Title: Flexible All-carbon Photovoltaics with Improved Thermal Stability

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Abstract: 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.

Keywords: nanocarbon p/n junctions, flexible photovoltaics, thermal stability, graphene nanoribbons.

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 1.5G 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 [under molecular dynamics \(MD\) simulation](#). [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, in our previous report on MD simulation, spontaneous dissociation of C_{60} 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/cm².

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 2,000 r.p.m. for 1h. (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 minutes 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 (Figure S1). A typical procedure of preparing nano-carbon ink starts from dissolving C₆₀s directly in toluene and then stirring for 30 minutes. Highly purified SWCNTs were then added to C₆₀ dispersions, followed by tip-sonication for 4 hours at an output power level of 15%. The emulsion process begins with the simultaneous injection of the C₆₀:SWCNT dispersion (mass ratio of 6 µg SWCNT to 30 µg C₆₀s) 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 C₆₀: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 C₆₀: SWCNT with GNRs at air/organic/water interfaces. Capillary forces resulting from gradual solvent evaporation allow for C₆₀: 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 C₆₀: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 TiO₂ nanoparticles (P25, Sigma Aldrich) was then directly spun cast onto the C₆₀:SWCNT:GNR layer, effectively preventing the diffusion of subsequent metal deposition. TiO₂ 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 cm². Current-voltage characteristics of photovoltaic cells were taken using a Keithley 2400 source measuring unit under AM 1.5G 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

Figure 1a schematically illustrates the representative snapshots of C₆₀:SWCNT assembly using MD simulation after 1 ns at different temperatures. The binary C₆₀:SWCNT composite remains intact up to 300K (only 5.6% at (150K) and 10.4% (300K) of C₆₀s originally resided on the surface dissociate), presumably due to the weak van der Waals (vdW) force. However, the percentage of dissociated C₆₀s exceeds 50% when the surrounding temperature gradually rises to 400K, as shown in Figure 1b. This can be attributed to the additional external stimuli in the form of thermal turbulence that effectively helps to circumvent the local minimum of Lenard-Jones (L-J) potential barrier, thus propelling more fullerenes away from SWCNTs. Further we quantify the dissociation rate (k) as the percentage of C₆₀s dissociated during the

simulation period of 1 ns. The variation of dissociation rate with temperature summarized in Figure 1c showed a clear monotonic increasing trend, indicating the structural stability decreases with increasing temperature. To further quantitatively describe dissociation process, we adopted the following equation from TST[21] to quantify our MD simulation results:

$$k = f \cdot e^{\left(\frac{-E_b}{k_B \cdot T}\right)} \quad (1)$$

where f is the attempt frequency, E_b is the activation energy or energy barrier, k_B is the Boltzmann constant and T is temperature. We fit the simulation data to this equation and obtained values of the attempt frequency and energy barrier; the fitted Eq. (1) is also shown as a dashed line in Figure 1c. The best fit attempt frequency f is $1.72 \times 10^{12} \text{ s}^{-1}$, which is well within the range reported in literature for a variety of processes that can be described by TST, and the energy barrier E_b is 0.13 eV.[21-23]

Figure 2 schematically illustrates the energetic profile for the dissociation process. For the C_{60} :SWCNT case shown in Figure 1a, the energy barrier that a C_{60} must overcome in order to dissociate is the same as the L-J energy well depth (E_0) associated with the vdW interaction between SWCNT and the C_{60} , i.e. $E_b = E_0$. From our MD simulations, this energy barrier is 0.46 eV. However, as discussed above, the fit of our simulation data to Eq. 1 yields an energy barrier of 0.13 eV. Although this result is on the same order as the MD value, the discrepancy is not negligible and will be discussed next.

