



Carbon Nanosheets and Nanostructured Electrodes in Organic Photovoltaic Devices

**Cooperative Research and Development
Final Report**

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Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI.A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

CRADA number: CRD-08-321

CRADA Title: Carbon Nanosheets and Nanostructured Electrodes in Organic Photovoltaic Devices

Parties to the Agreement: Luna Innovations

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources
Year 1	\$ 00.00
Year 2	\$ 00.00
Year 3	\$ 00.00
TOTALS	\$ 00.00

Abstract of CRADA work:

Carbon nanosheet thin films were employed as nanostructured electrodes in organic solar cells. Due to the nanostructured texture of the carbon nanosheet electrodes, there was an increase in performance over standard ITO electrodes with very thick active layers. ZnO deposited via atomic layer deposition (ALD) was used as a hole blocking layer to provide for carrier selectivity of the carbon nanosheets.

Summary of Research Results:

Organic photovoltaic (OPV) devices have been fabricated on carbon nanosheet (CNS) coated quartz substrates that were grown by the team at Luna. A stainless steel shadow mask was developed to allow for the direct deposition and growth of pre-patterned CNS electrodes, as seen in Figure 1. This approach allowed for reproducible device area and aided in the device fabrication process.

The patterned CNS electrode coated substrates were initially used as-received and a blend of poly(3-hexylthiophene):[6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) was deposited onto the CNS electrode. Initial studies used an inverted architecture where the CNS electrode would serve as the electron contact due in part to their relatively low work function (-4.2 eV). The active layer blend was deposited from a solution of P3HT:PCBM with a total concentration of 60 mg/ml in 1,2-dichlorobenzene at a ratio of 1:1 by weight. This solution was spin coated at 500 RPM and allowed to dry slowly over the course of 30 minutes. This film deposition process was tailored to increase the expected film thickness beyond the optimized 225 nm active layer thickness that is used in our planar ITO electrode devices to

help to overcome the increased electrode roughness present in the CNS films. The resulting film was subsequently annealed at 110 °C for 10 minutes in an inert atmosphere. The films were then treated with a low power (30 watts) O₂ plasma for 10 seconds that results in increased surface energy of the active layer film surface that allows for improved wetting thereby enabling the deposition of poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS), which is an aqueous suspension of a conductive polymer that acts as an hole transport layer and electron blocking layer in the bulk heterojunction polymer:fullerene device. After this light plasma treatment, PEDOT:PSS was spin coated at 4000 RPM on top of the active layer. The PEDOT:PSS coated device stack was subsequently annealed for 2 minutes in air at 110 °C to drive water out of the film and to improve the contact properties of the PEDOT:PSS. Finally, the devices were completed by depositing 100 nm Ag electrodes through a shadow mask at a pressure of 10⁻⁷ Torr. Completed devices were then measured under a tungsten halogen based solar simulator to evaluate their PV performance.



Figure 1. Patterned CNS electrodes as deposited through the shadow mask.

Bulk heterojunction P3HT:PCBM devices resulted in relatively poor performance due to the conductive nature of the CNS coated substrates, as seen in Figure 2. While there was an observed photoresponse (both photocurrent and photovoltage) of the devices when illuminated these were quite low due to the very poor current density - voltage (J-V) characteristics of the devices. Although PEDOT:PSS was used as an electron blocking layer at the the Ag electrode, it is apparent that the CNS electrode is not a selective contact for electrons in the bulk heterojunction device thereby resulting in the observed poor device performance.

