

Supplementary Information

Development of TiO₂ mesocrystal reactive electrochemical membranes for rapid removal of organic pollutants from water

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1. Methods and materials

1.1 Reagents and materials (Text S1.1)

The flow-through titanium plate (Purity > 99%) was obtained from Baoji Yinggao Metal Materials Co., Ltd., China. Ethylene glycol (EG) acetone, and methanol were from Beijing Dikma Biochemical Co., Ltd., China. p-Nitrophenol (p-NP, $\geq 99.0\%$), p-Chlorobenzoic acid (p-CBA, $\geq 99.0\%$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, $\geq 99.0\%$) were all from Shanghai Macklin Biochemical Co., Ltd., China. COD reagent was from Hach Co., Ltd., USA. Sodium perchlorate (NaClO_4 , AR), sodium sulfate (Na_2SO_4 , AR), sodium chloride (NaCl , AR), sodium hydroxide (NaOH , AR), and sulfuric acid (H_2SO_4 , AR) were from China National Pharmaceutical Group Co., Ltd., China.

1.2 Physical characterization of electrodes (Text S1.2)

Field-emission scanning electron microscope (FESEM, ZEISS MERLIN Compact, Germany) was employed to investigate the morphology of the electrodes and particles. X-Ray diffraction (XRD, Bruker D8 Advance, Germany) patterns were applied for evaluating the crystal type of the electrode and powders. Transmission electron microscope (TEM, JEOL JEM 2100F, Japan) equipped with a high-angle annular dark field (HAADF) detector was employed to investigate the morphology and crystal structure of a single particle. The elemental compositions and chemical states of the electrode surfaces were analyzed by X-ray photoelectron spectrometer (XPS, Thermo 250xi, USA). The specific surface area and pore structure of the electrodes were measured on a nitrogen adsorption apparatus (Micromeritic ASAP 2020, USA). The band structure of the electrodes was analyzed by valence band X-ray photoelectron spectrometer (VB-XPS, Thermo 250xi, USA) and diffuse reflectance UV-Visible absorption spectrometer (Shimadzu UV3600IPlus, Japan).

1.3 Electrochemical characterization of electrodes (Text S1.3)

Before all electrochemical experiments, the electrodes were rinsed with acetone and large amounts of Milli-Q water. Electrochemical impedance spectroscopy (EIS) was used to determine the conductivity and charge transfer resistance. EIS for the active layer of the porous electrodes was fitted to the Transmission Line Modeling (TLM) using the ZView software. The parameters of EIS were the frequency range of $10^{-2}\sim 10^5\text{Hz}$ and amplitude of 5 mV. Impedance-Potential (IMPE) was used to

determine Mott-Schottky plots. The parameters of IMPE were the potential window of -1~1.5 (V_{SCE}), potential increment of 50 mV, frequency of 1000Hz, and amplitude of 5 mV. Cyclic voltammetry (CV) measured in the wide potential window (-1.5~3.2 V_{SCE}) was used to determine the current response and electroactivity of various electrodes. Linear sweep voltammetry (LSV) measurements were used to determine the oxygen evolution potential. The parameters of the LSV were the potential window of 1 ~ 3 (V_{SCE}), the scan rate of 10 mV s⁻¹, and the sensitivity of 0.1 A V⁻¹.

2. Results and Discussions

2.1 Surface area determination (Text S2.1)

The r-p-TiO₂-L electrode sample underwent sonication, and the resultant powders were collected for analysis. **Fig. S1a** showed the N₂ adsorption-desorption curves of the flow-through titanium substrate, the r-p-TiO₂-L electrode, and the powders collected from the r-p-TiO₂-L electrode. The results according to the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) models were summarized in **Table S1**. The BET surface area and the pore volume for the TiO₂ mesocrystals were determined to be 204.75 m² g⁻¹ and 0.41 m³ g⁻¹, respectively. It was worth noting that TiO₂ mesocrystals within the r-p-TiO₂-L electrode exhibited a narrow micropore size distribution of about 1.0 nm (**Fig. S1b**), indicating that the width of nanochannels between two tiny subunits was about 1.0 nm.

2.2 Band structure of electrodes (Text S2.2)

In n-type semiconductors, the E_F is close to the E_C (Lim et al., 2014), and the flat-band potential (E_{FB}) is equivalent to E_F (Grätzel, 2001). In this study, E_F was indirectly measured using E_{FB}. Electrochemical impedance spectroscopy was employed to analyze the electrodes and generate Mott-Schottky plots. These measurements were conducted using a conventional three-electrode system coupled with a computer-controlled potentiostat/galvanostat. The values of E_{FB} and the density of N_D were calculated using the Mott-Schottky equation (**Eq. S1**), as outlined below.

$$\frac{1}{C_{SC}^2} = \left(\frac{2}{e\epsilon_0\epsilon N_D A^2} \right) \left(E_{\text{apply}} - E_{FB} - \frac{k_B T}{e} \right) \quad (\text{S1})$$

Where C_{SC} is the space charge layer capacity (F); e is the elementary electron charge (1.6 × 10⁻¹⁹ C); ε₀ is the permittivity of vacuum (8.86 × 10⁻¹⁰ F cm⁻¹); ε is the dielectric constant of TiO₂ (Takeuchi et al., 1978; Tang et al., 1994; D. Mardare*, 2004) (anatase phase is 46); N_D is the donor state density (cm⁻³); A is the electrode area (m²); E_{apply} is the applied bias potential; E_{FB} is the flat band potential; k_B is the Boltzmann constant (1.38 × 10⁻²³ J · K⁻¹); T is the temperature (298 K).

