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## Supported 3-D Pt nanostructures: the straightforward synthesis and enhanced electrochemical performance for methanol oxidation in an acidic medium

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### Abstract

Noble metal nanostructures with branched morphologies [i.e., 3-D Pt nanoflowers (NFs)] by tridimensionally integrating onto conductive carbon materials are proved to be an efficient and durable electrocatalysts for methanol oxidation. The well-supported 3-D Pt NFs are readily achieved by an efficient cobalt-induced/carbon-mediated galvanic reaction approach. Due to the favorable nanostructures (3-D Pt configuration allowing a facile mass transfer) and supporting effects (including framework stabilization, spatially separate feature, and improved charge transport effects), these 3-D Pt NFs manifest much higher electrocatalytic activity and stability toward methanol oxidation than that of the commercial Pt/C and Pt-based electrocatalysts.

### Introduction

Direct-methanol fuel cells (DMFCs) are increasingly interested as power sources for portable applications due to some unquestionable advantages over analogous devices fed with hydrogen (Bianchini and Shen 2009; Baglioia et al. 2010). Affirmatively, methanol exhibits higher volumetric energy density, and its storage and transport is much easier as compared to hydrogen, while the oxidation of methanol currently is still kinetically limited at the anode (Siracusano et al. 2009; Yang et al. 2010). Based on this fact, there is great interest on developing novel and efficient anode electrocatalysts for DMFCs (Kim et al. 2007; Bong et al. 2010; Koenigsmanna and Wong 2011). Recently, inspired progress has been achieved by using hybrid metal nanostructures (e.g., alloy and core/shell structures of transition/noble metals), in which the high activity of the system has been demonstrated within a limited life-span (Bing et al. 2010; Yang et al. 2012). However, due to their some labile components like transition metals in strong acid mediums (e.g., sulfuric acid), obtaining longer stability for these hybrid electrocatalysts remains challenge.

Platinum (Pt)-group noble metals are the most effective electrocatalysts to facilitate both methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) for DMFCs (Zhou et al. 2011; Qiao and Li 2011). Most recently, the tunable catalytic activities and efficiencies of the Pt-based electrocatalysts by designing favorable morphologies and structures have been demonstrated (Wang et al. 2011; Lee et al. 2011). Particularly, the new

Pt nanoflowers (NFs) with highly branched morphologies have been proposed to be one of the desirable architectures that are promising for reaching an optimized activity and stability (Lim et al. 2009; Zhang et al. 2010). Typically, these Pt nanostructures were made up of feracious Pt branches and second noble metal seeds, such as Pd and Au nanocrystals (Peng and Yang 2009; Yeo et al. 2011). It has been shown that the high catalytic activity of such Pt NFs was closely resulted by the highly available surface area of their branched configuration (Kim et al. 2010; Lim and Xia 2011). Unlike the transition/noble metal hybrids, these unalloyed noble metal nanostructures are expected to have a relatively high thermal and chemical stability against oxidation (Sasaki et al. 2010). For technical applications, two important aspects which should be considered in exploitation of nanostructured Pt catalysts are their framework stabilization and charge transport. Therefore, the most feasible electrocatalysts for fuel cells are still based on Pt nanostructures supported on conductive carbon materials (known as Pt/C catalysts). However, most of the previously reported 3-D Pt NFs without carbon support. Only few studies discussed the electrocatalytic properties of the post-supported Pt NFs by physically loading the as-made Pt NFs onto a carbon support. Nevertheless, there has been no report published to date on the direct synthesis and characterization of 3-D Pt NFs on carbon supports via a simple and effective synthetic strategy.

In this investigation, we present a new carbon supported Pt NFs with three dimensional (3-D) structures for electrocatalysis applications, synthesized by a straightforward galvanic battery reaction approach. For this system, three features become apparent over previous reports (Lim and Xia 2011): (i) Novel carbon supported mode imparts a satisfactory framework stability for Pt nanostructures, (ii) unique 3-D Pt configuration allows a facile mass transfer, and (iii) good contact between Pt component and carbon matrix results in an efficient electron conduction of the catalyst systems (see schematic in Fig. 1e for details). With these merits, we demonstrated that the MOR electrocatalysts with high activity and desirable durability can be designed on the basis of the novel supported 3-D Pt nanostructures.

