

Carbon Nanotube as Metal Free Catalyst for 5-Hydroxymethylfurfural Electrooxidation

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Abstract: Carbon materials exhibit promising metal-free catalytic properties in various catalytic processes due to their adjustable physical and chemical characteristics. In this study, we developed a highly active carbon nanotube (CNT) by adjusting the surficial oxygen functionality as a metal-free electrode to mediate the electrooxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA), utilizing TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a co-catalyst. The oxygen-functionalized carbon nanotube (CNT) exhibited good HMF oxidation activity with an onset potential of 1.09 V and good stability of recycling 5 times. A systematic study of the CNT surface was conducted to reveal the mechanism of the HMF oxidation process on the CNT during the reaction. Phenolic groups on the CNT surface were confirmed to be active sites for the reaction; carbonyl groups also contributed to the activity by converting into phenolic groups during the reaction. Carbon shows no valence change during the catalysis process, allowing it to maintain structural stability compared to different metal catalysts. Therefore, carbon materials are promising electrode material for scalable and sustainable applications in the HMF electrochemical oxidation process.

Key words: carbon nanotube; HMF electrooxidation; metal free catalysis; dimensional stability; 2,5-furandicarboxylic acid

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Addressing the global energy crisis remains a paramount challenge for contemporary society and future generations. Central to this endeavor is the efficient inter-conversion between electrical and chemical energy^[1]. Among these processes, electrolytic water splitting is pivotal; however, its efficiency is fundamentally bottlenecked by the sluggish kinetics of the oxygen evolution reaction (OER)^[2-6]. While noble-metal catalysts, particularly Ir and Ru, exhibit high activity and chemical robustness^[7-8], their scarcity and prohibitive cost impede large-scale sustainable deployment. Conversely, although first-row transition metals offer a more abundant alter-

native, their catalytic performance and long-term stability remain insufficient under harsh OER conditions^[9-11].

An emerging strategy to circumvent these limitations is the replacement of OER with more thermodynamically favorable and value-added oxidation reactions. By coupling hydrogen evolution at the cathode with the synthesis of high-value chemicals at the anode, the overall electrolysis potential can be significantly reduced. Such milder oxidative environments not only facilitate the use of earth-abundant transition metals with enhanced stability but also mitigate the degradation of anodic materials. However, a critical challenge asso-

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ciated with this approach is the intrinsically insufficient electrical conductivity of these metals. To address this, carbonaceous scaffolds, such as graphene and multi-walled carbon nanotubes (CNTs), are frequently employed to ensure efficient charge transport^[12-15]. Beyond their role as supports, carbon materials, especially those doped with heteroatoms, have gained prominence as cost-effective, metal-free catalysts due to their environmental compatibility, high specific surface area, and exceptional electron transfer kinetics^[16-22]. Nevertheless, whether serving as active catalysts or conductive supports, the influence of surface functional groups and structural defects is ubiquitous and profound^[23-26]. The intricate nature of these surface properties has led to inconsistent findings in the literature, leaving the precise catalytic mechanisms a subject of ongoing debate.

Traditionally, FDCA is mainly produced *via* oxidation of HMF at elevated temperature (80–150 °C) and pressure (0.3–4.0 MPa) over noble metal-based catalysts (for example, Pt, Au, and Pd)^[27-29]. Despite the well-established methodologies, these processes heavily rely on fossil energy, organic solvents and external oxidants and suffer from severe side reactions like HMF degradation. The electrochemical oxidation of HMF to FDCA presents a promising alternative to the OER in water splitting, offering significant thermodynamic and economic advantages^[30-31]. The substitution of OER ($\Delta G = 474 \text{ kJ} \cdot \text{mol}^{-1}$) with HMF oxidation ($\Delta G = 289 \text{ kJ} \cdot \text{mol}^{-1}$) has attracted increasing attention as it reduces the electrolytic cell voltage and enables substantial energy savings^[32]. This shift not only lowers the energy consumption of hydrogen production but also generates FDCA, a high-value chemical that can substitute petroleum-based terephthalic acid in producing sustainable polymers like polyethylene 2,5-furandicarboxylate^[33-34]. To substitute the OER, anode reaction for HMF oxidation is a six electrons reaction: $\text{HMF} + 6\text{OH}^- \rightarrow \text{FDCA} + 4\text{H}_2\text{O} + 6\text{e}^-$; while for the cathode reaction is still water reduction to hydrogen like in water splitting process: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. The overall reaction produces FDCA at the anode side and H_2 at the cathode side: $\text{HMF} + 2\text{H}_2\text{O} \rightarrow \text{FDCA} + 3\text{H}_2$. The process enables carbon-neutral production of both hydrogen and FDCA, reducing reliance on fossil fuels and minimizing greenhouse gas emissions. Yet the six electrons reaction makes the products more complicated than the OER reaction with different oxidation reaction pathways (Figure 1)^[35-37]. The complicated oxidation process also brings dynamic changes of metal catalysts, leading to decreasing stability. Anyway, the use of biomass-derived HMF further enhances the sustainability profile, creating a closed-loop system that converts renewable resources into high-value chemicals and energy carriers.

