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# Effects of $SnO_2$ layer coated on carbon nanofiber for the methanol oxidation reaction

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ABSTRACT

Carbon nanofibers (CNFs) are used as active materials for electrodes in various energy devices, such as lithium ion secondary batteries, supercapacitors, and fuel cells. Recent studies have shown that nanoscale coatings on carbon nanotubes increase the output and lifespan of these devices owing to the improvement of their mechanical and chemical properties. Among various coating methods, atomic layer deposition (ALD) can adjust the thickness of the coating layer conformally without any directional growth. Therefore, ALD can coat particles with high aspect ratios, such as CNFs, even at nanometer levels of thickness.

In this work, we grew two different morphologies of a $SnO_2$ layer on CNF. We used two types of ALD equipment: flow-type ALD (static ALD), and fluidized bed reactor-type ALD (dynamic ALD). Static ALD could form a discontinuous $SnO_2$, while a uniform $SnO_2$ layer was formed by pre-inserting a layer of $Al_2O_3$. On the other hand, dynamic ALD formed a uniform $SnO_2$ layer without pre-insertion of an $Al_2O_3$ layer. X-ray photoelectron spectroscopy analysis revealed that both $Sn^{4+}$ and $Sn^{2+}$ were present in $SnO_2$ on the CNF deposited by static ALD, probably due to the formation of an interfacial layer between the $SnO_2$ and CNF. When the dynamic ALD method was used, only $Sn^{4+}$ was present in the $SnO_2$ on CNF. Cyclic voltammetry analysis was performed to characterize the electrochemical properties of the $SnO_2$-coated CNF as an electrode on a direct methanol fuel cell. It was revealed that the discontinuous $SnO_2$ on CNF deposited by static ALD showed the highest current efficiency as well as enhanced electrocatalytic stability.

## 1. Introduction

Carbon nanofilament materials, such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs), are promising active materials for electrodes in various energy devices. They present interesting advantages such as network structure, low cost, and electrical conductivity. CNF has especially good properties as a catalyst support material for direct methanol fuel cells (DMFCs), because it has a low electrical resistance ($\sim 10^{-7}$ to $10^{-5}$ Ω m), large specific surface area (448 $m^2/g$), and excellent thermal and chemical stability [1]. However, there are two major problems with DMFCs employing CNFs: 1) CO poisoning during methanol electrooxidation [2] and 2) non-uniform Pt dispersion by strong C-C bonding on the CNF surface [3]. CNF has strong C-C bonding, so its surface is very stable, which implies that reactive sites for uniform nucleation are scarce [4]. Stable surface-induced Pt aggregation reduces electrocatalytic activity. To overcome these problems, researchers have investigated Pt-based alloys such as Pt-Cu [5], Pt-Sn [6], and others. Alternatively, $SnO_2$, one of the most widely used metal oxide catalysts, can supply oxygen-containing species such as OH, and can perform two functions [7]: it can help remove the CO species at lower potentials [8,9], and it can enhance Pt dispersion on supported catalysts.

$$SnO_2 + H_2O \rightarrow SnO_2\text{-}OH_{ads} + H^+ + e^-$$

$$Pt\text{-}CO_{ads} + SnO_2\text{-}OH_{ads} \rightarrow Pt + SnO_2 + CO_2H + e^-$$

Recent studies have shown that nanoscale coating on CNTs or CNFs increases the output and lifespan of energy storage devices owing to the improvement of their mechanical and chemical properties [10]. Among the various coating methods possible, atomic layer deposition (ALD) demonstrates a good coverage irrespective of the shape and size of the object being coated [11,12]. Therefore, it has the advantage of being able to coat particles with a high aspect ratio, such as CNF, even at nanometer levels of thickness. In a previous study, $VO_x$-coated multiwalled carbon nanotubes (MWCNTs) by ALD were used for a supercapacitor [13]. In addition, $SnO_2$-coated CNTs were used for a gas

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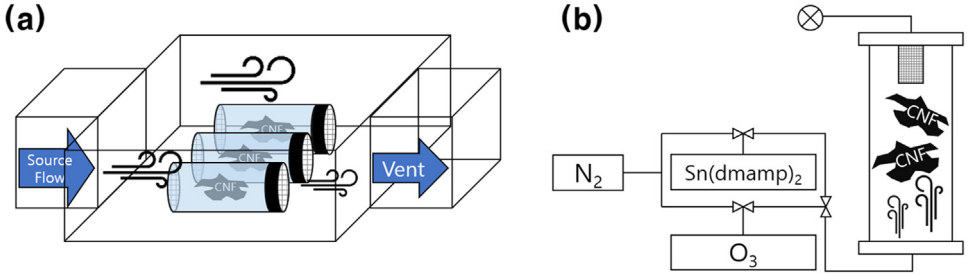


**Fig. 1.** Schematics of (a) static ALD and (b) dynamic ALD.

sensor [14].

In this study, CNF coated with $SnO_2$ by ALD is proposed to prevent CO-poisoning and non-uniform Pt dispersion. We can control the morphology of the $SnO_2$ layer on CNF by ALD [15]. Continuous film and island-type $SnO_2$ coatings can be formed on CNF by dynamic ALD or static ALD. Pt-coated CNFs with different $SnO_2$ morphologies were evaluated as a model electrode for DMFCs. The activity of the methanol oxidation reaction was monitored to elucidate the effect of different $SnO_2$ film morphologies.

