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Nanosheets/Mesopore Structured Co₃O₄@CMK-3 Composite as Electrocatalyst for Oxygen Reduction Reaction

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Abstract: Exploring highly effective and low-cost non-noble metal electrocatalysts for oxygen reduction reactions (ORR) will have a significance impact on the area of fuel cells and metal-air batteries. In this manuscript, we report a facile, efficient and environmental friendly method to deposit transition metal oxide nanosheets (NSs) on the backbone of ordered mesoporous carbon (CMK-3) via pyrolysis of the metal-precursor@CMK-3. The optimized CMK-3 catalyst with a coating of Co₃O₄ NS possesses a high surface area of 2396 m² g⁻¹ and demonstrates an excellent electrocatalytic activity towards ORR in alkaline media, which is much better than other transition metal oxide@CMK-3 catalysts and other carbon materialbased catalysts (such as carbon nanotubes). In addition, the asprepared catalyst possesses comparable electrochemical performances, and even superior durability and higher tolerance to methanol compared with commercially available Pt/C, which can be ascribed to the distinctive structure of nanosheets/mesopore (NSs/MP), indicative of great potential in the application of metal-air batteries.

Introduction

Developing new non-noble metal ORR electrocatalysts is of great importance for electrochemical devices directly in connection with the efficient energy conversion and storage technologies such as fuel cells and rechargeable metal-air batteries.^[1] It is well known that Pt and its alloys are the most efficient ORR catalysts until now, unfortunately, the high cost and low reserves of Pt prevent it from further development for commercialization.^[2] As a consequence, the alternative catalysts based on non-precious metals and metal oxide semiconductors have been investigated as potential ORR eletrocatalysts which has drawn widespread concern by research teams.^[3]

Metal or metal oxide catalysts constantly suffer from dissolution, disintegration, and agglomeration in the fuel cell applications, which is not conducive to the development of electrocatalyst.^[4] To overcome this obstacle, carbon matrices such as active carbon,^[2a] carbon nanotubes,^[5] graphene^[6] and porous carbon^[7] used to support metal oxides have been developed to ideal catalysts due to their high electro-conductivity, popular prices and ultrastability, which can improve the catalytic

[a] L. Gan, M. Wang, L. Hu, Dr. J. Fang, Prof. Y Lai, Prof. J. Li School of Metallurgy and Environment Central South University Changsha, Hunan, 410083 (China) E-mail: fangjing526@csu.edu.cn activity and durability of catalysts and maximize their electrochemical active sites. Self-ordered mesoporous carbon material, as a new kind of nanostructured material, possesses regular pore structure, large specific surface area and pore volume, good thermal stability and chemical stability, which has been widely explored as non-metal catalysts or as a characteristic support for metal catalysts.^[8] This interesting material was employed as a support by a mass of research groups for making catalysts with inorganic metal oxide and exhibiting a very good catalytic performance as electrode material.^[9]

Particularly, the bulk of CMK-3 possesses plenty of ordered interconnected pores, as an air diffusion electrode material, can provide valid gas diffusion channels which has been considered as potential electrocatalyst for ORR.^[10] Accordingly, the metal oxide loaded on the surface of CMK-3 can remain the gas diffusion path of CMK-3 and get amply effective activity area of three-phase interface (gas-catalyst-electrolyte) that are indispensable for fuel cell or metal-air battery.^[11] Wang et al.^[10] reported the high electrocatalytic performance of a mesoporous carbon Mn₃O₄@CMK-3 nanocomposite for oxygen reduction in alkaline solution. Nevertheless, the gas diffusion channels of CMK-3 may be blocked gradually with the loading increase of metal oxide nanoparticles (NPs), resulting in enhanced ohmic resistance and charge transfer resistance of ORR. Despite the tremendous progress in CMK-3-based catalyst NPs, little effects were done to the controllable assembly of non-precious metal oxide with other micromorphology supported on this threedimensional carbon networks as ORR catalysts.^[12]



Scheme 1. The schematic display for the synthesis process of $\text{Co}_3\text{O}_4@\text{CMK-3}$ composite.

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Here, we demonstrate a NSs/MP structured Co₃O₄@CMK-3 composite which is successfully synthesized by using CMK-3 as carbon support and Co(NO₃)₂ as a cobalt-precursor for exterior wall decoration, and the synthetic routine is illustrated in scheme 1. At first, the intermediate of CoOH or CoOOH nanosheets was fabricated by a solvothermal method and then calcinations the intermediates to graft ultrathin Co₃O₄ nanosheets onto highlyordered mesoporous carbon CMK- 3. The unique structure of the resulting metal oxide NSs@CMK-3 (Co₃O₄@CMK-3), an interconnected multihole structure of carbon nanorods with homogeneity deposition of Co₃O₄ NSs, leads to high electrical conductivity, good stability, excellent catalytic activity and anticrossing effects for ORR. These electrochemical properties were practically comparable or even superior in some ways to those observed for a commercial Pt/C (20 wt%) with the same mass, thus leading to a novel electrocatalyst for ORR. What's more, Co₃O_{4@}CMK-3 composites derived from different feed dosages of CMK-3 and Co₃O₄ supported on carbon nanotubes (Co₃O₄@CNTs), other metal oxide@CMK-3 hybrid were also prepared as referential samples, which verifies that the high activity of Co₃O₄ NSs deposit on the outer wall of CMK-3 with mesoporous architecture accounts for the excellent electrochemical catalytic performance of Co₃O_{4@}CMK-3.

