

Supporting information

Suppression Effect of Small Organic Molecules on Oxygen Reduction activity of Fe/N/C Catalysts

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1. Materials and methods

1.1 Synthesis of Fe/N/C catalyst

1.1.1 Synthesis of PDA-Fe/N/C

The PDA-Fe/N/C catalyst was prepared through high-temperature pyrolysis of the mixture of PmPDA-coated KJ600 carbon black and FeCl₃, according to the previous method.¹ In brief, to the mixture of KJ600 carbon black (2.0 g) grafted with sulfophenyl group, *m*-phenylenediamine (*m*-PDA, 15 g) and concentrated HCl (36%, 50 mL), as well as (NH₄)₂S₂O₈ (2 M, 140 mL) and FeCl₃ (1 M, 40 mL), were added to form a *Pm*-PDA-coated carbon black. After centrifugal separation and washing, the obtained powder (0.3 g) was mixed with FeCl₃ (1 M, 0.9 mL). The obtained precursor was pyrolyzed at 950 °C in Ar atmosphere for 1 h. The pyrolyzed sample was acid leached in 1 M HCl solution at 80 °C for 8 h followed by centrifugation and washing. Finally, the obtained powder was again pyrolyzed at 950 °C for 3 h to obtain the final catalyst.

1.1.2 Synthesis of PANI-Fe/N/C

The PANI-Fe/N/C catalyst was synthesized as previously reported methods.² In brief, KJ EC 300 carbon black was treated in 1 M HCl solution to remove metal impurities. Acid-treated KJ EC-300 (0.5 g) was first dispersed in 200 mL deionized water, and then aniline (2.0 mL), concentrated HCl (36%, 12.5 mL), (NH₄)₂S₂O₈ (2 M, 35mL) and FeCl₃ (1M, 10 mL) was added. The obtained suspension was kept below 10 °C for 12 hours to form a PANI-coated carbon black. The obtained precursor was pyrolyzed at 950 °C in Ar atmosphere for 1 h. The pyrolyzed sample was acid leached in 1 M H₂SO₄ solution at 80 °C for 8 h followed by centrifugation and washing. Finally, the obtained powder was again pyrolyzed at 950 °C for 3 h to obtain the final catalyst.

1.1.3 Synthesis of AT-Fe/N/C

The AT-Fe/N/C was synthesized by a traditional two-step pyrolysis and acid leaching process, according to the previous method.³ In brief, acid-treated KJ-600 (0.25g) was first dispersed in deionized water by sonication and then 2-aminothiazole (2-AT, 0.5g) and NaClO (8%, 15 ml) were added to into the suspension. Then the suspension was transferred into a 100 ml autoclave and performed solvothermal synthesis at 110 °C for 36 h to form poly-AT coated carbon black. Finally, FeCl₃ (1 M, 10 ml) solution was added into the above suspension. The suspension containing Fe, polymer and carbon was dried at 100 °C to evaporate solvent and to get solid power. The subsequent heat-treatment was performance in Ar atmosphere at 900 °C for 1 hour. The pyrolyzed sample was then acid leached in 1 M HCl solution at 80 °C for 7 h followed by centrifugation and washing. Finally, the obtained powder was again pyrolyzed at 950 °C for 3 h to obtain the final catalyst.

1.1.4 Synthesis of SNW-Fe/N/C

The SNW-Fe/N/C was prepared through high-temperature pyrolysis of precursor containing element Fe, nitrogen and carbon, according to the previous method.⁴ The precursor was synthesized through the dehydration condensation between melamine (0.626 g, 5.0 mmol), terephthalaldehyde (1 g, 7.5 mmol) with DMSO (18 mL) in 25 mL Teflon lined autoclave at 170 °C for 72 h. The formed SNW was in-situ coated on KJ600 carbon black (0.5 g). The obtained SNW/C (1.0 g) was mixed with FeCl₃ (3 mmol) in ethanol and the solvent was removed through rotary evaporator and further dried at 70 °C for 12 h. The obtained precursor was further pyrolyzed at 800 °C in Ar atmosphere for 1h, followed by acid leaching in 0.1 M H₂SO₄ at 80 °C for 8 h, and the second heat treatment at 800 °C in Ar atmosphere for 3h.

