Supporting Online Material for

Ultralow loading Pt decorated coral-like Pd nanochain networks with enhanced activity and stability towards formic acid electrooxidation

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Experimental Section

Materials: Poly-(N-vinyl-2-pyrrolidone) (PVP·K30, molecular weight: 30000-40000), H_2SO_4, KOH, hydrazine (N_2H_4, 80%), $PdCl_2$ and H2PtCl6 were purchased from Beijing Zhongxihuabo Factory (Beijing, China). Pt/C catalysts were purchased from BASF. Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) were obtained from Aldrich. Water (18 Ωm) used throughout all experiments was purified with the Millipore system.

Apparatus: Transmission electron microscope (TEM) and high-resolution (HRTEM) measurements were made on a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. Field emission scanning electron microscope (FESEM) was made on a JSEM-7500F scanning electron microscope operating at 3 kV. XPS

measurement was performed on a PHI Quantera spectrometer (ULVAC-PHI,Inc.) with Al Kα X-ray radiation as the X-ray source for excitation. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 40 mA) radiation, and diffraction patterns were collected at a scanning rate of 5 ^{o}/min and with a step of 0.02 ^{o}. CV experiments were performed with a CHI 660C electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China).

Synthesis of Pd-coral-like nanochain networks (PdCNNs): 5ml 56 mmol L^{-1} $PdCl_2$ aqueous solution and 31.3mg PVP with the initial molar ratio of 1:1 were added to 20ml of ultra-pure water by continuously stirring for 30min. The pH of solution was controlled by KOH (1.0M) aqueous solution. After stirring for 1h, 1ml N_2H_4 (80%) was added to the mixture followed by continuously stirring for 12h. The product was collected by centrifugation, washed several times with water and dissolved in 1 mL of ultra-pure water for further experimental.

Synthesis of Pt-on-PdCNNs: The Pt-on-PdCNNs were prepared by a spontaneous displacement reaction. 0.1 mL of the above solution was added into 2.9 mL of ultra-pure water, and then 19 mmol L^{-1} H_2PtCl_6 aqueous solution with different Pt/Pd ratios were added into solution. After ultrasonic blending for 30 min, the solution was then heated to 60 ^{o}C under magnetic stirring and left reacting for 5 h at N_2 atmosphere. Finally, the product was collected by centrifugation, washed one times with water and dissolved in 1 mL of ultra-pure water for further experimental.

Electrocatalytic experiment: A conventional, three-electrode cell consisting of glassy carbon (GC) with a diameter 5 mm as the working electrode, Pt wire as the counter electrode, and a salt bridge connected to the reference electrode compartment was used for all electrochemical measurements. The reference electrode was a reversible hydrogen electrode (RHE) in the same electrolyte as the electrochemical cell. All potentials throughout this paper are referred to RHE. Working electrodes were prepared by mixing the catalyst with Nafion (0.05 wt % Nafion dissolved in ethanol) solution. The mixture was sonicated and about 10.0 μL was applied onto a glassy

carbon disk and dried at infrared lamp. After solvent evaporation, a thin layer of Nafion-catalyst ink remained on the GC surface to serve as the working electrode. Cyclic voltammetry (CV) was carried out at room temperature in a deaerated 1 M HCOOH + 0.5 M H_2SO_4 solution to evaluate the catalyst activity for formic acid oxidation. For CO stripping voltammetry, CO was adsorbed at 0.1V (RHE) in 0.5 M H_2SO_4 solution for 10 min, excess CO in the electrolyte was then purged out with N_2 for 10 min, and then two first cycles were recorded at 50 mV s^{-1} at the beginning with 0.1V.

