

Supporting Information

For

Synthesis of Mn doped and anatase/rutile mixed-phase TiO₂ nanofibers for high photo activity performance

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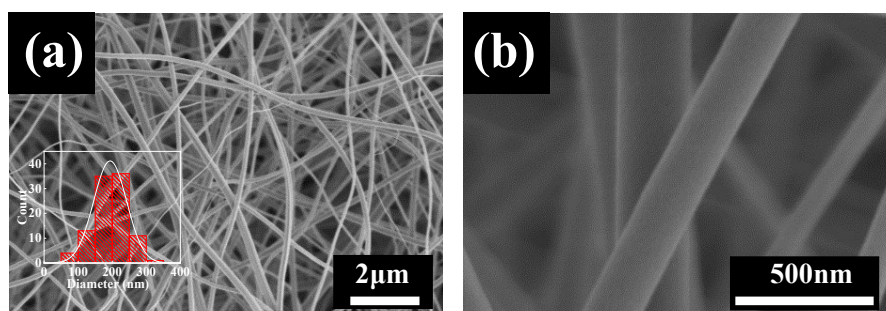


Figure SI 1: (a, b) SEM images of PVP-Mn@TiO₂-0.10 annealed at 600 °C for 1 hour in air with the histograms of diameter distribution analysis.

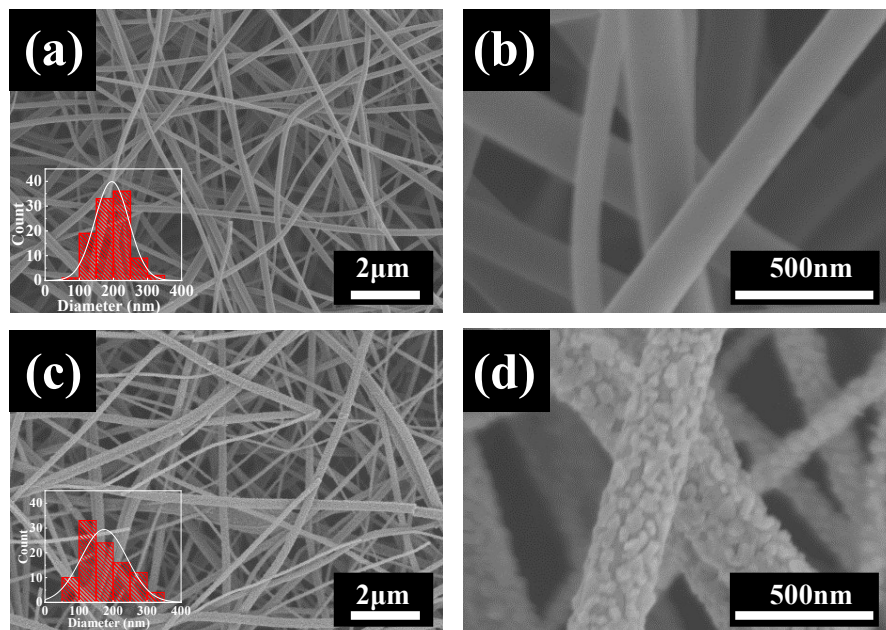


Figure SI 2: SEM images of PVP-Mn@TiO₂-0.10: (a, b) annealed at 450 °C for 1 hour under the N₂ atmosphere; (c, d) annealed at 750 °C for 1 hour under the N₂ atmosphere with each histograms of diameter distribution analysis.

Table SI 1: The diameter distribution result of PVP-Mn@TiO₂-0.10 after different treatment.

