

# NANOTECHNOLOGY

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Highlights **2012**



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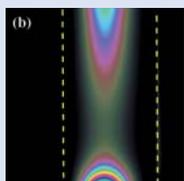
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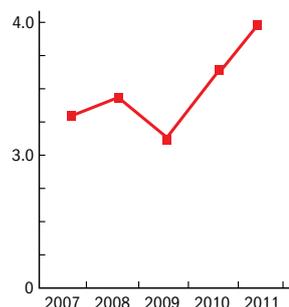


#### Front cover image:

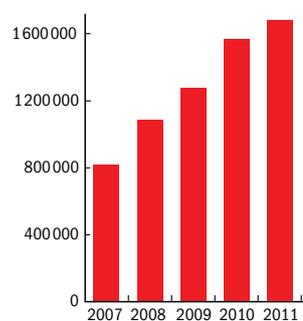
Contour map for the density probability of an electron state in a graphene ring calculated at the absolute minimum eigen-value as a function of the radial coordinate (horizontal axis) and the relative height of the core barrier (vertical axis).

Leonardo Villegas-Lelovsky *et al* 2012 *Nanotechnology* **23** 385201.

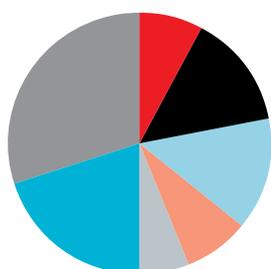
### Impact factor



### Yearly downloads



### Subject distribution



- Biology and medicine
- Electronics and photonics
- Energy at the nanoscale
- Patterning and nanofabrication
- Sensing and actuating
- Materials: synthesis or self assembly
- Materials: properties, characterization or tools

## Dear colleagues,

Ideas, discoveries and inspired innovations continue to fuel avid research activity in nanotechnology. It is perhaps no surprise then that *Nanotechnology* continues to attract such eminent papers and animated readers across the world. Downloads – currently around 150,000 per month – are increasing, as is our impact factor, which was 3.979 in the 2011 ISI Journal Citation Report.

As always, an exacting editorial policy is required to ensure that the researchers we serve receive the quality they expect. Rejection rates remain high at around 75% and the exemplary rigour of our peer review process is widely noted throughout the community.

Not just thorough, the journal is notably timely too. We publish weekly and our current average receipt-to-acceptance time is 75 days, with articles generally published within three weeks of acceptance.

Our special issues, solely dedicated to specific burgeoning research topics, provide an intense hit of the latest results from leading scientists specially invited to contribute. In 2012 we published special issues on nanowires for energy, ensuring sustainability with green nanotechnology, nanotechnology-based flexible electronics and plasmonics in optoelectronics.

In addition to regular research articles, the journal continues to publish topical reviews that put the latest progress in context. Our new ‘Publisher’s Pick’ feature on the *Nanotechnology* homepage provides a snappy news-style LabTalk piece to flag up research that we think will particularly interest our readers and an author interview where you can meet the researchers themselves. You can also follow up on previously published work at our ‘One year on’ link on the homepage. In addition, 2012 saw the first of our video abstracts, to complement our multimedia portfolio so that we continue to provide for all of the evolving needs of our community. Our editorial features ensure that the papers we publish receive the visibility they deserve.

Coming up, we have more special issues in preparation, not to mention the celebration of our 25th volume. As to the real surprises – the insights of genius and the visionary breakthroughs – for that it’s over to you, the researchers. In the meantime, these highlights give a glimpse of some of the gems that the journal has had to offer over the past year, with many more exciting papers to come at [iopscience.org/nano](http://iopscience.org/nano).



**Mark Reed**  
Editor-in-chief, *Nanotechnology*  
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[iopscience.org/nano](http://iopscience.org/nano)

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# Biology and medicine

Applications of nanotechnology have already provided medicine with a number of therapeutic tools, which are less invasive and debilitating than those they replace. However, certain challenges remain, stimulating researchers to push boundaries further in exploring and repairing living bodies with nanoscience.

The quest to identify new therapeutics to treat cancer continues to drive a huge amount of research activity. One of the issues facing the application of nanoparticles as diagnostic and therapeutic tools is the requirement for ready dispersion *in vivo*. Carbon nanotubes have a number of beneficial attributes as biomedical materials, but they tend to clump rather than disperse in aqueous solutions, such as those in living organisms. Researchers in China reported how they had used water-soluble chitosan to prepare and characterize a novel biomaterial, through conjugating multiwalled carbon nanotubes and phycocyanin – a water-soluble photoharvesting pigment. The new material could be stably dispersed in water and demonstrated photoinduced cytotoxicity. While it is early days for this technology, it may be promising as a future photodynamic and photothermal therapy for the treatment of cancer.

Nanotechnology also has an important role to play in biomedical devices. Researchers in the US described how they used 4(5)-(2-mercaptoethyl)-1H-imidazole-2-carboxamide for DNA sequencing. When tethered

to a pair of electrodes, the molecule traps other target molecules in a tunnel junction. Surprisingly large recognition-tunnelling signals are generated for all naturally occurring DNA bases A, C, G, T and 5-methylcytosine. This development may provide a cheaper approach to DNA sequencing compared with currently available techniques.

Graphene, the wonder material of nanoscale science and technology over the past few years, has not yet received in-depth exploration for biological applications. Now researchers in India and the US have reported a non-toxic versatile multicomponent graphene-based nanostructured system for cellular imaging. The multicomponent nanostructure system involves three components;  $\text{Fe}_3\text{O}_4$  nanoparticles, a poly(amido amine) dendrimer and a fluorescent near-infrared probe cyanine 5.0 on a graphene oxide surface. The final material is biocompatible, has strong near-infrared optical absorbance and exhibits superparamagnetic properties.

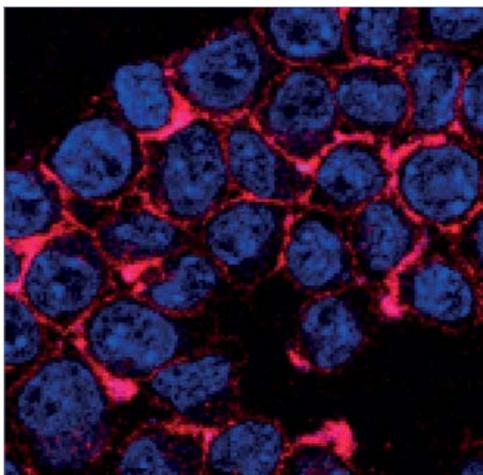
Increased understanding of the behaviour of nanomaterials has greatly facilitated their application in biosystems, and combinations of functionalities are increasingly being applied in a single nanomaterial to outsmart some of the challenges in developing next generation medical technologies. The articles highlighted here are just some of the results of the fruitful symbiosis between research in bioscience and nanotechnology.



Section Editor: Jeff Karp

## Section scope

This section of *Nanotechnology* focuses on the forefront of nanoscaled materials and techniques in biological and medical research. Biological applications of nanotechnology have garnered significant attention in recent years for their potential benefits in emerging fields of biotechnology and medicine, and consequently this section includes some of the most-read and most-cited articles in the journal. We welcome submissions of innovative work in a variety of fields including, but not limited to, the use of nanoparticles as delivery vehicles for drugs or gene therapies, nanoscale materials for directing cell phenotype and function, nanoscale materials used in tissue engineering and regenerative medicine, nanostructured medical devices, the use of DNA to create useful materials, the development of nanoscale approaches for biosensing or diagnostic applications, the use of nanomaterials for probing biological processes, investigations of the metabolic behaviour and biosafety of nanotechnology and novel methods for high-resolution cell and tissue imaging. Published material covers both *in vivo* and *in vitro* investigations, maintaining excellent standards of novelty and interest.



Confocal laser scanning microscopic image of MCF-7 breast cancer cells.

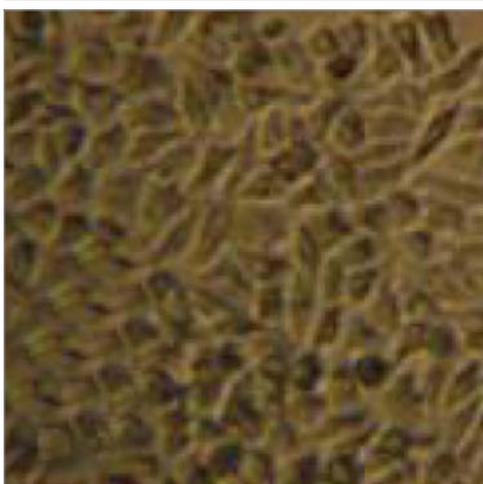
## Cellular imaging using biocompatible dendrimer-functionalized graphene oxide-based fluorescent probe anchored with magnetic nanoparticles

Prateek S Wate, Shashwat S Banerjee, Archana Jalota-Badhwari, Russel R Mascarenhas, Khushbu R Zope, Jayant Khandare and R Devesh K Misra

2012 *Nanotechnology* **23** 415101

We describe a novel multicomponent graphene nanostructured system that is biocompatible, and has strong NIR optical absorbance and superparamagnetic properties. The fabrication of the multicomponent nanostructure system involves the covalent attachment of 3 components;  $\text{Fe}_3\text{O}_4(\text{Fe})$  nanoparticles, PAMAM-G4- $\text{NH}_2$  (G4) dendrimer and Cy5 (Cy) on a graphene oxide (GO) surface to synthesize a biologically relevant multifunctional system. The resultant GO-G4-Fe-Cy nanosystem exhibits high dispersion in an aqueous medium, and is magnetically responsive and fluorescent. *In vitro* experiments provide a clear indication of successful uptake of the GO-G4-Fe-Cy nanosystem by MCF-7 breast cancer cells, and it is seen to behave as a bright and stable fluorescent marker. The study also reveals varied cellular distribution kinetics profile for the GO nanostructured system compared to free Cy. Furthermore, the newly developed GO nanostructured system is observed to be non-toxic to MDA-MB-231 cell growth, in striking contrast to free G4 dendrimer and GO-G4 conjugate. The GO-G4-Fe-Cy nanostructured system characterized by multifunctionality suggests the merits of graphene for cellular bioimaging and the delivery of bioactives.

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MWNT-CS-PC induced morphologic changes in MCF-7 cells observed by phasecontrast microscopy.

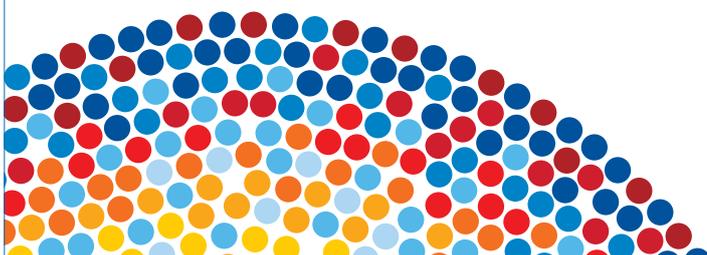
## Preparation, characterization and cytotoxicity of carbon nanotube–chitosan–phycocyanin complex

Xiaoxia Liao and Xuewu Zhang

2012 *Nanotechnology* **23** 035101

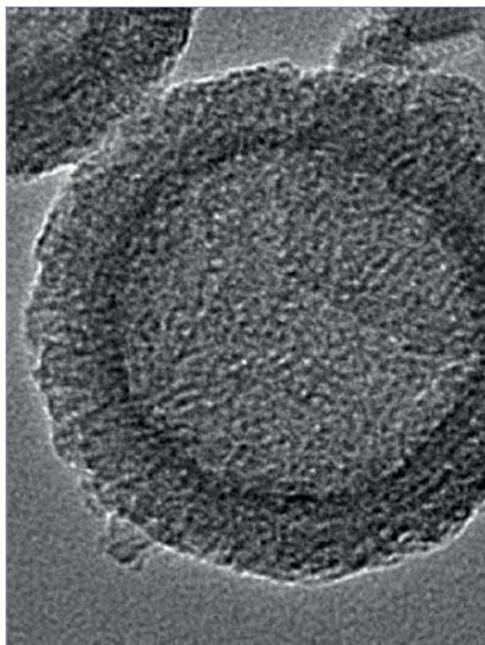
Photodynamic therapy (PDT) or photothermal therapy (PTT) using nanomaterials has shown great prospect for cancer treatment. Phycocyanin (PC) is a photoharvesting pigment and is also an attractive candidate for PDT. The multiwalled carbon nanotube (MWNT) is a potent candidate for PTT due to its extraordinary photo-to-thermal energy conversion efficiency upon excitation with near-infrared (NIR) light. To date, although MWNT-CS complexes have been well studied, no report about the reconjugation of MWNT-CS with phycocyanin is available in the literature. Here, by using water-soluble chitosan (CS), we prepared and characterized a novel biomaterial, MWNT-CS-PC, with the potential for PDT and PTT. The cytotoxicity experiments found that MWNT-CS-PC exhibited cell growth inhibition activity. Moreover, with irradiation of NIR light (808 nm) or visible light (532 nm), the photoinduced cytotoxicity was indeed enhanced. These results suggest that MWNT-CS-PC may potentially serve as a future photodynamic and photothermal therapy for cancer.

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TEM micrographs of the carboxy-HMSCs.

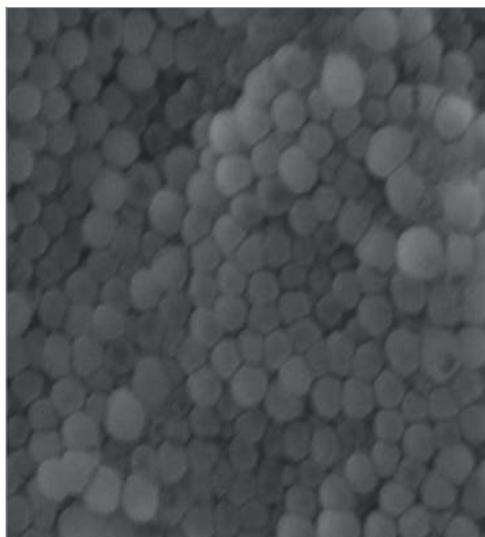
## Intracellular protein delivery by hollow mesoporous silica capsules with a large surface hole

Ji-Sun Lim, Kiwon Lee, Jong-Nam Choi, Yong-Kyung Hwang, Mi-Yeon Yun, Hee-Jin Kim, Yong Sun Won, Sung-Jin Kim, Hyockman Kwon and Seong Huh

2012 *Nanotechnology* **23** 085101

We prepared cell membrane-permeable hollow mesoporous silica capsules (HMSCs) by a simple new method. CTAB micellar assembly in cholesterol emulsion gave rise to a novel capsular morphology of the HMSC particles. The HMSCs consisted of mesostructured silica walls with a large surface hole (25–50 nm) and the average particle dimension was 100–300 nm. They exhibited high surface areas of up to 719.3 m<sup>2</sup> g<sup>-1</sup> and a mesoporous range of pores of 2.4–2.7 nm. The surface-functionalized HMSCs could also be prepared by a similar co-condensation method using tetraethoxysilane with various organoalkoxysilane precursors in the presence of cholesterol. These organically modified HMSCs could be further modified on demand. For example, a carboxy-functionalized HMSC could be surface-functionalized by a green fluorescent 5-aminofluorescein (AFL) through an amidation reaction to afford a fluorescent AFL–HMSC. The hollow capsular morphology of the HMSCs with a large surface hole enabled us to develop very efficient intracellular delivery systems for membrane-impermeable ions, molecules, and various functional proteins. Non-covalent sequestration and delivery of proteins as well as covalent linkage of fluorescent molecules on the silica surface are effective for this system. The highly negatively charged green fluorescent probe mag-fluo-4 could be intracellularly delivered into HeLa cells by HMSC without any difficulty. The HMSCs could also effectively transport large functional proteins such as antibodies into HeLa cells. The efficiency of protein delivery by HMSC seems to be 3–22-fold higher than that of mesoporous silica nanospheres (MSNs) based on confocal laser scanning microscopy (CLSM) analysis.

