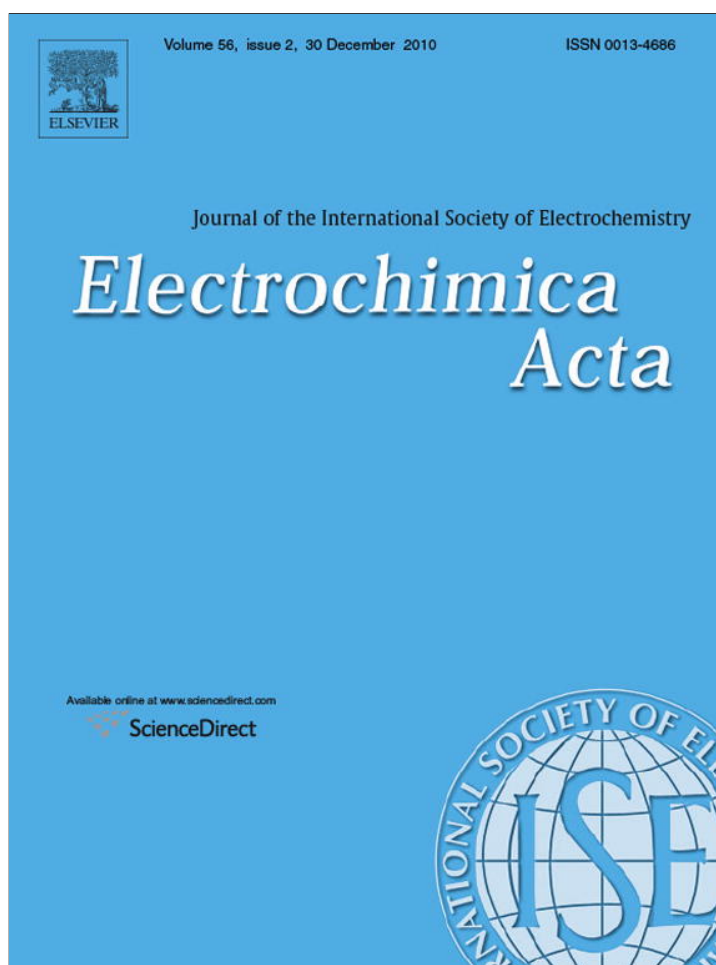




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A comparison of the electrocatalytic activities of ordered mesoporous carbons treated with either HNO₃ or NaOH

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ABSTRACT

Ordered mesoporous carbon (OMC) was treated with HNO₃ or NaOH. The two treated OMCs have many oxygen-containing functional groups. Those treated with HNO₃ have more acidic surface groups than those treated with NaOH. Nicotinamide adenine dinucleotide (NADH) and H₂O₂ were selected as marker molecules for the comparison of the electrocatalytic property of the OMCs. A comparison between the cyclic voltammograms shows that the oxidation peak potential of NADH is 0.614 V at a bare glassy carbon electrode (GCE), 0.205 V at OMC/GCE, 0.223 V at NaOH-treated OMC/GCE, and 0.0 V at HNO₃-treated OMC/GCE (vs. Ag/AgCl). The results indicate that the HNO₃-treated OMC/GCE exhibits the highest electrocatalytic activity for NADH oxidation. Thus, acidic groups rather than other oxygen-containing functional groups, play a very important role in the catalytic activity of OMC.

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1. Introduction

Ordered mesoporous carbon (OMC) has attracted enormous interest because of their unique structural, mechanical and electronic properties [1–5]. Great efforts have been devoted to its promising application fields, such as molecule separation, adsorption, sensors, energy storage, capacitors and especially electrocatalysis [6–10]. Recently, it was reported that OMC as electrode material could facilitate electron transfer on electrode/electrolyte interface for both oxidation and reduction processes and show excellent electrocatalytic property in electrochemical reaction. For example, Jia et al. [11] used OMC modified electrode to study the oxidation of dopamine. The electrochemistry of dopamine at the OMC modified electrode was surprisingly improved with a selective determination of dopamine in the presence of ascorbic acid. Zhu et al. [12] has done much research on the electrochemistry of various electroactive molecules such as uric acid, epinephrine, acetaminophenol and ascorbic acid using mesoporous carbon paste electrode. Compared with carbon nanotube paste electrode, it was found that the mesoporous carbon paste electrode improved electron transfer kinetics and catalytic capability of these molecules. In another research, the direct electron transfer of redox protein

(hemoglobin) could be accelerated by mesoporous carbons [13]. The marvelous electrocatalytic character of OMC towards the oxidation of nicotinamide adenine dinucleotide (NADH) has been reported [14]. Further, the OMC has been used as supports of electrocatalysts for direct methanol fuel cells (DMFC) [15,16].

Although the OMC showed so excellent electrocatalytic capability, the electrocatalytic mechanism of OMC is not clear until now. There are just a few speculations that the high electrocatalytic activity observed at OMC is attributed to the presence of a large number of oxygen-containing functional groups and edge plane-like defective sites (EDS) on the surface of OMC [11,17]. Therefore grafting oxygen groups on the OMC were widely used to improve the electrocatalytic activity of OMC [18,19]. The surface of OMC contains different types of oxygen-containing functional groups, such as carboxyl, phenolic hydroxyl, lactone, quinone, ether, and so on. However, the question that arises is: are all the oxygen-containing functional groups responsible for the good electrocatalytic properties of OMC? Considering the application aspects, it is important and necessary to investigate the influence of surface oxygen-containing functional groups on the electrocatalysis of OMC.

