

## Poster Session 5

### D1

# Tuning the Threshold Voltage of Carbon Nanotube Transistors by n-Type Molecular Doping for Robust and Flexible Complementary Circuits

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Tuning threshold voltage of a transistor is crucial for realizing robust digital circuits. For Silicon transistors, the threshold voltage can be accurately controlled by doping, mainly through ion implantation. However, it remains challenging to tune the threshold voltage of single-wall nanotube (SWNT) thin-film transistors (TFTs). In this work, we report a method to controllably n-dope SWNTs using 1H-benzoimidazole derivatives processed via either vacuum evaporation or solution coating.<sup>[1]</sup> The threshold voltages of our polythiophene-sorted SWNTs TFTs can be continuously tuned over a wide range. Photoelectron spectroscopy (PES) measurements confirmed that the SWNT Fermi energy decreased with increased doping concentration. Utilizing this approach, we proceeded to fabricate SWNT complementary inverters by inkjet printing of the dopants. We observed an unprecedented high noise margin of 28V at  $V_{DD} = 80V$  (70% of  $1/2V_{DD}$ ) and a gain of 85. Additionally, equally robust SWNT CMOS inverters (noise margin 72% of  $1/2V_{DD}$ ), NAND and NOR logic gates with rail-to-rail output voltage swing and sub-nanowatts power consumption were fabricated onto a highly flexible substrate for the first time.

[1] H.Wang, et al., PNAS, 2014, Accepted

## **Novel hierarchical nanostructure based on nitrogen doped carbon nanotubes and maghemite for electrochemical water oxidation**

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We have developed a new type of nanostructured anode material and studied its performance for catalyzing the oxygen evolving half reaction (OER) associated with electrolysis of water. The hybrid material, comprising a hierarchical iron oxide/nitrogen doped carbon nanotube structure, was used as a direct electrode for electrochemical water splitting without any further modification. The electrode is prepared in a bottom up process by CVD growth of NCNTs on the fibers of a conductive carbon paper, followed by a hydrothermal growth of iron hydroxide nanorods on the surface of the nitrogen doped carbon nanotubes (NCNTs). The iron hydroxide nanorods are then transformed to maghemite. The resulting hierarchical nanostructure exhibit large surface area, and ideal attachment of maghemite nanorods to NCNTs which are further well attached to the carbon paper. The hybrid electrode demonstrates very good electrochemical water oxidation activities in 0.1 M KOH. For a current density of 1 mA cm<sup>-2</sup> (geometric surface) an overpotential of only 392 mV is needed. By combining electrochemical water oxidation with isotope ratio mass spectrometry we show that only water is oxidized.

## **High Bias Characteristics of Individual, Suspended Carbon Nanotube p-n Junction Photodiodes**

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We have recently investigated p-n junction diodes formed by electrostatic doping of individual, suspended, single-walled carbon nanotubes (CNTs) using two gate electrodes positioned beneath a free standing nanotube that bridges source and drain electrodes. The electrostatic field imposed by the two gates polarizes the nanotube along its length, thereby allowing independent control of the "doping" in the nanotube without introducing impurities or defect states. These pn-devices exhibit rectifying diode behavior and finite photoresponse under illumination. Several interesting phenomena are observed at high bias that arise from Schottky contacts formed between the nanotube and its metal contact electrodes and electron tunneling between the n- and p-doped regions. A model is developed explaining this behavior showing evidence for plasmon-induced band gap shrinkage with electrostatic doping.

## D4

# Photoconductivity spectroscopy of individual suspended carbon nanotubes

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To investigate photoconductivity of chirality-identified carbon nanotubes, we have fabricated field-effect transistors with individual air-suspended nanotubes <sup>[1]</sup>. Trenches are etched into SiO<sub>2</sub>/Si substrates, and Pt/Ti are deposited on both sides of the trenches. By ethanol chemical vapor deposition, carbon nanotubes are grown over the trenches. We have also constructed a system which can simultaneously measure photocurrent and photoluminescence excitation spectra <sup>[2]</sup>. Nanotubes are excited with a wavelength-tunable continuous wave Ti:sapphire laser, and photoluminescence is detected by an InGaAs photodiode array attached to a spectrometer. Photoluminescence imaging and excitation spectroscopy allows us to locate the nanotubes and identify their chirality. For photocurrent microscopy, excitation laser is modulated by an optical chopper and a lock-in amplifier is used for detection.

Work supported by KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

[1] S. Yasukochi, T. Murai, S. Moritsubo, T. Shimada, S. Chiashi, S. Maruyama, and Y. K. Kato, Phys. Rev. B 84, 121409 (2011).

[2] Y. Kumamoto, M. Yoshida, A. Ishii, A. Yokoyama, T. Shimada, and Y. K. Kato, Phys. Rev. Lett. 112, 117401 (2014).

**D5**

## **Large thermoelectric power of highly concentrated semiconducting single-wall carbon nanotube film**

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High-performance flexible thermoelectric devices are highly needed. From a thermoelectric engineering standpoint, single-wall carbon nanotubes (SWCNTs) possess many desirable properties. In this work, we report our study on the thermoelectric properties of SWCNT films with different semiconducting/metallic ratios, combined with first-principles transport simulations.

