



Hollowed carbon capsule based Pt–Fe/carbon electrocatalysts prepared by chemical vapor infiltration method

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ABSTRACT

A new type of hollowed carbon capsule (HCC) material has been fabricated and utilized as a support for Pt–Fe catalyst by means of chemical vapor infiltration (CVI) method. The supported Pt–Fe/HCC catalyst was found to possess cavities with sizes around 20–40 nm and well-dispersed Pt–Fe alloy particles embedded on the internal graphitic carbon walls and hence can be used as potential electrocatalyst for fuel cells. Preliminary performance tests by cyclic voltammetry revealed that the supported Pt–Fe/HCC catalyst has electrochemical properties compatible to a common commercial catalyst. The formation mechanism of the HCC material is also proposed.

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1. Introduction

Direct methanol fuel cell (DMFC), which can use methanol as fuel without processing, has become a promising portable power source especially for transportation applications accounting for environmental protection issues. Undoubtedly, the fabrication and assembly of electrode materials dictate the efficiency, stability and costs of DMFC. The anode electrocatalysts commonly used nowadays are mostly made of Pt based alloys supported on carbon materials. As such, the physical and electrochemical properties of the carbon supports, such as carbon nanotube (CNTs), carbon mesoporous materials (CMMs), and activated carbons etc., are critical to the overall performance of fuel cell electrodes. Thus, the developments of novel carbon materials with high surface area, electrical conductivity, and electrochemical stability have drawn much research attentions [1–4]. Owing to their CO-tolerance during DMFC operations, bifunctional alloy catalysts such as Pt–Ru supported on carbon materials have become benchmarks of anode electrocatalysts [2,5]. However, supported Pt–Ru catalysts are also drawback by their cost ineffectiveness, as a result, alternative CO-tolerance alloy catalysts such as Pt–Fe, Pt–Co, Pt–Ni, and Pt–Mo have been extensively studied [6].

We report herein, a novel method to fabricate a new type of carbon material, namely hollowed carbon capsule (HCC) by chemical vapor infiltration (CVI) method. The Pt–Fe supported HCC was characterized using cyclic voltammetry (CV) measurements, high-resolution trans-

mission electron microscopy (HRTEM), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and X-ray diffraction (XRD).

2. Experimental

2.1. Materials synthesis

The HCC supported Pt–Fe catalyst was prepared using collapsed mesoporous MCM-48 silica as template and means of a CVI process after loading the metal catalyst. First, the templating mesoporous MCM-48 silica was synthesized following a conventional hydrothermal procedure [7] under the following chemical molar compositions: 5.0 SiO₂: 1.5 NaOH: 0.16 Brij-30 (C₁₂H₂₅(OCH₂CH₂)₄OH): 0.84 C₁₆TMABr (C₁₆H₃₃(CH₃)₃NBr): 400 H₂O. In brief, aqueous solution of colloidal silica and sodium hydroxide were mixed with a homogeneous solution of C₁₆TMABr and Brij-30 while adjusting the pH of the gel to 10 using glacial acetic acid, then allowed for crystallization for 2 days. Finally, the resultant product was filtered, washed and then calcined in air at 833 K. Subsequently, a desirable (1:1) molar ratio of H₂PtCl₆·6H₂O_(aq) and FeCl₃_(aq) were mixed with the MCM-48 template followed by drying under a vacuum evaporator. As a result, the Pt–Fe precursors were homogeneously adsorbed in the mesoporous silica. Finally, the dried powder was put into a homemade quartz reactor, reduced under hydrogen while ramping the temperature from room temperature (RT; 298 K) to 1093 K, and then proceeded by the carbon coating by CVI process with a gas flow ratio of C₂H₂/H₂ (50 sccm/50 sccm) [8]. The as-synthesized product was finally underwent a template removal treatment: first by washing with HF solution, followed by repeated washing with deionized water, then dried to obtained the supported Pt–Fe/HCC catalyst. We also performed similar

