Pd@MC-PVA composite electrocatalyst for ethanol electrochemical oxidation

Guoqing Zhang1, *, Binbin Jin1 and Yongqing Zhao2
1Chongqing Key Laboratory of Inorganic Special Functional Materials, Yangtze Normal University, Chongqing, China
2School of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, China

*Corresponding author e-mail: zhangguoqing@yznu.edu.cn

Abstract. By a simple and effective intermittent microwave heating (IMH) method, Pd anchored on mesoporous carbon (MC) and Poly (vinyl alcohol), (PVA) (Pd@MC-PVA) composite was successful synthesized for ethanol electrochemical oxidation. Both cyclic voltammetric and chronoamperametric measurements indicate that the performance of Pd@MC-PVA was significant improved for ethanol oxidation. The activity of Pd@MC-PVA for ethanol oxidation is four times higher than that of Pd@MC with the same Pd loading in alkaline media. The activity enhancement could attribute to a good Pd dispersion and utilization on MC because of strong hydrophilic and excellent conductivity.

1. Introduction
Carbon materials such as onion-like carbon [1], actinozoan-like carbon [2], straw-like carbon [3] and carbon particles [4] have been of continuous research interest, since fullerenes in 1985[5] and carbon nanotube in 1991[6] were found. They have a wide range of applications including metal atomic chain [7], gas/energy storage [8, 9], nano devices [10], supports of catalyst [11], and adsorbents [12], because of their intrinsic properties of large BET surface area, low weight, self-sinter, chemical inertia and excellent conductivity and so on. As we know, as a support of electrocatalyst, it is necessary that possessing an enough conductivity and large surface area can enable the fast charge transfer and increase the gas/liquid interfacial area. In the previous reports, it was found that the carbon material with hollow structure and large micropores could effectively enhance the performance of electrocatalyst [13, 14].

Diverse approaches have been established for carbon surface modification. The most widely used technique to functionalize the carbon surface involves oxidizing it with acid or ozone, which oxygenated functionalities, such as carboxylic acid, esters are generated. Moreover, the low bonding densities, and the pore structure damage during oxidative treatment are drawbacks [15]. Though some methods retained the carbon structure, it needed two separated synthesis steps, which make the process quite complex.

We report here on a promising and one-step synthesis of highly hydrophilic ordered MC-PVA composite with larger surface area by a rapid IMH. The resulting composite retains the ordered pore structure of the carbon. The synthesis strategy can be extended to various compositions of hydrophilic
and hydrophobic mesoporous materials-organic polymer. The resultant material exhibiting chemical properties of the polymers, as well as electric conductivity of MC, served as Pd based electrocatalyst support for ethanol oxidation in alkaline media.

2. Experimental

2.1. Preparation of the Pd@MC-PVA electrocatalyst

Chemicals were of analytical grade and used as received. 1 g of the molecular sieve SBA-15 was impregnated with 1.25 g of glucose aqueous solution, 0.14 g of sulphuric acid together with 0.35 g of PVA (87-89% hydrolyzed, Mw 13,000-23,000, Sigma-aldrich) in 5 g water. The mixture was put into a drying oven for 6 h at 373 K, and subsequently the oven temperature was increased to 433 K and maintained for 6 h. The experiments were controlled by a water-bath thermostat. After treatment in the oven, the sample turned dark brown. Then it was further heated by IMH technique, i.e., at 1000 W for 2 min, following 2 min at rest, and the same procedure was repeated two times. When the dark brown sample turned dark black, it was washed with 5wt % hydrofluoric acid at room temperature to remove the silica template. Then it was filtered, washed with ethanol, dried at 393 K, and labeled as MC-PVA. Without adding PVA in the reactant mixture, the obtained sample was labeled as MC.

Pd@MC-PVA and Pd@MC were prepared by the reduction of PdCl\(_2\) (4.7 ml, 0.1 mol dm\(^{-3}\)) in aqueous solution on MC-PVA or MC (50.0 mg) powders. The formic acid (5 ml, 1 mol dm\(^{-3}\)) used as reducing agent. The Pd loadings on the Pd@MC-PVA and Pd@MC were controlled at 20 -µg cm\(^{-2}\).

