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Advances in Structural Modulation of Heterogeneous Molecular Catalysts on Carbon Support for Efficient Electrochemical Nitrate Reduction Reaction

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INTRODUCTION

Electrochemical nitrate reduction provides a sustainable way to remove NO_3^-, generating valuable NH_3 under ambient conditions. However, high costs and complex reaction pathways present challenges for its efficiency. Effective NO_3^- electroreduction requires a catalyst that efficiently adsorbs intermediates like $*NO_3$, $*NO_2$, and $*NO$, ideally with low binding energy. Molecular catalysts, characterized by well-defined active sites fully exposed to reactants, enable systematic tuning of catalytic activity and selectivity, crucial for enhancing efficiency in electrocatalysis system. The downsizing of active sites to near-atomic scales maximizes surface-to-core ratios, promoting high turnover frequencies (TOFs) and enabling precise control over catalytic performance Recent advances in heterogenization strategies involve immobilizing molecular catalysts onto solid matrices, such as N-doped carbon and NGQDs, with strong electronic conductivity and a large surface area, which emerge as ideal hosts to enhance catalyst stability and facilitate integration into aqueous electrolytes. This work focused on investigating the immobilization of molecular iron (Fe) and copper (Cu) sites within NGQDs' matrix and single-atom catalyst (SAC), strategically occupying its defective sites that demonstrated exceptional performance in NO_3RR.

STRATEGY & EXPERIMENTAL

SYNTHESIS

- To synthesize Fe SAC, 1000 mg of **g-C_3N_4**, 120 mg **$C_6H_{12}O_6$** and certain amounts of metal salts (006 mmol, corresponding to 24 mg **$Fe(NO_3)_2{\cdot}9H_2O$** were mixed into 40 ml in DIW, ultrasonicated (3h), followed by stirring (24 h), and was further subjected to an evaporation to achieve a dried mixture.
- Then, further ground into a fine powder and treated with a pyrolysis in a tube furnace at 900°C under Ar .
- During electrochemical process, 200 μL of $CuCl_2$ aqueous solution (2 mM in water) was injected stepwise into the KOH solution. The CV polarization curve can reach steady state after 30 cycles, and the resultant powder denoted as Fe SAC-Cu.

RESULTS & DISCUSSION

EVOKING DYNAMIC Fe-Nx ACTIVE SITES via MOLECULAR Fe on NGQDS

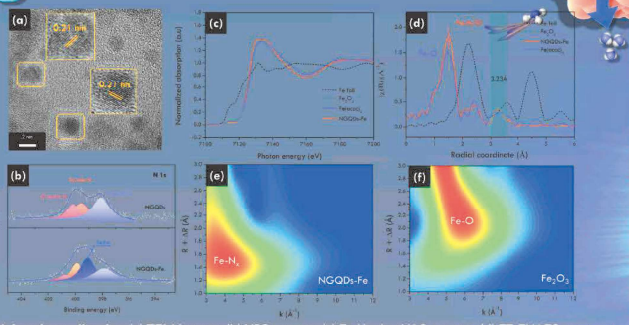

Fig 1. Local coordination. (a) TEM images, (b) XPS spectra, (c) Fe K-edge XAS spectra, (d) FT-EXAFS curves at Fe K-edge of NGQDs-Fe, Wavelet-transformed of the Fe K-edge (e). NGQDs-Fe and (f). Fe_2O_3.

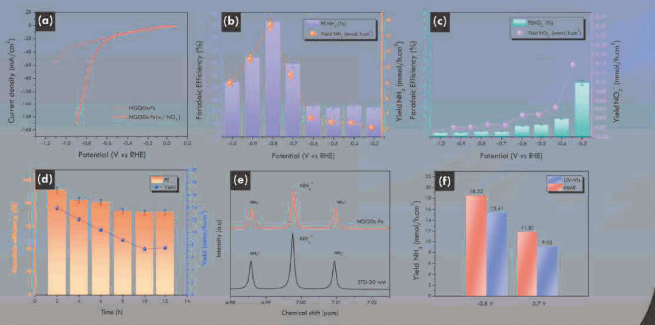

Fig 2. Electrocatalytic NO_3^-RR. (a) LSV curves, (b) NH_3 FE and yield rate (Y_{NH3}), (c). NO_2^- FE and yield rate (Y_{NO2-}), (d) NMR spectra, (e) NH_3 quantification comparison

