Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Supplementary materials

## Manipulating the Interaction of Pt NPs with N-hollow Carbon Spheres by F-doping for Boosting Oxygen Reduction/Methanol Oxidation Reactions

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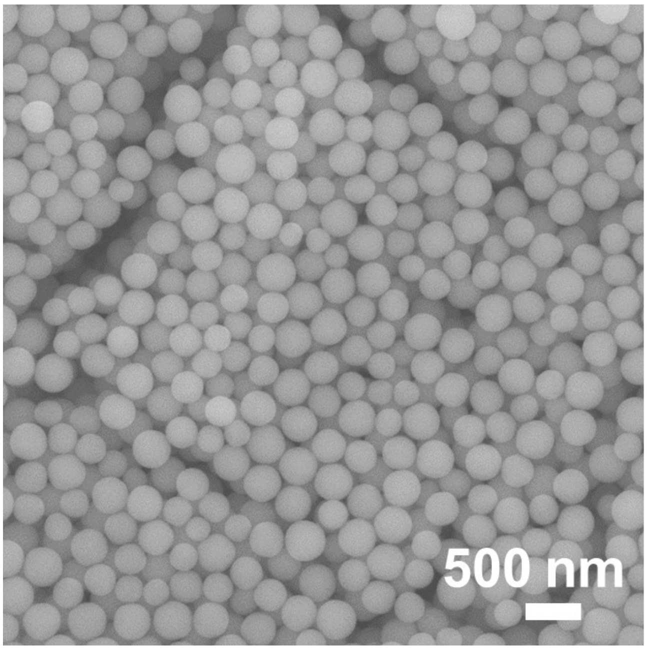


