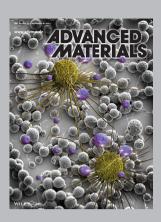
# ADVANCED FUNCTIONAL MATERIALS

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#### Fuel Cells

On page 4585, D. E. Morse and co-workers report a biologically inspired, kinetically controlled, catalytic approach to synthesizing a new family of nanocrystalline platinum-based catalysts. A novel composite of multiwalled carbon nanotubes and carbon black serves as the matrix for the in situ nucleation and growth of the Pt nanocrystals, providing access to new combinations of porosity, mesoscale morphology, conductivity, and electrochemical activity for hydrogen oxidation.



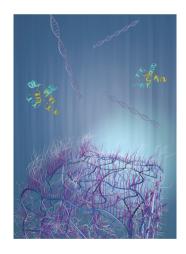
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#### Stimuli-Responsive Materials

A self-healing, long-lasting, antifouling coating is made by S. Minko and co-workers from antifouling polymers grafted to the surface and inside a polymer network film. On page 4593, they show how, if the grafted polymers are detached from the surface in the course of aging, the antifouling effect is spontaneously recovered by the rearrangement of the internally grafted polymers at the interface. 3D-grafted structures demonstrate four-fold longer stability than 2D surface grafted structures. Cover image courtesy of Ella Marushchenko.



#### **Polymer Gels**

O. Kuksenok and A. C. Balazs perform computational studies on photoresponsive polymer gels functionalized with spirobenzopyran chromophores. On page 4601, they these materials undergo 3D shape changes under nonuniform illumination. The repeated motion of the light along the gel results in well-controlled, directed sample movement. These results point to a robust method for controllably reconfiguring the morphology of polymer gels and driving the self-organization of multiple reconfigurable pieces into complex architectures. This image was designed by Mr. Nicholas Moellers.



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#### **EDITORIAL**

J. Aizenberg\*, P. Fratzl\*......4398-4399

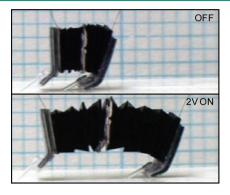
New Materials through Bioinspiration and Nanoscience

#### **FEATURE ARTICLES**

#### **Humidity-Sensitive Actuators**

H. Okuzaki, \* T. Kuwabara, K. Funasaka, T. Saido ......4400–4407

**Humidity-Sensitive Polypyrrole Films for Electro-Active Polymer Actuators** 

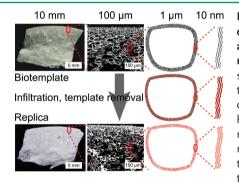


Humidity-sensitive polypyrrole films can provide an insight to the development of an origami robot fabricated by folding the polypyrrole film. The principle lies in the electrically induced changes in the elastic modulus caused by desorption of water vapor due to Joule heating, which is responsible for amplifying a contraction of the film to more than a 100-fold expansion.

#### **Biotemplating**

- O. Paris,\* G. Fritz-Popovski,
- D. Van Opdenbosch,
- C. Zollfrank\*.....4408-4422

Recent Progress in the Replication of **Hierarchical Biological Tissues** 



Biotemplating combines the hierarchical structure of natural materials with a broad range of available constituent materials by using biological tissues as scaffolds or casting molds for the synthesis of inorganic porous materials or composites. The replication of the entire hierarchical structure of biological materials down to nanometer length scales requires several important steps such as the thermal or chemical preparation of the template, its infiltration with the precursor, the subsequent transformation to a solid, and finally the template removal.

#### **Biomimetics**

A. R. Studart\* ......4423-4436

**Biological and Bioinspired Composites** with Spatially Tunable Heterogeneous **Architectures** 

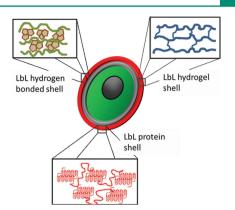
Load bearing materials in biology and in engineering differ markedly in their microstructural design. While biological materials exhibit highly heterogeneous microstructures (left), their synthetic counterparts are often designed to be homogeneous and isotropic (middle). Creating heterogeneous architectures with properties locally tuned to match non-uniform loading conditions should lead to bioinspired composites with extended durability using bioresorbable or environmental-friendly building blocks (right).



