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Electrocatalytic properties of platinum on hard carbon spherules derived from deoiled asphalt for methanol oxidation

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Abstract

In the present contribution, hard carbon spherules (HCSs) were synthesized from a deoiled asphaltene and were used as supporting materials for platinum (Pt) electrocatalyts. Pt nanoparticles were well dispersed on the surface of HCSs by an impregnation–reduction method. The morphology and microstructure of the as-prepared Pt/HCSs composites were studied by means of X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) techniques. The electrocatalytic properties of the Pt/HCS electrode for methanol oxidation were investigated by cyclic voltammetry and high electrocatalytic activity was observed.

Keywords: DMFC; Hard carbon spherules; Electrochemical properties

1. Introduction

Pt and Pt-based alloy particles play an important role in the chemical industry [1,2]. It has been shown that nanosized Pt particles with a high density of active sites usually exhibit superior catalytic properties. In addition to catalyst preparation, the choice of a suitable carbon support is one of the key factors affecting the performance of supported catalysts. It has been proved that the structure of a carbon support [3–6] can influence the structure of the corresponding catalyst layer and, as a result, the electrochemical properties of the catalyst. For instance, it was found that carbons with sulfur- or nitrogen-containing functional groups could enhance the activity of the resulting catalysts [7]. Recently, the emergence of novel carbon materials, such as carbon nanotubes (CNTs) [8], carbon spheres [9,10], and graphitic carbon nanofibers [11,12], provides new choices of carbon supports. The deposition of Pt, Ru and PtRu on CNTs has been reported and the as-prepared catalysts have better performance than other carbon-supported catalysts [13,14]. However, the synthesis of Pt nanoparticles with uniform size and good dispersion over the carbon supports as electrocatalytic materials remains to be a challenge.

The treatment and property exploration of asphaltene are becoming an increasingly important problem. Recently, asphaltene was found to be a potential precursor of onion fullerene structures [15]. As a carbon-rich by-product of petroleum processing, deoiled asphalt can release CH_4, CO, H_2, N_2, CO_2, H_2S and low molecular hydrocarbons upon thermal treatment and thus can be used as an inexpensive and readily available carbon source for preparing novel structural carbon materials.

In this paper, well-dispersed hard carbon spherules (HCSs) prepared from a deoiled asphalt were used as the support of Pt nanoparticles and the electrocatalytic properties of the resulting Pt/HCS electrode for methanol oxidation were investigated.

2. Experimental

2.1. Synthesis and characterization of Pt/HCS catalysts

HCSs were prepared by a chemical vapor deposition (CVD) method with a deoiled asphalt (supplied by China University of Petroleum, Beijing) as a precursor. A quartz tube of 35 mm

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diameter was inserted into a cylindrical furnace whose temperature was controlled with its central zone at 900 °C in an argon atmosphere. A 1 g deoiled asphalt was stored in a quartz boat in the quartz tube in a cool zone outside the furnace, and the pyrolysis of the deoiled asphalt was initiated by shifting the tube so that the quartz boat was moved into the reaction zone of the furnace. A 0.03 g HCSs were collected from the tube wall after the experiment. For the better anchoring of Pt nanoparticles, the as-produced HCSs were oxidized in a concentrated HNO_3 solution for 4 h.

The typical impregnation–reduction method was employed to prepare HCS-supported Pt catalyst with formaldehyde as a reducing agent. To use this method to synthesize Pt/HCS with Pt loading of 40 wt%, 0.060 g HCSs were uniformly dispersed in a 5.5 mL aqueous solution of H_2PtCl_6 (7.4 g/L) by ultrasonic mixing. Then, 20 mL formaldehyde was dropwise added into the H_2PtCl_6 solution at 60 °C and 0.8 mL H_2O_2 was added to stabilize the Pt particles under continuous stirring for 5 h. The solid product was rinsed with deionized water repeatedly and filtered. Finally, the product was dried at 70 °C for 12 h in a vacuum oven.

