Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

The electrochemical discrimination of pinene enantiomers by the cyclodextrin metal-organic framework

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1. General Methods

1.1 Chemicals and Instrumentation

Gamma-cyclodextrin, 1-Butyl-3-methylimidazolium Tetrafluoroborate ([Bmim]BF_4), alpha-(+)-pinene, alpha-(-)-pinene, beta-(-)-pinene were purchased from TCI. Beta-(+)-pinene was purchased from Siga-Aldrich. Potassium hydroxide was purchased from Hengshan Chemical Industry Commpany, Tianjin, China. Nafion D-521 dispersion liquid (5% w/w in water and 1-propanol, ⩾0.92 meq/g exchange capacity) and Nafion N-117 membrane (0.180 mm thick, ⩾0.90 meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Water used in experiment was purchased commercial ultrapure water. All organic solvent were purchased from J&K without further purification.

X-ray powder diffraction (XRD) data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation. The FT-IR spectra were measured with a Bruker Alpha infrared spectrometer with ATR operator station. Scanning electron microscope (SEM) images was performed by JSM-7500F (operating voltage, 5 kV) and ZEISS MERLIN Compact (operating voltage, 10 kV). Transmission electron microscopy (TEM) image was performed by a FEI Tecnai G2 at an accelerating voltage of 200 kV. Data of cyclic voltammetry (CV) and electrochemistry impedance spectroscopy (EIS) were collected by a Metrohm Autolab PGSTAT302N electrochemical workstation (made in Switzerland).

1.2 CD-MOF-1 Synthesis

CD-MOF-1 [S1, S2] (**1**): gamma-cyclodextrin (1.30g, 1 mmol) and KOH (0.45g, 8 mmol) were dissolved in water (20 ml). The aqueous solution was filtered after filter paper (slow), and methanol was allowed to vapor diffuse into the solution. The crystals were growing during the process of vapor diffusing. After fourteen days, the crystals were filtered and washed with methanol (3 × 50 ml) though filter paper. Then, the crystals were soaked in dichloromethane for three days, at the beginning of each day transporting the crystals into new dichloromethane after filtered. Next, the crystals were left to vacuum dry for 12 hours. The crystals were stored in an Ar glove box. Elemental analysis: C: 40.36%, H: 5.65%, Calcd. for **1**$[(C_{48}H_{80}O_{40})(KOH)_2(H_2O)_2]_n$: C, 39.90; H, 5.80.

1.3 Electrochemical Section

1.3.1 Working electrode modifying methods

Firstly, **1** was grinded into tiny piece. Mixing 5mg **1** with 0.95 mL methanol, then adding 50 μL Nafion D-521 dispersion liquid into the suspension. Ultrasonic vibrating the suspension for forty minutes (keep the temperature lower than 40℃). Putting 20 μL suspension onto glass carbon electrode (GCE**,** *Φ*=3 mm), a transparent film would coat the GCE after the suspension was dried, this GCE was named **1-GCE**. Putting 20 μL suspension onto platinum electrode (PE, *Φ*=1 mm), a transparent film would coat the PE after the suspension was dried, this PE was named **1-PE**.

1.3.2 Reference electrode, auxiliary electrode & electrolyte

Reference electrode (RE): 0.1 M AgNO3-acetonitrile solution as electrode solution was filled into a silver ion electrode (SIE).

Auxiliary electrode (AE): a platinum wire electrode was used as the auxiliary electrode in the whole work.

Electrolyte: 0.5 M [Bmim]BF_4 in acetonitrile solution.

1.3.3 EIS preparing and testing

0.37 g **1** was pressed into a round piece by a powder pressing machine, the height of the piece is 2.08 mm, and the diameter of the piece is 13.04 mm. Then, both faces were covered by a film of conductive silver paint.

Selecting one round face of the sample as the working electrode, and the opposite face were used as both reference electrode and auxiliary electrode. EIS data were test though open circuit potential (OCP) method. The frequency was range from 0.01 to 1.00×10^6 Hz.

2. Material Measurement

2.1 Infrared Spectrum

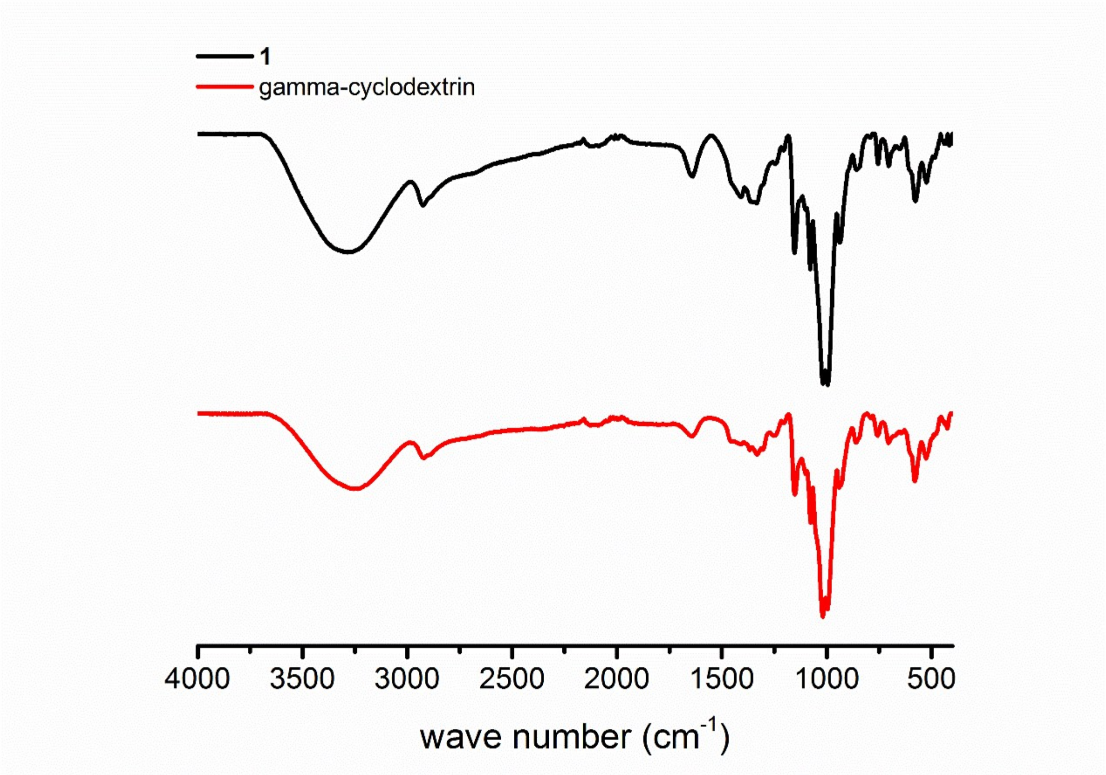


Fig. S1 Infrared spectrum of gamma-cyclodextrin (red line) and **1** (black line).

