

# LARGE-SCALE SYNTHESIS AND CONNECTIONS ADJUSTMENT OF THE CARBON NANOTUBE FOAMS

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## ABSTRACT

Carbon nanotubes (CNTs) catch the attention of many social science researchers, due to the remarkable mechanical, thermal, and electrical properties. Among the assemblies of the CNTs, CNT foams are self-assembled three dimensional (3D) network structures that have ultra-low densities, high conductivity, and novel chemical stability, which made them have great potential to use as structure components, heat and electric insulation, cushioning and energy absorption, molecular adsorption and filtration, scaffolds and templates, and composites. [1, 2] However, the mass production technology of the CNT foams is still the bottleneck restricting the industrialization and forward practical applications. In this paper, a novel large-scale synthesis technology of the highly stable carbon nanotube foams is reported. During the production, growing conditions of the floating catalyst chemical vapour deposition method (FCCVD) is modified to control the CNTs fabrication in the reaction zone,[3] and an ideal self-assembled CNT 3D network, which can be continually produced, is finally got. The 3D network can be collected by a rotating barrel, and a CNT foam with 1.5 m in length, 1 m in width, and 2-5 cm in thickness is obtained after 8 hours rolling. However, due to the weak connection points between CNTs, this as-formed foam is easy to collapse, even in the conditions of gent pressure and solvent spraying. In order to maintain the structure of the CNT foam and make the foam stable, we further explore welding technology between the CNTs. high temperature BNs directly growing, metal ion sputtering, Al<sub>2</sub>O<sub>3</sub> atomic layer deposition, and amorphous carbon (AC) welding are compared. It is found that the AC welding can firmly fix the contact points of the CNTs, and increase the mechanical robustness of the CNT foam. This joint-welded CNT foam shows remarkable elastic recoverability on both tensile and compressive strains, and could keep their electrical resistances almost unchanged during stretching, compressing and bending. The FCCVD directly growing with AC welding provides a way to produce large quantity high stable CNT foams that are close to meter scale and lays the foundations for the industrial application.

## 1. INTRODUCTION

CNTs have superb mechanical and physical properties, and recently have been assembled into macroscopic assemblies, such as yarns, films and foams and so forth, for real engineering applications[4-8]. Among these CNT assemblies, CNT foams (also known as CNT foam or sponge) have ultralow density, high porosity, and huge specific surface area, making them a prime candidate for have enormous potential in functional applications like biological tissues/artificial muscle[9],vibration energy damping[1] and reusable sorbents for environment remediation[10].

Great efforts have been made in the last decade in fabricating CNT foams and investigating their properties. Similar to the traditional foams like SiO<sub>2</sub> foams and PI foams, CNT foam can be manufactured by critical point drying of solution-processed hydrogels containing dispersed micrometre long CNTs. CNTs are randomly distributed in the foam, and held together primarily

through van der Waals interactions at discrete nanotube nodes. Thus, the as-made CNT foams have quiet low mechanical performance and are prone to experience plastic deformation under compressive loading. CNT foams can also be fabricated using one-step chemical vapour deposition (CVD) process. By pre-depositing catalyst on the substrate with low catalyst density, Xu *et al.* made a rubber-like foam composing of randomly oriented and sparse CNTs[11]. These CNTs are several millimetres long and intertwined with each other, endowing the foam with better mechanical properties and thermal stability. On the other hand, Gui *et al.*, fabricated the CNT foams through FCCVD process[12]. The catalyst powders were dissolved in the liquid carbon source to make a solution and then continuously injected into quartz tube housed in a heated furnace. The CNT foam was collected by the quartz substrate that was placed in the reaction zone. The compressive strength and modulus of these CNT foams are relatively weak comparing with the polymeric and metallic foams, and they cannot fully recover after releasing from the compressive loadings. Thus, a wealth of researches has been implemented to enhance the compressive performance of CNT foams. For example, Kim *et al.* transformed the inelastic CNT foam into a super-elastic material by coating it with graphene nanosheets [13]. This coating increases the Young's modulus and energy storage modulus by a factor of  $\sim 6$ , and the loss modulus by a factor of  $\sim 3$ . Moreover, the hybrid foam can recover to its original shape quickly after compression release. Yang *et al.* casted a uniform mesoporous-silica (m-silica) layer with tuneable thickness on the surface of CNTs in CNT foams[14], and the foam can then be compressed to 60% without collapse. Alternatively, recent studies have found that the compressive mechanical performance as well as the recoverability of CNT foam can also be effectively enhanced by either in-situ or post coating of amorphous carbon on CNTs in the foam[15, 16].