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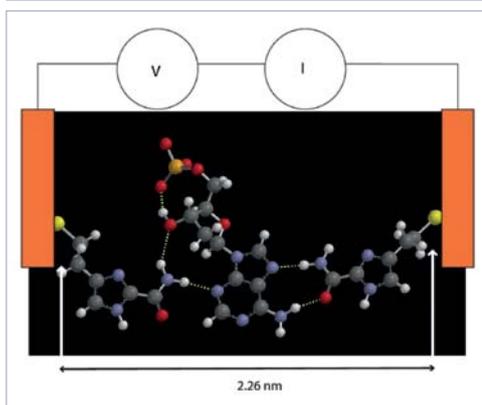
Top view SEM image of fibrin nanoconstructs depicting the assembly of fibrin nanotubes.

## Fibrin nanoconstructs: a novel processing method and their use as controlled delivery agents

G Praveen, P R Sreerexha, Deepthy Menon, Shantikumar V Nair and Krishna Prasad Chennazhi

2012 *Nanotechnology* **23** 095102

Fibrin nanoconstructs (FNCs) were prepared through a modified water-in-oil emulsification–diffusion route without the use of any surfactants, resulting in a high yield synthesis of fibrin nanotubes (FNTs) and fibrin nanoparticles (FNPs). The fibrin nanoconstructs formed an aligned structure with self-assembled nanotubes with closed heads that eventually formed spherical nanoparticles of size ~250 nm. The nanotubes were typically ~700 nm long and 150–300 nm in diameter, with a wall thickness of ~50 nm and pore diameter of about 150–250 nm. These constructs showed high stability against aggregation indicated by a zeta potential of –44 mV and an excellent temperature stability up to 200 °C. Furthermore, they were found to be enzymatically degradable, thereby precluding any long term toxicity effects. These unique fibrin nanostructures were analyzed for their ability to deliver tacrolimus, an immunosuppressive drug that is used widely to prevent the initial phase of tissue rejection during allogenic transplantation surgeries. Upon conjugation with tacrolimus, a drug encapsulation efficiency of 66% was achieved, with the *in vitro* release studies in PBS depicting a sustained and complete drug release over a period of one week at the physiological pH of 7.4. At a more acidic pH, the drug release was very slow, suggesting their potential for oral–intestinal drug administration as well. The *in vivo* drug absorption rates analyzed in Sprague Dawley rats further confirmed the sustained release pattern of tacrolimus for both oral and parenteral delivery routes. The novel fibrin nanoconstructs developed using a green chemistry approach thus proved to be excellent biodegradable nanocarriers for oral as well as parenteral administrations, with remarkable potential also for delivering specific growth factors in tissue engineering scaffolds.



The 4(5)-(2-mercaptoethyl)-1H-imidazole-2-carboxamide adaptor molecule (left and right side) trapping dAMP (middle) via a network of hydrogen bonds (dotted white lines).

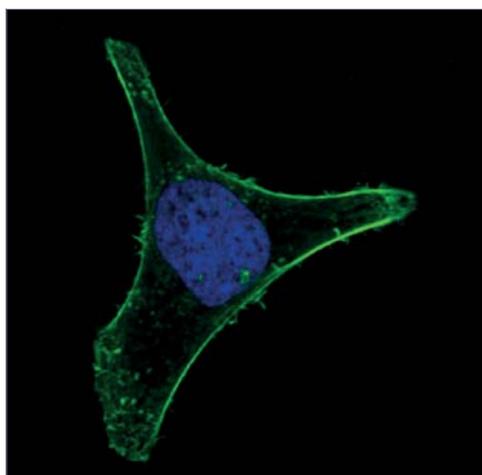
## Chemical recognition and binding kinetics in a functionalized tunnel junction

Shuai Chang, Shuo Huang, Hao Liu, Peiming Zhang, Feng Liang, Rena Akahori, Shengqin Li, Brett Gyarfas, John Shumway, Brian Ashcroft, Jin He and Stuart Lindsay

2012 *Nanotechnology* **23** 235101

4(5)-(2-mercaptoethyl)-1H-imidazole-2-carboxamide is a molecule that has multiple hydrogen bonding sites and a short flexible linker. When tethered to a pair of electrodes, it traps target molecules in a tunnel junction. Surprisingly large recognition-tunneling signals are generated for all naturally occurring DNA bases A, C, G, T and 5-methyl-cytosine. Tunnel current spikes are stochastic and broadly distributed, but characteristic enough so that individual bases can be identified as a tunneling probe is scanned over DNA oligomers. Each base yields a recognizable burst of signal, the duration of which is controlled entirely by the probe speed, down to speeds of  $1 \text{ nm s}^{-1}$ , implying a maximum off-rate of  $3 \text{ s}^{-1}$  for the recognition complex. The same measurements yield a lower bound on the on-rate of  $\sim 1 \text{ M}^{-1} \text{ s}^{-1}$ . Despite the stochastic nature of the signals, an optimized multiparameter fit allows base calling from a single signal peak with an accuracy that can exceed 80% when a single type of nucleotide is present in the junction, meaning that recognition-tunneling is capable of true single-molecule analysis. The accuracy increases to 95% when multiple spikes in a signal cluster are analyzed.

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Confocal image of HeLa cells stained for F-actin.

## Functionalized $\text{Fe}_3\text{O}_4@Au$ superparamagnetic nanoparticles: *in vitro* bioactivity

J Salado, M Insausti, L Lezama, I Gil de Muro, M Moros, B Pelaz, V Grazu, J M de la Fuente and T Rojo

2012 *Nanotechnology* **23** 315102

The interaction of nanoparticles with cells has been a focus of interest during the past decade. We report the fabrication and characterization of hydrosoluble  $\text{Fe}_3\text{O}_4@Au$  nanoparticles functionalized with biocompatible and fluorescent molecules and their interaction with cell cultures by visualizing them with confocal microscopy. Gold covered iron oxide nanoparticles were synthesized by reducing metal salts in the presence of oleylamine and oleic acid. The functionalization of these particles with an amphiphilic polymer provides a water soluble corona as well as the possibility to incorporate different molecules relevant for bio-applications such as poly(ethylene glycol), glucose or a cadaverine derived dye. The particle size, and the presence of polymer layers and conjugated molecules were characterized and confirmed by transmission electron microscopy, thermogravimetric measurements and infrared spectroscopy. A complete magnetic study was performed, showing that gold provides an optimum coating, which enhances the superparamagnetic behaviour observed above 10–15 K in this kind of nanoparticle. The interaction with cells and the cytotoxicity of the  $\text{Fe}_3\text{O}_4@Au$  preparations were determined upon incubation with the HeLa cell line. These nanoparticles showed no cytotoxicity when evaluated by the MTT assay and it was demonstrated that nanoparticles clearly interacted with the cells, showing a higher level of accumulation in the cells for glucose conjugated nanoparticles.

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# Electronics and photonics

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AIXTRON manufactures turn-key deposition systems for graphene, carbon nanotubes and semiconducting nanowires using chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD). These tools have a proven track record and cover 2" to 12" wafer-scale production. Also see the Materials: synthesis or self assembly category on p27. Visit [www.aixtron.com](http://www.aixtron.com).

Device down-sizing continues to drive developments in electronics and photonics, placing nanotechnology at the forefront of research in the industry. While manipulating the behaviour of systems with nanoscale features can introduce some challenges, the new properties that arise from these also open up new approaches to device design.

Achieving good electrical contact to nanowires is notoriously difficult. Researchers at the National Institute of Standards and Technology in the US have identified the processes that cause degradation in nanowire contacts following annealing. They show that poor wetting behaviour of Ni and Au on SiO<sub>2</sub> leads to excessive void formation, and that this can be prevented by the use of a specific adhesion layer of Ti/Al/Ni.

Recent research into nanowire networks has demonstrated transparent, conductive and flexible properties that lend them to a range of next-generation devices. Researchers at the Middle East Technical University in Turkey have fabricated Ge photodetectors using carbon nanotubes and silver nanowires as solution deposited and transparent electrodes. The

photodetectors demonstrate network-enhanced performance, are transparent and flexible, as well as having high efficiency, and a fast response and recovery time.

The exceptional properties of graphene have inspired a generation of electronics and photonics researchers, working at the nanoscale with organic materials. However, high contact and sheet resistance compared with indium tin oxide and rapid deterioration under high current injection have hampered applications of graphene in inorganic devices. Now researchers in Korea have demonstrated an effective approach around these difficulties. They introduced silver nanoparticles onto the graphene via a self-agglomeration process, and then effectively applied the nanoparticle-combined graphene as a current spreading layer onto InGaN/GaN blue LEDs.

In electronics and photonics research size matters, and the very features that raise challenges can also open up new approaches to overcome them. Among these highlighted papers are many more examples of the continuing innovation and creativity in electronics and photonics research at the nanoscale.

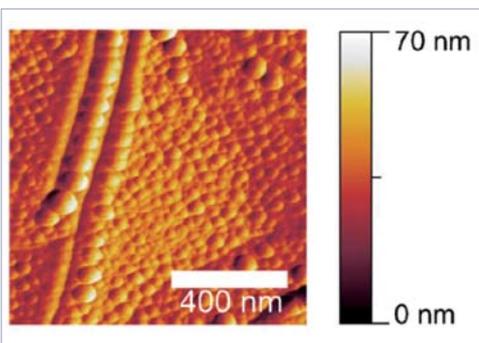


**Section Editor:**  
Meyya Meyyappan

## Section scope

Nanoscale materials and systems are an increasingly integral feature of advances in electronics and photonics device technology. Shrinking device footprints and novel optical device elements have transformed the products available to consumers and industry, as well as catalysing rapid progress in our understanding of the fundamental physics at the heart of nanoscale systems. This section is dedicated to research into new and improved electronic and photonic devices and the advances in our understanding of nanostructure properties that fuel the progress. Only reports describing a clear and significant advance in the field may be considered for publication. Research published in the section deals with a number

of fields including plasmonics, non-volatile memory devices, LEDs, understanding and manipulating fluorescence, novel photonic sources and detectors, the interaction of low-dimensional systems with light and electric fields and the potential for optoelectronic interfacing, as well as the physics that underlines these systems, and much more.



AFM image of a QD layer grown on top of a buffer consisting of GaAs layers and a strained-layer superlattice of 10 periods of In<sub>0.06</sub>Ga<sub>0.94</sub>As (10 nm) and GaAs (20 nm).

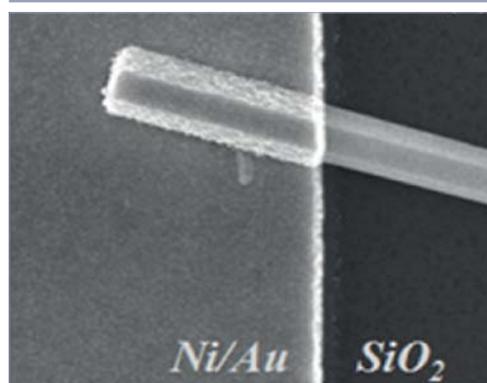
## Single-photon emission from electrically driven InP quantum dots epitaxially grown on CMOS-compatible Si(001)

M Wiesner, W-M Schulz, C Kessler, M Reischle, S Metzner, F Bertram, J Christen, R Roßbach, M Jetter and P Michler

2012 *Nanotechnology* **23** 335201

The heteroepitaxy of III–V semiconductors on silicon is a promising approach for making silicon a photonic platform. Mismatches in material properties, however, present a major challenge, leading to high defect densities in the epitaxial layers and adversely affecting radiative recombination processes. However, nanostructures, such as quantum dots, have been found to grow defect-free even in a suboptimal environment. Here we present the first realization of indium phosphide quantum dots on exactly oriented Si(001), grown by metal–organic vapour-phase epitaxy. We report electrically driven single-photon emission in the red spectral region, meeting the wavelength range of silicon avalanche photodiodes' highest detection efficiency.

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SEM image of nanowire with the same Ni/Au thicknesses deposited on Ni/Au contact for a NW device on a SiO<sub>2</sub> substrate.

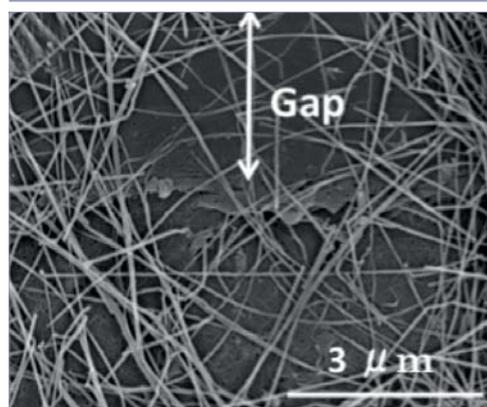
## Microstructure evolution and development of annealed Ni/Au contacts to GaN nanowires

Andrew M Herrero, Paul T Blanchard, Aric Sanders, Matt D Brubaker, Norman A Sanford, Alexana Roshko and Kris A Bertness

2012 *Nanotechnology* **23** 365203

The development of Ni/Au contacts to Mg-doped GaN nanowires (NWs) is examined. Unlike Ni/Au contacts to planar GaN, current–voltage (*I*–*V*) measurements of Mg-doped nanowire devices frequently exhibit a strong degradation after annealing in N<sub>2</sub>/O<sub>2</sub>. This degradation originates from the poor wetting behavior of Ni and Au on SiO<sub>2</sub> and the excessive void formation that occurs at the metal/NW and metal/oxide interfaces. The void formation can cause cracking and delamination of the metal film as well as reduce the contact area at the metal/NW interface, which increases the resistance. The morphology and composition of the annealed Ni/Au contacts on SiO<sub>2</sub> and the p-GaN films were investigated by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS) and x-ray diffraction (XRD) measurements. Adhesion experiments were performed in order to determine the degree of adhesion of the Ni/Au films to the SiO<sub>2</sub> as well as observe and analyze the morphology of the film's underside by SEM. Device degradation from annealing was prevented through the use of a specific adhesion layer of Ti/Al/Ni deposited prior to the nanowire dispersal and Ni/Au deposition. *I*–*V* measurements of NW devices fabricated using this adhesion layer showed a decrease in resistance after annealing, whereas all others showed an increase in resistance. Transmission electron microscopy (TEM) on a cross-section of a NW with Ni/Au contacts and a Ti/Al/Ni adhesion layer showed a lack of void formation at the contact/NW interface. Results of the XRD and TEM analysis of the NW contact structure using a Ti/Al/Ni adhesion layer suggests Al alloying of the Ni/Au contact increases the adhesion and stability of the metal film as well as prevents excessive void formation at the contact/NW interface.

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TEM image of the as-synthesized Ge NWs.

