Supporting Information

Impact of Pt Particle Size Distribution on HER Pathway and Performance

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1. Experimental

1.1 Materials

All chemicals were purchased from reagent companies and used directly without further purification. Dopamine ($C_8H_{11}NO_2$, 98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tris hydrochloride ($C_4H_{11}NO_3$, 99.9%) was obtained from Saiguo Biotechnology Co., Ltd. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BR) was purchased from Energy Chemical. Trimethylbenzene (C_9H_{12}, 99.7%), ethanol (C_2H_5OH, 99.7%), and sulfuric acid (H_2SO_4, 99.7%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Chloroplatinic acid (H_2PtCl_6, 99.9%) was acquired from Shanghai Macklin Biochemical Technology Co., Ltd. The 20% commercial Pt/C (20%-Pt/C, 20%) was purchased from JM Company (USA). Nafion perfluorosulfonic acid resin ($C_7HF_{13}O_5SC_2F_4$, 10%) was obtained from Shengernuo Technology Co., Ltd.

1.2 Synthesis of PDA Nanospheres

2 g of 3,3′,5,5′-tetramethylbenzidine (TMB) and 2 g of Pluronic F-127 (F127) were added to the aqueous phase (250 mL of water + 250 mL of trimethylbenzene) respectively. After being stirred uniformly, the mixture was sonicated for 30 minutes. Then, an appropriate amount of tris(hydroxymethyl)aminomethane (approximately 100 mg) was added to adjust the pH of the solution to 8.5. Subsequently, 600 mg of DA was added, and the mixture was stirred at room temperature for 24 hours. The product was washed twice with alcohol and ethanol respectively, centrifuged, and then placed in a blast drying oven for 24 hours to obtain PDA nanospheres. The size of PDA nanospheres was regulated by changing the polymerization time (8 h, 16 h, 24 h, and 32 h respectively), resulting in PDA nanospheres with sizes of 130 nm, 200 nm, 400 nm, and 550 nm.

1.3 Synthesis of Pt/C Catalysts

100 mg of PDA nanospheres were weighed and dissolved in distilled water. After

ultrasonic homogenization, 26.34 mg of H_2PtCl_6 was added, and the mixture was stirred at room temperature for 24 hours. Then, it was washed twice with alcohol and distilled water respectively, centrifuged, and placed in a blast drying oven for 24 hours to obtain Pt/C catalyst precursors with Pt^{4+} supported on PDA nanoparticles of different sizes. Subsequently, the samples were placed in a tube furnace and subjected to carbonization treatment at 1000 °C under the protection of N_2 inert atmosphere, yielding Pt/C-130, Pt/C-200, Pt/C-400, and Pt/C-550 catalysts. The carbonization temperature of 1000 °C was determined as the optimal annealing temperature for the Pt/C-200 catalyst after annealing at different temperatures.

1.4 Physical characterization

The morphology of the catalyst samples was characterized using a scanning electron microscope (SEM, TESCAN VEGA, Czech Republic). The composition of the catalysts was analyzed by X-ray diffraction (XRD, Rigaku SmartLab SE, Japan). Additionally, the microstructure and crystallographic information of the catalysts were characterized via transmission electron microscopy (TEM, FEI Tecnai G2 F20, Japan). The surface elemental species and chemical bonds of the catalysts were determined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, USA). The elemental contents in the catalysts were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 720, USA).

1.5 Electrochemical characterization

All the HER electrochemical performance tests in this experiment were conducted using a three-electrode system on a Chenhua CHI660E electrochemical workstation. A 0.5 M H_2SO_4 solution was used as the electrolyte, with an Ag/AgCl electrode as the reference electrode, a graphite rod as the counter electrode, and a glassy carbon electrode (with a diameter of 3 mm) drop-coated with the catalyst as the working electrode. Specifically, 2 mg of the catalyst was weighed and added, along with 20 μL of Nafion, to a mixed solution composed of 600 μL of water and 400 μL of isopropanol. Subsequently, this mixture was subjected to ultrasonic treatment for 30 minutes to

obtain a uniformly dispersed liquid. Using a pipette, 5 μL of this dispersion was dropped onto the surface of the glassy carbon electrode. The catalyst suspension was dried under infrared lamp illumination to prepare the working electrode for subsequent electrochemical tests.

