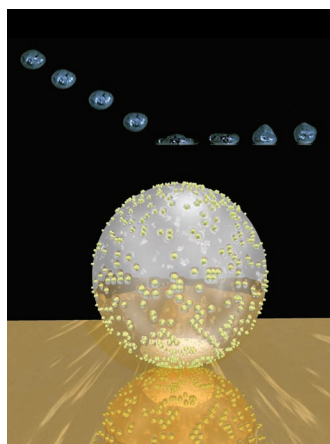


# ADVANCED FUNCTIONAL MATERIALS

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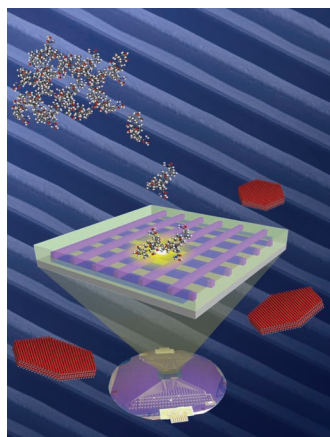


## Liquid Metals

On page 144, Kourosh Kalantar-zadeh, Arnan Mitchell, and co-workers introduce liquid metal marbles by encapsulating droplets of liquid metal in micro/nanoparticles that are insulating or semiconducting. The physical properties of the liquid metal marbles are investigated. The ability to form active electronic junctions using liquid metal marbles and its use as a highly sensitive, electrochemical-based, heavy metal ion sensor is demonstrated.

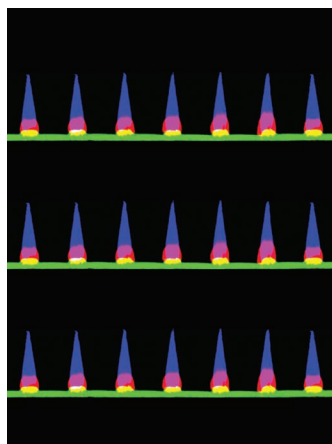
## Drug Delivery

Skin patches containing micrometer-scale needles ("microneedles") provide a safe, convenient, and pain-free approach for effective delivery of vaccines and pharmaceuticals. Paula T. Hammond, Darrell J. Irvine, and co-workers report on page 161 the design and use of a composite microneedle architecture for rapid cutaneous delivery and coordinated control over the release of antigen and adjuvant vaccine components for improved immunization in mice.



## Lithography

Force position arrays which are able to track the position of micro- or nanometer-sized objects require an extremely high spatial resolution down to the nanometer range. On page 191, Kittitai Subannajui, Andreas Menzel, Margit Zacharias, and co-workers report methods which combine advanced lithographic processes and piezoelectric materials on a large scale. The structures are achieved by phase-shift lithography and atomic-layer-deposition-based spacer lithography.



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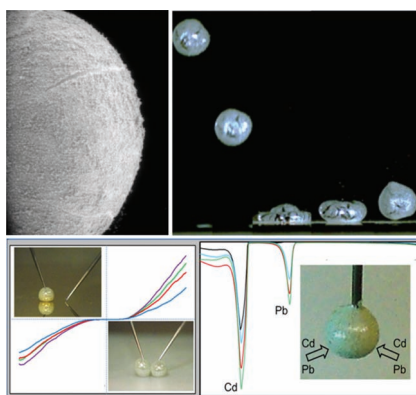
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## FULL PAPERS

## Metals

V. Sivan, S.-Y. Tang,  
A. P. O'Mullane, P. Petersen,  
N. Eshtiaghi, K. Kalantar-zadeh,\*  
A. Mitchell\* .....144–152

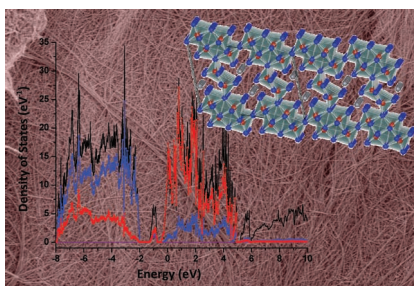
## Liquid Metal Marbles



Liquid metal marbles are formed by encapsulating droplets of liquid metal in micro/nanoparticles that are insulating or semiconducting. The physical properties of the liquid metal marbles are investigated. The ability to form active electronic junctions using liquid metal marbles and its use as a highly sensitive, electrochemical-based, heavy metal ion sensor is demonstrated.

