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# Construction of hollow carbon polyhedron supported Pt catalyst for methanol electrocatalytic oxidation



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#### ABSTRACT

In this work, the hollow Pt/CP (carbon polyhedron) catalyst derived from ZIF-8 was obtained via a simple hydrothermal method for electrocatalytic methanol oxidation reaction (MOR). Compared with Pt/CB (carbon black) catalyst, the hollow Pt/CP had the higher ESCA, which was 60 m<sup>2</sup> g<sup>-1</sup>, while the Pt/CB was only 41 m<sup>2</sup> g<sup>-1</sup>. Similarly, the I<sub>f</sub>/I<sub>b</sub> of the hollow Pt/CP was 7.5, which was also obviously about 3 times higher than the Pt/CB (2.5). All the results verified that the electrocatalytic oxidation activity of hollow Pt/CP was greatly better than Pt/CB. According to a series of characterizations, it can be discovered that the hollow Pt/CP catalyst derived from ZIF-8 had more rich oxygen-containing functional groups, smaller Pt nanoparticles size, more Pt content, larger specific surface area, and so on, which were good for the improvement of MOR activity.

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#### 1. Introduction

The pressure on the environment was mounting with the world's population being bigger. Besides, the pressure on energy was also very serious [1]. Therefore, the requirements of sustainable development were also very important and necessary. So, the current exploration and research on new energy were very urgent. Nowadays, the application of nuclear energy, hydrogen energy, solar energy, and other new energy source had achieved initial results. Also, due to the need for sustainable energy development and energy demand, fuel cells were one of the research hotspots. Fuel cells can directly transform the energy in chemical fuels to electricity, and this reaction had high efficiency and was friendly to the environment. Generally, hydrogen, as well as liquids such as alcohols, aldehydes, and so on can be used as fuel. Among them, methanol has become the most promising fuel due to its simple molecular structure, low cost, and low CO<sub>2</sub> emissions. The direct methanol fuel cell (DMFC) was very promising research which had some advantages such as high energy density, low operating temperature, convenient fuel storage, low pollutant emission, low cost, and so on [2,3]. Compared with traditional battery devices, DMFC had higher power density with long service life and rechargeable which was almost moment. Also, methanol fuel cell vehicles had

\* Corresponding author. *E-mail address:* tangzhicheng@licp.cas.cn (Z. Tang). the lowest cost. The anode catalytic material of DMFC is a key factor that determines its performance and commercial application. To maximize energy efficiency, researchers had conducted extensive exploration of catalysts. And the transition metals' application was more common at present. Among them, Pt was the most effective active ingredient. However, the existing Pt-based catalysts have the following problems: (1) Pt is easily adsorbed by reaction intermediate products (such as CO), resulting in catalyst poisoning; (2) the cost of Pt-based catalysts is too high. So, it was very necessary to find effective and low-cost materials that can reduce the Pt's content.

Based on the shortcomings of Pt-based catalysts, to maximize the active advantage of a small amount of Pt, the carrier's characteristic structure was used to achieve the requirement which had low content and high activity, such as carbon paper, graphene oxide, multi-walled carbon nanotubes, carbon nanofiber and so on [4–8]. At the same time, MOFs have the characteristics of high porosity, rich pore structure, high specific surface area, pores that can be easily controlled, various skeleton components and structure changes, easy to realize functionalization, and so on, whose application was very pervasive [9]. Currently, Ni-MOF, Co-MOF, HKUST, and other MOFs were widely used [10–13]. Some MOFs structures with special morphology, such as 3D flower-like [14], polyhedron [15], and so on, also have good application potential.

Based on the above advantages, the use of carbon materials derived from MOFs as carriers to prepare electro-catalysis for methanol oxidation reaction (MOR) has a promising application prospect. The most important carbonization method was to use high-temperature calcination to obtain a carbon material with a MOF's morphology. The materials with MOFs' unique morphology which can provide a special reaction channel were very advantageous for molecular's mass transfer, adsorption, desorption, and such advantages were particularly useful for MOR. Because of the special morphology and active components' dispersion displayed activity tends to be better.

In this paper, we prepared a hollow CP dodecahedron structure derived from ZIF-8, and test the electrocatalytic activity of the catalyst for MOR in alkaline medium. Compared with carbon black, it was discovered that hollow CP support had obvious structural advantages, which were conducive to the subsequent loading and dispersion of Pt, and the electron transport in the reaction. When the hollow Pt/CP was used in MOR, the catalytic performance was better than Pt/CB.

