Electronic Supplementary Information

Highly effective Electrosynthesis of Hydrogen Peroxide from Oxygen on Redox-active Cationic Covalent Triazine Network

Lan-Zhen Peng,^{‡a,b} Pei Liu,^{‡b,c} Qing-Qing Cheng,^b Wen-Jing Hu,^b Yahu A. Liu,^d Jiu-Sheng Li,^b Biao Jiang,^b Xue-Shun Jia,^a Hui Yang^{*,b,c} and Ke Wen^{*,b,c}

^a Department of Chemistry, Shanghai University, Shanghai 200444, China

^b Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China. Emails:

yangh@sari.ac.cn, wenk@sari.ac.cn,

^c School of Physical Science of Technology, ShanghaiTech University, Shanghai 201210, China

^d Medicinal Chemistry, ChemBridge Research Laboratories, San Diego, CA 92127, USA

1. Physical Characterization

Solvents and reagents were purchased from Energy Chemical or Sinopharm Chemical Reagent Co., Ltd without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker Avance-III NMR Spectrometer or a 500 MHz one. The FT-IR spectra were obtained on a PerkinElmer Spectrum Two FT-IR spectrometer using attenuated total reflection (ATR) technique. The ¹³C Cross-Polarization Magic Angle Spinning (CP-MAS) NMR spectra were performed on a Bruker ASX 500 MHz at 125.8 MHz and a MAS frequency of 25 kHz. Thermogravimetric analysis (TGA) was carried out on a SDT Q600 thermogravimetric analyzer, and the samples were heated to 1000 °C at a rate of 10 °C min⁻¹ under nitrogen atmosphere.

The scanning electron microscopy (SEM) and energy dispersive X-ray absorption spectroscopy (EDS) analyses were conducted on a Hitachi S-4800 cold-cathode field-emission scanning electron microscopy (FE-SEM) at 2.0 KeV -10.0 KeV. Bruker AXS D8 ADVANCE X-ray diffractometer with a Cu K_{α} ($\lambda = 1.5418$ Å) radiation source operated at 40 kV and 40 mA were used to collect Powder X-ray diffraction (XRD). Diffraction patterns were collected at a scanning rate of 2° per min with a step size of 0.02°. Nitrogen adsorption/desorption isotherms were measured by a JW-BK122W Area and Pore Size Distribution Analyzer at 77K after the samples were degassed at 120 °C for 24 h under vacuum. Specific surface areas were determined through Brunauer-Emmett-Teller (BET) model, and pore size distributions (PSDs) were calculated using Barret-Joyner-Halenda (BJH) theory. X-ray Photoelectron Spectroscopy (XPS) was used to collect on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with the monochromatic Al K_{α} source (12 kV, 4 mA, h = 1486.6 eV) under ultrahigh vacuum (10^{-7} Pa), referenced to the C 1s signal at 284.6 eV. EPR spectra were recorded on a JES FA200 EPR spectrometer. Elemental analysis (C, H, N) was carried out on an elementar vario MICRO cube Elemental Analyzer.

2. Electrochemical measurements

The working electrode was prepared and the electrocatalytic activity and selectivity of H_2O_2 were evaluated, referenced to our previous report.¹ The catalyst ink was prepared by mixing cCTF:Cl⁻ catalyst (12 mg), water (0.6 mL), isopropanol (0.3 mL), and Nafion solution (10 wt%, 0.1 mL), followed by ultrasonication. Then, 10 µL of dispersion was dropped onto the pre-polished RDE or RRDE and left to air dry overnight at room temperature. The linear sweep voltammetry (LSV) curves were recorded in O₂-saturated 0.1 M KOH solution with different rotating speeds and at a scan rate of 10 mV s⁻¹. All electrochemical measurements were performed using a CHI 730E workstation. The glass carbon and Ag/AgCl were used as the counter and reference electrodes, respectively.

The Koutecky–Levich (K-L) plots were carried out at different rotating speeds and electron transfer numbers were obtained by the K-L equation:

$$I^{-1} = I_k^{-1} + (0.62nFC_{O2}D_{O2}^{2/3}\gamma^{-1/6})^{-1}\omega^{-1/2}$$

where *I* is the measured current, I_k is the kinetic current, n is the number of transferred electrons, F is the Faraday constant (96,500 C mol⁻¹), C_{O2} is the concentration of oxygen (1.2 × 10⁻⁶ mol cm⁻³), D_{O2} is the diffusion coefficient of oxygen (1.9 × 10⁻⁵ cm² s⁻¹), γ is the kinematic viscosity (0.011 cm² s⁻¹) in 0.1 M KOH solution and ω (rad/s) is the rotating speed of the electrode.

