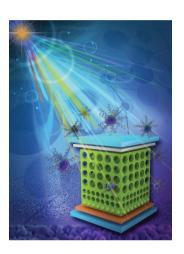
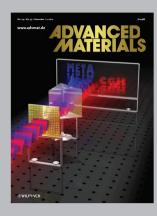
# ADVANCED FUNCTIONAL MATERIALS

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#### Solar Cells

A solid-state dye-sensitized solar cell with 7.3% efficiency is fabricated using crack-free, organized, mesoporous  ${\rm TiO_2}$  films with high surface areas and good interconnectivity. On page 26, Jong Hak Kim and coworkers demonstrate the role of the hybrid template, i.e., alumina nanoparticles grafted with a hydrophilic polymer. This template can be used for the preparation of various mesoporous inorganic oxide films.



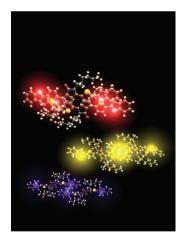
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#### Structure-Property Relationships

Heteroatom substitutions in the end-groups of three diketopyrrolopyrrole-containing small molecules are investigated to evaluate how such substitutions affect physical properties, charge transport, and the performance in bulk heterojunction solar cells. As reported by Thuc-Quyen Nguyen and co-workers on page 47, the single-crystal structures of three compounds reveal the differences in material properties arise from changes in intra- and intermolecular interactions in the solid state, which are caused by heteroatom substitutions. This study demonstrates a systematic investigation of structure–property relationships in conjugated small molecules.



#### **Metal Nanoparticles**

The coincidence lattice formed between a Mo(001) surface and a MgO thin film is used to prepare Fe nanoparticle ensembles with high spatial uniformity. As reported by Jacek Goniakowski, Niklas Nilius, and co-workers on page 75, the ordered growth of Fe is initiated by regular work function modulations and geometric distortions of the oxide layer across the coincidence cell.



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### **EDITORIAL**

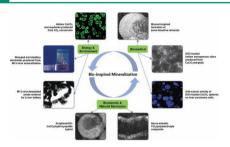
J. Ritterbusch......9 Change is the Only Consistency

#### **FEATURE ARTICLE**

#### **Biomineralization**

S. Kim, C. B. Park\*.....10-25

Bio-Inspired Synthesis of Minerals for Energy, Environment, and Medicinal Applications



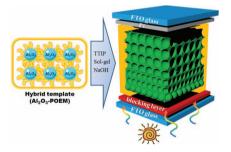
The continuously expanding application scope of bio-inspired (or biomimetic) mineralization is reviewed. Current applications of bio-inspired mineralization range from energy to healthcare through the development of advanced functional materials via the interconnection and combination of different reseach fields.

#### **FULL PAPERS**

#### Solar Cells

J. T. Park, W. S. Chi, D. K. Roh, S. H. Ahn, J. H. Kim\*.....26–33

Hybrid Templated Synthesis of Crack-Free, Organized Mesoporous TiO<sub>2</sub> Electrodes for High Efficiency Solid-State Dye-Sensitized Solar Cells

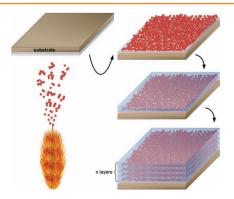


Crack-free, 10- $\mu$ m-thick, organized, mesoporous  $TiO_2$  films with high surface areas and good interconnectivity are synthesized using an efficient hybrid template, i.e.,  $Al_2O_3$  grafted with poly(oxyethylene) methacrylate ( $Al_2O_3$ -POEM). A solid-state dye-sensitized solar cell with 7.3% efficiency at 100 mW cm $^{-2}$  is fabricated. This is one of the highest efficiencies observed for N719 dye.

#### **Nanocomposites**

G. A. Sotiriou, C. O. Blattmann, S. E. Pratsinis\*.....34–41

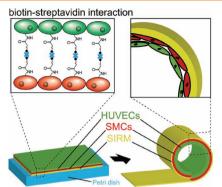
Flexible, Multifunctional, Magnetically Actuated Nanocomposite Films



Multilayer polymer nanocomposite films with high filler-loading are made by flame aerosol deposition and in situ annealing, followed by polymer spin coating. By repeating the process a number of times, multilayer films with the same or different filler composition are made. The resulting films exhibit superior filler-specific performance, which is attributed to the high filler-loading with exceptional homogeneity within the polymer films.