#### 2. Experimental

#### 2.1. Synthesis of catalysts

#### 2.1.1. Synthesis of ZIF-8

Refer to the previous literature [15] and make some adjustments to get ZIF-8. In a typical synthesis, 1.116 g  $Zn(NO_3)_2 \cdot 6H_2O$  was dissolved in methanol (15 mL) to form uniform solution, 2-Methylimidazole (1.232 g) was dissolved with stirring in methanol (30 mL) to get other clear solution. Then the two solutions with methanol were put together under stirring for 5 min. The mixture was kept reacting at hydrothermal reactor for 4 h. The powders were collected by centrifugation, washed with methanol for several times, and dried overnight at 110 °C.

#### 2.1.2. Synthesis of hollow CP

The above ZIF-8 was put in the tube furnace, carbonized at 900°C under argon atmosphere. The heating rate was 1 °C min<sup>-1</sup>, and heating time was 2 h. The purpose of this calcination condition was to completely remove Zn.

#### 2.1.3. Synthesis of hollow dodecahedron Pt/CP

Subsequently, 100 mg of hollow CP was dissolved in 100 mL ethylene glycol solution under ultrasonic conditions. After, added 3.3 mL of  $H_2PtCl_6\bullet GH_2O$  (38.6 mM  $L^{-1}$ ) and added dropwise 1 M NaOH to adjust the pH of the mixed solution to 8, the above solution was heated to 130 °C and reacted for 3 h. Then, using centrifugation (10,000 rpm min<sup>-1</sup>, 3 min), washed with distilled water and ethanol for three times, severally, and dried overnight at 60°C. The above experimental process was shown in Scheme 1.

#### 2.2. Apparatus and measurements

The XRD (X-ray diffraction) analysis was characterized by a Rigaku D/MAX-RB diffractometer to analyze the catalyst structure with Cu K $\alpha$  ( $\lambda$ =0.154 nm; 60 kV and 55 mA) diffraction source. To observe the catalysts' morphology and Pt nano-particles (NPs)' distribution size we used the TEM (transmission electron microscope, JEOL JEM-2010 transmission electron microscope at 200 kV). Raman spectrometer with 532 nm laser was employed to obtain Raman spectra (A RM 2000 microscope confocal). In order to know the composition on the samples' surface, the XPS (X-ray photo-electron spectroscopy) was performed on a VG ESCALAB 210 employing Mg K $\alpha$  as X-ray. Also, to detect the information of surface area and pore size distribution, N<sub>2</sub> adsorption-desorption isotherm was inspected by adsorbing N<sub>2</sub> at 76.2 K on a Micromeritics ASAP 2020 determinator for viewing the pore structure and specific surface area. FTIR (Fourier transform infrared spectroscopy) was also

used to find the elements' interaction. SEM (Scanning electron microscopy) image was obtained on SU-8020 to observe the morphology of Co-MOFs.

Electrochemical experiments were done at room temperature on a CHI660c electrochemical workstation (Chenhua, Shanghai), and counter electrode was a platinum wire and the reference electrode was Ag/AgCl. The preparation of working electrode: 5.0 mg catalyst and 25 mL of 0.05% Nafion solution was dispersed in 1 mL ethanol through ultrasound for 30 min. Then dropping ink 25  $\mu$ L of the above on the GCE surface, and then let it dry naturally, which was used as the working electrode.

