

# ADVANCED FUNCTIONAL MATERIALS

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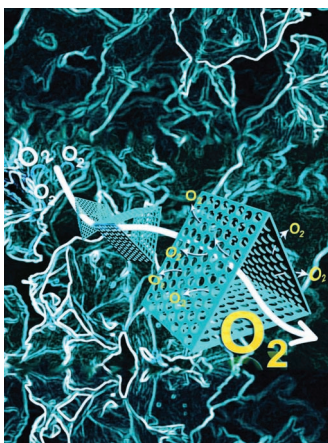
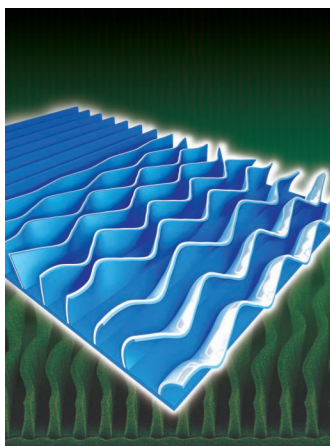


## Nanotechnology Meets Plant Sciences

The cell wall of plant cells is a physical barrier for nanoparticle uptake that limits nanotechnology development in plant sciences. On page 3576, Brian G. Trewyn, Kan Wang, and co-workers report using gold-plated mesoporous silica nanoparticles, which have increased performance as projectiles through the biolistic method, to co-deliver proteins and plasmid DNA into walled plant cells.

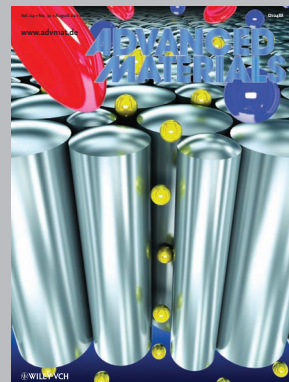
## Nanowalls

On page 3723, Won Bo Lee, Kookheon Char, and co-workers report the fabrication of Janus nanowalls and the phenomenon of lateral buckling in the walls. To realize Janus nanowalls, metal films are deposited on one side of the polymeric nanowalls. During the metal deposition, the nanowalls themselves buckle laterally because of the compressive residual stress in the metal films and geometric constraints.



## Lithium Ion Batteries

On page 3699 Xin-Bo Zhang and co-workers report the synthesis of free-standing hierarchically porous carbon (FHPC) derived from a graphene oxide gel in nickel foam by a facile in situ sol-gel method. As a cathode for  $\text{Li-O}_2$  batteries, the FHPC electrode exhibits a large capacity and high rate capability. This study opens up a promising strategy for the development of high-efficient oxygen electrodes for  $\text{Li-O}_2$  batteries.



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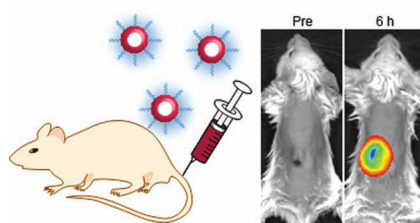
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# FULL PAPERS

## Biomedical Applications

K. Hayashi,\* M. Nakamura, H. Miki,  
S. Ozaki, M. Abe, T. Matsumoto,  
K. Ishimura .....3539–3546

### Near-Infrared Fluorescent Silica/ Porphyrin Hybrid Nanorings for In Vivo Cancer Imaging

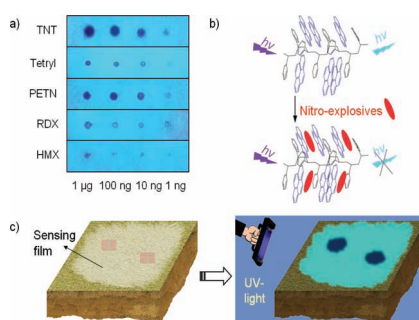


Near-infrared fluorescent silica/porphyrin hybrid nanorings (HNRs) are synthesized using a one-pot sol-gel reaction with a porphyrin-binding silica precursor. They are functionalized with amino groups and are easily modified with polyethylene glycol (PEG). The PEGylated HNRs (PEG-HNRs) accumulate in tumors through multiple factors such as their size, uncharged surface, unique shape, and long circulation time in blood, resulting in the acquisition of clear images of tumor.

