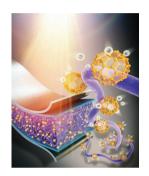
# ADVANCED FUNCTIONAL MATERIALS

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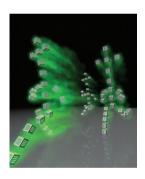


#### **Conjugated Polymers**

On page 3991 C. E. Park, S.-K. Kwon, Y.-H. Kim, and coworkers report recently advanced donor polymers with a novel acceptor unit, dithieno[3,2-b:2',3'-d]phosphole oxide (DTP) for high-performance solar cells. Surprisingly, the introduction of this DTP unit in the polymer chains shows superior charge transfer properties with highly polarizable characteristics, and a power conversion efficiency of 7.08% is achieved.

#### **Controlled Release**

Porous chemically loaded voxels can be dispensed in arrays on both rigid and flexible substrates to enable dynamic patterns and provide proof-of-concept for a chemical display. Simulations and experiments which are used to design the animation of a running man are described by D. H. Gracias and team on page 3998. Graphics: Jinpyo Hong and Martin Rietveld.

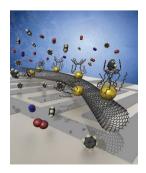


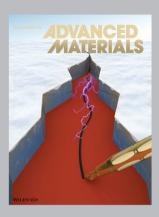
#### Piezochromic Materials

Turn-on and color-tuned piezochromic luminescence of acridonyl-tetraphenylethene (AD-TPE) with high-contrast is obtained by B. Xu, W. Tian, and colleagues in response to external mechanical stimuli. The results on page 4005 indicate that the unique behavior is driven by a switching of the excited state in solid state from localized excited (LE) state to intramolecular charge transfer (ICT) state under mechanical stimuli, which will inspire a new approach to realize the piezochromic luminescent materials and give a new insight into the nature of the piezochromic behavior.

#### Bezene Detection

A resistive sensor for detecting traces of benzene in air is built by P. Ballester, E. Llobet, and co-workers on page 4011 by covalently attaching quinoxaline-bridged resorcin[4]-arene cavitands to gold nanoparticles anchored on oxygen plasma treated carbon nanotubes. The inclusion of benzene in the aromatic cavity of the cavitand results in a measureable change of the electrical resistance of the functionalized carbon nanotube material.





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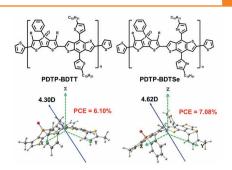


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Two novel copolymers, PDTP-BDTT and PDTP-BDTSe, containing dithienophosphole oxide units bring superior charge transfer properties by highly polarizable characteristics, which is beneficial for good performance in polymer solar cells.



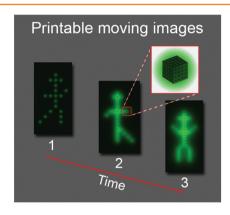
#### **FULL PAPERS**

#### **Conjugated Polymers**

K. H. Park, Y. J. Kim, G. B. Lee, T. K. An, C. E. Park, \* S.-K. Kwon, \* Y.-H. Kim\*.....3991-3997

**Recently Advanced Polymer Materials** Containing Dithieno[3,2-b:2',3'-d] phosphole Oxide for Efficient Charge Transfer in High-Performance Solar Cells

Information displayed in a chemical display is geometrically encoded within voxels that can be printed on a variety of substrates including flexible surfaces. Spatial and temporal programmed chemical release is used to generate an animation of a running man.



#### **Controlled Release**

Y. V. Kalinin, S. Pandey, J. Hong, D. H. Gracias\*.....3998-4004

A Chemical Display: Generating Animations by Controlled Diffusion from **Porous Voxels** 

Tuning the solid state luminescence of organic materials under mechanical stimuli is an attractive subject for both the fundamental research and practical application in the optical recording and sensing. Herein, a structurally welldefined molecule, acridonyl-tetraphenylethene is reported, whose molecular crystals exhibit an intriguing turn-on and color-tuned luminescence with high contrast in response to the mechanical stimuli such as grinding and hydrostatic pressure.

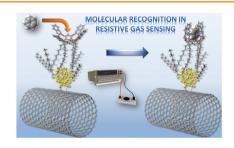


#### **Piezochromic Materials**

Q. Qi, J. Qian, X. Tan, J. Zhang, L. Wang, B. Xu.\* B. Zou. W. Tian\* ......4005-4010

Remarkable Turn-On and Color-**Tuned Piezochromic Luminescence:** Mechanically Switching Intramolecular Charge Transfer in Molecular Crystals

A new functionalization of multiwalled carbon nanotubes (MWCNTs) is engineered with a cavitand using molecular recognition via host-guest strategy for gas sensing application. The quinoxaline-walled thioether-legged cavitand is self-assembled as a monolayer onto gold nanoparticle decorated oxygen plasma MWCNTs. The sensor shows unprecedented high sensitivity toward traces of benzene vapors.