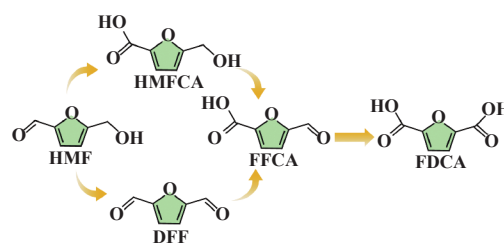


Figure 1 Possible oxidation reaction pathways of HMF to FDCA

Herein, we report the development of highly graphitic carbon nanotubes (CNTs) as an efficient, metal-free electrocatalytic platform for the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation of HMF to FDCA. By systematically tailoring the surface functionality of the CNTs, we aim to decouple the specific contributions of various oxygen-containing groups to the overall catalytic activity. Through a comparative study between clean and oxygen-functionalized CNT (oCNT) surfaces, we demonstrate that the density of surface defects and specific functionalities, rather than the carbon scaffold alone, dictate the HMF oxidation kinetics. This work provides deep insights into the structure-activity relationships of carbonaceous electrodes, offering a scalable and sustainable strategy for the electrochemical upgrading of biomass-derived intermediates.

1 Experimental section

The pristine CNT was treated with mixed nitric and sulfuric acid solution (NSA, 65% nitric acid and 98% sulfuric acid with a volume ratio of 1:1) to introduce oxygen containing functional groups on the CNT surface. In a typical procedure, 10 g pristine CNT was mixed with 500 mL of the acid solution at 105 °C and stirred for 4 h. Resulting nitrous gases were neutralized with $3 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution. Afterwards, the oxidized CNT was filtered and washed thoroughly with flow cell for several hours to remove residual acid and impurities. The CNT was then dried in a drying oven at 100 °C for 20 h, yielding the oxidized CNT powder denoted as oCNT. The electrochemical measurements were conducted in a three electrodes system, which was controlled by using a potentiostat/galvanostat (BioLogic VSP, France). A platinumized Pt wire, an Ag/AgCl electrode, and $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH solution were used as a counter electrode, reference electrode, and electrolyte, respectively. Raman spectra were measured by a Thermo Scientific DXR Raman Microscope with a $50\times$ objective and a 532 nm laser. TEM and HRTEM images were observed with a double Cs-corrected JEOL ARM 200 transmission electron microscope with a cold field emission gun, operated at 200 kV.

2 Results and discussion

In the absence of catalysts, the bare GC electrode, considered a carbon model with minimal surface functionality, exhibited a small oxidation current between 1.35 V and 1.5 V, likely attributed to the oxidation of TEMPO or the onset of OER in the presence of TEMPO, as shown in Figure 2(c). Upon the addition of HMF, an additional current response was observed beyond 1.53 V, suggesting the inherent but limited activity of GC. In contrast, the oCNT sample displayed significantly enhanced electrocatalytic performance, achieving a 400 mV cathodic shift at a current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ compared to GC. The onset potential for HMF oxidation on oCNTs was 1.09 V, notably lower than the theoretical OER potential of 1.23 V. This superior activity is ascribed to the abundant oxygenated functional groups and defective structures on the oCNT surface as confirmed by XPS (Figure 2 (a)–(b)), whereas the GC electrode (treated at 2000 °C) lacks such active sites. The oxygen functionalities on the oCNT surface were further quantified by deconvoluting the high-resolution C 1s and O 1s spectra. The C 1s spectrum was resolved into four constituent peaks: sp^2 -hybridized carbon (Peak I, 284.4 eV), sp^3 -hybridized carbon (Peak II, 284.8 eV), oxygenated carbon species (Peak III, 285.5 eV), and a π - π^* satellite peak (Peak IV, 289.1 eV). The O 1s spectrum was finely deconvoluted into five distinct peaks to identify the chemical environment of the surface oxygen: C=O in quinones (Peak I, 530.5 eV), C=O in ketones or aldehydes (Peak II, 531.7 eV), surface phenolic hydroxyls (Peak III, 532.5 eV), C—O—C in ethers/esters/anhydrides (Peak IV, 533.3 eV), and C—OH in carboxylic acids (Peak V, 534.5 eV). These results demonstrate the abundance of diverse functional groups on the oCNT surface, particularly the high density of surface phenolic and carboxylic species, which have been widely reported as potential active sites in carbon-based metal-free electrocatalysis. Based on our previous work, the oxygen functional groups on the oCNT can be selectively removed at different temperatures: carboxylic group (252 °C), lactone group on zig-zag edge (310 °C), anhydride group (515 °C), lactone group on armchair edge (610 °C), phenol group (800 °C) and carbonyl group (1000 °C). As shown in Figure 2(d), the removal of carboxylic and anhydride groups results in no change in the activity of the CNTs, which indicates that these groups do not contribute to the OER activity. All other groups contribute to the activity to some extent. Considering that anhydride and lactone groups undergo hydrolysis in the alkaline electrolyte into carboxylic and phenolic groups, only carboxylic, phenolic, and carbonyl groups remain during the reaction. It is well known that carbonyl groups can

transform into phenolic groups in the electrolyte. In alkaline media, the phenolic group exists in the C-O^- form, which is assigned as the main active site for HMF electrooxidation.

TEMPO, as a co-catalyst, plays a crucial role in the reaction. As shown in Figure 2(e), without the addition of TEMPO, the onset potential is 1.62 V (vs. RHE), significantly higher than that with TEMPO. Interestingly, the onset potential for HMF oxidation shows no obvious change with varying TEMPO concentrations. To further investigate the electrochemical behavior, we extended the scan potential to 1.95 V (vs. RHE). The CV curves reveal two oxidative processes for measurements involving TEMPO: the first process corresponds to HMF oxidation, while the second is attributed to the OER. The variation in activity occurs during the OER phase, indicating that the influence of TEMPO on carbon for the OER process (shown in Figure 2(f)) is more complex. As the focus of this work is HMF oxidation, this mechanism will be discussed in future studies. Since TEMPO concentration has no obvious influence on the reaction, we consider TEMPO to function as co-catalyst, which might form radicals to activate the HMF before the electrooxidation process.