## Sensors

Y. Wang, A. La, Y. Ding, Y. Liu,  
Y. Lei\* .....3547–3555

### Novel Signal-Amplifying Fluorescent Nanofibers for Naked-Eye-Based Ultrasensitive Detection of Buried Explosives and Explosive Vapors

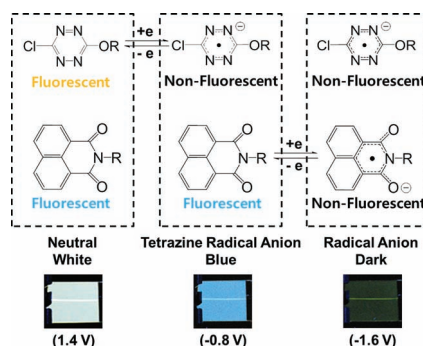


Novel electrospun fluorescent nanofibers are developed for the detection of part per trillion to part per billion level nitro explosive vapors and buried explosives using the naked eyes with UV excitation. The outstanding sensing performance can be attributed to the proposed “sandwich-like” conformation between pyrene and phenyl pendants of polystyrene, which may allow efficient long-range energy migration similar to a molecular wire thus achieving amplified fluorescence quenching.

## Organic Electronics

S. Seo, Y. Kim, Q. Zhou, G. Clavier,  
P. Audebert,\* E. Kim\* .....3556–3561

### White Electrofluorescence Switching from Electrochemically Convertible Yellow Fluorescent Dyad

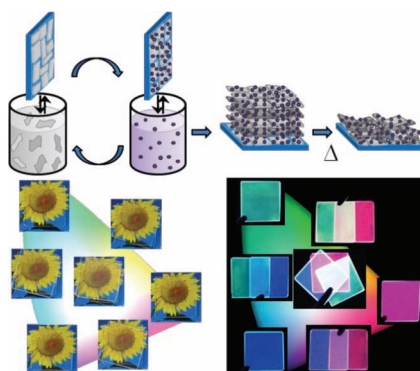


Multi-color fluorescence switching is achieved by blending a naphthalimide to the electrofluorochromic layer, to show white–blue–dark state of fluorescence. The reversible electrochemistry of the tetrazine and naphthalimide is accompanied by the fluorescence change in an electrochemical cell. The emission color can be tuned by quenching emission at selected wavelengths, reversibly, under low working potentials.

## Thin Films

B.-I. Lee, E.-s. Lee,  
S.-H. Byeon\* .....3562–3569

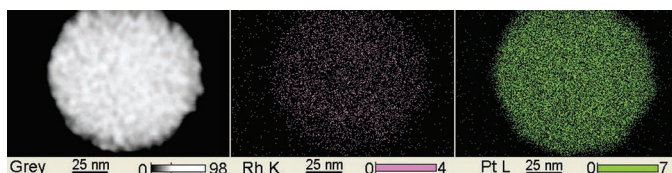
### Assembly of Layered Rare-Earth Hydroxide Nanosheets and SiO<sub>2</sub> Nanoparticles to Fabricate Multifunctional Transparent Films Capable of Combinatorial Color Generation



Antireflection and antifogging properties are integrated into transparent luminescent films by the layer-by-layer assembly of Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup> doped-hydroxocation nanosheets and negatively charged SiO<sub>2</sub> nanoparticles. Resulting multifunctional films exhibit efficient red, green, and blue emissions with controllable intensity. Multiple overlap of individual films generates combinatorial color and bright white-light under 254 nm UV irradiation.

## FULL PAPERS

**PtRh alloy 3D nanostructures are synthesized by controlling aggregation of nanoparticles** in oleylamine. The 3D alloy catalyst, composed of interconnected metallic particles, provides a large surface area and effective transport of reactive species. The properly prepared 3D porous nanostructures exhibit high electrochemical activity and good durability toward the methanol oxidation.

