

High peel strength aligned carbon nanotubes/etched Al foil composites with boosted supercapacitor and thermal dissipation performances

Juan Du^{1,2}, Le Kang², Haitao Zhou³, Jianhong Yang^{1,3}, De Chen⁴, Jia Qiao¹, Wangxing Li¹

1. School of Metallurgy and Environment of Central South University, Changsha, Hunan Province, People's Republic of China
2. Zhengzhou Non-ferrous Metals Research Institute Co. Ltd of CHALCO, Zhengzhou, Henan Province, People's Republic of China
3. School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu Province, People's Republic of China
4. Department of Chemical Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway

E-mail address: xingyangren82@163.com (Juan Du)

Abstract

The peel strength between the aligned carbon nanotubes (ACNTs) and substrate is a critical issue for the structural stability of the ACNTs-based composites. A poor ACNTs-substrate adhesion may cause unreliable and a short service life of the device. In this work, ACNTs are grown on the etched Al foil with largely improved bonding strength by a direct thermal chemical vapor deposition (CVD) synthesis. In the interface part of the ACNTs adjacent to the etched Al substrate, the ACNTs tangled together as 'tiny twine balls' with irregular shape are embedded in the pores of the etched Al foil, similar like the roots of a plant. Such unique structure generates strong bonding strength between as-grown ACNTs and etched Al substrate. The measured peel strength was 76.8 N m^{-1}

compared to the smooth surface Al foil without etching was 53.6 N m^{-1} . Besides, the ACNTs attached to etched Al foil firmly in comparison with the ACNTs have been separated from the smooth surface Al foil after peel strength testing. A ‘plant growth’ mechanism is proposed to illustrate the growth procedure. When the as-prepared ACNTs/etched Al foil composites are used as supercapacitor (SC) electrodes alone, they deliver the specific capacity (C_{sp}) of 11.3 F g^{-1} . By contrast, after the PANI or MnO_2 are post-synthesized on the ACNTs/etched Al substrate, the PANI/ACNTs and MnO_2 /ACNTs composites can reach a mass-normalized C_{sp} of 488.2 F g^{-1} and 117.6 F g^{-1} , respectively. The ACNTs/etched Al foil are also applied as thermal dissipation material for a 24W LED light. The final stable working temperature decreases from 106.3°C to 82.3°C and the temperature rise rate between 30°C and 82°C decreases from $0.19^\circ\text{C s}^{-1}$ to $0.04^\circ\text{C s}^{-1}$ after the ACNTs/etched Al foil are stuck to the backboard of LED light. The excellent electrical and outstanding thermal conductivities of ACNTs/etched Al foil composites are mainly attributed to the much higher bonding strength and improved interface contact. The results enlighten and promote the design and preparation of ACNTs composites with high peel strength to develop high-performance electrical and thermal management devices.

Key words: Aligned carbon nanotubes, Etched Al foil substrate, Peel strength, Supercapacitor, Thermal dissipation performance

1. Introduction

Carbon nanotubes (CNTs) have attracted extensive research since their discovery by Iijima in 1991 [1]. In 2004, the efficient synthesis of vertically aligned carbon nanotubes (VA-CNTs) films via chemical vapor deposition (CVD) growth was discovered by Hata *et al.* [2][3]. Being a typical of one-dimensional materials, aligned CNTs (ACNTs) possess good electrical and thermal

conductivities and high mechanical strength along the axial direction, which make them to be attractive materials for various applications [4][5], such as electrochemical double layer capacitors (EDLC) [6][7][8], lithium ion batteries [9][10], fuel cells [11][12], heat transfer and thermal dissipation [13][14], and electronic application [15]. However, it is impractical to directly use ACNTs as freestanding electrodes or thermal materials. A substrate is necessary to serve as a current or thermal collector to exploit the excellent properties of ACNTs. Sufficiently thin metal or alloy foils with high electrical and thermal conductivities and good machinability are suitable substrates for the ACNTs growth [16]. The CNTs grown on the flat metal or alloys substrates always show well alignment, uniform distribution and similar lengths, which are the ideal platforms for different applications [17][18][19].

During recent years, Al foil has aroused particular interest for being applied as the substrate for the ACNTs growth due to its various advantages. Firstly, Al foil is easy to get and the cost is very low compared to other substrates[9]. Secondly, an Al foil with good electrical and thermal conductivity is particularly suitable for electrochemistry or thermal transfer devices[20][21]. Thirdly, since the Al foil has natural oxidized surface, it does not require a pre-deposited buffer layer, which simplifies the preparation process[22]. Meanwhile, the high flexible property of Al foil also facilitates the continuous and large scale production for industry. It should be noted that for the electrical and thermal devices, the carbon nanomaterials-based electrodes are desired along with the seamless integration, long lifetime, and reliable performance, which all rely on the structure stability of the composites[23]. Especially, strong bonding between ACNTs and substrates can prevent the loss of CNTs, leads to the high reliability in practical applications[24]. Otherwise, the weak peel strength of ACNTs/substrate may cause a very short-time usage of such device[25]. Based on the previously reported works[17][26][27], the poor adhesion of ACNTs on the smooth

surface of Al foil or other substrates was a critical and often-neglected issue for the structural stability and service life of the composites, despite the initial performances were always excellent in certain applications. Extensive researches have been carried out to overcome this problem.

Shaijumon *et al.*[28] used gold interface material to improve the adhesion between ACNTs and Cu current collector for the supercapacitor (SC) electrode, demonstrating a significant improvement of the SC rate capability. M. Dharmendra *et al.*[14] used a diamond intermediate layer to improve the adhesion and heat transfer between the CNTs and the copper. Lin *et al.*[29] deposited a thin Al₂O₃ layer by atomic layer deposition as a thermal interface material to grow ACNTs on the copper substrate with largely improved adhesion. The effect of microwave treatment to embed CNTs with Ni nanoparticles in a Ti matrix to improve the adhesion was studied by Huan-Chieh Su *et al.*[30]. Seong Chu Lim *et al.*[31] provided a strong adhesion of CNTs onto the substrate is thermal deposition of indium and tin metal layers on an indium-tin oxide glass substrate, followed by thermal annealing. In addition, Lingbo Zhu *et al.*[32] proposed CNTs transfer technology by a solder reflow process, obtained good contact between CNTs and solder on the substrate. However, all those methods are multi-steps, moreover, some steps require complex and costly techniques, which are not feasible for scalable production. Especially, most of the methods have only limited improvements in the peel strength and performances of ACNTs/substrate for the devices application. Therefore, it is essential to develop a more facile and scalable process to grow ACNTs on metal substrates with good adhesion.

