Carbon Nanostructures in Organic Photovoltaics

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Center for Nanophase Materials Sciences is one of five DOE Nanoscale Science Research Centers.

Focus on Basic Science

www.cnms.ornl.gov
OPV R&D Capabilities

Synthesis, Purification
(small molecules, polymers, nanomaterials)

Processing
(small and large area)

Characterization
(+neutrons, +environment)

Theory, Modeling and Simulation

Critical R&D Capabilities Under the Same Roof
High-Impact Nanoscience Research
User Research Program

User proposal is 1-2 page long is expected to answer What-Why-How-When questions in the proposal form.
Next deadline: Wednesday, October 17, 2012
Successful applicants will be able to use CNMS facilities starting February 1, 2013

CNMS Scientific Themes:
Origins of Functionality at the Nanoscale
(Multiscale Functional Nanomaterials group)
Functional Polymer Architectures
Understanding Emergent Behavior

Proposal acceptance procedure: Internal feasibility review, external scientific review (2-3 reviewers/proposal). 30-40 percent of rated proposals

DOE-funded programs
Science Undergraduate Laboratory Internships (SULI) - Applications due October 1, 2012
Higher Education Research Experiences (HERE) – graduate students

Users Have Free Access to R&D Capabilities
Carbon Nanostructures for OPV

Graphene oxide

Graphene

Fullerenes

Chiral vector
\[ \mathbf{c}_{nm} = n\mathbf{\hat{a}}_1 + m\mathbf{\hat{a}}_1 \]

\((\mathbf{\hat{a}}_1, \mathbf{\hat{a}}_1)\) are the unit vector of 2D graphene lattice

\((n, m)\) indices

**Nanotube diameter**

\[ d_t = \sqrt{a(n^2 + nm + m^2)}/\pi \]

where \(a=0.246\text{nm}\)

**Chiral angle**

\[ q = \tan^{-1}\sqrt{3}m/(2n + m) \]

There is a potential to create all carbon PV

Sustainable

Capable of being continued with minimal long-term effect on the environment
Carbon Nanotubes

- **SWCNT** (m-SWNT, s-SWNT)
- **DWCNT**
- **MWCNT**

- Graphene
- Graphene Oxide
- Nanoparticles

Now CNTs are produced in commercial quantities

Estimated total capacity of CNT world-wide production in 2011 is 2,300-2,500 t.

(C-nano Technology, Showa Denko, Nanocyl Arkema, Bayer Materials Science and others)
Diversity of CNT Optical Properties

Energy of Van Hove transitions depend on the diameter of CNTs and doping

- Metallic SWNT: $v_1 \rightarrow c_1$ corresponds to the “first van Hove” optical transition
- Semiconducting SWNT: $v_2 \rightarrow c_2$ corresponds to the “second van Hove” optical transition
Multifunctionality of CNT in OPV

- Transparent Conductive Electrode (tunable work function)
- Dopant to improve charge carrier mobility
- Acceptor (tunable optical properties - diameter, doping)
- Direct polymer crystallization - order polymer at the interface
- Improve polymer thermal stability

Diverse family of carbon nanomaterials
Facilitates the design of all carbon PV
Why Search for ITO Alternative?

- Limited availability of Indium
- Instability in the basic/acidic environments
- Susceptibility to ion diffusion into polymer
- Limited transparency in the NIR
- Mechanical instability on bending for TCO
- Cost competitive due to reduction in nanomaterial cost/low processing cost
- Current leakage of FTO (fluorine tin oxide electrodes due to surface defects)

Nanomaterial based TCC- assembly of nanomaterials
Transparent Conducting Coating
Indium Price/Source analysis

US Import Sources (2003-06):
China, 45%; Japan, 18%; Canada, 16%; Belgium, 6%; and other 15%.

It's not only about the cost of In, but its sustainable supply
Spectral Selectivity Requirements
Transparent Conductive Coatings

Window Types for Solar Gain Control
- reducing cooling loads—and peak electric use—in new and existing buildings. R&D- "passive" or static control of solar gain, and dynamic modulation “active" (chromogenic) windows.”

High Performance Coatings (R&D-non metal)
- Chromogenic or Dynamic Windows (R&D reflective transition metal hydrides)

Daylight Enhancement Technologies
- (anticipated lighting energy savings of 40%–70%.)

