

Short communication

Novel carbon supported hollow Pt nanospheres for methanol electrooxidation

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Abstract

A carbon supported hollow Pt nanosphere electrocatalyst was prepared at room temperature in a homogeneous solution employing cobalt metal nanoparticles as sacrificial templates. TEM measurements showed that carbon supported Pt nanospheres were coreless and composed of discrete Pt nanoparticles with the crystallite size of about 2.2 ± 0.2 nm. XRD results showed that the hollow Pt nanospheres had a face-centered cubic structure. Electrochemical measurements demonstrated that the carbon supported hollow Pt nanosphere electrocatalyst exhibited enhanced electrocatalytic performance for methanol oxidation compared with carbon supported solid Pt nanoparticles.

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1. Introduction

Direct methanol fuel cells (DMFCs) are being widely studied for compact, high energy-density power sources [1–5]. As a cheap liquid fuel, methanol has several advantages over hydrogen. It is very easily handled, transported, stored, and has a high theoretical energy density [3,6]. It has been recognized that the success of fuel cell technology depends largely on two key materials: (1) the membrane and its methanol crossover rate [7–9] which can only be overcome by developing new membranes; (2) the anode catalyst which has slow anode kinetics [10–12] and which can only be overcome by developing new anode catalysts. With regard to a new DMFC anode catalyst, there are two major challenges, namely, the performance, including activity, reliability and durability, and cost reduction. Therefore, many efforts have focused on the development of techniques to achieve high catalytic performance and utilization efficiency [13–16].

Recently, hollow metal nanostructures have captured the attention of researchers due to the increased surface area, low density, cost-saving of material which make them exhibit catalytic

activities different from their solid counterparts [17,18]. Traditional ways to fabricate hollow nanostructures have focused on a templating method [19–24]. The templates include porous alumina [19,20], polystyrene spheres [21], silica spheres [22] and micelles [23,24]. Xia and co-workers have pioneered a method to prepare hollow metal particles based on a galvanic replacement reaction carried out in aqueous solutions [25]. The procedure of this method employed a sacrificial Ag nanoparticle with various morphologies, and used to reduce aqueous metal ions. This results in the formation of excellent hollow particles that take on the morphology of the sacrificial partner. Bai and co-workers extended a facile procedure for the synthesis of Pt hollow nanosphere catalysts by exploiting the replacement reaction between Co nanoparticles and H_2PtCl_6 [26]. The Pt hollow nanospheres prepared had a higher surface area and therefore exhibited enhanced electrocatalytic performance.

As it is well known, Pt and Pt-based particles electrocatalysts should be supported on carbon surface in practice [27,28]. The supported metal nanoparticles show a higher electrocatalytic activity and utilization efficiency than unsupported metal particles because of their large surface area on the supports [29]. Vulcan XC-72 (Cabot Corp.) is one of the well-known commercial carbon materials, which has been widely used as an electrocatalyst support due to its high surface area and abun-

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dant surface functional groups. Although Pt hollow nanospheres with an enhanced electrocatalytic performance have been synthesized [26], these hollow nanospheres have not been supported on a carbon surface to investigate their electrocatalytic performance. If the hollow Pt nanoparticles are supported on the XC-72 carbon surface, the electrocatalytic performance and utilization efficiency could be further improved. Therefore, herein we synthesized XC-72 carbon supported Pt hollow nanosphere electrocatalysts (HN-Pt/C) by a two-step method. Pt hollow nanospheres were firstly prepared by a replacement reaction between sacrificial Co nanoparticles and PtCl_6^{2-} ions, then were adsorbed onto a XC-72 carbon support. The electrochemical measurements demonstrated that the HN-Pt/C electrocatalysts show a much higher active surface area and a much better electrocatalytic performance for methanol oxidation in comparison to carbon supported solid Pt nanoparticles electrocatalysts (SN-Pt/C).

