

ADVANCED FUNCTIONAL MATERIALS

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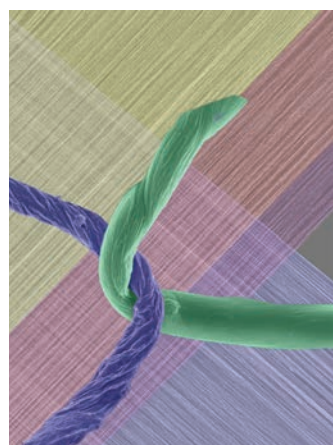
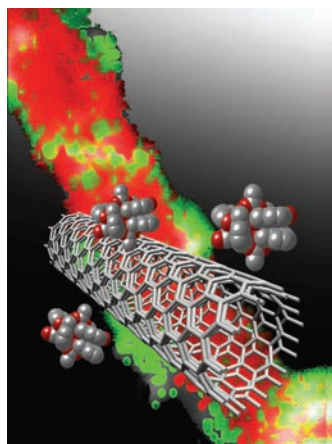


Zeolites

On page 916 Javier Pérez-Ramírez and co-workers establish different routes to prepare mesoporous Y and USY zeolites. Strategic combinations of optimized acid and base treatments, designed to steer clear of obstacles such as amorphization, pore blockage, and re-lumination, form a treasure map leading to modified zeolites with a high potential in adsorption and catalytic applications. Marcel Reich is gratefully acknowledged for the cover illustration.

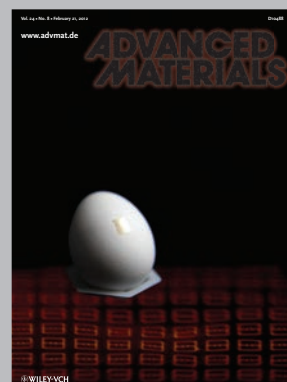
Single-Molecule Magnets

Attractive electrostatic interactions enable the grafting of cationic single-molecule magnets (SMMs) to the surface of chemically modified anionic multi-walled carbon nanotubes. As reported on page 979 by Eugenio Coronado, Carlos Martí-Gastaldo, and co-workers, physical measurements indicate that the chemical nature of the SMM unit remains intact, whereas its magnetic response is significantly affected by the grafting process, likely due to surface effects.



Carbon Nanotubes

Free-standing sheets made of aligned nitrogen-doped carbon nanotubes (CN_x) are reported on page 1069 by Xavier Lepró and co-workers. Similar to undoped carbon nanotubes (CNTs), such sheets can be twisted into strong, weavable, sewable, and knottable CN_x yarns without requiring the addition of CNT sheets to confine unaligned CN_x material. These yarns exhibit catalytic activity and larger capacitances than typical twist-spun CNT yarns.



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FEATURE ARTICLE

Surface Functionalization

A. Krueger,* D. Lang890–906

Functionality is Key: Recent Progress in the Surface Modification of Nanodiamond



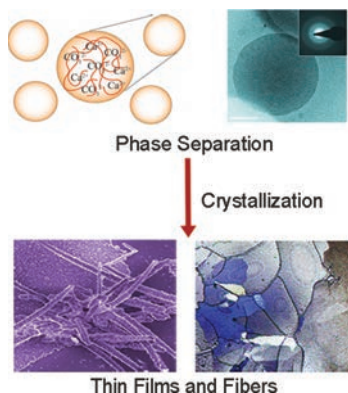
Surface chemistry on nanodiamond has developed into a field in its own right in recent years. The large variety of possible functionalization reactions on the surface of this purportedly inert material is presented. These modifications enable the application of nanodiamond in areas such as bioimaging, composites, or quantum engineering.

