# Flexible all-carbon photovoltaics with improved thermal stability

Chun Tang, Hidetaka Ishihara, Jaskiranjeet Sodhi, Yen-Chang Chen, Andrew Siordia, Ashlie Martini*, Vincent C. Tung*

*School of Engineering, University of California, 5200N. Lake Rd., Merced, CA 95343, USA*

A B S T R A C T

The structurally robust nature of nanocarbon allotropes, e.g., semiconducting single-walled carbon nanotubes (SWCNTs) and $C_{60}$s, makes them tantalizing candidates for thermally stable and mechanically flexible photovoltaic applications. However, $C_{60}$s rapidly dissociate away from the basal of SWCNTs under thermal stimuli as a result of weak intermolecular forces that "lock up" the binary assemblies. Here, we explore use of graphene nanoribbons (GNRs) as geometrically tailored protecting layers to suppress the unwanted dissociation of $C_{60}$s. The underlying mechanisms are explained using a combination of molecular dynamics simulations and transition state theory, revealing the temperature dependent disassociation of $C_{60}$s from the SWCNT basal plane. Our strategy provides fundamental guidelines for integrating all-carbon based nano-p/n junctions with optimized structural and thermal stability. External quantum efficiency and output current–voltage characteristics are used to experimentally quantify the effectiveness of GNR membranes under high temperature annealing. Further, the resulting $C_{60}$:SWCNT: GNR ternary composites display excellent mechanical stability, even after iterative bending tests.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

The discovery of graphene oxide's (GO) amphiphilicity has unlocked new opportunities for creating next generation carbon based composites with greater durability and improved material properties [1–4]. Spatially distributed graphitic patches on the basal plane mimic gecko's feet to facilitate interactions with the hard-to-process carbon nanomaterials while carboxylic groups simultaneously impart water processability. Unlike other surfactants that form hard-to-remove byproducts, GO can undergo an insulating-to-conducting transition under chemical or thermal reduction to yield reduced GO (rGO) [5]. This leads to an increase of graphitic domains, both in size and number, thus forming percolated networks for carrier transportation [6]. Furthermore, since the surfactant itself is the functional building block of the final assembly, a wide variety of new carbon based hybrids with uninterrupted interfaces are now possible through this unconventional self-assembly route [7,8]. Recently, we demonstrated that nano-carbon based solar cells comprised of geometrically tailored GO (graphene nanoribbons, GNRs, chemically unraveled from multiwalled carbon nanotubes), semiconducting single walled carbon nanotubes (SWCNTs) and fullerenes can be conveniently fabricated through the aqueous based solution processing route,

and have already delivered a power conversion efficiency (PCE) exceeding 1% under AM 1.5 G illumination [9–14]. While intense research efforts have been directed towards mending interspersed defects on basal plane to improve overall charge transport, little has been done regarding the mechanically and chemically robust nature of GNRs. The "membrane-like" morphology makes GNRs very "flimsy" and flexible objects that spontaneously undergo conformational transitions when not supported by substrates [15]. This can be explained by the abrupt decrease in flexural rigidity as a result of GNR's distinct dimensions, with thicknesses of only a few atomic layers, while lateral dimensions range from the submicron to micrometer levels. Combined with solvent-resistant and electrically conductive properties, this distinctive mechanical feature has opened up new research avenues to use GNRs as an impermeable and elastic barrier material for coating, transporting and interconnecting layers [16,17]. Indeed, our previous MD simulation-based study showed that spontaneous dissociation of C60 clusters from the basal plane of SWCNTs can be significantly suppressed upon assembly with GNRs [11].

Here we report that use of such GNR thin films as the protecting layer for $C_{60}$:SWCNT binary composites can withstand thermal stimuli and iterative mechanical stress. We perform MD simulations of GNR-protected $C_{60}$:SWCNT, which provide insights into how thermal stimuli influence structural stability, the mechanisms for improving stability via atomically thin membrane, and the correlation between membrane size and stability. In addition, we analyze the results in the context of the transition state theory (TST),

revealing the underlying energetic mechanisms driving observed trends and suggest avenues for future device optimization. Lastly, photovoltaic cells built upon the conceptual design of GNR stabilized carbon nano junctions exhibit improved thermal stability and can sustain iterative mechanical bending without adversely affecting output characteristics.

## 2. Experimental section

### 2.1. Molecular dynamics simulations

MD simulations were performed using LAMMPS software. The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [18,19] was used to describe the covalent carbon–carbon bond interactions, the non-bonded interactions were described by the Lennard–Jones (L–J) potential with minimum energy 0.00284 eV and zero crossing distance 0.34 nm. For the initial structure, 144 $C_{60}$ molecules were placed next to a (7,6) SWCNT in a hexagonal pattern with the SWCNT-$C_{60}$ distance being 0.3 nm, as determined from energy minimization. To obtain ternary composites, GNRs of various sizes were added to the system and simulated at 300 K as described in our previous report [11]. The time step was set to 1 fs, and the Nosé–Hoover thermostat was used to control the temperature during simulation [19]. Stability simulations were then performed for both $C_{60}$:SWCNT and $C_{60}$:SWCNT:GNR structures at temperatures ranging from 150 K to 700 K. When the SWCNT-$C_{60}$ distance was larger than 0.75 nm, the $C_{60}$ was assumed to have dissociated from the SWCNT. The percent of $C_{60}$ molecules dissociated from the surface of the SWCNT at 1 ns was calculated at each temperature point for each GNR size.

