

# Facile growth of carbon nanotube electrode from electroplated Ni catalyst for supercapacitor

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## ABSTRACT

A facile growth of carbon nanotubes (CNTs) was facilitated by the use of direct-current plating technique for catalyst preparation. Ni nanoparticles (NPs) were deposited on Cu foil at different applied voltages of 1.0, 1.5 and 2.0 V. The Ni-deposited foil was subsequently used as catalyst for CNTs synthesis by chemical vapour deposition (CVD) method. CVD was carried out at 800 °C using ethanol as carbon source. A voltage of 1.5 V was the optimum condition to deposit uniform Ni NPs that had a narrow size distribution of  $55\pm 3$  nm, which in turn, yielded synthesized CNTs with a uniform diameter of approximately  $60\pm 5$  nm with graphitic layers parallel to the CNTs axis. On the other hand, electroplated Ni at 1.0 V produced CNTs with graphitic layers at an angle to the CNTs axis, while electroplated Ni at 2.0 V produced curly CNTs with a wide distribution of diameters. These results show that Ni NPs size distribution could be controlled by electroplated voltage. Our observation was that Ni NPs with a narrow distribution of sizes and a uniform diameter is a key to uniform CNT synthesis. Furthermore, the synthesized CNTs electrode shows a faradic pseudo capacitance property, which can be attributed to the existence of oxidized Ni NPs. These results propose that the synthesized CNTs are promising materials for future super capacitor application. The optimization of ratio of Ni NPs and CNTs may improve the supercapacitors performance. Copyright © 2015 VBRI Press.

**Keywords:** Electroplating; carbon nanotube; chemical vapor deposition; pseudocapacitor.



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required. Chemical vapor deposition (CVD) is one of the presently available methods for CNT synthesis. Metal catalyst is an essential ingredient in the CVD approach [4, 5]. As for catalyst film preparation, evaporation and sputtering techniques are normally utilized [6-8], but these techniques are time-consuming and high cost. For practical application, facile catalyst preparation is absolutely required. Electroplating, a proposed technique for such preparation, is simple to set up, low cost, fast, can deposit to a selected area and does not need vacuum [9-11]. In this study, facile growth of CNTs was made possible by using direct-current (DC) electroplating for Ni nanoparticles (NPs) catalyst preparation; with the Ni-deposited catalyst, CNTs was synthesized by using CVD with ethanol as carbon source. The effects of DC-electroplating voltage on the morphology and structure of the CNTs were investigated. Furthermore, for demonstration of a potential application, supercapacitors based on the synthesized CNTs were fabricated and their electrochemical properties were determined.

## Introduction

Carbon nanotube (CNT) is one of the most promising materials in nanotechnology due to its large effective surface area and excellent mechanical and electrical properties. CNT shows a great potential for improving the performance of electronics devices, energy storage devices and sensors [1-3]. Important for large-scale applications, a simple synthesis method for mass production of CNT is

## Experimental

### Materials

Cu foils 99.9% pure (0.05 mm × 4 mm × 20 mm) were used as a substrate for Ni NPs preparation (Nilaco Corporation, Japan). Ni ingot was applied as cathode and commercial Ni electroplating solution was used as electrolyte in the electroplating process. Prior to electroplating, Cu foils were cleaned in ethanol and acetone and then ultrasonically cleaned for 10 minutes in distilled water. For CNT synthesis, ethanol (99.9%, Labscan) was used as carbon source and Ar (99.995%) was used as carrier gas. H<sub>2</sub>SO<sub>4</sub> (98%, Sigma Aldrich) was prepared in the concentration of 1 M for using as electrolyte in the measurements of electrochemical properties.

### Ni catalyst preparation by electroplating

DC electroplating technique was used for Ni deposition on Cu foil. The Cu foil and the Ni ingot were connected as anode and cathode, respectively. Electroplating temperature, time and distance between electrodes were fixed at 45°C, 5 min and 100 mm, respectively, while the applied voltages were varied from 1.0, 1.5 to 2.0V. The Ni catalyst-electroplated Cu foil was used for CNT synthesis by CVD.

