Facile and High-Throughput Fabrication of Carbon Nanotube Carpet-PDMS Structures toward Flexible Supercapacitors

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ABSTRACT

Flexible electronics have a wide range of applications in wearable and multifunctional electronics. Consequently, technologies for flexible energy storage need to be developed for flexible electronic devices. Here, we develop a facile fabrication technique utilizing vertically aligned carbon nanotubes (VACNTs), which enables high-throughput fabrication of flexible supercapacitors. Our unique technique ensures a strong adhesion between VACNTs and polydimethylsiloxane (PDMS), which facilitates a stable charge/discharge under varied strains. The measured capacitance is 170 μF/cm² at a high scanning rate of 1 V/s. In addition, the strong adhesion between VACNTs and PDMS enables the structure to sustain various bending strains. The capacitance under bending strains was found to be consistent under the bending angle varying from 0 to 180 degrees.

Keywords: flexible supercapacitors; vertically aligned carbon nanotubes; PDMS; fabrication process

1 INTRODUCTION

Energy storage devices are of great importance for society development. Supercapacitors have a much higher power density (from 5 to 55kW/kg) than Li-ion battery (from 0.4-3 kW/kg), which makes supercapacitors ideal for high power demanding devices, such as regenerative braking and load leveling systems [1]. Typically, supercapacitors can exhibit extremely high cycle stability and can be charged in seconds [2], and therefore supercapacitors have great potential to complement batteries and electrolytic capacitors in a variety of applications.

Electrical double-layer capacitors (EDLCs) are one type of supercapacitors, in which the electrode surface area plays a crucial role in the performance of a supercapacitor. To date, many different kinds of carbon materials, such as activated carbon [3], carbon fibers [4], carbon aerogels [5], graphene [6,7], and carbon nanotubes [8,9] have been utilized for fabricating EDLCs. High surface area, high electrical conductivity, high mesoporosity, and high electrolyte accessibility are the important properties desired for an ideal electrode material [10]. Carbon Nanotubes are promising electrode materials for supercapacitors owing to their excellent mechanical, electrical, and optical properties. The accessible mesopores in carbon nanotubes are responsible for the good capacitance properties [11,12] and vertically aligned nanotubes in VACNTs allow easier access for electrolyte ions to form an electrical double layer. Besides, the vertically aligned structure indicates a combined charge capacity from all individual tubes, which will enhance the effective surface area and energy density for the supercapacitors [13].

The conventional supercapacitors are too bulky and rigid to meet the requirements of small, thin, light-weight, environmentally friendly, and mechanical compliance for flexible and portable electronics [11,12,14]. Therefore, the recent research on flexible supercapacitors has heavily focused on the mechanical flexibility with the high electrochemical properties while following the significant trend of portable and wearable electronics [11]. Several fabrication methods have been studied to fabricate flexible supercapacitors. Flexible supercapacitors based on different structures with different materials have been discussed, such as reduced graphene oxide (rGO)/single-walled carbon nanotubes (SWNTs) [14], single-walled carbon nanotube films with continuous reticulated architecture [9], hierarchically structured carbon nanotube-graphene fibres [15], three-dimensional carbon nanostructure with vertically aligned carbon nanotubes on carbon nanofibers [16], nanostructured graphene composite papers [17], highly aligned carbon nanotube sheets [18], graphite oxide films wrote by direct laser [19], crumpled graphene papers [6], and wrinkled graphene [7].

The fabrication of flexible supercapacitors in large quantities is known to be complicated and needs a lot of handwork [6,7,18]. For example, to apply electrode materials onto flexible substrates, researchers use direct coatings which heavily relies on the physical adhesion of the electrode materials on the substrate [11] or stacking the electrode and electrolyte to construct the structures [7,9]. A key problem is that the electrode/substrate interface delaminates under large strain, which seriously limits the flexibility of supercapacitors [15,18,19].

In this work, we demonstrate a facile fabrication process to create a flexible supercapacitor based on a VACNTs-PDMS structure with ionic-liquid electrolytes. We utilize PDMS as a flexible substrate and transfer VACNTs onto partially cured PDMS. The VACNTs-PDMS structure acts as an electrode for flexible supercapacitors. After assembling the electrode with liquid or solid electrolyte, the flexible supercapacitors can be integrated into flexible electronics as energy storage devices. This fabrication process allows the construction of flexible VACNT-PDMS structures operable under large strains (stretching, bending, and twisting).

