Silver nanoparticles encapsulated in N-doped porous carbon matrix as high active catalysts towards oxygen reduction reaction via electron-transferring to outer graphene shells

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1. Experimental Details

Materials Preparation: $Zn(NO_3)_2 \cdot 6H_2O(>99\%)$, AgNO₃(>99.8%) was purchased from Sinopharm Chemical Reagent Co. Ltd (AR grade, China). ,2-Methylimidazole (99%) was purchased from J&K Chemical. Nafion solution (5 wt%) were purchased from Sigma-Aldrich. All reagents were directly used without further treatment.

Preparation of Zn-MOFs nanosheets: The Zn-MOFs nanosheets were prepared at the room temperature, which 0.33g Zn(NO₃)₂·6H₂O and 0.985g 2-Methylimidazole were respectively dissolved in 90ml deionized water to form transparent solution, and then mixed together and magnet stirred for 24 hour. Finally, the Zn-MOFs nanosheets was obtained by vacuum drying after washed with deionized water for 3 times.

Preparation of NC: The powder of Zn-MOFs nanosheets was transferred into a ceramic boat and placed in a tube furnace. The sample was heated to 900 °C with a heating rate of 5 °C min⁻¹ and kept at 900 °C for 3h under flowing nitrogen gas and then naturally cooled to room temperature. The obtained material was directly used without further treatment.

Preparation of Ag doped Zn-MOFs: 100 mg as-prepared Zn-MOFs nanosheets was uniformly dispersed in 20 ml deionized water by continues ultrasonic processing. Followed by injection of 0.7ml, 0.8ml, or 0.9ml AgNO₃ solution (5mg/ml with the solvent of deionized water). The corresponding samples were labeled AgNC-0.7, AgNC-0.8 and AgNC-0.9 respectively. After magnet stirred for 24 hours, the mixture was washed with deionized water for 3 times. Finally, the sample was obtained by vacuum drying and saved under vacuum conditions.

Preparation of Ag@NCs: The power of Ag doped Zn-MOFs was transferred into a ceramic boat and placed in a tube furnace. The sample was heated to 900 °C with a heating rate of 5 °C min⁻¹ and kept at 900 °C for 3h under flowing nitrogen gas and then naturally cooled to room temperature. The obtained material was directly used without further treatment.

2. Materials characterization

The powder X-ray diffraction patterns of the samples were collected on Rigaku D/MAX- γA

with Cu-K α radiation (λ =1.54178 Å). The morphology of as-prepared samples was observed by field emission scanning electron microscope (FESEM) on a JEOL JSM-6700 M scanning electron microscope. Transmission electron microscopy (TEM) images were performed on a Hitachi H7650 transmission electron microscope with an accelerating voltage of 200 kV. XPS was measured on an ESCALAB 250 X-ray photoelectron spectrometer using Al K α radiation. The HAADF STEM images were imaged by using a Titan 80-300 scanning/transmission electron microscope operated at 300 kV, equipped with a probe spherical aberration corrector. TGA was carried out using a Shimadzu-50 thermoanalyser under flowing nitrogen atmosphere and with a heating rate of 10 °C min-1. XPS was performed on an ESCALAB 250 X-ray photoelectron spectrometer using Al Ka radiation. The specific surface area was evaluated at 77 K (Micromeritics ASAP 2020) using the Brunauer–Emmett–Teller (BET) method applied to the adsorption branch. The data was normalized and analyzed using Athena and Artemis software. The background subtraction and normalization procedures were carried out using standard routines with default parameters determined by the Athena software.