In the present study, OMC is treated with HNO₃ or NaOH in liquid phase and obtains different oxygen-containing functional groups. In these procedures, OMC treated by HNO₃ produces the highest concentration of acidic groups, such as carboxyl, hydroxyl and quinone [20]. The results of Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) clearly identify that acidic groups on the surface of OMC are responsible for the favorable electrochemical proper-

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ties. It is consistent with the previous observations for other carbon electrodes [21–23].

2. Experimental

2.1. Reagents and apparatus

NADH was obtained from Sigma–Aldrich. H_2O_2 , HNO_3 and NaOH were obtained from Beijing Chemical Co. Ltd. All other chemicals not mentioned here were of analytical reagent grade and were used as received. Double-distilled water was used to prepare aqueous solutions throughout. The 0.1 M phosphate buffer solution (PBS pH = 7.0), which was made up of NaH_2PO_4 , Na_2HPO_4 and H_3PO_4 , was employed as a supporting electrolyte.

Electrochemical experiments were performed with a CHI830b Electrochemical Workstation (Shanghai Chenhua Instrument Corporation, China) in a conventional three-electrode cell. The working electrode used was glassy carbon (GC) electrode (3 mm diameter). A platinum electrode was applied as the counter electrode and an Ag/AgCl (in saturated KCl solution) electrode served as reference electrode. All solutions were purged with high-purity nitrogen for at least 5 min to remove oxygen prior to the beginning of the experiments. In this paper, all experiments were carried out at room temperature.

Small angle X-ray diffraction (XRD) patterns were obtained on an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA and using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). Infrared spectrum of the sample was recorded with Nicolet Magna 560 FT-IR Spectrometer with KBr plate. XPS measurement was performed on an Escalab 250 spectrometer (Thermo Electron Corp.) with Al KR radiation (1486.6 eV) as the X-ray source for excitation. Raman spectra were recorded at ambient temperature on a Renishaw Raman system model 1000 spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

2.2. Synthesis and treatment of OMC

The mesoporous silicates (SBA-15) were prepared using Pluronic P123 (non-ionic triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as a surfactant and tetraethoxysilane (TEOS) as a silica source, as described [24]. OMC was synthesized using SBA-15 as a template, and sucrose was used as a carbon source according to a reported carbonization procedure [1,25]. In a typical synthesis, 2 g of P123 was completely dissolved in a solution composed of 15 ml of deionized water and 60 ml of hydrochloric acid (2 M), and the temperature of the solution was raised to 311 K. After 2 h, 4.18 g of TEOS was added to the solution and the mixture was magnetically stirred until the TEOS dissolution. Then the mixture was remained stirred for 20 h at 311 K, after the mixture was placed in an oven at 373 K for 48 h. The resultant white precipitate was filtered, dried without washing, and calcined at 823 K. The calcined SBA-15 was impregnated with aqueous solution of sucrose containing sulfuric acid. 1 g of template (SBA-15) was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5 g of water, and keeping the mixture in an oven at 373 K for 6 h. Subsequently, the oven temperature was raised to 433 K for another 6 h. A similar process was repeated. The template–polymer composites were heat-treated in high-purity nitrogen flow at 1173 K for 6 h to carbonize the polymer. After dissolution of the silica framework in 0.1 M NaOH, the obtained mesoporous carbon material was denoted as OMC.

The obtained OMC was treated with HNO_3 or NaOH. 10 mg of OMC was dispersed in 20 ml 5 M HNO_3 or 8 M NaOH and the mixture was stirred for 7 or 4 h at 80 °C. After that treatment, samples were centrifuged and washed thoroughly with distilled water until the pH was close to 7, and further dried at 70 °C overnight. The HNO_3 -

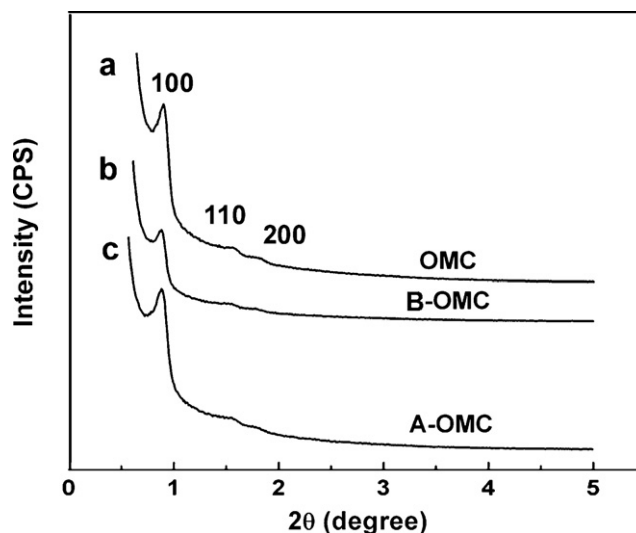


Fig. 1. The low-angle XRD patterns of original OMC (a), B-OMC (b) and A-OMC (c).

treated OMC and NaOH-treated OMC were denoted as A-OMC and B-OMC, respectively.

