

Supporting information

Porous N-Doped Graphitic Carbons Assembled One-Dimensional Hollow
Structures as High Performance Electrocatalyst for ORR

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EXPERIMENTAL SECTION

Materials and Characterization Methods

All chemical reagents were used as received. Polyvinylpyrrolidone (PVP, M_w : 55000) and Nafion solution were purchased from Sigma Aldrich, and all other chemicals, including cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), thioglycolic acid (TGA), potassium tellurate (K_2TeO_3), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (Hmim), sodium borohydride (NaBH_4), potassium hydroxide (KOH), sodium hydroxide (NaOH) and Pt(20 wt%)/C were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Transmission electron microscopy (TEM) images were collected on a Tecnai F30 operated at 300 kV. Element distribution mapping was performed on JEM-ARM200F transmission electron microscope. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Raman scattering spectra were monitored by Jobin Yvon LabRAM HR Evolution Raman Spectrometer. N_2 sorption isotherm at 77 K was carried out Micromeritics 3Flex Surface Characterization Analyzer after being degassed in vacuum at 200 °C for 12 h. The contents of Zn, Te, and Cd elements were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALab 250 X-ray photoelectron spectrometer. Linear-sweep voltammetry (LSV) was measured on a conventional three-electrode cell using a CHI660C electrochemical workstation. Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy

(EIS) were carried out in a ZAHNER ENNIUM electrochemical workstation. Ag/AgCl and platinum wire were used as reference and counter electrodes, respectively, in all electrochemical measurements.

Synthetic Procedures

Preparation and Assembly of CdTe QDs: We used a modified method to synthesis of TGA-CdTe QDs. In a typical procedure, Cd(CH₃COO)₂•2H₂O aqueous solution (50 mL, 4 mM) and TGA (18 μL) were added into a 250 mL round-bottom flask, and pH value of the mixture was adjusted to 10.7 using NaOH solution (1 M) under magnetic stirring; K₂TeO₃ aqueous solution (50 mL, 0.8 mM) and NaBH₄ (80 mg) were added in turn; the resulting solution was refluxed for 20 h at 100 °C. The reddish orange product corresponding to emission wavelength of 596-604 nm was obtained.

PVP methanolic solution (12.5 mL, 5 wt%) was introduced into the CdTe QD solution (100 mL), and the pH value of the mixture was adjusted to 9 using HCl solution (0.5 M). Prior to the addition of acetone (100 mL) and keeping for 15 min, the final solution was stirred for 24 h in the dark. Afterwards, the mixture was concentrated by centrifugation and washed with methanol for three times. Finally the nanowire (NW) sample assembled by CdTe QDs was re-dispersed into methanol (114.5 mL).

Preparation of CdTe@ZIF-8 Nanofibers: CdTe NW methanolic solution (1 mL) concentrated to ~ 10 μL was dispersed into Hmim methanolic solution (5 mL, 20 mM) without turbulence for 10 min, and then Zn(NO₃)₂•6H₂O methanolic solution (5 mL, 20 mM) was added. The resulting solution was kept room temperature for 24 h. The

sample was concentrated by centrifugation, washed with methanol and dried in a vacuum oven at 60 °C. The final product was subjected to characterization and preparation of N-doped graphitic carbons.

Preparation of one-dimensional hierarchical porous/hollow N-doped graphitic carbons (One-H/P-C): N-doped graphitic carbons were prepared by pyrolysis of ZIF-8-based precursors. A ceramic boat loading about 200 mg CdTe@ZIF-8 nanofibers was placed into a tubular furnace, and heated under N₂ atmosphere with temperature increase rate of 5 °C/min. The pyrolysis reactions were performed at 800, 900, and 1000 °C with different times including 3, 5, and 10 h. The black samples obtained were subjected to characterization and electrochemical measurements.

ZIF-8 rhombic dodecahedral nanocrystals that were synthesized by mixing Zn(NO₃)₂•6H₂O methanolic solution (50 mL, 100 mM) with Hmim methanolic solution (50 mL, 100 mM) were also used as precursors to prepare N-doped graphitic carbons under identical conditions.

Electrochemical Measurements

Preparation of Catalyst Ink: Electrocatalysts (2 mg) were dispersed into ethanol (980 μL), and then Nafion solution (20 μL, 5 wt%) was added. The mixture was formed well-dispersed suspension by ultrasonication.