The surface morphology of the HCSs and the Pt/HCS catalysts was observed on a field-emission scanning electron microscope (FESEM JEOL JSM-6700F). X-ray diffraction (XRD) measurements were carried out on a D/max-3C X-ray diffractometer using Cu Kα radiation (1.5405 Å) to characterize the structure of the Pt/carbon catalysts. The XRD spectra were used to determine the crystallographic identity of the produced material and to calculate the mean particle size based on the broadening of the most prominent peak in the XRD profile. The Scherrer's [16] equation, as described as follows, was used to calculate the average particle diameter D (in Å).

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

where θ is the angle of the peak, β the full width at half maximum (FHWM) of the corresponding XRD peak, λ the X-ray radiation wavelength in angstroms (Å) and K is a constant very close to unity (0.9 for Ni [16]) and is related both to the crystallite shape and to the way in which β and D are defined.

2.2. Preparation and characterization of electrodes

Electrochemical experiments of the as-prepared 40 wt% Pt/HCS catalysts were carried out on an electrochemical interface (Autolab PGSTAT302). A standard three-electrode cell was used with saturated calomel electrode (SCE) as the reference electrode and platinum foil as the counter electrode. The working electrode was made by casting of Nafion-impregnated catalyst ink on to a 4 mm diameter glassy carbon plate electrode. The catalyst loading was about 1 mg cm^{-2}. All the potentials measured in this study are reported with respect to the SCE. A 1.0 M H_2SO_4 or 2.0 M CH_2OH/1.0 M H_2SO_4 was used as the electrolyte. All the reagents used were of analytical grade.

3. Results and discussion

3.1. Morphology and structure of HCSs and Pt/HCS catalysts

The SEM image of the HCSs is shown in Fig. 1. It can be seen that the HCS particles are monodispersed with an average diameter less than 1 μm. Their perfect spherical shape and uniform size can be seen in the image. Obviously, the surfaces of the carbon spherules are very smooth, different from the rough surface of mesocarbon microbeads (MCMB) [17] or spongy carbon nanobeads [18].

Fig. 2 is a typical SEM image of the HCS-supported catalysts that present very uniform and high dispersion of metal nanoparticles on the carbon surface. In addition, particle aggregation can be also observed.

The powder XRD patterns of the raw HCSs and the supported catalysts are shown in Fig. 3. The broad and shallow diffraction peak at about 24° corresponds to the HCSs for supporting metals. As for the Pt/HCS catalyst, the synthesized Pt nanoparticles supported on the HCSs form a face-centered cubic (fcc) structure and the peaks at ca. 39.7°, 46.2° and 67.6° belong to Pt (1 1 1), (2 0 0) and (2 2 0), respectively. The mean size of Pt particles was estimated to be 3.5 nm by the Scherrer's equation.

3.2. Electrochemical characterization of Pt/HCS electrodes

Well-defined hydrogen absorption–desorption features are seen in the cyclic voltammogram curve (Fig. 4, dashed line) of the Pt/HCS electrode in 1.0 M H_2SO_4 solution at room temperature. The real surface area of Pt on the Pt/HCS catalysts could be estimated from the amount of charge (Q_H) associated with hydrogen adsorption (shaded area) on Pt surface. This area

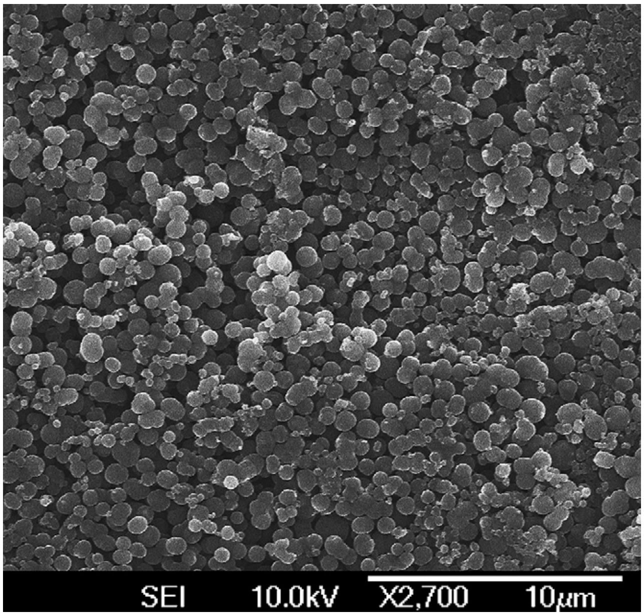

Fig. 1. SEM image of the HCSs.