As illustrated in Figure 1, the electrochemical oxidation of HMF to FDCA can proceed *via* several potential pathways. To elucidate the specific reaction pathway, we performed chronoamperometry (CA) at various potentials (1.36 V, 1.56 V, and 1.76 V) and analyzed the products using high-performance liquid chromatography (HPLC) (Figure 3). At an applied potential of 1.36 V, the oxidation products include HMFCa, FDCA, and FFCA (Figure 3(a)). The catalytic activity at this potential is relatively low, requiring approximately 80 h for complete HMF conversion. HMFCa emerges as the dominant intermediate, indicating that the aldehyde group of HMF is more susceptible to oxidation into a carboxyl group than the hydroxymethyl group. After the HMFCa yield reaches approximately 60%, its concentration plateaus. Meanwhile, the yield of FDCA increases steadily, eventually reaching 25%. Interestingly, the yield of FFCA initially increases but begins to decline after 20 h of oxidation. As shown in Figure 3(b), the charge balance for the products is not closed, suggesting that some electrochemically formed intermediates undergo subsequent chemical transformations. In this context, it is highly probable that the aldehyde groups in FFCA undergo a chemical conversion into other species.

When the potential is increased to 1.56 V, FDCA becomes the predominant product, achieving a 100% yield within 26 h (Figure 3(c)). HMFCa is detected as the primary intermediate, with its concentration peaking within the first 5 h before it is further oxidized to FDCA.

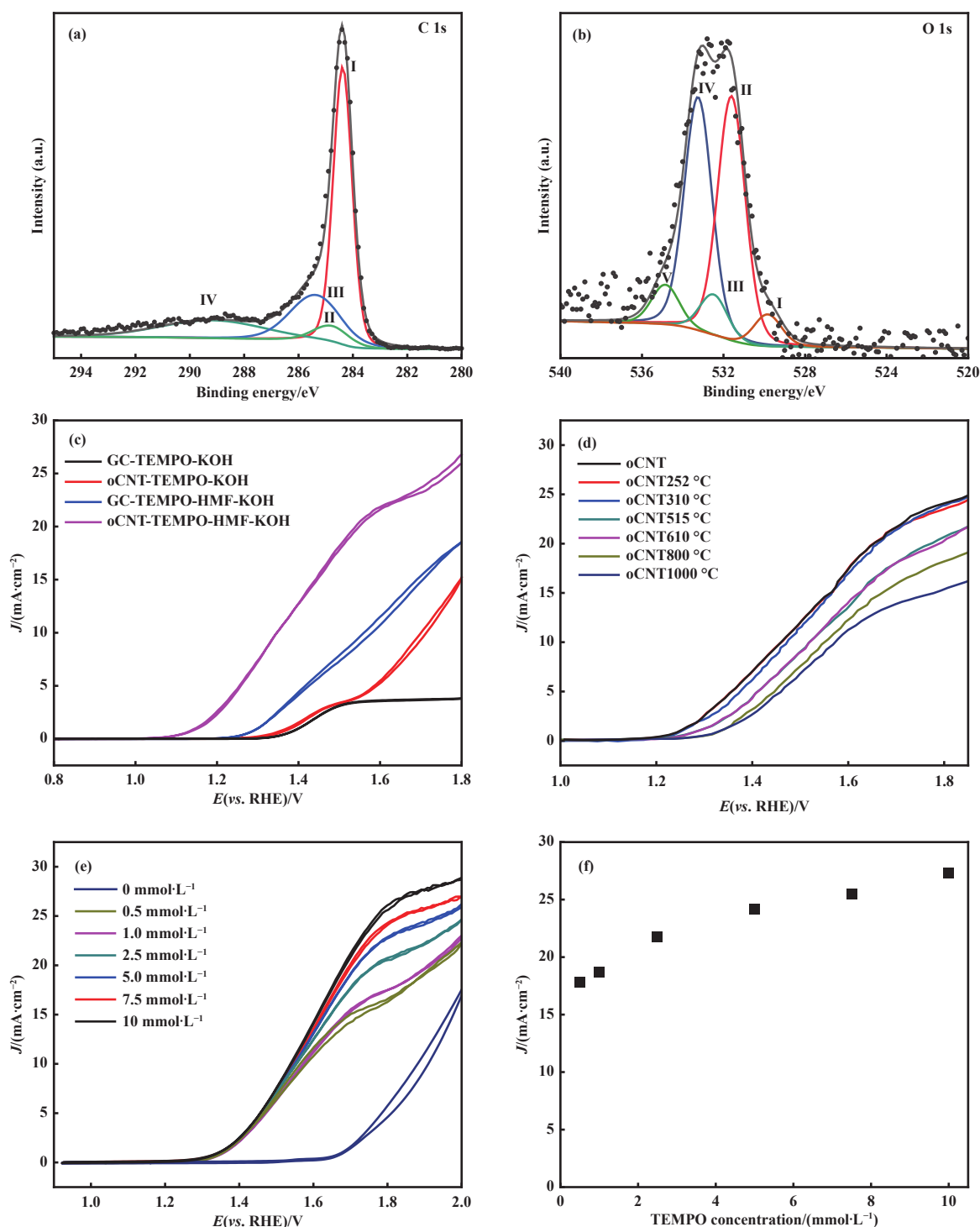


Figure 2 (a) C 1s XPS spectra of oCNT; (b) O 1s XPS spectra of oCNT; (c) Cyclic voltammogram (CV) of the naked electrode GC; (d) CV of different temperature treated oCNT for HMF electrooxidation (number denoted the treated temperature for CNT); (e) CV of the oCNT sample for HMF electrooxidation with different amount of TEMPO; (f) The trend of HMF oxidation activities vs TEMPO concentration

Note: oCNTs with and without TEMPO normalized to the geometric area of the active electrode area. CV is conducted from 1 V to 1.8 V (RHE) at 5 mV·s⁻¹ with automatic iR-compensation using uncompensated resistance (Ru) from electrochemical impedance spectroscopy (EIS). The Ru of the system is determined as 35 Ω for all samples by EIS.

