Electronic Supplementary Information

Role of iron in preparation and oxygen reduction reaction activity of nitrogen-doped carbon

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Experimental Section

Synthesis of Platelet SBA-15: Thin disk-shaped platelet SBA-15 ordered mesoporous silica was synthesized according to some modification of a previously reported procedure.[1] Typically, 1.0 g of Pluronic P123 triblock copolymer (Aldrich, Mn = 5800) was dissolved in 40 g of 2.0 M HCl aqueous solution. The mixture solution was stirred for 3 h at 35 ^oC. Once the solution became clear, 2.25 mL of TEOS (Aldrich, 98%) and 0.161 g of $ZrOCl_2$•$8H_2O$ (Sigma Aldrich, 99.5%) were added and the so-formed colloidal suspension was kept being stirred at the same temperature for 24 h. Afterward, the solution was transferred to a teflon vessel, which was sealed and crystallized for further 24 h at 90 ^oC in an oven under static conditions. The resulting white product was filtered, washed with deionized water and then dried in an oven at 80 ^oC. Prior to use for characterization and guest inclusion experiments, the as-synthesized SBA-15 powder was calcined in air at 550 ^oC for 12 h in order to remove the organic template from the pores for the formation of calcined SBA-15.

Synthesis of Ordered Mesoporous Carbon: Ordered mesoporous carbon (OMC) was synthesized by a typical "nanocasting method" using calcined platelet SBA-15 as a template and phenol/paraformaldehyde resin as carbon precursor. Typically, 0.470 g of phenol was introduced into 1.0 g of SBA-15 template by heating it at 140 ℃ for 12 h under vacuum. The resulting phenol-incorporated SBA-15 template was then reacted with paraformaldehyde (0.340 g) under vacuum at 145 °C for 12 h to produce a composite of phenol−paraformaldehyde resin/SBA-15. The composite polymer was then carbonized at 900 ^oC for 5h under Ar flow. After carbonization, the platelet SBA-15 template was removed by hydrofluoric acid (HF) treatment overnight for 12 h.

For the synthesis of Fe-treated OMC (OMC (Fe)), first, 5 ml of 0.5M $FeCl_2$ solution was vacuum infiltrated into1.0 g of SBA-15 template for 3 h. The mixture solution was then dried at 50 ^oC overnight to get a dried $FeCl_2$/SBA-15 mixture. Then, carbon precursor, phenol/paraformaldehyde resin, was nanocasted onto the prepared $FeCl_2$/SBA-15 mixture to get OMC (Fe) precursor. The remaining carbonization and silica removal processes for the synthesis of final OMC (Fe) catalyst are the same as mentioned above for OMC sample.

Synthesis of Phthalocyanine-Treated Ordered Mesoporous Carbons: For the synthesis of phthalocyanine-treated OMCs, i.e., (N-OMC (Pc)) and N-OMC (FePc), phthalocyanine (Pc) or iron phthalocyanine (FePc) is used as a carbon precursor, respectively. In brief, 250 mg of Pc or FePc is mixed with 500 mg of platelet mesoporous SBA-15 homogeneously, in dry condition, by using a vortex mixer for 30 min. The obtained homogeneously mixed composite was then pyrolyzed in Ar flow by keeping the synthesis conditions same as mentioned above. Silica etching from the resultant N-OMC (Pc)/SBA-15 and N-OMC (FePc)/SBA-15 mixtures was carried out by HF treatment overnight for 12 h, otherwise mentioned separately.