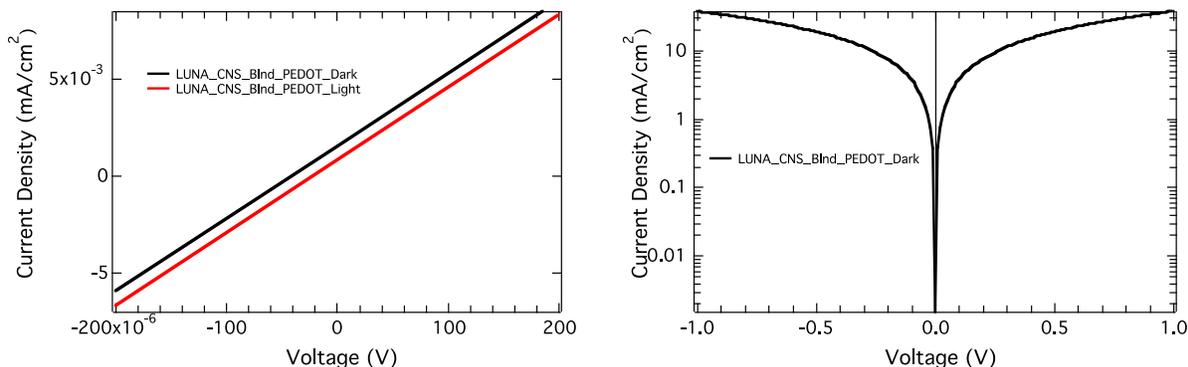


Figure 2. Current density vs. voltage (J-V) characteristics of a CNS/P3HT:PCBM/PEDOT:PSS/Ag device. Left: light vs. dark IV curve for CNS device demonstrating a photoresponse under light (red) vs. dark (black). Right: Dark IV curve in log/linear plot showing poor diode characteristics due to the lack of a hole blocking layer on the CNS surface.

Therefore, it was imperative that a hole blocking layer be used at the active layer / CNS interface so as to provide a selective contact at this interface, which will help to further define the diode characteristics of the device and would likely result in improved bulk heterojunction device characteristics. Hole blocking layers such as TiO_2 or ZnO can both be deposited using conformal deposition techniques such as atomic layer deposition (ALD) and sol-gel techniques. ALD has already been used to conformally coat the CNS. Additionally, the deposition of such materials at the interface of the large surface CNS films and the active layer would allow for more efficient hybrid OPV where the ZnO or TiO_2 materials can act as the electron acceptor in such a system and the enhanced interfacial area and the high conductivity of the CNS network should allow for higher device performance in these systems as well.

Upon the device results obtained above, we concluded that a hole blocking layer is required on the CNS samples in order to enhance the diode characteristics. The deposition of TiO_2 on CNS samples had previously been achieved through an acid treatment of the CNS films followed by atomic layer deposition (ALD) of TiO_2 . [Rooth et al. Atomic layer deposition of titanium dioxide nanostructures using carbon nanosheets as a template. *J Cryst Growth* (2009) vol. 311 (2) pp. 373-377]

An ALD chamber at NREL was used for the deposition of hole blocking layer materials. This system had been used to successfully deposit Al_2O_3 , TiO_2 and ZnO . As such, we explored the possible nucleation strategies other than the acid treatment described in the above reference. The use of an O_2 /Argon plasma treatment of the CNS films followed by a single layer deposition of trimethylaluminum resulted in a favorable nucleation strategy for the growth of ZnO thin films via ALD. The single layer of trimethylaluminum results in a nucleation layer that cannot self passivate through a dimerization process that may occur with linear precursors such as the diethyl zinc used for the ZnO growth. This process resulted in the successful nucleation and growth of ZnO on the CNS substrates as observed in x-ray fluorescence elemental analysis as seen in Figure 3 below.