US DOE Building Technology Program -achieve 50% to 70% whole building energy improvements  
Source: BTP DOE EERE

Flexible electronics and solar applications dominate the publications in nanomaterial-based transparent conductive coatings

Market: Architectural windows and glass facades-float glass 4 bl. m²/year
First Figure of Merit TCC

Sheet resistance

$$Rs = \frac{1}{\sigma t},$$  where $\sigma$ is the electrical conductivity in $\Omega^{-1} \text{ cm}^{-1}$ (absolute value, \textit{does not depend} on the size of the square) and $t$ is the coating thickness in cm.

$$T = \frac{I}{I_0} = \exp(-\alpha t)$$  where $\alpha$ is the optical absorption coefficient measured in $\text{cm}^{-1}$

$$FOM = \frac{T}{Rs};$$

$$\frac{dFOM}{dt} = \frac{\sigma \exp(\alpha t) - \alpha t \alpha \exp(\alpha t)}{\exp(2\alpha t)} = 0, \quad t_{\text{max}} = \frac{1}{\alpha}$$

\textit{TCC with maximum transmittance} $T = 1/e = 37\%$ does sound useful
TCC Figures of Merit

\[ FOM_1 = \frac{T}{R_s} \]
max FOM observed at T=37%

\[ FOM_1 = \frac{T^x}{R_s} \]
where \( x = 10 \). max FOM at T=90%

\[ FOM_1 = \frac{T^x}{R_s} = \sigma \cdot t \cdot \exp(-10\alpha \cdot t), \ t_{max} = 1/10 \cdot \alpha \]

When reflection losses cannot be neglected:
\[ FOM_2 = \sigma \cdot t \{(1 - R^2)[\exp(\alpha \cdot t) - R^2\exp(-\alpha \cdot t)]^{-1}\}^{10} \]

\[ FOM_3 = \frac{\sigma}{\alpha} = -\{R_s \cdot \ln(T + R)\}^{-1} \]

\[ FOM_4 = \frac{\sigma_{op}}{\sigma_{dc}} = 2R_s(T^2 - 1) \sqrt{\frac{\varepsilon_0}{\mu_0}} = (T^2 - 1) \frac{R_s}{188}, (\text{ohm}) \]

For film thickness<< wavelength of light optical conductivity is constant

\( T \) is the optical transmittance, and \( R_s \)-electrical sheet resistance (ohm/sq) \( R_s = \frac{1}{\sigma t} \) where \( \sigma \) is the electrical conductivity in \( \Omega^{-1}\text{cm}^{-1} \), \( t \) is the coating thickness (cm), \( \alpha \) is the optical absorption coefficient (cm\(^{-1}\)) and \( R \) is the reflectivity.

Figure of Merit for SWNT

Conductivity of two component system

\[
\sigma_1 = \frac{N_1 e^2}{\gamma_1 mV (\omega^2 + \gamma_1^2)} + \frac{N_2 e^2}{\gamma_2 \omega^2} \frac{\gamma_2 \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma_2^2 \omega^2} \\
S_{\square} = \sigma_1(0) d = \frac{N_1 e^2}{mV \gamma_1} d.
\]

Ideal Drude metal mSWNT – free charge carriers >2000cm⁻¹
Lorentz oscillator s-SWNT to characterize bound charge carriers < 2000cm⁻¹.
Assumption: \( \pi - \pi^* \) and inter band transitions not counted for.
Reflection is small

\[
- \log T = \epsilon(\omega) \frac{N_2}{V} d.
\]

\[
M(\omega) = \frac{S_{\square}}{-\log T(\omega)} = \frac{N_1}{N_2} \frac{1}{\epsilon(\omega) m \gamma_1} \frac{e^2}{d}.
\]

where \( V \) is the volume of the system, \( N1, m, \) and \( \gamma_1 \) are the number of free carriers, the electron mass (effective mass of the carriers), and the width of the free-carrier conductivity the relaxation rate.