4392

#### **FEATURE ARTICLES**

Biologically inspired materials with tailored properties have proven to increase stability of encapsulated cells in a hostile environment, and hence can expand applicability for biomedical, biotechnology, and bioelectronics applications. This Feature Article addresses some of the recent studies of inorganic and organic gels, polymeric and biomolecular microgels, and ultrathin conformal shells from polymers and proteins for efficient cell protection.



#### **Biomimetics**

I. Drachuk, M. K. Gupta, V. V. Tsukruk\*......4437–4453

Biomimetic Coatings to Control Cellular Function through Cell Surface Engineering

Investigation of the structural organization of chitinous materials—the second most abundant organic material on earth—leads to understanding of the principles of natural materials design. These designs are beginning to be harnessed to fabricate bioinspired composites with tunable properties that mimic living materials, which might provide useful for environmental challenges, as well as medical applications.

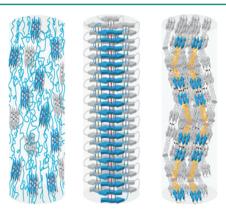


#### **Biomimetics**

J. G. Fernandez, D. E. Ingber\*.....4454-4466

Bioinspired Chitinous Material Solutions for Environmental Sustainability and Medicine

Spider dragline, lacewing egg stalk and mussel byssus: three extraordinary protein fibers with similar sequence motifs but widely differing mechanical properties and a wealth of potential uses as biomaterials.

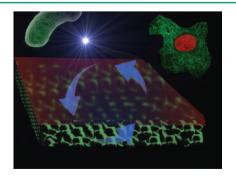


#### **Fibers**

E. S. Lintz, T. R. Scheibel\*.....4467–4482

Dragline, Egg Stalk and Byssus: A Comparison of Outstanding Protein Fibers and Their Potential for Developing New Materials

Significant advances in surface nanoarchitecture for bio-applications such as biocompatible surfaces, antifouling systems, implantation, stem cell research, organon-chip, and lab-on-chip are reviewed. The design of intelligent surfaces with both space- and time-dependent functionality requires selected materials, methodology used for nanostructuring, an active cell surface interface, patterning, drug depots in the substrate, and stimuli response (including multi-trigger response of system and self-regulation).



#### **Biosurfaces**

E. V. Skorb,\*

D. V. Andreeva ......4483-4506

Surface Nanoarchitecture for Bio-Applications: Self-Regulating Intelligent Interfaces

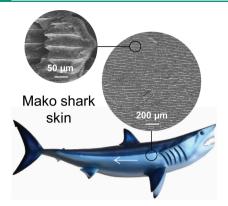
#### **FEATURE ARTICLES**

#### **Bioinspired Materials**

G. D. Bixler,

B. Bhushan\*.....4507-4528

Fluid Drag Reduction with Shark-Skin Riblet Inspired Microstructured Surfaces

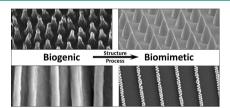


Engineering marvels found throughout living nature provide inspiration to researchers solving technical challenges. For example, the skin from fast-swimming sharks intrigues researchers because its riblet microstructure leads to low drag, self-cleaning, and antifouling properties. An overview of shark skin related studies that have been conducted in both open and closed channel flow experiments is presented. Adapted with permission.<sup>[24]</sup> Copyright 2012, Royal Society of Chemistry.

#### **Self-Assembly**

T. Kraus, D. Brodoceanu, N. Pazos-Perez, A. Fery\*......4529–4541

Colloidal Surface Assemblies: Nanotechnology Meets Bioinspiration



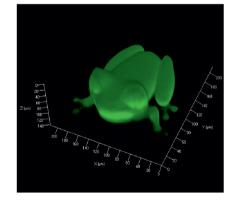
Particle-based routes to microstructure surfaces are discussed and two biomimetic approaches are reviewed: the fabrication of surface structures that are inspired by biogenic examples and the development of fabrication processes that are inspired by biological processes. Both strategies yield surfaces which mimic functional aspects of biological models or go beyond.