Linear Sweep Voltammetry (LSV) Tests： The LSV tests were performed at a scan rate of 5 mV s^{-1} within the voltage range of -0.2 V to -0.7 V. All test results were corrected with 90% iR compensation according to the equation: $E_{correct} = E_{RHE} - iR_s$, where Rs represents the solution resistance obtained from EIS. The Tafel curves were derived by processing the LSV test data according to Equation (1), and the reaction pathway in the HER process was determined based on the Tafel slope:

$$\eta = a + b \lg |j| \quad (1)$$

where b is the Tafel slope and j is the current density.

Electrochemical Impedance Spectroscopy (EIS) Tests： The EIS tests on the catalysts were carried out over a frequency range of 10^{-2} to 10^{5} Hz with an amplitude of 5 mV.

Measurement of Electrochemical Active Surface Area via Hydrogen Adsorption-Desorption Method： Cyclic voltammetry scans were performed within an appropriate potential range. During the scanning process, the curve of current versus potential was recorded. When the potential was scanned from negative to positive, the hydrogen atoms adsorbed on the catalyst surface underwent desorption, resulting in an obvious desorption current peak. The obtained curve was integrated to calculate the charge of the hydrogen desorption peak (QH). The electrochemical active surface area of the catalyst was calculated using Equation (2) based on the known charge for hydrogen adsorption per active site (theoretical value Q0 = 210 μC/cm^2):

$$ECSA = \frac{QH}{Q0 * m} \quad (2)$$

where m is the mass of the catalyst.

