



## Highly efficient platinum nanocatalysts synthesized by an open-loop reduction system with a controlled temperature loop

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### ABSTRACT

In the present study, highly homogeneous platinum nanocatalysts with enhanced electrocatalytic activity were uniformly deposited on carbon nanotubes directly grown on a silicon plate (Pt/CNTs/Si) as the electrode catalysts for direct methanol fuel cells (DMFCs) by a novel homemade open-loop reduction system (OLRS). Compared with a traditional reflux system that maintains the ratio of water to ethylene glycol (EG) at  $\sim 160^\circ\text{C}$  for  $\sim 4$  h, the gradual concentration increase of EG in the precursor solution can be accomplished by distilling off water in the OLRS while increasing the temperature to  $130^\circ\text{C}$ . This process with simultaneous increases in precursor concentration and in reaction temperature rendered high-quality Pt nanoparticles to precipitate with a high-density dispersion on the pretreated CNTs. The OLRS is not only able to only shorten the reduction time ( $< 1.5$  h) but is also able to enhance the electrocatalytic activity of the electrodes by creating a preferential orientation of Pt (1 1 1) facets for the methanol oxidation reaction (MOR). Cyclic voltammetry and electrochemical impedance spectroscopy were conducted to evaluate the mass activity (MA) and charge transfer resistance (Rct) of the prepared electrodes for the MOR. Compared with the electrodes prepared by traditional Pt reductions (MA:  $100\text{--}360\text{ A g}^{-1}$  and Rct:  $40\text{--}80\ \Omega\text{-cm}^2$ ), the Pt/CNTs/Si-based electrodes prepared at  $130^\circ\text{C}$  in the OLRS exhibited superior electrocatalytic properties, including an MA of  $435\text{ A g}^{-1}$  and an Rct of  $\sim 30\ \Omega\text{-cm}^2$ .

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### 1. Introduction

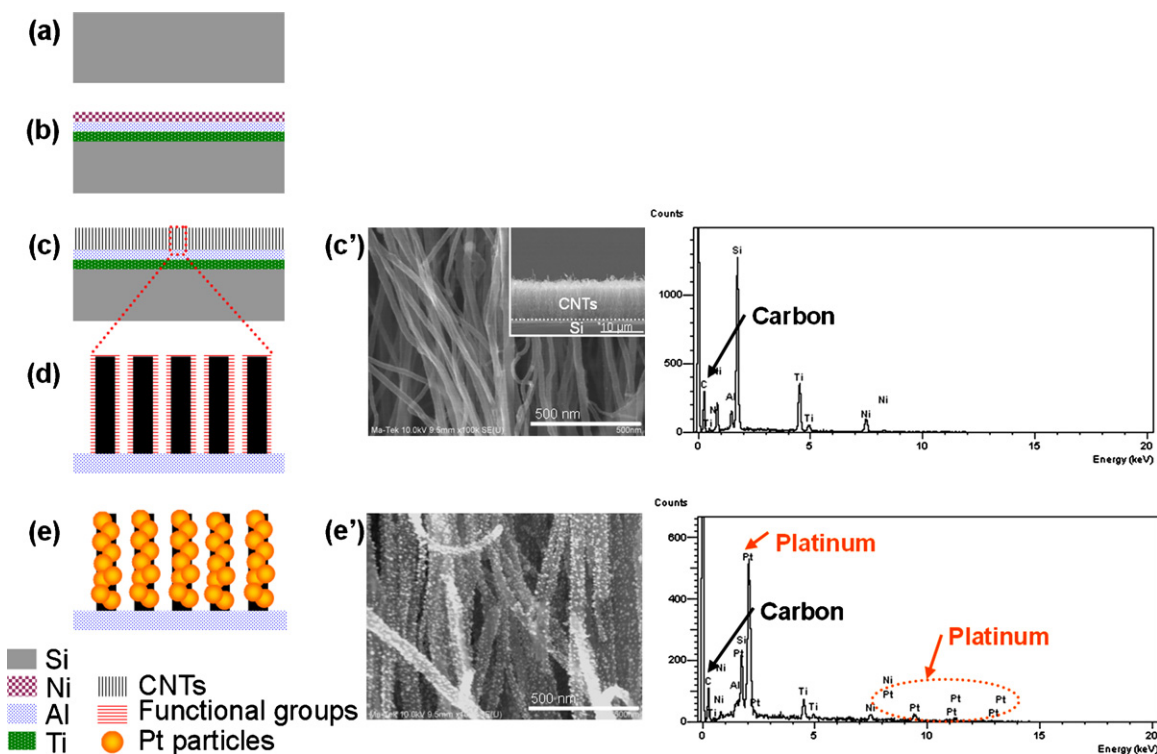
Direct methanol fuel cells (DMFCs) utilize methanol as the anode fuel, mainly because it offers a high energy density, low pollution, fast refueling, and a low operating temperature [1–3]. Compared with polymer electrolyte membrane fuel cells (PEMFCs), which use hydrogen as the fuel, DMFCs offer advantages, such as fuel storage and transportation safety as well as the ability to operate at room temperature. Therefore, DMFCs have a potential application as green micro-power sources for portable electronics.

In DMFCs, electrodes with small particles and uniform dispersion of metal catalysts are used to obtain a high surface area with better electrocatalytic performance and catalyst utilization; various carbon materials have been considered for use as the catalyst supports. Recently, carbon nanotube (CNT) nanostructures with a large specific surface area, superior mechanical properties, and electrochemical corrosion resistance in acidic or basic electrolyte solutions have been widely used in many engineering applications [4–6]. However, chemical oxidative treatments are required on the

outer surface of pristine CNTs to convert the intrinsic hydrophobicity of the inert graphite layers into hydrophilicity [7]. As a result of the pretreatment, the conjugated aromatic rings of the CNT surfaces can be modified with oxygen-containing functional groups [8] to serve as the metal catalyst-anchoring sites for facilitating catalyst nuclei formation and deposition.

