

Enhanced Water Oxidation of CoP/CNTs via Interfacial Charge Transfer

Induced by Poly Dimethyl Diallyl Ammonium Chloride

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1. Experimental section

1.1. Reagents and Solutions.

Commercial multiwalled carbon nanotubes (CNTs) was purchased from Beijing Deke Daojin Science And Technology Co., Ltd (<http://www.dknano.com>). Poly-(dimethyl diallyl ammonium chloride) (PDDA, Mw 400,000-500,000, 20 wt.%) and CoCl_2 were purchased from Shanghai Macklin Biochemical Co., Ltd. All other chemicals were of analytical reagents grade and used without further purification. Ultra-pure water ($18.25 \text{ M}\Omega\cdot\text{cm}$, $25 \text{ }^\circ\text{C}$) was used for the whole experiment.

1.2. Equipment.

All electrochemical measurements were performed on a CHI 760D electrochemical workstation (Shanghai CH Instruments Co., China). Electrochemical impedance spectroscopy (EIS) was obtained from the impedance measurement unit (IM6e, ZAHNER elektrik, Germany). Scanning electron microscope (SEM) was recorded by JSM-6700F microscope (Japan). High-resolution transmission electron microscopy (HRTEM) was recorded from using a Talos F200x (Thermo Fischer) (Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was obtained from Thermo ESCALAB 250XI XPS (American). X-Ray Diffraction (XRD) was recorded from (XRD Focuss D8 Brooke AXS Co. Ltd., Germany). Raman spectroscopy was conducted with a Raman spectrometer (Renishaw InVia). Fourier transform infrared spectroscopy (FT-IR) was recorded from FT-1760X (Waters, American). The zeta potential measurements were performed with a dynamic light scattering instrument (SZ-100, Horiba, Kyoto, Japan).

1.3. Preparation of PDDA@CNTs

To synthesize PDDA@CNTs, the commercial CNTs were firstly refluxed in concentrated nitric acid to obtain -COOH functional CNT. CNTs were obtained through centrifugation and washing with water until near neutral and vacuum dried at 60 °C. Then 150 mg of CNTs were dispersed in 50 mL H₂O with ultrasonication for 1 h. Subsequently, 10 mL 2mg·mL⁻¹ PDDA solution dispersed in water was added to the above solution. After sonication for 30 min, PDDA@CNTs were finally obtained *via* vacuum-filtration, washing with water and dried at 60 °C.

1.4. Preparation of CoP/PDDA@CNTs hybrid catalysts

According to the previous report with a little modification,¹ 20 mg of PDDA@CNTs was dispersed in 20 mL of water with ultrasonication for 1 h. Subsequently, 2 mL of CoCl₂ aqueous solution (10 mM) and 1 mL of NaH₂PO₂ solution (15 mg·mL⁻¹) were added to the above solution under stirring, respectively. After 30 min, 4 mL of NaBH₄ aqueous solution (0.1 M) was added dropwise under stirring for 20 min. Finally, CoP/PDDA@CNTs were obtained after centrifugation and washing with water/ethanol thoroughly and drying at 60 °C. CoP/CNTs and CoP PDDA were also prepared through the similar method without the addition of PDDA and CNTs, respectively.

1.5 Electrochemical measurements

Electrochemical measurements were performed with a three-electrode setup with a saturated calomel electrode (SCE) as the reference electrode and a platinum electrode as the counter electrode, a glassy carbon electrode (GCE, 0.1256 cm²) as the

working electrode. The catalyst suspension was prepared by dispersing 5 mg of various catalysts into 1 mL of the mixed solvent containing 200 μL of water, 800 μL of ethanol and 20 μL of 5% Nafion. For the preparation of the catalytic electrodes, 5 μL of the catalyst suspension was dropped onto GCE and dried at room temperature naturally. Linear sweep voltammetry (LSV) was employed to investigate the OER activities of various electrodes with a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$ in 1 M KOH. All data were corrected for iR loss unless otherwise noted. The catalytic stability of the electrodes was recorded as a function of reaction time. Before the electrochemical test, $E_{(\text{RHE})} = E_{(\text{SCE})} + 0.0591\text{pH} + 0.24$.