Flexible TCE Figure of Merit

introducing mechanical properties into FOM

\[ \Pi_{TC} = \frac{\sigma \varepsilon_c}{\alpha} \text{ ohm}^{-1} \]

\( \varepsilon_c \) - critical strain before critical failure which caused a device malfunction

\[ \Pi_{TC} = 0.15, \text{ SWNT LBL} \]
\[ \Pi_{TC} = 0.07, \text{ ITO} \]

100nm ITO on a PET \( \varepsilon_c = 1.1\% \) tension and 1.7\% in compression
\( \varepsilon_c \) is thickness dependent 0.83\% (200nm) 1.69\% (50nm thick)

N.A. Kotov ACS Nano 2010 4 (7), 3725-3734

CNTs demonstrate higher (better) FOM for flexible applications
Assembly of CNT-based TCE

Optimize the network of conducting nanotubes, reduce resistance of junctions and...
Characterization of Bundle and Junction Elements

• Ratio of Rj/Rb resistances correlates well with that measured on single bundles by others.
• Quantify effects of dopant on bundle and junction
Effect of nanotube length/aspect ratio

Gel electrophoresis and size exclusion chromatography (SEC) density gradient (iodixanol)

Possible problem: chiral rather than size dependent separation

The changes in conductivity can be quantitatively described by the generalized effective medium approximation.

Data extracted from J. Obrzut, ACS Nano 2 (9), 1879 (2008).

Demonstrates advantage of using length-separated tubes, compared to mixed length
Effect of s-/m- CNT on the FOM of TCC

Networks of m-SWNT show 1000x smaller Rs

HNO3 doped

s-/unsorted CNTs show 200000 ohm/sq.
m-CNT- 150 Ohm/sq and 80% transmittance


density gradient ultracentrifugation (DGU), dielectrophoresis, chemical selection, electrical breakdown, chromatography
DGU is commercialized by Nanointegris
The Effect of Number of Walls

0.6-0.9 nm, double wall carbon nanotubes with a diameter of 1.5-2.7 nm. Li, Appl. Phys. Lett. 91 (5), 053115 (2007).

DWNTs coatings are a factor of 2.4 better conducting compared to SWNTs. M. Hersam, Nat Nano 4 (1), 64 (2009).

Assuming aspect ratio of CNTs is the same

The tubes with a smaller number of walls exhibit better properties, and highly enriched DWNT take the lead in this group
Effect of metal decoration on the electro-optical properties

A two order of magnitude reduction in sheet resistance of Pd-FWNT was achieved,
Best TCC- about 274 ohm/sq. 81.65 % T @550 nm.

Li, ACS Nano 5 (8), 6500 (2011).

Pd-FWNT > Au-DWNTs > acid-DWNTs > Au-SWNTs > pristine DWNTs > pristine SWNTs
Summary on CNT based TCE

Resistive Touch Screen Display
88-90% T - 200-500 Ohm/sq

Capacitive Touch Screen Display
88-92% 100-1500 Ohm/sq.

LCD (pixel)
87-90% T 30-300 Ohm/sq.

Flat panel Display
80% 100 Ohm/sq.

Matches Requirements for Touch Screen Applications
CNT as Transparent Conducting Electrodes

PV efficiency with CNT electrode

Jsc, mA/cm²

Voc, V
CNT in active layer (P3HT-PCBM)

PV efficiency with CNT in Active Layer

CNTs as acceptor replacement in OPV

**Semiconducting SWNTs - P3HT**

- 3% s-SWNT “Optimal” concentration of CNTs
- $V_{oc} = 1.04V$ (3% SWNT)
- IQE of 26% is achieved for 1300-1400 nm
- Efficiency 0.72%. AM1.5, is governed by carrier recombination

DOI: 10.1021/nl202796u
Nanoengineering Coaxial Carbon Nanotube–Dual-Polymer Heterostructures

- CoMoCAT SWNTs coated with P3HT or F8BT polymers
- Preferential binding of P3HT to SWNT observed
- Red-shift (NIR) and broadening of absorbance spectra of polymers
- Functionality depends on Initial wrapper
  - F8BT acts as a barrier layer limiting electron-hole recombination hole (P3HT) and electrons (CNT)
  - P3HT acts as template to induce nanotube-seed morphology

Carbon Active Layer

Voc of 0.59 V and a power conversion efficiency of 0.21%

circuit current ($J_{sc}$) of 1.23 mA/cm², an open circuit voltage (Voc) of 0.59 V, and a fill factor of 0.29, giving rise to a power conversion efficiency of 0.21%.