2.2 X-ray powder diffraction (XRD)

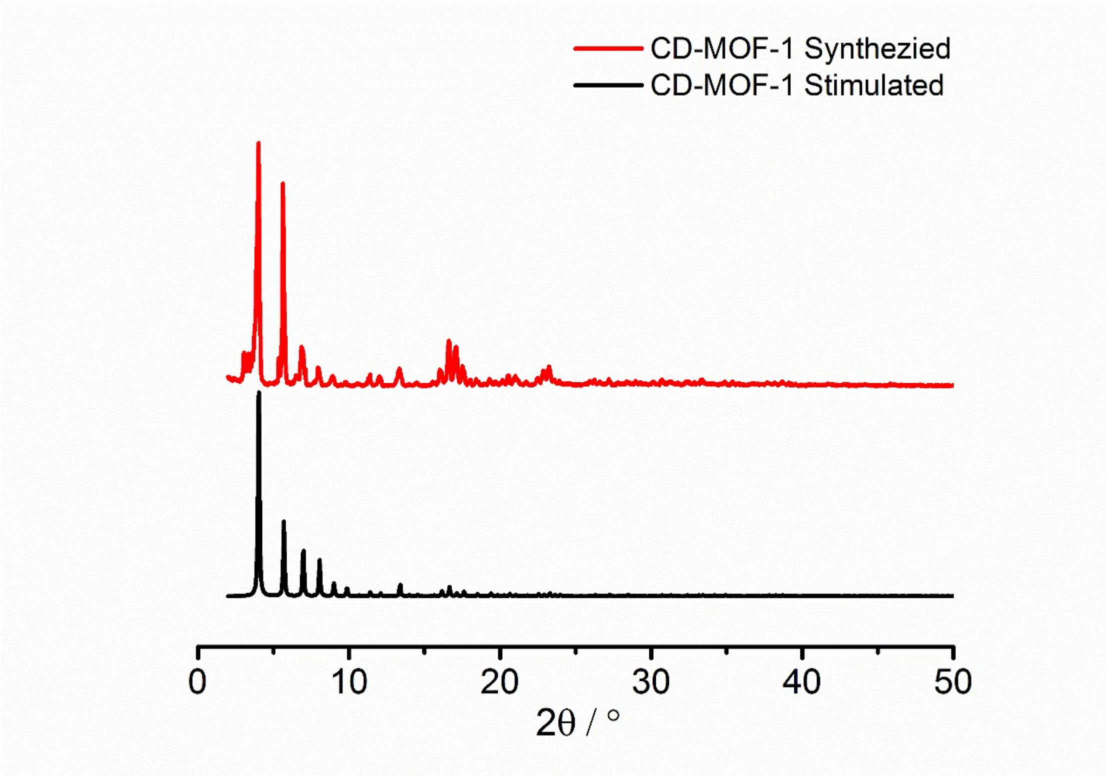


Fig. S2 X-ray powder diffraction data of **1** compared with calculated patterns derived from their crystal structures.

3. Electrochemistry Measurement

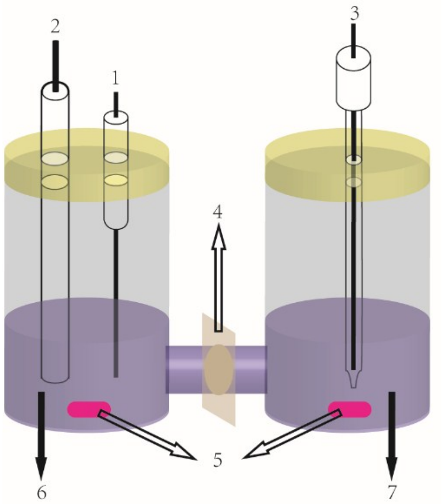


Fig. S3 The schematic diagram of the electrolysis device: 1. auxiliary electrode; 2. working electrode; 3. reference electrode; 4. Nafion 117 membrane; 5. magnetic stirrer; 6. Pinene with selected concentrations in electrolyte; 7. electrolyte.

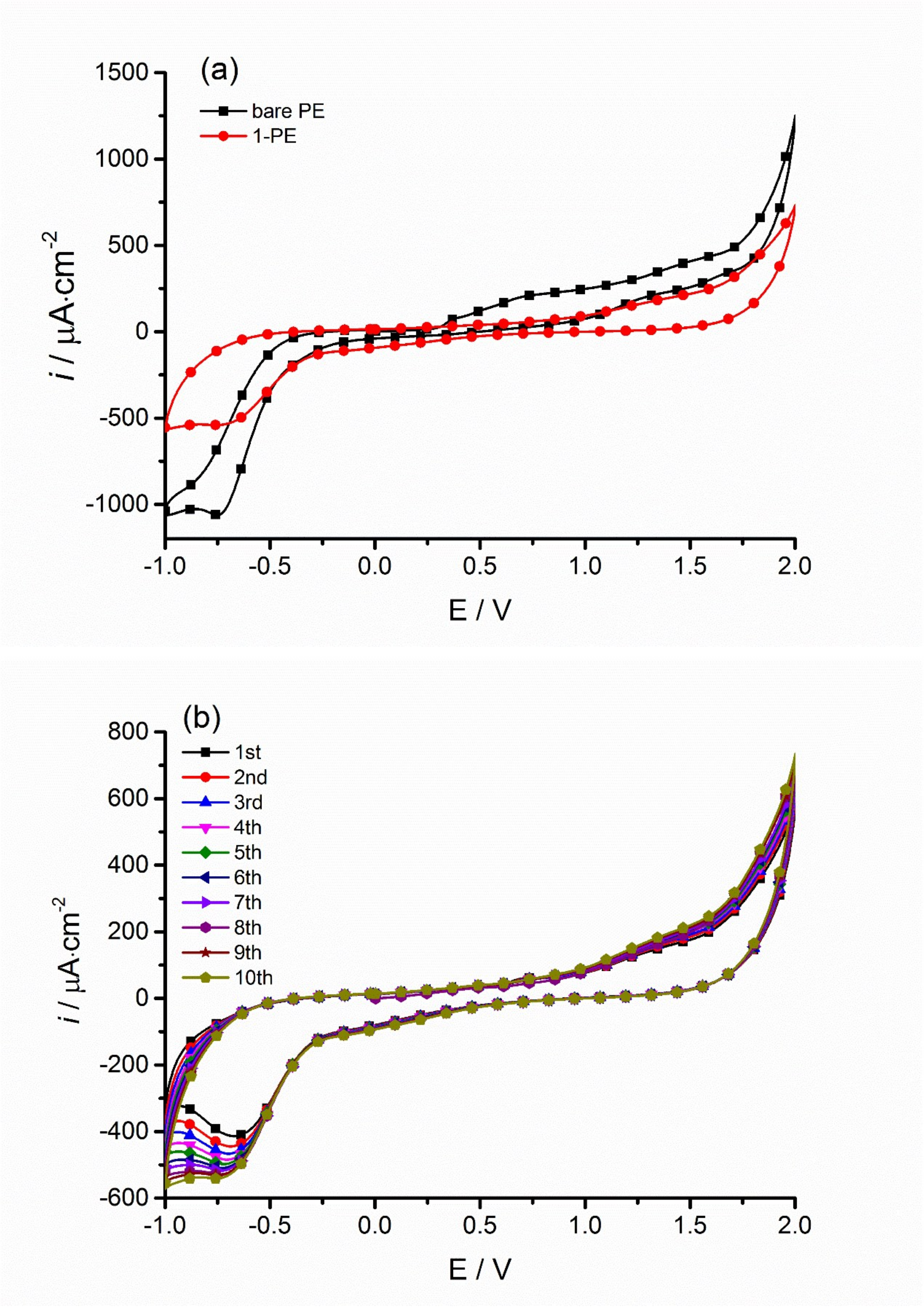


Fig. S4 Electrochemical behavior of **1-PE** in electrolyte as the scan rate of 10 mV s^{-1} (a) CV measurements of **1-PE** (red line) and bare PE (black line) (b) CV measurements of **1-PE** for ten cycles