Hydrogen peroxide selectivity and electron transfer number (n) were calculated based on RRDE measurement using the following equations:

$$H_2O_2$$
 (%) =200 $j_r/(N j_d+j_r)$
 $n=4j_d/(j_d+j_r/N)$

Where j_d is the disk current, j_r is the ring current, and N (N= 0.34) is the collection efficiency which was corrected under the same electrochemical conditions with Fe^{2+}/Fe^{3+} couple.² A potential of the ring electrode was maintained at 1.4 V/RHE promising the ring positive current.

3. Experiment Section

3.1. Synthesis the cCTN:Cl- catalyst and characterization

A mixture of 2,4,6-tris(4-aminophenyl)-1,3,5-triazine $(TAPT)^3$ (354.0 mg, 1.0 mmol) with 1,1'-bis(4-cyanophenyl)-[4,4'-bipyridine]-1,1'-diiumdichloride $(DNP^{++}-2CI^{-})^4$ (841.5 mg, 1.5 mmol) in a mixed solvent of MeCN and H₂O (50 mL, 10:1, v/v) in a sealed tube was sonicated for 30 min, then the reaction kettle was sealed off and heated at 120 °C for 72 h (Scheme S1). After cooling down naturally to room temperature, a reddish brown precipitate was collected by filtration and washed with THF, and dried at 120 °C under vacuum to afford cCTN:Cl⁻ (0.71 g, 59.2%).



Scheme S1. Synthesis of the cationic viologen-based redox-active covalent triazine networks via Zincke reaction under solvothermal condition.



Fig. S1. ¹³C CP/MAS solid state NMR spectrum of cCTN:Cl⁻.



Fig. S2. Thermogravimetric analysis of TAPT, DNP⁺⁺-2Cl⁻, cCTN:Cl⁻ under nitrogen.



Fig. S3. Field-Emission Scanning Electron Microscopy (FE-SEM) image of cCTN:Cl⁻ (A) powder morphology; (B) supernatant acetonitrile solution of cCTN:Cl-, which was dispersed by ultrasonication; (C) and (D)high-resolution TEM of cCTN:Cl⁻.



Fig. S4. PXRD pattern of cCTN:Cl⁻, indicated that the morphology is amorphous.



Fig. S5. (A) XPS survey spectrum of cCTN:Cl⁻, (B) High-resolution XPS spectra of C 1s, (C) N 1s; (D) Cl 2p for cCTN:Cl⁻. The N1s spetra for cCTN:Cl⁻ are deconvoluted to four peaks. The peaks located at 398.3 and 399.7 eV are belong to the triazine ring and some reduced viologen species; the peaks of Quanternary-N are assigned to the nitrogen atom of dicationic viologen moieties; the N-oxide peaks of 405.7 eV are originated from the nitrogen groups.



Fig. S6. The EDS elemental mapping of cCTN:Cl⁻ showed the ions were dispersed evenly.



Fig. S7. (A) N_2 adsorption isotherm of cCTN:Cl⁻ at 77K; (B) Pore size distribution of cCTN:Cl⁻ from N_2 adsorption isotherm using Barrett-Joyner-Halenda (BJH) theory.



Fig. S8 (A) CV of cCTFs in N₂-saturated 0.1M KOH solution at different scan rates (B) CV of cCTFs in O₂-saturated 0.1M KOH solution at a scan rate of 50 mV S⁻¹; (C) Polarization curves of the ORR on cCTN:Cl⁻ and cCTFs at 1600 rpm in O₂-saturated 0.1 M KOH solution (solid lines) and the ring current for H₂O₂ production (dash lines); (D) H₂O₂ selectivity and electron transfer number of the ORR on the electrocatalysts of cCTN:Cl⁻, cCTFs, respectively. These results demonstrate that the material made by the ionothermal method have the more positive onset potential for ORR activity (0.80 V vs. RHE) than cCTN:Cl⁻'s onset potential (0.75 V vs. RHE), but the selectivity (~70%) is much lower than cCTN:Cl⁻ (~85%) toward ORR to produce H₂O₂ in alkaline solution.



Fig. S9. (A) XPS survey spectrum of cCTN:Cl⁻; (B) High-resolution XPS spectra of C 1s, (C) N 1s; (D) Cl 2p for cCTN:Cl⁻ after 8 h stability test.

Table S1.	Combustion	elemental	analysis	of	cCTN	J: (Cl
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Theoretical value				Elemental analysis			
	C%	N%	H%	C%	N%	H%	
Calc. C ₃₆ H ₂₅ Cl ₃ N ₆	66.73	12.97	3.89	55.51	13.30	4.69	

References

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