Figures

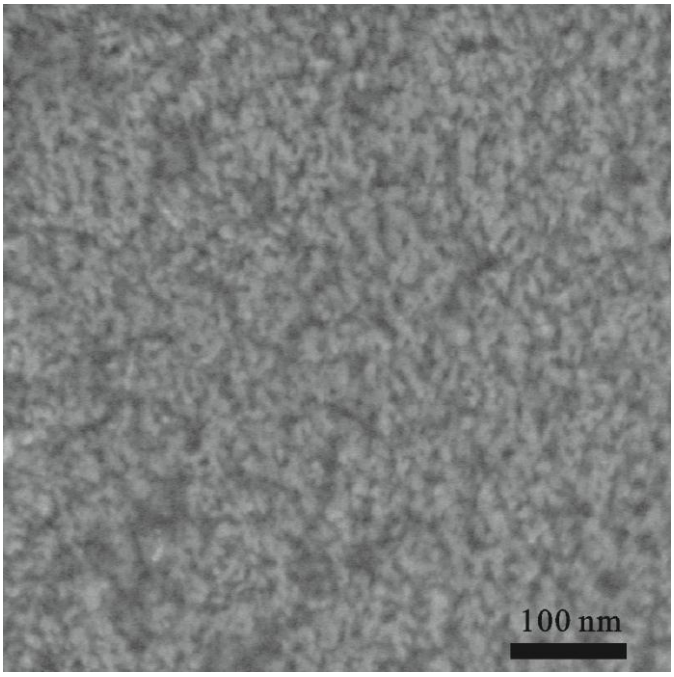

Figure S1 FESEM image of PdCNNs (pH= 7)