## **Experimental**

### **Sample preparation**

Typically, the carbon-supported Co nanoparticles (Co/ Carbon) (The initial content of Co is 20 wt%, synthesized by 700 °C heat treatment of anion exchange resin and Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] (1.0 g) were ultrasonically dispersed in 100 ml ethanol/water mixed solution (1:4 in volume), and then 12 ml of H<sub>2</sub>PtCl<sub>6</sub> (18.5 mg Pt/ml) was added into above solution drop by drop, under synchronous supersonic treatment and mechanical agitation and then stirred at 45 °C for 30 min. The black product was centrifugally separated and washed with distilled-deionized, and then dried at 80 °C under vacuum. The Pt content of this sample was 18.34 wt%. The controlled experiment on higher Pt-content sample (37.52 wt%) were attained by using 24 ml of H<sub>2</sub>PtCl<sub>6</sub> with other condition being equal. Before characterization, the residual Co component in the as-prepared samples was dissolved by 5 wt% HCl treatment.

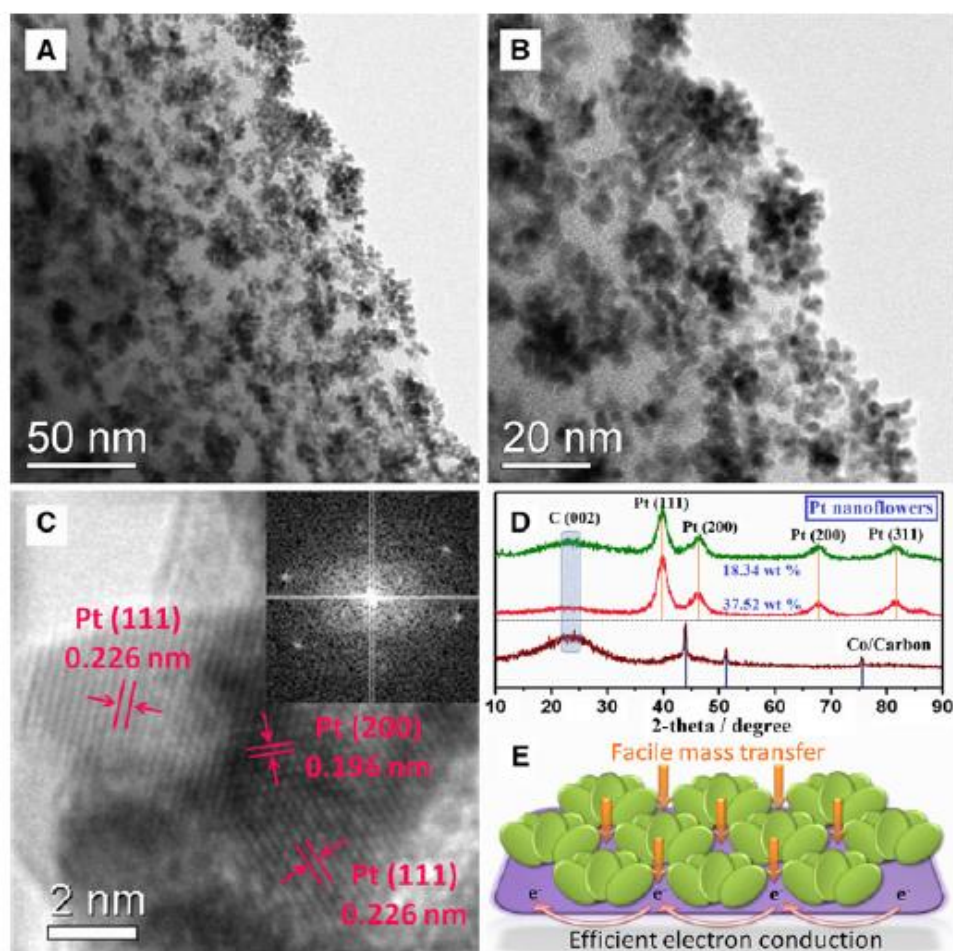
## Sample characterization

X-ray powder diffraction (XRD) measurements were carried out on a D/Max-III (Rigaku Co. Ltd., Japan) using Cu Ka radiation and operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) investigations were carried out on a JEOL JEM-2010 (JEOL Ltd., Japan) at 200 kV. And inductively coupled plasma-atomic emission spectrometry (ICP-AES) were used to analyze the Pt content of samples.

