

Carbon Nanotube Film by Filtration as Cathode Catalyst Support for Proton-Exchange Membrane Fuel Cell

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A simple filtration method is developed to prepare a partially oriented superhydrophobic film of carbon nanotubes (CNTs) that have been catalyzed with uniform small Pt nanoparticles (2.8 nm) at high metal loading (30 wt %). A proton-exchange membrane fuel cell with the oriented CNT film as the cathode achieves higher single-cell performance than those with carbon black and a disordered CNT-film-based cathode probably because of the enhanced electrocatalytic activity of Pt/CNT and improved mass transport within the oriented film.

Carbon nanotubes (CNTs) have been studied as an electrocatalyst support for proton-exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).^{1–10} Some early investigations found that by using the normal paste method and simply replacing carbon black particles with disordered multiwalled CNTs as the support for Pt catalyst nanoparticles higher PEMFC and DMFC performances were achieved.^{1–5} There was also an effort to form a single-walled carbon nanotube (SWNT) film via the electrophoretic method for studying the effect of SWNTs as a catalyst support in fuel cells.⁶

It is believed that an oriented CNT film may offer much improved fuel cell performance over that of disordered CNTs because of its unique microstructure. First, the electronic conductivity of CNTs is much higher along the tubes than across the tubes, and there is no energy loss when electrons transfer along the tubes.^{11,12} Second, higher gas permeability is expected with the oriented CNT film. Third, an oriented film may also exhibit superhydrophobicity,¹³ which can greatly facilitate water removal within the electrode, thereby improving mass transport in a PEMFC or DMFC.

In our previous studies, we proposed the idea of growing an aligned multiwalled carbon nanotube (MWNTs) film

directly on a carbon paper substrate by the chemical vapor deposition (CVD) method with subsequent deposition of Pt nanoparticles on the MWNTs to form the composite electrode. The unique advantage of this approach is that the deposited Pt nanoparticles are almost guaranteed to be in electrical contact with the external circuit^{9,10} and much improved Pt utilization (e.g., 60%) has been achieved.¹⁰ With the aforementioned direct CVD method, however, it has been difficult thus far to prepare Pt catalyst nanoparticles with a uniform small diameter (e.g., <5 nm) at high Pt loading (e.g., 30 wt %), two critical properties of a high-performance electrocatalyst. Also, we found that it is difficult to grow an aligned CNT film directly on carbon paper by the CVD method because of the rough nature of the carbon paper. In addition, although the CVD process is well suited to the fabrication of micro fuel cells, the process is expensive to scale up if films with large areas (e.g., hundreds of cm²) are desired.

In the present study, with an attempt to overcome the abovementioned disadvantages, we have developed a simple, versatile, and inexpensive filtration method¹⁴ for the preparation of an oriented Pt/CNT film for PEMFCs (Figure 1). In contrast to our previous effort where we deposited Pt nanoparticles after the CNT film was formed,^{9,10} here we deposit the Pt catalyst nanoparticles on the CNTs before the film formation and then use filtration as a means to form an oriented film of Pt/CNT on the Nafion membrane, which is then used as the catalyst layer in the fabrication of the membrane electrode assembly (MEA) for PEMFC. The method is simple, convenient, and easy to scale up. This new approach allows us to take advantage of all of the known methods for depositing metal (e.g., Pt) nanoparticles on the CNTs with precise control on the particle size, distribution, and loading. It also offers a convenient method of preparing alloy electrocatalysts, such as PtRu/CNT, PtNi/CNT, and PtSn/CNT.

Specifically for this study, ethylene glycol (EG) was used as a reducing agent and solvent to prepare Pt supported on CNTs with a high metal loading (30 wt % Pt).² The Pt/CNT suspension was then filtered through 0.2- μ m-pore hydrophilic nylon filter paper. Because the nylon filter is hydrophilic and the CNTs are hydrophobic, the CNTs tend to “stand up” on the filter and self-assemble into an

