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Rational design of inexpensive, highly active, and long-term stable non-precious metal electrocatalysts for oxygen reduction reaction (ORR) is of significant importance for large-scale applications of fuel cells in practice. In this paper, we reported, for the first time, the construction of 2D layered mesoporous transition metal-nitrogen-doped carbon/nitrogen-doped graphene(meso–M–N–C/N–G, M = Fe, Co, and Ni) electrocatalysts using 4, 4-bipyridine as nitrogenand carbon sources and mesoporous KIT–6/N–G generated by in-situ forming KIT–6 on graphene nanosheets as a template. The meso–Fe–N–C/N–G electrocatalysts showed super electrocatalytic performance for ORR. Excitingly, its catalytic activity and durability were superior to Pt/C, making it a good candidate as an ORR electrocatalyst in fuel cells. The results suggested that the outstanding electrocatalytic performance of electrocatalystswas attributed to the unique mesoporous structure, high surface area, ultrasmall size of Fe or FeO_x nanocrystals embedded in 2D layered N–G nanosheets, excellent electron transportation, homogeneous distributions of high-density pyridinic N and graphitic N, graphitic C, and abundant metal active sites (Fe–N_x). The synthetic approach can be used as a versatile route toward the construction of various 2D layered graphene-based mesoporous materials.

INTRODUCTION

Over the past decades, polymer electrolyte membrane fuel cells (PEMFCs) have been considered as one of the most promising techniques to replace internal combustion engines and steam engines due to their high energy conversion efficiency, low operation temperature, and low environmental impact.¹The oxygen reduction reaction (ORR) occurring at the cathode of PEMFCs is the rate-limiting factor of energyconversion due to the sluggish kinetics. Therefore, efficient ORR electrocatalysts are highly desired for practical applications.^{1b,2} Platinum (Pt) and its alloys are the most effective catalysts for ORR,³ but its high cost and poor stability have been the main bottlenecks that hamper the widespread commercialization of PEMFCs.⁴ Therefore, it is necessary to develop alternative inexpensive materials with high electrocatalytic activity and long-term stability to promote the commercialization of PEMFCs.⁵

So far, a large amount of alternative non-precious metal catalysts (NPMCs) have been exploited to catalyze the ORR, including heteroatom (e.g., nitrogen, boron, sulphur, and phosphorus)-doped carbon (e.g., carbon nanotube and graphene) materials,^{2a,5} transition metal oxides,⁶ nitrides,⁷ carbides,⁸ chalcogenides,⁹ and transition-metal-coordinating macrocyclic compounds.¹⁰ Recent studies suggest that codoping of non-precious transition metal elements (e.g. Fe and Co) could largely improve the electrocatalytic activity and durability of N-C materials, which have been considered as a family of promising NMPCs for ORR.¹¹ It has been found that the ORR performance of M-N-C catalysts not only depends largely on the chemical composition of active sites,¹² but also greatly relies on the accessibility of active sites.^{12b,13} Nevertheless, the M–N–C catalysts are generally prepared by the direct pyrolysis of a mixture precursor comprising a transition metal salt, a nitrogen-contained organic precursor, and a carbon-based supporting material or a nitrogencontained organic metal complex at high temperature under inert or ammonia gas condition.¹⁴Although the obtained M–N– C catalysts usually possess high specific surface area and the chemical compositions of active sites are tunable, the presence of rich micropores could induce problems in oxygen transport and reduce the accessibility of active sites.¹⁵ It can be expected that the ordered mesoporous NPMCs with large surface area and suitable pore size could be more promising for ORR catalysis due to its easy accessible active sites and low mass-transfer resistance.^{2a,16} However, most of the pores existed in these mesoporous catalysts are embedded in bulk particles, which isunfavorable to the effective utilization of

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active sites because a longer diffusion distance for reactants is needed to access active sites.^{2a,17} It can be anticipated that combining the mesoporous M–N–C materials with two-dimensional (2D) N-doped graphene to form 2D layered meso-M/N–C/N–graphene (meso-M/N–C/N–G) nanocomposites may further improve the electrocatalytic performance due to the easy accessible active sites and the excellent electron transport performance.

Herein, we report a novel route to fabricate a series of 2D layered meso-M/N–C/N–G nanocomposites using KIT–6/N–graphene as template, 4, 4-bipyridine as nitrogen and carbon source, and metal nitrate as metal source. The meso-M–N–C/N–G nanocomposites possess high specific surface area, homogeneous distribution of ultra-small M–N–C nanoparticles less than 5 nm, and mesopores with size of ~3.6 nm generated from the assembly of nanoparticles on the surface of 2D N–graphene nanosheets. Very encouragingly, the Fe- and Cobased versions of meso-M/C-N/N-G nanocomposites, especially meso–Fe–N–C/N–G nanocomposites, show the highest ORR activity, which exhibit superior activity and durability to Pt/C catalyst in acidic and alkaline media. To the best of our knowledge, this is the first report on the highest ORR performance for 2D meso–Fe–N–C/N–G nanocomposites,

which might be viable ORR catalysts for high-performance PEMECs.

The fabrication process of meso-M-N-C/N-G nanocomposites is depicted in Scheme 1. A typical synthesis of meso-M-N-C/N-G involves four steps. First, ordered mesoporous KIT-6 wasin-situ assembled on the surface of graphene oxide (GO) to form compact KIT-6/GO nanocomposite using tetraethyl orthosilicate as silicon source and P123 as soft template; Subsequently, the obtainedKIT-6/GOnanocomposite was calcined under air atmosphere to remove P123 andtransform GO into graphene (G) to obtain KIT-6/G nanocomposite, which werefurther calcinedunder NH₃ atmosphere to achieve theKIT-6/N-G template.Then, the KIT-6/N-Gwas added into a solution containing 4,4'-bipyridine and FeCl₃·6H₂O dissolved in water-ethanol solvent to form suspension under ultrasonic condition. The M–N–C precursors were introduced into the pore channels of KIT-6/N-G during the solvent evaporation process. The resulting product was further annealed at 900 °C and the KIT-6 template was subsequently removed via HF etching. The synthesis process of other meso-M/N-C/N-G nanocomposites is similar as meso-Fe-N-C/N-G nanocomposites, except for using different precursors and feeding the precursors in differentsequences.



