Construction of Pr/CDs/SSS/PbO$_2$ composite electrode for highly efficient degradation of organic pollutants

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S1. Chemicals and materials

Titanium Plate offered by OxyMetals Ltd (China). Praseodymium Nitrate Hexahydrate (Pr(NO$_3$)$_2$·6H$_2$O) from Shanghai Titan Technology Co(Shanghai, China). Lead Nitrate (Pb(NO$_3$)$_2$), Nitric Acid (HNO$_3$), Hydrochloric Acid (HCl) and Citric Acid (C$_6$H$_8$O$_7$) were provided by Luoyang Chemical Reagent Factory (Luoyang, China). Sodium p-styrenesulfonate (SSS), stannous chloride dihydrate (SnCl$_2$·2H$_2$O), antimony trichloride (SbCl$_3$) and tert-butanol (C$_4$H$_{10}$O) were supplied by Shanghai Maclean's Biochemical Technology Co Ltd (Shanghai, China). Sodium fluoride (NaF) was provided by Tianjin kwangfu Fine Chemical Research Institute (Tianjin, China). Anhydrous sodium sulfate (Na$_2$SO$_4$), methylene blue trihydrate, anhydrous ethanol, N,N-dimethylformamide (DMF), and urea (CO(NH$_2$)$_2$) were supplied by Tianjin Komeo Chemical Reagent Co. Isopropanol (C$_3$H$_8$O) and acetone (CH$_3$COCH$_3$) were provided by Hongyan Reagent Factory, Hedong District, Tianjin (Tianjin, China). Oxalic acid dihydrate (C$_2$H$_2$O$_4$·2H$_2$O) was provided by Shanxi Tongjie Chemical Reagent Co Ltd (Shanxi, China).

S2. Electrode preparation

The preparation of Pr/CDs/SSS/PbO$_2$ composite electrode consisted of four steps.

2.1. Pre-treatment of titanium plates

The oxidised layer on the surface of the titanium plate was firstly polished off using sandpaper; then it was submerged in a mixture of acetone, ethanol and deionised water (1:1:1, v/v) and ultrasonicated for 15 min to remove the particles and grease from

the surface of the titanium plate; subsequently, it was etched with a 15 wt% oxalic acid solution for 4 h at 90 °C; and finally, the pretreated titanium plate was rinsed with deionised water and retained in a 1 wt% oxalic acid solution and kept in 1 wt% oxalic acid solution.

2.2. Preparation of SnO_2-Sb_2O_3 intermediate layer

20 g $SnCl_2·2H_2O$ and 2 g $SbCl_3$ were dissolved in a mixed solution of 100 mL isopropanol and 13.2 mL hydrochloric acid, and stirred for 30 min to obtain the coating solution; then the pre-treated titanium plate was thermally coated, and dried at 100 °C for 10 min in a blast drying oven to view the crystal formation on its surface, and then coated again, and repeated the operation for 6 times, and finally its placed in a muffle furnace calcined at 500 °C for 2 h, the SnO_2-Sb_2O_3 interlayer was produced, recorded as Ti/SnO_2-Sb_2O_3.

2.3. Preparation and coating of N-CDs

Preparation of N-CDs: $C_6H_8O_7$ was used as the carbon source and $CO(NH_2)_2$ as the nitrogen source. 3 g $C_6H_8O_7$ and 2.81 g $CO(NH_2)_2$ were dissolved in 60 mL of DMF, after which the reaction was carried out in a microwave synthesizer at 180 °C and 4 MPa for 30 min, the solution was taken out when it was completely cooled down to room temperature. Then, loaded into a MD55 dialysis bag, and dialysed until the solution was colourless. Finally, the dialysed solution was sublimated in a cooler to obtain the N-CDs powder.

Coating of N-CDs: The above-prepared N-CDs were heated up to 700 °C for 2 h with 5 °C min^{-1} in N_2 atmosphere, and 50 mg of the carbonated N-CDs was dissolved in 0.5 mL of anhydrous ethanol. Firstly, 50 mg of carbonated N-CDs was dissolved in 0.5 mL of anhydrous ethanol and stirred for 8 h. Then, 0.1 mL of DuPont membrane solution was added and stirred for 24 h. Secondly, the N-CDs solution was added dropwise on the surface of Ti/SnO_2-Sb_2O_3 and pushed flat with a glass rod. Finally, it was placed in a vacuum drying oven for 10 h at 60 °C, and cooled down to room temperature to obtain the N-CDs coatings.

