Carbon Black Supported FM-N-C (FM=Fe, Co, Ni) Single-Atom Catalysts Synthesized by Self-Catalysis of Oxygen Coordinated Ferrous Metal Atoms†

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Carbon nanomaterials have abundant sources, but are difficult to use directly as the support of single atom catalysts (SACs) due to the lack of strong anchoring force to restrict the moving and aggregation of metal atoms in the high-temperature heat treatment. Herein, we report a “self-catalysis” method for the synthesis of ferrous metal single-atom catalysts (SACs) FM-N-C (FM=Fe, Co, Ni) with ~2 wt% metal loadings on carbon black support. The combination of experimental and theoretical evidences reveals the self-catalytic process from FM atoms to FM-N₄ species which involves (1) adsorption of FM ions on the surface-oxidized carbon nanoparticles *via* oxygen coordination bonds (FM-O); (2) catalytically decomposition of ammonia to nitrogen radicals on FM atoms; (3) replacement of oxygen coordination with nitrogen. The precoordination of FM with oxygen is found the key to the synthesis, which reduces the energy barriers of the ammonia decomposition and the nitrogen bonding to FM atoms, thus enables the formation of FM-N₄ species at a mild temperature of 600 °C. The synthesized FM-N-C SACs exhibit high catalytic activities towards O₂ and/or CO₂ reduction reactions. Different from the metal-organic framework based SACs in which the MOF support is significantly changed in size and weight, the self-catalysis technique is “mini-invasive” to the carbon support, thus benefiting the structural design of SACs by taking the advantage of the abundant morphologies of carbon nanomaterials.

Introduction

Single-atom catalyst (SAC) refers to the heterogeneous catalyst with atomically dispersed metal sites.¹⁻² SACs have attracted considerable attention because of the well-defined active site structure, the highest atomic efficiency and the excellent catalytic activity and selectivity.³⁻⁸ Among various SACs, the nitrogen coordinated metal single-atoms on carbon support (M-N-C) are one major class that plays an important role in electrocatalysis.⁹⁻¹⁴ For instance, Fe-N-C and Co-N-C SACs show high activities for oxygen reduction reaction (ORR),¹⁵⁻²⁰ Ni-N-C SACs exhibit high selectivity towards carbon dioxide reduction reaction (CO₂RR).²¹⁻²⁴ Most synthesis methods of M-N-C SACs need a high temperature pyrolysis (usually close to 1000 °C) to decompose the precursor and generate atomic M-N_x species on the carbon support.^{20, 25-26} Metal-organic-frameworks (MOFs) are the most popular support precursors.²⁷⁻³⁰ However, MOF supports are subjected to the big morphology/size changes and the large mass loss (usually >70%) that causes a lot of waste disposal.

Carbon nanomaterials, such as CNT, graphene, carbon black, etc., have abundant sources, diverse structures, high electrical conductivity and low cost.³¹⁻³³ Carbon nanomaterials can withstand high-temperature heat treatment and transfer the original nanostructures to the final catalyst, which is significant for the precise morphology and structural design of the catalyst.³⁴⁻³⁶ To date, carbon nanomaterials have mainly been successfully used as carriers for noble metal catalysts, such as Pt/C.³¹ Carbon black has also been used as the support of non-precious metal catalysts (NPMCs), such as Fe-N-C and Co-N-C for tens of years. Nevertheless, the early research of NPMCs has a problem of metal agglomeration due to the lack of strong metal/carbon interaction to restrict the aggregation of metal atoms at the high temperature, which causes the loss of atomic active sites and relatively low catalytic activity.³⁷⁻³⁹ Until 2009, Dodelet et al. developed a highly active Fe-N-C catalyst using 1,10-phenanthroline to coordinate and disperse a lot of Fe atoms on carbon black (BP2000).⁴⁰ Zhang et al. successfully applied this strategy to prepare a series of Ketjenblack supported SACs with high metal loadings.²⁴ In addition to the above coordination strategy, most carbon nanomaterial-supported SACs are prepared by pyrolyzing M, N, C precursor mixtures at a high temperature of about 1000 °C, and then performing acid leaching to remove metal nanoparticles (NPs). Although a few M-N-C SACs have been reported without acid leaching, their metal loadings are usually less than 1wt%.^{23, 41-43} There is still a need of new and efficient technologies for preparing SACs on carbon nanomaterial support.