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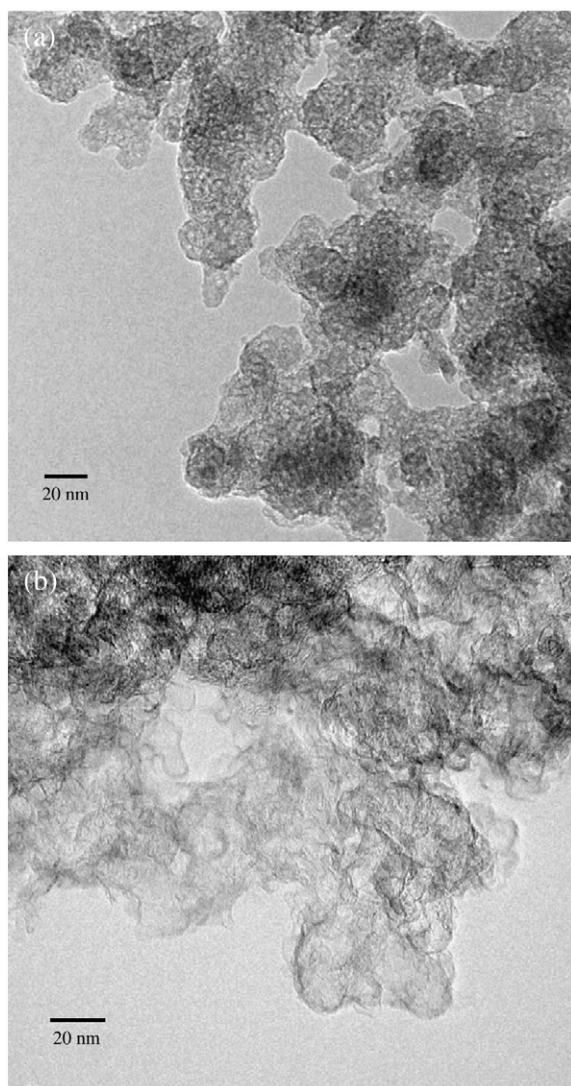


Fig. 1. TEM images of (a) MCM-48 silica-carbon composite obtained after the CVI process at 1093 K in the absence of metal loading, and (b) HCC material after removal of silica template.

experiments but under a CVI process at 1073 K, which led to the formation of Pt–Fe catalyst supported on solid carbon capsule (named as Pt–Fe/SCC; see below).

2.2. Materials characterization

The pore structures of all the silica templates and porous carbon materials were examined by a small-angle powdered XRD (Philips X'Pert PRO) using $\text{CuK}\alpha$ (0.154 nm) radiation (45 kV, 40 mA). The morphology and physical properties of the materials were also examined by HRTEM using a JEOL JEM-2100F instrument operated at 200 keV. Powdered sample suspended in acetone, was first agitated by ultrasonication, then dispersed and dried on a copper grid prior to the TEM measurement. Additional elemental analysis by ICP-AES (Jarrell-Ash, ICAP 9000) indicated that the supported Pt–Fe/HCC and Pt–Fe/SCC catalysts both contain ca. 30 wt.% Pt and 7.5 wt.% Fe.

To probe the electrochemical properties of the electrodecatalysts, cyclic voltammetry (CV) measurements were conducted on an Autolab PGSTAT302 instrument, which operate through three electrodes, namely the Ag/AgCl reference electrode, the working electrode, and the counter electrode using a Pt wire. The electrocatalytic activity of various electrodecatalysts, namely Pt–Fe/HCC, Pt–Fe/SCC, and the commercial Johnson-Matthey Pt–Ru supported on activated carbon