FULL PAPERS

Biomimetics

B. Cantaert, Y.-Y. Kim, H. Ludwig, F. Nudelman, N. A. J. M. Sommerdijk, F. C. Meldrum*907–915

Think Positive: Phase Separation Enables a Positively Charged Additive to Induce Dramatic Changes in Calcium Carbonate Morphology

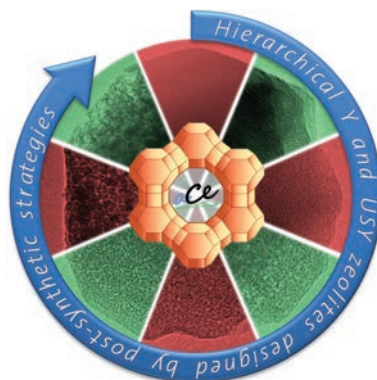


Taking inspiration from biomineralization, acidic additives are widely used to control calcium carbonate precipitation. It is shown that the positively charged additive poly(allylamine hydrochloride) (PAH) is also highly effective and it can direct the growth of thin films and fibers of CaCO_3 . These results are attributed to microphase separation of PAH in the presence of carbonate ions.

Zeolite Catalysts

D. Verboekend, G. Vilé, J. Pérez-Ramírez*916–928

Hierarchical Y and USY Zeolites Designed by Post-Synthetic Strategies

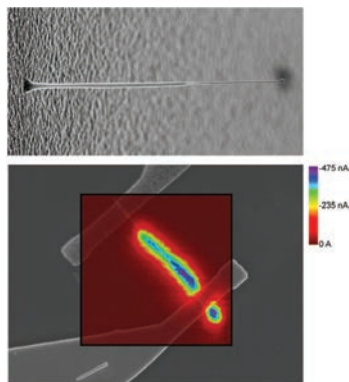


Strategic combinations of acid and base treatments to design a broad family of hierarchical Y and USY zeolites are presented. The selection of different starting zeolites combined with a comprehensive set of post-synthetic modifications enables the substantiation of the contradictory relationship between the sensitive FAU framework and its high Al content. The sorption and catalytic properties of the hierarchical Y and USY zeolites are superior compared to their conventional counterparts.

Nanowires

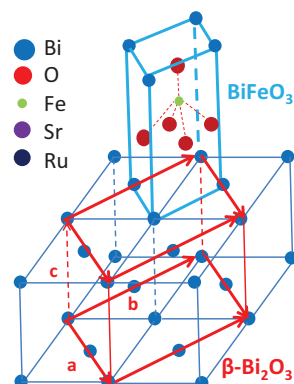
C. Gutsche,* A. Lysov, D. Braam, I. Regolin, G. Keller, Z.-A. Li, M. Geller, M. Spasova, W. Prost, F.-J. Tegude929–936

n-GaAs/InGaP/p-GaAs Core-Multishell Nanowire Diodes for Efficient Light-to-Current Conversion



Scanning photocurrent spectroscopy is used to study the photovoltaic response of single heterostructure n-GaAs/InGaP/p-GaAs core-multishell nanowire diodes. The proposed structure allows a selective wet etching of the individual shells and therefore a simple fabrication process. On the basis of a systematic characterization, good optoelectronic properties are demonstrated.

A tetragonal BiFeO_3 phase with a giant c/a ratio is successfully developed on SrTiO_3 substrates with low compressive misfit strain. It is demonstrated that the parasitic $\beta\text{-Bi}_2\text{O}_3$ phase plays a critically important role in inducing the formation of the super-tetragonal BiFeO_3 phase on SrTiO_3 substrates, providing a new route that does not involve strain engineering.

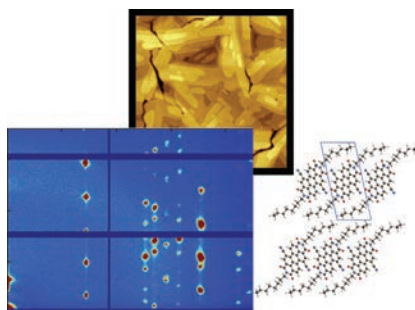


Ferroelectric Materials

H. Liu, P. Yang, K. Yao, K. P. Ong, P. Wu, J. Wang*937–942

Origin of a Tetragonal BiFeO_3 Phase with a Giant c/a Ratio on SrTiO_3 Substrates

A multiscale investigation of N, N' -bis(n -octyl)- x,y -dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI8-CN2) shows the same molecular arrangement in the bulk and in thin films sublimated on SiO_2/Si wafers. A complete structural determination and morphological studies disclose the growth mechanisms occurring at different deposition temperatures, which appear to be highly correlated with the trend of the electrical parameters that are measured in PDI8-CN2-based field-effect transistors.

