



# High performance all-carbon composite transparent electrodes containing uniform carbon nanotube networks



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## ABSTRACT

Indium tin oxide-free, flexible transparent electrodes (TEs) are crucial for the future commercialization of flexible and wearable electronics. While carbon-based TEs containing carbon nanotube (CNT) networks show promise, they usually exhibit poor dispersion properties, limiting their performance and practicality. In this study, we report a highly efficient and bending durable all-carbon composite TE (ac-TE) that employs uniform CNT networks on a monolayer graphene/polyethylene terephthalate (PET) substrate via a simple air spray deposition method. The air-sprayed CNT/graphene assembly was free-standing on solution, making a polymer-free transfer of carbon composites to target substrates possible. The excellent performance of the ac-TEs was attributed to the uniformly networked CNTs on the polycrystalline graphene with a well-controlled density, effectively bridging the line defects and filling the tears/voids or folds necessarily existing in the as-processed graphene. The sheet resistance of the ac-TEs was increased only 6% from its original value at a bending radius of 2.7 mm, while that of the pristine graphene/PET assembly increased 237%. Mechanical bending of the ac-TEs worsened the electrical performance by only ~1.7% after 2000 bending cycles at a bending radius of 2.5 mm. Degradation of the performance by the bending was the result of line defects formation in the graphene, demonstrating the potential of the uniform CNT networks to achieve more efficient and flexible carbon-based TEs. Furthermore, the chemically-doped ac-TEs showed commercially suitable electronic and optical properties with much enhanced thermal stability, closer to practical TEs in flexible devices.

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## 1. Introduction

Indium tin oxide (ITO) is one of the most frequently used materials for transparent electrodes (TEs). However, its growing cost and brittleness against bending hinder its utilization for future flexible and wearable applications [1,2]. Various suggestions have been proposed for ITO alternatives, including metal nanowires, conducting polymers, carbon nanotubes (CNTs), and their hybrids [3–5]. Graphene (Gr), a two dimensional (2D) material, has received great attention in various research fields thanks to its

unique properties such as low electron-phonon scattering, high carrier mobility, ambipolar electrical field effect, and quantum Hall effect [6]. In addition, its mechanical strength is predicted to exceed any other material and monolayer graphene only absorbs approximately 2.3% of visible light [7]. Recently, it has been demonstrated by numerous research groups that graphene has great potentials for various applications such as field effect transistors, energy storage materials, chemical and bio-sensors, cell imaging, barrier materials, TEs, and more [8–15].

Although the theoretical properties of graphene suggest that it would be an excellent ITO alternative, large-area graphene grown by chemical vapor deposition (CVD) often presents a higher sheet resistance value ( $R_{sh}$ ), several hundreds of ohm/sq, than ITO-based TEs [16–19]. The main reason for this higher sheet resistance is the presence of unavoidable structural defects such as grain boundaries, tears, folds, wrinkles, and point defects in the as-processed

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graphene layer [16,17]. It is well known that these defects can disrupt the  $sp^2$  delocalization of  $\pi$  electrons in graphene and may result in charge scattering or trapping [6]. Until now, various approaches have been attempted to reduce the deleterious effects of structural defects in the CVD-grown graphene (CVD-Gr). In a growth point of a view, enlarging graphene domain size by controlling the growth parameters or enhancing stitching of graphene domains by controlling orientation of the underlying Cu surface effectively improved the electrical properties of graphene; however, the real properties of the CVD-Gr still stayed far behind when compared to those of the defect-free pristine graphene [16–19]. In other approach, hybridization of graphene with other conducting materials, such as conducting polymers, metal nanowires, and metal grids can minimize the structural defects in the CVD-Gr while preserving its high transparency [20–23]. However, environmental stability of metallic and polymer materials is problematic for long-term usage. For example, polymers are very sensitive to heat and humidity and metals are easily oxidized in an ambient condition.

Among all of these techniques, CNT-Gr hybridization seems to be a promising method to combine the merits of 1D and 2D carbon materials. CNT networks are a unique class of nanomaterials demonstrating great potential for flexible electronics with electrical characteristics that exceed those of amorphous silicon and organic semiconductors, benefiting from the outstanding intrinsic electrical properties of CNTs within the network [22]. Numerous CNT-Gr hybridization methods have been reported, yet no single method has emerged to realize industrial level commercialization of flexible CNT-Gr macro-electronics at this moment. Since the pristine graphene layer is inert and hydrophobic, it is hard to obtain CNT-Gr hybrid films with uniform CNT networks; the hybridization methods generally suffer from difficulties in deposition efficiency and film uniformity due to the aggregation of CNTs and coffee ring effects [23–26]. For example, substrate-supported CVD synthesis of CNTs with graphene enables structure and property control, but it is not compatible with plastic substrates owing to the high temperature process ( $\sim 1000^\circ\text{C}$ ) [23]. Solution deposition of CNTs onto arbitrary substrates is useful for applications in flexible and wearable applications; however, the solution-based methods to hybridize CNT-Gr are limited to the use of graphene oxide (GO) or reduced GO materials at this moment [24–26], making it difficult to achieve good electrical properties of the resulting devices. Recent studies related to hybridizing CNT networks with pristine graphene grown by CVD suggest that the ability to understand and engineer the CNT arrangement within the network is important to control the performance of carbon-based TEs [27–29] and further improvements in sheet resistance ( $R_{sh}$ ), transmittance, and environmental stability must be achieved for future commercial flexible TE applications. Since CNTs and graphene in their pristine form are insufficient to satisfy demands for commercial applications, the chemical modification and/or doping strategies can be introduced to optimize the optoelectronic performance and environmental stability of the carbon-based TE materials [30–32].