Scheme 1.Schematic illustration shows the synthetic process of meso-M/N–C/N–G nanocomposites.

RESUNTS AND DISCUSSION

XRD patterns (Figure 1a) indicate that the obtained meso- Fe– N–C/N–G, meso-Co–N–C/N–G, and meso-Ni–N–C/N–G nanocomposites are composed of amorphous carbon derived from 4,4'-bipyridine and graphitic carbon resulted from Ngraphene.¹⁸ The broad nature of diffraction peak at 23.2° implies that the meso-M–N–C/N–G nanocomposites consist of disordered graphitic structure with low crystallinity.^{1a} The sharp diffraction peaks located at 26.3° and 42.7° indicates the presence of graphite with high crystallinity, which is different from the XRD results of traditional graphene free Fe-N-C catalysts (most of carbon is amorphous) reported in literatures.^{12b,18} Obviously, the abundant graphite is in favor of improving the electron transport performance of meso-M– N–C/N–G nanocomposites.

To investigate the nature of carbon property, Raman spectra are acquired for meso-Fe–N–C/N–G, meso-Co–N–C/N–G, and meso-Ni–N–C/N–G nanocomposites (Figure 1b). The Raman spectra display four peaks at 1360, 1590, 2696, and 2923 cm⁻¹ assigned to the D band, G band, 2D band, and D+G band of graphitic carbon with high crystallinity, respectively. The D band corresponds to sp³ defects and disordered sites, while the G band relates to the sp²-hybridized graphitic carbon layer. ¹⁹ It can be clearly seen that the position and the intensity of these bands are almost the same for all meso-M–N–C/N–G nanocomposites, indicating that the structure of all the carbon is identical and shows turbostratic features, as observed from the XRD patterns (Figure 1a).²⁰ The relative intensity ratio of

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the G and D band peaks (I_G/I_D) is used to estimate the amount of defects and disordered structures in carbon structure. The high I_G/I_D value suggests the presence of more ordered graphitic carbon, which is in favor of improving the electrical conductivity and beneficial for the electron transfer during ORR.²¹ In contrast, the small I_G/I_D value implies the existence of large numbers disordered and defect carbon, which is also beneficial for enhancing catalytic activity of the ORR because of the increased active sites. $^{\rm 22}$ The $I_{\rm G}/I_{\rm D}$ values of meso-Fe–N– and C/N-G, meso-Co-N-C/N-G, meso-Ni–N–C/N–G nanocomposites are calculated to be approximately 1.15, 1.21, and 1.16, respectively. For comparison, the Raman spectra of graphene and meso-Fe–N–C indicate that the I_G/I_D value of graphene and meso-Fe-N-C are 1.3 and 1.08, respectively (FigureS1). Obviously, the I_G/I_D values of all meso-M–N–C/N–G nanocomposites are larger than graphene-free meso-Fe-N-C catalyst and smaller than N-graphene. These results means that the formation of meso-M-N-C/N-G nanocomposites not only can improve the electrical conductivity, but also increase the numbers of active sites, and result in outstanding electrocatalytic performance.



Figure 1. (a) XRD patterns, (b) Raman spectra, and (c) N_2 adsorption/desorption isotherm of meso-M–N–C/N–G nanocomposites. Inset to panel (c) is the corresponding pore size distribution. (d) EIS curves of meso-Fe–N–C/N–G and meso-Fe-N-C nanocomposites.

The surface areas and pore features of meso-M–N–C/N–G nanocomposites are explored by N₂ sorption technique (Figure 1c). All meso-M–N–C/N–G nanocomposites exhibit a typical IV isotherms with a distinct hysteresis loop in the curve at relative pressures (P/P₀) from 0.42 to $1.0,^{23}$ suggesting the presence of mesopores. The BJH pore size distribution curves (inset in Figure 1c) further confirm the presence of highly uniform mesoporous structure in meso-M–N–C/N–G nanocomposites with a pore size centered at ~3.6 nm. The H3-type hysteresis loop at P/P₀ between 0.8 and 1.0 indicates that the presence of macropores derived from the stack of layer structured meso-Fe–N–C/N–G nanocomposites. Apparently, the meso-Fe–N–C/N–G nanocomposites exhibit different adsorption-desorption curves and BJH pore size distribution

curves in comparison with meso-Co-N-C/N-G and meso-Ni-N-C/N-G nanocomposites, and the additional mesopores with a pore size centered at ~6.3 nm exist in meso-Fe-N-C/N-G nanocomposite. The surface area and pore volume are determined to be 776 $m^2 \cdot g^{-1}$ and 1.31 $cm^3 \cdot g^{-1}$ for meso-Fe–N– C/N–G, 468 $m^2 \cdot g^{-1}$ and 0.83 $cm^3 \cdot g^{-1}$ for meso-Co–N–C/N–G, and 436 $m^2 \cdot g^{-1}$ and 0.81 $cm^3 \cdot g^{-1}$ for meso-Ni–N–C/N–G, respectively (Table S1). This mesoporous architecture with large specific surface are beneficial for facilitating the exposure of more active sites and the diffusion of reactants during the catalytic process.²⁴The electrochemical impedance (EIS) test results of meso-Fe-N-C and meso-Fe-N-C/N-G nanocomposites further suggest that the meso-Fe-N-C/N-G possesses superior electron transport performance to graphene-free meso-Fe-N-C due to its small curve radius (Figure 1d). The outstanding conductivity is beneficial for enhancing electrocatalytic performance.