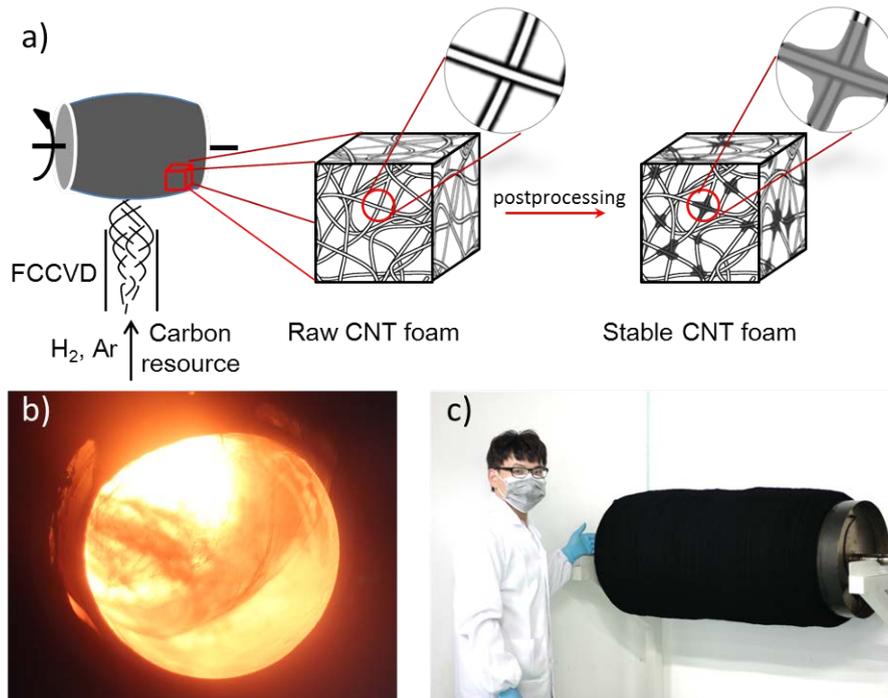
To date, the carbon foam, no matter derived from CNT-based suspensions or CVD method, usually have excellent compressive reversibility, but experience crack or plastic deformation upon stretching. Meanwhile, it is difficult to realize the large-scale manufacture of CNT foams by using the aforementioned methods, which is a key barrier for their engineering applications. In 2004, Li *et al.* reported a convenient and scalable method of producing CNT foams, films and fibers using the FCCVD method[3]. Instead of forming powder CNTs in the furnace as reported by Gui *et al.*[12], a free-standing sock-like elastic CNT foam was formed in the furnace, which can be continuously pulled out to be either collapsed into a fiber or layer-by-layer collected to form a CNT foam. This foam is ultralight and has highly natural entanglement structure during formation.

In this study, we produce CNT foams using Li's FCCVD method, and investigate compressive property. In order to maintain the structure of the weak CNT foam a high temperature BNs directly growing, metal ion sputtering,  $\text{Al}_2\text{O}_3$  atomic layer deposition, and amorphous carbon (AC) welding are compared. It is found that the AC welding can firmly fix the contact points of the CNTs, and increase the mechanical robustness of the CNT foam. This joint-welded CNT foam shows remarkable elastic recoverability on both tensile and compressive strains, and could keep their electrical resistances almost unchanged during stretching, compressing and bending. The notable elasticity makes the AC deposited CNT foam a prime candidate of elastic conductor for stretchable electronics.

