

## Supporting Information

Boosting Electrocatalyzed Hydrogen Evolutions with Electropolymerized Thiophene Substituted  
Co<sup>III</sup>Corroles

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## 1. Experimental Section

### 1.1 General.

All reagents were commercially analytic pure grade and directly used except where noted. All the electrochemical analyses were done in an inert atmosphere by dissolving the products in *o*-DCB containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were obtained using a three-electrode cell on a Chi-730D electrochemistry workstation. The electrodes used in electrochemical measurements were platinum wire ( $\Phi = 0.2$  mm), glassy carbon electrode ( $\Phi = 3$  mm), and Ag/AgCl as a counter, working and reference electrodes, respectively. FTIR-spectra were taken on Nicolet Nexus 470 FT-IR spectrophotometer and UV-Vis absorption spectra were noted on the Shimadzu UV3600 spectrophotometer.

### 1.2 Synthesis of 5,10,15-*meso*-trithiophene-H<sub>3</sub>corrole

2-thiophenealdehyde (5 mmol, 0.5608g) and 1.0 mL concentrated HCl acid were firstly dissolved in 100 mL pure water, and 30 mmol freshly distilled pyrrole (2.1 mL) was slowly added. The mixture was stirred at room temperature over 30 mins, then, mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub> (40 mL X 3) and dried by Na<sub>2</sub>SO<sub>4</sub>. After removal of organic solvent. The target compound was successfully obtained as a light-yellow solid-state compound in 81.2% yield (927 mg). *meso*-Thiophene-dipyrromethane (2 mmol, 0.4566g), 2-thiophenealdehyde (1.0 mmol, 0.1122 g) were dissolved in a mixed solvents containing 50 mL MeOH and 50 mL 5% HCl solution, and stirred at room temperature over 1h. After extracted by CH<sub>2</sub>Cl<sub>2</sub> (20mL X 3), chloranil was added (3 mmol, 0.7388 g) and the mixture was refluxed at 55°C for 4h. after removal of organic solvent, the residue was purified by silica gel column (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give the pure H<sub>3</sub>-*meso*-trithiophene-Corrole in a 47.8% yield (260 mg).



## 2. HR-ESI-mass spectra

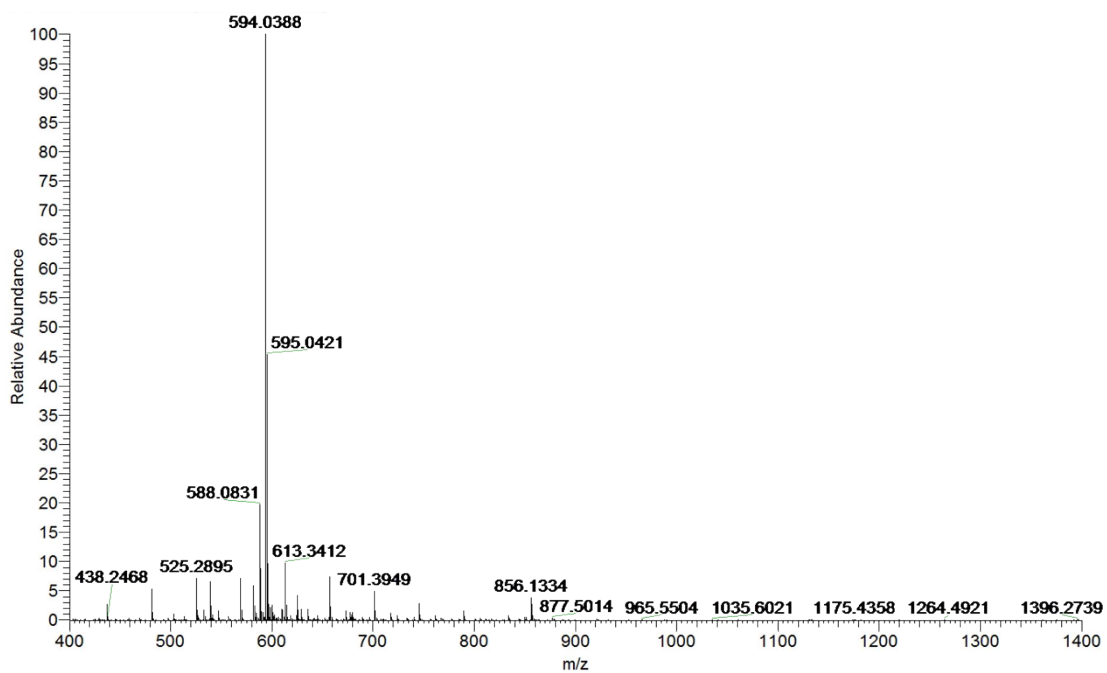
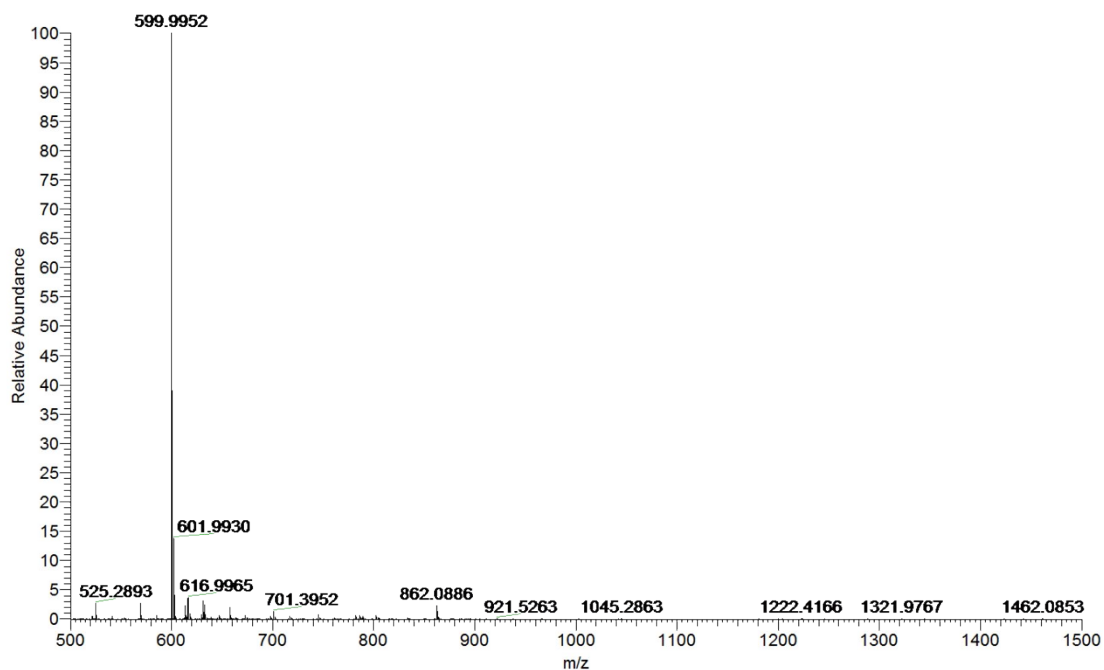