2.4. Preparation of Pr/CDs/SSS/PbO$_2$ composite electrode

The preparation of Pr/CDs/SSS/PbO$_2$ composite electrodes was achieved by electrodeposition. Specifically, 250 mL of electrolyte was composed of 5 mM Pr(NO$_3$)$_2$·6H$_2$O, 0.2 M Pb(NO$_3$)$_2$, 0.01 M NaF, and 5 mL (1 wt%) of SSS solution, the prepared N-CDs/PbO$_2$-coated electrodes were used as the anode and the titanium plates with the same dimensions were used as the cathode using a constant-voltage and constant-current DC power supply with a current of 30 mA cm^{-2} for 1 h. As a control group, 1 mM Pr/CDs/SSS/PbO$_2$ composite electrodes were prepared under the same synthesis conditions. The electroplating time was 1 h. As a control group, 1 mM Pr(NO$_3$)$_2$·6H$_2$O, 2 mM Pr(NO$_3$)$_2$·6H$_2$O, 3 mM Pr(NO$_3$)$_2$·6H$_2$O, and 7 mM Pr(NO$_3$)$_2$·6H$_2$O doped Pr/CDs/SSS/PbO$_2$ composite electrodes were prepared under the same synthesis conditions, and were noted as Pr/CDs/SSS/PbO$_2$-1, Pr/CDs/SSS/PbO$_2$-2, Pr/CDs/SSS/PbO$_2$-3, Pr/CDs/SSS/PbO$_2$-5, and Pr/CDs/SSS/PbO$_2$-7, respectively.

S3. Electrocatalytic degradation experiment

Methylene blue (MB) was tested as a model pollutant for degradation, electrocatalytically treating 300 mL of aqueous pollutant solution containing 0.1 M Na$_2$SO$_4$ as well as different concentrations of MB. a Pr/CDs/SSS/PbO$_2$ electrode (3 × 5 cm) was used as an anode, and a Ti plate of the same dimensions as a cathode at a spacing of 3 cm. The effects of MB concentration, current density, and solution pH on the MB degradation.

S4. Characterisation of prepared electrodes

The crystal structure of the electrode was characterised using an X-ray diffractometer (XRD, Bruker D8 Advance, Germany)with a scanning rate of 10° min^{-1} and 10~80°; the micro-size and morphological features of the electrode were observed using a scanning electron microscope (SEM, JSM-6390LV, Japan); the elemental composition and distribution of the electrode were also analysed using nergy-dispersive spectroscopy (EDS) was used to analyse the elemental composition and distribution of the electrodes; X-ray photoelectron spectroscopy (XPS, Thermo

ESCALAB 250 XI, USA) was used to analyse the elemental content and chemical valence of the electrodes.

The electrochemical performance of the prepared electrodes was evaluated at room temperature using an electrochemical workstation (CHI760E). Platinum sheet electrode was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode. All the tests were carried out in 0.2 M Na$_2$SO$_4$ solution, where the cyclic voltammetry curve (CV) was tested in the voltage range of 0~2 V with a scan rate of 100 mV s-1, the steady-state polarisation curve (SCV) was tested in the voltage range of 0~3 V, the electrochemical alternating current impedance spectroscopy (EIS) was performed with an amplitude of 5 mV and a frequency range of 0.01~100 kHz. The CP2K2023.1 code was applied for geometric optimization and energy at the level of Perdew–Burke–Ernzerh of (PBE) method equipped with DZVP-MOLOPT-SR-GTH basic sets. A 400Ry plane wave cutoff for the auxiliary grid was set. A Broyden mixing method was applied to accelerate the convergence to the requested total energy threshold value of10^{-6} Hatree for the total energy difference between two consecutive SCF iteration steps.

S5. Methods of analysis

During the electrolysis process, samples were taken at 30 min intervals, about 5 mL each time, and finally the degradation efficiency of MB was tested at 664 nm using a UV-visible spectrophotometer (UV-3600Plus) with the following **Eq. S1**:

$$\eta_{MB} = \left(A_0 - A_t \right)/A_0 \times 100\%$$

(S1)

where A_0 and A_t represent the absorbance of MB at the initial time and t moment, respectively, and η_{MB} represents the degradation rate of MB.

The kinetics were fitted based on the change in MB concentration during catalytic oxidation, which obeyed the approximate first-order reaction kinetics:

$$\ln \frac{C_0}{C_t} = kt$$

(S2)

where C_0 and C_t (mg L^{-1}) refer to the pollutant concentration at the initial and t

moments, respectively, and k (min⁻¹) represents the reaction rate constant.