Notably, no FFCA is detected at this higher potential, suggesting that the pathway through the hydroxymethyl group oxidation is bypassed. Instead, both the hydroxy-

methyl and aldehyde groups of HMF are efficiently converted into carboxyl groups. At 1.56 V, the Faradaic efficiency is significantly improved, with the electro-

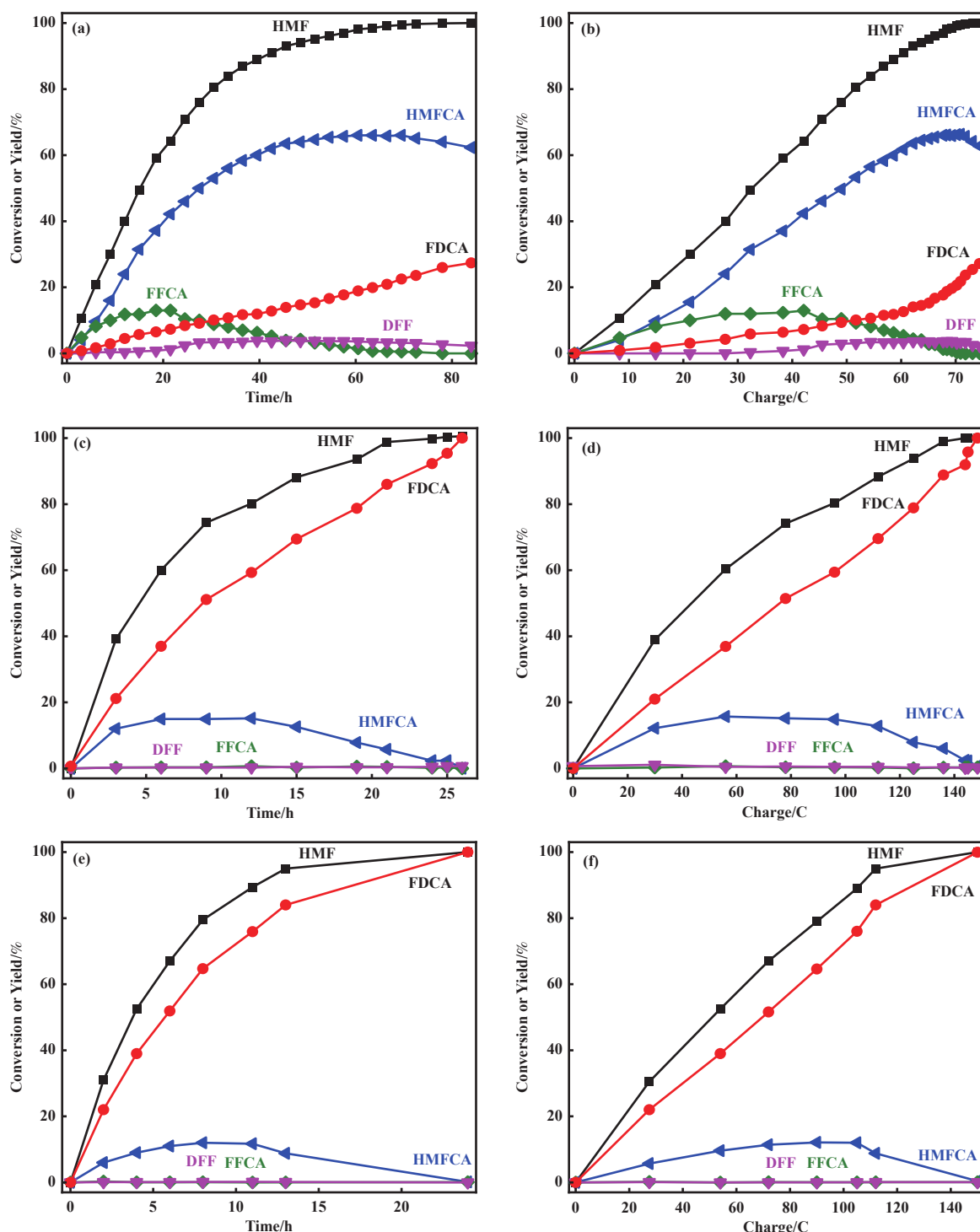


Figure 3 (a) The HMF conversion and products test under CA condition at 1.36 V (vs. RHE); (b) The charge used for the processes at 1.36 V (vs. RHE); (c) The HMF conversion and products test under CA condition at 1.56 V (vs. RHE); (d) The charge used for the processes at 1.56 V (vs. RHE); (e) The HMF conversion and products test under CA condition at 1.76 V (vs. RHE); (f) The charge used for the processes at 1.76 V (vs. RHE)

chemical charge primarily consumed for HMF-to-FDCA conversion (Figure 3(d)). Further increasing the potential to 1.76 V (Figure 3(e)–(f)) accelerates the reaction kinetics, achieving over 90% conversion within 12 h. Similar to the results at 1.56 V, HMFCa remains the only detectable intermediate, while others are present in

negligible amounts. These findings confirm that the oxidation pathway predominantly follows the HMF→HMFCa→FDCA route. The detection of FFCA only at lower potentials, compared to the exclusive presence of HMFCa at higher potentials, may be closely related to the states of the C-O⁻ active sites on the carbon surface at

different polarization levels.