Herein, we demonstrate a synthesis method based on the self-catalysis function of ferrous metal single-atoms, for the synthesis of carbon black (BP2000) supported nitrogen-coordinated ferrous metal SACs FM-N/BP (FM=Fe, Co, Ni) at a mild temperature of 600 °C. Experimental and theoretical results indicate that the oxidized BP2000 supported FM ions can capture and decompose ammonia into nitrogen radicals which further replace oxygen coordination to form FM-N₄

species. The coordination of FM ions with surface oxygen on BP2000 is the key prerequisite to the synthesis, which reduces the energy barrier of the ammonia decomposition and facilitates the bonding of nitrogen radicals with FM ions. The synthesized FM-N-C SACs possess quite high loadings of 1.6~2.1 wt% of metal single atoms. The high electrocatalytic activities of FM-N/BP SACs were demonstrated towards ORR and CO₂RR.

Results and discussion

BP2000 carbon black was chosen as the support because of its high specific surface area and abundant micropores that are beneficial for loading a large number of FM atoms. The synthesis mechanism and procedure of FM-N/BP SACs are described in Scheme 1 and Fig. S1†, respectively. Briefly, BP2000 was refluxed in concentrated acids at 60 °C for 1 h, and then oxidized at 10 °C for 40 h to obtain surface oxidized BP2000, denoted as O/BP. Compared to pristine BP ($I_D/I_G = 1.276$), we observed a decrease in the I_D/I_G ratio in the Raman spectra of O/BP ($I_D/I_G = 1.184$) after the oxidation and acid treatment (Fig. S2†). It is because the concentrated acids can remove some carbon defects.⁴⁴⁻⁴⁵ X-ray photoelectron spectroscopy (XPS) detected only C and O elements on O/BP, indicating the HNO₃ and H₂SO₄ treatment did not dope N and S into O/BP. Oxygen functional groups of C-O and C=O (Fig. S3†) could adsorb FM ions through attraction between the anion and the cation. After adsorbing FM ions, the FM-O/BP were collected by filtration and dried. Transmission electron microscopy (TEM) did not detect metal nanoparticles or clusters on each FM-O/BP materials (Fig. S4†). FM-O/BP was further heated in ammonia at a mild temperature of 600 °C to convert to the final FM-N/BP SACs. Different from the recent several reports that Fe precursor mixed with N-doped carbon matrix transforms to Fe oxides at ~300 °C and forms the final Fe-N-C SAC at high temperature (~1000 °C),⁴⁶⁻⁴⁷ TEM images in Fig. S5† show that there are no metal nanoparticles on the FM-O/BP treated 300 °C in NH₃ probably due to the metal-O coordination and physical obstacle of surface-grafting amino groups shown in Fourier transform infrared spectroscopy (FTIR) spectra (Fig. S6†)⁴⁸⁻⁵⁰.

Scanning electron microscopy (SEM), TEM and X-ray diffraction (XRD) characterizations show that the catalyst Fe-N/BP and BP2000 have almost identical particle morphology, size (20~30 nm) and low crystallinity as shown in Fig. 1a, b, and Fig. S7~S9†. And their pore size distributions are very close (Fig. 1c, Table S1†). XRD and TEM did not detect any metal nanoparticles or clusters on each FM-N/BP catalyst. The scanning transmission electron microscopy (STEM) elemental mappings show the uniformly and densely distributed FM and N elements on BP2000 (Fig. 1d and Fig. S10†). Atomic-resolution high-angle annular dark-field STEM (HAADF-STEM) was used to observe the FM atoms on the three catalysts. As shown in Fig. 2, all the three catalysts show a large number of monodispersed bright spots as highlighted by circles, corresponding to atomically dispersed Fe, Co and Ni on each catalyst. As determined by inductively coupled plasma atomic optical emission spectrometry (ICP-OES), the metal contents in each catalyst are Fe 1.6 wt%, Co 2.1 wt% and Ni 2.0 wt%, higher than that of most previously reported carbon nanomaterial supported Fe-SACs (Table S2†). The high loadings of FM single atoms on FM-N/BP can be attributed to the mild pyrolysis temperature (600 °C). Otherwise, the adsorbed metal ions would aggregate into metal NPs at higher temperatures (e.g. 700 °C) due to the lack of strong interaction between FM atoms and carbon support as shown in Fig. S11†.