### 2.2. Experimental fabrication and characterization

Nanocarbon composites comprised of $C_{60}$s and SWCNTs were created using an electrohydrodynamic assembly. The thickness of each layer was determined through cross-sectional SEM (ULTRA-55 FESEM), and Dektak Profilometer (Dektak 150). External quantum efficiency measurements were conducted using QE-R by Enli, Taiwan, connected with an ORIEL solar simulator at a constant light intensity of 100 mW/cm$^2$.

The details behind the interfacial assembly process are described, beginning with the raw materials used. $C_{60}$ powders (Nano C) are used as purchased without further purification. The synthesis of GNRs began with suspending MWCNTs (Sigma Aldrich) in concentrated sulfuric acid ($H_2SO_4$) for a period of 12 h and then treated them with 500 wt% potassium permanganate ($KMnO_4$). The immersion of $H_2SO_4$ enables the exfoliation of the nanotube and the subsequent graphene structures. The reaction mixture was stirred at room temperature for 1 h and then heated to 70 °C for an additional 1 h. A vial containing 1 mL of DI-water was used to monitor the exfoliation process. The reaction was completed when droplets of reactant completely dispersed without visibly distinguishable precipitation. When all of the $KMnO_4$ had been consumed, we quenched the reaction mixture by pouring over ice containing a small amount of hydrogen peroxide ($H_2O_2$ 10 mL). The solution was filtered over a polytetrafluoroethylene (PTFE) membrane, and the remaining solid was washed with hydrochloric acid (HCl) followed by ethanol/ether. The matte black pellet was re-dispersed in a mixture of methanol and DI-water ($V/V$, 1:9 volume ratio) and centrifuged at 2000 rpm for 1 h. (6,5) SWCNTs were purchased from SWeNT and were extensively purified using a modified density gradient ultracentrifugation with assistance of poly(9,9-dioctylfluorene) (PFO) [20]. In brief, 1.25 mg/mL SWCNTs were tip-sonicated using a horn-tip sonicator for 45 min in a 12.5 mg/mL solution of PFO in toluene.

Bundles and catalyst material were removed through a 3 h centrifugation at 31,000$g$ in a fixed angle rotor. The resulting supernatant (top 85% of a 3 cm vial) was carefully extracted and then centrifuged for another 18 h at 31,000$g$. Isolated or small bundles of SWCNTs were moved a total distance of 0.8 cm and filtered into pellet. The pellet was iteratively re-dispersed through a low power, horn micro-tip sonication in toluene (output level at 15% for 1 h), and re-centrifuged to remove residual polymer. Next, the SWCNT pellets were re-dispersed into a mixture of chlorobenzene and THF ($V/V$, 1:1 volume ratio) and re-centrifuged at 31,130$g$. The resulting SWCNT pellet was iteratively washed with copious amounts of acetone, ethanol and deionized (DI) water. Finally, a high temperature annealing was used to further remove any residual polymers and carbonaceous byproducts (Fig. S1). A typical procedure of preparing nano-carbon ink starts from dissolving $C_{60}$s directly in toluene and then stirring for 30 min. Highly purified SWCNTs were then added to $C_{60}$ dispersions, followed by tip-sonication for 4 h at an output power level of 15%. The emulsion process begins with the simultaneous injection of the $C_{60}$:SWCNT dispersion (mass ratio of 6 μg SWCNT to 30 μg $C_{60}$s) in toluene with the GNR (2 μg) dispersion in DI water and methanol ($V/V$, 9:1) through a coaxial electrohydrodynamic spraying setup. The feeding rate of each constituent were kept at 22 μL/min for $C_{60}$:SWCNT and 2 μL/min for GNR solution, respectively, through computerized syringe pumps. Deposition time of 13 min was found to deliver the highest photovoltaic performances. In the presence of a strong electric field, the nano-carbon ink forcibly disseminates into highly charged, self-dispersing droplets with nearly monodispersed diameter distribution in the sub-micron to nanometer ranges. Each droplet serves as a "nano-reactor", triggering the assembly process of $C_{60}$:SWCNT with GNRs at air/organic/water interfaces. Capillary forces resulting from gradual solvent evaporation allow for $C_{60}$:SWCNT composites in the organic phase to accumulate at these interfaces. Furthermore, these structures are then stabilized by the vdW forces when in contact with 2-D graphitic membranes. This alternative approach was found to create dense networks of ternary nano-carbon composites over the entire substrate. To mimic the high temperature environment in MD simulation and TST, assembly of the $C_{60}$:SWCNT:GNR active layers was conducted on a preheated hotplate at elevated temperatures throughout the course of the deposition position. Subsequently, the samples were again annealed for 1 h and a dense layer of $TiO_2$ nanoparticles (P25, Sigma Aldrich) was then directly spun cast onto the $C_{60}$:SWCNT:GNR layer, effectively preventing the diffusion of subsequent metal deposition. $TiO_2$ nanoparticles were dispersed in a mixture of methanol and DI water ($V/V$, 1:1). Next, the samples were annealed at 200 °C for 1 h to remove excess solvents. Lastly, the device was transferred to a vacuum chamber for Ag electrode evaporation (80 nm). In the case of flexible photovoltaics, PET/ITO was used as the flexible conductive substrate with a total device area of 0.4 cm$^2$. Current–voltage characteristics of photovoltaic cells were taken using a Keithley 2400 source measuring unit under AM 1.5 G spectrum simulation and light intensity was calibrated via KG-5 Silicon Diode using an Oriel 9600 solar simulator.

## 3. Results and discussion

### 3.1. Theoretical analysis

Fig. 1a schematically illustrates the representative snapshots of $C_{60}$:SWCNT assembly using MD simulation after 1 ns at different temperatures. The binary $C_{60}$:SWCNT composite remains intact up to 300 K (only 5.6% at 150 K and 10.4% at 300 K of $C_{60}$s originally resided on the surface dissociate), presumably due to the van der