In this paper, hybridization of single-walled CNTs (SWCNTs) with graphene was demonstrated by simple air spray deposition method to reproducibly achieve uniform thin films with a controllable morphology of CNTs over large areas, as illustrated in Fig. 1. To obtain high performance all-carbon composite TEs (ac-TEs), we chose SWCNTs for the base of the CNT film on graphene since the prior experimental results suggest that the optoelectronic performance of the SWCNTs is much superior to that of multi-walled CNTs [33–40]. We found that air spray deposition with simultaneous heat treatment inhibited the coffee ring effect and aggregation of SWCNTs on the graphene layer, leading to uniform formation of a 2D hybrid carbon film. Moreover, we investigated

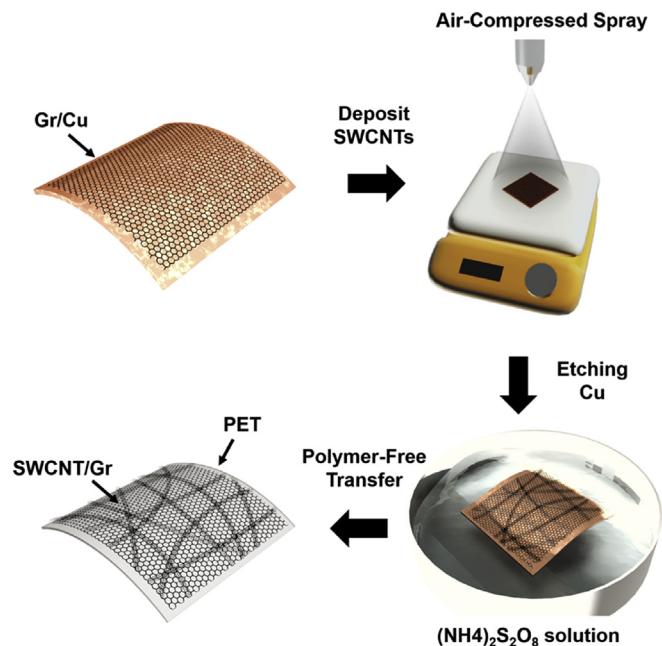


Fig. 1. Schematic illustration of SWCNT/Gr hybrid structure formed using a simple air spray deposition method. The hybrid 2D carbon films were transferred to an oxygen plasma treated PET substrate without the use of any supporting polymer layer.

the mechanical and electrical bending stabilities of the ac-TEs with effective bending radii for wearable devices, applicable to human neck ( $\sim 400$  mm), wrist ( $\sim 10$  mm) and finger ( $\sim 4$  mm). The electrical performance of the ac-TEs containing uniform CNT networks can withstand over 2000 cycles of the bending test with a bending radius of  $\sim 2.5$  mm, while the pristine Gr/PET assembly showed a large increment in the resistance. We demonstrate that the employment of uniform CNT networks on graphene via the air spray deposition method effectively alleviates the formation of line defects in graphene during the bending test, allowing more efficient and bending durable carbon-based TEs. The thermal stability of the chemically-doped ac-TEs with commercially suitable electronic and optical properties was significantly improved by the hybridization of SWCNTs with graphene.

## 2. Materials and experiment

### 2.1. Synthesis of graphene on Cu foil and its transfer

Monolayer graphene was grown on a polycrystalline copper (Cu) foil using a CVD method demonstrated elsewhere [16,17]. Briefly, 25- $\mu\text{m}$ -thick Cu foil (Alfa Aesar, 99.8% purity) was electro-polished in phosphoric acid for 15 min and rinsed with distilled water followed by isopropyl alcohol. The Cu foil was loaded into a quartz tube and the temperature was increased to  $1050^\circ\text{C}$  in a  $\text{H}_2$  environment (270 mTorr) for 15 min to remove native oxides in the Cu. The graphene was synthesized by introducing  $\text{CH}_4$  gas under  $\text{H}_2$  gas insertion (10 and 5 sccm respectively, 86 mTorr) for 10 min. For graphene transfer, poly(methyl methacrylate) (PMMA) was spin-coated onto the Gr/Cu assembly and the Cu foils were etched in an aqueous solution of 0.1 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . After being rinsed in distilled water, the PMMA/Gr was transferred onto the  $\text{O}_2$  plasma-treated PET substrate. The PMMA/Gr/PET assembly was dried on a hot plate at  $\sim 100^\circ\text{C}$  for 10 min. Finally, the PMMA was removed by washing with acetone.

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