Figure S1 High-resolution mass spectra of **1a** (top) and **1b** (bottom).

### 3. $^1\text{H}$ NMR spectra

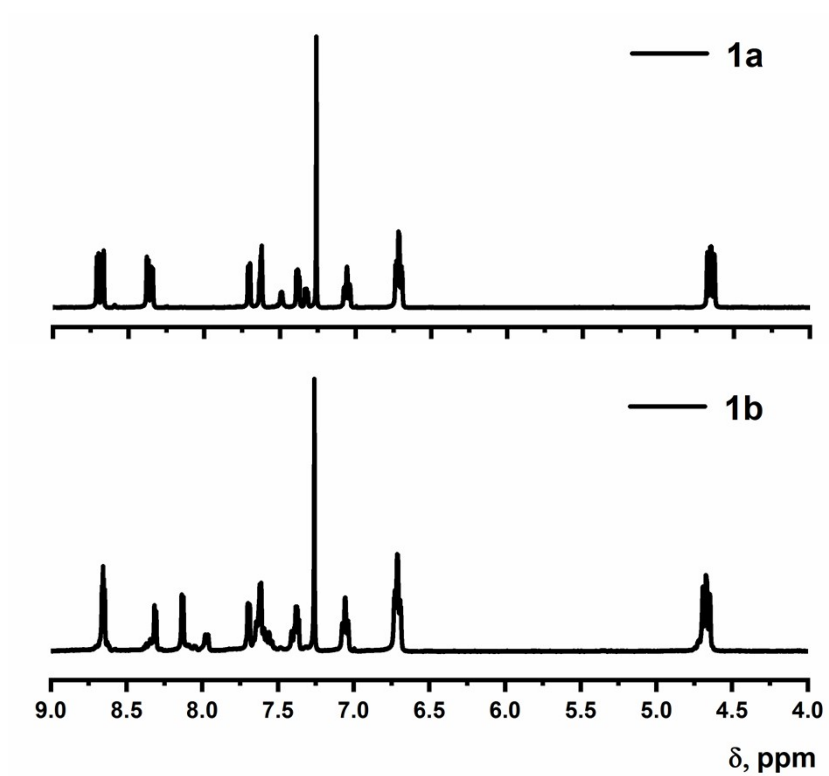


Figure S2  $^1\text{H}$  NMR spectra of 1a (top) and 1b (bottom) in  $\text{CDCl}_3$ .

#### 4. UV-vis absorption spectra

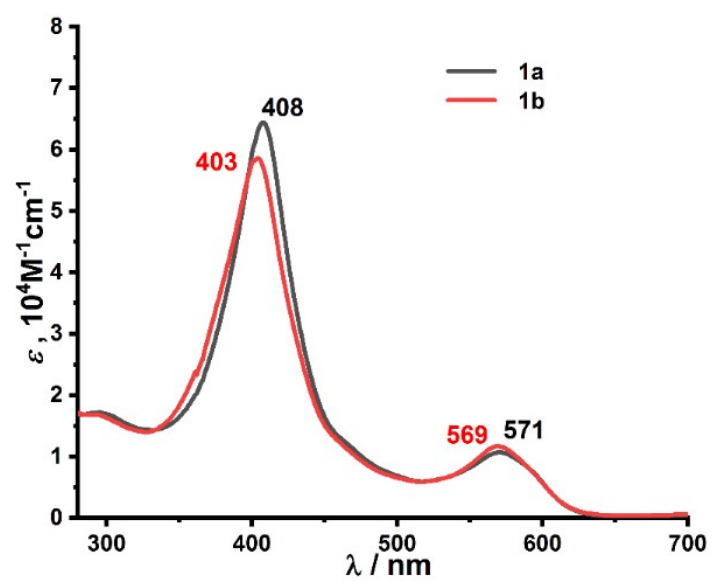


Figure S3 UV-vis absorption spectra of Co<sup>III</sup>corroles **1a** (black) and **1b** (red) in CH<sub>2</sub>Cl<sub>2</sub>.