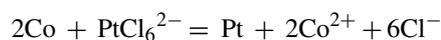
2. Experimental details

2.1. Reagents

Vulcan XC-72 carbon with a specific surface area (BET) of $240 \text{ m}^2 \text{ g}^{-1}$ and an average particle size of 40 nm was purchased from Cabot Corp. Nafion (perfluorinated ion exchange resin, 5 wt% solution) was obtained from Aldrich. A platinum precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), cobalt chloride (CoCl_2), sodium borohydride (NaBH_4), sulfuric acid and citric acid were of A.R. grade, and were purchased from Shanghai Chemical Products Ltd. Deionized water was used to prepare the solutions and high-purity nitrogen gas was used in the experiments.

2.2. Preparation of Pt/C electrocatalysts

A HN-Pt/C electrocatalyst was prepared by a two-step method. In a typical synthesis, 300 mL of 0.4 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was mixed with 0.4 mM citric acid solution which was used as a stabilizer. The solution was purged with N_2 for 15 min, then 20 mL of 40 mM NaBH_4 was added dropwise into the above solution under vigorous stirring giving rise to a brown Co hydrosol. The Co hydrosol was aged for 1 h to decompose the residual NaBH_4 . Afterwards, 100 mL of 0.8 mM H_2PtCl_6 was added dropwise under vigorous stirring. The color of the solution became blackish brown gradually, which showed that a trans-metallation reaction occurred. The Co nanoparticles were oxidized to Co^{2+} ions by PtCl_6^{2-} according to the equation as follows [26]:



After 60 min, to ensure that cobalt element was completely oxidized by slightly excessive PtCl_6^{2-} , carbon supports (48 mg dispersed in 20 mL H_2O) were then added to the above solution. After stirring for another 60 min, the product was collected by filtration and washed several times with deionized water and acetone. For comparison, SN-Pt/C electrocatalyst was directly synthesized by adding NaBH_4 solution into H_2PtCl_6 solution. Then, the Pt nanoparticles were adsorbed on carbon supports.

The solid products were dried at 80°C for 12 h in a vacuum oven.

2.3. Characterizations of Pt/C electrocatalysts

Energy dispersion X-ray spectra analysis (JSM-T20 field emission scanning electron microscopy) was used to determine the metal mass fraction of Pt/C catalysts. XRD patterns were obtained on a Thermo X'Tra X-ray diffractometer equipped with $\text{Cu K}\alpha$ as radiation source ($\lambda = 0.154056 \text{ nm}$) and operating at 40 kV and 40 mA. TEM images were recorded on a JEM-200CX transmission electron microscopy with an acceleration voltage of 160 kV. Sample preparation for TEM examination involved the ultrasonic dispersion of the sample in ethanol and placing a drop of the suspension on a copper grid covered with perforated carbon film.

2.4. Electrochemical measurements

The electrocatalytic activities of the Pt/C electrocatalysts for methanol electrooxidation were measured by cyclic voltammetry and chronoamperometry using a CHI 660B potentiostat/galvanostat and a three-electrode test cell at 30°C . The electrolyte solution was 2.0 M CH_3OH in 1.0 M H_2SO_4 . A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All potentials in this work are reported with respect to SCE. The working electrode was a thin layer of Nafion-impregnated catalyst cast onto a vitreous carbon disk with 4.0 mm diameter held in a Teflon cylinder. The working electrode was obtained in the following way: a slurry was first prepared by sonicating a mixture of 500 mg of deionized water, 10 mg of Pt/C electrocatalyst, and 200 mg of Nafion solution; then 2.0 μL of the slurry was pipetted and spread onto the vitreous carbon disk; the electrode was finally dried at 80°C for 10 min. The active specific surface area of Pt particles was calculated according to the hydrogen electroadsorption curve. The potential was cycled between +1.25 and -0.25 V at 50 mV s^{-1} in 1.0 M H_2SO_4 electrolyte to obtain the voltammograms of hydrogen adsorption. All electrolyte solutions were deaerated with high purity nitrogen for 30 min prior to electrochemical measurement.