XPS was used to analyze the catalyst surface elements (Fig. S12†, Table S3†). The C1s spectra of all the samples are similar, including C-C, C=N(C-O), C-N(C=O) and $\pi \rightarrow \pi^*$ peaks (Fig. S13†). The FM 3d spectra indicate the coexistence of +2 and +3 valence states of FM atoms (Fig. S14†). Compared with the control sample N/BP that was prepared without FM ions, additional peaks corresponding to FM-N bonds appear in the N1s spectra of FM-N/BP (Fig. S15†). Moreover, the contents of pyridinic and pyrrolic N in FM-N/BP decrease while the contents of graphitic and oxidized N did not change significantly (Fig. S16a†, Table S4†). It suggests that the formation of FM-N_x species is closely related to the pyridinic N and pyrrolic N. Further calculations indicate that the number of N coordinated with FM atoms in FM-N/BP is about four times that of FM atoms (Fig. S16b†), suggesting the possible four coordination of FM-N_x species.

To understand the formation process of FM-N/BP catalysts, we first performed X-ray absorption spectroscopy (XAS) analysis on the catalyst intermediates FM-O/BP (ferrous metal ions adsorbed on oxidized BP2000 before the heat treatment) (Fig. S17a₁-c₁†). The absorption edges of FM-O/BP are close to those of metal oxides but far away from metal foils, suggesting that FM single atoms are highly oxidized in FM-O/BP. The Fourier-transformed extended X-ray absorption fine structure spectra (FT-EXAFS) of Fe-O/BP, Co-O/BP and Ni-O/BP in *R* space show only one dominant peak at 1.57, 1.62 and 1.62 Å, respectively, corresponding to the Fe-O, Co-O and Ni-O peaks respectively (Fig. S17a₂-c₂†). The Fe-Fe, Co-Co and Ni-Ni metal bonds are absent for all samples. The coordination structures around FM atoms were clarified by fitting the FT-EXAFS data of FM-O/BP (Table S5 and Fig. S17a₂-c₂). The optimized coordination numbers of

Fe-O, Co-O and Ni-O are 3.8, 3.8, and 4.2, respectively, implying that each ferrous metal single atom is likely coordinated with four oxygen atoms, *i.e.* FM-O₄ in the catalyst intermediates FM-O/BP.

After the ammonia treatment at 600 °C, the intermediates FM-O/BP were converted to the catalysts of FM-N/BP. The presence of pre-edge peaks (~7113 eV for Fe-N/BP, ~7711 eV for Co-N/BP, ~8334 eV for Ni-N/BP) suggests the formation of FM-N₄ square planar structure (Fig. 3a₁-c₁[†]). The FT-EXAFS spectra of FM-N/BP in Fig. 3a₂-c₂ show the main peaks at 1.49, 1.36 and 1.38 Å for Fe-N/BP, Co-N/BP and Ni-N/BP, respectively. By comparing with the reference materials as well as the fitting results (Table S6[†]), it can be inferred that the FM atoms are coordinated with four nitrogen atoms in the FM-N/BP catalysts. From the EXAFS results we see that the peak intensity of FM-O coordination (Fig. S17a₂-c₂) is significantly higher than that of FM-N coordination (Fig. 3a₂-c₂). This is because the Debye-Waller factor of FM-O/BP was 2.6-13.5 times that of FM-N/BP, not that FM-O was not completely converted to FM-N. Fig. 3d shows the EXAFS wavelet transforms (WT) plots of Fe based samples. We can see both Fe-O/BP to Fe-N/BP contain no Fe nanoparticles. We notice a slight negative migration of the intensity maximum of WT plots in k-space from Fe-O/BP to Fe-N/BP. And this migration is more obvious on Co and Ni samples (Fig. S18[†]). We know that the position of the maximum intensity in k-space is related to the atomic weight of the coordination atom. The higher the atomic weight of the coordination atom, the higher the position of the maximum intensity in k-space. Therefore, these negative migrations of the maximum intensity support the replacement of oxygen coordination with nitrogen coordination. In short summary, the above results suggest that the oxygen coordinated FM atoms have been successfully converted into the nitrogen coordinated FM atoms after the ammonia treatment at 600 °C. And ferrous metals should be atomically dispersed with a FM-N₄ coordination structure. Since the FM atoms participate in the decomposition of ammonia and the substitution of FM-N bonds to FM-O bonds, the behavior of FM single-atoms can be regarded as a self-catalysis process.