1.2 Electrochemical measurements

The ORR polarization curves were obtained on a CHI-760D bipotentiostat equipped with a rotating ring-disk electrode. Rotating speed was fixed at 900 rpm. To prepare catalyst ink, the Fe/N/C catalyst (6.0 mg) was dispersed in the mixture of ethanol (0.5 mL), deionized water (0.5 mL) and Nafion (5 wt%, 50 μL). The working electrode was prepared by dropping 25μL catalyst ink into a glassy carbon (GC, ϕ = 5.61 mm) disk with Pt ring. A GC plate was used as the counter electrode. A reversible hydrogen (RHE) electrode and Hg/HgO electrode were used as reference electrode in acid and alkaline media, respectively. The potential was quoted relative to reversible hydrogen electrode (RHE) scale. The potential difference between the Hg/HgO electrode and RHE was determined to be 0.918 V.

1.3 Adsorption capacity test

PDA-Fe/N/C catalyst or KJ600 carbon black (30 mg) was dispersed in 0.1 M NaOH or H₂SO₄ solution (30 mL) containing 5 mM small organic molecule (ethanol,

1,4-dioxane Or n-butanol) in a sealed bottle. After shaking for 15 minutes, the slurry was filtrated to obtain clear aqueous solution. Finally, 0.5 mL of above solution (after adsorption) or solution before adsorption was pipetted into a NMR tube, and then 0.30 mL of reference solution (400 mM DMSO in D₂O) was added. The concentration of organic molecules in aqueous solution before and after adsorption by PDA-Fe/N/C or KJ600 were quantified by nuclear magnetic resonance (NMR, 500 MHz, Avance III), with DMSO (CH₃SOCH₃) as internal standard.

1.4 Physical characterizations

The Ar adsorption/desorption isotherm was tested on ASAP 2020 physisorption analyzer (Micromeritics).

The N₂ adsorption/desorption isotherm was tested on Tristar 3000 physisorption analyzer (Micromeritics).

XRD patterns was measured on a Japan Rigaku DMax-gA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda=1.54$ Å). The morphology of Fe/N/C catalysts was characterized by field emission scanning electron microscopy (SEM, HITACHI S-4800).

X-ray photoelectron spectroscopy (XPS, Qtac-100 LEISS-XPS instrument) was performed to character the surface composition of Fe/N/C catalyst.