We found a giant Seebeck effect in highly concentrated semiconducting SWCNT films, which shows a comparable to that of commercial Bi<sub>2</sub>Te<sub>3</sub> alloys. Carrier doping on semiconducting SWCNT films leads to further improvement of the thermoelectric performance. These results are well reproduced by first-principles transport simulations based on a simple SWCNT junction model. The present study clarified that thermally resistive junctions play an important role in the giant Seebeck effect of semiconducting SWCNT films. Because major advantages of SWCNTs as a thermoelectric material is their printability and flexibility, these findings represent a major advance in the realization of emerging printed flexible thermoelectric devices. [1]

[1] Y. Nakai, K. Honda, K. Yanagi, H. Kataura, T. Kato, T. Yamamoto, and Y. Maniwa, Appl. Phys. Express 7, 025103 (2014).

**D6**

## **Macroscale Superlubricity in Centimeters Long Perfect Double-walled Carbon Nanotubes under Ambient Conditions**

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Friction and wear are two main causes for mechanical energy dissipation and component failure, especially in micro/nano-mechanical systems with large surface-to-volume ratio. The past decade has witnessed increasing research interest in superlubricity, a phenomenon where the friction almost vanishes between two incommensurate solid surfaces, which is also called structural superlubricity. However, all experimental structural superlubricity was obtained on micro/nano-scale and mostly under high vacuum. Multi-walled carbon nanotubes (MWCNTs), composed of coaxial cylindrical graphene layers with a high aspect-ratio, are ideal candidates to study superlubricity. The MWCNT shells can slide or rotate with respect to each other. Due to the difficulty in nano-manipulation, there are only a few experimental reports on the sliding or rotational behavior of MWCNT shells in the past two decades. The measured intershell friction was much higher than the theoretical values due to the presence of defects or deformations in MWCNTs. Besides, the manipulation of individual CNTs is also a challenge because of their nanosized diameters.

Here we show that macroscale superlubricity can be realized in centimeters long double-walled carbon nanotubes (DWCNTs) under ambient conditions. Centimeters long inner shells could be continuously pulled out from DWCNTs. The intershell friction was lower than 1 nN and independent of the DWCNT length. The shear strength of the DWCNTs is only several Pascals, four orders of magnitude lower than the lowest reported value. The perfect structure of the ultralong DWCNTs used in our experiments is essential to the macroscale superlubricity. The macroscale superlubricity in DWCNTs can be understood in view of the absence of either defects or large axial curvatures in the as-employed DWCNTs and the length-independent variation of the vdW interaction between CNT shells during the pull-out process. The observation of superlubricity in ultralong DWCNTs is a promising result for many practical applications, such as ultrasensitive sensors, fine positioning devices, gyroscopes, fast switches and more.

## **Hierarchical Nanostructured Carbon/Sulfur Hybrid Cathode for High-Performance Lithium-Sulfur Battery**

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Among various energy storage/conversion systems, lithium-sulfur batteries are considered as one of the most promising candidate due to not only very high theoretical energy density of 2600 Wh kg<sup>-1</sup> (based on lithium-sulfur redox couple) and wide operating temperature range benefiting from its unique multiple-electron-transfer chemistry, but also abundant reserves and environmental friendliness of sulfur. However, several intrinsic obstacles should be overcome for its applicability extension, including the ultra-low electrical conductivity of sulfur and its lithiated products, huge volumetric changes during charge and discharge, and the shuttling mechanism of soluble intermediate polysulfides.

Here, a hierarchical nanostructured carbon/sulfur hybrid in which the porous carbon was in situ integrated into graphene/single-walled carbon nanotube (SWCNT) hybrid matrix with small cyclo-S<sub>8</sub> molecule clusters was fabricated as advanced cathode material for lithium-sulfur battery application. The sp<sup>2</sup> graphene/SWCNT hybrid interlinked framework was served as robust conductive scaffold with good electrical conductivity and structure stability, while the micro-/mesoporous carbon accommodated sulfur and lithium polysulfides, provided accessibility for liquid electrolyte to active material, and suppress the shuttle behavior due to the spacial confinement. Therefore, such hierarchical all-carbon nanostructure hybridized with small cyclo-S<sub>8</sub> molecule clusters obtained an excellent electrochemical performance including an ultrahigh specific capacity of 1121 mAh g<sup>-1</sup> at 0.5 C, a favorable high-rate capability of 809 mAh g<sup>-1</sup> at 10 C, a very low capacity decay of 0.12 % per cycle, and an impressive cycling stability of 877 mAh g<sup>-1</sup> after 150 cycles at 1 C. As sulfur loading increasing from 50 wt % to 77 wt %, high capacities of 970, 914, and 613 mAh g<sup>-1</sup> were still available at current densities of 0.5, 1, and 5 C respectively. Even after 300 cycles at 1 C, reversible capacity of over 600 mAh g<sup>-1</sup> was achieved. Based on the total mass of packaged devices, gravimetric energy density of GSH@APC-S//Li cell was expected to be 400 Wh kg<sup>-1</sup> at a power density of 10000 W kg<sup>-1</sup>, matching the level of engine driven systems. Such novel hierarchical nanostructured carbon will shed a light on advanced energy storage systems such as supercapacitors, lithium-air battery, and sodium-ion battery.