**Fig. S1** The SEM image of $SiO_2$ nanospheres.

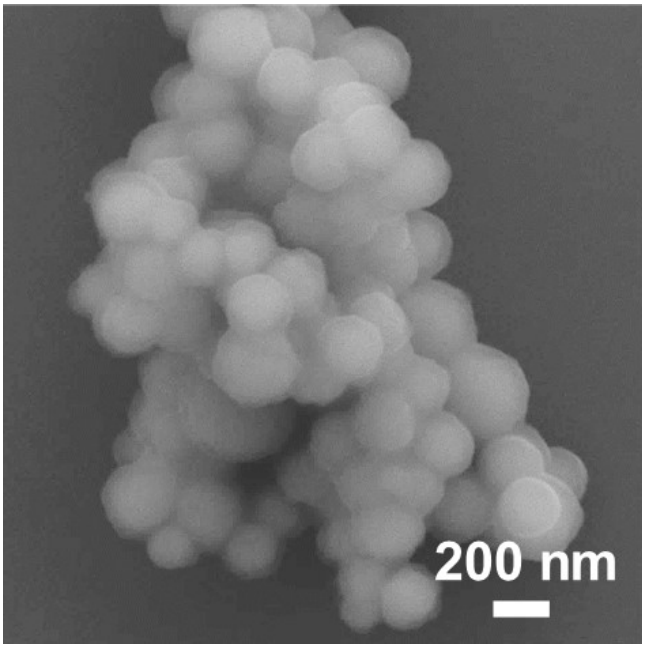


**Fig. S2** The SEM image of PDA@$SiO_2$ nanospheres with core-shell structure.

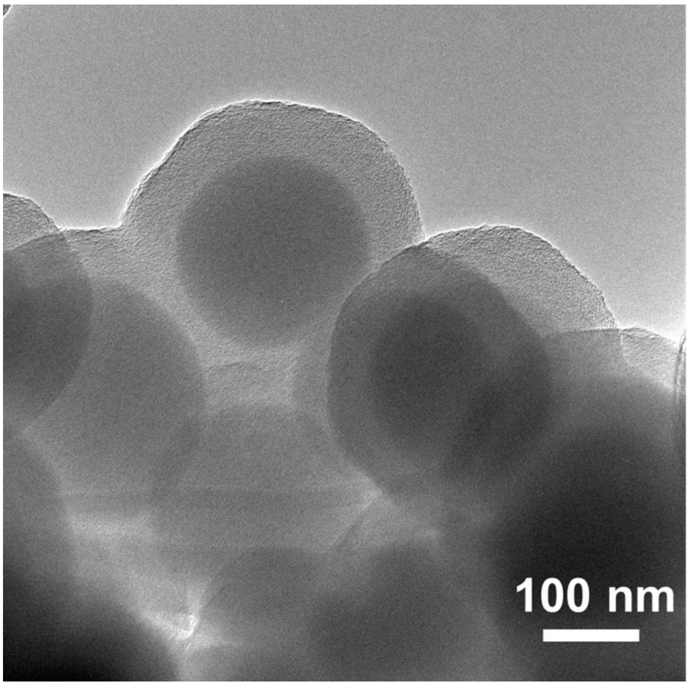


**Fig. S3** The TEM image of N-CS@$SiO_2$.

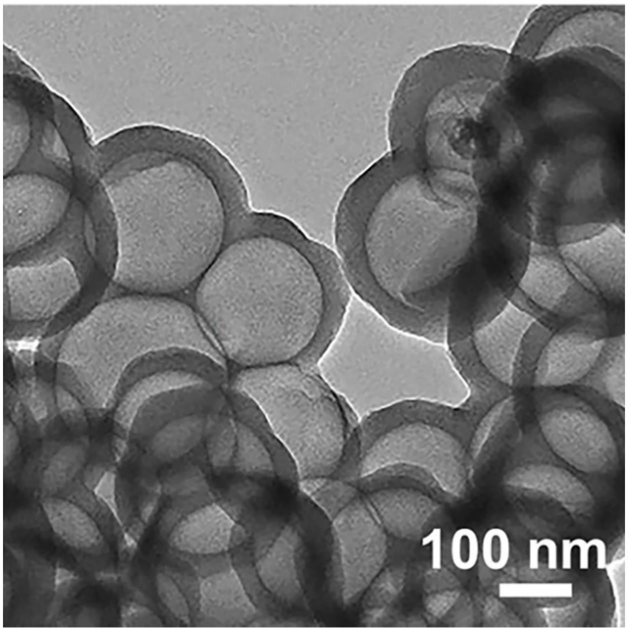


**Fig. S4** The TEM image of N-HCS.

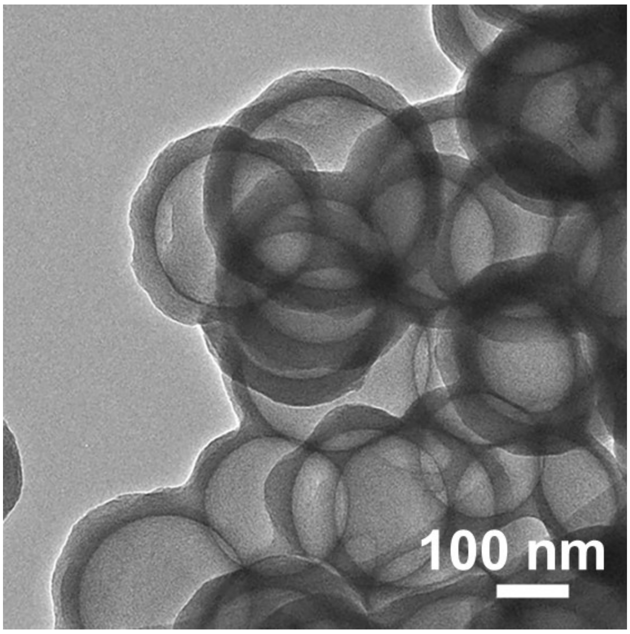


**Fig. S5** The TEM image of N, F-HCS.

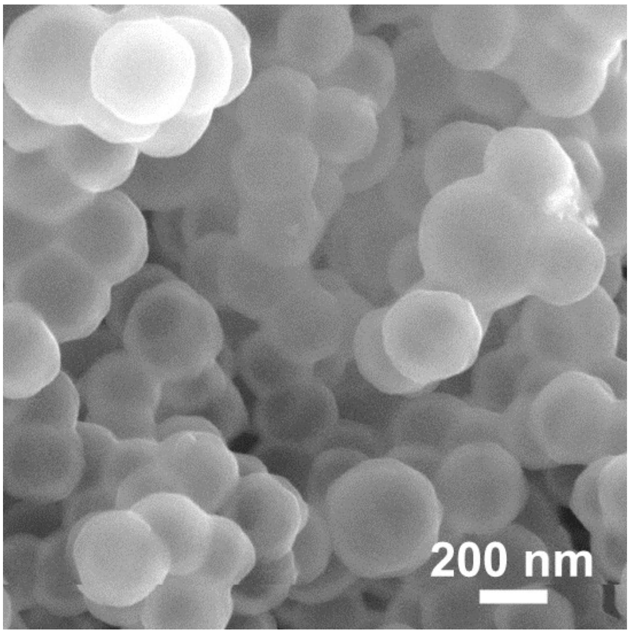


**Fig. S6** The SEM image of Pt@N-HCS.

**Table S1.** Pt mass low loading (wt%) from ICP-MS results of Pt@N, F-HCS and Pt@N-HCS.

| **Catalyst** | **Experimental Pt metal loading / wt%** |
|---|---|
| Pt@N, F-HCS | 4.8 |
| Pt@N-HCS | 4.9 |

