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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxx

ARTICLE TYPE

Metal (metal=Fe, Co), N codoped nanoporous carbon for efficient electrochemical oxygen reduction

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Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

Metal, N codoped nanoporous carbon (N-M-nC, M=Fe, Co) is prepared by in situ incorporation of the metal during the formation of the nanoporous carbon skeleton followed by NH₃ treatment. The samples exhibit superior catalytic performance for the oxygen reduction reaction (ORR) in alkaline electrolytes. M, N codoping shows a synergic effect with improved ORR performance compared to the sample with

¹⁰ only nitrogen dopant (N-nC), in the order of N-Fe-nC > N-Co-nC > N-nC, indicating that the M-N synergic effect is critical for high ORR performance in alkaline electrolyte. A detailed structural characterization of the catalysts is carried out, which suggests that the improved ORR performance should be attributed to the formation of active sites with M-N bonding. Other structural difference, including surface area, porosity and carbon structure, plays a minor role. The performance of the N-Fe-nC sample is

¹⁵ comparable to that of commercial Pt/C, including more positive onset and halfwave potential, comparable saturation current density and a dominant four-electron pathway, which suggests that nanoporous carbon can serve as an ideal platform for developing high performance ORR catalysts via proper doping.

Introduction

The electrochemical reduction of oxygen (known as the ²⁰ oxygen reduction reaction, ORR) is the cathode reaction in fuel cells (FCs). In the most widely used low temperature FCs with aqueous electrolytes such as polymer electrolyte membrane FCs and alkaline FCs, the ORR is six or more orders slower than the hydrogen oxidation reaction on the anode¹ and thus requires ²⁵ substantially higher loading of Pt catalysts. Even with the state of

the art technology, the Pt loading for the cathode is still 5-10 times higher than that in the anode². Therefore, developing cheap yet equally efficient ORR catalysts is of critical importance to reduce the cost of FCs. Replacing Pt with cheap, abundant ³⁰ elements is the ultimate but extremely challenging solution, which has inspired considerably enthusiasm in recent years.

To develop noble metal free ORR catalysts, an important strategy is to modify carbon materials with proper dopants to create the ORR active sites. The metal-N-C (M-N-C) catalysts by

- ³⁵ codoping of N and transition metals such as Fe³⁻⁵ and Co^{4, 6, 7} have been extensively studied. It has been demonstrated that by properly designed structure and well controlled processing, the M-N-C based catalysts may exhibit comparable performance to that of Pt. The active sites for this type of catalysts are proposed
- ⁴⁰ to be N-coordinated metal centers $MN_x^{2, 8}$. In acidic electrolyte, most high performance noble metal free catalysts reported are based on this type, in which the M-N synergy is essential.^{2, 9, 10} In alkaline electrolyte, the role of transition metals seems to be less critical. N-doped carbon without metal dopants is also found to
- ⁴⁵ show promising performance. Superior ORR performance has been reported for N doped carbon nanotubes and graphene

sheets.^{11, 12} It is proposed that the incorporated N atom will modulate the local electron density of carbon atoms, which will facilitate the O_2 adsorption and dissociation.^{11, 13, 14}

Although the term "metal free" is frequently adopted, the 50 existence of transition metals in these N-doped carbon materials cannot be completely excluded in most cases. For instance, growth of carbon nanotubes (CNT) or graphene is usually catalyzed by transition metals such as Mn, Fe, Co or Ni.¹⁵⁻¹⁷ It is 55 argued that the trace amount of transition metals may either serve as a component for the ORR active sites or assist the formation of the active sites¹⁸⁻²¹. Wang et al.²² demonstrated that manganese oxide in graphene prepared by the Hummer's method was responsible for the high-performance ORR catalysts reported 60 based on this type of graphene materials. N-doped carbon prepared from N containing organic molecules or polymers, such as polypyridine²³, polyacrylonitrile²⁴, melamine¹⁹, polyaniline²⁵, polypyrrole²⁶ etc may exclude the transition metals. However, the ORR performance is typically inferior compared to those derived 65 from CNT or graphene.^{18, 19, 27-30} There have been several recent efforts trying to elucidate the role of transition metals in the ORR performance based on these carbon materials which are more confidently to be regarded as metal free.³¹⁻³³ Masa et al.¹⁸ and Liu et al¹⁹ reported that trace metal residues significantly promote the 70 ORR performance in alkaline electrolyte of the N-doped commercial carbon blacks (Vulcan-72 and Black Pearl). However, the key structural changes caused by metal doping that lead to the enhanced ORR performance remain unclear.

