Electronic Supplementary Information:

Hydrophilic non-precious metal nitrogen-doped carbon electrocatalysts for enhanced efficiency in oxygen reduction reaction

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1. Experimental details

1) **Synthesis of hydrophilic carbon network as host:** All chemicals were used as received. Typically, 1.0 g triblock copolymer F127 was dissolved in 200 mL 50 mM 4, 4'-bipyridine water-ethanol (volume ratio of 1 : 17) solution, denoted solution A. Another solution, 50 mM $CuCl_2 \cdot 2H_2O$ was denoted solution B. The reaction was conducted by rapid mixing through pouring solution A (200 mL) into solution B (200 mL) under shaking to ensure sufficient mixing and the products were formed immediately. Subsequently, the collection of the resulting products was carried out through centrifugation with a speed of 4200 rpm for 60 min and washed for 3 times. The as-obtained polymers were pyrolyzed at 500 °C for 2.0 h with a heating rate of 60 °C h^{-1} under argon atmosphere. The host carbon (DUT-110) was obtained after the removal of the copper species using 4.0 M HNO_3 solution.

2) **Synthesis of highly hydrophilic ORR electrocatalysts:** Impregnation was used for introducing the Fe or Cu precursors in DUT-110 based on a certain molar ratio of Fe/N, Fe/Cu/N, and Cu/N, where the N content used for calculation came from XPS data (14.3 atom%). For all the three catalysts (Fe/N_1/3.2, Fe/Cu/N_1.3/1/8 and Cu/N_1/4), the same amount of support material (DUT-110, 250 mg) was employed for impregnation. For Fe/N_1/3.2, 144 mg $FeCl_3$ (dissolving in 700 μL H_2O) was impregnated into the pores of DUT-110. For Fe/Cu/N_1.3/1/8, the metal precursor was 72 mg $FeCl_3$ and 67 mg $CuCl_2{\cdot}2H_2O$ (dissolving in 700 μL H_2O), while for Cu/N_1/4 was 134 mg $CuCl_2{\cdot}2H_2O$ (dissolving in 700 μL H_2O). Subsequently, the composite materials were dried at 80 °C overnight and further heated to a temperature up to 900 °C with a heating rate of 2.0 °C min^{-1} and left at this temperature for 1.0 h in an argon atmosphere. Thereafter, the samples were allowed to cool down naturally. The composite samples with metals were transferred to a round bottom flask and dispersed in 100 mL of aqueous sulfuric acid (*ca.* 2.0 mol L^{-1}). These mixtures were refluxed at 110 °C for 24.0 h. After cooling down, the leached samples were re-collected by centrifugation and subsequently undergoing 8 cycles of washing with deionized water and centrifugation to remove acid residues as much as possible. The thermal treatment under argon was repeated with exactly the same temperature profile as before. The samples were then used for further analysis and application.

3) **Synthesis of less hydrophilic ORR electrocatalysts groups of Fe/N_PANI+Fe and Fe/N_IL+Fe:** The synthesis of group of Fe/N_PANI+Fe and Fe/N_IL+Fe was based on the previous work.[1] The key difference with that of hydrophilic ORR electrocatalysts lies in host carbon, where the highly hydrophobic carbon black (Ketjen EC 600J) was employed for these less hydrophilic catalysts. The N-source and Fe-source for Fe/N_PANI+Fe group are polyaniline and $FeCl_3$, respectively; while for Fe/N_IL+Fe group, N-source and Fe-source are heteroatom-containing ionic liquid, N, N-ethyl-methyl-imidazolium and $FeCl_3$. The pyrolysis and leaching treatment were kept identical with that of the hydrophilic class as described above.

4) **Structural characterization:** Scanning electron microscope (SEM) and the Energy Dispersive X-ray Spectroscopy (EDS) mapping investigations were carried out with a Hitachi SU8020 instrument. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) as well as the STEM elemental maps were obtained with a FEI Titan^3 80-300 with a