The energy shown in Figure 2a corresponds to the ideal case when the C_{60} : SWCNT system is in an energetically optimized configuration, i.e. all the SWCNT- C_{60} separations are exactly at the energy minimum distance (0.3 nm). However, in real simulations and experiments, the C_{60} molecules vibrate around their equilibrium states such that there is a distribution of SWCNT- C_{60} distances. We observe this to be the case in our simulations. Figure 3 shows the L-J interaction energy of all the C_{60} molecules with the SWCNT and the corresponding SWCNT- C_{60} distance in our simulation. At 150 K after 0.1 ns of simulation

time (Figure 3a), even though the majority of the C_{60} s are trapped around the equilibrium SWCNT- C_{60} distance of 0.3 nm (corresponding to L-J energy of 0.46 eV), less than half of them are within $\pm 2\%$ of the minimum energy distance. More importantly, some of the C_{60} molecules exhibit large positional oscillations and the SWCNT- C_{60} distances are beyond 0.455 nm, which corresponds to a SWCNT- C_{60} interaction energy of 0.13 eV (the fit E_0 value) or weaker. At ambient or elevated temperatures, these molecules will tend to dissociate from the SWCNT surface. C_{60} oscillations increase with temperature, subsequently increasing the number of C_{60} molecules that are, on average, further from the SWCNT. This is illustrated for the same system at 300 K and 0.1 ns in Figure 3b. The time-dependent evolution of the L-J energy of all the C_{60} molecules is shown in Figure 3c: we can clearly see that the initial model has a very narrow distribution of L-J energy around 0.46 eV. As the simulation proceeds, the number of C_{60} s at the energy minimum state decreases, with more of them redistributed to higher energy states, in particular, to states where their interaction energy is 0.13 eV or weaker. This means that at ambient conditions, an activation energy less than E_0 is required to initiate the dissociation process. This explains why, in our TST fitting, we obtained an energy barrier less than the minimum vdW energy for a single SWCNT- C_{60} interaction.

In the case of C_{60} :SWCNT:GNR composites, the GNR provide an additional energetic resistance (E_w) to dissociation, as shown in the energy profile in Figure 2(b); hence the total energy barrier is $E_b=E_0+E_w$. To verify this hypothesis and explore the physical meaning of E_w , we performed additional simulations of GNR protected C_{60} :SWCNT assembly. We considered GNRs of four different sizes: $19.5 \times 4.2 \text{ nm}^2$, $19.5 \times 8.5 \text{ nm}^2$, $19.5 \times 12.8 \text{ nm}^2$, $19.5 \times 17.0 \text{ nm}^2$. Our results show that, upon [interacting with](#) GNR, the stability of the system is significantly improved. For example, at 500 K, the dissociation rate decreases from 55.6% for the C_{60} :SWCNT alone to 4.17% when stabilized by a $19.5 \times 4.2 \text{ nm}^2$ GNR, despite the fact that the GNR does not fully cover the C_{60} : SWCNT structure. The maximum dissociation rate

for this GNR is found to be 27.8% at 700 K. When stabilized by a larger GNR, the dissociation rate is further suppressed, as shown in Figure 4a.

This behavior can still be described by TST, but with a higher energy barrier due to both SWCNT- C_{60} interactions and the [interaction with graphene](#), as illustrated by Figure 1a. We refit the simulation results for C_{60} :SWCNT structures assembled with GNR of different sizes to Eq. (1); the attempt frequency was not changed. As shown in Figure 4b, increasing the [contacting area](#) decreases the disassociation rate which in turn increases the energy barrier obtained from fitting the data to Eq. 1. The contribution from SWCNT- C_{60} interactions, E_0 , is constant, but that from the GNR, E_w , increases with [contacting area](#). Thus, the energy barrier can be written as a linear function of the [contacting area](#):

$$E_b = E_0 + 0.0011 \times A, \quad (2)$$

where $E_0 = 0.13$ eV, and A is the [contacting area](#). Note that A is not the area of the GNR because there is maximum amount of coverage possible that occurs when the GNR assembles completely around the structure. Increasing the GNR size more results in a scroll-like configuration where the GNR is folding around itself. The extra area due to the overlapping of the GNR nanoscroll does not provide additional stability for the C_{60} molecules. This occurs when the GNR area is above 205 nm^2 . Therefore, as shown in the inset of Figure 4b, we observe the saturation of E_b at a GNR area of approximately this magnitude.