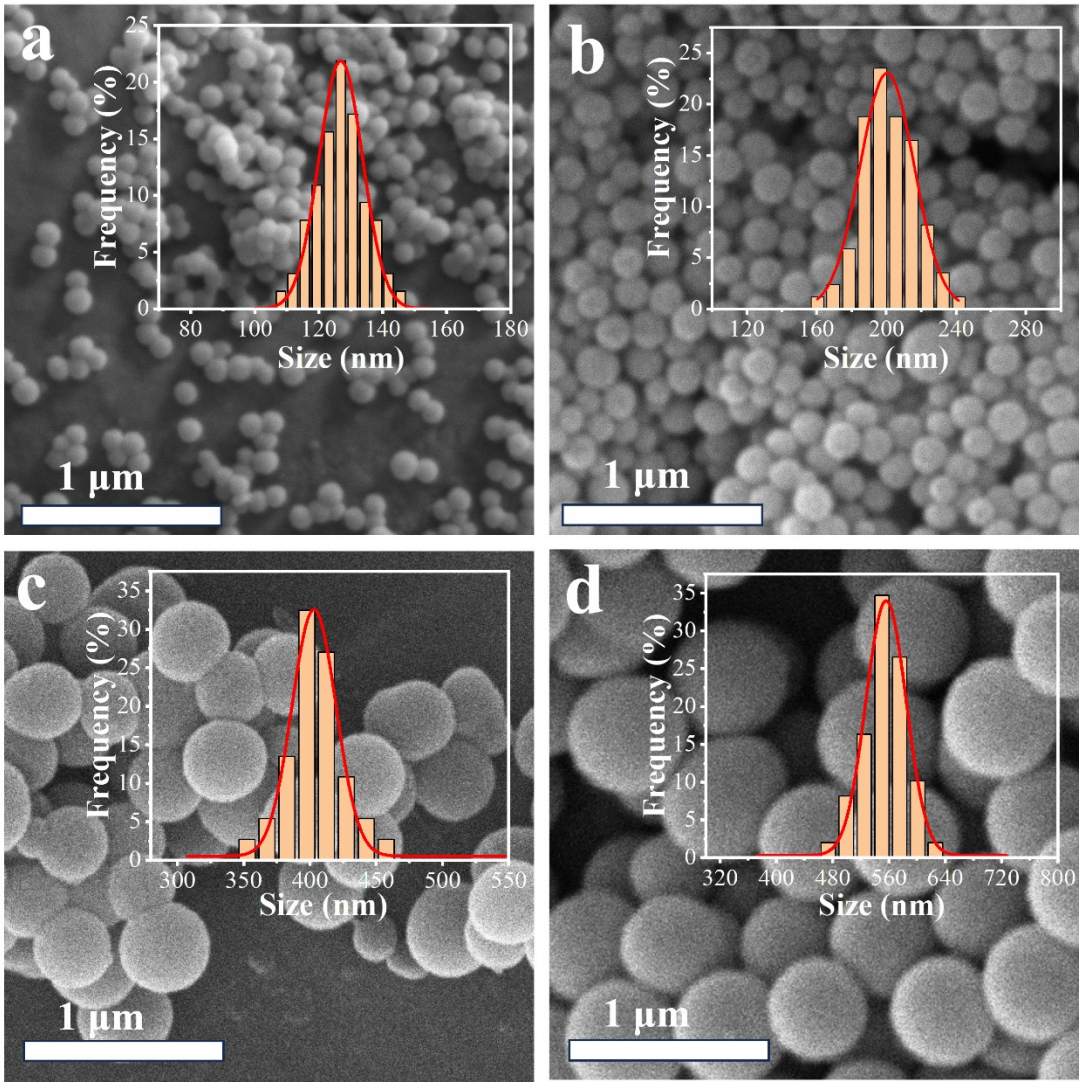


Fig. S1. Morphology and Size of Pt^{4+}-Loaded PDA Nanospheres with Different Sizes: (a) 130 nm; (b) 200 nm; (c) 400 nm; (d) 550 nm