The small size and homogeneous dispersion of Pt-based catalysts on supporting materials are highly desired attributes of DMFC electrocatalysts and enhance both catalytic activity and catalyst utilization. In recent years, there have been at least two commonly used synthesis methods for catalyst preparation, including chemical reduction and electrodeposition. Compared with electrodeposition [9–11], chemical reduction offers the advantages of easy preparation, direct reaction, and smaller particle sizes ( $\sim 2\text{--}4$  nm) of the synthesized catalysts [12]. However, catalyst preparation usually takes much longer ( $\sim 18\text{--}24$  h) as a result of the slow reaction rate of catalyst nucleation and growth at lower temperatures ( $60\text{--}90^\circ\text{C}$ ) [13]. As a result, the recently developed reflux technique greatly elevates the reaction temperature ( $\sim 140\text{--}160^\circ\text{C}$ ) close to the boiling point of the reactants. This technique supplies heat to chemical reactions over a period of time during which the distilled product vapors condense and return to the system from which they originated. The reflux system can potentially shorten

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**Fig. 1.** Fabrication process of the Pt/CNTs/Si-based electrode catalysts: (a) a silicon plate substrate, (b) deposition of Ni/Al/Ti thin films, (c) growth of vertically aligned CNTs, (d) hydrophilic treatment of the CNT surfaces, and (e) reduction of Pt catalyst particles. (c') and (e') show high-magnification SEM images and EDX spectra of (c) and (e). The inset of (c') shows the vertically aligned CNT layer directly grown on a Si plate.

the reduction time ( $\sim 3\text{--}4$  h) of catalysts and promote the desired electrocatalytic characteristics (i.e., small size and homogeneity of catalyst particles). Wang and Hsing [14] demonstrated that the particle size (2.0–3.5 nm) of Pt catalysts dispersed on carbon black (CB) can be controlled by reflux and that the prepared catalysts exhibited high catalytic activities in a PEMFC. Li et al. [15] prepared CNT-supported Pt (Pt/CNTs) by both the aqueous solution reductions of a Pt salt (formaldehyde, HCHO) and a Pt ion salt in ethylene glycol (EG) for comparison. The Pt/CNTs electrode catalysts synthesized by the EG method, in which NaOH was added to adjust the pH of the precursor solution, had a highly homogeneous dispersion of Pt nanoparticles on CNTs with a mean size of 2.6 nm. The Pt/CNTs electrode catalysts exhibited higher catalytic activity and enhanced electrode performance for the MOR in DMFCs than those prepared by the HCHO method. Later, Bock et al. [16] reported that the preparation of CB-supported Pt-based catalysts with a particle size range of 0.7–4.5 nm was carried out under reflux by adjusting the pH values of the reaction medium in the EG solution, which promoted the electrocatalytic activity of the MOR. Additionally, Li's team [17] further investigated the effect of the ratio of water to EG on Pt particle size in the Pt/CNTs electrodes during preparation by the EG method. The reflux process was conducted to maintain the water content for buffering the Pt formation rate in the EG-water system. They found that smaller and more homogeneous Pt nanoparticles (2.0–4.5 nm) were obtained by increasing the concentration of EG. More recently, Sarma et al. [18] used EG as a reducing agent in the precursor solution for the reflux process, resulting in a homogeneous size distribution (1.5–2.0 nm) and good catalyst stability. However, the reflux system's requirements for pressure control and a sealed environment in conjunction with only a limited decrement of the reduction time still provide room for the improvement in the catalyst preparation.

In the present study, an alternative open-loop reduction system (OLRS) is developed to provide a simple, rapid, and highly

efficient method of preparing Pt nanocatalysts for the electrode catalysts in DMFCs. This system achieves both the advantages of easy catalyst preparation by traditional chemical reduction and also a high reaction temperature for short reduction time by the reflux technique. Compared with the aforementioned reflux system, our novel OLRS reduced at  $130^\circ\text{C}$  can effectively shorten the reduction time of Pt catalysts more than 50% ( $<1.5$  h) at atmospheric pressure. Furthermore, highly homogeneous Pt nanocatalysts (particle size:  $3.6 \pm 0.4$  nm, ranging from 2.5 to 5.0 nm) were uniformly dispersed on CNTs (particle size:  $\sim 3.0$  nm compared with the best performing Pt/CNTs electrocatalysts in previous studies [14,15,17]).

## 2. Experimental

The OLRS deposition of Pt nanocatalysts is employed for the MOR in DMFCs, which consist of a silicon (Si) plate as a substrate on which a dense and uniformly distributed layer of CNTs is directly grown as a carbon support for the deposition of Pt nanoparticles. The fabrication process and fabricated materials of the Pt/CNTs/Si-based electrode catalysts are illustrated in Fig. 1 and described in the following sections in detail.

### 2.1. Growth of carbon nanotubes (CNTs)

A (100) bare Si substrate was employed as the electrode plate (p-type, electrical resistivity: 1–10  $\Omega\text{-cm}$ , Swiftek Corp.). A composite layer of nickel/aluminum/titanium (Ni/Al/Ti) was added by RF-sputtering for the purpose of promoting CNT growth, electron conduction (current collector), and adhesion promotion between the CNTs and Si. The film thickness and surface resistivity of the Ni/Al/Ti layer were 20/50/175 nm and  $1.2 \Omega\text{sq}^{-1}$ , respectively. Fig. 1(c') shows that the layer of vertically aligned CNTs was directly grown on the Ni-deposited Si substrate in a quartz-tube furnace by thermal chemical vapor deposition (TCVD). In this process, a

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