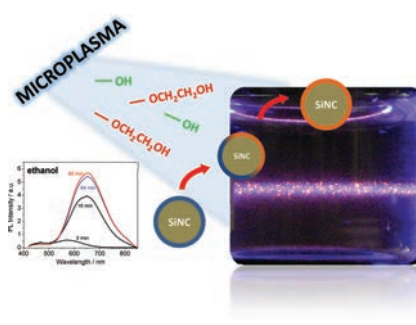


Organic Electronics

F. Liscio, S. Milita,* C. Albonetti, P. D'Angelo, A. Guagliardi, N. Masciocchi, R. G. Della Valle, E. Venuti, A. Brillante, F. Biscarini943–953

Structure and Morphology of PDI8-CN2 for n-Type Thin-Film Transistors

Surface engineering of silicon nanocrystals directly in water or ethanol by an atmospheric-pressure dc microplasma is reported. Microplasma processing stabilizes the optoelectronic properties of silicon nanocrystals that remain stable after several days of storage. The microplasma treatment in ethanol drastically enhances the silicon nanocrystals' photoluminescence intensity and causes a red-shift of the photoluminescence maximum.

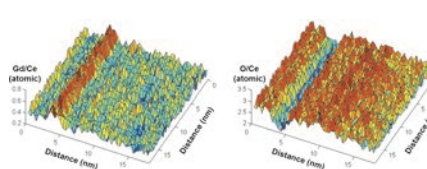


Quantum Dots

D. Mariotti,* V. Švrček, J. W. J. Hamilton, M. Schmidt, M. Kondo954–964

Silicon Nanocrystals in Liquid Media: Optical Properties and Surface Stabilization by Microplasma-Induced Non-Equilibrium Liquid Chemistry

3D concentration ratio maps of Gd/Ce and O/Ce near grain boundaries of gadolinia-doped ceria are acquired using energy dispersive spectroscopy in scanning transmission electron microscopy. The higher concentration of oxide ion vacancies at grain boundaries facilitates the oxygen surface exchange.



Fuel Cells

W. Lee,* H. J. Jung, M. H. Lee, Y.-B. Kim, J. S. Park, R. Sinclair, F. B. Prinz965–971

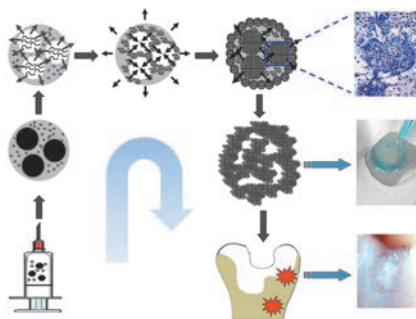
Oxygen Surface Exchange at Grain Boundaries of Oxide Ion Conductors

FULL PAPERS

Biomaterials

K. Su, T. T. Lau, W. Leong, Y. H. Gong,
D.-A. Wang*972–978

Creating a Living Hyaline Cartilage Graft Free from Non-Cartilaginous Constituents: An Intermediate Role of a Biomaterial Scaffold

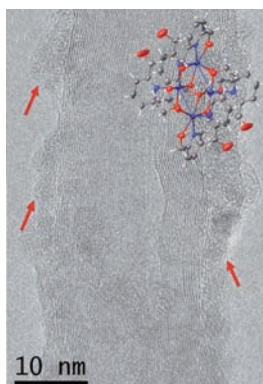


The living hyaline cartilage graft (LhCG) fabrication process is studied. The micro-tissues undergoing phase transfer cell culture (PTCC) interact and secrete extracellular matrices (ECMs), forming an intricate interpenetrating network of ECM within the hydrogel scaffold. With the removal of the alginate scaffold, the structural integrity of the construct remains intact and a pure, scaffold-free LhCG is formed that is ready for implantation.