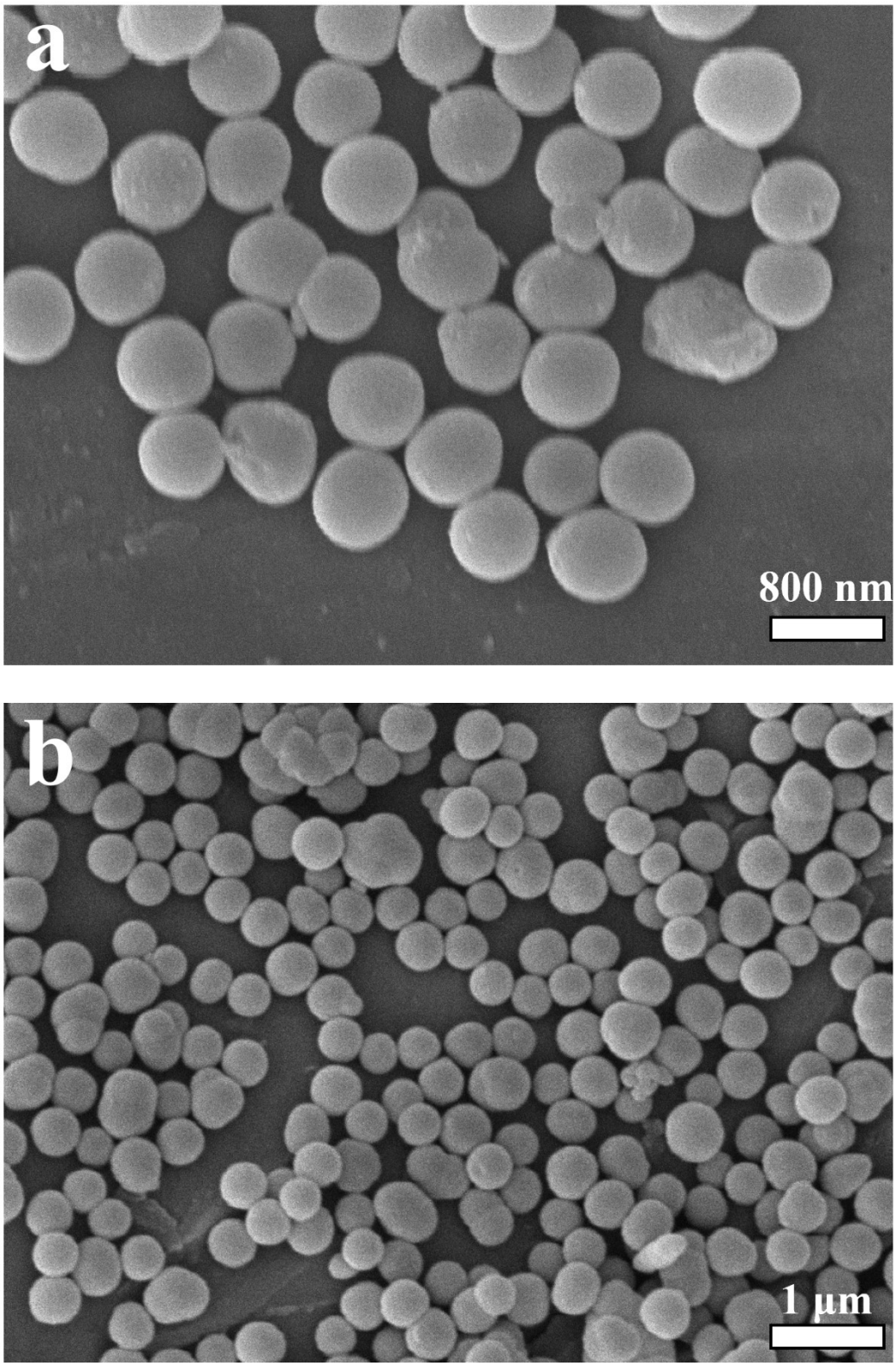


Fig. S2. SEM Morphologies of Pt/CS-200 Before and After Carbonization: (a) Before