**Table S2.** The proportion (%) of bonding types of deconvoluted C 1s peaks determined by XPS for Pt@N, F-HCS and Pt@N-HCS.

| **Sample** | **Proportion (%) of C 1s bonding types** | | | | |
|---|---|---|---|---|---|
| | **O-C=O** | **C-N/C-O/C-F** | **C-N/C-O** | **C-N/C=N** | **C=C/C-C** |
| Pt@N-HCS | 6.4 | NA | 7.1 | 16.4 | 70.1 |
| Pt@N, F-HCS | 6.5 | 11.4 | NA | 13.5 | 68.6 |

**Table S3.** The proportion (%) of bonding types of deconvoluted N 1s peaks determined by XPS for Pt@N, F-HCS and Pt@N-HCS.

| **Sample** | **Proportion (%) of N 1s bonding types** | | |
|---|---|---|---|
| | **Pyridinic-N** | **Pyrrolic-N** | **Graphitic-N** |
| Pt@N-HCS | 19.5 | 35.3 | 45.2 |
| Pt@N, F-HCS | 42.5 | 16.9 | 40.6 |

**Table S4.** The proportion (%) of bonding types of deconvoluted Pt 4f peaks determined by XPS for Pt@N, F-HCS and Pt@N-HCS.

| **Sample** | **Proportion (%) of N 1s bonding types** | |
|---|---|---|
| | **$Pt^{x+}$** | **$Pt^0$** |
| Pt@N-HCS | 20.8 | 79.2 |
| Pt@N, F-HCS | 30.3 | 69.7 |

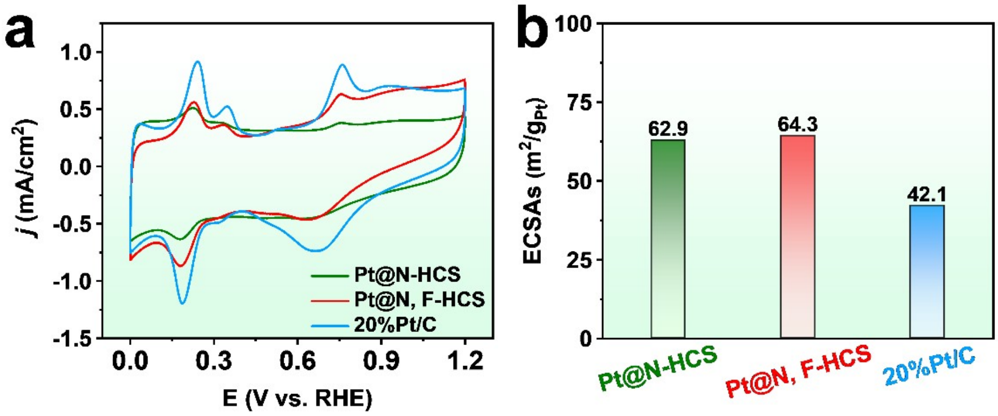


**Fig. S7** (a) CV curves of Pt@N, F-HCS, Pt@N-HCS and 20%Pt/C in Ar-saturated 0.1 M KOH solution with scan rate of 50 mV/s. (b) The corresponding ECSAs of Pt@N, F-HCS, Pt@N-HCS and 20%Pt/C catalysts.

