

# Facile grown carbon nanotubes as thermo-electrochemical cell electrodes by chemical vapor deposition at atmospheric pressure

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**Abstract.** A convenient low cost approach to synthesize carbon nanotubes (CNTs) by chemical vapor deposition at atmospheric pressure is reported. CNTs are grown directly on the nickel substrate without any extra catalyst to make the thermo-electrochemical cell (TEC) electrodes. The as-prepared CNT electrodes are first applied to make the TEC electrodes with the current density of  $56 \text{ mA.m}^{-2}$  and the power density up to  $1.24 \text{ W.m}^{-2}$ . The relative conversion efficiency of the TECs can reach 0.86%. The results suggest that the facile growth of CNTs under atmospheric pressure offers a promising approach for practical applications of the CNT-based TEC electrodes.

## 1. Introduction

Due to large aspect ratio, high surface area, good conductivity and thermal conductivity, carbon nanotubes (CNTs) show great potential in many applications, such as energy storage [1], field emission [2], and gas sensors [3]. Many methods, including arc discharge, laser ablation, and chemical vapor deposition (CVD), have been used to prepare CNTs in the past decades [1]. Among these methods, CVD method has been widely applied to produce CNTs due to its advantages of mild temperature, easy control, and low cost [4-6]. Early reports focused mainly on the preparation of CNTs on non-conducting substrates. However, synthesis of CNTs on these substrates usually needs the catalyst films deposition. In addition, to produce the CNT electrodes, the as-prepared CNTs are required to move to a conducting substrate, or need a post treatment process, which is time consuming and low efficient [7]. CNT synthesis on the conducting substrates can be used directly as electrode materials without any transfer process or post treatment [7]. In many cases, low pressure CVD can be used to produce CNTs, but it does not meet the demand of low cost and scaled growth, which is very important for the practical applications of CNT-based electrodes.

As a sustainable energy source, low-grade heat ( $<130^\circ\text{C}$ ) can be easily obtained in many fields, e.g. exhaust gases from industries, solar energy, and geothermal energy [8]. Thermo-electrochemical cells (TECs), also called thermo-cells or thermogalvanic cells, are promising for harvesting the low-grade heat due to merits of low cost, simple structure, direct energy conversion, and continuous operation [9]. Recently, CNTs show great advantages to produce TEC electrodes for excellent conductivity, high specific surface area, and quick electron transfer ability [10] [11]. Chemical vapor deposition at atmospheric pressure was employed to prepare the CNT electrodes, due to good electrical contact



property [9] [11]. Currently, the key issues for practical applications include the reduction of the cost of the CNT electrodes and the improvement of the energy efficiency for CNT-based TECs.

In this study, CNTs were grown directly on the nickel substrate by CVD at atmospheric pressure without any extra catalyst, and the low cost CNT electrodes were investigated for TEC application. The as-obtained CNTs were first used to make the TEC electrodes with the current density of  $56 \text{ mA.m}^{-2}$  and the power density up to  $1.24 \text{ W.m}^{-2}$ . The relative energy conversion efficiency of the TEC is 0.86%. These investigation suggests that convenient synthesis of CNTs on the catalytic substrate by atmospheric pressure CVD may offer a promising way to develop the practical CNT-based TEC devices.

## 2. Experimental

### 2.1. Synthesis of CNTs on nickel substrate

Firstly, nickel substrates (purity: 99.9%; thickness:  $200 \mu\text{m}$ ) were cleaned by acetone, alcohol and purified water for 15-30 min, respectively. Subsequently, the nickel substrates were placed in a middle zone of the high-temperature furnace (HEFEI KEJIN MATERIALS TECHNOLOGY CO, LTD, OTF-1200X-50, inner tube diameter: 44 cm, tube length: 100 cm). Then CNTs were grown facilely on these substrates by CVD at atmospheric pressure using  $\text{C}_2\text{H}_2$  (20 sccm) as the precursor at  $625^\circ\text{C}$  under Ar flow of 100 sccm.

### 2.2. Characterization

The structural properties of the samples were analyzed by scanning electron microscopy (SEM; JEOL JSM-7100F), X-ray diffraction (XRD; GmbH SMART APEX) and Raman spectroscopy (Renishaw Invia Raman Microscope).