Here we report highly efficient M-N-C (M=Fe and Co) ORR 75 catalysts in alkaline electrolyte based on nanoporous carbon

materials and study the role of transition metals in detail. A direct advantage of the nanoporous structure in catalysis is the high surface area which can enhance the density of active sites. ORR catalysts based on nanoporous carbon are gaining increasing s interest in recent years.^{27, 34, 35} We prepare the nanoporous carbon

- based ORR catalysts using the well-known block copolymer soft template method³⁶, which is versatile in porosity control and also allows us to obtain a truly metal free carbon materials as the basis to study the effect of the metals. Metal incorporation is achieved
- ¹⁰ during the formation of the carbon skeleton with intentional metal doping while N doping is realized by annealing in NH₃ atmosphere. By controlling the metal doping and the annealing atmosphere, metal free nanoporous carbon (nC), metal doped nC (M-nC), nitrogen doped nC (N-nC) and metal, nitrogen codoped
- ¹⁵ nC (N-M-nC) can be obtained, which allows us to study the M-N synergic effect on a more accurate basis. We demonstrate that for the nanoporous carbon system in alkaline electrolyte, M, N codoping shows improved ORR performance compared to single doping of N, in the order of N-Fe-nC > N-Co-nC > N-nC. The
- ²⁰ results suggest that the M-N synergic effect is also critical for high ORR performance in alkaline electrolyte. The performance of N-Fe-nC is comparable to that of the commercial Pt/C catalyst.

Experimental section

Materials and Chemicals.

- ²⁵ 1,3-diphenol ($C_6H_6O_2$, 99 %), ferrous sulphate (FeSO₄·7H₂O, 99%), cobalt sulphate (CoSO₄·6H₂O, 99%) were purchased from XILONG Chemical. HCl (37.0-40.0 wt %) was purchased from Beijing Yili Fine Chemicals Corporation. Tri-block copolymer F127 (MW=12600, EO106PO70EO106) was purchased from
- ³⁰ Sigma Chemicals. Carbon supported platinum catalysts (Pt/C, nominally 10 % on carbon black) and nafion (5 wt% solution in ethanol and water) were purchased from Alfa Aesar.

Synthesis of the Catalysts.

- The preparation procedure of N-M-nC is illustrated in Figure ³⁵ 1, which is adapted from the method in ref ^{37, 38}. Tri-block copolymer F127 and 1,3-diphenol are dissolved in deionized water and ethanol to give the soft template. The solution pH is adjusted to 1 by adjusting hydrochloride acid. Then the corresponding divalent metal sulphates are added to the solution.
- ⁴⁰ After continuous stirring for 2 h, formaldehyde is added to initiate the polymerization. Metal is incorporated into the polymeric precursor through the interaction with the functional groups on the template, likely the hydroxyl group in the 1,3diphenol. The hybrid precursor is subjected to a delicate heating
- ⁴⁵ program to remove the template. The resulted nanoporous carbon is heated again in NH₃ stream for N doping. The nanoporous carbon without metal doping is prepared by the same protocol except that the metal sulphate is not added. The samples are denoted as nC, N-nC, M-nC and N-M-nC for undoped, N-doped,
- ⁵⁰ M-doped, and N, M codoped nanoporous carbon, respectively, where M = Fe or Co.

Materials Characterization.

The structure and morphology of products are characterized by X-ray diffraction (XRD, Rigaku D/max 200 diffractometer, Cu $_{55}$ K α), and high-resolution transmission electron microscopy

(HRTEM, JEM 2100, 200 kV). Thermogravimetric analysis (TGA) is carried out on a Q600 SDT thermoanalyzer (Thermal Analysis Corporation, USA). Nitrogen adsorption-desorption isotherms are measured on an Autosorb IQ gas sorption analyzer ⁶⁰ (Quantachrome) at 77 K. Before testing, samples are degassed at 200 °C for 2 h. The surface area and pore size distribution is determined by the Brunauer–Emmett–Teller (BET) and

- Quenched Solid Density Functional Theory (QSDFT) methods assuming a slit/cylinder pores model, respectively. The detailed 65 QSDFT method is seen in supporting information. The X-ray
- ⁶⁵ QSDFT method is seen in supporting information. The X-ray photoelectron spectroscopy (XPS) analysis is performed on an AXIS-Ultra spectrometer (Kratos Analytical) using monochromatic Al Ko radiation (225 W, 15 mA, 15 kV). Eighty sweeps are carried out for Co 2p and Fe 2p, five sweeps for N 1s.
 ⁷⁰ The content of C, H and N was determined by the combustion method on an elemental analyser (Vario EL). The content of metal is estimated by TGA in air, assuming the residue are the pure Fe₃O₄ or Co₃O₄ phases.