Electrochemical double-layer capacitance (C_{dl}) was determined from cyclic voltammograms measured in a non-Faradaic region at different scan rates ($\nu = 40, 60, 80, 100$ and $120 \text{ mV}\cdot\text{s}^{-1}$) in the potential range 1.2 to 1.55 V versus SCE.² The current differences at 1.275 V against scan rates were fitted to obtain the C_{dl} : $C_{\text{dl}} = I_c/\nu$, where C_{dl} , I_c , and ν are the double-layer capacitance ($\text{mF}\cdot\text{cm}^{-2}$) of the electroactive materials, charging current ($\text{mA}\cdot\text{cm}^{-2}$), and scan rate ($\text{mV}\cdot\text{s}^{-1}$).

Electrochemical impedance spectra (EIS) experiments were performed with the three-electrode cell system in 1M KOH. The amplitude of the sinusoidal wave was 10 mV, and the frequency scan range was from 10 kHz to 100 mHz.

2. Result and discussion

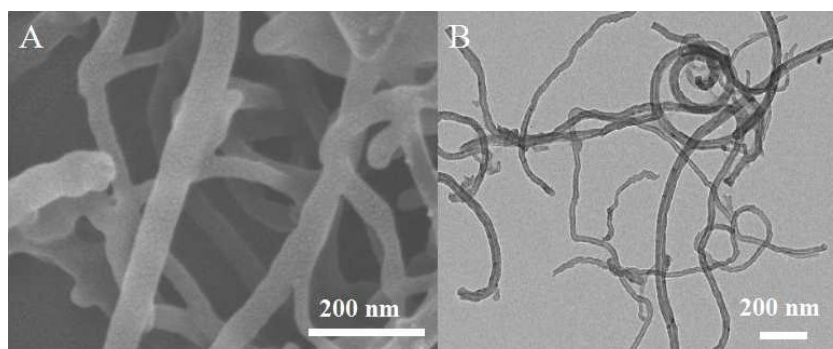


Figure S1 SEM (A) and TEM (B) images of CNTs.

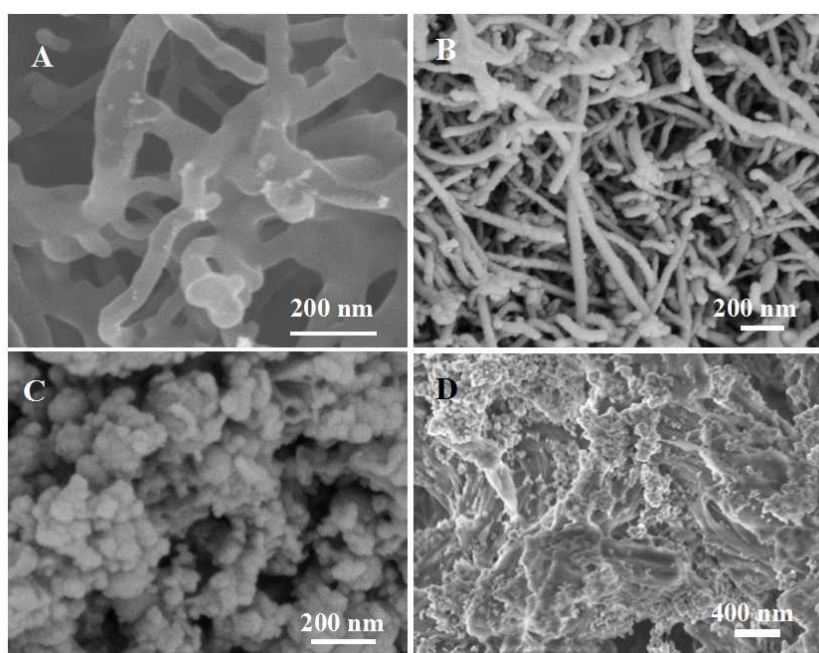


Figure S2 SEM images of PDDA@CNTs (A), CoP/CNTs (B), CoP (C) and CoP/PDDA.