## Nanowires

P. M. Marley, A. A. Stabile,  
C. P. Kwan, S. Singh, P. Zhang,  
G. Sambandamurthy,\*  
S. Banerjee,\* .....153–160

Charge Disproportionation and Voltage-Induced Metal–Insulator Transitions Evidenced in  $\beta$ - $\text{Pb}_x\text{V}_2\text{O}_5$  Nanowires

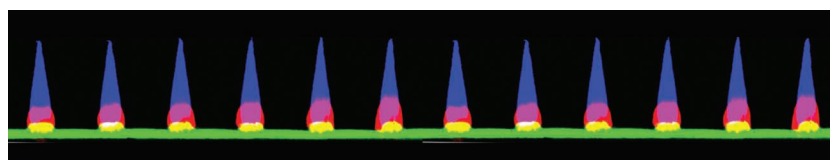
A synthetic route to nanowires of  $\beta$ - $\text{Pb}_x\text{V}_2\text{O}_5$  and evidence of an unprecedented voltage-induced metal–insulator transition in these materials is presented. X-ray diffraction and X-ray absorption spectroscopy experiments are consistent with charge ordering and electronic structure calculations suggest the appearance of a mid-gap state.

## Biomedical Applications

P. C. DeMuth, W. F. Garcia-Beltran,  
M. L. Ai-Ling, P. T. Hammond,\*  
D. J. Irvine\* .....161–172

## Composite Dissolving Microneedles for Coordinated Control of Antigen and Adjuvant Delivery Kinetics in Transcutaneous Vaccination

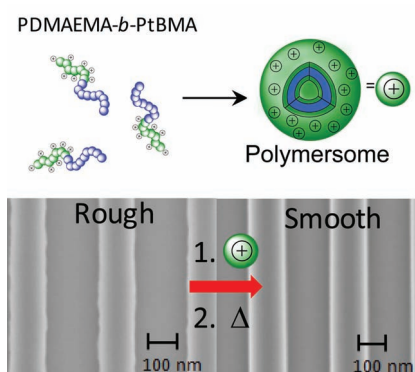
Composite polymer microneedles encapsulating drug-loaded, controlled-release poly(lactide-co-glycolide) (PLGA) matrices in a rapidly soluble poly(acrylic acid) (PAA) matrix provide rapid transcutaneous implantation of long-lived depots for sustained delivery of vaccines and drug cargos in vivo. Microneedle delivery of a rationally designed subunit vaccine formulation enhances adaptive immunity relative to traditional needle-based administration.



## Block Copolymers

Y.-M. Chuang, K. S. Jack, H.-H. Cheng,  
A. K. Whittaker, I. Blakey\* .....173–183

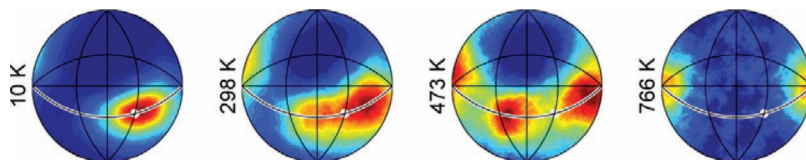
## Using Directed Self Assembly of Block Copolymer Nanostructures to Modulate Nanoscale Surface Roughness: Towards a Novel Lithographic Process



A novel process is developed to modulate the nanometer-scale roughness of surfaces. This is achieved through the directed self assembly of positively charged polymersomes, composed of block copolymers, onto negatively charged surfaces, which is followed by an annealing step that allows the selective reflow of the block copolymer to reduce the nanoscale surface roughness. The application of this method to smooth lithographically produced features is demonstrated.

## FULL PAPERS

**Pair distribution function analysis of the lead-free piezoelectric  $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$**  is used to reveal the thermal evolution of the cations' local environment. In particular, a "bifurcated" polarization rotation of the bismuth cations is observed, essentially convoluting previous suggestions of (singular) polarization rotation and of phase coexistence.

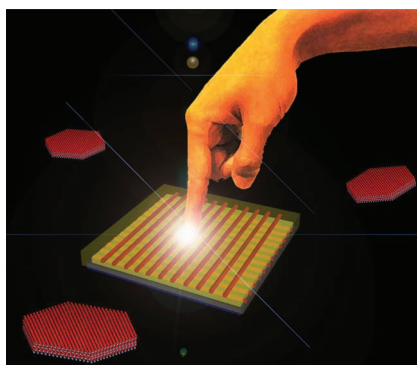


## Ferroics

D. S. Keeble,\* E. R. Barney,  
D. A. Keen, M. G. Tucker, J. Kreisel,  
P. A. Thomas.....185–190

## Bifurcated Polarization Rotation in Bismuth-Based Piezoelectrics

**Advanced lithographic processes combined with piezoelectric materials** have the potential to fabricate extremely high resolution force position arrays on a large scale. Nanometer-scale piezoelectric lines fabricated on Si wafers by phase-shift lithography and atomic-layer-deposition-based spacer lithography techniques are utilized to enable a new and simple path for devices that define the position with micro- and nanometer resolution.