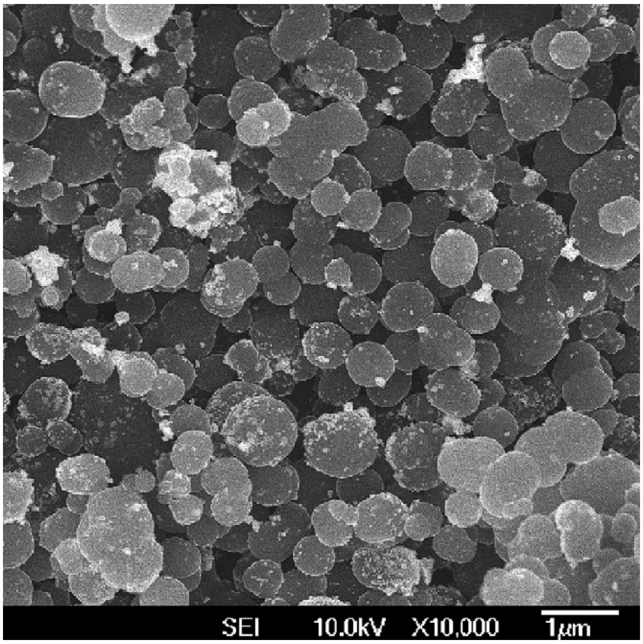

Fig. 2. SEM image of synthesized Pt nanoparticles supported on HCSs.

is normalized to the mass of Pt in the catalyst (S_S, specific surface area). S_S can be obtained from the following equation:

$$S_S = \frac{Q_H}{M_{Pt} Q_{Href}} \tag{2}$$

where Q_H is the amount of charge of the electroabsorption of hydrogen atoms on the Pt surface, M_{Pt} the mass of Pt and Q_{Href} is assumed to be 0.21 mC/cm^2 corresponding to a surface density of 1.3×10^{15} atom/cm^2 of Pt [19]. The value of Q_H of the as-prepared catalysts is 9.16 mC. The specific surface area of Pt thus can be estimated as $S_S = 10.9$ m^2/g.

For comparison, background cyclic voltammogram was performed on a Pt-free HCSs pasted electrode of the same geometric area (Fig. 4, solid line). In the absence of the Pt nanoparticles, no hydrogen absorption region was observed.

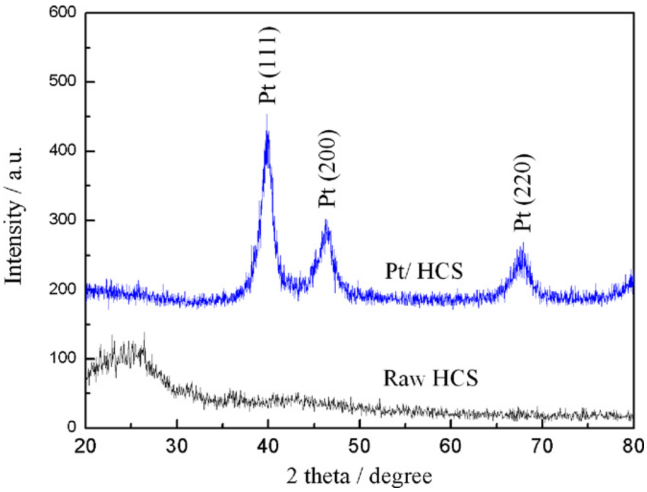

Fig. 3. XRD patterns of raw HCSs and Pt/HCS catalyst.