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The structure, morphology, and elemental composition of meso-Fe-N-C/N-G and meso-Co-N-C/N-G are characterized by TEM and SEM. The typtical TEM images indicate that a large amount of plicated layered structure can be observed in meso-Fe-N-C/N-G and meso-Co-N-C/N-G as marked by yellow arrows (Figure 2a and d), indicating the existence of N-G nanosheets. The partial enlarged image of Figure 2a and d display that the obvious pore chanal structure parallelly and vertically disperied on the meso-M-N-C/N-G surface.The regular dark and light images suggest the presence of ordered mesoporous structure duplicated from mesoporous KIT-6 template in meso-M–N–C/N-G (M = Fe and Co) (Figure 2b and e). According to the HRTEM images (Figure 2c andf), it is observed that there are ultrasmall nanoparticles uniformly distributed on N-G nanosheets, which are identified to be Fe/Fe₂O₃ and Co/CoO nanoparticles for meso-Fe-N-C/N-G and meso-Co-N-C/N-G, respectively. The lattice spacings of 0.202 and 0.269 nm are consistent with the (111) crystal plane of Fe and the (114) crystal planes of Fe_2O_3 (Figure 2c)⁵ and the lattice fringes with the planar distances of 0.190 and 0.247 nm correspond to the (101) crystal planes of Co and the (101) crystal planes of CoO (Figure 2f).^{2b} This observation is in accordance with the previous reports that Fe or Co in Fe-N-C or Co-N-C electrocatalysts usually exists in form of Fe/FeOx or Co/CoO_x .^{5,20,25} Due to the confinement of pore channel of mesoporous KIT-6 template, the Fe/Fe₂O₃ or Co/CoO nanoparticles have relatively smaller particle sizes (~5 nm), In comparison, the size of Fe or Co species in most of Fe-N-C or Co-N-C electrocatalysts synthesized via the direct pyrolysis of their precursors under high temperature without effective restriction effect is usually larger (>10 nm) and uncontrollable, $^{\rm 2b,5,20,25}$ leading to the numbers of exposed active sites is limited and the interaction between Fe or Co species and N–G is weaker. The smaller size of Fe/FeO_x or Co/CoO_x nanoparticles can facilitate their coordination with the surrounding N-C and N-G components and form more Fe-N_x or Co-N_x species on surface of Fe/FeO_x or Co/CoO_x to enhance the electrocatalytic performance due to the increase of active sites.⁵ The SEM (Figure 2g) and elemental mapping images (Figure 2h-k) and EDX spectra (Figure S2) further

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confirms the uniform distribution of Fe, Co, N, and C in meso-Fe–N–C/N–G and meso-Co–N–C/N–G. In addition, it also confirms that N element is well-distributed in graphene nanosheets, suggesting the successful doping of N into graphene to form N-G layers, resulting in the meso-M–N–C/N–G with ultrafine Fe/Fe₂O₃ and Co/CoO nanoparticles well-organized on surface of ordered mesoporous N-C matrix. The unique mesoporous structure in meso-M–N–C/N–G may be beneficial for the enhancement of electrocatalytic activity and electrochemical kinetics because of the increase of active sites and their favorable mass transport. Furthermore, the incorporated N–G nanosheets beneath Fe/Fe₂O₃ and Co/CoO may facilitate electron transportation during the redox process.²⁶



Figure 2. TEM images of (a-c) meso-Fe–N–C/N–G and (d-f) meso-Co–N–C/N–G nanocomposites; (g) SEM images and EDX elemental mapping images of (h) overlap, (i) C, (j) N, and (k) Fe of meso-Fe–N–C/N–G nanocomposites.

The XPSsurvey spectra of N-G, meso-Fe-N-C, and meso-Fe-N-C/N-G nanocomposites under different temperature reveal the presence of C, O, limited N as well as certain amount of Fe elements (Figure 3A). The asymmetric peakof C1s can be deconvoluted into a core peak located at 284.6 eV and two satellite peaks located at 285.8 and 287.1 eVassigned to C-C, C=N&C-O and C-N&C=O, respectively (Figure 3B).^{28a}For meso-Fe-N-C/N-G and meso-Fe-N-C nanocomposites, the high resolution XPS spectra of N1s can be fitted into four peaks at 398.6, 399.9, 401.1, and 403.2 eV assigned to pyridinic N, pyrrolic N, graphitic N, and quaternary N^+ – O^- (Figure 3C), respectively, suggesting that N is indeed doped into the mesoporous carbon molecular skeleton.^{2b,27} The N1s spectra of N-G reveal that the doped N atoms are existed in the form of ammonia N (396.3 eV), pyridinic N (398.6 eV), pyrrolic N (399.9eV), and graphitic N (401.1 eV). It is generally accepted

that graphitic N and pyridinic N may act as the efficient active sites for ORR, while other N species such as pyrrolic N and quaternary N^+-O^- have little effect on the electrochemical performance of carbon materials.²⁸ Meanwhile, the pyridinic N and pyrrolic N might coordinate with Fe to form Fe–N_x moieties, which also makes positive contributions to ORR activity and durability.²⁹ Furthermore, previous studies suggested that the graphitic N may possess superior electrocatalytic performance to pyridinic N for ORR.³⁰ According to the different types of N atomic percentages and Fe contents in the nanocomposites (Table S2 and Figure 3D),^{12b} it can be seen clearly that the N contents and N species in different nanocomposites are distinct. For N–G, the pyridinic N specie is dominant and the quaternary N⁺–O⁻ specie is absence.



Figure 3. (A) XPS survey spectra and high-resolution spectra of (B) C1s and (C) N1s. (D) Concentrations of N dopants in N–G, meso-Fe–N–C, and meso-Fe–N–C/N–G nanocomposites obtained at different temperatures. (E) O1s of (a) N–G, (b) meso-Fe–N–C, and (c-f) meso-Fe–N–C/N–G nanocomposites obtained by calcining at 600, 700, 800, and 900 °C, respectively. (F) Fe2p XPS spectra of meso-Fe–N–C/N–G nanocomposite obtained by calcining at 900 °C.

However, meso-Fe–N–C and meso-Fe–N–C/N–G nanocomposites are ammonia–N free, and the pyridinic N and graphitic N are main N species. For meso-Fe–N–C/N–G nanocomposites, the total N contents gradually decrease as the carbonization temperature increases. Meanwhile, the graphitic N contents first increase slightly as the temperature is raised from 700 to 900 °C and then decrease; while those of pyridinic N, pyrrodic N, and quaternary N⁺–O⁻ display a gradually decreasing trend because of its poor thermal stability and can be converted into graphitic N at higher carbonization temperature.^{26,11c,31} Considering the highest contents of graphitic N species in meso-Fe–N–C/N–G nanocomposites, the excellent

