**Title:** Aligned Carbon Nanotubes for Highly Efficient Energy Generation and Storage Devices

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**Abstract:**
As we proposed originally, the major objective of this project is to develop efficient energy generation and storage devices (e.g., solar cells, fuel cells, supercapacitors) by using vertically-aligned carbon nanotube arrays and carbon nanomaterials. We have demonstrated the use of aligned CNT arrays could enhance performance for many energy generation and storage devices. The aligned structure has also facilitated the surface functionalization and allowed an effective device construction. The growth of well-aligned CNTs with controllable length, diameter, and spacing has served the base for all of the work performed in this project. This project has led to about 23 journal publications, 4 book chapters, and received numerous commentaries appeared in scientific, business, and popular press (please see: “Events & News” at http://case.edu/cse/eche/daigroup/news.html and many others on internet).

**Subject Terms:**
Nanotubes, graphene, functionalization, aligned arrays, energy-related devices
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ABSTRACT

As we proposed originally, the major objective of this project is to develop efficient energy generation and storage devices (e.g. solar cells, fuel cells, supercapacitors) by using *vertically-aligned* carbon nanotube arrays and carbon nanomaterials. We have demonstrated the use of aligned CNT arrays could enhance performance for many energy generation and storage devices. The aligned structure has also facilitated the surface functionalization and allowed an effective device construction. The growth of well-aligned CNTs with controllable length, diameter, and spacing has served the base for all of the work performed in this project. This project has led to about 23 journal publications, 4 book chapters, and received numerous commentaries appeared in scientific, business, and popular press (please see: “Events & News” at [http://case.edu/cse/eche/daigroup/news.html](http://case.edu/cse/eche/daigroup/news.html) and many others on internet).
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I. ACCOMPLISHMENTS AND NEW FINDINGS

1. SUMMARY OF ACCOMPLISHMENTS ON CARBON NANOTUBES FOR ENERGY APPLICATIONS

1.1 Density Control of Vertically-aligned Carbon Nanotube Arrays for Advanced Nanoelectrodes (J. Mater. Chem. 2010, 20, 3595.)

We have developed a facile, but effective and versatile, lift-up method to controllably remove vertically-aligned carbon nanotubes (VA-CNTs) from their growth substrates. The intrinsic micron-scale roughness of the VA-CNT top surface and commercially available adhesive tapes enabled us to make selective contacts between the constituent nanotubes in a VA-CNT array and an adhesive layer for selective lift-up of VA-CNTs from the growth substrate (Figure 1). As a result, we can region-selectively control the CNT density to tailor the spacing between VA-CNTs, opening a new way to fabricate novel CNT nanoelectrode arrays attractive for electroanalyses and many other applications, including for energy storage and conversion.

1.2 Multilevel, Multicomponent Microarchitectures of Vertically-aligned Carbon Nanotubes for Diverse Applications (ACS Nano 2011, 5, 994.)

In this study, a simple multiple contact transfer technique has been developed for controllable fabrication of multilevel, multicomponent microarchitectures of vertically-aligned carbon nanotubes (VA-CNTs). Three dimensional (3-D) multicomponent micropatterns of aligned single-walled carbon nanotube (SWNTs) and multiwalled carbon nanotubes (MWNTs) have been fabricated, which can be used to develop a newly-designed energy-efficient touching sensor with reversible electrical responses for potential applications in electronic devices (Figure 2). The demonstrated dependence of light diffraction on structural transfiguration of the resultant CNT micropattern also indicates their potential for optical devices. Further introduction of various components with specific properties (e.g., ZnO nanorods) into the CNT micropatterns enabled us to tailor such surface characteristics as wettability and light response. Owing to the highly generic nature of the multiple contact transfer strategy, the methodology developed here could provide a general approach for interposing a large variety of multicomponent elements (e.g. nanotubes, nanorods/wires, photonic crystals, metal oxides for energy storage and conversion, etc.) onto a single chip for multifunctional device applications.
Figure 2. (A) A schematic illustration of the multiple contact transfer for multicomponent micropatterns of VA-SWNT/VA-MWNTs. (b) SEM image of aligned MWNTs transferred onto the Scotch tape after the first contact transfer. (c) Aligned SWNTs/MWNTs micropattern on Scotch tape after the second contact transfer. (d) An enlarged view of the selected region in (c). (B) (a, b) Schematic illustrations of the 3-D VA-MWNT/VA-SWNT multicomponent micropatterns at the decompression and compression state, respectively; (c) Current-voltage responses (i) and (ii) corresponding to (a) and (b), respectively; and (d) Current response to the compression-decompression cycles at a voltage of 5 V. Tested pattern area: 1 mm². (adapted from ACS Nano 2011, 5, 994.)
1.3 Soluble P3HT-Grafted CNTs for Efficient Bilayer-heterojunction Photovoltaic Devices (Macromolecules 2010, 43, 6699.)