Preparation of Electrode: The resulting catalyst ink was dropped on the surface of glassy carbon (5 mm diameter for LSV, and 3 mm diameter for CV and EIS), and dried at room temperature in air. It was used as the working electrode with a catalyst loading of ~0.15 mg/cm².

Ag/AgCl (3.5 M KCl) and polished Pt wire (~58 mm² for CV measurement and ~610 mm² for LSV measurement) were used as the reference electrode and the counter electrode, respectively.

Electrochemical Measurement: CV tests were measured in O₂ (N₂) saturated 0.1 M KOH solution after bubbling O₂ (N₂) for 30 min with a scan rate of 10 mV s⁻¹ between -1.0 V and 0.2 V vs Ag/AgCl. LSV tests on a rotating disk electrode (RDE) were measured in O₂ saturated 0.1 M KOH solution at a sweep rate of 10 mV s⁻¹ between -0.8 V and 0.1 V vs Ag/AgCl with different rotation speeds from 400 to 2400 rpm. The durability of catalysts was performed on a RDE in O₂ saturated 0.1 M KOH solution at a sweep rate of 50 mV s⁻¹ between -0.8 V and 0.1 V vs Ag/AgCl with rotation of 1600 rpm. Afterwards, methanol (3 mL, 3M) was directly added to the measurement system for studies of methanol crossover. EIS was measured in O₂ saturated 0.1 M KOH solution at 0.85 V vs RHE in the frequency range of 0.01 Hz to 10 kHz with oscillation potential amplitudes of 5 mV.

Electron transfer numbers are calculated based on the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{0.5}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limited current densities, ω is the angular velocity, n is the transferred electron number, F was the Faraday constant, C_0 was the bulk concentration of O₂.

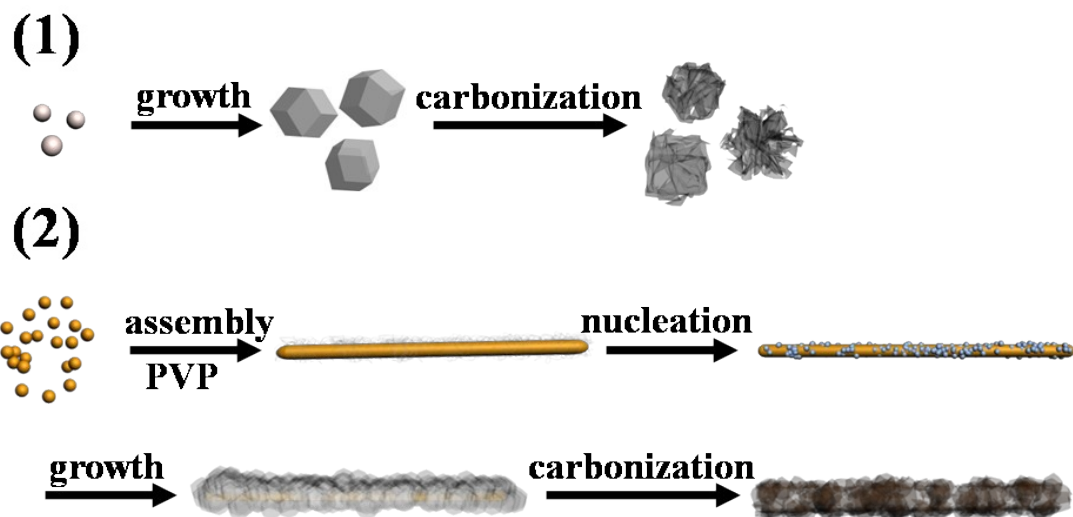


Figure S1. Schematic of preparation process of porous carbons derived from MOFs (1) without and (2) with nanowires assembled by CdTe quantum dots as hard templates.