## 2. EXPERIMENT METHOD

### 2.1 Fabrication of as-formed FCCVD CNT foam

As shown in the Figure 1a, a tube furnace (BEO, BTF-1200C) was used as reaction equipment. Argon was pumped into the quartz tube to evacuate the air. Ethanol with 1% ferrocene and thiophene was atomized and injected into the quartz tube as carbon resource, when the tube was heated up to  $1300^\circ\text{C}$  with a heating rate of  $5^\circ\text{C}$  per min. Under the atmosphere of hydrogen and argon, CNTs were produced in the tube and self-assembled to a 3D network floating in the airflow. The as-formed CNT foam was collected by a rotating barrel.



**Figure 1** a) the schematic of production of stable CNT foam; b) the self-assembled CNT network formed by FCCVD; c) the mass-production of the CNT foam

## 2.2 High temperature BNs directly growing

The BNs on CNT foam were grown in a horizontal electric furnace (BEO, BTF-1200C) consisting of an alumina tube 150 cm in length and 6 cm in diameter. The powders of B, MgO, and Fe<sub>2</sub>O<sub>3</sub>, the molar ratio of 2:1:0.5, were mechanically mixed in a planetary ball mill for 4 h. In this experiment, 500mg of the mixed powders was placed in an alumina crucible as the precursor. The original CNT foam was cut into a small piece by laser with dimensions of 50 mm × 35 mm × 10 mm, and positioned in the alumina crucible with 5-10 mm distance to the precursor powders. Then, the crucible was put at the centre of the heating zone in the alumina tube. After a 5 min Ar purge, the tube was heated up to 1200 °C in an Ar flow of 200 standard cubic centimetres per minute (sccm). When the temperature was steady at 1200 °C, the Ar flow was substituted for a 200 sccm NH<sub>3</sub> flow and maintained for 30-60 min. The NH<sub>3</sub> flow was returned to 200 sccm Ar and the tube was cooled down to room temperature in air, when the reaction finished.

## 2.3 Al<sub>2</sub>O<sub>3</sub> atomic layer deposition

An atomic layer deposition system (ENSURE NANOTECH, LabNano-9100) was employed to conduct the atomic layer deposition of Al<sub>2</sub>O<sub>3</sub>. After the divided CNT foam enclosing at the centre of the deposition area, the reaction region was vacuumed to  $4 \times 10^{-2}$  Pa and heated up to 250 °C. When the reaction condition reached the target and kept stable, Trimethylaluminum (TMA) and H<sub>2</sub>O was injected into the chamber as the precursor by pulses of 20 sccm N<sub>2</sub> flow. During the exposure, the TMA together with the H<sub>2</sub>O vapour chemisorbed and reacted on the substrate surface, resulting Al<sub>2</sub>O<sub>3</sub> deposition. The N<sub>2</sub> flow was close down and the system was cooled down to room temperature in air after 1 h reaction.

## 2.4 Metal ion sputtering

The Ni ion sputtering was managed by an automatic magnetron sputtering system (JINSHENGWEINA TECHNOLOGY, MSP-620). When the foam was placed at the reaction chamber, the system was vacuumed to  $8 \times 10^{-4}$  Pa. Subsequently, Ni particles were sputter-deposited and anchored on the surface of the CNT foams with a 20 W/cm<sup>2</sup> sputtering power in 80 sccm argon flow. After 1 h sputtering, the system was cooled down to room temperature in air.

## 2.5 Amorphous carbon welding

The collected foam was replaced into the furnace used in section 2.1, and then heated to 720°C under Argon atmosphere with a heating rate of 10°C per min. After the temperature kept stable, Acetylene with hydrogen was injected into the tube as carbon resource. With 2h treatment, amorphous carbon coated on the tube wall of CNTs and welded them.

## 2.6 Characterization of properties

The surface characteristics were probed by a SEM (FEI, Quanta 400F). The compressive property was measured by an Instron universal testing machine (Instron, 3365) equipped with a 10N load cell. The test was under the set strain rate of 20mm/min for 10 cycles. The electrical variation was recorded simultaneously during loading and unloading stress–strain curves.