In this study, CH$_2$OH-terminated regioregular poly(3-hexylthiophene) (P3HT) was grafted onto carboxylic groups of acid-oxidized carbon nanotubes (CNTs) via esterification reaction (Figure 3). The P3HT-attached CNTs (P3CNTs) are soluble in common organic solvents, facilitating an intimate mixing with free P3HT chains for strong electronic interactions. The optical and electrochemical properties of the resultant nanocomposite were found to be different from the conventional composite, in which the pristine CNT and P3HT were physically mixed together (P3HT/CNT). Electrochemical measurements on the onset oxidation and reduction potentials of the P3CNT showed positive shifts by 0.06 and 0.1 eV, respectively, with respect to the corresponding values of pure P3HT, indicating that P3CNT has a lower highest occupied molecular orbital (HOMO) energy level and a lower lowest unoccupied molecular orbital (LUMO) energy level than those of pure P3HT. Bilayer photovoltaic devices with a thin film of pure P3CNT as the electron-donor and C$_{60}$ as the electron-acceptor layer showed an increase in the power conversion efficiency by about 40% with respect to their counterpart based on pure P3HT.

1.4 Highly-Efficient Metal-Free Growth of Nitrogen-Doped Single-Walled Carbon Nanotubes on Plasma-Etched Substrates for Oxygen Reduction (JACS 2010, 132, 15127.)

In this study, we have for the first time developed a simple plasma-etching technology to effectively generate metal-free particle catalysts for efficient metal-free growth of undoped and/or nitrogen-doped single-walled carbon nanotubes (Figure 4). Compared with undoped CNTs, the newly-produced metal-free nitrogen-containing CNTs were demonstrated to show a relatively good electrocatalytic activity and long-term stability towards oxygen reduction reaction (ORR) in acidic medium. This finding will have a large impact not only on the fuel cell field and the catalyst community, but also on the nanotube growth as the metal residuals from metal nanoparticles used as catalysts for the conventional CNT growth often cause detrimental effects undesirable for various applications, including...
electronic and biological systems. However, possible use of CNTs produced by the metal-free growth has been largely precluded by its low growth efficiency. Owing to the highly generic nature characteristic of the plasma etching technique, the methodology developed in this study can be applied to many other substrates for efficient growth of metal-free CNTs for various applications, ranging from energy related to electronic and to biomedical systems.

1.5 Polyelectrolyte-Functionalized Carbon Nanotubes as Metal-Free Electrocatalysts for Oxygen Reduction (J. Am. Chem. Soc. 2011, 133, 5182.)

In this study, we found that quaternary ammonium functional groups along the PDDA backbone have a strong electron-accepting ability to withdraw electrons from carbon atoms in the nanotube carbon plane to induce the net positive charge (Figure 5), facilitating the ORR catalytic activity of the nitrogen-free CNTs adsorbed with the PDDA chains.

As shown by the XPS spectra in Figure 6A, only a pronounced C 1s peak was observed for the pristine nonaligned carbon nanotube (CNT) and vertically-aligned carbon nanotube (ACNT). The presence of a trace amount of O in the CNT sample is possibly due to the incorporation of physically adsorbed oxygen. Upon PDDA functionalization, a N 1s peak appeared and the intensity of the O 1s peak increased for both PDDA-CNT and PDDA-ACNT. The newly appeared N 1s peak comes from the adsorbed PDDA chain while the observed intensity increase in the O 1s peak for both PDDA-CNT and PDDA-ACNT indicates an enhanced oxygen absorption onto the PDDA-functionalized CNTs, suggesting an additional advantage as the ORR electrode. Figure 6B shows the high-resolution N 1s XPS spectra, in which the principle peak at around ~402 eV for pure PDDA is attributed to the charged nitrogen, N+. Compared to the N 1s XPS peak in pure PDDA, the PDDA N 1s peak position for PDDA-CNT and PDDA-ACNT shifted negatively to lower binding energy by ~0.5 eV, which indicates the occurrence of charge-transfer from CNT or ACNT to the N species of PDDA to positively charge carbon.
atoms in the conjugated electron-rich nanotube carbon plane.