### 2.3. TEC tests

For the TEC test, the test process is the same as the description in our previous reports [12]. Briefly, the Cup-Shaped device was used in the course of the TEC measurements. The separation of two CNT electrodes was 4 cm and the electrodes with different areas from  $0.5$  to  $6 \text{ cm}^2$  were tested. The temperatures of two sides were controlled by ice water and heating tape, respectively, and monitored by OMEGA thermocouple probes. The parameters of TEC were achieved by the KEITHLEY 2440 multimeter.

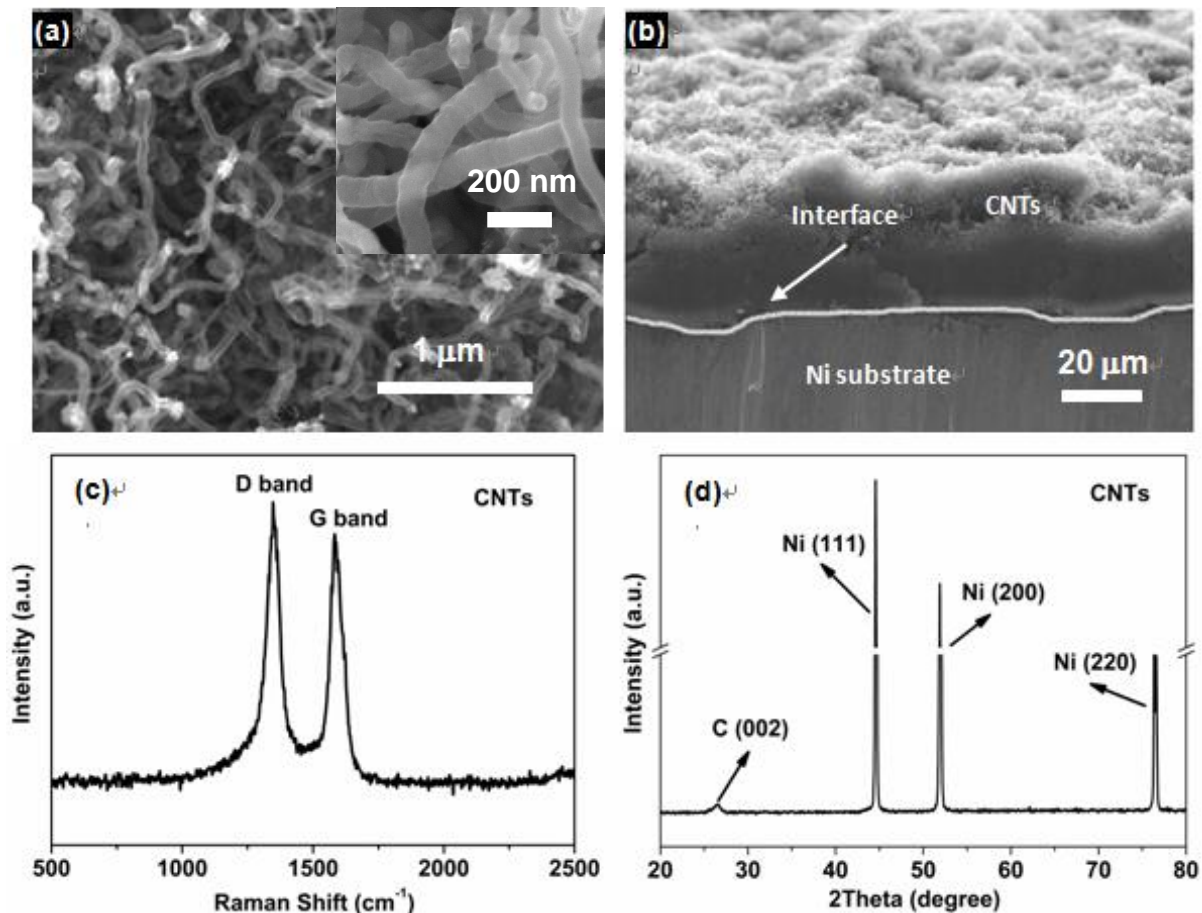
## 3. Results and discussion

SEM, Raman and XRD characterizations are shown in Figure 1. From the SEM images (See inset in Figure 1a), CNTs of diameters 60–90 nm were grown on the Ni substrate. The cross sectional SEM images (Figure 1b) show clearly that CNTs connect tightly with the nickel substrate, benefiting the enhancement of the adherence between the CNT electrode and the nickel substrates. As shown in Figure 1c, Raman spectrum shows obvious characteristic peaks of the CNTs, i.e. D band and G band [12]. XRD characterization (Figure 1d) indicates that the peaks at  $26.4^\circ$ ,  $44.5^\circ$ ,  $51.8^\circ$  and  $76.4^\circ$  can be attributed to (002) crystallographic planes of CNTs [13] [14], and (111), (200) and (220) planes of Ni from the nickel substrate [15], respectively.

