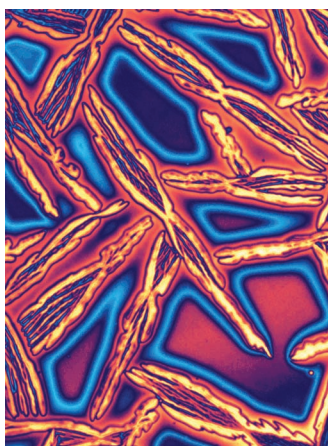


ADVANCED FUNCTIONAL MATERIALS

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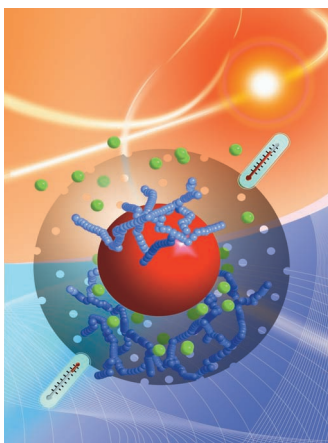


Solar Cells

On page 1399, Tao Wang, David G. Lidzey, and co-workers characterize the nanostructure of poly-[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT):(6,6)-phenyl C₇₀-butyric acid methyl ester (PC₇₀BM) bulk heterojunction (BHJ) solar cells upon thermal annealing using a optical probes including grazing incidence wide-angle X-ray scattering, spectroscopic ellipsometry, and photoluminescence spectroscopy. The measurements allow the film nanostructure to be correlated with both charge-carrier mobility and the performance of a photovoltaic device.

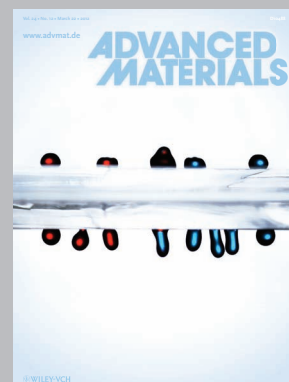
Stimuli-Responsive Materials

As reported by Munish Chanana, Luis M. Liz-Marzán, and co-workers on page 1436, dual-responsive gold nanoparticles exhibit fully reversible thermoresponsive and pH-sensitive optical and physicochemical properties. This occurs due to the pH-sensitive protein coating grafted with thermosensitive polymer brushes.



Drug Delivery

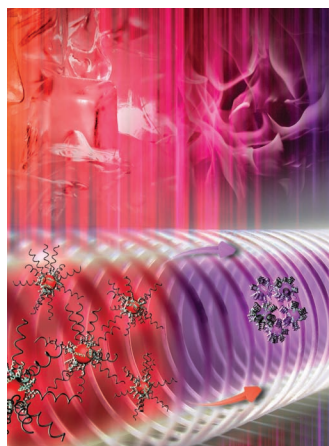
Multifunctional rattle-type microspheres integrating the advantages of being mesoporous, luminescent, and temperature responsive into one single entity are fabricated. As reported by Ziyong Cheng, Jun Lin, and co-workers on page 1470, the composite shows red emission and can potentially be applied as a spin-lattice relaxation time (T_1)-positive contrast agent due to the Gd₂O₃:Eu³⁺ core. The rate of drug release can be regulated via a change in temperature due to controlled switching of the hydrogel.



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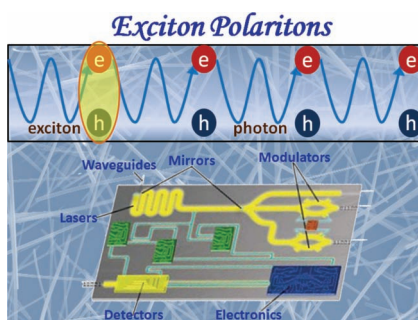
www.small-journal.com

HIGHLIGHT

Photonics

Y. Yan, Y. S. Zhao*1330–1332

Exciton Polaritons in 1D Organic Nanocrystals



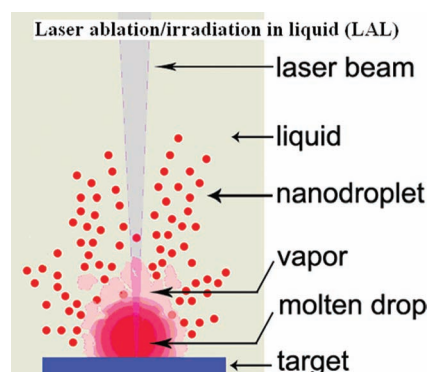
Nanophotonic circuits meet exciton polaritons (EPs) in organic nanomaterials: Great possibilities for the use of organic 1D crystalline nanostructures as building blocks are emerging. These remarkable studies will contribute significantly to the development of EP-based on-chip photonic devices in the near future.