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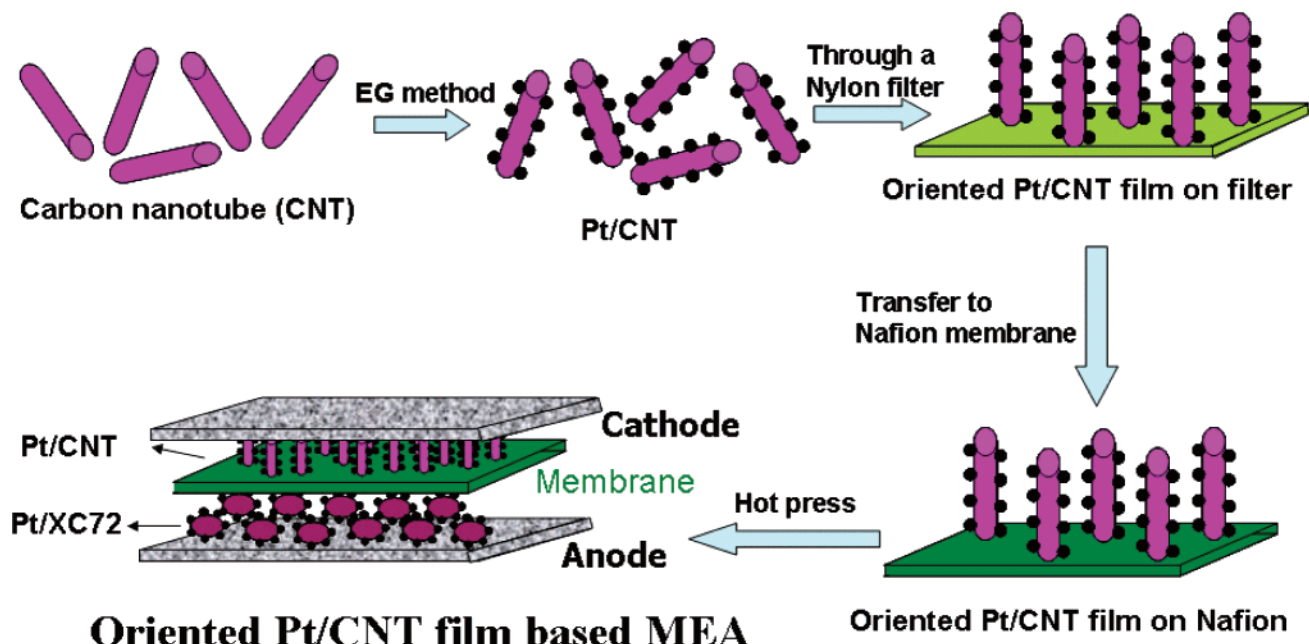


Figure 1. Schematic of the fabrication process for the oriented Pt/CNT-film-based MEA.

oriented film. The deposited film was then transferred onto a Nafion membrane by pressing the CNT-coated side of the filter onto the Nafion membrane. After the transfer, a 5 wt % Nafion solution was sprayed onto the surface of the Pt/CNT film (1.0 mg dry Nafion/cm²) to complete the cathode preparation. Finally, the anode, the oriented Pt/CNT-film-coated Nafion membrane, and a gas diffusion layer were hot pressed to obtain a membrane electrode assembly (MEA) with the oriented Pt/CNT film serving as the cathode catalyst layer. Note that a carbon black-based E-TEK electrode was used as the anode.

The CNTs used in this work were commercial products synthesized by the CVD method (multiwalled carbon nanotubes, Material & Electrochemical Research Corp.). To achieve a uniform Pt deposition on the outer walls of the nanotubes, the CNTs were surface oxidized by a 2.0 M H₂SO₄/4.0 M HNO₃ mixture for 6 h under refluxing conditions. The oxidized and washed CNTs were then suspended in EG solution and mixed with hexachloroplatinic acid in EG solution. After adjusting the pH of the solution to above 13 with 1 M NaOH in EG, the mixture was held at 140 °C for 3 h under reflux conditions to reduce Pt. After filtration, washing, and drying, we obtained the Pt/CNT catalyst with a metal loading of 30 wt %.

For MEA preparation, both the anode and cathode consist of a carbon paper backing layer, a gas diffusion layer, and a catalyst layer. Carbon papers (Toray Corp.) treated with PTFE (10 wt % PTFE in the cathode and anode) were employed as the backing layers. To prepare the diffusion layer, 5 wt % PTFE solution and carbon black XC-72 (Cabot Corp.) (weight ratio of carbon black to pure PTFE = 7:3) were mixed in ethanol by ultrasonication, and then the slurry was sprayed onto the carbon paper as a gas diffusion layer with a carbon loading of 4 mg/cm² in both the anode and cathode. The anode catalyst layer includes two layers. The first layer has a Pt electrode area loading of 0.1 mg Pt/cm² (20 wt % Pt/C, E-TEK). It consists of a 70 wt % Pt/C catalyst and 30 wt % PTFE. The second layer also has a Pt electrode area loading of 0.1 mg Pt/cm² (20 wt % Pt/C, E-TEK), but it is composed of 70 wt % Pt/C catalyst and 30 wt % Nafion (not PTFE). A 5 wt % Nafion solution was finally sprayed onto the surface of the anode (1.0 mg Nafion/cm²) to form a thin Nafion layer. The MEA