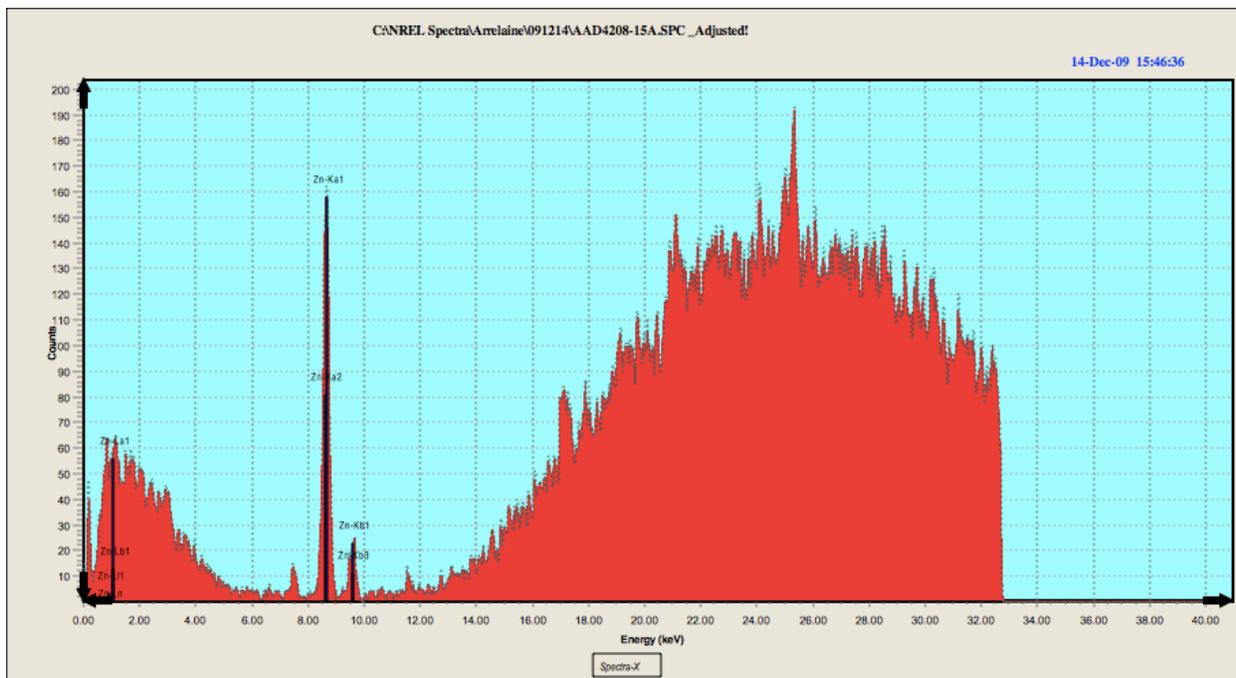


Figure 3. Above is a x-ray fluorescence (XRF) spectrum showing the presence of Zn on the CNS film, indicating the successful deposition of ZnO on the CNS substrate.

The CNS films were coated with 40 and 100 nm conformal films of ALD ZnO and evaluated in inverted devices. The 40 nm ALD ZnO thickness proved to be the best ZnO thickness, which agrees well with our previous work on solution deposited ZnO films for planar inverted device architectures. Devices on relatively thick CNS films ($\sim 2 \mu\text{m}$) coated with ALD ZnO are shown in Figure 4. The device performance was observed to be very poor with little to no PV effect. There were changes observed with illumination, however in order to prevent shorting in these thick CNS devices the active layer thickness had to be drop cast resulting in an active layer thickness of $\sim 9 \mu\text{m}$. Such thick active layers result in poor charge transport and extraction compounding the already low carrier mobility in the organic semiconductors.

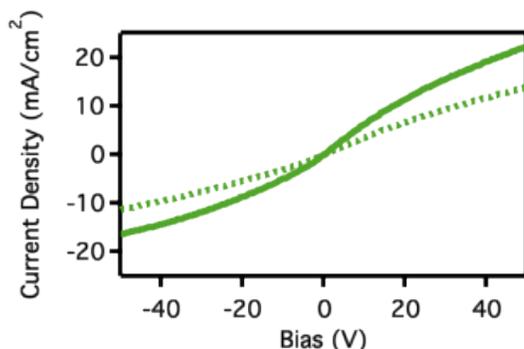


Figure 4. J-V characteristics of ALD ZnO coated thick CNS films.

The surface roughness of the CNS films and films coated with spin coated P3HT:PCBM were evaluated using atomic force microscopy (AFM). As seen in Figure 5, the surface roughness is reduced after coating the CNS films with the active layer. The electrical properties of the active layer coated CNS films was investigated with conducting AFM measurements. As seen in Figure 6, the conductivity of the coated CNS film is quite non-uniform. Current - voltage (I-V) scans at high current locations demonstrated high conductivity shunt pathways for current to flow directly into the CNS, whereas reasonable diode characteristics are observed in low current areas. This indicates that when coated with an adequate thickness of the active layer, the CNS/ZnO/P3HT:PCBM stack can function effectively as a diode, suggesting that reducing the shunt pathways could lead to functional devices.