## 5. Electrochemistry

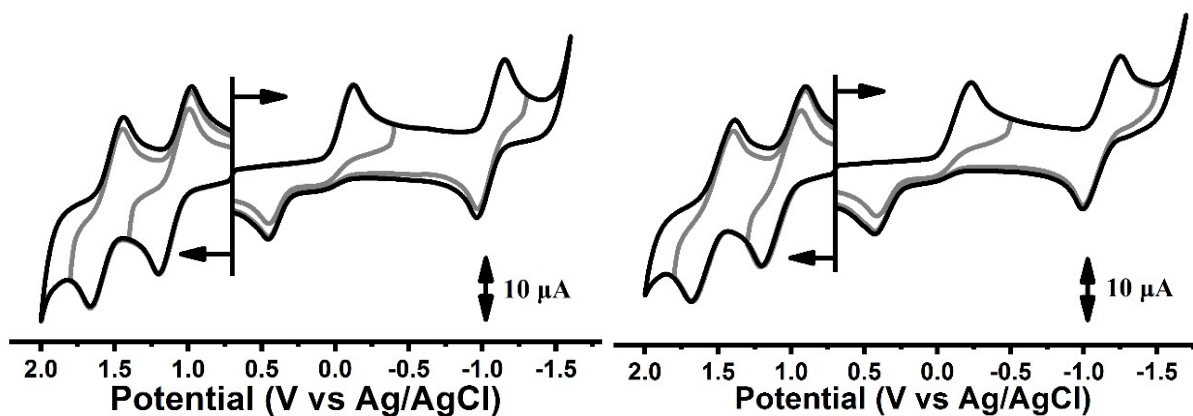


Figure S4 CV curves of Co<sup>III</sup>corroles **1a** (left) and **1b** (right) in *o*-dichlorobenzene (*o*-DCB) with 0.1M TBAP.

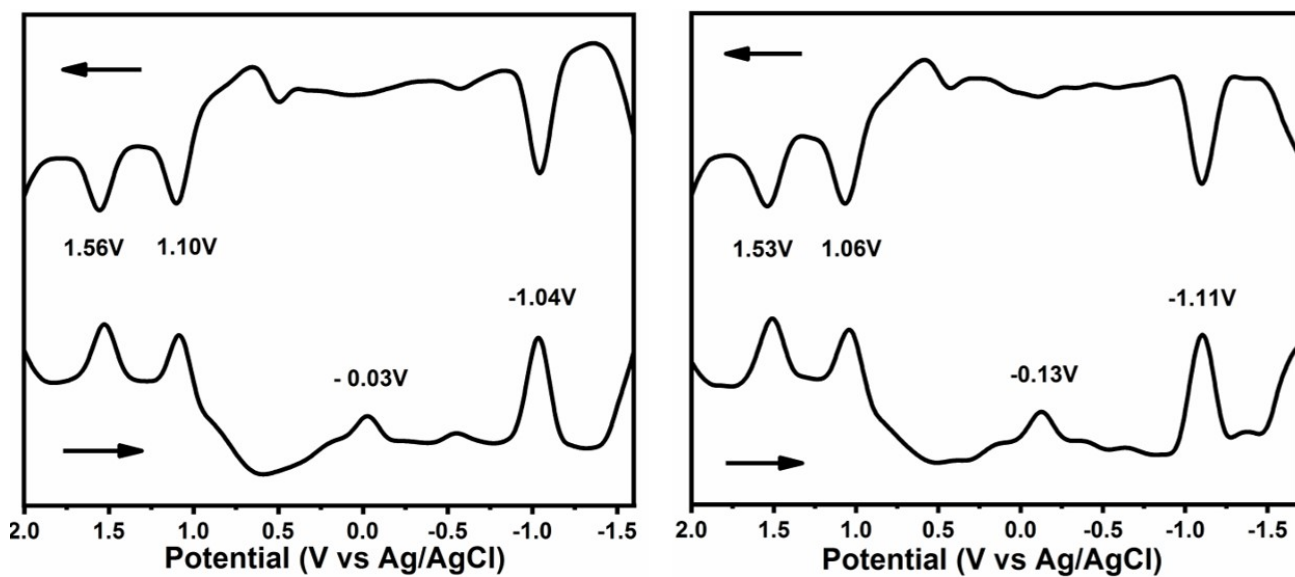


Figure S5 DPV measurements of **1a** (left) and **1b** (right) in *o*-DCB containing 0.1M TBAP.

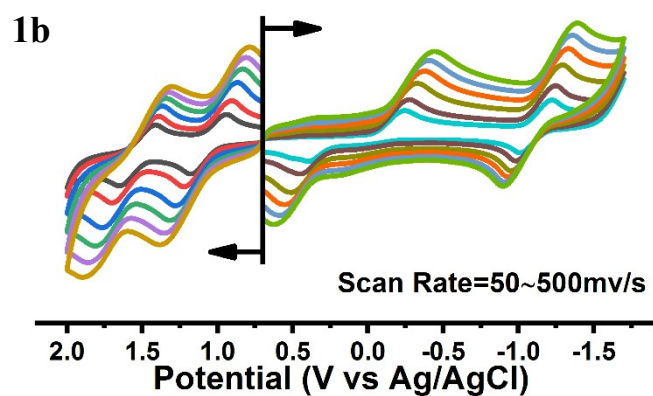
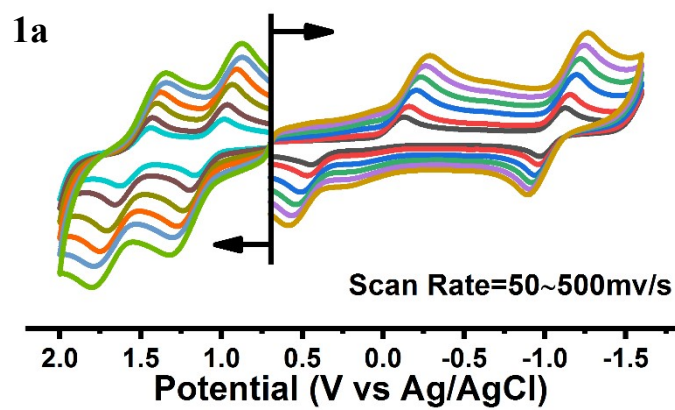