(denoted as Pt–Ru/AC with 30 wt.% Pt and 15 wt.% Ru on Vulcan XC-72) were performed on a μ Autolab potentiostat at a scan rate of 10 mV/s. The glossy carbon thin-film electrode was prepared by the following steps: first, ca. 10 mg of bimetal-loaded carbon samples were suspended in 5 mL deionized water followed by agitation under ultrasonication for 30 min. Then, ca. 7.5 μL of the resultant suspension mixture was withdrawn and injected onto the glassy carbon electrode followed by drying in air at 333 K for 1 h. Finally, ca. 7.5 μL of 1% Nafion solution was then pipetted onto the sample under N_2 environment at ambient temperature (298 K) for ca. 10 min. The methanol oxidation experiments were done at ambient temperature. Electrooxidation of methanol was carried out with an electrolyte of 0.5 M H_2SO_4 and 1.0 M methanol between -0.2 and 1.0 V under inert (N_2) environment.

3. Results and discussion

It may be envisaged that during the CVI process at elevated temperature, the mesostructure of the MCM-48 silica would be collapsed to form a coral-like structure with cavities of ca. 20–40 nm in diameter. Fig. 1a shows the coral-like, mesostructured silica-carbon composite obtained after the CVI process but in the absence of metal loading. Upon removal of silica template by HF treatment, the formation of hollowed carbon capsule (HCC) material with an

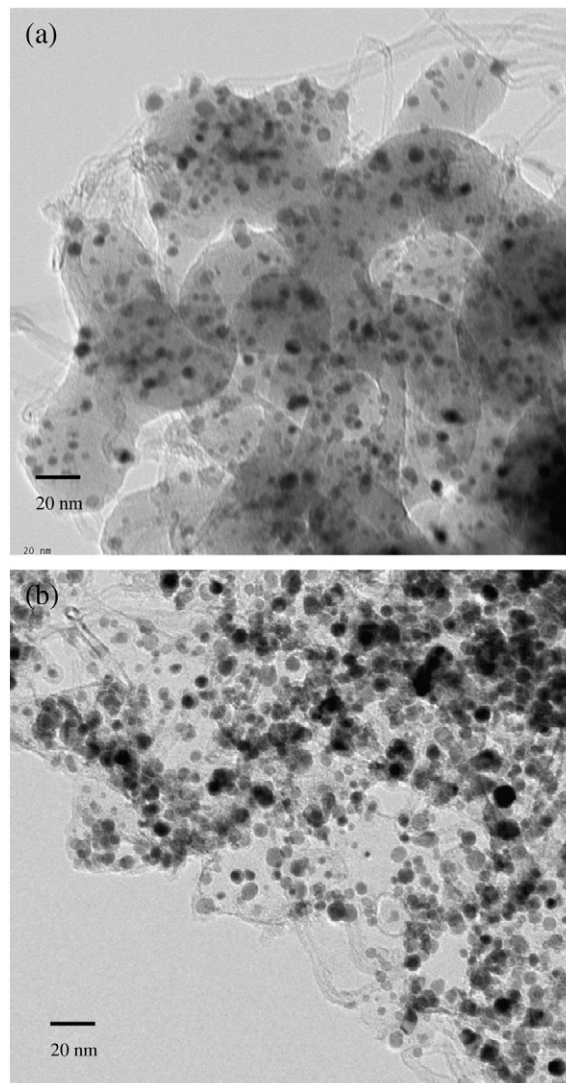


Fig. 2. TEM images of (a) MCM-48 silica and Pt–Fe/HCC composite obtained after the CVI process at 1093 K, and (b) supported Pt–Fe/HCC catalyst after removal of silica template.

averaged cavity size of ca. 20–40 nm can be readily observed, as shown in Fig. 1b. The cavity size of such HCC material has been proposed to be most preferable for mesoporous carbon supported metal catalysts especially during direct methanol fuel cell (DMFC) operation [9].

