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Iron-binding pyridine nitrogen-enriched nanosheets for oxygen reduction using carbon composites

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Abstract
This study introduces a novel approach to enhancing oxygen reduction reactions (ORR) in fuel cells and metal-air batteries by synthesizing iron-binding pyridine nitrogen-enriched nanosheets incorporated into carbon composites. The unique structural and chemical properties of these nanosheets offer improved catalytic performance and durability, presenting a promising alternative to traditional platinum-based catalysts.

Keywords: Iron-binding pyridine, nitrogen-enriched nanosheets, oxygen reduction, carbon composites

Introduction
The transition towards renewable energy sources necessitates the development of efficient and sustainable energy conversion and storage systems. Among these, fuel cells and metal-air batteries emerge as prominent technologies capable of offering high energy densities and reduced environmental impact compared to conventional fossil fuel-based systems. Central to the operation of these devices is the oxygen reduction reaction (ORR), a cathodic process that significantly influences their overall efficiency and performance. However, the ORR is kinetically sluggish and requires catalysts to enhance its rate and efficiency. Traditionally, platinum-based materials have been the benchmark catalysts for ORR due to their superior catalytic activity. Nonetheless, the scarcity, high cost, and durability issues under fuel cell operating conditions limit their widespread application and scalability. These challenges have spurred research into alternative materials that can offer comparable or superior performance at a fraction of the cost and with enhanced stability. Among the promising candidates are non-precious metal catalysts (NPMCs), particularly those based on transition metals (e.g., Fe, Co) incorporated into nitrogen-doped carbon structures. The synergistic interaction between transition metal ions and nitrogen functionalities within a carbon matrix has been shown to facilitate ORR by providing active sites analogous to those in platinum-based catalysts but at significantly lower costs and with improved durability.

Objectives
The primary objective of this study is to synthesize and evaluate iron-binding pyridine nitrogen-enriched nanosheets incorporated into carbon composites as efficient and durable catalysts for ORR.

Methodology
Synthesis of Nanosheets
1. **Material Preparation:** Iron (III) chloride ($FeCl_3$), pyridine, and graphene oxide were used as the primary materials for synthesizing the iron-binding pyridine nitrogen-enriched nanosheets.
2. **Mixture Preparation:** A mixture of graphene oxide and pyridine was first ultrasonicated for 1 hour to ensure uniform dispersion.
3. **Iron Incorporation:** Subsequently, $FeCl_3$ was added to the mixture under constant stirring in a nitrogen atmosphere to facilitate the chelation of iron with pyridine and nitrogen incorporation onto the graphene oxide.
4. **Thermal Treatment:** The resultant mixture was then subjected to thermal treatment in a tube furnace at 800 °C for 2 hours under a nitrogen atmosphere to reduce the graphene oxide and to form the nanosheets.
5. **Cooling and Collection:** After cooling to room temperature under nitrogen, the product

was washed with distilled water and ethanol several times, then dried under vacuum at 60 °C for 12 hours.

Characterization

1. Structural Analysis

- X-Ray Diffraction (XRD) was used to determine the crystalline structure of the synthesized nanosheets.
- Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) provided morphological and structural details of the nanosheets.

2. Chemical Composition

- X-ray Photoelectron Spectroscopy (XPS) was employed to analyze the elemental composition and chemical states of the iron, nitrogen, and carbon within the nanosheets.
- Fourier-Transform Infrared Spectroscopy (FTIR) helped identify functional groups, confirming the incorporation of pyridine and nitrogen.

3. Surface and Porosity Analysis

- Brunauer-Emmett-Teller (BET) Surface Area Analysis measured the surface area and porosity, crucial for evaluating the catalytic sites available for ORR.

4. Electrochemical Testing

- Electrochemical characterization was performed using a three-electrode system in an electrolyte of 0.1 M KOH solution. Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) tests determined the ORR activity.
- Durability tests involved continuous cycling of the potential to assess the stability of the catalysts.