Figure S6 The CV measurements of **1a** and **1b** in *o*-dichlorobenzene (oDCB) containing 0.1 M TBAP under scanning speed from 50 to 500 mV/s



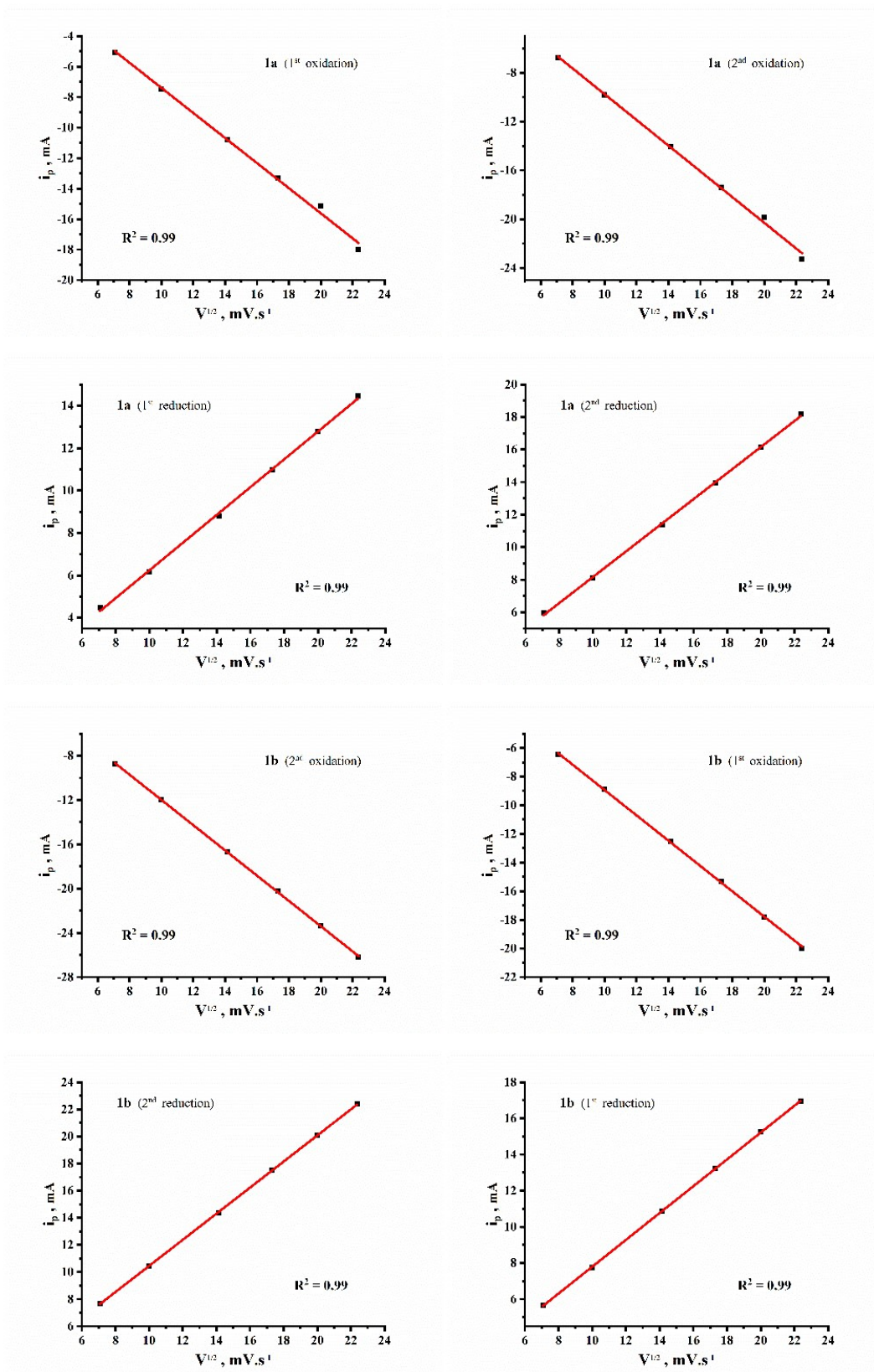


Figure S7 The dependence of square root of the scan-rate ( $v^{1/2}$ ) vs the peak current ( $i_p$ ) of **1a** in oDCB containing 0.1 M TBAP