2. The ORR activity recovery of Fe/N/C catalyst after removal of adsorbed SOMs

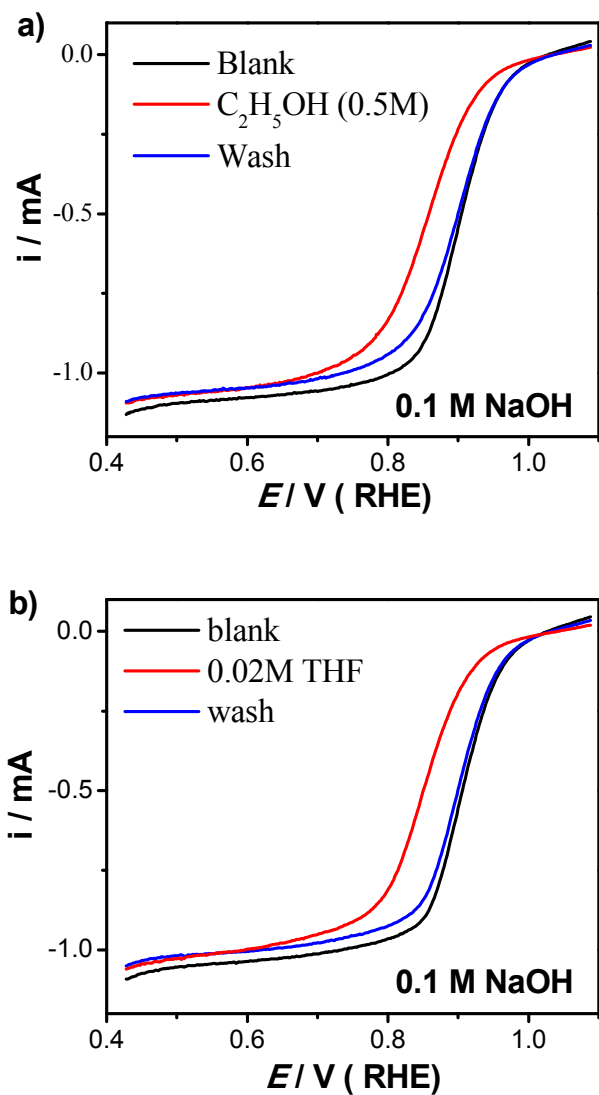


Figure S1. Polarization curves of poisoned PDA-Fe/N/C before and after immersing in deionized water for 3-5 min. The original ORR polarization curve was also shown for comparison. Conditions: Catalyst loading: 0.60 mg cm^{-2} ; Scan rate: 10 mV s^{-1} ; Rotating rate: 900 rpm. SOMs used here were ethanol (0.5 M) and THF (0.02 M).

Obviously, the ORR activity of PDA-Fe/N/C was almost recovered after removing adsorbed ethanol or THF by washing the poisoned electrode.

3. XRD patterns and SEM images of four ORR catalysts

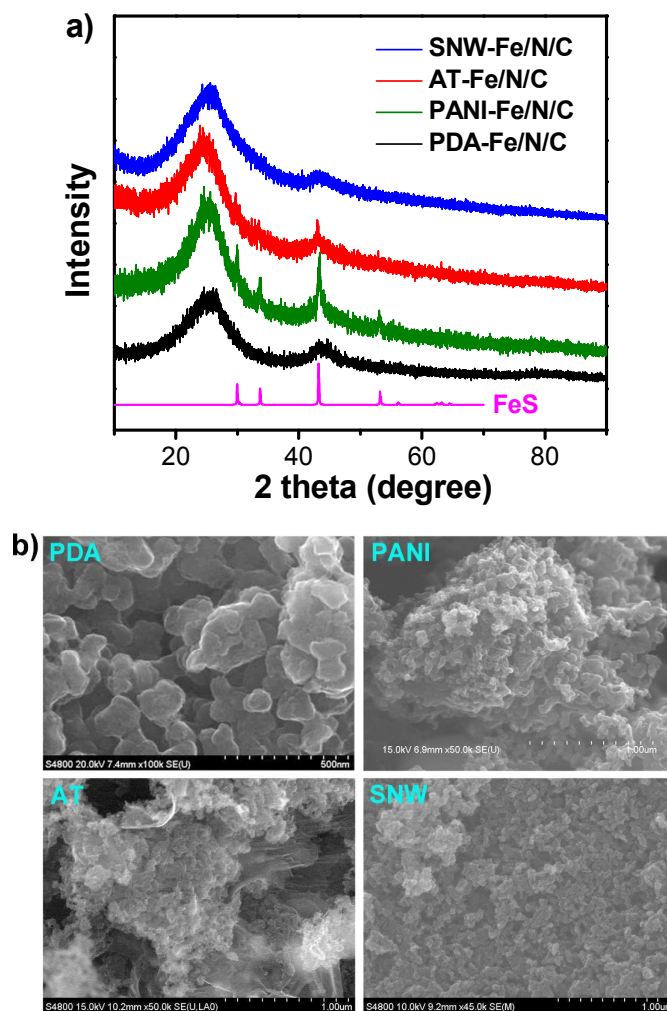


Figure S2. a) XRD patterns and b) SEM images of four different ORR catalysts prepared from different nitrogen sources (SNW-Fe/N/C, AT-Fe/N/C, PANI-Fe/N/C, and PDA-Fe/N/C).