#### 3. Result and discussion

#### 3.1. Electrochemical performance

#### 3.1.1. CV curve

All the tests were done under an N<sub>2</sub>-saturated condition at room temperature. In this system, the counter electrode was platinum wire and the Ag/AgCl electrode was used as a reference electrode, respectively. Glassy carbon electrode (GCE, 3.0 mm diameter) was buffed sequentially with 0.3 and 0.05 mm alumina oxide (Al<sub>2</sub>O<sub>3</sub>) powder 20 min, severally. Then it was ultrasonic for 2 min to wash (first use deionized water, then used deionized water and ethanol mixed solution, last use deionized water), respectively, then catalysts dropped to this electrode, which was treated as the working electrode. The working electrode was prepared by dropping 25  $\mu$ L of the catalyst ink on the GCE surface, and then evaporated the ethanol. The as-prepared working electrode was activated by CV (cyclic voltammetry) in 1 M NaOH and the potential range was from -1 V to 0.6 V (vs. Ag/AgCl) with a scan rate 50 mV  $s^{-1}$ . As the catalysts were used in the MOR, the electro-catalytic activities of catalysts were got by CV in a condation which containing 1 M NaOH and 1 M methanol from -1 to 0.4 V with a scan rate 50 mV s<sup>-1</sup> (vs. Ag/AgCl), respectively. The CA (Chronoamperometry) for the MOR was obtained at a potential of -0.2 V for 3600 s. In a frequency scope from 100 kHz to 0.1 Hz with stationary potential mode amplitude of 5 mV, the EIS (electrochemical impedance spectroscopy) data were tested in Nyquist diagrams form.

In the following experiments, to further get the electrochemical behaviors of hollow Pt/CP and Pt/CB. Fig. 1A depicted the CV curves of the two catalysts in N<sub>2</sub>-saturated with 1 M NaOH. The sweep potential was -1-0.6 V, scan rate was 50 mV s<sup>-1</sup>. According to literatures [16-18], the current peak between -1 V-0.6 V is caused by the typical hydrogen adsorption and desorption on the surface of the Pt catalyst (vs Ag/AgCl), The oxidation peak between -1-0.6 V was caused by the absorption and desorption of hydrogen on the Pt surface, it can be found that hollow Pt/CP had a larger electric double layer than Pt/CB, indicating that hollow Pt/CP had a larger electrochemically active surface area (ESCA). Also, this can be used to get the ESCA of hollow Pt/CP and Pt/CB. We used the following equation to obtain the ESCA. where  $Q_H$  (in mC cm<sup>-2</sup>) was the charge for hydrogen desorption, 0.21 (in mC cm<sup>-2</sup>) represent the charge required to oxidize a monolayer of H<sub>2</sub> on bright Pt and [Pt] was the loading of Pt on the electrode (in mg cm<sup>-2</sup>)] [19], and the  $\Delta Q_{\rm H}$  was the average value of  $Q_{\rm H}$ .

## $\text{ESCA} = \frac{\Delta Q_{\text{H}}}{0.21 * [\text{Pt}]}$

The calculated data are shown in the Table 1. And the According to the above formula, we can get the ESCA of hollow Pt/CP was 60 m<sup>2</sup> g<sup>-1</sup>, and the Pt/CB was 41 m<sup>2</sup> g<sup>-1</sup>. From this result, we can know the hollow Pt/CP had better ESCA and a larger electric double layer, which was helpful for the methanol oxidation. The bigger ESCA might be due to the hollow CP structure had a large specific surface area and excellent pore size channels



Scheme 1. The catalyst preparation process and simple reaction process.

Table 1

Hydrogen	adsorption	and	desorption	charges	and	mean	valu	es
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catalyst	Pt (mg cm <sup>-2</sup> )	Q' (mC $cm^{-2}$ )	Q" (mC cm <sup><math>-2</math></sup> )	$Q_{\rm H}~(mC~cm^{-2})$	$Q_{\rm H}/[{\rm Pt}] \ ({\rm mC} \ {\rm mg}^{-1})$
Pt/CP	0.24	45	15	30	125
Pt/CB	0.24	26	16	21	87

#### Table 2

Kinetic parameters for the MOR at selected potentials and electrode active surface area (ECSA) and  $l_{\rm f}/l_{\rm b}$  of the electrocatalysts.

Sample	$\text{ESCA}_{\text{H}} \ m^2 \text{g}^{-1}$	Methanol oxidation current density $mAcm^{-2}$	$I_{\rm f}/I_{\rm b}$
Pt/CB	41	0.30	7.5
Hollow Pt/CP	60	0.25	2.5

and had smaller Pt particles with good dispersion. These structural advantages might be beneficial to the molecules' adsorption and activation.