2 EXPERIMENTAL SECTION

2.1 VACNTs Growth Process

The substrate of Si chip with 5 nm Al and 3 nm Fe as catalyst deposited on the surface was prepared by physical vapor deposition (PVD). Then the substrate was placed in atmosphere pressure chemical vapor deposition (APCVD) chamber. The furnace temperature was increased to 750˚C with 500 sccm Ar flow. VACNTs were grown at 750˚C for 15 minutes with 60 sccm H_2 and 100 sccm C_2H_4. Then the chamber was cooled down to room temperature while keeping Ar flowing. The CVD setup and recipe are shown in Fig.1. The structure and morphology of the VACNTs were characterized by scanning electron microscopy (SEM).

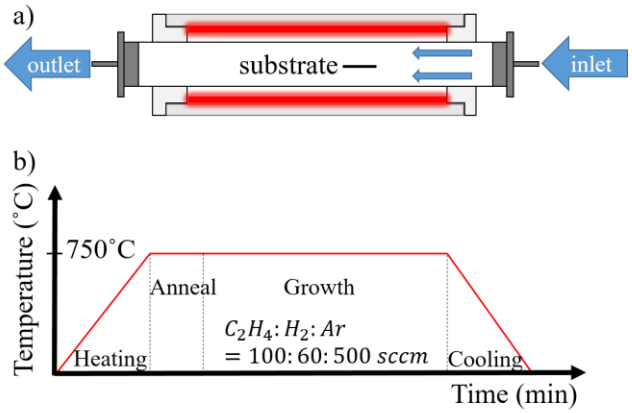

Figure 1: a) APCVD setup and b) Recipe.

2.2 Transfer of VACNTs onto PDMS

In order to achieve a good transfer of VACNTs, we developed a directly transfer method. To form a PDMS substrate, a liquid mixture of PDMS base and curing agent (Sylgard 184 Silicone Elastomer, Dow Corning) were mixed with a ratio of 10:1 and degassed under reduced pressure in a vacuum pump to remove bubbles. Then the liquid PDMS was heated on a hot plate at 65˚C for about 30 minutes before it was fully cured. The VACNTs sample was placed face-to-face onto the almost cured PDMS. The liquid PDMS infiltrated between carbon nanotubes, which ensured a strong adhesion between PDMS and VACNTs where the viscoelastic property of PDMS provided strong adhesion between VACNTs and PDMS. After PDMS was fully cured, the VACNTs with PDMS can be peeled off from original SiO_2 substrate slowly because of the stronger adhesion between PDMS and VACNTs than that between VACNTs and SiO_2 substrate. This strong adhesion will enable the VACNT-PDMS structure to sustain larger strain. Figure 2 schematically shows the transfer procedures. As the SEM images before and after transferred shown in Figure 3, VACNTs were successfully transferred onto PDMS.

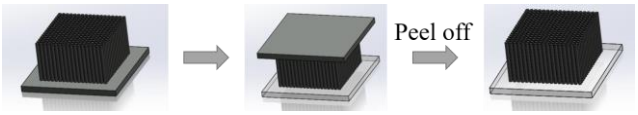

Figure 2: Transfer process schematic.