#### **FULL PAPERS**

A simple method is reported for stepwise formation of 2D multicellular structures through biotin-streptavidin (SA) interaction and further construction of controlled 3D multilayered tissue-like structures using the stress-induced rolling membrane (SIRM) technique. The bilayer of two types of cells on the SIRM is transformed into 3D tubes in which two types of cells directly interact and communicate with each other, mimicking tubular structures.



Stress-Induced Rolling Membrane (SIRM)

#### **Biomimetics**

P. Gong, W. Zheng, Z. Huang, W. Zhang,\* D. Xiao,\* X. Jiang\*.....42-46

A Strategy for the Construction of Controlled, Three-Dimensional, Multilayered, Tissue-Like Structures

The effects of heteroatom substitutions on the functional properties of diketopyrrolopyrrole-containing molecules are systematically investigated to identify the internal structure-property relationships. While the optical absorption and energy levels are insensitive to the heteroatom substitution, the materials' single crystal structures, capability of film formation, carrier mobility, and photovoltaic performance are significantly changed by the heteroatom substitutions.

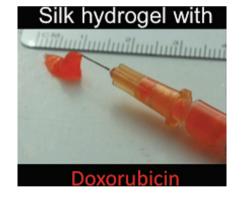


#### Structure-Property Relationships

J. Liu, B. Walker, A. Tamayo, Y. Zhang, T.-O. Nguyen\*......47-56

Effects of Heteroatom Substitutions on the Crystal Structure, Film Formation, and Optoelectronic Properties of Diketopyrrolopyrrole-Based Materials

Self-assembling silk hydrogels that can retain and then deliver doxorubicin locally are described. These systems are manufactured under aqueous conditions and release the payload in amounts that can be fine-tuned, resulting in a significant antitumor response in breast cancer xenografts. Thus, silk hydrogels are well-suited for the local delivery of chemotherapy and provide a promising approach to improve breast cancer therapy.



#### **Drug Delivery**

F. P. Seib, E. M. Pritchard, D. L. Kaplan\* ......58-65

Self-Assembling Doxorubicin Silk Hydrogels for the Focal Treatment of **Primary Breast Cancer** 



Hydrogel-like biomaterials are often too soft to support robust cell adhesion, yet methods to increase mechanical rigidity can compromise their bioactivity. Nanoparticle templating is reported as a strategy toward porous, layer-by-layer assembled, thin polyelectrolyte films with sufficient mechanical rigidity to promote robust cell adhesion and high loading capacity for bioactive species. This is potentially ideal for cellcontacting applications.

## Biomolecule Nanoparticule loading dissolution

#### **Biomaterials**

C. Wu, S. Aslan, A. Gand, J. S. Wolenski, E. Pauthe.\* P. R. Van Tassel\*......66-74

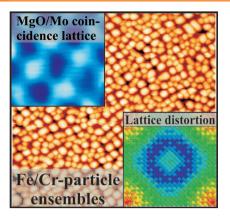
Porous Nanofilm Biomaterials Via Templated Layer-by-Layer Assembly

### **FULL PAPERS**

#### Thin Films

S. Benedetti, F. Stavale, S. Valeri, C. Noguera, H.-J. Freund, J. Goniakowski,\* N. Nilius\*.......75–80

Steering the Growth of Metal Ad-particles via Interface Interactions Between a MgO Thin Film and a Mo Support

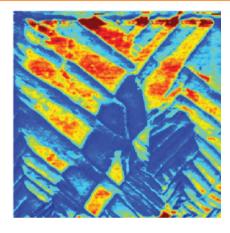


Fe and Cr deposition onto a MgO/Mo coincidence lattice leads to the development of uniform particle ensembles with small size distribution. The underlying modulations in the adsorption potential arise from variations in the MgO lattice parameter, the MgO-Mo binding length, and the work function, which in turn originate from different atomic registers at the metal/oxide interface.