## Electrochemical measurement

The electrochemical measurements were conducted on a PARE TAT 2273 instrument (Princeton Applied Research, USA). Specified catalyst ink (containing 10 lg Pt) was pipetted and spread on the glassy-carbon disk electrode. A Pt foil and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. The MOR curves for the as-prepared catalysts were obtained at 25 and 50 °C with a sweep rate of 50 mV s<sup>-1</sup>, by using a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution containing 1 M methanol as electrolyte.

**Fig. 1** Typical TEM images of the carbon-supported 3-D Pt nanoflowers: a Low magnification TEM image. b High magnification TEM image. c High-resolution TEM image (the *inset* is the fast Fourier transform image). d XRD patterns. e Schematic model of the carbon-supported 3-D Pt nanoflowers



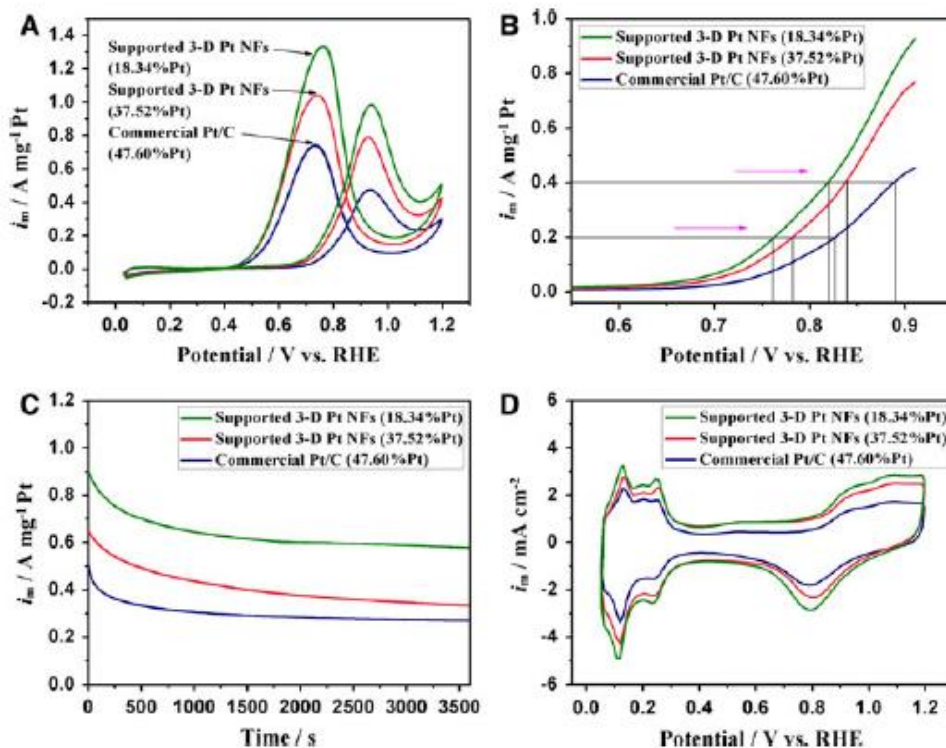
## Results and discussion

In the present study, the 3-D Pt NFs were synthesized and dispersed on carbon support by a simple and efficient cobalt-induced/carbon-mediated galvanic reaction approach. The carbon-supported Co nanoparticles (Co/Carbon) and  $\text{H}_2\text{PtCl}_6$  were used as precursors for the preparation of supported Pt NFs. The galvanic replacement reaction was easily induced by Co component due to the large reduction potential gap between the  $\text{PtCl}_6^{2-}/\text{Pt}$  (0.735 V vs. SHE) and  $\text{Co}^{2+}/\text{Co}$  (-0.277 V vs. SHE) redox couples:  $2\text{Co} + \text{PtCl}_6^{2-} = \text{Pt} + 2\text{Co}^{2+} + 6\text{Cl}^-$ . On the other hand, the galvanic battery reaction could take place in synchronism with the replacement reaction because of the carbon-mediated functionality. Therein, the Co acts as anode and C acts as cathode, where Co is oxidized to  $\text{Co}^{2+}$  and the released electrons pass through the conducting carbon to reduce  $\text{PtCl}_6^{2-}$  into metal Pt on cathode. It should be noted, the 3-D Pt branches will epitaxially grow on the preformed Pt nanocrystalline by galvanic reduction, rather than the random aggregates of Pt nuclei that were preformed in solution. Depending on this modified galvanic mechanism, we realized that the supported 3-D Pt NFs can be one-step synthesized without the use of given oriented seeds and capping reagents.

Transmission electron microscopy images in Fig. 1a revealed the excellent carbon supported architectures of these 3-D Pt nanostructures. From a higher magnification TEM image (Fig. 1b), it can be observed that large numbers of Pt NFs with size of 10–20 nm were well grown on the surface of the carbon matrix in spatial structures. The average size of the individual Pt nanoparticles was measured to be 3.0 nm by the TEM measurement from 100 randomly selected nanoparticles. The Pt content of this sample was determined to be 18.34 wt% by ICP-AES analysis. It is noted that the 3-D configuration of the Pt branches was still clearly observed when the Pt content was increased up to 37.52 wt% for a controlled sample (TEM images do not show). To