Fig. 1B showed the CV curves in the 1 M NaOH and 1 M methanol, the oxidation peak at -0.4-0.2 V was attributed to the methanol oxidation on the catalyst, the other peak at -0.2-0.6 V belonged to the oxidation of intermediate species such as CO [20]. The first oxidation peak of hollow Pt/CP was 0.3 mA cm<sup>-2</sup>, which was about 1.5 times higher than the Pt/CB (0.25 mA cm<sup>-2</sup>). Hollow Pt/CP had good catalytic activity, which might be due to its large specific surface area and smaller Pt, which was conducive to the reaction of methanol on the surface. Besides, the Pt<sup>0</sup> was also a favorable factor that was good for improving activity and was conducive to better contact between methanol and active sites. And the hollow Pt/CP has more Pt. To obtain the CO tolerance of the catalyst, it was expressed by the ratio of I<sub>f</sub> (forward peak current density) and I<sub>b</sub> (backward peak current density) [21]. The larger of the  $I_f/I_b$  ratio, the stronger the catalyst's resistance to the CO-like substances produced during the CH<sub>3</sub>OH oxidation process. The I<sub>f</sub>/I<sub>b</sub> of the hollow Pt/CP was 7.5, which was higher than the Pt/CB (2.5) about 3 times, higher  $I_f/I_b$  meant there was more CH<sub>3</sub>OH was oxidized to CO<sub>2</sub>, more intermediates of carbonaceous were effectually removed [22]. And Table 2 summarized and compared the ESCA data of the two catalysts, and the hollow Pt/CP had better ESCA and higher  $I_f/I_b$ .

Fig. 1C showed the CV curves in 1 M NaOH with 1 M methanol at different scan rate (10mV s<sup>-1</sup>, 20 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup>, 80 mV s<sup>-1</sup>, 100 mV s<sup>-1</sup>). The first half of the CV was selected to analyze changes in current density. It can be discovered that as the sweep rate increased, the methanol oxidation peak gradually increased, which meant the peak current also increased. The square root of sweep speed had a linear relationship with the current density, which meant the diffusion was the controlling step in the methanol oxidation process [23]. As Fig. 1D shown, there was a linear relationship between  $E_p$  (peak potential) and ln(v) at different scanning speeds, which meant this methanol oxidation reaction was not reversible [24]. And in Fig. 1E had shown the specific activity and mass activity of the two simples, as the results shown, the hollow Pt/CP had higher specific activity, which was about 1.5 times higher than Pt/CB, and the mass activity of hollow Pt/CP was also better than Pt/CB. This result may indicate that under the same load conditions, the Pt on hollow CP was more uniformly dispersed so that having a smaller Pt nanoparticle size, and more active sites were exposed.

### 3.1.2. Chronoamperometric curve and electro-chemical impedance tests

The chronoamperometry can test the long-term stability of hollow Pt/CP and Pt/CB in methanol oxidation at -0.2 V, which was in 1.0 M NaOH containing 1.0 M methanol for 3600 s. As Fig. 2A



**Fig. 1.** The CV curves of hollow Pt/CP and Pt/CB in 1 M NaOH without methanol (A) the insert was Pt/CB CV curves with methanol (B) at 50 mv/s, and at different scan rate for the forward scan of hollow Pt/CP and Pt/CB (C). Insert: plot of peak current density vs. square root of scan rate and the plot of  $E_p$  vs. ln(v) (D) of hollow Pt/CP. (E) Corresponding activity of hollow Pt/CP and Pt/CB.

shown, the hollow Pt/CP had higher current density at the first, but decreased after 200 s. The reason may be that the intermediate products produced during the reaction poisoned the catalyst, so its activity decreased with time. In order to compare the conductivity of the two catalysts, the EIS impedance spectrogram was used. As Fig. 2B shown, the hollow Pt/CP had a smaller radius. The diameter of the semicircle can be used to explain the conductivity of catalyst, and to illustrate the charge transferability in the methanol oxidation reaction [25]. From the experimental data, got equivalent circuit (inserted in Fig. 2B), where the R<sub>S</sub> represents the solution resistance, the capacitance of electrode double layer used C<sub>dl</sub> to present, and R<sub>CT</sub> meant the charge-transfer's resistance [26]. The R<sub>s</sub> of hollow Pt/CP was 11  $\Omega$ , and the Pt/CB was 9  $\Omega$ , and R<sub>CT</sub> was 166.6  $\Omega$ , 202.9  $\Omega$ , respectively. And it can be found that when compared with R<sub>ct</sub>, the R<sub>s</sub> can be ignored, which meant that the resistance of solution can be ignored. From the results, the smaller radius of hollow Pt/CP meant its high conductivity and strong charge transferability. And from the above results, we can know the activity of hollow Pt/CP was better than the Pt/CB. In order to further explain the physical structure of catalysts, the distribution of elements and the carbon materials' composition, and other structural features were as follows.