### CNT synthesis by chemical vapor deposition

The CNT synthesis procedure was as follows. A quartz tube reactor was filled with Ar gas at a flow rate of 500 sccm and the Ni catalyst-electroplated Cu foil was heated to 800°C. Ethanol was vaporized and directed into the quartz tube by Ar bubbling for 20 min to grow the CNTs.

### Characterization of Ni nanoparticles and CNTs

The morphology of the electroplated Ni was characterized by atomic force microscopy (AFM; SEIKO SPA400) with a monocrystal silicon tip (NT-MDT; HA\_NC ETALON). The morphology, diameter and structure of the graphitic layer, and the crystallinity of the synthesized CNTs were characterized by field emission scanning electron microscopy (FESEM; Hitachi SU-8030), transmission electron microscopy (TEM; JEOL JEM-2010) and Raman spectroscopy (Thermal Scientific; DXR™ SmartRaman Spectroscopy), respectively.

### Measurement of electrochemical properties

Electrochemical measurements were carried out in a three-electrode setup connected to an electrochemical workstation (Metrohm AUTOLAB PGSTAT 302). The CNT synthesized on Ni-electroplated Cu foil (an area of 4 mm × 10 mm) was used as working electrode. Pt and Ag/AgCl electrodes were used as counting and reference electrode, respectively. 1M H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as electrolyte. Electrochemical properties were characterized by cyclic voltammetry (CV) and galvanostatic charge/discharge (CD) technique. CV tests were done at the potential range of -0.3 to 0.2 V at a scan rate of 5, 20 and 100 mVs<sup>-1</sup>. CD tests were performed at a current of 5 mA. The specific capacitance ( $C_{sp}$ , Fg<sup>-1</sup>) was

evaluated from CV curves according to the following equation;

$$C_{sp} = \frac{\int_{V_1}^{V_2} i(V) dV}{2(V_2 - V_1)mv} \quad (1)$$

where  $\int_{V_1}^{V_2} i(V) dV$  is total voltammetric charge obtained by integration of positive and negative sweep in CV curve,  $V_2 - V_1$  is potential window width (V),  $m$  is a total mass of active materials (g),  $v$  is a scan rate (Vs<sup>-1</sup>) [12].

## Results and discussion

Fig. 1(a-c) show the AFM images of the Ni NPs on Cu foils electroplated at the voltages of 1.0, 1.5 and 2.0 V, respectively. Ni NPs were formed at all of these electroplating voltages. At the applied voltage of 1.0 V, small and larger clusters of Ni NPs were formed; their average sizes were 44±7 nm and 120±14 nm, respectively. At the applied voltage of 1.5 V, Ni NPs with a narrow distribution of sizes were formed with an average size of 55±3 nm. When the applied voltage was increased to 2.0 V, the sizes of the formed Ni NPs increased to approximately 103±12 nm. Thus, the size of formed Ni NPs can be controlled by varying electroplating voltages.

