

Polyaniline Modified Surface of Electrode for Boosting the Electrocatalysis on Hydrogen Evolution Reaction and Ethanol Oxidation Reaction

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EXPERIMENT :

1. Chemical and reagents

Aniline (99%), formic acid (90%), and aniline (AR) were purchased from Aladdin Ltd. Co.. P-toluenesulfonic acid (TsOH, AR), p-toluenesulfonic acid sodium salt (96%), glycerol (AR), ethanol (AR), H₂AuCl₄ (99.99%), and K₂PtCl₆ (99.9%) were purchased from Macklin Ltd. Co.. All the chemicals in present study were used as received without further purification. Ultrapure water (18.2 Mohm, Ultrapure system) was used as solvent for preparing solution.

The type of carbon paper employed in this work was TGP-H-060 (Toray) with 0.19 mm of thickness.

2 Preparation of Carbon Paper-polyaniline-Pt electrode

The p-toluenesulfonic acid (1.92 g) was dissolved in 100 mL of water and then aniline (0.93 g, 0.1 mol) was added, followed by adjusted to pH=1 with HCl. The resulted solution was taken as electrolytes and the PANI was electrochemical loaded onto the carbon paper (CP, 1.0 ×1.5 cm²; the loading area was controlled at 1.0 ×1.0 cm²) by using a conventional three-electrode system, in which carbon rod and Ag/AgCl (saturated KCl solution) were taken as the counter electrode and the reference electrode, respectively. The potential for electropolymerization was set as 0.75 V (vs Ag/AgCl). After electropolymerization, the CP electrode was washed with ultrapure water and then dried for the further applications.

In the 100 mL of water, K₂PtCl₆ (48.8 mg) and concentrated H₂SO₄ (2.67 mL) were added with stirring. The resulted solution was taken as electrolyte for Pt catalysts growth. The cathode current was set as -3.75 mA for a certain of time. After washed with water, the as-prepared CP-PANI-Pt composites was taken as electrode for electrocatalysis.

3. Structural characterization

The X-ray diffraction patterns were recorded on a Rigaku diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning speed of 5 or 0.5 degrees min⁻¹, and the work current and voltage were 20 mA and 40 kV respectively. The surface morphologies were characterized on a scanning electron microscope (SEM, JSM-7800F & TEAM Octane Plus). The transmission electron microscopy (TEM) and the high resolution transmission electron microscopy (HRTEM) images were collected on a transmission electron microscope (JEM-2100 & X-Max80). The X-ray photoelectron spectrum (XPS) of the as-prepared samples

were investigated with an electron spectrometer (Escalab-250Xi Thermo Scientific, USA). Al K α radiation was taken as the X-ray source. The raw data was calibrated by using the O 1s . The Fourier transform infrared (FTIR) spectra of the samples were recorded using an IR spectrometer (Affinity-1). In typically, the samples was collected from the electrode and mixed with KBr powder by grinding, and then the result mixture was made into the pellet under the 5 MPa of pressure for the FTIR characterization. The Raman spectra were determined by a Raman spectrometer (inVia, Renishaw, UK) using a 532 nm laser as the excitation source. A SDC-350 Contact Angle system was used to measure the contact angles (CAs) at room temperature, where the employed volume of water droplet was 5 μ L. Five independent measurements were used to calculate the average contact angles.

All the electrochemical measurements were conducted using an electrochemical workstation (Ivium-n-Stat, Netherlands) with three electrodes cell. Carbon rod was used as the count electrode and a Ag/AgCl (saturated KCl solution) or a Hg/Hg₂Cl₂ (saturated KCl solution) was used as the reference electrode. A solution of H₂SO₄ (100 mL, 0.5 mol L⁻¹) was used as electrolyte. For oxidation of organic compounds, a concentration of formic acid (or ethanol, or glycerol) was added and mixed with stirring. The electrochemical characterization was performed with a scanning rate of 20 mV s⁻¹.

