



## Original article

## High loading Pt nanoparticles on ordered mesoporous carbon sphere arrays for highly active methanol electro-oxidation

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## ABSTRACT

Three-dimensionally (3D) ordered mesoporous carbon sphere arrays (OMCS) are explored to support high loading (60 wt%) Pt nanoparticles as electrocatalysts for the methanol oxidation reaction (MOR). The OMCS has a unique hierarchical nanostructure with ordered large mesopores and macropores that can facilitate high dispersion of the Pt nanoparticles and fast mass transport during the reactions. The prepared Pt/OMCS exhibits uniformly dispersed Pt nanoparticles with an average size of ~2.0 nm on the mesoporous walls of the carbon spheres. The Pt/OMCS catalyst shows significantly enhanced specific electrochemically active surface area (ECSA) ( $73.5 \text{ m}^2 \text{ g}^{-1}$ ) and electrocatalytic activity ( $0.69 \text{ mA cm}^{-2}$ ) for the MOR compared with the commercial 60 wt% Pt/C catalyst.

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## 1. Introduction

Due to their high power density and energy-conversion efficiency, direct methanol fuel cells (DMFCs) are promising candidates for portable, transportation and mobile applications [1–4]. Pt nanoparticles supported on carbon materials have been recognized among the most active electrocatalysts for methanol oxidation [5–7]. However, the use of carbon material supported Pt catalyst usually leads to a thicker catalyst layer in the membrane-electrode assembly (MEA) of the DMFC compared with the use of the same mass of unsupported Pt catalyst, resulting in the increased inner electrical resistance and diffusion length in the catalyst layer. Due to this issue, the design of catalysts with higher loading of Pt nanoparticles on the carbon supports may be a promising strategy for the fabrication of thin-layered MEA.

Since high Pt loading can unavoidably lead to the increased size and agglomeration of Pt particles, great efforts have been focused on developing various carbon materials with particular structures to improve the distribution and restrict the growth of the Pt nanoparticles. In this regard, a variety of nanostructured carbon materials, such as graphene [8,9], carbon black [10–12], carbon nanotubes [13–16], and mesoporous carbons [17–19], have been applied to achieve a high Pt loading (>50 wt%) catalyst while maintaining a high dispersion of small nanoparticles. Among them,

ordered mesoporous carbon materials [17,20] have been considered as promising high loading catalyst supports, because they provide a high surface area for highly dispersed Pt nanoparticles and ordered uniform mesopores for ion diffusion. In our previous study, a hierarchical nanostructured carbon (OMCS) with a mesopore size of ca. 8 nm had been used as a catalyst support to disperse Pt with low Pt loading (20 wt%) [21]. The preliminary results showed that the OMCS-supported Pt (20 wt%) catalyst has significantly enhanced electrocatalytic performance compared with the carbon black-supported Pt. Inspired by the results, herein we employ the OMCS to support Pt nanoparticles with high Pt loading (60 wt%). The higher loading of Pt nanoparticles supported on OMCS is very important for reducing the diffusion layer thickness and mass transport resistance. In addition, the ordered bicontinuous macropores (between the close-packed mesoporous carbon spheres) facilitate the mass transport of fluids, allowing for enhanced access of reactant molecules to the active sites, while the mesopores provide the large surface area for high dispersion of Pt nanoparticles. In this work, we first demonstrate the preparation of high loading (60 wt%) Pt nanoparticles supported on OMCS and investigate their electrocatalytic properties for the methanol oxidation reaction (MOR).

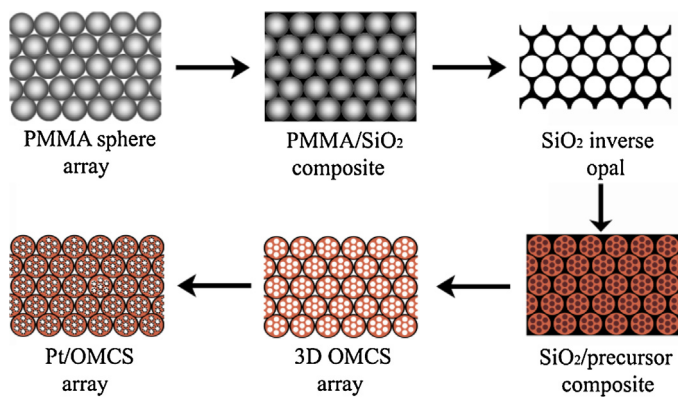
## 2. Experimental

## 2.1. Synthesis of the Pt/OMCS catalyst

Scheme 1 illustrates the procedure for the fabrication of the Pt/OMCS. The detailed preparation is described below.

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**Scheme 1.** Schematic for the formation process of the Pt/OMCS.

Synthesis of 3D ordered mesoporous carbon sphere arrays (OMCS): Monodisperse PMMA microspheres with *ca.* 460 nm in diameter were synthesized using a previously reported method [22]. The resulting PMMA microsphere suspension was then transferred to a glass bottle and allowed to stand for several weeks at room temperature to allow the spheres to precipitate completely. After the water was evaporated, PMMA colloidal crystal monoliths were formed. The prepared PMMA colloidal crystal monoliths were heated at 120 °C for 15 min to induce a stronger contact between each of the spheres. Then, the PMMA colloidal crystal monolith was immersed in the silica precursor solution (TEOS:0.1 mol L<sup>-1</sup> HCl:ethanol = 1:1:1.5 in weight ratio) for 1 h and then removed carefully from the solution and dried in air at room temperature for 24 h. The freestanding silica inverse opal was obtained after removal of the PMMA spheres by heating at 450 °C for 5 h. For the formation of the ordered mesoporous carbon sphere arrays, 1.0 g silica inverse opal was immersed in 4.0 g of a homogeneous ethanol solution containing 1.0 g of resol (Mw < 500) and 0.5 g of amphiphilic triblock copolymer Pluronic F127 for 1 h. The impregnated composites were maintained at 25 °C for 6 h to evaporate the ethanol, followed by heating at 100 °C for 24 h. The resulting composites were then heated in N<sub>2</sub> at 350 °C for 2 h at a heating rate of 1 °C min<sup>-1</sup> to remove the F127, and at 5 °C min<sup>-1</sup> rising to 900 °C, followed by a 2 h soak for further carbonation [23,24]. Finally, the OMCS was obtained by etching the silica inverse opal with a 5 wt% HF solution for 48 h.