CEOS aberration corrector for the objective lens operated at an acceleration voltage of 80 kV. Sample preparation was gentle pressing of TEM Lacey grids on the material. XPS spectra were acquired with an Escalab spectrometer (250Xi, USA) equipped with an Mg K_{α} monochromatic source. All the spectra were calibrated using the C 1s neutral-carbon peak at 284.8 eV. A Shirley background was subtracted prior to peak fitting. The peak areas were normalized with theoretical cross-sections to obtain the relative surface elemental compositions. Raman spectra were measured on a Renishaw Ramascope RM 2000 Raman microscope (50x, NA = 0.75) with a REM Laser from Laserquantum (wavelength: 532 nm). The parameters of peaks were extracted by the curve fitting on the Renishaw Wire 2.0 software, where a mixed Gaussian and Lorentzian function was used, and the maximum of the first curve is defined at 1170 cm^{-1}. Water physisorption (298 K) measurements were carried out on a Quantachrome Hydrosorb 1000 instrument. O_2 physisorption (90 K) measurements were performed on a Quantachrome Quadrasorb apparatus (Quantachrome Instruments, Boynton Beach, USA). Nitrogen adsorption isotherms were measured on a BELSORP adsorption analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was used to estimate specific surface area (S_{BET}) based on adsorption points in the relative pressure of $0.05<P/P_0<0.16$. Pore size distributions (PSDs) were derived from the adsorption branches of the isotherms based on non-localized density functional theory (NLDFT, nitrogen on carbon slit adsorption branch kernel). Prior to gas or vapor sorption measurements, the samples were degassed at 423 K for at least 12 h.

5) **Electrochemical characterization and ORR activity:** ORR activity and stability of the catalysts were tested using a rotating disk electrode (RDE) in a three-electrode electrochemical glass cell. Platinum gauze and reversible hydrogen electrode (RHE, gaskatel) were used as counter and reference electrodes, respectively. The catalyst powders were deposited by ink-casting as thin films on glassy carbon (GC) electrodes (Ø = 5 mm, as working electrode) with a loading of 0.8 mg cm^{-2}. For that purpose, the catalyst powder was suspended in a mixture of 850 μL Millipore water, 100 μL isopropanol and 50 μL Nafion solution (5 wt% stock solution) followed by sonication. Finally, 10 μL of the homogenized catalyst ink was deposited on the electrode and dried (at 60 °C) to generate a thin catalyst film. Electrochemical measurements were performed in 0.10 M KOH (pH ~ 13) as alkaline environments, respectively. Prior to electrochemical measurements, N_2 was

purged through the electrolyte. First, a cyclic voltammogram (CV) was recorded with a scan rate of 10 mV s^{-1} and rotation speed of 1500 rpm to evaluate the background currents (non-faradic current). For ORR measurements, the electrolyte was bubbled with O_2. The linear sweep voltammograms (LSV) were recorded with a scan rate of 10 mVs^{-1} at a rotation speed of 1500 rpm. For comparison, all electrocatalysts were compared with a platinum benchmark catalysts from ETEK (Pt/C 20 wt%), employing a catalyst electrode loading of 10 μg_{Pt} cm^{-2}. In this work, mass activity (I_m) of this series of highly hydrophilic doped catalysts is defined by the following equation of

$I_m = I_k/m_{catalyst}$ ($mA/mg_{catalyst}$) with I_m: the mass activity, $m_{catalyst}$: the catalyst loading on the glassy carbon electrode (mg/cm^2) and I_k: the kinetic current. I_k was calculated by the relationship $I_k = (I_{@0.8} \times I_{lim})/(I_{lim} - I_{@0.8})$ between $I_{@0.8V}$, the current density at 0.8 V, and I_{lim}, the limiting current density at 0.4 V respectively, both extracted from the LSV curves. The specific activity ($I_{specific}$) is defined as following: $I_{specific} = I_m/S_{BET}$ ($mA\ m^{-2}$)