TEC properties of the CNTs were tested by Cup-Shaped device [12]. As shown in Figure 2a, the seebeck coefficient can be obtained with the value of  $\sim 1.45 \text{ mV.k}^{-1}$ , in agreement with the literatures [8] [13]. The current densities ( $J_{\text{SC}}$ ) rise with increasing the temperature differences (Figure 2b). When the temperature difference is  $60^\circ\text{C}$ ,  $J_{\text{SC}}$  and  $J_{\text{SC}}/\Delta T$  are  $56.0 \text{ A.m}^{-2}$  and  $0.933 \text{ A.m}^{-2}\text{K}^{-1}$ , respectively. The energy conversion efficiency ( $\eta$ ) can be calculated by the following formula [8] [13]:

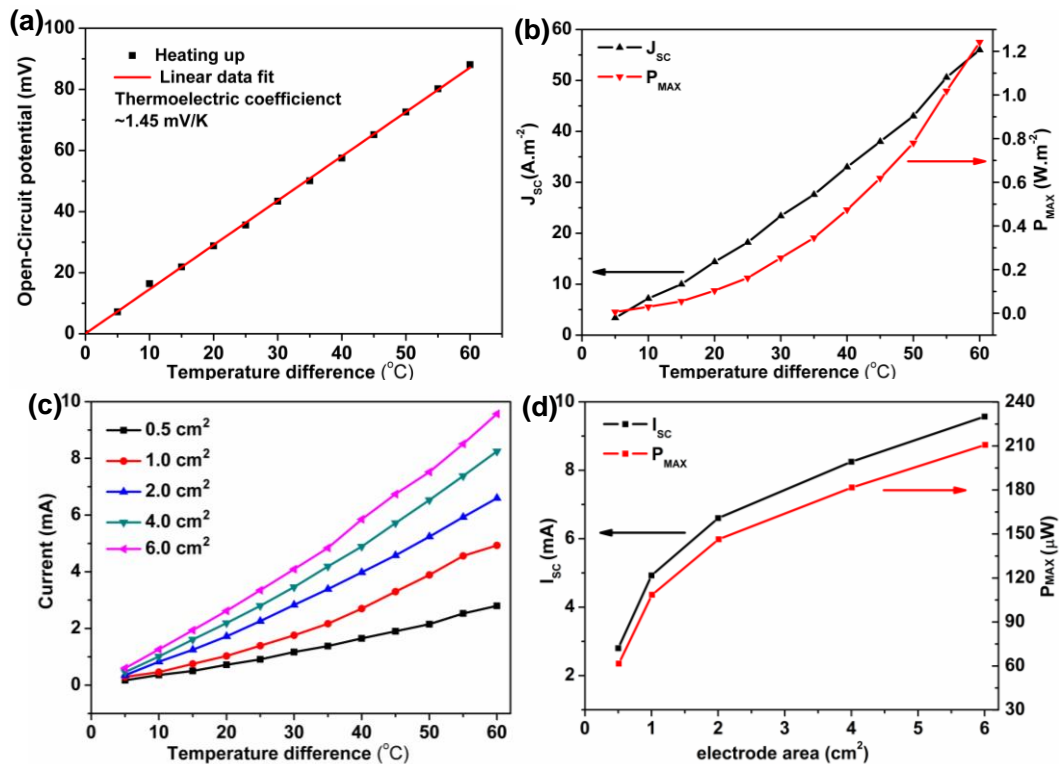
$$\eta = \frac{0.25v_{oc}I_{sc}}{Ak(\Delta T/d)} \quad (1)$$

$V_{oc}$  and  $I_{sc}$  represent the open-circuit potential and the short-circuit current, respectively.  $A$  is the effective test area of the CNT electrode,  $k$  is the thermal conductivity of the test electrolyte,  $\Delta T$  and  $d$  are the temperature difference and the distance between two identical CNT electrodes, respectively.

