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Article

Enhanced electrocatalytic activity for H_2O_2 production by the oxygen reduction reaction: Rational control of the structure and composition of multi-walled carbon nanotubes

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ABSTRACT

Hydrogen peroxide (H_2O_2) is a very useful chemical reagent, but the current industrial methods for its production suffer from serious energy consumption problems. Using high-activity and high-selectivity catalysts to electrocatalyze the oxygen reduction reaction (ORR) through a two-electron (2e^-) pathway is a very promising route to produce H_2O_2 . In this work, we obtained partially oxidized multi-walled carbon nanotubes (MWCNTs) with controlled structure and composition by oxidation with concentrated sulfate and potassium permanganate at 40 °C for 1 h (O-CNTs-40-1). The outer layers of O-CNTs-40-1 are damaged with defects and oxygen-containing functional groups, while the inner layers are maintained intact. The optimized structure and composition of the partially oxidized MWCNTs ensure that O-CNTs-40-1 possesses both a sufficient number of catalytic sites and good conductivity. The results of rotating ring disk electrode measurements reveal that, among all oxidized MWCNTs, O-CNTs-40-1 shows the greatest improvement in hydrogen peroxide selectivity (from ~ 30% to ~ 50%) and electron transfer number (from ~ 3.4 to ~ 3.0) compared to those of the raw MWCNTs. The results of electrochemical impedance spectroscopy measurements indicate that both the charge-transfer and intrinsic resistances of O-CNTs-40-1 are lower than those of the raw MWCNTs and of the other oxidized MWCNTs. Finally, direct tests of the H_2O_2 production confirm the greatly improved catalytic activity of O-CNTs-40-1 relative to that of the raw MWCNTs.

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1. Introduction

As a chemical raw material, the annual worldwide output of hydrogen peroxide (H_2O_2) is about 4.5 million tons, which fully demonstrates the importance of this chemical [1]. As an efficient green oxidant, hydrogen peroxide is widely used in pulp

bleaching, chemical synthesis, energy conversion, sewage treatment, and other applications [2–7]. At present, the industrial production of H_2O_2 mainly relies on the anthraquinone method, which consumes a considerable amount of energy and produces a large number of chemical pollutants due to the multistep hydrogenation and oxidation reactions [8,9]. Further-

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more, there are various safety risks associated with the storage and transportation of concentrated H_2O_2 [10]. H_2O_2 can also be directly synthesized from hydrogen and oxygen in the presence of noble metal catalysts, in acidic aqueous solution [11,12] or by plasma methods [13]. However, the direct synthesis of H_2O_2 also has some disadvantages, such as the risk of explosion of the gas mixture and the high cost of the noble metal catalysts.

An attractive alternative method for the in situ synthesis of H_2O_2 is the direct electroreduction of O_2 dissolved in alkaline media (Eq. (1)) or in acid media (Eq. (2)) to H_2O_2 , where the oxygen reduction reaction (ORR) undergoes a two-electron pathway [14–16]:

One of the key steps to promote the ORR to synthesize H_2O_2 is to develop catalysts with high activity and selectivity. Some noble metals such as Au, Pt, Pd, and Ag have been reported to show good catalytic activity for H_2O_2 generation from the ORR [17–22]. However, the high cost of precious metals could limit the bulk use of these catalysts. As a matter of fact, it is widely believed that carbonaceous materials are the most suitable alternatives as cathodic catalysts to produce H_2O_2 from the ORR, due to their advantages in terms of catalytic selectivity, cost, and environmental compatibility [23–25]. Recent papers have reported the use of N-doped non-metallic carbon materials [26,27] or non-noble metal and carbon gel complexes [28] for the electrochemical generation of H_2O_2 . These carbon materials exhibit good catalytic activity, but their structure-activity relationships need to be further studied. As types of carbon materials, multi-walled carbon nanotubes (MWCNTs) and zero-valent metal compounds have recently been used to catalyze the ORR for H_2O_2 production [29–31]. Because the metal dissolves gradually, there is still room to improve the stability of these carbon nanotube-based materials. Recently, Lu et al. [32] reported the direct use of MWCNTs as non-metallic materials to catalyze the ORR-based production of H_2O_2 , after the oxidation of commercially available carbon nanotubes. On the other hand, the authors did not investigate systematic changes in the structure and catalytic properties of the MWCNTs at different oxidation levels.