observed, respectively. After precipitation and the subsequent calcination treatment, the homogeneous Co₃O₄ covered on the surface of CMK-3 matrix in the form of standing NSs as shown in Figure 1C, more importantly, the pore structure of CMK-3 doesn't collapse during the low-temperature calcining process. As we can seen from the TEM image in Figure 1D, the surface of CMK-3 is covered with burrs and the NSs/MP structure of the Co₃O₄@CMK-3 composite can also be clearly observed. Additionally, as shown in Figure S1A, B, the Co₃O₄ NSs were uniformly aggregated in formation of the sphere-like structure. A comparison of Co₃O_{4@}CMK-3 composites derived from various CMK-3 mass was also prepared, in Figure S1C-E, the welldistributed Co₃O₄ NSs were epitaxial grown on the surface of CMK-3. But the Co₃O₄ NSs are hardly observed on the surface of CMK-3, when the usage of CMK-3 increased to 20 mg. What's more, Co₃O₄ supported on carbon nanotubes (Co₃O₄@CNTs) and other metal oxide@CMK-3 hybrid was also successful prepared (Figure S2).

Results and Discussion



Figure 1. Typical SEM and TEM images of the bare CMK-3 template (A, B) and the calcined $Co_3O_4@CMK-3$ composites with the best component ratio (C, D).

The morphology structure of the pristine CMK-3 template and the $Co_3O_4@CMK-3$ with the well-defined morphology after calcination are shown in Figure 1. The ordered threedimensional CMK-3 matrix consisted of plenty of rod-like aggregates in the micrometer scale (Figure 1A) and the sufficient ordered mesoporous channels of CMK-3 derived from SBA-15 with a diameter of ~1.9 um (Figure 1B) can be clearly



Figure 2. TEM images of $Co_3O_4@CMK-3$ (A, B) hybrid nanostructures; HRTEM image (C) and SAED pattern (D) of the corresponding Co_3O_4 nanosheets; High angle annular dark field scanning transmission electron microscopy image of $Co_3O_4@CMK-3$ composites (E) and the corresponding elemental mapping images of carbon (F) oxygen (G) and cobalt (H).

The morphology and microstructure view of $Co_3O_4@CMK-3$ were further conducted by a transmission electron microscopy analysis. A typical TEM image, as presented in Figure 2A, indicating that the $Co_3O_4@CMK-3$ possess a NSs/MP structure without any structure collapses after heat treatment process. In order to observe the NSs in more details, a magnifying TEM image of the $Co_3O_4@CMK-3$ composites is shown in Figure 2B. The stand upright Co_3O_4 NSs can be clearly observed on the

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backbone of CMK-3. Moreover, the thickness of a single ultrathin Co_3O_4 NSs is about 3.2 nm which is calibrated by Digital Micrograph software, which could offer very convenient transportation path for oxygen and the diffusion of the generated H₂O. In the HR-TEM images shown in Figure 2C, the interplanar distance of Co_3O_4 NSs is 2.46 Å, corresponding to the (311) crystal plane of Co_3O_4 . Additionally, three main diffraction rings were obtained in the SAED patterns (Figure 2D), which are readily assigned to the (111), (220) and (311) planes of the Co_3O_4 phase, in good agreement with X-ray diffraction (XRD) results. Atomic-resolution HAADF image of the Co_3O_4 @CMK-3

as shown in Figure 2E. Energy-dispersive X-ray (EDX) elemental mapping confirmed that C, O, Co are principal elemental components of the Co_3O_4 @CMK-3 which were also performed on the single nanorod (Figure 2F-H). In the carbon mapping, inferior carbon signal was detected out of the CMK-3 due to the nanorod lies on the carbon film. What's more, the Co and O are both homogeneously distributed around the template. More importantly, the difference between the cross sections diameters of the C mapping and the Co, O mappings demonstrate that the Co_3O_4 NSs deposit on the surface of CMK-3 and form a "core-shell" structure.



Figure 3. (A) X-ray diffraction patterns (B) Thermal gravity analysis in air (C) Nitrogen adsorption-desorption isotherm of the bare CMK-3 and Co₃O₄@CMK-3 composites with different component ratios.

Figure 3A shows the diffraction pattern of the assynthesized CMK-3 and the Co₃O₄ NSs@CMK-3 with different component ratios. It can be clearly seen that two broad diffraction peaks at 22.9° and 43.3° exist in the XRD pattern of CMK-3 which matching well with the (002) and (101) planes of the graphitic structure, respectively, indicating that the CMK-3 have good electro-conductivity due to the graphite phase. Besides, under the same calcination temperature, the amount of Co₃O₄ in the composites had little effect on the crystallinity of the final products and all of them presented the three main characteristic peaks centered at 31.2°, 36.8° and 59.3° corresponding to the (220), (311) and (511) lattice planes of the standard Co₃O₄ (JCPDS card No. 43-1003), respectively. Meanwhile, with the increasing amount of CMK-3 in the composites, the characteristic broad peak of CMK-3 in the range of 20-25° can be observed, especially the composites with 15 and 20 mg CMK-3.

