



Well-dispersed platinum nanoparticles supported on hierarchical nitrogen-doped porous hollow carbon spheres with enhanced activity and stability for methanol electrooxidation



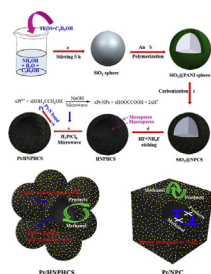
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HIGHLIGHTS

- HNPCHS have been successfully prepared.
- Pt NPs with small size were evenly deposited on HNPCHS.
- Pt/HNPCHS possesses higher catalytic activity, CO-tolerance and stability toward MOR.
- HNPCHS provides an ideal channel for fuels and products transport.
- Nitrogen functional groups improve dispersion of Pt NPs and strengthen CO-tolerance.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical nitrogen-doped porous hollow carbon spheres (HNPCHS) with porous-thin mesoporous shell and hollow macroporous core structure have been prepared via in-situ oxidation polymerization method using polyaniline as the precursor. After carbonization at 900 °C, the average diameter of HNPCHS is ca. 140 nm with shell thickness of ~1 nm. Pt nanoparticles with high dispersion and small size have been successfully deposited on the HNPCHS by a microwave-assisted polyol process to synthesize Pt/HNPCHS catalyst. The obtained samples are characterized by physical characterization and electrochemical measurements. Electrochemical studies reveal that the prepared Pt/HNPCHS catalyst possesses notably higher catalytic activity and CO-tolerance, and better stability toward methanol electrooxidation in comparison with Pt/nitrogen-doped porous carbon and the commercial Pt/C catalysts. It is likely that enhanced catalytic properties of the Pt/HNPCHS could be due to the high dispersion of small Pt nanoparticles, the presence of nitrogen species, developed porous-thin mesoporous shell and hollow macroporous core structure of support HNPCHS. As a result, the as-developed Pt/HNPCHS present attractive advantages for the application in fuel cell electrocatalyst.

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1. Introduction

Direct methanol fuel cell (DMFC) has attracted great attention as an environmentally friendly power sources for portable electronic devices due to their high energy density, easily handling liquid fuel, low operating temperatures (60–100 °C) and quick start-up [1–8]. Despite of these advantages, however, some obstacles still limit the

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broad applications of DMFCs: (i) the sluggish kinetics of the anode methanol oxidation reaction (MOR), (ii) methanol crossover through Nafion membrane, (iii) high costs of the Pt-based electrocatalysts and (iv) CO poisoning of anode catalyst by carbon monoxide from methanol electrooxidation [9–11]. To overcome the problems mentioned above, the widely accepted strategy is to develop Pt-based catalyst with high dispersion and small particle size or Pt-based alloys such as Pt–Pb [12–15], Pt–Bi [16], Pt–Mn [17], Pt–Zn [5,18], Pt–Ni [19,20], Pt–Au [21], Pt–Rh [22], Pt–Cu [23], Pt–Co [14,17,19] and Pt–Ru [24,25] based on the bifunctional mechanism and electronic effect [26]. Additionally, the design of carbon materials as supports with well-developed porosity, large surface area, nanoscaled morphology, good electric conductivity and high inertness in harsh chemical and electrochemical conditions are essential to electrocatalysts [9,27–32]. So the preparation of carbon supported Pt-based catalysts with excellent properties still is a challenge.

Until now, there have been considerable efforts focused on the synthesis of porous carbon materials with high surface area and large pore volume [33–41]. Hollow carbon microspheres with a specific structure of hollow cores and carbon shells have attracted extensive attention due to the outstanding features including high specific surface area and surface permeability, low density, well-defined interior voids, good electronic properties and possible applications in drug delivery, active material encapsulation, lithium-ion battery, catalyst supports, sensing, hydrogen storage, biomedical applications and damping materials [42–50]. In addition, hierarchically ordered porous carbon materials, especially those possessing well-defined macropores and interconnected micropores or mesopores have attracted much attention in fuel cell [28,51–54]. The probable reason is mesopores and micropores allow facile molecular transport of reactions and products in MOR and ORR, meanwhile, the main function of macropores is to act as the transport avenues into the interior of carbon particles. For example, Yu have reported a new type of carbon capsules with hollow core and mesoporous shell structures supported Pt–Ru catalysts exhibited much higher specific activity for methanol oxidation than commercial E-TEK supported catalysts by about 80% due to the high surface area and well-developed interconnected bimodal porosity [54]. Zhang et al. have reported hierarchically ordered porous carbons with macropores and mesopores can greatly enhance catalytic activity as supports for noble metals [28]. Yu et al. successfully prepared PtRu NPs supported on the bimodal porous carbons presented much better performance than its E-TEK counterpart [52]. It may also be due to the three-dimensionally interconnected macroscale and mesoscale bimodal porosity is beneficial to facile diffusion of fuels and products to and from the catalyst. Unfortunately, although the above pioneering works are very interesting, Pt NPs are very difficult to deposit directly and evenly onto such surfaces without active functional groups because of the relatively inert surface of carbon.