To further elucidate the oxidative behavior of various substrates, we compared their net current densities by subtracting the OER background. As shown in Figure 4(a), the onset potential for HMF is approximately 1.2 V. Two distinct oxidative processes are observed in the net linear sweep voltammetry (LSV) curve, corresponding to the oxidation of the hydroxymethyl and aldehyde groups, respectively. For the HMFCFA sample (Figure 4(b)), the onset potential shifts to 1.3 V, which is attributed to the oxidation of the hydroxymethyl group. By comparing these two substrates, it can be inferred that the earlier onset potential of 1.2 V for HMF originates from the aldehyde group oxidation, indicating that the aldehyde group is more easily oxidized than the hydroxymethyl group on this catalyst. This is further supported by the LSV of DFF (Figure 4(c)), which contains only aldehyde groups and also exhibits an onset potential near 1.2 V. These observations explain why HMF oxidation preferentially avoids the DFF pathway. However, the nature of the substituents on the furan ring introduces complexity to the oxidation behavior. For the FFCA (Figure 4(d)),

the oxidation of the remaining aldehyde group becomes more difficult compared to that in DFF. In summary, for HMF, which contains both hydroxymethyl and aldehyde groups, the oxidation of the aldehyde group dominates, leading to the formation of HMFCFA. This confirms that HMF electrooxidation on oCNTs follows the HMFCFA route rather than the DFF route. The oxidation of the hydroxymethyl group can theoretically produce either aldehyde or carboxyl groups. Since hydroxymethyl oxidation requires a higher overpotential, the resulting aldehyde intermediate is immediately further oxidized to a carboxyl group under these conditions. This explains why FFCA intermediates are negligible at potentials exceeding 1.56 V. As previously discussed, the C-O^- groups on the carbon surface likely facilitate this process. We hypothesize that the C-O^- sites may form $\text{C-O}^\bullet$ radicals, which more readily extract electrons from the more electron-rich aldehyde groups compared to the hydroxymethyl groups.

The catalytic performance of the metal-free oCNT catalyst is promising, however, long-term stability is a critical parameter for potential scaling and industrial

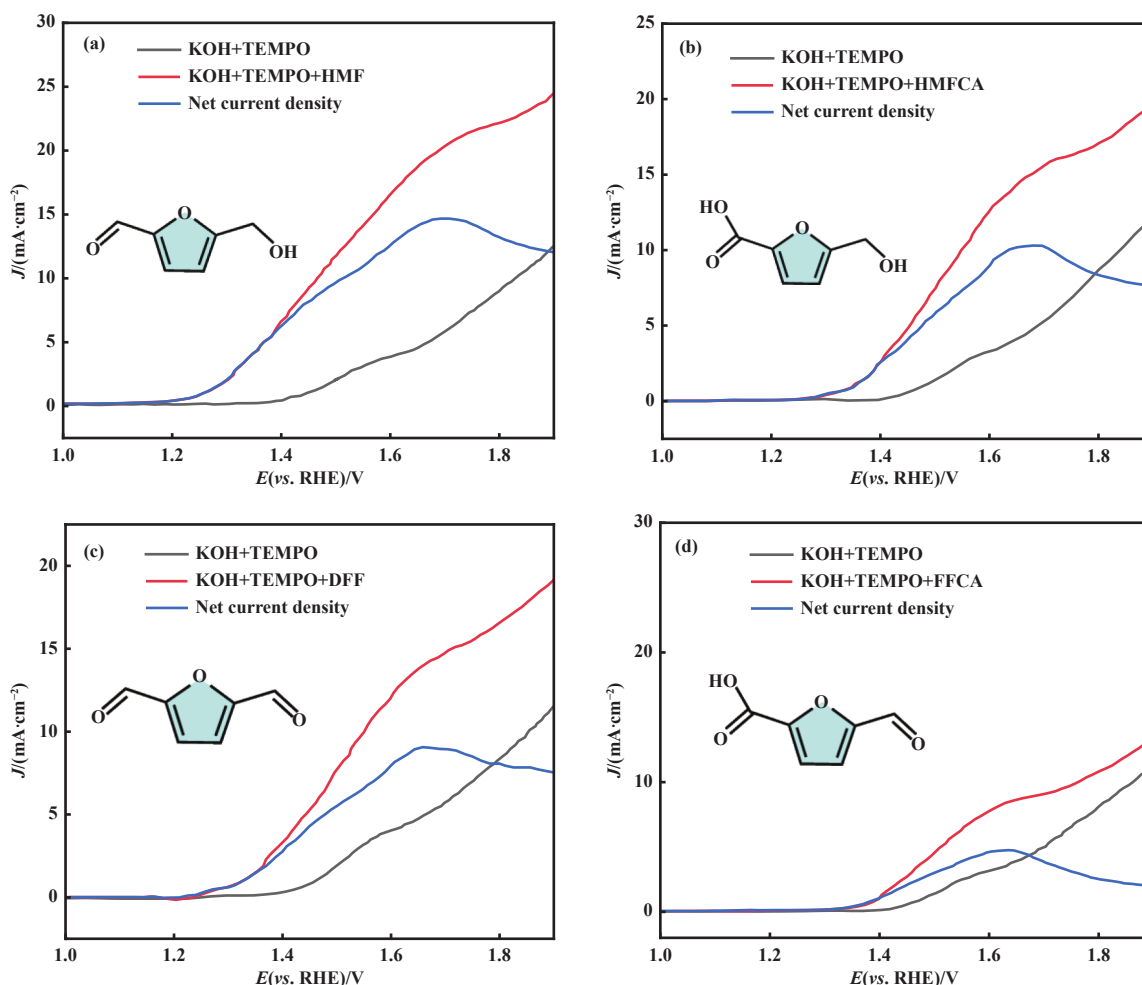


Figure 4 LSV curves and their net current density by subtracting the LSV curve of OER process at same condition: (a) HMF, (b) HMFCFA, (c) DFF, and (d) FFCA

