

Figure. S1. No  $\text{Ti}^{3+}$  self-doping Ti/TiO<sub>2</sub>-NTs

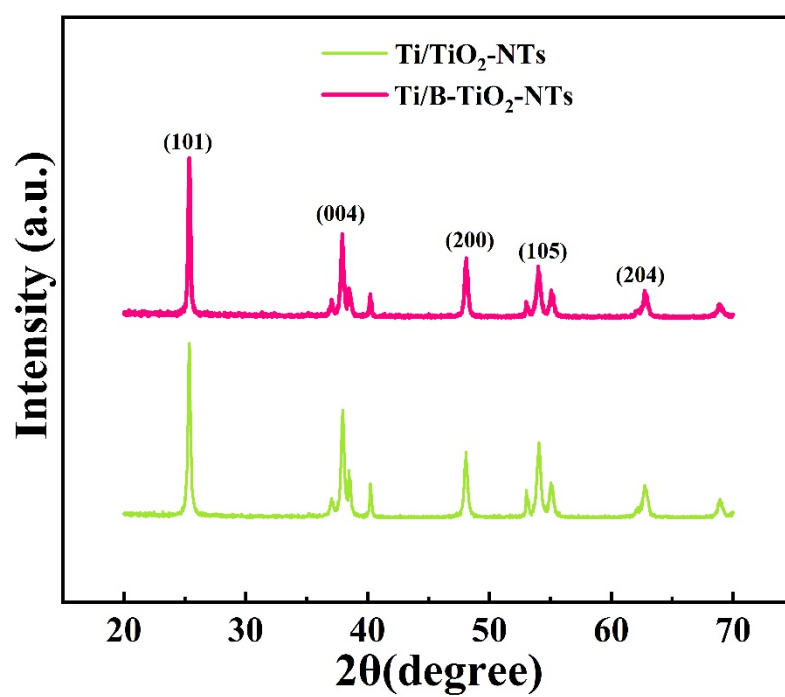


Figure. S2. XRD patterns of no  $\text{Ti}^{3+}$  self-doping Ti/TiO<sub>2</sub>-NTs and  $\text{Ti}^{3+}$  self-doping Ti/B-TiO<sub>2</sub>-NTs.

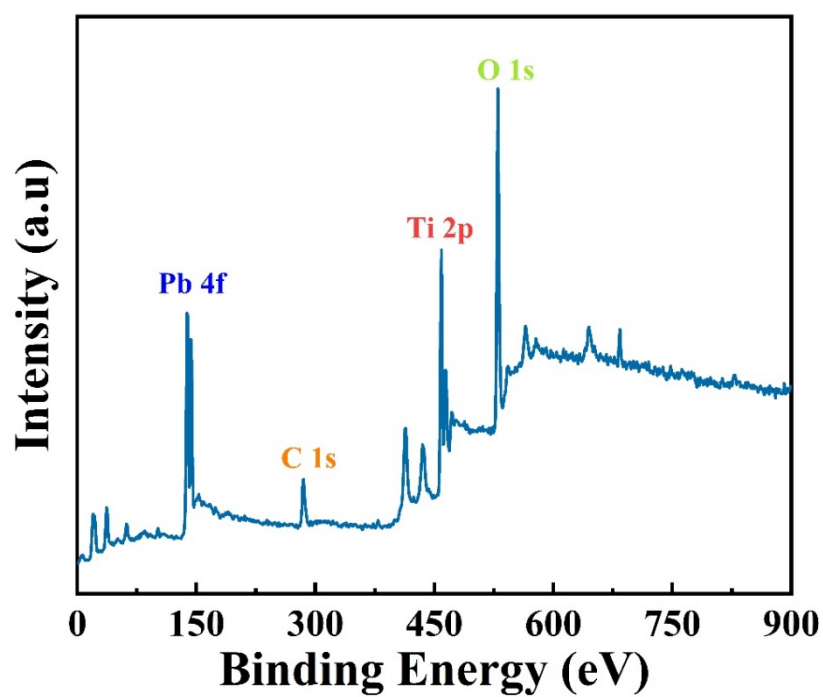


Figure. S3. XPS survey spectra of the Ti/B-TiO<sub>2</sub>-NTs/PbO<sub>2</sub>-SDS electrode.