## 3. RESULTS AND DISCUSSIONZZ

The as-formed foams are fabricated by FCCVD method that is invented by Li. This method synthesizes CNTs in the gas phase and produces CNT 3D networks directly (Figure 1b), which is much easier than traditional sol-gel processing. A 1.5 m × 1.0 m × 5~10 mm foam can be produced in 8 h (Figure 1c), showing the potential of mass-produce. However, due to the weak connections between CNTs, the 3D networks in foam are quite deformable, which troubles the application. Hence, structure enhancement is necessary.

There are four methods, high temperature BNs directly growing, metal ion sputtering, Al<sub>2</sub>O<sub>3</sub> atomic layer deposition, and amorphous carbon (AC) welding, being used to modify the foam structure. Figure 2 exhibits the foams after post processing. After the growth of BNs, white BNs platelets coated on the CNT foams, but the foams were corroded and collapsed during the processing. An obvious metallic luster can be observed after Ni sputtering, indicating the sputtering sprayed a thin layer of Ni on the foam surface. Al<sub>2</sub>O<sub>3</sub> coating made the foam turn white, and there were no obvious change after AC welding.

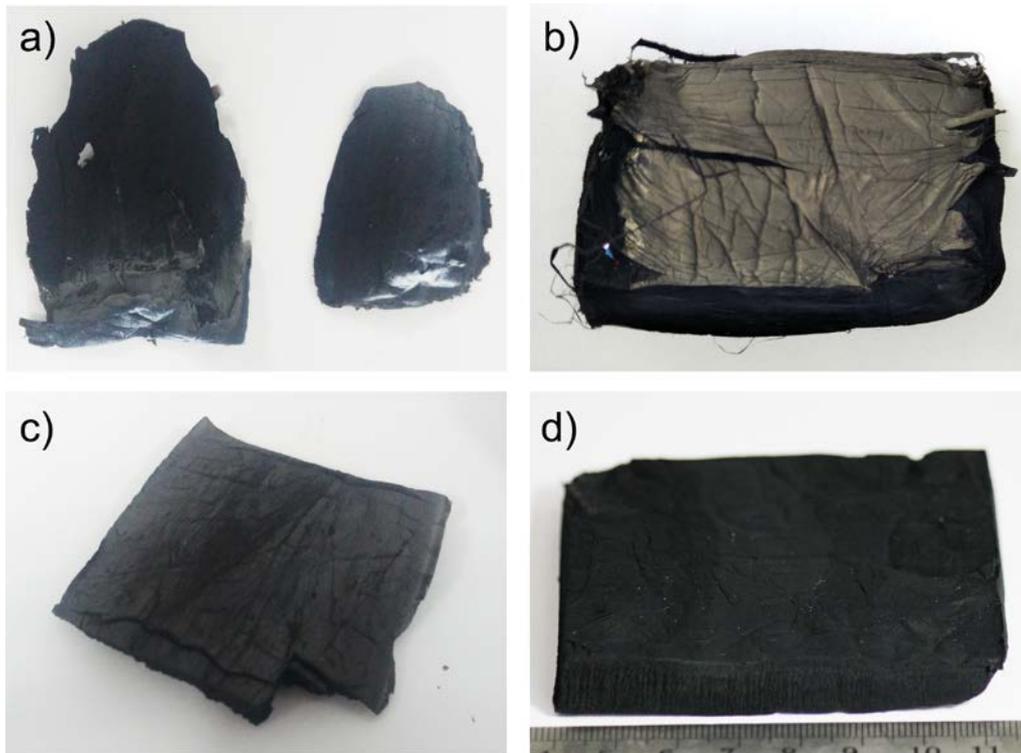
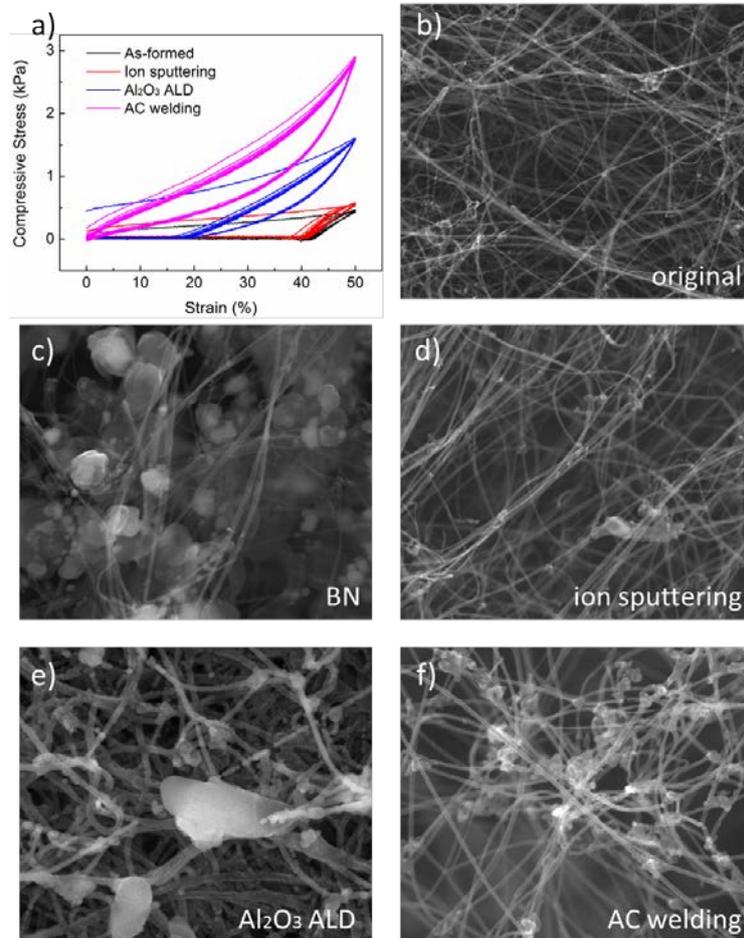