applications. In this section, we evaluate the electrochemical stability of the oCNT catalyst at a constant potential of 1.56 V for 24 h (Figure 5(a)). After each 24 h cycle, the spent electrolyte was replaced with fresh electrolyte containing HMF and TEMPO, while the oCNT anode was reused without any intermediate treatment. After five consecutive cycles, a slight decrease in FDCA selectivity was observed. This may be attributed to the strong adsorption of reaction intermediates on the oCNT surface, which partially blocks the active sites. The CA curves in Figure 5(b) exhibit a consistent trend. It is important to note that the observed decrease in oxidation rate is partially due to the static (non-flow) nature of our batch-type electrochemical cell. As the reaction proceeds, the depletion of the HMF substrate leads to a lower concentration, which inherently requires longer reaction times to achieve complete conversion. This suggests that the oCNT catalyst would likely exhibit even better performance in a continuous-flow industrial process where substrate concentrations are maintained. Regarding the structural integrity of the catalyst, although no significant carbon oxidation (CO_2

evolution) was macroscopically observed at the oCNT anode, potential surface corrosion must be considered. This consideration is supported by the Raman spectra (Figure 5(c)), which show a slight decrease in the intensity of peaks related to amorphous carbon and disordered defects. Crucially, the electrochemical process has no discernible impact on the graphitic structure of the CNT backbone. This structural robustness is further confirmed by the Transmission Electron Microscopy (TEM) images in Figure 5(d)–(e), which reveal that the morphology of the CNTs remains intact before and after the stability tests. These findings collectively demonstrate that the oCNT catalyst possesses excellent structural and electrochemical stability for HMF electro-oxidation. Furthermore, compared with recently reported HMF electrocatalysts, oCNT exhibits excellent stability, conversion rate, and Faradaic efficiency, demonstrating that oCNT is a promising metal free catalyst for HMF oxidation (Table 1).

In the final section, we investigate the reaction kinetics of the HMF electrooxidation process. Figure 6 (a)–(b) display the linear sweep voltammetry (LSV)