The thermal behavior of the as-synthesized CMK-3 and the $Co_3O_4@CMK-3$ composites with different component ratios was investigated through thermogravimetric (TG) analysis (Figure 3B). For the pure CMK-3, very limited and andante decomposition occurred before 500 °C followed by a dramatic decrease in the weight loss between 500-700 °C, which is attributed to the oxidation of the amorphous carbon consist in the CMK-3. Finally the decomposition nearly finished and the curve kept stabilized after 700 °C with little residual component that might come from the remaining SiO₂ during the synthesis of CMK-3. The existence of Si in the component was verified by our subsequent XPS measurement. In the other four

Co₃O₄@CMK-3 composites, the weight loss increased regularly with the increasing addition of CMK-3. In the case of the Co₃O₄@CMK-3 composites with 15 mg CMK-3 templates, a sharply declining (56% by weight) appeared at 500 °C, which can be assigned to the oxidation of the CMK-3. Thus the high interfacial area contact can accelerate the oxidation rate of the C that directly combines with the interfacial oxygen from the oxide, which is between the NSs oxide and the MP CMK-3. After the temperature increased to 800 °C, the Co₃O₄@CMK-3 shows a total weight loss of 65.8% thus 34.2% of the Co₃O₄ remained in the composite, indicating that it is essential to keep the heat treatment temperature below 500 °C during the preparation process, which could prevent CMK-3 from oxidizing by the oxygen from the oxide. This is also why we hold the calcinations temperature at 400 °C in the manuscript, in order to consume the chemically labile species but not destroy the pore structure of CMK-3.

As depicted in Figure 3C, the nitrogen adsorption –desorption isotherm of CMK-3 and other four Co_3O_4 NSs@CMK-3 composites are both exhibited a Type IV isotherm, which unequivocally confirmed that all of Co_3O_4 @CMK-3 composites are successfully prepared and keeping mesoporous structure of CMK-3. What's more, a pronounced hysteresis loop was presented at both raw CMK-3 and Co_3O_4 @CMK-3 composites in the low relative pressure range of 0.4-0.6, which resulted from their mesoporous structure. After the modification of the Co_3O_4 NSs, the calculated BET surface area increased from 1086 m² g⁻¹ (CMK-3) to 1470 m² g⁻¹ (CO₃O₄@CMK-3 composite derived from 5 mg CMK-3), 1805 m² g⁻¹ (10 mg CMK-

3) and 2396 m² g⁻¹ (15 mg CMK-3), but decreased to 946 m² g⁻¹ (20 mg CMK-3), which clearly demonstrated that a suitable amount of CMK-3 can effectively prevent the Co_3O_4 from aggregating which working as a rigid support for depositing Co_3O_4 NSs and lead to high surface area for the composite. Furthermore, the NSs/MP structure of Co_3O_4 @CMK-3 achieves

larger specific surface area and exhibits excellent effective interfacial contacts area among the three-phases, which is considered to be very beneficial to promote charge transfer and provide more active sites during the ORR. While the mass of CMK-3 rise to 20 mg, the Co_3O_4 layer was self-aggregated and blocked a part of the specific surface areas of CMK-3.



Figure 4. XPS spectra of (A) overall, (B) Co 2p and (C) O 1s of Co₃O₄@CMK-3 composites.

The detailed surface element chemical states of Co₃O₄@CMK-3 composites are further characterized by X-ray photoelectron spectroscopy (XPS) spectroscopy as shown in Figure 4, and all of the XPS spectroscopy was corrected by setting C 1s peak at 284.6 eV.^[13] The full survey spectrum of Co₃O₄@CMK-3 composites (Figure 4A) indicates the presence of O, Co, C, and Si, where the Si (2p) peak comes from the remnant of the SiO₂ during the hard template synthesis process of CMK-3. In Figure 4B, the peaks at binding energies of 779.9 eV and 795.9 eV should be ascribed to the Co^{3+} in $2p_{3/2}$ and 2p_{1/2} states, respectively. Meanwhile, the other two major peaks at 785.6 eV and 802.4 eV can also be attributed to the Co2+ in 2p_{3/2} and 2p_{1/2} states, respectively, suggesting the co-presence of Co³⁺ and Co²⁺ in the sample, and the ratio of Co³⁺: Co²⁺ is about 2 : 1.^[14] This result was further confirmed by our previous XRD analysis. In Figure 4C, the O 1s XPS spectrum was deconvoluted into three photoelectron peaks of 529.5 (Q1), 530.6 (O2) and 531.6 (O3) eV that can be corresponded to the lattice oxygen defect in the spinel Co₃O₄,^[15] the hydroxyl groups and a small amount of adsorbed moisture on the surface, respectively.