Materials Characterization: Surface morphologies of OMC materials were examined by a ultra-high resolution UHR-SEM and UHR-TEM techniques by using Hitachi S-5500 microscopes with an acceleration voltage of 30 kV. To confirm the crystallinity and uniformity of ordered mesoporous structure, X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab X-ray diffractometer attached with Cu Kα radiation operating at 30 mA and 40 KV and with a diffracted beam monochromator. Surface area and pore characteristics were characterized by recording nitrogen sorption isotherms at −196 ^{o}C using a Micromeritics ASAP-2020 accelerated surface area and porosimetry system. Specific surface areas of the samples were determined by nitrogen adsorption data in the relative pressure range from 0.05 to 0.2 using the Brunauer–Emmett–Teller (BET) equation. Total pore volumes were determined from the amount of gas adsorbed at the relative pressure of 0.99. Pore size distribution (PSD) was calculated from the adsorption branches by the Barrett–Joyner–Halenda (BJH) method. The elemental composition and their bonding properties were analyzed by an X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS system using a monochromated Al KR X-ray source). Electrical conductivity measurements for all the samples were done using a home-built 4-point probe apparatus by varying the applied pressure according to previously reported work.[2] The cell was made of a non-conducting teflon block carved into a hollow cylinder, which was covered by two metallic brass pistons, one as a base and the other as a lid, to which the pressure was applied. Fine powdered carbon sample was filled into the hollow teflon chamber, which in turn was sealed using two brass pistons, and resistivity measurement was performed by increasing the applied pressure as shown in Fig S 8b. Current was applied to the sample through the metallic pistons, and voltage was measured across the two metallic probes placed in the middle of teflon block. Keithley model 6220 and model 2182A were used as the DC current source and voltmeter, respectively. The current was varied from 0 to 10 mA, and the corresponding voltages were measured. The electrical conductivity of the samples was estimated using the formula;

$$\sigma = L/RA$$

where σ is the electrical conductivity, R is the resistance of the sample, A is the cross sectional area of the sample (0.126 cm^2) and L is the distance between the two voltage probes (0.2 cm). While measuring the resistivity, pressure was applied to the metallic pistons by using steel plates of known weights.

Electrochemical Measurements: All of the electrochemical analyses were carried out at room temperature in a conventional three-electrode arrangement using rotating ring-disk electrode (RRDE) connected to an electrochemical analyser (BioLogic VMP3). A glassy carbon RRDE (GC-RRDE) coated with as-synthesized OMC or commercial Vulcan XC-72-supported Pt catalyst was used as the working electrode, whereas an Ag/AgCl with saturated KCl and a Pt wire were used as reference and counter electrodes, respectively. All the potentials were measured and reported vs. Ag/AgCl (with sat. KCl solution) reference electrode. The catalyst ink was prepared by dispersing 5.0 mg of corresponding OMC or Pt/C (20 wt%) catalyst, respectively, in a mixture of 0.1 ml 5.0 % nafion solution and 0.9 ml deionized water The dispersed ink was drop casted over GC-RRDE and dried at $50^{o}C$ in oven. Catalyst loading amount was kept 395 µg cm^{-2} for all the OMC and Pt/C samples. The cyclic voltammetry (CV) profiles were recorded in O_2-saturated 0.1 M KOH or 0.1 M $HClO_4$ solution for ORR with scan rate of 50 mV/s in the potential range from +0.5 to -1.0 V in alkaline medium or from +1.1 to -0.2 V in acid medium, respectively. Before recording, the working electrodes were cycled for 20 cycles for stabilization of current density. RRDE measurements were performed by recording linear sweep voltammetry (LSV) curves in the oxygen-saturated 0.1 M KOH or 0.1 M $HClO_4$ solution. The LSV curves for ORR were recorded between +0.2 and -1.0 V in alkaline medium or +1.0 and -0.2 V in acid medium at potential scan rate of 10 mV/s, where the Pt ring potential was measured at set potential of +0.5 V. The electron number (*n*) and HO_2^- percentage were calculated by following equations;

$$n = \frac{4I_D}{I_D + {}^{I_R}\!/_{N}}$$

$$\%HO_2^- = 200 \times \frac{{}^{I_R}\!/_{N}}{I_D + {}^{I_R}\!/_{N}}$$

Where I_D, I_R and $N = 0.424$ are the disk current, ring current and collection efficiency, respectively for the employed RRDE.

References

1. S. Y. Chen, C. Y. Tang, W. T. Chuang, J. J. Lee, Y. L. Tsai, J. C. C. Chan, C. Y. Lin, Y. C. Liu and S. F. Cheng, *Chem. Mater*, 2008, **20**, 3906.
2. D.-S. Yang, S. Chaudhari, K. P. Rajesh and J.-S. Yu, *ChemCatChem*, 2014, **6**, 1236.