#### Hydrogels

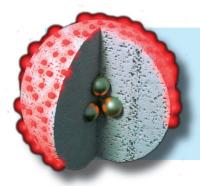
J. Torgersen,\* X.-H. Qin, Z. Li, A. Ovsianikov, R. Liska,\*

J. Stampfl\*.....4542-4554

Hydrogels for Two-Photon Polymerization: A Toolbox for Mimicking the Extracellular Matrix



Advances in the fabrication of hydrogel structures via two-photon polymerization are presented. Biocompatible synthetic and naturally derived hydrogel precursors polymerizable with water-soluble two-photon photoinitiators are discussed. Hydrogel constructs can be fabricated in situ, in the presence of cells and tissues mimicking key elements of the natural extracellular matrix. The potential of two-photon polymerization for exploring cell-cell and cell-extracellular matrix interactions is shown.



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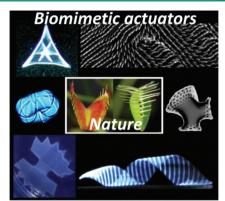
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## **FEATURE ARTICLE**

Active motion is intrinsic to many kinds of organisms and inspires development of synthetic actively moving materials. This paper discusses basic principles of design as well as recent advances in the development and applications of biomimetic hydrogel based actuating systems.

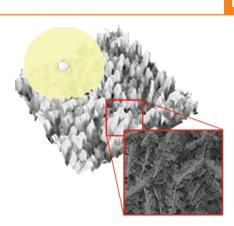


#### **Biomimetics**

L. Ionov\* ......4555-4570

Biomimetic Hydrogel-Based Actuating Systems

Single step production of bio-inspired hierarchical fluorinated wax crystalline surfaces, which exhibit superoleophobic characteristics, is reported. The marked surface roughness and re-entrant curvature, in combination with the low surface energy of the fluorinated wax, results in high contact angles of lowsurface-tension liquids and low contactangle hysteresis values.

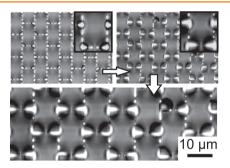


#### **FULL PAPERS**

#### Superoleophobic Materials

- S. Pechook, N. Kornblum, B. Pokroy\*.....4572-4576
- **Bio-Inspired Superoleophobic** Fluorinated Wax Crystalline Surfaces

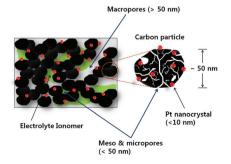
Localized patterning of hydrophilic regions on microstructured post arrays can be used to control the spatial distribution and size of water condensation droplets at the micrometer scale. The evolution of the droplet growth and coalescence is observed in situ by optical and electron microscopy. Freezing of the droplets is controlled by heterogeneous nucleation seed particles (AgI) on the post tips.



#### Micropatterning

- L. Mishchenko, M. Khan, J. Aizenberg, B. D. Hatton\*.....4577-4584
- Spatial Control of Condensation and Freezing on Superhydrophobic Surfaces with Hydrophilic Patches

Biologically inspired, kinetically controlled synthesis is used to develop a new family of nanocrystalline Pt-based catalytic electrodes. A novel carboncarbon composite of carbon black and multiwall carbon nanotubes is formed for the control of mesoscale morphology and used as the matrix for nucleation and growth of nanocrystalline Pt, providing access to new combinations of porosity, conductivity and electrochemical hydrogen oxidation.