DFT calculations provide an in-depth understanding on the self-catalysis of FM single atoms. Taking Fe-N/BP for example, we designed three catalyst intermediate models for comparison: oxidized BP2000 (O/BP), Fe adsorbed on BP2000 (Fe/BP) and Fe adsorbed on oxidized BP2000 (Fe-O/BP), which are corresponding to the final catalysts N/BP, Fe(N)/BP and Fe-N/BP respectively. The adsorption energy of ammonia on O/BP, Fe/BP, Fe-O/BP are calculated to be -0.016, -1.109 and -1.088 eV respectively, indicating that Fe atom has a strong adsorption to ammonia (Fig. S19[†]), because of the hybridization of the band of the host.⁵¹ Fig. 4a and b show the density of states (DOSs) of Fe/BP and Fe-O/BP with an adsorbed NH₃. The Fe 3d orbital partially overlaps with the N 2p of ammonia, forming an interaction between Fe and NH₃. It is worth noting that the overlap between Fe 3d and the adjacent C 2p in Fe/BP is very strong, which makes it difficult for the nitrogen radicals (generated by the ammonia decomposition) to break and replace the C-Fe bond. In comparison, the overlap of the state density orbit of the Fe 3d and the neighboring O 2p in Fe-O/BP is much weaker. In this case, the Fe-O bond can be more easily changed to Fe-N bond. Thus, the pre-coordination of Fe and O is crucial to the formation of Fe-N₄ species on the carbon black by the self-catalysis of Fe atom.

Fig. 4c shows the energy barrier is ~5.0 eV for a NH₃ molecule to dissociate a hydrogen. However, this energy barrier is reduced to only 1.5 eV for the NH₃ adsorbed on the Fe atom of Fe-O/BP. This decrease in dissociation energy means that Fe atom in Fe-O/BP can greatly reduce the activation energy of ammonia and facilitate its decomposition into nitrogen radicals. The conversion process from a Fe-O coordination to a Fe-N coordination is shown in Fig. 4d. The system formation energy decreases from -4.786 to -5.485 eV, implying a thermodynamically feasible conversion. It is deduced that the conversion process from Fe-O/BP to Fe-N/BP includes the following steps: (I) ammonia gas is preferentially adsorbed on the Fe ion; (II) ammonia is easily decomposed generating nitrogen radical under the catalysis of Fe ion; (III) the nitrogen radical replaces one oxygen coordination because of the more stable Fe-N bond than Fe-O bond; (VI) the remaining Fe-O bonds are gradually converted into Fe-N bonds by repeating the above process. Co-O/BP and Ni-O/BP have the similar conversion processes to Fe-O/BP as shown in Fig. S20[†], S21[†]. The self-catalysis of FM single atoms not only reduces the energy consumption for the SACs preparation, but also presents a mini-invasive characteristic that only changes the coordination structure around FM atoms while makes negligible change to the carbon support.