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electrocatalytic performance of the nanocomposites toward ORR is anticipated.²⁷ In addition, the Fe contents gradually decrease with the increase of calcination temperature because of the volatilization of FeCl₃ compounds during the pyrolysis.^{11c} Meanwhile, more Fe species may be embedded in the mesoporous N-C matrix by increasing the pyrolysis temperature, leading to the decrease of Fe on the surface of the nanocomposites. The O1s spectra can be fitted into three peaks at 533.2, 531.4, and 530.6 eV assigned C–OH coordination, C–O–C coordination, metalto oxideresidues and C=O coordination (Figure 3E), respectively.³² For Fe2p spectra, the peaks at 711.2 and 723.6 eV can be assigned to the binding energies of the Fe2p_{3/2} orbitals of Ncoordinated ${\rm Fe}^{^{3+}}$ or ${\rm Fe}^{^{2+}}$ species, respectively, indicating that most of the Fe species in the surface of Fe or FeO_x in meso-Fe-N–C/N–G are existed in the form of Fe– N_x complex.³³ This is favorable for the enhancement of ORR activity. The Fe2p_{1/2} spectra can be divided into two peaks with the binding energies at 714.5 and 726.2 eV, which should be ascribed to Fe^{3+} species. The peak at 720.3 eV is a satellite peak (Figure 3F). The survey and high resolution XPS spectra of N, C, and O in meso-Co-N-C/N-G, meso-Ni-N-C/N-G, and meso-Fe-N-C/N-G nanocomposites with different Fe (Co, Ni)/N molar ratios are similar as those of meso-Fe-N-C/N-C nanocomposites (Figures S3 and S4). This indicates that the active sites are identical in all meso-M-N-C/N-G nanocomposites because the C, N, and O species in these nanocomposites are consistent with meso-Fe-N-C/N-C (Table S3). The high resolution XPS scanning of Co2p_{3/2} is fitted into two peaks with the binding energies at 778.6 and 780.4 eV corresponding to Co²⁺ and Co-Nx species, respectively. The high resolution Ni2p spectra indicates that the $Ni2p_{3/2}$ and $Ni2p_{1/2}$ peaks are centered at the binding energies of 856.3 and 873.8 eV accompanied by two satellite bands, respectively, implying the presence of Ni element in the form of a divalent state.³

The ORR activity and kinetics of meso-Fe-N-C/N-G nanocomposites are evaluated using rotation-disk electrode (RDE) technique in 0.1 M KOH and 0.1 M HClO₄ media at room temperature. In order to achieve the optimal electro-catalytic activity, the effects of the calcination temperature and the molar ratio of FeCl₃·6H₂O to 4, 4'-bipyridine on the ORR activity are studied. It is found that the best ORR activity can be obtained in meso-Fe-N-C/N-G nanocomposites prepared by calcining at 900 °C (Figure 4a and b) and the optimal molar ratio of FeCl₃·6H₂O to 4, 4'bipyridine is 1:1 based on the highest onset and half-wave potentials (Figure 4c and d). The comparative study of ORR activity of different nanocomposites is performed by a RDE in O2-saturated 0.1 M KOH and 0.1 M HClO₄ media. The meso-Fe-N-C/N-G nanocomposites display better and comparable ORR activity in alkaline media and acidic media, respectively, compared with commercial Pt/C (20 wt %) at the same mass loading content. The cyclic voltammogram (CV) curves of Pt/C and meso-Fe-N-C/N-G show apparent cathodic peaks in O2-saturated 0.1 M KOH and 0.1 M $HCIO_4$ compared with that in N_2 -saturated solution with the adsorption and desorption peaks of hydrogen as well as the surface oxidation and reduction peaks for Pt/C catalyst and only a featureless double-layer charging current for meso-Fe-N-C/N-G nanocomposites(Figure 5a). The oxygen reduction peak appeared at

0.86 and 0.89 V versus RHE for Pt/C and meso-Fe–N–C/N–G nanocomposite in 0.1M KOH solution implies that the meso-Fe–N– C/N–G nanocomposites exhibit superior electrocatalytic activity to Pt/C toward ORR.^{34b,c} The cathodic peak potential for meso-Fe–N– C/N–G in 0.1 M HClO₄ media is 0.72 V, which is slightly lower than that for Pt/C (0.73 V), indicating an outstanding ORR activity for meso-Fe–N–C/N–G nanocomposites in acidic condition.^{34b,c} In order to further reveal the ORR activity ofdifferent nanocomposites,the linear sweep voltammetry (LSV)tests are also carried out (Figure 5b

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Figure 4. Rotating disk electrode (RDE) voltammograms of meso-Fe–N–C/N–G nanocomposite prepared at different pyrolysis temperatures in O₂-saturated (a) 0.1 M KOH and (b) 0.1 M HClO₄ media. RDE voltammograms of meso-Fe–N–C/N–G nanocomposite obtained by pyrolyzing the mixtures containing different molar ratios of FeCl₃·6H₂O and 4,4'-bipyridine at 900 °C in O₂-saturated (c) 0.1 M KOH and (d) 0.1 M HClO₄ media. Rotation speed is fixed at 1600 rpm and potential sweep rate is set at 10 mV/s.

and c and Table 1). The LSV polarization curves for ORR show that the onset potentials of N-G, meso-N-C/N-G, Fe-N-C, meso-Pt/C, and meso-Fe-N-C/N-G Fe-N-C, meso-Fe-N-C/G, nanocomposites are 0.87, 0.90, 0.91, 0.92, 0.93, 0.98, and 1.03 V vs. RHE, respectively, and the corresponding half-wave potentials are 0.78, 0.81, 0.82, 0.84, 0.85, 086, and 0.89 V vs. RHE, respectively, in 0.1 M KOH media. Clearly, the ORR activity is increased following the order of N-G < meso-N-C/N-G < Fe-N-C < meso-Fe-N-C < meso-Fe-N-C/G < Pt/C < meso-Fe-N-C/N-G, and the meso-Fe-N-C/N-G possesses the best electrocatalytic performance toward ORR in alkaline media. The ORR activity of meso-Fe-N-C/N-G nanocomposites is greatly enhanced relative to that of metal-free N-G and meso-N-C/N-G nanocomposites. The possible reason is that the introduction of Fe can form Fe-N_x active sites, which may meso-Fe-N-C/N-G enhance the electroactivity of