In this work, we present a scalable technique to directly grow ACNTs on etched Al foil substrate with strong mechanical adhesion by a catalyst floating CVD method. The ACNTs/etched Al foil interface exhibits strong mechanical adhesion, as well as the new composites exhibits good SC electrochemical and thermal dissipation performances. A ‘plant growth’ mechanism for the high

bonding strength between the as-grown ACNTs and etched Al foil is proposed. This work also provides a versatile and adaptable method to fabricate CNTs or ACNTs on different kinds of substrates with strong peel strength for various applications.

2. Experimental

2.1 Synthesis of ACNTs on Al foil, PANI/ACNTs and MnO₂/ACNTs composites.

For comparison, both of the etched Al foil (JCC, 99.7%, thickness 30 μm) and ordinary (smooth surface) Al foil without etching (HEC, 99.4%, thickness 25 μm) were cleaned with ethanol and placed in the center of quartz tube (heating zone) with diameter of 3.5 inch to grow ACNTs by using floating catalysts CVD method[10]. A programmable syringe pump was used to inject the catalyst/carbon source (ferrocene (Sigma-Aldrich) in ethanol (Sinopharm), 0.05 mol L⁻¹) into the quartz tube, with the tip of the injection nozzle located at the center of the preheating zone (360°C) of the furnace. When the temperature of the quartz tube reached the reacting temperature of 630°C, the catalyst/carbon source solution was injected into the quartz tube at the rate of 30.6 mL h⁻¹, along with the H₂/Ar (Yuanzheng Technology, the volume ratio was 1:9) was employed as the carrier gas with a total flow rate of 1000 sccm, it spent 1h for the injecting of catalyst/carbon source into the quartz tube. Briefly, the PANI were synthesized by one-step method on a conventional three-electrode system. An aqueous electrolyte solution of 1 M H₂SO₄ (Sinopharm) with 0.1 M aniline (Sigma-Aldrich) was used for the CV electrochemical deposition of PANI on the ACNTs/etched electrode. The deposition of PANI was carried out at the potentials between -0.2-0.8 V (vs. Ag/AgCl reference electrode) at the scan rate of 10mV s⁻¹ for 19 scan cycles[33]. MnO₂ was prepared by immersing ACNTs/etched Al foil in 0.2 M KMnO₄ (Sinopharm) aqueous solution for 1.5 h at the temperature of 70 °C[10], after that, a thin layer of nanostructured MnO₂ was deposited on the surface of ACNTs. The resulting MnO₂/ACNTs-etched Al foil was rinsed with deionized

water and ethanol and finally dried at 60 °C in vacuum oven for 24 h.

2.2 Materials characterization and peel strength testing

The morphology of the ACNTs and Al foil was investigated by field emission scanning electron microscopy (FESEM, FEI Quanta 250 FEG). Raman spectra were recorded on a Renishaw in Via Raman Microscope by using a 514 nm laser as the excitation source. To explore the peel strength of the ACNTs on the substrate, a qualitative way was using a tweezers to scrape or pull the ACNTs to exam whether the ACNTs were easily detached from the substrates. Moreover, in this work, the peel strength test was also quantitatively carried out in a Linklab XLW electromechanical tester. The testing method based on ASTM D3330 to test the peel strength of pressure-sensitive tape at 180° angle on the ACNTs/Al foil. Before testing, the ACNTs/Al foil composites were cut into ribbon foils with a width and length of 1.5cm and 15cm, respectively. The 3M VHB tape (wideness 25 mm) was placed on a PVC plate, flowing the carbon nanotube forest were attached on the 3M VHB tape. After that, a steel roller (2 kg) covered with rubber was used to roll the tape and the Al foil/carbon nanotube film above firmly for three times at the rate of 300 mm min⁻¹ to ensure a good contact between the ACNTs and 3M VHB tape. Consequently, the tape attached with carbon nanotube forest was placed on the PVC plate, then one end of the PVC plate was clamped to the testing machine tightly. During the testing, the Al foil/ACNTs film were moved away at the rate of 300 mm min⁻¹ by seizing the free end and back upon itself at an angle of 180°. The test schematic is showed as Fig.4. The contact area used for determining the peel strength was the geometrical area of the surface of the carbon nanotube forests covered with the tape. Therefore, the contact area was calculated by the wideness of carbon nanotube/Al foil film plus the length of the carbon nanotube forest/Al foil being removed at least for 20 to 80 mm from the start point.

2.3 Electrochemical and thermal dissipation measurements

The electrochemical properties and capacitance measurements of ACNTs/etched Al foil as the electrodes were studied in three-electrode system using 0.2 M Na₂SO₄ solution as the electrolyte. A silver/silver ion electrode (Ag/Ag⁺) was used as the reference electrode and a Pt mesh was used as the counter electrode. All the electrochemical measurements were carried out using a Potentionstat/Galvanostat (Princeton Applied Research, VersaSTAT MC). The cyclic voltammetry (CV) tests were carried out at various scan rates of 5, 10, 20, 50, 100 mV s⁻¹ between 0.2-0.6 V vs. Ag/AgCl reference electrode. The galvanostatic charge/discharge (GCD) curves were measured at various current densities of 0.2 A g⁻¹, 0.4 A g⁻¹, 1 A g⁻¹ between 0.2-0.6 V vs. Ag/AgCl reference electrode.