## **Single-Walled Carbon Nanotube Networks for Ethanol Vapor Sensing Application**

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Networks of pristine high quality single walled carbon nanotubes (SWNTs), the SWNTs after Ar-plasma treatment (from 2 to 12 min) and carbon nanobuds (CNBs) have been tested for ethanol vapor sensing. It was found that the pristine high quality SWNTs do not exhibit any ethanol sensitivity, while the defect introduction in the tubes results in the appearance of the ethanol sensitivity. The CNB network showed the ethanol sensitivity without plasma treatment. Both CNB and low defective (after 3 min treatment) SWNT networks exhibit significant drift in the resistance baseline, while heavily plasma-treated (9 min) SWNTs exhibited high ethanol vapor sensitivity without the baseline change. The mechanisms of the ethanol sensitivity and stability after the plasma irradiation are attributed to the formation of sensitive dangling bonds in the SWNTs and formation of defect channels facilitating an access of the ethanol vapor to all parts of the bundled nanotubes.

## **Carbon nanotube graphene hybrid film and its thermionic emission**

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We have fabricated an ultra-thin freestanding carbon nanotube/graphene hybrid film<sup>[1]</sup>. Such a square-centimetre-sized hybrid film can realize the overlaying of large-area single-layer chemical vapour deposition graphene on to a porous vein-like carbon nanotube network. The vein–membrane-like hybrid film, with graphene suspended on the carbon nanotube meshes, possesses excellent mechanical performance, optical transparency and good electrical conductivity. The ultra-thin hybrid film features an electron transparency close to 90%, which makes it an ideal gate electrode in vacuum electronics and a highperformance sample support in transmission electron microscopy.

The pore size of the CNT film can be decreased by increasing the number of the layers<sup>[2]</sup>. With smaller pore size, the graphene on CNT film can be Joule heated to a temperature as high as 1,800 K in vacuum without any change in the graphene structure. We have studied the thermionic emission of the graphene and derived the work function of graphene, ranging from 4.7 to 4.8 eV with the average value being 4.74 eV. Because the substrate influence can be minimized by virtue of the porous nature of the CNT film and the influence of adsorbents can be excluded due to the high temperature during the thermionic emission, the measured work function of graphene can be regarded as intrinsic.

[1]. Lin, X.Y.; Liu, P.; Wei, Y.; Li, Q.Q.; Wang, J.P.; Wu, Y.; Feng, C.; Zhang, L.N.; Fan, S.S.; Jiang, K.L., Development of an ultra-thin film comprised of a graphene membrane and carbon nanotube vein support. *Nature Communications*, 2013, 4, 3920.

[2]. Zhu, F.; Lin, X.Y.; Liu, P.; Jiang, K.L.; Wei, Y.; Wu, Y.; Wang, J.P.; Fan, S.S., Heating graphene to incandescence and the measurement of its work function by thermionic emission method. *Nano Research*, 2014, DOI. 10.1007/s12274-014-0423-1.

## **Robust Transistor of Single Wall Carbon Nanotube in a Network Structure, Rubber Materials and Gel**

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Ambient and wearable electronics have received increasing attention for realizing a safe, secure and comfortable smart community, requiring the devices that possess a similar feelings and comparable robustness to clothes. We developed the transistor from all soft organic materials, such as single wall carbon nanotube (SWNT) in a network structure, rubber materials and gel so that all components integrally stretch and absorb applied loadings and impact. The transistor is the side-gated transistor of SWNT channel, ion-gel gate dielectric, and the conductive SWNT rubber electrodes. The transfer characteristic of the side-gated transistor shows that the transistor operates at low voltage and shows high ON/OFF current ratio of 10<sup>4</sup>. We evaluated robustness and stretchability of the transistor systematically by measuring the transistor performance before and after various loadings such as press, bending, stretching and twisting. Our results indicate that the transistor really combines stretchability and robustness comparable to clothes.

## Waveguide-integrated light-emitting carbon nanotubes

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Carbon nanotubes can be envisioned as wave-guide integrated light sources for future on-chip data communication due to their unique structural, electrical and optical properties. The challenge thereby is to integrate and electrically contact solution processed nanotubes across CMOS compatible waveguide structures and to enforce efficient coupling of light from the nanotube into the waveguide. We will show how light from an electrically-driven carbon nanotube can be coupled directly into a photonic waveguide<sup>[1]</sup>. We realize wafer scale, broadband sources integrated with nanophotonic circuits allowing for propagation of light over centimeter distances. Moreover, we show that the spectral properties of the emitter can be controlled directly on chip with passive devices using Mach-Zehnder interferometers and grating structures. The direct, near-field coupling of electrically generated light into a waveguide, opposed to far-field fiber coupling of external light sources, opens new avenues for compact optoelectronic systems in a CMOS compatible framework.

[1] S. Khasminkaya, F. Pyatkov, B. S. Flavel, W. H. P. Pernice, R. Krupke, *Advanced Materials* (2014) in press

## **High uniformity networks of individual SWCNTs for thin film transistors from a novel floating catalyst reactor**

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Single-walled carbon nanotube (SWCNT) networks have a significant potential for the future electronics, both as transparent and flexible conductive electrodes <sup>[1]</sup> and as thin film transistors (TFT) <sup>[2,3]</sup>. Controlled fabrication of reproducible and uniform SWCNT networks, with appropriate density, high individual tube fraction and controlled tube diameter and length is especially important for realisation of SWCNT-TFT based integrated circuits.