3. Results and discussion

Fig. 1 shows typical EDX spectrums of the Pt/C electrocatalysts. The EDX analysis showed that the Pt mass percentage of HN-Pt/C and SN-Pt/C electrocatalysts was 19.8 and 20.3%, respectively, which are coincided with the ratio of Pt to carbon in the starting mixture. XRD patterns of the Pt/C catalysts are shown in Fig. 2. The rather wide diffraction peaks at $2\theta = 25.0^\circ$ are attributed to XC-72 carbon. The other diffraction peaks can be readily indexed to face-centered cubic platinum. The calculated interplanar spacing of hollow Pt nanospheres is 0.226 nm for Pt(1 1 1), 0.196 nm for Pt(2 0 0), and 0.138 nm for Pt(2 2 0), which are consistent with the standard powder diffraction file of Pt (JCPDS No. 04-0802). The breadth of the XRD peaks also indicated that small Pt crystallites were obtained. Using the

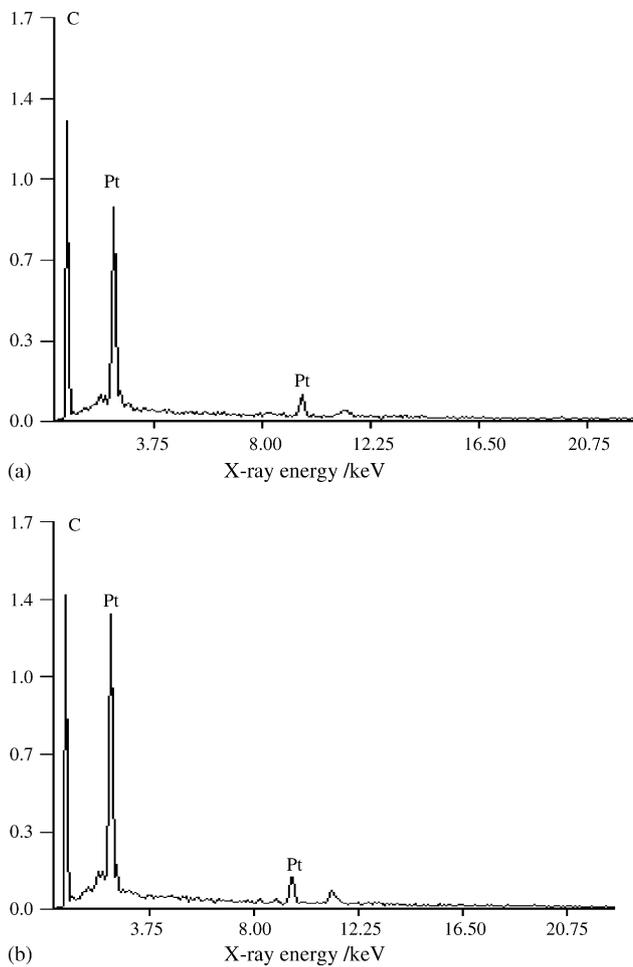


Fig. 1. EDX spectrum of (a) SN-Pt/C and (b) HN-Pt/C electrocatalysts.

Scherrer equation $D_c = 0.9\lambda/\beta \cos \theta$ (where $\lambda = 0.154056$ nm, β is the full width at half-maximum in radians), the average crystallite size (D_c) was estimated to be 2.2 ± 0.2 and 4.6 ± 0.2 nm, respectively, for hollow Pt nanospheres and solid Pt nanoparticles.

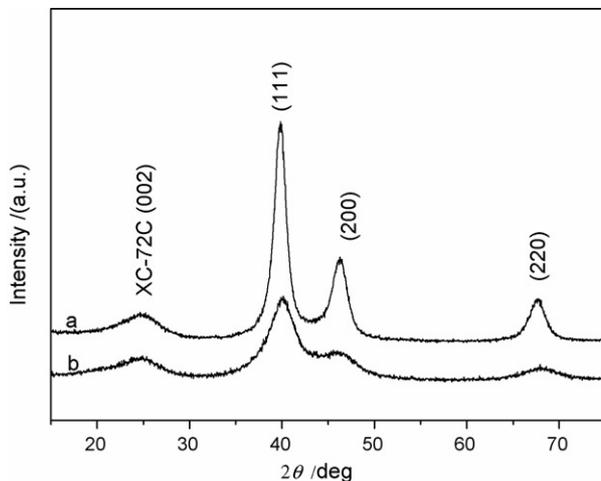


Fig. 2. XRD patterns of (a) SN-Pt/C and (b) HN-Pt/C electrocatalysts.