Figure 6C clearly indicates a significant enhancement in the ORR electrocatalytic activity for the PDDA-adsorbed CNTs (i.e., PDDA-CNT) through the intermolecular charge-transfer. Compared with the PDDA-CNT electrode, the PDDA-ACNT electrode shows even a more positive shift in both the onset potential (-0.07 V) and the peak potential (-0.28 V) with a more pronounced increase in the current density. Apart from the charge-transfer effect, therefore, the alignment structure has also played a role in the ORR process by facilitating the electrolyte diffusion, as we previously demonstrated for the VA-NCNT electrode (Science 2009, 323, 760). As a control, we have also performed the ORR test on a solution-cast PDDA/GC electrode and bare GC electrode, showing no ORR activity. Therefore, the observed enhancement in the ORR electrocatalytic activity for the PDDA-functionalized CNT electrodes could be attributed exclusively to the intermolecular charge-transfer schematically shown in the left side of the slide.

Results from the linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) for each of the electrode materials, including the CNT-based and commercial Pt/C electrocatalysts, in O$_2$-saturated 0.1 M KOH at a scan rate of 10 mV s$^{-1}$ and a rotation rate of 1600 rpm are given in Figure 6D. As can be seen in Figure 6D, the ORR at the bare carbon nanotube electrode commenced around -0.24 V (onset potential), followed by a continuous increase in the current density with no current plateau. The ORR onset potential at the PDDA-CNT electrode significantly shifted positively to -0.14 V and the limiting diffusion current at -0.4 V became about 3 times stronger with a relatively wide plateau in respect to the bare CNT electrode. Compared to both the PDDA-CNT and bare CNT electrodes, the strongest limiting diffusion current with a very wide current plateau was observed for ORR at the PDDA-ACNT electrode due, most probably, to an efficient four-electron pathway. The ORR current density at -0.4 V at the PDDA-ACNT electrode is 1.5 and 4.5 times that at the PDDA-CNT and bare CNT electrode, respectively, indicating that the combined effects of the PDDA adsorption and the aligned CNT structure are responsible for the high ORR electrocatalytic activity observed for the PDDA-ACNT electrode. Although the onset potential of ORR on PDDA-ACNT (-0.09 V) is still lower than that of the Pt/C electrode, its limiting diffusion current density is close to that of the Pt/C catalyst.

With many existing polyelectrolytes and more to be developed, the adsorption-induced intermolecular charge-transfer should provide a cost-effective solution approach to large-scale production of various carbon-based efficient metal-free ORR catalysts for oxygen reduction in fuel cells, and even new catalytic materials for applications beyond fuel cells (e.g., metal-air batteries, electrochemical biosensors).

2. SUMMARY OF ACCOMPLISHMENTS ON GRAPHENE FOR ENERGY APPLICATIONS

2.1. Nitrogen-Doped Graphene with High Electrocatalytic Activities for Oxygen Reduction

(ACS Nano 2010, 4, 1321.)