4. The sensitivity of five different catalysts to 1,4-dioxane

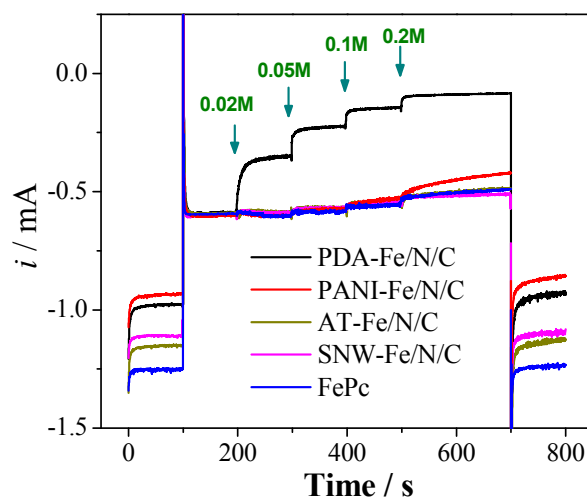


Figure S3. Chronoamperometric response of three different catalysts with the addition of 1,4-dioxane in O_2 -saturated 0.1 M NaOH solution. Conditions: Catalyst loading: 0.60 mg cm^{-2} ; Scan rate: 10 mV s^{-1} ; Rotating rate: 900 rpm. Potential was initially set at 0.50 V (diffusion limited current region) for 100 s, and then switched to about $E_{1/2}$. At 200 s, the 1,4-dioxane was added stepwise to reach solution concentration of 0.02, 0.05, 0.1, and 0.2 M. Finally, the potential was back to 0.50 V, to check the diffusion limited current (that is, no catalyst was stripped from electrode surface in the solution containing organic molecules).