2.2. Characterization of material

The morphology and microstructure of the materials was explored by field emission scanning electron microscopy (FESEM) (JSM-6700F, Japan), transmission electron microscopy (TEM) (JEM-2100F, Japan), and XRD (D/max-2400 Rigaku, Japan) with CuKa radiation (l=1.54178 Å) operating at 50.0 kV and 200.0 mA. All electrochemical measurements were conducted in a three-electrode electrolytic cell with an electrochemical workstation (CHI760C, CH Instruments, Shanghai, China). Platinum foil (3.0 cm\(^2\)) and Hg/HgO (1.0 mol dm\(^{-3}\) KOH) were used as counter and reference electrodes, respectively.

3. Results and discussion

As show in Figure 1, the synthesized MC-PVA presents a rod-like morphology with relatively uniform length of 1 µm. The ordered pores are 6 nm in diameter; the centers of adjacent pores are 10 nm apart. It is useful for the transport and hold of electrolyte. The examination of hydrophilicity as shown in figure 1 c and d by the water contact angle measurement instrument indicate that the contact angle of MC-PVA is 26.8°, much less than 80.4° of MC, and less than 79.1° observed for pure carbon material [16, 17]. Thus, the fast IMH partially burned PVA greatly improves the hydrophilicity of the MC-PVA, which enables accelerating the analysts to approach the material surface [18, 19]. It is advantageous for species such as the electrolyte ions, reactant and production to transport in the
material and to increase the active sites for oxidation reaction. The microstructure examined by XRD display a typical amorphous carbon peak assigned to (002); the ordered arrangement of the carbon nanorods in MC-PVA gives rise to a well-resolved XRD peaks shown in inset of figure 1(e), which can be assigned to (100), (110), and (200) diffractions of the hexagonal space [20, 21]. A significant diffraction peaks were located at around 0.6 degree, suggesting that this carbon sample has kept the original hexagonal mesostructure [22].

Figure 2 Cyclic voltammograms of Pd@MC and Pd@MC-PVA in 1.0 mol dm$^{-3}$ KOH (a)/ 1.0 mol dm$^{-3}$ ethanol solution (b), 303 K, scan rate: 50 mV s$^{-1}$.

Cyclic voltammograms of Pd@MC and Pd@MC-PVA were shown in figure 2. The onset potential, peak potential and peak current density of ethanol oxidation on Pd@MC and Pd@MC-PVA electrodes are ~0.49 V, ~0.151 V, 10.0 mA cm$^{-2}$ and ~0.55 V, ~0.185 V, 27.1 mA cm$^{-2}$ respectively. The similar onset and peak potential on two electrodes are due to the similar structure of carbon support. However, the peak current density of Pd@MC-PVA is 2.7 times more than that of Pd@MC, just owing to the better hydrophilic and conductivity of Pd@MC-PVA. As shown in figure 2(a), we can sure that the improvement of catalytic activity was owed to the good hydrophilic and conductivity of MC-PVA, which was able to give the more active center for the electrocatalytic reaction and species transportation.

Figure 3 Electrochemical impedance spectroscopy (EIS) of (a) Pd@MC (b) Pd@MC-PVA at different potentials in 1.0 mol dm$^{-3}$ KOH/1.0 mol dm$^{-3}$ ethanol solution.

From EIS in figure 3, resistance values were obtained at potential range from ~200 mV to 0 mV. The lower resistance of Pd@MC-PVA than that of Pd@MC can be seen. The reason is that IMH partially burned PVA, which greatly improve the hydrophilicity and simultaneously create some micropores on the surface of material.

Figure 4 (a) shows the relationship between the normalized charge of ethanol oxidation reaction and scan rate on Pd@MC and Pd@MC-PVA electrodes. $Q_{\text{mean}}$ is the integrated charge of anodic peak for ethanol oxidation at different scan rates and $Q_{\text{max}}$ is the one at the scan rate of 2 mVs$^{-1}$. We can see
from the curves that the charge decreasing of Pd@MC is similar to that of Pd@MC-PVA, but the decreasing slope of Pd@MC-PVA is faster than that of Pd@MC. That is because the remnants PVA in MC-PVA can significantly improve the hydrophilicity and conductivity, which create faster mass and electron transportation; and the new micropore on the surface of material is helpful for transportation of gas molecules producing from electrocatalytic reaction.