In this study, we have prepared partially oxidized MWCNTs, whose outer layers were destroyed and oxidized while the inner layers remained intact, by carefully controlling the conditions of the oxidation treatment. The as-prepared samples were characterized by various physicochemical methods, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR). Compared to commercial raw MWCNTs, the partially oxidized MWCNTs possess a greatly improved selectivity toward H_2O_2 . When the oxidation level of the oxidized MWCNTs is too low or too high, the improvement in catalytic performance over that of raw MWCNTs is limited, due to the compositional and structural changes being too small or too large. Only with an appropriate degree of oxidation, leading to limited structural changes, the oxidized MWCNTs possess good conductivity as well as a sufficient number of catalytic activity sites, and their ORR catalytic performance to produce H_2O_2 can be improved to the

greatest extent. This conclusion was further verified by various electrochemical measurements and by assessing the performance of in situ H_2O_2 generation from the ORR after the oxidation of the MWCNTs.

2. Experimental

2.1. Chemicals

Raw MWCNTs (diameter = 30–50 nm, length = 0.5–2 μm) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, KOH, and polytetrafluoroethylene (PTFE, 60 wt%, emulsion) were purchased from Shanghai Aladdin Reagent Co., Ltd. All other reagents, including H_2SO_4 , KMnO_4 , H_2O_2 (30 wt% in H_2O), HCl, and $\text{C}_2\text{H}_5\text{OH}$ were purchased from Guangzhou Chemical Reagent Factory. All reagents were of analytical grade and used without further purification. Deionized (DI) water was used in all experiments.

2.2. Preparation of partially oxidized MWCNTs

Partially oxidized MWCNTs were prepared via a very simple surface oxidation treatment. Typically, 30.0 mg raw MWCNTs, 30.0 mL concentrated sulfuric acid, and 150.0 mg KMnO_4 powder were added into a three-necked, round-bottomed glass flask, which was placed in a water bath. Then, the flask was equipped with a reflux condenser, magnetic stirrer, and thermometer. After stirring the mixture for 1 h at different temperatures (20, 30, 40, 50, and 60 $^\circ\text{C}$), excess H_2O_2 (15.0 mL) was slowly added into the flask until no bubbles formed, followed by the addition of 150.0 mL DI water. Next, the slurry was removed, cooled down naturally to room temperature, filtered through a millipore membrane (0.45 μm), and washed with plenty of 1.0 mol L^{-1} aqueous HCl solution and deionized water until the washings became neutral, with a pH value of 7.0. Finally, the black residue was dispersed in an appropriate quantity of water and then dried by the freeze-drying method.

Moreover, when the oxidation temperature was kept at 40 $^\circ\text{C}$, the reaction time was changed to 1, 2, and 3 h. The corresponding partially oxidized MWCNT products were denoted as O-CNTs-X-Y, in which X and Y represent the reaction temperature and time, respectively.

2.3. Characterization of oxidized MWCNTs

The morphology and structure of the products were characterized by TEM (JEM-2010HR). Wide-angle XRD patterns were recorded on a Bruker D8 X-ray diffractometer using Cu K α radiation (40 kV, 26 mA). The surface functional groups of the samples were investigated by FT-IR spectroscopy (Bruker EQUINOX 55). The Raman spectra of the samples were recorded on a HORIBA Jobin Yvon, LabRam HR800 laser confocal microspectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer.

2.4. Electrochemical measurements

All electrochemical tests were performed on a computer-controlled standard three-electrode system connected to an Auto84480 instrument at room temperature. Platinum foil (1.0 cm × 1.0 cm) and Ag/AgCl (saturated KCl) were used as counter and reference electrodes, respectively. Without specification, all potentials were referenced to the reversible hydrogen electrode (RHE) scale, using Eq. (3) [33]:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Ag/AgCl})} + 0.197 + 0.059 \times \text{pH} \quad (3)$$

where 0.197 V is the standard potential of the Ag/AgCl reference electrode in a saturated aqueous solution of KCl at 25 °C.

A glassy carbon disk (of 0.2475 cm² area) was used as the working electrode. The catalyst ink was prepared by mixing the as-prepared oxidized MWCNTs catalysts (2.0 mg), a Nafion® solution (5.0 wt%, 20.0 μL), and ethanol (500.0 μL), followed by ultrasonication for 1 h. Then, 10.0 μL of the ink suspension was dropped onto the glassy carbon disk and dried naturally. All measurements were conducted in O₂-saturated 0.1 M KOH (pH ~ 13) with a scan rate of 10 mV s⁻¹; the corresponding electrochemical polarization curves in N₂-saturated electrolytes were also recorded as a reference.