5. The protonation of pyridinic N in acid medium

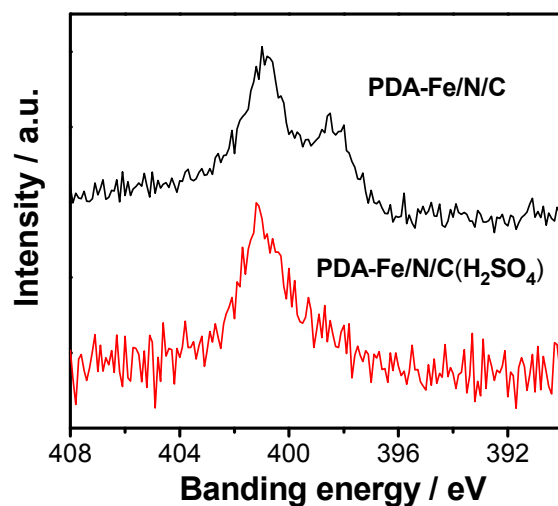
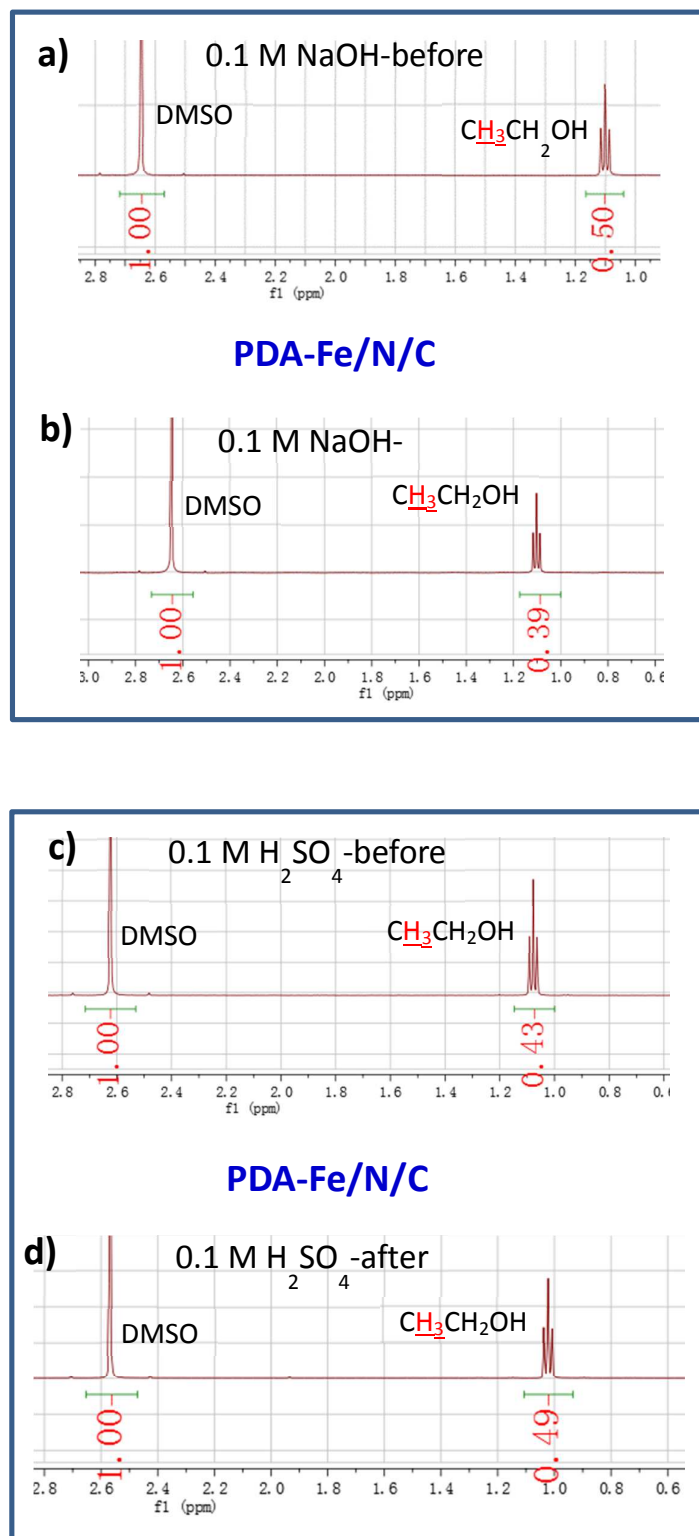
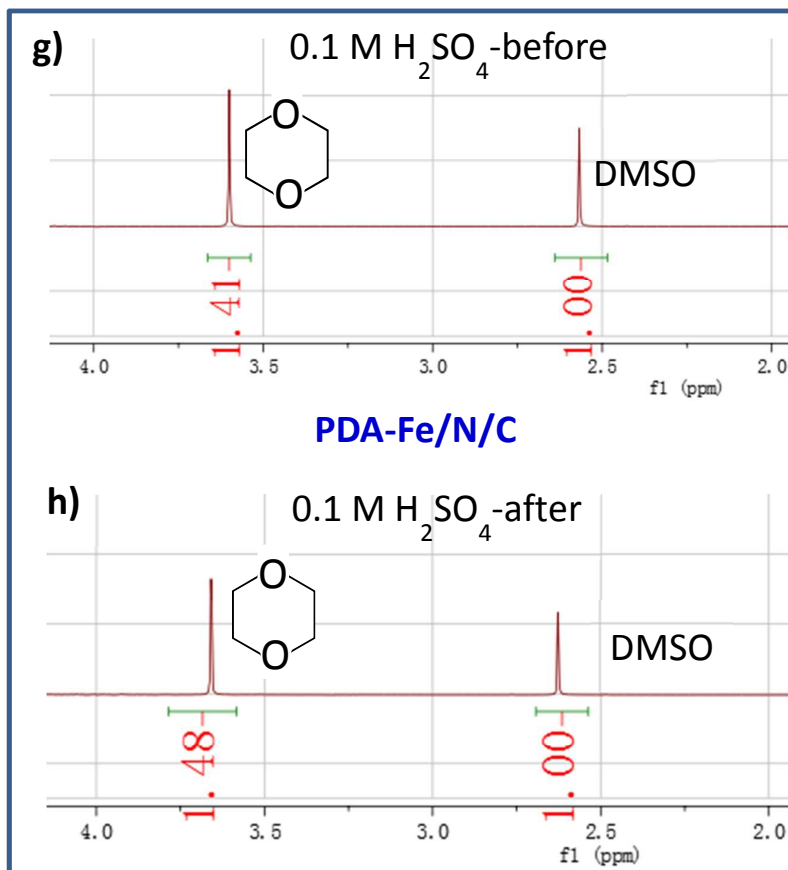
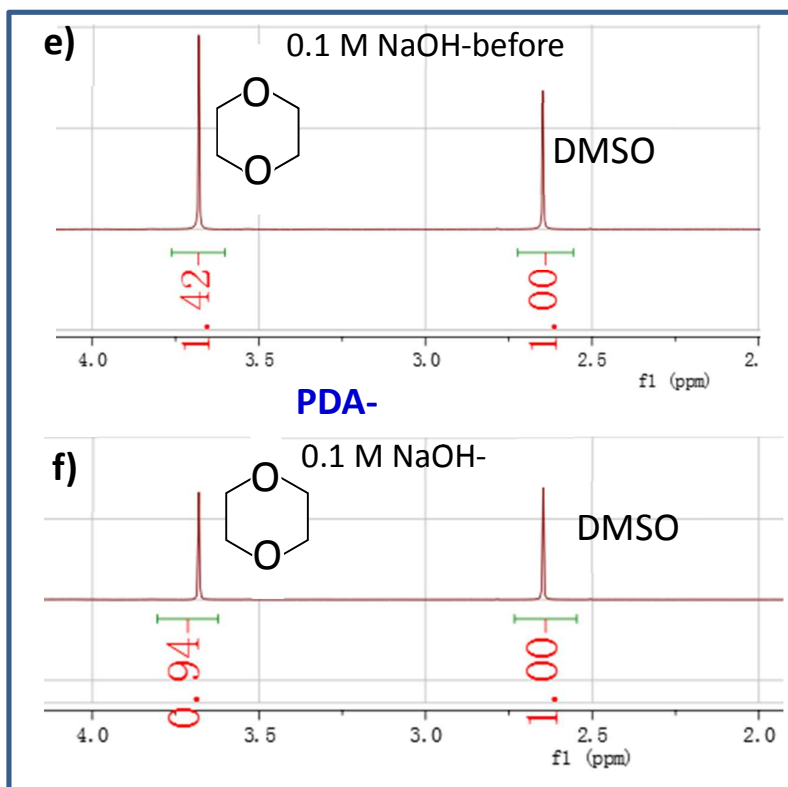


