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# Microscopic and Spectroscopic Analyses of Pt-Decorated Carbon Nanowires Formed on Carbon Fiber Paper

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**Abstract:** We report the synthesis of carbon nanowires (CNWs) via chemical vapor deposition using catalytic decomposition of ethanol on nanosized transition metals such as Co, Fe, and Ni. Dip-coating process was used for the formation of catalytic nanoparticles, inducing the growth of CNWs on the surface of the carbon fiber paper (CFP). The liquid ethanol used as carbon source was atomized by an ultrasonic atomizer and subsequently flowed into the reactor that was heated up to a synthesis temperature of 600–700°C. Microscopic images show that CNWs of <50 nm were densely synthesized on the surface of the CFP. Raman spectra reveal that a higher synthesis temperature leads to the growth of higher crystalline CNWs. In addition, we demonstrate the successful decoration of platinum nanoparticles on the surface of the prepared CNWs/CFP using the electrochemical deposition technique.

**Key words:** carbon fiber paper, carbon nanowires, catalysts, ethanol, Pt decoration

## Introduction

Carbon nanowires (CNWs) such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been considered the most attractive one-dimensional carbonaceous nanomaterials because of their superior properties and various applications (Boehm, 1997). Many approaches were developed to improve the methods for growing CNWs for various applications. Chemical vapor deposition (CVD) has advantages in synthesizing CNWs, including small amounts of impurities and lower processing temperature, compared with other methods such as laser ablation (Zhang et al., 2001) and arc discharge (Li et al., 2003). It has been generally known that CVD growth of the CNWs is induced via vapor–liquid–solid mechanism using nanosized transition metals (Moisala et al., 2003) prepared on substrates (Dikonimos Makris et al., 2005) as long as the temperature of the substrate is properly sustained during the process (Chlowalla et al., 2001). Recently, some studies have reported the use of carbon substrates for the CNW growth. Zhu and colleagues demonstrated the synthesis of CNTs on carbon fiber-supported iron (Fe) catalyst using methane gas (De Riccardis et al., 2006). In addition, De Riccardis and colleagues synthesized CNTs on carbon fiber coated with nickel nanoparticles using electrochemical deposition, and explained the anchorage effect of the CNTs. The carbon substrates, especially functionalized with CNWs, have good diffusion of transition metal particles and excellent electrical property. These merits lead to the easy formation of nanocatalysts such as palladium and platinum (Pt) on the substrate (Li & Shing, 2006). The research on the deposition of Pt nanoparticles on the surface of CNTs grown on the carbon substrates attracts attention from many engineers, because this hierarchical structure can enhance the performance of catalytic reactors or nanodevices (Benard et al., 2005).

Herein, we report the dense growth of CNWs on carbon fiber paper (CFP) using ethanol (Murakami et al., 2003). The ultrasonic atomizing system adopted in this work enables a fine control and a continuous supply of the liquid ethanol into the reactor (Jeong et al., 2007). For the CNW growth, various transition metals such as Co, Fe, and Ni were formed on the surface of the CFP using the dip-coating process. In addition, we demonstrate the decoration of Pt nanoparticles on the surface of the prepared CNWs/CFP using the electrochemical deposition technique. Microscopic and spectroscopic analyses support the hierarchical configuration of as-formed Pt-CNWs/CFP.

## Materials and Methods

### Materials

Nickel (Ni), Cobalt (Co), and iron (Fe) acetate (Aldrich) were used as catalysts (0.01 wt% in ethanol, individually). A CFP was dipped into the prepared solution, and it was then dried at 100°C. Finally, the CFP was reduced in a mixture of gas ($H_2$ of 2 vol% in $N_2$) at 500°C for 2 h.