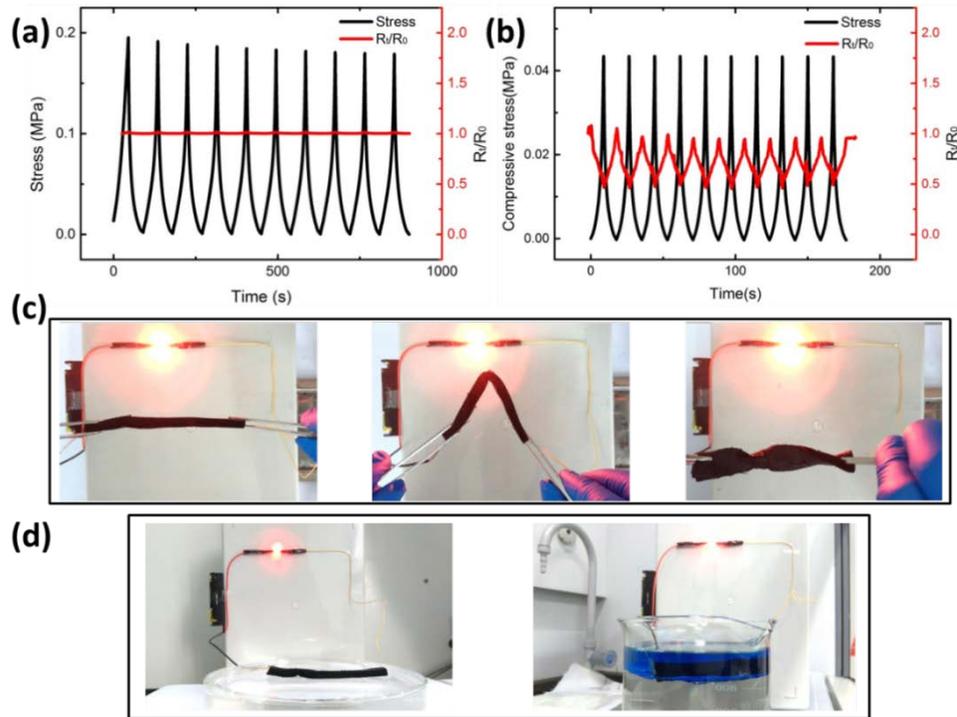
Figure 2. The photos of foams after high temperature BNs directly growing (a), metal ion sputtering (b), Al<sub>2</sub>O<sub>3</sub> atomic layer deposition (c), and amorphous carbon (AC) welding (d).