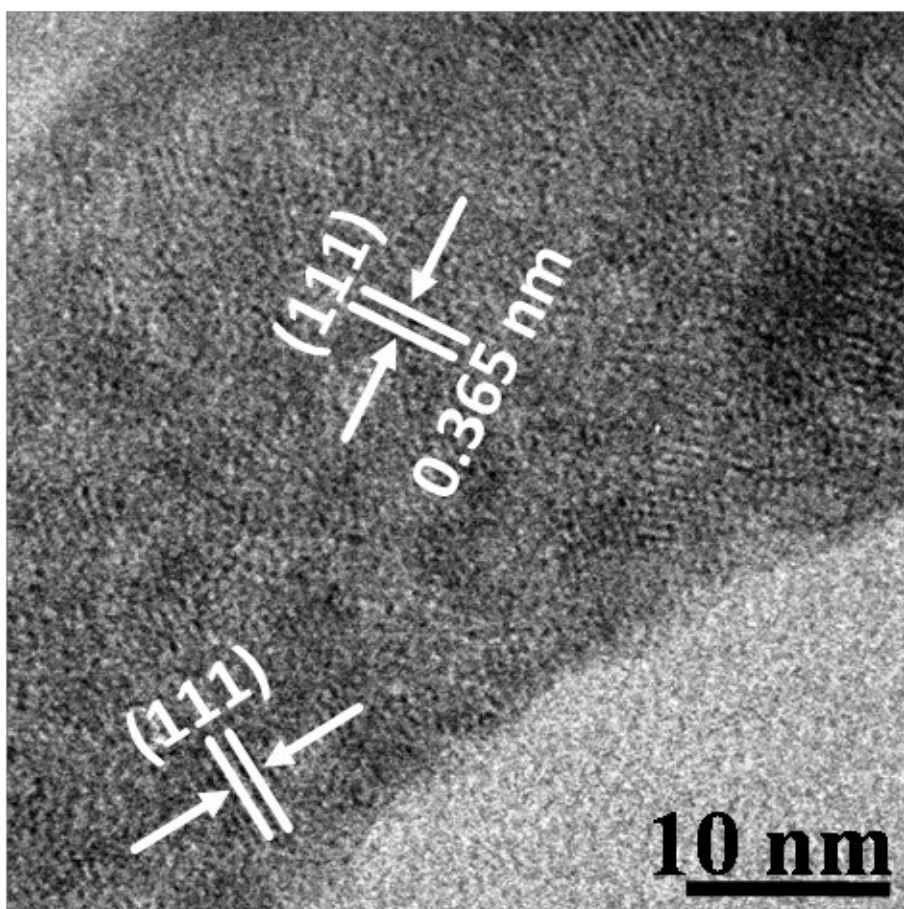
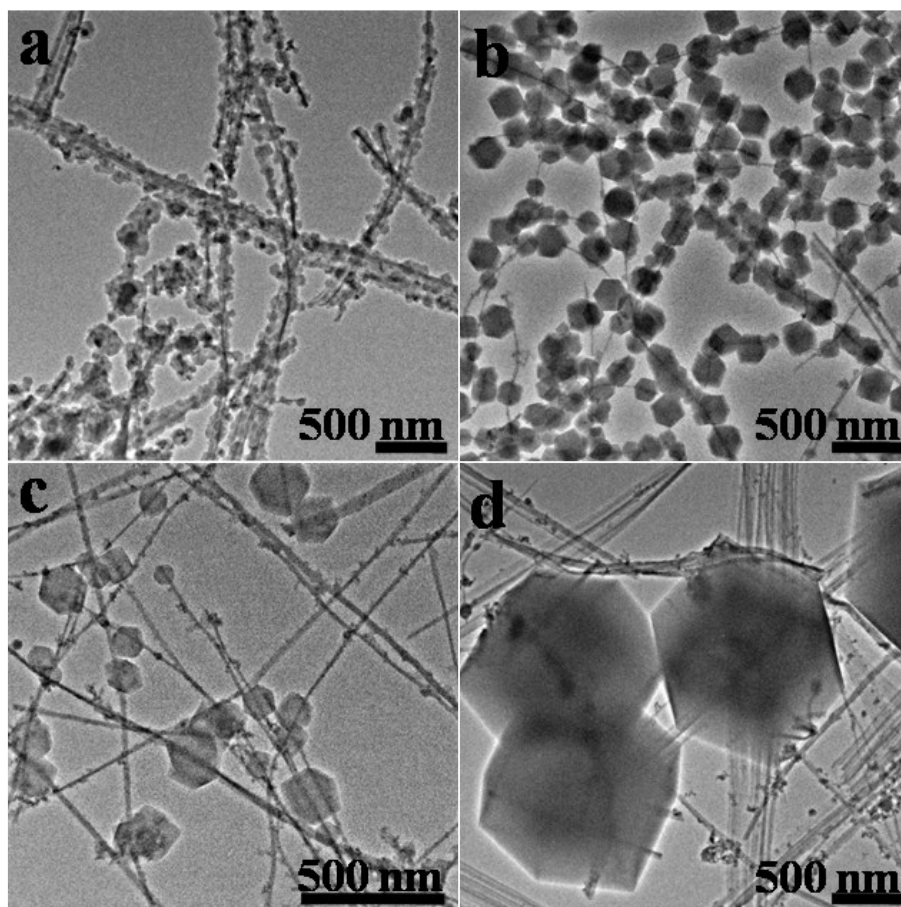


Figure S2. HRTEM images of CdTe QDs assembled nanowires.