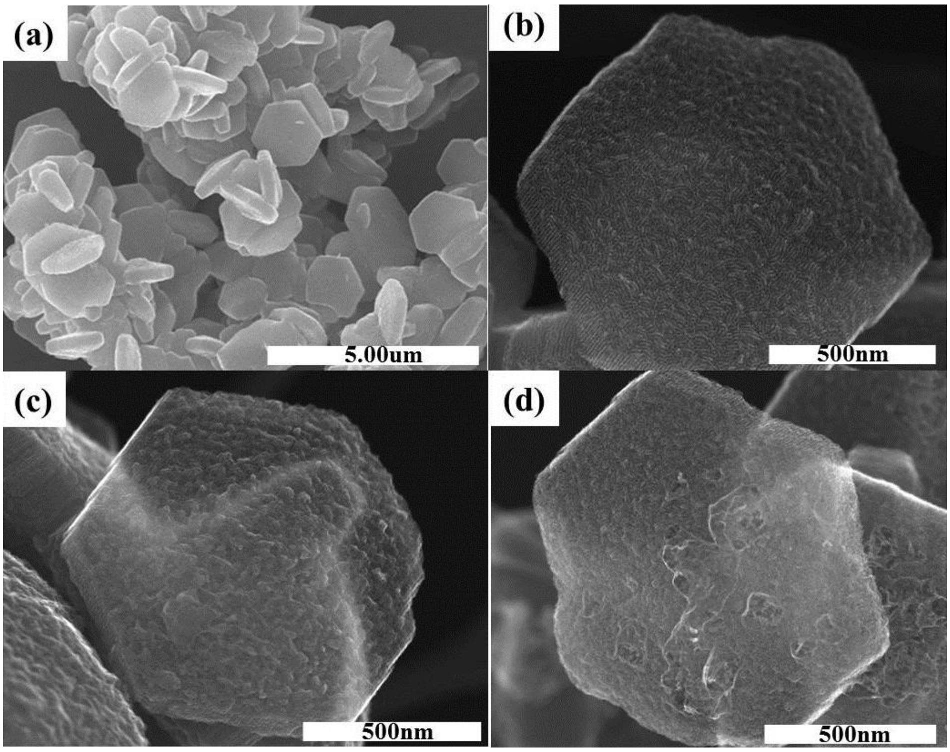


Fig. S1 (a) SEM image of as-synthesized platelet N-OMC (FePc) for large scale view. UHR-SEM images of as-synthesized platelet (b) OMC, (c) N-OMC (Pc) and (d) OMC (Fe).

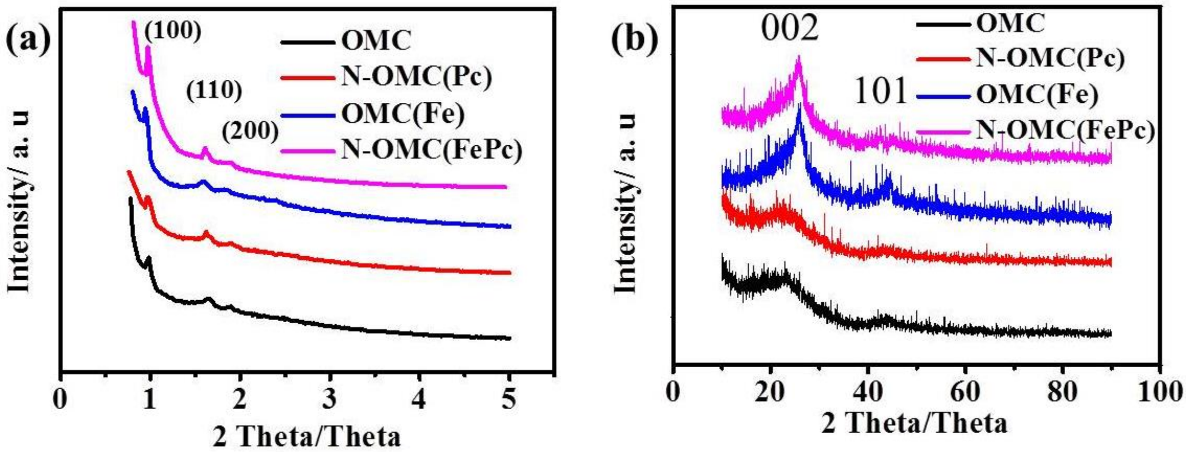


Fig. S2 (a) Small-angle and (b) wild-angle XRD patterns for all the platelet OMCs.