3. Electrochemical measurements details

The electrochemical tests were carried out in a three-electrode system on an electrochemical workstation (CHI760E). A glassy carbon (GC) electrode (diameter of 5 mm with surface area of 0.196 cm²) was used as a working electrode, while platinum foil was utilized as the counter electrode. The potential was recorded using Ag/AgCl (3.5 M KCl) electrode as the reference electrode. All of the potentials were 4 calibrated to the reversible hydrogen electrode (RHE) according to Nernst equation. To prepare the working electrode, typically, 4 mg of catalyst and 30µL Nafion solution (Sigma Aldrich, 5 wt %) were dispersed in 1 mL ethanol solution by sonicating for 1 h to form a homogeneous ink. Then 10 µL of the dispersion was loaded onto a glassy carbon electrode (loading 0.2 mg/cm²). Before ORR catalytic activity testing, oxygen was used to purge the 0.1 M KOH solution for 30 min to keep the solution oxygen saturation. Before Cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) tests, the working electrodes were activated using CV test at a scan rate of 100 mV s⁻¹ for several times. The linear sweep voltammetry (LSV) were applied at a scan rate of 10 mV s⁻¹. The polarization curves of the ORR was measured from 0.2 to 1.1 V (vs. RHE) at a scan rate of 10 mV s⁻¹ with a series of rotating electrode speeds using a MSR Electrode Rotator (Pine Research Instrumentation). The Pt/C (20 wt% Pt) catalyst which is considered to be one of the best ORR electrocatalysts was used as the reference material with the same loading amount. The RDE tests were measured at various rotating speed from 400 to 2025 rpm with a sweep rate of 10 mV·s⁻¹. The electron transfer number (n) was calculated by the slopes of their Koutecky– Levich (K-L) plots' (J⁻¹ vs. w^{-1/2}) linear fit lines from the K-L equation:

$$1/J = 1/J_{K} + 1/J_{L} = 1/J_{K} + 1/Bw^{1/2}$$
(S1)
B = 0.62nFC₀D₀^{2/3}V^{-1/6} (S2)

where J is the measured current density, J_K a

nd J_L are the kinetic-and diffusion limiting current densities, w is the angular velocity, n is transferred electron number, F is the Faraday constant (96485 C mol⁻¹), D₀ is the diffusion coefficient of O₂ (1.9×10-5cm² s⁻¹), C₀ is the bulk concentration of O₂ (1.2×10⁻⁶ mol cm⁻³), V is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹), and k is the electron-transfer rate constant.

4. Computational details

The Vienna Ab-initio Simulation Package (VASP) (Phys. Rev. B 1993, 48, 13115) code has been used for our calculations. This code solves the Kohn-Sham equations of density functional

theory (DFT) using a plane-wave basis set and the projector augmented wave (PAW) method (Phys. Rev. B 1994, 50, 17953). The generalized gradient approximation (GGA) of Perdew–Becke–Ernzerhof (PBE) is used for the exchange-correlation functional (Phys. Rev. Lett. 1996, 77, 3865). Ag (111), Ag (220) and Ag (200) are the most used facet in calculation. From the XRD and HRTEM results in experimental analysis, the most exposed lattice plane is Ag (111). So we build different graphene layers on Ag (111) to observe the change of electrons transfer value from Ag core to graphenes. The Ag (111) slab was represented by four Ag layers constructed from a (2 × 2) unit cell in which the down two layers of the flat surface were fixed. A vacuum equivalent to 15 Å was inserted to avoid the artificial interaction between slabs. To ensure the accuracy of the calculated results, the cutoff energy was set to 400 eV for the plane-wave expansion of the electronic wave function. All structures were optimized with a convergence criterion of 1×10^{-5} eV for the energy and 0.01 eV/Å for the forces. Brillouin-zone integration was performed with $5 \times 5 \times 1$ Monkhorst-Pack grid. The free energies of intermediates are obtained according to previous work using equation:

$\Delta G = \Delta E + \Delta Z P E - T \Delta S + e U$ (S3)

Where ΔE is the binding energy of adsorption species OH*, O* and OOH*, ΔZPE , ΔS and U are the zero point energy changes, entropy changes and applied potentials, respectively. The equilibrium potential U0 for four electron transfer ORR at pH = 14 is determined to be 0.402 V versus NHE or 1.23 V versus RHE according to the Nernst equation (E=E0-0.0591pH). The free energy diagrams of the oxygen reduction reactions (ORR) have been calculated according to the method developed by Nørskov et al (J Phys Chem B 108, 17886-17892 (2004)). In alkaline media (pH = 14), the four-electron ORR pathway could be summarized by the following elementary steps:

$$O_2(g) + H_2O(l) + e^- + * \rightarrow 00H^* + 0H^-$$
 (S4)

$$00H^* + e^- \to 0^* + 0H^-$$
 (S5)

$$0^* + H_2 O(l) + e^- \to OH^* + OH^-$$
 (S6)

$$OH^* + e^- \rightarrow * + OH^-$$
(S7)

Where * stands for an active site on the catalytic surface, (l) and (g) refer to liquid and gas phases, respectively.