Fig. 2. Chronoamperometric curves (A) and EIS (B): insert: the equivalent circuit diagram of hollow Pt/CP and Pt/CB.



Fig. 3. (A) Nitrogen adsorption-desorption isotherms and (B) Pore-size distribution of hollow Pt/CP and Pt/CB.

Table 3Textural properties of the catalysts.

Sample	$S_{BET} \ (m^2g^{-1})^a$	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	Average pore diameter (nm) <sup>a</sup>	Pt nanoparticle size (nm) <sup>b</sup>	Pt crystallite size (nm) <sup>c</sup>	$I_D/I_G{}^d$
Pt/CB	156.72	0.385	18.58	3.27	2.8	1.17
Hollow Pt/CP	365.73	0.496	34.51	2.62	1.63	1.03

<sup>a</sup> From the BET.

<sup>b</sup> from TEM.

<sup>c</sup> from XRD pattern.

<sup>d</sup> from Raman spectrum.

#### 3.2. Characterization of the catalysts

#### 3.2.1. BET analysis

To investigate the specific surface area and pore size of the two catalysts, the nitrogen isotherms of adsorption-desorption were obtained and the results were shown in Fig. 3A. The isotherms of N<sub>2</sub> adsorption-desorption were carried out, and the results exhibited a type IV hysteresis, with a typical H1 hysteretic loop, which indicated the samples having mesoporous structure also including capillary condensation [27]. Hollow Pt/CP's isotherm was typical for mesoporous materials, but included step at low relative pressures, reflecting the framework's dynamic character [28,29]. Also, the BET surface area of hollow Pt/CP (365.7 m<sup>2</sup> g<sup>-1</sup>) was bigger than the Pt/CB (156.7 m<sup>2</sup> g<sup>-1</sup>). As the data made clear that the specific surface area of hollow Pt/CP was nearly 2.3 times that of Pt/CB. The pore size distribution was got by BJH which was shown in Fig. 3B. The hollow Pt/CP was at about 10–60 nm,

which was higher than the Pt/CB. Table 3 summarized the two samples' structural properties. Due to the hollow structure of CP, its specific surface area is much larger than CB. It was precise because of the large specific surface area and large pore diameter of CP that it was conducive to the loading and dispersion of Pt. Also, the big surface area was good for the methanol's adsorption and its activation. These results indicate that the hollow CP obtained by carbonization well maintains the characteristics of ZIF-8, that is, it has a large specific surface area and a good pore size. Moreover, the hollow Pt/CP had better pore volume and bigger pore diameter, which may be also useful for transmitting electronics and transferring. Generally, it was considered that the large surface area may be good for the adsorption and activation of the reaction molecule. So, the hollow Pt/CP may be more beneficial for improving the activity of MOR under the same content.



Fig. 4. The SEM (a), TEM (b) picture of ZIF-8 and TEM figures of hollow Pt/CP (c), (insert picture was the HRTEM of hollow Pt/CP), Pt/CB (d). Particle size analysis of Hollow Pt/CP (e), Pt/CB (f). The (g-l) EDX elemental mapping of hollow Pt/CP.

#### 3.2.2. Topography characterization

To get the two catalysts' morphology information and analyze the Pt's particle size in the catalysts, SEM and TEM were conducted. The results were shown in Fig. 4. From the SEM and TEM (Fig. 4a and Fig. 4 b), a dodecahedron ZIF-8 was formed. After being carbonized under an argon atmosphere, the precursor dodecahedron's morphology was still maintained, and then the Pt was evenly loading onto the surface. To compare the active component Pt's particle size distribution on the two supports, statistics were made on the Pt in the two catalysts [Hollow Pt/CP (Fig. 4e), Pt/CB (Fig. 4f)]. As the results have shown, the hollow Pt/CP had smaller Pt nanoparticles than Pt/CB and the mean size which was 2.62 nm. And the smaller Pt was good for the methanol oxidation [30]. And the HRTEM (High-resolution TEM) of hollow Pt/CP was showed in Fig. 4c Fig. 4 c insert, and the lattice spacing was 0.23 nm which was fit into the Pt (111), and the lattice plane was face-centered cubic (fcc) Pt [31]. Besides, we selected one of the dodecahedron structures to display the EDX elemental mapping of the hollow Pt/CP (Fig. 4g–l). It can be discovered that the C spread all over the area, the distribution of O and N was similar, and the Pt was evenly distributed throughout the frame. The resulting carbon material (hollow CP), holding the advantages of the ZIF-8 and N, Pt active species was highly dispersed and good conductivity, which was highly desired for the MOR [32]. From the distribution map of Pt elements, it can be found that the distribution of Pt at the edge of the dodecahedron is more than that in the interior. At the same time, we think that the distribution range of Pt is based on the structure of carbon in CP, which indicates that the CP has a hollow structure. And from the TEM results, we can know that the C material was amorphous carbon, which had a big surface area. This result was consistent with the BET results.