The cyclic compressive results of the CNT foams are shown in the figure 3a, and the loading and unloading stress curves up to the strain of 50%. The as-formed CNT foam and ion sputtering foam can only recover 10% after compressed to 50% strain. The Al<sub>2</sub>O<sub>3</sub> ALD foam has 30% elastic recovery when released from 50% strain, and the stress at 50% strain is 1.5 kPa, which is triple that of the original foam. The AC welding foam can sustain large deformations without fracture and recover most of the volume back. The curve can go back to the origin above the x axis, which indicates the complete recovery without any plastic deformation. The 10-time cyclic compression curve indicates the moderate structure of the welded CNT foam. However, the BN/CNT foams were hard to be measured, because they were fragmented and dilapidated.



**Figure 3** a) the cyclic compressive testing on the CNT foams with different connections adjustments; the SEM images of original (b), BN welding (c), ion sputtering (d), Al<sub>2</sub>O<sub>3</sub> ALD (e) and AC welding (f) CNT foams

The SEM images present the microstructure of the foams. The original foam is constituted by 3D intersected CNT networks with no enhancements at the interconnected points. This structure provides the high porosity and low density, but relative low mechanical properties. As shown in figure 3c, The BNs growing implants small BN plates into the foam. However, the growth of BNs destroys the existing CNT networks and leads collapse of the foams. Figure 3d exhibits the inlayer of the foam after ion sputtering. There is no obvious difference between this and the original one, demonstrating that the ion sputtering can only deposit Ni on the surface of the foam. The ALD method delivers the precursor into the inner layers and coats Al<sub>2</sub>O<sub>3</sub> on the tube walls and connections (Figure 3e). It partly enhances the networks and changes the mechanical behaviour of the foams. The structure of the foam after AC welding presents AC deposits at the contact points and fixed the 3D CNT networks, and it totally transforms the CNT foams from ductile to elastic.



**Figure 4** Electrical resistance variation of AC-CNT Foams under cyclic loading of (a) 25% tensile strain and (b) 98% compressive strain; a circuit constructed with the AC deposited FCCVD foam as lightweight conductive bulk. The brightness of LED stayed the same with bending and twisting the foam (c), as well as put the foam into water and oil(d).

The electrical conductivity of the AC deposited foam was 1.86~2.42 S/cm, larger than that of the other carbon-based foams [13, 17-19] as well as some stretchable conductors [20-22]. Moreover, as shown in figure 4a, the resistance of the AC-CNT foam only somewhat increased by 1% when stretched to strain of 25%, and the conductivity was almost unchanged after the foam was released to the unstrained state. Thus, AC-CNT foams could be used as lightweight stretchable conductor. As shown in Figure 4b, during compression, the conductivity of the AC-CNT foam varied almost linearly with the compressive strain, and was halved when pressed to a strain of 98%. It could be interpreted by that upon compression, CNTs in the foam would contact with each other, establishing new electrical pathways. Upon unloading, the foam recovered to its initial shape and the resistance returned to the original level. As a demonstration, Figure 4c showed that the current could pass through an AC-CNT foam strip to light a LED lamp, and the brightness of the lamp was almost unchanged even when the form strip was bended or twisted, which signified excellent flexibility of the AC-CNT foam. In Figure 4d, it showed there had no effect on the current circuit when put the foam into wet or oil environment, and revealed the environment reliability. In these respects, the elastic AC-CNT foams could be used as stretchable conductors or piezo-resistive sensors in many areas such as flexible devices and wearable electronics.

#### 4. CONCLUSIONS

In this work, we compared four different methods to modify the FCCVD as-formed CNT foams. It is found that the AC welding can thoroughly change the mechanical properties of the CNT foams by welding the connection points. These hyper elastic AC-CNT foams also hold many potential applications. For example, they had higher electrical conductivity than other carbon-based foams and stretchable conductors as well, making them promising stretchable lightweight conductors.

## 5. ACKNOWLEDGES

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