5th International Biennial Conference on Ultrafine Grained and Nanostructured Materials, UFGNSM15

Growth of Carbon Nano Tubes on Copper Substrate Suitable for Lithium Ion Battery Anode

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Abstract

We report formation of vertically aligned carbon nanotube on copper substrate. Carbon nanotubes with diameter around 30 nm and height of 0.3 µm are grown on a 100 µm copper foil. This growth was made possible by deposition of a barrier layer from Chromium. Having CNTs on a highly conductive substrate like Copper have many application in different energy devices and sensors. Using this structure as an anode, lithium ion battery have been fabricated, and specific capacity of 120 mAh/g was obtained after 30 cycles.

1. Introduction

Carbon nanotubes have unique mechanical and electronic properties, Wang et al. (1998), Qian-Gang et al. (2006), Collins and Zettl (1996), Dai (2002). These structures found applications in many research fields such as sensors, actuators, lightweight electromagnetic shields and many energy devises like super-capacitors and Lithium ion batteries, De Volder et al. (2013), Raffaelle et al. (2001). In recent years many researches have been focused on

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formation of carbon nanotubes directly on a conductive substrate. This would improve the performance of CNT based integrated circuits, sensors and energy devices, because of reducing the parasitic resistances. Among different conductive substrates, copper is an excellent choice for its high electrical and thermal conductivity, combined with a low economical cost, Li et al. (2009).

Among different CNT growth approaches, CVD is one of the most used techniques, Dahn et al. (2007). If CNT growth on Copper substrate with CVD method is desired, some problems can deteriorate achieving a proper growth. The main reasons for this might be the following: (i) The metal catalyst particles might diffuse into the base metal substrate at the elevated temperatures of the CVD process and will lose their catalytic function. (ii) High roughness of the copper surface might result in heterogeneous nucleation and may cause formation of discontinuous intermediate layers. This might influence the catalyst particle size distribution, thus affecting on the CNT growth. (iii) Copper can be easily oxidized above 300 °C in an air ambient during the catalyst annealing procedure, causing poor adhesion to the catalyst multilayers and the CNTs grown on it, Li et al. (2009).

One of the important applications of CNTs is in energy devices like Lithium ion batteries. CNT can improve the performance of electrodes of lithium ion batteries, Wu et al. (2014). In industrial lithium ion batteries, usually graphitic carbon electrodes are used as the anode, because of the safety and cycle efficiency, Dubose et al. (1995). But its specific capacity is limited to 375 mAh/g, Wu et al. (2014). If CNTs are used as the anode, higher specific capacitance in comparison with graphite can be obtained. Lithium ion can intercalate both into the channel between the nanotubes, and into the interior of the nanotubes themselves, Zhou et al. (2004). These mechanisms enhance the specific capacity of electrodes made by CNTs in compare with graphitic electrodes.

The present study concentrates on growing vertically aligned CNTs on a pure Cu substrate using DC-PECVD technique. Selecting a proper barrier layer between the Ni catalyst layer and Copper substrate, enables the growth of vertically aligned CNTs on this conductive substrate. The CNTs on Copper structure was used for fabrication of a lithium ion battery to examine its properties as an anode material. The fabricated battery was tested for 30 cycles and the CNTs show specific capacitance of 3315 mAh/g in the first cycle and 120 mAh/g after 30th cycle.

2. Experimental details

Commercial Cu foil with a thickness of 0.1 mm (purity: 99.7% Cu) was used in the present experiment. First, the Cu foil was cleaned by washing with deionized water (DI water), immersing in 10% HCl solution for 2 minutes, rinsing in DI water and drying with air flow. For CNT growth, the copper substrate was placed in an E-beam evaporation system and 3 nm of Ni catalyst layer was deposited on its surface. We have previously determined the parameters for growth of vertically aligned CNTs on Ni/Silicon substrate using a DC-PECVD system. But using the same process as CNT growth on Ni deposited silicon substrate, did not result in growth of CNTs on Ni coated Copper foil. The reason for these different behaviors is that the temperature involved in CNT growth by DC-PECVD activates the diffusion of the Ni catalyst material into the copper substrate, which would inhibit its activity. To overcome this problem, one possible strategy is the deposition of a thick catalyst layer (in the order of hundreds of nanometers), so part of the catalyst coating remains unaffected by diffusion during the process. Nevertheless, control over nucleation was difficult, and no dense arrays of CNTs were obtained. Alternatively, we have deposited an electrically conductive thin barrier layer between the copper substrates and the Ni catalyst layer, in order to achieve suitable surface conditions for a high nucleation density, combined with good electrical contact between the CNTs and the copper. It was observed that using a proper thickness of Chromium layer as a barrier layer between the copper substrate and the Ni catalyst layer can result in the growth of dense arrays of vertically aligned CNTs. Using an E-beam evaporation system, 50 nm of Cr and 3 nm of Ni thin film layer were deposited on the Copper substrate as the barrier layer and the catalyst, respectively. After this step, DC Plasma Enhanced Chemical Vapor Deposition (DC-PECVD) process was performed for CNT growth. In this system, upon heating to 680 °C under a hydrogen atmosphere, the Ni film was annealed. The hydrogen flow rate during the annealing process was set to 15 sccm. After one hour of annealing, hydrogen plasma with DC bias of about 600 V and current density of 3 mA/cm² was applied for 8 minutes. As a result, the Ni catalyst layer was activated and Ni nanoparticle islands were formed on the surface of sample. Then, C2H2 gas with the flow rate of 4.5 to 5.5 sccm was added to the chamber. In this stage, The DC plasma voltage with the voltage of about 700 V and the corresponding current density around 3 mA/cm² was
applied to the sample for 15 minutes. At the end of the growth period, samples were slowly cooled, within the furnace, under H₂ gas environment.