The electrocatalytic activity and selectivity toward H₂O₂ of the catalysts were investigated by polarization and rotating ring disk electrode (RRDE) measurements. For the latter measurements, the Pt ring electrode was polarized at 0.3 V (vs. Ag/AgCl) in the electrolytes. The electron transfer number (*n*) and the HO₂⁻ intermediate production percentage (%HO₂⁻) were calculated based on Eqs. (4) and (5), respectively [34,35]:

$$n = \frac{4 \times I_D}{I_D + I_R / N} \quad (4)$$

$$\% \text{HO}_2^- = \frac{4 - n}{2} \quad (5)$$

where *I_D* is the disk current, *I_R* is the ring current, and *N* (= 0.37) is the H₂O₂ collection efficiency of the Pt ring.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in O₂-saturated 0.1 mol L⁻¹ KOH at 0.75 V, in the frequency range from 100 kHz to 0.01 Hz, at a 5 mV amplitude and with a rotation rate of 1600 rpm.

The stability was evaluated at a constant potential of 0.6 V, in O₂-saturated 0.1 mol L⁻¹ KOH at room temperature (rotation rate 1600 rpm).

2.5. In situ synthesis and detection of H₂O₂

The in situ generation of H₂O₂ was investigated using the three-electrode system described above. Teflon-treated carbon paper (CP, 2.0 cm × 2.0 cm) loaded with the oxidized MWCNTs (~ 2.0 mg cm⁻²) was used as the working electrode, which was fabricated in three steps. First, the carbon paper was soaked in PTFE emulsion (2 wt%) for several minutes, and then thermally treated at 350 °C for 30 min, resulting in a PTFE content of 30 wt%. The oxidized MWCNTs (8.0 mg) were dispersed into a mixture containing 2.0 mL ethanol and 80.0 μL Nafion® solution (5 wt%). After ultrasonication the mixture for 30 min, the catalyst was finally loaded on the treated CP by drop-casting it on a heating plate at 80 °C. The measurements were carried out in a two-compartment cell with a Nafion®-117 membrane as the separator. The two compartments were filled with a aque-

ous solution (0.1 mol L⁻¹) of KOH. The electrolyte was saturated with oxygen by purging O₂ for at least 30 min before the tests. Moreover, during the H₂O₂ accumulation process, O₂ was bubbled into the solution at a flow rate of 600 mL min⁻¹. Sample aliquots (1.00 mL) in the cathode compartment were withdrawn from the solution at specific time intervals for further quantitative analysis. The concentration of H₂O₂ in the samples was determined by ultraviolet-visible spectrophotometry using K₂TiO(C₂O₄)₂ as color indicator at 400 nm [36].

The current efficiency of the H₂O₂ electrosynthesis was calculated using Eq. (6) [37]:

$$\text{CE}\% = \frac{nF c V}{\int_0^t I dt} \times 100\% \quad (6)$$

where *n* is the number of transferred electrons in the reduction of O₂ to H₂O₂ (*n* = 2), *F* is the Faraday constant (96485 C mol⁻¹), *c* is the H₂O₂ concentration (mol L⁻¹), *V* is the volume of electrolyte (L), *I* is the current intensity (A), and *t* is the electrocatalysis time (s).

3. Results and discussion

3.1. Structure and composition of oxidized MWCNTs (O-CNTs)

The oxidized MWCNTs were obtained through a facile oxidation process, by stirring a mixture of raw MWCNTs, concentrated sulfuric acid, and KMnO₄ at different temperatures for a given time. The crystal structures of the O-CNTs-X-Y prepared under various conditions were first investigated and analyzed by XRD (Fig. 1). All patterns show three graphitic peaks. The broad peak at 26.0° is attributed to the (002) plane of the graphitic structure of the CNTs, while the other two weak peaks at 42.4° and 44.7° correspond to the (100) and (101) diffractions of the CNTs, respectively [38,39]. No other peaks are observed in the patterns, indicating that no other impurities are introduced into the samples, or that the impurity content is negligible. By comparing the XRD patterns of the raw and oxidized MWCNTs, it can be easily found that the oxidation treatment reduces the intensity of the peaks. Moreover, increasing the reaction temperature (Fig. 1(a)) or the reaction time (Fig. 1(b)) results in a weaker XRD peak intensity of the oxidized MWCNTs. This behavior may be due to the increase in oxidation temperature or oxidation time, which could result in increased damage to the graphitic structure of the MWCNTs.