Fig. 5. The XRD patterns of hollow Pt/CP and Pt/CB and the XRD pattern belongs to the 13-42°data of hollow Pt/CP (B).



Fig. 6. FTIR spectrums of Hollow Pt/CP and Pt/CB.

#### 3.2.3. XRD analysis

The XRD was used to get the catalysts' phase structure. And the XRD patterns of the two catalysts were showed in Fig. 5. The results had shown that there were different crystal face peaks of C and Pt. Also, the XRD exhibited the characteristic face-centered cubic structure of Pt (JCPDS 87-0647) [33], which was agreed with the HRTEM result. There were three peaks of Pt in the spectrum. The diffraction peaks were at 39.6  $^\circ$  for Pt (111), 46.2  $^\circ$  for Pt (200), 67.2 ° for Pt (220) [34,35]. The Pt (111) can be seen. As for the hollow Pt/CP, insert the corresponding pattern into Fig. 5. It can be found from Fig. 5 that there are two peaks in the range of  $13^{\circ}-42^{\circ}$ , one of which belongs to C (002) and the other belongs to Pt (111). The different crystal planes' of corresponding Pt peaks were not very obvious. In the hollow Pt/CP, Pt (111) crystal plane mainly existed. But the crystal faces of Pt's characteristics (200), (220), (311) were almost inconspicuous. To explain the dispersion degree of Pt in the catalyst and get the fine crystallite size of Pt (111). From the XRD pattern, the Pt/CB was 2.8 nm, the hollow Pt/CP was 1.63 nm. This result showed that the Pt's dispersion in hollow Pt/CP was very good. This result may due to the big surface area and appropriate pore size which was in favor of the Pt's fine dispersion, and Pt was evenly distributed on the carbon, which was agreed with TEM results. And the XRD pattern of the hollow Pt/CP also illustrated this result again. The diffraction peak at 24.6° was ascribed to the C (002), which was attributed to the amorphous carbon. To better understand the various functional groups on the carbon surface, we used FTIR to make a more detailed analysis.

#### 3.2.4. FTIR analysis

We used the FTIR since FTIR was highly sensitive to the catalyst's surface chemistry. As Fig. 6 shown, there were mainly four distinct characteristic peaks. The broad peak presence of -OH ( $v_{O-H}$  at about 3400 cm<sup>-1</sup>), C = O can be discovered ( $v_{C=O}$ 



Fig. 7. O1s (A), Pt4f (B) XPS, and C1s (C) XPS spectra of Hollow Pt/CP and Pt/CB.

at 1627 cm<sup>-1</sup>) [36]. As the study had showed, they were C-H of olefin, C = O, -OH, and C-H of saturated alkanes. And the peak at around 1300 cm<sup>-1</sup> belonged to the C-N stretch [37]. As the results showed, oxygen-containing functional groups' intensity in hollow Pt/CP was higher than the Pt/CB. In particular, as for the hollow Pt/CP, the -OH was higher than the Pt/CB, which meant the hollow Pt/CP had better hydrophilicity. Also, the -OH was good for adhering more Pt<sup>4+</sup> in H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O to the carbon material derived from ZIF-8, thereby the hollow Pt/CP obtaining more Pt, which was the main reason for its higher activity than Pt/CB. And the C = O band intensity of the hollow Pt/CP was also higher than Pt/CB, which made the catalyst favor the oxidation of the one-carbon compound. And the detailed analysis of the catalyst surface elements will be showed below.

