Supplementary Information (SI) for Dalton Transactions.
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Supporting Information

ZnO-templated Hollow Amorphous Carbon: Oxygen Adsorption and Doping Synergy for Enhanced ORR Catalysis

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SEM\TEM Related

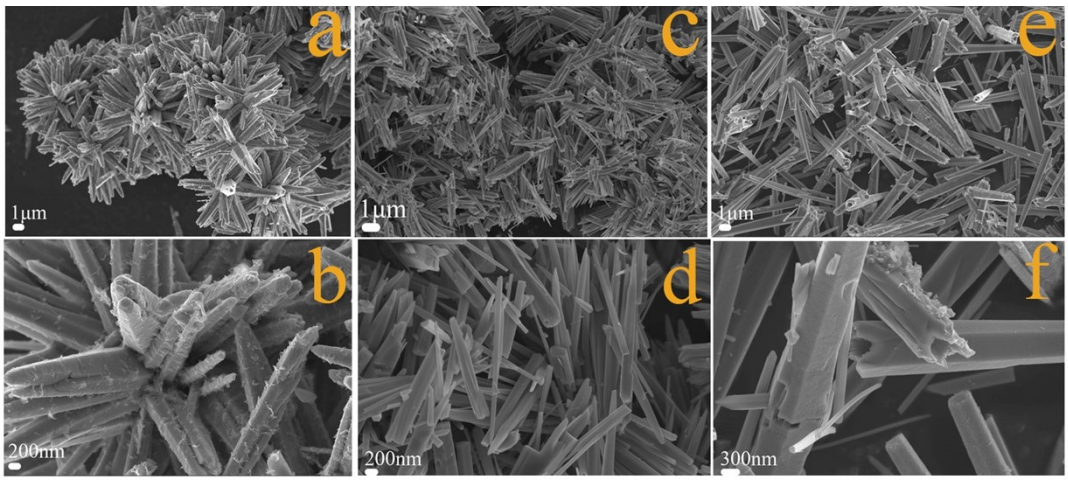

Figure S1. SEM image of ZnO nanomaterials:（a, b）ZnO-8；（c, d）ZnO-12；（e, f）ZnO-14

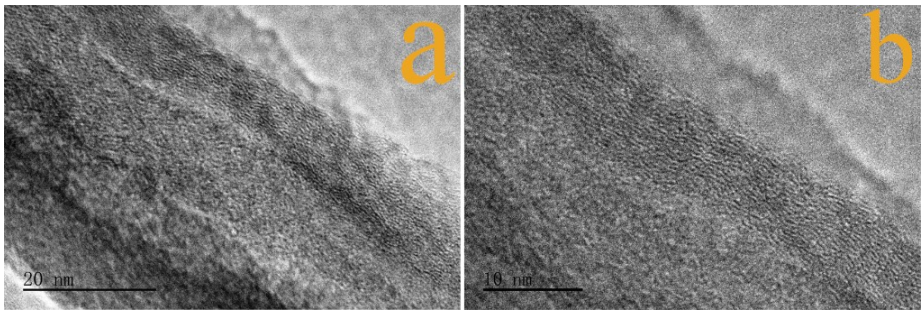

Figure S2. (a, b) HRTEM images of ZIF8/ZnO-12

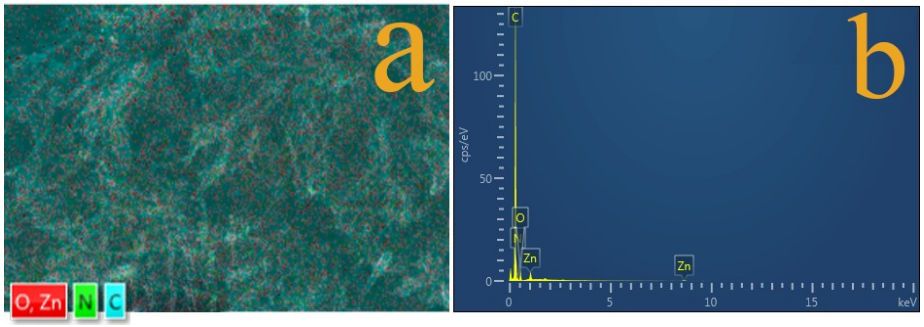

Figure S3. (a) SEM of ZIF8/ZnO-12;(b) EDS spectrums of ZIF8/ZnO-12

Table S1. Element content analysis table of ZIF8/ZnO-12

Element	Line Type	k factor	Apparent concentration	Wt%	Wt% Sigma	Atomic percent
C	K series	0.72334	72.33	90.46	0.15	93.34
N	K series	0.00000	0.00	0.00	0.00	0.00
O	K series	0.01875	2.14	8.30	0.15	6.43
Zn	L series	0.01609	1.61	1.24	0.03	0.23
Total:				100.00		100.00