The morphology of the electrocatalysts was investigated by TEM. Fig. 3(a) shows a typical TEM image of SN-Pt/C catalysts, it can be seen from which that Pt particles dispersed on carbon surface are solid. The mean size of Pt particles is approximately 4.8 ± 0.3 nm. Fig. 3(b) shows a typical TEM image of HN-Pt/C catalysts. It is found that the center of Pt nanospheres is brighter than the edges. The individual Pt nanospheres are composed of an empty core with a shell, that is, a hollow structure. The average diameter of the nanospheres was statistically calculated to be 24.5 ± 0.3 nm. Another feature is that the shell is incomplete

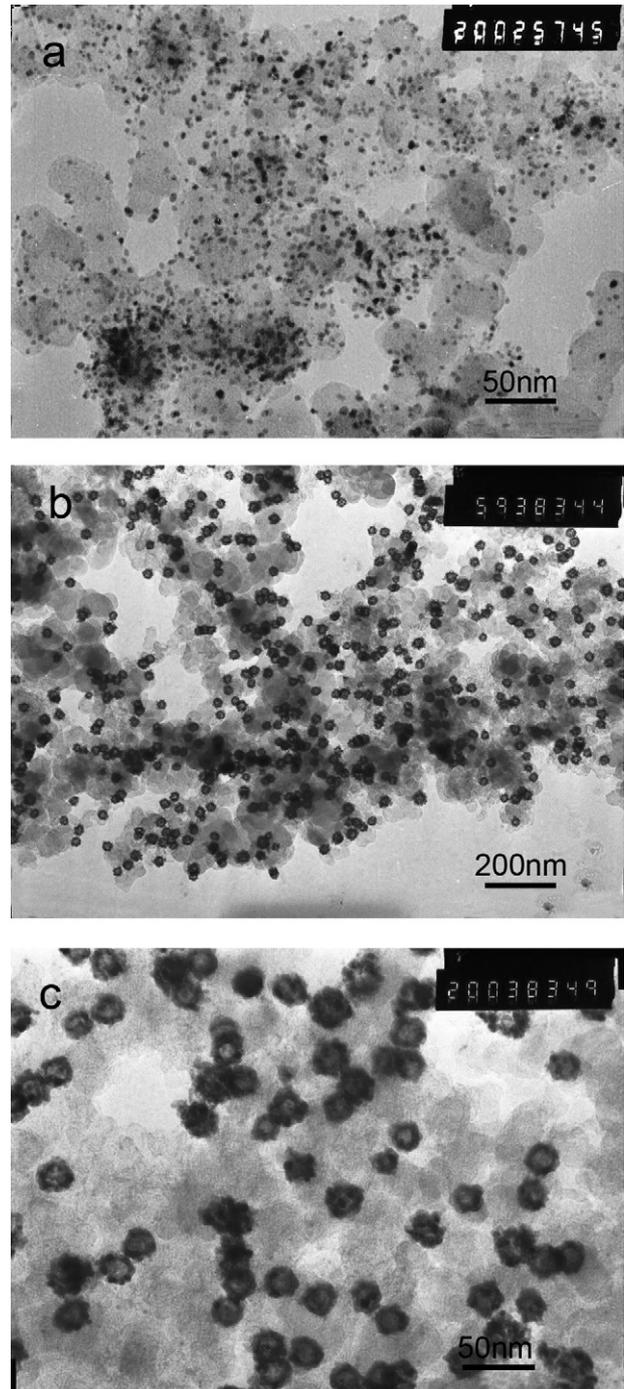


Fig. 3. TEM images of: (a) SN-Pt/C and (b and c) HN-Pt/C electrocatalysts.

and porous, not solid. As shown in Fig. 3(c), the shells of the Pt hollow nanospheres seem to be rough and consist of discrete Pt nanoparticles. This feature endows the hollow Pt nanospheres with a high active surface area.