We used a modified chemical vapor deposition (CVD) method to produce graphene thin film on a SiO$_2$/Si substrate in large scale. In a typical experiment, a thin layer of nickel film (~300nm) was first deposited on a SiO$_2$/Si substrate by sputter coating, which was then heated up to 1000ºC within a quartz tube under a high purity argon atmosphere. Thereafter, a nitrogen-containing reaction gas mixture (NH$_3$:CH$_4$:H$_2$:Ar = 10:50:65:200 standard cubic centimeters per minute) was introduced into the quartz tube and kept flowing for 5 minutes, followed by purging with a flow of NH$_3$ and Ar only for another 5 minutes. The sample was then rapidly moved out from the furnace center (1000ºC) under Ar protection. The resultant N-containing graphene (designated as: N-graphene)
film can be readily etched off from the substrate by dissolving the Ni catalyst residues in an aqueous solution of HCl (1M), allowing the freestanding N-graphene sheets to be transferred onto substrates suitable for subsequent investigation. The resultant N-graphene was demonstrated to act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction via a four-electron pathway in alkaline fuel cells (Figure 7). To our knowledge, this is the first use of graphene and its derivatives as metal-free catalyst for oxygen reduction. The ease with which graphene materials and their N-doped derivatives can be produced by various low-cost large-scale methods, including the chemical vapor deposition, chemical reduction of graphite oxide, exfoliation of graphite, microwave plasma reaction, and atmospheric pressure graphitization of silicon carbide, suggests considerable room for cost effective preparation of metal-free efficient graphene-based catalysts for oxygen reduction. This work indicates that the important role of N-doping to ORR discovered in our previous study on nitrogen-doped carbon nanotubes can be applied to various carbon materials for the development of other low-cost, metal-free efficient ORR catalysts for fuel cell applications, even new catalytic materials for applications beyond fuel cells.

2.2 Polyelectrolyte-Functionalized Graphene as Metal-Free Electrocataystics for Oxygen Reduction (ACS Nano 2011, 5, 6202.)

We have previously found that nitrogen-doped carbon nanotubes and graphene could actively catalyze ORR via a four-electron process; free from the crossover and CO poisoning effects due to the electron-accepting ability of the nitrogen atoms that creates a net positive charge (via intramolecular charge-transfer) on adjacent carbon atoms in the nanocarbon structures to readily attract electrons from the anode for facilitating the O₂ adsorption and the ORR process. In the present work, poly(diallyldimethylammonium chloride), PDDA, was used as an electron acceptor for functionalizing graphene (Figure 8) to impart electrocatalytic activity for oxygen reduction.
reaction (ORR) in fuel cells. Raman and X-ray photoelectron spectroscopic (XPS) measurements indicate the charge transfer from graphene to PDDA. The resultant graphene positively-charged via the intermolecular charge-transfer with PDDA was demonstrated to show remarkable electrocatalytic activity toward ORR with better fuel selectivity, tolerance to CO posing, and long-term stability than that of commercially available Pt/C electrode. The observed ORR electrocatalytic activity induced by the intermolecular charge-transfer provides a general approach to various carbon-based metal-free ORR catalysts for oxygen reduction. This work demonstrated yet another novel concept for using the intermolecular charge-transfer to develop low-cost, metal-free ORR catalysts useful in a wide range of energy-related devices (e.g., fuel cells, metal-air batteries) for Air Force applications.

2.3 Soluble P3HT-Grafted Graphene for Efficient Bilayer-heterojunction Photovoltaic Devices (ACS Nano 2010, 4, 5633.)

In this study, we used a simple esterification reaction to chemically graft CH$_2$OH-terminated regioregular poly(3-hexylthiophene) (P3HT) onto carboxylic groups of the graphene oxide (GO). The resultant P3HT-grafted GO sheets (G-P3HT) are soluble in common organic solvents, facilitating the structure/property characterization and device fabrication by solution processing. The covalent linkage and strong electronic interaction between the P3HT and graphene moieties in G-P3HT were confirmed by spectroscopic analyses and electrochemical measurements. Because of the extensive electron delocalization between the chemically-linked P3HT and graphene moieties in the G-P3HT, a bilayer photovoltaic device based on the solution-cast G-P3HT/C$_{60}$ heterostructures (Figure 9) showed a 200 % increase of the power conversion efficiency ($\eta = 0.61 \%$) with respect to its counterpart based on the P3HT/C$_{60}$ mixture under AM 1.5 illumination (100 mW/cm$^2$). To our knowledge, this is the first time for graphene sheets chemically-bonded with P3HT being used in photovoltaic cells. This work demonstrated a novel concept for interfacial molecular engineering to develop organic soluble G-P3HT for a wide range of optoelectronic devices for applications interested to Air Force.
In this study, a simple lithiation reaction was developed to covalently attach monosubstituted C₆₀ onto graphene nanosheets. Detailed spectroscopic (e.g., FTIR, Raman) analyses indicated that C₆₀ molecules were covalently attached onto the graphene surface through monosubstitution. Transmission electron microscopic (TEM) observation revealed that these monosubstituted C₆₀ moieties acted as nucleation centers to promote the formation of C₆₀ aggregates of ~5 nm in diameter on the graphene surface. The resultant C₆₀–grafted graphene nanosheets were used as electron acceptors in P3HT-based bulk heterojunction solar cells to significantly improve the electron transport, and hence the overall device performance, yielding a power conversion efficiency of ~1.22% (Figure 10). These results indicate that C₆₀–grafted graphene sheets are excellent electron accepting/charge transporting materials for constructing efficient polymer solar cells and for many other applications. This will directly support the missions of AFOSR and this work will also contribute significantly towards strengthening the national capability for research and development of advanced solar cell systems.