As described earlier, the HCC supported Pt–Fe catalyst was fabricated by first incorporation the Pt–Fe onto the mesoporous MCM-48 silica, then proceeded by carbon coating using the CVI process at 1093 K. The TEM images of the resultant product before and after removal of the silica template are shown in Fig. 2a and b, respectively. It can be clearly seen that the synthesis of the HCC supported Pt–Fe catalyst is accompanied by the growth of carbon nanotubes (CNTs) owing to the presence of Fe catalyst during the carbonization process. Moreover, the TEM image prior to the removal of silica template (Fig. 2a) clearly show that the Pt–Fe particles were well isolated between the interfaces of the silica template and the carbon film, leading to a uniformly dispersed Pt–Fe alloy particles in the internal surfaces of the HCC after removing the silica template (Fig. 2b). Further examinations of the supported Pt–Fe/HCC catalyst by HRTEM (Fig. 3a and b) indicate that the size of Pt–Fe particles span over a typical range of 2–10 nm. Furthermore, the walls of the HCC materials exhibit highly graphite structures. In addition, most of the Pt–Fe alloy particles are well isolated and appear to be embedded in the graphitic carbon walls.

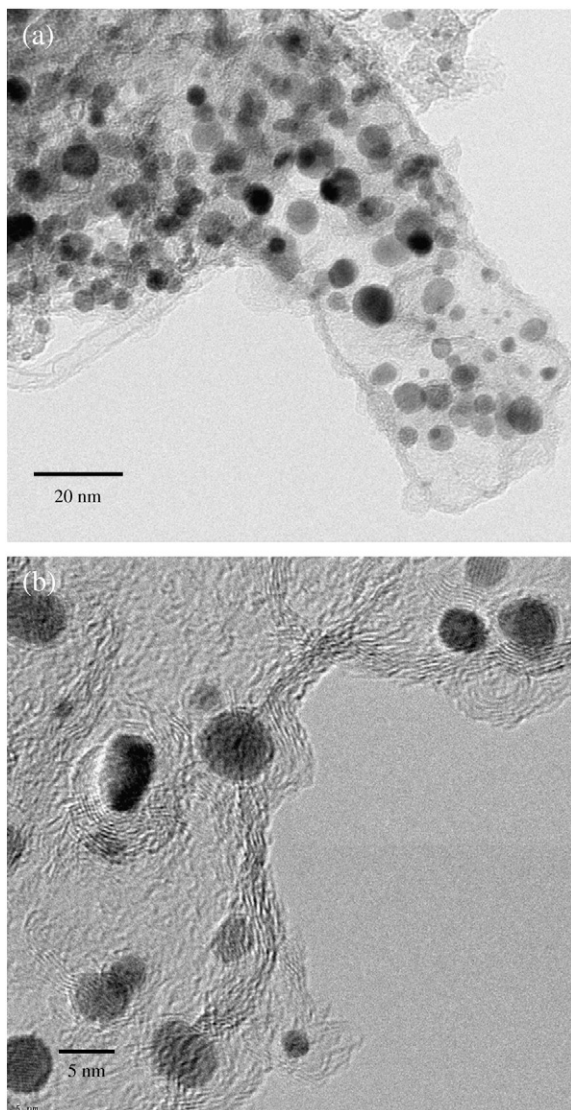


Fig. 3. (a) TEM and (b) HRTEM images of Pt–Fe/HCC catalyst.

