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# Pt nanoparticles incorporated into phosphorus-doped ordered mesoporous carbons: enhanced catalytic activity for methanol electrooxidation

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ABSTRACT

Phosphorus-doped ordered mesoporous carbons (POMCs) with different P content are successfully synthesized by hard template method using SBA-15 as hard template, sucrose as carbon precursor and triphenylphosphane as phosphorus precursor. Pt nanoparticles with size of 3.5 ± 0.4 nm are deposited on the framework of POMCs. The doping of P into OMCs facilitates the dispersion of Pt nanoparticles and accelerates the formation of oxygen-containing functional groups. Pt/POMCs nanocomposites were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, nitrogen adsorption–desorption and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry and chronoamperometry studies exhibit that the Pt/POMCs, especially Pt/$P_7$OMCs, have larger electrochemical active surface area (ECSA), higher electrocatalytic activity, more negative onset potential and long-time stability for the electrooxidation toward methanol than that of Pt/OMCs, PtRu/XC and commercial Pt/C catalysts. These enhanced performances indicate that Pt/$P_7$OMCs catalyst may be an excellent anode catalyst for direct methanol fuel cell (DMFC).

## 1. Introduction

Great efforts have been made to design and develop direct methanol fuel cell (DMFC) as energy sources owning to its high energy density, easily handling liquid fuel, quick start-up and environmental friendly [1,2]. Anode catalysts of DMFC can activate electrochemical reactions, leading to increase the rate of fuel oxidation and oxygen reduction [3]. Therefore, the preparation and performance of anode catalysts are research priorities in the development of DMFC. However, as one of the exclusive anode catalyst for methanol electro-oxidation, commercial Pt/C catalyst is still insufficient activities and easily poisoned by reaction intermediates such as CO [4–6]. This is mainly attributed to the poor methanol electro-oxidation kinetics [5,7], low catalyst efficiency and CO poisoning [6,8,9] of the catalysts employed for the methanol oxidation reaction (MOR) in the anode.

To overcome the problems mentioned above, it is necessary to develop novel electrocatalysts with much enhanced methanol oxidation activity/stability and higher CO-tolerance. It has been reported that Pt-based or Pt alloy catalysts play a significant role in improving electrocatalytic activity and stability, such as Pt/CNTs [6], Pt/OMCs [10], Pt/N-doped graphene [11], Pt-Ni-P CNTs [12], Pt–Ru–P [13] and Pt–Sn–P/C [14]. To date, the precious metals like Pt supported on the heteroatom-doped carbon materials as anode electrocatalysts to improve electrocatalytic activity of MOR have attracted a tremendous attention of researchers. It has been proved that the performance of catalyst is closely associated with the nature of the supporting materials [15]. The size, morphology and distribution of the Pt particles also have a close relationship with the supporting materials. Therefore, special attention has been paid to use the various carbon materials including graphene [16], carbon nanotubes [17], activated carbon fibers [18,19], ordered mesoporous carbons (OMCs) [7,20] and other carbonaceous materials. Compared to other carbon materials, OMCs as electrocatalyst support for fuel cells has been reported [21,22] due to its excellent characteristics such as high surface area, tunable pore size and large pore volume with narrow pore size distribution. These super features promote the facile molecular transport of reactants and products [23,24].

Heteroatoms such as N, P, S [11,12,25,26] doping into carbon materials offer a good choice to increase the catalytic performance of Pt-based catalysts in DMFC. Heteroatoms bonded with carbon framework can introduce defect sites due to different bond length,

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electronegativity and atomic size, and thereby can induce uneven charge distribution, which have significant effects on some of the properties of catalyst such as catalytic property [20,27]. Phosphorus, as one of the N-group elements, often shows similar properties with nitrogen [26]. The same as N atom, P has a larger atomic radius and higher electron-donating ability which make it an astute choice as a dopant to carbon materials [20]. It also has been reported that the addition of P can drastically reduce the size of Pt nanoparticles (NPs) [13,14] and improve the distribution of Pt NPs on carbon support. Furthermore, the introduction of P may largely increase the number of oxygen-containing functional groups, which promotes the CO-tolerance towards MOR [12,20,26]. Recently, P-doped multiwalled nanotubes [28] and P-doped OMCs [20] exhibit high electro-catalytic activity for the oxygen reduction reaction (ORR). Pt supported on P-doped CNTs [26] and Pt-Ni-P composites [12] illustrate better activities toward the MOR. Thence, by the synergistic effect of the suitable carbon support OMCs, doping heteroatom P and small size Pt NPs, we expected to obtain an electrocatalyst with excellent catalytic activity, better CO-tolerance and much higher stability.

In this work, Pt/POMCs as efficient anode electrocatalysts for MOR were synthesized using hard template method. Pt NPs incorporated inside the P-doped ordered mesoporous carbons (Pt/POMCs) via a simple impregnation–reduction method using formic acid as reductant. Both the physical and electrochemical properties of Pt/POMCs were studied. Pt/$P_7$OMCs was found to be an excellent electrocatalyst with higher electrochemical active surface area (ECSA), much smaller size of Pt NPs and sharply enhanced electrochemical properties.