In general, the real surface area of Pt particles is one of the important parameters to determine the catalytic properties of electrocatalysts for methanol electrooxidation since this reaction is surface-sensitive. The active specific surface area of Pt particles for Pt/C catalysts could be estimated from the hydrogen adsorption curves [28]. Fig. 4 shows cyclic voltammograms of the Pt/C electrocatalysts in 1.0 M H₂SO₄, the hatched region in which is attributed to the hydrogen adsorption and the hatched area represents the integrated charge for the hydrogen adsorption. The active specific surface area of Pt particles in m² g⁻¹ can be calculated from the following formula assuming a correspondence value of 0.21 mC cm⁻² (calculated from the surface density of 1.3 × 10¹⁵ atom cm⁻²), a value generally admitted for polycrystalline Pt electrodes and the Pt loading [30]. The specific surface area of HN-Pt/C was calculated to be 138.7 m² g⁻¹ Pt, which is much higher than 73.0 m² g⁻¹ Pt of SN-Pt/C electrocatalysts.

$$A_{EL} \text{ (m}^2\text{g}^{-1} \text{ Pt)} = \frac{Q_H}{0.21 \times 10^{-3} C \text{ (g Pt)}}$$

where A_{EL} is the active specific surface area of Pt particles, Q_H the amount of charge exchanged during the hydrogen atom electroadsorption and C is the coulomb.

Fig. 5 shows the cyclic voltammograms of methanol electrooxidation over HN-Pt/C and SN-Pt/C electrocatalysts prepared in this work and a commercial E-TEK Pt/C (20% Pt) catalyst in 2 M CH₃OH/1 M H₂SO₄ electrolyte at 30 °C. It can be seen from Fig. 5 that the electrooxidation of methanol began at about 0.40 V versus SCE. The current peaks at about 0.67–0.70 V versus SCE in the forward scan are attributed to methanol electrooxidation. As shown in Fig. 5, the peak current of HN-Pt/C and SN-Pt/C electrocatalysts is 12.0 and 6.6 mA, respectively. From the current measurements, it is clear that the catalytic activity of the hollow Pt nanospheres is almost twice

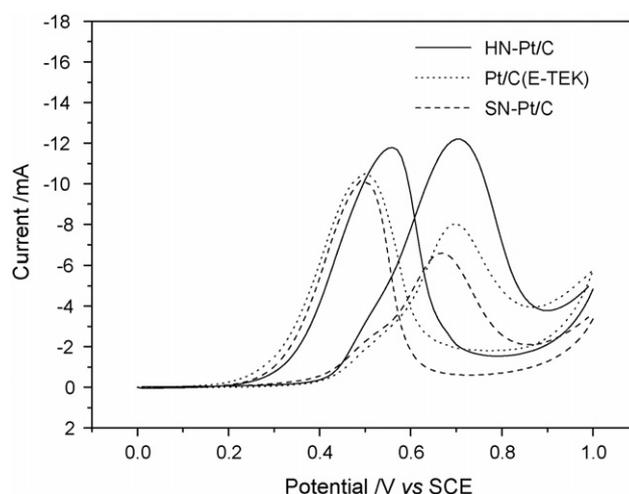


Fig. 5. Cyclic voltammograms of methanol electrooxidation on Pt/C catalysts in 2.0 M CH₃OH/1.0 M H₂SO₄ electrolyte at a scan rate of 20 mV s⁻¹ at 30 °C.

that of the solid Pt nanoparticles. In addition, the HN-Pt/C catalyst exhibited higher current peak than the E-TEK Pt/C catalyst. The facts demonstrated that the HN-Pt/C catalyst displayed better electrocatalytic activity for methanol electrooxidation than the E-TEK Pt/C and SN-Pt/C electrocatalysts. The improvement in electrocatalytic activity is due to the hollow Pt nanospheres which possess higher active surface area, and is related to the electrocatalytic activity of methanol.