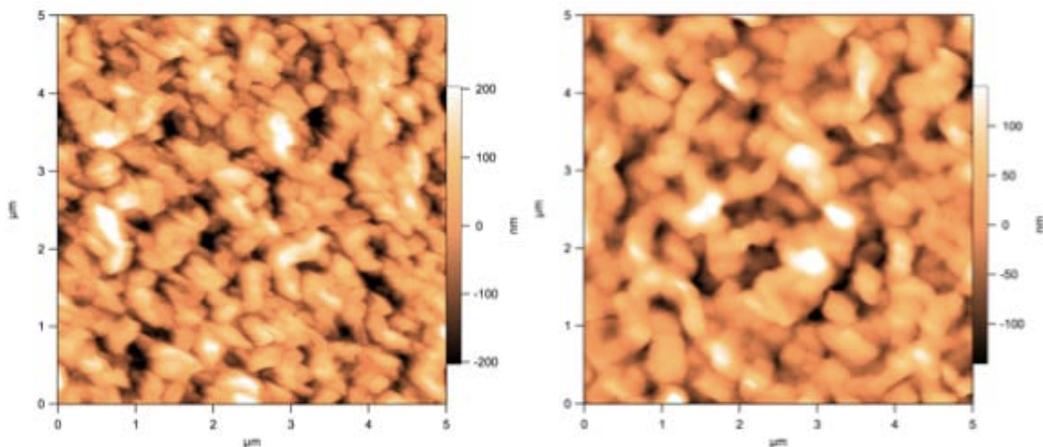


Figure 5. AFM topography images of CNS film (left) and P3HT:PCBM coated CNS film (right).

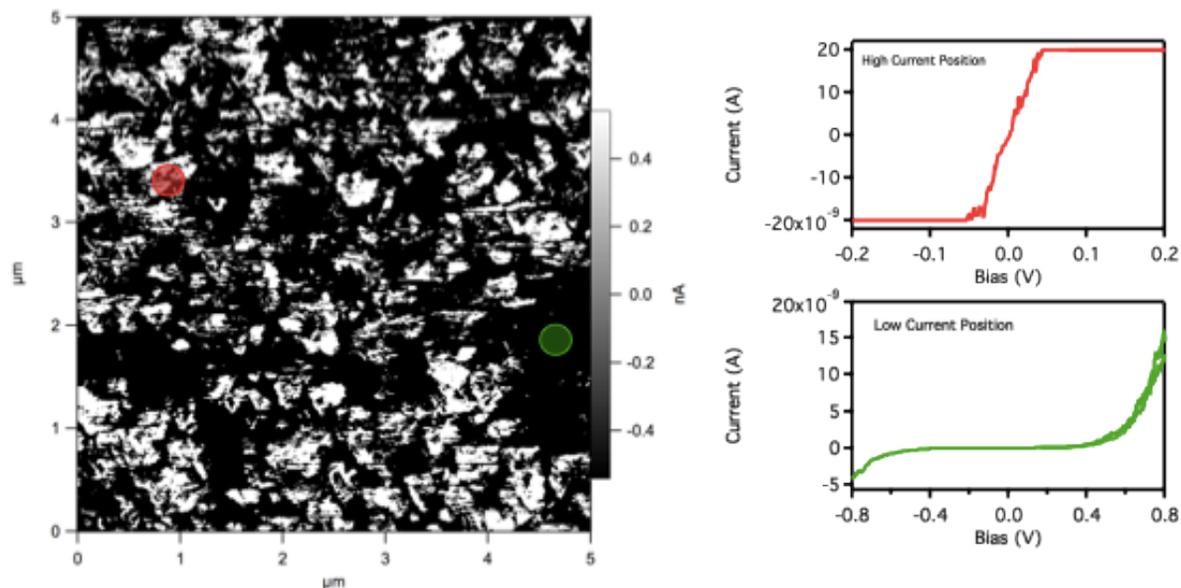


Figure 6. Conductive AFM images of P3HT:PCBM coated CNS film (left) and current - voltage scans of high current (top, right) and low current locations (bottom, right).