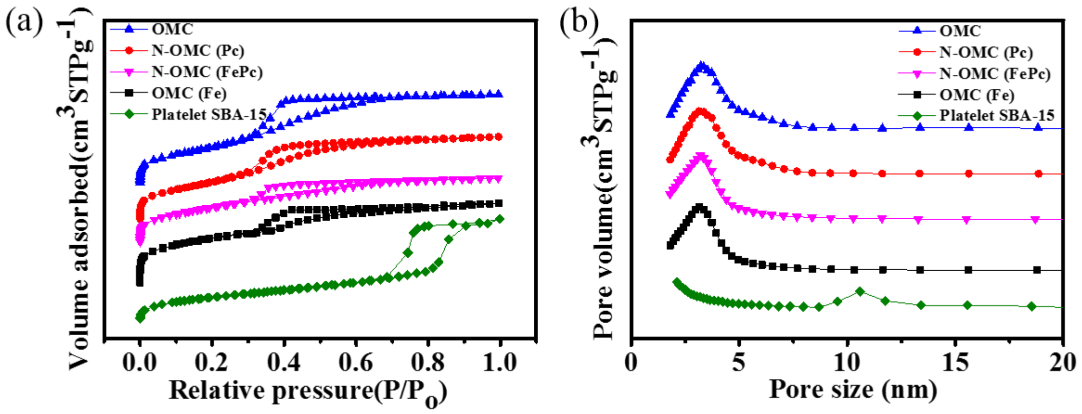


Fig. S3 (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of all the different platelet OMC samples along with the parent platelet SBA-15.

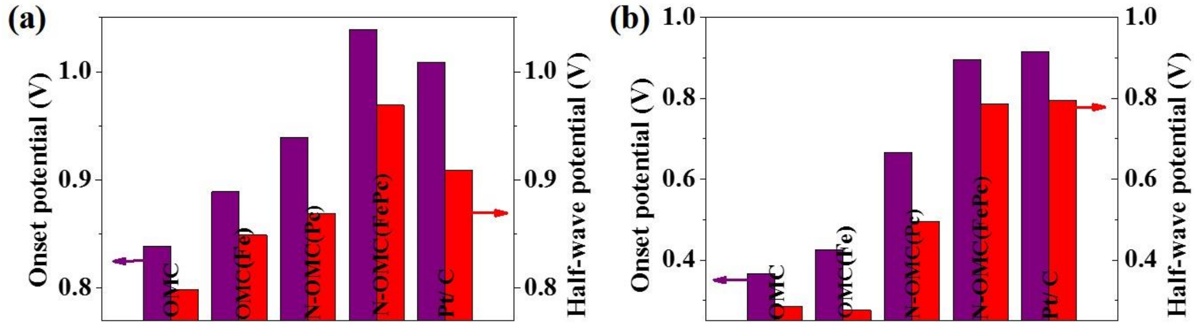


Fig. S4 The half-wave potential and onset potential of platelet OMC, OMC (Fe), N-OMC (Pc), N-OMC (FePc), and Pt/C at a rotation rate of 1,600 rpm in O2-saturated (a) 0.1 M KOH solution and (b) 0.1 M HClO$_4$ solution. Notice that here the potentials used were referenced to a reversible hydrogen electrode (RHE) by converting parameters determined in Ag/AgCl reference electrodes to those in RHE.