Electrochemical Preparation and Characterization.

To prepare the working electrode, 2 mg of samples are ultrasonically dispersed in a mixed solution of 100 μ L isopropanol and 100 μ L Nafion (0.5 wt%) for about 1 h. Then 7 μ L of suspension is dropped onto a glassy carbon rotating ring disk (RDE, 5 mm, Pine Research Instrumentation, USA) surface so and dried for 5 min under infrared light and 2 h at room temperature.

All electrochemical measurements of the samples, including cyclic voltammograms (CVs) and linear scan polarization curves are performed at room temperature in 0.1 M KOH solutions. The selectrolyte is purged with oxygen for at least 30 min prior to each measurement. The data is recorded using a CHI 760D bipotentiostat (CHI Instruments, Inc., USA). The reference electrode is a Ag/AgCl (3.5 M KCl-filled) electrode in 0.1 M KOH solution. The counter electrode was a platinum foil.

⁹⁰ The number of electron transferred during the ORR is calculated based on measurements on a rotating ring-disk electrode (RRDE, 5.61 mm of disk outer diameter, Pine Research Instrumentation, USA). The electrode preparation and measurement conditions follow the same way as the RDE ⁹⁵ measurement. Before experiments, the Pt ring was activated by potential cycling from 0 to 1.4 V (vs. RHE) at a scan rate of 50 mV s⁻¹ for at least 10 minutes. The number of electron transferred (n) is calculated using the following equation.³⁹

$$n = \frac{4I_d}{I_d + \frac{I_r}{I_r}}$$
 (Equation 1)

Where N=0.37 is the collection efficiency, I_d is the disk current, I_r is the ring current, respectively.

Results and discussion

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Structural characterization of the catalysts

Figure 2 shows the transmission electron microscopy (TEM) images of nC, Fe-nC, N-nC and N-Fe-nC. The nC sample has a nanoporous structure with pore diameter of 5 nm separated by walls with thickness of 5 nm (Figure 2a). The pores exhibit one-dimensional ordering (Figure 2b), which is confirmed by the clear
 diffraction peak in the small angle X-ray diffraction (SA-XRD) pattern (Figure S1). The Fe-nC sample exhibits similar

nanoporous structure (Figure 2c). However, the long range ordering of the pore alignment is significantly weakened. The diffraction peak in the SA-XRD pattern becomes broader and less well-defined (Figure S1). Although the level of the doped Fe is

⁵ only 1-2 wt% (Table S1), it may interfere the formation of the long range ordering structure through the interaction with the template copolymer or the monomers. Doping of Co shows the similar effect, i.e., the nanoporous structure is largely unaffected (Figure S4a, S4b) while the long range order of the pores is lost ¹⁰ (Figure S1).

The nanoporous nature of these samples is further confirmed by nitrogen adsorption measurements (Figure 3a). The nC and MnC samples exhibit similar specific surface area around 700 m^2g^{-1} (Table S1). A well-defined Type H2 hysteresis loop is observed

- ¹⁵ in the isotherms of all these samples, which is originated from the capillary condensation effect in nanoscale pores.⁴⁰ Correspondingly, there is a narrow peak at 5 nm in the pore size distribution patterns (Figure 3b) of these samples. This result is in very good agreement with the near uniform pore size observed in
- ²⁰ TEM images. These samples also contain pores smaller than 1.5 nm in width, which is indicated by the rapid uptake in the low pressure region of the isotherms (Figure 3a).

Thermal treatment in NH_3 causes a notable N doping effect. The N content is 4.85 wt%, 2.47 wt% and 2.75 wt% for the N-nC,