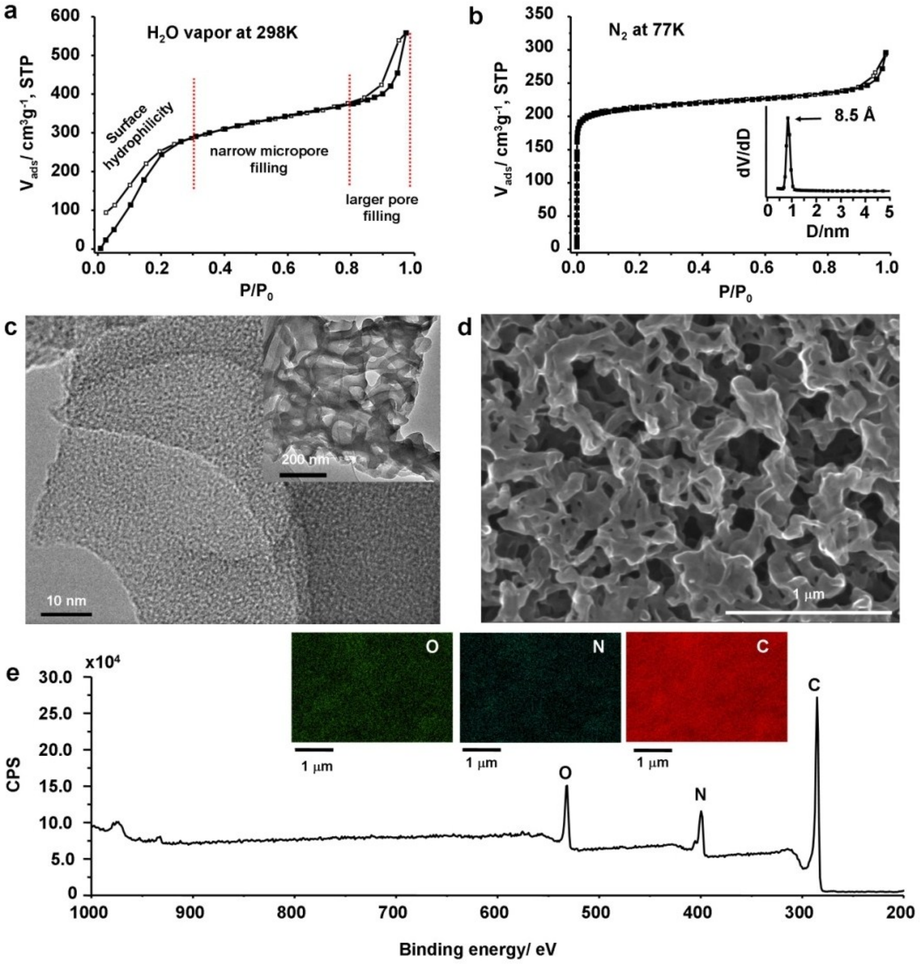

Fig. S1 Structural characterization of host DUT-110. (a) H_2O vapor adsorption (solid symbols) and desorption (empty symbols) isotherm at 298 K. (b) N_2 adsorption (solid symbols) and desorption (empty symbols) isotherm at 77 K and the corresponding PSD (inset, adsorption branch based on NLDFT theory). (c) TEM images with low (inset) and high magnification. (d) SEM image. (e) XPS survey spectrum showing surface compositions. Inset shows the SEM-EDS compositional maps of area in d) for C, N and O accordingly.

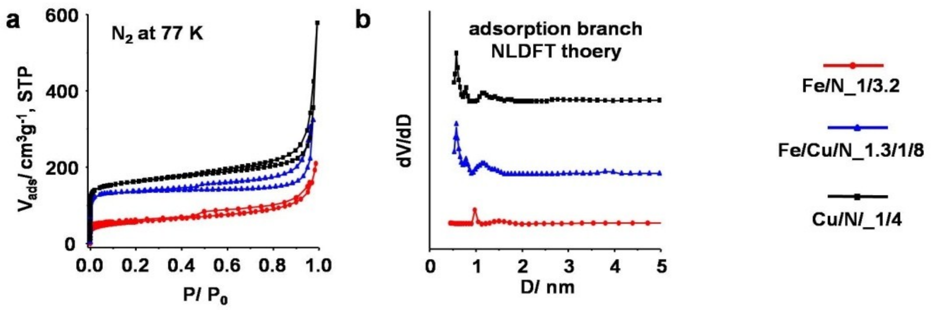

Fig. S2 (a) N_2 adsorption isotherm at 77 K. (b) Pore size distribution based on N_2 adsorption data by NLDFT theory.

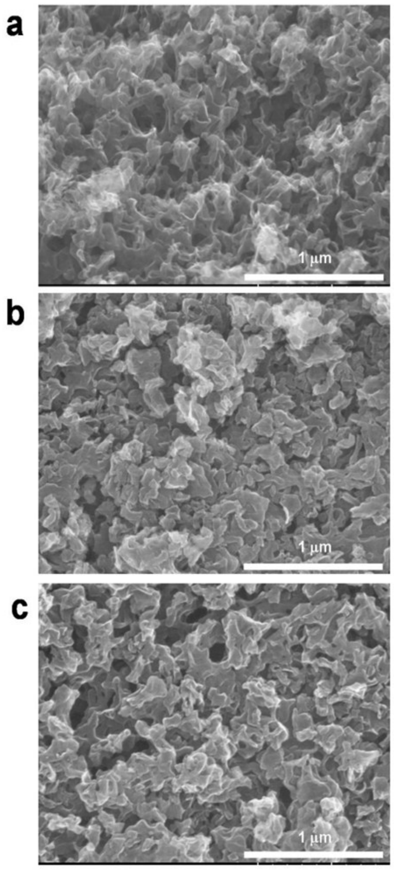

Fig. S3 SEM images for Fe/N_1/3.2 (a), Fe/Cu/N_1.3/1/8 (b), and Cu/N_1/4 (c).