Carbon Nanotubes

C. Bosch-Navarro, E. Coronado,*
C. Martí-Gastaldo,*
B. Rodríguez-González,
L. M. Liz-Marzán979–988

Electrostatic Anchoring of Mn_4 Single-Molecule Magnets onto Chemically Modified Multiwalled Carbon Nanotubes

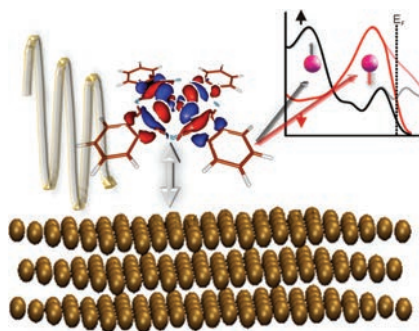


Two different routes that enable the electrostatic grafting of cationic single-molecule magnets (SMMs) onto the surface of chemically modified anionic multiwalled carbon nanotubes (MWNTs) are described. The chemical nature and physical properties of the resulting hybrids are discussed on the basis of the experimental techniques. The chemical nature of the SMM unit remains intact, while its magnetic response is significantly affected by the grafting process.

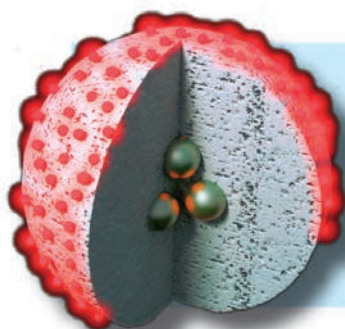
Organic Electronics

S. Lach,* A. Altenhof, K. Tarafder,
F. Schmitt, E. Ali, M. Vogel, J. Sauther,
P. M. Oppeneier, Ch. Ziegler989–997

Metal–Organic Hybrid Interface States of A Ferromagnet/Organic Semiconductor Hybrid Junction as Basis For Engineering Spin Injection in Organic Spintronics



Metal–organic open-shell molecules such as transition metal phthalocyanines (MPc) chemisorb on ferromagnetic surfaces and form hybrid interface states involving electronic states from the molecule and the substrate. These interface states are often spin-split and thus can act as a spin-filter. Shown is the CuPc semi-occupied orbital (SOMO) with its $d_{x^2-y^2}$ character chemisorbed on Co(001) and corresponding spin-resolved photoemission data with high spin-down polarization directly at the Fermi level E_F .



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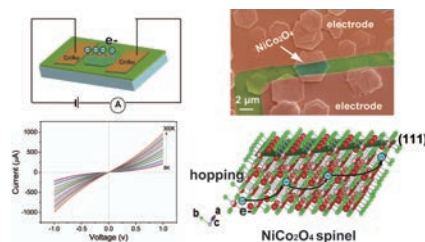
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Micrometer-sized NiCo_2O_4 platelets are prepared from their corresponding hydroxide precursor. Then, the electrical transport within an individual NiCo_2O_4 nanoplate is investigated. The mechanisms of electrical conduction in the low-temperature range ($T < 100$ K) can be explained in terms of the Mott's variable-range hopping model. At high temperatures ($T > 100$ K), both the variable-range hopping and nearest-neighbor hopping mechanisms contribute to the electrical transport properties of the NiCo_2O_4 nanoplate.

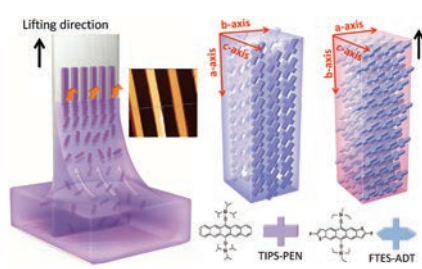


Nanostructures

L. F. Hu, L. M. Wu,* M. Y. Liao,
X. H. Hu, X. S. Fang*998–1004

Electrical Transport Properties of Large, Individual NiCo_2O_4 Nanoplates

Self-aligning, highly crystalline, uniform soluble acene crystal arrays are facilely grown via an optimized one-step dip-coating process. The optimized crystals grow only at a particular substrate lifting-rate in the presence of low boiling point solvents. This is because the rate of input/output flows at the contact line is well-balanced with the optimal substrate lifting rate. The study provides a simple and reproducible method for creating high-performance uniform organic semiconductor thin films over large areas of substrates with a variety of geometries.