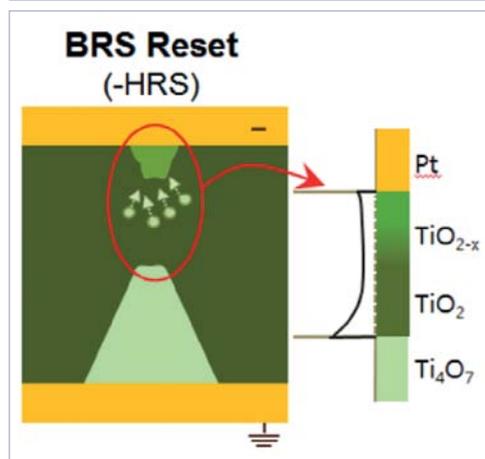
## Transparent, highly flexible, all nanowire network germanium photodetectors

Burcu Aksoy, Sahin Coskun, Seyda Kucukyildiz and Husnu Emrah Unalan

2012 *Nanotechnology* **23** 325202

We report on the fabrication and characterization of all nanowire (NW) network photodetectors. For this purpose, germanium (Ge) NW networks are used as active semiconducting elements, whereas single walled carbon nanotube (SWNT) and silver (Ag) NW networks are used as the contacts. Following their synthesis, all NW networks are deposited through simple solution based methods. Photoresponse characteristics and transparency of the photodetectors for different Ge NW densities are measured. The fabricated devices show a large response with short relaxation times (<10 ms), are flexible and transparent within the visible spectrum.

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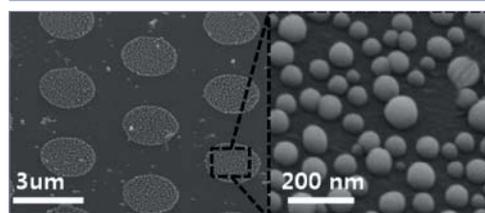
Schematic diagram representing BRS reset processes under positive and negative biases, respectively, and their resulting band diagrams.

## Memristive tri-stable resistive switching at ruptured conducting filaments of a Pt/TiO<sub>2</sub>/Pt cell

Kyung Jean Yoon, Min Hwan Lee, Gun Hwan Kim, Seul Ji Song, Jun Yeong Seok, Sora Han, Jung Ho Yoon, Kyung Min Kim and Cheol Seong Hwang

2012 *Nanotechnology* **23** 185202

A tri-stable memristive switching was demonstrated on a Pt/TiO<sub>2</sub>/Pt device and its underlying mechanism was suggested through a series of electrical measurements. Tri-stable switching could be initiated from a device in unipolar reset status. The unipolar reset status was obtained by performing an electroforming step on a pristine cell which was then followed by unipolar reset switching. It was postulated that tri-stable switching occurred at the location where the conductive filament (initially formed by the electroforming step) was ruptured by a subsequent unipolar reset process. The mechanism of the tri-stable memristive switching presented in this article was attributed to the migration of oxygen ions through the ruptured filament region and the resulting modulation of the Schottky-like interfaces. The assertion was further supported by a comparison study performed on a Pt/TiO<sub>2</sub>/TiO<sub>2-x</sub>/Pt cell.



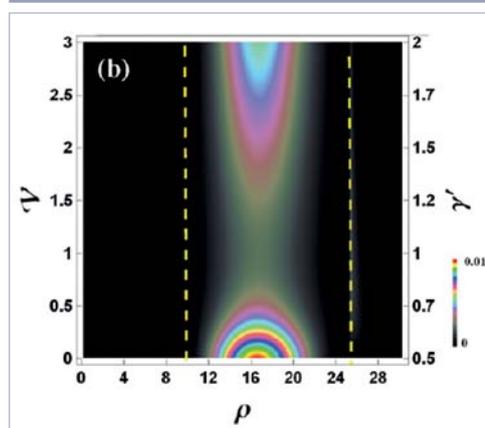
SEM image showing graphene with Ag nanoparticles only in selectively patterned micro-circles (MAGR).

## A self-assembled Ag nanoparticle agglomeration process on graphene for enhanced light output in GaN-based LEDs

Jae-Phil Shim, DoHyung Kim, Minhyeok Choe, Takhee Lee, Seong-Ju Park and Dong-Seon Lee

2012 *Nanotechnology* **23** 255201

We introduce Ag nanoparticles fabricated by a self-assembled agglomeration process in order to enhance the electrical properties, adhesive strength, and reliability of the graphene spreading layer in inorganic-based optoelectronic devices. Here, we fabricated InGaN/GaN multi-quantum-well (MQW) blue LEDs having various current spreading layers: graphene only, graphene with Ag nanoparticles covering the surface, and graphene with Ag nanoparticles only in selectively patterned micro-circles. Although the Ag nanoparticles were found to act as an additional current path that increases the current spreading, optical properties such as transmittance also need to be considered when the Ag nanoparticles are combined with graphene. As a result, LEDs having a graphene spreading layer with Ag nanoparticles formed in selectively patterned micro-circles displayed more uniform and stable light emission and 1.7 times higher light output power than graphene only LEDs.



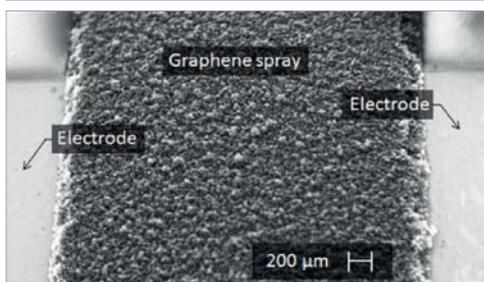
Contour map for the density probability of an electron state in a graphene ring calculated at the absolute minimum eigen-value as a function of the radial coordinate (horizontal axis) and the relative height of the core barrier (vertical axis).

## Voltage-driven ring confinement in a graphene sheet: assessing conditions for bound state solutions

Leonardo Villegas-Lelovsky, Carlos Trallero-Giner, Victor Lopez-Richard, Gilmar E Marques, Cesar E P Villegas and Marcos R S Tavares

2012 *Nanotechnology* **23** 385201

We have systematically studied the single-particle states in quantum rings produced by a set of concentric circular gates over a graphene sheet placed on a substrate. The resulting potential profiles and the interaction between the graphene layer and the substrate are considered within the Dirac Hamiltonian in the framework of the envelope function approximation. Our simulations allow microscopic mapping of the character of the electron and hole quasi-particle solutions according to the applied voltage. General conditions to control and operate the bound state solutions are described as functions of external and controllable parameters that will determine the optical properties ranging from metallic to semiconductor phases. Contrasting behaviors are obtained when comparing the results for repulsive and attractive voltages as well as for variation of the relative strength of the graphene-substrate coupling parameter.



SEM image of bulk-sprayed graphene showing intimate contact between sheets.

## Large photocurrents in single layer graphene thin films: effects of diffusion and drift

James Loomis and Balaji Panchapakesan

2012 *Nanotechnology* **23** 265203

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This paper reports large photocurrents in air-assisted depositions of single layer graphene (derived from reduced single layer graphene oxide) upon illumination with near-infrared (NIR) light. NIR-induced charge carrier generation and subsequent separation at the metal-graphene interface resulted in photocurrent generation. Varying bias voltages were applied to test samples and allowed for evaluating photoresponses in either diffusion- or drift-dominated regions. In the diffusion-dominated region, position-dependent effects of photoconductivity were demonstrated. The photocurrent exhibited increase when the positive electrode was illuminated, decrease when the negative electrode was illuminated, and negligible response when the area between the electrodes was illuminated. At a 100  $\mu\text{V}$  bias voltage, a per cent change in current from  $\sim 150\%$  (40 mW NIR) to  $\sim 1800\%$  (335 mW NIR) is reported. Such large photocurrent responses result from built-in electric fields and optically generated temperature gradients (maximum NIR-induced temperature rise  $\sim 70^\circ\text{C}$ ). The per cent photocurrent change was observed to depend on both annealing temperature and NIR power, but not resistance value. In the drift-dominated realm, a Gaussian photocurrent profile was obtained, signaling drift of charge carriers with increase in localized electric field, akin to the classic Haynes-Shockley experiment. A minority carrier mobility value of  $\mu \sim 700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is reported. The simple low cost graphene devices presented in this paper were fabricated without lithographic processing and are ideal candidates for assorted infrared imaging applications.

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# Patterning and nanofabrication

Advances in patterning and fabrication are increasing the level of control we have over the structures applied in nanotechnology. Combined with a growing knowledge of the effects of morphology and patterning, these advances have empowered the material design aspect in the development of new technology.

Integrating III-V nanowires into silicon electronics may improve transistor performance while minimizing costs. However, research into the growth of InAs nanowires on silicon substrates has not yet demonstrated the control over diameter, vertical alignment and yield required for device integration. Sepideh Gorji Ghalamestani and colleagues at Lund University in Sweden introduced a thin yet high-quality InAs epitaxial layer using metalorganic vapour phase epitaxy. Using these thin epitaxial layers they were able to demonstrate well aligned nanowire growth, including precise position and diameter control across the full wafer. The device characteristics of transistors fabricated in this way showed high uniformity, suggesting that the approach may be applied on manufacturing scales.

Researchers in Korea have developed a new and efficient approach to synthesizing patterns of silver nanoparticles. “The fact of the matter is that the synthesis of metal nanoparticles in precisely

pre-designed shapes and sizes is not an easy task, and it is even more difficult to arrange the nanoparticles in a targeted pattern,” they point out. However, they successfully demonstrate an approach to site-selective synthesis in pre-patterned trenches. Localized surface plasmon resonances can be excited in the final structure so that electromagnetic fields can be enhanced and reradiated, even at larger angles than the critical angle of total internal reflection.

Researchers at the University of Michigan in the US examine the feasibility of ion beam irradiation as a means of fabricating semiconductor nanospikes for specific device applications. They report the first investigation into the electrical conduction properties of individual nanospikes created by ion erosion. Using a novel *in situ* transmission electron microscope nanoprobe approach they identify a number of features in the electrical response of the structures that result from their unique ion-damaged structures.

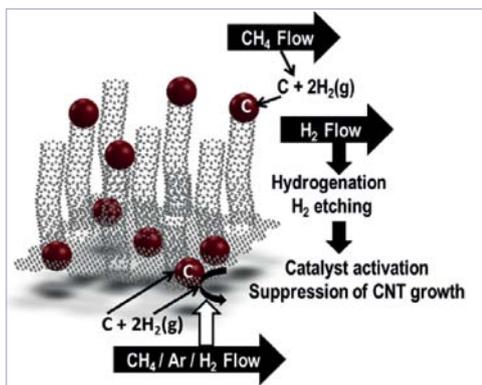
As the capabilities in nanoscale fabrication and patterning advance, so too, it seems, do the inventive ways of applying them. The papers in this selection of highlights report just some of the fruits of research at the frontiers of nanoscale control in material design.



**Section Editor:**  
Sergei Kalinin

## Section scope

As device sizes approach the nanoscale the effects from various fundamental forces, which are neglected at the macroscale, are dominant. In order to explore and utilize these unique conditions it is a continual goal of nanoscientists to improve methods of accurately fabricating devices and patterning surfaces at the nanoscale. This section focuses on comprehensive presentations of novel methods to increase the resolution, control and efficiency of nanoscale production and demonstrate new applications based on these nanofabricated materials. A wide range of lithography techniques are covered in this section including both bottom-up and top-down methods. We emphasise the need for articles to demonstrate real improvements in techniques by direct comparison with other methods. These improvements can take many forms. For example, demonstrating improvement in the control of a technique, increasing the area or conditions in which the technique can be performed, increasing speed or output of the technique or reducing the costs of fabrication.



Schematic illustrating direct CNT growth on planar graphene with methane feedstock. The pyrolysis of methane supplies carbon and hydrogen to the system.

## Out-of-plane growth of CNTs on graphene for supercapacitor applications

Youn-Su Kim, Kitu Kumar, Frank T Fisher and Eui-Hyeok Yang

2012 *Nanotechnology* **23** 015301

This paper describes the fabrication and characterization of a hybrid nanostructure comprised of carbon nanotubes (CNTs) grown on graphene layers for supercapacitor applications. The entire nanostructure (CNTs and graphene) was fabricated via atmospheric pressure chemical vapor deposition (APCVD) and designed to minimize self-aggregation of the graphene and CNTs. Growth parameters of the CNTs were optimized by adjusting the gas flow rates of hydrogen and methane to control the simultaneous, competing reactions of carbon formation toward CNT growth and hydrogenation which suppresses CNT growth via hydrogen etching of carbon. Characterization of the supercapacitor performance of the CNT-graphene hybrid nanostructure indicated that the average measured capacitance of a fabricated graphene-CNT structure was  $653.7 \mu\text{F cm}^{-2}$  at  $10 \text{ mV s}^{-1}$  with a standard rectangular cyclic voltammetry curve. Rapid charging-discharging characteristics ( $\text{mV s}^{-1}$ ) were exhibited with a capacitance of approximately 75% ( $490.3 \mu\text{F cm}^{-2}$ ). These experimental results indicate that this CNT-graphene structure has the potential towards three-dimensional (3D) graphene-CNT multi-stack structures for high-performance supercapacitors.

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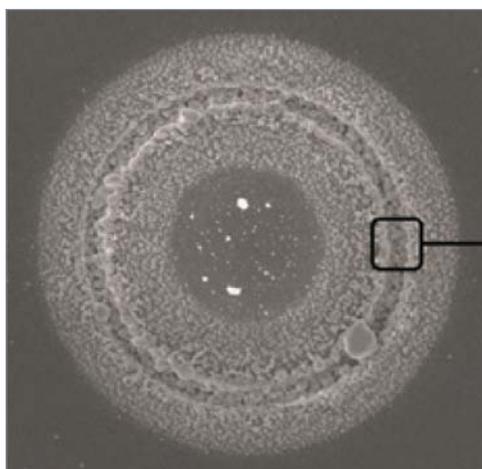
30° tilted SEM image of the lithographically defined InAs nanowires with different diameters and spacings.

## Uniform and position-controlled InAs nanowires on 2" Si substrates for transistor applications

Sepideh Gorji Ghalamestani, Sofia Johansson, B Mattias Borg, Erik Lind, Kimberly A Dick and Lars-Erik Wernersson

2012 *Nanotechnology* **23** 015302

This study presents a novel approach for indirect integration of InAs nanowires on 2" Si substrates. We have investigated and developed epitaxial growth of InAs nanowires on 2" Si substrates via the introduction of a thin yet high-quality InAs epitaxial layer grown by metalorganic vapor phase epitaxy. We demonstrate well-aligned nanowire growth including precise position and diameter control across the full wafer using very thin epitaxial layers (<300 nm). Statistical analysis results performed on the grown nanowires across the 2" wafer size verifies our full control on the grown nanowire with 100% growth yield. From the crystallographic viewpoint, these InAs nanowires are predominantly of wurtzite structure. Furthermore, we show one possible device application of the aforementioned structure in vertical wrap-gated field-effect transistor geometry. The vertically aligned InAs nanowires are utilized as transistor channels and the InAs epitaxial layer is employed as the source contact. A high uniformity of the device characteristics for numerous transistors is further presented and RF characterization of these devices demonstrates an  $f_t$  of 9.8 GHz.