All carbon PV Active Layer

Single chirality (6,5) S-SWCNT- C60

Efficiency depends on chiral purity of SWNTs. Admixture of other chiralities results in performance depletion

All carbon Active Layer PV

Single chirality 98% pure (6,5) S-SWCNT- C70

- s-SWCNT-PC70BM fullerene-rGO
  - Reported efficiency 1.3%
  - Calculated efficiency limit
    - 13% for 0.75-1.2 nm, and 9% for 1.2–1.7nm

- max Voc achieved Jsc is 10x smaller (thicker layer needed)

J. Grossman ACS Nano, Just Accepted (2012)
Towards All-Carbon Photovoltaics

• Progress in c-PV depends on efficient chiral separation of semiconducting nanotubes.
Graphene based TCE

Source – natural graphite powder, high purity, CVD

$5/kg graphite compared to more than $500/g for CNT

CVD growth- transfer

**Acidic route:** Graphite $\rightarrow$ GO $\rightarrow$ deposition $\rightarrow$ reduction (thermal or hydrazine) $\rightarrow$ Gr/Gr-O (significant number of defects R.S. Ruoff Carbon 2007, 45, 1558

**Organic solvent route:**
- N-methyl-pyrrolidone
- DMF


K. S. Novoselov Nano Letters 2008 8 (6), 1704-1708

**Surfactant route:**
- SDBS


**Electrochemical route:**
Graphene Figure of Merit

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88-90%T-200-500ohm/sq

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LCD (pixel)
87-90%T 30-300ohm/sq.

Flat panel Display
80% 100ohm/sq.
Roll-to-roll production of 30-inch graphene films for transparent electrodes

Sukang Bae¹, Hyeongkeun Kim¹³, Youngbin Lee¹, Xiangfan Xu⁶, Jae-Sung Park⁷, Yi Zheng⁵, Jayakumar Balakrishnan⁵, Tian Lei¹, Hye Ri Kim², Young Il Song⁶, Young-Jin Kim¹³, Kwang S. Kim⁷, Barbaros Özyilmaz⁵, Jong-Hyun Ahn¹,⁴, Byung Hee Hong¹,¹² and Sumio Iijima¹⁸

The outstanding electrical¹, mechanical²,³ and chemical⁴,⁵ properties of graphene make it attractive for applications in flexible electronics⁶-⁸. However, efforts to make transparent conducting films from graphene have been hampered by the lack of efficient methods for the synthesis, transfer and doping of graphene at the scale and quality required for applications. Here, we report the roll-to-roll production and wet-chemical doping of predominantly monolayer 30-inch graphene films grown by chemical vapour deposition onto flexible copper substrates. The films have sheet resistances as low as ~125 Ω·sq⁻¹ with 97.4% optical transmittance, and exhibit the half-integer quantum Hall effect, indicating their high quality. We further use layer-by-layer stacking to fabricate a doped four-layer film and measure its sheet resistance at values as low as ~30 Ω·sq⁻¹ at ~90% transparency, which is superior to commercial transparent electrodes such as indium tin oxides. Graphene electrodes were incorporated into a fully functional touch-screen panel device capable of withstanding high strain.

30 Ohm/sq 90% transmittance

ORNL’s Graphene 40 -inch
**Programmatic**

1. Consider a model of non-linear, innovation-driven science and technology development for OPV
2. Coordination between Federal, State, business investments/programs
4. Engage existing infrastructure of DOE user-SHARE facilities (to min capital cost)
5. NSF/ONR can co-sponsor travel grants for students, faculty to use DOE capability

**Develop approaches to interrogate the structure and functionality of interface.**

**In situ diagnostics of structure (neutrons)- functionality evolution during OPV assembly and degradation.**
The purpose of this workshop is to review current state of research activities in nanomaterial-based photovoltaics from theory to fundamental properties of materials and devices and to facilitate discussions and collaboration between scientists and companies.
ITO/CNT/Graphene

Graphene

MWNT

CoMo

HiPCO

Arc/LA

AM1.5

ITO

DWNT

Different Transmittance, Similar conductivity

Transmittance consideration- max. purity needed

SWNTs electrodes on glass

100 1000 10000

Wavelength (nm)
High Nanotube purity

Raw SWNT: 451 °C
Purified SWNT: 754 °C

Pure CNTs are thermally stable in air
Effect of dopant on equivalent circuit model parameters

Direct observation of bundle (R1) and junction (R2) change as a function of doping
Equivalent circuit modeling

For macroscopic assessment, averaged properties of bundles and junctions can be obtained. Ratio of $R_j/R_b$ resistances correlates well with that measured on single bundles by others.
Doping affects nanotube junction and bundles