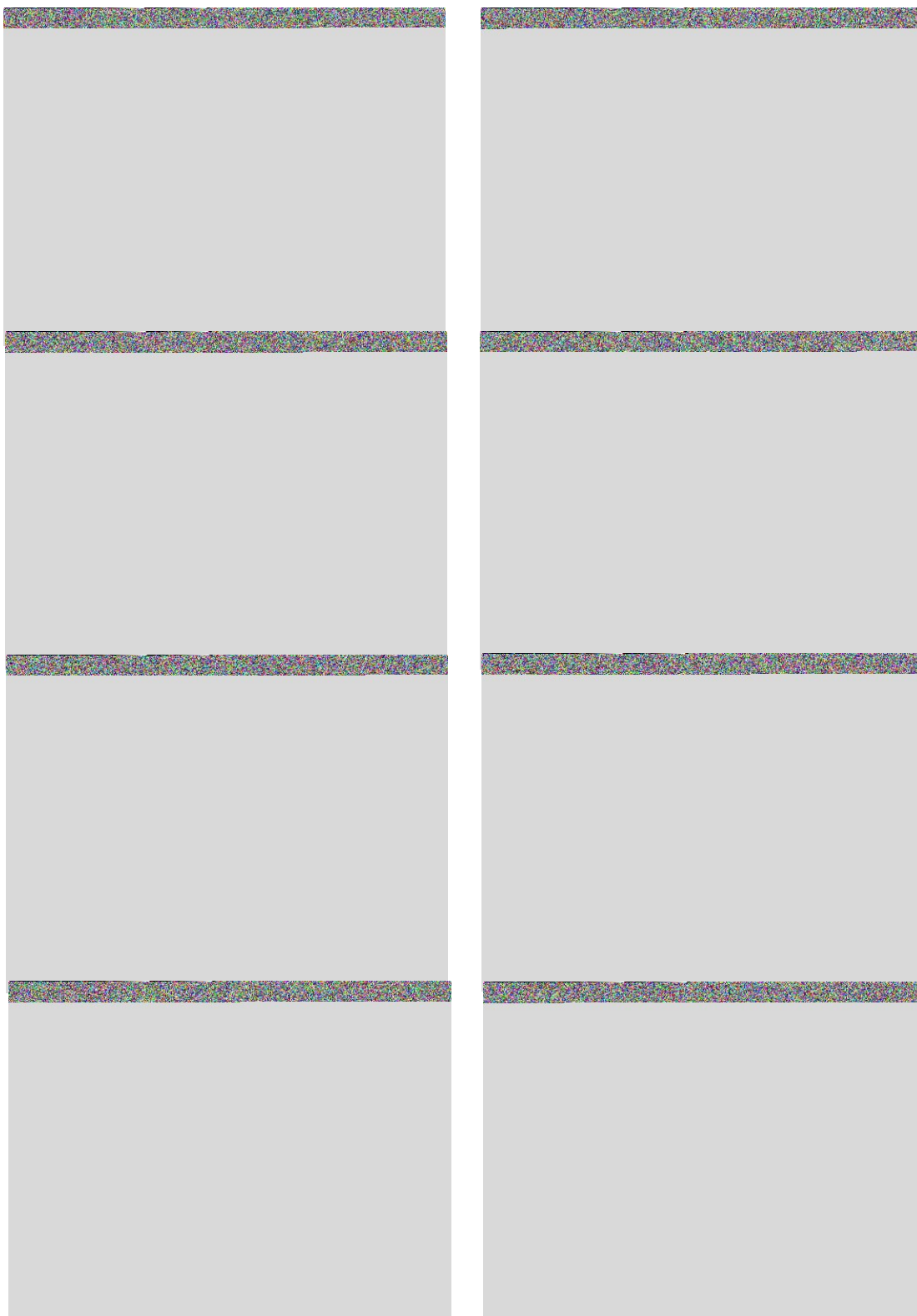


Figure S8 The dependence of square root of the scan-rate ( $v^{1/2}$ ) vs the peak current ( $i_p$ ) of **1b** in oDCB containing 0.1 M TBAP.

## 6. Photographs

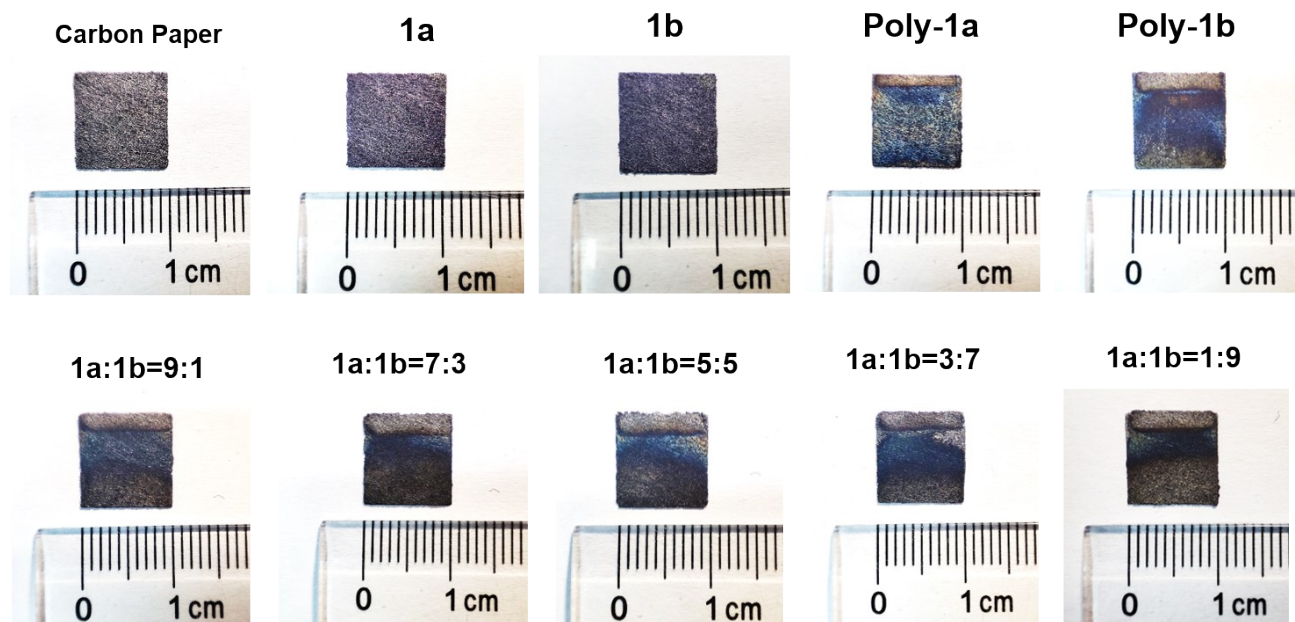


Figure S9 The photographs of carbon paper, direct deposition of **1a** and **1b**, electropolymerized **1a**, **1b** and co-polymers.