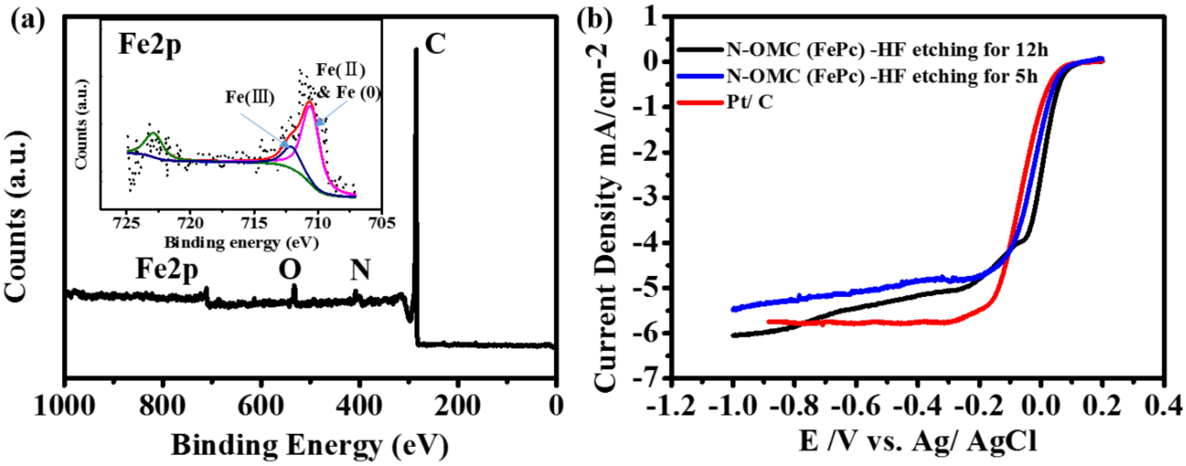


Fig. S5 (a) Survey spectrum along with high-resolution Fe 2p XPS spectrum of N-OMC (FePc) sample prepared with 5h HF-etching, and (b) LSV curves of N-OMC (FePc) samples prepared by HF etching for different periods along with Pt/ C.