The ORR electrocatalytic properties of electrocatalysts were first tested by cyclic voltammetry (CV). As illustrated in Figure 5A, the composite with 15 mg CMK-3 reveals the best ORR performances compared to the other three control samples, due to the big BET surface area. In addition, the higher activity of the electrocatalysts can also be concluded from the larger onset potential (E_{onset}) and peak current (I_{peak}). Lower values of E_{onset} and I_{peak} for the catalysts with 5 mg and 10 mg CMK-3 are due to the fact that a comparatively more Co₃O₄ NSs have partially blocked the active sites of CMK-3, while the less average amount of Co₃O₄ NSs were obtained by using 20 mg templates, which can vastly reduce the catalytic activity. So that the other compared samples were prepared by using 15 mg templates in this paper. As depicted in Figure 5B, the Co₃O₄@CMK-3 shows an ORR E_{onset} of 1.03 V (vs RHE) and a peak potential of 0.90 V, which is more positive than the pure CMK-3 (E_{onset} of 0.84 V and peak potential of 0.75 V), suggesting the Co3O4 NSs can enhance the catalytic activity for ORR. It is worth mentioning that a slight but well-defined backward peak was obtained at CMK-3 electrode around 1.02 V, but was absented at Co₃O₄@CMK-3 electrode. This is powerful evidence that CMK-3 has a gas channel, which does not allow the electrolyte to penetrate and oxygen cannot be consumed due to the sluggish ORR kinetics on the bare CMK-3. However, the Co₃O₄ NSs deposited on the surface of CMK-3 preserves the gas diffusion channels, so as the Co₃O₄ NSs not only fabricates a unique three-phase interface, but also provides ORR with highly active sites. That's to say, one side of the Co₃O₄ NSs exposes to the air transport within the CMK-3, while the other side can fully contact the electrolyte. More importantly, the performance of Co₃O₄@CMK-3 is comparable to that of Pt/C with the same mass (Eonset of 1.01 V and peak potential of 0.90 V).



Figure 5. (A) CVs of Co_3O_4 @CMK-3 electrodes synthesized by using different amount of CMK-3 template. (B) CVs of Co_3O_4 , CMK-3, Co_3O_4 @CMK-3 and Pt/C electrodes.



Figure 6. (A) RDEs of Co₃O₄, CMK-3, NiO@CMK-3, ZnO@CMK-3, Co₃O₄@CMK-3 and Pt/C electrodes (from left to right). (B) RDEs at various rotating rates and Koutecky-Levich plots (inset) of Co₃O₄@CMK-3 electrode (*j* represents the corrected current attributable to O₂). (C) RRDE test of Co₃O₄. CMK-3, Co₃O₄@CMK-3 and Pt/C electrodes. (D) Comparison of electron-transfer number on different electrodes at 0.6 V. Scan rate: 10 mV s⁻¹.

To further evaluate the activity and dynamics property, the as-obtained samples were prepared on rotating disk electrode (RDE) for linear sweep voltammetry (LSV) in an O₂-saturated 0.1 M KOH solution, and the working electrode was rotated at 1600rpm in order to remove the emerging bubbles during the electrochemical measurements. As demonstrated by Figure 6A, both Co₃O₄@CMK-3 and Pt/C show a sharply increasing LSV curve. The Co₃O₄@CMK-3 exhibits an E_{onset} of 0.98 V, a E_{1/2} of 0.80 V and limiting current density of 5.52 mA cm⁻², which is in close proximity to that of Pt/C (Eonset of 0.99 V, E1/2 of 0.81 V and limiting current density of 5.12 mA cm⁻²) and other catalysts in the literature (Table 1). In contrast, the LSV curve from bare CMK-3 shows a relatively slow current increase and negative E_{1/2} of 0.74 V, implying that the pristine CMK-3 mainly occurs in a two-electron-transfer during the ORR process. We also ran a comparison with Co₃O₄@CNTs, Co₃O₄ NSs deposited on the surface of CNTs, which is prepared by the same method shown in this work. As shown, the performance of Co₃O₄@CNTs including Eonset, E1/2, and limiting diffusion current is still far behind the as-prepared Co₃O₄@CMK-3. The superior electrocatalytic performance of Co₃O₄@CMK-3 comes from the NSs/MP structure which could expand the reaction area. More importantly, due to the hollow nature, CNTs possess gas diffusion channels, but the oxygen would be unable to get pass the carbon hollow tubes, resulting in slowly ORR electron transfer process. But in CMK-3, this situation is completely different, oxygen could be lightly passed through gas channels because all pores inside the CMK-3 are connected and at the same time contact with highly active Co₃O₄. The other metal oxide deposited on CMK-3 (ZnO@CMK-3, NiO@CMK-3) was also tested as another control sample. Though having the same formation NSs/MP structure as the Co₃O₄@CMK-3, the ORR catalytic properties of metal oxide@CMK-3 are still behind the

as-prepared Co₃O₄@CMK-3 in terms of E_{onset}, E_{1/2}, and limiting current density, proving the superiority of the surface method for highly active Co₃O₄ depositing on mesoporous carbons (CMK-3) over other transition metal oxide @CMK-3.