There was an increase of N_D from 6.32 × 10²⁰ cm⁻³ for the p-TiO₂-L electrode to 9.32 × 10²⁴ cm⁻³ for the r-p-TiO₂-H electrode and 7.03 × 10²⁵ cm⁻³ for the r-p-TiO₂-L electrode. The calculated E_F was 0.4, 0.06, and 0.2 (vs. SHE) for the p-TiO₂-L electrode, r-p-TiO₂-L electrode, and r-p-TiO₂-H electrode,

respectively.

Valence band edge (E_V) and work function of the electrodes could be calculated using **Eq. S2** and **S3** according to the valence band X-ray photoelectron spectrometer (VB-XPS) spectrum. The tangent line AB was the largest slope. The tangent line CD was parallel to the trailing line. The intersection point of the AB and CD is marked by W.

$$E_V(\text{vsSHE}) = \Phi_A - 4.44 + E_0 \quad (\text{S2})$$

Where Φ_A is the work function of the instrument (4.6eV), E_0 is the corresponding binding energy at the intersection point W, and the values were 3.35, 2.92, and 3.07eV for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively. Therefore, the calculated E_V was 3.51, 3.08, and 3.23 V_{SHE} for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively.

$$\Phi = \Phi_A + \Delta V \quad (\text{S3})$$

Where Φ_A is the work function of the XPS instrument (4.6eV), ΔV is the differential value (eV) of the binding energy between the tangent point of line AB and the inflection point at the tail of the curve, and the values were 2.09, 1.41 and 1.76 eV for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively. Therefore, the values of work function were 6.69, 6.01, and 6.36 eV for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively.

The optical band gap (E_g) can be calculated by the Tauc equation (**Eq. S4**) (Carbajo et al., 2018) derived from UV-Visible (UV-vis) absorption spectrometer and Tauc plots.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (\text{S4})$$

With Tauc curves, the intersection point of the tangent line and the X-axis can be obtained and the abscissa value of this point is the E_g value of the tested electrodes. The values of E_g were 3.19, 2.97, and 2.78 eV for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively.

E_C can be calculated by subtracting E_g from E_V . Thus, the values of E_C were 0.32, 0.3, and 0.26 V_{SHE} for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively.

2.3 EIS analysis for porous electrodes fitted to Transmission Line Modeling (TLM) (Text S2.3)

The equivalent circuit for porous electrodes was illustrated in **Fig. 4a**. The impedance plots were segmented into high, medium, and low frequency regions, which corresponded respectively to the outer layer, active layer, and support layer. The impedance behavior in the high and low frequency regions, attributed to the outer and support layers, mirrors that of the plate electrode (Jurczakowski et al., 2004).

Meanwhile, the irregular plots observed in the medium-frequency region are characteristic of the active layer and can be explained by the TLM (Bisquert, 2000; Jing and Chaplin, 2016).

The TLM can be described as **Eq. S5**.

$$Z_{al} = \frac{1}{r_m + r_s} \left[\frac{\left\{ \frac{1}{r_m + r_s} \left[2r_m r_s + (r_m^2 + r_s^2) C_\lambda + \frac{L}{\lambda} r_m r_s S_\lambda \right] Z_O Z_B \right\}}{\left[\lambda S_\lambda (r_m + r_s) + (Z_O + Z_B) C_\lambda + \frac{1}{\lambda (r_m + r_s)} Z_O S_\lambda \right]} \right] \quad (S5)$$

Where $C_\lambda = \cosh(L/\lambda)$, $S_\lambda = \sinh(L/\lambda)$, and L is the dimensionless depth of the electrode active layer (set to unity). r_s (ohm) and r_m (ohm) are the ionic resistance and electronic resistance; Z_B (ohm) is the boundary impedance, which in this case represents the electronic plane connecting the active and support layers and is set to a low value (e.g., $1 \times 10^{-7} \Omega$) due to sufficient electrical contact between the two layers; λ is a parameter related to Z_{active} , given by **Eq. S6**. Z_{active} (ohm) represents the interfacial impedances of the active layer, given by **Eq. S7**. Each interfacial impedance contains a time constant characterizing the interfacial response to a variable frequency ΔE signal.

$$\lambda = \left[\frac{Z_{active}}{r_m + r_s} \right]^{0.5} \quad (S6)$$

$$Z_{active} = \frac{1}{\frac{1}{r_{ct}} + j\omega\Phi T_p} \quad (S7)$$

where r_{ct} is the resistance to charge transfer of the active layer (ohm); T_p is a constant associated with the capacitance of the active layer ($F s^{\phi-1}$); j is the notation for the imaginary unit ($\sqrt{-1}$); ω is the radial frequency (radians s^{-1}); ϕ is related to the angle of rotation of a purely capacitive line on the complex plane plots (dimensionless), and is equal to 0 for a pure resistor and 1 for a pure capacitor.