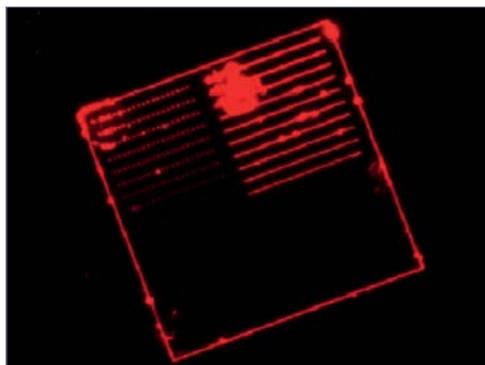
SEM images of circular-shaped trenches packed with Ag nanoparticles. The image shows over-dense coverage, due to the over-exposure of the fluorine layer by FIB.

## Site-selective synthesis of silver nanoparticles in pre-patterned trenches and their localized surface plasmon resonances

Hansik Yun, Il-Min Lee, Sang Hyuk Im, Seung-Yeol Lee and ByoungHo Lee

2012 *Nanotechnology* **23** 015306

A method for depositing silver nanoparticles in a pre-patterned trench by site-selective synthesis is described. In the trench patterns with various shapes, silver nanoparticles can be selectively nucleated and grown only on polyvinylpyrrolidone (PVP) domains by attraction (or repulsion) between silver ions and the hydrophilic PVP island domains in a silica matrix of the trench (or the hydrophobic fluorosilane layer). Regarding the silver nanoparticles in the trench, localized surface plasmon resonance (LSPR) could be excited by obliquely incident light, reradiating the enhanced electromagnetic field in the far- and near-fields. Even in the case of a large angle incidence in total internal reflection (TIR), the patterned silver nanoparticle clusters underwent strong scattering with a high intensity, due to the LSPR effect.



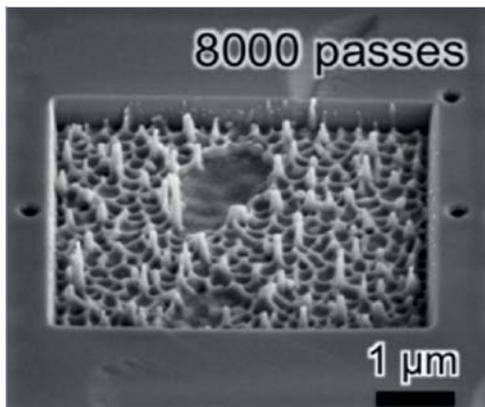
Fluorescent image captured in N21 channel after QD attachment.

## Site-selective assembly of quantum dots on patterned self-assembled monolayers fabricated by laser direct-writing

Chong Wu, Yongsheng Wang, Xuemingyue Han, Xinming Hu, Qianyi Cheng, Baohang Han, Qian Liu, Tianling Ren, Yonghong He, Shuqing Sun and Hui Ma

2012 *Nanotechnology* **23** 235302

A simple and efficient route for quantum dot (QDs) patterning using self-assembled monolayers (SAMs) as templates is described. By means of a laser direct-writing (LDW) technique, SAMs of octadecylphosphonic acid formed by adsorption on native oxide layer of titanium film were patterned through laser-induced ablation of the SAM molecules. This technique allows the creation of chemical-specific patterns accompanied by slight change in the topography. Using atomic force microscopy and friction force microscopy, the dependence of feature size and characteristics on the irradiation dose was demonstrated. Upon immersion of a substrate with patterned SAMs bearing thiol as the terminal group into a dispersion of QDs resulted in the assembly of QDs on the specific thiol-terminated areas. Patterns of QDs with different photoluminescent wavelength were generated. The LDW technique, which is convenient and flexible due to its path-directed and maskless fabrication process, provided a new powerful approach for patterning materials on surfaces for various applications.



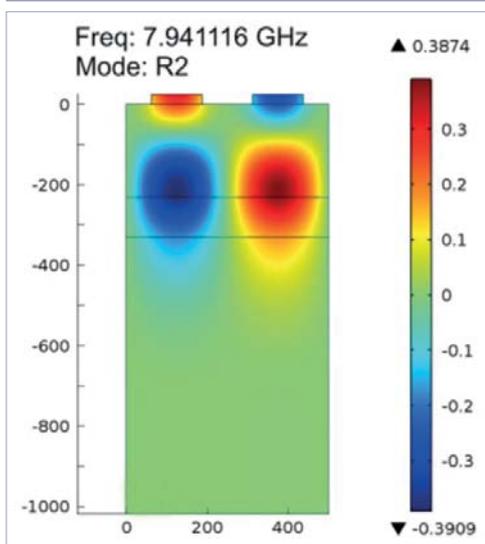
SEM images showing a region of rough InAs film grown on nC InP through the process of irradiation with a 7.3 pA FIB using a 100 ns spot dwell time.

## Electrical transport in ion beam created InAs nanopikes

K A Grossklaus, J R Jokisaari, X Q Pan and J M Millunchick

2012 *Nanotechnology* **23** 315301

Ion beam irradiation has previously been demonstrated as a method for creating nanowire-like semiconductor nanostructures, but no previous studies have reported on the electrical properties of those structures. In this work we describe the creation and *in situ* transmission electron microscopy electrical characterization of nanoscale InAs spike structures on both InAs and InP substrates fabricated using a focused ion beam erosion method. Those InAs 'nanospikes' are found to possess internal structures with varying amounts of ion damaged and single crystalline material. Nanospike electrical behavior is analyzed with respect to model electronic structures and is similar to cases of barrier limited conduction in nanowires. The different electrical responses of each nanospike are found to be the result of variation in their structure, with the conductivity of InAs nanospikes formed on InAs substrates found to increase with the degree of nanospike core crystallinity. The conductivity of InAs nanospikes formed on InP substrates does not show a dependence on core crystallinity, and may be controlled by the other internal barriers to conduction inherent in that system.



FEM calculation result for DL1. The image shows the vertical component of the displacement field for the R3 mode.

## Ultrahigh-frequency surface acoustic wave transducers on ZnO/SiO<sub>2</sub>/Si using nanoimprint lithography

S Büyükköse, B Vratzov, D Ataç, J van der Veen, P V Santos and W G van der Wiel

2012 *Nanotechnology* **23** 315303

Ultrahigh-frequency surface acoustic wave devices were fabricated on a ZnO/SiO<sub>2</sub>/Si substrate using step-and-flash nanoimprint lithography combined with hydrogen silsesquioxane (HSQ) planarization. Excellent critical dimension control was demonstrated for interdigital transducers with finger electrode widths from 125 down to 65 nm. Fundamental and higher-order Rayleigh modes up to 16.1 GHz were excited and detected, which is the highest frequency for ZnO-based transducers on silicon reported so far. Surface acoustic modes were confirmed with numerical simulations. Simulation results showed good agreement with the experimental data.

# Energy at the nanoscale

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Angstrom Engineering designs and manufactures turn-key thin-film deposition equipment for research and pilot production. Our capabilities include physical vapour deposition and chemical vapour deposition processes, such as LPCVD, PECVD, evaporation and sputtering. We offer many standard configurations as well as the ability to engineer a solution to meet your specific application. Please contact our engineering team to discuss your application and requirements.

Energy continues to hold priority attention in government, industry and academia. New energy-generating mechanisms will always capture interest, but increasingly research efforts are focusing on understanding the limiting factors of current technologies to maximize their economic and environmental viability.

Solar energy remains one of the most promising directions for renewable energy research. Organic photovoltaics allow economies in cost but increasing the efficiency remains a challenge, and requires an understanding of the limiting factors. A collaboration of researchers in the US and China have explained some of the anomalies in the efficiencies of heterojunction device structures, strengthening the foundations for designing nanostructured photovoltaic devices with optimized efficiencies.

Aggregation and increased interparticle resistance have led to degradation in the electrochemical performance of the ferrite nanoparticles. Now Yun-Ho Jin *et al* have demonstrated enhanced cyclability and high capacity

with ferrite nanoparticles coated with carbon. Such ferrite nanostructures provide relatively cheap and environmentally innocuous candidates for anode materials with a high theoretical capacity for lithium ion batteries.

Carbon-nanotube-coated paper has been demonstrated to be effective as a supercapacitor and a promising candidate for energy storage. However, so far it has been used with ionic liquid electrolytes, which lead to leakage and integrity problems. Researchers in Korea have now demonstrated supercapacitors using carbon nanotube coated paper and gel electrolytes based on silica and ionic liquids.

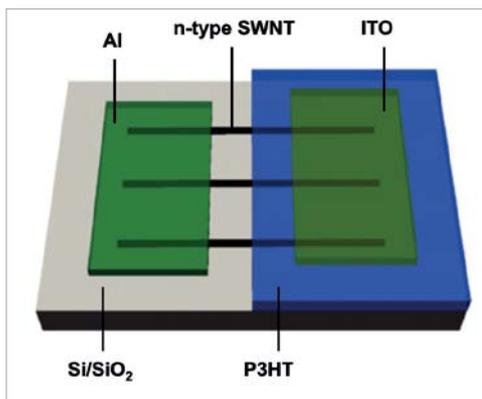
In 1927, when Werner Heisenberg stated the fundamental compromise in the knowledge of time and energy in a system, little would he have known how preoccupied we would be by those same variables 85 years later. In some ways the race is on to find new means for meeting our energy demands before we run out of time. And as these highlights demonstrate, the research community is well primed to meet the challenge.



Section Editor: John Vajo

## Section scope

Nanoscale science and technology research forms a fundamental component in the development of alternative energy sources. In view of mounting awareness of the current limitations of the world's energy resources, research in this field is becoming increasingly important. The new section in *Nanotechnology* focuses on innovative techniques based on nanostructures that can be applied towards all forms of energy generation and storage, and embraces both advances in the fundamental science involved as well as technological innovations. Papers published in the new section describe ways to improve the efficiency, stability and processibility of photovoltaic devices, hydrogen storage units, fuel cells, and a range of other energy-related fields of research. The reports cover work towards the development of sophisticated new nanomaterials and fabrication techniques, as well as studies that aim to deepen our understanding of the fundamental mechanisms at work in the latest energy generating and storing devices.



Schematic of a planar heterojunction solar cell based on a P3HT film on top of laterally aligned SWNTs.

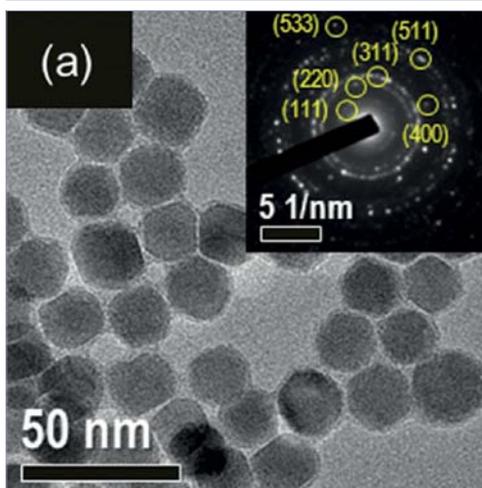
## Anomalous thickness-dependence of photocurrent explained for state-of-the-art planar nano-heterojunction organic solar cells

Geraldine L C Paulus, Moon-Ho Ham and Michael S Strano

2012 *Nanotechnology* **23** 095402

Due to their simple geometry and design, planar heterojunction (PHJ) solar cells have advantages both as potential photovoltaics with more efficient charge extraction than their bulk heterojunction (BHJ) counterparts, and as idealized interfaces to study basic device operation. The main reason for creating BHJs was the limited exciton diffusion length in the active materials of the PHJ: if an exciton is generated at a distance greater than its diffusion length from the hetero-interface of the PHJ, it would be very unlikely to be able to contribute to the photocurrent. Based on this argument one expects a maximum in the photocurrent of PHJs for a thickness of the active layer equal to the exciton diffusion length ( $\sim 10$  nm). However, in two recently developed PHJs that have appeared in the literature, a maximum photocurrent is observed for 60–65 nm of poly(3-hexylthiophene) (P3HT). In this work, we explore this anomaly by combining both an optical  $T$ -matrix and a kinetic Monte Carlo simulation that tracks the exciton behavior in the PHJs. The two systems considered are a P3HT/single walled carbon nanotube (SWNT) device, and a P3HT/phenyl-C61-butyric acid methyl ester (PCBM) device. The model demonstrates how a bulk exciton sink can explain the shifted maximum in the P3HT/SWNT case, whereas in the P3HT/PCBM case the maximum is mainly determined by PCBM molecules interdiffusing in the P3HT upon annealing. Based upon the results of this model it will be possible to more intelligently design nanostructured photovoltaics and optimize them toward higher efficiencies.

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TEM image of  $\text{Fe}_3\text{O}_4$  nanoparticles.

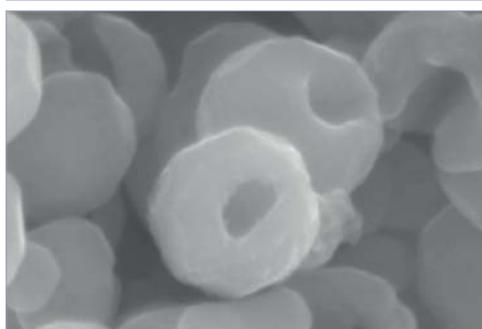
## Synthesis of core/shell spinel ferrite/carbon nanoparticles with enhanced cycling stability for lithium ion battery anodes

Yun-Ho Jin, Seung-Deok Seo, Hyun-Woo Shim, Kyung-Soo Park and Dong-Wan Kim

2012 *Nanotechnology* **23** 125402

Monodispersed core/shell spinel ferrite/carbon nanoparticles are formed by thermolysis of metal ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ) oleates followed by carbon coating. The phase and morphology of nanoparticles are characterized by x-ray diffraction and transmission electron microscopy. Pure  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  nanoparticles are initially prepared through thermal decomposition of metal-oleate precursors at  $310^\circ\text{C}$  and they are found to exhibit poor electrochemical performance because of the easy aggregation of nanoparticles and the resulting increase in the interparticle contact resistance. In contrast, uniform carbon coating of  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  nanoparticles by low-temperature ( $180^\circ\text{C}$ ) decomposition of malic acid allowed each nanoparticle to be electrically wired to a current collector through a conducting percolative path. Core/shell  $\text{Fe}_3\text{O}_4/\text{C}$  and  $\text{CoFe}_2\text{O}_4/\text{C}$  nanocomposite electrodes show a high specific capacity that can exceed  $700\text{ mAh g}^{-1}$  after 200 cycles, along with enhanced cycling stability.

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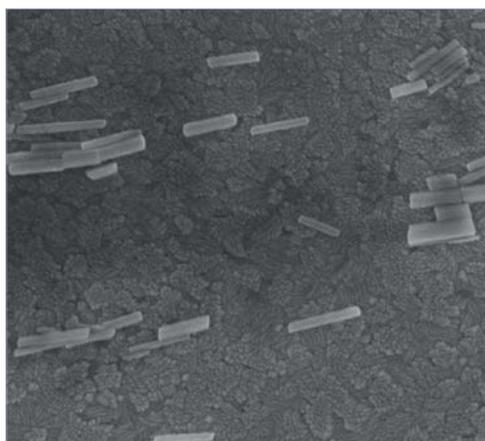
FESEM images of the as-prepared  $\text{CoFe}_2\text{O}_4$  nanospheres.