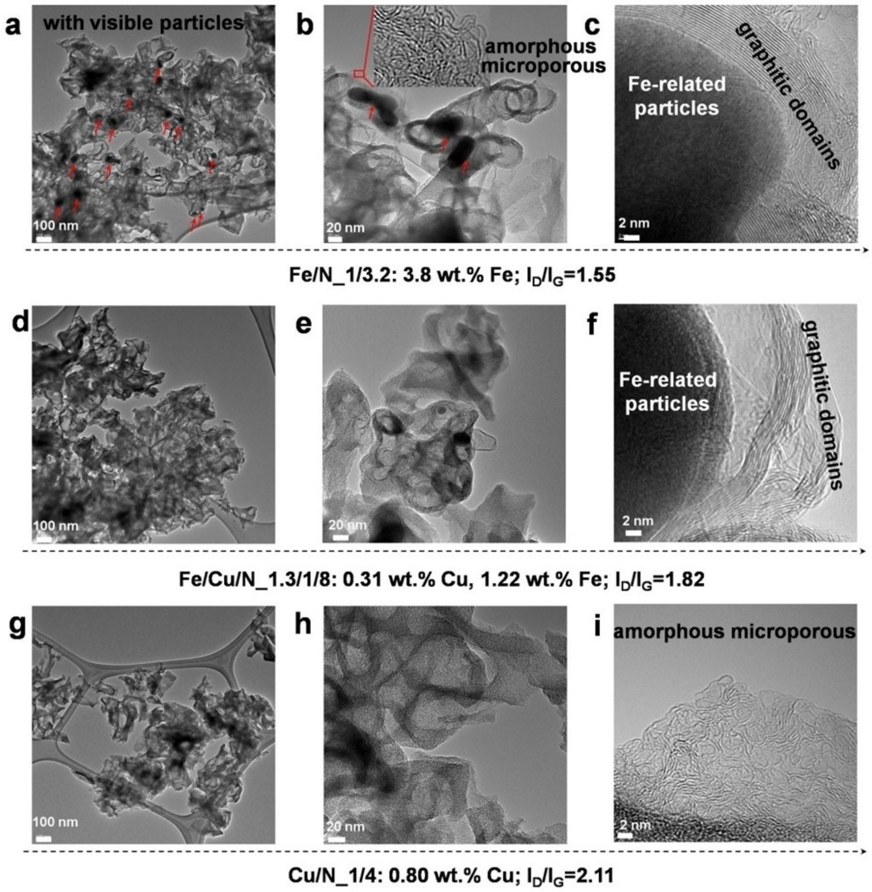

Fig. S4 Microstructure observation of the group of hydrophilic materials. (a-c) TEM images of Fe/N_1/3.2. (d-f) TEM images of Fe/Cu/N_1.3/1/8. (g-i) TEM images of Cu/N_1/4. The Fe and Cu content refers to their overall content determined by ICP; while the I_D/I_G is calculated based on Raman spectra.

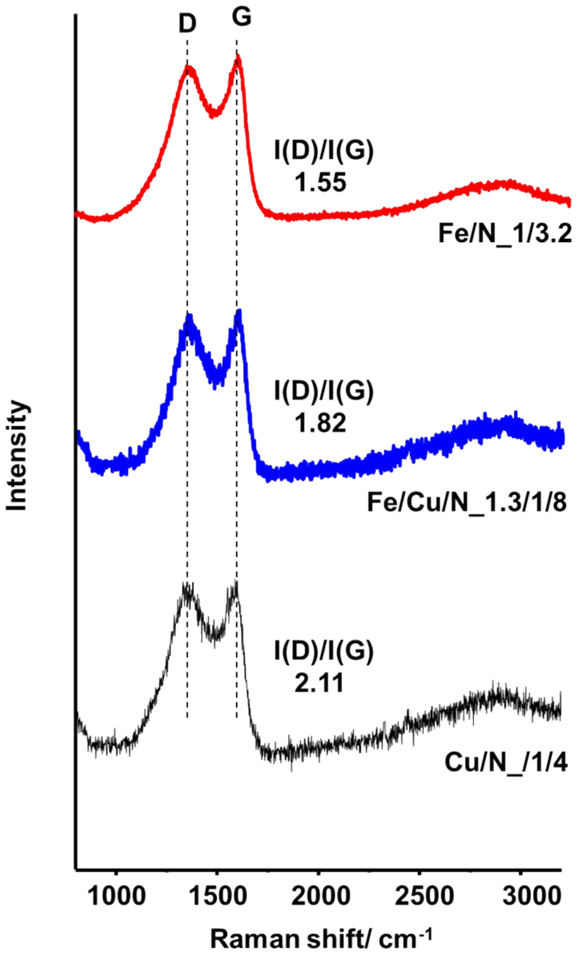

Fig. S5 Raman spectra of Fe/N_1/3.2, Fe/Cu/N_1.3/1/8 and Cu/N_1/4. (please see the fitting details in Table S1 in the following).