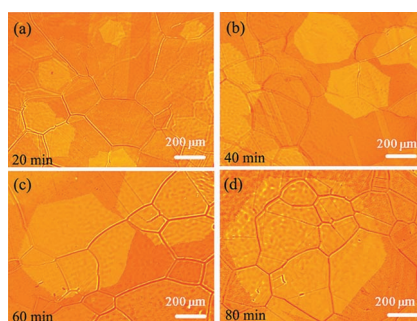


## Nanodevices

K. Subannajui,\* A. Menzel,\* F. Güder,  
Y. Yang, K. Schumann, X. Lu,  
M. Zacharias\* .....191–197

## Large-Scale Nano Piezo Force Position Arrays as Ultrahigh-Resolution Micro- and Nanoparticle Tracker

**The key to synthesizing large graphene grains by ambient pressure chemical vapor deposition (APCVD)** is to maintain a low nucleation rate and to provide a continuous drive for graphene growth. An optimized process enables  $\approx 100$  nuclei/ $\text{cm}^2$  on a finely polished and annealed substrate. A continuous increase in carbon supply and flow rate drives the graphene growth to  $\approx 1.2$  mm, the largest reported on a Cu substrate.

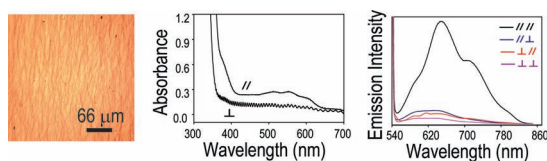


## Graphene

T. Wu, G. Ding, H. Shen,\*  
H. Wang, L. Sun, D. Jiang, X. Xie,\*  
M. Jiang.....198–203

## Triggering the Continuous Growth of Graphene Toward Millimeter-Sized Grains

**A novel method making use of block copolymer self-assembly in nematic liquid crystals (LCs)** is described for preparing macroscopically oriented nanofibrils of  $\pi$ -conjugated semiconducting polymers. Upon cooling, a diblock copolymer composed of regioregular poly(3-hexylthiophene) (P3HT) and a liquid crystalline polymer (LCP) in a block-selective LC solvent can self-assemble into oriented nanofibrils exhibiting highly anisotropic absorption and polarized photoluminescence emission.



## Semiconducting Polymers

X. Tong, D. Han, D. Fortin,  
Y. Zhao\* .....204–208

## Highly Oriented Nanofibrils of Regioregular Poly(3-hexylthiophene) Formed via Block Copolymer Self-Assembly in Liquid Crystals

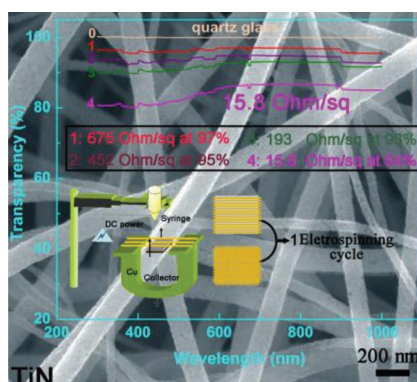


## FULL PAPERS

## Electrodes

H. Li, W. Pan,\* W. Zhang, S. Huang,  
H. Wu.....209–214

### TiN Nanofibers: A New Material with High Conductivity and Transmittance for Transparent Conductive Electrodes

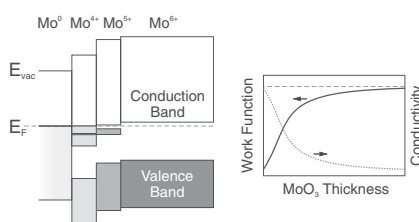


TiN nanofibers are successfully fabricated and assembled on quartz glass via electrospinning. High conductivity and transmittance are found in the TiN nanofiber network. A sheet resistance of 15.8 Ohm  $\text{sq}^{-1}$  at 84% transparency can be achieved, which makes electrospun TiN nanofibers promising candidates for new transparent electrode materials.

## Metal Oxides

M. T. Greiner,\* L. Chai,  
M. G. Helander, W.-M. Tang,  
Z.-H. Lu .....215–226

### Metal/Metal-Oxide Interfaces: How Metal Contacts Affect the Work Function and Band Structure of $\text{MoO}_3$

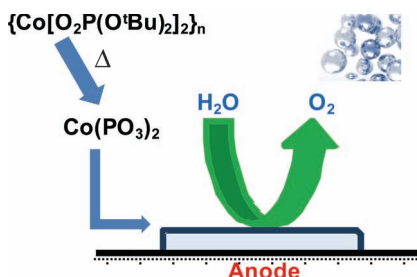


Metal/metal-oxide interfaces are important for many electronic devices. It is shown that chemical and electronic interfacial interactions between metals and oxides result in nanometer-scale changes to the work function and electronic band structure for  $\text{MoO}_3$ .