Here, we report our recent progress in developing controlled synthesis of SWCNTs by a novel type of floating catalyst reactor. Iron catalyst particles are created by physical evaporation of iron targets by an electric spark discharge. Concentration of catalyst particles can be controlled by adjusting the discharge energy and thus the concentration of SWCNTs grown in the gas phase can be controlled precisely. This allows us to reduce bundling of the SWCNTs in the gas phase, leading to SWCNT networks consisting mainly of individual tubes after membrane filtration at the reactor outlet.

In addition to high individual fraction, these SWCNT networks exhibit small mean tube diameter of 1.1 nm and mean length of 3-4  $\mu\text{m}$ . To estimate the uniformity of the networks, we fabricated SWCNT-TFT arrays on Si-substrates, based on filter dissolution transfer technique <sup>[2]</sup>. With optimal network density, the SWCNT TFTs exhibit excellent characteristics with high charge carrier mobility of  $\sim 100 \text{ cm}^2/\text{Vs}$  and high ON/OFF-ratio  $1\text{E}^5\text{-}1\text{E}^7$ . The SWCNT networks were found to be uniform over the  $1\text{cm}^2$  area of the test arrays, consisting of several hundred individual devices. All the tested devices with  $100\mu\text{m}\times 100\mu\text{m}$  channel dimensions exhibited similar TFT-characteristics. We have also fabricated network devices with very small mean SWCNT diameter of 0.86 nm. These devices fabricated at lower reactor temperature have smaller mean SWCNT length and charge carrier mobility, but exhibit excellent uniformity and small ON-current spread.

[1] A. Kaskela, A. G. Nasibulin, M. Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, and E. I. Kauppinen, "Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique," *Nano Lett.*, vol. 10, no. 11, pp. 4349–4355, Nov. 2010.

[2] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1–6, Feb. 2011.

[3] D.-M. Sun, M. Y. Timmermans, A. Kaskela, A. G. Nasibulin, S. Kishimoto, T. Mizutani, E. I. Kauppinen, and Y. Ohno, "Mouldable all-carbon integrated circuits," *Nature Communications*, vol. 4, Aug. 2013.

## **Thin film electronics based on direct deposition of aerosol-synthesized SWCNTs**

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High purity single-walled carbon nanotubes (SWCNTs) can be synthesized using a floating-catalyst method<sup>[1]</sup>. SWCNTs synthesized in this manner can be further fabricated into thin films using a variety of methods, such as membrane filtration and subsequent transfer of the film from the filter onto a substrate by pressing or dissolving the filter, and by aerosol sampling techniques such as electrostatic and thermal precipitation<sup>[2]</sup>.

Here, we report our recent progress in developing improved dry, single-step and direct deposition methods for aerosol-synthesized SWCNTs. We have designed and built new plate-to-plate thermal and electrostatic precipitators that can be used to efficiently deposit thin films of SWCNTs on a variety of substrates. These methods preserve the high quality of aerosol-synthesized SWCNTs, which give them excellent performance as transparent conducting electrodes<sup>[3]</sup> and thin film transistors<sup>[4,5]</sup>. Additionally, direct deposition is compatible with a wide range of substrates, doesn't require the use of special filters and eliminates substrate and SWCNT exposure to potentially harmful chemicals. The deposition method and parameters are shown to have a significant effect on the resulting SWCNT network morphology and resulting electrical properties.

- [1] A. Moisala, A.G. Nasibulin, D.P. Brown, H. Jiang, L. Khriachtchev, and E.I. Kauppinen, "Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor," *Chemical Engineering Science* vol. 61, pp. 4393-4402, July 2006
- [2] M.Y. Timmermans, D. Estrada, A.G. Nasibulin, J.D. Wood, A. Behnam, D-M. Sun, Y. Ohno, J.W. Lyding, A. Hassanien, E. Pop, and E.I. Kauppinen, "Effect of carbon nanotube network morphology on thin film transistor performance," *Nano Research* vol. 5, pp. 307-319, May 2012
- [3] A. Kaskela, A. G. Nasibulin, M. Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, and E. I. Kauppinen, "Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique," *Nano Lett.*, vol. 10, no. 11, pp. 4349-4355, Nov. 2010.
- [4] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1-6, Feb. 2011.
- [5] D.-M. Sun, M. Y. Timmermans, A. Kaskela, A. G. Nasibulin, S. Kishimoto, T. Mizutani, E. I. Kauppinen, and Y. Ohno, "Mouldable all-carbon integrated circuits," *Nature Communications*, vol. 4, Aug. 2013.

## **Carbon nanotubes network for $10^8$ on/off ratio field effect transistors**

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Carbon nanotubes networks in field-effect transistors (FETs) generally show limited performances with on/off ratio much inferior ( $10^5$ ) respect to the one of single strand nanotube transistors ( $10^8$ ). Here we report the fabrication of FETs utilizing semi-aligned networks of polymer wrapped semiconducting carbon nanotube as active layer. Semiconducting SWNTs were selected by polymer wrapping using poly-9,9-di-n-dodecyl-fluorenyl-2,7-diyl (PF12) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT), and are aligned on a  $\text{SiO}_2$  surface by Blade coating. Field effect transistors fabricated in this way show carrier mobility ranging from  $0.42 \text{ cm}^2/\text{Vs}$  to  $3.71 \text{ cm}^2/\text{Vs}$  and record high on/off ratio of  $10^8$ . FETs based on PF12-wrapped SWNT shows almost symmetric ambipolar characteristic, while devices fabricated with P3DDT-wrapped SWNTs display significantly lower electron current. This results evidence that the wrapping polymer has influence not only on the quality of SWNTs dispersion, but also on the device performance. Finally, we demonstrate the importance of controlling the wrapping polymer concentration as it has significant influence on the transport characteristics.