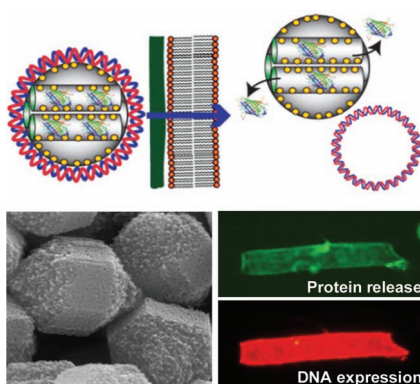


## Fuel Cells

Y. Zhang,\* M. Janyasupab, C.-W. Liu,  
X. Li, J. Xu,\* C.-C. Liu .....3570–3575

**Three Dimensional PtRh Alloy Porous Nanostructures: Tuning the Atomic Composition and Controlling the Morphology for the Application of Direct Methanol Fuel Cells**

**Gold functionalized mesoporous silica nanoparticles** are loaded with fluorescent proteins (eGFP) and coated with plasmid DNA expressing the red fluorescent protein mCherry. These nanoparticles are introduced to living plant cells using the biolistic method. This methodology delivers both protein and plasmid DNA, resulting in plant cells that exhibit both fluorescences.

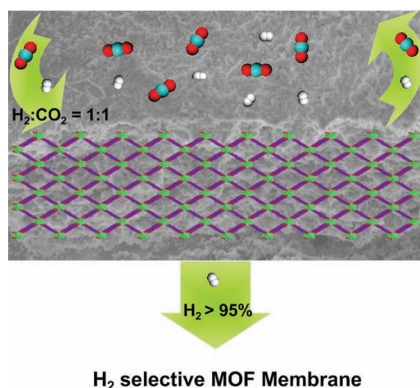


## Silica Nanoparticles

S. Martin-Ortigosa, J. S. Valenstein,  
V. S.-Y. Lin, B. G. Trewyn,\*  
K. Wang\* .....3576–3582

**Gold Functionalized Mesoporous Silica Nanoparticle Mediated Protein and DNA Codelivery to Plant Cells Via the Biolistic Method**

**Continuous  $\text{NH}_2\text{-MIL-53(Al)}$  metal-organic framework (MOF) membranes are prepared successfully on macroporous glass frit discs** assisted with colloidal seeds to be evaluated for hydrogen gas separation. As-prepared membrane is studied by single and binary gas permeation of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{CO}_2$  at different temperatures. The supported  $\text{NH}_2\text{-MIL-53(Al)}$  membranes exhibit high permeance and high selectivity, which result in a very high separation power. The robust membranes with high performance are expected in potential applications for hydrogen recycling.

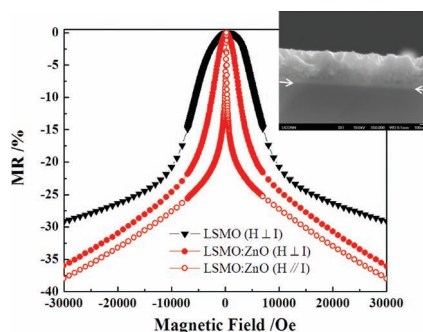


## Hydrogen-Selective Membranes

F. Zhang, X. Zou, X. Gao, S. Fan,  
F. Sun, H. Ren, G. Zhu\* .....3583–3590

**Hydrogen Selective  $\text{NH}_2\text{-MIL-53(Al)}$  MOF Membranes with High Permeability**

**A  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3\text{:ZnO}$  composite film** is fabricated by spin-depositing a  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  phase in between ZnO nanorods hydrothermally grown on a (0001)- $\text{Al}_2\text{O}_3$  substrate. This unique nanocomposite fabrication method results in an enhanced low-field magnetoresistance effect that is believed to be due to spin polarized tunneling through modified  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  grain boundaries in the composite film.



## Composites

M. Staruch, H. Gao, P.-X. Gao,  
M. Jain\* .....3591–3595

**Low-Field Magnetoresistance in  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3\text{:ZnO}$  Composite Film**

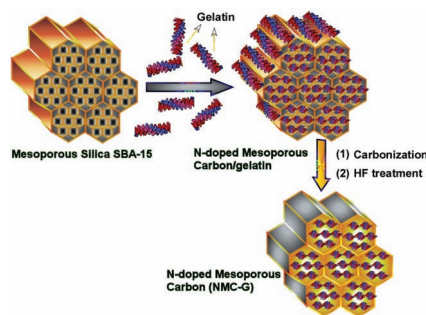


## FULL PAPERS

## Ceramics

G. P. Mane, S. N. Talapaneni,  
C. Anand, S. Varghese,  
H. Iwai, Q. Ji, K. Ariga,  
T. Mori, A. Vinu\* .....3596–3604

### Preparation of Highly Ordered Nitrogen-Containing Mesoporous Carbon from a Gelatin Biomolecule and its Excellent Sensing of Acetic Acid