- ²⁵ N-Fe-nC, N-Co-nC samples, respectively. For the nC sample, the nanoporous structure is well maintained after N doping, as shown in the TEM images (Figure 2d, Figure S2). However, the long range order of the pores become poorer, as suggested by the poorly defined peak in the SA-XRD pattern (Figure S1). On the
- ³⁰ other hand, the M-nC samples experience a more notable change of the pore structure after thermal treatment in NH₃. As shown in the TEM image, the pore arrangement of the N-Fe-nC sample is significantly disrupted (Figure 2e and Figure S3c). Some pores are merged together, forming larger mesopores. This is in
- ³⁵ agreement with the SA-XRD results where no diffraction peaks are observed (Figure S1). Moreover, the carbon shell also becomes thinner and shows clear graphite layers (Figure 2f). Similar phenomena are also observed in the N-Co-nC sample (Figure S1, S4).
- ⁴⁰ Figure 3 summarizes the nitrogen sorption isotherms and the pore size distribution curves of the nC based samples, which clearly demonstrates that thermal treatment in NH₃ enlargers the BET surface area and enhances the porosity of both nC and M-nC samples. The BET surface area is 1006, 871, 845 m²g⁻¹ for the N-
- ⁴⁵ nC, N-Fe-nC and N-Co samples, all of which are significantly promoted compared to the samples prior to thermal treatment in NH₃. The shape of the isotherms and the pore size distribution curves is quite similar for N-nC and nC, indicating that the change of the pore structure is not significant during the N-
- ⁵⁰ doping process. On the other hand, the N-M-nC samples exhibit a very unique adsorption profile for nitrogen, i.e, the Type H3 hysteresis at the higher relative pressure⁴¹, which is not observed for the M-nC samples (Figure 3b). The pore structure analysis results derived from the nitrogen sorption isotherms are in very
- ⁵⁵ good agreement with the TEM results, both of which indicate that the incorporated metals amplify the change of pore structure during the thermal treatment in NH₃, with additional mesopores created.

The structural change of the nC based samples resulted from 60 thermal treatment in NH₃ is further studied by Raman spectroscopy. The spectra in the 1000-2000 cm⁻¹ region can be deconvoluted into four components following the approach by Sharifi et al⁴² and Nitze et al⁴³ : the I band at 1180-1190 cm⁻¹, the D band at 1330 cm⁻¹, the D" band at 1470-1520 cm⁻¹ and the G 65 band at 1590 cm⁻¹ (Figure S6). The I band is impurity related. Both the D and D" bands are due to defect induced Raman active modes, where D is related to irregular lattice spacing and D" to disorder in graphene layer stacking⁴². Some authors also attribute the D" band to the distortion of the hexagonal symmetry in ⁷⁰ graphene, such as five member rings²¹. We use the integrated band ratios I_G/I_D and $I_G/I_{D''}$ to characterize the ordering in the graphitic structure, as summarized in Figure 4 for the nC based samples. Both the I_G/I_D and I_G/I_D, ratios are similar for N-nC and nC, indicating that the carbon structure is not significantly 75 affected by N-doping. On the other hand, the N-M-nC samples exhibit much higher I_G/I_{D⁷} ratio compared to the M-nC samples, despite that the I_G/I_D ratio is almost similar. This indicates that the incorporated metal will improve the ordering of the graphitic structure during the thermal treatment in NH₃, which is in 80 agreement with the thin graphitic layer structure observed in TEM (Figure 2 and Figure S3 and Figure S4).

The incorporation of metal also affects the nitrogen doping mechanism during the NH₃ treatment, as shown by the X-ray photoelectronic spectroscopy (XPS) (Figure 5). The N 1s spectrum of N-nC can be deconvoluted into peaks corresponding to pyridinic (398.6±0.3 eV), pyrrolic (400.3±0.3 eV) and graphitic (402 eV) nitrogen, respectively, with pyrrolic N being the major component. Such N chemical bonding is commonly observed in N-doped carbon materials.^{6, 44} For the N-M-nC samples, however, the peak at 398.6 eV becomes dominant. As nitrides also contribute to the 398.6 eV peak^{21, 34}, this change in the XPS spectra can be attributed to the M-N bonding formation. Unfortunately, due to the low metal content, the Fe and Co spectra are too noisy to provide sufficient information on bonding 95 (Figure S5).

