

Supporting Information

Morphology-Tuning-Induced Highly Efficient Regeneration of Pt/C Nanoelectrocatalysts

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1. 1. Materials. The carbon black BP2000 was purchased from Asian-Pacific Specialty Chemicals Kuala Lumpur. Methanol (CH₃OH), sulfuric acid (H₂SO₄), Nafion solution (5 wt %), and H₂PtCl₆ · 6H₂O salt were purchased from Sigma-Aldrich. Ammonium fluoride (NH₄F) was purchased from Beijing Chemical Works, China. All the chemicals were used as delivered without further treatment. Ultrapure water with the specific resistance of 18.23 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration. A glassy carbon electrode (4 mm in diameter) was purchased from Tianjin Aida Hengsheng Tech. Co., China. The gas CO with high purity (99.99%) was purchased from Changchun Gas Co., China.

1. 2. Synthesis of fresh Pt/C (Pt 10 wt.%) Electrocatalyst and the sintering. Vulcan XC-72 and H₂PtCl₆ were used as the carbon support and platinum precursor, respectively. The carbon support (1.0 g) was dispersed with known amounts of Pt precursor in 100 mL de-ionized water and 50 mL ethylene glycol followed by sonication of about 30 min for even dispersion. After that, a solution prepared by mixing ethylene glycol with sodium borohydride (molar ratio of ethylene glycol: NaBH₄ = 10:1) was added slowly drop-by-drop into the above solution with vigorous stirring. The mixture was kept stirring for 4 h at 100°C to permit the complete reduction of Pt from its metal salt. The black precipitate was isolated on a filter, washed with de-ionized water and then dried at 120°C overnight to give a carbon-supported Pt catalyst. The Pt content was finally determined by ICP to be 10 wt. % Pt. The prepared Pt/C catalyst was put in a quartz crucible which was heated in N₂ atmosphere (flow rate: 200 mL/min) within a tubular furnace, and the temperature was increased to the set temperature (900°C) with a ramp rate of 5°C min⁻¹, followed

by a dwell time at this temperature for 3 h. The sintered Pt/C with Pt 10 wt.% was labeled as **Pt-S**.

1. 3. Synthesis of BP-F. In a typical synthesis, a given amount of NH_4F (1.8g) and BP (100mg) were firstly dispersed in 10 ml H_2O . The mixture was sonicated for about 2 h and then stirred overnight. The resulting suspension was dried under vacuum at 40 °C and then pyrolyzed at 1000 °C for 1h under argon atmosphere with flow rate of 80 mL/min. After that, the sample was cooled down to room temperature and collected from the quartz tube.

1. 4. The regeneration of sintered Pt/C. The regeneration of sintered Pt/C was based on a fact that $\text{O}_2/\text{CH}_3\text{Cl}$ can dissolve Pt nanoparticles into PtCl_6^{2-} in a sealed refluxing methanol liquid environment, while the PtCl_6^{2-} can be reduced back into Pt^0 by methanol when the temperature rises up to 160°C. By combining these two processes together, we designed a redispersion or regeneration reaction system containing the following components: O_2 , CH_3Cl and methanol plus Pt/C in a sealed glass reactor from SynthWare®. According to parameters from the Manufacture, the glass ware as shown in Fig. S1 can stand high pressure up to 8 bar with thick wall.

