2012 Spring Meeting
May 14 – 18
Strasbourg, France

PROGRAMME

CONFERENCE SYMPOSIA

MATERIALS FOR ENERGY
A  Advanced Silicon Materials Research for Electronic and Photovoltaic Applications III
B  Thin Film Chalcogenide Photovoltaic Materials
C  Solid State Ions: Mails and Charge Transport across and along Interfaces of Functional Materials
D  Unconventional Thermoelectrics: from new materials to energy conversion devices
E  Actinide compounds and properties
F  Solid proton conductors (in honor of Prof. G. Alberti)

BIO / ORGANIC / POLYMERIC MATERIALS
G  Functional Biomaterials
H  Organic and Hybrid Materials for Flexible Electronics: Properties and Applications
I  Biological applications for organic electronic devices
J  DNA Directed Programmable Self-assembly of Nanoparticles into Meta Materials for energy and other applications
K  Surface modifications of carbon-related materials II

MATERIALS FOR ELECTRONIC / PHOTONIC / PLASMONIC
L  Novel Functional Materials and Nanostructures for innovative non-volatile memory devices
M  More than Moore: Novel materials approaches for functionalized Silicon based Microelectronics
N  Control of light at the nanoscale: materials, techniques and applications
O  Applied Nanophotonics: Nanophotonic Functional Materials and Devices

ADVANCED MATERIALS AND NANO MATERIALS
P  Advanced Hybrid Materials III: design and applications
Q  Science and technology of nanotubes, graphene and 2D layered materials
R  Novel materials for heterogeneous catalysis
S  Physics and Applications of Novel gain materials based on Nitrogen and Bismuth Containing III-V Compounds
T  Carbon- or Nitrogen-Containing Nanostructured Thin Films

METHODS AND ANALYSIS
V  Laser materials processing for micro and nano applications
W  Current Trends in Optical and X-Ray Metrology of Advanced Materials for Nanoscale Devices III
X  Quantitative Microscopy of Energy Materials
Y  Advanced materials and characterization techniques for solar cells
procedures and multi-parametric analyses to better characterized the inhomogeneous material obtained. Herein, we propose the implementation of novel chemical apparatuses as a controlled, efficient and sustainable approach for the scalable chemical functionalization of CNTs. In particular, we have investigated the functionalization of CNTs with classical reactives, including azomethinylides, diazonium salts and organolithium compounds, in flow conditions. The characterization of these products with a set of subsidiary techniques (UV-vis and Raman spectroscopy, TGA, DLS) shows that our approach affords products tailor able for specific applications, with a particular interest for the controlled compatibilization in polymeric organic solar cells.1. (a) Salice, P.; Menna, E., et al., Chem. Commun. 2011, 47 (32), 9092-9094; (b) Menna, E.; Salice, P., et al. Italian Patent PD2011A000153. 2. Cataldo, S.; Salice, P., Menna, E.; Pignatario, B., Energy Environ. Sci. 2012, doi: 10.1039/C1EE02276H.

The effect of carbon nanotube tip functionalization on electronic tunneling. 

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**Resume**: Modification of carbon nanotubes by doping and functionalization is widely used to control individual nanotubes’ properties and interaction with surrounding media such as polymer matrix. As it is known from experiments and theoretical calculations, sidewall modification can increase nanotube-matrix interaction but reduce nanotube conductivity significantly. In this work we investigate the effect of doping and functionalization on carbon nanotube tip electrical properties. Using density functional calculations, we show that doping with boron and nitrogen and functionalization with –COOH group modify the local density of electronic states of several nanotube tip models, which can boost or decrease tunneling currents between carbon nanotubes while having negligible effect on individual nanotube conductivity itself. Thus, a possibility is opened to increase electrical characteristics of CNT based materials and devices by tip region modification and selecting appropriate type and amount of dopant/chemical group. This work is a part of Marie Curie Initial Training Network “CONTACT” (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/.

3-D Nanostructured Si-Ge-Single Wall Carbon Nanotube Free-Standing Anodes for High Energy Density Lithium Ion Batteries

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**Resume**: Alternative active materials for lithium ion batteries are under investigation to meet energy storage demands. Silicon and Ge are promising anode materials demonstrating capacities up to 3000 mAh/g, much higher than state-of-the-art graphite. Recent work shows free-standing single wall carbon nanotubes (SWCNTs) as viable anode support materials due to their robust mechanical and electrical properties. A 3-D hybrid structure of Ge and SWCNTs which enhances lithium diffusion has demonstrated 1000 mAh/g capacity at a C/20 rate with ≤ 8 % reduction in energy density as the discharge rate is increased to 1C in full batteries. The electrochemical performance of nanostructured electrodes containing both Si and Ge within a SWCNT network is presently evaluated. Ge nanoparticles are incorporated into SWCNT electrodes by solution processing, and Si is deposited through a chemical vapor deposition process. Characterization of the materials by Raman spectroscopy, XRD, and SEM confirm the presence of Ge within the CNT network coated with a thin layer of Si. Electrochemical testing of the Si-Ge:SWCNT electrodes shows high reversible capacity exceeding 1000 mAh/g. The addition of the Si coating enhances the electrode capacity along with reducing the surface area and the first cycle loss, resulting in a high...
The effect of carbon nanotube tip functionalization on electronic tunneling

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ITN “CONTACT”: http://www.contactproject.eu/

The research aim of ITN “CONTACT” is the tailored industrial supply-chain development of CNT-filled polymer composites with improved mechanical and electrical properties

Synthesis  Modeling  Processing
Dispersion  Characterization  Application
Applications of polymer-CNT composites:

- I've made a composite with 2 w.% of nanotubes!
- Indeed… and looks like all of them are here.