Figures S1-S15 and Tables S1-S2:

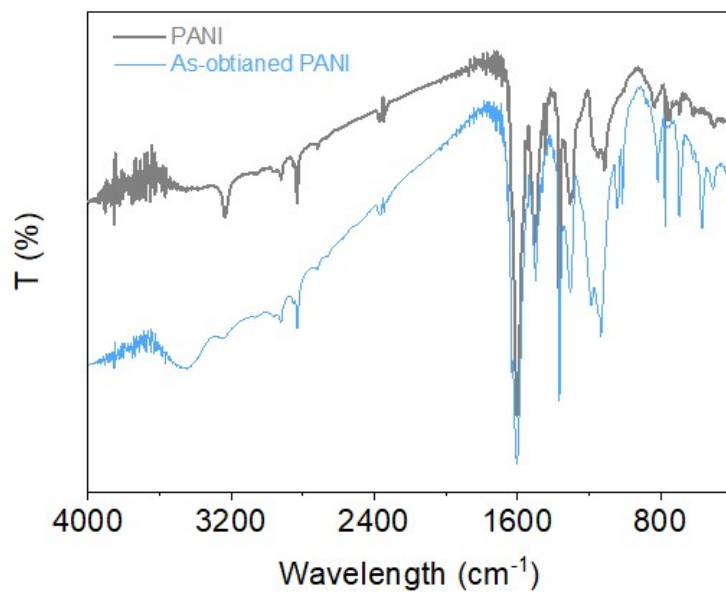


Figure S1. The FTIR spectrum of the as-prepared PANI via electropolymerization (Blue line) and commercial PANI (Grey line).

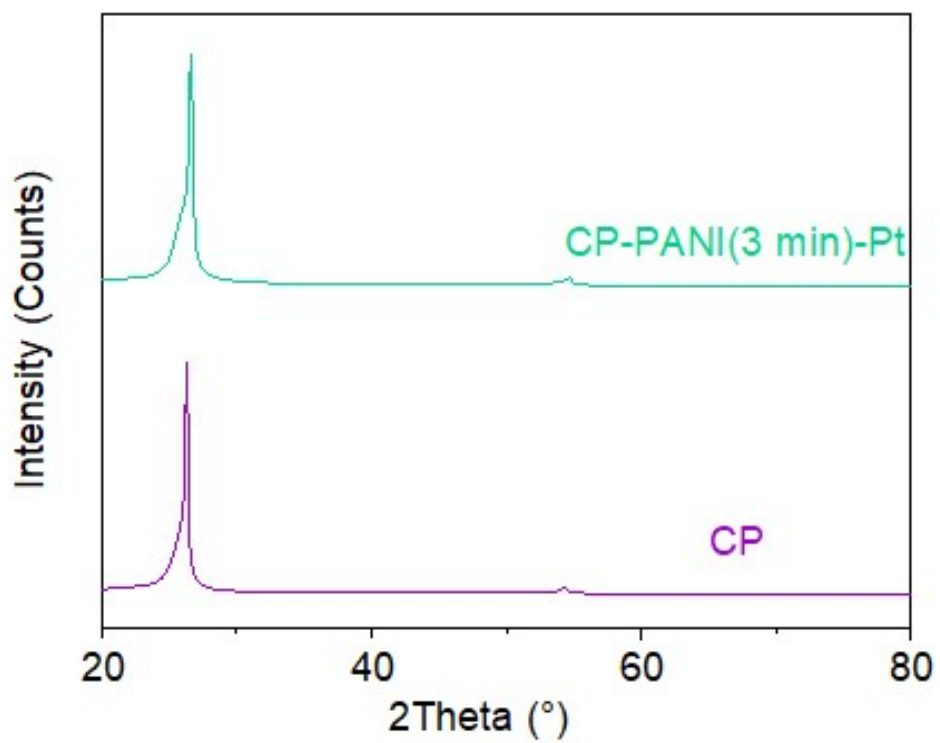


Figure S2. The XRD patterns of the carbon paper and the CP-PANI-Pt electrode.