was obtained by hot pressing the anode, an oriented Pt/CNT-coated Nafion membrane, and a cathode gas diffusion/backing layer with a pressure of 140 atm at 135 °C for 1.5 min. For comparison, two other cathode catalyst layers were prepared. One was prepared by mixing 20 wt % Pt/C E-TEK catalyst with PTFE solution (weight ratio of Pt/C to pure PTFE = 7:3) and depositing the mixture onto the gas diffusion layer. The other was prepared by just spraying 30 wt % Pt/CNT catalyst onto the gas diffusion layer. Both cathode layers were sprayed with Nafion with a 1.0 mg/cm² loading. The Pt loading of the cathodes was 0.2 or 0.25 mg of Pt/cm². The single-cell performance of the 5 cm² MEAs was conducted using an automated fuel cell test station.

The XRD pattern (Bruker α XS, D8ADVANCE) of the Pt/CNT sample is shown in Figure 2a. The diffraction peak observed at 23–27° can be attributed to the hexagonal graphite structure (002), which shows that CNTs have good electric conductivity. The Pt diffraction peaks show that Pt has a face-centered cubic (fcc) crystal structure. From the isolated Pt (220) peak, the mean particle size calculated with the Scherrer equation is 2.6 nm. A typical transmission electron microscopy (TEM, Philips TECNI12) image of 30 wt % Pt/CNT (Figure 2b) shows that spherical Pt nanoparticles with a narrow size distribution (2–5 nm and averaged at 2.8 nm) have been deposited on the CNTs, which is consistent with the XRD analysis. Considering the fact that multiwalled CNTs have a relatively small surface area (100 m²/g) compared with that of carbon black (237 m²/g), it is interesting that a small Pt particle size can still be obtained with this method at such a high metal loading (30 wt %).

The scanning electron microscopy (SEM, Philips XL30-FEG) image of the cross section of the Pt/CNT-film-coated Nafion membrane (Figure 2c) shows a thin film of ca. 5 μ m thickness on the Nafion membrane. Most CNTs are standing up, although they are not fully vertical to the membrane. It is believed that a CNT film with better orientation can be obtained with further optimization of the filtration process.

The contact angles (CA) (Figure 3) of the oriented Pt/CNT film (Figure 3a) and the nonoriented Pt/CNT film (Figure 3b) (spraying Pt/CNT onto the cathode diffusion