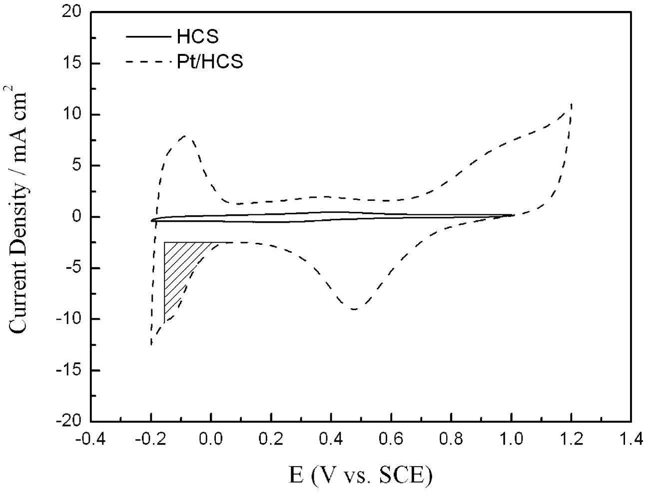

Fig. 4. Cyclic voltammogram curves of the Pt-free HCSs (solid line) and Pt/HCS (dashed line) electrodes in 1.0 M H_2SO_4 solution at room temperature at scan rate of 50 mV/s.

Fig. 5 shows the cyclic voltammograms of the methanol electrooxidation over the Pt/HCS catalyst in the electrolyte of 2.0 M CH_3OH and 1.0 M H_2SO_4 at room temperature. The scanning rate used here is 50 mV/s. The voltammetric features are in good agreement with those in the published works [20,21]. The current peak between 0.7 and 0.9 V versus SCE in the forward scan is attributed to methanol electrooxidation on the catalyst. In the backward scan, the re-oxidation of methanol is clearly observed due to the reduction of oxide of platinum.

The HCS support used in our study have been treated by the concentrated HNO_3 solution, resulting in a high density of functional groups such as carboxyl, hydroxyl and carbonyl groups on the surface of the HCSs. After platinum salt precursors were mixed with the surface-oxidized HCSs, the Pt ions would interact with and attach onto these surface functional groups on the HCSs via coordination reactions or in-exchange reactions, thus functioning as a nucleation precursors that were finally reduced to Pt nanoparticles on the HCSs [22]. The function groups of the surface-oxidized HCSs were suitable for heterogeneous nucleation and interrupts particles agglomeration.

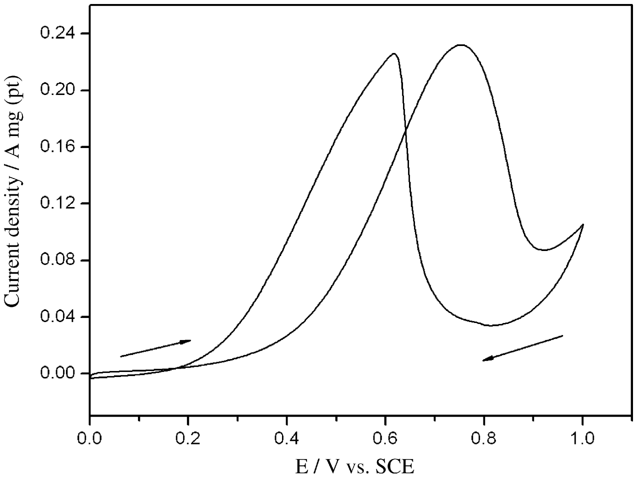

Fig. 5. Cyclic voltammogram curve of Pt/HCS electrodes in 1.0 M H_2SO_4 + 2.0 M CH_3OH solution at room temperature at scan rate of 50 mV/s.

Therefore, the synthesized Pt nanoparticles were very uniform in size, and well dispersed on HCSs surface. The high electrocatalytic activity of the Pt/HCS catalyst can be attributed to the high dispersion of the Pt nanoparticles.

From the above results, it can be concluded that the HCSs derived from the deoiled asphalt are excellent candidate to be used as the catalyst support for methanol oxidation.

4. Conclusions

The hard carbon spherules synthesized from a deoiled asphalt was used as the support of Pt electrocatalyts. The Pt nanoparticles with a mean diameter of 3.5 nm were uniformly dispersed on the surface of the HCSs. The electrocatalytic properties of the obtained Pt/HCS electrode for methanol oxidation were investigated by cyclic voltammetry and their high electrocatalytic activity was observed.

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