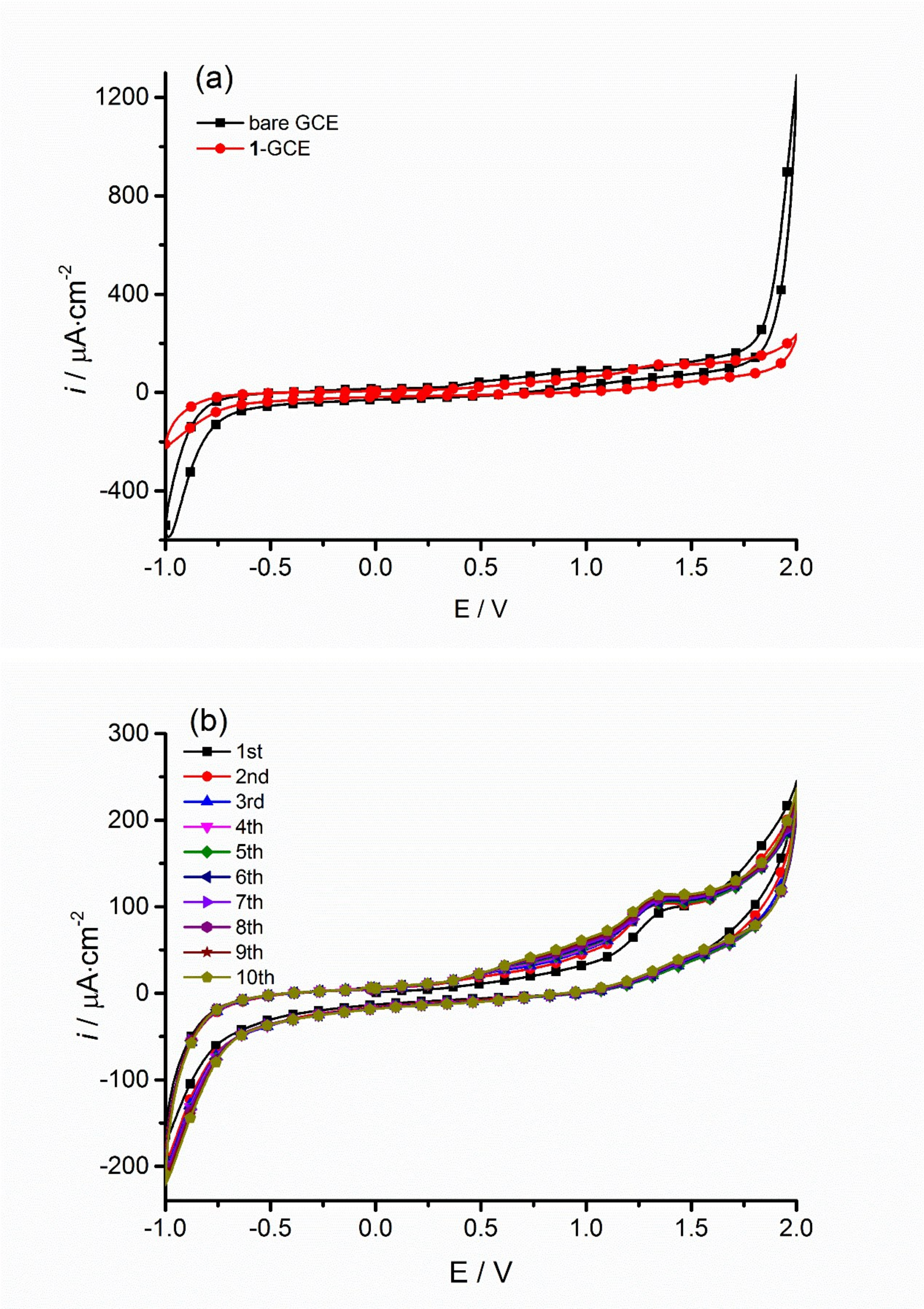


Fig. S5 Electrochemical behavior of **1-GCE** in electrolyte as the scan rate of 10 mV s^{-1} (a) CV measurements of **1-GCE** (red line) and bare GCE (black line) (b) CV measurements of **1-GCE** for ten cycles.

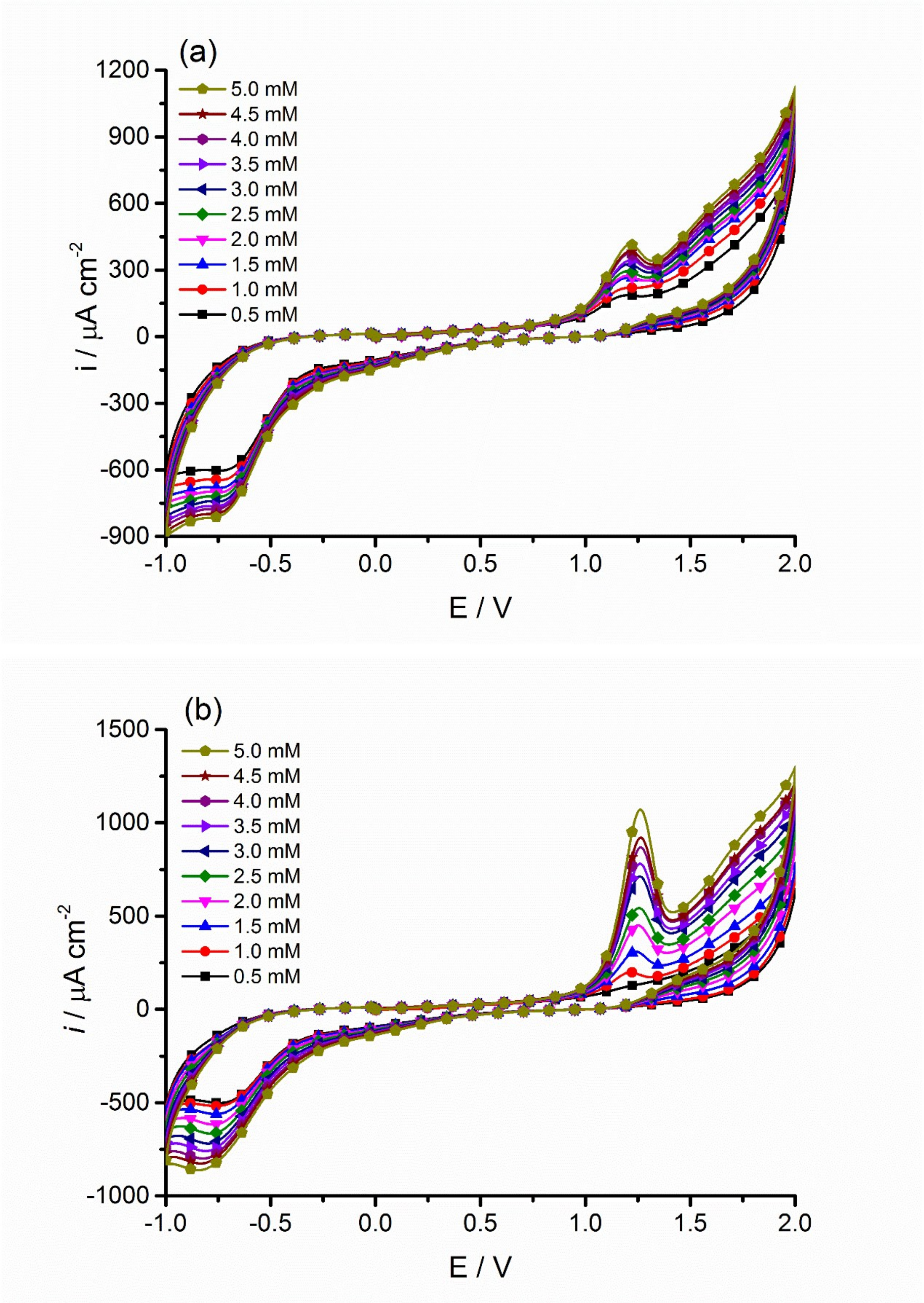


Fig. S6 CV signals of SA and RA with the same scan rate (10 mV s^{-1}) at **1-PE** (a) CV of SA at different concentrations (b) CV of RA at different concentrations.