The total organic carbon (TOC) values of the pollutants were obtained by testing with a TOC analyser (Vario TOC select, Germany), and their mineralisation efficiency (MCE) was calculated by the following **Eq. S3**[1]:

$$MCE = \frac{\Delta(TOC)_{\exp}}{\Delta(TOC)_{theor}}$$
(S3)

where $\Delta(TOC)_{exp}$ and $\Delta(TOC)_{theor}$ (mg L⁻¹) represent the actual and theoretical TOC removal obtained during the reaction, respectively. Assuming that all the consumed electrical energy is used for the mineralisation of MB, the reaction equation is as follows:

$$C_{16}H_{18}N_3ClS + 34H_2O \rightarrow 16CO_2 + \frac{3}{2}N_2 + SO_2 + HCl + 51H^+ + 51e^-$$
(S4)
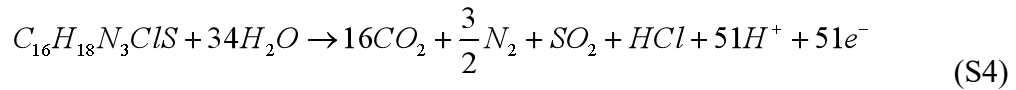
Therefore, the theoretical TOC value can be calculated by the following **Eq. S5**[2]:

$$\Delta(TOC)_{theor} = \frac{\frac{It}{n_eF}n_cM \times 10^3}{V}$$
(S5)

where I (A) refers to the applied current, t (s) represents the electrolysis time, n_e represents the number of electrons transferred in the reaction of equation (3), F (96485 C mol⁻¹) represents Faraday's constant, n_c represents the number of carbon atoms in the target pollutant, M (12 g mol⁻¹) represents the molar mass of elemental C, and V (L) represents the solution volume.

In addition, the energy consumption during electrolysis can be calculated using the following **Eq. S6**[3]:

$$E_c = \frac{U_{cell}It}{V \lg(TOC_0 / TOC_t)}$$
(S6)

where E_c (kWh L⁻¹) is the energy consumption during electrolysis, U_{cell} (V) is the electric field potential, I (A) is the applied current, t (s) is the reaction time, V (L) refers to the solution volume, and TOC_0 and TOC_t refer to the TOC values at the initial and t moments, respectively.

