Applied Surface Science 256 (2009) 33–38

Contents lists available at ScienceDirect

Applied Surface Science

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

Poly(sodium-p-styrenesulfonate) assisted microwave synthesis of ordered mesoporous carbon supported Pd nanoparticles for formic acid electro-oxidation

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ARTICLE INFO

Article history:
Received 30 October 2008
Received in revised form 15 June 2009
Accepted 23 June 2009
Available online 22 July 2009

PACS:
82.45.Yz
82.45.Jn

Keywords:
Pd nanoparticles
Ordered mesoporous carbons
PSS assisted
Microwave synthesis
Formic acid
Electro-oxidation

ABSTRACT

Pd nanoparticles highly dispersed onto the surface of ordered mesoporous carbons (OMCs) were synthesized successfully by poly(sodium-p-styrenesulfonate) (PSS) assisted microwave synthesis. Here, PSS served as a bifunctional molecule both for solubilizing and dispersing OMCs into aqueous solution and for jointing Pd^{2+} to facilitate the subsequent uniform formation of Pd nanoparticles on their surfaces. The effects of PSS on structural and electrochemical properties of Pd/OMCs were investigated. It was found that the addition of PSS facilitated Pd nanoparticles to disperse on the carbon surface. Electrochemical properties showed that Pd catalysts prepared with addition of PSS displayed better electrochemical activity and stability for formic acid electro-oxidation than those without PSS.

1. Introduction

Direct formic acid fuel cells (DFAFCs) have attracted considerable interest recently as portable power applications [1–3]. Formic acid (HCOOH) is a liquid like methanol but it has a lower crossover through the Nafion-based membrane and a higher kinetic activity than methanol. Thus DFAFCs can be operated at a higher voltage than direct methanol fuel cells [4,5]. Pd based catalysts were found to possess superior performance in HCOOH oxidation in DFAFCs compared with Pt based catalysts [6,7]. Unfortunately, a poor dispersion state of Pd catalysts on the support is partially blamed for low catalyst activity in DFAFCs [3,8]. To achieve a higher efficiency of the catalyst, Pd has to be well-dispersed on the support. For this reason, it is desirable that the support material provides a suitable specific area and surface chemistry as well as a good electrical conductivity.

The OMCs have high surface areas and large pore volumes and are attractive support materials for noble metal nanoparticles (such as Pt, Pt–Ru, etc.) in fuel cell electrodes [9–11]. However, it is difficult to achieve highly dispersed metal catalyst due to the inert surface of the OMCs. In addition, the functionalization of OMCs has also not been studied in a large extent, because these conventional methods for the surface functionalization of OMCs processes involve either tedious procedures or harsh treatments to modify OMCs surfaces [11–13]. Recently, it was found that modification of OMCs with surfactants or polymers is mild and effective to graft organic motifs on the surface of OMCs [14,15]. Therefore, it is desirable to develop these ways that provide well-dispersed Pd nanoparticles with narrow particle distribution on the surfaces of modified OMCs. Meanwhile, preparing Pd nanoparticles on OMCs is not a sufficient investigation in DFAFCs.

Microwave synthesis has received considerable attention as a new, promising method for nanomaterials due to its rapid, uniform, and effective heating. In this paper, we introduce PSS into the microwave polyol process to prepare Pd nanoparticles supported on OMCs. This method is an efficient way to prepare Pd catalyst with uniform size and good dispersion on the carbon surface. The effects of the presence of PSS on structural and electrochemical properties of Pd/OMCs were investigated. It was found that the addition of PSS improved the wettability of carbon support and facilitated Pd nanoparticles to settle there. The

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0169-4332/$ – see front matter.
doi:10.1016/j.apsusc.2009.06.132

catalysts were compared with the unmodified catalyst with regard to dispersion and electrocatalytic activity.

2. Experiment

2.1. Synthesis of SBA-15 and OMCs

OMCs synthesized using SBA-15 as a hard template and benzene vapor as a carbon source was employed as catalyst support. SBA-15 was prepared according to the procedure reported by Su et al. [12] using Pluronic P123 (Sigma–Aldrich) in aqueous medium. Afterward, the SBA-15 template/carbon composite was obtained through deposition of carbon on the surface of the SBA-15 carried out using a CVD method with the benzene as the carbon precursor. After carbonization at 900 °C and removal of the silica template with HF solution, the OMCs were obtained.

2.2. Preparation of Pd catalysts

The OMCs were firstly modified by means of oxidation treatment in 1.0 M HNO_3 at room temperature for 0.5 h (OMCs-o) in order to create oxygen surface groups [13].

A typical run for the catalyst having 20 wt% Pd was carried out as follows: 1.88 mL of 0.075 mol mL^{-1} $PdCl_2$ solution was added to 20 mL ethylene glycol, adjusting pH to 11 by addition of the 2.0 M sodium hydroxide solution. Then 60 mg of OMCs-o were mixed with 10 mL of PSS solution and subsequently dropped into the Pd precursor solution. After 30 min of sonicating, the suspension was then exposed in the middle of a microwave oven (LG MG-5021 MW1, 800 W, 2450 MHz) for 90 s at 700 W and cooled to room temperature naturally. The product was isolated by centrifugation, washed with acetone and then dried in a vacuum oven at 353 K overnight, named as Pd/OMCs-o-*x*. Herein x represents the initial molar ratio of PSS to Pd (e.g., 3, 5 and 7). For comparation, the Pd/OMCs catalyst was synthesized under the same procedure.