Average values for double-layer capacitances (C_{dl} (F)) is given to **Eq. S8**.

$$C_{dl, i} = \left(\frac{T_i}{[r_s^{-1} + r_{ct, i}^{-1}]^{1-\phi}} \right)^{1/\phi} \quad (S8)$$

The values of $R_{ct, active}$ were 3.06×10^{12} , 2276, and 1.2Ω for the p-TiO₂-L, r-p-TiO₂-H and, r-p-TiO₂-L electrodes, respectively. The Nyquist fitting plots for these electrodes are depicted in **Fig. S2 ~ S4**. The results are summarized in **Table S2**.

2.4 Calculation of the width of d_{SC} (Text S2.4)

The capacitance (C) of the electrode is composed of the double layer capacitance (C_{dl}) and the space charge capacitance (C_{SC}), as detailed in **Eq. S9**.

$$\frac{1}{C} = \frac{1}{C_{dl}} + \frac{1}{C_{SC}}$$

(S9)

It can be assumed that the width of the space charge layer is far longer than the Helmholtz layer. Thus, C_{dl} is much larger than C_{SC} , corresponding to $1/C \approx 1/C_{SC}$. $1/C_{SC}$ can be calculated by **Eq. S10**.

$$\frac{1}{C_{SC}} = \frac{2\pi f Z_{im}}{-i}$$

(S10)

Where i is an imaginary unit, f is the frequency of the electrochemical impedance (1 kHz), and Z_{im} is the imaginary part of the impedance.

A plot of $1/C_{SC}^2$ against E_{apply} should yield a straight line, from which the E_{FB} can be determined from the intercept on X-axis. The N_D can be obtained from the slope.

Considering the space charge layer as parallel plate capacitor, C_{SC} can be calculated by **Eq. S11**.

$$C_{SC} = \frac{\epsilon_0 \epsilon A}{d_{SC}}$$

(S11)

The width of the d_{SC} can be calculated by substituting Eq. S7 into S1, thus obtaining **Eq. S12** (van de Krol et al., 1999; Beranek et al., 2005).

$$d_{SC} = \left[\frac{2\epsilon_0 \epsilon (E_{apply} - E_{FB})}{eN_D} \right]^{\frac{1}{2}}$$

(S12)

The width of the space charge layer (d_{SC}) was calculated to be 430.6, 0.8, and 1.6 nm with the potential of +2.4 V_{SHE} for the p-TiO₂-L, r-p-TiO₂-L, and r-p-TiO₂-H electrodes, respectively.

2.5 Service lifetime of the TiO₂ mesocrystal REM (Text S2.5)

The lifetime of the TiO₂ mesocrystal REM was determined by the time when the cell potential was 5 V higher than the initial value, which can be calculated by **Eq. S13** (Hine et al., 1979).

$$T_1 \times i_1^n = T_2 \times i_2^n$$

(S13)

where T_1 is lifetime obtained at high current density ($i_1 = 40$ mA/cm²), T_2 is lifetime obtained at low current density ($i_2 = 10$ mA/cm²), and n is a coefficient.

The service lifetime of TiO₂ mesocrystal REM was 10 h and 168 h at current density of 40 mA/cm² and 10 mA/cm², respectively. n in **Eq. S15** is calibrated as 2.02 for the TiO₂ mesocrystal REM. The service lifetime at the actual operating current of 5 and 3 mA/cm² can be estimated as 691.5 and 1987.9

h, respectively.

2.6 $\cdot\text{OH}$ adsorption and details for DFT calculations (Text S2.6)

The adsorbed H_2O is converted to $\cdot\text{OH}$ during the electrochemical process. As discussed above, both the H and Ti adsorption patterns can produce surface-absorbed $\cdot\text{OH}$ while the O adsorption pattern cannot. O atom in H_2O participates in the formation of hydrogen-bond and chemical bond for the H and Ti adsorption patterns, which could produce $\cdot\text{OH}$ easily. A hydrogen bond can be formed by the reaction between the O atom of $\cdot\text{OH}$ and the H atom in reduced TiO_2 (H adsorption pattern). A chemical bond can be formed by the reaction between the O atom of $\cdot\text{OH}$ and the Ti atom in reduced TiO_2 (Ti adsorption pattern). Adsorption energy at the two adsorption patterns is calculated by DFT calculation.

In addition, mesocrystals consist of subunits and nanochannels, and some organic compounds might diffuse into these nanochannels (**Fig. S8**). To elucidate the effect of crystal structure on the adsorption energy of $\cdot\text{OH}$, models of crystals with different structures were constructed by VESTA software. This model is based on a standard planar framework, distinguishing only between the interior and exterior of the nanochannels, and does not fully replicate the complex nanochannel structures found in the mesocrystals. **Fig. S9** showed the basic configuration of common $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ bulk crystals and $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ mesocrystals with nanochannels width of 10 Å. **Fig. 7c** showed the basic configuration of $\cdot\text{OH}$ adsorbed at the Ti adsorption pattern on the surface of common $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ bulk and $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ mesocrystals by a chemical bond. **Fig. 7d** showed the basic configuration of $\cdot\text{OH}$ adsorbed at the H pattern on the surface of common $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ bulk and $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ mesocrystals by a hydrogen bond. The orange dotted line was the edge of individual crystals.