1. 5. Physical and electrochemical characterization of catalysts. The morphology and dimensions of as-prepared samples were obtained using transmission electron microscopy (TEM) obtained on a JEM-2100F microscopy with an accelerating voltage of 200 kV. Subangstrom resolution HAADF STEM images were obtained on a FEI TITAN ChemiSTEM equipped with a CEOS (Heidelberg, Ger) probe corrector, operating at 200 kV. The Brunauer-Emmett-Teller (BET) surface areas and pore volumes were obtained from 77 K N_2 sorption isotherms using ASAP 2020 instrument. The final Pt contents in the catalysts were obtained from ICP (ICAP-6000, Thermo Fisher Scientific). The activity of Pt/C for methanol electro-oxidation was evaluated by cyclic voltammetry (CV) on glassy carbon electrodes. Fabrication of the working electrodes was done by pasting catalyst inks on a glassy carbon rotating disk electrode (4 mm in diameter). Its apparent surface area (0.1256 cm^2) was used to normalize the ORR activity of the catalysts. The carbon ink was formed by mixing 5 mg of Pt/C catalysts, 100 μL of 5 wt % Nafion solution in alcohol, and 900 μL of ethanol in a plastic vial under ultra-sonication. A 10- μL aliquot of the carbon ink was dropped on the surface of the glassy carbon rotating disk electrode, yielding an approximate catalyst loading of 0.05 mg. The electrolyte was 0.5 M H_2SO_4 or 0.5 M H_2SO_4 + 0.5 M CH_3OH solution; the counter and the reference electrodes were a platinum wire and a SCE electrode, respectively. The potential of the electrode was controlled by an EG&G (model 273) potentiostat/galvanostat system. Cyclic voltammetry was performed from 0.0 to 1.0 V at 50 mV s^{-1} .

2. The regeneration of Pt/C catalysts.

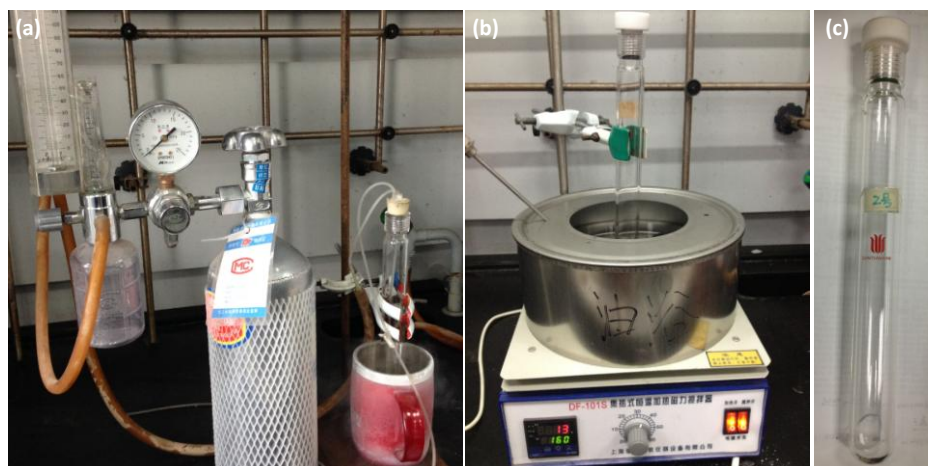


Figure S1.(a) The collection process of CH_3Cl with liquid N_2 . (b) The setup for the regeneration of sintered Pt/C electrocatalyst at 160°C sealed in a glass reactor. (c) The glass reactor with a PTFE stopper used in the system shown in (b).