### Growth of CNWs of the CFP

For growth of the CNWs, the synthesis temperature was controlled between 600 and 700°C. The reactor was heated


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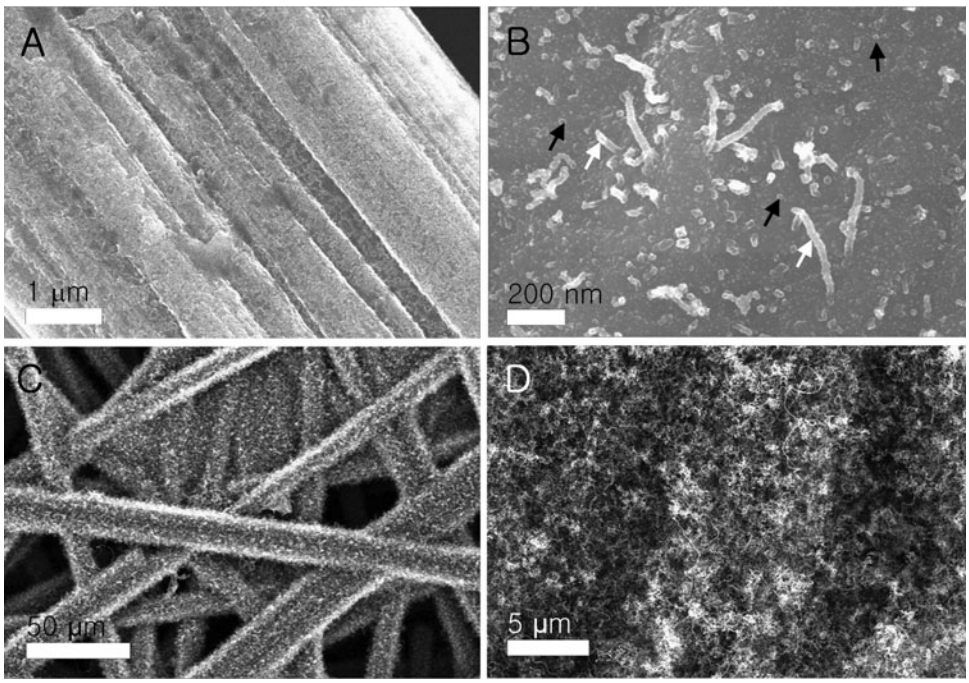


**Figure 1.** SEM images: (**A**) Ni thin film coated on carbon fiber paper (CFP), (**B**) tiny nanowires formed after exposure to ethanol for 30 s, and (**C, D**) mature carbon nanowires grown on the surface of the CFP.

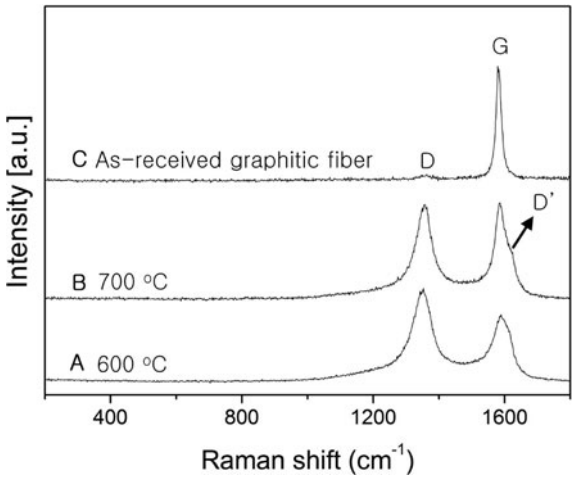


**Figure 2.** Raman spectra of carbon nanowires grown at different synthesis temperatures: (**A**) 600°C and (**B**) 700°C; (**C**) Raman spectrum of as-received carbon fiber paper.

