



# Hollow hemisphere-shaped macroporous graphene/tungsten carbide/platinum nanocomposite as an efficient electrocatalyst for the oxygen reduction reaction



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## ABSTRACT

Hollow hemisphere-shaped macroporous graphene/tungsten carbide/platinum (HMG/WC/Pt) nanocomposite has been synthesized as an efficient electrocatalyst for the oxygen reduction reaction (ORR). The HMG/WC/Pt sample has been systematically characterized by the X-ray diffraction (XRD), Scanning electron microscope (SEM) and Transmission electron microscopy (TEM). The analysis results indicate that the sample has an interesting three-dimensional hollow hemisphere-shaped macroporous architecture. The results also demonstrate the successful integration of WC and Pt nanoparticles on the HMG, in which the WC nanoparticles are in size of about 10 nm and the Pt nanoparticles are in size of about 3 nm. The as-prepared HMG/WC/Pt electrode displays excellent electrocatalytic performances for the ORR in 0.1 mol L<sup>-1</sup> HClO<sub>4</sub> electrolyte. The mass activity ( $i_m$  at 0.9 V) of HMG/WC/Pt is 206 mA mg<sup>-1</sup> Pt, which is about 85% higher than that of Pt/C (112 mA mg<sup>-1</sup> Pt). It also displayed a very high activity retention of 84.5% after 2000 cyclic voltammetry cycles for the HMG/WC/Pt, while that of the Pt/C is only 70.5%. The HMG/WC/Pt nanocomposite would be a promising electrocatalytic material for the ORR in Fuel cell applications.

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## 1. Introduction

Oxygen reduction reaction (ORR) is one of the important basic electrochemical reactions, which involves the processes of oxygen adsorption on the electrode surface and reduction into water or hydrogen peroxide [1]. ORR has an important academic significance and application value in the fuel cell, metal air batteries, chlor-alkali industry and corrosion protection, etc [2–4]. Taking the fuel cell as examples, the anode reaction is related to the types of fuel and electrolyte, while the cathode reaction is the ORR with oxygen as the sole oxidant [5]. Compared with the fuel oxidation reaction in anode, the ORR in cathode is more difficult to occur, which becomes the main restricting factor to affect the reaction rate and conversion efficiency of fuel cell [6]. Due to its slow reaction rate and high overpotential of ORR, it is difficult to obtain

high catalytic current near equilibrium potential in fuel cell application. So it is necessary to use appropriate catalyst materials to reduce the overpotential, improve the reaction rate and efficiency of ORR, in order to manifest its value in practical technical application [7]. At present, an efficient catalytic material for ORR is the carbon black-supported noble metal platinum (Pt) electrocatalyst [8]. However, the high cost and low stability of Pt greatly limits its development and application in commercial catalysts. Therefore, it is of great significance to design the ORR catalytic materials with high activity and high stability to promote the research of related fields.

Supporting Pt nanoparticles on the surface of carbon materials can greatly increase the surface area and utilization of Pt, so as to increase catalytic activity and reduce the consumption of Pt [9]. The selection of carbon materials is very important for the preparation of highly active and stable ORR catalytic materials. At present, the commercial carbon black (Vulcan XC-72) is prone to chemical and electrochemical corrosion in acidic conditions within the potential range of oxygen reduction reaction [10]. The

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corrosion of carbon black often leads to exfoliation of Pt from support and loss of catalytic activity, which makes the service life of catalyst material to be greatly shortened. With this in mind, an excellent carbon support materials for ORR electrocatalyst should possess the following characteristics: good conductivity, high specific surface area as well as high stability [11]. For this purpose, nanostructured graphite carbon materials with high surface area and high conductivity have been selected as the high-performance support materials for ORR electrocatalyst. For example, Graphene has the characteristics of large specific surface area, fast electron conduction rate and high structural stability, has been used as novel support for ORR electrocatalyst [12]. The unique two-dimensional planar structure of graphene provides a good platform for the uniform distribution of Pt nanoparticles, and the dangling bond on surface of graphene can interact with the catalyst particles, in which the catalytic activity and stability of the catalyst were greatly increased [13].

In addition to improving the utilization of noble metals by support materials, the use of co-catalyst components can also help to enhance the catalytic performances of noble metal catalysts [14]. For example, some co-catalyst components (e.g. transition metal oxide, carbide, nitride and so on) not only can be used as the support material of noble metals, but also can be used as additive phase to enhance the catalytic activity and stability of noble metals by so-called synergistic effect [15]. Li et al. prepared a carbon black-supported Pt-Mn<sub>3</sub>O<sub>4</sub> composite and proved a remarkable activity for oxygen evolution reaction because of the synergistic effect [16]. A similar result was also obtained for the Pt-SnO<sub>2</sub>/C composite when used as an ORR electrocatalyst for proton exchange membrane fuel cell [17]. Particularly, the Pt-WC/C composite catalysts reported by Shen et al. showed outstanding catalytic performances for the ORR, in which much lower overpotential and larger current density were achieved compared with commercial carbon black supported Pt catalysts [18]. It is predicted that the electron transfer phenomenon is occurred between transition metal carbides and noble metals, which can change the surface electronic structure of noble metals and enhanced their catalytic activity, stability and reduce the possibility of being poisoned [19]. A similar study on the Pt metal and WC composite catalyst was also carried out by Mustain group, which showed that WC not only played a role of carrier and but also strengthened ORR catalytic activity by reducing the overpotential and activation energy of the reaction [20].