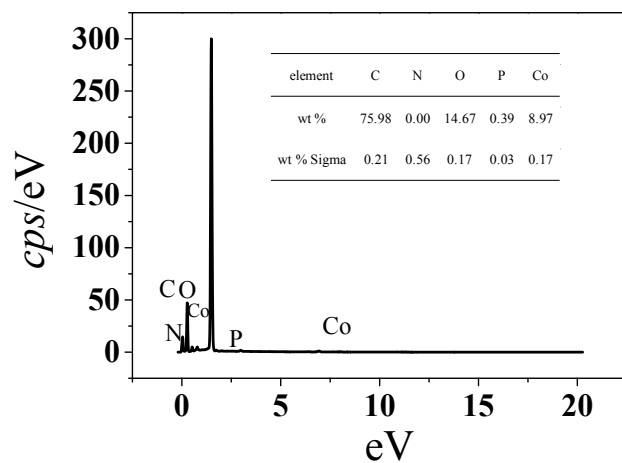


Figure S3 EDS image of CoP/PDDA@CNTs.

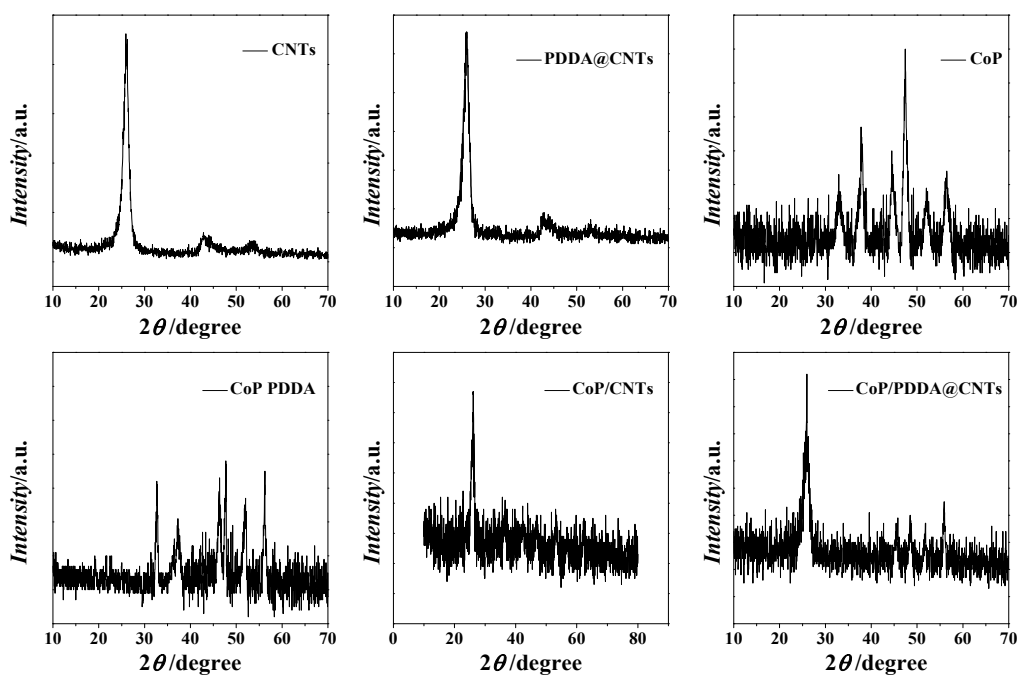


Figure S4 XRD patterns of CNTs, PDDA@CNTs, CoP, CoP/CNTs, CoP PDDA and CoP/PDDA@CNTs.