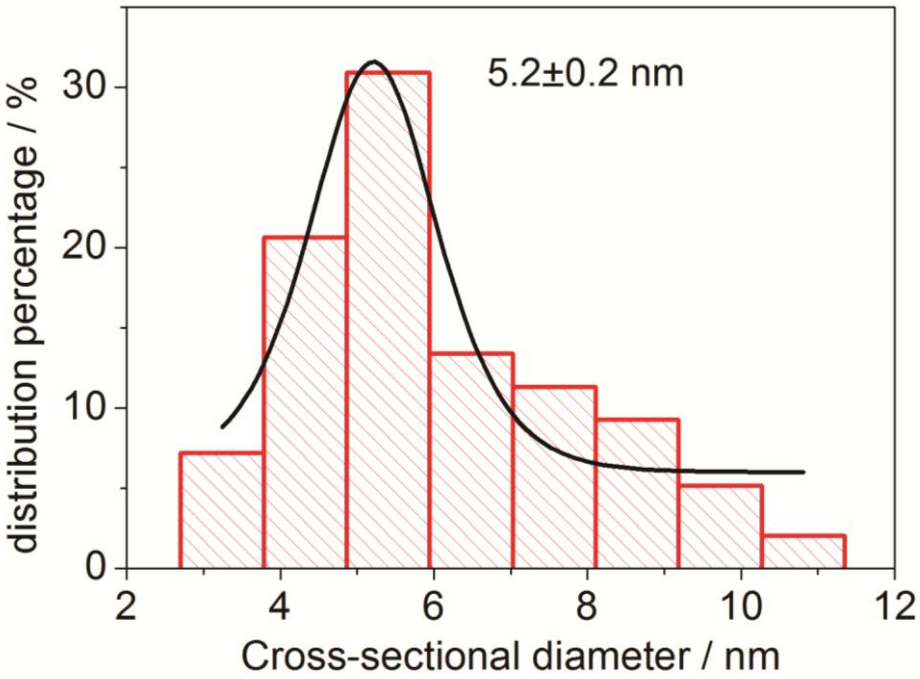

Figure S2 histogram of cross-sectional diameter of PdCNNs

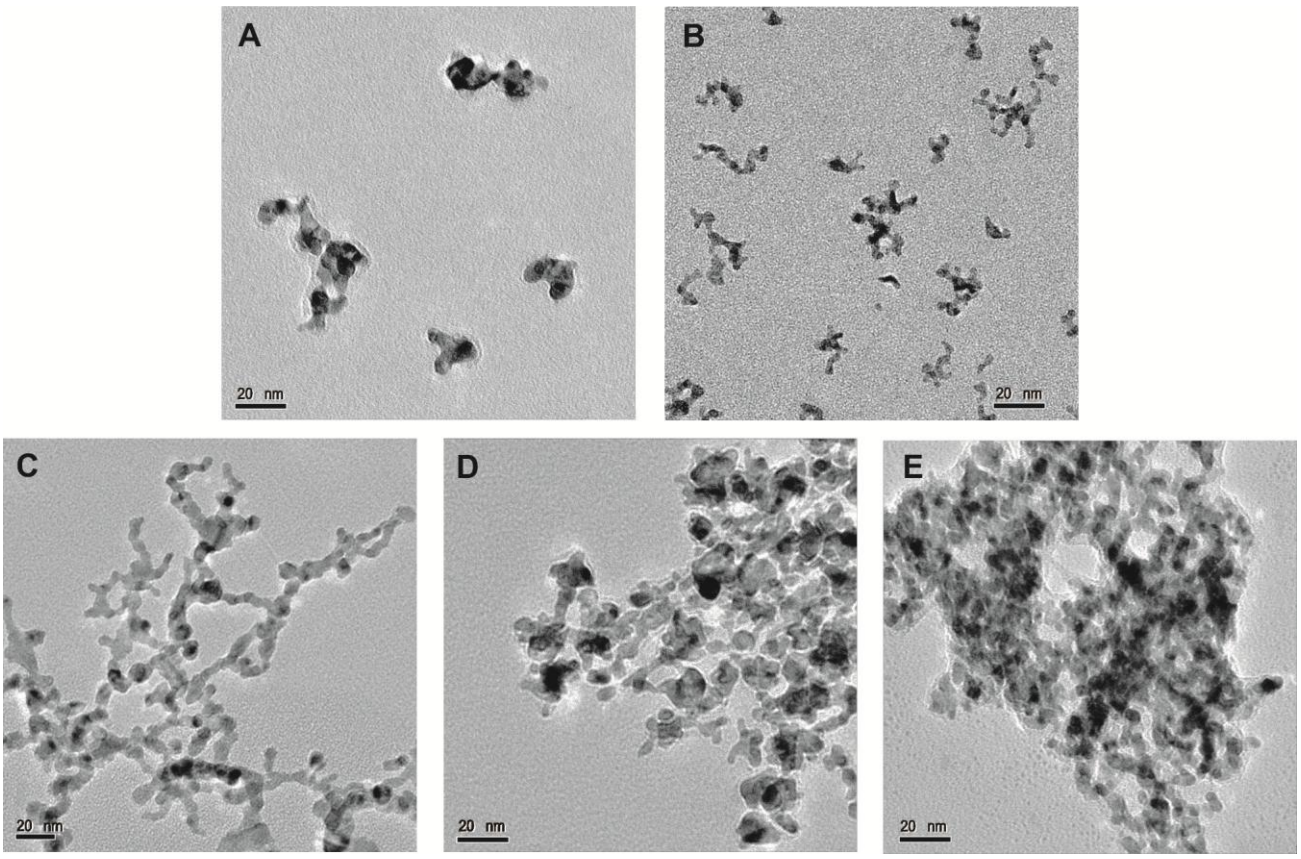

Figure S3 TEM images of PdCNNs synthesized with different pH value (A) pH= 2; (B) pH= 5; (C) pH=7; (D) pH=10; (E) pH=12