FigureS3. TEM images of samples prepared under different conditions: (a) 1 mL 20 mM, (b) 10 mL 20 mM, (c) 5 mL 7.5 mM and (d) 5 mL 100 mM of $\text{Zn}(\text{NO}_3)_2$ methanolic solution and identical amount of Hmim methanolic solution. Methanolic solution of CdTe NWs was concentrated from 1 mL to 10 μL before being added.

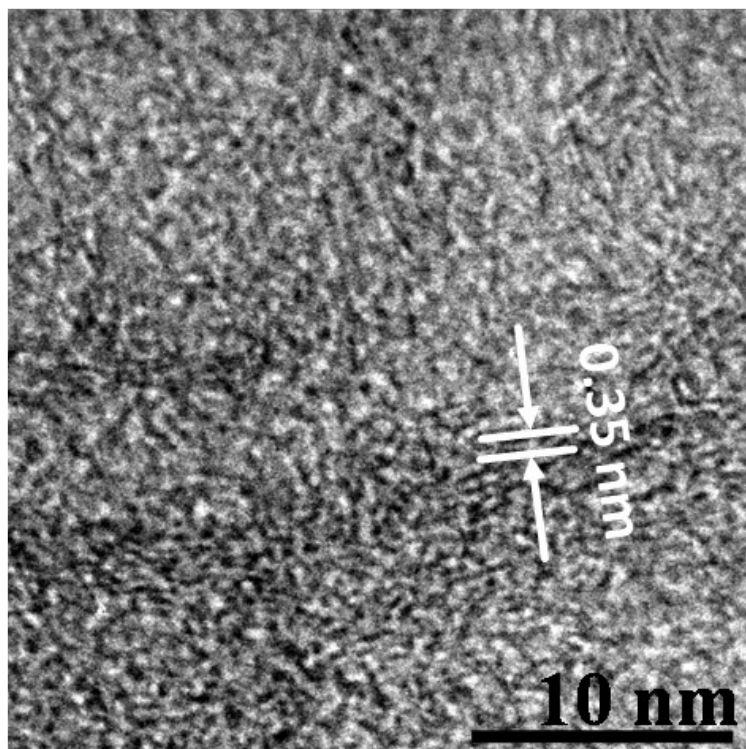


Figure S4. HRTEM images of One-H/P-C-1000-3 derived from CdTe@ZIF-8 nanofibers

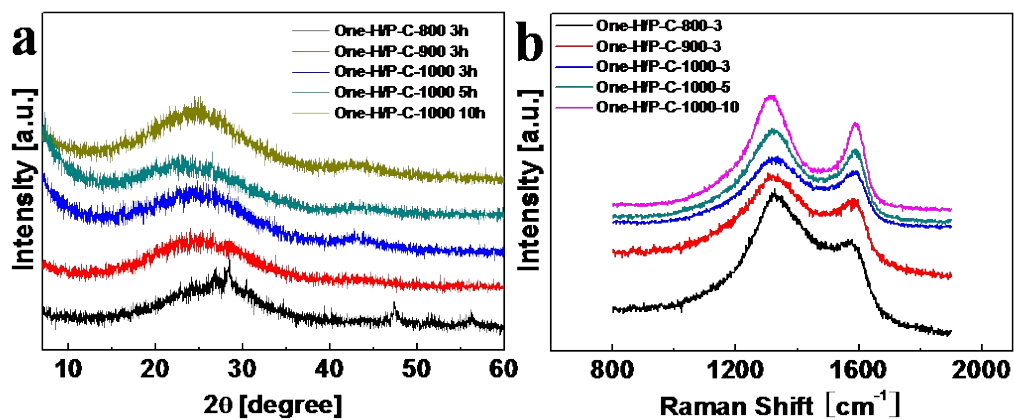


Figure S5. (a) PXRD patterns and (b) Raman spectra of the series of One-H/P-C- T - t samples ($T = 800, 900,$ and 1000 ; $t = 3, 5,$ and 10).