3.2 Experimental Findings

To validate our theoretical prediction on the improved thermal stability of all-carbon composites, GNRs of four different dimensions (e.g., width of 20, 25, 50 and 140 nm) are prepared through the oxidative cutting of multiwalled carbon nanotubes (Figure S2).[24] Figure 5a features the tip of a coaxial nozzle for electrohydrodynamic emulsion process. The synergistic assembly of C_{60} :SWCNT:GNR composites starts with atomization of a solution of the precursors into an electrospray of micro/nano droplets in a coaxial manner.[25] This step is achieved by simultaneously injecting the solution at a certain feeding rate. As a result, each

precursor contacts at the interfaces and is suspended toward the heated substrates, causing the solvent to begin evaporating and inducing the synergistic assembly of GNR onto the C₆₀:SWCNT structures (Figure 5b). Surface-active GNR membranes, which are known to adhere to the different interfaces to minimize the surface energy, start to undergo dimensional transitions to assemble around the binary assembly of C₆₀:SWCNT bundles.[11] Experimental observations are in accordance with MD simulations, which suggest that the vdW force drives the GNRs to preferentially adhere the C₆₀ surface. On the other hand, the assembling pattern is determined primarily by the aspect ratio of the GNR membranes. While the resulting thin film appeared to be uniform over the entire substrate, the morphological features at nanoscale were found to contain networks of slightly porous nanostructures as shown in Figure 5d. In a close-up view of high resolution scanning electronic microscopy (HRSEM) images, most of the networks consist small bundles (in some rare cases, few individual SWCNTs as shown in inset of Figure 5d). Next, the C₆₀:SWCNT:GNR active layers were thermally annealed to cleanly restore the graphitic patches on the basal plane, thus creating electrically addressable carbon-carbon interfaces in the final assembly. In addition, the solvent resistant nature of the all-carbon composites after thermal annealing formed the foundation for subsequent solution processing of TiO₂ as a transporting layer for charge carriers and a blocking layer to prevent the shorting (Figure 5e).

Figure S3 schematically shows the photovoltaic device architecture (starting from the bottom: glass/indium tin oxide (ITO) substrates, GO:SWCNT hole transporting layer, C₆₀:SWCNT:GNR photoactive layer, TiO₂ nanoparticles, and finally a thermally deposited silver electrodes). To quantitatively investigate the thermal stability of C₆₀:SWCNT photoactive layers, external quantum efficiency (EQE) measurements of the photovoltaic devices were first performed (Figure 6a). The EQE provides elegant insights into the stability of the C₆₀: SWCNT structures, because it is a direct measure of how efficiently the dissociated electron-hole pairs are collected at the opposite electrodes. Tightly bounded

excitons generated within the SWCNT active layer will not undergo dissociation and propagation if there are (a) unfavorable energetics inhibiting the propagation of charge carriers or (b) no built-in electric field stemmed from p-n junctions, i.e., n-type C₆₀ and p-type SWCNTs, in a close proximity to provide an external driving force.[26-28] To examine the temperature effect on the stability, we specifically adapted a modified electrohydrodynamic assembling process (see Methods section) that allows us to both systematically and qualitatively explore the correlation between stability and thermal fluctuation of the GNR stabilized all-carbon p-n junctions. Without GNR barrier layers, the control cells comprised of only C₆₀: SWCNT binary composites exhibited a weak photoresponse under elevated temperatures. In particular, photoresponse originated from fullerenes is greatly diminished, indicating the unwanted dissociation of fullerene clusters from the SWCNT backbones. Alternatively, the EQE of the device with GNR protecting layers showed a significantly improved response across the visible to NIR range under short circuit conditions (short circuit current, J_{sc} of 4 mA/cm²), as a result of much-preserved integrity of carbon nano-p/n junctions. The EQE peaks at 25.4 % in the visible region and 13.7 % in the NIR. Even at a higher annealing temperatures, up to 500 K, the covering of GNR membranes still effectively suppresses the leaking of C₆₀s from photoactive layers. Although the overall EQE has decreased, with a peak efficiency of 19.8%, most of the signature characteristics from individual graphitic allotropes are clearly present. The moderate decrease of EQE, especially in the visible range (450 nm for C₆₀), can be attributed to the presence of free C₆₀s that were not fully protected by the GNR membranes, making them vulnerable to thermal turbulence at high annealing temperatures. Meanwhile, the photoresponse from semiconducting SWCNT at around 975 nm did not reduce significantly, indicating the robust protection of GNR that is resistant to external disturbance. This experimental observation demonstrates the key role of GNR in stabilizing the photoconductive carbon nanocomposites. The observed trend is in a good agreement with our MD simulations and the framework of TST. MD results show that