The adsorption energy of $\cdot\text{OH}$ was calculated based on DFT+U methods using the Vienna Ab-initio Simulation Package (VASP) (Kresse and Hafner, 1993; Kresse and Furthmüller, 1996b,a). The electron-ion interactions were described by using the projector augmented wave (PAW) (Blöchl, 1995; Kresse and Joubert, 1999) method. The exchange and correlation energies were determined with the Perdew, Burke, and Ernzerhof (PBE) (Perdew and Wang, 1992; Perdew et al., 1996) functional with the on-site Coulomb Repulsion U term. In this work, $U(\text{Ti}) = 4.2$ eV for all the calculations. The van der Waals interaction was considered using the DFT-D3 method with Becke-Jonson damping dispersion correction. The cutoff energy for the plane wave-basis expansion was set to 400 eV. The

convergence criterion of the electronic structure was set to 10^{-4} eV, and the atomic relaxation was continued until the forces acting on atoms were smaller than 0.02 eV $\text{\AA}^{-1}$. The Brillouin-zone sampling was conducted using Monkhorst-Pack (MP) grids of special points with the separation of 0.04 $\text{\AA}^{-1}$, and a Gaussian smearing of 0.05 eV was applied to speed up electronic convergence (Momma and Izumi, 2011). The results for DFT calculation were summarized in **Table S3**.

Supplementary Figures

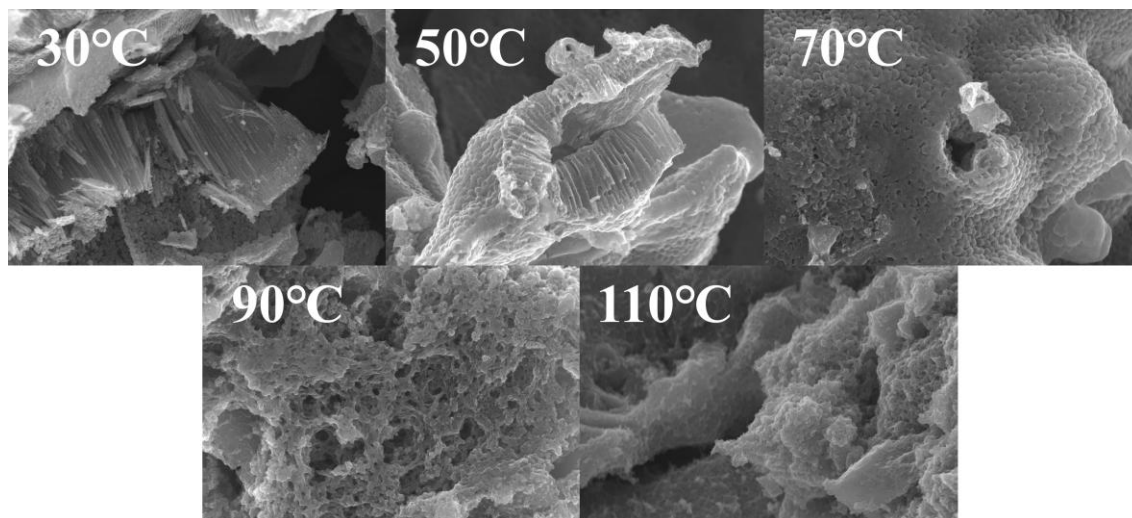


Fig. S1. SEM images of the electrodes at different anodization temperatures.

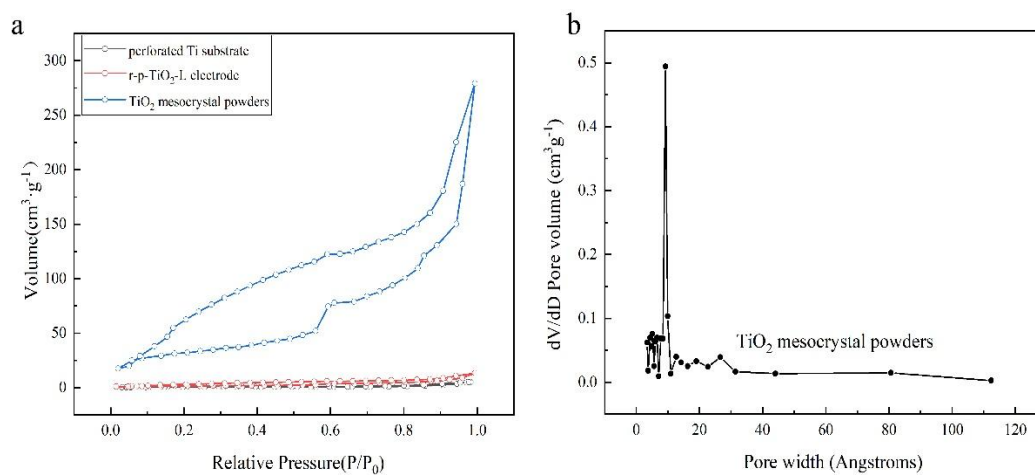


Fig. S2. (a) N_2 adsorption-desorption curves for the flow-through titanium plate, the r-p-TiO₂-L electrode, and the TiO₂ mesocrystal powders. (b) Pore size distribution of the powders collected from the sonication of r-p-TiO₂-L electrode.