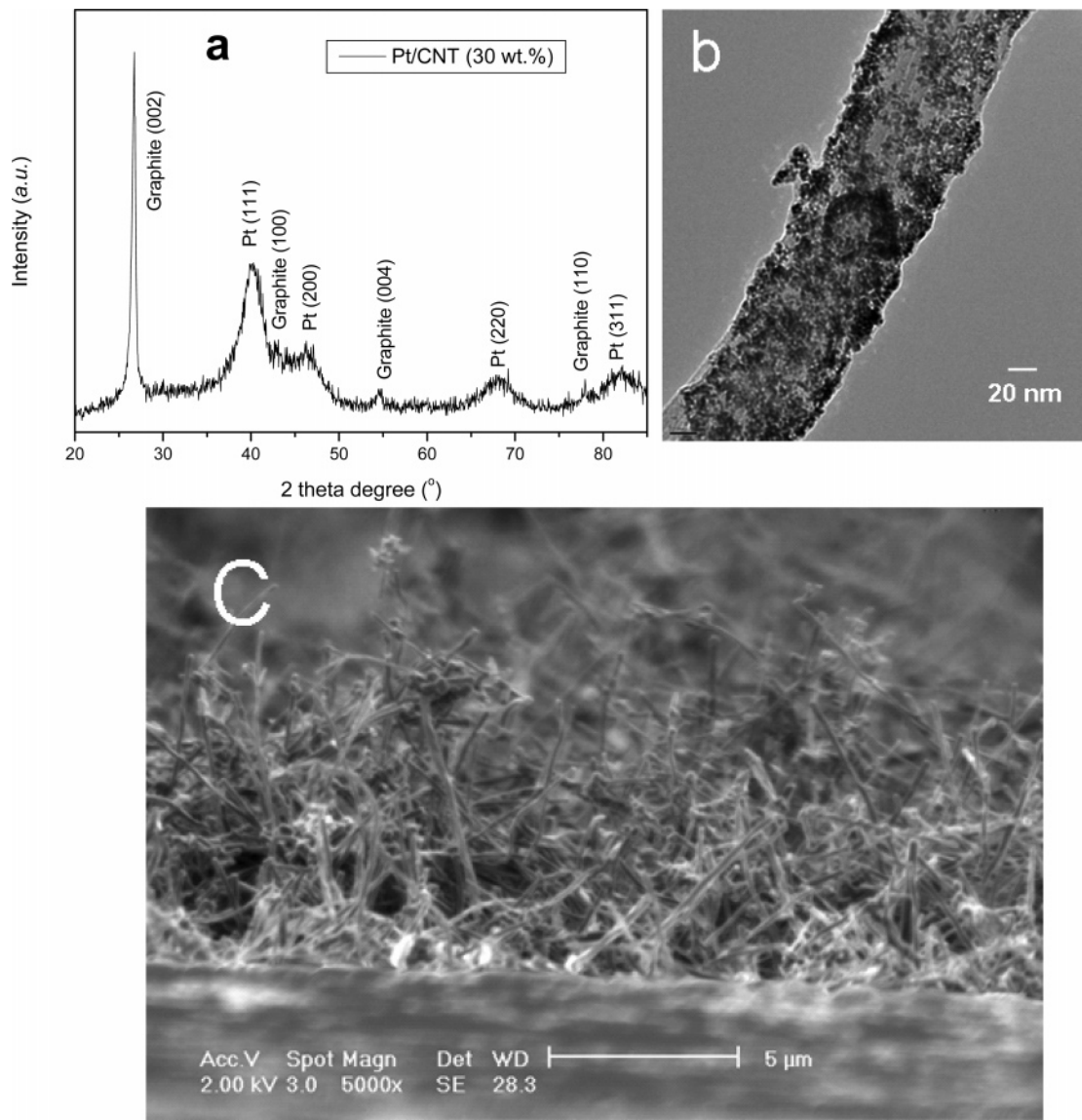


Figure 2. (a) Powder XRD pattern of the Pt/CNT catalyst, (b) TEM micrograph of the Pt/CNT catalyst, and (c) SEM micrograph of the oriented Pt/CNT film on a Nafion membrane.

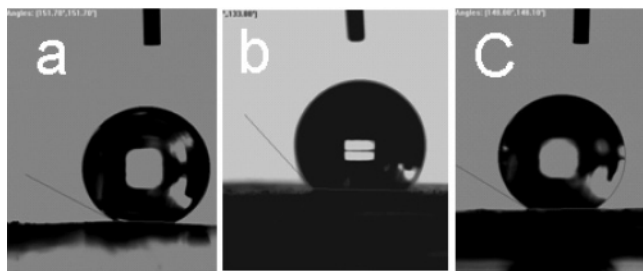


Figure 3. Surface contact angles of (a) the oriented Pt/CNT film, (b) the nonoriented Pt/CNT layer, and (c) the Pt/C layer with PTFE (30 wt %).

layer directly and without PTFE) are 151.7 and 134.2°, respectively. It is interesting that large contact angles are obtained even though these CNTs have been treated with a mixture of nitric acid and sulfuric acid before the Pt deposition. We speculate that hydrophilic functional groups (e.g., $-\text{COOH}$) were generated during the acid reflux process but may have been subsequently used for anchoring Pt nanoparticles.² It has been reported that an oriented pristine CNT film shows higher hydrophobicity than a nonoriented one.¹³ The CA measurements in this study show that the Pt/CNT film prepared by the filtration

method is more hydrophobic probably because its orientation is better than that of the Pt/CNT film formed by the spraying method. Note that the catalyst layer with 70 wt % Pt/C and 30 wt % PTFE offers a CA of only 147.2° (Figure 3c), which is lower than that of the oriented Pt/CNT film without any PTFE. In a fuel cell electrode, PTFE is commonly added to serve as a binder and to provide hydrophobicity for water management within the electrode structure. However, the PTFE added to the electrode often covers the Pt catalytic sites, thus lowering the activity of the Pt catalyst. Furthermore, the use of PTFE requires sintering at high temperatures (e.g., 340 °C), which tends to lead to the aggregation of Pt particles. Thus, the elimination of PTFE without sacrificing hydrophobicity and electrode integrity can be beneficial to the maximization of Pt utilization.