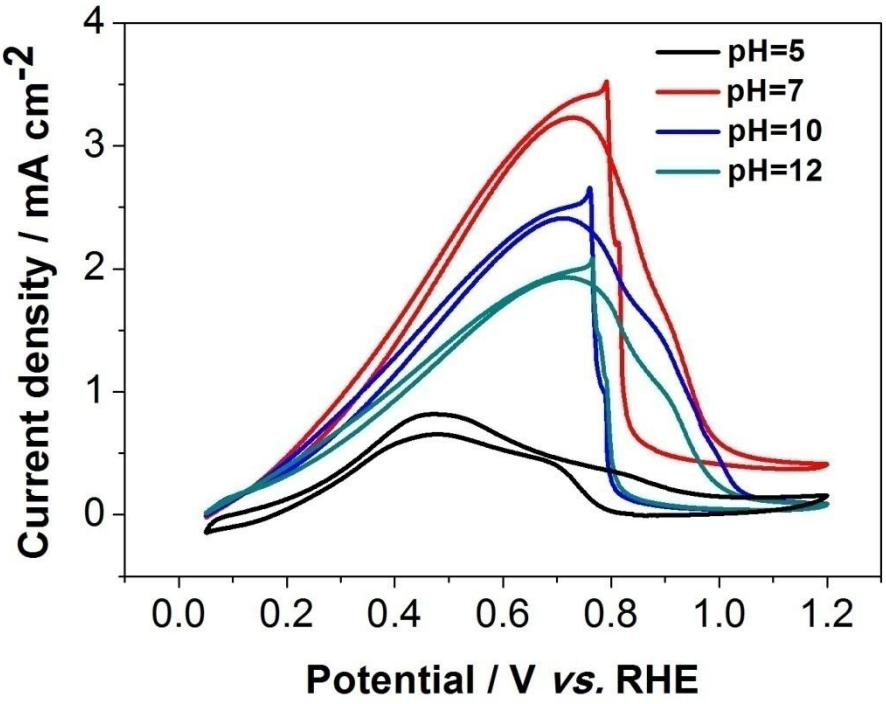

Figure S4 CVs of PdCNNs synthesized at different pH value in the synthesis in 0.5 M H_2SO_4 + 1.0 M HCOOH at the scan rate of 50 mV s^{-1}.

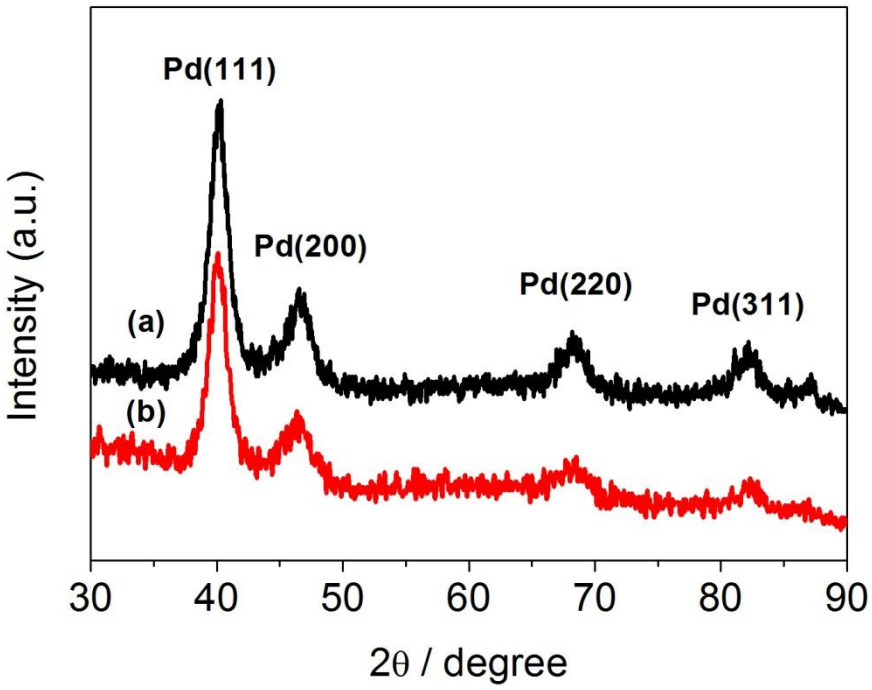

Figure S5 XRD pattern of (a) PdCNNs, (b) Pt-on-PdCNNs.