further insight into the structure of the Pt branches, high-resolution TEM (HR-TEM) image of two coterminous Pt NPs was measured (see Fig. 1c). It reveals that the two nanocrystals have the lattice spacing between the (111) planes of 0.226 nm and the mutual lattice spacing between the (200) planes of 0.196 nm. The inset shows a fast Fourier transform (FFT) image of this high-resolution image, where the spots have a clear rectangular symmetry and a pair dim spots, corresponding to the (111) and (200) diffractions of single-crystalline Pt NPs, respectively. The crystalline structures of the as-prepared samples have been investigated by the powder XRD, and the resultant patterns are shown in Fig. 1d.



Fig. 2 a CV curves at  $50 \text{ mV s}^{-1}$ . b Linear-sweep voltammograms. c Chronoamperometric curves at  $0.90 \text{ V}$  in an aqueous solution containing  $0.5 \text{ M H}_2\text{SO}_4$  and  $1 \text{ M}$  methanol. d CV curves at  $50 \text{ mV s}^{-1}$  in  $\text{N}_2$ -sparged  $0.5 \text{ M H}_2\text{SO}_4$  solution. All these curves were recorded at a temperature of  $25 \text{ }^\circ\text{C}$



The MOR performance of the as-prepared catalysts was first tested at  $25 \text{ }^\circ\text{C}$  in contrast with commercial product. As shown by the CV curves at  $50 \text{ mV s}^{-1}$  (see Fig. 2a), the mass activity ( $i_m$ ) at the first peak potential of the commercial Pt/C (47.60 wt% Pt, TKK, Japan), supported 3-D Pt NFs (37.52 wt% Pt), and supported 3-D Pt NFs (18.34 wt% Pt) were 579, 781, and  $982 \text{ mA mg}^{-1}$ , respectively. It is obvious that the  $i_m$ -peak values of our samples are far better than those of commercial Pt/C and reported Pt-based electrocatalysts results (Kim et al. 2007; Bong et al. 2010; Koenigsmanna and Wong 2011). The corresponding oxidation potentials of the supported Pt NFs were obviously lower than that of the commercial Pt/C catalysts (see Fig. 2b), further suggesting that the MOR was easier to proceed the oxidation on the Pt nanostructures with 3-D configuration (Zhang et al. 2010). Furthermore, it can be seen from the chrono-amperometric measurements (see Fig 2c) that the steady-state Pt-mass activity appeared in the order of supported 3-D Pt NFs (18.34 wt% Pt)[supported 3-D Pt NFs (37.52 wt% Pt)]commercial Pt/C (47.60 wt% Pt). Expressly, the supported 3-D Pt NFs (18.34 wt% Pt) system exhibited the highest Pt-mass activity with the lower decay rate compared with the others, suggesting its superior electrocatalytic stability toward MOR. By combination of hydrogen adsorption/desorption method and CV technique (Fig 2d), the electrochemical surface area (ECSA) of the three catalysts were  $113.2$ ,  $82.7$ , and  $60.3 \text{ m}^2 \text{ g}^{-1}$  for supported 3-D Pt NFs (18.34 wt% Pt), supported 3-D Pt NFs (37.52 wt% Pt), and commercial Pt/C (47.60 wt% Pt), respectively. All these results indicated that the carbon supported 3-D Pt NFs behaved an optimized performance with high activity and good stability at a suitable Pt content of 18.34 wt%.