The damage to the structure of the MWCNTs caused by the oxidation treatment under different conditions can be confirmed by inspecting the morphologies of the samples, which were investigated by TEM. Typical images of the OCNTs-X-Y are shown in Figs. 2 and 3. Fig. 2(a) and (b) shows that, when the reaction time is kept constant (1 h), the MWCNTs maintain their tubular morphology after the oxidation treatment at the lower reaction temperature (20 °C), and the degree of damage to the MWCNT walls is relatively small. Upon increasing the reaction temperature to 40 °C, the tubular structure of the MWCNTs is generally retained, while the walls of the nanotubes begin to break down, as shown by the defects clearly visible in the MWCNTs (Fig. 2(c)) after the oxidation treatment. As the reaction temperature is further increased to 60 °C, the

Fig. 1. XRD patterns of O-CNTs-X-1 (a) and O-CNTs-40-Y (b) samples.

nanotube walls are thoroughly etched and the oxidized products completely lose their tubular shape (Fig. 2(d)). When the reaction temperature is maintained constant, the time of the oxidation treatment plays a similar role to the treatment temperature in the destruction of the structure of the MWCNTs, that is, the etching degree of the MWCNT walls increases with an increase in reaction time. After a certain oxidation time, the walls become partially corroded. On the other hand, when the oxidation time is long enough, the walls are completely corroded and the as-prepared O-CNTs entirely lose their tube-like structure (Fig. 2(e) and (f)).

The high-resolution transmission electron microscopy (HRTEM) images illustrate more clearly the changes affecting the MWCNT walls during the oxidation process. For the commercial MWCNTs, the images show very clear stripes due to the high crystallinity, the graphite layers are evenly arranged, and the tube walls are intact (Fig. 3(a)). With an increase in oxidation degree, the structure of the MWCNT walls is gradually destroyed. For partially oxidized MWCNTs samples such as O-CNTs-40-1, which was treated at 40 °C for 1 h, the HRTEM image (Fig. 3(b)) shows that the outer layers of the MWCNT walls suffer significant damage. Noticeable amounts of defects and ruptures are present on the outer layers of the nanotube wall (corresponding to the outer side of the red dotted line in Fig. 3(b)), while the stripes corresponding to the graphite layers are still visible on the inner wall, indicating that the oxidation treatment has little impact. The thinned graphitized

MWCNT walls appear to be covered with an amorphous carbonaceous coating. In this case, if the MWCNTs are further oxidized by increasing the oxidation temperature or extending the treatment time, the damage to the MWCNT walls will propagate from the outer to the inner layers of the nanotube walls, the amorphous carbonaceous layer will gradually thicken, and finally the MWCNT walls will be completely destroyed. Only a very small number of rather short stripes representing the graphite structure can be seen in Fig. 3(c). Incidentally, a small number of darker areas are observed in the figure, where the MWCNTs stack together or have thicker micro-ends.

To further understand the effects of the oxidation treatment on the number of defects and on the structure and crystallization of the O-CNTs, Raman spectroscopy was employed to characterize the obtained MWCNTs samples. The spectra of all materials are presented in Fig. 4. All spectra show a strong D band at $\sim 1330\text{ cm}^{-1}$, which is related to structural defects, disorder, and vacancies in the graphene lattice. A G band at about 1580 cm^{-1} , associated with the crystalline graphitic structure of the CNTs [40], can also be observed. The intensity ratio of the D and G peaks (I_D/I_G) was used to inspect the structural damage in the O-CNTs caused by the oxidation treatment. In general, the I_D/I_G ratios of the O-CNTs are higher than those of the raw MWCNTs, which indicates that the oxidation process destroys the MWCNT structure and creates crystal defects in the graphitic structure [41]. This result is consistent with the XRD and TEM results discussed above. Fig. 4(a) and (b) also

Fig. 2. TEM images of MWCNT samples obtained under different oxidation conditions: raw MWCNTs (a), O-CNTs-20-1 (b), O-CNTs-40-1 (c), O-CNTs-60-1 (d), O-CNTs-40-2 (e), and O-CNTs-40-3 (f).

Fig. 3. High-resolution TEM images of raw commercial MWCNTs (a), O-CNTs-40-1 (b), and O-CNTs-60-1 (c). The inner images in (a) and (b) show partial enlargements. The outer parts of the red lines of the walls in (b) are damaged.