2.3. Electrode preparation

Prior to the modification, the GC electrode of 3 mm diameter was polished with 1.0, 0.3 and 0.05 μm alumina slurry in turn, and was sonicated successively in 1:1 nitric acid, absolute alcohol and double-distilled water. The cleaned electrode was dried with high-purity nitrogen gas. The preparative procedure of modified electrode was as follows: 5 mg of the OMC was dispersed in 10 ml of N,N-dimethylformamide (DMF) with the aid of ultrasonic oscillation to give a 0.5 mg ml^{-1} black suspension, then 5 μl of OMC suspension was cast onto a glassy carbon electrode (GCE). The solvent was evaporated under an infrared lamp to obtain the OMC modified electrode (OMC/GCE).

3. Results and discussion

3.1. Characterizations of original and treated OMCs

Fig. 1 displays the low-angle XRD patterns of original and treated OMCs. The original OMC exhibits three diffraction peaks, which can be attributed to (1 0 0), (1 1 0) and (2 0 0) reflections for 2-D hexagonal structure ($p6mm$) (curve a). It suggests that the ordered hexagonal mesostructure is successfully replicated from the silica template. Meanwhile, three diffraction peaks were also detected in the samples of B-OMC and A-OMC, which means that ordered mesostructure has been nicely maintained (curves b and c) after the treatment with NaOH or HNO_3 . It has been reported that an ordered structure of OMC can maintain even in boiling 5 M aqueous solution of NaOH, KOH, or HNO_3 over a week, showing strong resistance from the attack of acids or alkalis [18,26].

The increase of the oxygen content can be seen from the FT-IR analyses. FT-IR spectra of the original OMC, B-OMC and A-OMC are shown in Fig. 2. Fig. 2 demonstrates that the peaks at 1730, 3441 and 1200 cm^{-1} are attributed to the characteristic absorption of the oxygen-containing functional groups. In contrast to the original OMC (curve a), the A-OMC appears a higher intensity absorption peak at 1730 and 3441 cm^{-1} assigned to the C=O and O–H stretching vibration (curve c), which indicates that lots of acidic groups such as carboxyl, phenolic hydroxyl and quinone are introduced to the surface of A-OMC. But the two absorption peaks on the B-OMC (curve b) are similar to the spectrum of the original OMC. How-

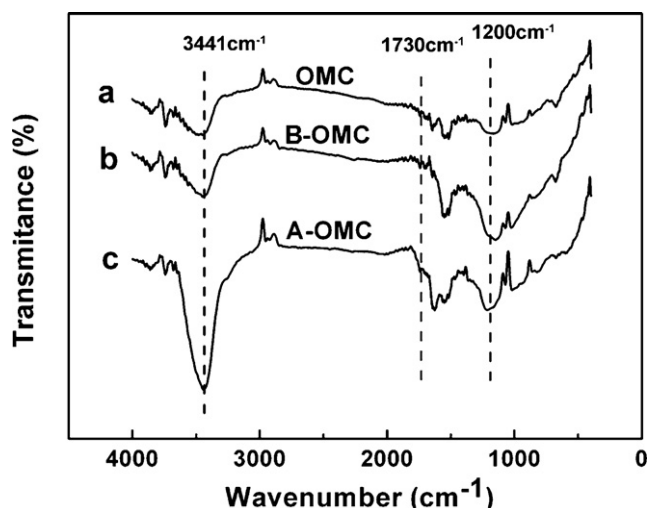


Fig. 2. FT-IR spectra of original OMC (a), B-OMC (b) and A-OMC (c).

ever, a marked increase in the absorbance intensity is observed in the absorption spectrum of B-OMC at peak 1200 cm^{-1} (curve b), which is attributed to a stretching mode of C–O–C groups in the ether structure [27]. These results illustrate that different oxygen-containing functional groups are formed on the surface of OMC that is treated with HNO_3 or NaOH .

However, FT-IR spectrum is very difficult to quantify the content of oxygenated species. Consequently, XPS is used to further characterize the change of oxygenated species. The XPS of the original OMC (curve a), B-OMC (curve b) and A-OMC (curve c) are shown in Fig. 3. The XPS analysis of the original OMC reveals the presence of

Table 1

XPS data of original OMC and treated OMCs.

Samples	C (at.%)	O (at.%)	O/C (at. conc.%)
OMC	90.08 ± 0.005	9.92 ± 0.008	0.110 ± 0.003
A-OMC	88.10 ± 0.004	11.90 ± 0.006	0.135 ± 0.004
B-OMC	83.76 ± 0.01	16.24 ± 0.008	0.194 ± 0.007

a small amount of oxygen functional groups at peak 532 eV (curve a), but an increase of oxygen content was detected in the B-OMC (curve b) and A-OMC (curve c). This is consistent with the results of FT-IR spectroscopy. The surface atomic concentrations of C and O were calculated from the corresponding peak areas of the XPS spectra (Table 1).

Fig. 3 also displays typical XPS C 1s spectra of original OMC (curve d), B-OMC (curve e) and A-OMC (curve f). The C 1s spectrum of original OMC has a peak at 289 eV (curve d) which mainly represents carbonyl peak [28]. The C 1s spectrum of B-OMC has almost no change at 289 eV (curve e). It can be indicated that there are no significant changes in the content of acidic groups in B-OMC. So it is true that NaOH as alkaline agent produces other oxygen functional groups instead of acidic groups, which is consistent with FT-IR results. As expected, an increasing carbonyl peak was observed in the XPS spectrum of A-OMC (curve f), indicating more acidic groups formed on the surface of A-OMC [28].