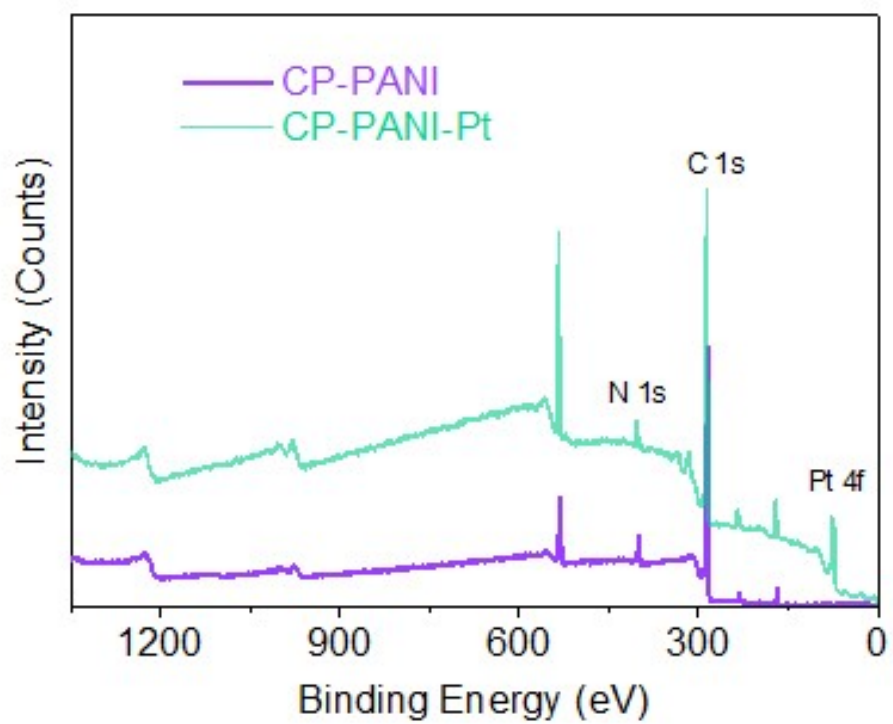


Figure S3. The XPS of the CP-PANI and the CP-PANI-Pt electrode.

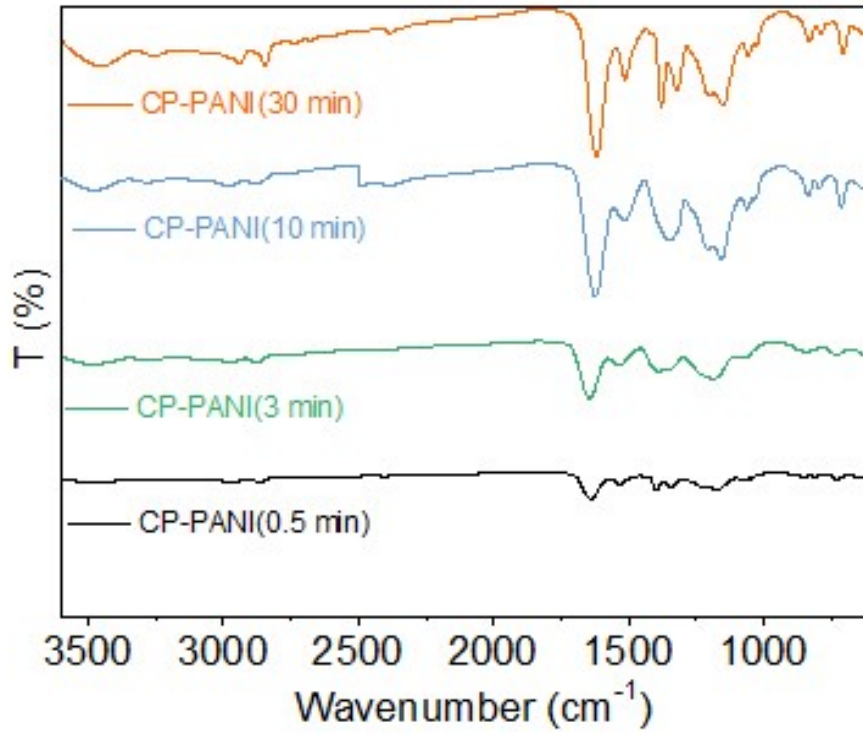


Figure S4. The FTIR spectrum of the PANI obtained by using loading time and the IR peak become stronger as prolonging the loading time, illustrating the PANI layer becoming thicker.