Fig. 4. Raman spectra of O-CNTs-X-1 (a) and O-CNTs-40-Y (b) samples.

shows that, at low oxidation levels, the I_D/I_G ratio increases with an increase in oxidation degree, until it reaches a maximum at higher oxidation degrees. Further increasing the oxidation level leads to a decrease in the I_D/I_G ratio, due to the fact that the oxygen-bonded saturated sp^3 configuration C, which forms the defects, could be desorbed in the form of C=O and O=C=O species, thus resulting in the decrease in intensity of the D band [42].

In order to investigate the changes in chemical composition of the oxidized MWCNTs, the functional groups of the as-prepared samples were characterized by FT-IR. As shown in Fig. 5, the spectra of the O-CNTs show noticeable changes in the intensity of the characteristic peaks of several functional groups, compared to those of the raw MWCNTs. The wide absorption peak at $\sim 3438\text{ cm}^{-1}$ is the characteristic vibration peak of the hydroxyl (–OH) in the acidic functional groups on the MWCNTs [43]. The bands at ~ 2920 , 1722 , and 1655 cm^{-1} are attributed to the stretching vibrations of the C–H [44], C=O [45], and C=C [30] groups of the MWCNTs, respectively. In addition, with a further increase in the oxidation degree, C–O–C ($\sim 1229\text{ cm}^{-1}$) and C–O ($\sim 1050\text{ cm}^{-1}$) [46] signals appear in the FT-IR spectra. Overall, these typical bands reveal that oxygen-containing functional groups, some of which (–COOH and C–O–C) were reported to favor the electrosynthesis of H_2O_2 [32], have been introduced on the surface of the O-CNTs.

In order to better understand the effect of the oxidation treatment on the elemental contents on the MWCNT surface,

the chemical states of all oxidized MWCNTs samples were studied by XPS. The corresponding results are given in Fig. 6. The oxygen content of the MWCNTs before oxidation is negligible, as only one C1s peak is visible in the recorded spectra of the raw samples, indicating the absence of any oxygenated functional groups. The O1s peak appears in the spectra of the oxidized MWCNTs and its intensity gradually increases with an increase in oxidation level, denoting a corresponding increase in the oxygen content (Fig. 6(a) and (d)). The high-resolution C1s spectra (Fig. 6(b) and (e)) could be deconvoluted into six specific bands including those of C=C, C–C, C–O, C=O, and O=C–O groups at 284.7, 285.1, 286.1, 287.0, and 288.9 eV, respectively, as well as the $\pi-\pi^*$ transition at 290.5 eV [47,48]. Moreover, the deconvolution of the high-resolution O1s spectra (Fig. 6(c) and (f)) suggests the presence of two oxygenated species on the surface of the O-CNTs: C=O at 531.6 eV and C–O at 533.2 eV [47]. The high-resolution C1s and O1s spectra thus support the conclusions of the FT-IR analysis discussed above. The relative contents of oxygen-containing groups in the samples were obtained by measuring the relative peak areas in Fig. 6(e) and (f), and the results are summarized in Table 1. The data in the table clearly show that the oxidation treatment resulted in a sustained increase in the relative content of oxygen-containing groups on the surface of the MWCNTs.

3.2. ORR electrocatalytic activity of O-CNTs

Fig. 5. FT-IR spectra of O-CNTs-X-1 (a) and O-CNTs-40-Y (b) samples.

Fig. 6. XPS survey spectra (a) along with high-resolution C1s (b) and O1s (c) spectra of O-CNTs-X-1 samples; XPS survey spectra (d) along with high-resolution C1s (e) and O1s (f) spectra of O-CNTs-40-Y samples.

According to the above analysis, the oxidation treatment of the MWCNTs gradually destroys their structure and introduces defects and oxygen-containing functional groups on their surface. Defects and oxygen-containing functional groups can alter the electronic structure of carbon materials; this leads to different binding energies of the intermediates generated during the ORR process to the active sites of the carbon-based materials, which in turn affect the ORR catalytic activity of the catalysts [49,50]. According to density functional theory (DFT) calculation results reported elsewhere, the defects introduced in the MWCNTs have weak cohesion with oxygenated species, which ensures that the O–O bonds are preserved, thus improving the selectivity toward H₂O₂ formation [51]. Moreover, the C–O–C and –COOH functional groups bind OOH*, the only intermediate involved in the two-electron reduction of O₂, at very favorable energies for the two-electron oxygen reduction to H₂O₂, indicating high reactivity in the electrochemical synthesis of H₂O₂ [32]. Defects and oxygen-containing functional groups such as C–O–C and –COOH thus result in the ORR to produce