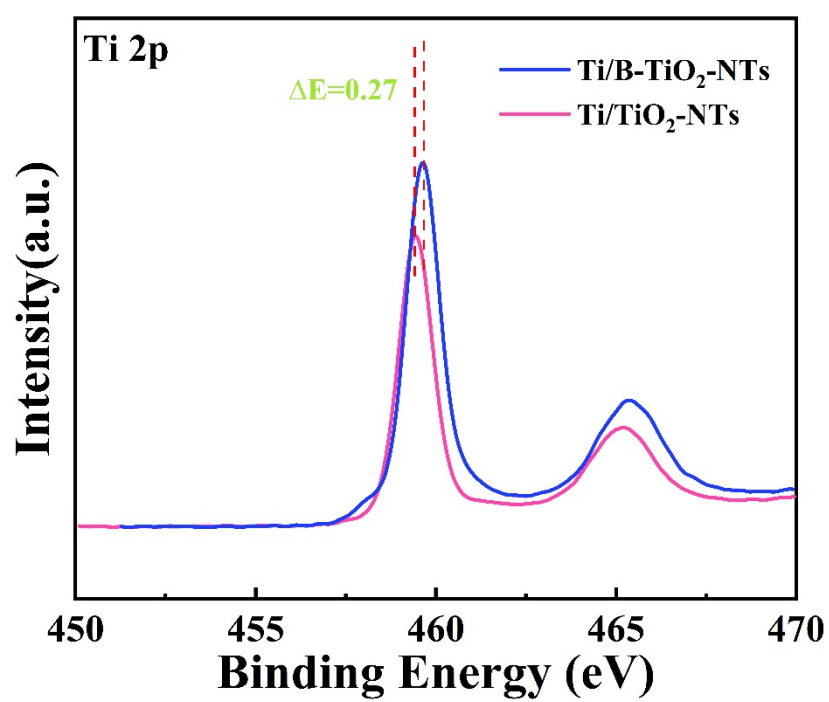


Figure. S4. XPS spectra of Ti 2p orbital of Ti/TiO<sub>2</sub>-NTs and Ti/B-TiO<sub>2</sub>-NTs.

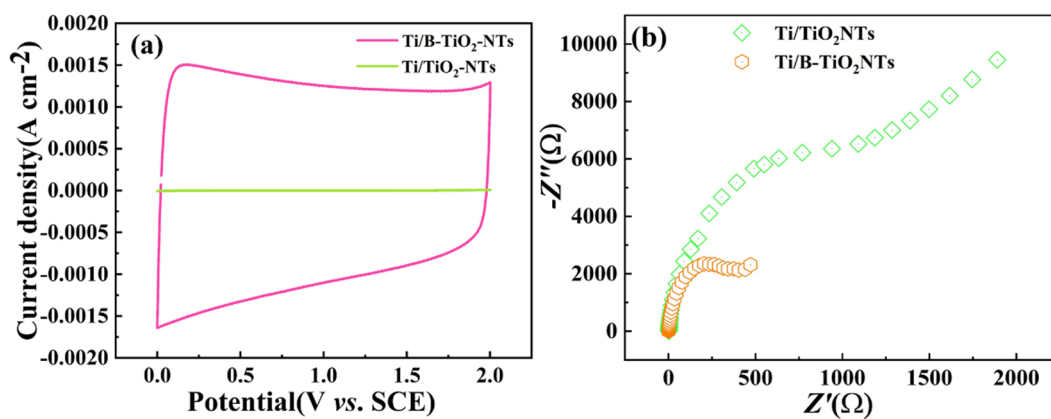


Figure. S5. (a) Cyclic voltammograms of of the Ti/B-TiO<sub>2</sub>-NTs and Ti/TiO<sub>2</sub>-NTs electrode; (b) EIS of of the Ti/B-TiO<sub>2</sub>-NTs and Ti/TiO<sub>2</sub>-NTs electrode.