The electrocatalytic performance of the catalysts

The ORR performance of the nanoporous carbon based catalysts in 0.1 M aqueous KOH solution is shown in Figure 6, which is measured on a rotating ring-disk electrode (RRDE). The 100 M-N synergy is first illustrated in Figure 6a using Fe as the metal dopant. The samples without N doping (nC and Fe-nC) are rather poor ORR catalysts. Nitrogen doping significantly promote the ORR activity. The N-nC sample shows an onset (E_{on}) and half wave potential (E_{1/2}) of -0.090 and -0.167 V (vs. Ag/AgCl), 105 respectively and saturate current density (jsat) of 5.12 mA cm-2, which is already very close to that of the commercial Pt/C catalyst (E_{on} = -0.051 V, $E_{1/2}$ = -0.132 V, j_{sat} =5.64 mA cm⁻²). The N-Fe-nC sample shows even more remarkable performance: Eon= -0.044 V, $E_{1/2}$ = -0.125 V (vs. Ag/AgCl) and j_{sat}=5.62 mA cm⁻² 110 Notably, the onset and half wave potential are more positive than that of Pt/C, which means lower overpotential during fuel cell operations. The performance is in line with noble metal free ORR catalysts^{7, 27, 30, 45, 46}. A parallel study on the Co doped samples is also carried out. Figure 6b summarized the linear scanning 115 polarization curves of the three N doped sample. Both N-Fe-nC and N-Co-nC outperform nC in terms of the potential, while N-

Co-nC is slightly less efficient compared to N-Fe-nC ($E_{1/2}$ = -0.145 V (vs. Ag/AgCl), j_{sat}=4.82 mA cm-2).

To further assess the electrocatalytic mechanism, we calculate the number of electron transferred (n) and the yield of hydrogen 5 peroxide on the basis of disk and ring current (Equation 1). The n

- of the N-Fe-nC is 3.88-3.98 in the range of -0.8 V to -0.2 V (vs. Ag/AgCl), indicating a dominant four-electron process and low peroxide formation ratio (0.5-6 %) (Figure 6c). The selectivity is also very close to that of Pt/C. The N-Co-nC sample exhibits
- ¹⁰ lower n value of 3.51-3.66 and higher peroxide yield around 15%. However, for the N-nC sample, n is only 3.41 at -0.8 V (vs. Ag/AgCl), corresponds to a relatively high peroxide formation ratio of 30 %. The selectivity also improves in the order of N-nC < N-Co-nC < N-Fe-nC.
- ¹⁵ The N-Fe-nC sample is further characterized for the methanol tolerance and the stability. As shown in Figure S7, after introducing methanol into the alkaline medium, the peak corresponding to oxygen reduction at -0.18 V (vs Ag/AgCl) of the N-Fe-nC remains unchanged. While for the Pt/C, the ORR
- ²⁰ peak in the CV curve disappears after methanol introduction. The long-term operation stability of the N-Fe-nC sample is assessed after 300 CV cycles between -1.0 and 0.2 V at 50 mV/s in oxygen saturated 0.1 M KOH. As shown in Figure S8, both $E_{1/2}$ and j_{sat} remain unchanged. The above results show the N-Fe-nC ²⁵ has very good methanol tolerance and long-term stability.

Discussions

The soft template method allows us to prepare metal-free nanoporous carbon and control the M and N doping. Thus, the effect of the M and N dopants on the ORR performance can be ³⁰ evaluated on a more accurate basis. Clearly, nitrogen is essential to achieve good ORR performance, as the two samples without N

- (nC and Fe-nC) are both rather inefficient catalysts. N doping on nC results in reasonably good ORR performance (only 35 mV more negative in $E_{1/2}$ compared to Pt/C). In terms of the potential, ³⁵ this performance is in fact among the highest results for N-doped
- carbon derived from N containing organic molecules or polymers.^{18, 47} The good activity may be attributed to the high surface area of the nanoporous carbon which can accommodate more surface active sites. However, the selectivity is poor with
- ⁴⁰ more than 20% peroxide formation. Several previous reports on N-doped carbon materials derived from organic precursors also suffered from the low selectivity^{18, 47-50}. The overall performance of the N-nC sample, in terms of both the potential and the selectivity, is inferior compared to the N-doped carbon samples ⁴⁵ based on graphene or carbon nanotubes.^{11, 12}

The ORR performance of the three N doped samples clearly suggests that there is a synergic effect of M and N on the ORR performance even in alkaline electrolyte. The improved ORR performance due to the M-N synergy can be correlated to the

- ⁵⁰ structural changes originated from the metal doping. We will focus on the difference between the N-M-nC and N-nC samples. A notable difference in N chemical bonding is suggested by the N1s XPS spectra (Figure 5) where the N-M-nC samples exhibit a more dominant component at 398.6 eV compared to N-nC. This
- ⁵⁵ binding energy is usually attributed to nitrogen atoms with pyridinic structure, while N atoms in the nitride and MNx form also contribute to this component. 17a, ^{21, 51} Therefore, the higher 398.6 eV component for the N-M-nC samples can serve as an

indication of M-N bond formation. Similar N 1s patterns with dominant 398.6 eV component have been previously observed in ORR catalysts derived from pyrolysis of N-chelated Fe complexes^{10, 52} where Fe-N bonding is highly probable and has been confirmed by EXAFS. Previous studies by X-ray absorption techniques^{53, 54} and Mossbauer spectroscopy^{55, 56} also suggest that 65 NH₃ treatment of metal-loaded carbon will result in formation of

the N-coordinated metal structure MNx. Therefore, the improved ORR performance of N-M-nC compared to N-nC in alkaline electrolyte can be attributed to the formation of the MN_x structure which can serve as the ORR active centers.