The electrochemical capacitance testing of PANI/ACNTs-etched Al foil was studied at the potentials between -0.2-0.7 V (vs. Ag/AgCl reference electrode) in 1M H₂SO₄ solution, and the electrochemical capacitance measurement of MnO₂/ACNTs-etched Al foil was carried out at the potentials between -0.2-0.8 V (vs. Ag/AgCl reference electrode) in 0.2 M Na₂SO₄ solution. Both the CV response of the PANI and MnO₂ electrodes were measured at scan rate of 5 mV s⁻¹. The specific capacitance (C_{sp}) for ACNTs, PANI/ACNTs, MnO₂/ACNTs was evaluated from the CV curves, according to the equation below

$$C_{sp} = \frac{I}{2M(dV/dt)}$$

Where I is the sweeping current, and dV/dt is the scanning rate of voltage, M is the effective mass of the ACNTs, PANI/ACNTs, MnO₂/ACNTs electrode, respectively.

The thermal dissipation performance of ACNTs/Etched Al foil was demonstrated by testing the working temperature of a 24 W LED light of which was with and without pasting the ACNTs/Al foil on the backboard.

3. Results and discussion

3.1 The ACNTs growth on Al foil with etching pit and smooth surface

Fig. 1 showed the typical FESEM of the cross-section and top view of the Al foil with etching pit and smooth surface. As shown in Fig.1-D, the surface of the etched Al foil has been etched into different pits and ravines. The depth of the etched pits or ravines was between $4\mu\text{m}$ ~ $6\mu\text{m}$ (Fig.1-B). In contrast, the ordinary Al foil demonstrated much more smoother surface than the etched Al foil (Fig.1-A and C). There was no obvious pits or ravines on the surface of the ordinary Al foil no matter of which was observed from the cross-section or top view.

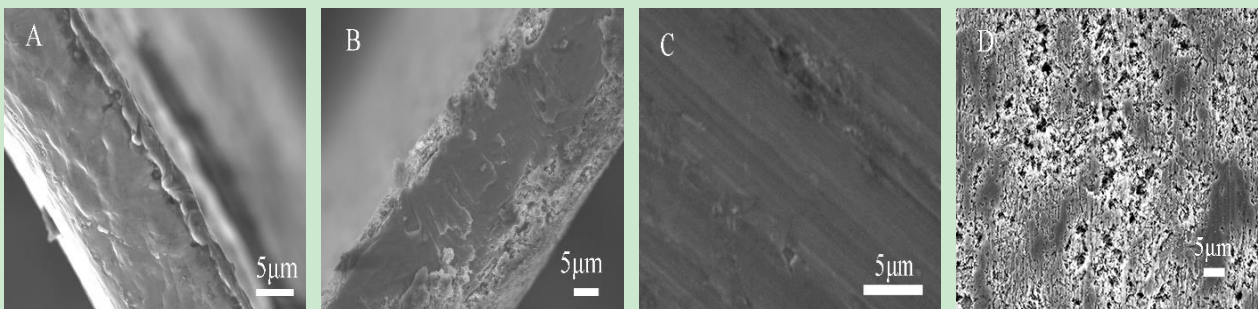


Fig.1 FESEM images of the native surface of ordinary Al foil with smooth surface (A, C-the cross section and top view respectively) and etched Al foil with etching pit surface (B, D-the cross section and top view respectively)

Vertically aligned multi-wall carbon nanotubes (ACNTs) could be grown effectively both on the Al foil with smooth and etched surface. The side view of the carbon nanotube forest revealed the vertical growth of CNTs (Fig.2A and B). A pronounced growth and a fairly even distribution of CNTs on the Al foil with smooth surface was observed, however, some part of the CNTs forest have detached from the substrate. Conversely, CNTs forest grown on the etched Al foil were attached to the substrate well. Especially for the root and top part of the forest, the CNTs trended to tangle together with a state of disordered and intricate structure. Nevertheless, they were still in directional

alignment over a large surface area of the etched Al foil. Apparently, the degree of alignment of the CNTs being grown on smooth surface Al foil was slightly better than on etched Al foil. From the top view it was shown that the CNTs forest grown on the both Al foil were disordered and tangled together (Fig.2C and D).

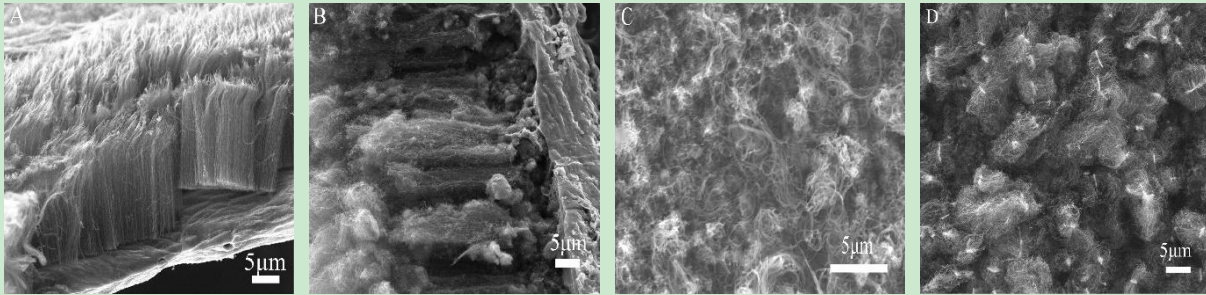


Fig.2 FESEM images of the as-grown carbon nanotubes on the ordinary Al foil with smooth surface (A, C-Acquired from the side and top view of the CNTs respectively) and on the etched Al foil with etching pit surface (B, D- Acquired from the side and top view of the CNTs respectively)

3.2 Raman characteristics of as-grown ACNTs on etched and ordinary Al foil substrate

Raman spectra is usually used to characterize the graphitization of as-grown CNTs. The G-band intensity is related to a graphitization ($1550-1650\text{ cm}^{-1}$) and the D-band intensity is related to defect-induced (1350 cm^{-1}) optical mode. The G-band to D-band intensity ratio (I_G/I_D , G/D ratio) corresponds to the graphitization of CNTs, which can be regarded as an indication of the quality of as-grown CNTs. A higher I_G/I_D ratio indicates the better graphitization of CNTs. On the contrary, a lower I_G/I_D ratio means more defects and amorphous carbon in the as-grown CNTs. Fig.3 showed Raman spectra and I_G/I_D ratio of as-grown CNTs on Al foil with smooth and etched surface respectively. The high degree of crystallinity of carbon nanotubes were verified from Raman spectroscopy for CNTs grown on both smooth and etched Al foil. Second order features at $\sim 2709\text{ cm}^{-1}$ (CNTs on smooth surface Al foil) and $\sim 2711\text{ cm}^{-1}$ (CNTs on etched Al foil) were also observed in the spectrum, which were associated with the D band variation. No remarkable

as-called “radial breathing modes” (RBM, 75-300 cm^{-1}) representing the single and double walled nanotubes with diameters between 1 and 2 nm were observed for CNTs either grown on smooth or etched Al foil. However, the higher I_G/I_D ratio of CNTs grown on etched Al foil proved its higher graphitization degree than the CNTs grown on smooth surface Al foil.