#### Ferroic Materials

R. K. Vasudevan, M. B. Okatan, C. Duan, Y. Ehara, H. Funakubo, A. Kumar, S. Jesse, L. Q. Chen, S. V. Kalinin,\* V. Nagarajan\* .....81–90

Nanoscale Origins of Nonlinear Behavior in Ferroic Thin Films

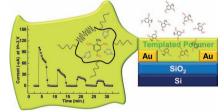


The nanoscale origins of Rayleigh behavior in ferroic materials have remained elusive, despite the widespread applicability of this phenomenological law. Using band-excitation piezoresponse force microscopy, individual nanoscale measurements on Pb(Zr,Ti)O $_3$  films probe a distinctly non-Rayleigh regime. The collective average of the individual measurements leads directly to macroscopic Rayleigh-type nonlinearity. These results point to the nanoscale origins of nonlinearity in a variety of disordered ferroics.

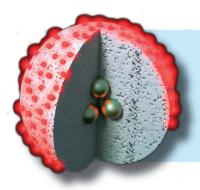
#### Sensors

H. Kong, J. Sinha, J. Sun, H. E. Katz\* ......91–99

Templated Crosslinked Imidazolyl Acrylate for Electronic Detection of Nitroaromatic Explosives



When exposed to 2,4,6-trinitrotoluene (TNT) explosive, templated polymers show greatly increased conductivity changes, even at very low TNT concentration, accompanied by a confirming color change from colorless to deep red. At very low relative humidity, the relative conductivity increase is the highest (about 4000 times) yet reported in response to TNT exposure.



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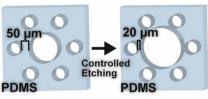
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#### **FULL PAPERS**

In three-dimensionally patterned microvascular gas exchange units, the membrane thickness between microchannels is closely related to the mass transfer rates. The relationship between the membrane thickness in microvascular contactors and absorption rates via a selective etching process is studied.







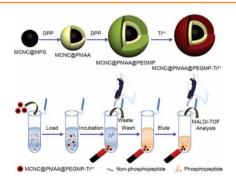
#### Structure-Property Relationships

D. T. Nguyen, Y T. Leho,
A. P. Esser-Kahn\*.....100–106

The Effect of Membrane Thickness on a Microvascular Gas Exchange Unit



High-quality magnetic composite microspheres composed of a magnetic colloid nanocrystal cluster (MCNC) core, a poly (methylacrylic acid) (PMAA) interim layer, and a Ti4+-immobilized poly(ethylene glycol methacrylate phosphate) (PEGMP) shell are elaborately designed and fabricated via a two-step distillation-precipitation polymerization (DPP) and a Ti4+-immobilization process. The as-synthesized MCNC@ PMAA@PEGMP-Ti<sup>4+</sup> composite microspheres show excellent performance in selective enrichment of phosphopeptides from complex biological samples.

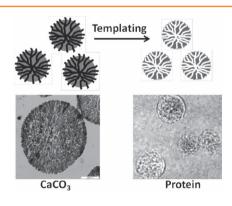


#### **Composite Materials**

W. F. Ma, Y. Zhang, L. L. Li, Y. T. Zhang, M. Yu, J. Guo, H. J. Lu,\* C. C. Wang\*......107–115

Ti<sup>4+</sup>-Immobilized Magnetic Composite Microspheres for Highly Selective Enrichment of Phosphopeptides

A straightforward yet mild templating method for producing porous protein microparticles is presented. The resulting particles show low polydispersity, high inner surface area, and, consequently, enhanced enzymatic activity. Due to the mesoporous structure, the particles exhibit an extraordinary deformability with an elastic modulus. Overall, the material parameters can be adapted to match the requirements of pharmaceutical applications.

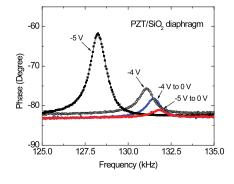


#### **Mesoporous Materials**

S. Schmidt, M. Behra, K. Uhlig, N. Madaboosi, L. Hartmann, C. Duschl, D. Volodkin\*.....116–123

Mesoporous Protein Particles Through Colloidal CaCO<sub>3</sub> Templates

A significant phenomenon of reversed remnant polarization is observed in a bent  $Pb(Zr_{0.52}Ti_{0.48})O_3$  (PZT) diaphragm. The resonant peaks at -4 and -5 V indicate that negative polarization is induced in the PZT film by these negative biases. However, after removing the negative bias, the negative polarization switches to the positive direction. The flexoelectric polarization reverses the negative remnant polarization.



#### **Microelectromechanical Systems**

Z. Wang,\* X. X. Zhang, X. Wang,W. Yue, J. Li, J. Miao, W. Zhu\*....124–132

Giant Flexoelectric Polarization in a Micromachined Ferroelectric Diaphragm