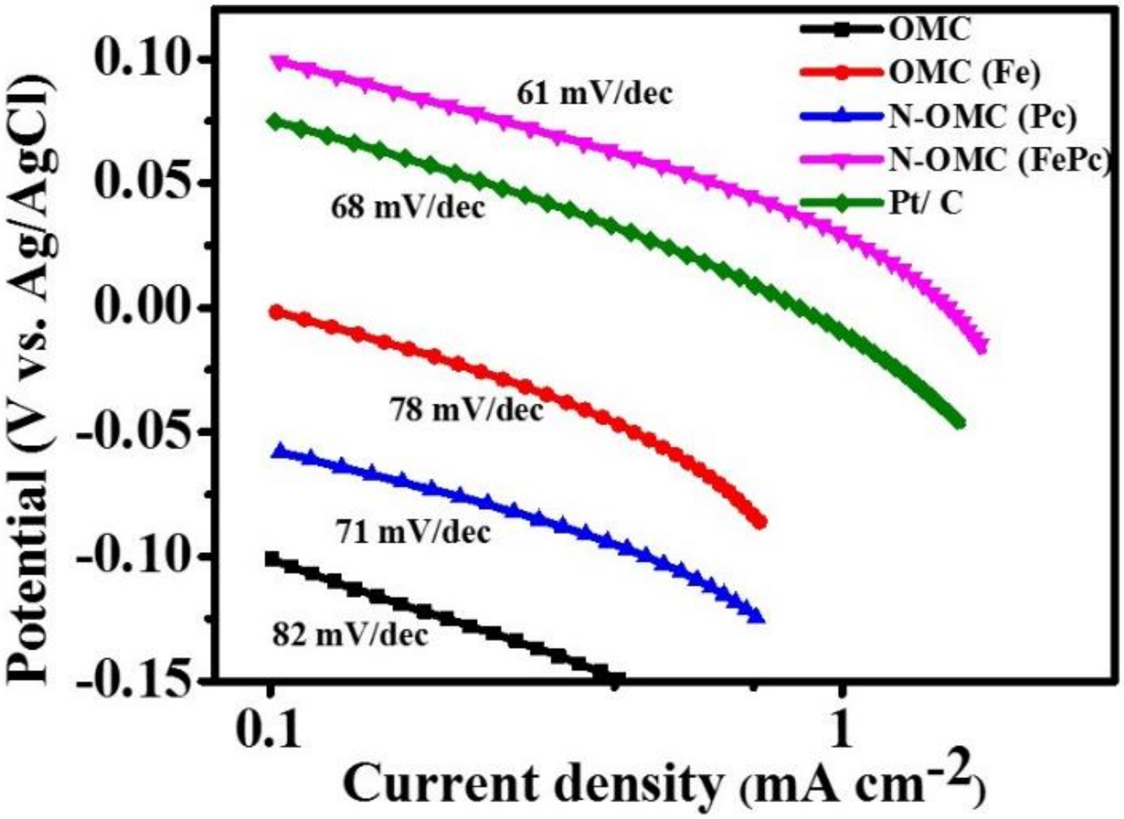


Fig. S6 Tafel plots of the platelet OMC, OMC (Fe), N-OMC (Pc), N-OMC (FePc), and Pt/C derived by the mass transport correction of corresponding LSV data recorded at 10 mV s^{-1} in 0.1 M KOH solution in Fig. 3a.

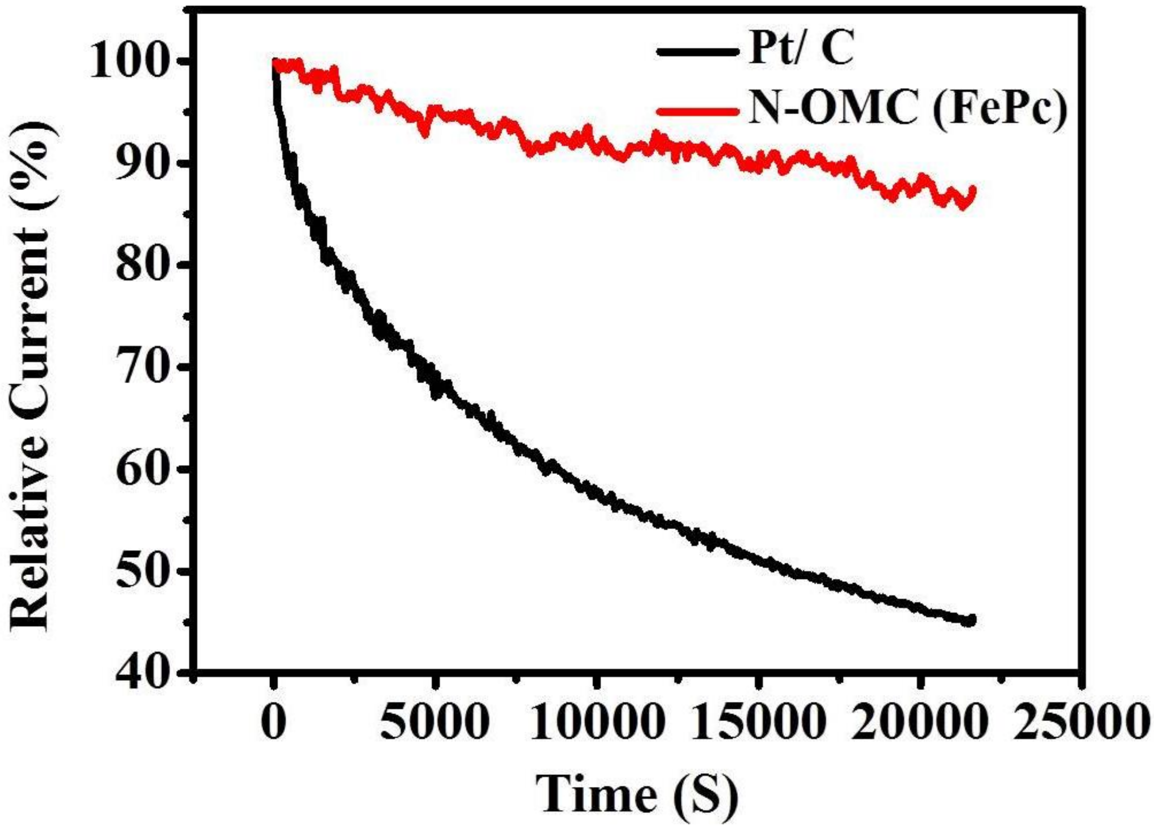


Fig. S7 Relative chronoamperometric J-t responses of platelet N-OMC (FePc) and Pt/C electrodes at −0.3 V vs. Ag/AgCl in O_2-saturated 0.1 M KOH solution.