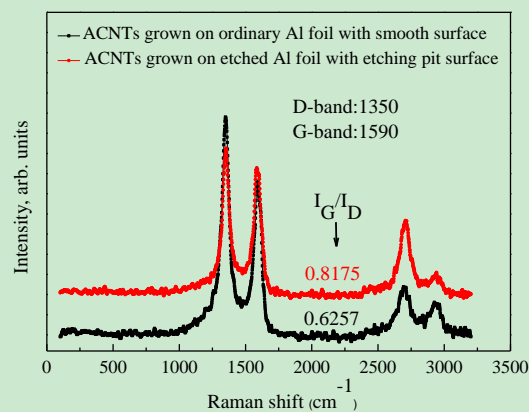


Fig.3 The Raman spectra of as-grown CNTs on smooth and etching pit surface Al foil, respectively

3.3 Peel Strength of as-grown ACNTs /Al foil substrate with different surface morphology

The adhesion between ACNTs and substrate interface should be mechanically strong for reliable bind-free integration into different technologies. Fig.4 was the schematic of the peel strength test for ACNTs grown on the etched and smooth surface Al foil. As shown in Fig.5, the stable peel strength determined for ACNTs grown on etched Al foil was much higher than the ACNTs grown on ordinary Al foil. From the small inset picture in Fig.5, it was observed that the ACNTs grown on smooth surface Al foil have totally been peeled away from the substrate, as a result, the smooth surface Al foil was exposed clearly after peeling test. In contrast, the ACNTs grown on etched Al foil were still attached to the substrate well except some black carbon particles on the top of ACNTs was stuck onto the tape. This experimental phenomenon directly confirmed that the as-grown ACNTs have a much stronger adhesion strength to the etched Al foil than to the

smooth surface Al foil substrate.

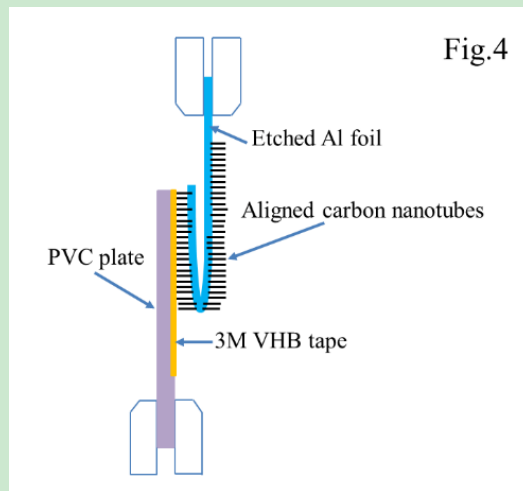


Fig.4 The schematic of peel strength test

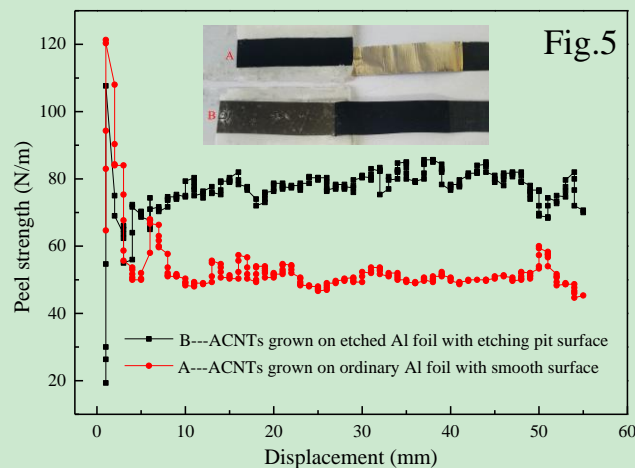


Fig.5 Peel strength as a function of displacement, used to determine the adhesion strength of ACNTs grown on the smooth and etching pit surface Al foil respectively, the inset picture is the ACNTs and Al foil after peeling test, which A is ACNTs grown on Al foil with smooth surface, B is ACNTs grown on etched Al foil with etching pit surface

In addition, another simple and fast method to compare the adhesion property of ACNTs grown on ordinary and etched Al foil was using tweezers or blade to scrape ACNTs grown on the Al substrate. As a result, the ACNTs grown on ordinary Al foil was easily separated from the substrate by scraping, while no obvious ACNTs was scraped off from the etched Al foil after scraping. In

order to understand the mechanism of great adhesion strength of ACNTs to the etched Al foil substrate, top and side view FESEM were used to inspect the nanostructure binding way between ACNTs and etched Al foil before and after scraping by the blade, as be shown in Fig.2 B, D and Fig.6. It could be observed that the top of ACNTs fell down densely on the same direction after scraping, compared to the ACNTs were only tangled together loosely before scraping. The ACNTs below the top surface are still stand vertically on the etched Al foil (Fig. 6A, B). The root ends of the CNTs tangled together were just as small twine ball particles with indefinite shape which were embedded in the pit of the etched Al foil, as Fig. 6C, D showed. Obviously, the FESEM demonstrated that the major reason for the great adhesion between as-grown ACNTs and the etched Al foil was that the ACNTs had been planted into the etching pit of etched Al foil during the grown process.