Table S1. The ratio of I_G to I_D of N-doped graphitic carbon series according to Raman spectra of Figure S5b.

Sample	I_G/I_D
One-H/P-C-800-3	0.54
One-H/P-C-900-3	0.81
One-H/P-C-1000-3	0.86
One-H/P-C-1000-5	0.88
One-H/P-C-1000-10	0.90

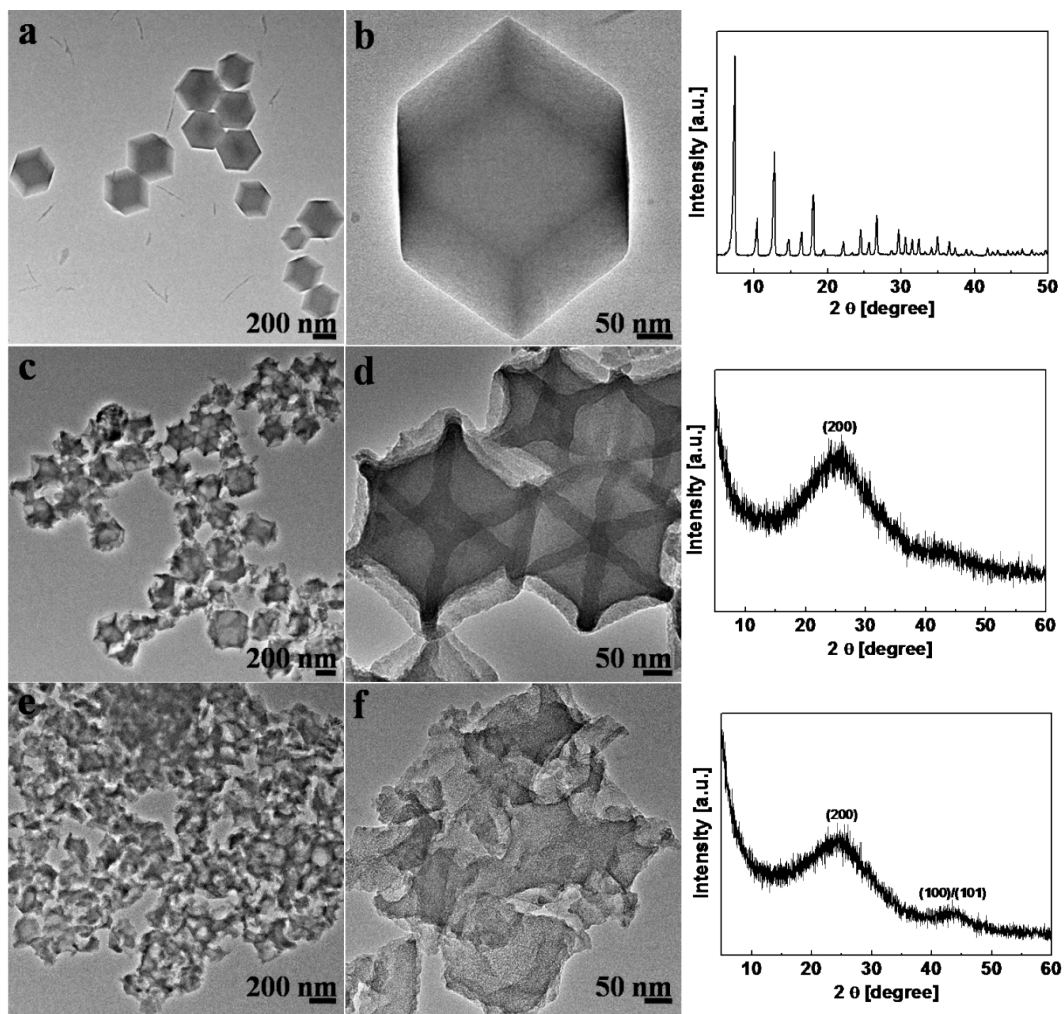


Figure S6. TEM images of (a, b) ZIF-8 rhombic dodecahedra, and N-doped graphitic carbons by pyrolysis of ZIF-8 rhombic dodecahedra at (c, d) 800 °C and (e, f) 1000 °C for 3 h. The right row shows corresponding to their PXRD patterns.