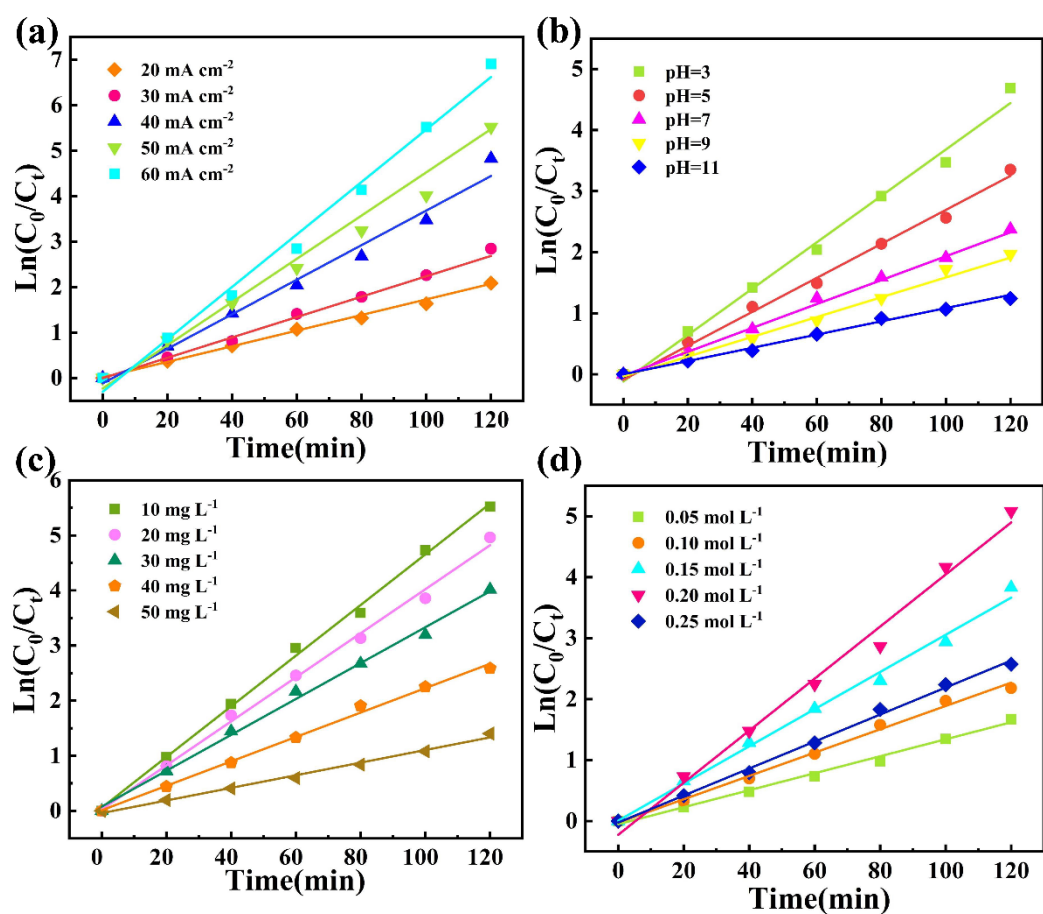


Figure. S6. Pseudo-first-order kinetic fitting curves at different current density (a), initial MB concentration (b), initial pH (c) and electrolyte concentration (d).

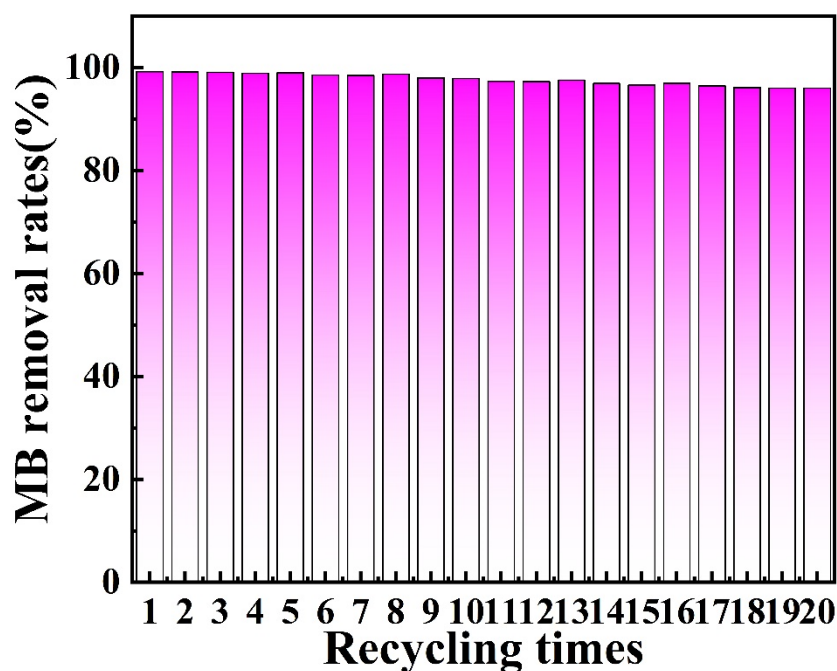


Figure. S7. Repetitive experiment of Ti/B-TiO<sub>2</sub>-NTs/PbO<sub>2</sub>-SDS electrode in electrochemical oxidation of MB for 120 min. Conditions: current density: 40 mA cm<sup>-2</sup>, initial MB concentration: 30 mg L<sup>-1</sup>, initial pH = 3, T = 25 °C, Na<sub>2</sub>SO<sub>4</sub> concentration = 0.2 M.