Figure 10. (A) Schematic representation of C₆₀-grafted graphene as electron transport materials. (B) J–V curves of the photovoltaic devices with the C₆₀–G:P3HT (1:1 wt/wt), the C₆₀:P3HT (1:1 wt/wt), or the C₆₀/G mixture (10 wt% G):P3HT (1:1 wt/wt) as the active layers after annealing treatment (130 °C, 10 min). (adapted from J. Phys. Chem. Lett. 2011, 2, 1113.)

2.5 Voltage-induced Light Emission from Large-area Graphene Films (Appl. Phys. Lett. 2010, 96, 143107.)

In this study, voltage-induced incandescent light emission from large-area graphene films was demonstrated. Stable, bright and uniform incandescent emission with a low turn-on voltage (~6 V) was obtained for a free-standing graphene film (0.5 cm × 1 cm) under appropriate vacuum (0.05 Torr) or Ar protection.

In a typical experiment, an aqueous dispersion of graphene oxide (GO) was prepared from exfoliation of graphite by acid oxidation. The obtained GO was then solution-cast into a large-area film on a quartz plate, followed by thermal reduction in the mixed gas of Ar (400 SCCM)/H₂ (70 SCCM) at 900 °C for 3 h. Alternatively, free-standing graphene films were fabricated by vacuum filtration of chemically reduced GO dispersion, followed by thermal treatment according to a previously-reported method. To investigate the optical emission behavior of the graphene film, two parallel gold electrodes (width 1 mm; length 10 mm; separation distance 5 mm) were deposited on the quartz-supported graphene film by sputter-coating through a physical mask. The device was then placed in a vacuum chamber (0.05 Torr) before applying an external voltage for light emission measurements. Light emission was detected by a spectrometer (Ocean Optics) and a photometer (Minolta LS-110) at room temperature. The temperature of the graphene film during light emission...
was measured remotely by an infrared pyrometer (RAYTEK Marathon MM). Similarly, the free-standing graphene film was adhered to two metal electrodes and suspended above the quartz substrate for light emission measurements (Figure 11). The emission spectra fit well to the blackbody emission model with the emission intensity being exponentially proportional to the external voltage and inversely proportional to the gas pressure. Our results indicate great promise of graphene-based incandescent emitters for flexible flat-lighting applications, providing a body of information that will allow Air Force to design lighting-related systems to accomplish missions that are impossible with current devices and methods.

3. SUMMARY OF ACCOMPLISHMENTS ON CARBON NANOTUBE AND GRAPHENE / POLYMER NANOCOMPOSITES FOR ENERGY APPLICATIONS


In this study, stable aqueous dispersions of polymer-modified graphene nanosheets (GNs) were prepared via in-situ reduction of exfoliated graphite oxides in the presence of cationic poly(ethyleneimine) (PEI). The resultant water-soluble PEI-modified graphene sheets were then used for sequential self-assembly with acid-oxidized multiwalled carbon nanotubes, forming hybrid carbon films (Figure 12).

