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Short Communication

Metal-Free COF@CNT Composites as Efficient Electrocatalysts for Overall Water Splitting

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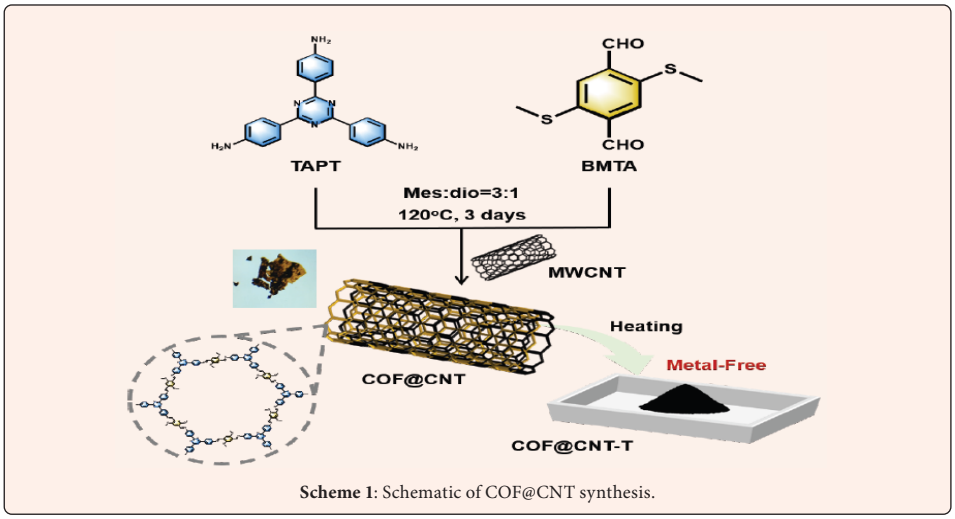
Abstract

There is an urgent need to develop efficient electrocatalysts to promote the conversion and storage of green energy for achieving zero carbon emissions. Covalent organic frameworks (COFs) possess highly porous structures, while carbon nanotubes (CNTs) exhibit excellent stability and conductivity. The combination and synergistic effect of these materials can significantly enhance electrocatalytic performance in water splitting. In this study, a composite of TAPT-BMTA COF and CNT was synthesized and systematically characterized using powder X-ray diffraction, thermogravimetric analysis, and nitrogen adsorption measurements. Furthermore, we investigated the influence of pyrolysis temperature on the electrocatalytic performance by pyrolyzing the COF@CNT composites at various temperatures. The results demonstrated that the COF@CNT-600 sample exhibited superior electrochemical activity, with an OER overpotential of 321 mV and an HER overpotential of 71.6 mV at a current density of 10 mA cm^{-2}.

Introduction

The extensive consumption of fossil fuels leads to substantial carbon dioxide emissions, posing significant environmental challenges. Water splitting for hydrogen production is recognized as a critical bottleneck in the sustainable conversion and storage of renewable electricity generated from solar, wind, and hydropower [1]. To achieve efficient hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), there has been considerable interest in developing electrocatalysts that incorporate inexpensive 3d transition metals, or even metal-free alternatives [2,3].

Covalent organic frameworks (COFs) are a class of materials synthesized from organic monomers linked by covalent bonds, exhibiting significant potential across various applications such as energy storage, [4] gas separation, [5] and electrochemical sensing [6]. This versatility is attributed to their unique, highly ordered porous structure [7,8] and exceptional design flexibility [9]. Moreover, COFs serve as effective metal-free electrocatalysts due to their well-defined skeletal architecture and high porosity, which facilitate synergistic effects in catalytic processes. For instance, the π-π conjugated structure of C4-SHz COF and its rich network of active sites enable rapid electron transfer. Consequently, this material demonstrated an overpotential of 320 mV at a current density of 10 mA cm^{-2}, showcasing excellent OER activity and long-term stability [10]. In another notable example, COF-C_4N represents a novel phenazine-conjugated, two-dimensional COF featuring a graphene-like crystal structure. This material exhibits an ordered crystalline arrangement and demonstrates OER performance with an overpotential of 349 mV at 10 mA cm^{-2} and a Tafel slope of 64 mV dec^{-1} [11]. Additionally, catalytically active functional groups can be incorporated into the framework via condensation reactions or post-synthetic modifications, thereby enhancing its electrocatalytic efficiency. Despite the exceptional porosity of COFs, their inherent conductivity remains relatively low. On this occasion, carbon nanotubes (CNTs), renowned for their exceptional conductivity, have emerged as a prevalent matrix material in electrode applications, finding extensive use in supercapacitors, batteries, and electrocatalysis [12-14]. The integration of covalent organic frameworks (COFs) with CNTs can effectively address the inherent conductivity limitations of COFs. CNTs serve as an efficient electron conductor, and this synergistic combination enhances the overall electrochemical performance. The schematic diagram for synthesizing COF@CNT and subsequent thermal treatment is shown in Scheme 1.