Normally, the CNTs usually began to grow on the surface of the catalyst nanoparticles, it was speculated that with the distribution of the catalyst nanoparticles in the etching pits of etched Al foil, the CNTs began to grow. However, the narrow space of the etching pit of etched Al foil and the nonuniform distribution location of the catalyst particles in the etching pit compelled the CNTs to be unoriented growth. As a result, the CNTs became to tangle together at the beginning of growth. Whereafter, when the CNTs grew out of the etching pit, they turned to be oriented growth to keep alignment gradually because of the effect of van der waals force. Consequently, the strong attachment of as-grown ANCTs to the etched Al substrate should employ “Plant growth” mechanism. At the beginning of the growth, the ACNTs have been planted into the etching pit of etched Al substrate to keep from being separated subsequently in case, just like the seeds were deeply rooted into the soil to avoid the following grown plants to be separated from the soil. In conclusion, the result indicated that reliable binder-free integration between the CNTs and the

etched Al foil could be achieved by the direct synthesis. It was reasonable to believe that there would be no more a reliability issue and an obstacle for long-term usage of ACNTs devices to a certain extent.

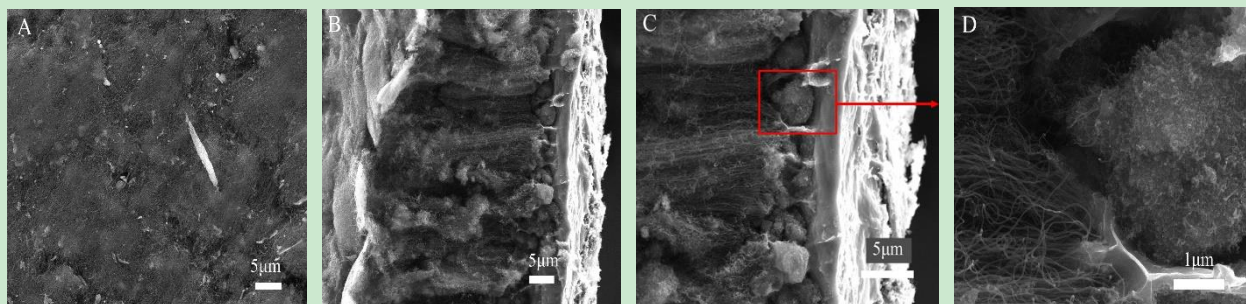


Fig.6 Top and side view SEM of ACNTs grown on etched Al foil after scraping by a blade, A- the top view of ACNTs, B-the side view of the ACNTs, C-the root ends morphology of ACNTs which directly attach to the etching pit of etched Al substrate, D-the higher magnification of the root ends of ACNTs which are embedded in the etching pit of the etched Al substrate

3.4 Electrochemical performance of as-grown ACNTs on etched Al foil

The original ACNTs grown on etched Al foil was hydrophobic greatly. Therefore, for the sake of improving the hydrophilicity of as-grown ACNTs to test the electrochemical performance in aqueous solution, electrochemical oxidizing pretreatment has been carried out in 1M Na₂SO₄ solution by galvanostatic electrolysis at the current density of 1.5 mA cm⁻² for 10min. Fig.7A displayed the CV measurements of a double-layer capacitance of ACNTs grown on etched Al foil at various scan rates. The approximating rectangular and symmetric shape of the CVs performed at high scan rate of 100 mV s⁻¹ suggested a fast ion diffusion facilitated by the patterned and aligned structure of the ACNTs and low contact resistance between the ACNTs and the etched Al foil substrate. The charging and discharging curves at different current densities were shown in Figure 7B. The symmetrical charging and discharging curves were almost linear in the total range of

potential, which showed a very good capacitive behavior of ACNTs. Traditionally, the way to lower the contact resistance between the nanotubes and collector electrodes in double layer capacitors was typically achieved by mixing nanotubes with conductive binders and coating this composite on the current collector electrodes. However, this process drastically modified the properties of CNTs electrode, leading to adverse effects on the electrochemical performance of the double layer capacitance, which was a major issue in developing CNTs-based supercapacitors. In our study, the ACNTs were directly grown on the current collector electrodes with great adhesion on the substrate. Therefore, it was more facilitative and no problem mentioned above would arise. The specific capacitance (C_{sp}) value for the ACNTs grown on etched Al foil was calculated from the CV measured at 5 mV s^{-1} (Fig.7A) and was found to be about 11.3 F g^{-1} . The facilitating ion diffusion, good adhesion and low contact resistance made the ACNTs grown on etched Al foil to be well suited for being as electrode alone or substrate for synthesizing composite materials which could be applied in supercapacitor as well as batteries, fuel cell. As a preferable substrate, ACNTs/etched Al foil have been served as a current collector for PANI and MnO_2 deposition. The electrochemical voltammetry performance of ACNTs/etched Al foil before and after PANI or MnO_2 coating were shown in Fig.8.

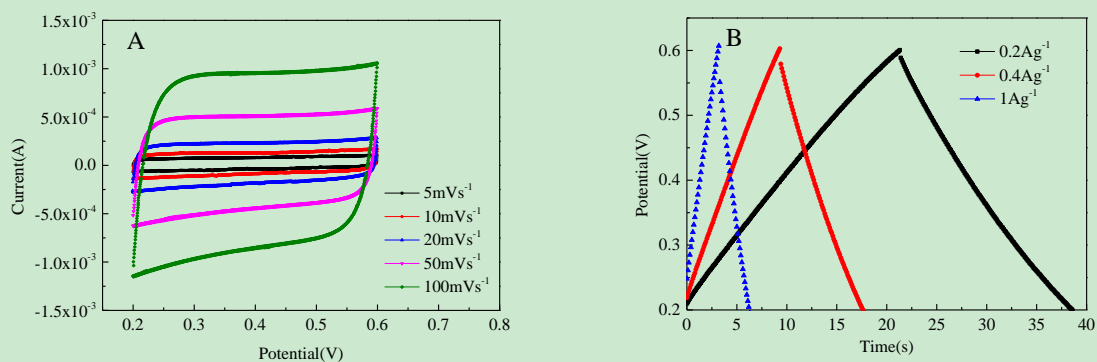


Fig.7 Electrochemical properties measured in 0.2M Na₂SO₄ solution. (A) Cyclic voltammograms measured for ACNTs grown on etched Al foil at scan rates ranging from 5 mV s⁻¹ to 100 mV s⁻¹; (B) Charge–discharge cycles taken at different current density of 0.2A g⁻¹, 0.4A g⁻¹ and 1A g⁻¹ (based on the mass of ACNTs).