FEATURE ARTICLES

Nanomaterials

H. B. Zeng,* X.-W. Du,* S. C. Singh,*
S. A. Kulinich,* S. K. Yang, J. P. He,
W. P. Cai1333–1353

Nanomaterials via Laser Ablation/Irradiation in Liquid: A Review

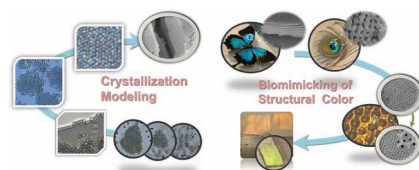


Laser ablation of solid targets in liquid medium has been elaborately developed to prepare nanomaterials with special morphologies and microstructures, as well as to achieve one-step functionalization. The synthetic strategies based on laser ablation in liquid (LAL) are summarized and nanostructures derived from the peculiarity of LAL are highlighted along with a review of their applications and future challenges.

Colloids

Y. Y. Diao, X. Y. Liu*1354–1375

Controlled Colloidal Assembly: Experimental Modeling of General Crystallization and Biomimicking of Structural Color



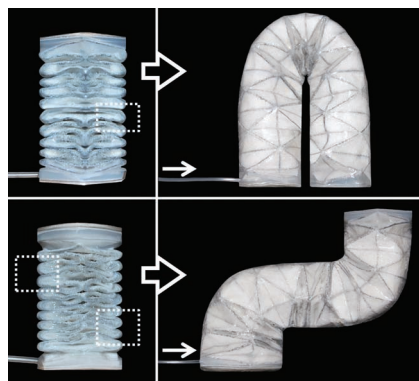
As a unique and new modeling approach, electrically controlled colloidal assembly enables the acquisition of comprehensive knowledge about nucleation, surface/kink kinetics, and crystal growth at the single growth unit level that has never been acquired before. In practical applications, colloidal crystallization can be adopted to produce structural colors on silk fabrics.

FULL PAPER

Composite Materials

R. V. Martinez, C. R. Fish, X. Chen,
G. M. Whitesides*1376–1384

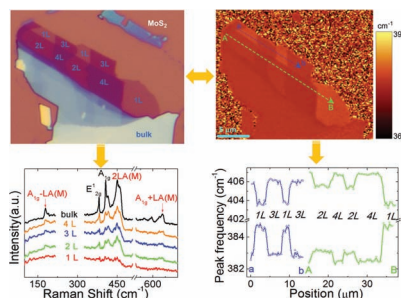
Elastomeric Origami: Programmable Paper-Elastomer Composites as Pneumatic Actuators



Soft pneumatic actuators based on composites consisting of elastomers with embedded sheet or fiber structures that are flexible but not extensible combine soft lithography, for fabrication, with the principles of origami, for structural design. These actuators respond to pressurization with a wide range of motions, such as bending, extension, contraction, and twisting.

FULL PAPERS

Raman frequencies of E_{2g}^1 and A_{1g} peaks can be used to identify the layer number of ultrathin molybdenum disulfide (MoS_2) flakes. The systematic Raman characterizations using various laser lines suggest a clear evolution of the coupling between the electronic transition and phonon when MoS_2 is scaled down from three- to two-dimensional geometry.

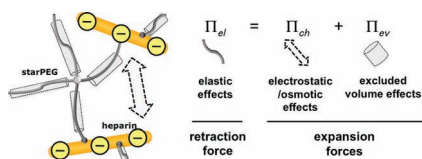


Layered Materials

H. Li, Q. Zhang,* C. C. R. Yap,
B. K. Tay,* T. H. T. Edwin,
A. Olivier, D. Baillargeat 1385–1390

From Bulk to Monolayer MoS_2 :
Evolution of Raman Scattering

A mean field approach is applied to develop extracellular matrix (ECM)-inspired biohybrid hydrogels that allow for the independent variation of physical and biomolecular properties. Using this material, multiple combinations of matrix parameters are identified to effectively stimulate morphogenesis of human endothelial cells and differentiation of human mesenchymal stem cells.