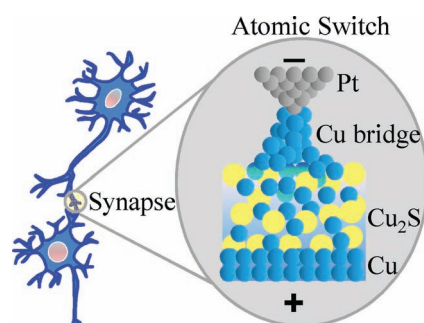


Highly basic and well-ordered nitrogen-doped mesoporous carbon with tunable pore diameters is prepared and its sensing capability for acidic molecules is demonstrated. It is found that the prepared material is highly basic and stable and shows excellent selectivity for sensing acetic acid.

## Nanoelectronics

A. Nayak,\* T. Ohno, T. Tsuruoka,  
K. Terabe, T. Hasegawa,  
J. K. Gimzewski, M. Aono ....3606–3613

### Controlling the Synaptic Plasticity of a $\text{Cu}_2\text{S}$ Gap-Type Atomic Switch

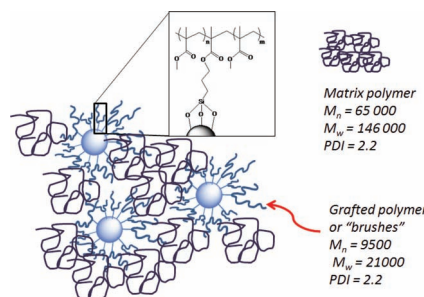


Features of human memory are mimicked by a  $\text{Cu}_2\text{S}$  gap-type atomic switch, which behaves as a biological synapse element under voltage pulse stimulation. The fact that it responds to the presence of air and the change of temperature distinguish it as an advanced synthetic synapse with the potential to perceive environment, similar to the human brain.

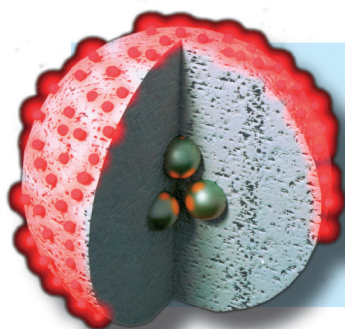
## Quantum Dots

M. Wong, J. Guenther, L. Sun,  
J. Blümel, R. Nishimura,  
H.-J. Sue\* .....3614–3624

### Synthesis and Fabrication of Multifunctional Nanocomposites: Stable Dispersions of Nanoparticles Tethered with Short, Dense and Polydisperse Polymer Brushes in Poly(methyl methacrylate)



Nanoparticles tethered with short, dense and polydisperse polymer brushes exhibit excellent compatibility and stability in a poly(methyl methacrylate) matrix, despite the large mismatch in molecular weights of matrix polymer and grafted polymer. Polymer brushes are prepared through free radical polymerization, which is generally applicable to a wide range of nanoparticle-nanocomposite combinations. The tunability of multifunctional properties of these hybrid materials is reported.



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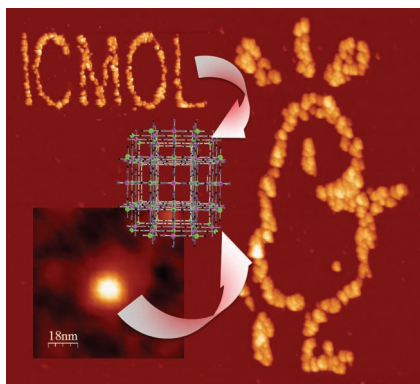
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## FULL PAPERS

**Local oxidation nanolithography combined with self-assembled monolayers** result in an efficient method for the precise organization of different diameter anionic Prussian-blue analogue nanoparticles (NPs) on silicon surfaces. The electrostatic forces, which fix the NPs on the oxide patterns, guarantee their electronic decoupling from the surface and ensure the prevalence of their interesting physical properties.