#### **Benzene Detection**

P. Clément, S. Korom, C. Struzzi, E. J. Parra, C. Bittencourt, P. Ballester,\* E. Llobet\* ......4011-4020

Deep Cavitand Self-Assembled on Au NPs-MWCNT as Highly Sensitive Benzene Sensing Interface

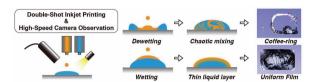
#### **FULL PAPERS**

#### Thin Films

Y. Noda,\* H. Minemawari, H. Matsui, T. Yamada, S. Arai, T. Kajiya, M. Doi, T. Hasegawa\* ...... 4022-4031

Underlying Mechanism of Inkjet Printing of Uniform Organic Semiconductor Films Through Antisolvent Crystallization

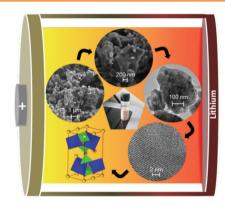
Double-shot inkiet printing utilizing antisolvent crystallization has the ability to form uniform organic semiconductor films, which, as demonstrated, is attributed to the unique nature of initial contact dynamics between chemically different microdroplets before occurrence of solute crystallization. Among three kinds of unique dynamics, the "wetting" can create a thin solution layer on antisolvent droplet surface, which eventually eliminates the coffee-ring effect.



#### **Energy Storage**

G. Pagot, F. Bertasi, G. Nawn, E. Negro, G. Carraro, D. Barreca, C. Maccato, S. Polizzi, V. Di Noto\*.........4032-4037

High-Performance Olivine for Lithium Batteries: Effects of Ni/Co Doping on the Properties of LiFe Ni Co, PO4 Cathodes

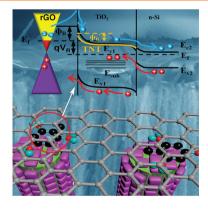


Five high voltage olivine cathodes for lithium batteries, based on lithium transition metal phosphates, are synthesized and characterized. The effect of differing degrees of cobalt and nickel doping on structure, morphology, and electrochemical properties of the different materials is studied; high performances in terms of voltage, specific capacity, specific energy, and cyclic life are obtained.

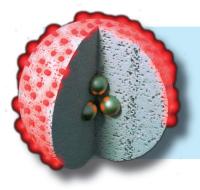
#### Nanosensors

Z. Yang, X. C. Dou, \* S. L. Zhang, L. J. Guo, B. Y. Zu, Z. F. Wu, H. B. Zeng\*.....4039-4048

A High-Performance Nitro-Explosives Schottky Sensor Boosted by Interface Modulation



A high-performance Schottky sensor is fabricated for the detection of trace nitro-explosives vapors. The sensitivity of the silicon nanowires array/TiO2/rGO sensor is boosted with the insertion of TiO<sub>2</sub>. Superior selectivity is shown even when compared with interfering gases of 10 ppm.



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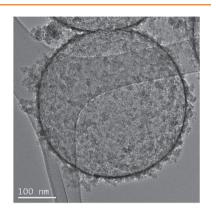
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#### Ultrathin hollow silica nanoshells can be synthesized by substituting in organically modified trialkoxysilanes into existing nanoshell syntheses. The resulting nanoshells have much thinner shell walls, which result in dramatic improvement in applications as ultrasound contrast agents.



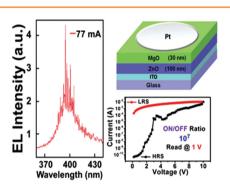
### **FULL PAPERS**

#### **Biomedical Imaging**

A. Liberman, J. Wang, N. Lu, R. D. Viveros, C. A. Allen, R. F. Mattrey. S. L. Blair, W. C. Trogler, M. J. Kim, A. C. Kummel\*......4049-4057

Mechanically Tunable Hollow Silica Ultrathin Nanoshells for Ultrasound **Contrast Agents** 

Electrically driven random laser memory (RLM) diodes based on Pt/MgO/ZnO/ ITO structure are fabricated. Both the random laser action and nonvolatile resistive random access memory functionality are well demonstrated. The dual functional RLM device paves a new route to advance the traditional memories using electrical detection toward faster parallel optical reading processes.