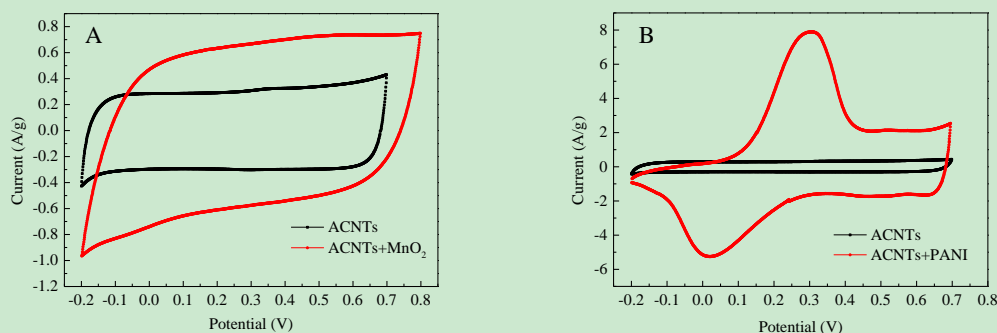


Fig.8 (A) CV curves of the ACNTs/etched Al foil and MnO₂/ACNTs-etched Al foil. (B) CV curves of the ACNTs/etched Al foil and PANI/ACNTs-etched Al foil.

The ACNTs before coating showed very small current response in the CV curve. In contrast, after depositing PANI or MnO₂ on the ACNTs, the PANI/ACNTs or MnO₂/ACNTs composites showed a much larger current density than the ACNTs alone, which indicated a great increase in the capacitance because of the redox reaction of PANI or MnO₂. The C_{sp} of PANI coating together with the ACNTs reached 488.2 F g⁻¹, and the C_{sp} of MnO₂ coating together with the ACNTs was 117.6 F g⁻¹. By growing PANI or MnO₂ directly onto the surface of ACNTs/etched Al foil which were served as a current collector, the interfacial resistance of the composite electrodes would reduce because they were all binder-free. Moreover, the ACNTs could not only enhance the mechanical property of PANI or increase the electrical conduction of MnO₂, but also optimized the electrolyte ion diffusion path for the redox reaction of the composite electrodes. Most important of all, the bind-free and 3D microscopically open structure of composite materials would make the advantages of the PANI, MnO₂, ACNTs-etched Al foil be fully utilized.

3.5 The thermal dissipation performance of ACNTs grown on etched Al foil

ACNTs have been known for their excellent thermal dissipation property. Herein, ACNTs were grown directly on etched Al foil with good adhesion forming a single-step composite for thermal dissipation. For demonstrating the thermal dissipation performance of as-grown ACNTs/etched Al foil composite, the temperature variation testing experiment of a LED light after being turned on was designed. The schematic illustration of the experiments was shown in Fig.9. The structure designed for the experiments was consisted of a thermometer chip mounted on a fixed position of the backboard of a 24W LED light. And silicone thermal conductive adhesive was used to make sure that the ACTNs/etched Al foil composite was mounted on the LED backboard tightly. Reference measurements were also done without anything being pasted on or only with etched Al foil being stuck on the backboard of LED respectively, but otherwise under the same conditions. The ambient temperature stabilized at 25°C during the testing process for all the experiments.

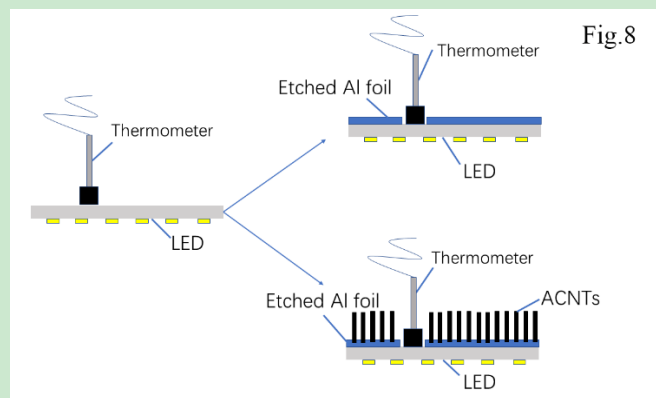


Fig.9 A schematic illustration of testing process of the temperature variation of LED light after being turned on, which was without and with the etched Al or ACNT/etched Al foil as thermal dissipation substrate being attached on.

In the experiments, the temperature of the backboard of LED light increased rapidly after it was turned on, as shown in Fig.10. It took 273s for the temperature of LED backboard increasing from 30°C to 82°C, while after the etched Al foil being pasted on the backboard of LED, it spent

287s for the same temperature increasing process (as shown in the inset table of Fig.10). The final stable working temperature of LED backboard with and without etched Al foil being pasted on was 106.8°C and 106.3°C respectively. Almost the same temperature increasing rate (From 30°C to 82°C) and final stable working temperature of LED with and without etched Al foil being pasted on indicated that the thermal dissipation performance was almost no difference between these two testing conditions. However, after the ACNTs/etched Al foil composite being mounted on the backboard of LED, it took 1192s for the temperature increasing from 30°C to 82°C. The working temperature increasing rate (From 30°C to 82°C) was much slower than without ACNTs/etched Al being pasted on. Moreover, the final stable working temperature of LED with ACNTs/etched Al foil being mounted on was 82.3°C, which was also much lower than without ACNTs/etched Al composite being mounted on the LED, comparatively. Obviously, efficient cooling performance for LED light with ACNTs/etched Al foil composite being pasted on during its working process was achieved. The microfin structures and excellent thermal conductivity of aligned carbon nanotube arrays enabled efficient thermal dissipation from the heated backboard of LED light which was also suitable for other modern electronics thermal dissipation application and so on. The as-grown ACNTs having great adhesion on etched Al substrate were more light, flexible, high surface area to volume ratio together with the high heat transfer coefficient at the same time which was mechanically and physically superior compared to some other thermal dissipation materials. All those properties accompanied with the relatively simple fabricating method made the ACNTs/etched Al foil composites to be a strong candidate for future thermal management applications.