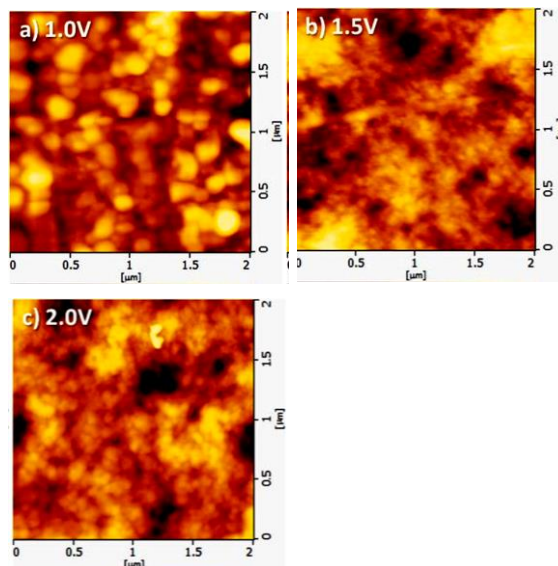
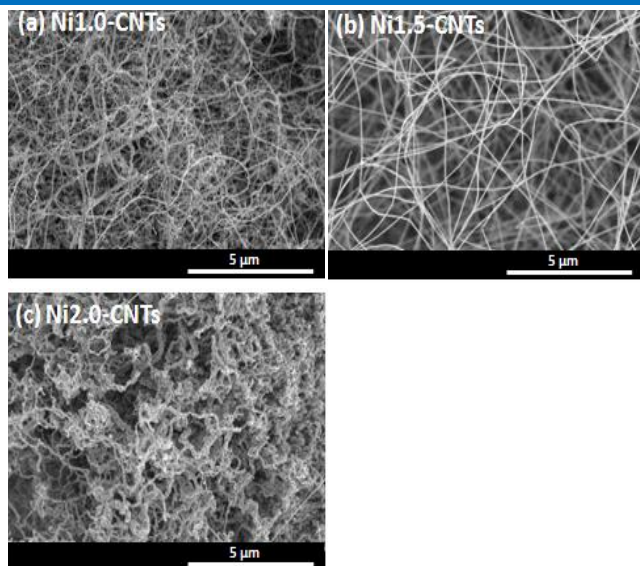


Fig. 1. AFM images of Ni NPs on Cu foils electroplated at the voltages of (a) 1.0 V, (b) 1.5 V and (c) 2.0 V.

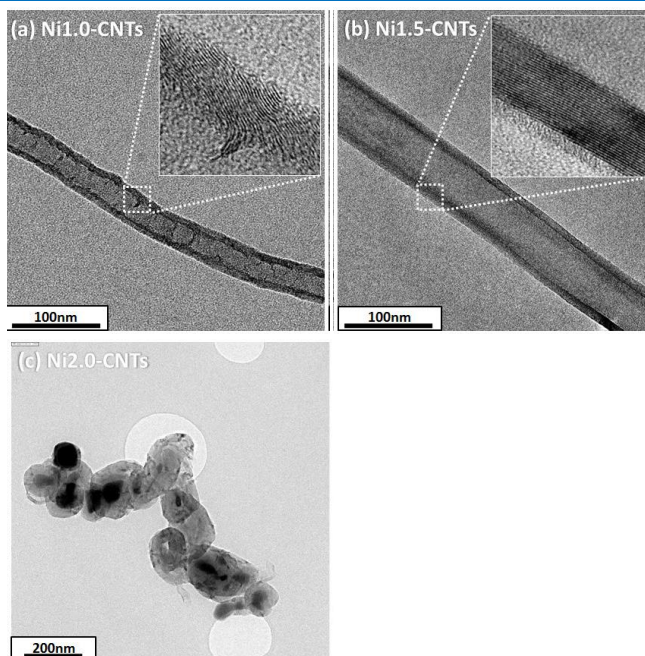
Fig. 2(a-c) show SEM images of the CNTs synthesized by using Ni NPs catalysts that were deposited at electroplating voltages of 1.0, 1.5 and 2.0 V, respectively (hereafter referred to as Ni1.0-CNTs, Ni1.5-CNTs and Ni2.0-CNTs, respectively). After CVD, the surfaces of all Cu foils were visually observed to be wholly covered with black powder. All of the formed Ni NPs were able to act as catalyst producing tubular shaped CNTs, but the synthesized CNTs were different in their morphology and structure. The Ni1.0-CNTs were a tangled network while the Ni1.5-CNTs were straight with high aspect ratio and the Ni2.0-CNTs were curly and agglomerated.