The polarization curves of the membrane electrode assembly (MEA) based on oriented Pt/CNT, nonoriented Pt/CNT, and Pt/C (with 30 wt % PTFE) as the cathode catalyst layers are shown in Figure 4. Oriented Pt/CNT-based MEA exhibits higher performance than Pt/C and nonoriented Pt/CNT-based MEAs. Higher performance in the activation-controlled region (low current density) may be attributed to the enhanced specific activity of Pt

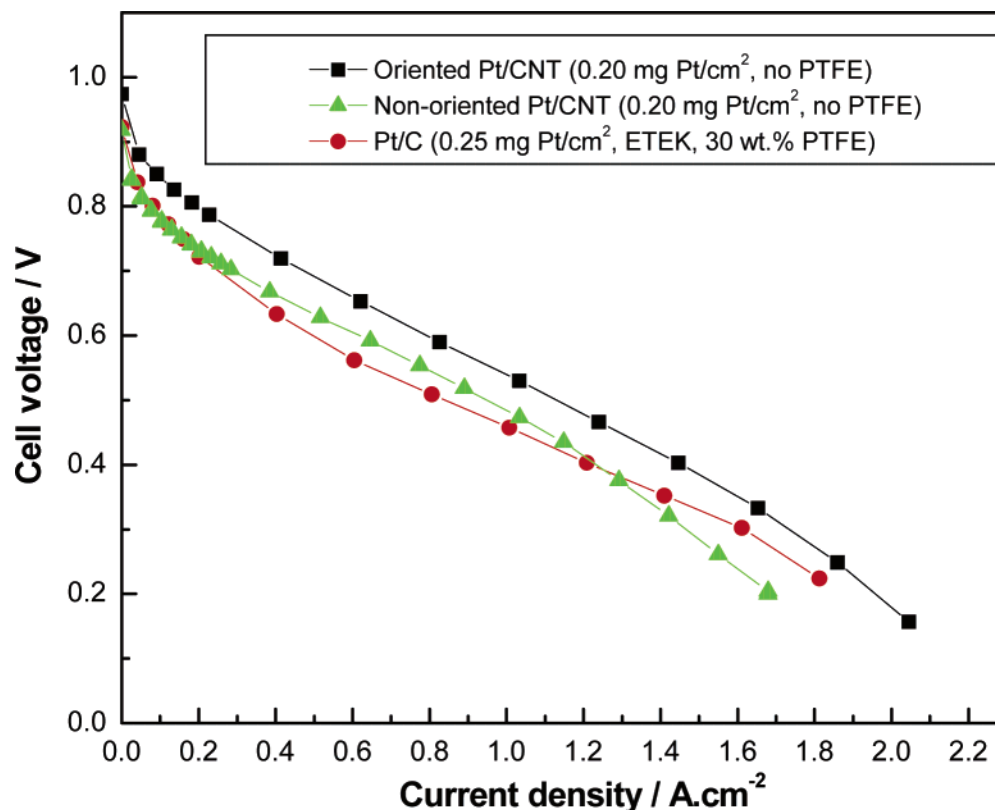


Figure 4. I - V curves of PEMFCs with the oriented Pt/CNT film, the nonoriented Pt/CNT film, Pt/C with 30 wt % PTFE as the cathode catalyst layers. 0.2 mg of Pt/cm² (Pt/C, 20 wt %, E-TEK) in the anode, and Nafion 112 as the membrane. Test conditions: cell and O₂ humidification at 70 °C; H₂ humidification at 85 °C, H₂ and O₂ pressure and flow rate at 0.2 MPa and 0.2 L/min, respectively.

due to the unique interaction of Pt and CNT.¹⁵ The elimination of the electronically insulating PTFE and the possibly improved electron transfer through the oriented CNTs in the oriented Pt/CNT catalyst layer may help to improve Pt utilization and reduce the ohmic resistance of the electrode, which can provide improved performance over the whole current density range. At the mass transfer-controlled region (high current density), the superhydrophobicity of the oriented Pt/CNT film can help to repel water from the cathode, whereas the MEAs with non-oriented Pt/CNTs and Pt/C show lower performance that is mainly due to "flooding" of the electrode and the resulting mass transport difficulty. Careful optimization of the structure of the oriented CNT film (e.g., CNT alignment, film thickness, Nafion content, etc.) is likely to improve the power density of the PEMFC further.

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In summary, we have demonstrated a simple, fast, inexpensive, and scalable filtration method of preparing a partially oriented superhydrophobic CNT film via self-assembly of CNTs that have been precatalyzed with small Pt nanoparticles (2.8 nm) at high metal loading (30 wt %). When such a film is used as the cathode, higher PEMFC performance is achieved because of improved Pt utilization and mass transport. This method can be easily extended to the preparation of oriented CNT-supported bimetallic electrocatalysts such as PtRu, PtNi, and PtSn, which are useful for both PEMFCs and DMFCs.

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