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# Atomic layer deposition assisted Pt-SnO<sub>2</sub> hybrid catalysts on nitrogen-doped CNTs with enhanced electrocatalytic activities for low temperature fuel cells

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## ABSTRACT

Nitrogen doped carbon nanotubes (CN<sub>x</sub>) of a high nitrogen concentration were synthesized directly on carbon paper as the skeleton of a 3D composite electrode. Ultra-fine SnO<sub>2</sub> nanoparticles about 1.5 nm were deposited on CN<sub>x</sub> with atomic layer deposition (ALD) technique. Pt nanoparticles from 1.5 to 4 nm were deposited on CN<sub>x</sub>/carbon paper and SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper with ethylene glycol reduction method. Three dimensional Pt/CN<sub>x</sub>/carbon paper and Pt-SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper composite electrodes were obtained, respectively. They were characterized over oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) for low temperature fuel cells. With similar sizes of Pt nanoparticles, the electrochemical surface area (ECSA) of Pt-SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper is larger than that of Pt/CN<sub>x</sub>/carbon paper. Pre-deposited SnO<sub>2</sub> nanoparticles promote the electrocatalytic activity of Pt toward ORR, carbon monoxide (CO) stripping and MOR. The underlying mechanisms for the enhanced activities are discussed.

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## 1. Introduction

Fuel cell is a promising choice for clean energy because of its eco-friendly system, high energy conversion efficiency and high power density. Low temperature fuel cells, involved with proton-exchange membranes as the solid electrolyte, draw a great deal of attentions because of its low operating temperature and wide applications including automobiles, on-site power generation, back-up power, fork-lifts, and portable electronic devices. Although hydrogen is an ideal fuel for low temperature fuel cells (proton-exchange membrane fuel cell, PEMFC), challenges remain in the production and storage of H<sub>2</sub>. To bypass these disadvantages, the direct methanol fuel cell (DMFC) has been developed with aqueous

methanol as the fuel. Methanol, as a liquid at room temperature, makes storage and transport much easier. Methanol also contains a high energy density (6 kWh kg<sup>-1</sup>), involving 6 electrons in the complete oxidation to CO<sub>2</sub> [1].

Despite considerable advances in recent years, technical and economical barriers still exist, hindering the widespread application of low temperature fuel cells. Both PEMFC and DMFC are limited by the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode. The cell voltage is therefore lowered to ~0.4–0.7 V at practical current densities compared to the thermodynamic voltage of 1.23 V [2]. This drawback results in the reduced efficiency of the energy conversion in low temperature fuel cells. The slow kinetics of ORR requires a high loading of Pt at the cathode to reduce oxygen

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effectively. But the high price and low reserve of Pt prohibit the commercialization of low temperature fuel cells.

Different from the PEMFC, the DMFC is also limited by the poor electrocatalytic activity toward methanol oxidation reaction (MOR) at the anode, which accounts for a further voltage loss of more than 0.3 V [2]. The slow kinetics of MOR is mostly due to the surface poisoning on Pt by reaction intermediates, mainly CO, formed by dehydrogenation of methanol. Endeavors to mitigate the poisoning of Pt have been focusing on the addition of co-catalysts, particularly Ru [2,3]. However, Ru is also an expensive noble metal. Further reduction of the cost and improvement of anodic catalytic performance for DMFC are still the key issues.

Besides alloying Pt with other transition metals, the addition of metal oxides is also investigated to enhance the electrocatalytic activity for MOR and ORR. Many studies have demonstrated that the addition of metal oxides to Pt results in more active electrocatalysts for both ORR and MOR. It was reported that TiO<sub>2</sub> enhanced both the activity and durability of Pt for the ORR [4] and MOR [5,6]. Sun *et al.* showed that Pt/WO<sub>3</sub>/C was more active for ORR in sulfuric acid than Pt/C catalysts [7]. Jafri *et al.* demonstrated that the electrocatalytic activity of Au toward ORR can be improved by adding MnO<sub>2</sub> or ZnO [8]. Sasaki *et al.* found that niobium oxides improved the activity of Pt over ORR [9]. Xu *et al.* studied the positive effect of CeO<sub>2</sub> on Pt/C toward alcohol electrooxidation [10,11]. The enhanced activities were attributed to the high dispersion of Pt nanoparticles, electronic effect and/or bifunctional mechanism of metal oxides.