XPS Related

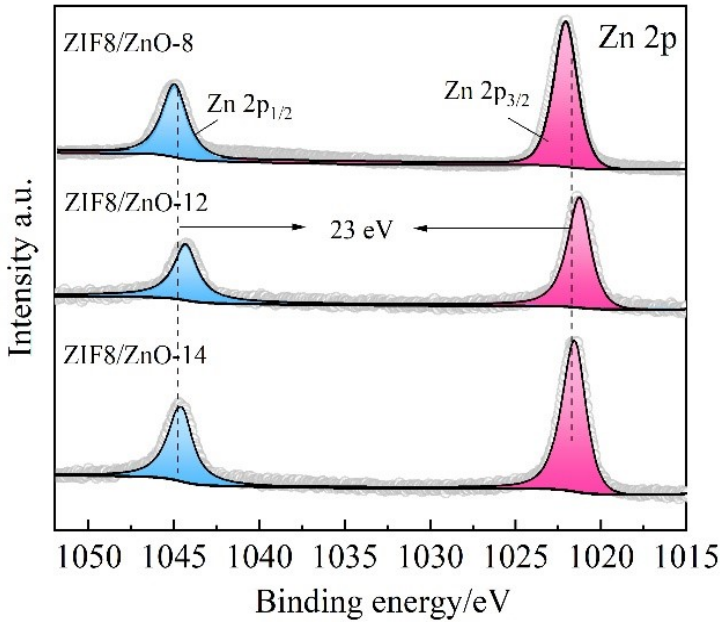

Figure S4. XPS spectrum of Zn2p

ZABs Related

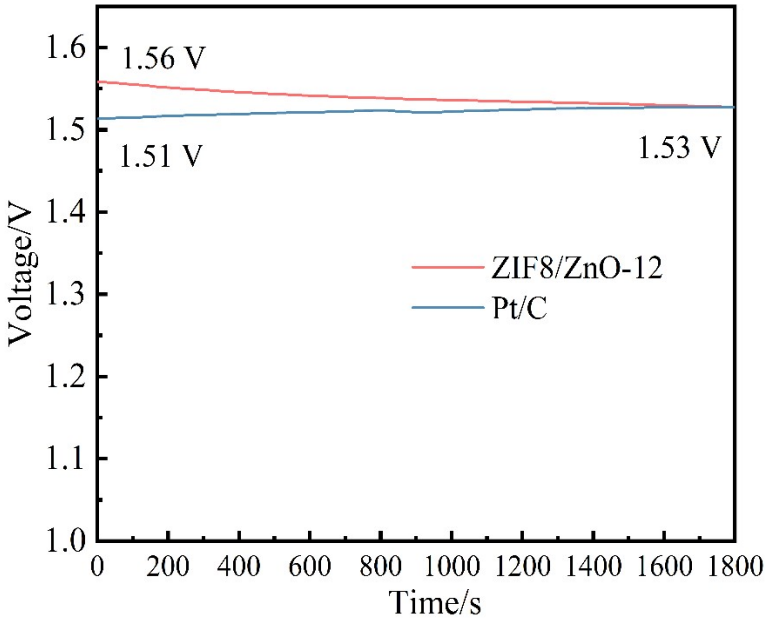

Figure S5. Open circuit voltage test of ZIF8/ZnO-12 and Pt/C

DFT Related

Density functional theory (DFT) calculations were performed using the quantum espresso (QE)[1, 2] based on the pseudopotential plane wave (PPW) method. The perdew-Bueke-Ernzerhof (PBE) functional [3] was used to describe exchange-correlation effects of electrons. We have chosen the projected augmented wave (PAW) potentials [4, 5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a energy cutoff of 400 eV in all relaxation processes. The convergence criteria were set to 10^{-4} eV for the energy and -0.002 eV/Å for the force. The k-point meshes were set of 2 × 3 × 1, 3 × 3 × 1for geometry optimization and electronic self-consistent, respectively. All constructions possess larger than 15 Å vacuum region to minimize the interactions between adjacent image cells[6]. The model is primarily built on a 6×6×1 graphene supercell with pyridinic nitrogen doping. The established model is shown in the figure S6.

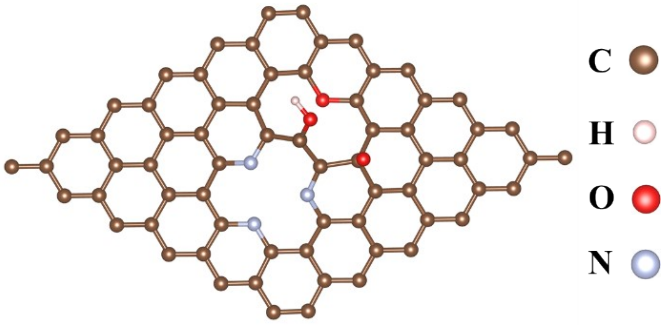

Figure S6. Atomic configuration diagram of doped adsorbed O-combination catalyst

The free energies of reactants and each intermediate state at an applied electrode potential U were calculated as follows: $G(U) = \Delta E + \Delta ZPE - T\Delta S - neU$, where n is the electron number of such state and ΔE represents the change in enthalpy which is considered from the DFT total energy value, ΔZPE represents the change in zero point energy and ΔS represents the change in entropy. Since it is difficult to obtain the exact free energy of OOH, O, and OH radicals in the electrolyte solution, the adsorption free energy ΔG_{OOH*}, ΔG_{O*}, and