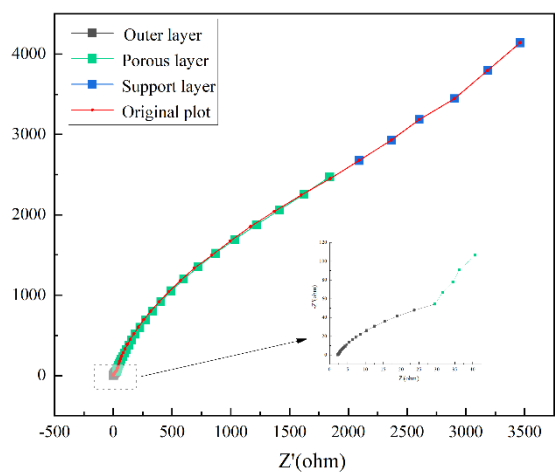


Fig. S3. Nyquist fitting plots of the p-TiO₂-L electrode

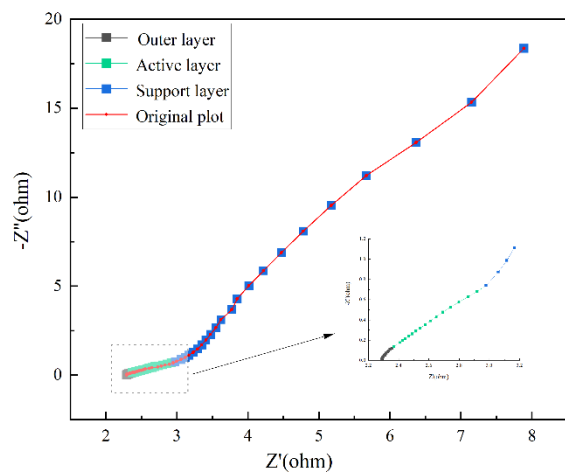


Fig. S4. Nyquist fitting plots of the r-p-TiO₂-H electrode

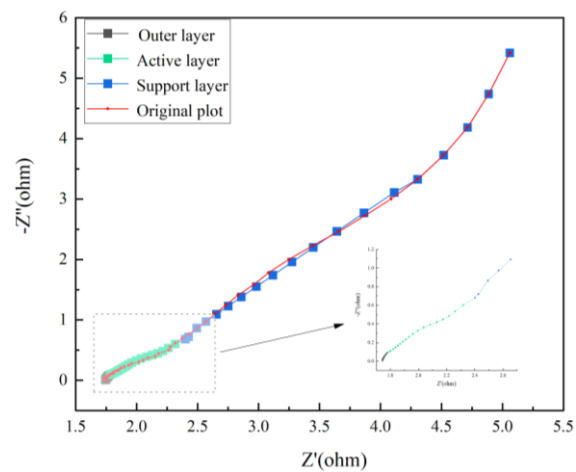


Fig. S5. Nyquist fitting plots of the r-p-TiO₂-L electrode

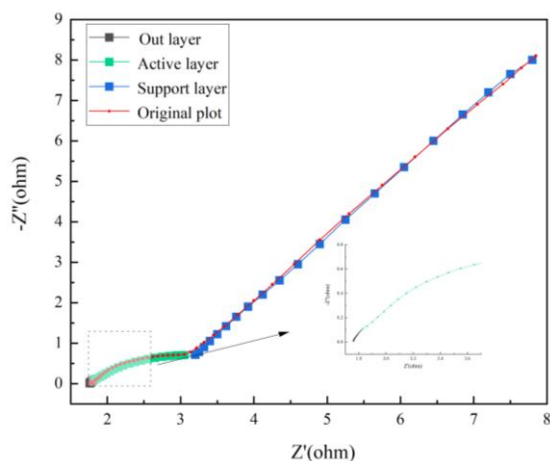


Fig. S6. Nyquist fitting plots of the r-p-TiO₂-L electrode after a period of operation.

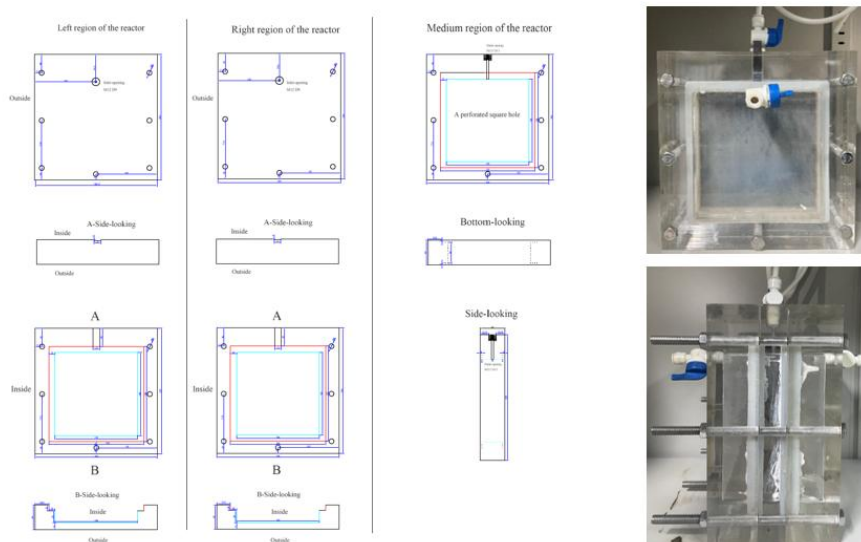


Fig. S7. (a) Diagram for designing the reactor of REM and **(b)** photograph of the actual device.