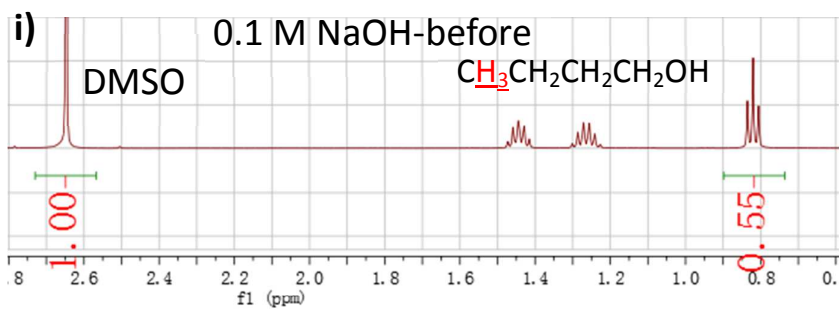
Figure S4. High-resolution N 1s spectra of PDA-Fe/N/C before and after the addition of H₂SO₄. The amount of H₂SO₄ added was 0.04 mmol / mg_{cat}.

In the PDA-Fe/N/C catalyst, the peak at around 398.2 eV can be attributed to pyridinic N. After the addition of H₂SO₄, this peak disappeared, and the pyridinic N converted into pyridinium cation, whose binding energy shifted to 401 eV.⁵

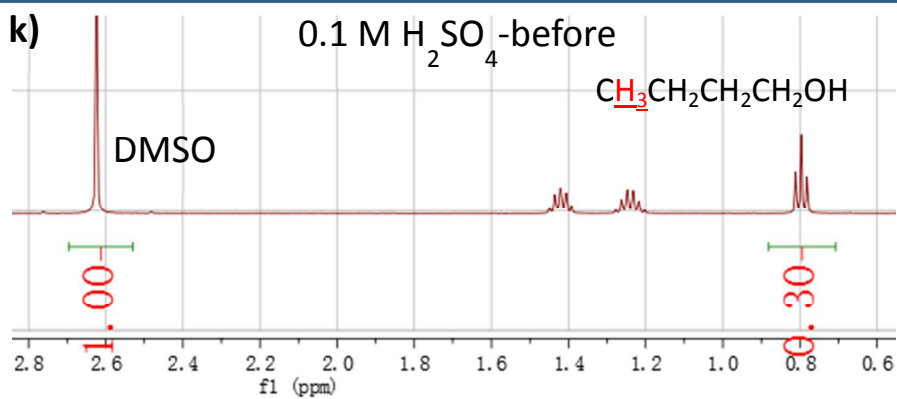
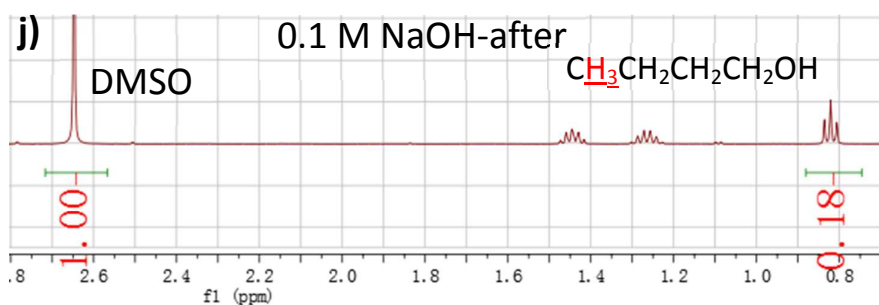
6 . NMR spectra of organic molecule solution before and after the adsorption by PDA-Fe/N/C or KJ600 carbon black