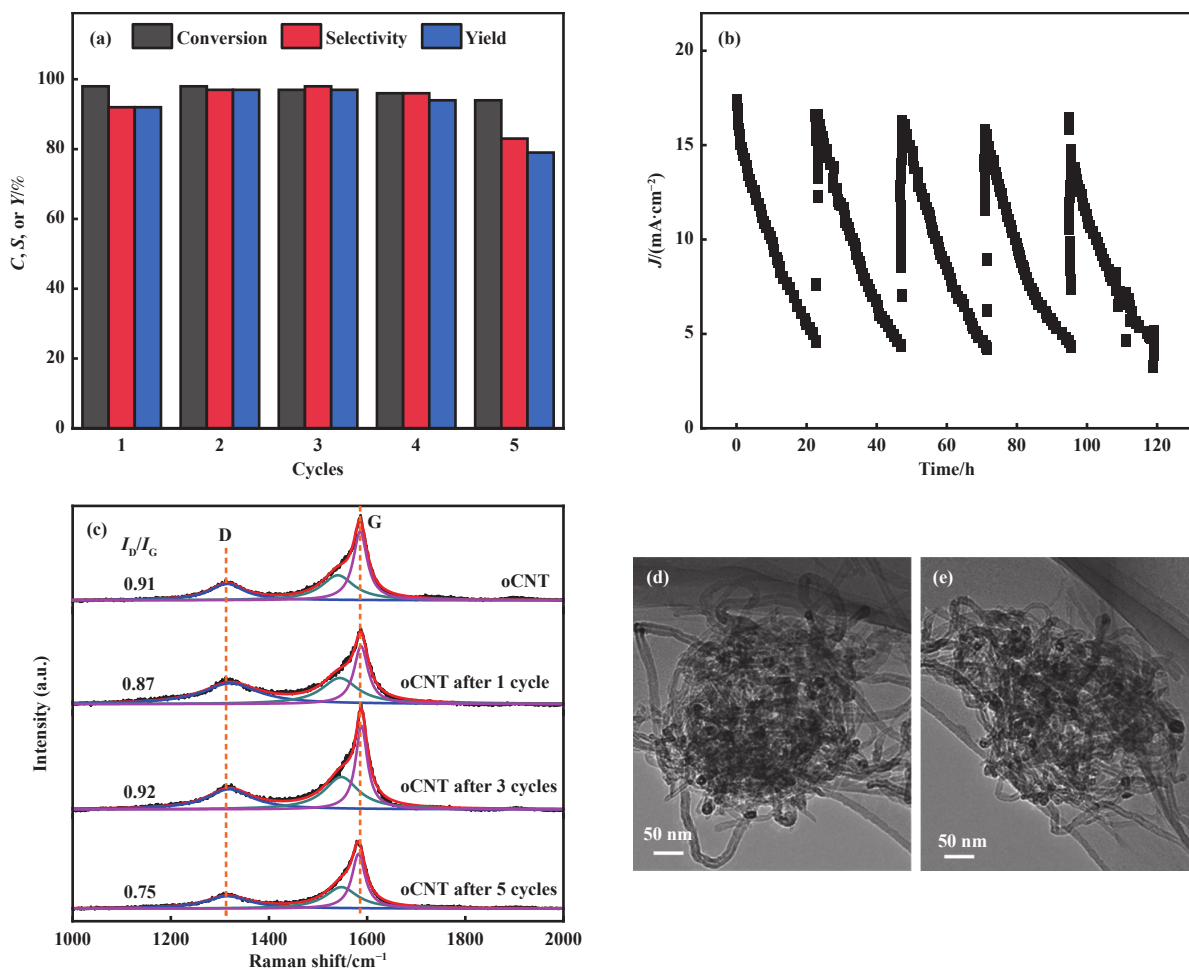


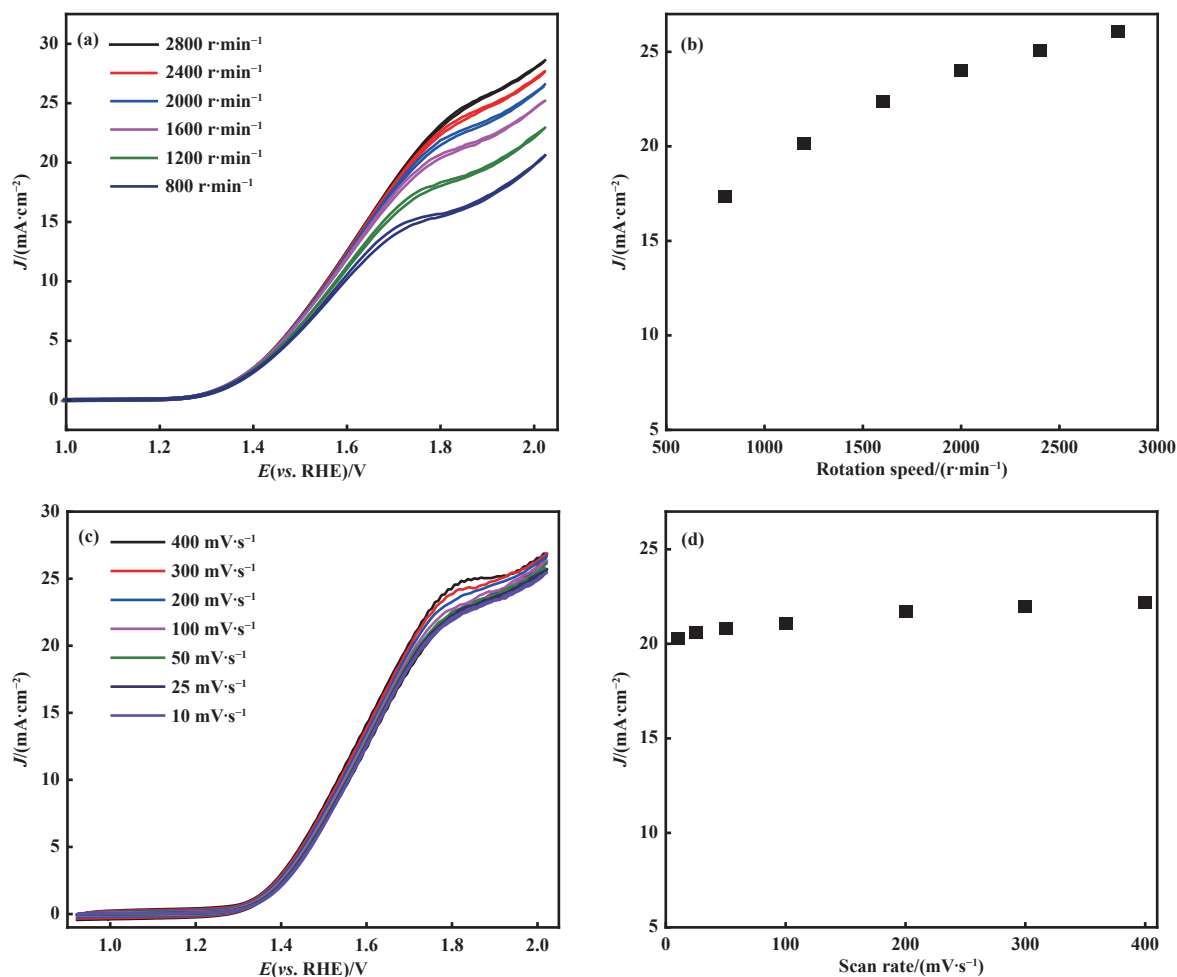
Figure 5 (a)–(b) The recycling experiment of the HMF electrooxidation at 1.56 V; (c) Raman spectra of oCNT samples before and after reactions; HRTEM images of the oCNT (d) before and (e) after 5 cycles CA measurement

Table 1 Comparison of key performance metrics for HMF oxidation catalysts

Catalyst	Conversion _{HMF} /%	FDCA Yield	F.E./%	Stability
Ni ₉ S ₈ /BNC ^[38]	>99	92.7%	93.3	5 cycles
Ni-Co/NF ^[39]	100	96.2%	94.6	100 h
<i>h</i> -CoOOH ^[40]	—	99%	>98	30 cycles
VO ₂ /Ni ₃ S ₂ ^[41]	97.1	96%	96	98 h
NiSe-CoNiSe ₂ /NF ^[42]	99.93	4.92 mmol·cm ⁻² ·h ⁻¹	98.92	8 cycles
RuSe ₂ @CoSe ₂ /NF ^[43]	98.15	97%	96.82	100 h
NiCoMoO ₄ ^[35]	95	—	88.2	140 h
oCNT (This work)	100	100%	—	100 h

curves at various rotation speeds. The rotation speed has no discernible impact on the reaction mechanism, as the onset potential remains constant across all speeds. However, at higher potentials, the current density exhibits a linear dependence on the rotation speed. This phenomenon is closely related to the competitive relationship between HMF oxidation and the OER. Given that the HMF oxidation rate is extremely rapid, it leads to a local depletion of HMF near the electrode surface. Consequently, in the absence of sufficient substrate

supply, the OER becomes more dominant, contributing to the increased current density. By increasing the rotation speed, the mass transfer of HMF is enhanced, effectively replenishing the substrate at the electrode interface and allowing HMF oxidation to proceed continuously. Figure 6(c)–(d) illustrate the influence of scan rates on the catalytic performance. Interestingly, varying the scan rate shows no significant effect on the current density. Typically, the scan rate substantially influences the double-layer capacitance and non-Faradaic