Table	1.	Comparison	of	the	ORR	performance	of	various	well-developed
electro	cat	alysts in the lit	tera	ture					

Catalysts	E _{onset} vs. RHE (V)	E _{1/2} vs. RHE(V)	Limiting current density (mA cm ⁻²)	Ref
Co ₃ O ₄ @CMK-3	0.98	0.80	5.52	This work
Co@Co ₃ O ₄ /NC- 1	0.92	0.80	4.50	[16]
Fe/Fe ₂ O ₃ @Fe- N-C-1000	0.88	0.75	6.41	[17]
N-Co ₉ S ₈ /G	0.94	-	6.00	[18]
Co ₃ O ₄ /N-rmGO	0.94	-	3.36	[19]
NC@Co-NGC DSNC	0.92	0.82	5.30	[20]
ZnCo ₂ O ₄ /N-CNT	0.95	0.87	3.00	[21]
N,S-CN	0.89	0.74	4.30	[22]
Mo-Doped MCG	0.74	-	2.79	[23]
WN/N-carbon black hybrids	0.80	-	2.70	[24]
GNPC	0.92	-	5.20	[25]

The LSV curve of Co₃O₄@CMK-3 at various rotating rates is obtained, as shown in Figure 6B. The current density increases with the acceleration of rotation rates, which can be ascribed to the thinning diffusion layer, indicating that the NSs/MP structure is expected to increase charge transfer. In addition, the Koutecky-Levich (K-L) equations could be used to calculate the kinetic parameter of electron-transfer numbers (n). As seen from the inset picture in Figure 6B, the good linearity of the K-L plots indicates the first-order reaction kinetics toward the consumption of O2. [26] Dramatically, similar n value was calculated to be about 3.91 by analyzing the slopes of the K-L plots at the potential range of 0.55-0.70 V, indicating that the $Co_3O_4@CMK\mathchar`-3$ composite favours a four-electron-transfer reduction during the ORR process, which is remarkably similar to that catalyzed by the commercial Pt/C catalyst (n= 4.0, LSV polarization curves seen in Figure S3), while n in the other cases is 1.2, 2.5, 2and 2.9, 3.1 for Co₃O₄, CMK-3, ZnO@CMK-3, NiO@CMK-3, and Co₃O₄@CNTs, respectively (Figure 6D, LSV polarization curves seen in Figure S4,S5).

This was further confirmed by RRDE measurement which monitors the intermediate of peroxide species (HO₂⁻) produced during the ORR process. The ring and disk currents were recorded in Figure 6C which shows a more direct reaction pathway of $Co_3O_4@CMK-3$ compared to other catalysts. The

result shows that both $Co_3O_4@CMK-3$ and Pt/C exhibit negligible HO₂⁻ yields. This result is in close agreement with the analysis of the K–L plots, verifying a mainly 4e reduction of $Co_3O_4@CMK-3$ for ORR. We also compare the bare CMK-3 catalyst, in which the average HO₂⁻ yield value is much higher than that of $Co_3O_4@CMK-3$ during the same potential range. This strongly suggests that the ORR active sites of our catalyst originate from the Co_3O_4 . The advantages of $Co_3O_4@CMK-3$ for ORR could be concluded as following: 1. The $Co_3O_4@CMK-3$ possess the NSs/MP structure which could provide more threephase interfacial areas for ORR. 2. The composite of Co_3O_4 NSs and heat-treatment CMK-3 provide lager BET surface area, sufficient active sites and good conductivity, reflecting in better ORR catalysis performance.



Figure 7. (A) Long-term stability test; (B) Methanol tolerance test of $Co_3O_4@CMK-3$ and Pt/C by chronoamperometry. All chronoamperometric tests were conducted at -0.35 V (vs Ag/AgCl) in O_2 -saturated 0.1 M KOH. The stability test was operated at a rotation rate of 1600 rpm.

Finally, long-term durability is used to evaluate the oxygen reduction performance which is also a significant factor for their practical application in metal-air batteries or fuel cells. The chronoamperometry curves of $Co_3O_4@CMK-3$ and Pt/C at a constant potential of 0.35 V (vs Ag/AgCl) were shown in Figure 7A, obviously, the $Co_3O_4@CMK-3$ possesses superior stability with a more slight current attenuation of 10% after 10 h of continuous electrolysis, compared to the Pt/C that manifested a current decay of 36%, this current declining was attributed to the active species peeled off during the oxygen reduction reaction. More importantly, like other Pt-free catalyst, $Co_3O_4@CMK-3$ shows stronger tolerant to methanol, in contrast to Pt/C (Figure 7B), which is a crucial property for fuel cells which employ methanol. This indicated that the long-term stability of $Co_3O_4@CMK-3$ is better than that of Pt/C.