For ORR, the onset potential is calculated by:

$$U_{\text{RHE}}^{\text{onset}} = -\max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}$$
(S8)

 $\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4$ wre free energies of reaction barriers of (S1)-(S4) and calculated by:

$$\Delta G_1 = \Delta G_{\rm OOH^*} - 4.92 \tag{S9}$$

$$\Delta G_2 = \Delta G_{0^*} - \Delta G_{00H^*} \tag{S10}$$

$$\Delta G_3 = \Delta G_{\rm OH^*} - \Delta G_{\rm O^*} \tag{S11}$$

$$\Delta G_4 = -\Delta G_{\mathrm{OH}^*} \tag{S12}$$

When U=1.23 V, the ΔG_i (i=1~4) with largest uphill energy barrier value represents the RDS of the models.



Figure S1 Field emission scanning electron microscopy (SEM) images of a) Zn-MOF precursors; b) 0.7-Ag/Zn-MOF; c) 0.9-Ag/Zn-MOF.



Figure S2 Transmission electron microscopy (TEM) image of a) NC; b) Ag@NC-0.7; c) Ag@NC-0.8; d) Ag@NC-0.9.



Figure S3 a-h) Representative high-resolution transmission electron microscopy (HRTEM) images of Ag@NC-0.8; i) Carbon shell thickness statistics of the carbon shells around metal nanoparticles for Ag@NC-0.8.



Figure S4 XRD pattern of Zn-MOF and other three kind of precursors with different content of Ag.



Figure S5 XRD patterns of Ag@NC-0.7, Ag@NC-0.8, Ag@NC-0.9.



Figure S6 Thermogravimetric analysis (TGA) curves of a) 0.8 Ag/Zn-MOF and b) Zn-MOF under nitrogen atmosphere.



Figure S7 Infrared radiation (IR) spectroscopy of a) Ag@NC-0.8 and b) 0.8 Ag/Zn-MOF.



Figure S8 Pore size distribution curves of Ag@NC-0.8 and NC.



Figure S9 a) Nitrogen adsorption and desorption isotherm and b) pore size distribution curves of Ag@NC-0.7.



Figure S10 a) Nitrogen adsorption and desorption isotherm and b) pore size distribution curves of Ag@NC-0.9.



Figure S11 XPS spectrum of N 1s of NC.



Figure S12 XPS spectrum of a) N 1s and b) Ag 3d of Ag@NC-0.7.



Figure S13 XPS spectrum of a) N 1s and b) Ag 3d of Ag@NC-0.9.



Figure S14 XPS survey of a) NC b) Ag@NC-0.7 c) Ag@NC-0.8 d) Ag@NC-0.9.



Figure S15 CV curves of a) 20wt% Pt/C, Ag@NC-0.8 b) Ag@NC-0.7 c) Ag@NC-0.9 d) Pure NC

in O₂-saturated 0.1 M KOH.



Figure S16 a) RDE polarization curves of pure a)NC b) Ag@NC-0.7 c) Ag@NC-0.9 d) 20wt% Pt/C of different rotations rates varies from 400 to 2025 rpm and Electron-transfer number obtained from the Koutecký–Levich (K-L) equation.



Figure S17 RRDE curves of Ag@NC-0.8 and 20wt% Pt/C.



Figure S18 The TEM images, XRD, and XPS data of Ag@NC-0.8 after durability test of 5000 cycles have been added in the supporting information.



Fig. S19. DFT calculated models shown with 2*2 cell. (a-d) The profile of interface at one to four layers graphitic carbon shell wrapped Ag core.

Table S1 Chemical compositions of Ag@NC-0.7, Ag@NC-0.8, Ag@NC-0.9 by Inductively Coupled Plasma-Atomic Emission Spectrometry.

Samples	Content of Ag (wt %)	Content of Zn (wt %)
Ag@NC-0.7	9.29	6.82
Ag@NC-0.8	13.65	4.06
Ag@NC-0.9	17.75	4.37

Table S2 Summary of the specific surface area, pore volume, pore diameter, micropore area, micropore volume and external surface area of various samples.