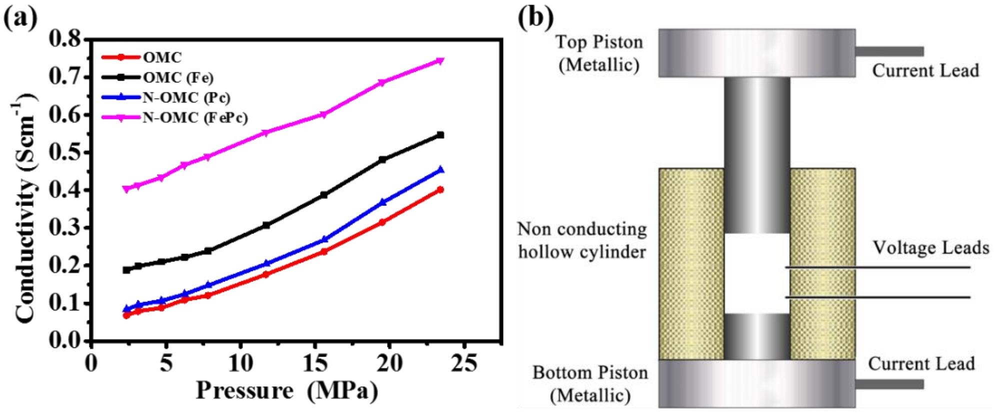


Fig. S8 (a) Variation in electrical conductivity of platelet OMC, OMC (Fe), N-OMC (Pc), N-OMC (FePc) under different pressures. (b) A diagram of the cell for measurement of electrical conductivity.

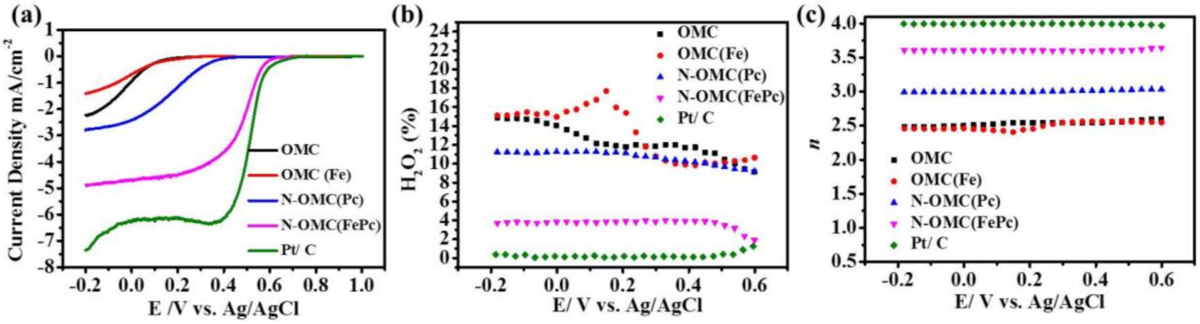


Fig. S9 (a) LSV curves at a scan rate of 10 mV s^{-1} and a rotation rate of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ solution, (b) percentage of H_2O_2 yield and (c) electron transfer number of platelet OMC, OMC (Fe), N-OMC (Pc), N-OMC (FePc) and Pt/C as functions of electrode potential.