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nanocomposite.^{2b,35} The ORR activity of meso-Fe-N-C/N-G is higher than that of graphene-free Fe-N-C and meso-Fe-N-C nanocomposites because the incorporated graphene nanosheets in meso-Fe-N-C/N-G could improve the electron conductivity, which has been proven by EIS tests (Figure 1d). The ORR activity of meso-Fe-N-C nanocomposites is superior to bulk Fe-N-C due to its open mesoporous structure. The existence of mesopores in meso-Fe-N-C nanocomposites not only can increase the numbers of exposed active sites but also can enhance the accessibility of active sites because of the outstanding mass transfer efficiency.^{16a,11c} These features are all beneficial for improving electrocatalytic property.^{27,36} Furthermore, compared with meso-Fe-N-C/G, the better ORR activity of meso-Fe-N-C/N-G may suggest that after doping N atoms in graphene, the numbers of active sites are effectively increased because of the formation of more pyridinic N as confirmed by XPS characterization. Meanwhile, the electron conductivity can be further enhanced due to the electron-rich characteristic of N atom, which is also in favor of electrocatalytic reaction.³⁶ More importantly, the half-wave potential and the limited current density at 0.5 V of meso-Fe-N-C/N-G nanocomposites are 30 mV and 0.22 mA·cm⁻², which are higher than those of benchmark Pt/C.In fact, to the best of our knowledge, the presently developed meso-Fe-N-C/N-G nanocomposites possess the best catalytic performance toward ORR compared with the leading results of M-N-C catalysts reported in recent studies (Table S4).



Figure 5. (a) Cyclic voltammograms of Pt/C (20 wt%) and meso-Fe–N–C/N–G nanocomposites in N₂- and O₂-saturated 0.1 M KOH and 0.1 HClO₄ media at a scan rate of 50 mV·s⁻¹. (b) LSV curves of different catalysts at a rotation rate of 1600rpm in O₂-saturated 0.1 M KOH media with a scan speed of 10 mV/s. (c) LSV curves of different catalysts at a rotation rate of 1600 rpm in O₂-saturated 0.1 M HClO₄media with a scan speed of 10 mV/s. (d) Tafel plots of meso-Fe–N–C/N–G nanocomposites and Pt/C (20 wt%) catalystin O₂ saturated 0.1 M KOH solution.

Generally, the ORR kinetics is more sluggish in acidic media than in alkaline media, especially for NPMCs.³⁷ So, the electrocatalytic activity of meso-M–N–C/N–G nanocompositesfor ORR in acidic media (0.1 M HClO₄) is also studied. The results reveal that all meso-M–N–C/N–G nanocomposites display excellent

electrocatalytic activity and their ORR activity follows the same order as that in alkaline media, except that the ORR activity of meso-Fe-N-C/N-G is slightly lower than Pt/C (Figure 5c). The halfwave and onset potentials of Pt/C and meso-Fe-N-C/N-G nanocomposites from their LSV curves are 0.73 V, 0.85 V vs. RHE and 0.72 V, 0.83 V vs. RHE, respectively. The onset and half-wave potentials of meso-Fe-N-C/N-G nanocomposites are only 20 and 10 mV, more negative than those of Pt/C. The limiting current density of Pt/C catalyst and meso-Fe-N-C/N-G nanocomposites at 0.50 V is 4.9 and 4.57 mA·cm⁻², respectively. The above results indicate that our meso-Fe-N-C/N-G nanocomposites possess excellent ORR activity in both alkaline and acidic media, which may have a bright application prospect. Obviously, the limiting current density of Fe-N-C catalyst in alkaline and acidic media is different, suggesting that the FeNx and C-N species in meso-Fe-N-C/N-G nanocomposites may show different ORR activities, and the FeN_x species may possess superior ORR activity toC-N species in acidic media.^{18,38} In addition, the meso-Co-N-C/N-G and meso-Ni-N-C/N-G nanocomposites also exhibit remarkable electrocatalytic activity toward ORR, and their onset and half-wave potentials can reach 0.97 V, 0.84 V. vs RHE and 0.92 V, 0.81 V. vs RHE, respectively, in alkaline media (Figure S6). The mass-transfer corrected Tafel plots within a potential range between about 0.8 V and 0.95 V vs. RHE of Pt/C and meso-Fe-N-C/N-G electrocatalysts were calculated to accurately compare their ORR activities. The Tafel plots are obtained after the measured currents were corrected for diffusion to give the kinetic currents in the mixed activation-diffusion region, according to the equation:³⁹

$$j_k = \frac{jj_d}{j_d - j_d}$$

Where j is the overall measured current density, j_k is the kinetic current density, j_d is the diffusion limiting current density. The results were shown in Figures 5d and S6. As seen in Figures 5d and S6, the meso-Fe-N-C/N-G exhibits a Tafel slope of $63\text{mV}\cdot\text{dec}^{-1}$ in alkaline media, which is smaller than that of Pt/C catalyst (79 mV·dec⁻¹), however, the Tafel slope of meso-Fe-N-C/N-G is $97\text{mV}\cdot\text{dec}^{-1}$). These results further than that of Pt/C catalyst (91 mV·dec⁻¹). These results further verify that the meso-Fe-N-C/N-G catalyst possesses the faster ORR electrocatalytic reaction kinetics than Pt/C catalyst in alkaline media and the slower ORR electrocatalytic reaction kinetics than Pt/C catalyst in acid media.

Table 1.The ORR catalytic performance of different catalysts in alkaline and acidic media.