The difference is significant enough that the current density at 0.4 V can be used as an indicator of the catalytic activity of the catalysts under moderate polarization conditions. The Pt/C catalysts were therefore biased at 0.4 V versus SCE and the changes in their polarization currents with time were recorded shown in Fig. 6. For each catalyst, the methanol electrooxidation current decreased moderately with time. The decay in the electrocatalytic activity is due to that the intermediate products of methanol oxidation such as CO which are easily adsorbed on the Pt nanoparticles, and inhibit the methanol electrooxidation reaction. It should be worth noting that HN-Pt/C electrocata-

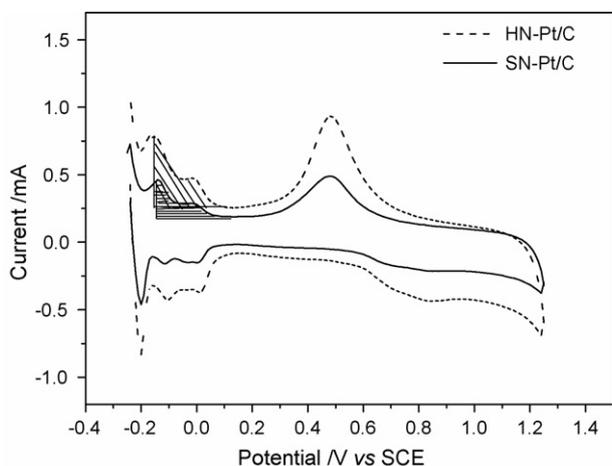


Fig. 4. Cyclic voltammograms of Pt/C catalysts in 1.0 M H₂SO₄ at a scan rate of 50 mV s⁻¹ at 30 °C. The hatched area represents the amount of charge of the electroadsorption of hydrogen on Pt surface.

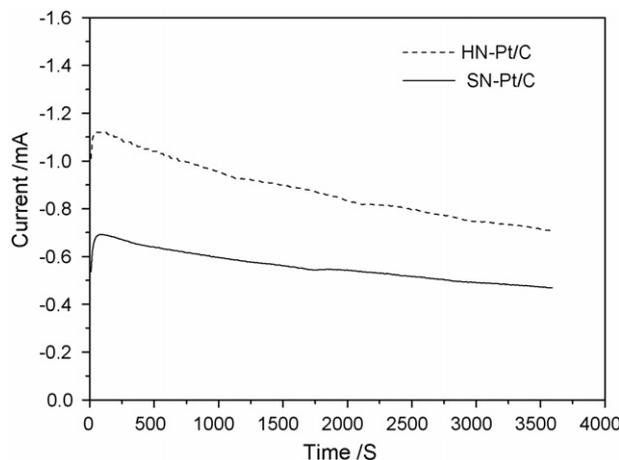


Fig. 6. Polarization current vs. time plots for the electrooxidation of methanol in 2 M CH₃OH/1 M H₂SO₄ electrolyte at 0.4 V (vs. SCE) at 30 °C.

lyst exhibited a much higher initial and ultimate polarization current than SN-Pt/C, which indicated the former displays better catalytic performance for methanol electrooxidation than the latter.

4. Conclusions

A carbon supported hollow Pt nanosphere electrocatalyst was prepared at room temperature in a homogeneous solution with Co nanoparticles as sacrificial templates. TEM measurements showed that the carbon supported Pt hollow nanospheres were coreless and made of many incomplete nanoparticles. A better electrocatalytic performance for methanol oxidation of this HN-Pt/C catalyst was demonstrated with cyclic voltammetry and chronoamperometry. The improvement in electrocatalytic performance is due to the higher active surface area of the HN-Pt/C catalyst. The present method in this paper is simple, effective, and could be extended to the fabrication of other carbon supported metals or their bimetallic hollow nanospheres.

Acknowledgments

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