#### 3.2.5. XPS technique

The XPS was normally used to obtain the surface composition of catalysts and their electronic structure. Fig. 7 had shown the O1s (A) Pt4f (B), and C1s (C) spectrum. Form the O1s spectrum, there were four peaks at 532.08ev, 532.88ev, 533.5ev, 534.38 ev. The 532.08 ev was attributed to C–O, and 533.58 ev belonged to C = O, which was higher than the Pt/CB. The peak at 532.88 ev was C–OH. The 534.58 ev was carboxyl's O atom [38,39]. Func-

#### Table 4

Relative content of species in O1s peaks, O/C atomic ratio and  $Pt^0/(Pt^0+Pt^{2+})$  in Pt4f determined by XPS spectra of samples.

		Relative O1s peak area (%)				Pt <sup>0</sup> /(Pt <sup>0</sup> +Pt <sup>2+</sup> )(%)
Samples	O/C	C-OH	C-0	C = 0	-0H	
Pt/CB	0.48	36	15	38	11	32
Hollow Pt/CP	0.63	41	17	27	15	48

tional groups such as hydroxyl had a certain increase in the catalyst's hydrophilicity. And these groups' intensity in the hollow Pt/CP was higher than that of Pt/CB. As for the C1s spectrum, the peak at 285.08 ev was the carbon (sp<sup>3</sup> C–C), and the peak at 284.18 ev was ascribed to the C–N [40,41]. To have a visualized analysis, we listed the mass ratio of O/C and the oxygen relative percentage in the four different functional groups in Table 4. For the hollow Pt/CP, the content of the oxygen on the surface was higher than that of Pt/CB. The most important was that the carboxyl group was the key addition of functional groups in oxygen was as the data showed. The results indicated that the -COOH will legitimately fix the Pt ions precursor via electrostatic or coordination action, thereby more Pt nanoparticles were dispersed on the



Fig. 8. Raman spectrums of Hollow Pt/CP and Pt/CB, insert was the Raman spectrums from 1300 to 1700 cm<sup>-1</sup> of Pt/CB.

hollow CP surface after the reduction which was the ethylene glycol method. Also, this result was agreed with former research [42]. As for the Pt4f spectrum, the  $Pt4f_{7/2}$  and  $Pt4f_{5/2}$  existed. The more intense doublet (71.0 eV and 74.5 eV) was deemed to Pt(0) species [43] which was in favor of the catalytic activity. The other two peaks belonged to Pt (II), which may be the PtO or Pt(OH)<sub>2</sub> [44]. As the results had shown, the intensity of Pt(0) in the hollow Pt/CP was higher than the Pt/CB. We calculated the proportion of Pt(0)in the entire spectrum and found the proportion of Pt(0) in hollow Pt/CP was 48%, which was higher than that of Pt/CB (32%). This meant that the hollow CP was more conducive to the formation of Pt(0) which was good for increasing catalytic activity. This was due to the structural advantage of hollow CP over carbon black, which had more carboxyl groups made it easier for the precursor of Pt to be fixed to the CP and be reduced to Pt. Such consequences also displayed that the oxidation activity of hollow Pt/CP was higher than that of Pt/CB in MOR. The carbonized carbon could supply more electronic traps which made the  $e^-$  can easily transfer to the surface of porous carbon [45], which was good for the MOR.

#### 3.2.6. Raman spectroscopy

To explore the structural defects difference of the hollow Pt/CP and Pt/CB, the Raman was conducted. The results were showed in Fig. 8. The two strong peaks were at 1369 cm<sup>-1</sup> and 1584 cm<sup>-1</sup>, which were respectively called D (Disordered carbon) and G (Graphtic carbon) peak. The G peak belonged to the bond's stretching for all chain structure or ring structure's sp<sup>2</sup> atom pairs. The D peak was attributed to disordered carbon atom structure [46,47]. Graphene-like carbon has the G and D peaks, which lie at~1560 and 1360 cm<sup>-1</sup>, respectively [48]. The G peak position shows dispersion (excitation wavelength dependence). The D peak position means disordered sp<sup>3</sup> carbon, which gives a broad feature in 1100 cm<sup>-1</sup>–1350 cm<sup>-1</sup>, the shape of which corresponds to the density of states [49]. Also, it redounded to the amorphous or disordered carbon [50]. The D and G meant the carbon atoms which were hexagonally bonded, and the carbon frames were distorted on the defect sites in the graphitic networks, respectively [51]. In order to know the graphitization degree, using the D-band to G-band intensity ratio, and the higher intensity of ratio meant the sample with higher defects or disorder [52-54], and the disorder of the carbon structure may come from carbon's other electronic structure, such as sp<sup>2</sup>, sp<sup>3</sup> on carbon chain or carbon ring in the hollow CP, which was good for the later reaction. The results had shown that hollow Pt/CP had higher I<sub>D</sub>/I<sub>G</sub>, and the carbonation at a high temperature can lead to more defects or disorder. More structural defects made the obtained hollow CP material more conducive to the dispersion of precious metal-Pt and were useful for catalytic reactions to provide more active sites and facilitated better contact between methanol and catalyst. The above characterization results indicate that the activity can be influenced by the material's surface area, surface properties, the active components' particle size, and so on [55].