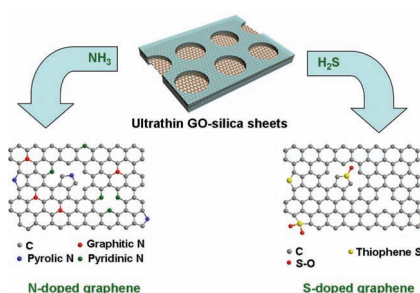


## Nanopatterning

E. Coronado,\* A. Forment-Aliaga,\*  
E. Pinilla-Cienfuegos, S. Tatay,  
L. Catala, J. A. Plaza .....3625–3633

Nanopatterning of Anionic  
Nanoparticles based on Magnetic  
Prussian-Blue Analogues

**Heteroatom (N or S)-doped graphenes** are synthesized via thermal reaction between graphene oxide and guest gases ( $\text{NH}_3$  or  $\text{H}_2\text{S}$ ) on ultrathin graphene oxide-porous silica sheets at high temperatures. It is found that both N and S-doping can occur to form the different binding configurations in the graphene and both N and S-doped graphene sheets exhibit excellent electrocatalytic properties for oxygen reduction reaction.

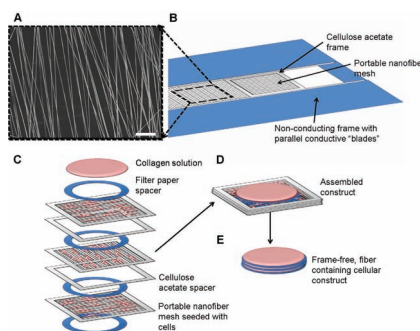


## Fuel Cells

S. B. Yang, L. J. Zhi, K. Tang,\*  
X. L. Feng,\* J. Maier,  
K. Müllen\* .....3634–3640

Efficient Synthesis of Heteroatom (N or  
S)-Doped Graphene Based on Ultrathin  
Graphene Oxide-Porous Silica Sheets for  
Oxygen Reduction Reactions

**A novel engineering strategy is devised to create a nanofiber-hydrogel composite scaffold**, which displays the characteristic morphological cues of native corneal tissue. Investigation of cell response to nanofibrous topographical cues, combined with media supplementation, highlights that orthogonal arrangement of adult human derived corneal stromal (AHDCS) cells in 3D constructs with the presence of insulin and ascorbate promotes keratogenesis, which could be a new strategy for generation of complex corneal tissue.

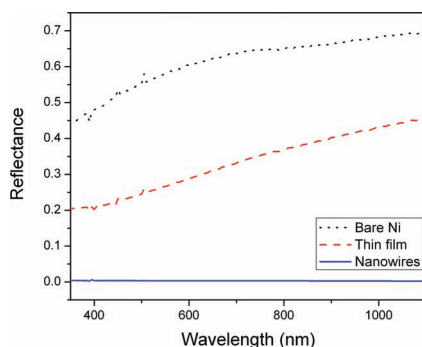


## Scaffolds

S. L. Wilson, I. Wimpenny,  
M. Ahearne, S. Rauz, A. J. El Haj,\*  
Y. Yang\* .....3641–3649

Chemical and Topographical Effects on  
Cell Differentiation and Matrix Elasticity in  
a Corneal Stromal Layer Model

**Single-crystalline, metallic  $\text{Ni}_x\text{Si}$  nanowire arrays** are grown on flexible metal foil substrates, without the need for lithography, etching, or catalysts. The optical properties of these NW arrays demonstrate broadband suppression of reflection due to light scattering, and high electrical conductivity ( $10^{-4} \Omega\text{-cm}$ ), suggesting their use as an efficient and low-cost back electrode material for photovoltaics.