RESULTS & DISCUSSION

TANDEM ELECTROCATALYST via MOLECULAR Cu on Fe SAC

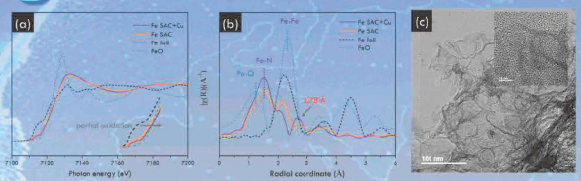

Fig.3. (a) Fe K-edge XAS spectra of Fe SAC-Cu and Fe SAC, (b). FT-EXAFS spectra at Fe K-edge, (c).TEM image

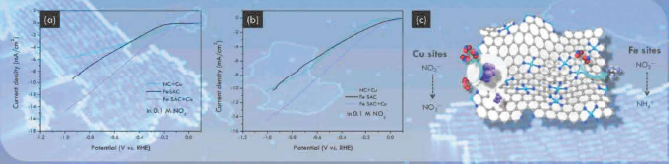

Fig. 4. LSV curves of the NC-Cu, Fe SAC, and Fe SAC-Cu in0.1 M KOH under the presence of (a) 0.1 M NO_3^-, (b). 0.1 M NO_2^-, and (c) Schematic illustration of the reaction pathway using dual Fe-Cu sites.

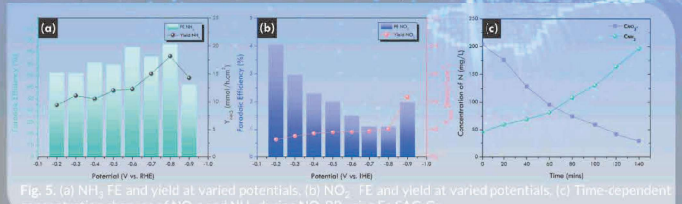

Fig. 5. (a) NH_3 FE and yield at varied potentials, (b) NO_2^- FE and yield at varied potentials, (c) Time-dependent concentration changes of NO_3^- and NH_3 during NO_3RR using Fe SAC-Cu.

Research Experiences

Master Degree (2019-2021): Metal organic framework (MOF)-based and its derivative material for efficient oxygen evolution reaction (OER)
Doctoral Degree (2021-2024): Structural Modulation of Heterogeneous Molecular Catalysts on Carbon Support for Efficient Electrochemical Energy Conversions (OER, NO_3RR)

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REFERENCES

[1] **M. Rinawati**, Y.S. Chiu, L.Y. Chang, C.Y. Chang, W.N. Su, N.L.W. Septiani, B. Yuliarto, W.H. Huang, J.L. Chen, & M.H. Yeh*, *"Evoking the Dynamic Fe-Nx Active Sites through the Immobilization of Molecular Fe Catalyst on N-doped Graphene Quantum Dot for the Efficient Electroreduction of Nitrate to Ammonia"*, J. Mater. Chem. A, 2024,12, 22070-22081.
[2] **M. Rinawati**, L.Y. Chang, C.Y. Chang, M. Rinawati, C.C. Chang, L.Y. Chang, D. Kurniawan, W.H. Chiang, W.N. Su, B. Yuliarto, W.H. Huang, J.L. Chen, & M.H. Yeh*, *"Pioneering molecularly-level Fe sites immobilized on graphene quantum dots as a key activity descriptor in achieving highy efficient oxygen evolution reaction"*, Chemical Engineering Journal, 2024, vol.489, 151436.
[3] **M. Rinawati**, Y.X. Wang, W.H. Huang, Y.T. Wu, Y.S. Cheng, D. Kurniawan, S.C. Haw, W.H. Chiang, & M.H. Yeh*, *"Unraveling the efficiency of heteroatom-doped graphene quantum dots incorporated MOF-derived bimetallic layered double hydroxide towards oxygen evolution reaction"*, Carbon, 2022, vol.200, 437-447
[4] **M. Rinawati**, Y.X. Wang, K.Y. Chen, & M.H. Yeh*, *"Designing a spontaneously deriving NiFe-LDH from bimetallic MOF-74 as an electrocatalyst for oxygen evolution reaction in alkaline solution"*, Chemical Engineering Journal, 2021, vol.423, 130204.