Fig. 4 shows the Raman spectra of original OMC (curve a), B-OMC (curve b) and A-OMC (curve c). They both show two characteristic peaks of the D band at 1340 cm^{-1} and the G band at 1595 cm^{-1} . The D band is associated with the presence of defects in the graphite layer. The G band corresponds to the Raman-active E_{2g} , resulted from the vibration mode corresponding to the movement in the opposite directions of two neighboring carbon atoms in a single

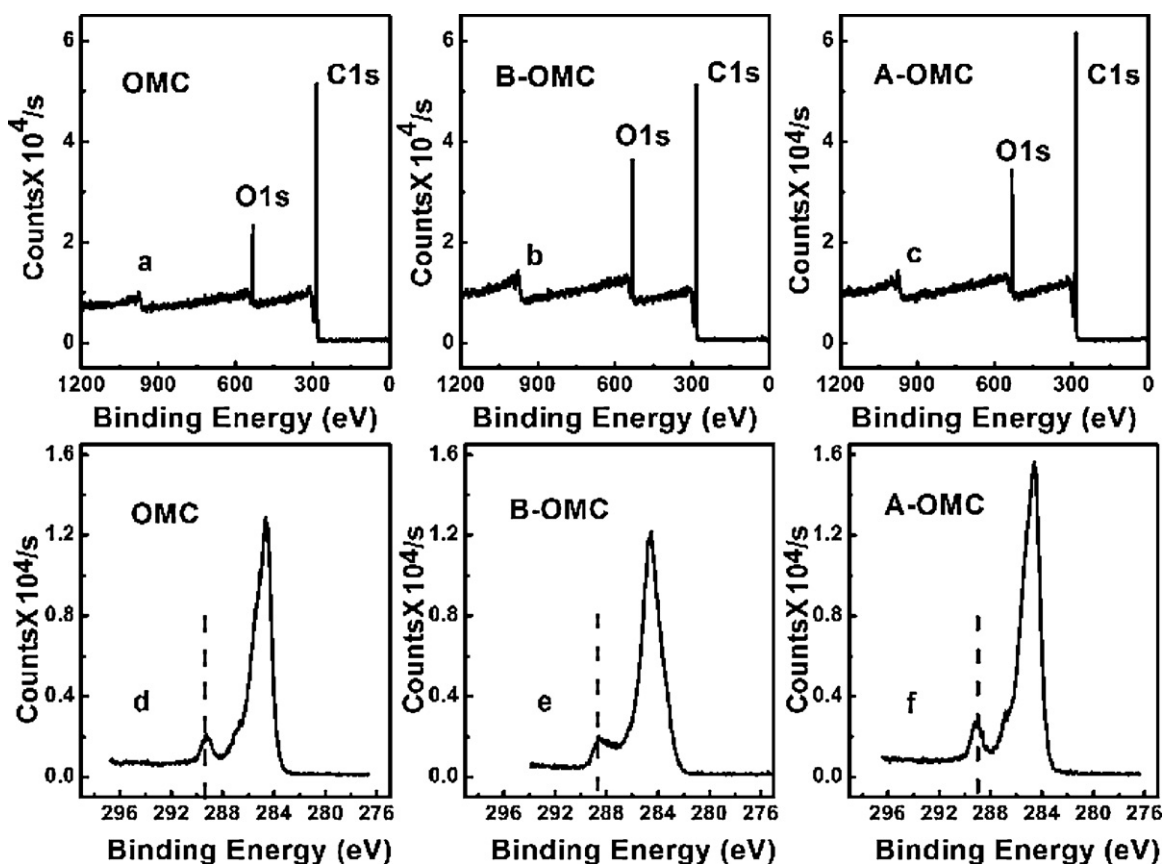


Fig. 3. XPS spectra of original OMC (a), B-OMC (b) and A-OMC (c). C 1s spectra of original OMC (d), B-OMC (e) and A-OMC (f).

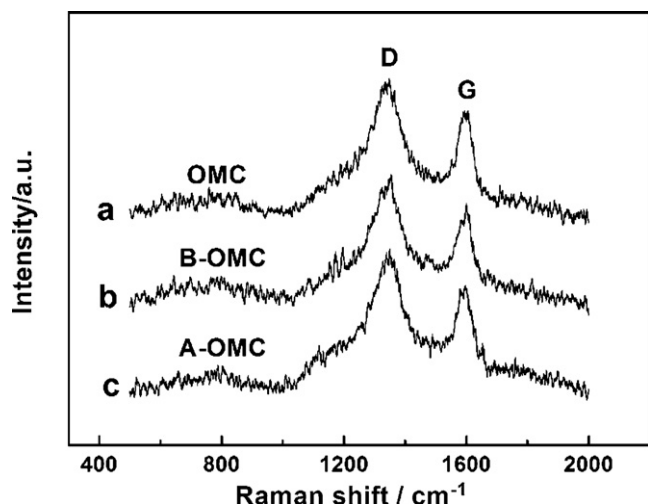


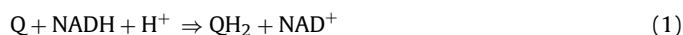
Fig. 4. Raman spectra of OMC (a), B-OMC (b) and A-OMC (c).

crystal graphite sheet [29]. Therefore, the relative intensity ratio of the D and G lines (I_D/I_G ratio) is proportional to the number of defect sites in graphite carbon [29,30]. The I_D/I_G ratio of original OMC, B-OMC and A-OMC is 1.10, 1.07 and 1.08, respectively, indicating that the original OMC and treated OMCs contain the same amount of EDSSs. So it is significant to further investigate the influence of the oxygen content on the electrocatalytic activity of OMC.