A further investigation was made on the mass transportation behavior of this modified hydrophilic material by studying the relationship between anodic peak current density and the square root of scan rate on Pd@MC and Pd@MC-PVA as shown in inset of Figure 4 (b). The Pd@MC shows a linear relationship from 5 mVs\(^{-1}\) to the end while the linear relationship on Pd@MC-PVA appears at a high scan rate of 7.5 mVs\(^{-1}\). The result further reveals that the oxidation of ethanol on Pd@MC is mostly limited by the concentration polarization; and oxidation of ethanol on Pd@MC-PVA is controlled dominantly by activation polarization at low scan rates.

![Figure 4](image)

(Figure 4) (a) Plot of normalized charge of anodic peak and scan rate (b) plot of the peak current density against the square root of the rate on Pd@MC and Pd@MC-PVA. 

Stability of Pd@MC and Pd@MC-PVA was also compared through the steady-state measurement. Figure 5 shows their curves at 3 mA cm\(^{-2}\). Oxidation of ethanol on Pd@MC-PVA was relatively stable at low potentials of -0.2 V. On the Pd@MC, the potential was finally shifted to a high value for oxygen evolution after -0.15 V, due to the loss of the catalytic activity possibly. It is because that the relative inferior conductivity of Pd@MC leads to adsorbed species on electrocatalyst surface blocking the access of ethanol molecules into electrocatalyst bulk.

![Figure 5](image)

(Figure 5) Chronopotentiometric curves of ethanol oxidation on Pd@MC and Pd@MC-PVA.

4. Conclusion

This work reported that Pd@MC-PVA composite electrocatalyst was successfully synthesized by a simple and effective IMH method. The experimental results show that the as-obtained material is an attractive electrocatalyst for ethanol oxidation. Good electron transfer on Pd@MC-PVA surface can be contributed to the strong hydrophilicity of material. The stability and catalytic activity examinations indicated that significant improvement of Pd@MC-PVA electrocatalyst catalytic activity, comparing with Pd@MC, could be attributed to the modification of MC by PVA. It is proved substantially that a
large surface area, strong hydrophilicity and good conductivity of Pd@MC-PVA accelerate the process of surface reaction and decrease the concentration polarization for ethanol oxidation.