Carbonization; (b) After Carbonization

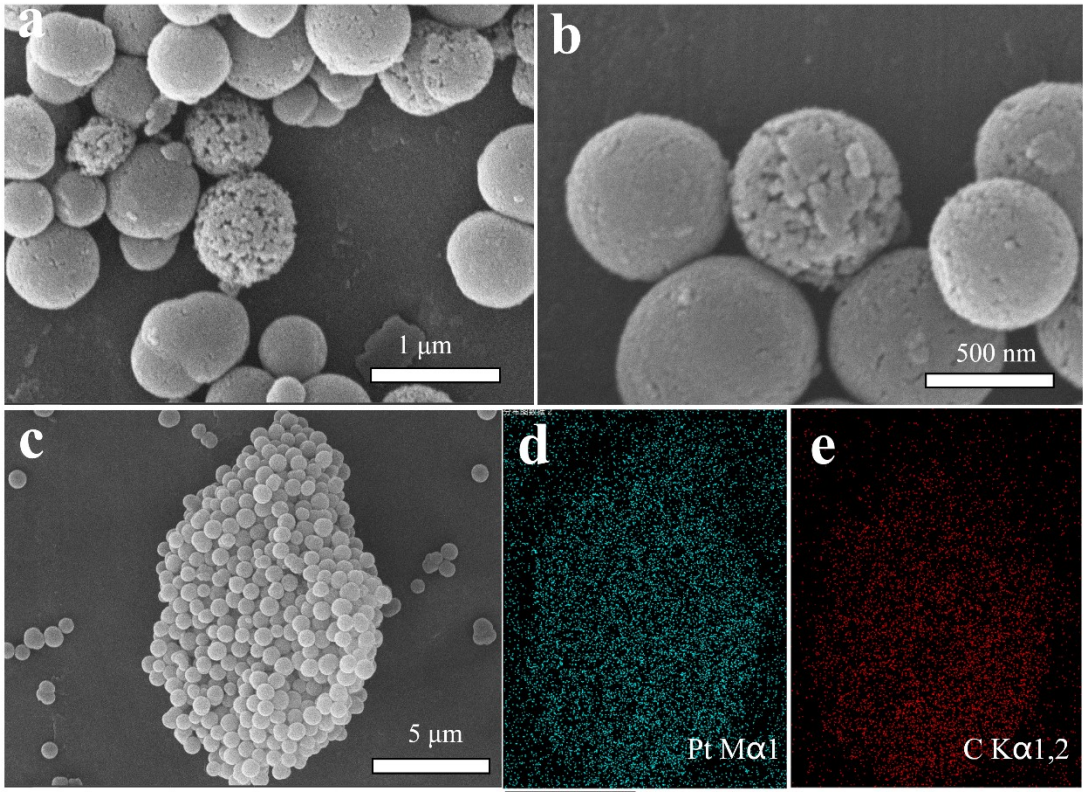
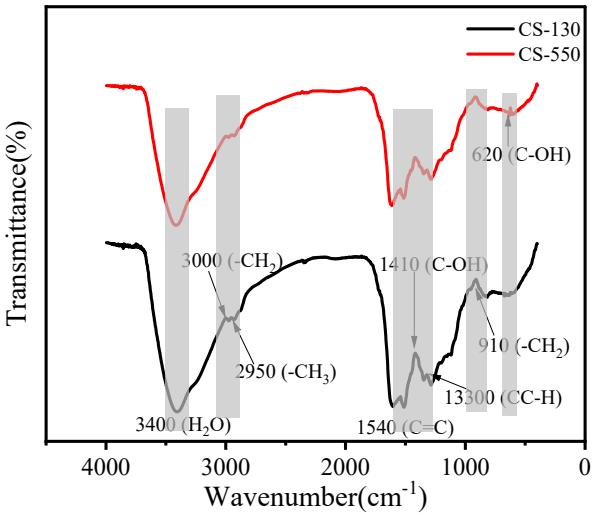