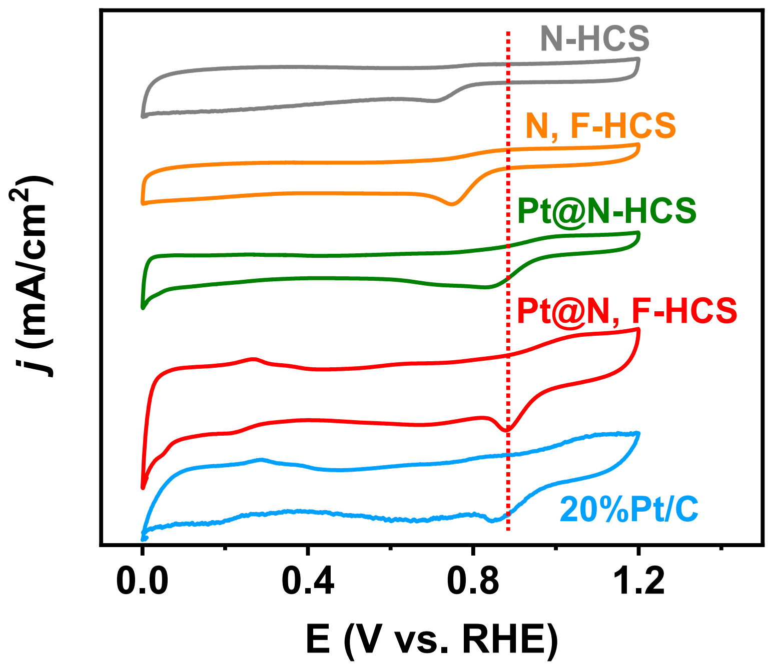


**Fig. S8** CV curves of Pt@N, F-HCS, Pt@N-HCS, N, F-HCS, N-HCS and 20%Pt/C under $O_2$ saturated condition in 0.1 M KOH solution with scan rate of 5 mV/s.

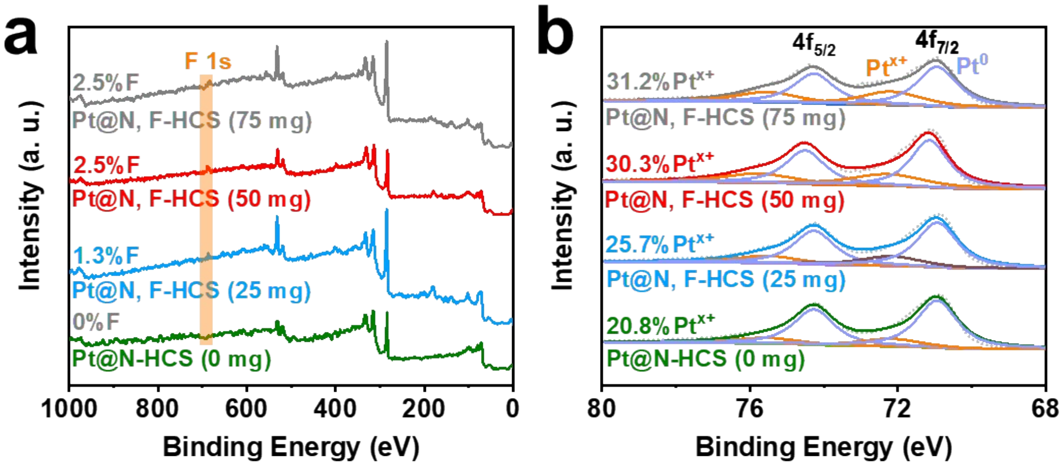


**Fig. S9** (a) XPS all spectrums of Pt@N, F-HCS samples with different F sources (0 mg, 25 mg, 50 mg and 75 mg). (b) Pt fine spectrums of Pt@N, F-HCS samples with different F sources (0 mg, 25 mg, 50 mg and 75 mg) and $Pt^{x+}$ contents (20.8%, 25.7%, 30.3% and 31.2%).