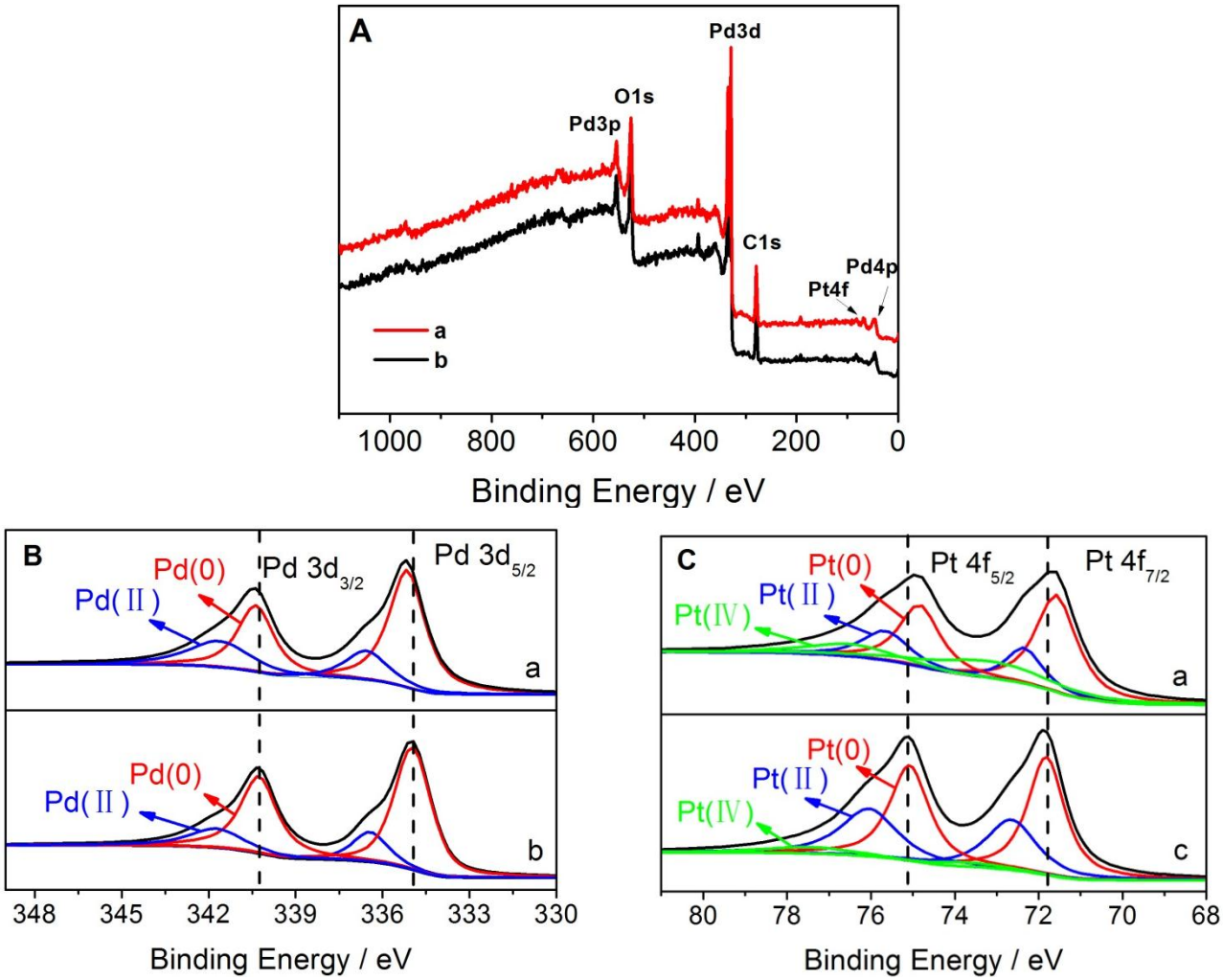

Figure S6 XPS of different catalysts, a: Pt-on-PdCNNs, b: PdCNNs, c: Pt/C (20 wt%, BASF). (A) Wide-range XPS