The glass reactor is 19 cm long with diameter 2.6 cm. The total inner volume is about 35 mL. For the redispersion reaction, 6 mg sintered Pt/C with or without additional carbon black was dispersed in 1 ml methanol in the above glass reactor by sonication. After that, a tinny stir bar was added into the reactor. Before any collection, the glass reactor was purged with CH_3Cl to remove air and then cooled down with liquid nitrogen (LN_2) to catch CH_3Cl and O_2 , respectively at appropriate flow rates. By controlling the collection time, the ratio among O_2 , CH_3Cl and methanol can be tuned precisely. After the collection of CH_3Cl and O_2 , the glass reactor was sealed by a stopper with screw thread made of poly(1,1,2,2-tetrafluoroethylene) (PTFE) as shown in Fig. S1. About one fourth of the glass reactor was inserted into an oil bath to warm up to 160°C gradually with stirring from the tiny stir bar. After the temperature raised up, some methanol will become vapor at the bottom and cool down into liquid at the top of the glass reactor due to the much lower temperature there. The liquid methanol will flow down to the bottom again to maintain the liquid phase for the dispersion of Pt/C. In this case some of the O_2 or CH_3Cl will stay in the liquid phase and others stay in the vapor. The pressure inside the glass reactor is less than 8 bar since the glass reactor only can stand up to 8 bar in maximum. During this redispersion process, the Pt will be oxidized and then reduced back repeatedly for many times to achieve the reformation or redispersion of Pt on support. After the temperature rises to 160°C , the reaction will be kept for 7 h. After that the solution was cooled down to room temperature. The stopper was loosed to release all the residual gas. The obtained ink of Pt/C in methanol will be centrifuged down and the PtCl_6^{2-} will stay in supernatant. The solid will be washed with water for three times, with ethanol for another three times, finally dried under vacuum at 80°C to get the final regenerated Pt/C. The PtCl_6^{2-} in supernatant will be recovered with reductant in the form of Pt black.

3. The absorption spectrum of PtCl_6^{2-} obtained from the supernatant after

centrifugation of the redispersion solution.

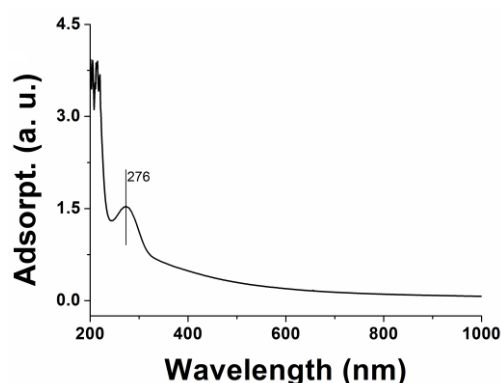


Figure S2. The UV-Vis adsorption spectrum of the supernatant obtained from the redispersion solution.

According to the literature (*J. Phys. Chem. B* **1999**, *103*, 3818-3827), the above Fig. S2 clearly shows the Pt nanoparticles were dissolved into solution in the form of PtCl_6^{2-} by $\text{O}_2/\text{CH}_3\text{Cl}$. This part of PtCl_6^{2-} will be collected in the form of Pt black by the reduction with NaBH_4 .

4. The CV data treatment.

In order to see the pure methanol-oxidation induced current on catalysts, the original CV data were treated as following: the catalyst was tested in a blank 0.5 M H_2SO_4 solution without methanol in CV as shown in the following black curve, then the electrode was removed to a solution of 0.5 M H_2SO_4 + 0.5 M CH_3OH and tested with CV (red curve in Fig. S3). For the pure methanol electro-oxidation induced current, it (green curve in Fig. S3) was obtained by subtracting black curve (blank data) from the red curve. Finally all the comparisons among different Pt/C catalysts are based on the background-corrected data (such as the green curve in Fig. S3).

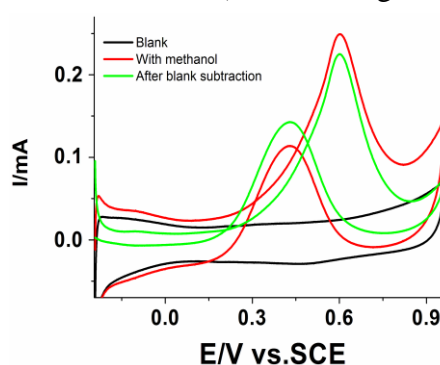


Figure S3. An example of CV data treatment based on the results from the regenerated PtS-9.¹

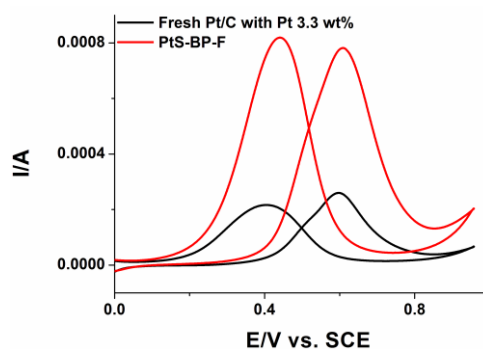


Fig. S4. The comparison between PtS-BP-F and fresh Pt/C with the same Pt 3.3wt.%. All these currents were obtained based on the same amount of catalyst loading of 0.05 mg.