Among various metal oxides, SnO<sub>2</sub> is vigorously researched because of its high electronic conductivity, and stability in low temperature fuel cell working conditions [12]. Previously, we reported SnO<sub>2</sub> nanowires as catalyst support, which enhanced the activity for ORR and MOR [13,14]. As a co-catalyst, SnO<sub>2</sub> was also found to enhance the activity of Au toward ORR [15–17]. The activity of Pt over MOR [1,18], ethanol oxidation [19] and ORR [20] was also enhanced by the addition of SnO<sub>2</sub>. This promotional role of SnO<sub>2</sub> in activity may be further improved if smaller sized SnO<sub>2</sub> can be obtained and thus higher specific surface area is offered. Atomic layer deposition (ALD), based on sequential and self-limiting surface reactions, provides a powerful method for the coating of ultra-fine metal oxides.

Our previous reports indicated that pristine nitrogen-doped carbon nanotubes (CN<sub>x</sub>) are active for nanoparticles deposition on the surface [21,22]. Compared with carbon nanotubes (CNTs), Pt deposited on CN<sub>x</sub> shows higher electrocatalytic activity and durability. In this work, combining the advantage of ALD technique and the intrinsic merits of CN<sub>x</sub>, SnO<sub>2</sub> nanoparticles were deposited on CN<sub>x</sub> by atomic layer deposition (ALD) [23], and investigated as the co-catalyst of Pt for low temperature fuel cells.

## 2. Experimental

### 2.1. Synthesis of CN<sub>x</sub>

CN<sub>x</sub> were directly synthesized on a commercial carbon paper (denoted as CN<sub>x</sub>/carbon paper) as reported previously [24]. Briefly, carbon paper sputtered with a 30 nm Al buffer layer

and then a 5 nm Fe catalyst film was placed at the heating center and 3 g melamine was placed at the upstream part of the quartz tube in a horizontal furnace. Melamine acted both as the carbon and nitrogen precursors to yield CN<sub>x</sub> at 800 °C. The nitrogen concentration is 10.4 at. % based on the X-ray photoelectron spectroscopy (XPS) measurement [24].

### 2.2. SnO<sub>2</sub> deposition with atomic layer deposition

Polycrystalline SnO<sub>2</sub> was deposited on the CN<sub>x</sub>/carbon paper (SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper) by atomic layer deposition (ALD) as described elsewhere [25]. SnCl<sub>4</sub> and deionized water as precursors were introduced into the reactor in an alternating manner. Nitrogen (20 sccm) was applied as the carrier gas, and reactor was kept at the pressure of 0.4 Torr. The reaction was set at 400 °C for 50 cycles.

### 2.3. Pt nanoparticles deposition

Pt nanoparticles were deposited on the SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper electrode by ethylene glycol reduction method. Briefly, the SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper electrode was refluxed at 160 °C for 3 h in 50 ml ethylene glycol solution containing 0.2 mM H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. Then the electrode was dried at 60 °C overnight in a vacuum oven. The obtained composite electrode is denoted as Pt-SnO<sub>2</sub>/CN<sub>x</sub>/carbon paper. Pt nanoparticles were also deposited on CN<sub>x</sub>/carbon paper, denoted as Pt/CN<sub>x</sub>/carbon paper, as a baseline for comparison.

### 2.4. Physical characterizations

The morphology of CN<sub>x</sub> was characterized with field emission scanning electron microscopy (SEM, Hitachi S-4800, 5 kV). The structure of CN<sub>x</sub> and dispersion of SnO<sub>2</sub> and Pt nanoparticles were investigated with transmission electron microscopy (TEM, Philips CM10, 80 kV). The energy dispersive spectroscopy (EDS) was taken with the above SEM at 20 kV. The Pt loading was tested with inductive coupled plasma-optical emission spectroscopy (ICP-OES, Varian Vista-Pro).

### 2.5. Electrochemical characterizations

The electrochemical characterizations were conducted with an Autolab potentiostat/galvanostat (Model PGSTAT-30, Ecochemie, Brinkman Instruments). Pt wire and Ag/AgCl (3 M NaCl) was served as the counter and reference electrode respectively. All potentials in this work are referred to the standard hydrogen electrode (SHE). Cyclic voltammograms were recorded in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. The electrocatalytic activity for ORR was evaluated in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> with linear scanning voltammetry at a scan rate of 50 mV s<sup>-1</sup>. The catalytic activity toward MOR was investigated in 0.5 M H<sub>2</sub>SO<sub>4</sub> with 1 M methanol. Since CO is an important reaction intermediate of the methanol oxidation, the CO stripping was also conducted. CO (99.5%) was purged for 30 min to achieve saturation. A monolayer of CO absorbed on Pt surface was obtained by purging N<sub>2</sub> for 30 min while with the working electrode polarized at 0.05 V. Voltammetry was applied for CO strip at last. All the electrochemical characterizations were conducted at room temperature.

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