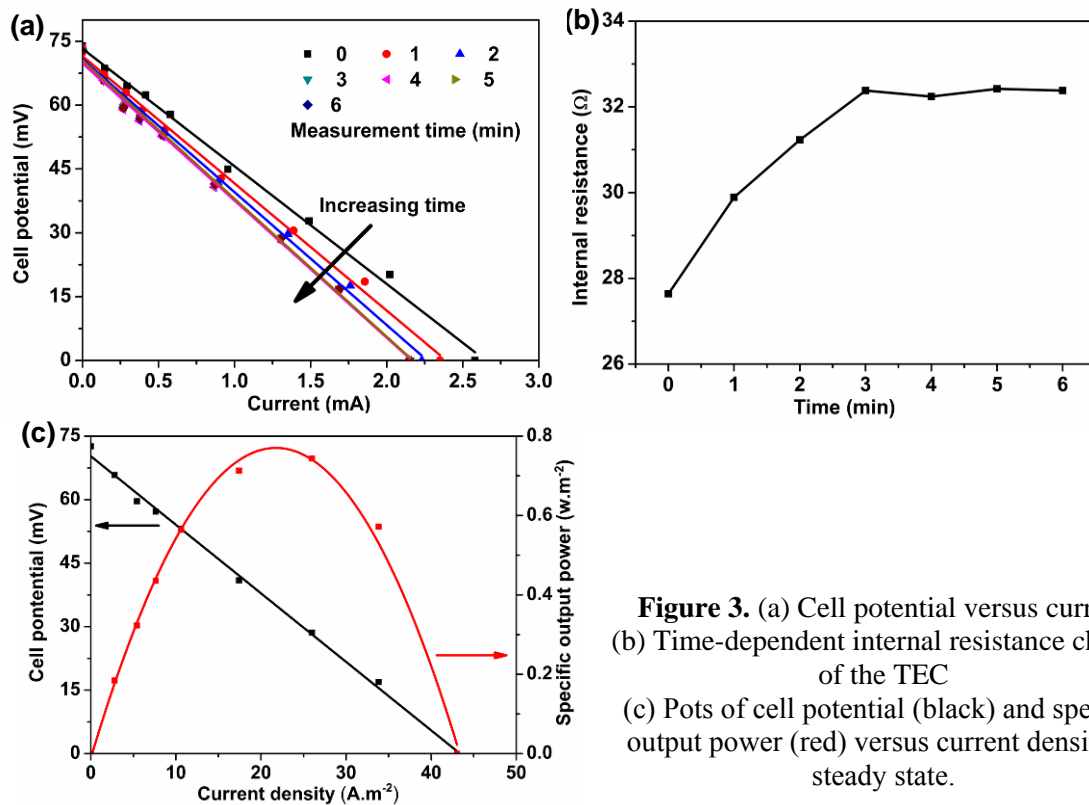


**Figure 1.** (a-b) SEM images, (c) Raman and (d) XRD results of the CNTs facily grown on the nickel substrate without any additional catalyst.