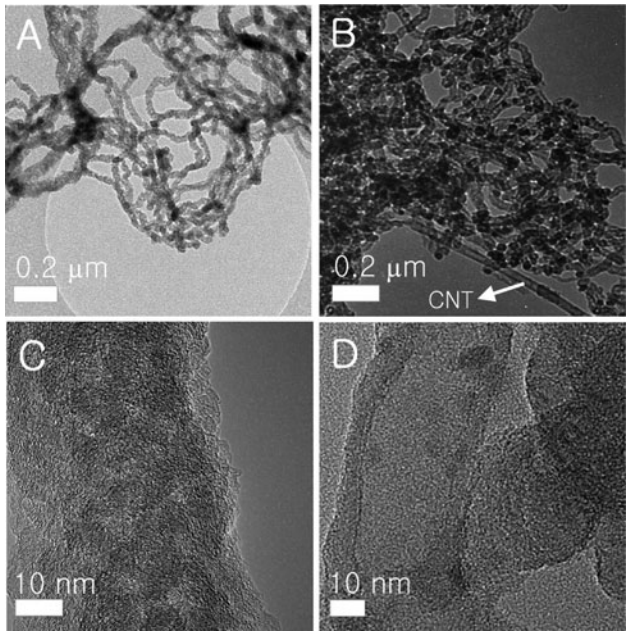


**Figure 3.** TEM and HRTEM images of CNWs grown at (**A, C**) 600°C and (**B, D**) 700°C. TEM, transmission electron microscopy; HR-TEM, high-resolution transmission electron microscopy; CNW, carbon nanowires.

up at a rate of 5°C/min. When the reactor reached the synthesis temperature, ethanol (99.5% dehydrated ethanol with maximum 0.005% water) was supplied into an ultrasonic atomizer by a syringe pump at 5 cc/min. The gaseous ethanol reacts with the catalytic nanoparticles formed on the CFP for 1 h. After synthesis, the furnace was cooled down with a continuous flow of $N_2$ gas.

## Deposition of Pt Nanoparticles on CNWs/CFP

Afterward, we deposited platinum nanoparticles on the surface of the CNTs grown on the CFP via electrodeposition. Platinum solution of 1 mM concentration was prepared by dissolving Pt in 0.5 M $H_2SO_4$ diluted in distilled water of 1 L volume. Next, the CNWs/CFP was immerged into the Pt solution. The range of the operating potential for the electrodeposition system was 0.1–1.0 V. The deposition time was 5 min.

## Characterizations

The products were characterized by energy-dispersive X-ray spectrometry (EDX; HORIBA), Raman spectroscopy (LabRam HR), X-ray photoelectron spectroscopy (XPS; AXIS-NOVA, Kratos Inc.), field-emission-scanning electron microscopy (FE-SEM; S-4700, HITACHI), transmission elec-