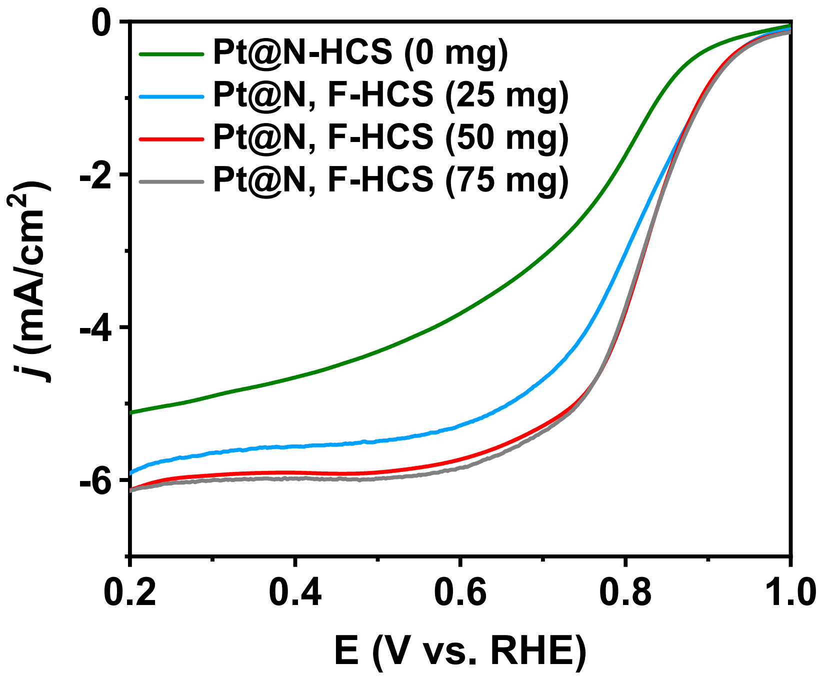


**Fig. S10** LSV curves of Pt@N, F-HCS catalysts with different F source amount (0 mg, 25 mg, 50 mg and 75 mg).

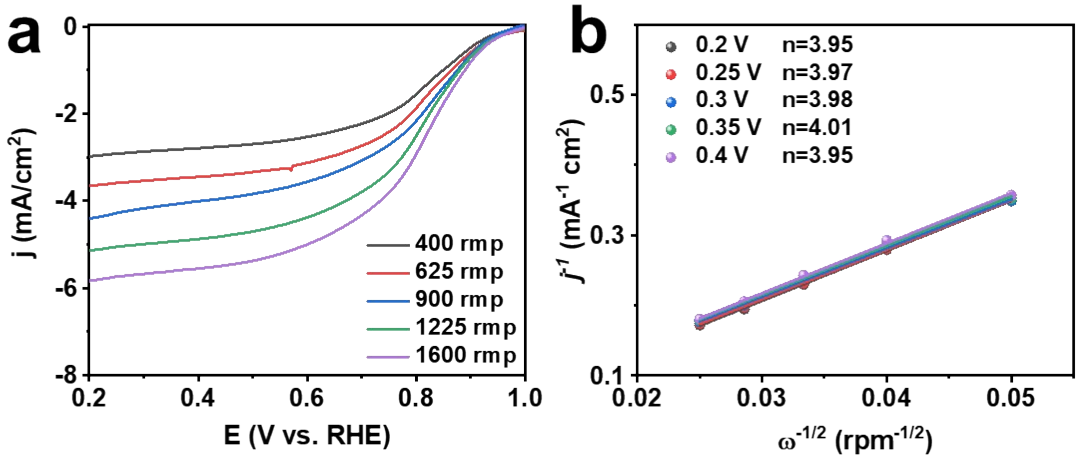


**Fig. S11** (a, b) RDE measurements of commercial 20%Pt/C in $O_2$-saturated 0.1 M KOH solution at 400-1600 rmp.

**Table S5.** Comparison ORR performance of the Pt@N, F-HCS with recently reported Pt-based catalysts in alkaline solution.

| **Catalysts** | **$E_{on}$ (V vs RHE)** | **$E_{1/2}$ (V vs RHE)** | **$j_L$ (mA/cm$^2$)** | **Tafel slope (mV/dec)** | **Ref** |
|---|---|---|---|---|---|
| **Pt@N, F-HCS** | **0.98** | **0.84** | **6.21 (0.2 V)** | **48.4** | **This work** |
| $Pt_2Pd_3$/CKN | 0.90 | 0.821 | 6.11 (0.4 V) | 83 | S1 |
| 3 nm Pt | 0.953 | 0.870 | 4.3 (0.4 V) | 68.2 | S2 |
| $PtP_2$@PNC | 0.97 | 0.82 | NA | NA | S3 |
| 3 wt % Pt/N-C | NA | 0.90 | 5.5 | 70 | S4 |
| Pt/MFO/NPC | 0.980 | 0.835 | 4.66 (0.4 V) | NA | S5 |
| FePt-NSC | 1.02 | 0.89 | 5.67 (0.4 V) | 63 | S6 |
| J.M.-Pt/C NCs | 0.91 | 0.844 | NA | NA | S7 |
| Pt@20N-CQDs | 0.925 | 0.834 | 3.83 (0.5 V) | NA | S8 |
| Pt/NC | NA | 0.82 | 4.35 (0.3 V) | 80 | S9 |
| Pt/GC | 0.92 | 0.828 | 5.6 (0.2 V) | 66 | S10 |

