

Stabilizing Cobalt Single Atoms on Nitrogen-Doped Carbon: A Low-Cost Route Toward Green Hydrogen Production

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Resumo/Abstract

RESUMO - Com o interesse cada vez mais crescente em produção de hidrogênio verde, eletrocatalisadores baseados em single-atoms com materiais de carbono altamente eficientes para reação de evolução de hidrogênio (HER) apresentam um papel importante para o desenvolvimento de novas tecnologias. Contudo, a obtenção de um material de carbono altamente condutivo e capaz de estabilizar átomos únicos em sua estrutura ainda apresenta um grande desafio. Neste trabalho, desenvolvemos uma síntese ionotermal de carbono dopado com nitrogênio e posterior coordenação de single-atoms de Co por troca catiônica para obtenção de nanofolhas de Co/NC. Para eletrocatalise de HER, o eletrodo Co/NC-900 apresentou o menor sobrepotencial (-0.0023 V) e cinética reacional mais rápida, com um coeficiente de Tafel de 73 mV dec⁻¹. Este estudo abre um novo caminho para o desenvolvimento de catalisadores sustentáveis de metais não nobres para HER.

Palavras-chave: átomos individuais, catalisadores, reação de evolução de hidrogênio, carbono dopado com nitrogênio.

ABSTRACT - With the growing interest in green hydrogen production, single-atom-based electrocatalysts with highly efficient carbon materials for the hydrogen evolution reaction (HER) play an important role in the development of new technologies. However, obtaining a highly conductive carbon material capable of stabilizing single atoms in its structure still presents a major challenge. In this work, we used ionothermal synthesis of nitrogen-doped carbon and subsequent coordination of single Co atoms by cation exchange to obtain Co/NC nanosheets, which were processed at different calcination temperatures. For HER electrocatalysis, the Co/NC-900 electrode showed the lowest overpotential (-0.0023 V) and fastest reaction kinetics, with a Tafel coefficient of 73 mV dec⁻¹. This study opens a new path for the development of sustainable non-noble metal catalysts for HER.

Keywords: single-atoms, catalysts, hydrogen evolution reaction, N-doped carbon.

Introdução

Hydrogen produced from clean carbon emission sources has been considered an ideal alternative to traditional fossil fuels. Water electrolysis technology offers a renewable route for H₂ production, in which catalysts play a key role in accelerating the reaction kinetics, reducing the energy barrier of the reaction (1). Currently, noble metals such as platinum (Pt) are the most efficient electrocatalysts for the hydrogen evolution reaction (HER). However, the high cost and scarcity of Pt in the environment ultimately limit the large-scale production of electrocatalysts (2). For this reason, the use of non-noble metals and more abundant in nature, has become the focus of research into their electrochemical properties for the production of HER catalysts (3).

Based on these motivations, this work presents a strategy for producing a low-cost electrocatalyst for HER using single Co atoms immobilized on a nitrogen-doped carbon matrix.

Experimental

Synthesis of Co/N-doped carbon materials

N-doped carbon materials (NC) were synthesized by a method recently developed by our group (4), which was inspired by the ionothermal method. Initially, cotton cellulose was mixed with NaCl, and after pulverization, combined with the systematic addition of hydrolyzed collagen. After this step, the mixture was subjected to pyrolysis at 400°C in N_{2(g)} for 2h, with a heating rate of 5°C min⁻¹. To evaluate the material's structural and electrocatalytic characteristics, a pyrolysis at 900°C was also performed for comparative purposes. The obtained NC materials were dispersed in an aqueous solution containing CoCl₂·6H₂O, which was then subjected to an ultrasonic bath for 1 hour. Finally, the obtained material was dried at 100°C.

Electrodes preparation

For electrode preparation, a dispersion method adapted from (5) was used. More precisely, 4 mg of catalyst was added to 1 mL of a mixture containing 40µL of 5wt% Nafion solution, water/isopropanol in a volume ratio of 3:1, and dispersed by ultrasonication for 2 h. Then, 5µL of the suspension was deposited on the glassy carbon electrode surface (GCE) with geometric area of 0.071cm² and allowed to dry at room temperature.

Results and Discussion

High-angle annular dark field scanning TEM (HAADF-STEM) was applied to probe the atomic structure of a single Co cations regarding NC matrix.