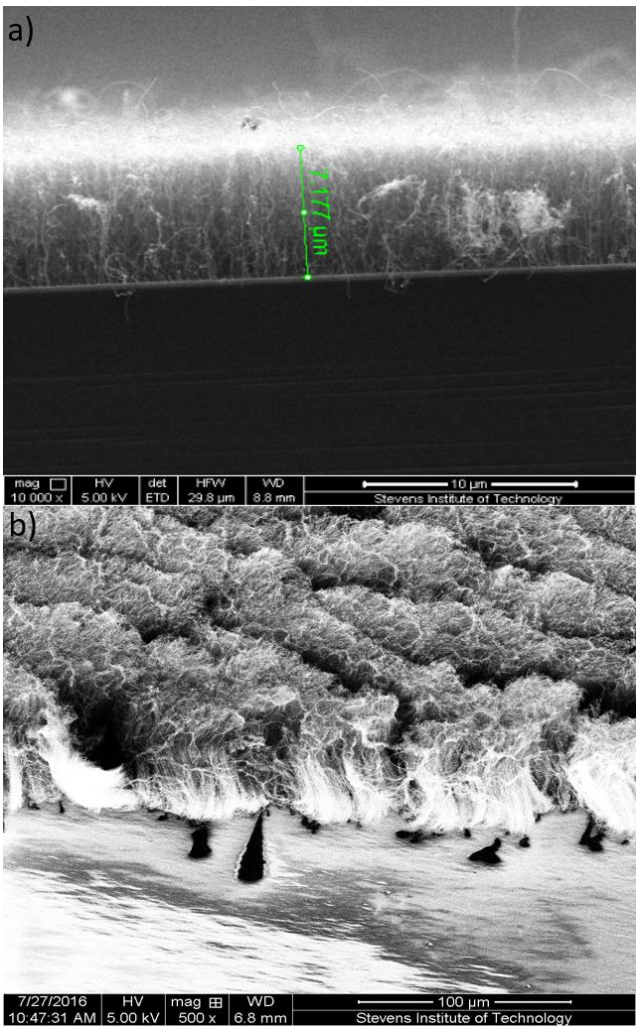

Figure 3: SEM images of a) VACNTs grown on SiO_2 substrates via APCVD, b) VACNTs on PDMS substrates.

2.3 Electrochemical Characterization

The electrochemical behavior was characterized using cyclic voltammetry (CV) in a three electrode configuration. The VACNTs was used as an electrode in the flexible supercapacitor. Platinum (Pt) foil was used as a counter electrode and Ag/AgCl (sat. KCl) as the reference electrode. CV measurements were performed within the

potential range of 0.0V-0.5V as scan rates of 50-1000 mV/s. The capacitances of the electrodes were calculated as a capacitance per area (F/cm^2). The average capacitance was normalized per area of the samples and was estimated according to the following equation [18,20,21]:

$$C = \frac{\int_{E_1}^{E_2} I\, dV}{\Delta V \times A} \quad (1)$$

where I is the current, A is the area of the supercapacitor, ΔV is the scanning rate, and E_1 and E_2 are the voltage.

The actual performance of a supercapacitor is usually measured by the power density and the energy density. Here, the power density is directly related to the rate at which energy can be transferred from the supercapacitor, while the energy density is the amount of energy stored per unit area of the supercapacitor in our case [11]. The average power during discharge was calculated by integrating the current density (I) versus voltage curves [18,20,21]:

$$P = \frac{1}{V \times A}\int_0^V I \times V dV \quad (2)$$

where V is the initial voltage during discharge. The discharged energy (E, in Wh) was obtained using equation [18,20,21]:

$$E = \frac{1}{3600\Delta V \times A}\int_0^V I \times V dV \quad (3)$$

2.4 Flexibility Test

To evaluate the flexibility and durability, we performed both the tensile strain measurements and the bending strain measurements. The structure was stretched from 0% to 20% and bent from 0 to 180 degree.

3 RESULTS AND DISCUSSION

Figure 4 shows the cyclic voltammetry (CV) curves recorded at a scanning rate of 1 V/s in 30% KOH solution. As can be seen, the structure showed good electrochemical stability and capacitive behaviors at scanning rate from 50 mV/s to 1 V/s. The capacitance can be calculated to be 170 μF/cm² at 1 . Figure 5 shows the CV curves of the structure at tensile and bending states. The results indicates that the supercapacitor exhibits a good flexibility under mechanial deformations.