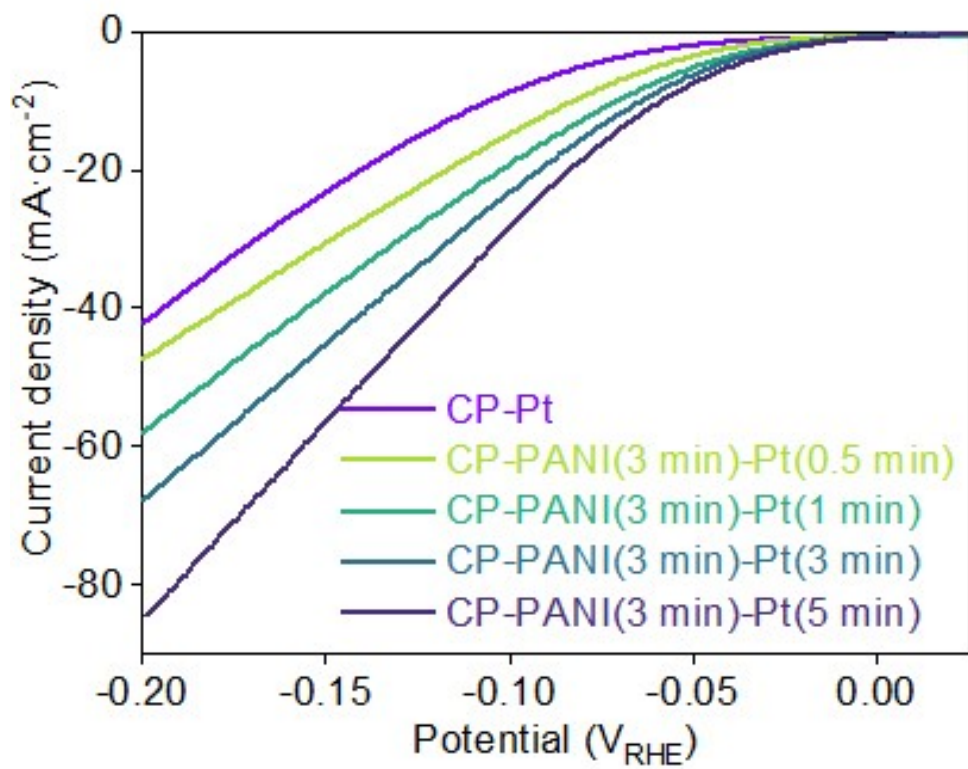


Figure S5. The HER performance by using PANI modified electrode with different Pt loading amount.

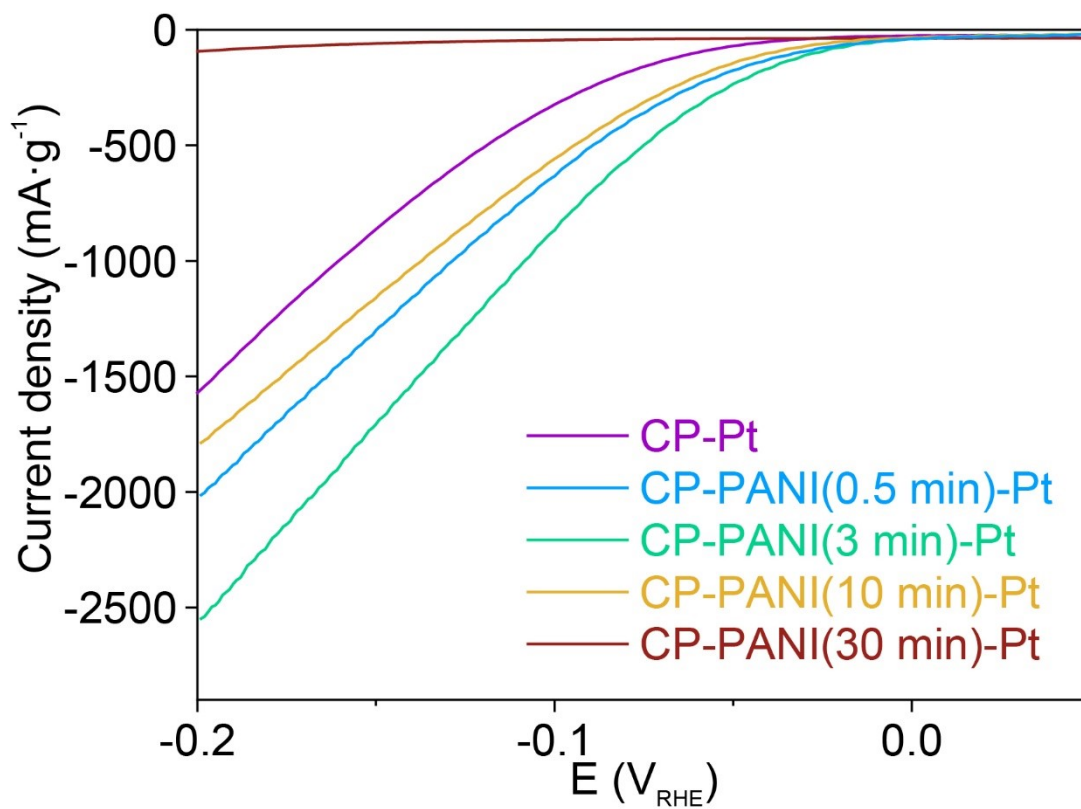


Figure S6. The polarization curves for HER on series of the as-prepared electrodes.