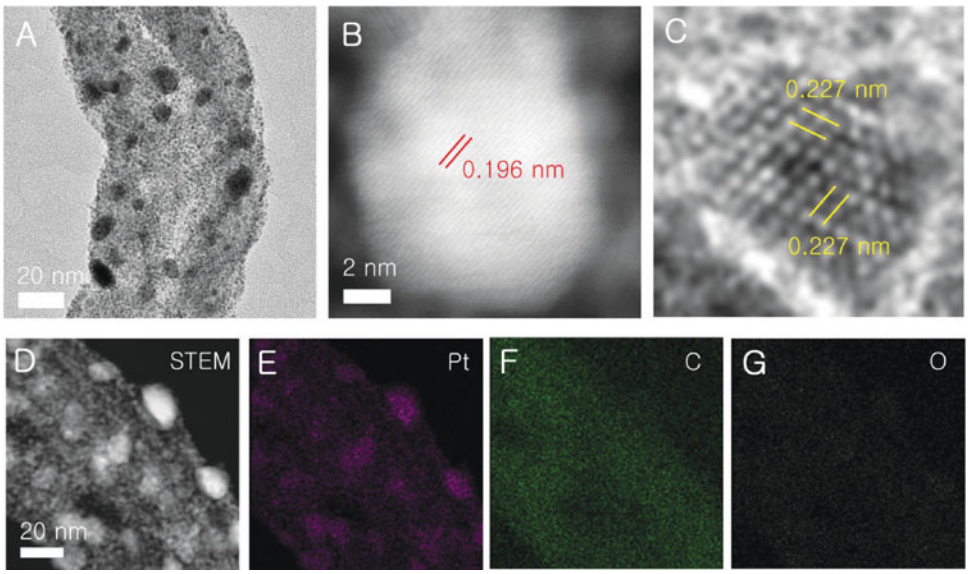


**Figure 4.** TEM, STEM, and EDX mapping images of the Pt-CNW hybrid materials: (**A**) Pt nanoparticles decorated on the CNWs, (**B, C**) lattice structures of Pt nanoparticles with diameter in the range of 2–10 nm, (**D–G**) EDX mapping images. TEM, transmission electron microscopy; STEM, scanning transmission electron microscopy; EDX, energy-dispersive X-ray spectrometry; CNW, carbon nanowires.

tron microscopy (TEM; a FEI Tecnai F30 Super-Twin), and $C_s$-corrected scanning transmission electron microscopy (STEM; JEM-ARM200F).

## Results and Discussion

Figure 1A shows that a Ni thin film uniformly covered the surface of the CFP. After exposure to ethanol for 30 s, some baby-like CNWs (white arrows), having a size of ~50 and 100 nm in diameter and length, are partially initiated on the surface of the CFP (Fig. 1B). The black arrows indicate the Ni nanoparticles that may be formed from reduction of the Ni thin film shown in Figure 1A. The Ni nanoparticle has a diameter of <50 nm, and the smallest particle is around 10 nm. Low- and high-magnetization SEM images reveal that the CNW layer uniformly covered the entire surface of the CFPs (Figs. 1C, 1D). The length of the CNWs is ~10 $\mu$m. Similar results are produced by CNW growth using Co and Fe catalysts.

Figure 2 shows the Raman spectra of the CNWs prepared at 600 and 700°C. The G-line and D-line were recorded at ~1,590 and 1,350 $cm^{-1}$, respectively. At 600°C, the D-line was more predominant than the G-line, and the $I_D/I_G$ was calculated to be 1.33 (Fig. 2A). This implies that the sample may include many carbonaceous particles or disordered graphitic structures. The $I_D/I_G$ decreases to 1.01 at 700°C (Fig. 2B). We also found a peak at ~1,620 $cm^{-1}$, called D' (Elias et al., 2009). Figure 2C shows the Raman spectrum of as-received CFP with high crystallinity, which did not change significantly after maintaining a temperature of 800°C during a synthesis time of 1 h. Thus, we suggest that higher synthesis temperature can lead to the growth of higher crystalline CNWs.

At 600°C, most of the CNWs resemble wavy CNFs of ~50 nm (Fig. 3A). Their structure seems to be composed of disordered and platelet lattice (Fig. 3C). The presence of CNTs is found in the product prepared at 700°C, but their yield is low (Fig. 3B). The inner diameter of CNTs is measured as ~30 nm (Fig. 3D). Nanoparticles of ~30 nm, leading to CNW growth, are mainly observed at CNF's tip.

Figure 4A shows that the CNWs are uniformly decorated with the nanoparticles, which are mostly quasi-spherical in shape. A STEM image shows that the nanoparticles on the surface of the CNWs are in the range of 3–10 nm (Fig. 4B). Two lattice spacings in small nanoparticles are measured as 0.196 and 0.227 nm (Fig. 4C), which can be assigned to the (0 0 1) and (1 1 1) planes of cubic Pt (Li et al., 2010). Mapping images of the Pt-CNWs hybrid materials clearly show the presence of the Pt nanoparticles on the surface of the CNWs (Figs. 4D–4G).