Scheme 1: Schematic of COF@CNT synthesis.

Synthesis Method

TAPT-BMTA COF was prepared using a modified method based on the procedure reported by Ma et al. For the synthesis of COF@CNT, 10 mg of MWCNT, 28.4 mg of 1,3,5-Tris-(4-aminophenyl)triazine (TAPT, 0.08 mmol), and 27.2 mg of 2,5-bis (methylthio) benzaldehyde (BMTA, 0.12 mmol) were added to 35 mL Pyrex tubes. The mixture was then combined with a solvent system consisting of 1,4-dioxane and homotrimethylbenzene in a ratio of 1:3 (v/v), along with 0.4 mL of 6 M acetic acid (AcOH). Subsequently, the tubes were subjected to three freeze-pump-thaw cycles to remove gas. The tubes were sealed and heated at 120°C for 3 days. At the end of the reaction, the product was collected by centrifugation and washed three times with tetrahydrofuran (THF). The COF@CNT was pyrolyzed at 400 °C, 600 °C and 800 °C under nitrogen atmosphere with a heating rate of 5 °C/min, and the obtained electrocatalysts were named COF@CNT-400, COF@CNT-600 and COF@CNT-800, respectively.

Results and Discussion

To confirm the successful synthesis of COF@CNT, PXRD spectra were obtained for both TAPT-BMTA COF and COF@CNT. The results revealed that the diffraction peaks of both samples were aligned, indicating that the synthesized COF@CNT structure matched the expected configuration (Figure 1a). Furthermore, thermogravimetric analysis (TG) was conducted to evaluate the thermal stability of COF@CNT. The data indicated that the framework began to decompose at 419 °C and fully disintegrated by 600 °C, leaving a residual mass of approximately 28% (Figure 1b).

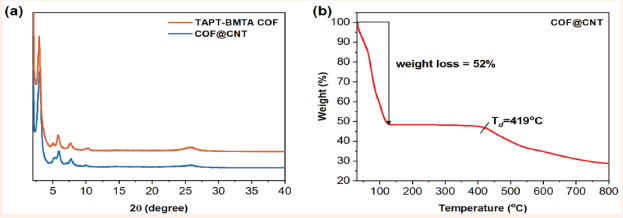


Figure 1: (a) The PXRD of TAPT-BMTA COF and COF@CNT. (b) The TG curve for COF@CNT.

To investigate the pore size of COF@CNT composites, nitrogen adsorption experiments were conducted. The results are presented in Figure 2a. The maximum adsorption capacity reached 462.3 cm^3/g, and the adsorption isotherm exhibited typical Type I characteristics, indicating a well-developed microporous structure. Furthermore, the pore size distribution calculated using density functional theory (DFT) confirmed the presence of micropores ranging from 1 to 2 nm and mesopores ranging from 3 to 5 nm (Figure 2b). These findings suggest that the material possesses a highly porous architecture. Additionally, specific surface area analysis revealed that the BET specific surface area of COF@CNT was 856.0 m^2/g (Figure 2c), while the Langmuir specific surface area was 1320.8 m^2/g (Figure 2d).

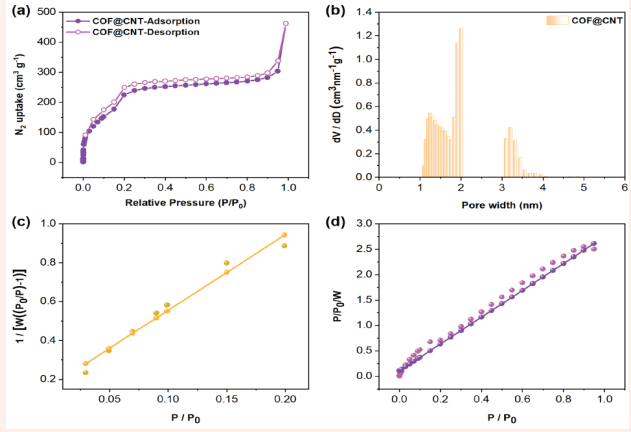


Figure 2: (a) The 77 K N_2 sorption isotherms of activated COF@CNT. (b)The pore size distributions of mesopore and micropore for COF@CNT. (c) The BET and (d) Langmuir fitting curves for the gas sorption isotherms of COF@CNT.