Table S1. Crystal sizes of  $\beta$ -PbO<sub>2</sub> grains on different electrodes.

| Electrode  | Half height width<br>(101 planes) | Intensity | Crystallite size (nm)<br>(101 planes) |
|--|-----------------------------------|-----------|---------------------------------------|
| Ti/B-TiO <sub>2</sub> -NTs/PbO <sub>2</sub> -<br>SDS | 0.385                             | 823       | 20.62                                 |
| Ti/B-TiO <sub>2</sub> -NTs/PbO <sub>2</sub>          | 0.228                             | 561       | 53.28                                 |
| Ti/TiO <sub>2</sub> -NTs/PbO <sub>2</sub>            | 0.137                             | 302       | 65.29                                 |

Table S2. The fitted EIS parameters.

| Electrode  | R <sub>ct</sub><br>( $\Omega$ cm <sup>-2</sup> ) | R <sub>s</sub><br>(m $\Omega$ cm <sup>-2</sup> ) | CPE<br>(mMho cm <sup>-2</sup> ) | W<br>(mMho cm <sup>-2</sup> ) | n     |
|--|--|--|---------------------------------|-------------------------------|-------|
| Ti/TiO <sub>2</sub> -NTs/PbO <sub>2</sub>            | 195  | 363  | 3.42                            | 103                           | 0.698 |
| Ti/B-TiO <sub>2</sub> -NTs/PbO <sub>2</sub>          | 40.7   | 298  | 5.65                            | 126                           | 0.845 |
| Ti/B-TiO <sub>2</sub> -NTs/PbO <sub>2</sub> -<br>SDS | 6.74   | 145  | 12.9                            | 138                           | 0.965 |

**Table S3. Comparison of the performance of PbO<sub>2</sub> electrodes with other reported degradation MB methods.**

| Catalyst   | MB concentration      | Conditions  | COD or TOC removal efficiency(%) | Ref          |
|--|-----------------------|---|----------------------------------|--------------|
| Ti/Sb <sub>2</sub> O <sub>3</sub> -<br>SnO <sub>2</sub> /Er-PbO <sub>2</sub> | 30 mg L <sup>-1</sup> | 0.1M<br>Na <sub>2</sub> SO <sub>4</sub> , 40mA/cm <sup>2</sup> , pH=3,<br>120min  | 65.34%                           | [1]          |
| PbO <sub>2</sub> -ZrO <sub>2</sub>   | 30 mg L <sup>-1</sup> | 0.2M<br>Na <sub>2</sub> SO <sub>4</sub> , 50mA/cm <sup>2</sup> , pH=3,<br>120min  | 72.7%                            | [2]          |
| S-TiO <sub>2</sub> NTA-<br>PbO <sub>2</sub>                                  | 20 mg L <sup>-1</sup> | 0.02M<br>Na <sub>2</sub> SO <sub>4</sub> , 20mA/cm <sup>2</sup> , pH=7,<br>120min | 49.4%                            | [3]          |
| OP-10<br>modified<br>PbO <sub>2</sub>  | 30 mg L <sup>-1</sup> | 0.15M<br>Na <sub>2</sub> SO <sub>4</sub> , 50mA/cm <sup>2</sup> , pH=5,<br>120min | 70 %                             | [4]          |
| Ti/B-TiO <sub>2</sub> -<br>NTs/PbO <sub>2</sub> -<br>SDS                     | 30 mg L <sup>-1</sup> | 0.2M<br>Na <sub>2</sub> SO <sub>4</sub> , 40mA/cm <sup>2</sup> , pH=3,<br>120min  | 80.6%                            | This<br>Work |

## References

- [1] Zhou, Y. Z. et al., Electrocatalysis enhancement of  $\alpha$ ,  $\beta$ -PbO<sub>2</sub> nanocrystals induced via rare earth Er(III) doping strategy: Principle, degradation application and electrocatalytic mechanism. *Electrochim. Acta*.2020,333,135535.
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- [3] Ying, S., Li Y.D., Yao Y.W., Xia Y., Jiao M.Y., Han E.S., Electrodeposition and Catalytic Performance of Hydrophobic PbO<sub>2</sub> Electrode Modified by Surfactant OP-10. *ECS Journal of Solid State Science and Technology*.2021, 10,123005.
- [4] Yang, C., Shang S.S., Li X.Y., Fabrication of sulfur-doped TiO<sub>2</sub> nanotube array as a conductive interlayer of PbO<sub>2</sub> anode for efficient electrochemical oxidation of organic pollutants. *J Hazard Mater.* 2021,258,118035.