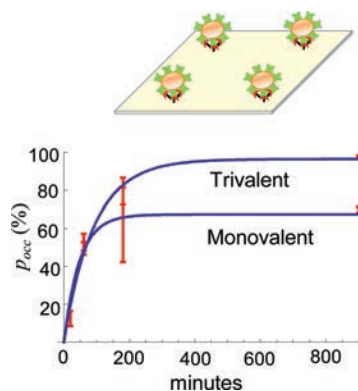


Organic Electronics

J. Jang, S. Nam, K. Im, J. Hur, S. N. Cha,
J. Kim, H. B. Son, H. Suh, M. A. Loth,
J. E. Anthony, J.-J. Park,* C. E. Park,*
J. M. Kim,* K. Kim1005–1014

Highly Crystalline Soluble Acene Crystal Arrays for Organic Transistors: Mechanism of Crystal Growth During Dip-Coating

Nanopatterns of quantum dots are generated on DNA origami with molecular precision. The quantitative studies of their binding kinetics show that the yield can be greatly improved by controlling many factors including the valency of the binding location, the biotin linker length, and the organization and spacing of the binding locations on the DNA.

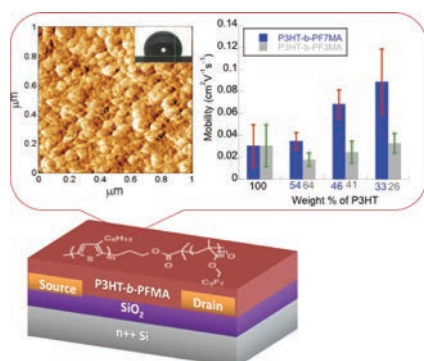


Nanopatterns

S. H. Ko, G.M. Gallatin,
J. A. Liddle*1015–1023

Nanomanufacturing with DNA Origami: Factors Affecting the Kinetics and Yield of Quantum Dot Binding

The attachment of a semifluorinated block can significantly improve upon the charge carrier properties of regioregular poly(3-hexyl thiophene) (P3HT) on bare SiO_2 . The mobilities of poly(3-hexyl thiophene)-*block*-polyfluoromethacrylates can approach up to $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with only 33 wt% of the P3HT block incorporated in the copolymer.



Semiconductors

J. Liu, D. Haynes, C. Balliet,
R. Zhang, T. Kowalewski,
R. D. McCullough*1024–1032

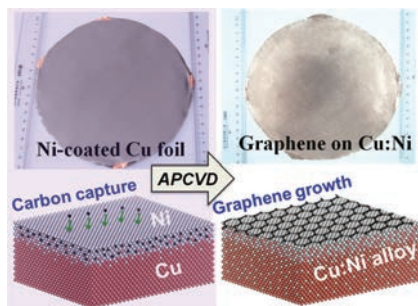
Self Encapsulated Poly(3-hexylthiophene)-poly(fluorinated alkyl methacrylate) Rod-Coil Block Copolymers with High Field Effect Mobilities on Bare SiO_2

FULL PAPERS

Graphene

D. Y. Wan, T. Q. Lin, H. Bi,
F. Q. Huang,* X. M. Xie, I.-W. Chen,
M. H. Jiang1033–1039

Autonomously Controlled Homogeneous Growth of Wafer-Sized High-Quality Graphene via a Smart Janus Substrate