## **Characterization of Dye-Sensitized Solar Cells with Counter Electrode made of Single-Walled Carbon Nanotubes**

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Dye-sensitized solar cells (DSSCs) have attracted much attention as alternatives to conventional Si-based solar cells because of the potential low cost bulk production. Platinum, however, which is used as counter electrodes of DSSCs, is known to be the highly demanded rare metal. It is also corrosive to iodine electrolyte and hence limits the kind of electrolyte. Hence, nano carbon materials such as carbon nanotubes or graphene can be good candidates for counter electrodes <sup>[1]</sup>. Here, we used the vertically aligned single-walled carbon nanotube (VA-SWNT) <sup>[2]</sup> and metal/semiconductor separated buckypapers as counter electrodes. In addition to the J-V characteristics, impedance technique and electrochemical measurement are employed. The result shows that the charge transfer resistance between VA-SWNT and iodine electrolyte is higher than that between Pt and electrolyte and therefore VA-SWNT has lower catalytic activity to iodine electrolyte. And it is also shown that there is a possibility to improve the catalytic activity by separating semi conducting and metal SWNTs.

[1] L. Kavan, J. Yum, M. Grätzel, *Nano Lett.*, 11, (2011), 5501.

[2] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, *Chem. Phys. Lett.*, 385, (2004), 298.

## **MICROFLUIDIC DEVICE WITH CARBON NANOTUBE CHANNEL WALLS FOR BLOOD PLASMA EXTRACTION**

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The human plasma biomarker analysis is promised to be a revolution for disease diagnosis and therapeutic monitoring. However, blood plasma is a complicated body fluid. For targeted plasma biomarker detection or untargeted plasma biomarker discovery, the challenges can be as difficult as identifying a needle in a haystack. Plasma extract from whole blood is the first step for plasma biomarker analysis. We report a new microfluidic device with channel walls made of nitrogen-doped carbon nanotubes (CNxCNT) as a point-of-care device to continuously extract plasma from human whole blood. The cross flow microfiltration principle is applied in this plasma extraction device. The blood sample is transported within the double spiral channels. The plasma diffuses through the porous CNxCNT wall into the spiral plasma channel while blood cells continue to flow inside the spiral blood sample channel.

## Highly Conductive CNT Thin Films for Organic Solar Cells

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Current transparent electrodes in electronic devices are made of indium tin oxide (ITO). Although it has the best electrical properties required for electronic applications, several drawbacks, such as its cost, its brittleness, have to be overcome to comply with the next generation of organic electronic devices. In this context, carbon nanotubes (CNTs) have been under investigation for several years, due to their excellent electrical and mechanical properties, to replace the ITO electrodes.

Using high quality CNT inks, transparent and highly conductive films have been made to prepare solar cells. CNT inks have been prepared by liquid ammonia reduction in order to fully individualize the CNTs without damaging them<sup>[1]</sup>, as it is commonly done by usual dispersion techniques, such as functionalization, ultrasonication and/or ultracentrifugation. This method allows to keep long CNTs in solution with excellent electrical properties.

This work is focused on organic solar cells on glass and on flexible substrates to study the CNT properties and to compare their efficiency to ITO. Spray-coated transparent and conductive films of SWNT ink prepared by reductive dissolution show higher conductive performances than films made of SWNT aqueous dispersion and a better uniformity than spin-coated TCFs. Integration of those TCFs into solar cells show comparable power efficiency than ITO solar cells. Moreover, CNT networks can be used to prepare flexible electrodes, thus new solar cell designs can be envisioned. We show that the performance of a SWNT-based solar cell, in absolute terms and in comparison to an ITO-based control device, depends not only on the quality of the SWNT transparent electrode itself but also on the active layer material and processing.

[1] S. Fogden, C. Howard, R. Heenan, N. Skipper, M. Shaffer, ACS Nano, 2012, 6(1), pp54-62, Scalable method for the reductive dissolution, purification, and separation of single-walled carbon nanotube.

## **SWNT Transparent Conductive Thin Films from SEERe-Nanotubide Inks**

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Linde Nanomaterials has developed a revolutionary new single walled carbon nanotube ink. Known as SEERe- Ink, it can be used to make ‘best in class’ transparent conductive thin films suited to a wide application spectrum including solar cells, touch screens, displays, electrochromic windows and thin-film transistors. The possible applications for SEERe- Ink also extends beyond the TCF market - the potential for further SWNT functionalisation open the way possible applications to include sensors, composites and within the healthcare sector.

Using reduction dissolution technology to produce nanotubide inks, Linde Nanomaterials has been able to produce TCFs which exceed the resistivity and transparency requirements commonly quoted in the literature as 100 ohms/sq at 90% transparency without affecting the other critical properties such as haze, environment stability, flexibility, hardness, adhesion and of course, cost.

This reductive dissolution technology begins by reducing SWNTs in liquid ammonia followed by dissolution in a polar aprotic organic solvent without the need for additional sonication. This mild dissolution technique results in solutions of long, undamaged, individualized SWNTs which can be deposited using spin or spray coating to make TCFs. This technique directly addresses the critical SWNT conductivity scaling factors of purity, length and bundle size to produce commercially viable TCFs.