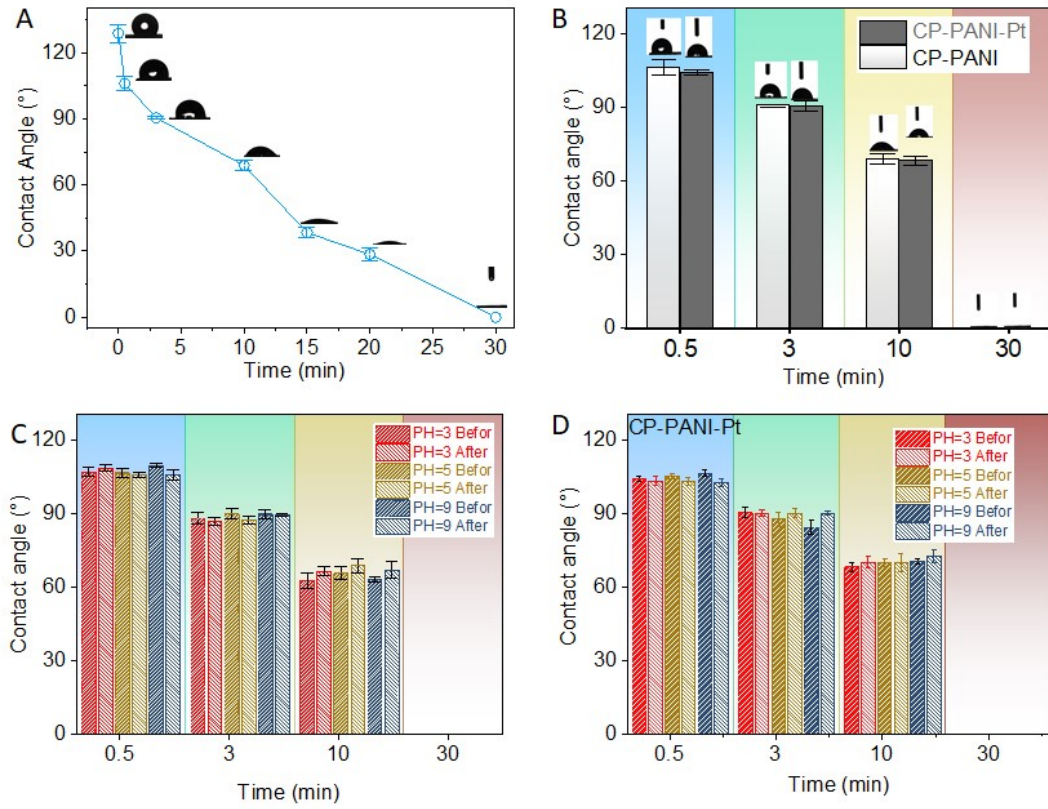


Figure S7. The contact angles of the surface of the as-prepared electrodes.