The electrocatalytic properties of Fe-N/BP, Co-N/BP and Ni-N/BP are examined. The electrochemical active surface area (ECSA) of 600, 592 and 607 m² g⁻¹ are obtained for Fe-N/BP, Co-N/BP and Ni-N/BP respectively by the electrochemical double layer capacitance method as shown in Fig. S22 (see experimental section for the method). Given the similar ECSAs for the three catalysts, the kinetics should be the dominant factor determining their electrocatalytic performance. The typical application of Fe-N-C and Co-N-C catalysts is catalyzing the ORR. The heat-treatment temperature of 600 °C was chosen based on the optimization of ORR activity and the sample purity. The sample treated at 500 °C shows a lower activity than that treated at 600 °C as shown in Fig. S23. The higher temperature of 700 °C will produce a similar ORR activity, but the high temperature also caused metal nanoparticles (Fig. S11) that should be

avoided in the SAC research. The LSV curves of the 600 °C-treated Fe-N/BP and Co-N/BP in O₂ saturated 0.1 M KOH solution are shown in Figure 5a. The half-wave potentials of Fe-N/BP and Co-N/BP are 0.90 and 0.86 V, respectively. The half-wave potential of Fe-N/BP is 30 mV more positive than that of Pt/C catalyst and superior to most other reports (Table S7[†]). The electron transfer numbers are close to 4 (Fig. S24[†]), and the catalysts display good stability in the alkaline electrolyte (Fig. S25[†]). In O₂ saturated 0.5 M H₂SO₄ solution, the half-wave potentials of Fe-N/BP and Co-N/BP are 0.78 and 0.76 V respectively (Fig. 5b), comparable to most other Fe-N-C catalysts as shown in Table S8. The electron transfer numbers are close to 4 (Fig. S26[†]). The potassium thiocyanate poisoning experiments indicates that the ORR activities originate from Fe and Co atoms (Fig. S27[†]).⁵²⁻⁵³ The kinetic currents (J_k) are calculated based on the Koutecky-Levich equation. The Fe-N/BP shows a high kinetic current density of 5.51 mA cm⁻² at 0.9 V, larger than Pt/C (2.76 mA cm⁻²) and Co-N/BP (1.58 mA cm⁻²) in the alkaline medium. While in acid medium, the J_k of Fe-N/BP and Co-N/BP are 0.19 mA cm⁻² and 0.05 mA cm⁻² at 0.9 V, respectively. In addition, both Fe-N/BP and Co-N/BP show good ORR stability and methanol tolerance in the acidic media (Fig. S28[†], S29[†]). HADDF-STEM images in Fig. S30 show a large number of atomically dispersed FM on carbon support without metal nanoparticles, suggesting that the atomic active sites were well maintained through the durability tests. It is worth mentioning that Fe-N/BP exhibits a much higher ORR activity than Fe(N)/BP (Fig. S31[†]). It means that the co-existence of FM and oxygen coordination (*i.e.* FM-O) is necessary for the formation of highly active FM-N₄ species in our experiment. Fe-N/BP was also assembled into a 5 cm² PEM fuel cell as the cathode catalyst, and the fuel cell achieved a peak power density of 672 mW cm⁻² (Fig. 5c).

Fig. 5d and Fig. S32[†] show the steady-state current densities of Ni-N/BP and Fe-N/BP in catalyzing the CO₂RR in CO₂ saturated 0.5 M KHCO₃ solution. Fe-N/BP exhibits a quite small overpotential, starting to produce CO₂RR current below -0.4 V (vs. RHE). Ni-N/BP shows a slightly larger onset overpotential of -0.42 V (defined by the potential at which the current density reaches 0.1 mA cm⁻²). CO and H₂ are the CO₂ reduction products, and no liquid product was detected by ¹H nuclear magnetic resonance (Fig. S33[†]). Ni-N/BP exhibits a Faradaic efficiency (FE) over 88% for CO at -0.72 V (Fig. 5e), which is much higher than 63% of Fe-N/BP (Fig. S34a[†]), and similar to other reported Ni-N-C catalysts (Table S9[†]), demonstrating its excellent activity and selectivity. The CO production turnover frequency (TOF) per metal single-atomic site was calculated based on the total mass loaded on the electrode as shown in Fig. 5f and Fig. S34b[†]. TOFs of CO production are 1712 h⁻¹ at -0.82 V for Ni-N/BP and 341 h⁻¹ at -0.57 V for Fe-N/BP. The TOF of Ni-N/BP is comparable to those of metal porphyrins and noble metal catalysts in aqueous solutions.⁵⁴⁻⁵⁵ After 10 h electrolysis, the current densities of Ni-N/BP and Fe-N/BP remained almost unchanged (Fig. S35[†]), showing remarkable stability.