5. Table S1. The BET and EASA measurements of Pt10, Pt-S, and PtS-BP-F

	BET / m ² g ⁻¹	EASA _{CO} (m ² /g)	EASA _H (m ² /g)
Pt10	167	55	63
Pt-S	185	24	27
PtS-BP-F	607	40	68

6. XPS spectra of F 1s for BP-F and PtS-BP-F.

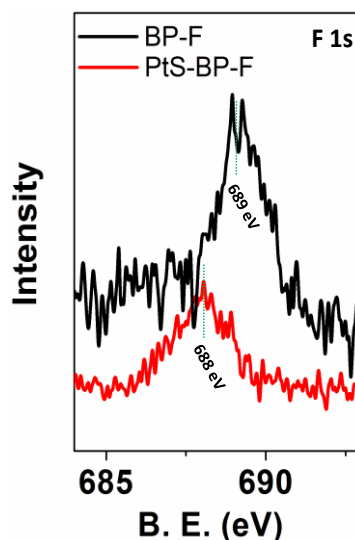


Fig. S5. XPS spectra of F1s in BP-F and PtS-BP-F.

7. Computational details

Spin-polarized density functional theory calculations in this study were performed using the Vienna ab initio simulation package (VASP).²⁻⁵ The interactions

between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented wave (PAW) method.⁶⁻⁷ The Perdew–Burke–Ernzerhof form of the Generalized-Gradient Approximation was employed to describe electron exchange and correlation.⁸ The wave functions at each k-point were expanded with a plane wave basis set and a kinetic cutoff energy up to 400 eV. Brillouin zone integration was approximated by a sum over special selected k-points using the Monkhorst–Pack method⁹ and they were set to $5 \times 5 \times 1$. The electron occupancies were determined using Gaussian broadening with a width of 0.05 eV. Geometries were optimized until the energy was converged to 1.0×10^{-5} eV/atom and the force was converged to 0.01 eV/Å. For an isolated Pt atom, calculation was performed in a large supercell with Γ -point sampling only. Graphene (carbon) supercells with a size of 3×3 (for Pt₁-Pt₃) and 4×4 (for Pt₄-Pt₅) were used (see Fig. S5), and the distance between graphene layers was set to 25 Å.

Furthermore, the climbing image nudged elastic band (CINEB) method¹⁰ was employed to locate the transition state (TS) and the reaction pathways. Once the initial and final configurations of a reaction path were selected, four intermediate images were interpolated between the initial and final configurations. The interpolated configurations are connected by springs, through which the highest-energy configuration climbs uphill to the saddle point. The minimum energy paths was confirmed until all the force components perpendicular to the tangent of the reaction pathway were reduced to be less than 0.01 eV/Å. The harmonic vibrational frequencies of the TSs were calculated to characterize the nature of the stationary point. The transition state was verified to have only one imaginary vibrational frequency.