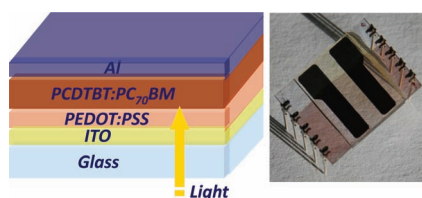


Hydrogels

U. Freudenberg, J.-U. Sommer,*
K. R. Levental, P. B. Welzel, A. Zieris,
K. Chwalek, K. Schneider, S. Prokoph,
M. Prewitz, R. Dockhorn,
C. Werner* 1391–1398

Using Mean Field Theory to Guide
Biofunctional Materials Design

In poly[N-9'-heptadecan-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT):(6,6)-phenyl C_{70} -butyric acid methyl ester (PC_{70}BM) photovoltaic thin-films, the glass transition temperature is not sensitive to the relative blend-ratio or film thickness, but is sensitive to thermal treatment, casting solvent, and substrate. The π - π stacking between PCDTBT reduces upon thermal annealing, an observation that is correlated with reduced hole-mobility in thermally annealed devices. Coarse phase-separation in PCDTBT: PC_{70}BM occurs upon annealing at or above 155 °C.

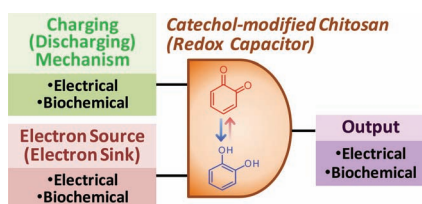


Solar Cells

T. Wang,* A. J. Pearson, A. D. F. Dunbar,
P. A. Staniec, D. C. Watters, H. Yi,
A. J. Ryan, R. A. L. Jones, A. Iraqi,
D. G. Lidzey* 1399–1408

Correlating Structure with Function in
Thermally Annealed PCDTBT: PC_{70}BM
Photovoltaic Blends

Catechol-modified-chitosan films are redox-active and can exist in oxidized or reduced states. These films can be reductively charged either electrochemically or enzymatically by mediated redox-cycling reactions. Oxidative-discharging is achieved by electrochemical mediator redox-cycling or by donating electrons to O_2 to generate a substrate (H_2O_2) for subsequent enzymatic (peroxidase) reactions. Thus, these films can inter-convert electrochemical and biochemical inputs/outputs.



Biomedical Applications

E. Kim, Y. Liu, W. E. Bentley,
G. F. Payne* 1409–1416

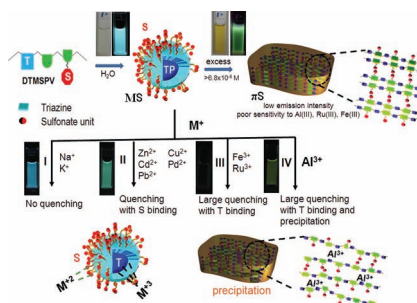
Redox Capacitor to Establish Bio-Device
Redox-Connectivity

FULL PAPERS

Self-Assembly

J. You, J. Kim, T. Park, B. Kim,
E. Kim*1417–1424

Highly Fluorescent Conjugated Polyelectrolyte Nanostructures: Synthesis, Self-Assembly, and Al^{3+} Ion Sensing

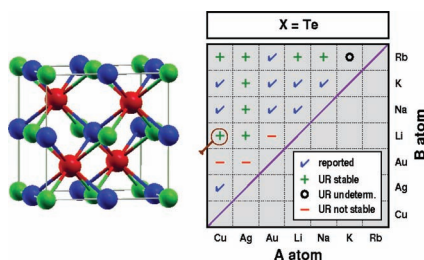


A highly fluorescent conjugated polyelectrolyte (DTMSPV) with high fluorescence quantum yield is synthesized for Al^{3+} sensing in aqueous solutions. The DTMSPV with dual metal binding sites is self-assembled into stable fluorescent nanostructures in aqueous solution. DTMSPV micelle-like structure (DTMSPV-MS) is sensitive and selective to Al^{3+} , showing a color change from blue to yellow. Al^{3+} in water is easily eliminated by filtration of precipitates formed by the complexation of the triazine units of the polymer and Al^{3+} .