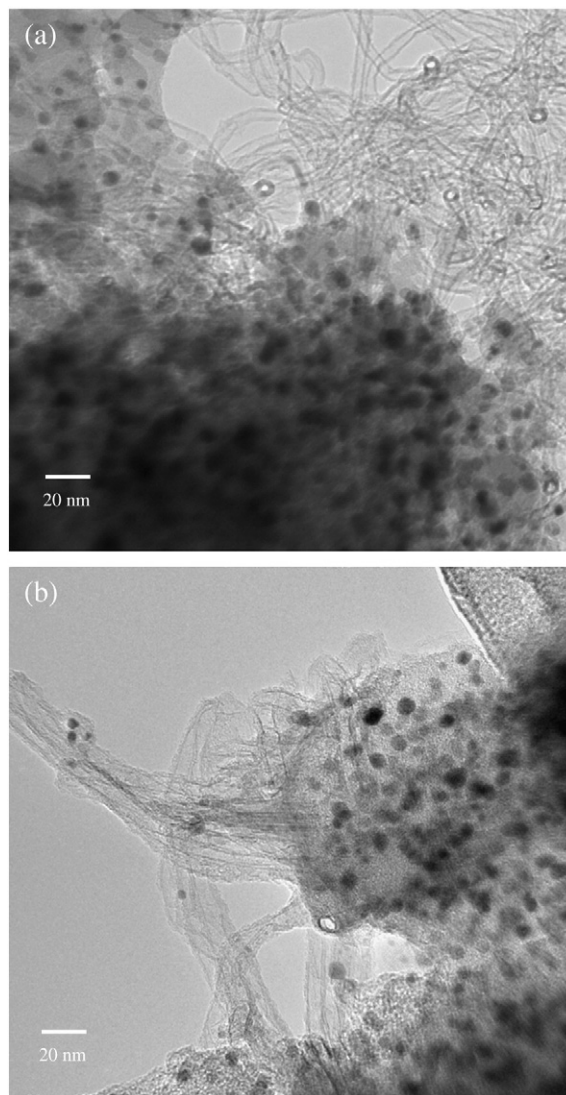


Fig. 4. TEM images of (a) MCM-48 silica and Pt–Fe/SCC composite obtained after the CVI process at 1073 K, and (b) supported Pt–Fe/SCC catalyst after removal of silica template.

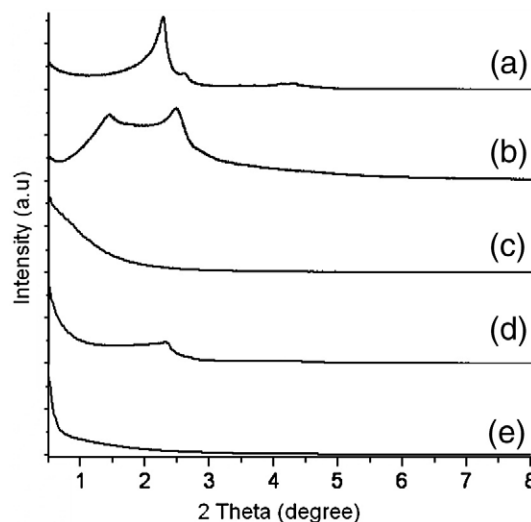


Fig. 5. XRD patterns of (a) MCM-48, (b) CMT-1, (c) Pt–Fe/SCC, (d) MCM-48 treated at 1093 K, and (e) Pt–Fe/HCC (see text).

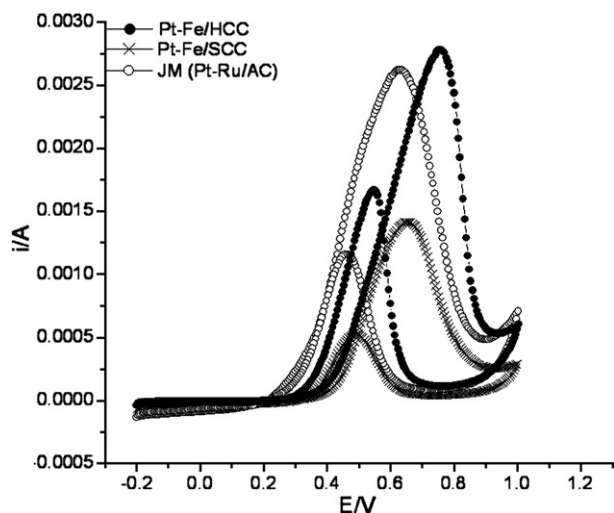


Fig. 6. Cyclic voltammograms of methanol oxidation on (a) Pt-Fe/HCC, (b) Pt-Fe/SCC, and (c) Johnson-Matthey XC-72.