## Hollow $\text{CoFe}_2\text{O}_4$ nanospheres as a high capacity anode material for lithium ion batteries

Ying Wang, Dawei Su, Alison Ung, Jung-ho Ahn and Guoxiu Wang

2012 *Nanotechnology* **23** 055402

Hollow structured  $\text{CoFe}_2\text{O}_4$  nanospheres were synthesized by a hydrothermal method. The uniform hollow nanosphere architecture of the as-prepared  $\text{CoFe}_2\text{O}_4$  has been confirmed by field emission scanning electron microscopy and transmission electron microscopy analysis, which give an outer diameter of 200–300 nm and a wall thickness of about 100 nm.  $\text{CoFe}_2\text{O}_4$  nanospheres exhibited a high reversible capacity of  $1266\text{ mA h g}^{-1}$  with an excellent capacity retention of 93.6% over 50 cycles and an improved rate capability.  $\text{CoFe}_2\text{O}_4$  could be a promising high capacity anode material for lithium ion batteries.



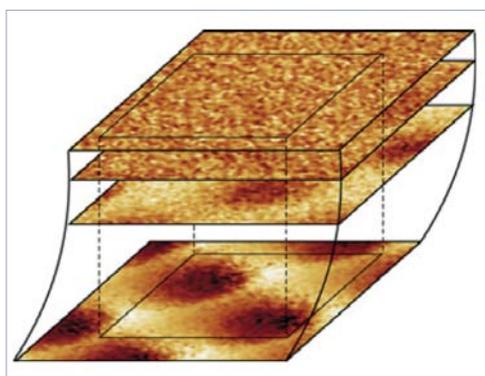
SEM image of NaF<sub>4</sub>:Yb/Er/Gd nanorod thin films on the front surface of a-Si:H solar cells.

## Core/shell structured NaF<sub>4</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup>/Gd<sup>3+</sup> nanorods with Au nanoparticles or shells for flexible amorphous silicon solar cells

Z Q Li, X D Li, Q Q Liu, X H Chen, Z Sun, C Liu, X J Ye and S M Huang

2012 *Nanotechnology* **23** 025402

A simple approach for preparing near-infrared (NIR) to visible upconversion (UC) NaF<sub>4</sub>:Yb/Er/Gd nanorods in combination with gold nanostructures has been reported. The grown UC nanomaterials with Au nanostructures have been applied to flexible amorphous silicon solar cells on the steel substrates to investigate their responses to sub-bandgap infrared irradiation. Photocurrent–voltage measurements were performed on the solar cells. It was demonstrated that UC of NIR light led to a 16-fold to 72-fold improvement of the short-circuit current under 980 nm illumination compared to a cell without upconverters. A maximum current of 1.16 mA was obtained for the cell using UC nanorods coated with Au nanoparticles under 980 nm laser illumination. This result corresponds to an external quantum efficiency of 0.14% of the solar cell. Mechanisms of erbium luminescence in the grown UC nanorods were analyzed and discussed.



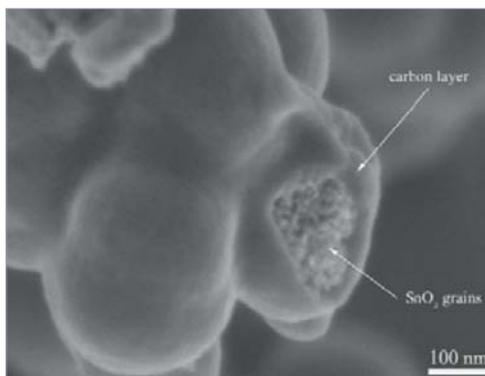
Schematic drawings of the postprocessing procedure to align constant height images one below the other.

## Three-dimensional dynamic force spectroscopy measurements on KBr(001): atomic deformations at small tip–sample separations

S Frey, S Kawai, R Pawlak, T Glatzel, A Baratoﬀ and E Meyer

2012 *Nanotechnology* **23** 055401

Three-dimensional dynamic force spectroscopy measurements were carried out above KBr(001) at low temperature in order to investigate the distance dependence of the tip–sample interactions. In particular, the recorded 3D frequency shift data as well as the extracted interaction force and potential energy fields were analysed with respect to influences of tip and/or sample deformations. We found that a postprocessing correction of the observed deformations significantly modifies the magnitude of the extracted interaction forces and also the image contrast.



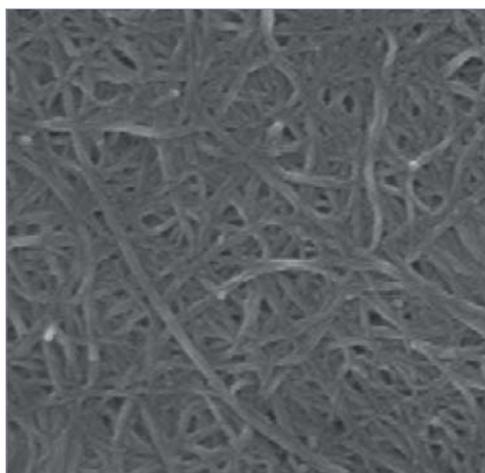
SEM image of SnO<sub>2</sub>@carbon nanostructures.

## Mesoporous SnO<sub>2</sub>@carbon core–shell nanostructures with superior electrochemical performance for lithium ion batteries

L B Chen, X M Yin, L Mei, C C Li, D N Lei, M Zhang, Q H Li, Z Xu, C M Xu and T H Wang

2012 *Nanotechnology* **23** 035402

SnO<sub>2</sub>@carbon nanostructure composites are prepared by a simple hydrothermal method. The composite exhibits unique structure, which consists of a mesoporous SnO<sub>2</sub> core assembled of very small nanoparticles and a carbon shell with 10 nm thickness. The mesoporous SnO<sub>2</sub>@carbon core–shell nanostructures manifest superior electrochemical performance as an anode material for lithium ion batteries. The reversible specific capacity of the composite is about 908 mAh g<sup>-1</sup> for the first cycle and it can retain about 680 mAh g<sup>-1</sup> after 40 charge/discharge cycles at a current density of 0.3 C. Moreover, it shows excellent rate capability even at the high rate of 4.5 C. The enhanced performance was attributed to the mesoporous structure and a suitable carbon coating.



High-magnification SEM image showing detailed morphology of carbon nanotubes.

## All-solid-state flexible supercapacitors based on papers coated with carbon nanotubes and ionic-liquid-based gel electrolytes

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Yu Jin Kang, Haegeun Chung, Chi-Hwan Han and Woong Kim

2012 *Nanotechnology* **23** 065401

All-solid-state flexible supercapacitors were fabricated using carbon nanotubes (CNTs), regular office papers, and ionic-liquid-based gel electrolytes. Flexible electrodes were made by coating CNTs on office papers by a drop-dry method. The gel electrolyte was prepared by mixing fumed silica nanopowders with ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf<sub>2</sub>]). This supercapacitor showed high power and energy performance as a solid-state flexible supercapacitor. The specific capacitance of the CNT electrodes was 135 F g<sup>-1</sup> at a current density of 2 A g<sup>-1</sup>, when considering the mass of active materials only. The maximum power and energy density of the supercapacitors were 164 kW kg<sup>-1</sup> and 41 Wh kg<sup>-1</sup>, respectively. Interestingly, the solid-state supercapacitor with the gel electrolyte showed comparable performance to the supercapacitors with ionic-liquid electrolyte. Moreover, the supercapacitor showed excellent stability and flexibility. The CNT/paper- and gel-based supercapacitors may hold great potential for low-cost and high-performance flexible energy storage applications.



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# Sensing and actuating

A new level of detail and precision has been enabled through developments in nanomaterial science. As well as enabling enhanced device capabilities by incorporating the latest understanding in material properties, a great deal of research attention is focused on improving the reproducibility, reliability and convenience of information retrieval at the nanoscale.

The extraordinary signal enhancements arising from structural and plasmonic properties of nanomaterials can hugely boost system sensitivities. Surface plasmon resonances allow access to the extremely weak yet unique spectral fingerprints from Raman scattering, which might otherwise be lost to practical purposes. However, particle aggregation and signal fluctuation can still cause problems. Researchers in the US and Canada conveniently sandwich fluorescent probes between a plasmonic gold nanoparticle core and a silica shell for surface enhanced Raman scattering. They also investigate how different shapes of gold core affect the response.

Graphene has famously extraordinary mechanical and electrical properties. Now researchers in the UK and US have successfully dispersed graphene nanoplatelets into a polydimethylsiloxane matrix resulting in a composite

with photomechanical properties for use in wireless devices. As they point out: “An optical-to-mechanical energy conversion factor of  $7\text{--}9\text{ MPa W}^{-1}$  obtained during testing showed an extraordinary photomechanical effect larger than not only all other carbon-based composites, but also any other material that exhibits a photomechanical effect.”

Biological systems can inspire new approaches to nanoscale actuation. Researchers in Spain have observed the conformational changes during virus morphogenesis for the first time. Viral terminases hydrolyse ATP molecules in the process of packaging DNA inside the preformed viral prohead. As Johann Mertens and his colleagues point out, the biomolecular machines involved in this process generate one of the highest mechanical powers observed in nature. The researchers used the bending of functionalized cantilevers as terminases immobilize on them to characterize the terminase interactions and observed irreversible conformational changes.

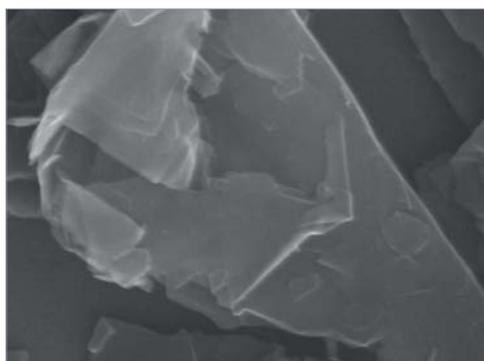
Any advancing technology achieves what was previously impossible. But progress in sensing and actuating seems to go further, building on novel nanomaterial properties to demonstrate the previously inconceivable.



**Section Editor:**  
Juergen Brugger

## Section scope

The possibility of using nanotechnology to convey and enhance information to a macroscopic scale has driven a wave of research into the fabrication and optimization of nanoscale sensor devices. Devices have been developed for such wide ranging applications as the detection of gases, such as ethanol and oxygen; biomolecules, like DNA; and mechanical forces. Progress is leading to applications in a multitude of fields such as food safety and gas alarms. The unique properties of nano materials, such as exceptional strength and massive surface-to-volume ratio compared with their macroscale counterparts, has allowed great enhancement of the sensitivity of sensors in many fields. This section invites submissions that show significant enhancement of the sensing capabilities of applied nano systems, as well as novel applications of nanoscale devices to the detection of mechanical phenomena, biological, material and chemical species.



SEM image of gold nanoparticles.

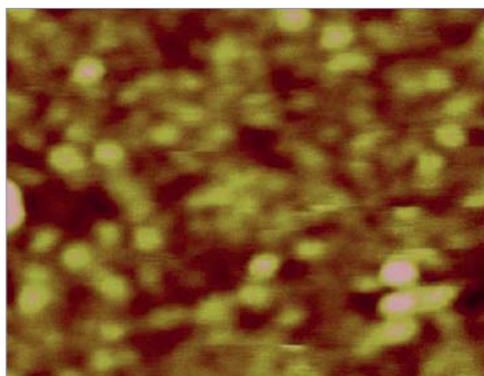
## Graphene-nanoplatelet-based photomechanical actuators

James Loomis, Ben King, Tom Burkhead, Peng Xu, Nathan Bessler, Eugene Terentjev and Balaji Panchapakesan

2012 *Nanotechnology* **23** 045501

This paper reports large light-induced reversible and elastic responses of graphene nanoplatelet (GNP) polymer composites. Homogeneous mixtures of GNP/polydimethylsiloxane (PDMS) composites (0.1–5 wt%) were prepared and their infrared (IR) mechanical responses studied with increasing pre-strains. Using IR illumination, a photomechanically induced change in stress of four orders of magnitude as compared to pristine PDMS polymer was measured. The actuation responses of the graphene polymer composites depended on the applied pre-strains. At low levels of pre-strain (3–9%) the actuators showed reversible expansion while at high levels (15–40%) the actuators exhibited reversible contraction. The GNP/PDMS composites exhibited higher actuation stresses compared to other forms of nanostructured carbon/PDMS composites, including carbon nanotubes (CNTs), for the same fabrication method. An extraordinary optical-to-mechanical energy conversion factor ( $\eta_M$ ) of 7–9 MPa W<sup>-1</sup> for GNP-based polymer composite actuators is reported.

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AFM topographic image of gp19 immobilized at 40 ng ml<sup>-1</sup> shows its arrangement in a monolayer of packed oligomers.

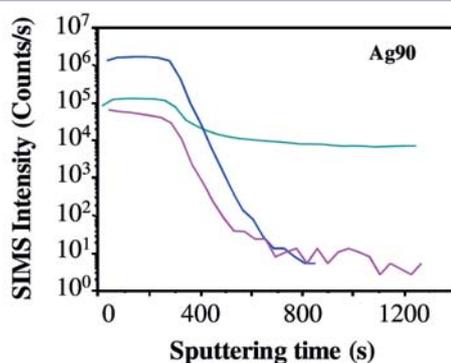
## Stepwise motion of a microcantilever driven by the hydrolysis of viral ATPases

Johann Mertens, María I Daudén, José L Carrascosa and Javier Tamayo

2012 *Nanotechnology* **23** 015501

The biomolecular machines involved in DNA packaging by viruses generate one of the highest mechanical powers observed in nature. One component of the DNA packaging machinery, called the terminase, has been proposed as the molecular motor that converts chemical energy from ATP hydrolysis into mechanical movement of DNA during bacteriophage morphogenesis. However, the conformational changes involved in this energy conversion have never been observed. Here we report a real-time measurement of ATP-induced conformational changes in the terminase of bacteriophage T7 (gp19). The recording of the cantilever bending during its functionalization shows the existence of a gp19 monolayer arrangement confirmed by atomic force microscopy of the immobilized proteins. The ATP hydrolysis of the gp19 terminase generates a stepped motion of the cantilever and points to a mechanical cooperative effect among gp19 oligomers. Furthermore, the effect of ATP can be counteracted by non-hydrolyzable nucleotide analogs.

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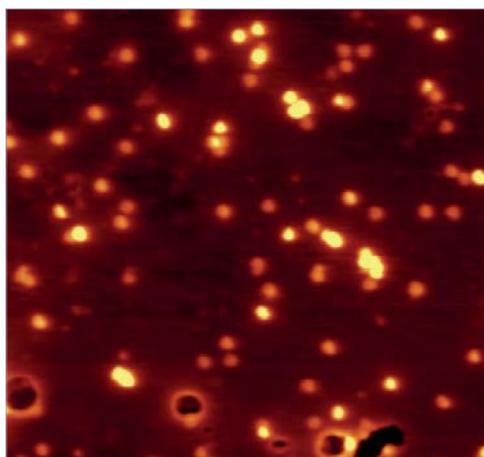
An image showing various positions of contact for AFM bending tests.