3.2. Electrocatalytic oxidation of NADH

To better understand the electrocatalytic property of the original and treated OMCs, NADH is introduced in the electrolyte as a probe in this study. Fig. 5 shows cyclic voltammetric responses to 0.5 mM NADH at different electrodes at pH 7.0. As shown in Fig. 5D, without NADH, the A-OMC/GCE exhibits a pair of well-defined redox waves at 0.0 V (curve a4), which could be ascribed to the redox process of the acidic groups produced on the surface of A-OMC [23]. However, no peaks are apparent at the bare GCE, OMC/GCE and B-OMC/GCE in the absence of NADH (curves a1–a3). Upon the addition of 0.5 mM NADH, the bare GCE only exhibits a weak peak at 0.614 V (curve b1). Compared with GCE (0.614 V), the OMC/GCE (curve b2, 0.205 V) displays a decrease in the overvoltage as well as a current increase, which implies that the OMC/GCE improves the oxidation process

of NADH and shows a good electrocatalytic activity. The better electrochemical performance of original OMC may be attributed to a large number of EDSSs and the oxygen-containing functional groups on the surface of OMC [11,17,31], which is consistent with the observed structure through Raman and FT-IR spectroscopy. However, the B-OMC/GCE (curve b3, 0.223 V) displays the similar peak potential and peak current with OMC/GCE for the oxidation of NADH, suggesting that the B-OMC possesses the same electrocatalytic activity as original OMC. It can be seen that electrocatalytic activity of B-OMC does not increase with increasing oxygen content of B-OMC. This means that not all the oxygen-containing functional groups seem to be responsible for the electrochemistry behavior of OMC. Nevertheless, different from the B-OMC/GCE, the A-OMC/GCE (curve b4, 0.0 V) shows a potential of about 600 and 200 mV more negative compared with that at bare GCE and OMC/GCE. It can be concluded that the A-OMC has better electrocatalytic activity than original OMC and B-OMC for the oxidation of NADH. Because the surface of both original OMC and treated OMC contains the same amount of EDSSs, the surface defects play a negligible role in comparing electrocatalytic activity of various OMCs in this work. Thus, the reason is quite likely due to the increase of acidic groups on the surface of A-OMC, which improves the electrocatalytic properties of A-OMC. It was reported that redox active quinones formed on the surface of carbon nanotubes were responsible for the electrocatalytic of NADH [23]. Thus, the well electrocatalysis of A-OMC can be attributed to surface quinones (Q) [23,32,33].



This is followed by the recycling of quinone species on the surface of A-OMC.



We can presume that the acidic groups formed on the surface of OMC have the similar role for catalytic property of OMC.

We also compare A-OMC/GCE with B-OMC/GCE for amperometric analysis of NADH. In Fig. 6, curve a presents a current–time curve recorded at 0.0 V at the A-OMC/GCE. At such a low potential, almost no current response is visualized at the B-OMC/GCE for the oxidation of NADH (data not shown). So the operation potential is 0.2 V for amperometric detection of NADH at the B-OMC/GCE (curve b). It could be seen that the response signals were increased after each addition of NADH. Plot of the steady state current versus NADH

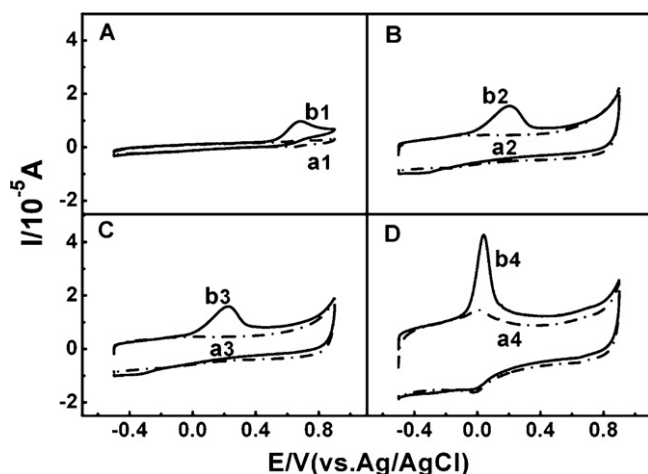


Fig. 5. CVs recorded at (A) bare GCE, (B) original OMC/GCE, (C) B-OMC/GCE, (D) A-OMC/GCE in the absence (a1, a2, a3 and a4) and presence (b1, b2, b3 and b4) of 0.5 mM NADH. Background electrolyte, 0.1 M PBS at pH 7.0. Scan rate: 50 mV s^{−1}.