## Carbon nanotube sponge as electrochemical capacitor electrodes capturing any capacitive particles

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Carbon nanotubes (CNTs) have been extensively studied as a promising material for next-generation electric storage devices such as electrochemical capacitors, lithium ion batteries, and metal-air batteries. We have systematically studied the millimeter-scale growth of single-wall CNTs (SWCNTs) by chemical vapor deposition (CVD) on substrates <sup>[1]</sup> and realized the semi-continuous scalable synthesis of few-wall CNTs (FWCNTs) by fluidized bed CVD (FB-CVD) <sup>[2]</sup>. Sponge-like matrices of long SW/FWCNTs, which can be easily made by their dispersion and filtration, are attractive because of their high conductivity, specific surface area, and their small pores (several tens nm) capturing active particles with good electrical contacts. In this work, we target at electrochemical capacitors, which have the highest power density among the electric storage devices and thus need high electric conductivity for electrodes. We demonstrate the simple fabrication of hybrid electrodes with activated carbon (AC) and manganese dioxide (MnO<sub>2</sub>) captured in CNT sponges for electrochemical capacitors with enhanced energy and power densities.

First we investigated the effect of individual and matrix structures of CNTs on the electrochemical property. 50- $\mu\text{m}$ -tall vertically aligned SWCNTs (VA-SWCNTs) were grown by CVD using C<sub>2</sub>H<sub>2</sub> <sup>[1]</sup> for 1 min and transferred to porous polymer membrane. Self-supporting 40- $\mu\text{m}$ -thick random network films of SWCNTs and FWCNTs were prepared by filtrating the dispersions of SWCNTs by on-substrate growth <sup>[1]</sup> and FWCNTs by FB-CVD <sup>[2]</sup>. Electrochemical performance was measured by cyclic voltammetry with a 3-electrode cell in 1 M Na<sub>2</sub>SO<sub>4</sub> aq. All CNT electrodes showed a constant specific capacitances from 5 to 1000 mV/s scan rates (equal to 0.8 s charge-discharge), showing that these three electrodes have sufficiently high electric conductivities.

Next we fabricated and evaluated the hybrid electrodes. Self-supporting AC-FWCNT hybrid films were fabricated by mixing AC and FWCNTs at a 9:1 weight ratio, dispersing them in ethanol, and filtrating the dispersion. Even with a contact only at one edge of the film, it kept a specific capacitance of 132 F/g at a high scan rate of 100 mV/s in a 1 M H<sub>2</sub>SO<sub>4</sub> aq. 10 wt% FWCNTs hold and make 90 wt% AC conductive, making it possible to eliminate the capacity-less metal current correctors and insulating polymer binders <sup>[3]</sup>. Self-supporting MnO<sub>2</sub>-FWCNT hybrid films were fabricated by electrodepositing MnO<sub>2</sub> in FWCNT matrices. By carefully adjusting the over-potential, sub- $\mu\text{m}$ -sized MnO<sub>2</sub> particles were uniformly formed whole over

the FWCNT sponge, yielding a high specific capacitance  $\sim 200$  F/g at 2 mV/s and in a 0.5-1.0 M  $\text{Na}_2\text{SO}_4$  aq. Any capacitive particles will be captured within CNT matrices.

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- [1] K. Hasegawa and S. Noda, ACS Nano 5, 975 (2011).
- [2] D. Y. Kim et al., Carbon 49, 1972 (2011).
- [3] R. Quintero et al., RSC Adv. 4, 8230 (2014).

## **Thermoacoustic Chips with Carbon Nanotube Thin Yarn Arrays**

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Aligned carbon nanotube (CNT) films drawn from CNT arrays have shown the potential as thermoacoustic loudspeakers. CNT thermoacoustic chips with robust structures are proposed to promote the applications. The silicon-based chips can play sound and fascinating rhythms by feeding alternating currents and audio signal to the suspending CNT thin yarn arrays across grooves in them. In addition to the thin yarns, experiments further revealed more essential elements of the chips, the groove depth and the interdigital electrodes. The sound pressure depends on the depth of the grooves, and the thermal wavelength can be introduced to define the influence-free depth. The interdigital fingers can effectively reduce the driving voltage, making the chips safe and easy to use. The chips were successfully assembled into earphones and have been working stably for about one year. The thermoacoustic chips can find many applications in consumer electronics and possibly improve the audiovisual experience.

[1] Y. Wei, X.Y. Lin, K.L. Jiang, P. Liu, Q.Q. Li, and S.S. Fan, *Nano Lett.* 13 (2013) 4795-4801.

## **Sub-10 $\mu\text{m}$ top-gate carbon nanotube thin-film transistors based on high-speed flexographic printing process**

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Among various thin film transistors (TFTs), carbon nanotube (CNT) TFTs have advantages such as high mobility, flexibility, transparency, printability, and so on. In the previous work, we developed a fully-lithography free and non-vacuum process to fabricate CNT TFTs based on flexographic printing technique, one of high speed printing methods, and achieved a high mobility of  $157 \text{ cm}^2/\text{Vs}$ .<sup>[1]</sup>

In this work, we have improved the resolution of the printing technique for miniaturizing printed CNT TFTs. Flexographic plates were fabricated by using micro-fabrication process. High-purity semiconductor CNTs were used for the channel. Top-gate CNT TFTs with a channel length of  $\sim 7 \mu\text{m}$  was fabricated. The devices showed an on/off ratio of 103 and a mobility of  $3.7 \text{ cm}^2/\text{Vs}$ . This work was partially supported by ALCA-JST, SICORP-JST, and Grant-in-Aid of MEXT.