Fig. S3. Morphological and Elemental Composition Analysis of Pt/CS-550: (a-c) SEM Morphology Images; (d, e) EDS Mapping Results



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2 **Fig. S4.** Comparison of FTIR spectra for PDA carbon spheres with CS-130 and CS-550.

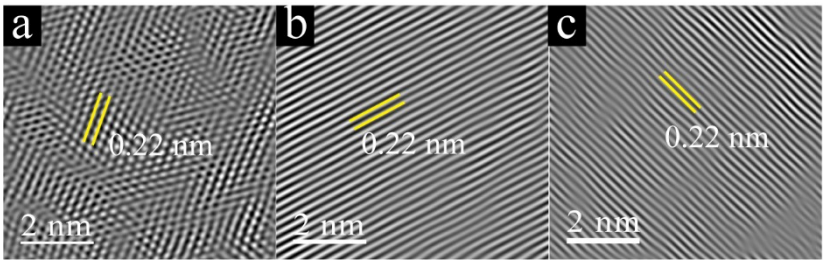


Fig. S5. (a–c) Inverse FFT images (IFFT) corresponding to regions 1#, 2#, and 3# in Fig. 2(g), respectively.

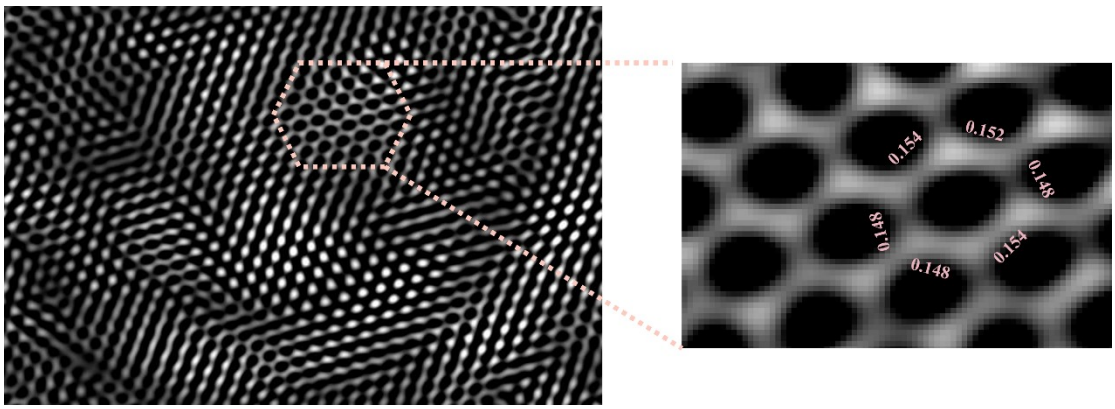
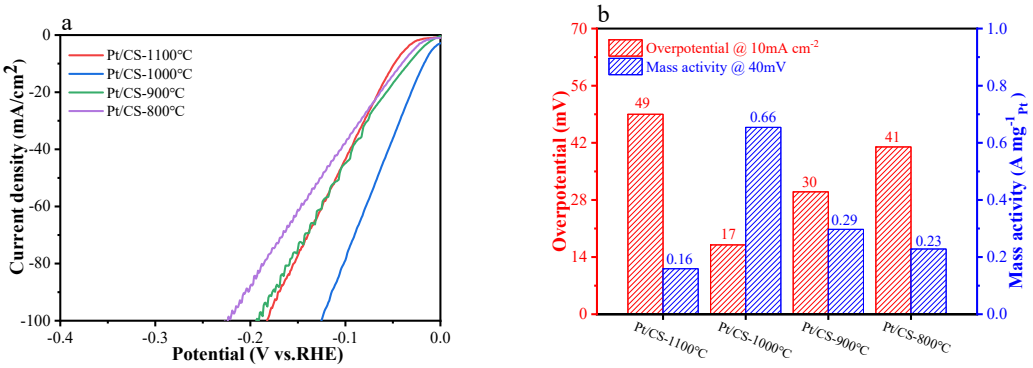


Fig. S6. Surface Structural Analysis of Pt/CS-200



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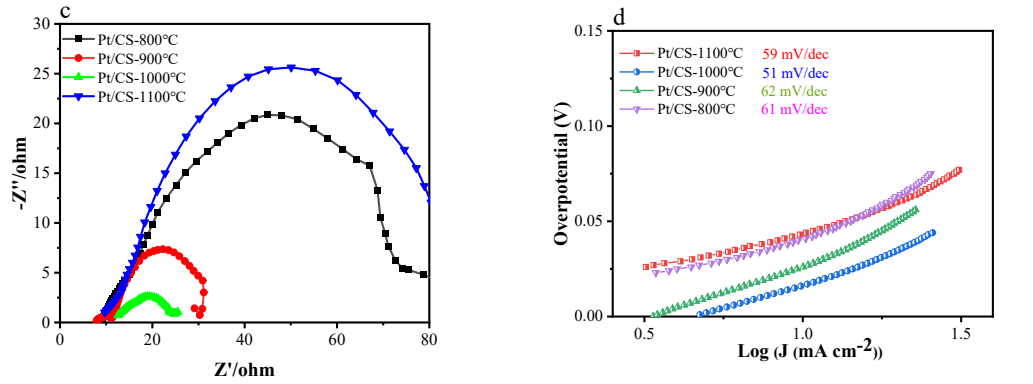

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4 **Fig. S7.** Pt/CS-200 at different carbonization temperatures: (a) LSV curves; (b)
5 Overpotential at 10 mA cm^{-2} and mass activity at 40 mV (bar chart); (c)
6 Electrochemical impedance spectra; (d) Tafel slopes.