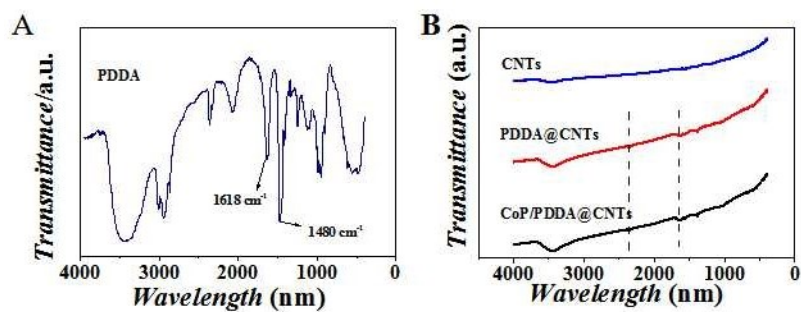


Figure S5 FT-IR spectra of PDDA (A), CNTs, PDDA@CNTs and CoP/PDDA@CNTs (B).

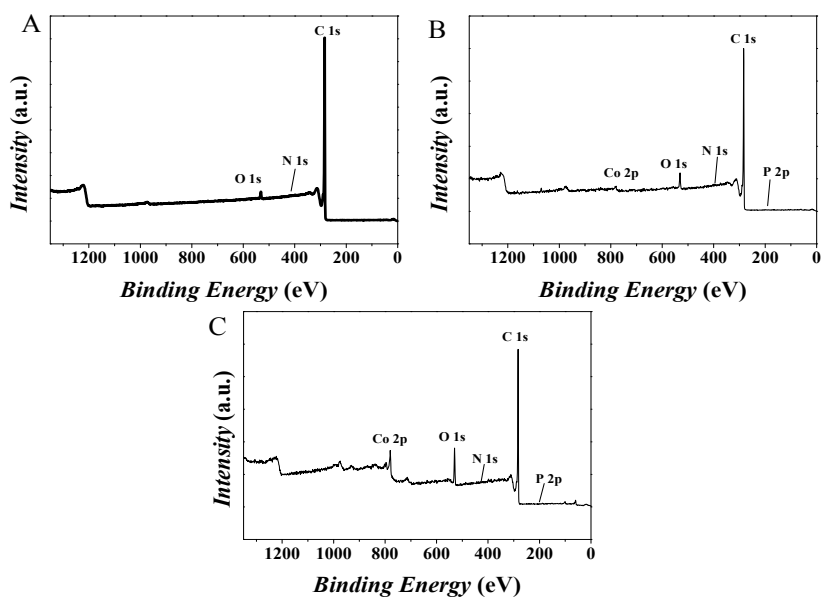


Figure S6 XPS full spectra of PDDA@CNTs (A), CoP/PDDA (B) and CoP/PDDA@CNTs (C).

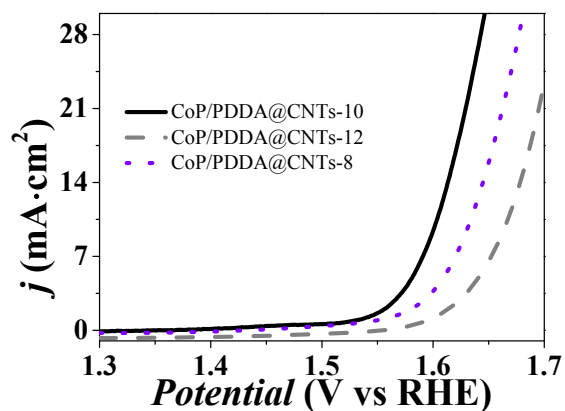


Figure S7 LSV curves of CoP/PDDA@CNTs-8, CoP/PDDA@CNTs-10 and CoP/PDDA@CNTs-12 in 1 M KOH solution.