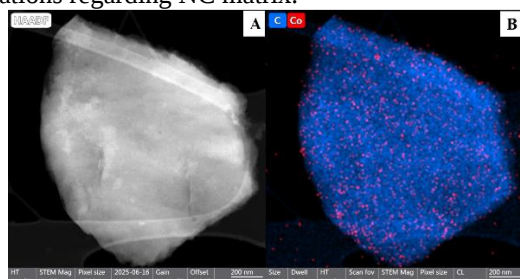


Figure 1. A) HAADF-STEM image of Co/NC-900 material. B) Corresponding EDS elemental mapping image.

Figure 1A show the NC nanosheet structure with a width of about 200 nm. The material's chemical composition is examined by EDS, shown in Figure 1B, where the line scan image confirms the uniform distribution of Co (red) over the surface of the NC network, suggesting that the metal cations are well coordinated and isolated by N-pyridine and N-pyrrole groups in the structure.

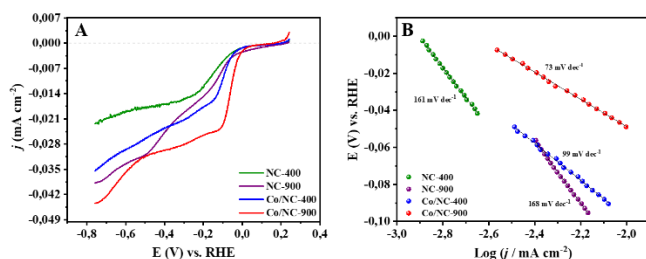


Figure 2. A) Electrocatalytic HER performance of catalysts at a scan rate of 2 mV s⁻¹. B) Corresponding Tafel plots.

For electrochemical HER, the linear sweep voltammetry (LSV) curves of different electrocatalysts (Figure 2A) show that the initial overpotential of Co/NC-900 is -0.0023 V. Meanwhile, the initial overpotentials of Co/NC-400, NC-900, and NC-400 are -0.037, -0.056, and -0.066 V, respectively. The kinetics of HER processes has been further evaluated based on Tafel slopes (Figure 2B). The Tafel slope of Co/NC-900 is 73 mV dec⁻¹, which is smaller than other electrodes. In this case, the HER process of the Co/NC-900 electrocatalysts follows the Volmer–Heyrovsky mechanism, and suggests that the kinetic process of HER at a low potential has enough high active sites and higher conductive structure.

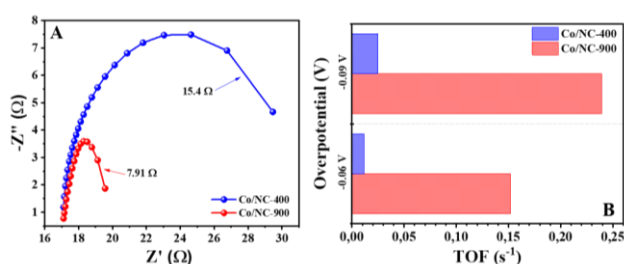


Figure 3: A) Nyquist plots of Co/NC-400 and Co/NC-900 electrodes. B) Corresponding TOFs of electrodes.

Nyquist plots in Figure 3 display that the Co/NC-900 exhibits much smaller resistance than Co/NC-400, suggesting fast electron transfer in the Co/NC-900 electrode/electrolyte interface during the HER process. Turnover Frequency (TOF) is also calculated to further evaluate the enhancement in intrinsic HER activity of electrodes. Specifically, the Co/NC-900 catalyst shows a TOF value of 0.15 s⁻¹ at an overpotential of 60mV, much higher than that of Co/NC-400 (0.012 s⁻¹). In addition, at a relatively large overpotential of 90mV, the TOF of Co/NC-900 can reach 0.24 s⁻¹, which is about 10 times that of Co/NC-400 catalyst.

Conclusions

In summary, benefiting from the synergistic effects of the synthesized material components, the intrinsic activity of the Co/NC catalyst obtained and investigated at temperatures of 400 and 900°C is remarkably improved, which is reflected in the high electrocatalytic activity in relation to HER in alkaline media, with Co/NC-900 standing out against comparative electrodes. In addition, the uniform distribution and spacing of Co atoms in the carbon structure prevents the aggregation of nanoparticles, thus ensuring good single-atom stabilization, corroborating the high TOF value found. This synthesis strategy provided a new approach to increase the efficiency of low-cost electrocatalysts for HER.

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