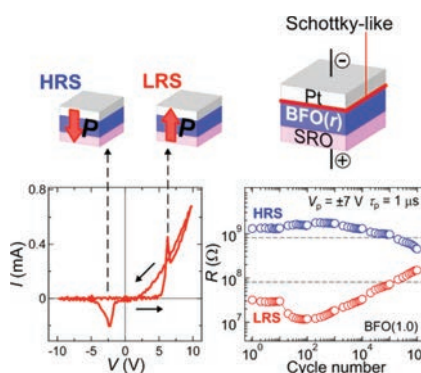


Homogenous growth of wafer-sized high-quality graphene is autonomously controlled by a novel substrate design in which a “smart” composite substrate with a self-evolving composition autonomously regulates the carbon content. The processing temperature spans from 1000 °C to 650 °C, the graphene layer number can be tuned from one to five, and the transparent conductive properties exceed the best reported for large-area graphenes.

Ferroics

A. Tsurumaki,* H. Yamada,
A. Sawa*1040–1047

Impact of Bi Deficiencies on Ferroelectric Resistive Switching Characteristics Observed at p-Type Schottky-Like Pt/Bi_{1-x}FeO₃ Interfaces

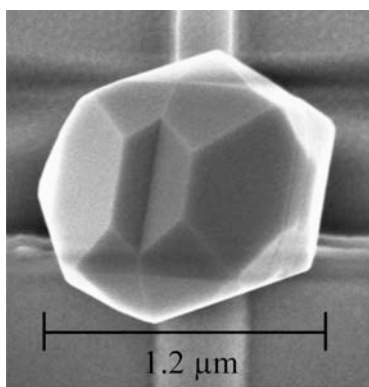


p-type Schottky-like Pt/BiFeO₃ interfaces show a bipolar-type resistive switching effect. A non-volatile resistive switching effect at Pt/BiFeO₃ interfaces induced by ferroelectric polarization reversal is reported. The devices show promising characteristics for use as non-volatile memories such as stable resistive switching without the need for any forming process, data retention of >10⁵ s at room temperature, and endurance of >10⁵ cycles.

Semiconductors

K. A. McComber, X. Duan, J. Liu,
J. Michel,* L. C. Kimerling...1049–1057

Single-Crystal Germanium Growth on Amorphous Silicon

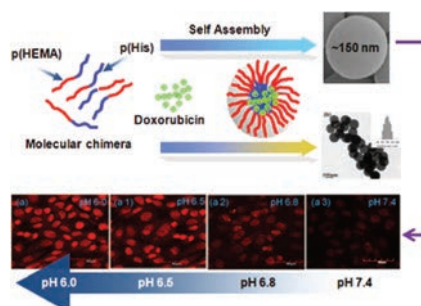


A method for the growth of single-crystal germanium on amorphous silicon by ultrahigh vacuum chemical vapor deposition at temperatures not exceeding 450 °C is presented. Growths proceed through constrictive channels and emerge with improved properties compared to as-deposited germanium. A description is given of the growth mechanism and its implications for design of the growth structure.

Biomedical Applications

R. P. Johnson, Y.-I. Jeong, E. Choi,
C.-W. Chung, D. H. Kang, S.-O. Oh,
H. Suh, I. Kim*1058–1068

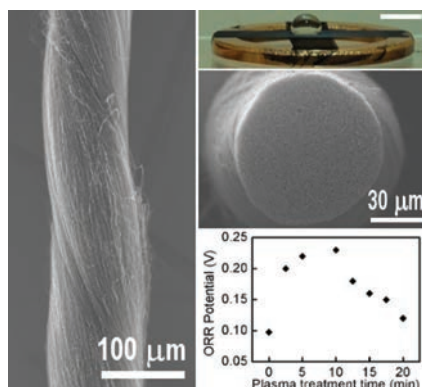
Biocompatible Poly(2-hydroxyethyl methacrylate)-*b*-poly(L-histidine) Hybrid Materials for pH-Sensitive Intracellular Anticancer Drug Delivery



Uniform nanomicelles are fabricated via self-assembly of a series of biocompatible poly(2-hydroxyethyl methacrylate)-*block*-poly(L-histidine) hybrid materials. They are shown to be a suitable carrier for the pH-sensitive delivery of doxorubicin.