Thinner CNS films were deposited and evaluated in order to reduce the CNS roughness and active layer thickness in hopes of increasing the device performance. Thin patterned CNS films resulted in reduced conductivity and increased series resistance, making it necessary to deposit a silver busbar on the CNS film in order to reduce the sheet resistance to levels similar to that of ITO as seen in Figure 7.

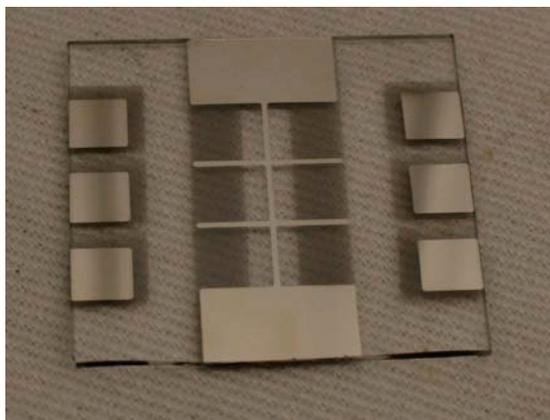


Figure 7. Thin patterned CNS electrodes with silver bus bar

Standard device architectures employing a CNS/P3HT:PCBM/Ca/Al device stack are shown in Figure 8 as a function of the active layer thickness. These were deposited on thin CNS films (~ 100 nm) and demonstrate increasing diode quality with increasing active layer thickness. Despite employing thinner CNS films, the optimized active layer thickness was still quite thick in order to avoid shunting of the devices. This indicates that while the CNS films are on average thinner, there is still a very large surface roughness with nanosheets that extend well beyond the measured CNS film thickness, which lead to efficient shunt pathways.