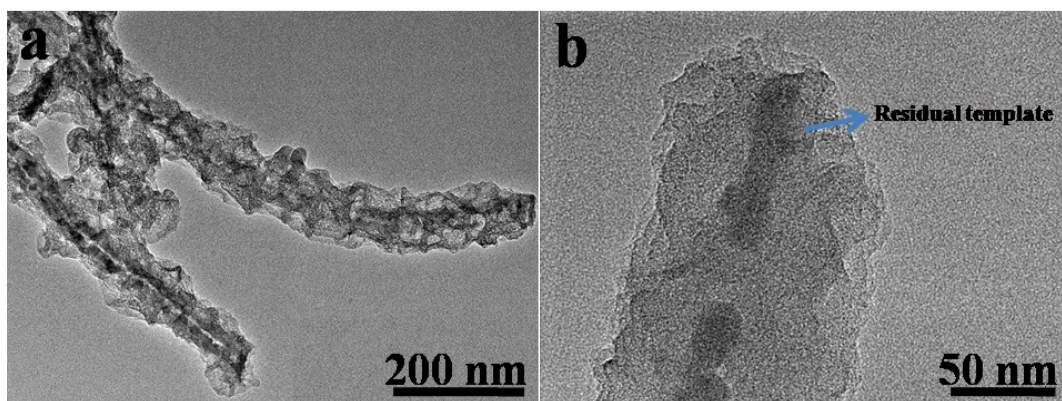


Figure S7. TEM images of (a, b) One-H/P-C-800-3 with different magnification.

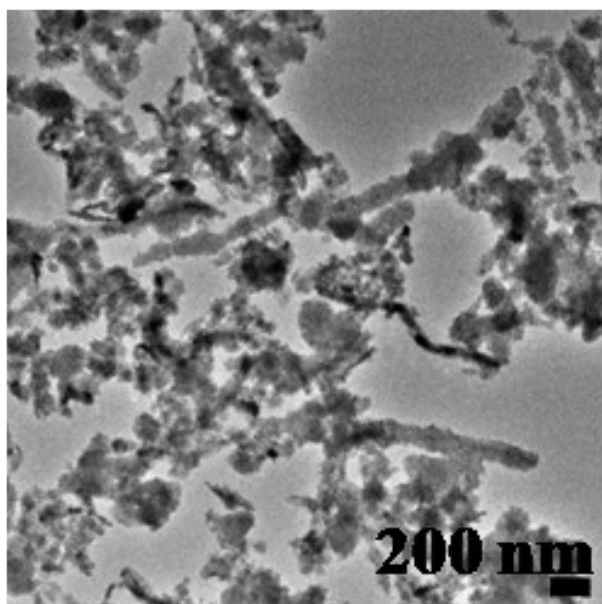


Figure S8. TEM images of One-H/P-C-1000-5.

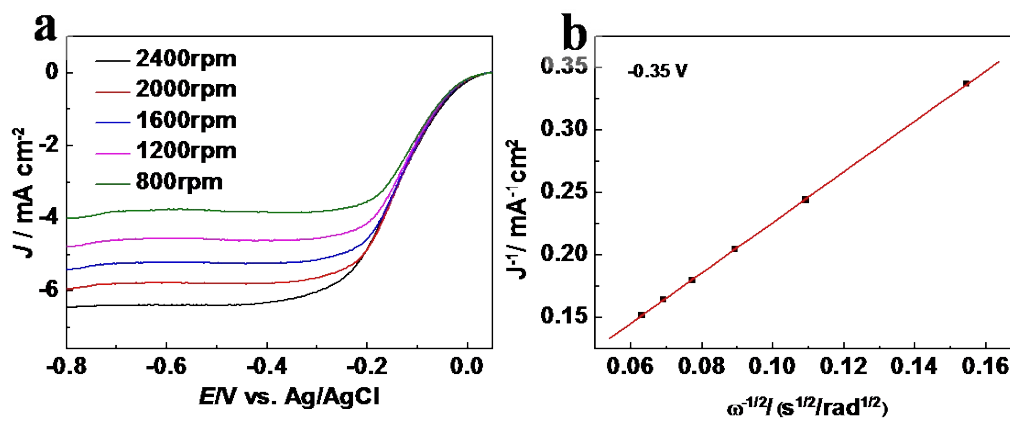


Figure S9. (a) LSV curves of Pt/C with different rotation speeds, and (b) K-L plots of Pt/C at -0.35 V.