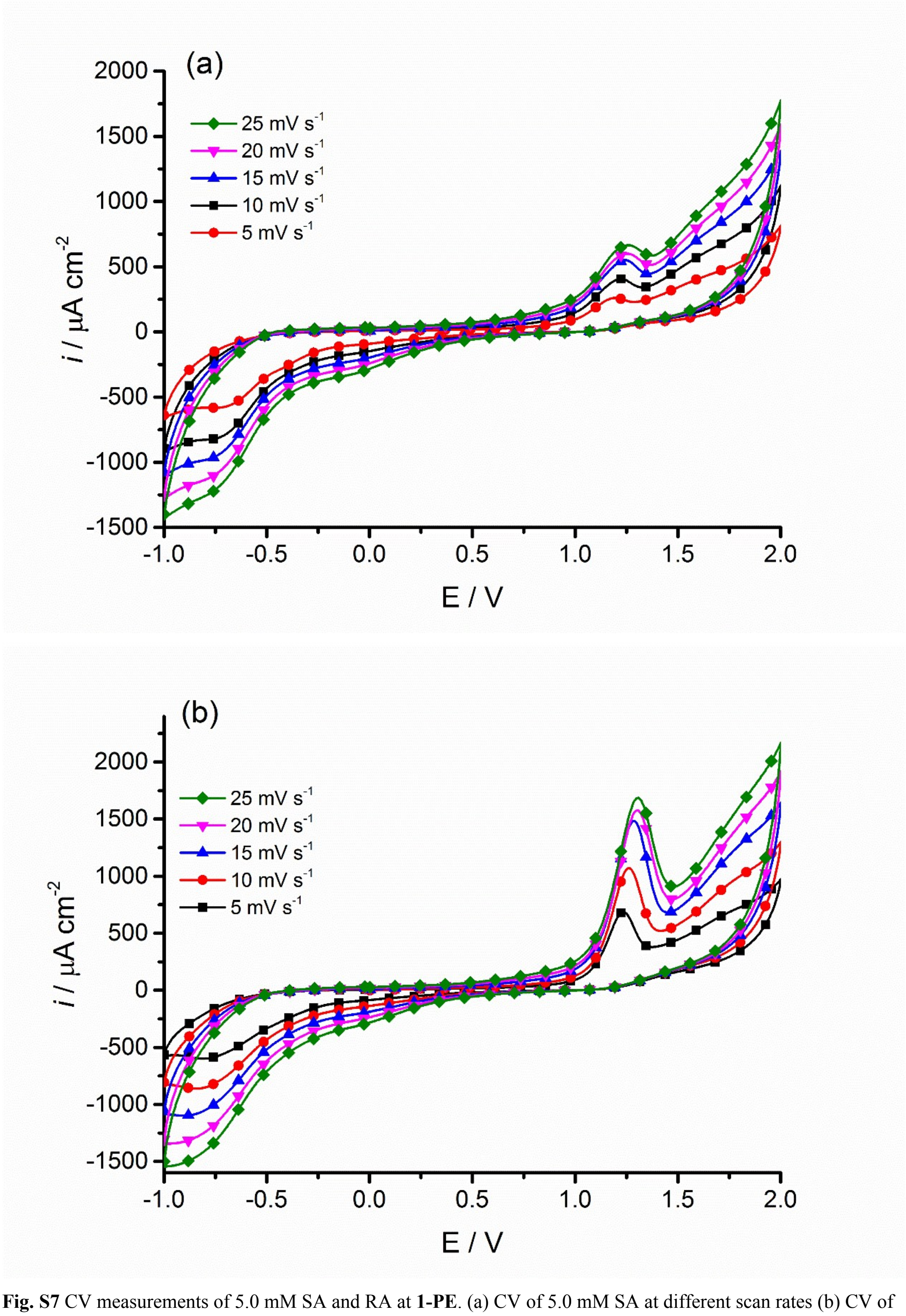
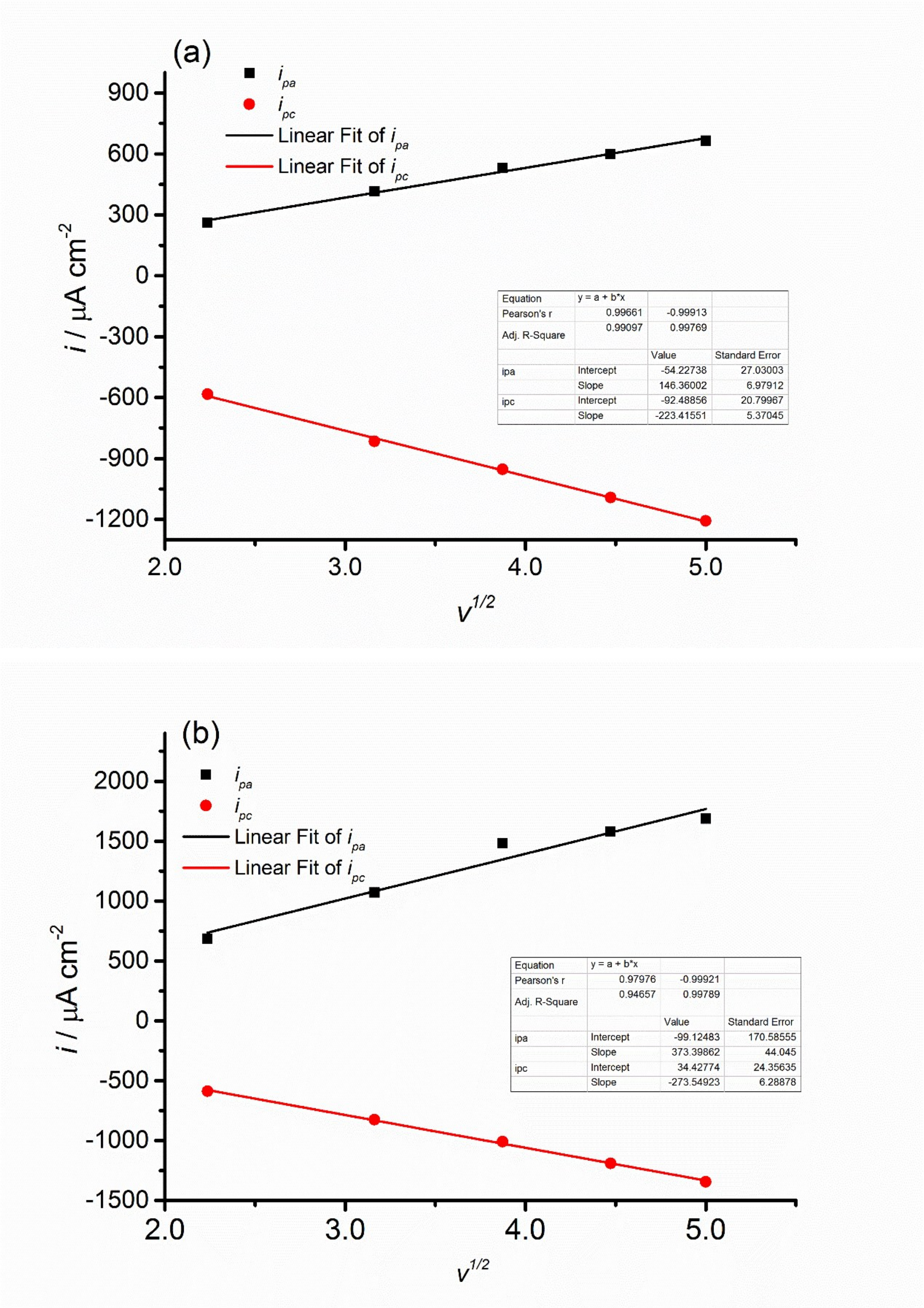


Fig. S7 CV measurements of 5.0 mM SA and RA at **1-PE**. (a) CV of 5.0 mM SA at different scan rates (b) CV of 5.0 mM RA at different scan rates



Equation	y = a + b*x		
Pearson's r	0.99661	-0.99913	
Adj. R-Square	0.99097	0.99769	
		Value	Standard Error
ipa	Intercept	-54.22738	27.03003
	Slope	146.36002	6.97912
ipc	Intercept	-92.48856	20.79967
	Slope	-223.41551	5.37045

Equation	y = a + b*x		
Pearson's r	0.97976	-0.99921	
Adj. R-Square	0.94657	0.99789	
		Value	Standard Error
ipa	Intercept	-99.12483	170.58555
	Slope	373.39862	44.045
ipc	Intercept	34.42774	24.35635
	Slope	-273.54923	6.28878

Fig. S8 (a) Plots of i_{pa} and i_{pc} vs square root of scan rate $v^{1/2}$, respectively, for Fig. S9a; (b) Plots of i_{pa} and i_{pc} vs square root of scan rate $v^{1/2}$, respectively, for Fig S9b.