the stability of the C₆₀: SWCNT structure decreases with increasing temperature, as exhibited by the continuous dissociation of C₆₀ molecules at elevated temperatures. The relationship between dissociation rate and temperature is consistent with the predictions of TST. Furthermore, introduction of GNRs provides an additional energy barrier to dissociation and thereby significantly improves the stability. The energy barrier due to incorporation of GNR is proportional to the interacting area over the C₆₀ molecular surface and saturates once the C₆₀s are fully covered by GNR, supporting experimental observations. The drastic enhancement in thermal resistance of such photoconductive all-carbon composites upon assembling with GNR broadens their versatility in thin film energy harvesting devices where the thermal stability is a great challenge.

To further systematically reveal the correlation between the interacting layers and thermal stability of carbon nano-p/n junctions, GNRs of diverse dimensions were explored. To this end, C₆₀: SWCNT nano-hybrids were assembled by GNR barrier layers of four widths: 20 nm, 25 nm, 50 nm, and 140 nm. With increasing width of the GNR, the EQE increases monotonically until it saturates at a critical GNR width of 50 nm (Figure 6b). It is found that when the GNR width is larger than 50 nm, the EQE saturates and then slightly reduces. This is explained by the formation of energetically unfavorable metal-semiconductor junctions as the semiconducting nature of graphene nanoribbons gradually falters due to the overlapping of graphitic domains. Several published studies have simultaneously discussed the drawbacks of integrating metallic like nano-carbon derivatives, e.g., bundles of carbon nanotubes and stacks of GO into organic photovoltaic cells, adversely affecting exciton extraction.[10-12, 29, 30] Our results illustrate a clear relationship between thermal stability and GNR size, offering key guidelines for designing optimized all-carbon nanocomposites with desired structural stability and photoconductivity. Additionally, photovoltaic output characteristics of C₆₀: SWCNT active layers protected by the stabilization of GNR sheets remain comparable upon thermal annealing at 400K for one hour, delivering V_{oc} of 0.51V, J_{sc}

of 3.9 mA/cm², FF of 60%, and a power conversion efficiency (PCE) of 1.21% (Figure 6c). In contrast, control cells without GNR protecting layers showed a much-reduced photovoltaic response both prior and after annealing. Specifically, the FF, which closely associates with the energetics of each layer decreases drastically even before thermal annealing, presumably due to the spontaneous dissociation at room temperature and the lack of energetically favorable hole transporting GNR layers.[17] In addition, C₆₀s start dissociating from the active layers upon annealing, leaving behind sparsely distributed carbon nano-p/n junctions. As a result, FF appreciably reduces from 60% to almost 31%.

Aside from the improved thermal stability, the carbon nano-p/n junctions assembled by GNRs also attain comparable output performance under high mechanical stress. The aforementioned low temperature electrohydrodynamic processing unlocks the opportunity to deposit photoconductive carbon solar inks directly onto flexible conductive substrates, e.g., Polyethylene terephthalate (PET)/ITO. Inset of Figure 6d features such a flexible photovoltaic device laminated onto a curvilinear surface. The flexible photovoltaic cells delivered V_{oc} of 0.51V, J_{sc} of 4.05 mA/cm², FF of 42%. In comparison to the rigid devices, the losses in both J_{sc} and FF could be due to the higher contact resistance of the flexible substrates stemmed from the degradation of underlying ITO conductive layer, possible non-uniform surface coverage and insufficient crystallinity of TiO₂ nanoparticles. The high temperature annealing process of TiO₂ (~400°C) is unlikely to be compatible with the underlying PET/ITO substrates, thus leading to undesired materials properties that adversely affect the transport of charge carriers. These issues should be well addressed with the rapid advancement of graphene or metal nanowire based transparent conductors in tandem with the use of alternative n-type transporting layers, including fullerene derivatives that can be processed at a relative low temperature, thus greatly improving the overall performance.[8, 31, 32] Nevertheless, the power conversion efficiency retains 85% with respect to the rigid counterparts. In addition, the photoconductive C₆₀:SWCNT:GNR composites supported on

flexible substrates were found to sustain iterative mechanical bending at 120° without significantly compromising overall performance. Figure 6d shows the device performance after mechanical bending of 100 times. No significant deterioration was observed regarding V_{oc} and J_{sc} , underscoring the potential of such all-carbon nanocomposites in flexible energy harvesting applications.