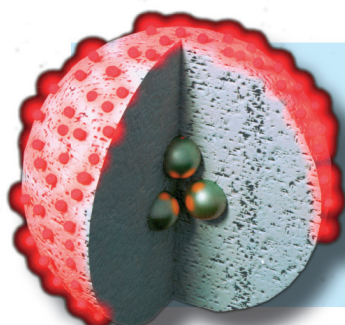
## Catalysis

H. S. Ahn, T. D. Tilley\*.....227–233

### Electrocatalytic Water Oxidation at Neutral pH by a Nanostructured $\text{Co}(\text{PO}_3)_2$ Anode



A nanostructured  $\text{Co}(\text{PO}_3)_2$  is prepared by the thermolytic molecular precursor method and then drop-cast onto an anode to perform water oxidation at neutral pH at a rate of 0.21  $\text{s}^{-1}$  and an overpotential of 440 mV. The catalytic onset overpotential is ca. 310 mV, which is 100 mV lower than that of comparable  $\text{Co}_3\text{O}_4$  nanoparticles under identical conditions.



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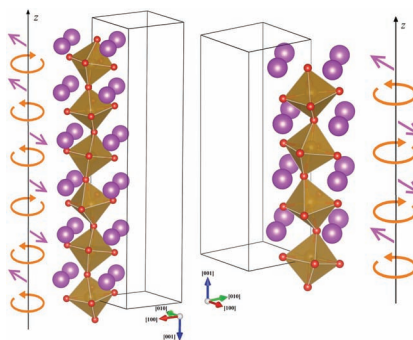
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## FULL PAPERS

A new family of nanometer-scale twinned octahedral tilting structures is found in multiferroic  $\text{BiFeO}_3$  by developing and/or using first-principle-based schemes. Among other properties, this complex tilting is coupled with unusual antiferroelectricity. These new and previously overlooked nano-twinned patterns originate from frustration and are likely to be present in a variety of compounds.

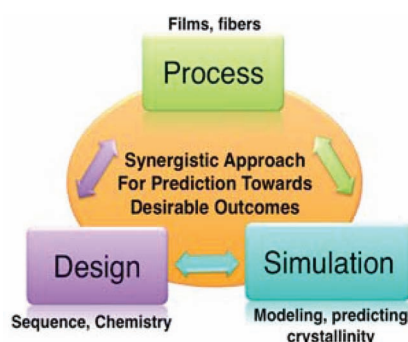


## Ferromagnetic Materials

S. Prosandeev,\* D. Wang, W. Ren, J. Íñiguez, L. Bellaiche .....234–240

## Novel Nanoscale Twinned Phases in Perovskite Oxides

Understanding sequence–structure–property relationships provides the opportunity to generate materials with pre-determined properties. A trinity approach combining controlled synthesis (genetically programmed), tailorable processing (via microfluidic focusing and film assembly), and molecular modeling with spider silk-like designs as target materials is reported. This iterative approach offers a robust discovery path in optimizing material designs with predictable functional outcomes.

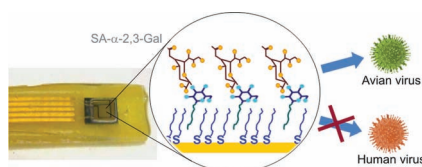


## Structure–Property Relationships

S. T. Krishnaji, G. Bratzel, M. E. Kinahan, J. A. Kluge, C. Staii, J. Y. Wong,\* M. J. Buehler,\* D. L. Kaplan\* .....241–253

## Sequence–Structure–Property Relationships of Recombinant Spider Silk Proteins: Integration of Biopolymer Design, Processing, and Modeling

Biomimetic architectures for the impedimetric discrimination of influenza virus phenotypes are tailored by a self-assembly process on gold substrates. Incorporated sialic acid molecules as sensing entities mimic receptors found on target cells of the influenza A virus. The resulting detector rapidly discriminates between avian and human strains of influenza A virus, acting as a reagentless, label-free diagnostic device for influenza phenotyping, which is important in surveillance and prediction of pandemics.



## Biomimetics

B. Wicklein, M. A. Martín del Burgo, M. Yuste, E. Carregal-Romero, A. Llobera, M. Darder, P. Aranda, J. Ortín, G. del Real, C. Fernández-Sánchez,\* E. Ruiz-Hitzky\* .....254–262

## Biomimetic Architectures for the Impedimetric Discrimination of Influenza Virus Phenotypes