In a typical experiment, we chemically reduced GO sheets with hydrazine in the presence of poly(ethyleneimine) (PEI) as stabilizer. The introduction of the charged soluble polymer chain unit onto graphene plane should result in a well-dispersed graphene-based material. The adsorption of the water-soluble cationic PEI chains onto graphene sheets (PEI-GNs) could not only render the GNs to be dispersible/soluble but also make it possible for controllably fabricating multicomponent hybrid films by sequential self-assembly with other negatively-charged nanomaterials (e.g., acid-oxidized CNTs in the present case).
The availability of solution-processable GNs allowed the formation of GN-based functional films through various solution processing methods, including filtration, solution-casting, electrophoretic deposition, and Langmuir-Blodgett deposition. However, most of the above mentioned techniques suffer from a lack of the film architecture/property control, leading to the loss of the surface area for energy storage due to graphene aggregation. For energy storage applications, therefore, we have used 1D carbon nanotubes (CNTs) to physically separate 2D GNs to preserve graphene’s high surface area through layer-by-layer self-assembling of graphene sheets and CNTs (Figure 12). These hybrid films were demonstrated to possess interpenetrating network carbon structures with well-defined nanopores, exhibiting a nearly rectangular cyclic voltammogram even at an exceedingly high scan rate of 1 V/s with an average specific capacitance of 120 F/g to be promising for supercapacitor electrodes. This will directly support the missions of AFOSR and this work will also contribute significantly towards strengthening the national capability for research and development of advanced energy storage systems.


In this study, we reported a new class of nanocomposite electrodes for the development of high-performance supercapacitors with environmentally friendly ionic liquid electrolytes. These new nanocomposite electrodes consist of the high-surface-area activated carbons, carbon nanotubes, and ionic liquids as the integrated constituent components. The resultant composites show significantly improved charge storage and delivery capabilities. In an ionic liquid electrolyte, the composites possess a superior capacitance (188 F/g) over a pure carbon nanotube electrode (20 F/g) and a conventional activated carbon electrode (90 F/g). Based on these nanocomposite electrodes and an ionic liquid electrolyte, we have further developed prototype supercapacitors (Figure 13) with a high cell voltage (4 V) and superior energy and power densities (50 Wh/kg and 22 kW/kg, respectively).
respectively, in terms of the mass of the active electrode material. The nanocomposite supercapacitors developed in the present study clearly outperform the current supercapacitor technology, providing a new approach in fabricating advanced supercapacitors with a high performance, inherently safe operation, and long lifetime.

3.3 Hole and Electron Extraction Layers Based on Graphene Oxide Derivatives for High-Performance Bulk Heterojunction Solar Cells (manuscript in preparation)

In this work, we have demonstrated, for the first time, that simple charge neutralization of the -COOH groups in GO with Cs₂CO₃ could reverse the charge extraction property in BHJ solar cells. GO can act as an excellent hole-extraction layer while its Cesium-derivative, GO-Cs, is an excellent electron-extraction material for BHJ solar cells, independent of the anode and cathode materials. Their excellent charge extraction performance can be attributed to their unique work functions, coupled with the work function tunability simply through charge neutralization of the periphery -COOH groups of GO with Cs₂CO₃ into COOCs groups, and the ambipolar transporting ability of their basal plane. The normal and inverted devices based on GO hole- and GO-Cs electron-extraction layers (Figure 14) both outperform the corresponding standard BHJ solar cells with state-of-the-art hole- and electron-extraction layers. Therefore, the present study opens new avenues for the design and development of novel charge extraction materials for high-performance solar cells and many other optoelectronic devices.

4. OTHER ENERGY-RELATED DEVICES

4.1 Novel Benzo[1,2-b:4,5-b']dithiophene-Benzothiadiazole Derivatives with Side Chains for High-Performance Solar Cells (Adv. Mater. 2011, 23, 4554.)

In this study, we have synthesized two D-A alternating copolymers (i.e., PBDT-OBT, PBDT-FBT, Figure 15) by polymerizing modified benzo[1,2-b:4,5-b']dithiophene (BDT) and benzothiadiazole (BT) as the D and A segments, respectively. The attached thiophene side chains on the phenyl ring of BDT were designed to afford a more electron rich donor to lower HOMO levels. On the other hand, the BT units as acceptor in PBDT-OBT and PBDT-FBT were also modified with alkynoxy (slightly more electron-rich) and fluorine (electron-deficient) moieties, respectively. Since the introduction of a fluorine atom led to a more delocalized LUMO wave function, PBDT-
FBT showed a lower LUMO level, and hence a higher short circuit current, \( J_{sc} \), and a higher power conversion efficiency, PCE. The photovoltaic properties of the resultant copolymers were investigated in typical bulk heterojunction devices using PC71BM as the acceptor. High PCEs of 5.64% and 6.21% were obtained for PBDT-OBT and PBDT-FBT, respectively. Therefore, these copolymers are promising donor materials for application in polymer solar cells.