Conclusions

In this paper, a simple, scalable and energy saving synthesis method has been developed based on the self-catalysis function of ferrous metal to prepare FM-N-C SACs. During the synthesis, FM atoms capture and decompose the ammonia molecule and create nitrogen radicals that readily replace the oxygen coordination, converting FM-O bonds to FM-N bonds on the carbon black support. The mild heat treatment at 600 °C prevents the aggregation of the FM atoms, thereby enables high densities of FM-N₄ species with FM loadings of 1.6~2.1 wt%. The self-catalysis synthesis is "mini-invasive" to the carbon support, thus suitable for precise catalyst structure design.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21673014, 21975010, 51920105001).

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Carbon Black Supported FM-N-C (FM=Fe, Co, Ni) Single-Atom Catalysts Synthesized by Self-Catalysis of Oxygen Coordinated Ferrous Metal Atoms

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Carbon nanomaterials have abundant sources but are difficult to use directly as a support for single atom catalysts (SACs) due to the lack of strong anchoring forces to restrict the aggregation of metal atoms during the high-temperature treatment.

Figures

Scheme 1. Schematic illustration of synthesis of FM-N/BP SAC by the self-catalysis of FM atoms.

Fig. 1. Characterizations of BP and Fe-N/BP. a) SEM images, b) TEM and inserted high-resolution TEM images and c) N₂ adsorption isotherms at 77 K and corresponding pore

Fig. 2. HAADF-STEM images of (a, b) Fe-N/BP, (c, d) Co-N/BP and (e, f) Ni-N/BP showing the atomically dispersed FM atoms on BP2000 support as highlighted by color circles.

Fig. 3. (a₁-c₁) Normalized XANES spectra at FM K-edge and (a₂-c₂) FT-EXAFS spectra of indicated samples and the R-space fitting for Fe-N/BP, Co-N/BP and Ni-N/BP. The insets in (a₂-c₂) show the schematic models of FM-N₄ moieties in the catalysts, Fe (brown), Co (magenta), Ni (green) and N (blue). (d₁-d₃) Wavelet transforms for the Fe k³-weighted EXAFS signals of Fe foil, Fe-O/BP and Fe-N/BP with optimum resolutions at 2.0 Å.

Fig. 4. Calculated partial density of states of (a) Fe/BP and (b) Fe-O/BP with adsorbed NH₃. For C 2p states calculation, only the C atoms adjacent to the Fe atom are considered. The Fermi level is set to energy zero. (c) The dissociation energy of free NH₃ and NH₃ adsorbed on Fe-O/BP (the energy of the initial state is taken as zero). (d) A possible pathway from Fe-O/BP intermediate to Fe-N/BP catalyst.

Fig. 5. Electrocatalytic tests. (a) LSV curves of Fe-N/BP, Co-N/BP and Pt/C in 0.1 M KOH electrolytes. (b) LSV curves of Fe-N/BP, Co-N/BP in 0.5 M H₂SO₄ and Pt/C in 0.1 M HClO₄. Both electrolytes are O₂-saturated. (c) Polarization curve and power density curve of Fe-N/BP as cathode catalyst in a PEMFC. 5 cm² single cell with 80 °C H₂/O₂ at flows of 0.3 L min⁻¹ for H₂ and 0.4 L min⁻¹ for O₂, 100%RH, 2 bar absolute pressure, NRE 211 membrane. (d) H₂, CO and total steady-state current densities of Ni-N/BP in CO₂-saturated 0.5 M KHCO₃ for the CO₂ reduction reaction test. (e) Faradaic efficiencies for producing CO and H₂, and (f) TOF for producing CO on the Ni-N/BP catalyst in an H-cell test. The catalyst mass loading is 0.2 mg cm⁻².