The electrochemical performance tests were conducted using a classical three-electrode system, with nickel foam serving as the working electrode for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) tests in a 1 mol/L KOH solution. Metal free and without pyrolysis COF@CNT exhibited electrocatalytic activity, with an OER overpotential of 337 mV at a current density of 10 mA cm^{-2} (Figure 3a), and corresponding Tafel slope of 77.4 mV/dec (Figure 3b). For the HER test, COF@CNT demonstrated overpotential of 87.4 mV at the same current density (Figure 3c), with corresponding Tafel slope of 110.4 mV/dec (Figure 3d).

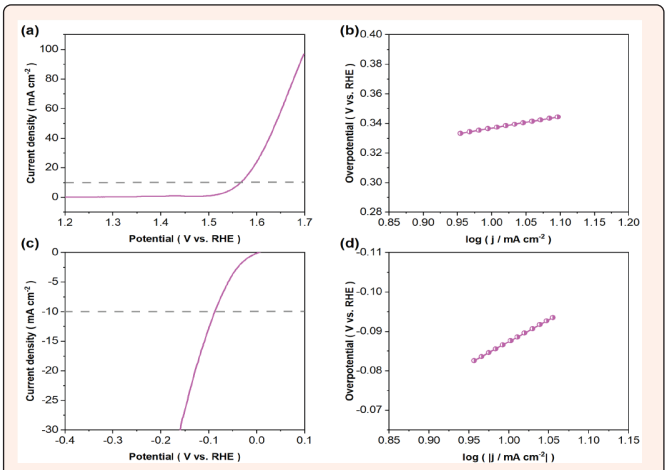


Figure 3: Electrochemical evaluations of different catalysts. The (a) LSV curves and (b) corresponding Tafel curves of different COF@CNT catalysts for OER. The (c) LSV curves and (d) corresponding Tafel curves of different COF@CNT catalysts for HER.

During these tests, the COF@CNT-T samples demonstrated varying electrocatalytic activities depending on the heat treatment temperatures (400 °C, 600 °C, and 800 °C). For the OER test, COF@CNT-400, COF@CNT-600, and COF@CNT-800 exhibited overpotentials of 330 mV, 321 mV, and 325 mV, respectively, at a current density of 10 mA cm^{-2} (Figure 4a), with corresponding Tafel slopes of 73.2 mV/dec, 71.3 mV/dec, and 71.9 mV/dec (Figure 4b). For the HER test, these samples demonstrated overpotentials of 82.1 mV, 71.6 mV, and 79.0 mV, respectively, at the same current density (Figure 4c), accompanied by Tafel slopes of 108.2 mV/dec, 91.4 mV/dec, and 107.2 mV/dec (Figure 4d). In summary, the electrocatalytic performance of the COF@CNT-T samples followed the trend: COF@CNT-600 < COF@CNT-800 < COF@CNT-400 for both OER and HER reactions, with the 600°C-treated sample exhibiting superior electrocatalytic activity.

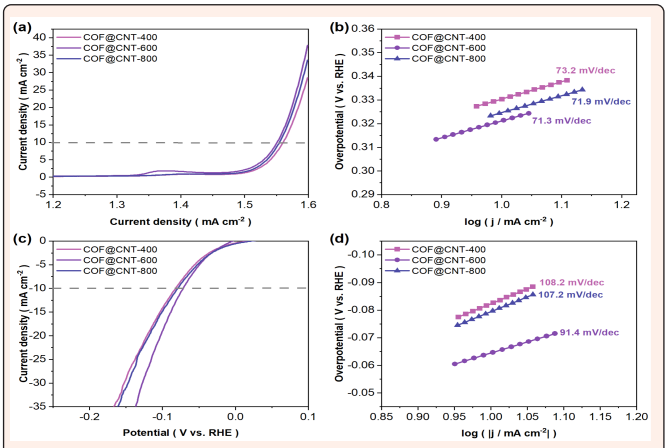


Figure 4: Electrochemical evaluations of different catalysts. The (a) LSV curves and (b) corresponding Tafel curves of different COF@CNT-T catalysts for OER. The (c) LSV curves and (d) corresponding Tafel curves of different COF@CNT-T catalysts for HER.

Conclusion

In summary, the TAPT-BMTA COF and CNT matrix composite was synthesized via a one-pot reaction and subsequently activated at high temperatures ranging from 400 to 800 °C. All the thermally modified COF@CNT-T nanocomposites were confirmed to be effective non-metal electrocatalysts for overall water splitting. The OER overpotential ranged from 321 to 330 mV, while the HER overpotential ranged from 71.6 to 82.1 mV at a current density of 10 mA cm^{-2}. Such performance can be attributed to the synergistic effect between the porous COFs and conductive CNTs, which results in lower overpotentials and Tafel slopes. This study provides a new direction for developing highly efficient metal-free bifunctional electrocatalysts for water splitting in energy conversion applications.

Acknowledgment

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