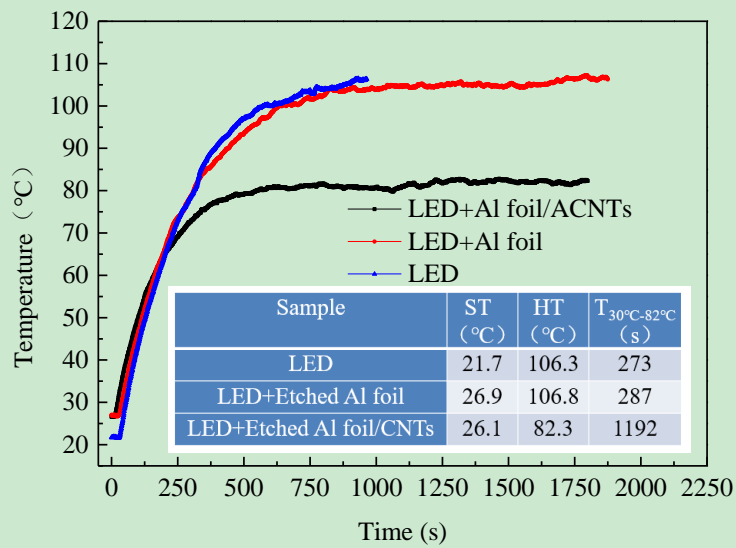


Fig.10 After it was turned on, the temperature variation of LED light, and the LED light with ACNTs/etched Al foil composites or etched Al foil being as thermal dissipation materials as function of time. The inset table was the final stable temperature and the temperature increasing time from 30°C-82°C of LED with and without ACNTs/etched Al foil composites or etched Al foil

Note: ST- The temperature was tested at the beginning of turning on the LED light,

HT- The final stable highest temperature value of the LED light reached after it turned on,

T_{30°C-80°C}- Time for the temperature of LED light increased from 30°C to 82°C.

4. Conclusion

In conclusion, this paper present that directly plant aligned carbon nanotube arrays on etched Al foil with high peel strength and low contact resistance in one-step by floating-catalyst CVD method. The etching pit surface structure of Al foil was advantageous both for CNTs growth and the root ends of as-grown CNTs being embedded into the micro-pit on the surface to keep great adhesion between each. The good electrical and thermal dissipation performance of the ACNTs/etched Al foil have been demonstrated that the excellently mechanical, electrical and thermal end-contaction dense bundles of ACNTs/etched Al foil composites were promising candidates for application in electrode, thermal dissipation materials and so on. In addition, for

optimal performance of the as-grown ACNTs/etched Al foil material, post-synthesis of metal elements, oxide, polymer material on the ACNTs/etched Al substrate to take full advantages of different materials to generate better synergistic effects was realizable. The advantage of directly growing ACNTs on etched Al foil with high peel strength was not only every individual carbon nanotube electrically and thermally end-connected in situ, but also demonstrated the feasibility of scalable production technique, long-term usage and reliability of ACNTs/etched Al foil composites, which would overcome several obstacles to the applications in energy storage devices, heat transfer and thermal management field.

Acknowledgment

This work was financially supported by Zhengzhou Non-ferrous Metals Research Institute Co.Ltd of CHALCO, the project funded by CHALCO.

References

- [1] S. Iijima, Helical microtubules of graphitic carbon, *Nature*. 354 (1991) 56.
<http://dx.doi.org/10.1038/354056a0>.
- [2] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes, *Science* (80-.). 306 (2004) 1362–1364. doi:10.1126/science.1104962.
- [3] D.F. Kenji Hata, Ijima, Yumura, (19) *United States* (12), 1 (2009). doi:US 2010/0311130 Al.
- [4] C. Wang, K. Takei, T. Takahashi, A. Javey, Carbon nanotube electronics – moving forward, *Chem. Soc. Rev.* 42 (2013) 2592–2609. doi:10.1039/C2CS35325C.
- [5] X. Wang, Z. Liu, Carbon nanotubes in biology and medicine: An overview, *Chinese Sci. Bull.* 57 (2012) 167–180. doi:10.1007/s11434-011-4845-9.

- [6] W. Lu, R. Hartman, L. Qu, L. Dai, Nanocomposite Electrodes for High-Performance Supercapacitors, (2011) 655–660.
- [7] W. Lu, L. Qu, K. Henry, L. Dai, High performance electrochemical capacitors from aligned carbon nanotube electrodes and ionic liquid electrolytes, *J. Power Sources*. 189 (2009) 1270–1277.
- [8] G. Yu, X. Xie, L. Pan, Z. Bao, Y. Cui, Hybrid nanostructured materials for high-performance electrochemical capacitors, *Nano Energy*. 2 (2013) 213–234.
- [9] H. Zhou, F. Lou, P.E. Vullum, M.-A. Einarsrud, D. Chen, F. Vullum-Bruer, 3D aligned-carbon-nanotubes@ Li₂FeSiO₄ arrays as high rate capability cathodes for Li-ion batteries, *Nanotechnology*. 24 (2013) 435703.
- [10] F. Lou, H. Zhou, F. Huang, F. Vullum-Bruer, T.D. Tran, D. Chen, Facile synthesis of manganese oxide/aligned carbon nanotubes over aluminium foil as 3D binder free cathodes for lithium ion batteries, *J. Mater. Chem. A*. 1 (2013) 3757–3767. doi:10.1039/c3ta00793f.
- [11] Y. Shen, Z. Xia, Y. Wang, C.K. Poh, J. Lin, Pt coated vertically aligned carbon nanotubes as electrodes for proton exchange membrane fuel cells, *Procedia Eng.* 93 (2014) 34–42. doi:10.1016/j.proeng.2013.11.037.
- [12] P. Sehwat, C. Julien, S.S. Islam, Carbon nanotubes in Li-ion batteries: A review, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 213 (2016) 12–40. doi:10.1016/j.mseb.2016.06.013.
- [13] T. Ji, Y. Feng, M. Qin, W. Feng, Thermal conducting properties of aligned carbon nanotubes and their polymer composites, *Compos. Part A Appl. Sci. Manuf.* 91, Part 1 (2016) 351–369. doi:http://doi.org/10.1016/j.compositesa.2016.10.009.
- [14] M. Dharmendra, S. Suresh, C.S. Sujith Kumar, Q. Yang, Pool boiling heat transfer

enhancement using vertically aligned carbon nanotube coatings on a copper substrate, *Appl. Therm. Eng.* 99 (2016) 61–71. doi:10.1016/j.applthermaleng.2015.12.081.