The maximum output power ( $P_{MAX}$ ) can be calculated by the equation:  $P_{MAX} = 0.25V_{oc} \times I_{sc}$ . The relative energy conversion efficiency ( $\eta_r$ ) is an important parameter of the TEC, which can be achieved by the equation:  $\eta_r = \eta / (\Delta T / T_h)$ , where  $T_h$  is the temperature of the hot side.  $P_{MAX}$  increases with raising the temperature difference from 5 to 60 °C (Figure 2c). When the temperature difference climbed to 60 °C,  $P_{MAX}$  and  $\eta_r$  were calculated to be 1.24 W.m<sup>-2</sup> and 0.86%, respectively. In comparison with the other CNT electrodes [9] [10], TEC performance of CNT electrode, facily grown on the Ni substrate, was not very excellent due to the poor quality of CNTs, as confirmed by the Raman characterization (Figure 1c). To get high quality of CNTs, one of the most effective ways is to decrease the oxidation layer on the surface of the Ni substrate. As shown in Figure 2d, the current of the TECs became higher with the increasing area of the CNT electrode, contributed to the increase of active sites [8] [16]. The current of TEC based CNT electrode could reach 9.57 mA with increasing the area to 6 cm<sup>2</sup> under the temperature difference of 60 °C. However, the increasing rates of  $I_{sc}$  and  $P_{MAX}$  decreased gradually with the increase of CNT electrode area and the curves exhibit nonlinear relationship (Figure 2d)), which might be related to the edge effect and the growth density of the CNTs [8], similar phenomenon could be observed in our previous reports [16].