It is well known that the chemical reaction catalyzed by electrocatalyst is influenced by the mass diffusion kinetics of actual electrodes [21]. In the mass diffusion process, the transfer rate of electrolyte ion in catalyst channel plays a decisive role in reaction process which directly affects the rate of catalytic reaction [22].

Because support material is a carrier of the noble metal catalyst, in a catalytic reaction process, mass transfer is mainly carried out in the pore structure of support material. According to the theory of mass transfer, the transfer resistance and diffusion distance in the channel are the two important factors which can affect the mass transfer kinetics. When the support material has a large number of interconnected pore structures, the diffusion distance of mass can be greatly shortened, and the mass transfer rate is greatly improved [23]. Particularly, some support materials with micron-sized macroporous structures can effectively reduce the mass transfer resistance and improve the mass transfer rate [24]. For the cathodic ORR electrocatalyst for fuel cell, the mass transfer problem of electrode materials, such as the diffusion of oxygen and the discharge of water, especially needs to be considered. It is worth noting that, the low catalytic efficiency caused by slow mass transfer is one of the major factors leading to the voltage loss of fuel cell [25]. In order to improve the mass transfer kinetics and catalytic efficiency, the development of macroporous skeleton-supported noble metals ORR electrocatalysts is a preferred strategy, which becomes one of key steps for manufacturing high-performance proton exchange membrane fuel cell in industry [26].

In the present investigation, we report the controlled synthesis of hollow hemisphere-shaped macroporous graphene/tungsten carbide/platinum (HMG/WC/Pt) nanocomposite as an efficient electrocatalyst for the ORR of fuel cell. For this new-style multi-component ORR electrocatalyst, there are several obvious structural advantages: (i) a novel hollow hemisphere-shaped graphene with unique macroporous structure is proposed as support material of ORR electrocatalysts, which provides a favorable pore structure for enhancing mass transfer in the catalytic reaction process; (ii) the high specific surface area and stable three-dimensional structure of hollow hemisphere-shaped graphene are achieved, which endow with well dispersion and high stability for the active components; (iii) ultrafine WC nanoparticles surrounded by ultrafine Pt nanoparticles are successfully designed on the surface of graphene, where the potential synergistic effect between WC and Pt can leads to greatly enhanced ORR catalytic performances for this composite electrocatalyst.

## 2. Experimental

### 2.1. Synthesis of materials

The HMG/WC composite support was synthesized by a synchronous high-temperature strategy with polystyrene (PS) microsphere as a sacrificial template, graphene oxide (GO) and ammonium metatungstate (AMT) as precursors. The GO was prepared using a modied Hummers' method and dispersed in deionized water [27]. Firstly, 160 mL of PS microsphere dispersion (5 mg mL<sup>-1</sup>, 3 μm mean size) was added into 100 mL GO solution (2 mg mL<sup>-1</sup>) dropwise followed by magnetic stirring for 60 min. Afterward, 50 mg of AMT was added into above mixture solution under stirring for another 60 min. The resulting mixture solution was concentrated by synchronous magnetic stirring and heating, followed by freeze-drying. Finally, the dried product was transferred to a tube furnace and calcined at 850 °C for 2 h under an Ar atmosphere with a heating rate of 5 °C min<sup>-1</sup>. As a comparison, HMG was also fabricated through the same process as HMG/WC but without the addition of AMT.

HMG/WC/Pt electrocatalyst was synthesized by a rapid microwave heating reduction method [28]. A certain amount of H<sub>2</sub>PtCl<sub>6</sub> and HMG/WC were mixed with ethylene glycol in an ultrasonic bath for 30 min. The mixed solution was put into a microwave oven, and was heated to the boiling point and maintained for 30 seconds. Afterward, the as-prepared product was washed with

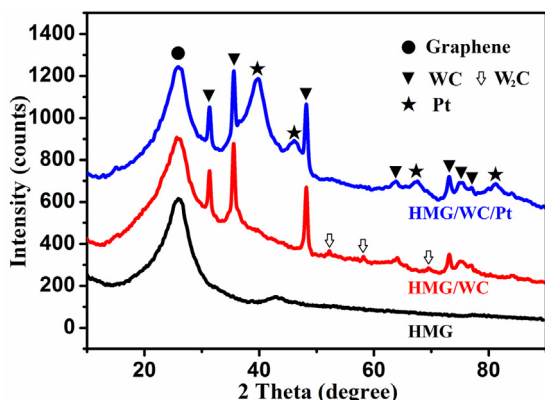


Fig. 1. XRD patterns of the HMG, HMG/WC and HMG/WC/Pt samples.

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