Catalyst	Media	Onset potential (V. vs RHE)	Half-wave Potential (V. vs RHE)	Diffusion- limiting current at 0.5 V (mA·cm ⁻²)			
Pt/C	Alkaline	0.98	0.86	5.19			
	Acidic	0.85	0.73	4.90			
Meso-Fe -	Alkaline	1.03	0.89	5.41			
N–C/N–G	Acidic	0.83	0.72	4.57			
Meso-Fe -	Alkaline	0.93	0.85	4.31			
N–C/G	Acidic	0.88	0.68	4.32			

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Meso-Fe-	Alkaline	0.92	0.84	4.23
N–C	Acidic	0.87	0.67	4.27
Fe-N-C	Alkaline	0.91	0.82	4.01
	Acidic	0.85	0.65	4.18
Meso-N-	Alkaline	0.90	0.81	3.82
C/N–G	Acidic	0.82	0.62	3.44
N–G	Alkaline	0.87	0.79	3.16
	Acidic	0.79	0.55	2.77

To gain further insight into the ORR kinetics and the catalytic mechanism, the RDE polarization curves of meso-Fe-N-C/N-G nanocomposites are performed in the potential range of 0.1-1.1 V at 400-2400 rpm (Figure 6a and c). The prominent platforms appeared in the potential range of 0.7-0.1 V in 0.1 M KOH media suggests that the ORR current of meso-Fe-N-C/N-G nanocomposites is fully mass-diffusion-limited in this potential range. However, the gradually increased ORR current in the potential range of 0.5–0.1 V in 0.1 M HClO₄ media indicates that the meso-Fe-N-C/N-G nanocomposites exhibit a sluggish ORR kinetics in acidic media. The limiting current density decreases from 3.68 to 6.81 mA·cm⁻² as the rotating speed decreases from 2500 to 400 rpm because the diffusion distance of the O₂-saturated electrolyte is shortened at high speed.⁴⁰The corresponding Koutecky–Levich (K-L) plots within the potential range from 0.3 to 0.6 V vs. RHE show a good linearity and parallelism both in alkaline and acidic media (Figure 6b and d), which confirms that the first-order reaction kinetics toward the oxygen concentration in the solution and the numbers of electrons transferred during the ORR are similar at different potentials.⁴¹ Furthermore, the electron transfer numbers (n) are calculated from the slope of K-L equation. For an alkaline electrolyte solution, the calculated value of n is approximately 3.99-4.11 over the entire potential range, indicating that the ORR on meso-Fe-N-C/N-G nanocomposites fully follow the four-electron-transfer pathway corresponding to the complete reduction of oxygen into water. Similarly, the calculated value is around 3.76-3.94 for an acidic electrolyte solution, which is slightly smaller than 4, suggesting that the ORR is dominant by a four-electron oxygen reduction process and only a fraction of two-electron process occur during ORR process. The ORR polarization curves of meso-Co-N-C/N-G nanocomposites at rotation rates from 400 to 1600 rpm in 0.1 M HClO₄ and 0.1 M KOH media (Figure S7) show that the corresponding K-L plots calculated based on



Figure 6. (a and c) LSV curves of meso-Fe–N–C/N–G nanocomposites at the rotation rates of 400 to 2400 rpm in 0.1 M KOH and 0.1 M HClO₄ media. (b and d) Corresponding Koutecky–Levich (K–L) plots at different potentials in 0.1 M KOH and 0.1 M HClO₄ media.

ORR polarization curves of meso-Co–N–C/N–G nanocomposites exhibit good linearity with a consistent slope, indicating the first order reaction kinetics for ORR with respect to O_2 concentration. The average electron transfer numbers are calculated from K-L equation to be about 4 at 0.30-0.60 V in alkaline and acidic media, which also suggests that the fourelectron pathway is dominate during the ORR process.

The stability of non-precious metal ORR catalysts is an important performance criterion in order to successfully project them as replacements of Pt-based catalysts.42 To assess the stability of meso-Fe-N-C/N-G nanocomposites, the accelerated durability test is carried out by comparing with Pt/C catalyst in 0.1 M KOH media (Figure 7a). Clearly, the polarization curves recorded after 5000 cyclic voltammograms test display only a slightly negative shift of half-wave potential of 8.1 mV for meso-Fe-N-C/N-G nanocomposites. However, the half-wave potential negatively shifts by 41.2 mV for Pt/C under the similar test media. Meanwhile, the diminishment of diffusion-limited current for Pt/C is obvious larger than that of meso-Fe-N-C/N-G nanocomposites. Then, the durability of meso-Fe-N-C/N-G and Pt/C for ORR is evaluated by continuous chronoamperometric measurements at 0.50 V. vs RHE in an O2-saturated 0.1 M KOH and 0.1 M HClO4 media.After having reacted for 10000s, the meso-Fe–N–C/N–G nanocomposites exhibit slight performance attenuation with 95.3 % and 92.3 % of the relative current persisted in alkaline and acidic media, respectively. In sharp contrast, the current density of Pt/C has a much greater loss, especially in acidic media, and the current loss reaches 17.6 % in alkaline media and 43.6 % in acidic medium due to the surface oxidization, particle dissolution/aggregation/Oswald ripening over time, and weak interactions with carbon support (Figure 7b).43 In addition, the resistance of the catalysts to methanol crossover is also of particular importance for practical applications.¹⁴It is revealed that after adding 10 % methanol into 0.1 M KOH or

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0.1 M HClO₄ electrolyte solutions as indicated by the arrows (Figure 7c and d), the ORR current of Pt/C significantlydecreases due to the oxidation of methanol on the electrode surface. However, the current density of meso-Fe–N–C/N–G nanocomposite has no noticeable change, except for a slight oscillation. The above results reveal that the meso-Fe–N–C/N–G nanocomposites indeed not only possesses excellent durability but also has outstanding tolerance to methanol crossover, which may be a promising candidate as cathode catalystto replace commercial Pt/C for direct methanol fuel cells.

We proposed a synergetic mechanism to explain the superior ORR performance of meso-Fe–N–C/N–G nanocomposites. As it can be seen in Scheme 2, the enhanced electrocatalytic activity and durability of meso-Fe–N–C/N–G nanocomposites may be attributed to the unique multi-component and 2D layered mesoporous structure. Firstly, the abundant pyridinic N and pyrrolic N in N–G can effectively enlarge the density of active sites, improve the electron transport performance, and enhance the synergistic effect between Fe–N–C nanocrystals and N–G through



Figure 7. (a) RDE polarization curves of meso-Fe–N–C/N–G and Pt/C before and after stability test in O_2 -saturated 0.1 M KOH media. (b) Current-time chronoamperometric response of meso-Fe–N–C/N–G and Pt/C at 0.5 V. vs RHE in O_2 -saturated 0.1 M KOH and HClO₄media. (c and d) Chronoamperometric response of meso-Fe–N–C/N–G and Pt/C at 0.5 V. vs RHE in O_2 -saturated 0.1 M KOH and 0.1 M HClO₄ media. The i-t curves are measured at a rotating speed of 1600 rpm.