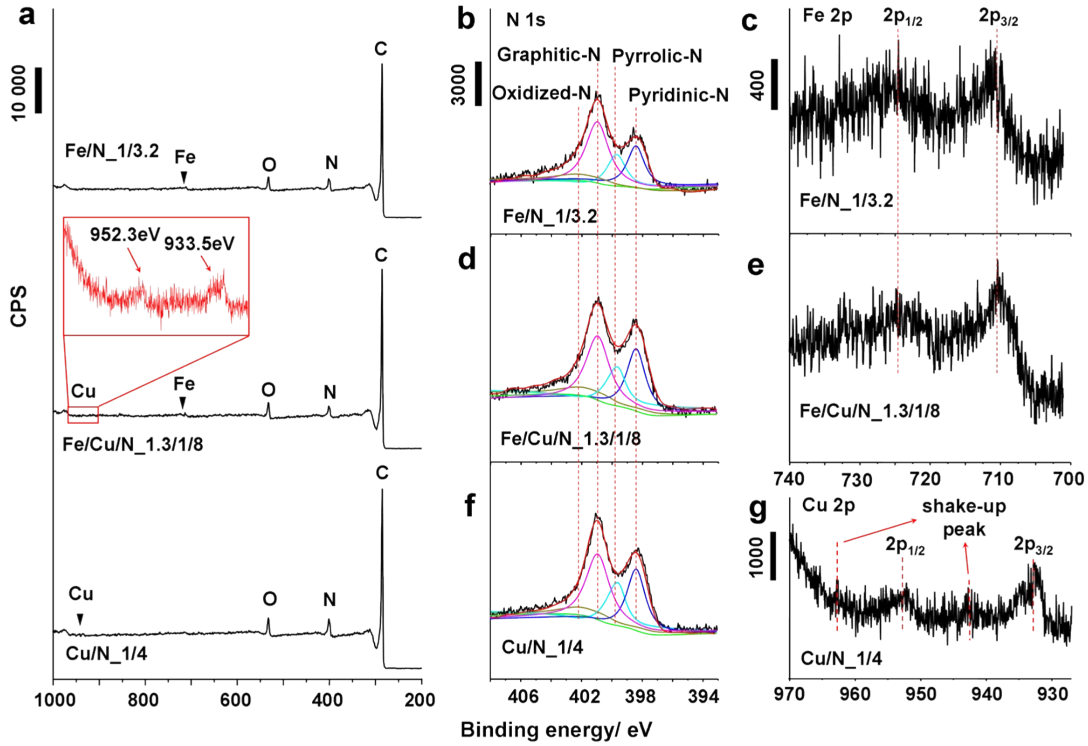

Fig. S6 (a) XPS survey spectra showing surface compositions. Inset shows the high-resolution Cu 2p for Fe/Cu/N_1.3/1/8. (b, d, f) High-resolution deconvoluted N 1s for Fe/N_1/3.2, Fe/Cu/N_1.3/1/8 and Cu/N_1/4, respectively. (c, e) High-resolution Fe 2p spectra for Fe/N_1/3.2 and Fe/Cu/N_1.3/1/8, respectively. (g) High-resolution Cu 2p spectrum for Cu/N_1/4. The lines in b, d, f label the peaks related to Pyridinic-N, pyrrolic-N, Graphitic-N and Oxidized-N; the lines in c, e label the peaks related to $2p_{1/2}$ and $2p_{3/2}$ of Fe^{x+} (x=2 or 3); while the line and arrow in g label the peaks related to $2p_{1/2}$ and $2p_{3/2}$ of Cu^{x+} (x=1 or 2) and accompanied shake-up peaks.

As shown, the three peaks at 398.4, 400.9, and 402.2 eV in the N 1s spectrum of Fe/N_1/3.2 (Figure S6b) can be assigned to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N, with ratio of 24.7, 14.0, 55.6 and 5.7 %, respectively. Similarly, Fe/Cu/N_1.3/1/8 exhibited 28.1 % pyridinic-N, 12.2 % pyrrolic-N, 53.2 % graphitic-N, and 6.5 % oxidized-N (Figure (Figure S6d), while Cu/N_1/4 showed slightly less graphitic-N (50.2 %) but similar pyridinic-N (27.4 %), pyrrolic-N (17.2 %) and oxidized-N (5.2 %) (Figure S6f).