## 7. Raman Spectra

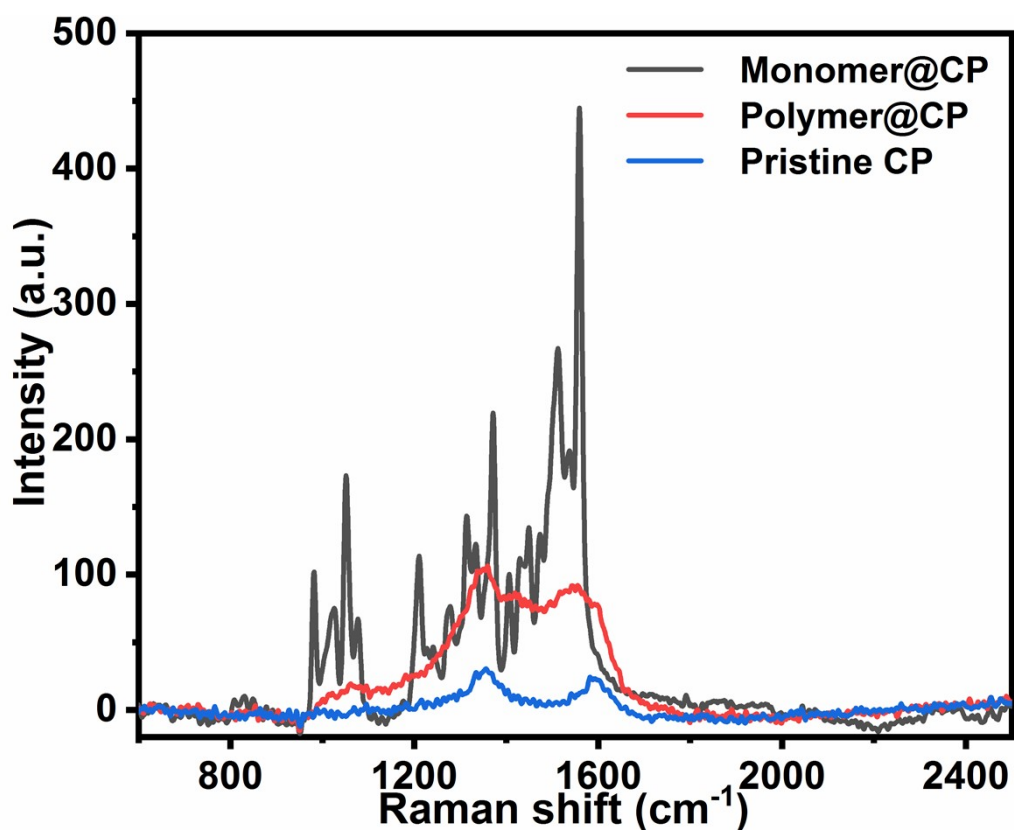


Figure 10 Raman spectra of pristine carbon paper (blue), direct drop-coating of 1a on the carbon paper (black) and electropolymerized 1a on the carbon paper (blue).