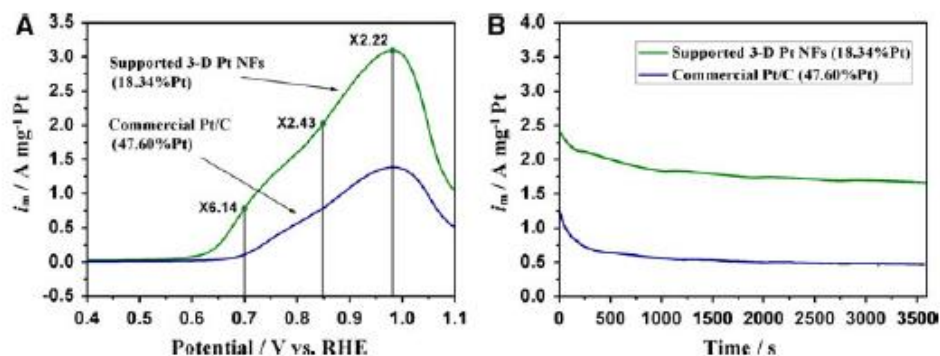


Fig. 3 a Linear-sweep voltammograms. b Chronoamperometric curves at 0.95 V in an aqueous solution containing 0.5 M  $\text{H}_2\text{SO}_4$  and 1 M methanol (temperature = 50 °C). c, d  $i_m$  values at various time of 250, 1,800, and 3,600 s at different temperatures (25 and 50 °C)

To further demonstrate its improved efficiency and durability, intensified MOR testing of the supported 3-D Pt NFs (18.34 wt% Pt) along with the comparison to commercial Pt/C (47.60 wt% Pt) was implemented at elevated temperature of 50 °C. The linear-sweep voltammograms in Fig. 3a shows that the oxidation activity was substantially increased relative to the case of 25 °C. Obviously, the improved performance is more prominent for the supported 3-D Pt NFs, significantly reflected by its lower onset potential and higher oxidation current. In particular, the oxidation current of the supported 3-D Pt NFs is 6.14 times higher than that of commercial Pt/C at 0.7 V. This result could be attributed to the unique 3-D configuration of the carbon-supported Pt NFs (see Fig. 1e), which provides considerable interface area and space to accommodate the fast mass transfer promoted by the elevated temperature. Besides the improved efficiency, the good durability of the electrocatalyst is well worth pursuing for DMFCs under such elevated environment. For this purpose, we further carried out the chrono-amperometric measurements at constant temperature of 50 °C, with the results shown in Fig. 3b. It is obvious that the supported 3-D Pt NFs have much higher Pt-mass activity than commercial Pt/C at 50 °C in the entire period, suggesting a high thermal and chemical stability of the our electrocatalyst system.

## Conclusions

Novel carbon-supported 3-D Pt NFs were synthesized and used as electrocatalyst for methanol oxidation. The as-obtained Pt NFs showed a unique structure grown on carbon matrix, facilitating fast electron and mass transport. Benefiting from the advantageous supporting effects and nanostructures, significantly improved efficiency and durability of the catalyst system at both 25 and 50 °C were demonstrated based on these supported 3-D Pt nanostructures, which suggests this novel nanomaterial is a promising candidate for fuel cell applications.

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