4.2 Highly Crystalline and Low Bandgap Donor Polymers for Efficient Polymer Solar Cells


In this study, we have developed a new class of highly crystalline, low bandgap D-π-A polymers (i.e., EI-PFDTBT) using ethylene bridging unit to ensure a coplanar configuration between the side chains and main chain. High efficiency polymer solar cells with a power conversion efficiency exceeding 5% have been constructed from the newly-synthesized polymer by solution-processing at elevated temperatures. Using the elevated-temperature solution-processing demonstrated in this study, therefore, high-performance PSCs could be constructed from many (semi-)crystalline polymers previously reported to be insoluble and incompatible with PCBM for photovoltaic applications.

II. JOURNAL PAPERS PUBLISHED FROM THIS PROJECT WITH ACKNOWLEDGEMENTS TO THE AFOSR GRANT AND BOOK CHAPTERS

JOURNAL PUBLICATIONS

1. D. Yu, L. Dai
   “Self-assembled graphene/carbon nanotube hybrid films for supercapacitors”

2. L. Qu, Y. Liu, J.-B. Baek, L. Dai
   “Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells”

3. L. Qu, Y. Zhao, Y. Hu, H. Zhang, Y. Li, W. Guo, H. Luo, L. Dai
   “Controlled removal of individual carbon nanotubes from vertically-aligned carbon nanotube arrays for advanced nanoelectrodes”


5. D. Yu, L. Dai
   “Voltage-induced incandescent light emission from large-area graphene films”
6. B. K. Kuila, K. Park, L. Dai
   “Soluble P3HT-grafted carbon nanotubes: synthesis and photovoltaic application”
7. D. Yu, Y. Yang, M. Durstock, L. Dai
   “Soluble P3HT-grafted graphene for efficient bilayer-heterojunction photovoltaic devices”
   “Metal-free carbon nanomaterials become more active than metal catalysts and last longer”
9. D. Yu, Q. Zhang, L. Dai
   “Highly-efficient metal-free growth of nitrogen-doped single-walled carbon nanotubes on plasma-etched substrates for oxygen reduction”
10. L. Dai
    “Layered graphene/quantum dots: Nanoassembly for highly efficient solar cells”
    Vertically-aligned carbon nanotube electrodes for lithium-ion batteries”
    “Controlled growth and modification of vertically-aligned carbon nanotubes for multifunctional applications”
    “Metal-free carbon nanomaterials become more active than metal catalysts and last longer”
14. L. Qu, R. A. Vaia, L. Dai
    “Multilevel, multicomponent microarchitectures of vertically-aligned carbon nanotubes for diverse applications”
15. W. Lu, R. Hartman, L. Qu, L. Dai
    “Nanocomposite electrodes for high-performance supercapacitors”
16. S. Wang, D. Yu, L. Dai
    “Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction”
17. D. Yu, K. Park, M. Durstock, L. Dai
    “Fullerene-grafted graphene for efficient bulk heterojunction polymer photovoltaic devices”
18. W. Lu, L. Dai
    “Carbon nanotubes for advanced energy conversion and storage”
“Polyelectrolyte-functionalized graphene as metal-free electrocatalysts for oxygen reduction”
ACS Nano 5, 6202, 2011.
20. Q. Peng, X. Liu, D. Su, G. Fu, J. Xu, L. Dai
“Novel benzo[1,2-b:4,5-b′]dithiophene-benzothiadiazole derivatives with variable side chains for high-performance solar cells”
“Multifunctional functional conjugated polymers with main-chain donors and side-chain acceptors for dye sensitized solar cells (DSSCs) and organic photovoltaic cells (OPVs)”
“Hole and electron extraction layers based on graphene oxide for high-performance bulk heterojunction solar cells”
(submitted)
23. J. Liu, H. Choi, J. Y. Kim, M. Durstock, L. Dai
“Highly crystalline and low bandgap donor polymers for efficient polymer solar cells”