#### 3.3. Catalytic mechanism

As the above results had shown, the hollow Pt/CP catalyst was the best in all two samples. From the characterization results, the hollow CP had a big surface area and favorable pore size which was good for dispersing metal-Pt. And the hollow CP also contained more hydroxyl groups, which connected more Pt precursors to the carrier, resulting in more elemental Pt. Besides, the hollow Pt/CP had more Pt<sup>0</sup> which was the most important active ingredient in MOR. All of these advantages made the hollow Pt/CP catalyst showed better methanol oxidation activity than Pt/CB. And the oxidation of methanol on the catalyst was mainly through methanol dehydrogenation into intermediates, dehydrogenation, and oxidation of these intermediates ultimately into CO<sub>2</sub>. Adsorption and dehydrogenation mainly occur at Pt sites. To better illustrate the performance of the hollow Pt/CP, the oxidation process of methanol on the catalysts was put down. The process of adsorption occurred in



Fig. 9. The mechanism diagram of hollow Pt/CP.

the voids of CP, which was further enhanced by the presence of Pt. Moreover, the pores of hollow Pt/CP also adsorbed water molecules which facilitated the oxidation of intermediates to CO<sub>2</sub>. The big surface area and porosity of the hollow Pt/CP played an important role in accelerating the methanol adsorption and subsequent oxidation by providing an extended active surface area [56–58]. The processes can be predicted as the following proposed mechanism, and the corresponding mechanism diagram was shown in Fig. 9.

 $CH_3OH + Pt \rightarrow Pt - CH_3OH_{ad}$ 

 $Pt - CH_3OH_{ad} \rightarrow Pt - CO_{ad} + H^+$ 

 $Pt + OH^- \rightarrow Pt - OH_{ad} + e^-$ 

 $Pt - OH_{ad} + Pt - CO_{ad} \rightarrow 2Pt + CO_2 + H_2O$ 

#### 4. Conclusions

In this work, the hollow CP support was successfully derived from ZIF-8, and it was discovered that the ZIF-derived hollow CP support had many structural advantages, such as a large specific surface area, good pore size, abundant oxygen-containing functional groups, like carboxyl, which were necessary for the subsequent loading and dispersion of Pt nanoparticles, and maybe benefit for the transport of electron. Based on the results of characterizations, we discovered that the hollow Pt/CP due to the special morphology had the bigger specific surface area, which was 365.7 m<sup>2</sup> g<sup>-1</sup> and the Pt/CB was 156.7 m<sup>2</sup> g<sup>-1</sup>, which was The high surface area was good for the Pt dispersion, the adsorption and activation of reactants. More importantly, the hollow Pt/CP had richer oxygen-containing functional groups, higher Pt<sup>0</sup>/(Pt<sup>0</sup>+Pt<sup>2+</sup>), which were beneficial to improve catalyst activity. In addition, the hollow Pt/CP had more structural defects, which was in favor of the ac-

tivity. Therefore, the hollow Pt/CP showed better activity than the Pt/CB, and a better ability to against CO-like substances toxic. This also shown that the ZIF-derived carbon material was very meaningful material as a substrate, which was useful for improving the activity and stability of the catalyst.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Credit authorship contribution statement

**Chengxiu Ding:** Writing – original draft. **Fang Dong:** Conceptualization, Writing – review & editing. **Zhicheng Tang:** Supervision, Funding acquisition.

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