-0, (b) TP-3 calcined for 200min at 400 °C: The X-ray diffraction (XRD) pattern of the membrane confirmed a pure anatase phase, which is the most-active phase. The crystallite size was estimated to be approximately 15.8 nm in TP-0 and 11.6nm in TP-3 by peak broadening analysis using Scherrer's equation based on the peak at (101).⁹

2.5 UV-vis diffuse reflectance spectra

UV-vis reflectance spectra were measured with a Shimadzu UV-2401TC UV-vis spectrophotometer using BaSO₄ as the background.

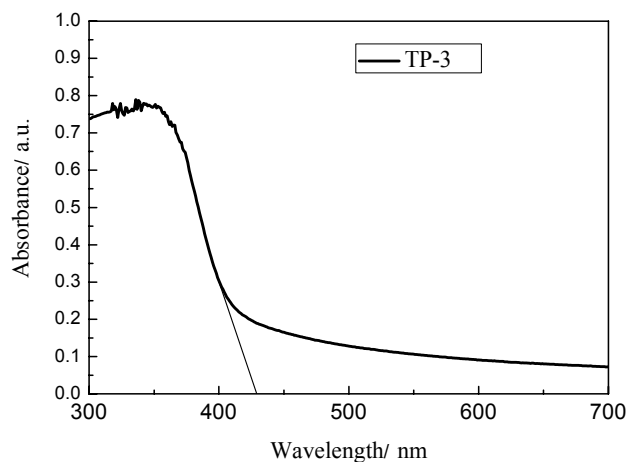


Figure S6. UV-vis adsorption spectra of the TiO₂ film of TP-3: An extension of the

absorption edge towards visible light region was observed and the maximum shifted to a longer wavelength of 430nm, indicating that the N, C-doped TiO₂ membranes possesses photoactivity in visible-light. The band gap was approximately 2.88eV,¹⁰ which is narrower than that of the pure TiO₂.

References

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