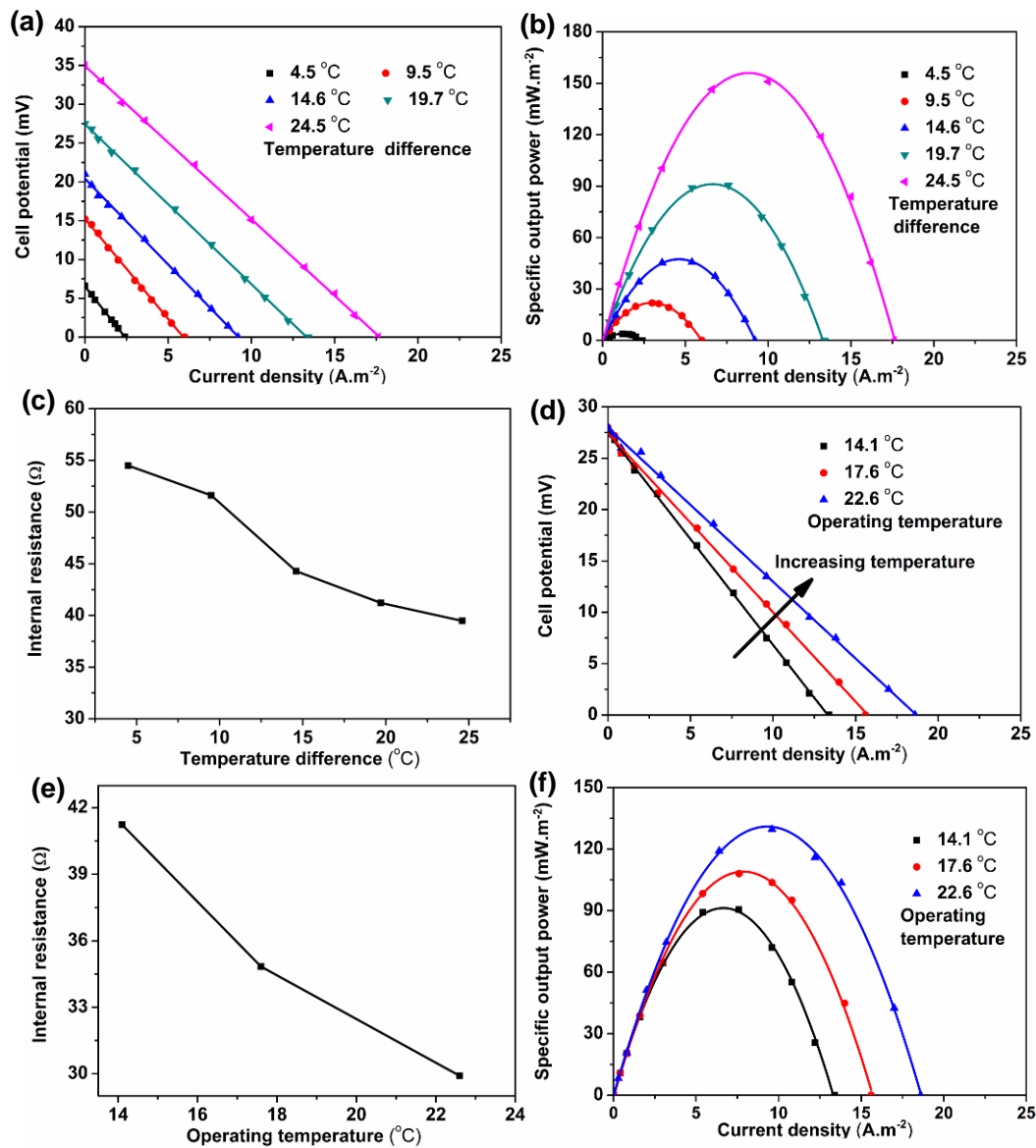


**Figure 2.** (a) Cell potential versus temperature difference for 0.4 M  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  redox couple, (b)  $J_{SC}$  and  $P_{MAX}$  versus temperature difference between the two test electrodes, each electrode area is 0.5 cm<sup>2</sup>, (c) Current versus temperature difference with different areas of the CNT electrodes, (d)  $I_{SC}$  and  $P_{MAX}$  versus the electrode area.



**Figure 3.** (a) Cell potential versus current (b) Time-dependent internal resistance change of the TEC (c) Plots of cell potential (black) and specific output power (red) versus current density at steady state.

Discharge properties of the TECs for CNT electrodes are shown in Figure 3. As shown in Figure 3a, the internal resistance (i.e. the slope of the E-I curves) of the TEC increased with the increasing time and the steady value of  $32.38\ \Omega$  was reached 3 min after the operation (Figure 3b). The operating temperature, i.e. the average of the temperatures at hot and cold electrodes, was fixed at  $29.2\ ^\circ\text{C}$  and the temperature difference was maintained at  $50\ ^\circ\text{C}$  during the measurements. The cell potential and the specific output power at steady state are shown in Figure 3c. The Cup-shaped TEC generated  $J_{\text{SC}}$  of  $43.0\ \text{A}\cdot\text{m}^{-2}$  (output current of  $2.15\ \text{mA}$ ) and  $P_{\text{MAX}}$  of  $0.78\ \text{W}\cdot\text{m}^{-2}$  (output power of  $39\ \mu\text{W}$ ).



**Figure 4.** (a) Cell potential vs current density and (b) specific output power vs current density under different temperature difference; (c) the internal resistance vs temperature difference; (d) cell potential vs the current density under different operating temperature; (e) the internal resistance vs operating temperature; (f) the specific output power vs current density under different operating temperature.



Generally, the value of  $V_{oc}$  in a TEC is mainly determined by the temperature difference. As shown in Figure 4a, with increasing the temperature difference, the cell potential and the current density increased from 6.6 mV and 2.4 mA.m<sup>-2</sup> at  $\Delta T = 4.5$  °C to 35.0 mV and 17.6 mA.m<sup>-2</sup> at  $\Delta T = 24.5$  °C, respectively, resulting in the improvement of  $P_{MAX}$  from 3.94 to 154.0 mW.m<sup>-2</sup> (Figure 4b). Meanwhile, the internal resistance of the TEC decreased from 54.49 to 39.48  $\Omega$  with increasing the temperature difference (Figure 4c). Under the same temperature difference of 19.7 °C (Figure 4d), when increasing the operating temperature, the current density increased from 13.4 to 18.6 mA.m<sup>-2</sup>, corresponding to the operating temperature of 14.1 and 22.6 °C, respectively, similar cases can be found in the previous reports [8] [17]. As shown in Figure 4e, the internal resistances of the TEC decrease by 27.4% (from 41.21 to 29.91  $\Omega$ ) due to the increasing operating temperature, resulting in the increase of  $P_{MAX}$  from 91.5 to 130.2 mW.m<sup>-2</sup> (Figure 4f). The decrease of the internal resistance is attributed to the improvement of ion transport and diffusion between the CNT electrodes [8] [17].

#### 4. Conclusions

In summary, CNTs were facilely grown on the nickel substrate by atmospheric pressure CVD method to make the TEC electrodes. The TEC based CNT electrodes can achieve the current density of 56 mA.m<sup>-2</sup> and the power density up to 1.24 W. m<sup>-2</sup>, and the relative energy conversion efficiency of the TEC is 0.86%. The results suggest that facilely grown low cost CNTs on the catalytic substrate may offer a promising way for the practical applications of CNT-based TEC devices.

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