Experimental parameters	Diameter (nm)
450 °C, 1 h, N ₂	195.49±9.80
600 °C, 1 h, N ₂	189.91±9.80
750 °C, 1 h, N ₂	173.64±13.31
600 °C, 1 h, Air	193.88±9.50

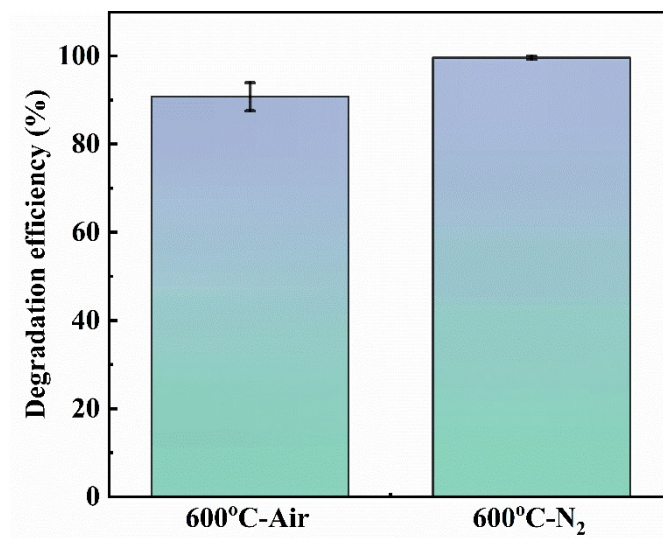


Figure SI 3: Photodegradation efficiency from Mn@TiO₂-0.10 nanofibers synthesized at different conditions.

Table SI 2: Comparison of photocatalytic contaminants removal rate and reuse cycle of various TiO₂ nanofibers based photocatalysts.

Photocatalysts	Light source	Target compound	Removal rate (min ⁻¹)	Reuse cycle	Ref.
Mn@TiO ₂	20 W, 325 nm	Methylene blue	5.22E ⁻²	5	This work
Fe ₂ O ₃ /TiO ₂	500 W Hg lamp	Rhodamine B	5.00E ⁻²	1	1
BN-Ag/TiO ₂	150 W visible light	Methylene blue	4.65E ⁻²	4	2
ZnTiO ₃ @TiO ₂	75 W Xenon lamp	Rhodamine B	3.14E ⁻²	10	3
BiOBr@TiO ₂	300 W Xe lamp	RhB	2.50E ⁻²	5	4
EPF(2/1)-TiO ₂	4 W, 350–400 nm	Methylene blue	5.02E ⁻²	10	5
TiO ₂ -BN	365 nm	ibuprofen	5.4E ⁻²	8	6
TiO ₂ /g-C ₃ N ₄	300 W Xe lamp	Rhodamine B	6.4E ⁻²	5	7
TiO ₂ /SnO ₂	300 W medium Hg lamp	Methylene blue	6.04E ⁻²	3	8

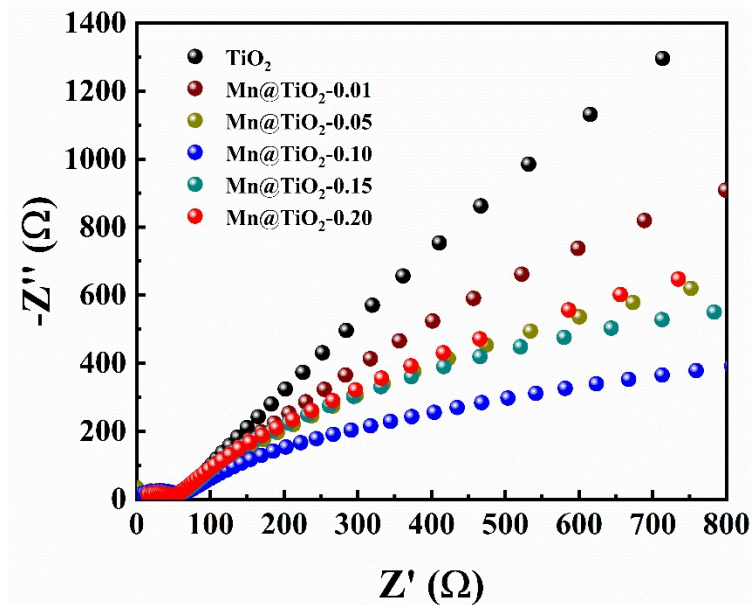


Figure SI 4: The electrochemical impedance spectroscopy (EIS) Nyquist plots of TiO_2 , $\text{Mn@TiO}_2\text{-0.01}$; $\text{Mn@TiO}_2\text{-0.05}$; $\text{Mn@TiO}_2\text{-0.1}$; $\text{Mn@TiO}_2\text{-0.15}$, and $\text{Mn@TiO}_2\text{-0.20}$.