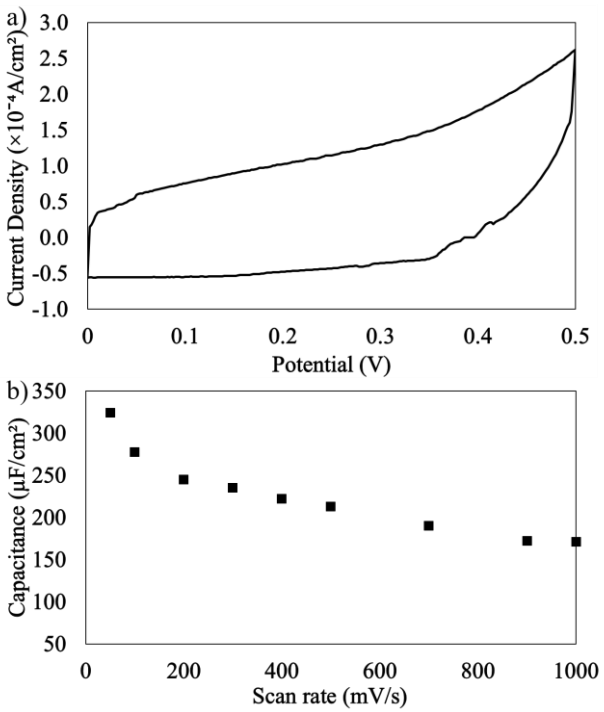

Figure 4: Electrochemical properties. a) Cyclic voltammetry curves of the flexible supercapacitors at a scan rate of 1 V/s. b) Dependence of capacitance on the scan rate from 50 mV/s to 1 V/s.

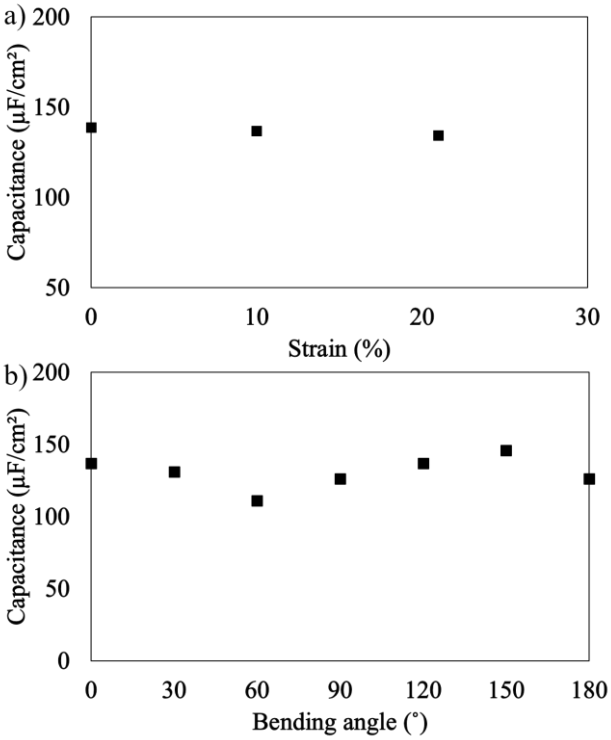

Figure 5: Flexibility and strechability. a) Performance under stretching strains from 0% to 20%. b) Performance under bending angles ranging from 0 to 180 degrees.

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4 CONCLUSION

We have demonstrated the facile fabrication process of the flexible supercapacitors using VACNTs on PDMS substrate. The direct transfer of VACNTs onto PDMS enables to fabricate flexible supercapacitors in large size with good electrochemical properties and flexibility. Our structure shows a high flexibility and stability under stretching to 20% and bending up to 180 degree. Therefore, these flexible supercapacitors are promising for applications in various flexible electronics.

REFERENCES

[1] X. Li and B. Wei, "Supercapacitors based on nanostructured carbon," *Nano Energy*, **2** (2), 159–173 (2013).

[2] P. Kanninen, N. D. Luong, I. V Anoshkin, A. Tsapenko, J. Seppälä, A. G. Nasibulin, T. Kallio, and others, "Transparent and flexible high-performance supercapacitors based on single-walled carbon nanotube films," *Nanotechnology*, **27** (23), 235403 (2016).

[3] J. Gamby, P. L. Taberna, P. Simon, J. F. Fauvarque, and M. Chesneau, "Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors," *Journal of power sources*, **101** (1), 109–116 (2001).

[4] L.-F. Chen, Z.-H. Huang, H.-W. Liang, W.-T. Yao, Z.-Y. Yu, and S.-H. Yu, "Flexible all-solid-state high-power supercapacitor fabricated with nitrogen-doped carbon nanofiber electrode material derived from bacterial cellulose," *Energy & Environmental Science*, **6** (11), 3331–3338 (2013).

