Journal of Electroanalytical Chemistry 825 (2018) 40–50

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Template, surfactant, stabilizer free controllable synthesis of various morphologies platinum decorated ordered mesoporous carbon nano architecture for high–performance electrochemical sensing

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ARTICLE INFO

Keywords:
Template free
Surfactant free
Various morphologies platinum
Ordered mesoporous carbon
Electrochemical sensing

ABSTRACT

In this work, spherical, flower and urchin–like platinum nanoparticles (PtNSs, PtNFs, PtNUs) decorated ordered mesoporous carbon (OMC) architecture were synthesized through a facile strategy without any template, surfactant and stabilizer. The different morphologies can be controlled by simple adjusting the proportion of precursor K_2PtCl_4, HCOOH and OMC at room temperature, this both simplifies the synthesis procedure and permits good mixing, with better interfacing between the two nanophases of K_2PtCl_4 and OMC. The formation mechanism of PtNUs, PtNFs and PtNSs decorated OMC (OMC–PtNUs, OMC–PtNFs and OMC–PtNSs) was deeply researched. The novel structure has the potential to possess high Pt utilization, high Pt activity surface and high specific surface area of OMC, which enables the excellent electrochemical sensing performance. Paracetamol (AP), methanol and glucose were employed as redox probes to study the electrocatalytic performance, which shows favorable electron–transfer kinetics. The novel structure should be a good model for constructing a promising electrochemical sensing platform for further research in pharmaceutical preparations and in biological fluids.

1. Introduction

Platinum nanoparticles (PtNPs) are an important electrocatalysts owing to their intrinsic catalytic properties. In the electrocatalytic application of PtNPs, some issues, such as the high cost, activity and durability, should be fully considered [1–7]. The rational design and synthesis of PtNPs with high surface area is an effective method to reduce cost, improve catalytic activity and long–term stability [8–11]. Much effort has been focused on the tuning of the specific structural feature of PtNPs to produce Pt catalysts with high surface area, so as to achieve high catalytic performance and utilization efficiency [12]. PtNPs with different morphology, such as nanofibers [13], nanowire [14], nanotubes [15], nanocages [16], nanodendrite [17] have been successfully produced.

So far, the common methods are template approach and surfactants guidance synthesis method. For instance, Kenya Kani et al. made use of cage–type mesoporous silica as a hard template and $C_{16}EO_8$ as a surfactant to synthesize the periodically arranged arrays of dendritic Pt nanospheres [18]. Ambrose A. Melvin and coworkers developed a method for synthesizing silica hollow spheres loaded with Pt NPs that using lauryl ester of tyrosine as surfactant and TEOS as a template [19]. A method to prepare Pt spheres with hollow interior and nanosponge shell by using silica particles as template and polyethylene–polypropylene glycol (F127) as surfactant was reported by Hamed Ataee–Esfahani et al. [20]. Cheng et al. developed a project for synthesizing flower–like Pt nanostructure that using polyvinyl pyrrolidone (PVP) as surfactant [21]. A method to prepare monodisperse $Pt_{2.6}Co_1$ nanoflowers by using cetyltrimethylammonium chloride (CTAC) as surfactant was reported by Jiang et al. [22]. Song and coworkers established an approach for synthesizing three–dimensional trimetallic Pt–Pd–Co alloyed nanoflowers that using oleylamine as surfactant, along with cetylpyridinium chloride (CPC) as the co–surfactant [23]. These are excellent works for preparing PtNPs with different morphologies, thus leading to high specific surface area. However, the above template synthesis approaches need additional procedures such as the preparation and removal of the templates, which is noneconomic for actual production. Generally speaking, the addition of template and surfactant are relatively time consuming, the cost is

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https://doi.org/10.1016/j.jelechem.2018.08.002
Received 26 May 2018; Received in revised form 1 August 2018; Accepted 4 August 2018
Available online 08 August 2018
1572-6657/

relatively high and complicated reaction procedures are needed, which limits the large-scale production of platinum nanomaterials. Hence, it remains an interesting challenge to develop a template, surfactant and stabilizer free route to direct synthesis of Pt NPs with different morphologies.

In recent years, nanostructured carbon materials have been considered as one of the most interest and significant electrode materials in the field of catalyst supports. To improve the Pt utilization and further enhance their catalytic activity, Pt catalysts are often dispersed onto a variety of carbon supports, including carbon nanotubes (CNTs), graphene, carbon nanofibers and other carbon materials [24]. Besides the above carbon materials, ordered mesoporous carbon (OMC) have been testified to be a very promising support material. OMC has been received extensive attention from the scientific community owing to its large surface area, porous structure, good thermal stability, flexible framework composition and chemical inertness [25–28]. The introduction of Pt NPs into OMC, which extends the applications of support materials and provides new characteristics such as catalytic and electrochemical activities. The combination of the two components brings together the advantages of the high surface area of OMC and the unique catalytic properties of PtNPs, which has made OMC based Pt nanocomposites be a good model for constructing preeminent electrochemical sensors for further detection of various molecules.

Based on the mentioned above, here we report a simple template, surfactant, and stabilizer free controllable method for the synthesis of various morphologies Pt decorated OMC nanocomposites (OMC–PtNPs). Three kinds of different morphologies including spherical, flower and urchin–like PtNPs with high specific surface area were prepared via adjusting the ratio of Pt precursor, reductant and supporter. The most significant thing is that Pt with different morphologies can be directly grown on OMC without any other heat treatment steps, which can preserve the intrinsic electronic structure of both the Pt NPs and OMC. Combine the advantages of PtNPs and OMC, the obtained OMC–PtNPs show high–performance electrochemical sensing performance for AP, methanol and glucose in pharmaceutical preparations and in biological field.