## Photovoltaics

N. P. Dasgupta, S. Xu, H. J. Jung,  
A. Iancu, R. Fasching, R. Sinclair,  
F. B. Prinz\* .....3650–3657

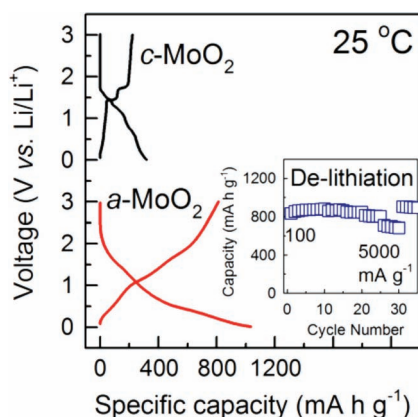
Nickel Silicide Nanowire Arrays for  
Anti-Reflective Electrodes in  
Photovoltaics

## FULL PAPERS

## Lithium-Ion Batteries

J. H. Ku, J. H. Ryu, S. H. Kim,  
O. H. Han,\* S. M. Oh\* .....3658–3664

### Reversible Lithium Storage with High Mobility at Structural Defects in Amorphous Molybdenum Dioxide Electrode

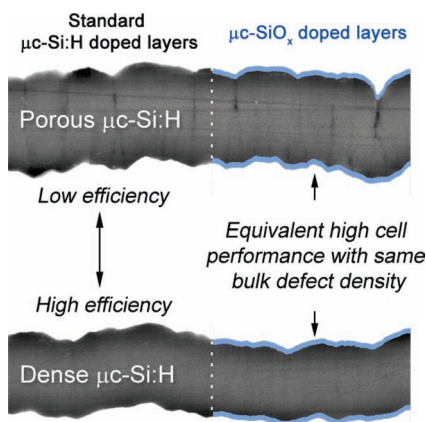


An amorphous  $\text{MoO}_2$  ( $\alpha\text{-MoO}_2$ ) electrode exhibits an unexpectedly high  $\text{Li}^+$  storage capacity (up to  $810 \text{ mA h g}^{-1}$ ), which is larger by a factor of four than that of its crystalline counterpart.  $\text{Li}^+$  ions are hosted by the structural defects in  $\alpha\text{-MoO}_2$  and opened vacancies and void spaces give a much faster charge/discharge rate as compared with the crystalline counterpart.

## Thin Films

G. Bugnon,\* G. Parascandolo,  
T. Söderström, P. Cuony, M. Despeisse,  
S. Hänni, J. Holovsky, F. Meillaud,  
C. Ballif .....3665–3671

### A New View of Microcrystalline Silicon: The Role of Plasma Processing in Achieving a Dense and Stable Absorber Material for Photovoltaic Applications

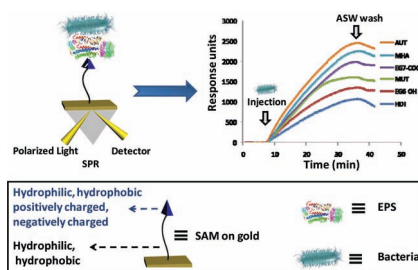


The growth of intrinsic microcrystalline silicon material at high deposition rates is studied for photovoltaic applications. The contribution of two distinct material phases on solar cell performance on textured substrates is shown. The porosity of the material is demonstrated through damp-heat experiments. Based on the developments, a single junction p-i-n microcrystalline record solar cell is presented.

## Surface Plasmon Resonance

A. Pranzetti, S. Salaün, S. Mieszkina,  
M. E. Callow, J. A. Callow, J. A. Preece,  
P. M. Mendes\* .....3672–3681

### Model Organic Surfaces to Probe Marine Bacterial Adhesion Kinetics by Surface Plasmon Resonance

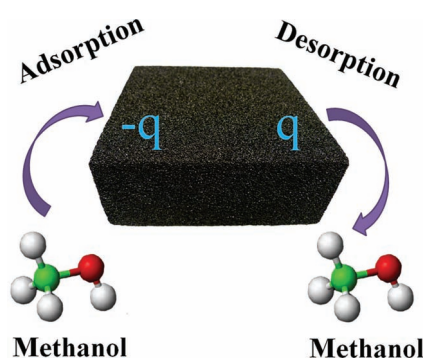


Surface plasmon resonance (SPR) spectroscopy, in combination with self-assembled monolayers (SAMs) that have different backbone structures and/or functional groups, is used for the first time to study the initial stages of bacterial adhesion to surfaces. The role of extracellular polymeric substances (EPS) in bacterial adhesion is also investigated. SPR spectroscopy is revealed as a powerful and unique way to probe bacterial adhesion in real time.