Previously, we reported the synthesis of a replicated carbon mesoporous material called CMT-1 [8], which was done under a similar CVI process but at 1073 K, a temperature that is slightly lower than the aforementioned synthesis of the supported Pt-Fe/HCC catalyst. It was anticipated that by performing a similar experiment with pre-loaded Pt-Fe precursors on MCM-48, followed by CVI process at 1073 K, we should obtain Pt-Fe based catalyst supported on CMT-1. However, to our surprise, the TEM images in Fig. 4a show that the resultant material did not possess the predicted CMT-1 structure, rather it formed a CNTs coexisting solid carbon capsule (SCC) material embedded with Pt-Fe particles inside after removal of the silica template (Fig. 4b). However, unlike Pt-Fe/HCC, the size of the Pt-Fe particles in Pt-Fe/SCC were found to be more uniform, typically in the range of 2–5 nm. In this context, the reason that a mesostructured carbon cannot be formed may be due to the high Pt-Fe loading, which may lead to distortion of the structural framework of the carbon, as proposed in our earlier study for the fabrication of PtRu/CMMs [2].

The aforementioned results are consistent with additional analyses by XRD, as shown in Fig. 5, which displays the small-angle diffraction patterns of the mesoporous MCM-48 silica template (Fig. 5a), CMT-1 carbon mesoporous material directly replicated from MCM-48 by CVI process at 1073 K without the metal loading (Fig. 5b), supported Pt-Fe/SCC catalyst fabricated by pre-doping Pt-Fe on MCM-48 proceeded by CVI process at 1073 K (Fig. 5c), the parent MCM-48 silica after treated at 1093 K (Fig. 5d), and supported Pt-Fe/HCC catalyst fabricated at 1093 K (Fig. 5e). Clearly, while performing the CVI process at a lower temperature (1073 K) in the presence of Pt-Fe

loading, the resultant Pt-Fe/SCC material (Fig. 5c) did not possess the expected CMT-1 mesostructure (Fig. 5b). In addition, for Pt-Fe/HCC prepared using a CVI process at 1093 K (Fig. 5e), the MCM-48 structure did collapse and aggregated, which agree well with the formation mechanism proposed for HCC by the TEM results.

Fig. 6 shows the cyclic voltammograms of Pt-Fe/HCC (30 wt.% Pt, 7.5 wt.% Fe), Pt-Fe/SCC (30 wt.% Pt, 7.5 wt.% Fe), and a commercial Johnson-Matthey catalyst (Pt-Ru/AC; 30 wt.% Pt, 15 wt.% Ru on XC-72 activated carbon). While it is clear that the averaged particle size for the Pt-Fe/HCC electrocatalyst is larger than the Pt-Ru/AC, however, the current density for the former (0.0028 A) is slightly higher than that of the latter (0.0026 A). This is ascribed due to the fact that: (i) the improved electrical conductivity of the coexisting CNTs and the excellent graphitic structure of HCC, (ii) the well-dispersed Pt-Fe catalyst, (iii) the introduction of secondary Fe metal that tends to enhance the utilization of Pt [6], and (iv) superior mass transport properties of the HCC support with typical cavity size of ca. 20–40 nm. On the other hand, the Pt-Fe/SCC catalyst being has the lowest current density, is mainly due to its structure leading to an overall decrease in the effective surface area of the Pt-Fe catalyst.

In conclusion, our results indicate that the Pt-Fe/HCC electrocatalyst so fabricated has comparative electrochemical properties compared to the commercially available Johnson-Matthey catalyst (30 wt.% Pt, 15 wt.% Ru on XC-72 activated carbon). On going research works aiming at decreasing the Pt-Fe particle sizes and fabricating a varieties of diversified and more cost-effective bimetal alloy catalysts such as Pt-Ru, Pt-Co, and Pt-Ni catalysts supported on HCC have been undertaken.

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