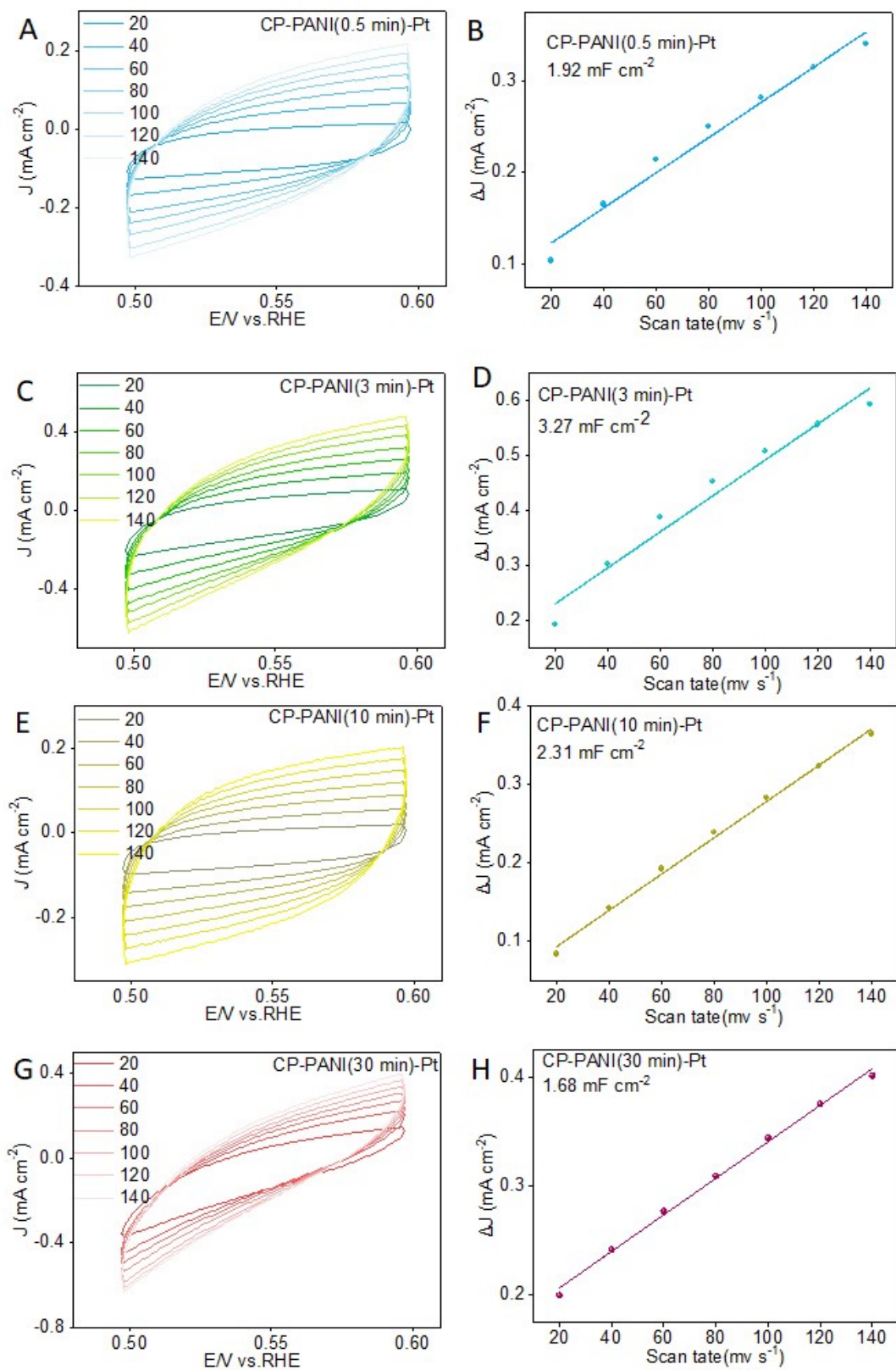


Figure S8 The double capacitance measurement of the as-prepared electrodes.

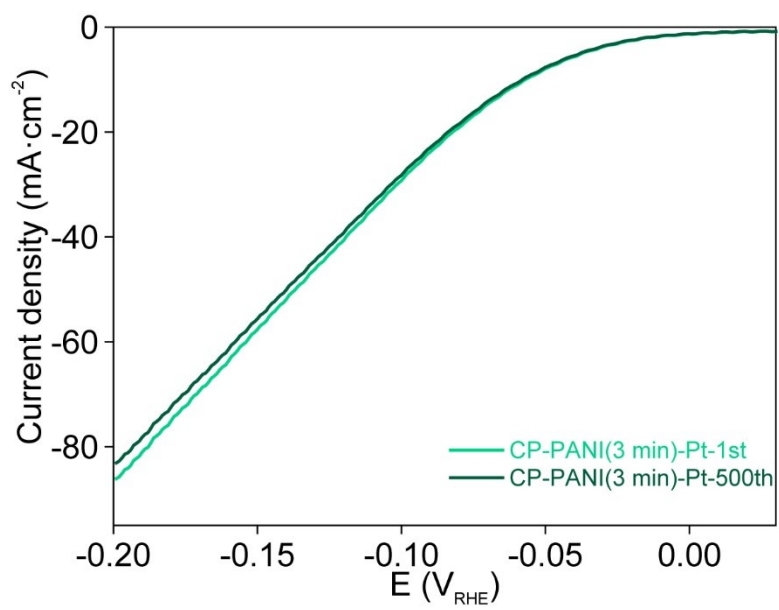


Figure S9. The LSV curves of HER on CP-PANI(3 min)-Pt electrode. The LSV curves of HER presents that the potential negative shift a little after test 500 circles, which indicates the good stability of CP-PANI(3 min)-Pt electrode.