The above data shows the mechanism for the enhanced electrochemical performance of the $Co_3O_4@CMK-3$ composite. We believe that the high active and unusual Co_3O_4 NSs deposition on the outer wall of the pristine CMK-3 play a significant role in its enhanced catalytic performance for ORR, Furthermore, the unique NSs/MP structure could alleviate the volume expansion and promote the electrons transport from electrode to catalyst during ORR, thus reducing the resistance in the ORR process which could improve the electrochemical performance. More importantly, the direct coverage of Co_3O_4 NSs on CMK-3 enables a strong bonding between Co_3O_4 and CMK-3, leading to excellent ORR stability. And the Co_3O_4 NSs

not only fully contact the electrolyte solution, but also at same time get improved oxygenation because of the interconnected pores in the CMK-3 (see scheme 2), indicating a brilliant ORR catalytic performance.



Scheme 2. Schematic representation of the $Co_3O_4@CMK-3$ structure for catalysis of ORR.

Conclusions

In summary, we have designed catalyst structure of highly active Co_3O_4 NSs couple with MP carbon support (CMK-3), resulting in comparability electrocatalytic activity in comparison to commercially Pt/C (20%) catalyst toward ORR. The Co₃O₄ NSs were vertically grown on the CMK-3 outer surface, rather than inner ordered pores because of the extreme hydrophobicity of CMK-3. This framework includes a highly active Co₃O₄ NSs layer and interconnected oxygen pervasion channels from the CMK-3, ensuring the Co₃O₄ NSs obtain abundant three phase interfacial areas. The electrochemical testing results verify that this unique NSs/MP Co₃O₄@CMK-3 composite possesses excellent electrocatalytic performance for ORR, which is superior to pure CMK-3 and other carbon material-based catalysts. We expect that this simple synthesis methodology for deposition of Co₃O₄ NSs on CMK-3 can be extended to other similar areas.

Experimental Section

Synthesis of materials

The fabrication process for 3D Co₃O₄@CMK-3 is demonstrated in Scheme 1. First, the ordered mesoporous carbon (CMK-3) was obtained by using a soft template method to synthesis the ordered silica template SBA-15, followed by a hard template casting and carbonization process according to the previous literatures.^[27] In a typical synthesis of Co₃O₄@CMK-3, 15 mg CMK-3 templates were first dispersed into 40 mL of deionized water under ultrasound for 5min at room temperature, and followed by addition of 145 mg Co(NO₃)₂+6H₂O, 35 mg hexamethylenetetramine (HMT) and 6.5 mg citric acid trisodium salt

dehydrate, respectively. After forming homogeneous solution, the resultant solution was transferred into a 100 mL round bottom flask, and keeping at 90 °C for 6 h with magnetically stirring in an oil bath. After that, the flask was cooled down to room temperature naturally and then the mixtures were washed via centrifugation at 8000 rpm for 5min with methanol for several times, and the obtained product was dried at 60°C overnight. Finally, the as-prepared product was further pyrolysis treatment at 400°C for 2 h at a temperature increase rate of 1°C min⁻¹ in Ar atmosphere. For comparison, the aggregated Co₃O₄ NSs, ZnO@CMK-3, NiO@CMK-3 and Co₃O₄@CNTs were synthesized via a similar procedure except for without addition of CMK-3, using Zn(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O replace of Co(NO₃)₂·6H₂O and using CNTs replace of CMK-3. Moreover, a series of Co₃O₄@CMK-3 composites were also prepared by adjusting the amounts of CMK-3 templates for comparison.

Physicochemical Characterization

The XRD measurement was carried out by X-ray difraction (Rigaku-TTRIII, Cu Ka, I =0.154056 nm). The morphology of products was obtained by field emission scanning electron microscopy (SEM,TESCAN MIRA3 LMU) and microstructure was observed through transmission electron microscopy (TEM, Titan G2 6020) which is equipped with energy dispersive X-ray spectrometry (EDS) to examine the homogeneity of the C, N, O, S, Fe and Co in the product. X-ray photoelectron spectra (XPS) were acquired on an ESCSLAB MK II X-ray photoelectron spectrometer with Mg K α as the excitation source. The Brunauer-Emmett-Teller (BET) surface area and pore volume were measured by using an automatic volumetric adsorption equipment of Mircomeritics ASAP2010. Thermo gravimetric analysis (Perkin-Elmer TGA 7) was carried out under a flow of air with a temperature ramp of 10 °C/min from room temperature to 800 °C.