After proper growth of CNTs on Copper substrate was obtained, it was used as the anode material in a Lithium ion battery. For this experiment CNTs grown on Copper foil was used as one electrode while Lithium foil was implemented as the other electrode of the battery. A polypropylene film was used as the separator, which was placed between these two electrodes to isolate them from each other. The battery electrolyte consist of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 wt) solution.

3. Results and discussion

SEM images of CNTs grown on copper substrate with different growth parameters are shown in Fig. 1. The result of CNT growth on 3nm Ni/50 nm Cr/Copper substrate is illustrated in part (a) of this figure. It can be seen that CNT growth had occurred for this sample, but the density of CNTs on the surface is low. Increasing the C₂H₂ flow rate in the growth process from 4.5 sccm to 5.5 sccm results in denser vertically aligned CNTs as can be seen in Fig. 1b. For comparison, the result of performing growth process on the sample without Cr barrier layer is illustrated in Fig. 1c. It is clear that no CNT growth was occurred in this case. The growth parameters for the sample in part (b) was used as the best condition among other tested experiments. Carbon nanotubes with diameter around 30 nm and height of 0.3 µm are grown on this sample.

![SEM images of CNTs grown on copper substrate with different growth parameters](image)

Fig. 1. SEM images of some of the different conditions for growth of CNTs. (a) 3 nm Ni/ 30 nm Cr/ Cu substrate. In the growth process C₂H₂ flow rate was 4.5 sccm for this sample; (b) 3 nm Ni/ 30 nm Cr/ Cu substrate. C₂H₂ flow rate was set to 5.5 sccm in this case. High density vertically aligned CNTs are obtained with this growth parameters; (c) The result of growth process on the sample without Cr barrier between the Ni catalyst layer and Cr substrate. No CNT growth was occurred on the surface.

After proper growth condition for CNTs on copper substrate was obtained as was illustrated in Fig. 1b, Lithium ion battery was fabricated using CNTs as one of the battery electrodes and Copper as an excellent conductor that would serve as the current collector of the battery. The schematic of the fabricated lithium ion battery can be seen in Fig. 2.
Figure 3 shows the galvanostatic charge-discharge curves for the fabricated battery with the CNTs on Copper foil, in the voltage range of 0.1 to 3.3 V. As can be seen in this figure, at the end of the first discharge cycle, large amount of specific capacity around 3315 mAh/g was obtained which was reduced in the next cycles. This large irreversible capacity in the first discharge process, can be related to the formation of Solid-Electrolyte-Interface (SEI) during the first cycle.

The cycling performances of CNTs on Cu substrate are shown in Figure. 4. It can be seen that after the 10th cycle, the capacity reaches an approximately constant value. At the end of the 30th cycle the charge capacity is 120 mAh/g.

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**Fig. 2.** schematic of (a) CNTs grown on Cu substrate; (b) configuration of the fabricated lithium ion battery based on CNTs on Copper foil.

**Fig. 3.** Profiles for the galvanostatic charge-discharge curve.

**Fig. 4.** Specific capacity as a function of cycle number for both charge and discharge cycles.
In addition, columbic efficiency is shown in Fig. 5, which shows that the fabricated battery has a columbic efficiency of more than 60% after 30 cycles.

![Columbic Efficiency Graph](image)

**Fig. 5.** Columbic efficiency as function of cycle number.

### 4. Conclusion

In summary, a proper condition for growth of carbon nanotubes on Copper surface was achieved. This growth was possible by deposition of a thin layer of Cr as a barrier layer on Cu substrate. The grown carbon nanotubes are fabricated on a highly conductive substrate, which enables implementing them in many modern applications such as anodes of Lithium ion batteries. This structure has been used for fabrication of a lithium ion battery, showing specific capacitance of 120 mAh and columbic efficiency of 60% after 30 cycles.

### Acknowledgements

The authors would like to thank Professor Mohajerzadeh and Dr. Samaneh Soleimani for their technical assistance. This work was funded by INSF.

### References