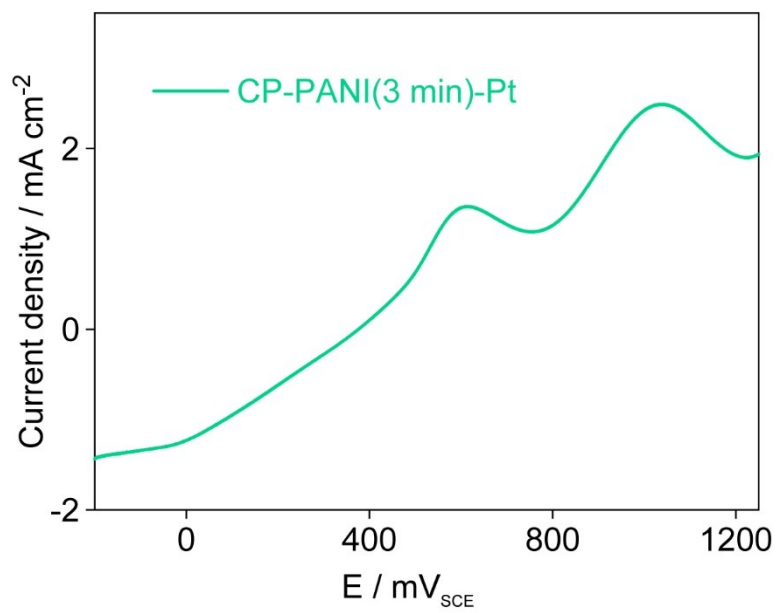


Figure 10. The LSV curve of EOR on the CP-PANI(3 min)-Pt electrode.

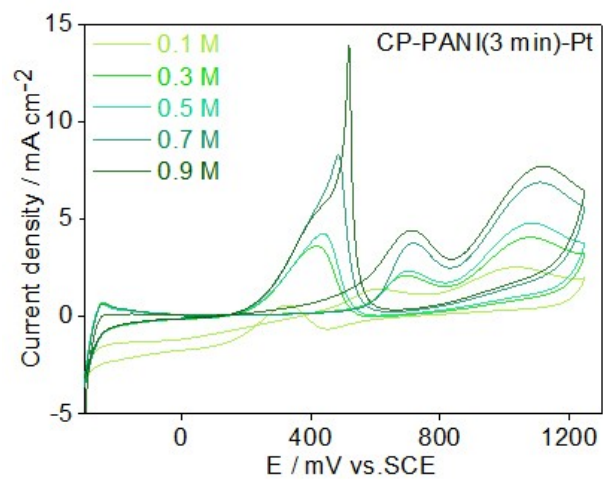


Figure S11 The EOR on the CP-PANI (3 min)-Pt electrode with different concentration of ethanol.

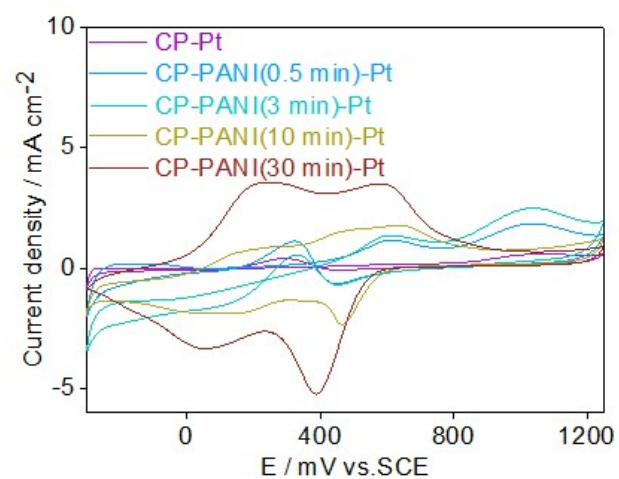


Figure S12. The EOR performance by using the CP-PANI-Pt electrodes with different thickness of PANI layers.

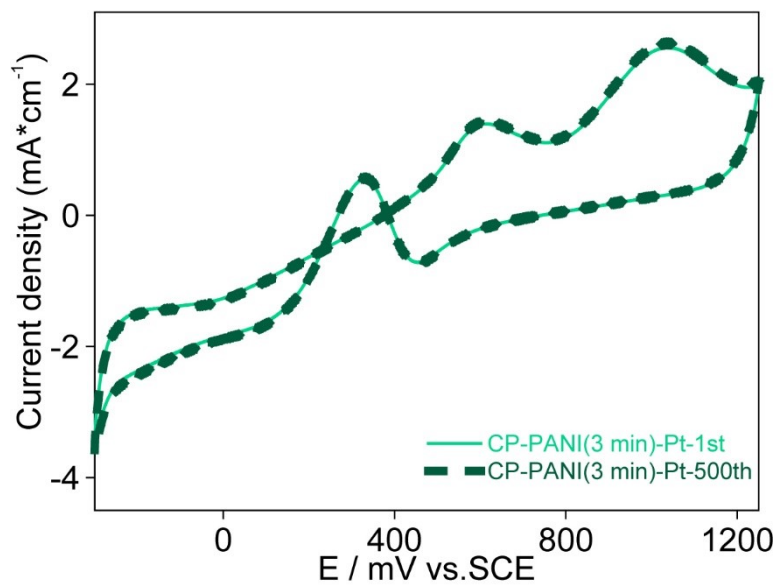


Figure S13. The CV curves of OER on CP-PANI(3 min)-Pt. The CV curves showed that the 500th circle was very closed to the first one, illustrating the high stability of the CP-PANI(3 min)-Pt.