coordination-chelating interaction of N and Fe atoms, and thus largely improve their ORR activity.44 Then, the unique mesoporous structure and evenly distributed Fe, N, and O species on the surface of meso-Fe-N-C/N-G nanocomposites are not only beneficial for improving the mass transport properties of O₂ and increasing the numbers of exposed active sites, but also helpful to facilitate the transport of electrolyte ions, reaction intermediates, and products⁴⁵ and prevent unwanted agglomeration of active sites,⁴⁶ which greatly contribute to the enhancement of electrocatalytic activity and stability. Meanwhile, the small size of mesopores (~3.6 nm) in meso-Fe-N-C/N-G nanocomposites is favorable for the adsorption of O₂ molecules. In addition, the uniform ultrasmall size of Fe or FeO_x nanocrystals and N-C nanoparticles can further increase the numbers of graphitic N, pyridinic N, and Fe-N_x species on the surface of meso-Fe-N-C/N-G nanocomposite because of the large surface-area-to-volume ratio and make the active sites evenly distributed on the N-G surface, resulting in excellent ORR activity. Finally, the thin 2D layered structure of meso-Fe-N-C/N-G nanocomposites can ensure the accessibility of the reactant molecules due to the short diffusion distance to active sites, leading to a further promoted ORR performance. The detail ORR mechanism of meso-Fe-N-C/N-G involves two pathways based on the different position of active sites as demonstrated in Scheme 2. On graphitic N active sites, the O₂ molecules are firstly adsorbed on adjacent C, and formed C-O-O intermediate. Then, the O₂ is step by step reduced through the four electron transfer pathway. In the process of the reaction, the graphitic N atoms convert into pyridinic-like N atoms in a subsequent coupled electron-proton transfer step through breaking of a C–N bond.⁴⁷ On Fe– N_x active sites, the O_2 · firstly displaces the OH- species and chemisorbs directly on the Fe^{2+} active site. Subsequently, the reaction proceeds to the ferrous-hydroperoxyl adduct via the superoxo and the ferric-hydroperoxyl states. Finally, the catalytic cycle in alkaline media undergoes a complete 4e transfer to regenerate the active sites via the formation of ferric-hydroxyl species.48 However, the analogous ferrous-hydroperoxyl adduct is FeII-(OHOH) in acidic media, and the adsorbed peroxide intermediate is reduced via a 2e⁻ process, resulting in the 2 e × 2 e mechanism.

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Scheme 2. The proposed synergetic mechanism for the enhanced catalytic performance of meso-Fe–N–C/N–G nanocomposites for ORR.

Conclusions

In summary, this work reports the development of a series of novel 2D layered mesoporous M-N-C/N-G (M = Co, Fe, and Ni) nanocomposites via a universal nanocasting method as super-efficient electrocatalysts for ORR in both alkaline and acidic media. The ORR activity of the mesoporous M-N-C/N-G nanocomposites is largely relied on the types of metal complex, the pyrolysis temperature, and the molar ratioof precursors. The optimal meso-Fe-N-C/N-G nanocomposites exhibit the highest ORR activityand durabilityboth in acidic and alkaline electrolytes, which are comparable or even superior to benchmark Pt/C. Moreover, the presence of methanol almost cannot influence the ORR current density. The characterizations display that the prominent performance is associated with beneficial factors including high surface area, unique mesoporous structure, and highly dispersed ultrafine Fe or FeO_x nanocrystals and N-C nanoparticles. It is expected that the developed unique 2D meso-Fe-N-C/N-G nanocomposites can serve as high-performance electrocatalysts for ORR in PEMFCs. The present synthetic methodology may provide a new cutting-edge technology to synthesize various 2D mesoporous composite materials for various applications.

Experimental Section

Materials preparation

Graphene was prepared by a modified hummer's method. Typically, 1 g of graphite power was slowly added into a mixed solution of concentrated sulfuric acid (130 mL) and phosphoric acid (30 mL) containing 6 g of KMnO₄ in a 250 mL ground flask at an ice bath. Then, the flask was transferred to an oil bath and keep at 50 °C for over 12 h under mechanical stirring. After naturally cooled to ambient temperature, the turbid liquid was slowly poured into a 500 mL of beaker containing 15 mL H₂O₂ and 100 mL deionized water with continually stirring, and the solution in beaker immediately turns into light yellow, indicating the formation of GO. After the turbid liquid was completely added, the solution was further stirred 2 h to ensure the complete oxidization of graphite. Subsequently, the obtained yellow turbid was centrifuged at 2000 rpm in a 10 mL of tube, and the black particles (unreacted graphite) were discarded. The turbid in the top of tube was washed with concentrated HCl, deionized water, and ethanol for three times, respectively. Then, the products were freeze dried overnight to obtain thegraphene.

KIT-6/N-graphene (KIT-6/N-G) nanocomposites were prepared according to a modified method reported previously.⁴⁹ Briefly, 6.0 g of triblock copolymer pluronic P123, 1 g of GO, and 6 g of n-butanol, 11.8 g of concentrated HCI were added into a 150 mL aqueous solution and continuously stirred at 45 °C for 24 h. Then, TEOS (12 g) was added to the

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above solution under vigorous stirring at the speed of 0.5 mL/min. Then, the mixture solution was kept under stirring at 45 °C for another 24 h. After refluxing treatment at 80 °C for 6 h, the dark yellow solid products were collected by filtration, washed with water and ethanol, and dried at 80 °C for 12 h in oven. In order to obtain KIT–6/N–G nanocomposites, the KIT-6/G was further calcined at 700 °C for 3 h in NH₃ atmosphere at the ramp of 2 °C / min to obtain KIT–6/N–G.