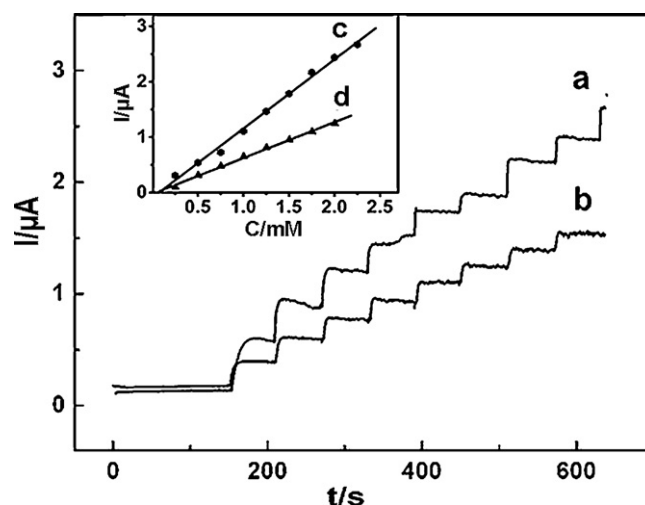


Fig. 6. Amperometric responses of the A-OMC/GCE (at 0.0 V (a)) and B-OMC/GCE (at +0.2 V (b)) with successive addition of 0.25 mM NADH into PBS (0.1 M, pH 7.0). Inset shows the related calibration curves at the A-OMC/GCE (c) and B-OMC/GCE (d).

concentration yielded the calibration curves is shown in inset of Fig. 6 (curves c and d). The B-OMC/GCE shows a weak response current and yields a sensitivity of $9.14 \text{ mA M}^{-1} \text{ cm}^{-2}$ with a detection limit of $1.20 \text{ } \mu\text{M}$ (curve d). Consistent with the high peak current of NADH at A-OMC/GCE (Fig. 5D, curve b4), the A-OMC/GCE also shows a high amperometric response to NADH (curve a). Calculated from the slope value of the corresponding calibration curve (curve c), the A-OMC/GCE produces a higher sensitivity of $18.28 \text{ mA M}^{-1} \text{ cm}^{-2}$ and a lower detection limit $0.65 \text{ } \mu\text{M}$ which are found to overmatch B-OMC/GCE (curve d) for amperometric detection of NADH. The results reiterate that the A-OMC/GCE shows better electrocatalytic activity than B-OMC/GCE, though both contain numerous oxygen-containing functional groups.

From above results, it can be seen that the A-OMC/GCE showed a good electrocatalytic activity for the oxidation of NADH, and it might be used as a chemically modified electrode to explore electroanalytical applications. So the stability study of NADH current at A-OMC/GCE was necessary. We studied amperometric responses of the A-OMC/GCE upon additions of 0.4 mM NADH at an applied potential of 0.0 V (data not shown). The response of the A-OMC/GCE remains stable and the current decay is very small with only 9.0% current diminutions at 900 s , implying that A-OMC/GCE is considerably stable.

3.3. Electrocatalytic reduction of H_2O_2

To further compare the electrocatalytic activity of A-OMC with B-OMC, the electrochemical response of an important molecule (H_2O_2) is studied at different electrodes with CVs (Fig. 7). As shown in Fig. 7A, with the addition of H_2O_2 to the solution, there is a faintness reduction peak current at GCE (curve b1) which is corresponding to the conversion of H_2O_2 to H_2O . The OMC/GCE displays a cathodic peak at -0.20 V and an enhancing peak current (curve b2). Obviously, the presence of OMC can efficiently promote the electro-reduction of H_2O_2 . Compared with GCE, the peak current signals of H_2O_2 on the B-OMC/GCE (curve b3) are also enhanced significantly, but the electrochemical response of H_2O_2 on the B-

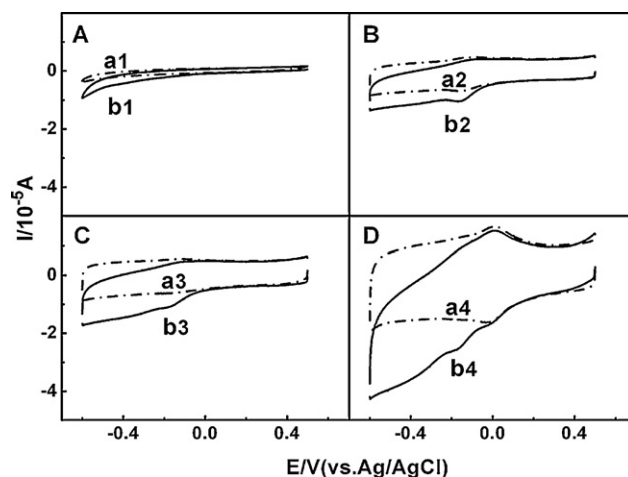


Fig. 7. CVs for $1.0 \text{ mM H}_2\text{O}_2$ at (A) bare GCE, (B) original OMC/GCE, (C) B-OMC/GCE, (D) A-OMC/GCE (solid lines). Dash dotted lines represent the background response (0.1 M PBS , $\text{pH } 7.0$). Scan rate: 50 mV s^{-1} .

OMC/GCE is similar to that on the OMC/GCE (curve b2). The results indicate that NaOH-treated OMC has the similar electrocatalytic property with original OMC. Noticeably, an enhancement of three times in reduction current of H_2O_2 is obtained at A-OMC/GCE over OMC/GCE in Fig. 7D (curve b4). This suggests that the A-OMC/GCE exhibits the highest electrocatalytic activity for the reduction of H_2O_2 compared with GCE, OMC/GCE and B-OMC/GCE, which may be due to the formation of lots of acidic groups on the surface of A-OMC.