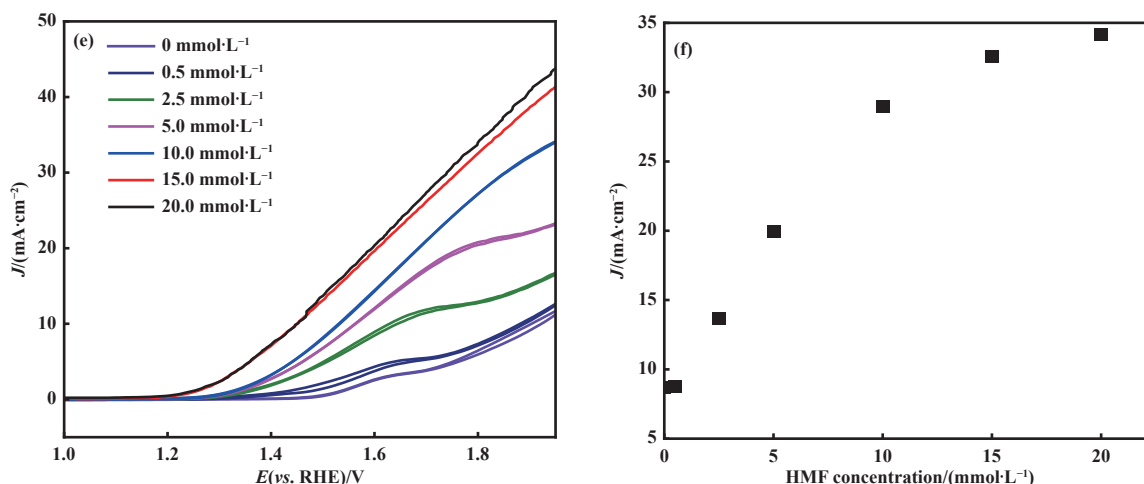


Figure 6 (a)–(b) The influence of rotation speed for the HMF electrooxidation reaction; (c)–(d) The influence of scan rate for the HMF electrooxidation reaction; (e)–(f) The influence of HMF concentration for the HMF electrooxidation reaction

current of the electrode. However, the results indicate that the non-Faradaic contributions are negligible compared to the total current, suggesting that Faradaic processes, specifically HMF electrooxidation, are the dominant reactions under the conditions. Finally, the effect of HMF concentration was investigated (Figure 6(e)–(f)). In the absence of HMF, the current originates solely from the OER and the background oxidation of the electrode system. At low HMF concentrations, the OER process remains visible at higher potentials, indicating that the rapid consumption of HMF necessitates a higher bulk concentration to maintain the reaction. Once the concentration reaches 15 mM, the current density becomes relatively independent of further concentration increases, suggesting a transition from a diffusion-controlled to a surface-kinetics-controlled regime. These kinetic insights provide crucial parameters for optimizing flow rates and substrate feeding strategies in large-scale industrial applications.

3 Conclusions

In summary, oCNTs represent a scalable and sustainable class of anode materials for the electrochemical oxidation of HMF to FDCA. Upon surface functionalization, the oCNTs exhibit remarkable catalytic activity, where surface phenolic hydroxyls and carbonyl groups are identified as the primary contributors to the enhanced electrocatalytic performance. The reaction kinetics and pathways were thoroughly investigated, revealing a dominant HMFCa-mediated route that is highly sensitive to the applied oxidative potential. Regarding durability, although the alkaline electrolyte may induce minor physical detachment of amorphous carbon species, the highly graphitic backbone of the CNTs remains structurally intact under the required oxidative potentials, ensuring the overall stability of the

electrode. Unlike metal-based catalysts, which typically undergo valence state fluctuations during catalysis, the carbon framework maintains its chemical and structural integrity without valence changes. Consequently, this metal-free catalyst exhibits exceptional dimensional stability. Given the structural diversity of carbon-based materials and the universal nature of surface oxygen functionalities, oCNT anodes hold great promise for broader, more cost-effective industrial applications in biomass valorization.

Data availability statement

Associated data in ScienceDB

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非金属催化剂碳纳米管催化 5-羟甲基糠醛电氧化研究

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摘要: 碳材料因其可调的物理化学特性, 在多种催化过程中展现出极具前景的无金属催化性能。本工作设计了一种高活性碳纳米管作为无金属碳催化剂, 以 TEMPO(2,2,6,6-四甲基哌啶-1-氧基) 为助催化剂实现了 5-羟甲基糠醛(HMF) 电氧化制备 2,5-呋喃二甲酸(FDCA) 的催化反应。作为探针阳极, 含氧官能团功能化的碳纳米管表现出良好的 HMF 氧化活性, 起始电位为 1.09 V, 并具有循环使用 5 次的良好稳定性。通过对碳纳米管表面的系统研究, 揭示了反应过程中 HMF 在碳纳米管上的氧化机理。碳纳米管表面的酚羟基被证实是该反应的活性位点; 羰基在反应过程中通过转化为酚羟基也对活性有所贡献。与几种金属催化剂相比, 碳在催化过程中未发生价态变化, 从而能够保持结构稳定性。因此, 碳材料是用于 HMF 电化学氧化过程的可扩展和可持续应用方面极具前景的电极材料。

关键词: 碳纳米管; HMF 电氧化; 无金属催化; 尺寸稳定性; 2,5-呋喃二甲酸