**Table S6.** Comparison ORR activity of the Pt@N, F-HCS with recently reported Pt-based catalysts in alkaline electrolyte.

| **Catalysts** | **MA (A/$mg_{Pt}$) @0.9V** | **SA (mA/$cm_{pt}^2$) @0.9V** | **Reference** |
|---|---|---|---|
| **Pt@N, F-HCS** | **1.76** | **2.73** | **This work** |
| 3 nm Pt | 0.4894 | NA | S2 |
| $PtP_2$@PNC | 0.1486 | NA | S3 |
| 3 wt % Pt/N-C | 0.238 | NA | S4 |
| J.M.-Pt/C NCs | 0.067 | NA | S7 |
| L-cysteine-decorated Pt/C | 0.23 | 0.44 | S11 |
| $PtNi_7$ | 0.210 | NA | S12 |
| np-AlCoFeMoCr/Pt | 0.81 | NA | S13 |
| PtPd MNs | 0.428 | 1.168 | S14 |
| Pd/Au-Pt | 0.604 | 1.34 | S15 |
| Pd@PtPd RDs | 0.17 | 0.42 | S16 |
| PtPd NNs | 0.42 | 0.91 | S16 |
| $Pt_{37}Cu_{56}Au_7$ | 0.871 | 1.85 | S17 |
| Pt@Pd/C | 1.38 | 1.84 | S18 |

**Table S7.** Comparison ORR activity of the Pt@N, F-HCS with recently reported similar-sized Pt NPs doped materials.

| **Catalysts** | **$E_{on}$ (V vs RHE)** | **$E_{1/2}$ (V vs RHE)** | **MA ($A/mg_{Pt}$) @0.9V** | **SA ($mA/cm_{pt}^2$) @0.9V** | **Tafel slope (mV/dec)** | **Ref** |
|---|---|---|---|---|---|---|
| **Pt@N, F-HCS** | **0.98** | **0.84** | **1.76** | **2.73** | **48.4** | **This work** |
| Pt-ECPA | NA | NA | 0.22 | 0.12 | 69.3 | S19 |
| Pt/C@NC | NA | 0.84 | 0.22 | 0.41 | NA | S20 |
| 10Pt/SGCN-550 | NA | 0.85 | 0.22 | 0.71 | NA | S21 |
| $Pt/TiO_2/C(R)$ | NA | 0.873 | 0.249 | 0.653 | 71 | S22 |
| Pt/AVC | NA | 0.81 | 0.93 | 1.14 | 113 | S23 |
| $P_{NS}$-Pt/C | NA | 0.925 | 1.00 | 1.81 | NA | S24 |
| $Pt_{0.1}$/N–C | 0.94 | 0.68 | 0.24 | NA | NA | S25 |
| Pt/N-OHPC | 0.90 | 0.76 | 0.553 | 0.93 | 79.5 | S26 |
| Pt/NPC | 0.969 | 0.823 | NA | NA | 80 | S5 |
| CN/Pt-140 | 0.827 | NA | 0.11 | 0.203 | 81 | S27 |
| Pt/CoNC-2D | 0.89 | 0.83 | 1.66 | NA | 49.5 | S28 |
| Pt/(B-C)600 | NA | 0.885 | 0.30 | 0.35 | NA | S29 |
| GQD-Pt NTAs | 1.02 | 0.87 | 1.14 | 2.24 | NA | S30 |
| Pt-TMIM-rGO | 0.975 | NA | 0.346 | 0.61 | NA | S31 |

**Table S8.** Electrochemical data for the MOR catalyzed by the synthesized Pt@N, F-HCS and comparison samples in 0.1 M KOH + 1 M $CH_3OH$.

| **Catalysts** | **Onset potential (V)** | **Peak potential (V)** | $\boldsymbol{I_f}$ **(mA/cm²)** | $\boldsymbol{I_b}$ **(mA/cm²)** | $\boldsymbol{I_f/I_b}$ |
|---|---|---|---|---|---|
| Pt@N-HCS | 0.34 | 0.79 | 50.24 | 9.68 | 5.19 |
| **Pt@N, F-HCS** | **0.28** | **0.76** | **59.98** | **10.50** | **5.71** |
| commercial 20%Pt/C | 0.38 | 0.85 | 34.82 | 8.35 | 4.17 |

**Table S9.** Comparison of MOR activity of the Pt@N, F-HCS with recently reported Pt-based catalysts in alkaline solution.