Electronic Structure

X. Zhang, L. Yu, A. Zakutayev,
A. Zunger*1425–1435

Sorting Stable versus Unstable Hypothetical Compounds: The Case of Multi-Functional ABX Half-Heusler Filled Tetrahedral Structures

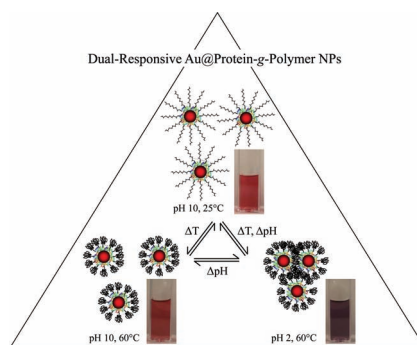


First-principles thermodynamics is used to determine the lowest-energy structures and stability with respect to decomposition of 488 hypothetical ABX Half-Heusler compounds from the groups I–I–VI, I–II–V, I–III–IV, II–II–IV and it is found that 235 are unstable against decomposition and 18 are too close to determine. 235 other unreported (UR) compounds are predicted to be new stable phases. The electronic structures of these predicted new compounds are evaluated, seeking potential new material functionalities.

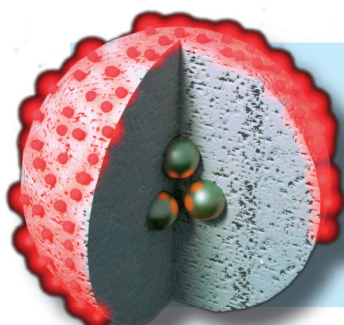
Nanoparticles

M. S. Strozyk, M. Chanana,*
I. Pastoriza-Santos, J. Pérez-Juste,
L. M. Liz-Marzán*1436–1444

Protein/Polymer-Based Dual-Responsive Gold Nanoparticles with pH-Dependent Thermal Sensitivity



Protein-coated gold nanoparticles (NPs) grafted with thermosensitive polymer brushes behave as truly smart dual-responsive materials. Proteins are naturally pH-sensitive and confer reversible U-shaped pH-responsive properties to the particles, whereas polymer brushes of oligo(ethylene glycol) methacrylates grafted by means of surface-initiated atom transfer radical polymerization add fully reversible thermoresponsive properties to the nanoparticles. Such Au@protein-g-polymer NPs exhibit pH-dependent thermoresponsive behavior with reversible optical properties.



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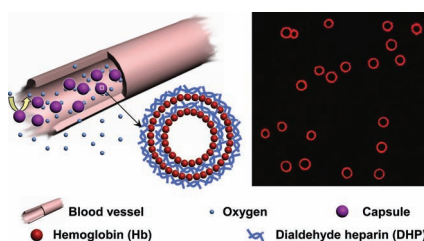
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FULL PAPERS

Biocompatible, biodegradable, and blood-compatible hemoglobin-based microcapsules used as blood substitutes are successfully fabricated by covalent layer-by-layer assembly. Given the advantages of the layer-by-layer assembly technique, the construction and behavior of these hemoglobin-based capsules are controllable and adjustable, which makes the obtained capsules promising candidates for applications as blood substitutes, oxygen carriers, and in other biomedical fields.

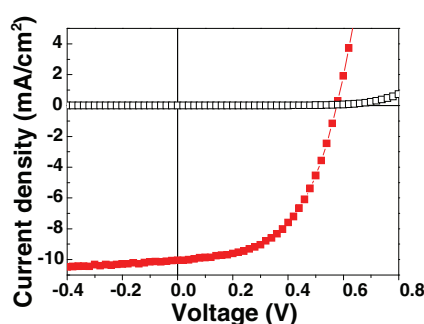


Biomedical Applications

Y. Jia, Y. Cui, J. B. Fei, M. C. Du,
L. R. Dai, J. B. Li,*
Y. Yang* 1446–1453

Construction and Evaluation of Hemoglobin-Based Capsules as Blood Substitutes

The use of vapor phase polymerized poly(3,4-ethylenedioxythiophene) (VPP-PEDOT) as a metal anode replacement in inverted bulk heterojunction and hybrid organic/inorganic solar cells is reported. The VPP-PEDOT and a work-function enhancing PEDOT:polystyrene sulphonate (PEDOT:PSS) layer are stamp transfer printed on top of the active photogeneration layer. The resulting device performance is equivalent to that for devices made with thermally evaporated Au anodes.

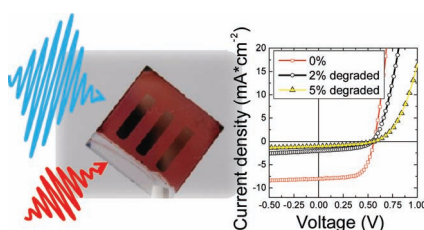


Solar Cells

X. Wang, T. Ishwara, W. Gong,
M. Campoy-Quiles, J. Nelson,*
D. D. C. Bradley* 1454–1460

High-Performance Metal-Free Solar Cells Using Stamp Transfer Printed Vapor Phase Polymerized Poly(3,4-Ethylenedioxythiophene) Top Anodes

The impact of light-induced degradation on the exciton and charge separation dynamics in the active layer of poly(3-hexylthiophene)/[6,6]-phenyl C₆₁-butyric acid methyl ester (P3HT/PCBM) organic solar cells is studied using optical pump-probe spectroscopy. The losses in excitons and polarons are quantified and compared to the degradation of solar cell performances in which the active layer has been selectively aged.