H₂O₂. Therefore, there is no doubt that the oxidation treatment of the MWCNTs can alter their corresponding catalytic activity. However, the catalytic activity of MWCNTs with different oxidation degrees can also vary depending on their different structures and oxygen contents. Therefore, RRDE measurements, where the amount of H₂O₂ generated at the disk electrode could be accurately determined by the ring current, were conducted in O₂-saturated 0.1 M KOH solution (pH = 13) to evaluate the ORR pathway for all oxidized MWCNT samples during the ORR process. The experimental results shown in Fig. 7 allow identifying the O-CNTs catalysts with the most suitable oxidation degree.

As clearly shown in the RRDE voltammograms of Fig. 7(a), the disk and ring currents corresponding to O-CNTs-60-1 are the smallest among the O-CNTs subjected to different treatment temperatures. This may be due to the very high level of oxidation of the O-CNTs-60-1 samples, whose structure changed to an amorphous carbonaceous state with low crystallinity (Figs. 2(d) and 3(c)), which does not promote electron transfer and transmission. Figs. 7(b) and 7(c) show an improvement in both the yield of H₂O₂ and the number of transferred electrons in the ORR-based synthesis of H₂O₂ when the MWCNT catalysts are oxidized. The same conclusion can be drawn from Figs. 7(e) and 7(f). Based on the previous conclusions, this could be due to the introduction of defects and catalytically active oxygen-containing functional groups on the surface of the MWCNTs in the oxidation process. More specifically, the sample subjected to an oxidation treatment at 40 °C for 1 h shows the best catalytic performance. Compared to those of the unoxidized MWCNTs and of the products obtained under other oxidation treatment conditions, the O-CNTs-40-1 sample exhibits a higher current and a lower overpotential, indicating a higher reactivity. In particular, compared to that of the com-

Table 1

Contents of oxygen-containing functional groups in O-CNTs, obtained from XPS measurements.

Sample	O content (at%)	Content of oxygen-containing functional groups (at%)	
		C–O	C=O
MWCNTs	0	—	—
O-CNTs-20-1	10.25	7.32	2.93
O-CNTs-30-1	14.51	11.49	3.02
O-CNTs-40-1	19.31	15.35	3.96
O-CNTs-50-1	28.81	24.18	4.63
O-CNTs-60-1	32.61	26.34	6.27
O-CNTs-40-2	27.09	21.67	5.42
O-CNTs-40-3	28.34	22.55	5.79

Fig. 7. RRDE voltammograms (rotation speed: 1600 rpm, scan rate: 10 mV s⁻¹) of O-CNTs-X-1 (a) and O-CNTs-40-Y (d) samples; hydrogen peroxide yield of O-CNTs-X-1 (b) and O-CNTs-40-Y (e) samples; electron transfer number of O-CNTs-X-1 (c) and O-CNTs-40-Y (f) samples.

mercial raw MWCNTs, the selectivity toward H₂O₂ of O-CNTs-40-1 shows a significant increase, from less than 30% to about 50%, and the corresponding number of transferred electrons (*n*) decreases from more than 3.4 to less than 3.0, which indicates that the ORR has a higher tendency to undergo a 2e⁻ pathway. It is worth pointing out that Figs. 7(b), (c), (e), and (f) also show that the selectivity toward H₂O₂ and the *n* value change significantly at negative potentials, which may be due to the side hydrogen evolution reaction.

In addition to the RRDE results, the results of the EIS measurements (Fig. 8) also reveal that O-CNTs-40-1h has the best catalytic activity, because its charge-transfer and intrinsic resistances are lower than those of the raw MWCNTs or of the other oxidized MWCNTs. Overall, these results support the preliminary conclusion that the partially oxidized O-CNTs-40-1 sample exhibits higher catalytic activity and selectivity in the ORR-based production of H₂O₂, compared to those of raw MWCNTs and of other oxidized MWCNTs with lower or higher

Fig. 8. Electrochemical impedance spectroscopy plots of O-CNTs-X-1 samples (a) and enlarged view of the high-frequency region of panel a (b); electrochemical impedance spectroscopy plots of O-CNTs-40-Y samples (c) and enlarged view of the high-frequency region of panel c (d).