FULL PAPERS

Weavable, sewable, and knottable yarns of N-doped nanotubes are fabricated by twist insertion into plasma-treated, free-standing sheets of oriented multiwalled carbon nanotubes. These yarns exhibit high specific strengths, large capacitances, and tunable catalytic activity for electrochemically driven oxygen reduction reactions. Catalytic activity as a function of processing conditions is correlated with nitrogen chemical species.

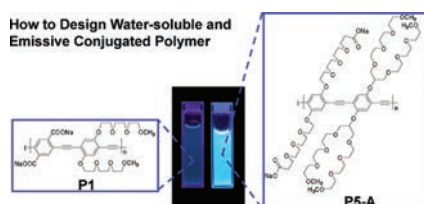


Carbon Nanotubes

X. Lepró,* R. Ovalle-Robles, M. D. Lima, A. L. Elías, M. Terrones, R. H. Baughman1069–1075

Catalytic Twist-Spun Yarns of Nitrogen-Doped Carbon Nanotubes

The correlation between the molecular design of conjugated polyelectrolytes (CPEs) and their solubility and emissive properties in water is systematically investigated by means of UV-vis and fluorescence spectroscopy and electron microscopy. Bulky and hydrophilic side chains and spacers are required to achieve complete water solubility and high quantum yield of CPEs in water, providing an important molecular design principle to develop functional CPEs.

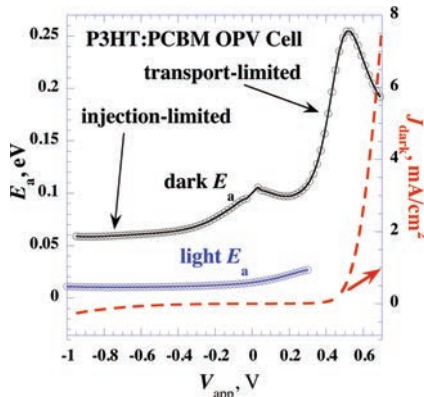


Sensors

K. Lee, H.-J. Kim, J. Kim*1076–1086

Design Principle of Conjugated Polyelectrolytes to Make Them Water-Soluble and Highly Emissive

Dark current and photocurrent activation energy spectra are measured for two types of poly(3-hexylthiophene) in pure films, films blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), and in bulk heterojunction organic photovoltaic cells. The cells show an unexpected transport limitation near the open circuit photovoltage. The results support a model of transport that combines the influence of short-range energetic disorder with long-range Coulomb fields from charged defects.

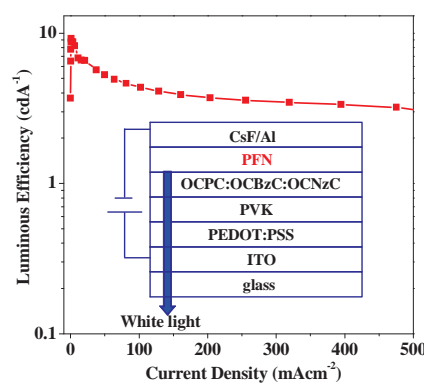


Photovoltaic Devices

Z. Liang, A. M. Nardes, J. van de Lagemaat, B. A. Gregg*1087–1091

Activation Energy Spectra: Insights into Transport Limitations of Organic Semiconductors and Photovoltaic Cells

Fully solution-processed fluorescent small-molecule white organic light-emitting diodes (WOLEDs) are fabricated. The methanol/water soluble conjugated polymer (PFN), as the electron-injection layer (EIL) material, plays a key role in the improvement of the device performance for solution-processed small-molecule-based WOLEDs. A high efficiency is obtained. The performance is the best ever reported for solution-processed fluorescent small-molecule WOLEDs using fully solution-processed techniques.



Light-Emitting Diodes

S. F. Xue, L. Yao, F. Z. Shen, C. Gu, H. B. Wu, Y. G. Ma*1092–1097

Highly Efficient and Fully Solution-Processed White Electroluminescence Based on Fluorescent Small Molecules and a Polar Conjugated Polymer as the Electron-Injection Material