## 2. Experimental

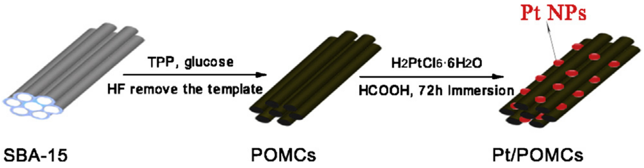
### 2.1. Reagents and apparatus

Pluronic P123 (non-ionic triblock copolymer, $PEO_{20}PPO_{70}PEO_{20}$) and Nafion (5 wt%) were purchased from Sigma-Aldrich. Triphenylphosphine and $H_2PtCl_6{\cdot}6H_2O$ were purchased from Aladdin and Sinopharm Chemical Reagent Co. Ltd. All other reagents used were of analytical grade and used as received without further purification.

The morphologies of the synthesized samples were characterized by powder X-ray diffraction (XRD). XRD was obtained on a an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Kα radiation (kα = 0.15406 nm). Transmission electron microscopy (TEM) (JEOL, JEM-2100F) was operated at 200 kV. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TG Analyzer. The Pt content was determined by TGA. The surface area and pore size of the synthesized OMCs and POMCs were determined by $N_2$ adsorption-desorption isotherms (ASAP 2020) and were obtained from the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. X-ray photoelectron spectroscopy (XPS) was measured using Thermo ESCA LAB spectrometer (USA). The binding energy was referenced to C 1s line at 284.6 eV for calibration. The error of the data represents the standard deviation of triplicate measurements.

### 2.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three electrode cell. An Ag/AgCl (in saturated KCl solution) and a platinum electrodes were served as the reference and counter electrodes, whereas the modified GC electrode as a working electrode. The procedures of GC electrode pretreatment are described according to previous reference [10]. Cyclic voltammetry (CV) measurements were performed in 0.5 M $H_2SO_4$ solutions with or without 1.0 M $CH_3OH$. The CO-stripping voltammetry based on the method reported by Liu. *et al.* [26] was measured in 0.5 M $H_2SO_4$ solution with a potential range of −0.2 to 1.0 V. Both the scan rate of CV and CO-stripping tests are 50 mV $s^{-1}$.



**Scheme 1.** The synthesis process of Pt/POMCs.

### 2.3. Preparation of Pt/OMCs, Pt/POMCs and modified electrode

Conventional ordered mesoporous silica SBA-15 was used as a hard template, which was prepared using Pluronic P123 and tetraethyl orthosilicate (TEOS) as the surfactant and silica source [29]. $P_x$OMCs were synthesized according to the method reported by Ryoo *et al.* [30], except triphenylphosphine (TPP) and glucose were added at the same time, and the mass ratio of TPP and glucose is x (x = 3.5; 7; 14). In a typical synthesis route, Pt/OMCs nanocomposite was prepared by the following procedure: 35 mg of OMCs was dispersed in 10 mL of double distilled water containing 31.4 mg $H_2PtCl_6{\cdot}6H_2O$. After ultra-sonication for more than 1 h and magnetic stirring for about 2 h at room temperature, the $H_2PtCl_6{\cdot}6H_2O$ could diffuse into the pores of OMCs. Then, the gained sample was dried under vacuum at 70 °C until get a fine and completely dry powder. And then 5 mL double distilled water and 2.5 mL HCOOH were added to redisperse the powder. The resultant suspension was stored at room temperature for 72 h. Finally, the product was centrifuged, collected and dried in an oven at 60 °C. The obtained composite was marked as Pt/OMCs. Pt/POMCs nanocomposites were synthesized in the same way of Pt/OMCs. The only difference is that the catalyst support is not OMCs but POMCs. The fabrication strategy is shown in Scheme 1.

Finally, more than 1 hour of ultrasonication was necessary to disperse 2 mg Pt/OMCs or Pt/POMCs into a mixture of 0.1 mL (5 wt%) Nafion and 0.9 mL distilled water. After dropping 3 μL of the suspension onto the electrode surface, the electrode was dried in air or an infrared lamp.

## 3. Results and discussion

### 3.1. Characterization of Pt/OMCs and Pt/POMCs

The influence of P doping on mesostructure of OMCs and POMCs was investigated by XRD. Fig. 1A shows the typical small-angle XRD patterns of OMCs and POMCs. For the OMCs, the XRD patterns show the well (100), (110) and (200) peaks with a hexagonal mesopore arrangement at 2θ of 0.98°, 1.70°, and 2.00°, which indicates the synthesis of ordered mesoporous structure. Partial deterioration of the XRD peaks is observed in POMCs. However, the existence of the main diffraction peak (100) illustrates that the framework hexagonal ordering of OMCs is basically retained. The phosphorus-doped mesoporous carbon samples (POMCs) with different P concentrations display gradual disappearance of the three peaks, indicating the loss of long-range structural order [31]. Fig. 1B exhibits the wide-angle XRD patterns of (a) Pt/OMCs, (b) Pt/$P_{3.5}$OMCs, (c) Pt/$P_7$OMCs, and (d) Pt/$P_{14}$OMCs. The diffraction peak located at about 24.52° is due to the (002) crystal face of carbon, while the peaks at 39.78°, 46.38°, 67.46° and 81.62° are corresponding to the (111), (200), (220) and (311) lattice planes of face-centered cubic structure of Pt. According to the Scherrer