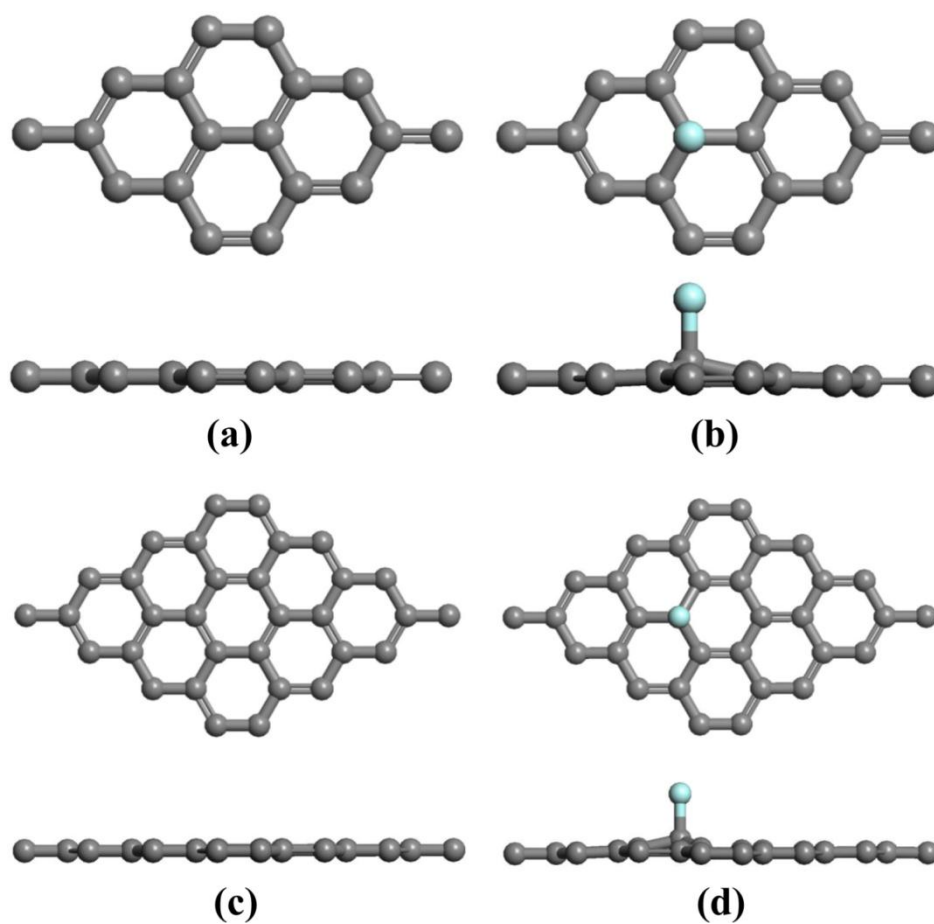


Figure S6. Optimized structures of (a) 3×3 , (c) 4×4 pristine carbon substrates and (b) 3×3 , (d) 4×4 fluorinated carbon substrates. The grey and cyan balls denote the carbon and fluorine atoms, respectively.