The N-M-nC samples are also different to N-nC in surface area, 70 pore structure and carbon structure. These structure difference may also contribute to the improved ORR performance. Therefore, for a fuller understanding on the M-N synergy, it is critical to evaluate the effect of these structure difference on the 75 ORR performance. A comparison between the N-Fe-nC and N-Co-nC samples is particularly informative. These two samples have very similar pore structure. The N-Co-nC sample even shows more ordered graphitic structure. As shown In Figure 4, we can see that the N-Co-nC sample exhibit much higher $I_G/I_{D''}$ ⁸⁰ ratio compared to the N-Fe-nC sample. However, the oxygen reduction reaction performance of the N-Co-nC sample is inferior to that of the N-Fe-nC sample, which strengthens the conclusion that the MN_x structure plays a more critical role in determining the ORR performance. This is in agreement with previous studies 85 in acidic electrolyte, which suggests that the Co based ORR catalysts are slightly less efficient compared to their Fe counterpart.9, 39 In addition, the specific surface area, which has been shown to positively correlated to ORR performance³⁴, is clearly not a determining factor in our case, as the less efficient ⁹⁰ N-nC sample in fact has the highest BET surface area. Therefore, the difference in surface area, pore structure and carbon structure are not the major reason for the improved ORR performance. The observed M-N synergy should be directly correlated to the formation of the MN_x active sites, which are more active than that 95 in metal-free N-nC samples.

Conclusions

In conclusion, we obtain high performance ORR catalysts by codoping of N and transition metals M (M=Fe or Co) into nanoporous carbon (N-M-nC). M, N codoping shows a synergic ¹⁰⁰ effect with improved ORR performance compared to single doping of nitrogen, in the order of N-Fe-nC > N-Co-nC > N-nC, indicating that the M-N synergic effect is critical for high ORR performance in alkaline electrolyte. The M-N synergic effect is attributed to the formation of active sites with M-N bonding (the ¹⁰⁵ MNx structure), while the change in surface area, porosity and carbon structure only plays a minor role. The N-Fe-nC catalyst outperforms the commercial Pt/C catalysts with 10 wt% Pt loading. Nanoporous carbon, though ORR inactive itself, may serve as an ideal platform to derive high performance ORR ¹¹⁰ catalysts via proper doping.

The authors acknowledge MOST of China (No. 2010CB631301) and NSFC (No. 21101007, U1201241 and 11375020, 21321001).

Notes and references

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† Electronic Supplementary Information available: Additional XPS spectra, XRD patterns, Raman spectra, electrochemical activity of the 10 samples, additional TEM images of the catalysts. See DOI: 10.1039/b000000x/

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Cite this: DOI: 10.1039/c0xx00000x

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Figure 2. TEM images of modified nanoporous carbon (nC): (a, b) nC, (c) Fe-nC, (d) N-nC (e, f) N-Fe-nC



Figure 3. N2 adsorption-desorption isotherms (a) and pore size distributions (b) of modified nanoporous carbon.



Figure 4. Summary of the I_G/I_D and I_G/I_{D^{**}} ratios in the Raman spectra of the nanoporous carbon based samples



Figure 5. High resolution XPS spectrum of N 1s for N-nC and N-M-nC



Figure 6. (a-b)Linear scanning polarization curves of the nanoporous carbon based ORR catalysts measured on a rotating ring and disk electrode in O2s saturated 0.1 M KOH at rotating rate of 1600 rpm. The ring potential is set to 0.5 V (vs. Ag/AgCl). The outer diameter of the RRDE disk is 5.61 mm. The catalysts loading is 0.28 mg cm⁻² according to the electrode preparation process. (c) The electron transfer number (n_e) and H₂O₂ yield (H₂O₂%) of the catalysts.

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Table of Content



Fe, N codoped nanoporous carbon (N-Fe-nC) exhibits superior oxygen reduction activity with lower overpotential and comparable electron transfer number compared with Pt/C.