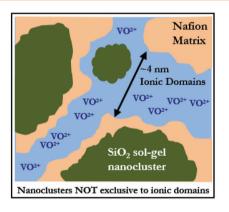


#### Memory

C.-S. Wang, C.-H. Nieh, T.-Y. Lin, Y.-F. Chen\* ......4058-4063

**Electrically Driven Random Laser** Memory

The morphology and crossover performance of Nafion-SiO<sub>2</sub> hybrid membranes for vanadium redox flow batteries are quantified. Reduced vanadium crossover is observed in hybrid membranes as well as neat Nafion membranes receiving thermal annealing. Contrast matching small-angle neutron scattering experiments show the presence of SiO2 nanoclusters on the order of 10 nm in diameter, which are much larger than a single ionic domain.

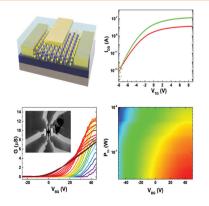


#### Vanadium Batteries

E. M. Davis,\* J. Kim, V. P. Oleshko, K. A. Page, C. L. Soles\* .......4064-4075

Uncovering the Structure of Nafion-SiO<sub>2</sub> Hybrid Ionomer Membranes for Prospective Large-Scale Energy Storage Devices

Few-layer ReS2 is successfully synthesized via chemical vapor deposition. Top-gated FET devices, back-gated four-terminal devices, and photodetectors are built based on the as-grown high-quality materials. All of them show great device performance, which distinguishes ReS2 a great platform for future applications in electronic and optoelectronic devices.



#### **Optoelectronics**

E. Zhang, Y. Jin, X. Yuan, W. Wang, C. Zhang, L. Tang, S. Liu, P. Zhou,\* W. Hu,\* F. Xiu\*.....4076-4082

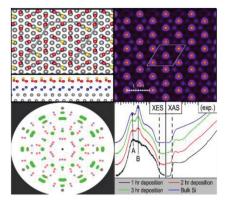
ReS2-Based Field-Effect Transistors and Photodetectors

#### **FULL PAPERS**

#### Silicene

N. W. Johnson,\* D. Muir, E. Z. Kurmaev, 

Stability and Electronic Characteristics of Epitaxial Silicene Multilayers on Ag(111)



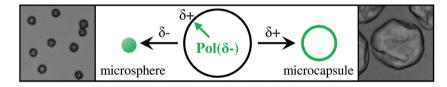
The stability and electronic structure of epitaxial silicene bilayers and multilayers on Ag(111) are explored through the complementary techniques of density functional theory calculations and synchrotron-based soft X-ray spectroscopy. Bilayers are predicted to have a novel AA-stacked structure and electronic characteristics similar to epitaxial silicene monolayers on Ag(111). The instability of multilayers is evident in the evolution of the Si L<sub>2,3</sub> X-ray emission spectrum.

#### **Supramolecular Materials**

R. M. Parker, J. Zhang, Y. Zheng, R. I. Coulston, C. A. Smith. A. R. Salmon, Z. Yu. O. A. Scherman. C. Abell\* ...... 4091–4100

**Electrostatically Directed Self-Assembly** of Ultrathin Supramolecular Polymer Microcapsules

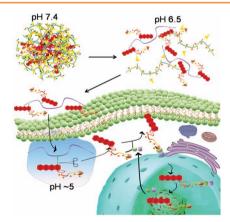
Charged copolymers are selectively partitioned to the interface of a microdroplet by a complementary charged surfactant for supramolecular cross-linking via cucurbit[8]uril. This dynamic assembly process is employed to controllably form hollow microcapsules or solid microparticles from a single solution. The ability to dictate the distribution of a mixture of charged copolymers is demonstrated by the single-step fabrication of distinct core-shell microcapsules.



#### **Drug Delivery**

L. Li, W. Sun, J. Zhong, Q. Yang, X. Zhu, Z. Zhou, Z. Zhang, Y. Huang\*.....4101-4113

Multistage Nanovehicle Delivery System **Based on Stepwise Size Reduction** and Charge Reversal for Programmed **Nuclear Targeting of Systemically Administered Anticancer Drugs** 

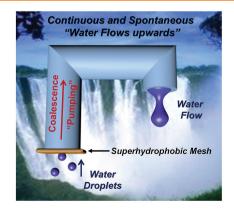


A cancer cell nuclear-targeted delivery system for in vivo application is achieved by a multistage responsive approach in which the size and charge of the nanovehicle can be transformable by adapting to the varying barriers.

#### **Water Transportation**

M. Cao, K. Li, Z. Dong, C. Yu, S. Yang, C. Song, K. Liu,\* L. Jiang ..... 4114-4119

Superhydrophobic "Pump": Continuous and Spontaneous Antigravity Water Delivery



Antigravity transportation of water is becoming a vital issue for the development of advanced devices and new technology. Herein, a centimeter-scale water selfascent driven only by the surface energy release of water droplets is reported via a superhydrophobic mesh, demonstrating the successful achievement of "water flows upward" without any external forces.