685.4031	770.0950	704.5300
0.16	0.21	0.29
6.81	6.04	7.86
4 536.3166	569.8430	493.2865
0.262517	0.278215	0.241025
149.0865	200.2520	211.2435
	0.16 6.81 4 536.3166 7 0.262517 149.0865	0.16 0.21 6.81 6.04 4 536.3166 569.8430 7 0.262517 0.278215 149.0865 200.2520

Table S3 Compariso	n of different form of	nitrogen of differen	nt samples by XPS n	neasurement.
Samples	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N

Ag@NC-0.7	26.7%	27.0%	46.3%	0
Ag@NC-0.8	39.3%	19.7%	41.0%	0
Ag@NC-0.9	42.7%	12.7%	30.9%	13.7%

Table S4 Comparison of ORR activity between different samples.

Samples	Onset Potential	Half-wave	j at E=0.7 V
	(V vs RHE)	Potential	$(mA cm^{-2})$
		(V vs RHE)	
Ag@NC-0.7	0.973	0.865	5.01
Ag@NC-0.8	1.014	0.904	5.82
Ag@NC-0.9	0.975	0.873	5.72
20wt% Pt/C	0.956	0.834	5.09
NC	0.918	0.760	1.96

Table S5. Bader charge analysis of Ag@C before and after oxygen atom adsorption. The bold values in right two columns represent the charge value of carbon site before and after oxygen atom adsorption.

Atom number	Charge (before adsortion)	Charge (after adsortion)
Ag1	11.0122	11.0096
Ag2	10.9093	10.8772
Ag3	10.9877	10.9877
Ag4	10.9847	11.0011
Ag5	11.0122	11.0095
Ag6	10.9093	10.8741
Ag7	10.9877	10.9975
Ag8	10.9848	10.9939
Ag9	11.0123	11.0085
Ag10	10.9093	10.8775
Ag11	10.9877	10.9857
Ag12	10.9846	10.9914
Ag13	11.0119	11.0092
Ag14	10.9093	10.8712
Ag15	10.9877	10.9846
Ag16	10.9849	10.9667
C1	4.0343	4.0199
C2	4.0718	4.0599
C3	4.0343	4.0875
C4	4.0718	4.0099
C5	4.0344	4.019
C6	4.0717	4.1416
C7	4.0345	2.9773

C8	4.0717	4.1931
О	/	7.0463

Table S6. Bader charge analysis of Ag@2C before and after oxygen atom adsorption. The bold values in right two columns represent the charge value at adsorbed site before and after oxygen atom adsorption.

Atom number	Charge (before adsortion)	Charge (after adsortion)
Agl	10.9952	11.0113
Ag2	10.9303	10.9309
Ag3	10.9967	10.9876
Ag4	10.997	10.9934
Ag5	11.0311	11.0133
Ag6	10.9189	10.929
Ag7	10.9886	10.9864
Ag8	10.9817	10.9845
Ag9	10.9921	11.0075
Ag10	10.9397	10.931
Ag11	10.9876	10.9875
Ag12	10.9807	10.9861
Ag13	11.0317	11.0018
Ag14	10.9302	10.9332
Ag15	10.9809	10.9893
Ag16	10.9762	10.9718
C1	4.0593	3.9519
C2	4.0365	4.1007
C3	3.9459	4.1413
C4	4.0437	3.9708
C5	4.0594	4.0286
C6	4.0363	4.1008
C7	3.946	4.0331
C8	4.0436	3.971
С9	4.0591	3.9089
C10	4.0365	4.1007
C11	3.9461	3.995
C12	4.0436	3.9707
C13	4.0593	3.0043
C14	4.0367	4.1009
C15	3.9462	3.9685
C16	4.043	3.9718
0	/	7.0362

Table S7. Bader charge analysis of Ag@3C before and after oxygen atom adsorption. The bold values in right two columns represent the charge value at adsorbed site before and after oxygen atom adsorption.