[1] K. Higuchi et al., Appl. Phys. Express 6, 085101 (2013).

## Light emission and detection with carbon nanotubes

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Carbon nanotubes (CNTs) are direct band gap materials that are not only useful for nanoelectronic applications, but also have the potential to make significant impact on the developments of nanoscale optoelectronic devices. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as light-emitting diodes <sup>[1,2]</sup>, photodetectors and photovoltaic (PV) cells <sup>[3,4]</sup>. Semiconducting single-wall CNTs (SWCNTs) are direct-gap materials that can efficiently absorb and emit light. The unique band structure of SWCNT suggests that multiple subbands absorptions can contribute to optoelectronic properties. By combining sufficient nanotubes with different diameters, it was also demonstrated that it is possible to gain a nearly continuous absorption response within a broad spectral range (from UV to infrared) to match the solar spectrum <sup>[5]</sup>. In addition, extremely efficient carrier multiplication (CM) effect has been observed <sup>[6]</sup>, which may potentially lead to a higher energy conversion efficiency than that defined by the Shockley-Queisser limit. More recently, efficient photovoltage multiplication was also realized via introducing virtual contacts in CNTs, making the output photovoltage of CNT based solar cells a tunable quantity via choosing the diameter of the tube and the number of virtual contacts introduced in the device <sup>[7]</sup>, making it possible for developing optoelectronic communications between nanoelectronic circuits and high performance infrared photodetectors <sup>[8-10]</sup>.

### References

- [1] Mueller T, M. Kinoshita M, M. Steiner M, V. Perebeinos V, Bol AA, Farmer DB and Avouris P (2010), *Nature Nanotech*, 5:27-31.
- [2] Wang S, Zheng QS, Yang LJ, Zhang ZY, Wang ZX, Pei T, Ding L, Liang XL, Gao M, Li Y and Peng LM (2011), *Nano Lett.*, 11: 23.
- [3] Lee JU, Gipp PP and Heller CM (2004), *Appl. Phys. Lett.*, 85:145.
- [4] Wang S, Zhang LH, Zhang ZY, Ding L, Zeng QS, Wang ZX, Liang XL, Gao M, Shen J, Xu HL, Chen Q, Cui RL, Li Y and Peng LM (2009), *J. Phys. Chem. C*, 113(17): 6892.
- [5] Lehman J, Sanders A, Hanssen L, Wilthan B, Zeng J and Jensen C (2010), *Nano Lett.*, 10, 3261.
- [6] Gabor, N.M., Zhong, Z.H., Bosnick, K., Park, J. & McEuen, P.L. (2010), *Science* 325, 1367.
- [7] Yang LJ, Wang S, Zeng QS, Zhang ZY, Pei T, Li Y and Peng LM (2011), *Nature Photonics*, 5:672.
- [8] Zeng Q.S., Wang S., Yang L.J., Wang Z.X., Pei T., Zhang, Z.Y., Peng L.-M., Zhou W.W., Liu J., Zhou W.Y. and Xie S.S. (2012), *Optical Materials Express* 2(6): 839
- [9] Yang L.J., Wang, S., Zeng, Q.S., Zhang, Z.Y. and Peng, L.-M. (2013) 8:1225.
- [10] Yu, D.M., Wang, S., Ye, L.H., Zhang, Z.Y., Chen, Y.B., Zhang J. and Peng L.-M. (2014) *Small* 10:1050.

## **Carbon Nanotube Thin Film Transistors for Printed Electronics**

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We present single-walled carbon-nanotube (SWCNT) thin-film transistors (TFT) fabricated on a plastic substrate using a hybrid manufacturing method. The device structure is a bottom-gate top-contact (BGTC) configuration. The SWCNT networks for the TFT channels were collected onto nitrocellulose membrane filters directly from a floating catalyst-CVD reactor <sup>[1]</sup>. SWCNT networks were transferred onto plastic PEN substrates, by dissolving the membrane filter by acetone <sup>[2]</sup>. Before the transfer process, the gate electrodes were shadow-evaporated and polyimide dielectric layer was ink-jet printed on the substrate. The source and drain electrodes were shadow-evaporated on top of the percolating SWCNT network. Finally, another layer of polyimide was ink-jet printed on top of the channel to function as a mask for O<sub>2</sub> plasma etching that removed the SWCNTs outside the channel area.

The TFTs were characterized by transfer and output curve measurements using a Keithley 4200 semiconductor characterization system in ambient conditions. The TFTs had parallel plate mobilities on the order of 8 cm<sup>2</sup>/Vs and on/off-ratios over 10<sup>5</sup>, with the measurement voltage ranging from -20 V to +20 V. The demonstrated process can be used to fabricate, for example, backplane circuits of flexible displays.

[1] Sun, D.-m., M.Y. Timmermans, Y. Tian, A.G. Nasibulin, E.I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, *Nature Nanotech.*, 2011. 6(3): p. 156-161.

[2] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1–6, Feb. 2011.