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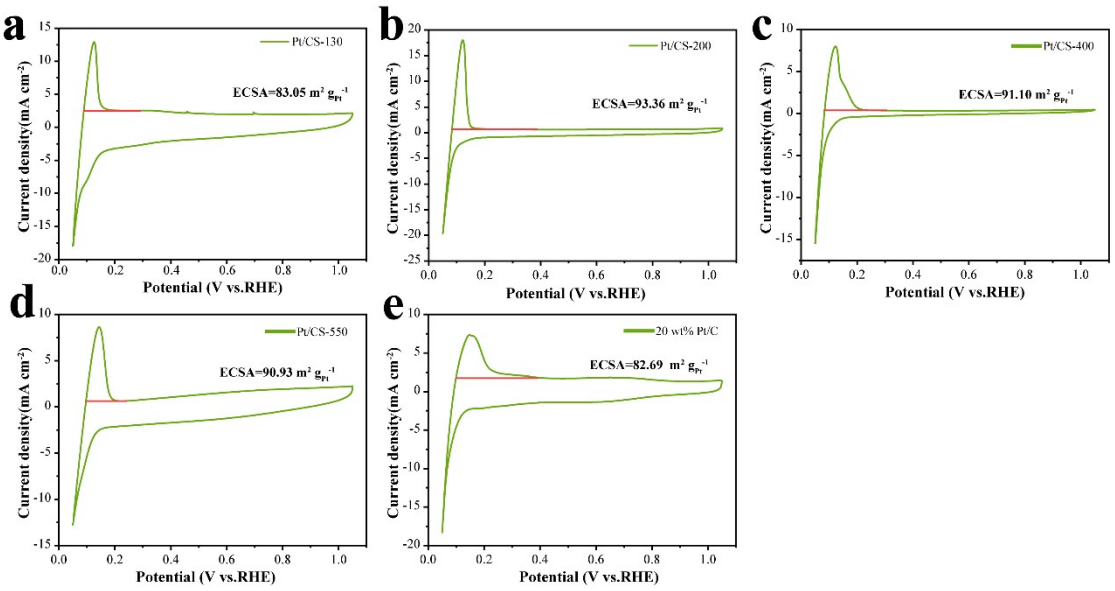

Fig. S8. Hydrogen Adsorption Test: Electrochemical Active Surface Area (ECSA) of Pt/CS-130 (a), Pt/CS-200 (b), Pt/CS-400 (c), Pt/CS-550 (d), and Commercial 20%-Pt/C (e).

Table S1. The fitting impedance parameters of Pt/CS-130, Pt/CS-200, Pt/CS-400, Pt/CS-550, and 20% wt Pt/C.

	Rs	Rct	CPE-T	CPE-P
Pt/CS-130	10.5	15.4	0.00122	0.500
Pt/CS-200	12.2	13.4	0.000679	0.530
Pt/CS-400	9.8	15.8	0.00106	0.663
Pt/CS-550	12.3	29.6	0.00103	0.706
20% wt Pt/C	8.7	17.2	0.000188	0.691

Table S2. ICP-MS statistics of Pt content of Pt/CS-130, Pt/CS-200, Pt/CS-400, and Pt/CS-550

samples	Pt content (wt%)
Pt/CS-130	12.37
Pt/CS-200	15.05
Pt/CS-400	15.98
Pt/CS-550	11.77

Table S3. Comparison of synthetic approach and HER activity of reported electrocatalysts under 0.5 M H_2SO_4 solution.

No.	Catalysts	Overpotential(mV)	Tafel slope (mV/dec)	Ref.
01	Pt/CS-200	17	29.8	This work
02	1 wt% Pt/ Mo_2C/C	19	28	[1]
03	g-C_3N_4@Pt	100	77	[2]
04	Pt NPs/DPC	30	31	[3]
05	L-PtNi-C	38	29.6	[4]
06	Pt/CoNC	15.2	45.6	[5]
07	C-ZIF-CuPt	46	45	[6]
08	Pt/C-0.2	17	48.43	[7]
09	$Pt_{1\ \%}$-$CoMoS_2$/C	118	68	[8]
10	Pt-WC-1,10/BMZ	23	40.1	[9]
11	Pt NCs	42	101	[10]
12	L-Pt/SC	23	24	[11]
13	C-rPDA-Pt/TiO_2 NSs	60	34.8	[12]

Refences

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