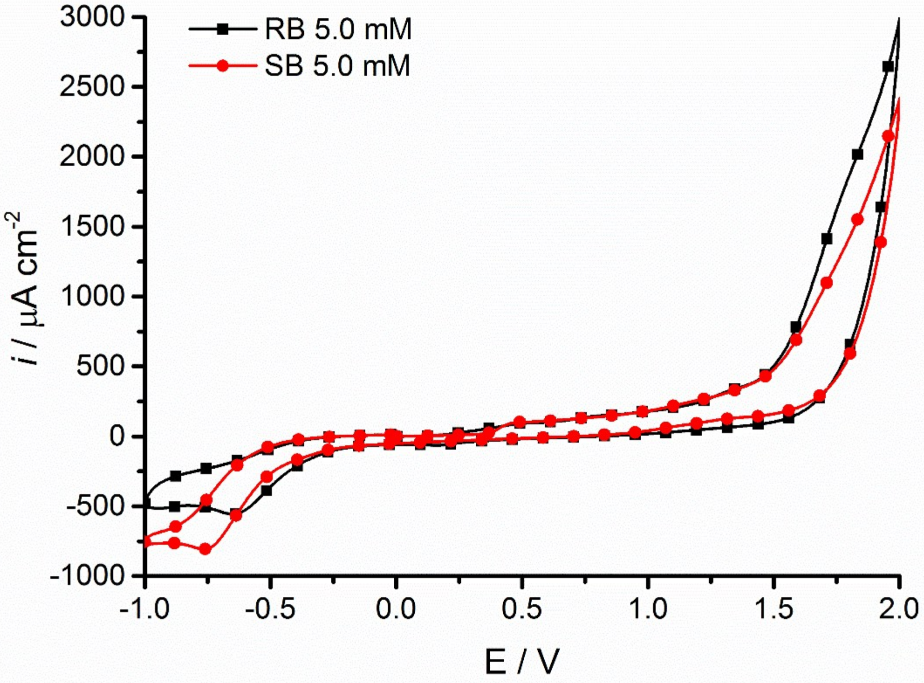


Fig. S9 CV signals of RB (black line) and SB (red line) at **1-PE** (scan rate: 10 mV s^{-1}, concentration: 5.0 mM)

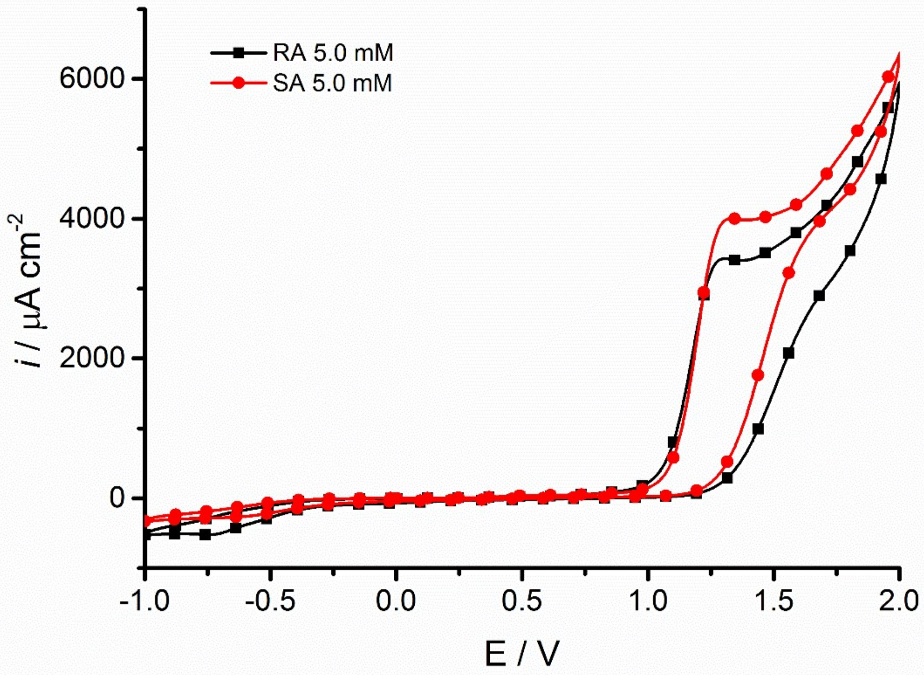


Fig. S10 CV signals of RA (black line) and SA (red line) under bare PE (scan rate: 10 mV s^{-1}, concentration: 5.0 mM).

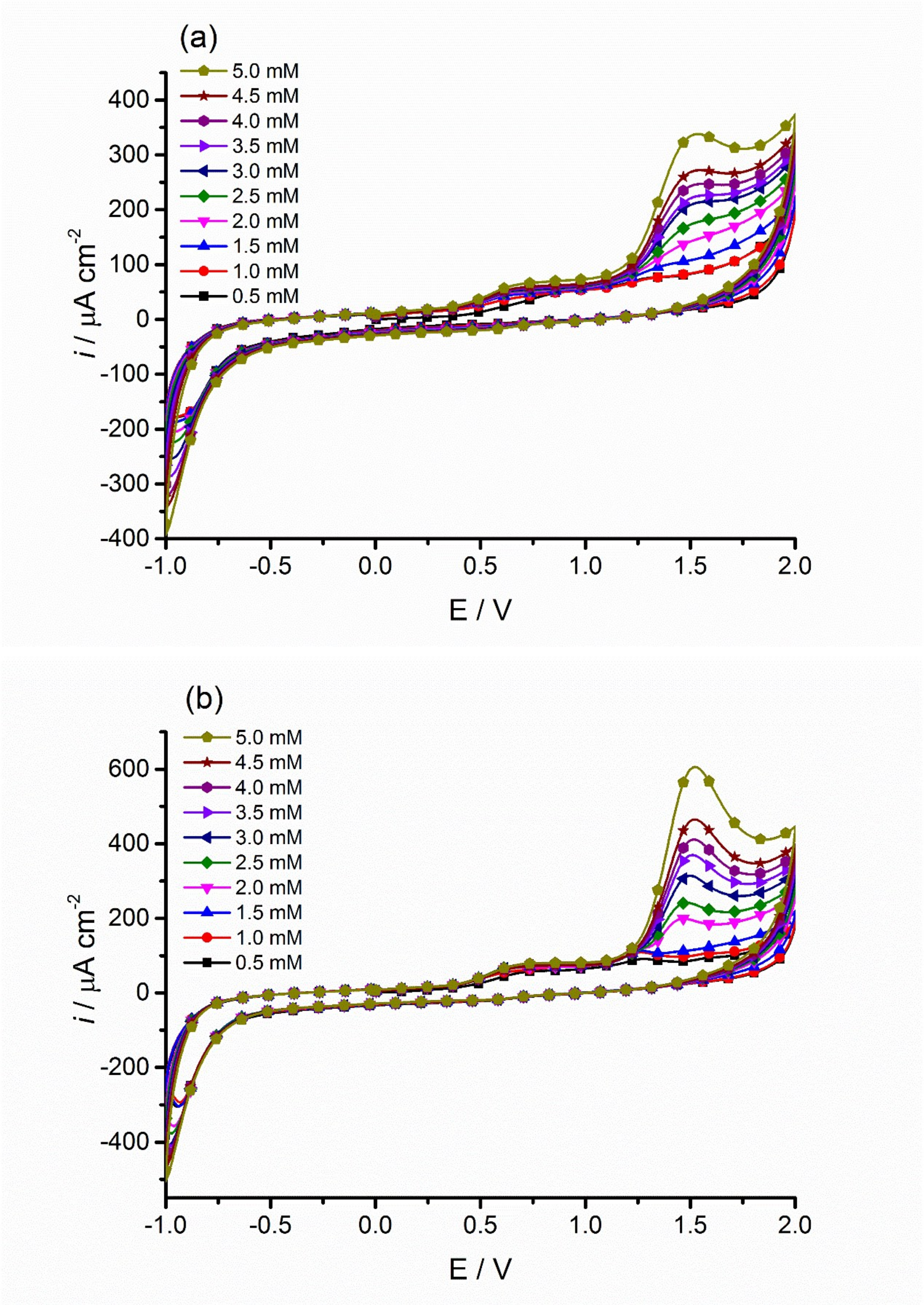
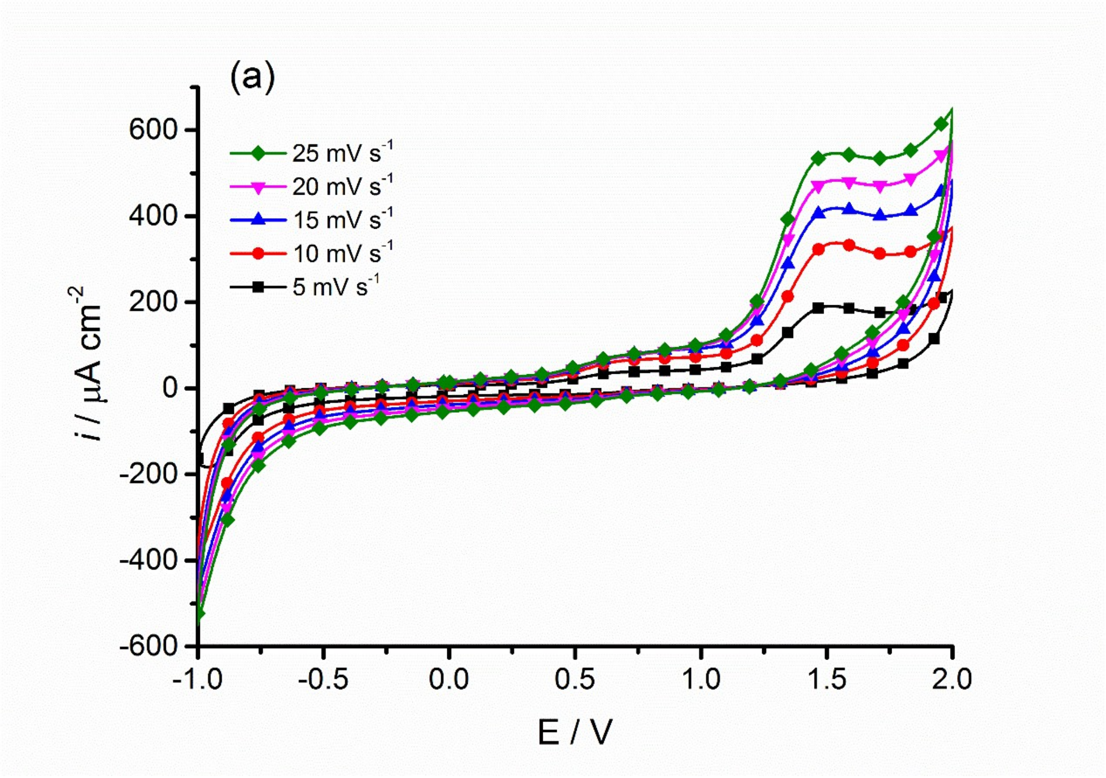