## Porous Materials

R. Paul, A. A. Voevodin, D. Zemlyanov,  
A. K. Roy, T. S. Fisher\* .....3682–3690

### Microwave-Assisted Surface Synthesis of a Boron–Carbon–Nitrogen Foam and its Desorption Enthalpy

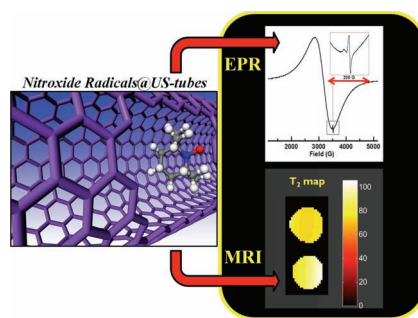


Carbon foams provide the combined advantages of large surface area and high thermal conductivity, which are critical for thermal energy storage, but they have low adsorption enthalpy for lightweight hydrocarbons. Microwave heating-assisted chemical treatment converts carbon foam to B–C–N foam. An enhanced adsorption enthalpy for B–C–N foams can enhance adsorption processes for thermal storage and utilization.



## FULL PAPER

Nitroxide radicals within ultrashort single-walled carbon nanotubes (US-tubes) are a promising new technology for magnetic resonance imaging (MRI) and electron paramagnetic resonance imaging (EPRI) biomedical applications. These materials display characteristic electron paramagnetic resonance (EPR) signals due to the incorporation of immobilized nitroxide spin probes in the US-tubes and short proton relaxation times for MRI.

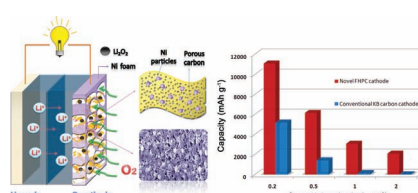


### Biomedical Applications

E. J. Rivera, R. Sethi, F. Qu, R. Krishnamurthy, R. Muthupillai, M. Alford, M. A. Swanson, S. S. Eaton, G. R. Eaton, L. J. Wilson\* .....3691–3698

### Nitroxide Radicals@US-Tubes: New Spin Labels for Biomedical Applications

Graphene oxide gel-derived, free-standing, hierarchically porous carbon in nickel foam without any additional binder is synthesized successfully by an in situ sol-gel method. As the cathode of Li-O<sub>2</sub> batteries, the as-synthesized electrodes have excellent performance with a high capacity and a high rate capability.

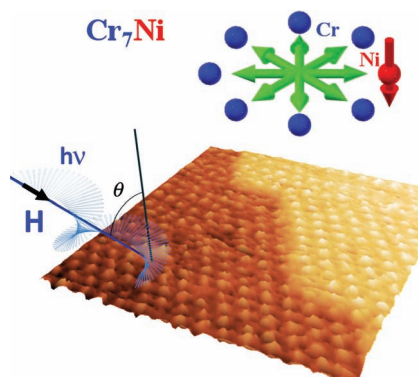


### Batteries

Z.-L. Wang, D. Xu, J.-J. Xu, L.-L. Zhang, X.-B. Zhang\* .....3699–3705

### Graphene Oxide Gel-Derived, Free-Standing, Hierarchically Porous Carbon for High-Capacity and High-Rate Rechargeable Li-O<sub>2</sub> Batteries

The experimental and theoretical determination of magnetic anisotropy in molecular spin clusters is addressed. The method used provides hints for the interpretation of X-ray magnetic dichroism (XMCD) spectra and the results are evidence for the interplay between the single ion magnetic anisotropy and that of the whole molecule.

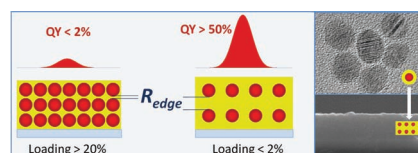


### Magnetic Materials

V. Corradini,\* A. Ghirri, E. Garlatti, R. Biagi, V. De Renzi, U. del Pennino, V. Bellini, S. Carretta, P. Santini, G. Timco, R. E. P. Winpenny, M. Affronte .....3706–3713

### Magnetic Anisotropy of Cr<sub>7</sub>Ni Spin Clusters on Surfaces

The emission quantum yield of CdSe nanocrystals embedded into a matrix of CdS semiconductor is tunable via inter-particle distance. The transmission electron microscopy images show the cross section of a film along with nanoparticle precursors used for its assembly.



