

# Free-standing conductive thin films from gold-carbon nanotube composites

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## Abstract

We report on the development of a method of formation of free-standing gold-carbon nanotube (CNT) composites. It is based on a quick and simple decoration of CNT films with the application of chloroauric aqueous solution. Flexible and conductive macroassemblies of any size and shape can be created with ease. Addition of as little as 1% of Au by weight allowed for reduction of resistance by more than a quarter. Higher Au doping resulted in further decrease of resistance, but not so significant. From the practical point of view, these composites are a new type of materials with high electrical conductivity, but also offer resistance to corrosion.

**Key words:** carbon nanotubes; macroassemblies; gold nanoparticles

## Introduction

Carbon nanomaterials such as carbon nanotubes (CNTs) and graphene have shown great promise for creation of materials of significantly improved characteristics as compared with the typical materials present around us from hundreds of years. High performance in terms of electrical [1, 2], thermal [3-5], mechanical [6, 7] and optical [8, 9] properties give us hope that we will be able to make full use of them to offer significant improvements on many fronts one day. However, the problem is in translation these encouraging properties from individual CNTs and graphene flakes to the macroscopic objects. Their macroscopic assemblies often have a sort of discontinuous nature with plethora of voids, which disrupts transport of phonons/electrons

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and load transfer. R&D community needs to either to reduce this number of voids by creating much longer CNTs/larger graphene flakes or find appropriate “glue”, to combine these individual elements without significant deterioration of their properties.

Deposition of Au onto CNTs can be accomplished by multi-step electroless liquid processing [10-12], electrodeposition [13] or physical methods such as sputtering [14, 15] or electron-beam evaporation [16]. One of the most facile approach is based on the use of  $\text{HAuCl}_4$  aqueous solution [17, 18], but it commonly uses CNT powder as “feed”. The technique has not been tested before on CNT macroassemblies such as free-standing thin films of tangible dimensions, what is crucial to evaluate their properties and practical potential.

Here we present a convenient method of manufacturing mechanically-strong free-standing Au-CNT composites of any size and shape. Au clusters improve electron transport between individual CNTs and their bundles, which results in increased electrical conductivity. The material offers high corrosion resistance compared to traditional metal conductors or CNTs typically doped with metals such as Cu or Al.

## **1. Experimental**

The CNT films were produced by a method reported elsewhere [19]. In brief, CNTs were combined with a binder (ethyl cellulose), dispersed and spray-coated onto a substrate, from which it can be delaminated as free-standing CNT films. Then, flash annealing with a blowtorch rapidly removes the binder making free of residue CNT film. For this study we employed both the CNT films with the binder (b) and binder-free (bf) to see the influence of its composition on deposition of Au. They are denoted as CNT-b and CNT-bf, respectively.

A gold ion solution was prepared by adding chloroauric acid ( $\text{HAuCl}_4$ , Sigma Aldrich, 99.9%) to deionized water, sonicated for 5 minutes, dripped onto the CNT films to fully cover their surface, and then left to dry in the ambient conditions. Equal volumes for deposition of 1%wt and 5%wt aqueous solutions were used.

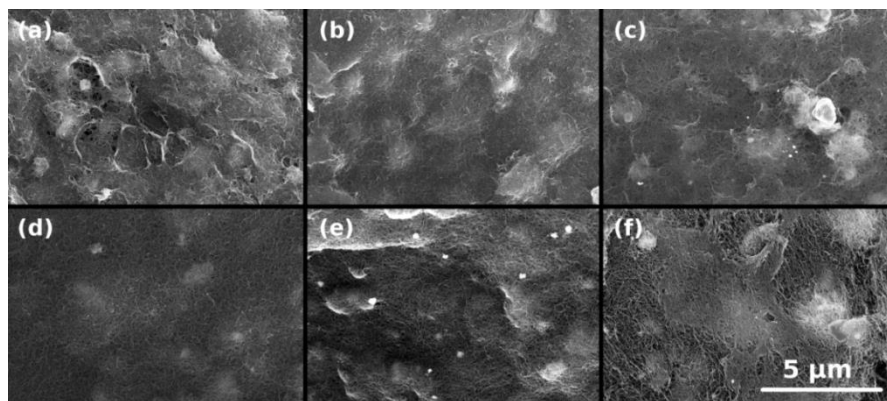
Scanning Electron Microscopy (SEM, FEI Nova NanoSEM) and Transmission Electron Microscopy (TEM, Tecnai Osiris) was used to probe the structure and quality of CNTs films on micro- and nanoscale.