Fig. S11 CV signals of SB and RB with the same scan rate (10 mV s^{-1}) at **1-GCE** (a) CV of SB at different concentrations (b) CV of RB at different concentrations.



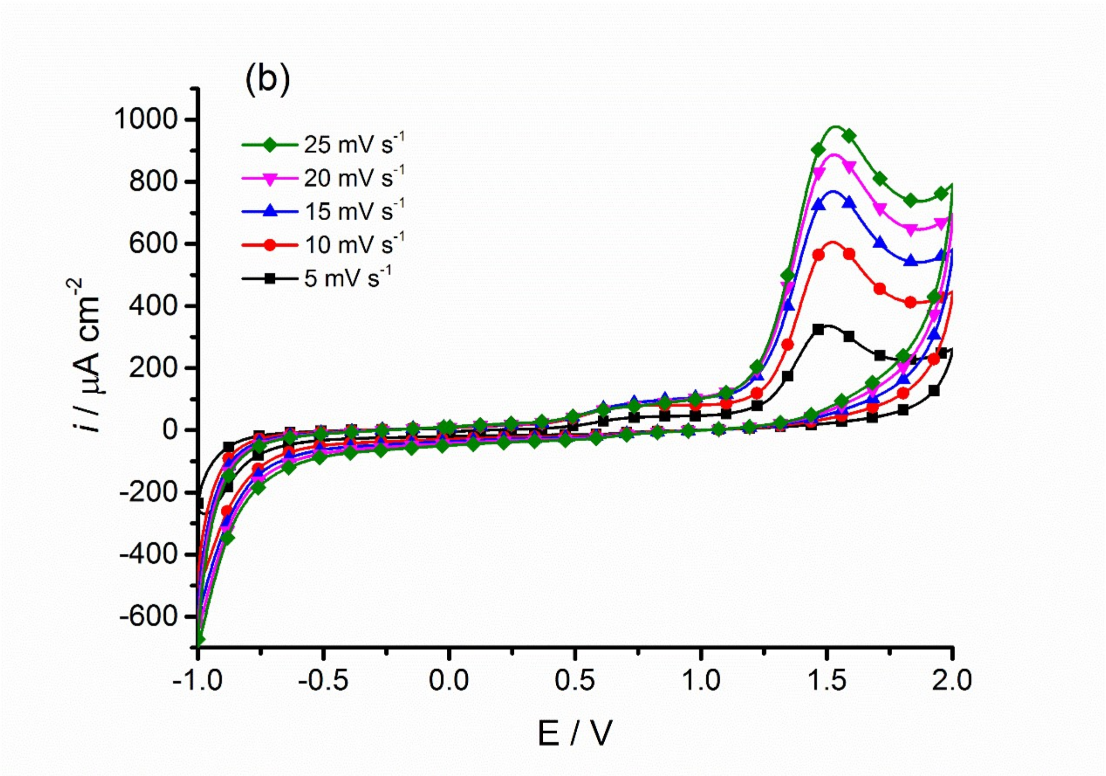


Fig. S12 CV measurements of 5.0 mM SB and RB at **1-GCE**. (a) CV of 5.0mM SB at different scan rates (b) CV of 5.0 mM RB at different scan rates