## 7. SEM, EDX and mapping analysis

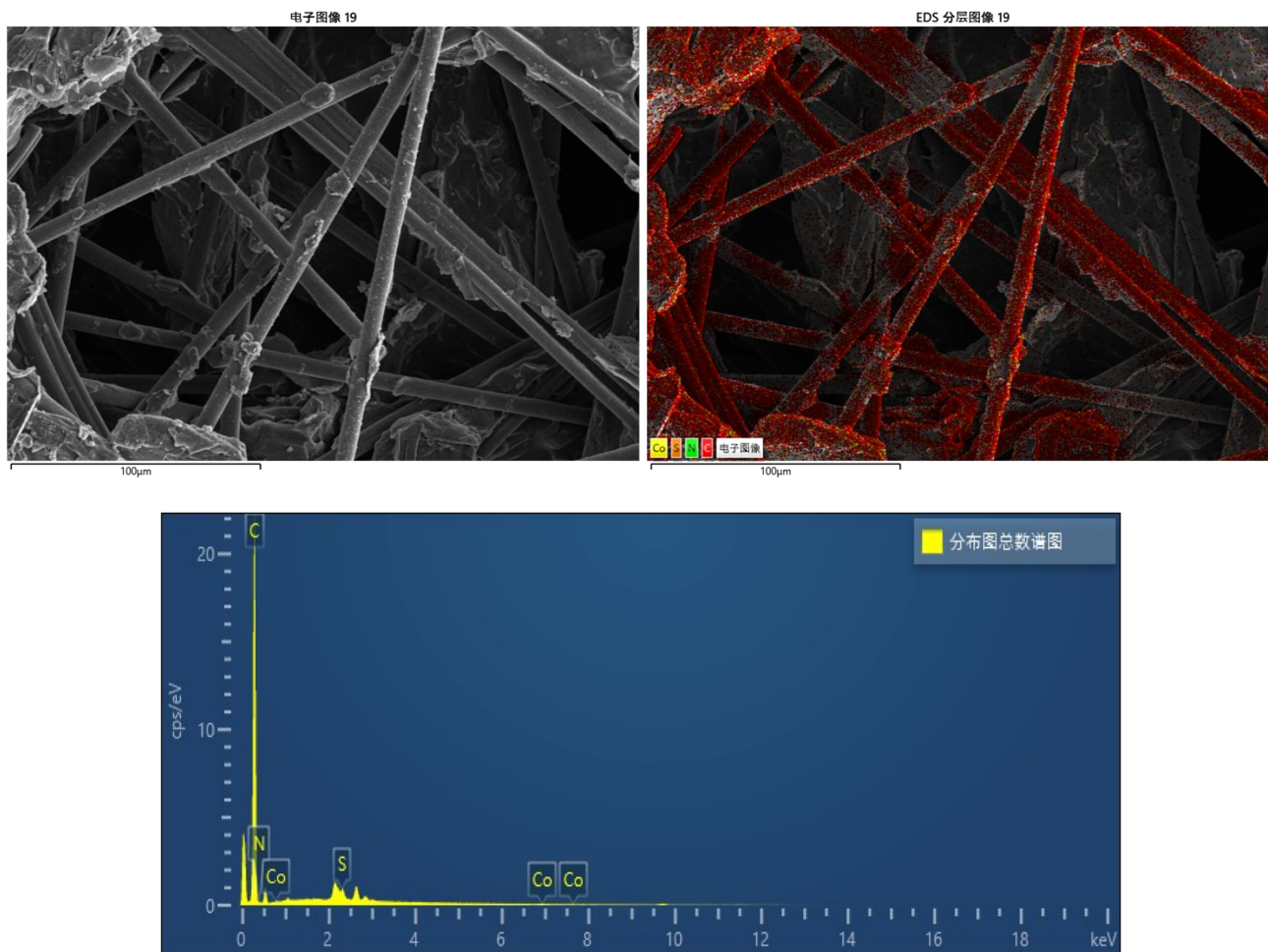


Figure 11 The overlay mapping and EDX analysis of electropolymerized **poly-1a**.

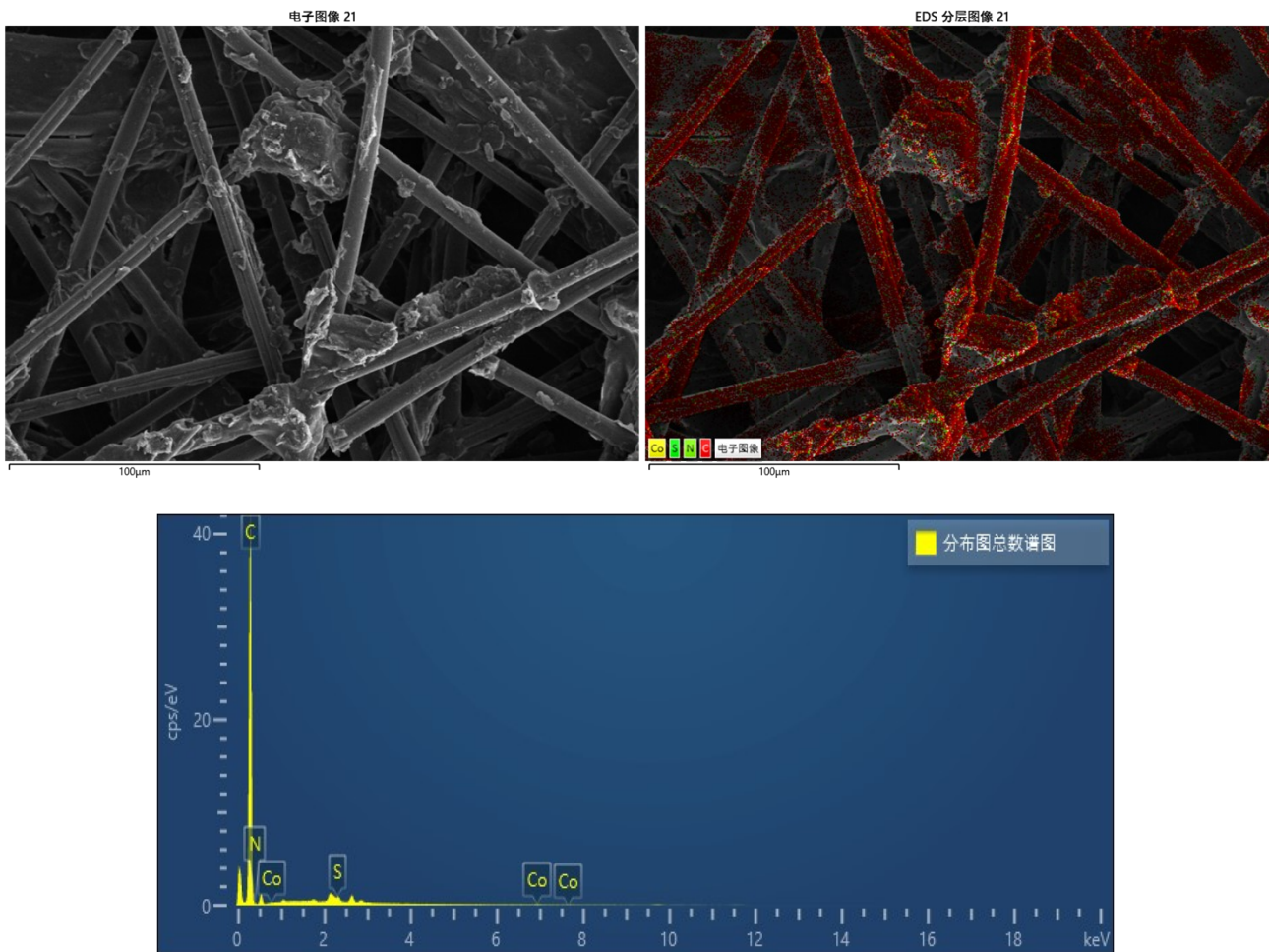


Figure S12 The overlay mapping and EDX analysis of electropolymerized **poly-1b**.