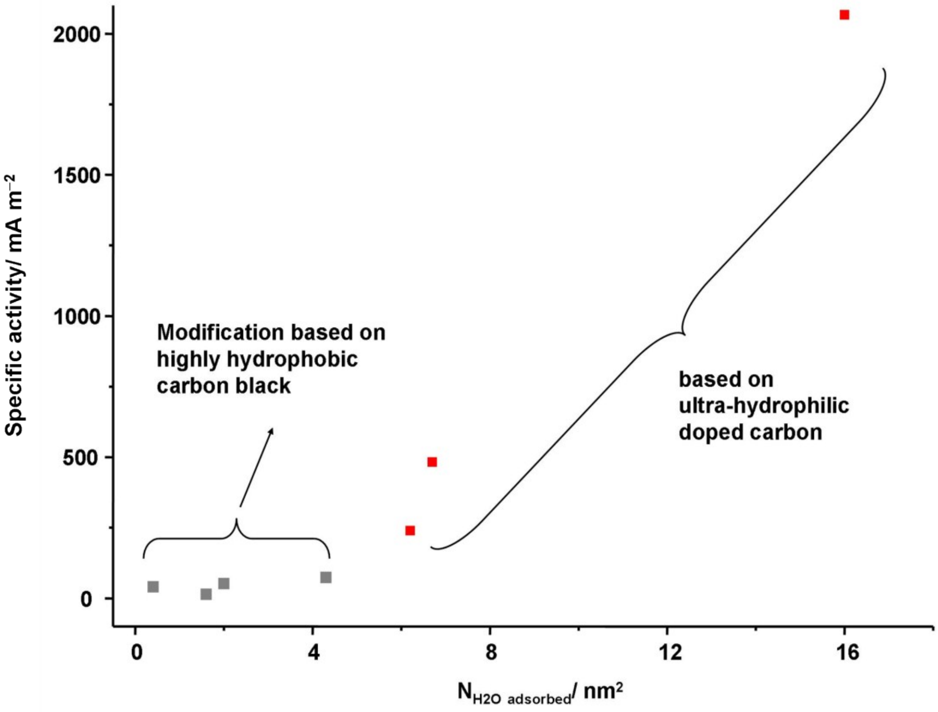

Fig. S7 The relationship between hydrophilicity in term of water molecules adsorbed per nm^2 based on adsorption data at P/P_0=0.3 and specific activity.

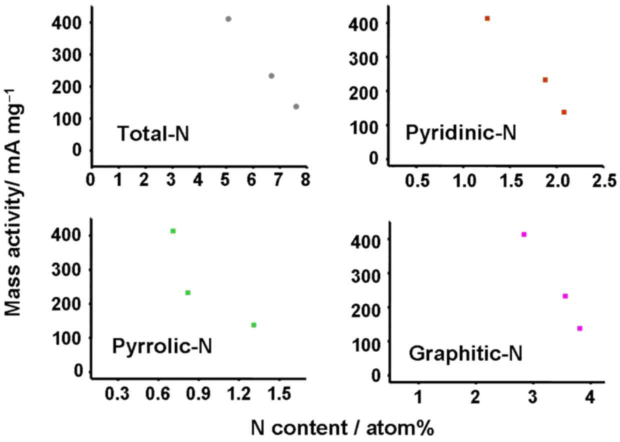

Fig. S8 The relationship between the content of N-species in terms of total N, pyridinic-N, pyrrolic-N and graphitic-N and the mass activity for the hydrophilic catalysts group. This indicates that there is no clear trend between mass activity and the N-doping properties.

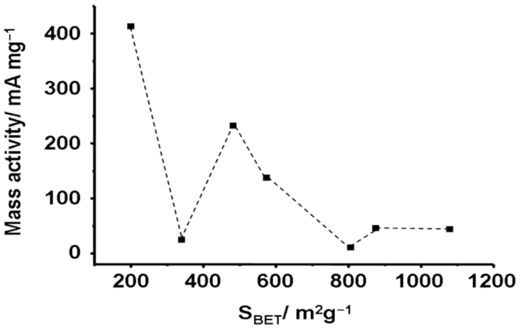

Fig. S9 The relationship between the surface area and the mass activity. As shown, there is also no clear trend between activity and specific surface area.