Fig. 9. Chronoamperometric responses of MWCNTs, O-CNTs-40-1, O-CNTs-40-3, and O-CNTs-60-1 at 0.6 V (rotation speed: 1600 rpm).

oxidation degree.

The long-term durability is an important parameter in the evaluation of electrocatalysts; hence, the stability of O-CNTs-40-1, raw MWCNTs, and oxidized MWCNTs with higher oxidation levels were studied by the chronoamperometric method. As shown in Fig. 9, O-CNTs-40-1 retains 90.5% of the initial current density after a 10000-s test, while the raw MWCNTs, O-CNT-40-3, and O-CNT-60-1 keep 83.6%, 72.2%, and 67.6% of their initial current, respectively, showing the outstanding stability of the partially oxidized O-CNTs-40-1 sample.

3.3. In situ synthesis of H_2O_2

Based on the results of the electrochemical tests discussed above, it is clear that O-CNTs-40-1 has higher catalytic activity, selectivity, and durability in the ORR-based synthesis of H_2O_2 than the raw MWCNTs and the oxidized MWCNTs with lower or higher oxidation degree. In order to further investigate the practical applicability of O-CNTs-40-1, some samples were loaded on Teflon-treated CP to obtain a CP@O-CNTs-40-1 electrode for the in situ production of H_2O_2 through the ORR.

Under different cathodic potentials, significantly different amounts of H_2O_2 accumulate on the CP@O-CNTs-40-1 electrode during the same time. As shown in Fig. 10, with the cathode potential ranging from 0.86 to 0.46 V over 40 min, the cumulative concentration of H_2O_2 increases and reaches its max-

Fig. 10. Influence of applied cathode potential on the in situ generated amount of H_2O_2 . Experimental conditions: pH 13; operating temperature 25 °C; O-CNTs-40-1 dosage 8.0 mg; oxygen flow rate 600 mL min⁻¹.

imum at 0.46 V. As the cathode potential continues to increase, the concentration of H_2O_2 decreases, which is due to the fact that both the decomposition of H_2O_2 and the evolution of H_2 at high potential begin to occur, inhibiting the $2e^-$ process of the ORR. Figs. 11(a) and (b) show the cumulative concentration of H_2O_2 and the corresponding current efficiency of different cathodes at 0.46 V. Compared to those of the electrode loaded with the raw MWCNTs, the H_2O_2 concentration and current efficiency of the CP@O-CNTs-40-1 electrode show great improvement. O-CNTs-40-1 clearly shows higher potential than the unoxidized raw MWCNTs as ORR catalyst to generate H_2O_2 in practical applications. Incidentally, the current efficiency of the CP@O-CNTs-40-1 electrode in Fig. 11(b) shows a slight decrease toward the end of the experiment, which can be attributed to the increased decomposition of H_2O_2 at this potential. The measured concentration of H_2O_2 is lower than its actual generated concentration, resulting in a slight decrease in the calculated current efficiency [52].

The results of the electrochemical measurements show that O-CNTs-40-1 has enhanced activity and selectivity in the electrocatalytic reduction of oxygen to H_2O_2 compared to the raw MWCNTs. In addition, O-CNT-40-1 shows a greater performance improvement compared to those of the other oxidized samples. These findings can be understood with the help of the physicochemical characterization experiments. MWCNTs that are completely non-oxidized or have a low degree of oxidation do not possess effective catalytic active sites, while oxidized MWCNTs with high degree of oxidation have a severely dam-

Fig. 11. Accumulation of H_2O_2 on different cathode materials over 40 min at 0.46 V (a) and corresponding current efficiency (b). Experimental conditions: pH = 13, operating temperature 25 °C, O-CNTs-40-1 dosage 8.0 mg, oxygen flow rate 600 mL min⁻¹.

aged graphitic structure and their electron transfer performance is greatly reduced, which is also not favorable for the reaction.