## 9. Normalized LSV measurements

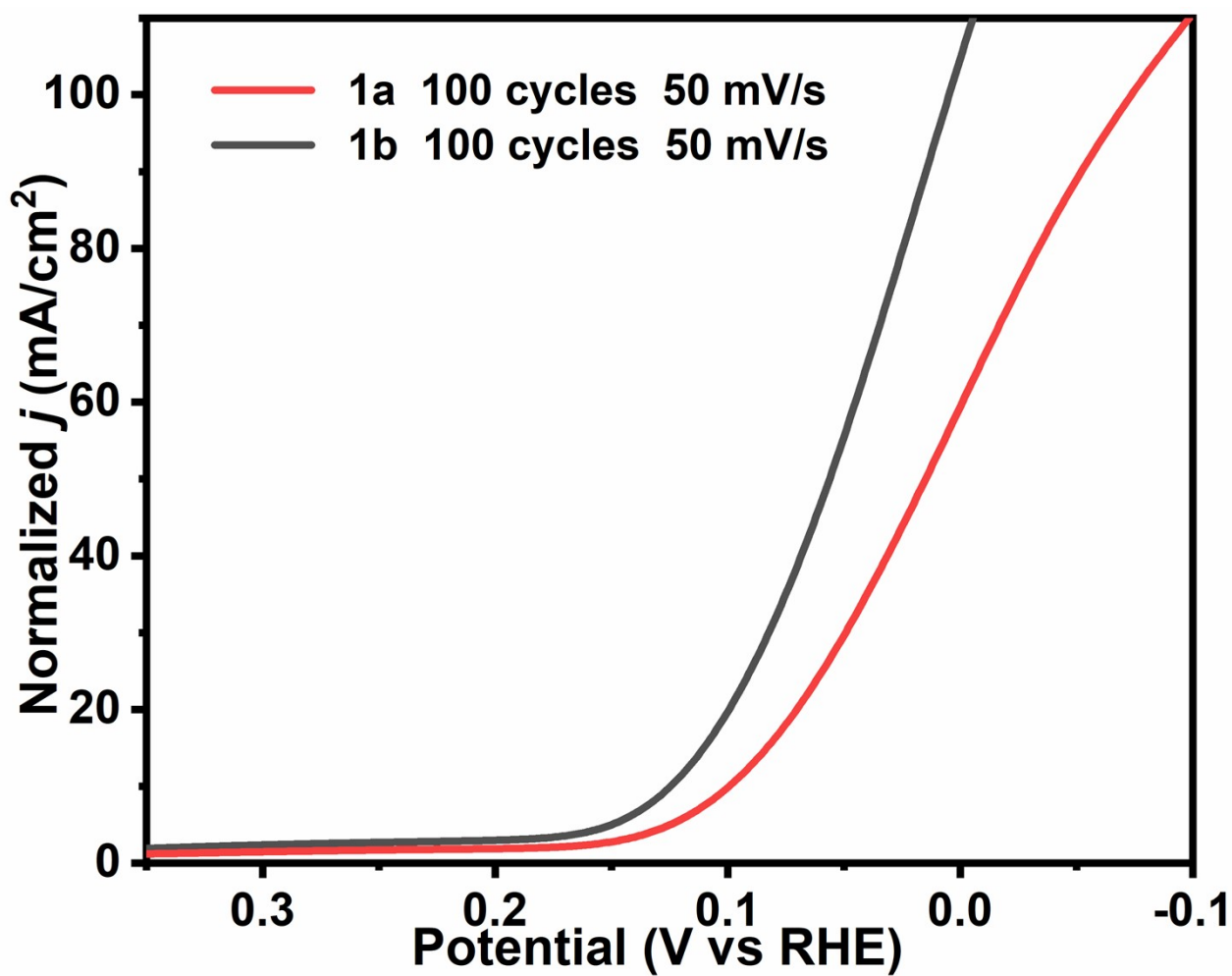


Figure S13 Normalized LSV measurement of electropolymerized **poly-1a** and **poly-1b** in 0.5M H<sub>2</sub>SO<sub>4</sub>

## 10. Tables

Table S1 The redox potentials of Co<sup>III</sup>corroles **1a** and **1b** derived from both DPV measurements

	$E_{1/2} \text{ Ox}^{\text{II}}$	$E_{1/2} \text{ Ox}^{\text{I}}$	$E_{1/2} \text{ Red}^{\text{I}}$	$E_{1/2} \text{ Red}^{\text{II}}$
<b>1a</b>	+1.56	+1.10	-0.03	-1.04
<b>1b</b>	+1.53	+1.06	-0.13	-1.11

Table S2 EDX analysis of different ratio of elements of electropolymerized **Poly-1a**

Element	wt%	At%
C	90.40	92.29
N	8.39	7.35
S	0.66	0.25
Co	0.55	0.11
Total	100.00	100.00

Table S3 EDX analysis of different ratio of elements of electropolymerized **Poly-1b**

Element	wt%	At%
C	92.96	94.32
N	6.29	5.47
S	0.34	0.13
Co	0.41	0.08
总量	100.00	100.00