XPS spectra reveal the existence of Ca, P, O, and C signals (Fig. 5A). From the high-resolution spectra (Figs. 5B–5D), the core-level binding-energy positions of C (1*s*), O (1*s*), Pt ($4f_{7/2}$), and Pt ($4f_{5/2}$) of the Pt-CNWs hybrid materials were detected at 284.3, 531.1, 71.3, and 74.6 eV, respectively. Deconvolution of the C1s peak confirms the main contribution of $sp^2$-hybridized C–C bond in the CNWs (Fig. 5B). The $sp^3$-hybridized carbon atom was assigned at 285.2 eV. The peaks related to the C–O and C=O species or hydroxyl functional groups were assigned at ~287 and 288.8 eV, respectively (Pinault et al., 2005). Detection of Pt(4f) signals support the fact that the Pt nanoparticles have been successfully synthesized on the surface of the CNWs prepared on the CFP (Fig. 5C).

## Summary

CNWs were synthesized by catalytic decomposition of ethanol on transition metal nanoparticles that were prepared by reducing the thin film formed on the surface of the CFP via dip-coating method. SEM images showed that CFP was completely covered with the CNWs of <50 nm. Most of the CNWs were CNFs. Raman spectra indicated that the crystallinity of CNWs was dependent on the synthesis temperature. This result was supported by TEM analysis of the

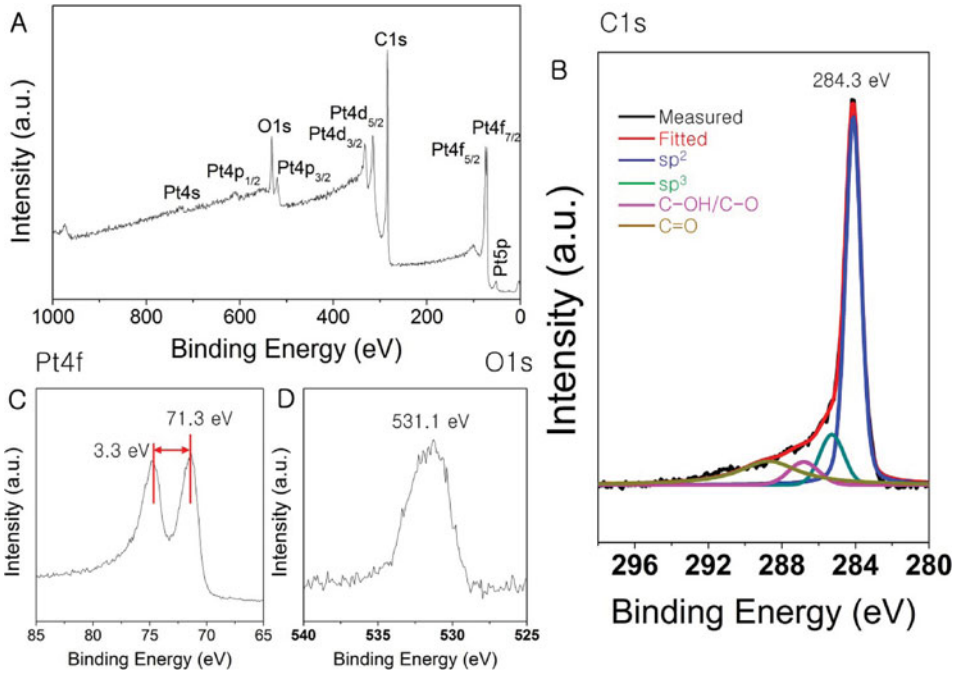


**Figure 5.** X-ray photoelectron spectroscopy spectra of the Pt-carbon nanowires hybrid materials: (**A**) survey and detailed scans of (**B**) C 1*s*, (**C**) Pt 4*f*, and (**D**) O 1*s*.

CNWs. Increase of synthesis temperature induced the growth of some CNTs in low yield. In addition, we successively decorated the Pt nanoparticles on the external surface of the CNWs synthesized on the CFP. HRTEM images clearly showed that the lattice structure of the nanoparticles deposited on the surface of the CNWs could be assigned to that corresponding to cubic Pt. EDX and XPS analyses strongly supported the Pt-CNWs hybrid configuration.

## Acknowledgment

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