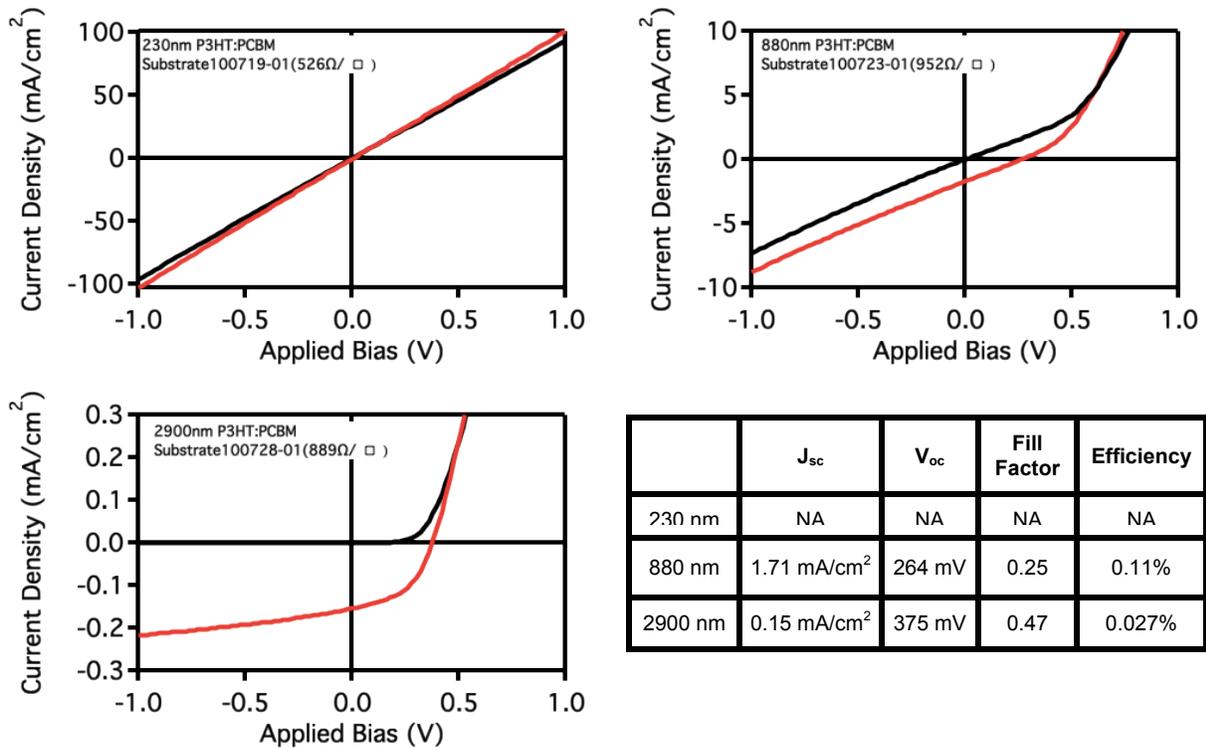
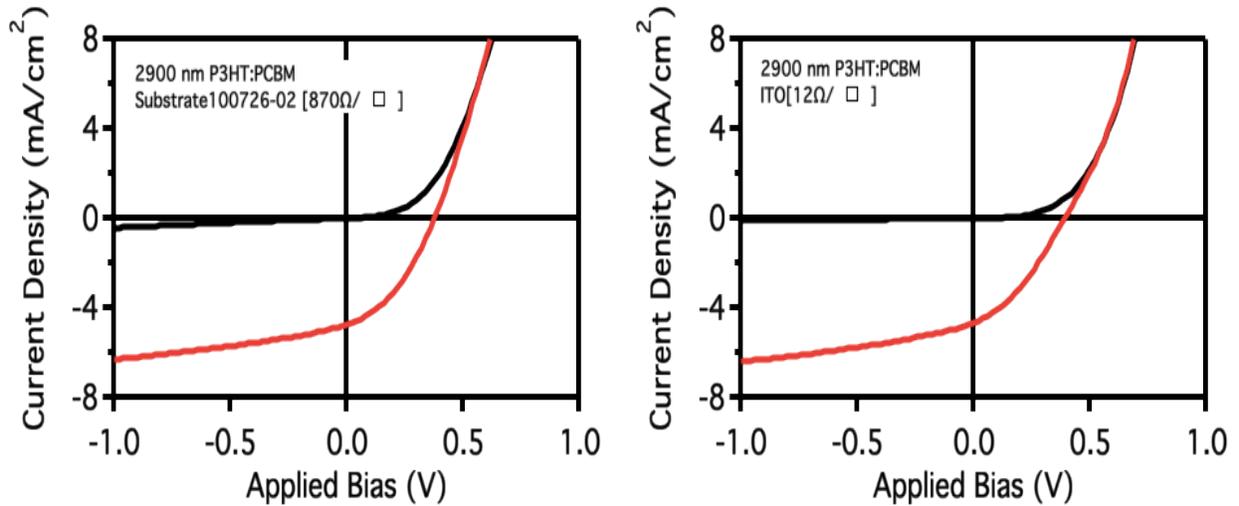


Figure 8. J-V characteristics of CNS/P3HT:PCBM/Ca/Al devices with increasing active layer thickness showing improved diode characteristics with thickness.

Inverted device architectures demonstrated improved performance relative to the standard device data presented above, with the inverted CNS-based device outperforming an equivalent ITO device as seen in Figure 9. The active layer thickness was optimized at 2.9 μm , still quite thick for planar device architectures, however the nanostructured CNS electrode provided increased current collection and fill factor relative to the ITO control. The open circuit voltage was slightly lower for the CNS device, which is likely due to the lower shunt resistance owed to the rough CNS electrode. The decreased shunt resistance results from an increased dark leakage current in the CNS device. This leakage current results in the smaller observed photovoltage in the CNS devices.



	J_{sc}	V_{oc}	Fill Factor	Efficiency	Shunt Resistance	Series Resistance
CNS	4.73 mA/cm ²	376 mV	0.38	0.66%	38 kΩ	356 Ω
ITO	4.66 mA/cm ²	390 mV	0.34	0.61%	167 kΩ	213 Ω

Figure 9. J-V characteristics of CNS/ZnO/P3HT:PCBM/PEDOT:PSS/Ag devices compared to equivalent planar ITO devices.

CNS electrodes demonstrate improved PV device performance with thick active layer systems owing to the nanostructured electrode morphology that allows for increased collection of carriers in a thick bulk heterojunction system. Additionally, transport in these nanostructured pathways is quite efficient resulting in improved fill factor.

Subject Inventions listing: n/a

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