#### A packing limit close to the theoretical body-centered-cubic packing density is identified for spherical block copolymer micelles in a matrix-forming material. Beyond the packing limit, the micelles coalesce at their interfaces thereby creating disorder. This work heralds new

design rules for creating ordered porous

frameworks of materials of arbitrary

composition.

## **Packing Limit** 63%

**Porogen Volume Fraction** 

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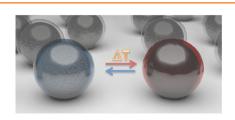
Mesoporous Materials

A. W. Wills, D. J. Michalak, P. Ercius, E. R. Rosenberg, T. Perciano, D. Ushizima, R. Runser,

B. A. Helms\*.....4120-4128

**Block Copolymer Packing Limits and** Interfacial Reconfigurability in the Assembly of Periodic Mesoporous Organosilicas

**Liquid-filled microcapsules** are used to reproduce the solution behavior of switchable valence tautomers in the solid state while enabling control over their interconversion temperature.



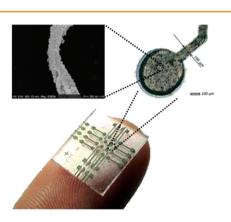
Microencapsulation

N. A. Vázquez-Mera, C. Roscini, I. Hernando,\*

D. Ruiz-Molina\*.....4129-4134

Liquid-Filled Valence Tautomeric Microcapsules: A Solid Material with Solution-Like Behavior

Multifunctionalized hybrid ires based on carbon nanotubes are prepared through different surface modification processes. These hybrid nanowires exhibit both the high electrical conductivity of metal and excellent mechanical properties of carbon nanotubes together with good dispersability. Flexible and stretchable electrodes based on the hybrid nanowires demonstrate stable electro-mechanical properties under large structural deformations.

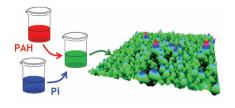


#### **Flexible Electronics**

N. Wang, D. Jiang, L. Ye, M. Murugesan, M. Edwards, Y. Fu, J. Liu\*.....4135-4143

Flexible Multifunctionalized Carbon Nanotubes-Based Hybrid Nanowires

Multifunctional supramolecular coatings are built up through simple dipcoating of substrates in an aqueous solution of polyamine in the presence of phosphate anions. It is shown that the derivatization of polyamine precursors with different chemical groups can endow films with predefined responsiveness or multiple properties, thus resulting in a one-pot and one-step preparation of substrate-adherent films displaying built-in functions.



#### **Surface Chemistry**

W. A. Marmisollé, J. Irigoyen,

D. Gregurec, S. Moya,

O. Azzaroni\*......4144–4152

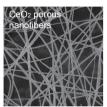
Supramolecular Surface Chemistry: Substrate-Independent, Phosphate-Driven Growth of Polyamine-Based Multifunctional Thin Films

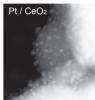
#### **FULL PAPERS**

#### **Photochemical Reduction**

P. Lu, B. Qiao, N. Lu, D. C. Hyun, J. Wang, M. J. Kim, J. Liu, Y. Xia\* ......4153-4162

Photochemical Deposition of Highly Dispersed Pt Nanoparticles on Porous CeO2 Nanofibers for the Water-Gas Shift Reaction



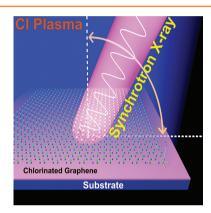


CeO2 porous nanofibers composed of an interconnected network of single crystalline and fully oxidized CeO<sub>2</sub> nanoparticles are fabricated through electrospinning and calcination. The hierarchically porous structure enables facile deposition of Pt nanoparticles using a photochemical method. The high porosity of CeO<sub>2</sub> nanofibers and the uniform distribution of Pt nanoparticles greatly improve their activity and stability toward the water-gas shift reaction.

#### **Graphene Doping**

X. Zhang, T. Schiros,\* D. Nordlund, Y. C. Shin, J. Kong, M. Dresselhaus,\* T. Palacios\*.....4163-4169

X-Ray Spectroscopic Investigation of **Chlorinated Graphene: Surface Structure** and Electronic Effects



Plasma-based chlorination on graphene is a unique surface functionalization to realize effective and noninvasive doping. Surface states of doped graphene are systematically investigated through synchrotron-based X-ray spectroscopy. Chlorine doping is a highly nonintrusive process, leaving long-range periodicity of electronic states of graphene intact. Strong substrate effects are observed and studied.

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