4. Conclusions

In summary, oxidized MWCNTs with different oxidation degrees were used to catalyze the oxygen reduction reaction and produce H_2O_2 . The experimental results show that, after the oxidation treatment, defects and oxygen-containing functional groups are introduced on the surface of the MWCNTs, which promotes H_2O_2 generation by the ORR through a two-electron process. Therefore, all oxidized MWCNTs have better catalytic activity and selectivity than the commercial non-oxidized MWCNTs. Among the oxidized MWCNTs, O-CNTs-40-1 exhibits the greatest improvement in H_2O_2 selectivity (from $\sim 30\%$ to $\sim 50\%$) and electron transfer number (from ~ 3.4 to ~ 3.0). In terms of structure and composition, the outer walls of O-CNTs-40-1 are damaged and destroyed by the oxidation treatment, resulting in the formation of a large number of defects, which promotes the ORR. At the same time, oxygen-containing functional groups such as $-\text{COOH}$ and $\text{C}-\text{O}-\text{C}$ introduced on the MWCNT surface are known to be the catalytic active sites for the ORR-based production of H_2O_2 . On the other hand, the inner layers of the nanotube walls are not corroded and keep their graphitic structure, which ensures that the material has good electrical conductivity. Therefore, the

present partially oxidized MWCNTs have good applicability in catalyzing the reduction of oxygen to H_2O_2 . The present work could provide useful information for the design of electrocatalysts capable of efficiently catalyzing the ORR for the in situ synthesis of H_2O_2 ; in particular, we showed that tailoring the surface oxidation degree and conductivity of carbon-based materials could significantly enhance their performance.

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Graphical Abstract

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Enhanced electrocatalytic activity for H_2O_2 production by the oxygen reduction reaction: Rational control of the structure and composition of multi-walled carbon nanotubes

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Multi-walled carbon nanotubes (MWCNTs) with tailored structure and composition were prepared and showed significantly improved performance in the electrocatalytic ORR to produce H_2O_2 , compared to that of the raw MWCNTs.

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对多壁碳纳米管的结构和组成进行精细调控提高其电催化氧还原反应制H₂O₂的催化活性

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摘要: 双氧水(H₂O₂)是一种重要的化工原料。目前, 其工业生产主要采用蒽醌法, 但工艺复杂、能耗高, 同时高浓度H₂O₂不宜储存和远距离运输。电催化氧气二电子还原(ORR)制备H₂O₂技术具有绿色环保、工艺简单等优点, 且可实现H₂O₂的原位生产, 受到了广泛关注。开发高效、廉价的非贵金属催化剂是ORR制备H₂O₂技术的关键。多壁碳纳米管(MWCNTs)作为一

种便宜易得、稳定环保的常用催化材料,具有一定的ORR催化活性,本文对MWCNTs进行表面氧化处理,通过优化氧化处理的条件调控其结构和表面的含氧官能团含量,提高MWCNTs电催化ORR制 H_2O_2 的性能.

物化表征结果表明,随着氧化处理温度的上升或时间的延长,MWCNTs的结构从外到内逐渐被破坏,管壁表面对 2e^- 路径ORR具有催化活性的缺陷和含氧官能团含量逐渐增加.但随着氧化程度进一步加深,MWCNTs的管壁被严重破坏,材料导电能力显著降低,从而不利于电催化ORR的进行.电化学测试结果表明,在所有的氧化MWCNTs样品中,O-CNTs-40-1(40 °C,氧化处理1 h)电流最大,相比未经处理的商业化MWCNTs的ORR起始还原电位正移最明显.而且催化ORR制 H_2O_2 的选择性提升幅度也最大,其中双氧水产率从约30%提升至50%左右,反应转移电子数则从3.4降低至3.0.电化学阻抗谱结果表明,O-CNTs-40-1具有最佳导电能力.将O-CNTs-40-1负载到聚四氟乙烯处理过的碳纸(CP)上作为电极,用于 0.1 mol L^{-1} KOH溶液中电催化ORR生成 H_2O_2 的实验结果显示,恒电位0.46 V(vs. RHE)40 min,CP@O-CNTs-40-1电极的 H_2O_2 累积浓度为 64.8 mg L^{-1} ,而CP@MWCNTs电极对应的浓度仅为 39.4 mg L^{-1} .且CP@O-CNTs-40-1电极在 H_2O_2 累积过程中对应的电流效率达到52%–65%.这表明比未经调控的MWCNTs,经过精准调控结构和组成之后的O-CNTs-40-1更加适合用作电催化ORR原位制备 H_2O_2 的催化剂.

通过精确调控结构和组成之后,MWCNTs外层断裂腐蚀而内层结构完好,使其同时具备足够的催化 2e^- 路径ORR活性位点和良好的导电能力,因而大幅提高了电催化ORR制备 H_2O_2 的性能.这为进一步探索优化设计碳基材料的结构,提升催化剂电催化ORR原位制备 H_2O_2 的性能提供了一种有用的思路.

关键词: 过氧化氢; 氧还原反应; 多壁碳纳米管; 电催化性能; 氧化处理

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