ΔG_{OH*} are used in the calculations. The equilibrium potential U_0 for ORR was determined to be 0.460 V alkaline media where the reactant and product are at the same energy level. The free energy of $H_2O(l)$ is derived as $G_{H_2O(l)} = G_{H_2O(g)} + RTln(p/p_0)$ since only $G_{H2O(g)}$ can be directly obtained by DFT calculations, where R is the ideal gas constant, T = 298.15K, p = 0.035 bar, and p0 = 1 bar. The free energy of OH^- was derived as $G_{OH^-} = G_{H_2O(l)} - G_{H^+}$, where $G_{H^+} = 1/2\, G_{H_2} - kBTln10 \times pH$. More information about the free energies of reactions can be found in the ref 7[7].

References

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J.Phys.:Condens.Matter, 21 (2009), 395502.

[2] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R.A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N.L. Nguyen, H.V. Nguyen, A. Otero-de-la-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A.P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, Journal of Physics: Condensed Matter, 29 (2017), 465901.

[3] K.B. John P. Perdew, Matthias Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett., 77 (1996) 3865-3868.

[4] P.E. Blöchl, O. Jepsen, O.K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, Physical Review B, 49 (1994) 16223-16233.

[5] G.K.D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, PHYSICAL REVIEW B, 59 (3) (1999) 1758-1775.

[6] Q. Zhang, C. He, J. Huo, Mechanism of complete dehydrogenation of ammonia borane in electrochemical alkaline environment, Computational Materials Science, 207 (2022), 111306.

[7] Y. Jiao, Y. Zheng, M. Jaroniec, S.Z. Qiao, Origin of the Electrocatalytic Oxygen Reduction Activity of Graphene-Based Catalysts: A Roadmap to Achieve the Best Performance, Journal of the American Chemical Society, 136 (2014) 4394-4403.