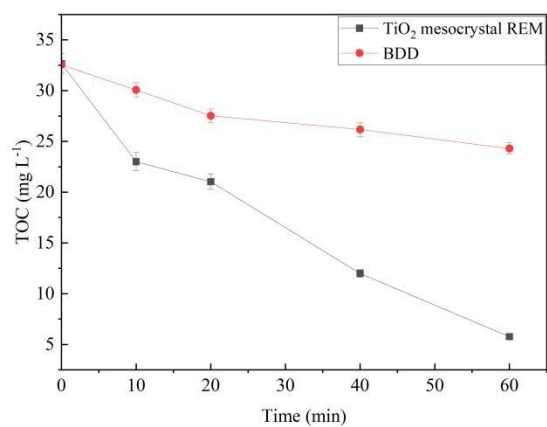


Fig. S8. Comparison of degradation performance between the TiO₂ mesocrystal REM and the BDD electrode (3 mA/cm², Membrane flux = 800 L/(m³·h), [p-NP]₀ = 51.2 mg/L, pH = 7 and

electrolyte is NaClO_4).

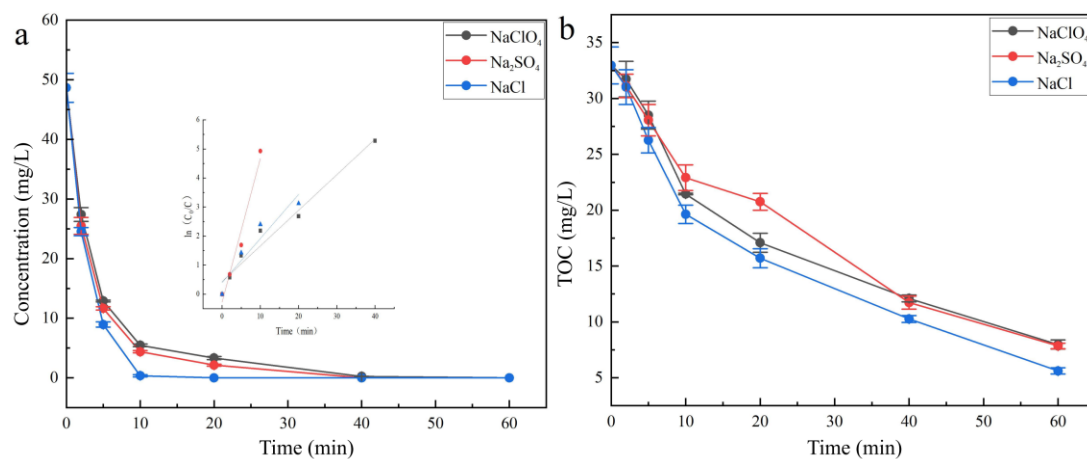


Fig. S9. Oxidation of p-NP by the TiO_2 mesocrystal REM under different electrolyte conditions: (a) concentration profiles (inset: pseudo-first-order kinetic fitting) and (b) TOC variation over reaction time.

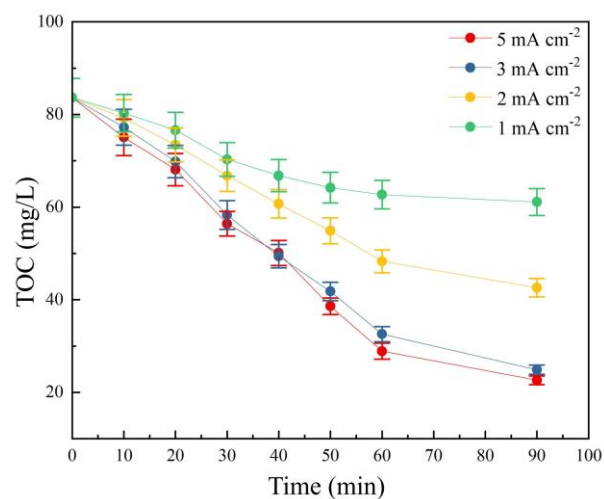


Fig. S10. TOC concentration during the treatment of coal chemical wastewater by the TiO_2 mesocrystal REM.

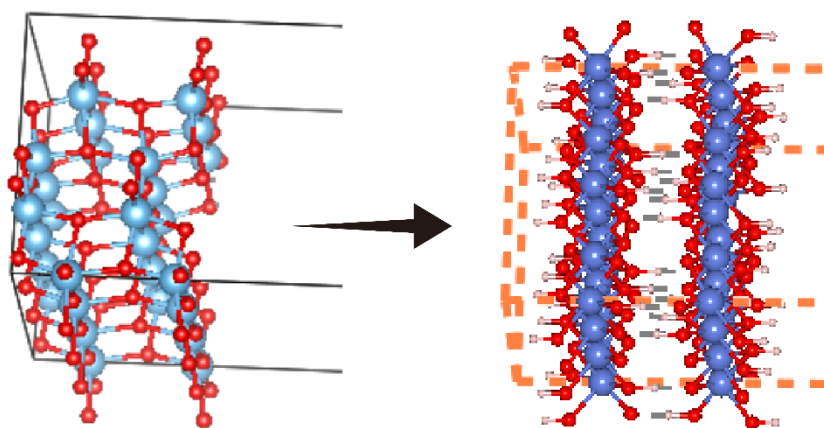


Fig. S11. Basic configuration for the transformation from TiO_2 to $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$.