To tackle this challenge, many studies have focussed on incorporation of heteroatoms (e.g., N, P, and S) on to the carbon supports so as to modify their surface [20,55–60]. Among them, various N-doped carbon-based materials including carbon nanotubes [61–63], magnetic carbon nanoparticles [64], graphite [65], graphene [66], shell–core nanostructured carbon [67], carbon nitride nanofibers [68–70] and porous carbons [10,29,52,71,72] have been received considerable attentions as a more effective route to improve the dispersion of metal nanoparticles. Studies have proven that the presence of N species in carbon materials will enhance the catalytic activity and improved the CO poisoning and dispersion as well as stability [73]. The enhancement in catalytic activity was probably ascribed to the following reasons: (i) Both modified nucleation and growth kinetics during catalyst nanoparticle

deposition not only decreased catalyst particle size but facilitated the dispersion of Pt NPs. (ii) The strong metal–support interaction is beneficial to enhance anchoring of Pt to the support, leading to an improved stability of the electrodes. (iii) N species on the carbon support surface could change the electron donor/accept characteristics of carbon, resulting in the enhanced catalytic activity toward oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) [29,74,75]. These imply that nitrogen-doped hollow carbon materials can be used as desirable electrode materials for DMFC.

In the present study, to obtain a particular carbon support with excellent dispersion and high methanol oxidation activity of Pt catalyst, aniline was selected as the carbon and nitrogen sources to prepare hierarchical nitrogen-doped porous hollow carbon spheres with mesoporous shell and hollow macroporous core. Pt NPs supported on HNPCHS are prepared by a simple microwave-assisted polyol procedure. Both the physical and electrochemical properties of Pt/HNPCHS were investigated. The results show that HNPCHS facilitates the formation of highly dispersed, smaller, uniform Pt NPs, resulting in enhanced Pt utilization rate and a higher methanol oxidation activity than commercial Pt/C. Hence, Pt/HNPCHS render future practical applications as supported electrocatalysts for DMFCs.

2. Experimental

2.1. Preparation of Pt/HNPCHS catalyst

The preparation of HNPCHS was composed of four steps and the schematic procedure for the synthesis of the HNPCHS was shown in Scheme 1. SiO₂ spheres with the diameter about 140 nm were synthesized according to the literature (Scheme 1a) [76]. The SiO₂@PANI was prepared by *in-situ* oxidation polymerization of aniline in the presence of SiO₂ spheres [77], the procedure was divided into two steps: (i) SiO₂ (0.12 g) and aniline (1 mL) were immersed in 1 M H₂SO₄ (50 mL) and kept for ultrasound about 30 min. (ii) After stirring for 3 h, ammonium persulfate solution (the molar ratio of aniline/ammonium persulfate is 4:1) was also immersed in 1 M H₂SO₄ (50 mL) and added drop by drop to the above solution, then the mixture was stirred at room temperature for 24 h. The black–green product was filtered and washed repeatedly with both water and ethanol and dried under vacuum at 60 °C for 12 h (Scheme 1b). For comparison, similar procedures were adopted for the preparation of PANI, except that none of SiO₂ spheres was added.

The as-prepared SiO₂@PANI composites were carbonized in a pure Ar atmosphere at 900 °C for 1 h to form SiO₂@nitrogen-doped porous carbon spheres, donated as SiO₂@NPCS (Scheme 1c). Finally, the HNPCHS with developed macropores and mesopores were obtained via the removal of the silica template in 2 M HF + 8 M NH₄F aqueous solution at room temperature for 10 min, washed with distilled water and alcohol three times, then dried at 60 °C for 12 h (Scheme 1d). At the same time, the nitrogen-doped porous carbon (NPC) was prepared by pyrolysis of PANI using the same method.

Pt catalysts supported on HNPCHS or NPC were synthesized by a simple microwave-assisted polyol procedure [78,79]. Briefly, in a 50 mL beaker, 20 mg of HNPCHS carbon support was mixed with 15 mL of ethylene glycol (EG) and stirred for 3 h to form uniform mixture ink. Then 0.684 mL of 0.03746 M H₂PtCl₆-EG was slowly dropped into the above suspension, followed by stirring for 2 h and adjusting the pH to 12 using 1 M NaOH-EG solution. After Ar gas was fed into the mixture ink for 15 min, the beaker and its contents were heated in a household microwave oven (2450 MHz, 800 W) for 60 s. Subsequently, the resulting suspension was stirred

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