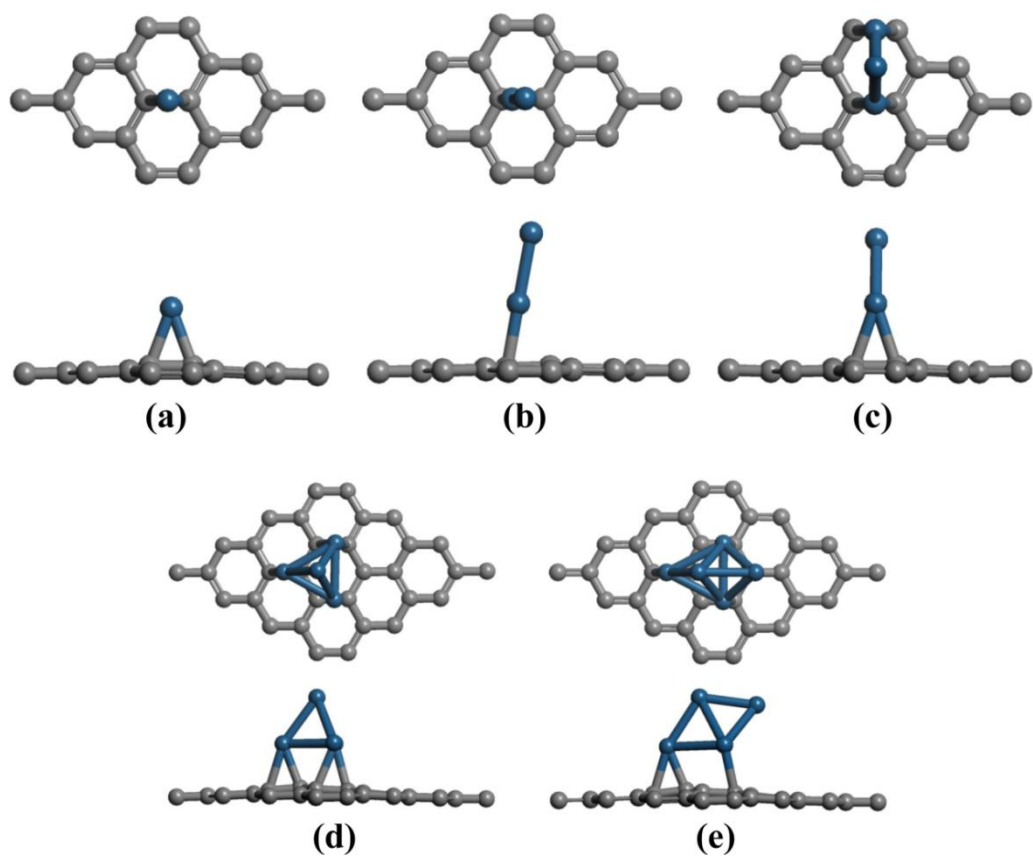


Figure S7. Lowest-energy configurations for (a) Pt₁, (b) Pt₂, (c) Pt₃, (d) Pt₄ and (e) Pt₅ binding on pristine carbon substrates.

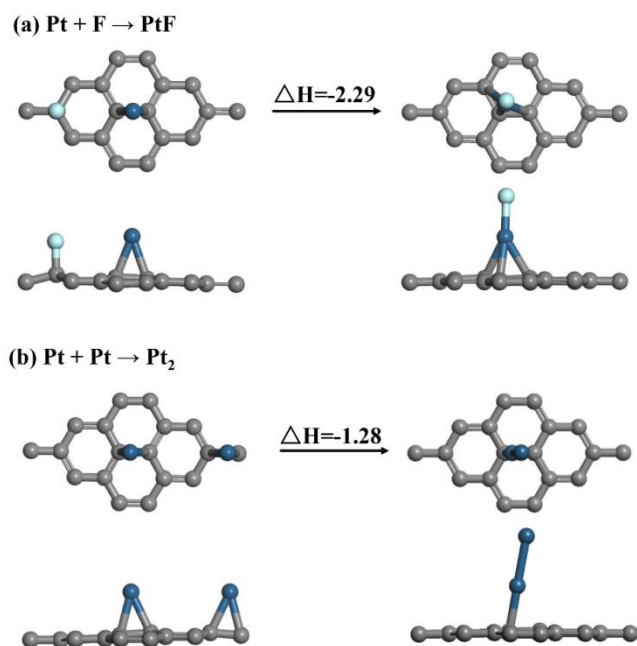


Figure S8. The configurations of reactants and products in (a) $\text{Pt} + \text{F} \rightarrow \text{PtF}$; (b) $\text{Pt} + \text{Pt} \rightarrow \text{Pt}_2$. ΔH is the heat of reaction. The energy unit is in eV.