## Ag/ZnO nanomaterials as high performance sensors for flammable and toxic gases

Mrunal A Khaderbad, Youngjin Choi, Pritesh Hiralal, Atif Aziz, Nan Wang, Colm Durkan, Pradyumna Thiruvenkatanathan, Gehan A J Amaratunga, V Ramgopal Rao and Ashwin A Seshia

2012 *Nanotechnology* **23** 025502

Ag/ZnO nanocomposites supported on polycrystalline Al<sub>2</sub>O<sub>3</sub> were synthesized by an unprecedented approach combining plasma enhanced chemical vapor deposition (PE-CVD) of ZnO matrices and the subsequent deposition of Ag nanoparticles (NPs) by radio frequency (RF) sputtering. The system structure, composition and morphology were investigated by glancing incidence x-ray diffraction (GIXRD), secondary ion mass spectrometry (SIMS), field emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray spectroscopy (EDXS). A tailored dispersion and distribution of silver particles could be obtained under mild conditions by the sole variation of the sputtering time. Gas sensing properties toward flammable and toxic gases, both reducing (CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>COCH<sub>3</sub>) and oxidizing (O<sub>3</sub>), were investigated in the temperature range 100–400 °C. Beside the high sensitivity, the developed sensors exhibited a response proportional to Ag content, thanks to catalytic and electronic effects promoted by silver NPs. In addition, discrimination between oxidizing and reducing analytes was enabled by a suitable choice of the adopted working temperature.



AFM image of a representative SERS active film.

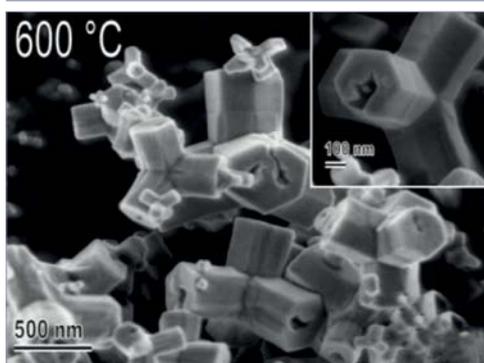
## Chitosan-coated anisotropic silver nanoparticles as a SERS substrate for single-molecule detection

Monica Potara, Monica Baia, Cosmin Farcau and Simion Astilean

2012 *Nanotechnology* **23** 055501

Surface-enhanced Raman spectroscopy (SERS) is a technique that has become widely used for identifying and providing structural information about molecular species in low concentration. There is an ongoing interest in finding optimum particle size, shape and spatial distribution for optimizing the SERS substrates and pushing the sensitivity toward the single-molecule detection limit. This work reports the design of a novel, biocompatible SERS substrate based on small clusters of anisotropic silver nanoparticles embedded in a film of chitosan biopolymer. The SERS efficiency of the biocompatible film is assessed by employing Raman imaging and spectroscopy of adenine, a significant biological molecule. By combining atomic force microscopy with SERS imaging we find that the chitosan matrix enables the formation of small clusters of silver nanoparticles, with junctions and gaps that greatly enhance the Raman intensities of the adsorbed molecules. The study demonstrates that chitosan-coated anisotropic silver nanoparticle clusters are sensitive enough to be implemented as effective plasmonic substrates for SERS detection of nonresonant analytes at the single-molecule level.

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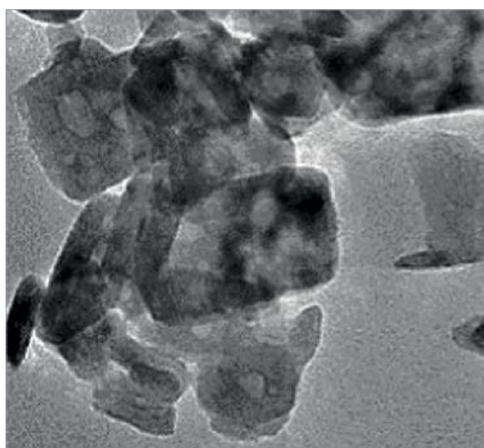
SEM images of ZnO structures. The inset is a close-up image.

## Synthesis of ZnO tetrapods for flexible and transparent UV sensors

Simas Rackauskas, Kimmo Mustonen, Terhi Järvinen, Marco Mattila, Olga Klimova, Hua Jiang, Oleg Tolochko, Harri Lipsanen, Esko I Kauppinen and Albert G Nasibulin

2012 *Nanotechnology* **23** 095502

ZnO tetrapods (ZnO-Ts) were synthesized in a vertical flow reactor by gas phase oxidation of Zn vapor in an air atmosphere. The morphology of the product was varied from nearly spherical nanoparticles to ZnO-Ts, together with the partial pressure of Zn and reaction temperature. MgO introduced during synthesis, increased the band gap, the optical transparency in the visible range, and also changed the ZnO-T structure. Fabricated flexible transparent UV sensors showed a 45-fold current increase under UV irradiation with an intensity of  $30 \mu\text{W cm}^{-2}$  at a wavelength of 365 nm and response time of 0.9 s.

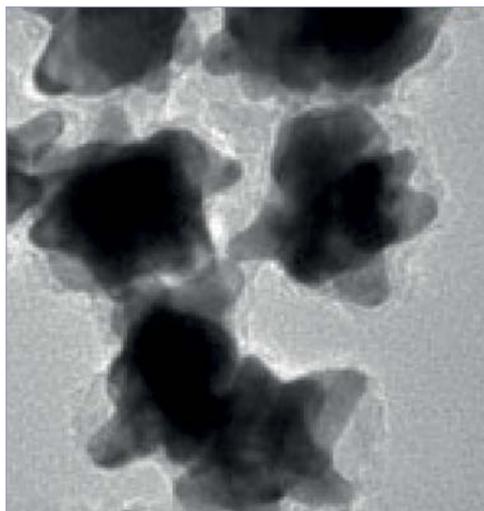
TEM image of graphene-WO<sub>3</sub> nanocomposite.

## Faster response of NO<sub>2</sub> sensing in graphene-WO<sub>3</sub> nanocomposites

Shubhda Srivastava, Kiran Jain, V N Singh, Sukhvir Singh, N Vijayan, Nita Dilawar, Govind Gupta and T D Senguttuvan

2012 *Nanotechnology* **23** 205501

Graphene-based nanocomposites have proven to be very promising materials for gas sensing applications. In this paper, we present a general approach for the preparation of graphene-WO<sub>3</sub> nanocomposites. Graphene-WO<sub>3</sub> nanocomposite thin-layer sensors were prepared by drop coating the dispersed solution onto the alumina substrate. These nanocomposites were used for the detection of NO<sub>2</sub> for the first time. TEM micrographs revealed that WO<sub>3</sub> nanoparticles were well distributed on graphene nanosheets. Three different compositions (0.2, 0.5 and 0.1 wt%) of graphene with WO<sub>3</sub> were used for the gas sensing measurements. It was observed that the sensor response to NO<sub>2</sub> increased nearly three times in the case of graphene-WO<sub>3</sub> nanocomposite layer as compared to a pure WO<sub>3</sub> layer at room temperature. The best response of the graphene-WO<sub>3</sub> nanocomposite was obtained at 250 °C.

TEM images gold nanostars, – MGITC–SiO<sub>2</sub>.

## Shape-dependent surface-enhanced Raman scattering in gold–Raman-probe–silica sandwiched nanoparticles for biocompatible applications

Ming Li, Scott K Cushing, Jianming Zhang, Jessica Lankford, Zoraida P Aguilar, Dongling Ma and Nianqiang Wu

2012 *Nanotechnology* **23** 115501

To meet the requirement of Raman probes (labels) for biocompatible applications, a synthetic approach has been developed to sandwich the Raman-probe (malachite green isothiocyanate, MGITC) molecules between the gold core and the silica shell in gold–SiO<sub>2</sub> composite nanoparticles. The gold–MGITC–SiO<sub>2</sub> sandwiched structure not only prevents the Raman probe from leaking out but also improves the solubility of the nanoparticles in organic solvents and in aqueous solutions even with high ionic strength. To amplify the Raman signal, three types of core, gold nanospheres, nanorods and nanostars, have been chosen as the substrates of the Raman probe. The effect of the core shape on the surface-enhanced Raman scattering (SERS) has been investigated. The colloidal nanostars showed the highest SERS enhancement factor while the nanospheres possessed the lowest SERS activity under excitation with 532 and 785 nm lasers. Three-dimensional finite-difference time domain (FDTD) simulation showed significant differences in the local electromagnetic field distributions surrounding the nanospheres, nanorods, and nanostars, which were induced by the localized surface plasmon resonance (LSPR). The electromagnetic field was enhanced remarkably around the two ends of the nanorods and around the sharp tips of the nanostars. This local electromagnetic enhancement made the dominant contribution to the SERS enhancement. Both the experiments and the simulation revealed the order nanostars > nanorods > nanospheres in terms of the enhancement factor. Finally, the biological application of the nanostar–MGITC–SiO<sub>2</sub> nanoparticles has been demonstrated in the monitoring of DNA hybridization. In short, the gold–MGITC–SiO<sub>2</sub> sandwiched nanoparticles can be used as a Raman probe that features high sensitivity, good water solubility and stability, low-background fluorescence, and the absence of photobleaching for future biological applications.

TEM images of pure SnO<sub>2</sub> nanorods.

## Needle-like Zn-doped SnO<sub>2</sub> nanorods with enhanced photocatalytic and gas sensing properties

Hongtao Huang, Shouqin Tian, Jing Xu, Zhong Xie, Dawen Zeng, Di Chen and Guozhen Shen

2012 *Nanotechnology* **23** 105502

Zn-doped SnO<sub>2</sub> nanorods have been prepared by a simple hydrothermal method on a large scale. The as-prepared samples were characterized by x-ray powder diffraction, scanning electron microscope, transmission electron microscope, energy dispersive spectrometer, x-ray photoelectron spectroscopy, UV–vis absorption spectra and photoluminescence spectra. Studies found that the products are needle-like single-crystalline nanorods grown along the [1 $\bar{1}$ 2] orientation. The photocatalytic properties of the synthesized Zn-doped SnO<sub>2</sub> were investigated by decomposing acid fuchsine, showing much higher photocatalytic activity than pure SnO<sub>2</sub> nanorods and bulk SnO<sub>2</sub> powders. An enhanced gas sensing ability toward methanal, ethanol and acetone gases is also achieved in high sensitivity and fast response. The origins of the enhanced performances are discussed.

# Materials: synthesis or self-assembly

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Control and innovation in nanoscale synthesis have redefined nanomaterials research. There have been some fortunate accidents that have led to revolutionary new materials, such as bucky balls and carbon nanotubes, but these tend to be the exception rather than the rule. Increasingly, rational, often *ab initio*, mechanistic design is taking prominence in approaches at the forefront of nanoscale synthesis research.

As an example, over the past few decades, zinc oxide nanowires have been intensely researched. However, general synthesis procedures have limited control in terms of length, vertical alignment, and the presence of residual catalyst seeds at the tip, which causes problems for integration. Zhong Lin Wang and colleagues in the US, China and Japan modified a generic technique to overcome all of these challenges. In addition, they developed a model to explain how the ultralong nanowires grow with the presence of residual catalyst seed at the substrate end.

Concomitantly, there has also been an enormous amount of creativity in producing functional structures. Weizhen He and colleagues in Korea, Japan, China and the US have reported on the synthesis of novel dye-sensitized solar cell (DSSC) structures that use a Ti mesh for both photoanodes and counter electrodes. The approach improves the flexibility and conductivity of the electrodes,

and may lead to greater versatility in DSSC design, since as the authors point out, the voids in the mesh substrate also allow light to enter the cell from the photoanode side, leading to possible frontal illumination.

Sustainability considerations are attaining mounting importance. For instance, methods that use biotemplates often have milder processing requirements and are hence attracting significant research interest. Researchers in Germany have demonstrated how 3 nm wide cobalt-iron alloy nanowires can be synthesized by simple wet chemical electroless deposition inside tubular tobacco mosaic virus particles. These as-prepared nanowires may find uses in high-density data storage, imaging, sensing and drug delivery. Sustainability and green nanotechnology was also the focus of a special issue in July 2012.

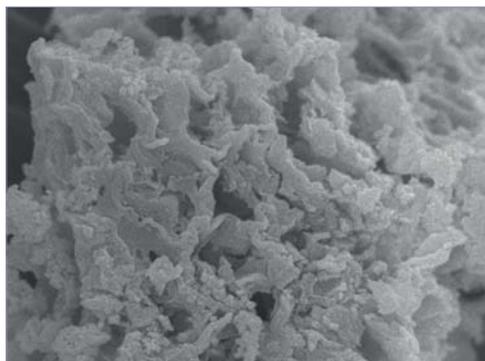
Synthesis has been empowered beyond the 'hit and miss' of previous approaches. This need not necessarily mean abandoning the wide-eyed curiosity to see 'what happens if...'. On the contrary, a deepening understanding almost always reveals more avenues to explore, more synthesis approaches for more applications to create, develop and investigate, and, perhaps, fewer dead ends to encounter. The research in this collection gives just a glimpse of the current fertile landscape in creating new nanomaterials using diverse and complementary strategies.



**Section Editor:**  
Stanislaus Wong

## Section scope

The success of nanotechnology in real-world applications hinges on the development of methods that allow for cheaper, faster, greener and more reliable modes of fabrication of high-quality nanostructures for implementation into devices. The synthesis of nanoscale materials is now performed via a huge variety of methods, including but not limited to, physico-chemical, optical and mechanical variations. This section continues to publish papers that demonstrate progress towards the development of previously unattainable and novel fabrication standards for existing nanostructures, as well as the fabrication of new structures wherein a clear, important and practical application can be convincingly demonstrated.



Representative low-magnification FESEM image of titania nanomaterials prepared by using yeast as template.

## Environment-friendly biomimetic synthesis of TiO<sub>2</sub> nanomaterials for photocatalytic application

Shu-Juan Bao, Chao Lei, Mao-Wen Xu, Chang-Jun Cai and Dian-Zeng Jia

2012 *Nanotechnology* **23** 205601

We have demonstrated an environment-friendly biomimetic synthesis method for the preparation of TiO<sub>2</sub> nanomaterials with different crystal phases and morphologies. This is the first time that it has been found that the crystal phase of TiO<sub>2</sub> can be controlled just by using different biotemplates, and cannot be changed by calcination up to 750 °C. In our experiment, anatase TiO<sub>2</sub> was obtained by using yeast and albumen templates, while rutile TiO<sub>2</sub> was formed by using dandelion pollen as the template.

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Low-magnification cross section SEM image of TNTs on the Ti-mesh substrate.

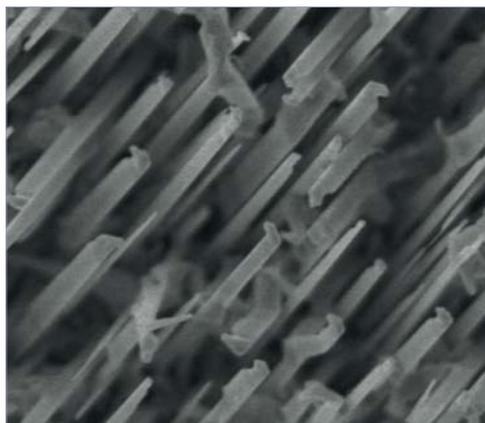
## Advantages of using Ti-mesh type electrodes for flexible dye-sensitized solar cells

Weizhen He, Jijun Qiu, Fuwei Zhuge, Xiaomin Li, Jae-Ho Lee, Yang-Do Kim, Hyung-Kook Kim and Yoon-Hwae Hwang

2012 *Nanotechnology* **23** 225602

We used Ti meshes for both the photoanodes and counter electrodes of dye-sensitized solar cells (DSSCs) to improve the flexibility and conductivity of the electrodes. These mesh type electrodes showed good transparency and high bendability when subjected to an external force. We demonstrated the advantages of cells using such electrodes compared to traditional transparent conducting oxide based electrodes and back side illuminated DSSCs, such as low sheet resistance, elevated photo-induced current and enhanced sunlight utilization. Nanotube layers of different thicknesses were investigated to determine their effect on the photovoltaic parameters of the cell. The overall efficiency of the best cells was approximately 5.3% under standard air mass 1.5 global (AM 1.5 G) solar conditions. Furthermore, the DSSCs showed an efficiency of approximately 3.15% due to the all Ti-mesh type electrodes even after illumination from the back side.