[5] J. Li, X. Wang, Q. Huang, S. Gamboa, and P. J. Sebastian, "Studies on preparation and performances of carbon aerogel electrodes for the application of supercapacitor," *Journal of Power Sources*, **158** (1), 784–788 (2006).

[6] J. Zang, C. Cao, Y. Feng, J. Liu, and X. Zhao, "Stretchable and high-performance supercapacitors with crumpled graphene papers," *Scientific reports*, **4**, 6492 (2014).

[7] T. Chen, Y. Xue, A. K. Roy, and L. Dai, "Transparent and stretchable high-performance supercapacitors based on wrinkled graphene electrodes," *Acs Nano*, **8** (1), 1039–1046 (2013).

[8] L. Dai, D. W. Chang, J.-B. Baek, and W. Lu, "Carbon nanomaterials for advanced energy conversion and storage," *small*, **8** (8), 1130–1166 (2012).

[9] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, and S. Xie, "Highly Stretchable, Integrated Supercapacitors Based on Single-Walled Carbon Nanotube Films with Continuous Reticulate Architecture," *Advanced Materials*, **25** (7), 1058–1064 (2013).

[10] W. Lu and L. Dai, *Carbon nanotube supercapacitors*. INTECH Open Access Publisher, 2010, (2010).

[11] W. K. Chee, H. N. Lim, Z. Zainal, N. M. Huang, I. Harrison, and Y. Andou, "Flexible graphene-based supercapacitors: a review," *The Journal of Physical Chemistry C*, **120** (8), 4153–4172 (2016).

[12] T. Chen and L. Dai, "Flexible supercapacitors based on carbon nanomaterials," *Journal of Materials Chemistry A*, **2** (28), 10756–10775 (2014).

[13] E. Frackowiak, K. Metenier, V. Bertagna, and F. Beguin, "Supercapacitor electrodes from multiwalled carbon nanotubes," *Applied Physics Letters*, **77** (15), 2421–2423 (2000).

[14] H. T. Jeong, B. C. Kim, M. J. Higgins, and G. G. Wallace, "Highly stretchable reduced graphene oxide (rGO)/single-walled carbon nanotubes (SWNTs) electrodes for energy storage devices," *Electrochimica Acta*, **163**, 149–160 (2015).

[15] D. Yu, K. Goh, H. Wang, L. Wei, W. Jiang, Q. Zhang, L. Dai, and Y. Chen, "Scalable synthesis of hierarchically structured carbon nanotube-graphene fibres for capacitive energy storage," *Nature nanotechnology*, **9** (7), 555–562 (2014).

[16] Y. Qiu, G. Li, Y. Hou, Z. Pan, H. Li, W. Li, M. Liu, F. Ye, X. Yang, and Y. Zhang, "Vertically aligned carbon nanotubes on carbon nanofibers: a hierarchical three-dimensional carbon nanostructure for high-energy flexible supercapacitors," *Chemistry of Materials*, **27** (4), 1194–1200 (2015).

[17] L. Liu, Z. Niu, L. Zhang, W. Zhou, X. Chen, and S. Xie, "Nanostructured graphene composite papers for highly flexible and foldable supercapacitors," *Advanced Materials*, **26** (28), 4855–4862 (2014).

[18] T. Chen, H. Peng, M. Durstock, and L. Dai, "High-performance transparent and stretchable all-solid supercapacitors based on highly aligned carbon nanotube sheets," *Scientific reports*, **4**, 3612 (2014).

[19] M. F. El-Kady and R. B. Kaner, "Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage," *Nature communications*, **4**, 1475 (2013).

[20] J. A. Lee, M. K. Shin, S. H. Kim, H. U. Cho, G. M. Spinks, G. G. Wallace, M. D. Lima, X. Lepró, M. E. Kozlov, R. H. Baughman, and others, "Ultrafast charge and discharge biscrolled yarn supercapacitors for textiles and microdevices," *Nature communications*, **4**, (2013).

[21] Y. Fu, X. Cai, H. Wu, Z. Lv, S. Hou, M. Peng, X. Yu, and D. Zou, "Fiber supercapacitors utilizing pen ink for flexible/wearable energy storage," *Advanced materials*, **24** (42), 5713–5718 (2012).