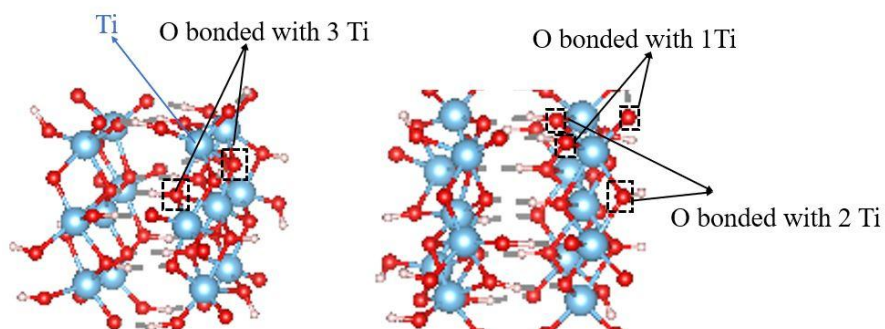


Fig. S12. Atom distribution at the edge of individual mesocrystal.

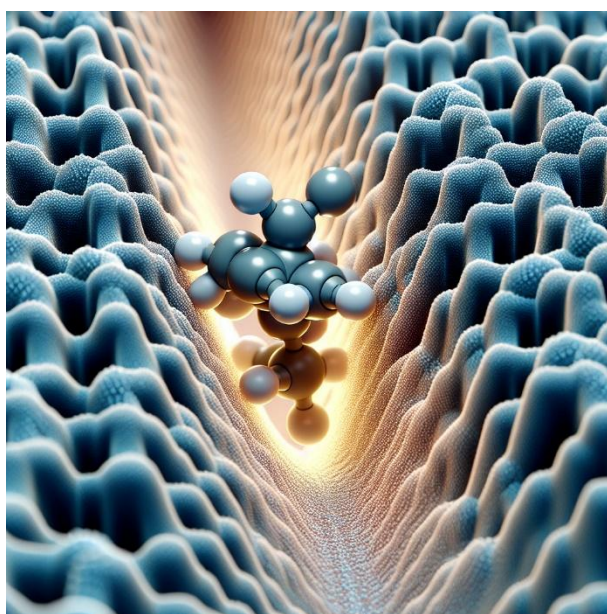


Fig. S13. Schematic diagram for the diffusion of organic compounds into the nanochannels of mesocrystals.

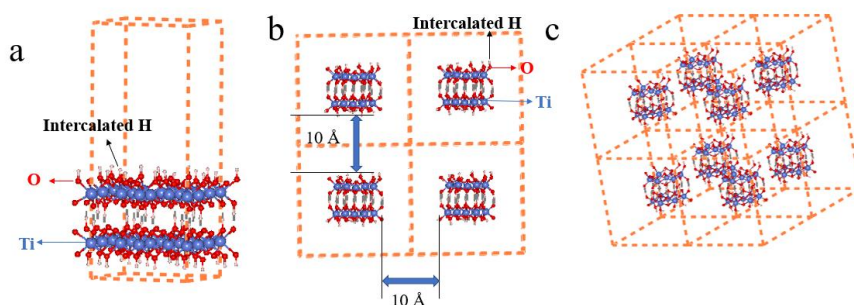


Fig. S14. Basic configuration for **(a)** common $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ bulk, **(b, c)** $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ mesocrystal with nanochannels width of 10 Å.