4. Conclusion

In summary, we have explored the 2-D soft GNR membranes as the barrier layers for photoconductive but thermally unstable C₆₀: SWCNT nano-p/n junctions. MD simulations show that the decreasing stability with surging temperature can be described by the TST. Geometrically tailored GNR increases the energy barrier for the C₆₀s to dissociate from the SWCNT surface, thus greatly suppress the influence of thermal stimuli. When the GNR width is beyond a critical value, the energy barrier saturates. Our MD simulations mesh well with the experimental measurements and uncover the mechanism of improved thermal and mechanical stability via the use of 2-D membranes. Experimental measurements show that incorporation of the soft graphitic membranes greatly improves the structural stability even under high temperature annealing up to 500 K. Further, the mechanically resilient nature of these nanocarbon composites were found to withstand iterative mechanical bending without significantly compromising the overall photovoltaic performance. The results presented here provide basic guideline to designing highly efficient, thermally stable and mechanically flexible carbon nano-p/n junctions based photovoltaic devices.

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6. Figures

Figure 1. (c) Representative snapshots of the C₆₀: SWCNT structures after 1 ns at different temperatures. (b) Percent of C₆₀ molecules dissociated from the (7,6) SWCNT surface at different temperatures; no GNR interaction is considered here. (c) Dissociation rate versus temperature extracted from (a; the square symbols are from MD simulations, and the dashed curve is fit to Eq. 1

Figure 2. Dissociation energy profile depicts energy difference for the SWCNT:C₆₀ structure (a) without and (b) with GNR interaction, respectively. Without GNR, the energy barrier for dissociation is equal to E_0 . When GNR is included, the energy barrier E_b is the sum of E_0 and E_w .

Figure 3. (a) At a temperature of 150 K, the distribution of SWCNT- C_{60} distance and the corresponding L-J energy between each C_{60} and the (7,6) SWCNT at 0.1 ns. Each point represents a C_{60} molecule; (b) the same system at a temperature of 300 K, 0.1 ns; (c) Time dependent distribution of SWCNT: C_{60} L-J energy at 300 K.

Figure 4. (a) Dissociation rate versus temperature for various $\text{C}_{60}:\text{SWCNT}$ structures stabilized by GNR membranes. The symbols are from MD simulations, and the curves are fits to Eq. 1. (b) The energy barrier obtained from TST fitting as a function of interacting area. The red line is a linear fit to the data, inset shows the same data plotted as a function of the GNR area.

Figure 5. Images of (a) the tip of coaxial electrohydrodynamic spraying and (b) emulsion droplets captured by a high-speed camera. (c) Dense networks of the ternary composites on ITO substrate pre-coated with GO:SWCNT modification layers. HRSEM images show the (d) nano-p/n junctions comprised of C_{60} :SWCNT [binary composites stabilized](#) by GNRs. Inset shows the close-up view of such all-carbon composites along with the snapshot taken from MD simulation. (e) Dense and pinhole free TiO_2 nanoparticles for both blocking and electron transporting layers. Scale bars are 200 nm.

Figure 6. (a) EQE characteristics of nano-p/n junctions with and without GNR protecting layers under high temperature annealing. Inset shows the device architectures. (b) Corresponding EQE with respect to the width of the GNRs that were used to stabilize the C₆₀:SWCNT structure. (c) Current-voltage output characteristics of nano-p/n junctions after annealing. (d) The C₆₀:SWCNT based photovoltaic not only shows an improved thermal stability and can withstand mechanical bending. Inset displays the device that was bent on a curvilinear glass vial for measurement.

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