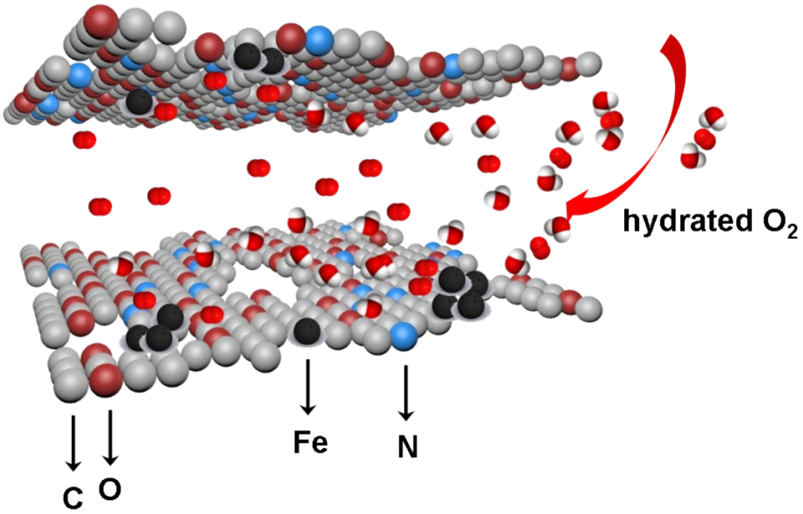

Fig. S10 Schematic representation of possible behavior of hydrated O_2 in the reaction interface.

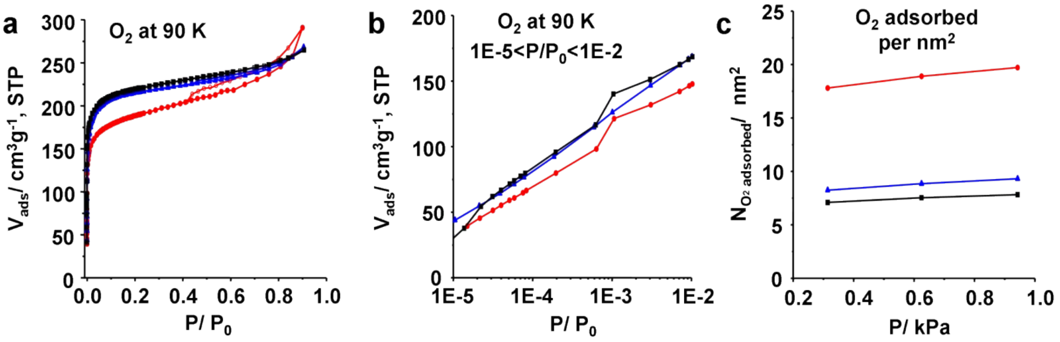

Fig. S11 (a, b) O_2 adsorption (solid symbols) and desorption (empty symbols) isotherm at different relative pressure range at 90 K. (c) The calculated number of O_2 molecules adsorbed per nm^2 in the same pressure range as that in (b).

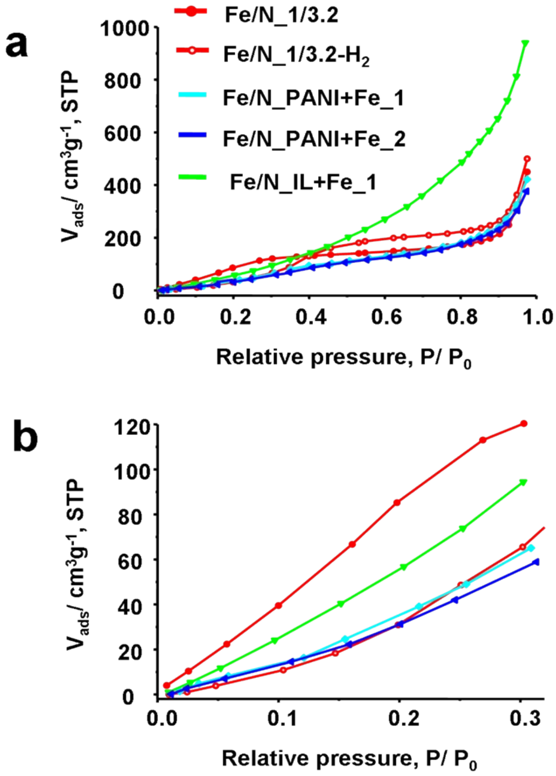

Fig. S12 The tuning of surface hydrophilicity of sample of Fe/N_1/3.2 by H_2 reduction and comparison with other catalysts.