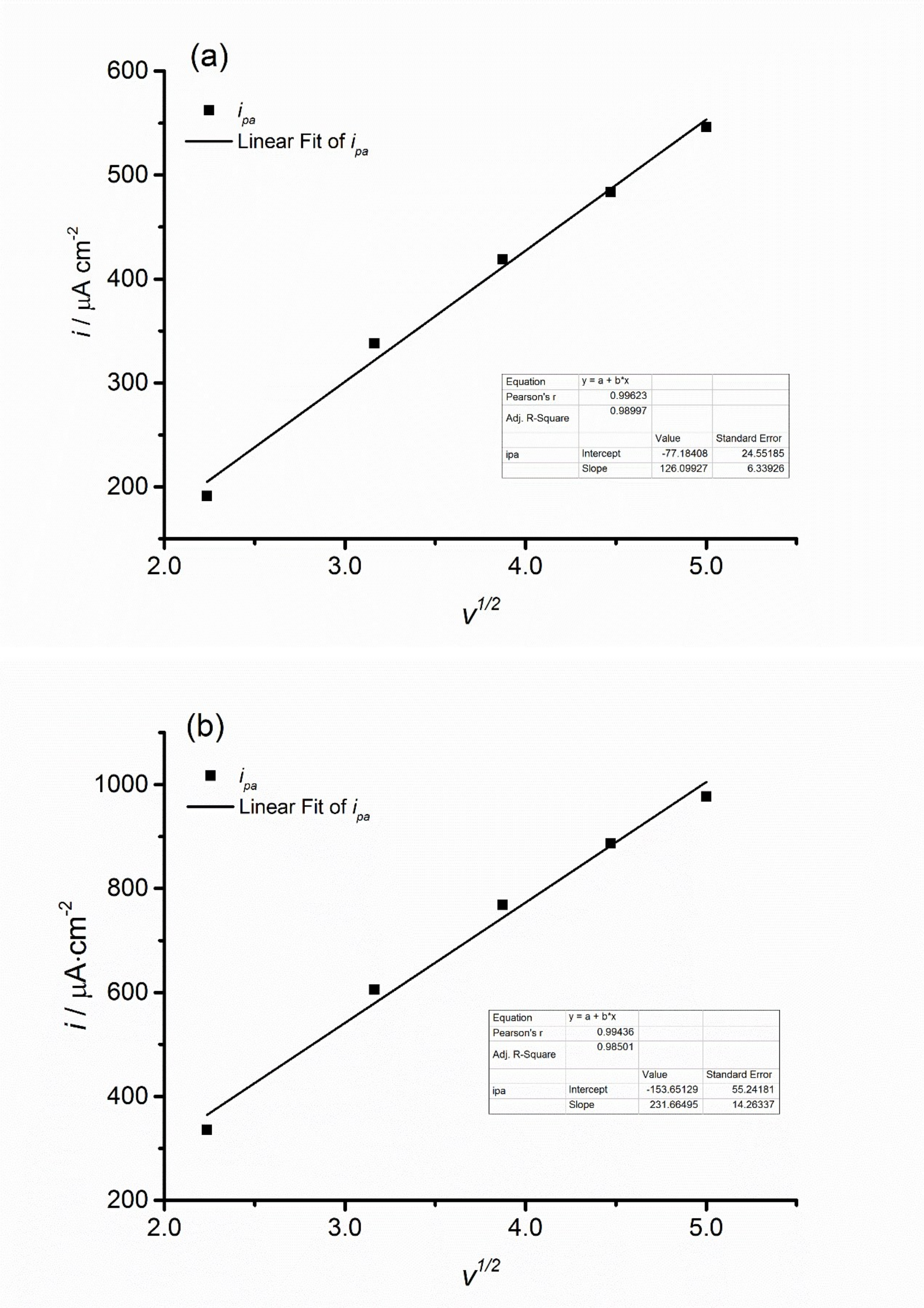


Fig. S13 (a) Plots of i_{pa} and i_{pc} vs square root of scan rate $v^{1/2}$, respectively, for Fig. S14a; (b) Plots of i_{pa} and i_{pc} vs square root of scan rate $v^{1/2}$, respectively, for Fig S14b.

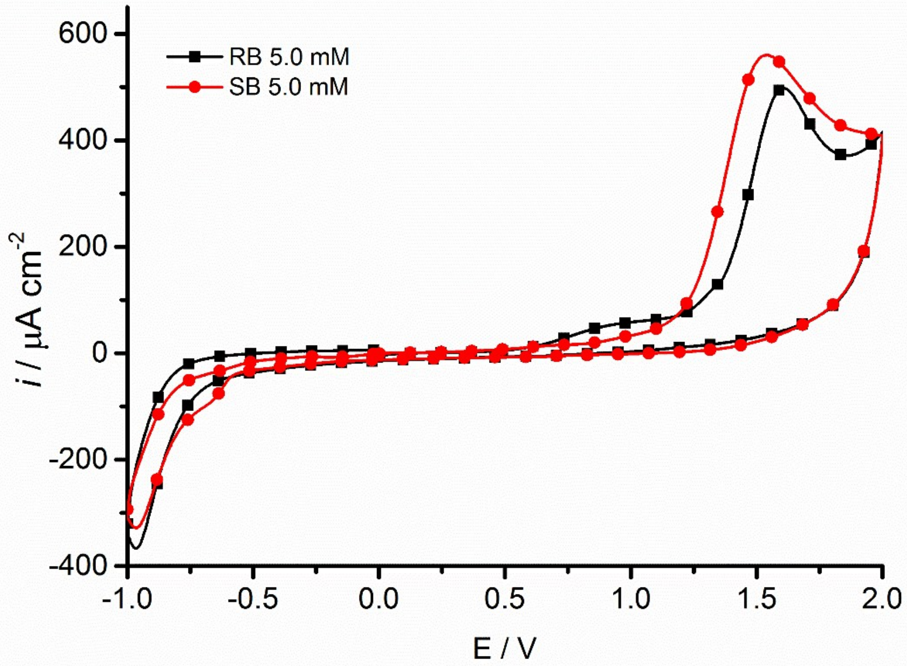


Fig. S14 CV signals of RB (black line) and SB (red line) at bare GCE (scan rate: 10 mV s^{-1}, concentration: 5.0 mM).

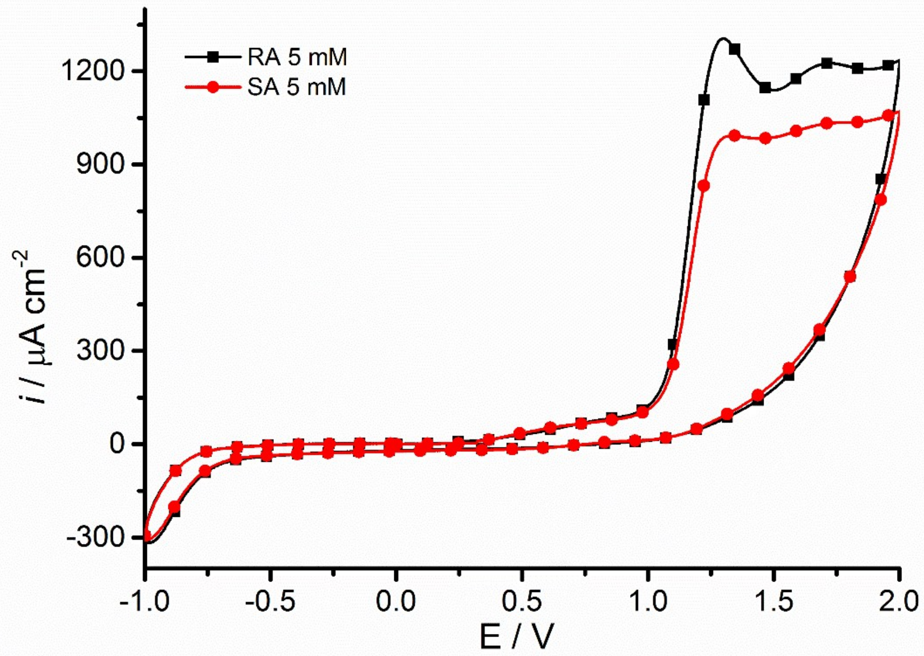


Fig. S15 CV signals of RA (black line) and SA (red line) at **1-GCE** (scan rate: 10 mV s^{-1}, concentration: 5 mM).