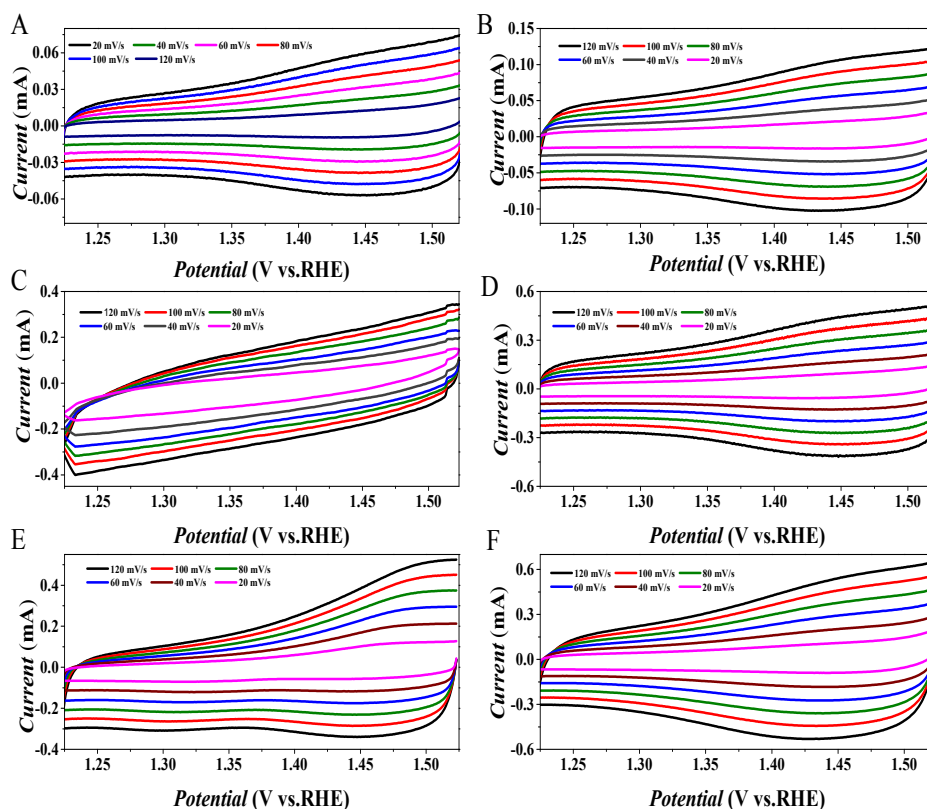


Figure S8 CV curves in potential range of 1.22-1.152 V versus RHE of CNTs (A), PDDA@CNTs (B), CoP (C), CoP/CNTs (D), CoP PDDA (E) and CoP/PDDA@CNTs (F)

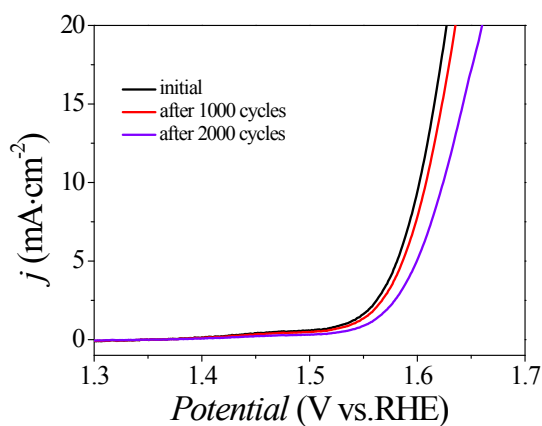


Figure S9 LSV curves of CoP/PDDA@CNTs in 1 M KOH before and after long-term 1000 and 2000 cycles