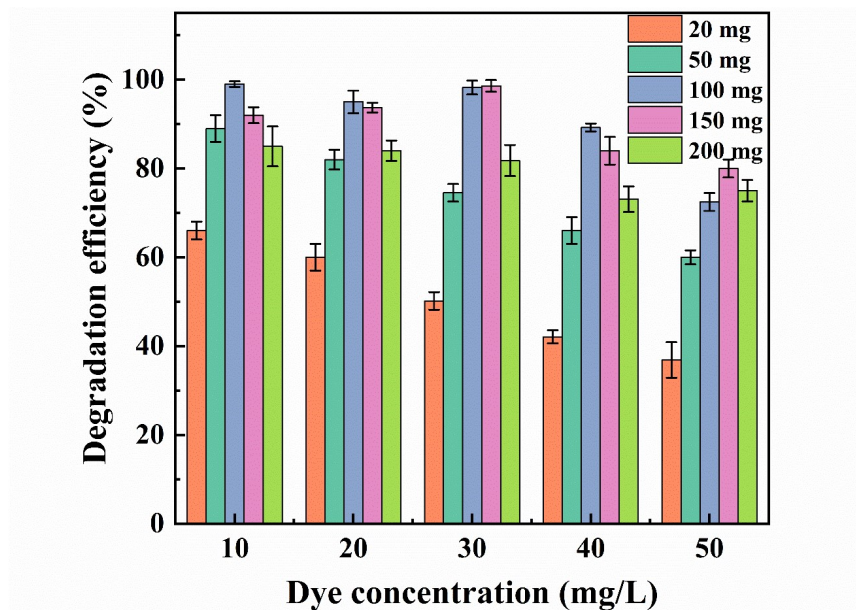


Figure SI 5: Effect of dye concentration and catalyst amount on the photodegradation efficiency of MB by $\text{Mn@TiO}_2\text{-0.10}$.

In order to explore the possibility of Mn@TiO₂ nanofilm applied for energy storage, the electrochemical properties were investigated by a three-electrode system in 1 M Na₂SO₄ aqueous electrolyte, using a Pt counter electrode and an Hg/HgO reference electrode. Figure SI 1 displayed the cyclic voltammetry curve (CV) collected for Mn@TiO₂ nanofilm at different scan rates. These CV curves are all in the shape of a deformed rectangle, corresponding to the typical properties of the carbon-based electrochemical double-layer capacitors. From Figure SI 6 (b), the curve demonstrated a well rectangular-like curve no matter whether under at a low or higher scan speed testing, which implied good Faraday capacitance reaction has occurred on the film surface. As offered in Figure SI 6 (b), the charging and discharge curves of the Mn@TiO₂-0.10 were reasonably symmetric with a good linear relation of discharge/charge voltage versus time. This result again certificated the ideal capacitive characteristic and speedy charge/discharge property of Mn@TiO₂ samples. In order to measure the real-life performance of the prepared Mn@TiO₂, the charge and discharge cyclic stability was analyzed. After 5000 cycles, the capacitance still maintains 91 % of the initial capacitance as shown in Figure SI 6, exhibiting an excellent electrochemical stability. Besides, the charge and discharge curves are all in the shape of triangle as shown in Figure SI 6 (c) inset. Table SI 3 enumerated the mass-specific capacitance of all samples. The loading amounts of Mn⁴⁺ were comparable in these electrodes. As expected, the higher Mn⁴⁺ containing electrodes performed substantially larger current density owned to its higher electrochemically active. This also could be owing to the raised surface area and interior charge transport speed⁹. Therefore, all electrochemical result makes it is possible to foresee the improvement of TiO₂ conductivity as well as practice expanding.