Plotting of MB standard curve

100 mg of MB was dissolved in 100 mL of deionised water to configure a standard solution of 100 mg L^{-1}, which was then diluted to 2.5, 5, 15, and 20 mg L^{-1}, and the absorbance values were tested at 664 nm using a cuvette with a luminous range of 10 nm, and deionised water as the reference solution, as shown in **Table S1**, and the standard curve of MB is shown in **Fig. S1**
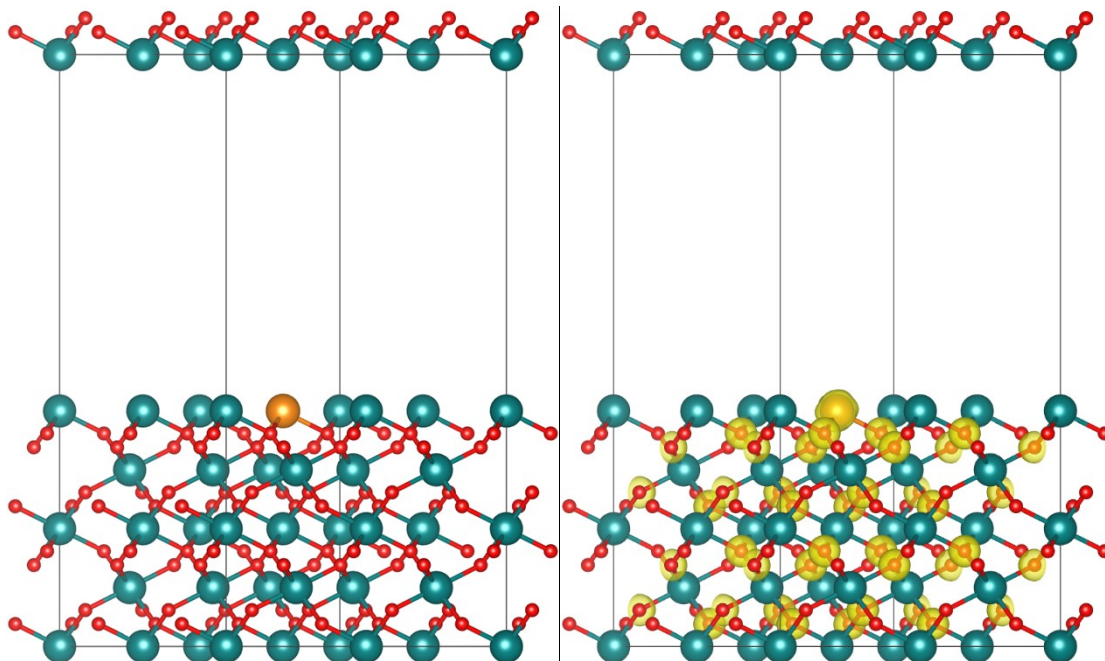
The standard curve of MB is shown in **Fig. S1**, and the standard curve equation is shown in **Eq. S7**:
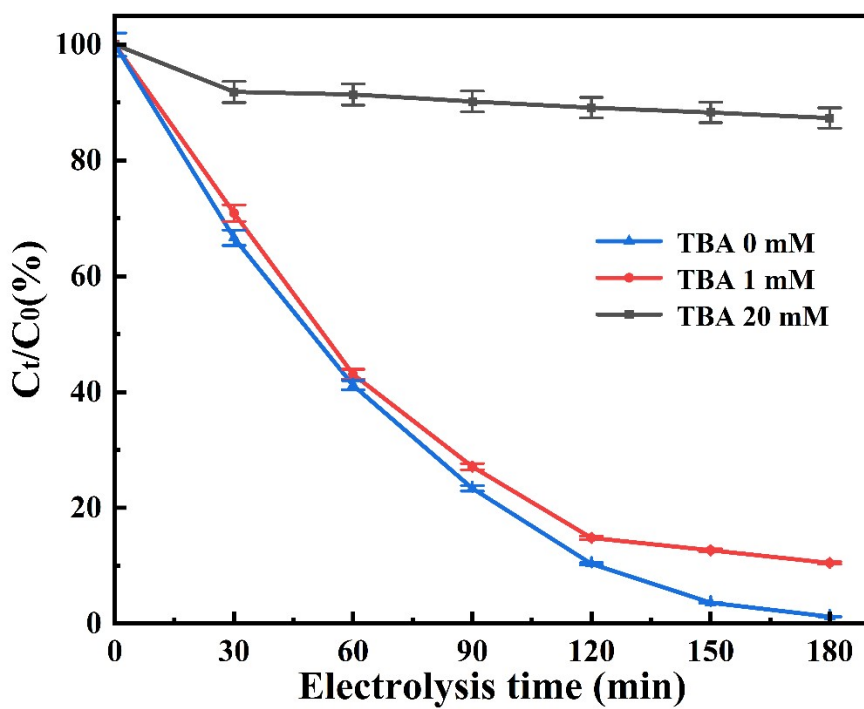
$$A = 0.15287c + 0.24068 \tag{S7}$$

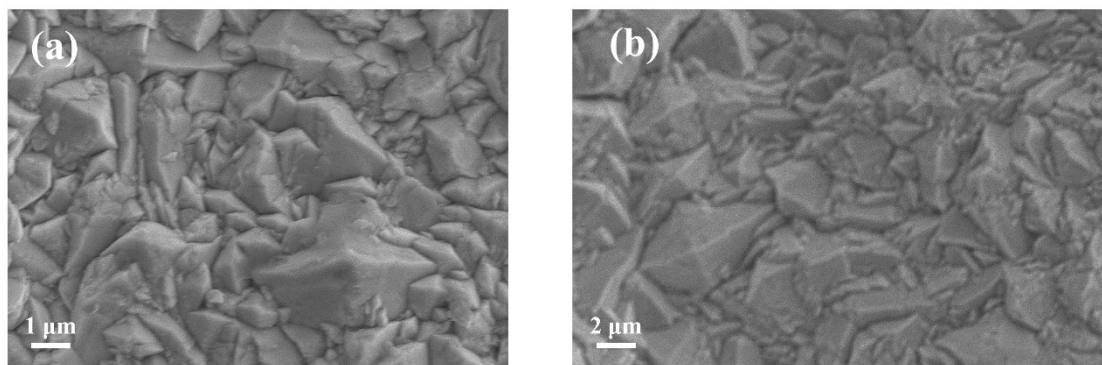where A is the absorbance, c is the solution concentration, and $R^2 = 0.99813$.
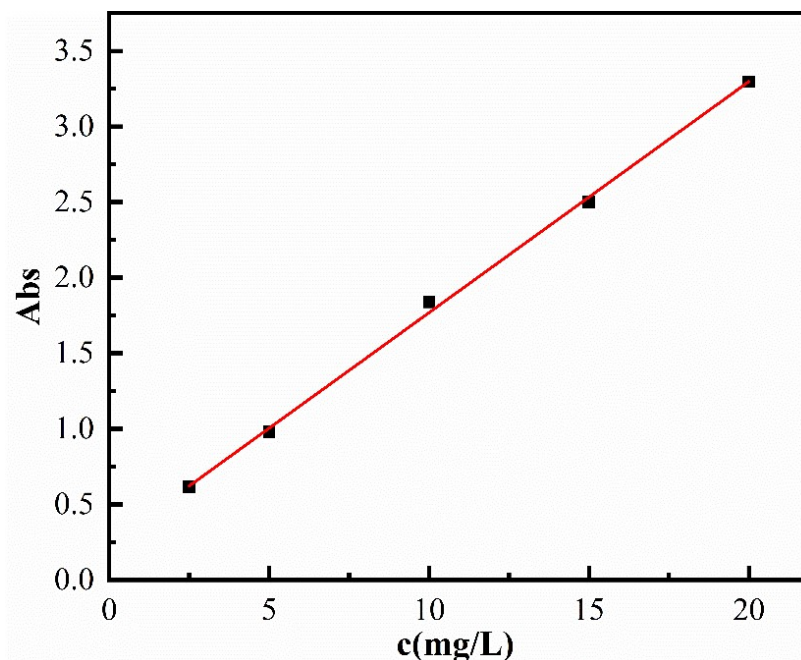
Fig. S1 Standard curve of MB.