2. Experimental

2.1. Reagents and apparatus

Formic acid (HCOOH), paracetamol (AP) and hydrofluoric acid were purchased from Sigma–Aldrich (MO, USA). Nafion, sodium hydroxide (NaOH), anhydrous ethanol, sucrose, H_2SO_4, potassium chloroplatinate (K_2PtCl_4), potassium chloride (KCl), phosphoric acid (H_3PO_4) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ordered mesoporous carbon (OMC) and mesoporous silica material (SBA–15) were prepared in our laboratory. The 0.1 M pH 7.4 phosphate butter solution (PBS), which was made up from Na_3PO_4, Na_2HPO_4 and NaH_2PO_4 was employed as a supporting electrolyte.

All of the electrochemical experiences were applied in a three electrode cell by using an Autolab Electrochemistry Workstation (PGSTAT 302 N, Metrohm, Switzerland). Working electrode was the modified glassy carbon electrode (GCE, diameter: 3.0 mm), a Pt wire served as the counter electrode and Ag/AgCl worked as the reference electrode, respectively. Scanning electron microscopy (SEM) images of the samples were recorded on a Philips XL–30 ESEM operating at 3.0 kV. Transmission electron microscopy (TEM) images were determined with a JEM–2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. Energy–dispersive X–ray (EDX) images were done using a JEM–2100F transmission electron microscope (JEOL, Japan) with an EDX unit (Noran) operating at 200 kV. X–ray diffraction (XRD) patterns were obtained on an X–ray D/max–2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Kα radiation (k = 0.15406 nm). X–ray Photoelectron Spectroscopy (XPS) was recorded by Thermo ESCA LAB spectrometer (USA). Fourier transform infrared (FTIR) spectroscopy of the sample was recorded with Nicolet Magna 560 FT-IR spectrometer with a KBr plate. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TG analyzer (TGAQ500). The temperature was increased by 10 °C per minute to 800 °C under ambient conditions.

2.2. Synthesis of OMC

OMC was prepared by using SBA–15 as a template and sucrose as a carbon source according to the method reported by Ryoo et al. [29]. The synthesis procedure of OMC was as follows: first of all, 0.5 g mesoporous silica material (SBA–15), 0.625 g of sucrose and 0.14 g of H_2SO_4 were dispersed in 2.5 g of water and then the above mixture was dried in a vacuum oven for 6 h at 100 °C. Subsequently, the vacuum oven temperature was climbed to 160 °C for another 6 h. In order to obtain fully carbonized and polymerized sucrose inside the pores of the silica template, we repeat the above thermal treatment steps. Then, the template–polymer composites were putted in a tube furnace in nitrogen flow at 900 °C and kept carbonizing for 6 h. Finally, the silica framework in the powder was etched by 5 wt% hydrofluoric acid. The filtered sediment was washed three times with excessive ethanol and dried in a vacuum oven at 50 °C overnight. Finally, OMC was obtained.

2.3. Synthesis of OMC–PtNUs, OMC–PtNFs and OMC–PtNSs

For the synthesis of OMC–PtNUs, a mixture of OMC (60 mg), 20.00 mL of K_2PtCl_4 (10.0 mM) and HCOOH (30.00 mL) was shaken for a while. After, the reaction was kept sonicating for 30 min and then stewing for 3 days at room temperature. Finally, the sample was centrifuged, washed with ethanol and water three times, respectively. OMC–PtNUs was obtained by dying the above sample in an oven for 5 h at 60 °C.

The synthesis procedure of OMC–PtNFs and OMC–PtNSs was similar to that of OMC–PtNUs, except that added different amount of reactant OMC (OMC–PtNFs: 60 mg OMC; OMC–PtNSs: 60 mg OMC), 20.0 mL K_2PtCl_4 (OMC–PtNFs: 20.0 mM K_2PtCl_4; OMC–PtNSs: 50.0 mM K_2PtCl_4), and HCOOH (OMC–PtNFs: 30 mL HCOOH; OMC–PtNSs: 30 mL HCOOH). The overall synthesis procedure of OMC–PtNUs, OMC–PtNFs and OMC–PtNSs composites is depicted in Scheme 1.

2.4. Electrode preparation

Before modifying of GCE, it was polished with 1.0, 0.30 and 0.05 μm alumina slurry, then washed by distilled water and sonicated for 30 s in anhydrous ethanol and nitric acid, respectively. After, 2.0 mg of the as–prepared OMC–PtNUs, OMC–PtNFs and OMC–PtNSs were dispersed into 1.0 mL nafion to form a homogeneous suspension via sonication. Finally, 10.0 μL of the suspension was dropped onto the polished GCE and the solvent was dried under an infrared lamp.

3. Results and discussion

3.1. Characterization of OMC–PtNUs, OMC–PtNFs and OMC–PtNSs

The special architecture of the nanocomposites were confirmed by SEM (Fig. 1). Fig. 1A, B show that Pt NFs with a uniform particle size (the average diameter is about 27.88 nm) are nicely loaded on the worm–like OMC (OMC–PtNFs). In addition, the inset of Fig. 1 A shows the EDX pattern of OMC–PtNFs, it can be clearly seen that Pt element are existence in OMC–PtNFs, which further elaborates that Pt NFs are successfully loaded on the OMC. Meanwhile, Fig. 1C, D show Pt NSs with diameter of 69.36 nm and closely restacked multilayer structure are loaded on the surface of OMC (OMC–PtNSs). Fig. 1E, F reveal Pt NUs with the average particle size diameter about 4.41 nm are decorated on the surface of OMC (OMC–PtNUs). The results indicate that the