| Catalysts | Electrolyte | MA ($A/mg_{Pt}$) | SA ($mA/cm_{pt}^2$) | Reference |
|---|---|---|---|---|
| **Pt@N, F-HCS** | **0.1 M KOH + 1 M $CH_3OH$** | **2.28** | **3.55** | **This work** |
| $PtNi_7$ | 0.1 M NaOH + 0.1 M $CH_3OH$ | 0.250 ± 0.10 | NA | S12 |
| Pt nanodendrites | 0.1 M KOH + 1 M $CH_3OH$ | 0.91 | 1.84 | S32 |
| Pt/NGDY | 1 M KOH + 1 M $CH_3OH$ | 1.449 | 0.154 | S33 |
| 10:5–Pt/$Ni(OH)_2$/N-CNTs | 0.1 M NaOH + 1 M $CH_3OH$ | 0.344 | 1.13 | S34 |
| Pt/N-CNTs | 0.1 M NaOH + 1 M $CH_3OH$ | 0.261 | 1.32 | S34 |
| GrPt | 1 M NaOH + 1 M $CH_3OH$ | 0.939 | NA | S35 |
| Pt–$Ce(CO_3)OH$/rGO-2 | 1 M KOH + 1 M $CH_3OH$ | 1.277 | NA | S36 |
| Pt/NiFe-LDH | 1 M KOH + 1 M $CH_3OH$ | 0.5123 | NA | S37 |
| Pt/NiFe-LDH/RGO | 1 M KOH + 1 M $CH_3OH$ | 0.9493 | NA | S37 |
| PdPtNi NPs | 1 M KOH + 1 M $CH_3OH$ | 1.167 | 2.18 | S38 |
| PtNi NPs | 1 M KOH + 1 M $CH_3OH$ | 0.872 | 2.02 | S38 |
| Au@Pt HUSs | 0.5 M NaOH + 1 M $CH_3OH$ | 0.22 | NA | S39 |