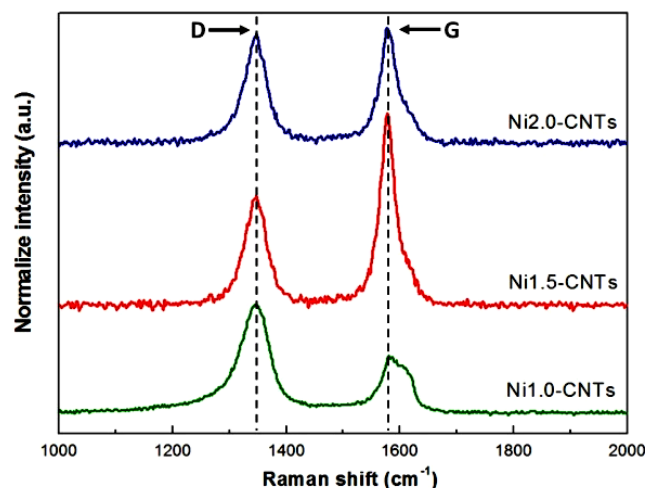
**Fig. 2.** SEM images of (a) Ni1.0-CNTs, (b) Ni1.5-CNTs and (c) Ni2.0-CNTs.

**Fig. 3(a-c)** shows TEM images of Ni1.0-CNTs, Ni1.5-CNTs and Ni2.0-CNTs, respectively. Insets are TEM images of graphitic layers of CNT walls at high magnification. Typical for TEM characterization, magnification in the range of  $\times 50000$  to  $\times 400000$  was used. Observed at low magnification, Ni1.0-CNTs and Ni1.5-CNTs were tubular in shape with diameters of approximately  $45 \pm 7$  nm and  $60 \pm 5$  nm, respectively. However, at high magnification, it was found that their graphitic layers were completely different. The inset in **Fig. 3(a)** shows that the graphitic layers of Ni1.0-CNTs were at an angle to the tube axis wall, while the inset in **Fig. 3(b)** shows clearly that the graphitic layers of Ni1.5-CNTs were parallel to the tube axis. Furthermore, the structure of Ni2.0-CNTs was completely different from those of Ni1.0-CNTs and Ni1.5-CNTs. Ni2.0-CNTs were largely curly with Ni catalyst inside and wide distribution of tube diameters (**Fig. 3(c)**).

**Fig. 4** shows Raman spectra of the synthesized CNTs. The exciting light was Ar ion laser at the wavelength of 532 nm (2.33 eV). Generally, in carbon material characterization, Raman spectra can be used to identify the existence of disordered carbon (*D*-band) and graphitic carbon (*G*-band). Two sharp peaks at Raman shift of approximately  $1350 \text{ cm}^{-1}$  (*D*-band) and  $1590 \text{ cm}^{-1}$  (*G*-band) were observed for all samples. The ratio of *G*-band and *D*-band ( $I_G/I_D$ ) can be used to evaluate the crystallinity of the CNTs. A higher  $I_G/I_D$  ratio indicates a higher degree of structural ordering and purity of CNTs [13]. In this study, it was found that the  $I_G/I_D$  of Ni1.0-CNTs, Ni1.5-CNTs and Ni2.0-CNTs were 0.53, 1.77 and 1.06, respectively. Ni1.5-CNTs showed the highest  $I_G/I_D$ . These results corresponded well to the SEM and TEM results, demonstrating that Ni1.5-CNTs were relatively higher purity and/or had lower defects inside the parallel graphitic layers. Moreover, they also showed that the electroplating voltage directly affected the morphology of Ni NPs. Small-sized Ni NPs with narrow distribution is key to uniform CNT synthesis.



**Fig. 3.** TEM images (a) Ni1.0-CNTs, (b) Ni1.5-CNTs and (c) Ni2.0-CNTs. Insets are TEM images of graphitic layers of CNT walls at high magnification.