Table S1 Structural parameters and ORR performance in 0.1 M KOH of three group samples investigated

Electrocatalyst	S_{BET} [a] (m^2g^{-1})	Fe content [b] (wt%)	N content [c] (atom%)	Water adsorbed at P/P_0=0.3 [d] (H_2O/nm^2)	$E_{1/2}$ [e] (V)	I_m [f] ($mAmg^{-1}$)	$I_{specific}$ [g] (mAm^{-2})
Group 1: Doped carbon-based electrocatalysts prepared through modification of ultra-hydrophilic carbon network by $FeCl_3$							
Fe/N_1/3.2	200	3.80	5.1	16	0.87	413	2067
Fe/Cu/N_1.3/1/8	482	1.22	6.7	6.7	0.89	233	482
Cu/N_1/4	574	0	7.6	6.2	0.86	138	239
Group 2: Doped carbon-based electrocatalysts prepared through modification of hydrophobic carbon black by polyaniline and $FeCl_3$							
Fe/N_PANI+Fe_1	340	6	7.2	4.6	0.85	25	74
Fe/N_PANI+Fe_2	875	3	7.3	2.0	0.9	46	52
Group 3: Doped carbon-based electrocatalysts prepared through modification of hydrophobic carbon black by ionic liquid and $FeCl_3$							
Fe/N_IL+Fe_1	1079	1.54	1.5	0.4	0.83	44	41
Fe/N_IL+Fe_2	806	1.48	2.4	1.6	0.81	11	14

[a] S_{BET}: specific surface area based on BET theory; [b] Fe content: overall Fe content determined by ICP technique; [c] N content determined by XPS measurement; [d] The number of water molecules adsorbed per nm^2 are calculated based on water vapour adsorption isotherm at relative pressure of 0.3 at 25 °C; [e] $E_{1/2}$: Half wave potential, the potential at which current reached half of the diffusion current (I_d at 0.4 V vs. RHE); [f] I_m: Mass activity calculated by equation of $I_m = I_k/m_{catalyst}$, $m_{catalyst}$ is the catalyst loading on the glassy carbon electrode (mg cm^{-2}) and I_k the kinetic current; [g] $I_{specific}$: specific activity defined as: $I_{specific} = I_m/S_{BET}$.

Table S2. Fitting details of Raman spectra for samples of Fe/N_1/3.2, Fe/Cu/N_1.3/1/8 and Cu/N_1/4.

ID	Curve name	Center	Width	Height	% Gaussian	Type	Area	Peak height	Area	All area
Fe/N_1/3.2	D2	1170	91.7794	66.344	100	Mixed	6.48E+03	I(D1)/I(G1): 1.73 I(D2)/I(G2): 0.15 I(G2)/I(G1): 1.16	I(D1)/I(G1): 2.44 I(D2)/I(G2): 0.17 I(G2)/I(G1): 0.64	I(D)/I(G) 1.55
	D1	1351.9	201.765	654.621	100	Mixed	1.41E+05			
	G2	1601.23	78.9678	440.649	100	Mixed	3.70E+04			
	G1	1543.06	143.014	378.641	100	Mixed	6.48E+03			
Fe/Cu/N_1.3/1/8	D2	1170	163.353	469.231	100	Mixed	8.16E+04	I(D1)/I(G1): 1.68 I(D2)/I(G2): 0.24 I(G2)/I(G1): 0.96	I(D1)/I(G1): 4.34 I(D2)/I(G2): 0.26 I(G2)/I(G1): 1.62	I(D)/I(G) 1.82
	D1	1351.48	205.031	3368.72	70.4371	Mixed	8.39E+05			
	G2	1544.6	153.689	1916.36	100	Mixed	3.14E+05			
	G1	1598.46	78.1899	2000.43	66.4126	Mixed	1.93E+05			
Cu/N_1/4	D2	1170	52.3019	28.0539	2.68453	Mixed	2.28E+03	I(D1)/I(G1):	I(D1)/I(G1):	

	D1	1362.49	241.743	623.272	100	Mixed	1.60E+05	1.19 I(D2)/I(G2): 0.12 I(G2)/I(G1): 0.46	3.2 I(D2)/I(G2): 0.08 I(G2)/I(G1): 0.54	I(D)/I(G) 2.11
	G2	1530.46	105.579	239.193	100	Mixed	2.69E+04			
	G1	1600.24	90.3597	521.568	100	Mixed	5.02E+04			

Table S3 Activity parameters comparison with reported non-precious metal nitrogen-doped carbon catalysts based on the RDE data in O_2-saturated 0.1 M KOH.

Material	E_{onset} [a] (V)	$E_{1/2}$ (V)	Ref
Fe/N_1/3.2	0.90	0.87	This work
Fe/Cu/N_1.3/1/8	0.92	0.89	
Cu/N_1/4	0.89	0.86	
MIL-88B-NH_2 derived C/Fe_3C	0.92	0.82	2
Soft-templated C/Fe_3C	0.87	0.82	3
N-Fe-CNT/CNP	0.97	0.92	4
Fe@mesoporous N-doped C	0.8	0.75	5

[a] onset potential is defined as the potential at which the current density reaches 1 mA cm^{-2}. All the potentials reported in this work were expressed versus the reversible hydrogen electrode (RHE).

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