Energy-Dispersive X-ray spectroscopy (EDX, Bruker Quantax coupled with Nova NanoSEM) detected the elemental composition at 10 keV emission voltage.

Thermogravimetric analysis (TGA, Mettler Toledo TGA/DSC system) measured changes in chemical and physical properties with temperature. The samples were heated to 1000°C at 10°C min<sup>-1</sup> rate in the flow of air at 20 ml min<sup>-1</sup>.

Electrical properties measurements were performed with the use of Keithley 2000 multimeter using a four probe method. 5 mm x 40 mm specimens were prepared for this purpose. An average and standard deviation among ten samples for each subset (CNT-b and CNT-bf subjected to 0%wt, 1%wt, 5%wt Au deposition) is given. Resistance was normalized to the measured initial resistance recorded at room temperature.

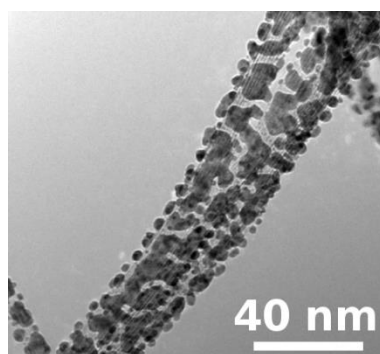
## 2. Results



**Fig. 1** SEM micrographs of the CNT films. (a) CNT-b (b) CNT-b with 1% wt Au deposition, (c) CNT-b with 5%wt Au deposition, (d) CNT-bf, (e) CNT-bf with 1%wt Au deposition, (f) CNT-bf with 5% wt Au deposition