Deposition of Pt on OMCS: ~0.05 g of the OMCS was dispersed in a 2 mL solution of 0.2 g of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in ethanol and ultrasonicated for 20 min. After drying at room temperature, the resulting powder was placed in a ceramic boat and reduced at 150 °C for 2 h in a H<sub>2</sub>/Ar flow.

## 2.2. Characterization

Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4700 FEG scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were carried out on a Hitachi H800 and a JEOL JEM-3010 transmission electron microscope, respectively (both operating at 200 kV). Powder X-ray diffraction (XRD) data were collected on a Shimadzu XRD-6000 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The actual Pt contents of the catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, Thermo Elemental).

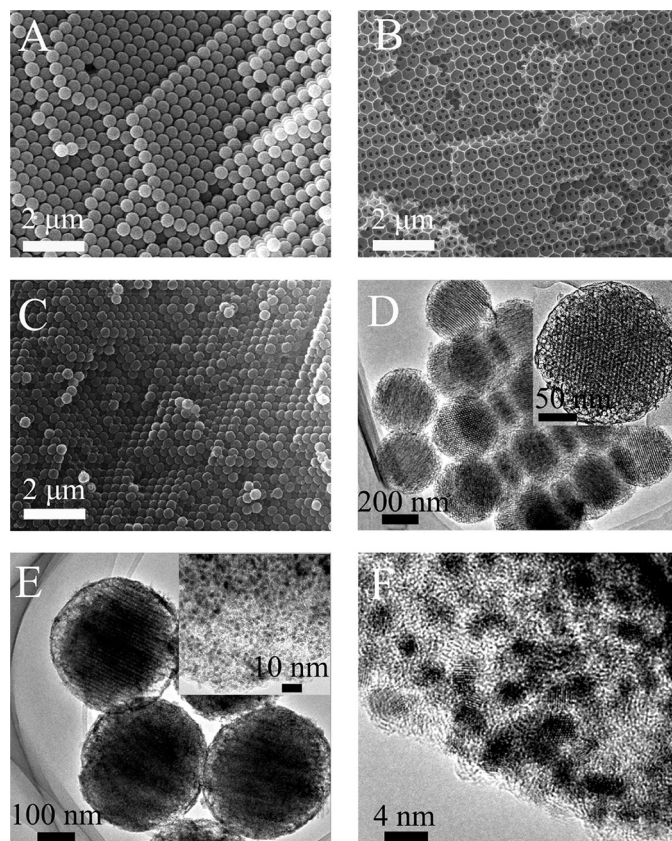
## 2.3. Electrochemical experiments

The electrochemical measurements were performed in a potentiostat/galvanostat (Reference 600, Gamry Instruments)

using a conventional three-electrode cell with a double junction Ag/AgCl (saturated KCl) electrode and a Pt wire as the reference and counter electrodes, respectively. To prepare the working electrode, 1 mg of the catalyst was ultrasonically dispersed in 1 mL of ethanol. Subsequently, 5  $\mu\text{L}$  of the suspension was deposited onto a 4 mm glassy carbon (GC) electrode. After the electrode was dried at room temperature, 5  $\mu\text{L}$  of a Nafion solution (5 wt%) was placed on the top of the GC substrate and dried to completion at room temperature. The total Pt loadings were controlled at  $\sim 0.02 \text{ mg cm}^{-2}$ . The cyclic voltammetry (CV) tests were performed in an Ar-saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution either with or without 1 mol L<sup>-1</sup> CH<sub>3</sub>OH at room temperature at a scan rate of 50 mV s<sup>-1</sup>. All the potentials were converted to the normal hydrogen electrode (NHE) scale using the equation  $E_{\text{NHE}} = E_{\text{Ag/AgCl, sat. KCl}} + 0.197 \text{ V}$ .

## 3. Results and discussion

Fig. 1A shows a typical SEM image of the 3D ordered PMMA sphere arrays (PMMA opal) prepared from highly monodisperse PMMA spheres (*ca.* 460 nm). The SEM image of the silica inverse opal with uniform macroporous structure fabricated from PMMA opal is shown in Fig. 1B. The size of the macropores is *ca.* 410 nm,  $\sim 11\%$  smaller than the original PMMA sphere diameter due to the volume shrinkage during the calcination process. Fig. 1C displays an SEM image of the OMCS and it retains the ordered face-centered cubic (fcc) structure in the PMMA opal after the two-step replication procedure. However, due to the shrinkage of carbon precursor during the carbonization process, the size of the carbon spheres reduced to  $\sim 380 \text{ nm}$ . Fig. 1D reveals a typical TEM image of



**Fig. 1.** SEM images of (A) PMMA opal, (B) silica inverse opal and (C) OMCS; TEM images of (D) OMCS (inset: higher magnification image of one mesoporous carbon sphere), (E) Pt/OMCS (inset: higher magnification image); (F) HR-TEM image of Pt/OMCS.

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