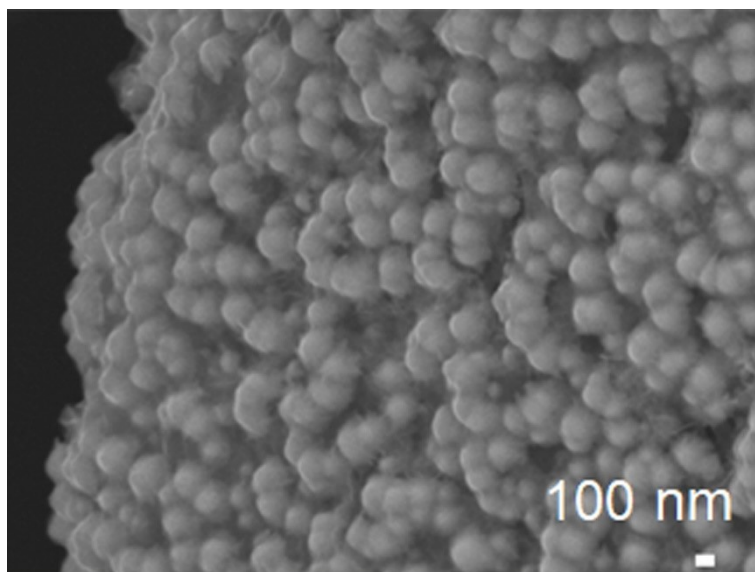


Figure S14. The SEM images of CP-PANI(3 min)-Pt after EOR test.

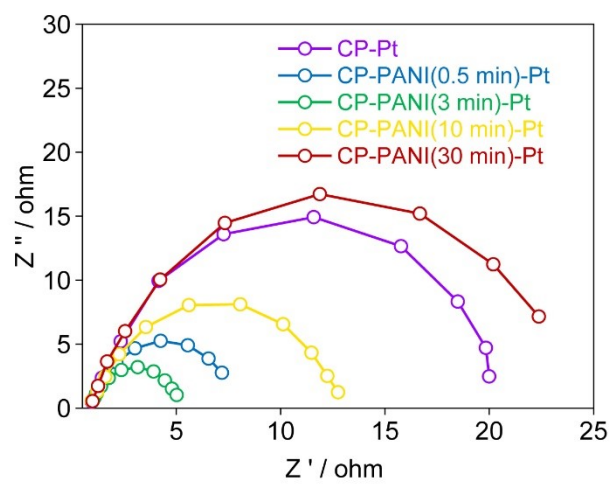


Figure S15. The ESI of the as-prepared electrodes.

Table S1. The Pt content of the series samples, which are test by ICP

Samples	Pt content ($\mu\text{g}\cdot\text{cm}^{-2}$)
CP-Pt	26.83
CP-PANI(0.5 min)-Pt	35.1
CP-PANI(3 min)-Pt	33.3
CP-PANI(10 min)-Pt	32.7
CP-PANI(30 min)-Pt	38.6

Table S2. The catalysis performance of the electrode in this work compared with other electrodes in other reported work.

Electrocatalyst	E_f (V) *	E_b (V) **	J_f (mA cm ⁻²)	Ref.
CP-PANI(3 min)-Pt	0.609	0.331	1.43	this work
Pt/Ti	0.71	0.52	0.88	<i>J.Power Sources</i> , 2011, 196 3119
Pt/TiO ₂ /Ti	0.76	0.53	1.81	<i>J.Power Sources</i> , 2011, 196 3119
HIF-Pt/C	0.66	0.52	4.5	<i>Angew. Chem.</i> 2010, 122, 421.
Pt/NbRuO	0.75	0.62	1.1	<i>J. Phys. Chem. C</i> 2011, 115, 3043
Pt@Sn/C	0.5	-	0.9	<i>J. Am. Chem. Soc.</i> , 2014, 136(31): 10862
PtSn/C	0.82	0.65	0.09	<i>Electrocatalysis</i> , 2016, 7, 193.
Pd@Pt	0.86	0.63	6.2	<i>Int. J. Hydrogen. Energ.</i> , 2013, 38, 12681.
PtRu/graphite	0.52	0.33	2.32	<i>Carbon</i> , 2010, 48, 78.

* E_f : the potential of the forward peak, the potential of the ethanol oxidation peak.

** E_b : the potential of the backward peak, generally characterizing the CO desorption.