Similar results are also reflected for the detection of different H_2O_2 concentrations at A-OMC/GCE and B-OMC/GCE in Fig. 8. Fig. 8A is the CVs of the A-OMC/GCE in 0.1 M PBS ($\text{pH } 7.0$) containing 0.0 , 1.0 , 2.0 and 3.0 mM of H_2O_2 . It can be clearly seen that the reduction currents increase with the addition of H_2O_2 , exhibiting excellent electrocatalytic activities towards the reduction of H_2O_2 . However, when the same concentration H_2O_2 appears, the peak

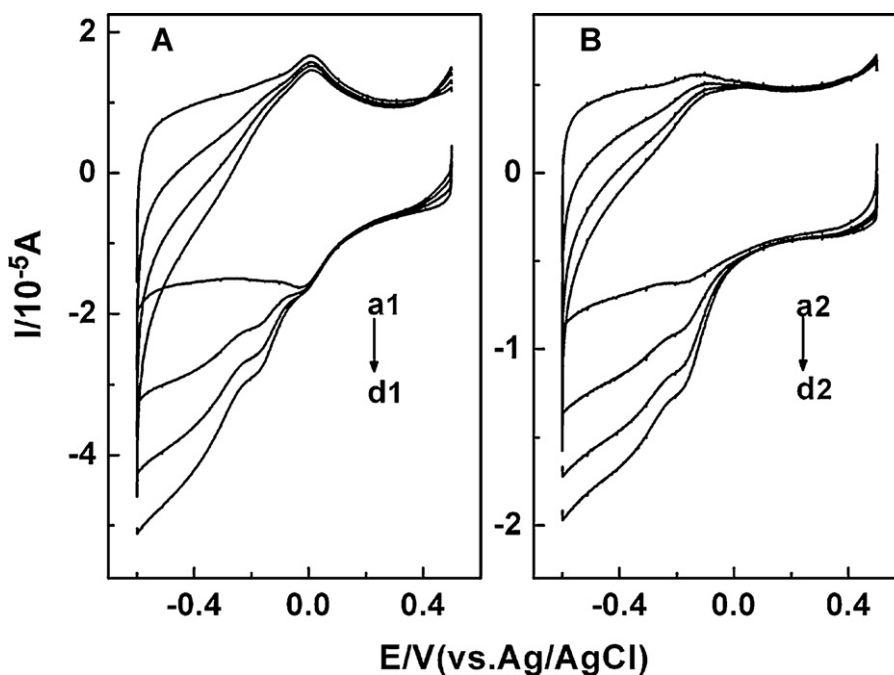


Fig. 8. CVs for (A) A-OMC/GCE and (B) B-OMC/GCE recorded in 0.1 M PBS $\text{pH } 7.0$ in the absence (a1 and a2) and presence of 1.0 mM (b1 and b2), 2.0 mM (c1 and c2) and 3.0 mM (d1 and d2) of H_2O_2 . Scan rate: 50 mV s^{-1} .

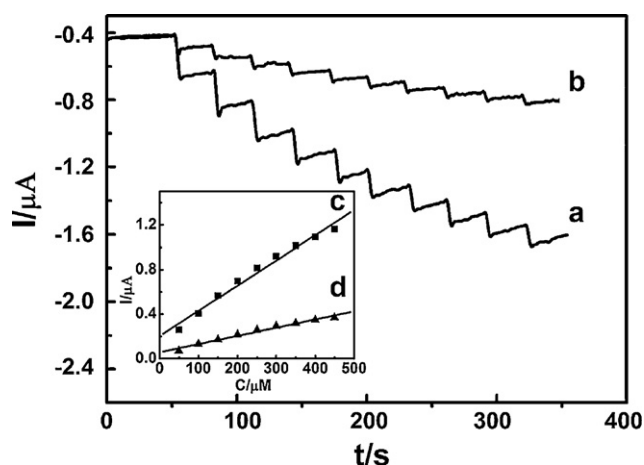


Fig. 9. Amperometric responses of the A-OMC/GCE (a) and B-OMC/GCE (b) with successive addition of 50 μM H_2O_2 into PBS at -0.2 V (0.1 M, pH 7.0). Inset shows the related calibration curves at the A-OMC/GCE (c) and B-OMC/GCE (d).

current of H_2O_2 is significantly lower at B-OMC/GCE than that at the A-OMC/GCE. These results are well consistent with the detection for NADH.

Fig. 9 shows the amperometric responses of the A-OMC/GCE (curve a) and B-OMC/GCE (curve b) upon additions of 50 μM H_2O_2 at an applied potential of -0.2 V . It can be seen that the response current was dramatically increased after each addition of H_2O_2 . Inset of Fig. 9 is the corresponding calibration plots. The detection limit, based on a signal-to-noise ratio of 3, was estimated to be around 1.66 μM for A-OMC/GCE, while it was 10.5 μM for B-OMC/GCE. From the slope of the calibration curves, much higher sensitivity of 35.29 $\text{mA M}^{-1}\text{ cm}^{-2}$ was obtained for A-OMC/GCE (curve c) and it was almost 3 times greater than that of B-OMC/GCE (10.57 $\text{mA M}^{-1}\text{ cm}^{-2}$, curve d). The results again showed that the A-OMC/GCE has better electrocatalytic property than B-OMC/GCE.