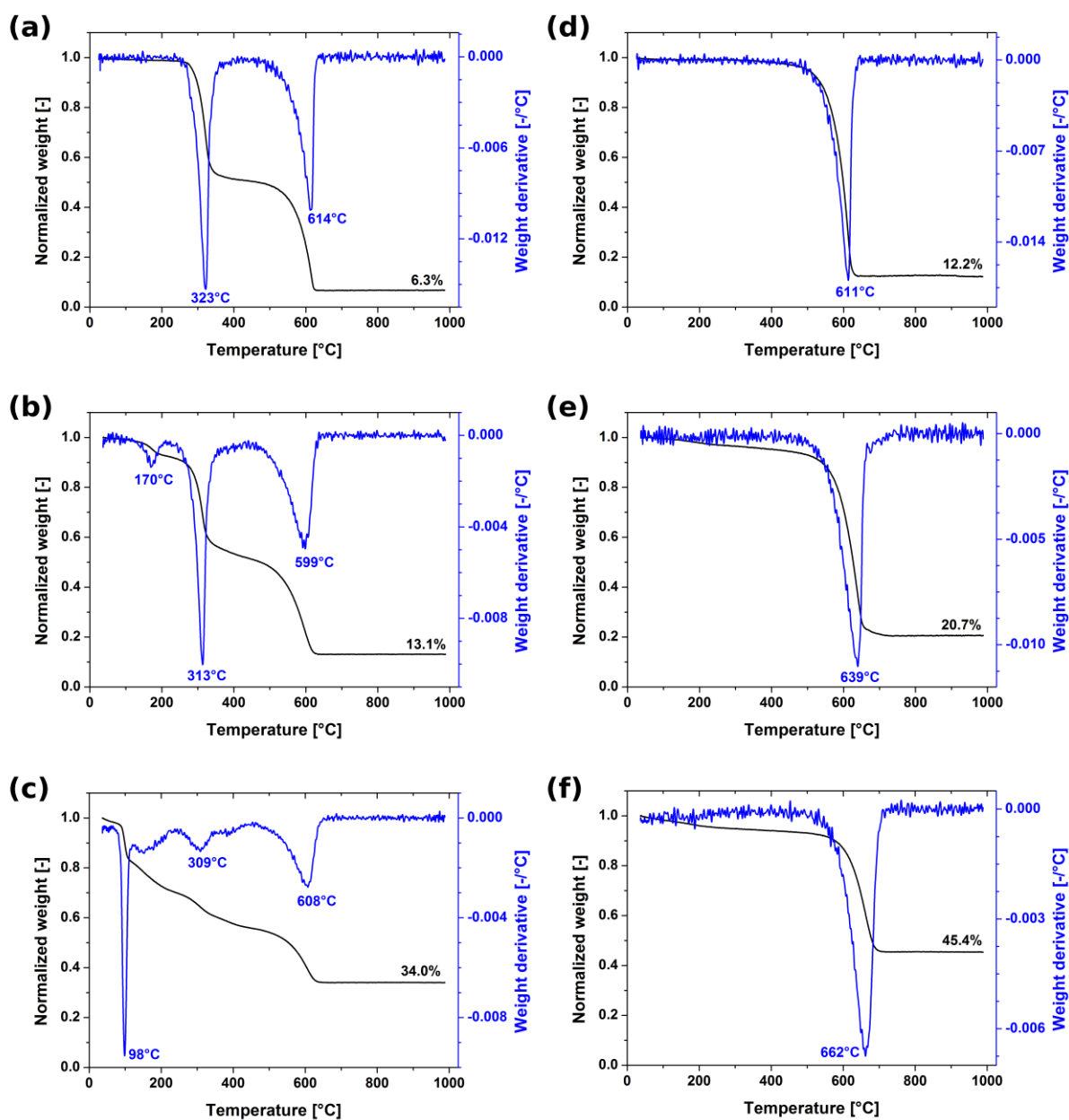
Two types of films were used for Au deposition: CNT-b (with the binder) and CNT-bf (binder-free). Fig. 1 shows microstructure of both of them with and without Au present. It is not

surprising that the CNT-bf is more porous because of the absence of ethyl cellulose, which created a sort of removable scaffolding for the CNT film formation. In fact, Au deposition seems to gradually increase the porosity of the binder-free material (Fig. 1d-f). Furthermore, deposition of Au appears to be uniform without excessive agglomeration of clusters. Because the process forms mostly Au in the nanoscale range [18], metal particles are not visible by SEM. High-resolution TEM (Fig. 2) showed that Au clusters size range from a few up to about 20 nm.



**Fig. 2** TEM micrographs of the CNT-bf with 5%wt Au deposition.

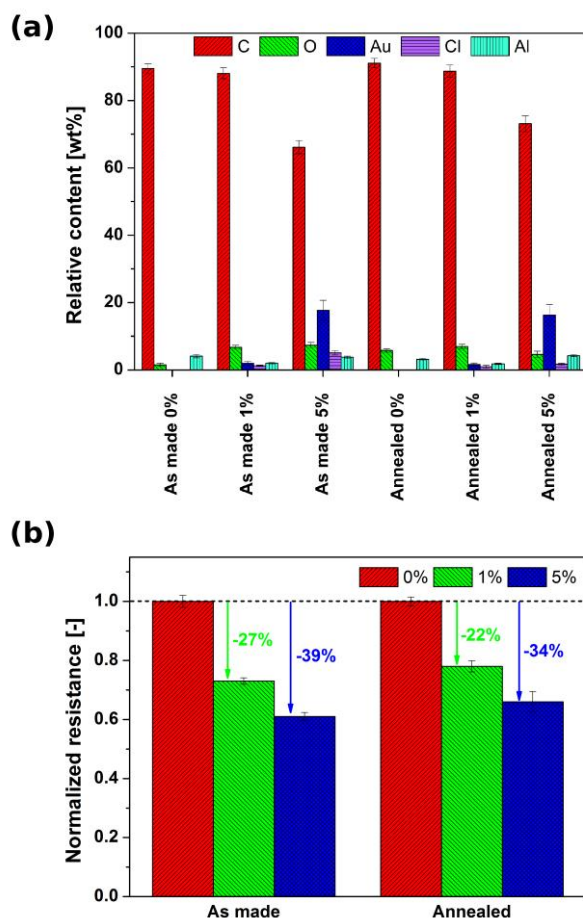
Furthermore, we carried out TGA to quantify the amount of Au deposited onto the surface. The samples in the left column, which represent the CNT-b materials with binder present, show typical, two-step influence of the oxidation of ethyl cellulose below 450°C [19]. This region coincides with the decomposition regime of Au compounds introduced using this method. Side-products of reaction between  $\text{HAuCl}_4$  and CNTs or various carbonaceous impurities commonly contaminating the sample are responsible for that low-temperature monotonic weight loss. Chlorine present in up to few wt% content (Fig. 4a) can also react with various functional groups making them volatile [20]. If we take into account that the CNT films produced this method using unpurified CNTs contain 6.3% (Fig. 3a, CNT-b) and 12.2% (Fig. 3d, CNT-bf) residual alumina catalyst, we can evaluate how Au addition scales with concentration of the doping solution. In the case of CNT-bf films, we see that Au content after TGA is about 8.5% (Fig. 3e, 1% wt Au solution) and 33.2% (Fig. 3f, 5% wt Au solution was used).