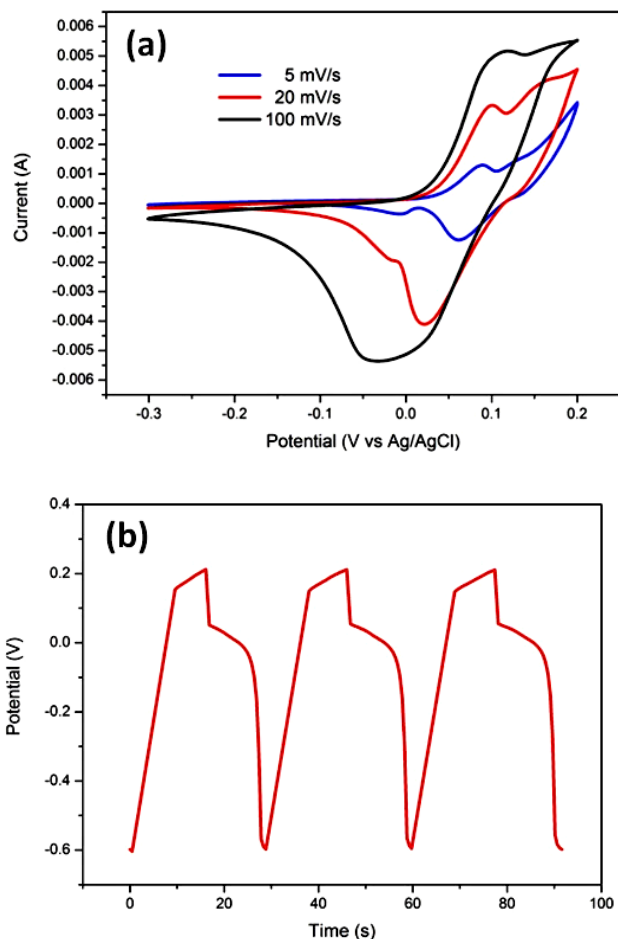


**Fig. 4.** Typical Raman spectra of (a) Ni1.0-CNTs, (b) Ni1.5-CNTs and (c) Ni2.0-CNTs.

To check their suitability for supercapacitor application, the electrochemical properties of Ni1.5-CNTs on Cu foil were determined. **Fig. 5(a)** shows cyclic voltammetry (CV) curves of Ni1.5-CNTs in the potential range of -0.3 to 0.2 V at different scan rates. Instead of showing the expected rectangular shaped curve of ideal electric double-layer capacitor, all of CV curves showed a pair of redox current peaks, indicating that faradic pseudocapacitance is the dominant electrochemical property. With increasing scan rate, the current increased and the gap between redox peaks widened while the shapes of the CV curves were retained, indicating reversibility of the redox reactions. This pseudocapacitive character might be caused by residual Ni NPs catalyst [14] from CNT synthesis. Evidently, X-ray photoelectron spectroscopy spectra showed a chemical shift of Ni 2p peaks, indicating that  $\text{Ni}_x\text{O}_y$  and  $\text{Ni}(\text{OH})_2$  were



formed after electroplating (data not shown). In addition, Ni NPs could also have been oxidized by residual oxygen inside the quartz tube during the CVD process. **Fig. 5(b)** shows a cycle of the galvanostatic charge-discharge curves at the current of 5 mA. In contrast to the symmetrical triangular shape of a typical electric double-layer capacitor, the discharge curves show nonlinearities, indicating an occurrence of faradaic reaction in the active electrode material and substantiating the results from the CV curves. The specific capacitance calculated from the CV curve at a scan rate of 5 mVs<sup>-1</sup> was approximately 53 Fg<sup>-1</sup>.



**Fig. 5.** (a) Cyclic voltammetry curves of Ni<sub>1.5</sub>-CNTs with different scan rate and (b) galvanostatic charge-discharge curves.

All of these preliminary results signified that facile growth of CNTs by Ni NPs catalyst, deposited using DC electroplating method was fully achieved. The synthesized CNTs showed a real potential for supercapacitor electrode application. However, further work and optimization are still necessary.

## Conclusion

Novel CNTs synthesis method that is simple and low cost was proposed. This method uses controllable electroplated Ni NPs as catalyst and ethanol as carbon source for CVD process. The electroplating voltage directly affected the size of Ni NPs, which, in turn, affecting the morphology and structure of the synthesized CNTs. By selecting the appropriate voltage, graphitic layers of CNTs can be made

parallel to the tube axis with a narrow distribution of tube diameters at 60±5 nm. The synthesized CNTs showed a real potential as supercapacitor with a specific capacitance of 53 Fg<sup>-1</sup> at a scan rate of 5 mVs<sup>-1</sup>. Further optimization of the amount ratio of oxidized Ni NPs and CNTs should improve the supercapacitor performance.

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