- [15] B. Liu, C. Wang, J. Liu, Y. Che, C. Zhou, Aligned carbon nanotubes: from controlled synthesis to electronic applications., *Nanoscale*. 5 (2013) 9483–502. doi:10.1039/c3nr02595k.
- [16] S. Talapatra, S. Kar, S.K. Pal, R. Vajtai, L. Ci, P. Victor, M.M. Shaijumon, S. Kaur, O. Nalamasu, P.M. Ajayan, Direct growth of aligned carbon nanotubes on bulk metals:, *Nat. Nanotechnol.* 1 (2006) 112–116. doi:10.1038/nnano.2006.56.
- [17] S.P. Patole, H.I. Kim, J.H. Jung, A.S. Patole, H.J. Kim, I.T. Han, V.N. Boraskar, J.B. Yoo, The synthesis of vertically-aligned carbon nanotubes on an aluminum foil laminated on stainless steel, *Carbon N. Y.* 49 (2011) 3522–3528. doi:10.1016/j.carbon.2011.04.051.
- [18] W. Lin, R. Zhang, K.S. Moon, C.P. Wong, Molecular phonon couplers at carbon nanotube/substrate interface to enhance interfacial thermal transport, *Carbon N. Y.* 48 (2010) 107–113. doi:10.1016/j.carbon.2009.08.033.
- [19] R. Yu, W. Fan, X. Guo, S. Dong, Highly ordered and ultra-long carbon nanotube arrays as air cathodes for high-energy-efficiency Li-oxygen batteries, *J. Power Sources*. 306 (2016) 402–407. doi:10.1016/j.jpowsour.2015.12.042.
- [20] S. Dörfler, I. Felhösi, T. Marek, S. Thieme, H. Althues, L. Nyikos, S. Kaskel, High power supercap electrodes based on vertical aligned carbon nanotubes on aluminum, *J. Power Sources*. 227 (2013) 218–228. doi:http://dx.doi.org/10.1016/j.jpowsour.2012.11.068.
- [21] Y. Wu, C.H. Liu, H. Huang, S.S. Fan, Effects of surface metal layer on the thermal contact resistance of carbon nanotube arrays, *Appl. Phys. Lett.* 87 (2005) 1–3. doi:10.1063/1.2133916.

- [22] C.C. Su, S.H. Chang, Effective growth of vertically aligned carbon nanotube turfs on flexible Al foil, *Mater. Lett.* 65 (2011) 2700–2702. doi:10.1016/j.matlet.2011.05.012.
- [23] I. Lahiri, D. Lahiri, S. Jin, A. Agarwal, W. Choi, Carbon nanotubes: How strong is their bond with the substrate?, *ACS Nano*. 5 (2011) 780–787. doi:10.1021/nn102900z.
- [24] H.C. Shim, Y.K. Kwak, C.-S. Han, S. Kim, Enhancement of adhesion between carbon nanotubes and polymer substrates using microwave irradiation, *Scr. Mater.* 61 (2009) 32–35. doi:10.1016/j.scriptamat.2009.02.060.
- [25] P. Jampani, a. Manivannan, P.N. Kumta, Advancing the Supercapacitor Materials and Technology Frontier for Improving Power Quality, *Electrochem. Soc. Interface*. 19 (2010) 57–62. https://www.electrochem.org/dl/interface/fal/fal10/fal10_p057-062.pdf.
- [26] I. Lahiri, D. Lahiri, S. Jin, A. Agarwal, W. Choi, Carbon Nanotubes: How Strong Is Their Bond with the Substrate?, *ACS Nano*. 5 (2011) 780–787. doi:10.1021/nn102900z.
- [27] S.M. Ubnoske, E.J. Radauscher, E.R. Meshot, B.R. Stoner, C.B. Parker, J.T. Glass, Integrating carbon nanotube forests into polysilicon MEMS: Growth kinetics, mechanisms, and adhesion, *Carbon N. Y.* 113 (2017) 192–204. doi:10.1016/j.carbon.2016.11.047.
- [28] M.M. Shaijumon, F.S. Ou, L. Ci, P.M. Ajayan, Synthesis of hybrid nanowire arrays and their application as high power supercapacitor electrodes, *Chem. Commun.* (2008) 2373. doi:10.1039/b800866c.
- [29] W. Lin, R. Zhang, K.S. Moon, C.P. Wong, Synthesis of high-quality vertically aligned carbon nanotubes on bulk copper substrate for thermal management, *IEEE Trans. Adv. Packag.* 33 (2010) 370–376. doi:10.1109/TADVP.2009.2034335.
- [30] H.-C. Su, C.-H. Chen, Y.-C. Chen, D.-J. Yao, H. Chen, Y.-C. Chang, T.-R. Yew, Improving the adhesion of carbon nanotubes to a substrate using microwave treatment, *Carbon N. Y.* 48

(2010) 805–812. doi:<http://dx.doi.org/10.1016/j.carbon.2009.10.032>.

- [31] S.C. Lim, H.K. Choi, H.J. Jeong, Y. Il Song, G.Y. Kim, K.T. Jung, Y.H. Lee, A strategy for forming robust adhesion with the substrate in a carbon-nanotube field-emission array, *Carbon* N. Y. 44 (2006) 2809–2815. doi:[10.1016/j.carbon.2006.03.030](https://doi.org/10.1016/j.carbon.2006.03.030).
- [32] L. Zhu, Y. Sun, D.W. Hess, C.P. Wong, Well-aligned open-ended carbon nanotube architectures: An approach for device assembly, *Nano Lett.* 6 (2006) 243–247. doi:[10.1021/nl052183z](https://doi.org/10.1021/nl052183z).
- [33] D. Chen, Towards the upper bound of electrochemical performance of ACNTs@polyaniline arrays as supercapacitors, *Energy & Environmental Science* 2 (2014). doi:[10.1039/C1EE01989A](https://doi.org/10.1039/C1EE01989A).