**Fig. 3** Thermograms of the CNT films. (a) CNT-b (b) CNT-b with 1%wt Au deposition, (c) CNT-b with 5%wt Au deposition, (d) CNT-bf, (e) CNT-bf with 1%wt Au deposition, (f) CNT-bf with 5%wt Au deposition

When CNT-b films were used, the Au content after TGA was 6.8% (Fig. 3b, 1%wt Au solution) and 27.7% (Fig. 3c, 5%wt Au solution). In both cases, we expected a fifth-fold increase, whereas the results show that they quadrupled. The reason for that may be that  $\text{HAuCl}_4$  that we

bought was not fully anhydrous and water weight loss contributed to the recorded thermograms. The explanation is supported by the fact that it was a consistent error in all of our experiments.



**Fig. 4.** (a) chemical composition of all samples as evaluated by EDX, (b) the influence of Au addition on electrical resistance of CNT films.

As a final step, we evaluated the influence of Au addition on electrical properties of CNT films (Fig. 4b). Even as small addition as that from 1%wt Au solution causes reduction in electrical resistance by a quarter. What is interesting is that further Au addition does not cause proportional decrease of resistance. The results show that small Au content helps with electrical percolation of the material by alleviating the problem of junction resistance. Lekawa-Raus *et al.* showed in a similar study that Ag nanoparticles can effectively join CNTs and their bundles to improve the electrical properties [21]. Addition of Au instead of Ag is important for long term

performance because Ag is prone to oxidation, but Au/CNT composite can preserve the corrosion-resistant nature of CNTs. From the electrical point of view, their conductivity is of the same order of magnitude  $6.30 \times 10^7$  S/m (Ag) vs.  $4.10 \times 10^7$  S/m (Au) [22].

### **3. Conclusions**

In brief, we proposed a simple route towards Au/CNT composite films of any size or shape. Doping of the material is very-straightforward and the process is based on a single step, which involves putting CNT film in contact with the H<sub>2</sub>AuCl<sub>4</sub> aqueous solution and leaving it to dry. By varying the concentration of the solution, one can tune the content of Au on the surface of the material. The presence of binder, removal of which does not cause significant improve in conductivity, did not interfere with the doping efficiency despite improved packing of the material. For some applications in which only electrical conductivity is the target, leaving the film with the binder has no influence, but assures better mechanical properties. We believe that such a simple method to create free-standing Au/CNT composites could be helpful in the real-life application of CNT macroassemblies wherein high electrical conductivity is important. It is important to stress that Au nanoparticles are not prone to oxidation as commonly used Cu, Al and Ag nanoparticles, therefore such Au/CNT composites can be useful in the applications where corrosion-resistance is of the essence.

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