#### **Fuel Cells**

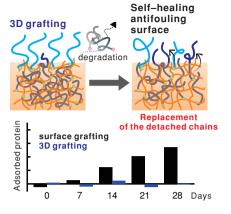
- C. S. Kong, H.-L. Zhang, F. Somodi, D. E. Morse\*.....4585-4592
- Bio-Inspired Synthesis of High-**Performance Nanocomposite Catalysts** for Hydrogen Oxidation

#### **FULL PAPERS**

#### **Stimuli-Responsive Materials**

H. Kuroki, I. Tokarev, D. Nykypanchuk, E. Zhulina, S. Minko\* ........4593–4600

Stimuli-Responsive Materials with Self-Healing Antifouling Surface via 3D Polymer Grafting

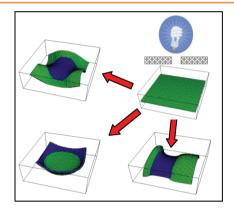


The self-healing long-lasting antifouling coating is developed using 3D polymer-grafting when antifouling polymers are grafted to the surface and inside the polymer network film. If the grafted polymers are detached from the surface in the course of aging, the antifouling effect is spontaneously recovered by the rearrangement of the internally grafted polymers at the interface. 3D grafted structures demonstrate 4-fold longer stability than 2D surface grafting.

#### **Polymer Gels**

O. Kuksenok, A. C. Balazs\*......4601–4610

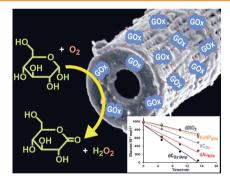
Modeling the Photoinduced Reconfiguration and Directed Motion of Polymer Gels



Computer simulations of polymer gels containing spirobenzopyran chromophores show that these materials can undergo both 3D shape changes and directed motion under non-uniform illumination. By illuminating the samples through photomasks, these gels can be molded remotely and reversibly into a variety of shapes. Furthermore, repeated motion of light in a specific direction results in the directed motion of the samples.

#### **Biocatalysis**

Rapid Flow-Through Biocatalysis with High Surface Area, Enzyme-Loaded Carbon and Gold-Bearing Diatom Frustule Replicas

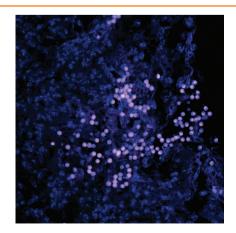


Electrically conductive microparticles possessing the hollow, hierarchically-porous architectures of diatom frustules can be attractive as enzyme supports. Freestanding, high-specific-surface-area carbon and gold-bearing frustule replicas (generated via shape-preserving conversion of diatom silica) functionalized with a high loading of glucose oxidase (GOx) exhibit rates of flow-through catalysis more than 80% greater than for GOx-bearing carbon black and gold nanoparticles.

#### **Immunotherapy**

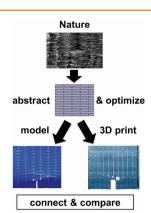
O. A. Ali, P. Tayalia, D. Shvartsman, S. Lewin, D. J. Mooney\* .....4621–4628

Inflammatory Cytokines Presented from Polymer Matrices Differentially Generate and Activate DCs In Situ



Macroporous poly(lactide-co-glycolide) (PLG) matrices mimic inflammatory environments by producing gradients of inflammatory cytokines. Controlled, in vivo presentation of GM-CSF, Flt3L, and CCl20 recruits a unique distribution of dendritic cells (DCs) that infiltrate the pores of the PLG extracellular matrix. The coordination of cell mobilization caused by these systems may be exploited for the design of vaccines and other immunotherapies.

Tough composites with bioinspired topologies and microscale features are designed, 3D printed and mechanically tested. Discrete simulation methods are used to identify fracture resistant composite topologies. Subsequently, additive manufacturing is used for rapid fabrication of the computationally conceived composites. In agreement with the simulation predictions the 3D printed composites exhibit fracture resistance far superior to their individual constituents.



### **FULL PAPER**

#### **Composites**

L. S. Dimas, G. H. Bratzel, I. Eylon, M. J. Buehler\* ......4629–4638

Tough Composites Inspired by Mineralized Natural Materials: Computation, 3D printing, and Testing