Atom number	Charge (before adsortion)	Charge (after adsortion)
Agl	11.0356	11.0336
Ag2	10.928	10.9137
Ag3	10.9835	10.9873
Ag4	10.986	10.9849
Ag5	11.0267	11.0116
Ag6	10.9003	10.9137
Ag7	10.9884	10.9871
Ag8	10.9843	10.985
Ag9	11	11.0158
Ag10	10.9327	10.9136
Ag11	10.9834	10.9872
Ag12	10.986	10.9849
Ag13	10.9936	10.9932
Ag14	10.8999	10.9135
Ag15	10.9884	10.9872
Ag16	10.9852	10.9851
C1	4.083	4.0482
C2	4.0579	4.0592
C3	4.0108	4.0471
C4	3.9452	3.946
C5	4.0579	4.0723
C6	3.9443	3.464
C7	4.0488	4.0482
C8	4.0579	4.0588
С9	4.0458	4.0471
C10	3.9452	3.9456
C11	4.0579	4.0777
C12	3.9443	4.0329
C13	4.0831	4.0482
C14	4.0579	4.0592
C15	4.0107	4.0471
C16	3.9452	3.946
C17	4.0579	3.957
C18	3.9443	3.9437
C19	4.0488	4.0482
C20	4.0579	4.0596
C21	4.0463	4.0471
C22	3.9452	3.9458
C23	4.0579	3.4638
C24	3.9443	3.91
0	/	7.0804

Table S8. The Bader charge analysis of Ag@4C before and after oxygen atom adsorption. The bold values in right two columns represent the charge value at adsorbed site before and after oxygen atom

		<u>C1 (0 1) (</u>
Atom number	Charge (before adsortion)	Charge (after adsortion
Agl	11.0119	11.0298
Ag2	10.9382	10.9244
Ag3	10.9839	10.9853
Ag4	10.9662	10.9681
Ag5	11.0314	11.025
Ag6	10.9255	10.9264
Ag7	11.0008	10.9858
Ag8	11.0061	11.0005
Ag9	10.9924	10.9899
Ag10	10.9265	10.9285
Ag11	10.9736	10.9854
Ag12	10.967	10.9732
Ag13	11.0131	10.9882
Ag14	10.9131	10.926
Ag15	10.986	10.9862
Ag16	11.0076	11.0049
C1	4.1062	4.1059
C2	4.0582	4.0573
C3	3.9768	3.9757
C4	3.9452	3.9443
C5	4.0576	4.0576
C6	4.0572	4.0858
C7	3.9441	3.9437
C8	3.9438	3.9139
C9	4.1073	4.1058
C10	4.0574	4.0573
C11	3.9765	3.9758
C12	3.9452	3.9443
C13	4.0575	4.0576
C14	4.057	4.0857
C15	3.944	3.9437
C16	3.9439	3.94
C17	4.1077	4.1058
C18	4.0573	4.0573
C19	3.9764	3.9757
C20	3.9452	3.9443
C21	4.0576	4.0576
C22	4.0575	4.0858
C23	3.944	3.9429
C24	3.9439	3.9151
C25	4.1072	4.1059
C26	4.0574	4.0573

C27	3.9763	3.9758
C28	3.9452	3.9443
C29	4.0576	4.0565
C30	4.0572	3.2069
C31	3.9439	3.9437
C32	3.944	3.914
0	/	6.8888

Table S9. Energy barrier values of each electrons transfer step for calculated models at U=0V (RHE).

Step energy	ΔG_1	ΔG_2	ΔG_3	ΔG_4
barrier (eV)				
Ag@C	-0.867	-2.955	-0.376	-0.722
Ag@2C	-0.473	-2.410	-0.927	-1.110
Ag@3C	-0.477	-4.466	1.131	-1.108
Ag@4C	-0.476	-1.976	-1.360	-1.108
Ag	-0.758	-2.012	-1.360	-0.790
Graphene	0.456	-1.778	-0.848	-2.749
Ideal catalyst	-1.23	-1.23	-1.23	-1.23

Table S10. The binding energy of adsorption species at U=0V (RHE).

Binding	ΔE_{00H*}	ΔE_{0*}	ΔE_{OH*}
energy (eV)			
Ag@C	3.703	1.0475	0.412
Ag@2C	4.097	1.9868	0.80
Ag@3C	4.093	-0.073	0.798
Ag@4C	4.094	2.4179	0.798
Ag	3.812	2.10	0.480
Graphene	3.548	5.0258	2.449
Ideal catalyst	3.34	2.41	0.92