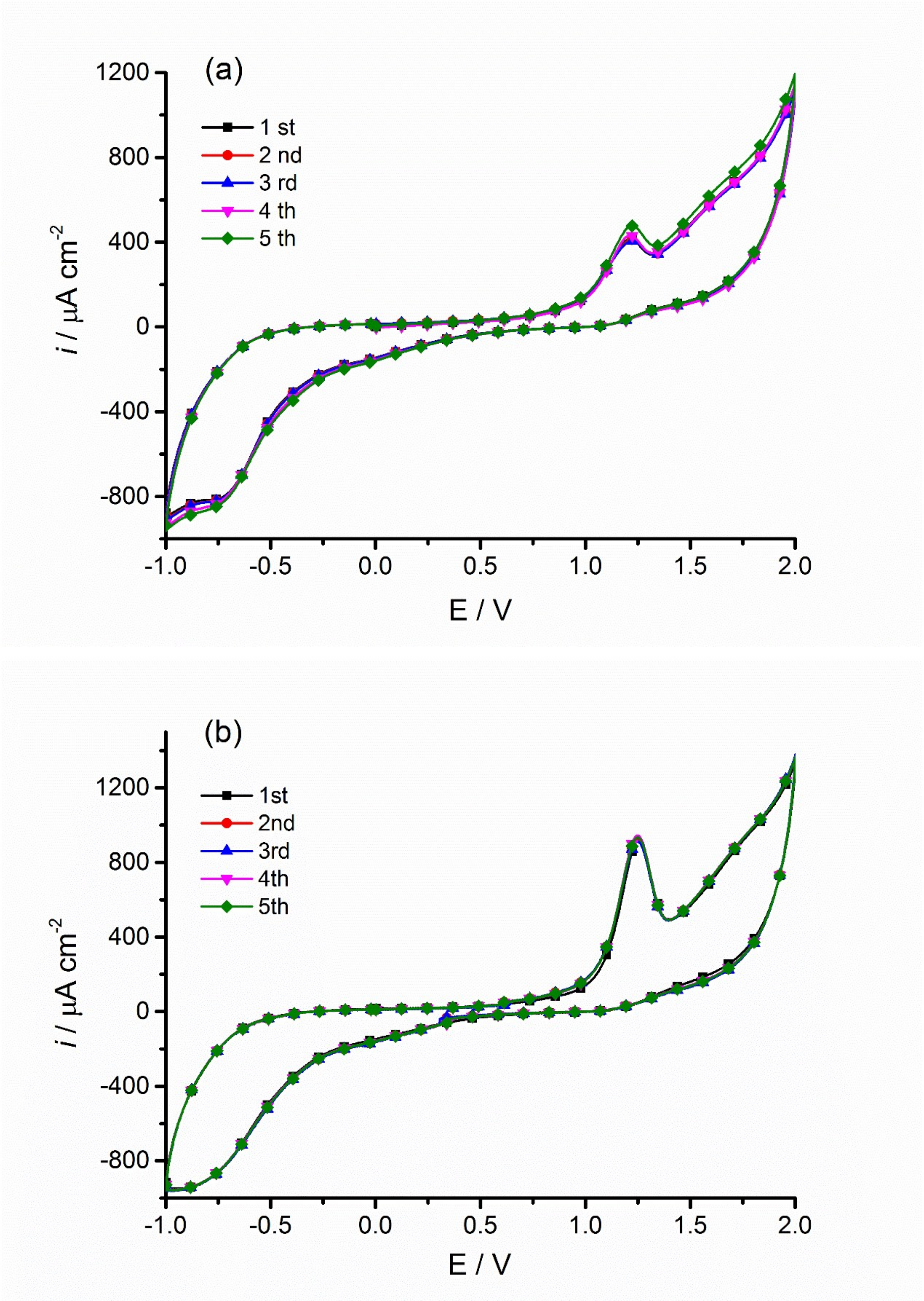


Fig. S16 **1-PE** reliability CV tests: testing 5.0 mM SA for five circles firstly (a), then washing the electrode **1-PE** in acetonitrile and testing 5.0 mM RA for five circles (b). (scan rate: 10 mV s^{-1})

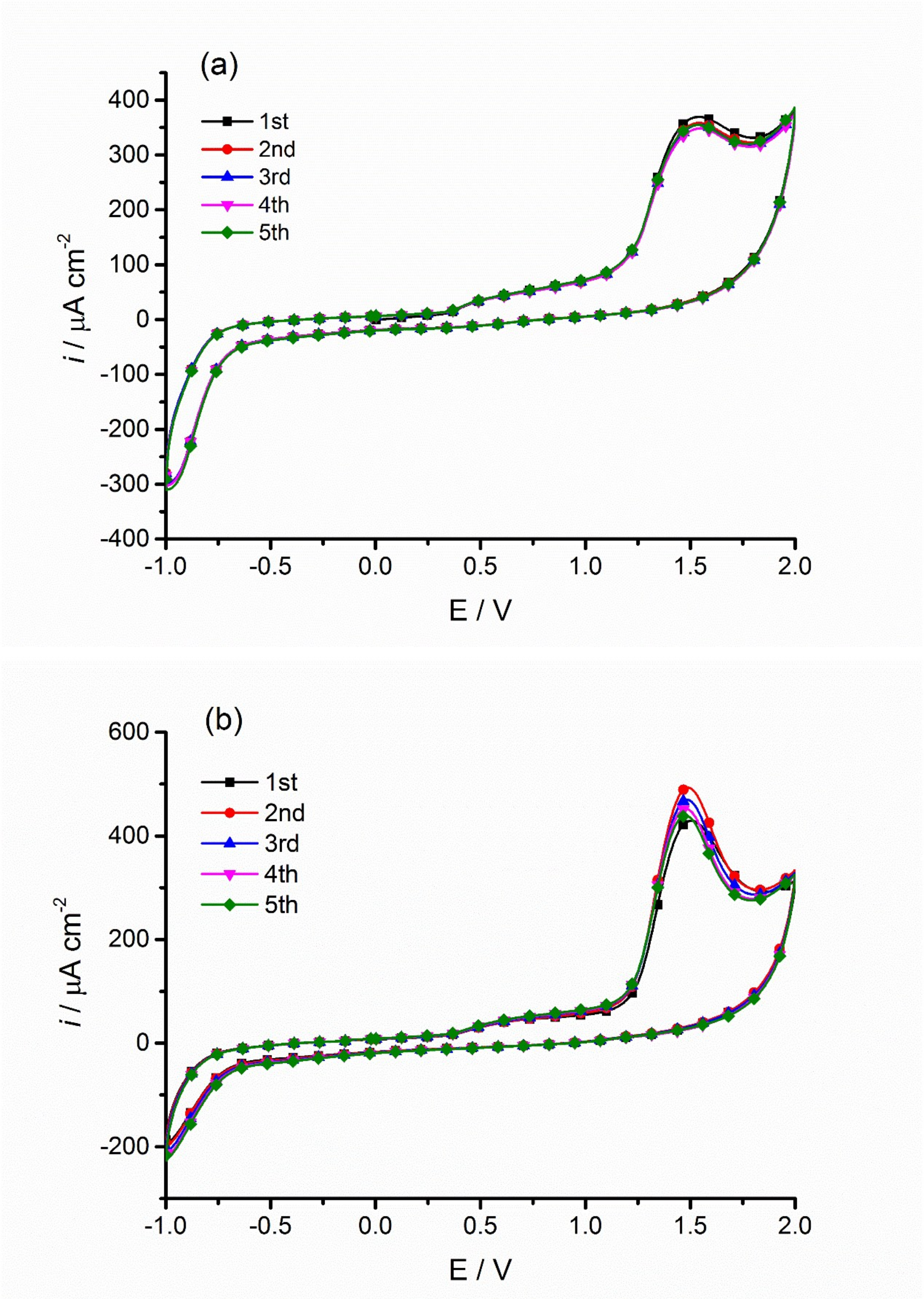


Fig. S17 1-GCE reliability CV tests: testing 5.0 mM SB under **1-GCE** for five circles firstly (a), then washing the working electrode **1-GCE** in acetonitrile and testing 5.0 mM RB for five circles (b). (scan rate: 10 mV s^{-1})

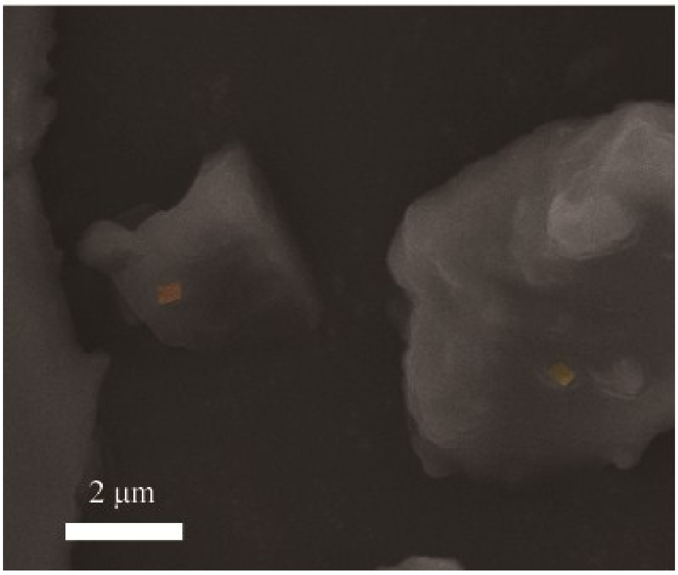


Fig. S18 SEM image of the collected coationg **1**-Nafion D521 after CV measurement (the nano cubic of **1** was marked in orange for clear).

References

S1 R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi and J. F. Stoddart. *Angew. Chem. Int. Ed.*, 2010, **49**, 8630.

S2 R. S. Forgan, R. A. Smaldone, J. J. Gassensmith, H. Furukawa, D. B. Cordes, Q. W. Li, C. E. Wilmer, Y. Y. Botros, R. Q. Snurr, A. M. Z. Slawin, and J. F. Stoddart. *J. Am. Chem. Soc.*, 2011, **134**, 406.