Fig. S2 The hybrid model constructed with (1 0 1) face of β-PbO2 and Pr atom, and (b) Charge density of Pr doping PbO_2、PBE // DZVP-MOLOPT-SR-GTH.

Fig. S3. The effect of TBA on electrocatalytic degradation of MB

Fig. S4. SEM images of (a) fresh Pr/CDs/SSS/PbO$_2$ and (b) recovered Pr/CDs/SSS/PbO$_2$ after 10 cycles.

Table S1 MB standard curve data

Name	C (mg L^{-1})	Absorbance (A)
1	2.5	0.615
2	5	0.797
3	10	1.839
4	15	2.500
5	20	3.296

Table S2 Degradation efficiency and calculated approximate first order kinetic rate constants for MB at different Pr doping concentrations (t = 180 min).

Pr doping concentration / Mm L^{-1}	0	1	2	3	5	7
η_{MB} / %	92.1	89.5	93.5	97.8	98.2	92.5
$k \times 10^3$ / min^{-1}	14.53	12.87	16.6	22.25	24.63	14.84
R^2	0.982	0.996	0.993	0.970	0.954	0.991

Table S3 Degradation efficiency and calculated approximate first order kinetic rate constants for MB at different MB concentrations (t = 180 min).

MB concentration / mg L^{-1}	50	100	150	200
η_{MB} / %	98.2	96.5	94.5	87
$k \times 10^3$ / min^{-1}	22.61	19.19	16.39	11.4
R^2	0.990	0.991	0.973	0.994

Table S4 Degradation efficiency and calculated approximate first order kinetic rate constants for MB at different current densities (t = 180 min).

Current density / mA cm^2	5	15	30	45
η_{MB} / %	76.7	84.6	96.5	99.4
$k \times 10^3$ / min^{-1}	7.86	10.65	19.19	27.13
R^2	0.993	0.992	0.991	0.936

Table S5 Degradation efficiency and calculated approximate first order kinetic rate constants for MB at different pH (t = 180 min).

pH	3	5	7	9	11
η_{MB} / %	90.6	98.8	92.5	91	86
$k \times 10^3$ / min^{-1}	13.9	24.63	15.63	14.46	11.56
R^2	0.990	0.954	0.965	0.974	0.976

Table S6 TOC Removal, Mineralisation Efficiency and Energy Consumption for the degradation process of MB by pure PbO_2 electrodes and Pr/CDs/SSS/PbO_2 electrodes (t = 180 min).

Name	PbO_2	Pr/CDs/SSS/PbO_2
TOC Removal / %	45.1	58.0
Mineralisation Efficiency / %	3.44	6.02
Energy Consumption / kWh L^{-1}	80.08	55.37

Table S7

Content of Pb ions in solution during degradation of azo wastewater by Pr/CDs/SSS/PbO_2 electrode

Name	Pb level/(μg L^{-1})
Rhodamine B	118.6
Methyl orange	117.8
Acidic Red	115.9
Methyl violet	118.3

References

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