(B) Pd 3d XPS (C) Pt 4f XPS

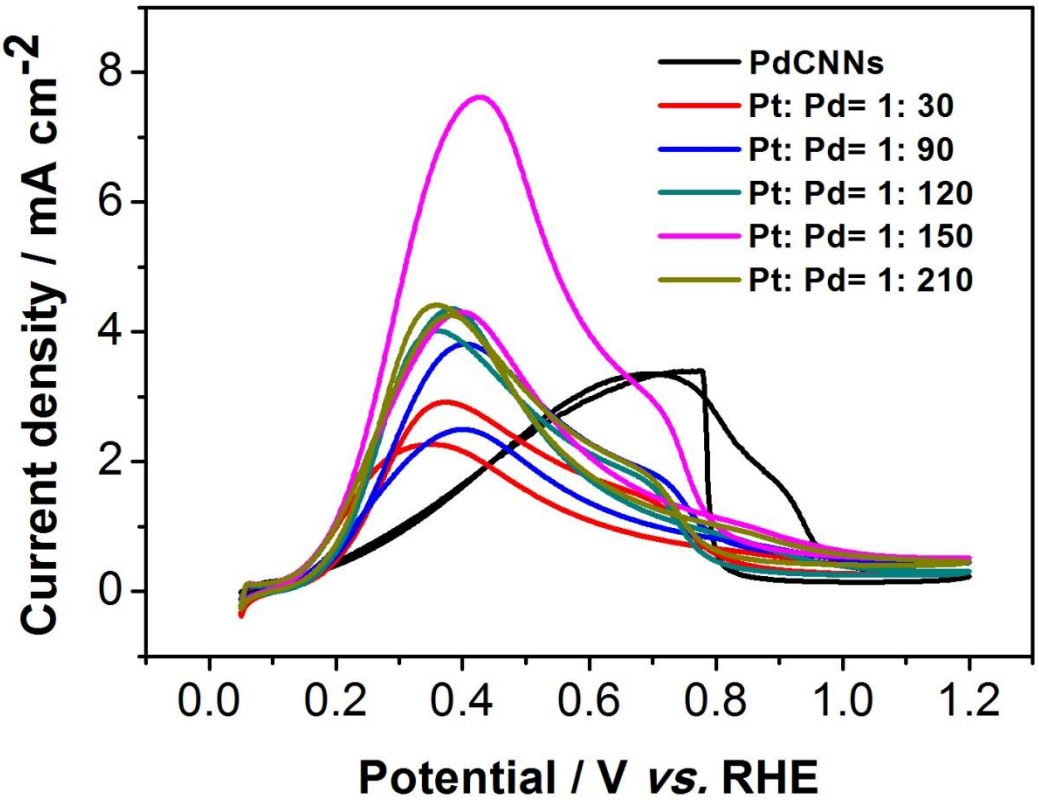

Figure S7 CVs of Pt-on-PdCNNs synthesized with different Pt/Pd molar ratios in 0.5 M H_2SO_4 + 1.0 M HCOOH at the scan rate of 50 mV s^{-1}.

Table S1 Catalyst characterization and catalytic performance (formic acid oxidation) of Pt-on-PdCNNs, PdCNNs, Pd/C (20 wt%) and Pt/C (20 wt%, BASF).

Catalysts	Metal Loading(μg)	ECSA (m^2/g_{metal})	I_{peak} (mA/cm^2)	I_{peak} (A / mg_{metal})
Pt-on-PdCNNs	50	32.92	7.62	2.51
PdCNNs	50	31.06	3.36	1.04
Pd/C	10	55.12	1.27	0.70
Pt/C	10	65.21	1.73	1.13