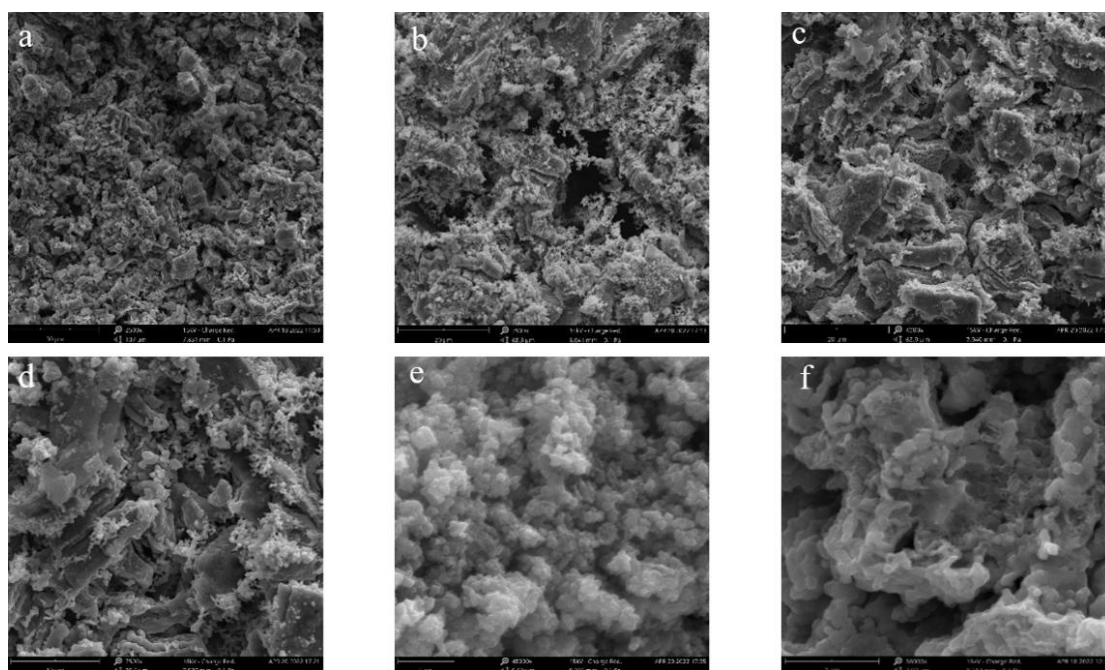


Fig. S15. SEM image of the electrode after long-term use, images a-c are at low magnification, while d-f are at high magnification.

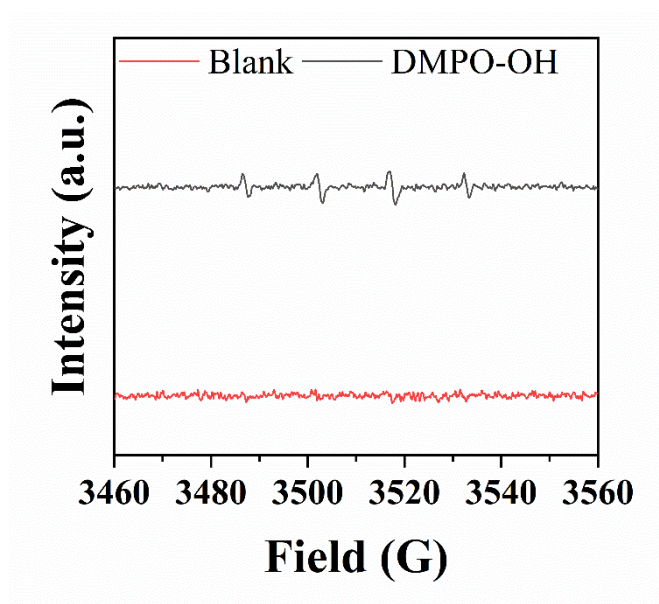


Fig. S16. SEM image of the electrode after long-term use.

Supplementary Tables

Table S1 Surface area results of the flow-through titanium plate, the r-p-TiO₂-L, and the powders collected from ultrasonication of the r-p-TiO₂-L

Parameters	flow-through Ti plate	r-p-TiO ₂ -L	powders
BET surface area (m ² g ⁻¹)	1.908	10.14	204.75
Micro surface area (m ² g ⁻¹)	1.817	5.7931	113.463
Pore volume (m ³ g ⁻¹)	0.001	0.0025	0.41

Table S2 EIS fitting results of the r-p-TiO₂-L, r-p-TiO₂-H and p-TiO₂-L

Outer layer					
Parameters	R _s (Ω)	T (F s ^{Φ-} ₁)	Φ	R _{ct} (Ω)	C _{dl} (F)
r-p-TiO ₂ -L	1.7	0.3	0.8	1.1	0.2
r-p-TiO ₂ -H	2.3	0.14	0.8	0.7	0.072
p-TiO ₂ -L	2.2	0.0005	0.9	353	0.0002
Active layer					
Parameters	r _m (Ω)	T (F s ^{Φ-} ₁)	Φ	R _{ct} (Ω)	C _{dl} (F)
r-p-TiO ₂ -L	3.6	0.65	1	1.2	0.65
r-p-TiO ₂ -H	3.7	0.51	0.55	2276	0.85
p-TiO ₂ -L	1021	0.003	0.92	3.06×10 ¹²	0.003

Table S3 Absolute energy and the adsorption energy of $\cdot\text{OH}$ at different adsorption patterns on the common $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ bulk and $\text{Ti}^{\text{III}}(\text{O})(\text{OH})$ mesocrystals

Absorption patterns	Absolute energy (eV)	Absorption energy (eV)
TiOOH bulk-non adsorbed	-626.18	-
TiOOH bulk -H pattern	-636.22	-2.94
TiOOH bulk -Ti pattern	-637.20	-3.93
TiOOH mesocrystal- non adsorbed	-512.59	-
TiOOH mesocrystal-H pattern	-520.87	-1.19
TiOOH mesocrystal-Ti pattern	-522.31	-2.63

Table S4 Water quality and inorganic salt ion indicators of coal chemical wastewater

water quality parameters	value	water quality parameters	value
pH	7.50	K^+ (mg/L)	465
TOC (mg/L)	85	Na^+ (mg/L)	590
COD (mg/L)	206	Ca^{2+} (mg/L)	0.51
turbidity (NTU)	1.38	Mg^{2+} (mg/L)	4.64
conductivity (S/cm)	18.91	Cl^- (mg/L)	743
TDS (mg/L)	190	NO_2^- (mg/L)	393
$\text{NH}_4\text{-N}$ (mg/L)	3.22	NO_3^- (mg/L)	354
TN (mg/L)	1.05	SO_4^{2-} (mg/L)	123
TP (mg/L)	2.56	PO_4^{3-} (mg/L)	N.D.

Supplementary References

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