2.3. Instrument and measurement

The porous structures of the carbon supports were measured by N_2 adsorption isotherm using Micromeritics ASAP 2010 at 77 K. Surface areas of the samples were calculated using the Bruauer–Emmett–Teller (BET) equation, while the pore size distributions were determined by the Barret–Hoyner–Halenda (BJH) method using the adsorption branch. X-ray diffraction (XRD) patterns were recorded by a Bruker D8 ADVANCE diffractometer using Cu Kα radiation (λ = 0.154056 nm). Transmission electron microscopy (TEM, FEI Tecnai G2) operating at 200 kV was applied to characterize the morphology and particle size distribution. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash 1100) was used to analyze the contents of Pd on the catalysts.

The catalytic performance of the Pd catalysts in room temperature HCOOH oxidation reaction was evaluated by cyclic voltammetry and chronoamperometry methods, using an electrochemical working station (CHI-660C, Chenhua, Shanghai) and a standard three-electrode cell. The working electrode was prepared as follows: 5 mg of the catalyst was mixed with 1 mL of ethanol and 50 μL of 5 wt% Nafion solution (Aldrich Chemical Co.). The mixture was sonicated for 30 min to obtain the slurry. Approximately 25 μL of the slurry was applied to the surface of the glassy carbon electrode to form a thin layer of ca. 0.1256 cm^2 in geometrical area. A saturated calomel electrode (SCE) and a platinum foil were used as the reference electrode and the counter electrode, respectively. All electrolyte solutions were deaerated with high purity nitrogen for 30 min prior to electrochemical measurement.

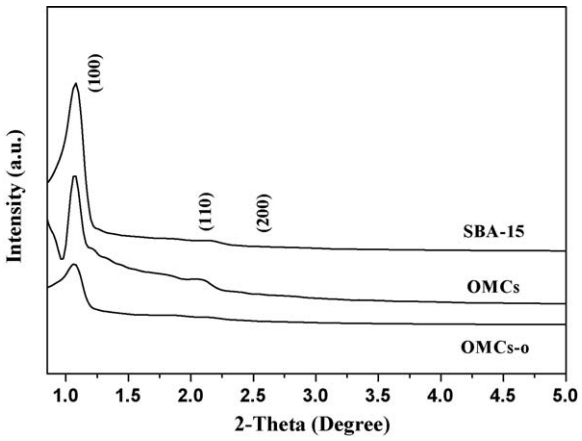

Fig. 1. XRD patterns of SBA-15, OMCs and OMCs-o.

3. Results and discussion

Fig. 1 shows the XRD patterns of OMCs and OMCs-o along with the parent SBA-15 template. The OMCs exhibit three well-resolved peaks, which can be assigned to (1 0 0), (1 1 0), and (2 0 0) reflection of 2D hexagonal lattice, similar to the XRD pattern of SBA-15 [1,12]. And OMCs-o also show similar XRD patterns indicating that hexagonally ordered structure is maintained after modification by the concentrated nitric acid. However, f-OMCs show a small peak suggesting a decrease of the structural order, although it still has a considerable degree of structural order. The more detailed structural characterizations are observed by TEM images (Fig. 2). In the (1 1 0) direction, the OMCs (see Fig. 2a) exhibit large domains of highly ordered stripe-like and hexagonally arranged arrays, originating from the mesoporous silica framework [16]. After oxidation treatments, The TEM image showed in Fig. 2c confirms that the OMCs-o still maintain the ordered structure although its degree of structural order is lower than that of the OMCs, as observed by XRD. Furthermore analysis of N_2 sorption isotherms and BJH pore size distributions (Fig. 3) of the SBA-15, OMCs and OMCs-o showed their type IV isotherms with an H1 and H2 hysteresis loops, respectively, which indicated the presence of cylindrical pore channels in these mesoporous materials [1,12,16]. SBA-15 presented a relatively broad pore size distribution centered at 6.5 nm, while OMCs and OMCs-o had a narrow pore size distribution centered at 4.4 and 4.2 nm, respectively. The detailed pore characteristics of the three samples resulting from N_2 sorption adsorption were summarized in Table 1. The specific surface areas of the SBA-15, OMCs and OMCs-o are 643, 931 and 764 $m^2\ g^{-1}$, respectively. Furthermore, the total pore volumes of the SBA-15, OMCs and OMCs-o obtained from the volume of nitrogen adsorbed at the relative pressure of 0.99 are 0.78, 0.83 and 0.69 $cm^3\ g^{-1}$, respectively.

Fig. 4 presents that the same pattern was replicated by all Pd/OMCs catalysts synthesized with or without different amounts of PSS. One broad diffraction around $2\theta = 23^\circ$ belongs mostly to the carbon support. The others could be indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections of the facecentered-cubic phase of Pd bulk [17,18]. As can be seen from (2 2 0) reflection, it gets narrower with the increase of the amount of PSS added, indicating the average sizes of Pd particles become larger. Moreover, Table 2 shows the average particle sizes of the catalysts estimated by the Scherrer formula [19,20]. The average size of Pd particles increases slightly from 4.9 to 5.5 nm when the amount of PSS added to the synthesis solution increases.

Fig. 5 shows the TEM images of the different catalysts prepared with or without PSS. As can be seen from Fig. 5a, there are few