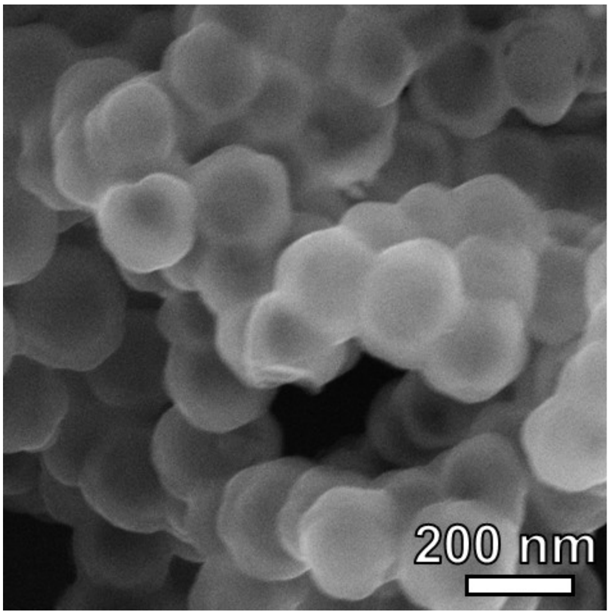


**Fig. S12** SEM image of Pt@N, F-HCS after MOR.

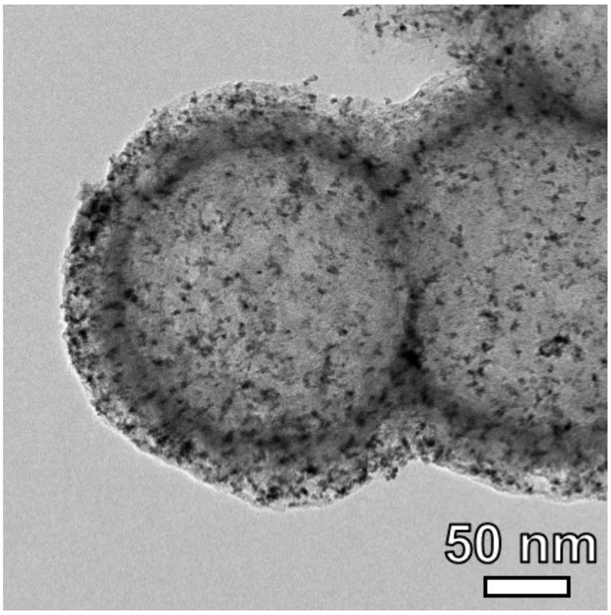


**Fig. S13** TEM image of Pt@N, F-HCS after MOR.

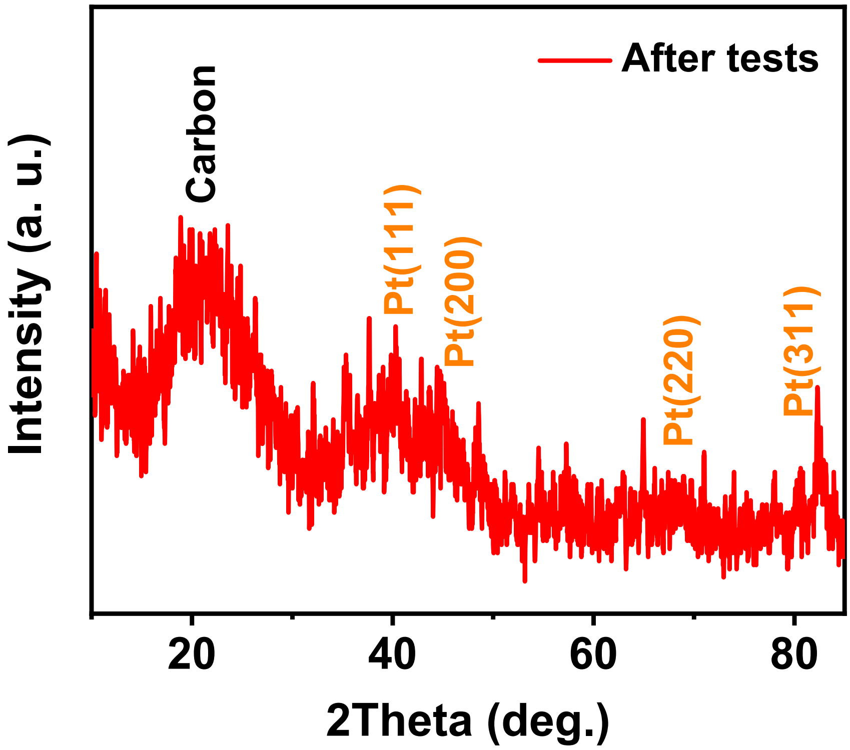


**Fig. S14** XRD pattern of Pt@N, F-HCS after MOR.

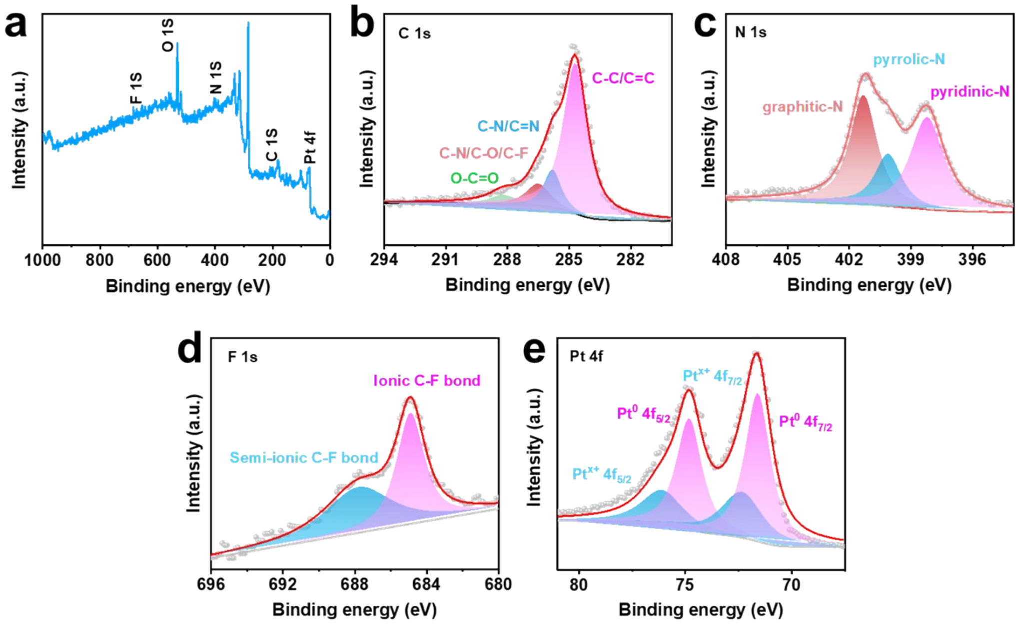


**Fig. S15** XPS patterns of Pt@N, F-HCS after MOR.

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