* Photographs from www.baytubes.com

Industrial scale CNT production:

* Micro photograph from www.baytubes.com
Project overview:

Atomistic level
- **Input:** atomic data, molecular geometry
- **Methods:** QC & MD
- **Results:** (modified) CNT properties – IP, EA, charge hopping probabilities etc.

Mesoscopic level
- **Input:** composite morphology, external fields, molecular properties;
- **Methods:** MC;
- **Results:** composite FE properties;

Application: Continuum level
- **Input:** device design, material properties;
- **Methods:** FEM, analytical modeling etc.;
- **Results:** device properties;

P1.11: GPGPU-assisted nanocomposite modeling and characterization
Mesoscopic level modeling:

Current inside CNT $\sim$ mA;
Current in tunneling junctions $\sim$ nA;
Ratio of effective time of inter- & intratube transport:

$$\frac{t_{\text{tun}}}{t_{\text{CNT}}} \sim 10^5$$

Mesoscopic Simulation:
Monte Carlo simulation of charge transport between CNTs under effect of:

\[ \vec{E}_{\text{tot}}(\vec{r}) = \vec{E}_{\text{ext}}(\vec{r}) + \vec{E}_{\text{e}}(\vec{r}) + \vec{E}_{\text{T}}(\vec{r}) + \vec{E}_{\text{pol}}(\vec{r}) \]

Field of free charges:
\[ \vec{E}_{\text{e}}(\vec{r}) = \sum \frac{\vec{p}_{ij}}{r_{ij}} \]

Polarization field:
\[ \vec{E}_{\text{pol}}(\vec{r}) = - \sum \frac{2(\vec{E}_{\text{tun}} + \vec{E}_{\text{pol}})}{r_{ij}} \vec{p}_{ij} \]

Thermal voltage fluctuations in contact region
\[ f(V_T) = A_T \exp\left(-\frac{CV_T^2}{2k_B T}\right) \]

**Electron transfer in the “tip region”:**

\[ W_{\text{tot}} = \frac{4\pi}{\hbar} \int_{\gamma} e^V \rho_{\sigma}(E_F - eV + \epsilon) \rho_{\sigma}(E_F + \epsilon) |M|^2 ds \]

\[ M_{\phi\phi} = \frac{\hbar}{2m} \int (\phi^* \nabla \psi - \psi \nabla \phi^*) ds \]

**Tersoff – Hamann**:
\[ \psi_n = \frac{A_n \exp(-\kappa_n r)}{r}, \quad \kappa_n = \frac{\sqrt{2m|E_n|}}{\hbar} \quad \Rightarrow \quad M_{ij} = \frac{\hbar}{2m} \frac{k_i k_j}{2\pi} e^{-\left(k_i + k_j\right)/\hbar} \]

Data required from atomistic level: LDOS $\rho(E)$ in contact region

* Theory of the scanning tunneling microscope
  J. Tersoff, D.R. Hamann, PRB 1985 Vol. 31(2) 805-813;
Intratube transport: decrease of conductivity with doping

Effect of the Chemical Functionalization on Charge Transport in Carbon Nanotubes at the Mesoscopic Scale
Alejandro López-Bezanilla, Nano Letters 2009 Vol. 9 (3) 940-944;

Properties variation in finite tube fragments:

Variation of electronic density:
Image compiled from ~100 dl/dV measurements
Odom T.W., Hafner J.W., Lieber C.M.
Scanning probe microscopy studies of carbon nanotubes
M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris
CNT-tip models:

This project has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

CNT-tip LDOS for the tubes with 4-7 layers:

LDOS for the pure CNT tip:
LDOS for the CNT tip with N adatom: peak displacement, additional peaks; gap narrowing

LDOS for the CNT tip functionalized with –COOH group: disappearing of a resonant state, gap closing;
Main conclusion:

While CNT side doping generally leads to a decrease in intra-tube conductivity, contact region functionalisation can improve inter-tube conductivity due to changes in LDOS;

The results of atomistic-level LDOS calculation can be introduced in mesoscale model in a simple way.

Missing in this picture (future work): e-phonon scattering;

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1. The work is a part of the CONTACT project for the tailored supply-chain development of CNT-filled composites with improved mechanical and electrical properties funded by Marie Curie Initial Training Network "CONTACT" (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/;

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THANK YOU!