The meso-M–N–C/N–G nanocomposites were prepared through a nanocasting method. For the synthesis of meso-Fe-N-C/N-G nanocomposites, typically, 2 mL of water was added to a 6 mL of ethanol solution containing FeCl₃·6H₂O (126 mg) and 4, 4'-bipyridine (80 mg) with a molar ratio of FeCl₃·6H₂O to 4, 4'-bipyridine at 1:1. After the solution became clear, 50 mg of KIT-6/N-G template was added into the above solution and stirring vigorously overnight to evaporate the solvent at room temperature. Then, the material was pyrolyzed at 900 °C in high-purity nitrogen atmosphere for 3 h with a heating speed of 3°/min. Finally, the obtained nanocomposites were etched with 5 wt % HF to remove KIT-6 template. For the synthesis of meso-Co-N-C/N-G and meso-Ni-N-C/N-G nanocomposites, firstly, 4, 4'-bipyridine (80 mg) was completely dissolved into ethanol solution (6 mL) containing 50 mg of KIT-6/N-G under ultrasonic condition, then 122 mg of $CoCl_2 \cdot 6H_2O$ or 121 mg of NiCl₂·6H₂O dissolved in water (2 mL) was slow dripped into the above suspension with a molar ratio of CoCl₂·6H₂O or $NiCl_2 \cdot 6H_2O$ to 4, 4'-bipyridine at 1:1. After vigorously stirring overnight to evaporate the solvent at room temperature, the obtained material was pyrolyzed at 900 °C in high-purity nitrogen atmosphere for 3 h with a heating speed of 3°/min. Finally, the obtained nanocomposites were etched with 5 wt% HF to remove KIT-6 template.

N-G was synthesized by the direct calcination GO at 900 C for 2h under NH_3 atmosphere.

Platinum, nominally 20wt% on carbon black, HiSPECTM 3000 (Pt/C) was obtained from Alfa Aesar (China).

Materials characterization

XRD was performed on a PANalytical Empyrean diffractometer with Cu Kalpha1 radiation (λ =1.5405Å) in the Bragg angle ranging between 20° and 80°. Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) characterizations were performed on a FEI Tecnai F20 field-emission transmission electron microscope (FE-TEM) quipped with an EDS detector at an acceleration voltage of 200 kV. The scanning electron micrographs were recorded with a HITACHI S4800 field-emission scanning electron microscope (FE-SEM). Surface area measurements were performed on an ASAP 2020 Brunauer-Emmett-Teller (BET) analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers. Raman spectra were acquired using a LabRAMHR800 spectrographer (Horiba). The excitation source was a helium-neon laser with a wavelength of 512.5 nm and an excitation power of 6 mW.

Electrochemical measurements

Electrochemical measurements were carried out on a CHI 760E electrochemical workstation (CH Instruments, Chenhua Co., China) assembled with a modulated speed rotator (RRDE-3A) in a standard three electrode system with a platinum wire as the counter electrode, a catalyst-modified glassy carbon electrode (GCE) with an area of 0.0707 cm² as the working electrode, and a saturated calomel electrode (SCE, 0.241 V vs RHE) as the reference electrode. All potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241 + 0.059*pH) V. The catalyst ink was prepared by ultrasonically mixing 3.0 mg of as-prepared catalyst with 15 µL of Nafion® (5%) solution, 0.15 mL of water, and 0.15 mL of ethanol for 30 min to form a homogeneous suspension. A total of 2 µL of well-dispersed catalyst ink was pipetted and spread onto the surface of a pre-polished rotation disk electrode (RDE) (d = 3 mm), and dried in air for 30 min before measurement, corresponding to a catalyst loading of 261 μ g/cm². Linear sweep voltammetry (LSV) polarization curves in the potential range of 0.2 to -0.9 V or 0.9 to -0.2 V (vs. SCE) for the oxygen reduction reaction (ORR) were acquired in an oxygen saturated 0.1 M KOH or 0.1 M HClO₄ electrolyte with a sweep rate of 10 mV s^{-1} at various rotating speeds from 400 to 2600 rpm. Before each measurement, the electrolyte was bubbled with O₂ for 30 min. A flow of O₂ was maintained over the electrolyte during the measurement to ensure a continuous O₂ saturation. Cyclic voltammetry was collected without rotation in the potential range of 0.2 to -0.9 V or 0.9 to -0.2 V (vs. SCE) with a scan rate of 50 $mV \cdot s^{-1}$ in nitrogen saturated 0.1 M KOH or 0.1 M HClO₄ solution. In this paper, all current densities were normalized to the geometric surface area of the disk electrode and all the electrochemical experiments were carried out at room temperature and ambient pressure. Koutecky-Levich plots $(J^{-1}vs \omega^{-1/2})$ were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) kinetic current density (jk) on the basis of the Koutecky-Levich equation (eqs 1-3).^{13b}

 $\frac{1}{j} = \frac{1}{j_{L}} + \frac{1}{j_{K}} = \frac{1}{Bw^{1/2}} + \frac{1}{j_{k}} (1)$ B= 0.62nFC₀D₀^{2/3}v^{-1/6} (2) $j_{K} = nFkC_{0}(3)$

where, j was the experimentally measured current density at specific potential, $j_{\rm K}$ was kinetic current density, $J_{\rm L}$ was the limiting diffusion current density, ω was the angular velocity, n was the electron transfer number, F was the Faraday constant (F = 96485 C mol⁻¹), C₀ was the saturated concentration of O₂ in 0.1 M KOH (1.2×10⁻⁶ mol·cm⁻³) or in 0.1 M HClO₄ (1.18×10⁻⁶), D₀ was the diffusion coefficient of dissolved oxygen in 0.1 M KOH (1.9 × 10⁻⁵ cm² s⁻¹) or in 0.1 M HClO₄ (1.93 × 10⁻⁵ cm²·s⁻¹), and ω was the kinematic viscosity of 0.1 M KOH (0.01 cm²·s⁻¹) or 0.1 M HClO₄ (8.93 × 10⁻³ cm²·s⁻¹). "n" can be calculated from the slope by the under plot of j⁻¹vs. $\omega^{-1/2}$ and j_k was calculated from the inverse of the intercept. Electrochemical impedance spectroscopy (EIS) of different catalysts were measured in the dark using a Zennium electrochemical workstation (Zahner, Germany) in a three-electrode system

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with a Ag/AgCl (3 M KCl) reference electrode as the reference electrode, Pt as the counter electrode, and 0.5 M H_2SO_4 solution as the electrolyte with frequency ranging from 100 mHz to 10 kHz and a potential amplitude of 10 mV under OCP condition.

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2D layered meso-M/N–C/N–G nanocomposites with high specific surface area, homogeneous distribution of ultra-small M–N–C nanoparticles less than 5 nm, and mesopores with size of ~3.6 nm exhibit excellent electrocatalytic activity toward oxygen reduction reaction (ORR) in acidic and alkaline media.