Electrochemical measurements

The ORR performances were studied on a standard three electrode system working in Solartron1470E electrochemical workstation. A Pt wire and an Ag/AgCI (3 M KCI) electrode served as the counter electrode and the reference electrode, respectively. The working electrodes were prepared as follows: All catalysts inks with the concentration of 4 mg mL⁻¹ were prepared by dispersing 4 mg catalyst in 750 µL ethanol, 215 µL water, 35 µL Nafion solution (5 wt.%, Alfa Aesar), followed by ultrasonic treatment for 0.5 h. Then, the resulting $10\mu L$ homogeneous suspensions were pipetted onto glassy carbon rotating disk electrode (RDE, PINE, 5 mm in diameter) to achieve electrocatatlysts loading of about 200 $\mu g \mbox{ cm}^{-2}$ The electrodes were then allowed to dry naturally in air. N2-saturated and O2-saturated 0.1 M KOH solutions at room temperature served as the electrolyte for ORR tests. LSV spectra were collected at a scan rate of 5 mV s⁻¹ at various rotation rates of 400-2025 rpm. The overall electron transfer number (n) during a typical ORR process can be calculated according to the slope of Koutecky-Levich equation: [2b, 28]

$$\frac{1}{J} = \frac{1}{J_{K}} + \frac{1}{J_{L}} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_{K}}$$
$$B = 0.2nF(D_{0})^{\frac{2}{3}}v^{-\frac{1}{6}}C_{0}$$

where J stands for the measured current density, n is the number of electrons transferred per oxygen molecule, J_K is the kinetic current density in amperes at a constant potential, J_L refers to the diffusion-limited current density, ω (rpm) is the angular velocity of the disk, C_0 represents for the bulk concentration of O_2 (1.2×10⁻³ mol L⁻¹), F is the Faraday constant (96485 C mol⁻¹), D_0 is the diffusion coefficient of O_2 (1.9×10⁻⁵ cm² s⁻¹) and v is the kinetic viscosity of the electrolyte (1.0×10⁻²)

cm² s⁻¹).^[29]

For rotating-ring-disk electrode (RRDE) measurements, the Pt ring is employed to collect the intermediate products while the glassy carbon disk is the main oxygen reaction place. The ring current and disk current was recorded respectively, while a LSV program was operated on disk electrode at a rate of 5 mV s⁻¹ and a constant potential (0.4 V vs. Ag/AgCl) test was applied on Pt ring. The n and the %HO₂⁻ field were calculated from the equations below:^[30]

$$\%HO_2^- = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

n = 4 × $\frac{I_d}{I_d + I_r/N}$

In the equation, I_d and I_r are corresponding to the ring current and disk current, respectively. N is 0.37 which stands for the current collection efficiency of the Pt ring.^[31]

In the measurements, the reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE) with high purity H₂ saturated 0.1 M KOH electrolyte. The scan rate of linear sweep voltammetry was 1 mV s⁻¹, and the thermodynamic potential of the RHE is calculated according to the average value of the two potentials at which the current crossed zero. In 0.1 M KOH, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.94$ V.

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Keywords: non-noble metal eletrocatalyst •oxygen reduction reaction • metal oxide nanosheets • nanosheets/mosepore

- a) G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* 2011, 332, 443-447; b) C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, *Angewandte Chemie* 2008, 47, 3588-3591; c) Y. Cheng, H. Zhang, C. V. Varanasi, J. Liu, *Scientific reports* 2013, 3, 3195; d) R. Zhang, S. He, Y. Lu, W. Chen, *Journal of Materials Chemistry A* 2015, 3, 3559-3567.
- [2] a) Y. Li, T. Li, M. Yao, S. Liu, *Journal of Materials Chemistry* 2012, 22, 10911; b) W. Niu, L. Li, X. Liu, N. Wang, J. Liu, W. Zhou, Z. Tang, S. Chen, *Journal of the American Chemical Society* 2015, 137, 5555-5562.
- a) D.-W. Wang, D. Su, *Energy & Environmental Science* 2014, 7, 576;
 b) M. Zhang, W. Yuan, B. Yao, C. Li, G. Shi, ACS applied materials & interfaces 2014, 6, 3587-3593.
- [4] a) Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *Journal of the American Chemical Society* **2012**, *134*, 9082-9085; b) M. Sun, H. Liu, Y. Liu, J. Qu, J. Li, *Nanoscale* **2015**, *7*, 1250-1269.
- [5] a) N. I. Andersen, A. Serov, P. Atanassov, Applied Catalysis B: Environmental 2015, 163, 623-627; b) S. Jiang, S. Song, Applied Catalysis B: Environmental 2013, 140-141, 1-8.
- [6] a) Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nature materials* **2011**, *10*, 780-786; b) C. Sun, F. Li, C. Ma, Y. Wang, Y. Ren,