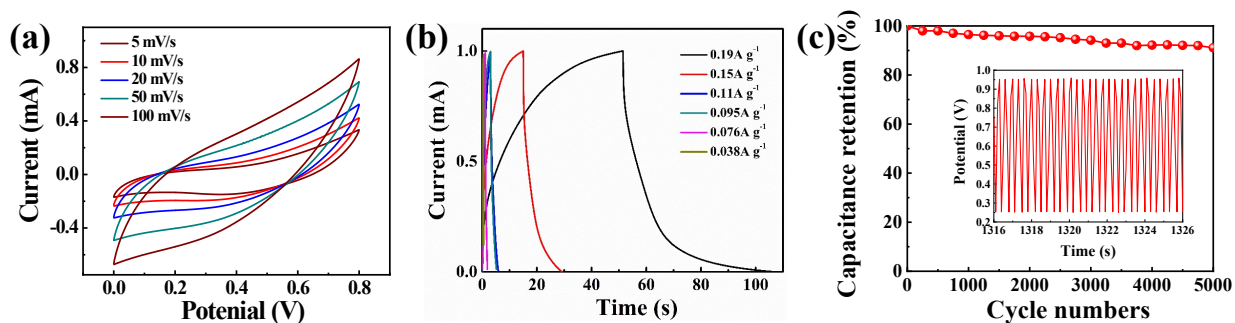


Figure SI 6: (a) CV curves collected of Mn@TiO₂-0.10 electrodes at the different scan rate; (b) Galvanostatic charge/discharge curves collected at different current densities for the sample operated within a voltage window of 1.0 V; (c) the long-term cyclic charge-discharge curve of Mn@TiO₂-0.10.

Table SI 3: mass specific capacitance of all samples.

Sample	Cm (F g ⁻¹)
TiO ₂	1.11
Mn@TiO ₂ -0.01	2.69
Mn@TiO ₂ -0.05	4.13
Mn@TiO ₂ -0.10	5.09
Mn@TiO ₂ -0.15	8.07
Mn@TiO ₂ -0.20	8.37

References

- 1 H. Liu, Z.-G. Zhang, X.-X. Wang, G.-D. Nie, J. Zhang, S.-X. Zhang, N. Cao, S.-Y. Yan and Y.-Z. Long, *J. Phys. Chem. Solids*, 2018, **121**, 236–246.
- 2 M. Nasr, L. Soussan, R. Viter, C. Eid, R. Habchi, P. Miele and M. Bechelany, *New J. Chem.*, 2018, **42**, 1250–1259.
- 3 K. S. Ranjith and T. Uyar, *ACS Sustain. Chem. Eng.*, 2018, **6**, 12980–12992.
- 4 Y. Cai, J. Song, X. Liu, X. Yin, X. Li, J. Yu and B. Ding, *Environ. Sci. Nano*, 2018, **5**, 2631–2640.
- 5 C. G. Lee, H. Javed, D. Zhang, J. H. Kim, P. Westerhoff, Q. Li and P. J. J. Alvarez, *Environ. Sci. Technol.*, 2018, **52**, 4285–4293.

- 6 L. Lin, W. Jiang, M. Bechelany, M. Nasr, J. Jarvis, T. Schaub, R. R. Sapkota, P. Miele, H. Wang and P. Xu, *Chemosphere*, 2019, **220**, 921–929.
- 7 L. Cui, S. Liu, F. Wang, J. Li, Y. Song, Y. Sheng and H. Zou, *J. Alloys Compd.*, 2020, **826**, 154001.
- 8 L. Zhang, W. Yu, C. Han, J. Guo, Q. Zhang, H. Xie, Q. Shao, Z. Sun and Z. Guo, *J. Electrochem. Soc.*, 2017, **164**, H651–H656.
- 9 X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong and Y. Li, *Adv. Mater.*, 2013, **25**, 267–272.