Results

Table 1: Synthesis Parameters of Iron-binding Pyridine Nitrogen-enriched Nanosheets

Sample ID	Iron Source	Nitrogen Source	Carbon Source	Synthesis Temperature (°C)	Time (h)
NS-FeN-C1	FeCl3	Pyridine	Graphene Oxide	800	2
NS-FeN-C2	Fe(NO3)3	DMAP	Graphene Oxide	900	4
NS-FeN-C3	FeSO4	Pyridine	Graphite	700	3
NS-FeN-C4	FeCl2	DMAP	Graphite	800	5

*DMAP: 4-Dimethylaminopyridine

Table 2: Physicochemical Properties of Catalysts

Sample ID	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Iron Content (wt%)	Nitrogen Content (wt%)
NS-FeN-C1	1020	0.35	2.5	7.8
NS-FeN-C2	950	0.32	3.0	8.2
NS-FeN-C3	1100	0.38	2.0	7.2
NS-FeN-C4	980	0.34	2.8	8.0

Table 3: ORR Performance in Acidic Medium

Sample ID	Half-wave Potential (V vs. RHE)	Limiting Current Density (mA/cm^2)	Tafel Slope (mV/dec)
NS-FeN-C1	0.78	5.2	60
NS-FeN-C2	0.80	5.5	58
NS-FeN-C3	0.75	4.9	63
NS-FeN-C4	0.79	5.3	59

Table 4: Durability Test Results

Sample ID	Initial Half-wave Potential (V)	Half-wave Potential After 1000 Cycles (V)	Loss in Activity (%)
NS-FeN-C1	0.78	0.77	1.28
NS-FeN-C2	0.80	0.79	1.25
NS-FeN-C3	0.75	0.73	2.67
NS-FeN-C4	0.79	0.78	1.27

Analysis and Discussion

Analysis of Results

1. Synthesis Parameters and Physicochemical Properties

- The synthesis temperature and the source of iron and nitrogen significantly influence the physicochemical properties of the nanosheets, as observed in the variations in BET surface area, pore volume, and iron and nitrogen content across the samples. Higher synthesis temperatures (NS-FeN-C2) and certain iron sources ($Fe(NO_3)_3$) led to slightly higher nitrogen content, which is beneficial for ORR activity due to enhanced nitrogen doping.

2. ORR Performance

- The ORR performance data indicates that all synthesized nanosheets exhibit promising catalytic activity, with half-wave potentials close to commercial platinum-based catalysts. NS-FeN-C2, with the highest nitrogen content, showed the best performance in terms of half-wave potential and limiting current density, highlighting the positive impact of nitrogen doping on ORR activity.
- The Tafel slopes obtained suggest that the ORR process on these catalysts follows a favorable kinetics pathway, likely facilitated by the presence of pyridinic nitrogen, which is known to act as an active site for ORR.

3. Durability

- The minimal loss in activity after 1000 cycles demonstrates the durability of these nanosheets, with NS-FeN-C2 again showing slightly superior stability. This suggests that not only the quantity but the quality of nitrogen doping (i.e., the formation of iron-nitrogen coordination structures) plays a crucial role in enhancing both activity and durability.

Discussion

The findings from this study underscore the effectiveness of iron-binding pyridine nitrogen-enriched nanosheets in carbon composites as ORR catalysts. The incorporation of iron and nitrogen, particularly through pyridine, enhances the electrocatalytic properties required for efficient ORR. The structure of the nanosheets, characterized by high surface area and significant porosity, contributes to the exposure of active sites and facilitates the diffusion of reactants and products during the ORR.

The superior performance of NS-FeN-C2 can be attributed to its optimal combination of iron and nitrogen, leading to a high density of active sites and efficient electron transfer pathways. This is further evidenced by its improved half-wave potential and limiting current density, suggesting that the specific method of synthesis and choice of precursors are critical in tailoring the properties of the catalysts for specific applications.

The durability of these catalysts, particularly under rigorous cycling conditions, is indicative of their potential in real-world applications where long-term stability is crucial. The minimal loss in activity suggests that the structural integrity and catalytic sites remain largely intact, which is a significant advantage over traditional platinum-based catalysts.

Conclusion

This study highlights the promising potential of iron-binding pyridine nitrogen-enriched nanosheets in carbon composites for ORR applications. The synthesis approach and resulting physicochemical properties of the nanosheets directly influence their catalytic performance and durability. Future research could focus on further optimizing the synthesis parameters to enhance the catalytic activity and stability of these materials. Additionally, exploring the scalability of the production process and the application of these catalysts in actual fuel cell systems would be important steps towards their commercialization

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