W. Yang, Z. Ma, J. Li, Y. Chen, Y. Kim, L. Chen, *Journal of Materials Chemistry A* **2014**, *2*, 7188.

- a) J. Xiao, L. Wan, X. Wang, Q. Kuang, S. Dong, F. Xiao, S. Wang, Journal of Materials Chemistry A 2014, 2, 3794; b) Y. J. Sa, K. Kwon, J. Y. Cheon, F. Kleitz, S. H. Joo, Journal of Materials Chemistry A 2013, 1, 9992; c) H. W. Liang, W. Wei, Z. S. Wu, X. Feng, K. Mullen, Journal of the American Chemical Society 2013, 135, 16002-16005.
- [8] A. Walcarius, Chemical Society reviews 2013, 42, 4098-4140.
- [9] a) B. Sun, H. Liu, P. Munroe, H. Ahn, G. Wang, Nano Research 2012, 5, 460-469; b) M.-S. Kim, D. Bhattacharjya, B. Fang, D.-S. Yang, T.-S. Bae, J.-S. Yu, Langmuir : the ACS journal of surfaces and colloids 2013, 29, 6754-6761.
- [10] Y.-g. Wang, L. Cheng, F. Li, H.-m. Xiong, Y.-y. Xia, Chemistry of Materials 2007, 19, 2095-2101.
- [11] N.-I. Kim, J. Y. Cheon, J. H. Kim, J. Seong, J.-Y. Park, S. H. Joo, K. Kwon, *Carbon* 2014, 72, 354-364.
- a) M.-Y. Cheng, B.-J. Hwang, *Journal of Power Sources* 2010, 195, 4977-4983; b) F. Wu, R. Huang, D. Mu, X. Shen, B. Wu, *Journal of Alloys and Compounds* 2014, 585, 783-789.
- [13] Y. Chu, J. Feng, Y. Qian, S. Xiong, RSC Advances 2015, 5, 40899-40906.
- [14] J. Li, Z. Zhou, K. Liu, F. Li, Z. Peng, Y. Tang, H. Wang, *Journal of Power Sources* 2017, 343, 30-38.
- [15] S. Xiong, J. S. Chen, X. W. Lou, H. C. Zeng, Advanced Functional Materials 2012, 22, 861-871.
- [16] A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A. J. R. Botz, R. A. Fischer, W. Schuhmann, M. Muhler, *Angewandte Chemie International Edition* **2016**, *55*, 4087-4091.
- [17] Y. Zang, H. Zhang, X. Zhang, R. Liu, S. Liu, G. Wang, Y. Zhang, H. Zhao, *Nano Research* **2016**, *9*, 2123-2137.
- [18] S. Dou, L. Tao, J. Huo, S. Wang, L. Dai, *Energy & Environmental Science* **2016**, *9*, 1320-1326.

- [19] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nature materials* 2011, *10*, 780.
- [20] S. Liu, Z. Wang, S. Zhou, F. Yu, M. Yu, C.-Y. Chiang, W. Zhou, J. Zhao, J. Qiu, Advanced materials 2017, 29, n/a-n/a.
- [21] Z.-Q. Liu, H. Cheng, N. Li, T. Y. Ma, Y.-Z. Su, Advanced materials 2016, 28, 3777-3784.
- [22] K. Qu, Y. Zheng, S. Dai, S. Z. Qiao, Nano Energy 2016, 19, 373-381.
- [23] Y. Dong, M. Liu, Y. Liu, S. Wang, J. Li, *Journal of Materials Chemistry* A 2015, 3, 19969-19973.
- [24] Y. Dong, J. Li, Chemical communications 2015, 51, 572-575.
- [25] Z. Song, N. Cheng, A. Lushington, X. Sun, Catalysts 2016, 6.
- [26] Z. Wang, S. Xiao, Z. Zhu, X. Long, X. Zheng, X. Lu, S. Yang, ACS applied materials & interfaces 2015, 7, 4048-4055.
- [27] a) L. Zeng, F. Xiao, J. Wang, S. Gao, X. Ding, M. Wei, *Journal of Materials Chemistry* 2012, 22, 14284; b) A. Jahel, C. M. Ghimbeu, L. Monconduit, C. Vix-Guterl, *Advanced Energy Materials* 2014, 4, 1400025.
- [28] J. Zhang, S. Wu, X. Chen, M. Pan, S. Mu, Journal of Power Sources 2014, 271, 522-529.
- [29] a) W. Ding, L. Li, K. Xiong, Y. Wang, W. Li, Y. Nie, S. Chen, X. Qi, Z. Wei, *Journal of the American Chemical Society* 2015, 137, 5414-5420;
 b) L. Lin, Q. Zhu, A. W. Xu, *Journal of the American Chemical Society* 2014, 136, 11027-11033.
- [30] M. Mohamed Jaffer Sadiq, S. Mutyala, J. Mathiyarasu, D. Krishna Bhat, Journal of Electroanalytical Chemistry 2017, 799, 102-110.
- a) D. S. Yang, D. Bhattacharjya, S. Inamdar, J. Park, J. S. Yu, *Journal of the American Chemical Society* 2012, *134*, 16127-16130; b) M. Favaro, L. Ferrighi, G. Fazio, L. Colazzo, C. Di Valentin, C. Durante, F. Sedona, A. Gennaro, S. Agnoli, G. Granozzi, *ACS Catalysis* 2015, *5*, 129-144.

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In this work, we uniformly deposition of Co_3O_4 nanosheets on the backbone of CMK-3. The Co_3O_4 nanosheets not only fully contact the electrolyte solution, but also at same time get improved oxygenation because of the interconnected pores in the CMK-3. And the other metal oxides can also be deposited on the surface of carbon supports.



L. Gan, M. Wang, L. Hu, J. Fang*, Y. Lai, J. Li

Page No. – Page No. Nanosheets/Mesopore Structured Co₃O₄@CMK-3 Composite as Electrocatalyst for Oxygen Reduction Reaction

Layout 2:

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Text for Table of Contents

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Page No. – Page No. Title