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References
[1] Ugarte, D., Curling and closure of graphitic networks under electron-beam irradiation. Nature, 359 (6397), (1992) 707-709.
[2] Mi, Y. Z.; Luo, Y., Actinozoan-Like Carbon Materials Prepared via a Solvothermal Route. Advanced Materials Research, 557-559, (2012) 983-986.
[3] Yong, X.; Yingliang, L.; Yuanzhu, M.; Dingsheng, Y.; Jingxian, Z.; Liqiang, C., A Simple Route to Form Straw-like Carbon Microbundles. Chemistry Letters, 34 (10), (2005) 1422-1423.
[4] Mukawa, K.; Oyama, N.; Shinmi, T.; Sekine, Y., Nanostructural Control of the Formation of Carbon Particles by Application of a Moderate Electric Field. Chemistry Letters, 46 (1), (2017) 19-21.
[5] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E., C60: Buckminsterfullerene. Nature, 318 (6042), (1985) 162-163.
[6] Iijima, S., Helical microtubules of graphitic carbon. Nature, 354 (6348), (1991) 56-58.
[7] Tang, D. M., Fabrication and Property Investigation of Carbon Nanotube-Clamped Metal Atomic Chains, Springer Berlin Heidelberg: Berlin, Heidelberg, (2013) 55-71.
[8] Elyassi, M.; Rashidi, A.; Hantehzadeh, M. R.; Elahi, S. M., Hydrogen Storage Behaviors by Adsorption on Multi-Walled Carbon Nanotubes. Journal of Inorganic & Organometallic Polymers & Materials, 27 (1), (2016) 1-11.
[9] Liu, T.; Davijani, A. A.; Sun, J.; Chen, S.; Kumar, S.; Lee, S. W., Hydrothermally Oxidized Single-Walled Carbon Nanotube Networks for High Volumetric Electrochemical Energy Storage. Small, 12 (25), (2016) 3423-3431.
[10] Chen, Y.; Zhang, J., Chemical vapor deposition growth of single-walled carbon nanotubes with controlled structures for nanodevice applications. Accounts of chemical research, 47 (8), (2014) 2273-2281.
[11] Nongwe, I.; Bepete, G.; Shaikjee, A.; Ravat, V.; Terfassa, B.; et.al, Synthesis of gold encapsulated in spherical carbon capsules with a mesoporous shell structure. A robust catalyst in a nanoreactor. Catalysis Communications, 53 (30), (2014) 77-82.
[12] Zhuang, Y.-T.; Jiang, R.; Wu, D.-F.; Yu, Y.-L.; et.al, Selenocarrageenan-inspired hybrid graphene hydrogel as recyclable adsorbent for efficient scavenging of dyes and Hg2+ in water environment. Journal of Colloid and Interface Science, 540, (2019) 572-578.
[13] Wu, Q.; Jiang, L.; Qi, L.; Yuan, L.; Wang, E.; Sun, G., Electrocatalytic activity and stability of Ag-MnOx/C composites toward oxygen reduction reaction in alkaline solution. Electrochimica Acta, 123 (123), (2014) 167-175.
[14] Lee, J. S.; Park, G. S.; Lee, H. I.; Kim, S. T.; Cao, R.; Liu, M.; et.al, Ketjenblack carbon supported amorphous manganese oxides nanowires as highly efficient electrocatalyst for oxygen reduction reaction in alkaline solutions. Nano Letters, 11 (12), (2011) 5362.
[15] Bahr, J. L.; Tour, J. M., Covalent chemistry of single-wall carbon nanotubes. Journal of Materials Chemistry, 12 (7), (2002) 1952-1958.
[16] Ueda, K.; Sato, Y.; Mori, M., Incorporation of N2 and CO into Organic Molecules: Amide Formation by Palladium-Catalyzed Carbonylation and Nitrogenation. Journal of the American Chemical Society, 122 (43), (2000) 10722-10723.
[17] Mancuso, R.; Raut, D. S.; Marino, N.; De, L. G.; Giordano, C.; Catalano, S.; Barone, I.; Andò, S.; Gabriele, B., A Palladium-Catalyzed Carbonylation Approach to Eight-Membered
Lactam Derivatives with Antitumor Activity. Chemistry - A European Journal, 22 (9), (2016) 3053-3064.

[18] Tanev, P. T.; Pinnavaia, T. J., A Neutral Templating Route to Mesoporous Molecular Sieves. Science, 267 (5199), (1995) 865-867.

[19] Abdel-Fattah, T. M.; Williams, P. A.; Wincheski, R. A.; Shams, Q. A., Catalyst Design Using Nanoporous Iron for the Chemical Vapor Deposition Synthesis of Single-Walled Carbon Nanotubes. Journal of Nanomaterials, 2013 (1-2), (2013) 1-7.

[20] Yu, C.; Fan, J.; Tian, B.; Zhao, D.; Stucky, G. D., High-Yield Synthesis of Periodic Mesoporous Silica Rods and Their Replication to Mesoporous Carbon Rods. Advanced Materials, 14 (23), (2002) 1742-1745.

[21] Bello, A.; Barzegar, F.; Momodu, D.; Dangbegnon, J.; Taghizadeh, F.; Manyala, N., Symmetric supercapacitors based on porous 3D interconnected carbon framework. Electrochimica Acta, 151, (2015) 386-392.

[22] Kim, T.-W.; Park, I.-S.; Ryoo, R., A Synthetic Route to Ordered Mesoporous Carbon Materials with Graphitic Pore Walls. Angewandte Chemie International Edition, 42 (36), (2003) 4375-4379.