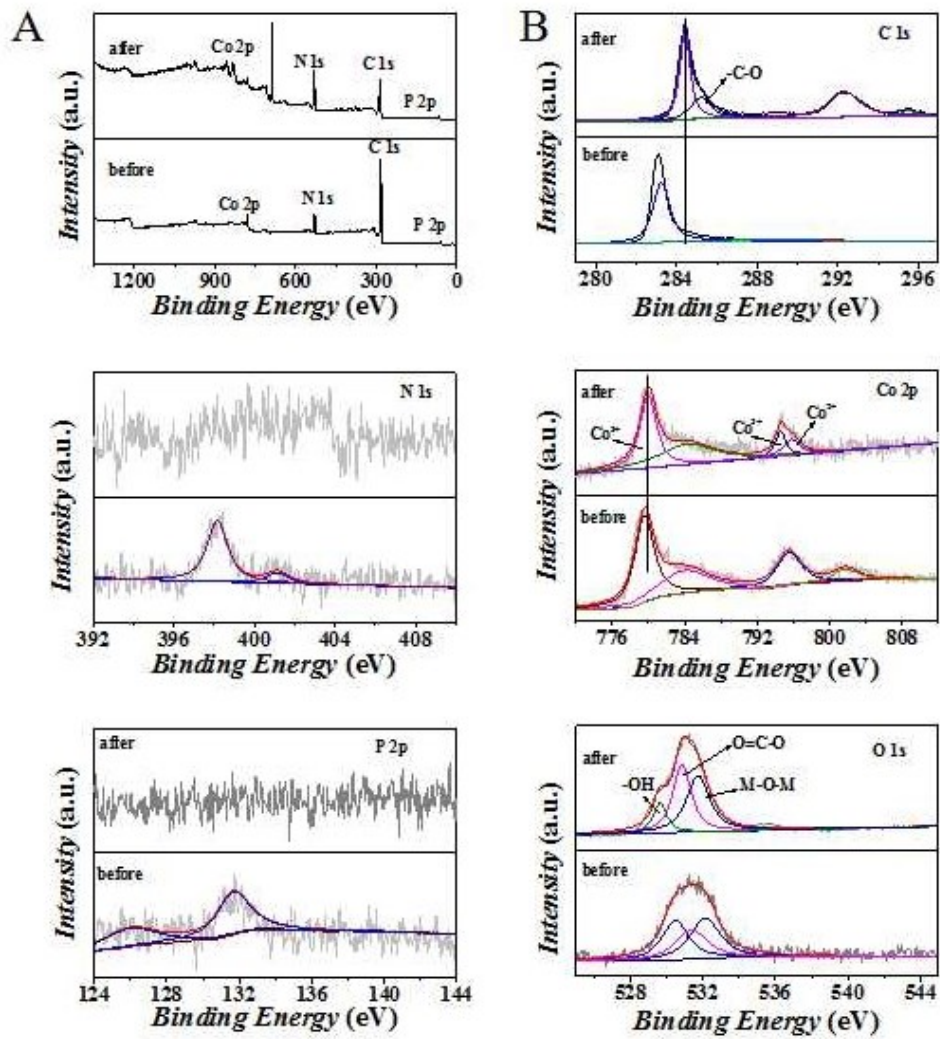


Figure S10 XPS full spectra (A), deconvoluted C 1s (B), N 1s (C), Co 2p (D), P 2p (E) and O 1s (F) XPS spectra of CoP/PDDA@CNTs before and after CV test.

Tabel S1 Electrochemical Catalytic Performance Values of Metal Phosphide Catalysts

materials	Tafel slope $\text{mV} \cdot \text{dec}^{-1}$	overpotential (V) at 10	loading ($\text{mg} \cdot \text{cm}^{-2}$	Refs
	¹	$\text{mA} \cdot \text{cm}^{-2}$	²⁾	
ultrafine CoP-CNT	50	0.330	0.28	²
CoP NPs/C	99	0.34	0.71	³
Co ₂ P/CNTs	68	0.29	0.75	⁴
Co ₂ P/NPCNT	53	0.37	0.75	⁵
CoP/CoP ₂ @NPCNT	58	0.30	0.2	⁶
s				
CoP/PDDA@CNTs	64	0.37	0.28	This work

References

- 1 C. S. Mo, J. H. Jian, J. Li, Z. S. Fang, Z. Zhao, Z. K. Yuan, M. J. Yang, Y. Zhang, L. M. Dai and D. S. Yu, *Energy Environ. Sci.*, 2018, **11**, 3334-3341.
- 3 C. C. Hou, S. Cao, W. F. Fu and Y. Chen, *ACS Appl. Mater. Interfaces*, 2015, **7**, 28412-28419.
- 4 J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu and W. Xing, *ACS Catal.*, 2015, **5**, 6874-6878.
- 5 D. Das and K. K. Nanda, *Nano Energy*, 2016, **30**, 303-311.
- 6 D. Das, A. Das, M. Reghunatha and K. K. Nanda, *Green Chem.*, 2017, **19**, 1327-1335.
- 7 H. Li, S. M. Xu, H. Yan, L. Yang and S. Xu, *Small*, 2018, **14**, 1800367.