BOOK CHAPTERS

1. W. Lu, L. Dai
4. Y. Xu, L. Dai

III. PERSONNEL SUPPORT

PROJECT PARTICIPANTS

Senior Personnel
Liming Dai (PI, CWRU)

Post-doctors
Dingshan Yu (Full time, CWRU)
Jun Liu (Part time, CWRY)

AFRL Collaborators
Michael Durstock (WPAFB)

Throughout the project, close collaboration was maintained with Dr. Michael Durstock at AFRL/MLBP in Dayton. Dr. Dai and his team will continue to work closely together with Dr. Durstock’s team to build a strong and long-term collaboration on energy initiatives to meet the Air Force needs.
IV. SIGNIFICANCE TO AIR FORCE AND CIVILIAN TECHNOLOGY CHALLENGES

Recent developments in military applications have placed renewed demands for new and improved high performance renewable power systems with significant improvements in weight to volume ratios and extraordinarily energy generation and storage capacities. This project brought together expertise and resources available at CWRU and AFRL. The outcome of the project directly supported the mission of AFOSR and AFRL and has contributed significantly towards strengthening the national capability for research and development of next generation power systems, including organic solar cells, fuel cells, and supercapacitors, by: 1) providing Air Force with a scientific rationale that led to innovations in the design of lightweight, flexible solar cells for Air Force applications, 2) providing a body of information that allowed Air Force to design renewable power systems to accomplish missions that are impossible with current devices and methods, 3) training graduate and/or post-doctoral students who assumed major responsibilities in critical defense- and civilian-related power system R&D, 4) bringing together multidisciplinary expertise and resources in the area of materials synthesis, characterization, device construction, and system integration from both CWRU and AFRL, and 5) enhancing academic collaboration with Air Force laboratories and other DoD national laboratories. The interests of this project to Air Force has been clearly evidenced by a substantial amount of the proposed work that has been carried out in the Wright-Patterson Air Force Research Laboratory in close collaboration with AFRL researchers. The outcomes of this project should also provide an opportunity for the domestic energy industry to create new jobs and strengthens the U.S. economy. This will further enhance our position to capture the economic and military benefits emerging from developments in this field. Our work has received numerous commentaries appeared in scientific, business, and popular press (please see: “Events & News” at http://case.edu/cse/eche/dagroup/news.html and many others on internet). Our technologies are envisioned to be transformative and having a large impact on the energy field, and their repercussions are continuing.

V. INTERACTIONS/TRANSITIONS

During this project period, the PI has been elected to be Fellows to the Royal Society of Chemistry and the American Institute of Medical and Biological Engineering and invited to serve as members of the Advisory Editorial Board for several international journals, including the Journal of Physical Chemistry (ACS), Nano Energy (Elsevier), Journal of Nano Energy and Power Research (American Scientific Publisher), and Journal of Molecular and Engineering Materials (World Scientific Publishing), while the PI and team members have presented the results from this project at many national and international conferences, including:


Co-Chair for “Nanomaterials and Nanotechnology in Fuels and Energy Production” at 241st ACS National Meeting & Exposition, Anaheim, California, March 27-31, 2011.

The 8th Annual Taiwan/U.S. Air Force Nanoscience Workshop, Seattle, Washington, April 5-6, 2011.


Invited talk at the National Meeting pf The Federation of Analytical Chemistry and Spectroscopy, Reno, NV, October 2 - 6, 2011.

Invited talk at the International Conference on One-dimensional Nanomaterials 2011 (ICON 2011), Beijing, China, December 7-9, 2011.

2010
Invited talk at the 12th International Ceramics Congress & 5th Forum on New Materials, Montecatini Terme, Italy, June 6-18, 2010.
Invited talk at the 2nd International Conference on Cellular and Molecular Bioengineering, Singapore, August 2-4, 2010.

2009
Invited talk at the ACS 238th National Meeting, DC, August 16-20, 2009.
Invited talk at the 2009 American Composite Society Annual Meeting, Delaware, September 15-17, 2009.
Invited talk at the International Green Energy Nanocarbon Conference, Chonju, South Korea, November 4-7, 2009.