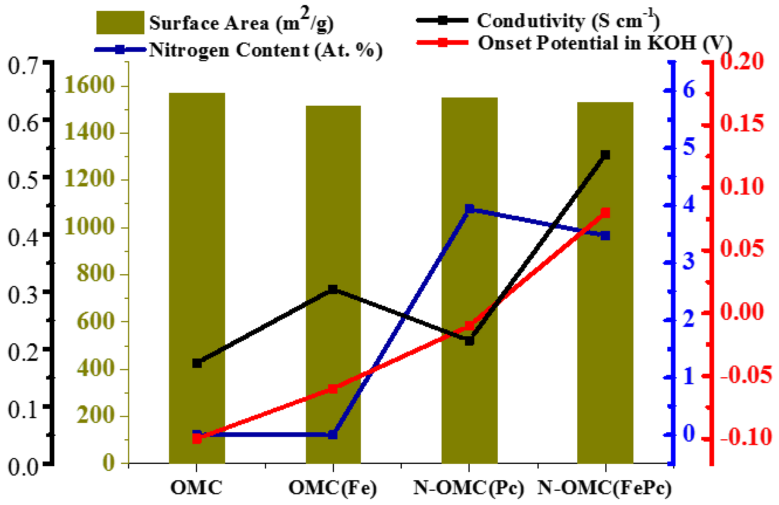
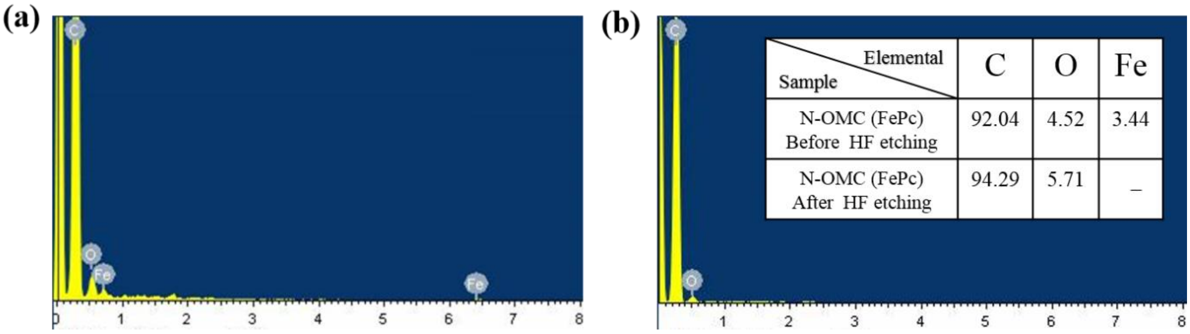


Fig. S10 Correlative effects of surface area, electrical conductivity, and nitrogen content on the onset potential of OMC, OMC (Fe), N-OMC (Pc) and N-OMC (FePc).



Sample \ Elemental	C	O	Fe
N-OMC (FePc) Before HF etching	92.04	4.52	3.44
N-OMC (FePc) After HF etching	94.29	5.71	_

Fig. S11 EDS elemental analysis of as-prepared N-OMC (FePc) composite (a) before and (a) after HF etching.

Table S1 Relative elemental amount of platelet OMC, N-OMC (Pc), N-OMC (FePc) and OMC (Fe).

Sample	C	O	N	Fe
OMC	94.68	5.32	-	-
N-OMC (Pc)	92.89	3.17	3.94	-
N-OMC (FePc)	93.38	3.14	3.48	
OMC (Fe)	92.52	7.48		-

Table S2 Textural properties of platelet SBA-15, OMC, N-OMC (Pc), N-OMC (FePc), OMC (Fe) and commercial 20 wt% Pt/C.

Sample name	**S_{BET} (m^2g^{-1})**	**V_{micro} (cm^3g^{-1})**	**V_{meso} (cm^3g^{-1})**	**V_{total} (cm^3g^{-1})**	**Pore size (nm)**
Platelet SBA-15	**821.8**	**0.14**	**1.54**	**1.68**	**11.6**
OMC	**1567.8**	**0.70**	**1.17**	**1.87**	**3.3**
OMC (Fe)	**1513.6**	**0.78**	**1.12**	**1.90**	**3.2**
N-OMC (Pc)	**1550.7**	**0.94**	**1.57**	**2.51**	**3.2**
N-OMC (FePc)	**1530.9**	**1.15**	**1.61**	**2.76**	**3.2**
Pt/C	**261**	**0.01**	**0.39**	**0.40**	**-**