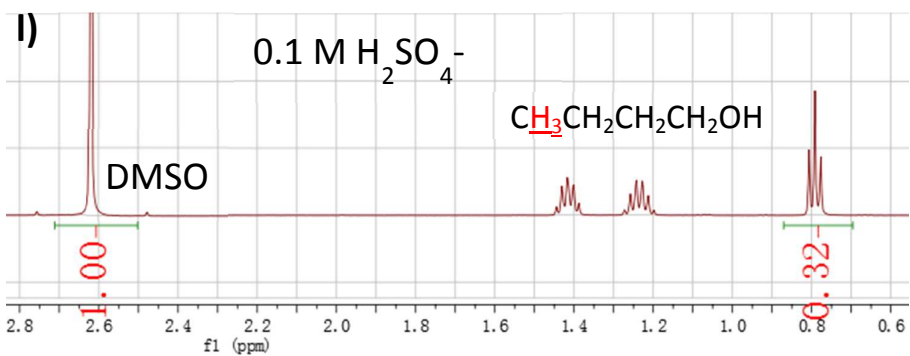




PDA-Fe/N/C



PDA-Fe/N/C



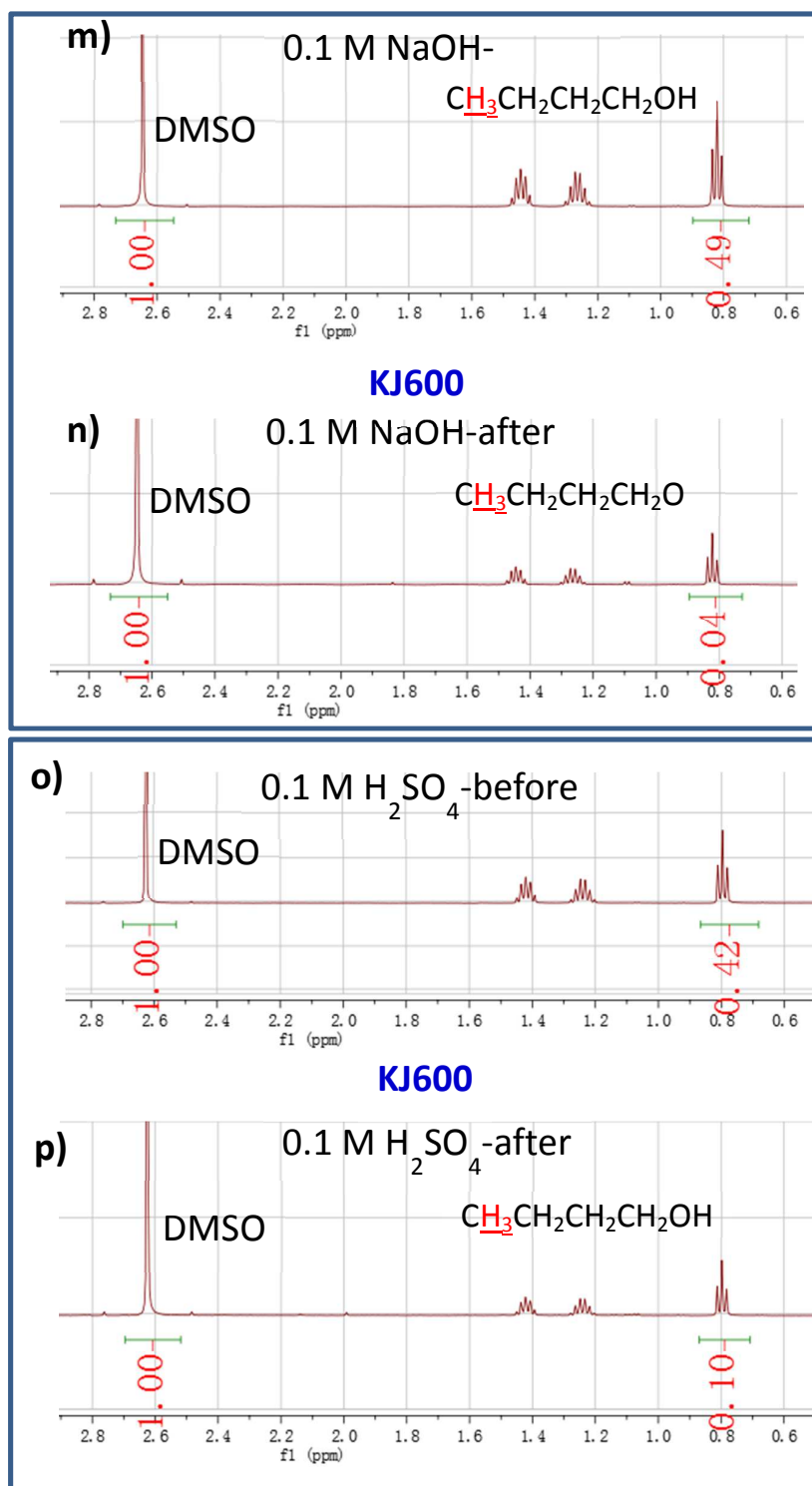


Figure S5. ^1H NMR spectra of ethanol, 1,4-dioxane and butanol before and after the adsorption of PDA-Fe/N/C (a-l) and KJ600 (m-o) under different pH environment. (a, b) Ethanol in 0.1 M NaOH; (c, d) Ethanol in 0.1 M H_2O_4 ; (e, f) Dioxane in 0.1 M NaOH; (g, h) Dioxane in 0.1 M H_2O_4 ; (i, j) Butanol in 0.1 M NaOH; (k, l) Butanol in

0.1 M H₂O₄; (m, n) Butanol in 0.1 M NaOH (KJ600); (o, p) Butanol in 0.1 M H₂O₄ (KJ600).

4. Comparison of N 1s spectra of KJ600 carbon black and PDA-Fe/N/C

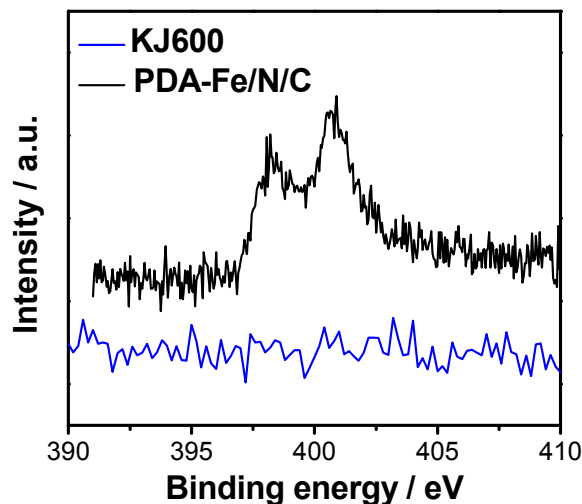


Figure S6. High-resolution N 1s spectra of PDA-Fe/N/C and KJ600 carbon black.

1. Wang, Q.; Zhou, Z. Y.; Lai, Y. J.; You, Y.; Liu, J. G.; Wu, X. L.; Terefe, E.; Chen, C.; Song, L.; Rauf, M.; et al., Phenylenediamine-Based FeN_x/C Catalyst with High Activity for Oxygen Reduction in Acid Medium and Its Active-Site Probing. *J. Am. Chem. Soc.* **2014**, *136*, 10882-5.
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3. Chen, C.; Yang, X. D.; Zhou, Z. Y.; Lai, Y. J.; Rauf, M.; Wang, Y.; Pan, J.; Zhuang, L.; Wang, Q.; Wang, Y. C.; et al., Aminothiazole-Derived N,S,Fe-Doped Graphene Nanosheets as High Performance Electrocatalysts for Oxygen Reduction. *Chem. Commun.* **2015**, *51*, 17092-5.
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