The foregoing analysis allows for the following observations. First, compared with original OMC, the surface defects play a negligible role for the improvement of electrochemical behavior of NADH and H_2O_2 at A-OMC/GCE from Raman results. Second, the increase of oxygen-containing functional groups on the surface of B-OMC does not cause any significant change in electrocatalysis of NADH (Fig. 5C, curve b3) and H_2O_2 (Fig. 7C, curve b3), which shows similar electrochemical property with the original OMC. Third, the increase in the density of oxygen-containing functional groups, especially acidic groups on the A-OMC, correlates with the enhancement of electrochemical behavior of NADH (Fig. 5D, curve b4) and H_2O_2 (Fig. 7D, curve b4). One can summarize that this correlation contributes to the increase of acidic groups on the surface of A-OMC. Up to now, the mechanism of the acidic groups able to improve the catalysis capability of OMC remains vague. Research in this direction is currently being done in our laboratory.

4. Conclusions

The A-OMC and B-OMC are obtained during the treated process of OMC with HNO_3 or NaOH , and the large difference in electrocatalytic properties becomes clearly visible. For the two OMCs, the treatment leads to the increase of oxygen-containing functional groups on the surface of OMC. Through all the experiments, A-OMC shows better electrocatalytic activity for the oxidation of NADH and the reduction of H_2O_2 than original OMC. However, B-OMC displays similar electrocatalytic property with original OMC. It is concluded that it is the acidic groups, not other oxygen-containing functional groups that is helpful to electrocatalytic property of OMC.

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References

- [1] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* 122 (2000) 10712.
- [2] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* 412 (2001) 169.
- [3] R. Ryoo, S.H. Joo, in: O. Terasaki (Ed.), *Studies in Surface Sciences and Catalysis*, vol. 148, Elsevier, Amsterdam, 2004, p. 241.
- [4] J. Lee, S. Han, T. Hyeon, *J. Mater. Chem.* 14 (2004) 478.
- [5] J. Lee, J. Kim, T. Hyeon, *Adv. Mater.* 18 (2006) 2073.
- [6] A. Vinu, M. Miyahara, K. Ariga, *J. Phys. Chem. B* 109 (2005) 6436.
- [7] M. Hartmann, A. Vinu, G. Chandrasekar, *Chem. Mater.* 17 (2005) 829.
- [8] H. Zhou, S. Zhu, M. Hibino, I. Honma, *J. Power Sources* 122 (2003) 219.
- [9] M. Zhou, L.P. Guo, Y. Hou, X.J. Peng, *Electrochim. Acta* 53 (2008) 4176.
- [10] J.C. Ndamaniha, Y. Hou, J. Bai, L. Guo, *Electrochim. Acta* 54 (2009) 3935.
- [11] N. Jia, Z. Wang, G. Yang, H. Shen, L. Zhu, *Electrochim. Commun.* 9 (2007) 233.
- [12] L.D. Zhu, C.Y. Tian, D.X. Zhu, R.L. Yang, *Electroanalysis* 20 (2008) 1128.
- [13] J.J. Feng, J.J. Xu, H.Y. Chen, *Biosens. Bioelectron.* 22 (2007) 1618.
- [14] M. Zhou, L. Shang, B.L. Li, L.J. Huang, S.J. Dong, *Electrochim. Commun.* 10 (2008) 859.
- [15] S.H. Joo, K.J. Kwon, D.J. You, C. Pak, H. Chang, J.M. Kim, *Electrochim. Acta* 54 (2009) 5746.
- [16] S.H. Joo, C. Pak, D.J. You, S. Lee, H. Lee, J.M. Kim, H. Chang, D. Seung, *Electrochim. Acta* 52 (2006) 1618.
- [17] G. Hu, Y. Ma, Y. Guo, S.J. Shao, *J. Electroanal. Chem.* 633 (2009) 264.
- [18] R. Liu, X. Wang, X. Zhao, P. Feng, *Carbon* 46 (2008) 1664.
- [19] A.H. Lu, W.C. Li, N. Muratova, B. Spliethoff, F. Schüth, *Chem. Commun.* (2005) 5184.
- [20] M.J. Lázaro, L. Calvillo, E.G. Bordejé, R. Moliner, R. Juan, C.R. Ruiz, *Micropor. Mesopor. Mater.* 103 (2007) 158.
- [21] R.L. McCreery, *Interfacial Electrochemistry*, Marcel, New York, 1999, p. 631.
- [22] A. Chou, T. Böcking, N.K. Singh, J.J. Gooding, *Chem. Commun.* (2005) 842.
- [23] M. Wooten, W. Gorski, *Anal. Chem.* 82 (2010) 1299.
- [24] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [25] H. Furukawa, M. Hibino, H.S. Zhou, I. Honma, *Chem. Lett.* 32 (2003) 132.
- [26] P.A. Bazula, A.H. Lu, J.J. Nitz, F. Schüth, *Micropor. Mesopor. Mater.* 108 (2008) 266.
- [27] M. Starsinic, R.L. Taylor, P.L. Walker Jr., P.C. Painter, *Carbon* 21 (1983) 69.
- [28] X.F. Yu, T. Mu, H.Z. Huang, Z.F. Liu, N.Z. Wu, *Surf. Sci.* 461 (2000) 199.
- [29] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* 46 (2008) 833.
- [30] A.C. Ferrari, J. Robertson, *Phys. Rev. B* 61 (2000) 14095.
- [31] M. Musameh, N.S. Lawrence, J. Wang, *Electrochim. Commun.* 7 (2005) 14.
- [32] B.W. Carlson, L.L. Miller, *J. Am. Chem. Soc.* 107 (1985) 479.
- [33] T. Kuwana, *Anal. Chem.* 50 (1978) 1315.