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SEM micrographs of GaN nanowires grown on *r*-sapphire substrate, using 5 nm Gold seed film.

## Using seed particle composition to control structural and optical properties of GaN nanowires

Xiang Zhou, Jordan Chesin, Samuel Crawford and Silvija Gradečak

2012 *Nanotechnology* **23** 285603

The morphology, structure, and optical properties of gallium nitride (GaN) nanowires grown using metal-organic chemical vapor deposition (MOCVD) on *r*-plane sapphire using gold and nickel seed particles were investigated. We found that different seed particles result in different growth rates and densities of structural defects in MOCVD-grown GaN nanowires. Ni-seeded GaN nanowires grow faster than Au-seeded ones, and they do not contain the basal plane stacking faults that are observed in Au-seeded GaN nanowires. We propose that stacking fault formation is related to the supersaturation and surface energies in different types of seed particles. Room temperature photoluminescence studies revealed a blue-shifted peak in Au-seeded GaN nanowires compared to the GaN near-bandgap emission. The blue-shifted peak evolves as a function of the growth time and originates from the nanowire base, likely due to strain and Al diffusion from the substrate. Our results demonstrate that seed particle composition has a direct impact on the growth, structure, and optical properties of GaN nanowires and reveal some general requirements for seed particle selection for the growth of compound semiconductor nanowires.

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Pristine TMV particles imaged by TEM. No staining procedure was applied. The virions are randomly distributed on the TEM grid, but show linear and lateral aggregation.

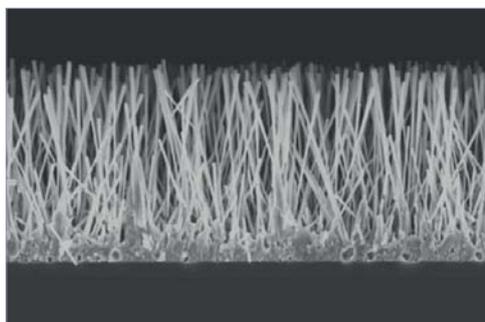
## Electroless synthesis of 3 nm wide alloy nanowires inside *Tobacco mosaic virus*

Sinan Balci, Kersten Hahn, Peter Kopold, Anan Kadri, Christina Wege, Klaus Kern and Alexander M Bittner

2012 *Nanotechnology* **23** 045603

We show that 3 nm wide cobalt–iron alloy nanowires can be synthesized by simple wet chemical electroless deposition inside tubular *Tobacco mosaic virus* particles. The method is based on adsorption of Pd(II) ions, formation of a Pd catalyst, and autocatalytic deposition of the alloy from dissolved metal salts, reduced by a borane compound. Extensive energy-filtering TEM investigations at the nanoscale revealed that the synthesized wires are alloys of Co, Fe, and Ni. We confirmed by high-resolution TEM that our alloy nanowires are at least partially crystalline, which is compatible with typical Co-rich alloys. Ni traces bestow higher stability, presumably against corrosion, as also known from bulk CoFe. Alloy nanowires, as small as the ones presented here, might be used for a variety of applications including high density data storage, imaging, sensing, and even drug delivery.

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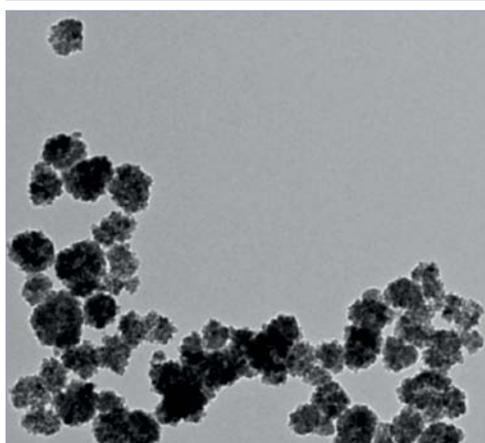
Cross-sectional view of synthesized ZnO nanowires using conventional source materials and without pretreatments.

## Synthesis of vertically aligned ultra-long ZnO nanowires on heterogeneous substrates with catalyst at the root

Guang Zhu, Yusheng Zhou, Sihong Wang, Rusen Yang, Yong Ding, Xue Wang, Yoshio Bando and Zhong lin Wang

2012 *Nanotechnology* **23** 055604

The synthesis of ultra-long high-quality ZnO nanowires with uniform size and orientation on heterogeneous substrates is highly desirable, not only for investigating the fundamental properties of ZnO nanowires, but also for fabricating integrated functional nanodevices. Here we present a novel and general technique for growing vertically aligned ultra-long ZnO nanowires on various substrates. More importantly, the metal catalyst is experimentally determined not at the tip ends of the nanowires but at the junction area between the nanowires and the underlying substrate. Based on detailed analysis and control group results, we then propose a three-stage growth mechanism, in which vapor–liquid–solid growth and vapor–solid growth compete with each other to become dominant.



HAADF-STEM image of Fe<sub>3</sub>O<sub>4</sub>@C core–shell nanoparticles (FCNPs).

## One-step solvothermal synthesis of Fe<sub>3</sub>O<sub>4</sub>@C core–shell nanoparticles with tunable sizes

J Zheng, Z Q Liu, X S Zhao, M Liu, X Liu and W Chu

2012 *Nanotechnology* **23** 165601

We report the synthesis of Fe<sub>3</sub>O<sub>4</sub>@C core–shell nanoparticles (FCNPs) by using a facile one-step solvothermal method. The FCNPs consisted of Fe<sub>3</sub>O<sub>4</sub> particles as the cores and amorphous uniform carbon shells. The content of Fe<sub>3</sub>O<sub>4</sub> is up to 81.6 wt%. These core–shell nanoparticles are aggregated by primary nanocrystals with a size of 10–12 nm. The FCNPs possess a hollow interior, high magnetization, excellent absorption properties and abundant surface hydroxyl groups. A possible growth mechanism of the FCNPs is proposed. The role of glucose in regulating the grain size and morphology of the particles is discussed. The absorption properties of the FCNPs towards Cr(VI) in aqueous solution is investigated. We demonstrate that the FCNPs can effectively remove more than 90 wt% of Cr(VI) from aqueous solution.

# Materials: properties, characterization or tools

The extraordinary properties of nanomaterials have found so many applications in real world technology that it would be hard to imagine life without them. As developments in nanotechnology fast-track device innovations from the realms of fantasy to the shop shelf, extraordinary discoveries in fundamental physics are also being unearthed in the properties of nanomaterials.

Nanostructures modify material properties – in fact the principle has been exploited for years. One example is in the efforts to improve the ductility of SiC, otherwise so promising for electronics applications. While the use of nanostructures in SiC nanowires has been very successful, the resulting superplasticity is not truly understood. Researchers in Australia, China, Hong Kong and the US have now shed light on the influence of microstructures on the brittleness and plasticity of SiC nanowires using molecular dynamics.

Field emission is another huge area of research activity in nanotechnology. So it may be a surprise to some to find that the famous Fowler-Nordheim theory for field emission is so often wrongly implemented with the use of a defective equation for the macroscopic current density. Yet as Richard G Forbes at the University of

Surrey explains, “It over-predicts the ‘macroscopic’ (i.e. large area field emission-average) emission current density, by a factor thought to typically lie between  $10^3$  and  $10^9$ .” In his theoretical paper highlighted here, he describes the origins of these errors and clarifies some points to aid correct mathematical representation of field-emission systems.

The tools to explore the properties of nanomaterials are also under constant renovation. Researchers in the US introduce a conducting metal shield onto a Kelvin probe microscope, which effectively shields the long-range electrostatic contributions from the macroscopic cantilever and all but the very end of the tip. They demonstrate a factor of five improvement in the spatial resolution with the modification.

The properties of nanomaterials are constantly rewriting the text books on what behaviour we can expect from a given system. They also provide the tools for probing nanoscale systems with unprecedented accuracy, sensitivity and resolution. *Nanotechnology* is now well into its second decade, but as this collection of highlights emphasizes, research into nanomaterial properties is still teeming with surprises, laying endless scope for new developments in the field.

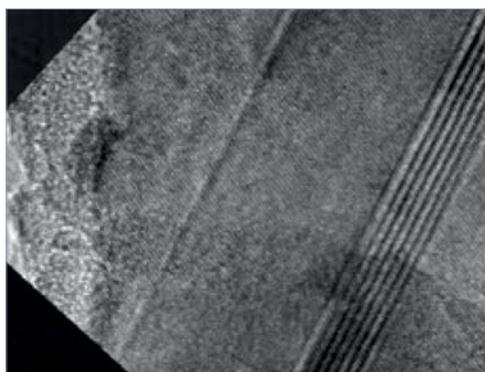


**Section Editor:**  
**Mervyn Miles**

## Section scope

Much of the progress in current technology is based on the unique and extraordinary properties of nanoscale structures and systems. This section is devoted to research that provides a deeper understanding of the way nanostructured materials interact and the factors that govern their behaviour. The section includes experimental research on the optical, magnetic, electrical, mechanical and quantum properties of nanostructures and systems, and looks at ways of manipulating the response to changes in the surrounding environment and external triggers for device applications. The section also covers theoretical studies that reveal potential new properties that have not yet been experimentally observed, as well as helping to explain the physics behind the reported properties of nanomaterials.

We also encourage submissions on new ways of characterizing the nanoscale structures and properties, including novel ways to image materials.



HRTEM detail of an NW that contains six  $3d_{111}$  periods made on the [011]ZA.

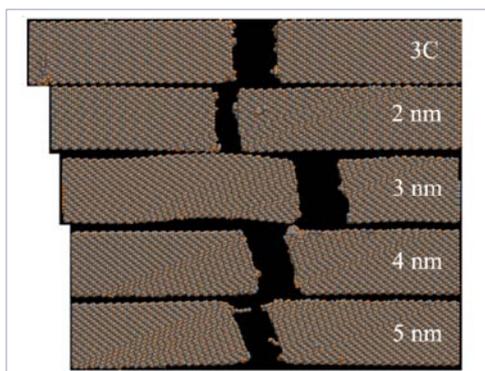
## Hidden defects in silicon nanowires

M I den Hertog, C Cayron, P Gentile, F Dhalluin, F Oehler, T Baron and J L Rouviere

2012 *Nanotechnology* **23** 025701

Recent publications have reported the presence of hexagonal phases in Si nanowires. Most of these reports were based on 'odd' diffraction patterns and HRTEM images—'odd' means that these images and diffraction patterns could not be obtained on perfect silicon crystals in the classical diamond cubic structure. We analyze the origin of these 'odd' patterns and images by studying the case of various Si nanowires grown using either Ni or Au as catalysts in combination with P or Al doping. Two models could explain the experimental results: (i) the presence of a hexagonal phase or (ii) the presence of defects that we call 'hidden' defects because they cannot be directly observed in most images. We show that in many cases one direction of observation is not sufficient to distinguish between the two models. Several directions of observations have to be used. Secondly, conventional TEM images, i.e. bright-field two-beam and dark-field images, are of great value in the identification of 'hidden' defects. In addition, slices of nanowires perpendicular to the growth axis can be very useful. In the studied nanowires no hexagonal phase with long range order is found and the 'odd' images and diffraction patterns are mostly due to planar defects causing superposition of different crystal grains. Finally, we show that in Raman experiments the defect-rich NWs can give rise to a Raman peak shifted to  $504\text{--}511\text{ cm}^{-1}$  with respect to the Si bulk peak at  $520\text{ cm}^{-1}$ , indicating that Raman cannot be used to identify a hexagonal phase.

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SiC nanowires with stacking defects at  $19.47^\circ$ . The image shows the patterns of the nanowires following fracture.

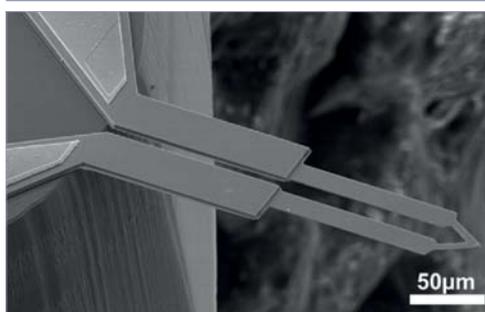
## Influence of microstructures on mechanical behaviours of SiC nanowires: a molecular dynamics study

Jun Wang, Chunsheng Lu, Qi Wang, Pan Xiao, Fujin Ke, Yilong Bai, Yaogen Shen, Xiaozhou Liao and Huajian Gao

2012 *Nanotechnology* **23** 025703

The tensile behaviours of [111]-oriented SiC nanowires with various microstructures are investigated by using molecular dynamics simulations. The results revealed the influence of microstructures on the brittleness and plasticity of SiC nanowires. Plastic deformation is mainly induced by the anti-parallel sliding of 3C grains along an intergranular amorphous film parallel to the  $(11\bar{1})$  plane and inclined at an angle of  $19.47^\circ$  with respect to the nanowire axis. Our study suggests that the wide dispersion of mechanical properties of SiC nanowires observed in experiments might be attributed to their diverse microstructures.

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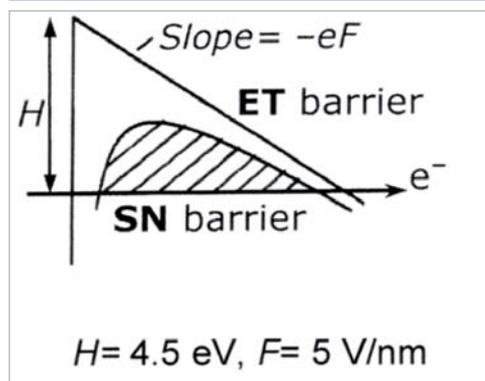
Scanning electron microscope (SEM) micrograph of the cantilever used in the experiment.

## Lorentz force actuation of a heated atomic force microscope cantilever

Byeonghee Lee, Craig B Prater and William P King

2012 *Nanotechnology* **23** 055709

We report Lorentz force-induced actuation of a silicon microcantilever having an integrated resistive heater. Oscillating current through the cantilever interacts with the magnetic field around a NdFeB permanent magnet and induces a Lorentz force that deflects the cantilever. The same current induces cantilever heating. With AC currents as low as 0.2 mA, the cantilever can be oscillated as much as 80 nm at resonance with a DC temperature rise of less than  $5^\circ\text{C}$ . By comparison, the AC temperature variation leads to a thermomechanical oscillation that is about 1000 times smaller than the Lorentz deflection at the cantilever resonance. The cantilever position in the nonuniform magnetic field affects the Lorentz force-induced deflection, with the magnetic field parallel to the cantilever having the largest effect on cantilever actuation. We demonstrate how the cantilever actuation can be used for imaging, and for measuring the local material softening temperature by sensing the contact resonance shift.



The exact triangular (ET) and Schottky–Nordheim (SN) barriers as calculated exactly, for  $H = 4.5 \text{ eV}$ ,  $F = 5 \text{ V nm}^{-1}$ .