## **Using Nanotube Transistors for Single-Molecule Studies of DNA Polymerase I**

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DNA polymerases are critical enzymes for DNA replication, and because of their complex catalytic cycle they are excellent targets for investigation by single-molecule experimental techniques. Recently, we studied the Klenow fragment (KF) of DNA polymerase I using a label-free, electronic technique involving single KF molecules attached to carbon nanotube transistors [1]. The nanotube sensitivity allowed a single KF molecule to be monitored over long durations as it processed thousands of template strands. Processivity of up to 42 nucleotide bases was directly observed, and statistical analysis of the recordings determined key kinetic parameters for the enzyme's open and closed conformations. Subsequently, we have used the same technique to compare the incorporation of canonical nucleotides to analogs like  $\alpha$ -thio-dNTPs, 2-thio-dTTP or dCTP, and 6-chloro-dGTP. The analogs had almost no effect on the closed conformation, during which the nucleotide is incorporated. Instead the entire effect of the analogs was during the open conformation. The thiolated and chlorinated analogs appear to interfere with KF's recognition and binding, two key steps that determine its ensemble turnover rate.

[1] T. J. Olsen, et. al., JACS 135, 7855 (2013).

## **LCNDs : Photonic Functionalization of MWCNT Towards Light Conversion Nanostructured Devices**

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As described by Lehn <sup>[1]</sup>, light conversion molecular devices (LCMD) are based on the property named “antenna effect”, that summarizes the sequence of events involving selective absorption (by a ligand as antenna), energy transfer and emission (by a central lanthanide ion). Highly sensitive photonic nanodevices based on this process have been developed in our group <sup>[2]</sup>. In this work, carbon nanotubes were covalently functionalized by a reaction with 4-azidobenzoic acid and then complexed with Eu<sup>3+</sup> salts under microwave irradiation. FT-IR and UV-vis confirmed the formation of the complexes and SEM showed that this procedure can decorate the CNT with a layer of crystalline fluorescent complexes, resulting in a highly efficient photonic CNT-Eu hybrid system we named light conversion nanostructured device (LCND). This device presents a better quantum efficiency than the non-hybrid ones.

- [1] Lehn, J. M.; *Angew. Chem., Int. Ed.* 1990, 29, 1304;  
[2] de Sá, G.F. et al.; *Coord.Chem. Rev.* 2000, 196, 165;

## **Thermoelectric devices based on sandwiched carbon nanotube forests and the effect of contact electrodes**

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Multi-walled carbon nanotube forests were grown by atmospheric-pressure chemical vapor deposition onto silicon substrates and incorporated as one of the materials in thermoelectric energy generators. In order to more carefully study the thermoelectric behavior of carbon nanotubes, the forests were transferred onto copper substrates. The first method to transfer the millimeter-long forests onto copper involved depositing the thin film catalyst directly onto copper and subsequently growing the forest directly over the top surface. The second method involved physically detaching the forest from its silicon substrate with the tip of sharp tweezers. In a symmetric copper-nanotube-copper configuration measured at temperatures between 300-380 K, this device exhibited a Seebeck coefficient of 16-20  $\mu\text{V}/\text{K}$ . In comparison, our previous measurements on a symmetric silicon-nanotube-silicon device produced a coefficient as high as 132  $\mu\text{V}/\text{K}$  in a similar temperature range. The order of magnitude decrease was attributed to the absolute Seebeck coefficient of copper being much smaller than that of silicon.

## Application of Nanoparticle Antioxidants to Enable Hyperstable Chloroplasts for Solar Energy Harvesting

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The chloroplast contains densely stacked arrays of light-harvesting proteins that harness solar energy with theoretical maximum glucose conversion efficiencies approaching 12%. Few studies have explored isolated chloroplasts as a renewable, abundant, and low cost source for solar energy harvesting. One impediment is that photoactive proteins within the chloroplast become photodamaged due to reactive oxygen species (ROS) generation. In vivo, chloroplasts reduce photodegradation by applying a self-repair cycle that dynamically replaces photodamaged components; outside the cell, ROS-induced photodegradation contributes to limited chloroplast stability. The incorporation of chloroplasts into synthetic, light-harvesting devices will require regenerative ROS scavenging mechanisms to prolong photoactivity. Herein, we study ROS generation within isolated chloroplasts extracted from *Spinacia oleracea* directly interfaced with nanoparticle antioxidants, including dextran-wrapped nanoceria (dNC) previously demonstrated as a potent ROS scavenger. We quantitatively examine the effect of dNC, along with cerium ions, fullerenol, and DNA-wrapped single-walled carbon nanotubes (SWCNTs), on the ROS generation of isolated chloroplasts using the oxidative dyes, 2',7'-dichlorodihydrofluorescein diacetate (H2DCF-DA) and 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide sodium salt (XTT). Electrochemical measurements confirm that chloroplasts processed from free solution can generate power under illumination. We find dNC to be the most effective of these agents for decreasing oxidizing species and superoxide concentrations whilst preserving chloroplast photoactivity at concentrations below 5  $\mu$ M, offering a promising mechanism for maintaining regenerative chloroplast photoactivity for light-harvesting applications.

Boghossian\*, A.A.; Sen\*, F.; Gibbons, B.M.; Sen, S.; Faltermeier, S.M.; Giraldo, J.P.; Zhang, C.T.; Zhang, J.; Heller, D.A.; Strano, M.S. Application of Nanoparticle Antioxidants to Enable

Hyperstable Chloroplasts for Solar Energy Harvesting. *Advanced Energy Materials* 3, 881-893 (2013).