## 2. Experiment

### 2.1. CNF synthesis

CNFs were synthesized by two steps. First, polyacrylonitrile (PAN, $M_w$ = 150,000) nanowires were synthesized by electrospinning. The solution for electrospinning was composed of 10 wt% PAN dissolved in N,N-dimethylformamide (DMF) with stirring for 5 h. For the electrospinning process, the feeding rate of solution was set at 0.03 mL/h. The distance between the collector and the syringe needle was fixed at 15 cm. The voltage and humidity were kept at 13 kV and 10%, respectively, during electrospinning. PAN nanowires were stabilized at 280 °C for 2 h in air and subsequently, carbonized at 800 °C for 2 h under a $N_2$ (99.999%) atmosphere. The prepared CNFs had a radius of about 240 nm.

### 2.2. CNF coating

CNFs were coated with $SnO_2$ by ALD, for which two types of ALD were used. The first is a flow-type ALD (Atomic Classic, CN-1, Korea) with a custom-made container for CNF, and the other is a fluidized bed reactor ALD (iPV d100, ISAC Research, Korea). The flow-type ALD and fluidized bed reactor ALD are denoted hereafter as static ALD (S-ALD) and dynamic ALD (D-ALD), respectively. In S-ALD, the container was constructed with Pyrex glass tubing (SCHOTT, Germany) closed with mesh and an aluminum cap. It was filled with CNFs and placed at the center of the S-ALD chamber.

In S-ALD, $SnO_2$ was deposited at 161 °C for 105 cycles with tetrakis-dimethylamino tin (TDMASn) and $H_2O$ as reactants for a target thickness of 5 nm. One cycle of ALD consisted of 1 s TDMASn feeding - 15 s $N_2$ purge - 1 s $H_2O$ feeding - 25 s $N_2$ purge process. To enhance the uniformity of the $SnO_2$ coating, $Al_2O_3$ was deposited on CNF at 161 °C for 5 cycles with trimethyl aluminum (TMA) and $H_2O$ as reactants for < 1 nm thickness. One ALD cycle consisted of 1 s TMA feeding - 5 s $N_2$ purge - 0.5 s $H_2O$ feeding - 25 s $N_2$ purge process.

In D-ALD, $Al_2O_3$ was processed at 120 °C for 5 cycles with TMA and $H_2O$ as reactants. $SnO_2$ was processed at 150 °C for 277 cycles with dimethylamino-2-methyl-2-propoxy-tin(II) ($Sn(dmamp)_2$) and $O_3$ as reactants for a 5 nm target. One ALD cycle consisted of 1 s $Sn(dmamp)_2$ feeding - 5 s purge - 0.5 s $O_3$ feeding - 25 s purge process.

We prepared four types of samples: $SnO_2$/CNF and $SnO_2/Al_2O_3$/CNF by S-ALD, and $SnO_2$/CNF and $SnO_2/Al_2O_3$/CNF by D-ALD, by using these coating methods.

### 2.3. Pt dispersion

All the $SnO_2$-coated CNF samples were coated with 40 wt% Pt. The CNF samples were dispersed in deionized (DI) water, following which $H_2PtCl_6{\cdot}xH_2O$ (Aldrich) was added to the dispersion. After this process, $NaBH_4$ (Aldrich) solution was added as a reducing agent. The samples were washed several times with DI water and freeze-dried at − 50 °C using liquid nitrogen.

### 2.4. Analysis method

Transmission electron microscopy (TEM) (JEM-2100F, JEOL) analysis and energy-dispersive spectroscopy (EDS) mapping data were used for investigating the morphology and chemical composition of the $SnO_2$ layer on CNF. Surface chemical states were observed by X-ray photoelectron spectroscopy (XPS) (MultiLab2000, ThermoFisher) using non-monochromatic Al Kα radiation. Electrochemical characteristics were investigated by a potentiostat/galvanostat (PGST302N, Eco Chemie, Netherlands). A conventional three-electrode system was used, consisting of a working electrode (glassy carbon electrode of area 0.07 $cm^2$), a counter electrode (Pt gauze), and a reference electrode (Ag/AgCl, saturated KCl). The electrolyte was a mixture of 0.5 M $H_2SO_4$ and 2 M $CH_3OH$. To measure methanol electrooxidation, all the CNF samples were prepared as mixed inks of 80 wt%-coated CNF and 20 wt % Nafion (Aldrich) in a mixture of 2-propanol (Aldrich) and DI water. Then, the inks of all samples were coated on glassy carbon electrodes. The activity of the methanol electrooxidation reaction was evaluated by cyclic voltammetry (CV) at a scan rate of 50 mV/s in the range of − 0.2–1.0 V. Fig. 1

## 3. Results and discussion

### 3.1. Morphology of $SnO_2$ layer

Morphology analysis and chemical mapping of the $SnO_2$-coated CNFs were conducted by TEM-EDS. Fig. 2 shows the TEM images and EDS mapping data of the $SnO_2$-coated CNFs. The amorphous $SnO_2$ layer was darker than CNF in the bright-field image, which was confirmed by EDS mapping.

Fig. 2(a) shows that $SnO_2$ was sparsely and discontinuously grown on the CNF surface by S-ALD, primarily due to the low reactivity and wettability of the TDMASn precursor and $H_2O$ vapor on the CNF surface. In contrast, a uniform $SnO_2$ layer was formed by inserting an $Al_2O_3$ layer on CNF by S-ALD, as shown in Fig. 2(b). The uniform distribution of both Sn and Al were confirmed by EDS mapping. Density functional theory shows that the TMA reaction requires a smaller activation energy than the TDMASn reaction. In the $Al_2O_3$ ALD reaction, the activation energies of TMA and $H_2O$ are 0.52 eV and 0.7 eV, respectively [14]. In the $SnO_2$ ALD reaction, the activation energy of TDMASn and $H_2O$ are 1.079 eV and 0.728 eV, respectively [15]. Therefore, the $Al_2O_3$ layer plays the role of the seed layer for the $SnO_2$ layer. It has been reported that various methods were used to functionalize its surface to form the uniform ALD film on the substrate