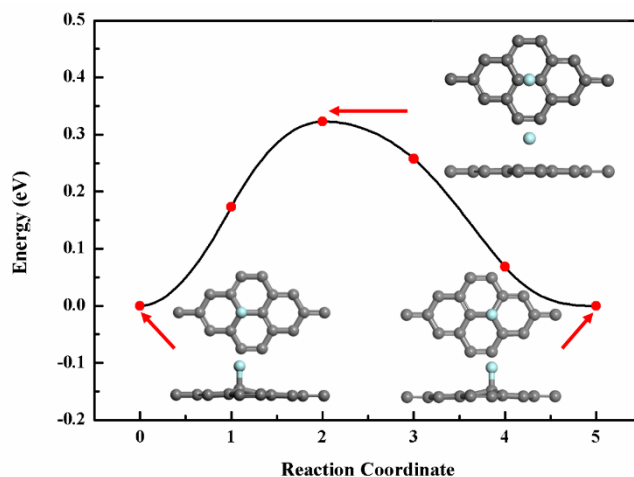


Figure S9. The reaction pathway for F atom migration on the carbon substrate.

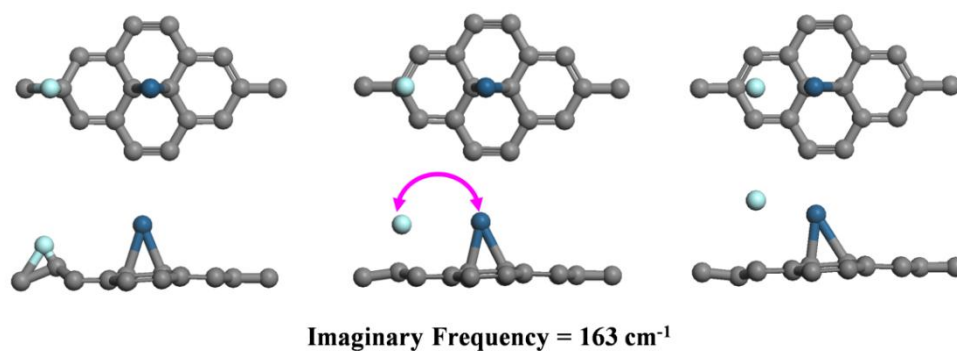


Figure S10. The vibrational mode of the imaginary frequency for the transition state.

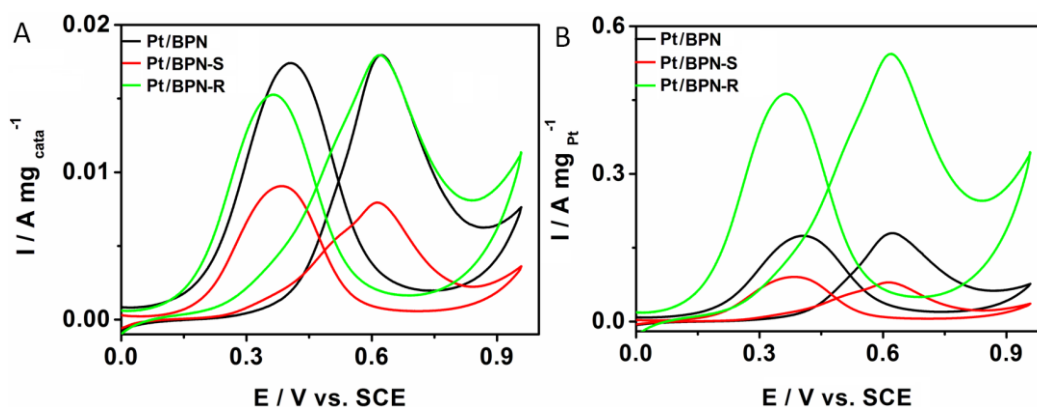


Figure S11. The electrocatalytic characterization of different Pt/C catalysts through cyclic voltammetry (CV) in 0.5 M H₂SO₄ and 0.5 M CH₃OH solution with scan rates of 50 mV/s. (A) The comparison of catalyst mass-normalized catalytic activity (mA/mg_{catalyst}) among different catalysts: fresh N-doped BP supported Pt (Pt/BPN, Pt 10 wt.%), sintered one (Pt/BPN-S) and regenerated one (Pt/BPN-R,

Pt 3.3wt.%) with additional BP-F. **(B)** The comparison of Pt mass-normalized catalytic activity (A/mg_{Pt}) among these three catalysts.

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