Doping affects nanotube junction and bundles.
Critical concentration of nanotubes percolation condition

\[ \varphi_{\text{crit}}(a) = 1 - \exp(-V_{\text{opt}}(a)) = 1 - \exp\left( -B_{\text{critical}} \frac{V}{V_{\text{excluded}}} \right) \]

- Considering nanotubes as randomly oriented capped cylinders with aspect ratio, \( a = \text{length/diameter} \)
- Same equation is valid for spheres, when \( a \ll 1 \), the for percolation of conducting spheres
- Condition of aspect ratio, \( a \geq 100 \) corresponds to high aspect ratio, critical number of contacts with rod is \( B = 1.20 \). for aspect ratio approaching infinity, \( \lim B = 1 \)

\[ \varphi_{\text{crit}}(a >> 1) = \frac{B_{\text{crit}}(a >> 1)}{2a} = \frac{0.6}{a} \]

- Critical fraction of nanotubes with aspect ratio, \( a = 100 \) needed to establish percolation

\[ \varphi_{\text{crit}}(a = 100) = 6 \cdot 10^{-3} \cdot 100\% = 0.6 \]

Effect of Nanotube Alignment

Effect of alignment on current in FET

(NanoNet)


NanoNet, A simulation tool for Thin films transistors based on network of nanotubes or nanowires By Ninad Pimparkar, Satish Kumar, Jayathi Murthy, Muhammad Alam Purdue University
Dopant mitigated the effects of different bundle size by making bundles more conductive (s-SWTNs doping)
Separation of individual SWNTs using surfactant and Density Gradient Ultracentrifugation separation of m/s SWNT


Doping of individual nanotubes

CNT network form unsorted SWNT m-SWNT vs. unsorted SWNT

Factor of x5.6 higher conductivity for m-SWNT

A. A. Green and M. C. Hersam Nano Lett., 2008, 8 (5), pp 1417–1422

The effect of doping is more pronounced than SWNT character

Yasumitsu Miyata, J. Phys. Chem. C 2008 112 (10), 3591-3596

Doping has similar effect on SC and m-SWNT
Assembly of Nanostructures (pure or composite)


A. A. Green Nano Lett., 2008, 8 (5), pp 1417–1422

Tae-Keun Hong ACS Nano 2010 4 (7), 3861-3868

Minimized Network Resistance
Graphene SWNTs composites

arc-discharged P3SWCNT (Carbon solutions Inc.)

Graphene MWNT LbL composites


Kim ACS Nano 2010 4 (7), 3861-3868
Silver nanowire network

Thin Films
T approaches 92% for sheet resistance approaching 100 Ohm/sq.

For thick films
(M/A 230 mg/m²),
T approaches 32% for Rs 0.5 ohm/sq.

In the middle range, which is of most interest for electrode applications, the film with M/A 70 mg/m² displays T 75% and Rs 3.4 ohm/sq.

- Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios
Woven Metal Wire TCC

8ohm/sq
T~80%

Nano imprinted TCE

T-78%. R-22ohm/sq
Thank you for your attention
High purity of CNTs is important for high transmittance in Solar or Photopic
Optical, Electrical Performance of Common Transparent Conductors

Capacitive Touch Screen Display
88-92% 100-1500ohm/sq.

Resistive Touch Screen Display
88-90%T 200-500Ohm/sq.

LCD (pixel)
87-90%T 30-300ohm/sq.

Flat panel Display
80% 100ohm/sq.

Purity of raw material is 50-90% Impurity negatively impacts the TCE figure of merit. SWNTs are mixtures of m-SWNT(1/3) and s-SWNT(2/3).

Methods for Catalytic Growth of Nanotubes

7-14 bundled SWNTs, with the individual tubes being 0.8-1.6 nm in diameter.

Raw materials
- HiPCO
- arc
- laser
- CVD

Purification
Dispersion
Separation
Deposition

Direct growth/assembly on device

A. carbon; Metal catalyst

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Flexible and Solar TCC Applications

- Solar cells (AM1.5 spectral response)- thermal stability, low cost
- Solid State Lighting (UV/vis)
- Voltage driven displays (VDD) electro-chromic, electrophoretic electro-wetting and liquid crystal displays
- Current driven display displays (p-n) diodes resistive touch screen and OLEDs
- Flat Panel Displays
- Static dissipation, EMI shielding

TCE Figure of Merit Depends on Application

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UT-BATTELLE