### Photovoltaics

E. Khon, S. Lambright, D. Khon, B. Smith, T. O'Connor, P. Moroz, M. Imboden, G. Diederich, C. Perez-Bolivar, P. Anzenbacher, M. Zamkov\* .....3714–3722

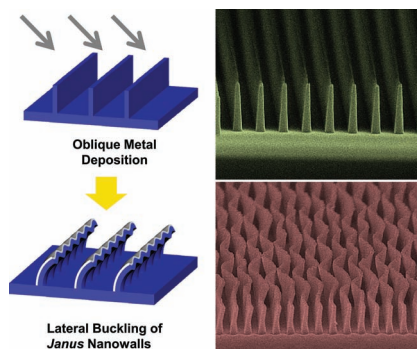
### Inorganic Solids of CdSe Nanocrystals Exhibiting High Emission Quantum Yield

# FULL PAPERS

## Surfaces

H. Yoon, A. Ghosh, J. Y. Han,  
S. H. Sung, W. B. Lee,\*  
K. Char\* .....3723–3728

### Lateral Buckling of High Aspect Ratio Janus Nanowalls

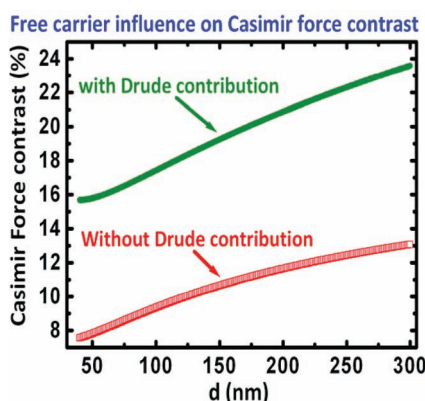


The fabrication of a novel structure – Janus nanowalls – and the phenomenon of lateral buckling within the wall are demonstrated. Metal films are deposited on one side of the polymeric nanowalls. During the metal deposition, the nanowalls themselves buckle laterally; this buckling is induced by the compressive residual stress in the metal film and geometric confining constraints.

## Dielectrics

G. Torricelli, P. J. van Zwol, O. Shpak,  
G. Palasantzas,\* V. B. Svetovoy,  
C. Binns, B. J. Kooi, P. Jost,  
M. Wuttig .....3729–3736

### Casimir Force Contrast Between Amorphous and Crystalline Phases of AIST

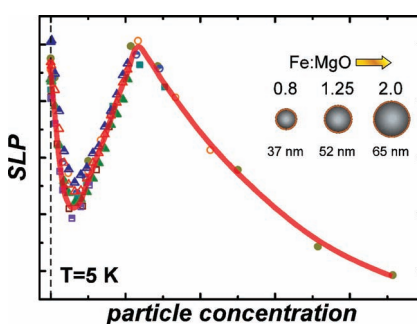


The Casimir force is measured to be higher for crystalline than for amorphous phase change materials. The contribution of free electrons (Drude term) and the change of bonding to the Casimir force contrast are determined. This finding suggests potential pathways to optimize the Casimir force contrast for applications.

## Nanoparticles

C. Martinez-Boubeta, K. Simeonidis,  
D. Serantes, I. Conde-Leborán,  
I. Kazakis, G. Stefanou, L. Peña,  
R. Galceran, L. Balcells, C. Monty,  
D. Baldomir, M. Mitrakas,  
M. Angelakeris\* .....3737–3744

### Adjustable Hyperthermia Response of Self-Assembled Ferromagnetic Fe-MgO Core-Shell Nanoparticles by Tuning Dipole-Dipole Interactions



The correlations arising from dipole-dipole interactions and their influence on the hyperthermia efficacy are studied both theoretically and experimentally and found to be in quantitative agreement. The calculation represents an analytical model of hyperthermia in magnetic interacting particle systems to explain in a simple way the ubiquitous behavior observed in this class of materials.