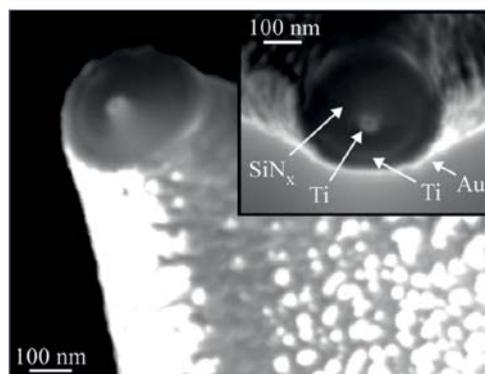
## Extraction of emission parameters for large-area field emitters, using a technically complete Fowler–Nordheim-type equation

Richard G Forbes

2012 *Nanotechnology* **23** 095706

In papers on cold field electron emission from large-area field emitters (LAFEs), it has become widespread practice to publish a misleading Fowler–Nordheim-type (FN-type) equation. This equation over-predicts the LAFE-average current density by a large highly variable factor thought to usually lie between  $10^3$  and  $10^9$ . This equation, although often referenced to FN's 1928 paper, is a simplified equation used in undergraduate teaching, does not apply unmodified to LAFEs and does not appear in the 1928 paper. Technological LAFE papers often do not cite any theoretical work more recent than 1928, and often do not comment on the discrepancy between theory and experiment. This usage has occurred widely, in several high-profile American and UK applied-science journals (including *Nanotechnology*), and in various other places. It does not inhibit practical LAFE development, but can give a misleading impression of potential LAFE performance to non-experts. This paper shows how the misleading equation can be replaced by a conceptually complete FN-type equation that uses three high-level correction factors. One of these, or a combination of two of them, may be useful as an additional measure of LAFE quality; this paper describes a method for estimating factor values using experimental data and discusses when it can be used. Suggestions are made for improved engineering practice in reporting LAFE results. Some of these should help to prevent situations arising whereby an equation appearing in high-profile applied-science journals is used to support statements that an engineering regulatory body might deem to involve professional negligence.

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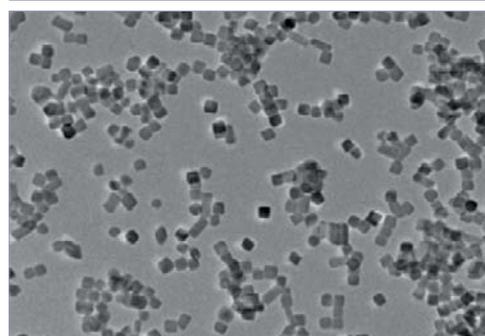
Scanning electron micrograph of a coaxial probe. (Inset) The thin films that form the shell (Ti/Au), the insulating layer ( $\text{SiN}_x$ ), and the core electrode (Ti) are visible at the tip.

## High spatial resolution Kelvin probe force microscopy with coaxial probes

Keith A Brown, Kevin J Satzinger and Robert M Westervelt

2012 *Nanotechnology* **23** 115703

Kelvin probe force microscopy (KPFM) is a widely used technique to measure the local contact potential difference (CPD) between an AFM probe and the sample surface via the electrostatic force. The spatial resolution of KPFM is intrinsically limited by the long range of the electrostatic interaction, which includes contributions from the macroscopic cantilever and the conical tip. Here, we present coaxial AFM probes in which the cantilever and cone are shielded by a conducting shell, confining the tip–sample electrostatic interaction to a small region near the end of the tip. We have developed a technique to measure the true CPD despite the presence of the shell electrode. We find that the behavior of these probes agrees with an electrostatic model of the force, and we observe a factor of five improvement in spatial resolution relative to unshielded probes. Our discussion centers on KPFM, but the field confinement offered by these probes may improve any variant of electrostatic force microscopy.



TEM image of the pristine Pt/ $\text{Ta}_2\text{O}_{5-x}$ / $\text{TaO}_{2-x}$ /Pt sample.

## Modeling for multilevel switching in oxide-based bipolar resistive memory

Ji-Hyun Hur, Kyung Min Kim, Man Chang, Seung Ryul Lee, Dongsoo Lee, Chang Bum Lee, Myoung-Jae Lee, Young-Bae Kim, Chang-Jung Kim and U-In Chung

2012 *Nanotechnology* **23** 225702

We report a physical model for multilevel switching in oxide-based bipolar resistive memory (ReRAM). To confirm the validity of the model, we conduct experiments with tantalum-oxide-based ReRAM of which multi-resistance levels are obtained by reset voltage modifications. It is also noticeable that, in addition to multilevel switching capability, the ReRAM exhibits extremely different switching timescales, i.e. of the order of  $10^{-7}$  s to  $10^0$  s, with regard to reset voltages of only a few volts difference which can be well explained by our model. It is demonstrated that with this simple model, multilevel switching behavior in oxide bipolar ReRAM can be described not only qualitatively but also quantitatively.

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# Topical Reviews

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## High-speed atomic force microscopy coming of age

**Toshio Ando**

2012 *Nanotechnology* **23** 062001

High-speed atomic force microscopy (HS-AFM) is now materialized. It allows direct visualization of dynamic structural changes and dynamic processes of functioning biological molecules in physiological solutions, at high spatiotemporal resolution. Dynamic molecular events unselectively appear in detail in an AFM movie, facilitating our understanding of how biological molecules operate to function. This review describes a historical overview of technical development towards HS-AFM, summarizes elementary devices and techniques used in the current HS-AFM, and then highlights recent imaging studies. Finally, future challenges of HS-AFM studies are briefly discussed.

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## The application of graphene as electrodes in electrical and optical devices

**Gunho Jo, Minhyeok Choe, Sangchul Lee, Woojin Park, Yung Ho Kahng and Takhee Lee**

2012 *Nanotechnology* **23** 112001

Graphene is a promising next-generation conducting material with the potential to replace traditional electrode materials such as indium tin oxide in electrical and optical devices. It combines several advantageous characteristics including low sheet resistance, high optical transparency and excellent mechanical properties. Recent research has coincided with increased interest in the application of graphene as an electrode material in transistors, light-emitting diodes, solar cells and flexible devices. However, for more practical applications, the performance of devices should be further improved by the engineering of graphene films, such as through their synthesis, transfer and doping. This article reviews several applications of graphene films as electrodes in electrical and optical devices and discusses the essential requirements for applications of graphene films as electrodes.

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## Carbon nanotube synthesis: from large-scale production to atom-by-atom growth

**Catherine Journet, Matthieu Picher and Vincent Jourdain**

2012 *Nanotechnology* **23** 142001

The extraordinary electronic, thermal and mechanical properties of carbon nanotubes (CNTs) closely relate to their structure. They can be seen as rolled-up graphene sheets with their electronic properties depending on how this rolling up is achieved. However, this is not the way they actually grow. Various methods are used to produce carbon nanotubes. They all have in common three ingredients: (i) a carbon source, (ii) catalyst nanoparticles and (iii) an energy input. In the case where the carbon source is provided in solid form, one speaks about 'high temperature methods' because they involve the sublimation of graphite which does not occur below 3200 °C. The first CNTs were synthesized by these techniques. For liquid or gaseous phases, the generic term of 'medium or low temperature methods' is used. CNTs are now commonly produced by these latter techniques at temperatures ranging between 350 and 1000 °C, using metal nanoparticles that catalyze the decomposition of the gaseous carbon precursor and make the growth of nanotubes possible. The aim of this review article is to give a general overview of all these methods and an understanding of the CNT growth process.

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## Nanowires for energy generation

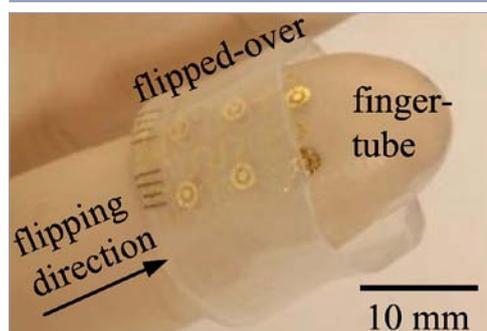
**Pritesh Hiralal, Husnu Emrah Unalan and Gehan A J Amaratunga**

2012 *Nanotechnology* **23** 194002

As a result of their morphology, nanowires bring new properties and the promise of performance for a range of electronic devices. This review looks into the properties of nanowires and the multiple ways in which they have been exploited for energy generation, from photovoltaics to piezoelectric generators.

# Media coverage

With the number of academic articles published worldwide increasing dramatically each year, it is becoming more difficult for important research to be identified by academics, students and the general public. The *Nanotechnology* editors actively work to identify important research and promote it to the interested community. As a result of these efforts, articles from *Nanotechnology* have been featured by international news organizations (BBC, FOX, ABC), popular scientific magazines (*New Scientist*, *Nature News*, *Cosmos*), scientific blogs and even in a *YouTube* video, which received more than 1 million hits. Below are two examples of *Nanotechnology* articles that you may have seen in the news in 2012.



Turning the elastomeric finger-tube inside out relocates the array on the inner surface of the finger-tube, shown here at the midway point of this flipping process.

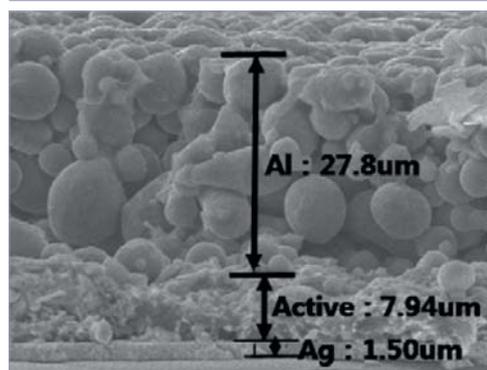
## Silicon nanomembranes for fingertip electronics

Ming Ying, Andrew P Bonifas, Nanshu Lu, Yewang Su, Rui Li, Huan Yu Cheng, Abid Ameen, Yonggang Huang and John A Rogers

2012 *Nanotechnology* **23** 344004

We describe the use of semiconductor nanomaterials, advanced fabrication methods and unusual device designs for a class of electronics capable of integration onto the inner and outer surfaces of thin, elastomeric sheets in closed-tube geometries, specially formed for mounting on the fingertips. Multifunctional systems of this type allow electrotactile stimulation with electrode arrays multiplexed using silicon nanomembrane (Si NM) diodes, high-sensitivity strain monitoring with Si NM gauges, and tactile sensing with elastomeric capacitors. Analytical calculations and finite element modeling of the mechanics quantitatively capture the key behaviors during fabrication/assembly, mounting and use. The results provide design guidelines that highlight the importance of the NM geometry in achieving the required mechanical properties. This type of technology could be used in applications ranging from human-machine interfaces to 'instrumented' surgical gloves and many others.

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Cross-sectional SEM images for the R2R gravure printed diode.

## Fully roll-to-roll gravure printed rectenna on plastic foils for wireless power transmission at 13.56 MHz

Hyejin Park, Hwiwon Kang, Yonggil Lee, Yongsu Park, Jinsoo Noh and Gyoujin Cho

2012 *Nanotechnology* **23** 344006

Wireless power transmission to inexpensive and disposable smart electronic devices is one of the key issues for the realization of a ubiquitous society where sensor networks such as RFID tags, price tags, smart logos, signage and sensors could be fully interconnected and utilized by DC power of less than 0.3 W. This DC power can be provided by inductively coupled AC from a 13.56 MHz power transmitter through a rectenna, consisting of an antenna, a diode and a capacitor, which would be cheap to integrate with inexpensive smart electronic devices. To integrate the rectenna with a minimum cost, a roll-to-roll (R2R) gravure printing process has been considered to print the rectenna on plastic foils. In this paper, R2R gravure printing systems including printing condition and four different nanoparticle based inks will be reported to print the rectenna (antenna, diode and capacitor) on plastic foils at a printing speed of 8 m min<sup>-1</sup> and more than 90% device yield for a wireless power transmission of 0.3 W using a standard 13.56 MHz power transmitter.

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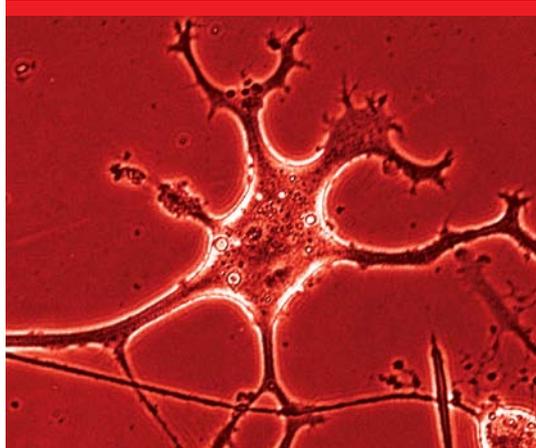
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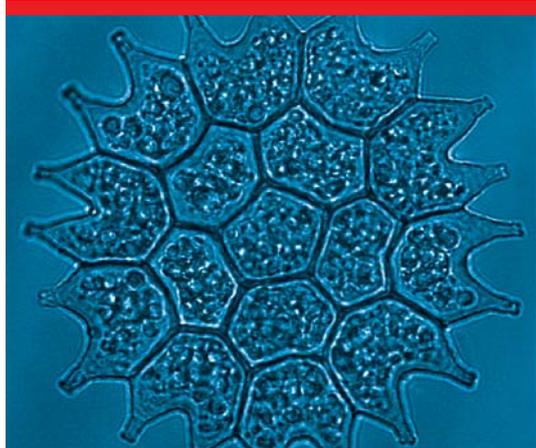
Journal section magazines highlighting the best content in three of *Nanotechnology*'s subjects



### NANOTECHNOLOGY

#### Biology and medicine

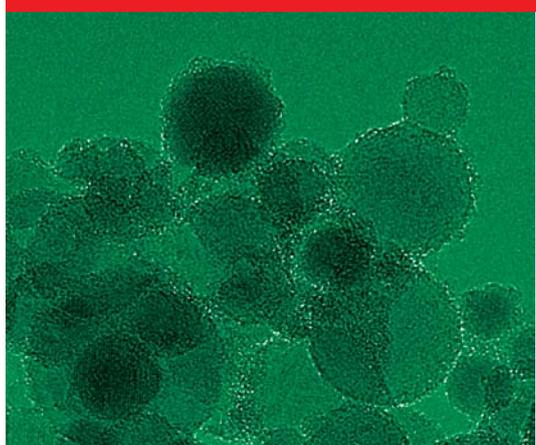
**Image left:** Nerve cell morphology after co-culture for 22 days. **Wei-Chin Huang, Jiunn-Der Liao, Chou-Ching K Lin and Ming-Shaung Ju** 2011 *Nanotechnology* **22** 275101.



### NANOTECHNOLOGY

#### Sensing and actuating

**Image left:** A bright field image of a *Pseudopediastrum* colony using an optical microscope. **D B Phillips, J A Grieve, S N Olof, S J Kocher, R Bowman, M J Padgett, M J Miles and D M Carberry** 2011 *Nanotechnology* **22** 285503.



### NANOTECHNOLOGY

#### Energy at the nanoscale

**Image left:** Freestanding Si nanospheres prepared from the gas phase and subsequently stain etched. **Bernhard Goller, Dmitry Kovalev and Olga Sreseli** 2011 *Nanotechnology* **22** 305402.

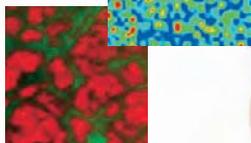
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