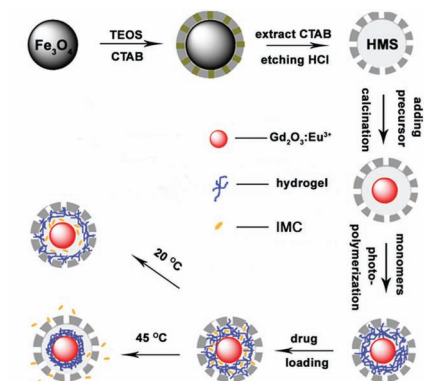


Solar Cells

F. Deschler, A. De Sio, E. von Hauff,*
P. Kutka, T. Sauermann, H.-J. Egelhaaf,
J. Hauch, E. Da Como* 1461–1469

The Effect of Ageing on Exciton Dynamics, Charge Separation, and Recombination in P3HT/PCBM Photovoltaic Blends

Hydrogel-modified luminescent rattle-type mesoporous silica microspheres are prepared. The composites have good compatibility and can act as a magnetic resonance (MR) contrast agent because of the Gd³⁺ ions. The drug release behavior is regulated via a change in temperature.



Drug Delivery

X. Kang, Z. Cheng,* D. Yang,
P. Ma, M. Shang, C. Peng,
Y. Dai, J. Lin* 1470–1481

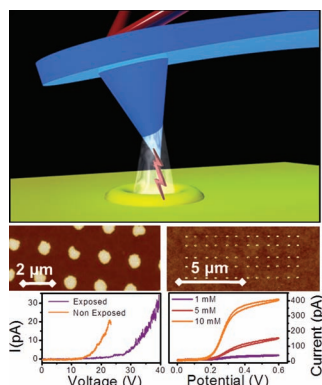
Design and Synthesis of Multifunctional Drug Carriers Based on Luminescent Rattle-Type Mesoporous Silica Microspheres with a Thermosensitive Hydrogel as a Controlled Switch

FULL PAPERS

Surface Patterning

C. Martin-Olmos, L. G. Villanueva,
P. D. van der Wal, A. Llobera,
N. F. de Rooij, J. Brugger,
F. Perez-Murano*1482–1488

Conductivity of SU-8 Thin Films through Atomic Force Microscopy Nano-Patterning

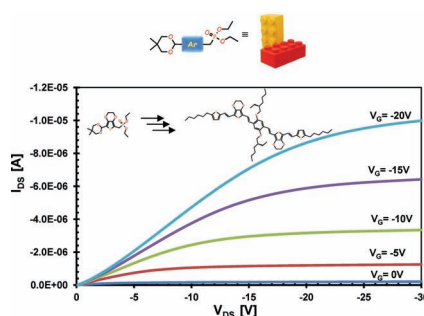


Atomic force microscopy (AFM)-based lithography of SU-8 ultrathin films and its applicability for the fabrication of nano-devices are investigated. It is shown that SU-8 presents outstanding insulating properties and extremely high dielectric strength. A physical-chemical mechanism responsible for the AFM-based patterning is proposed and the potential of this AFM nanopatterning demonstrated by the prototyping and testing of nanoelectrode arrays.

Organic Electronics

K. N. Shivananda, I. Cohen,
E. Borzin, Y. Gerchikov, M. Firstenberg,
O. Solomeshch, N. Tessler,
Y. Eichen*1489–1501

Sequence-Independent Synthesis of π -conjugated Arylenevinylene Oligomers using Bifunctional Thiophene Monomers

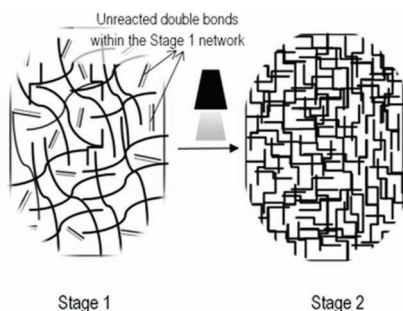


Wittig-Horner vinyl bond formation using bifunctional monomers provides an efficient, sequence-independent synthesis tool for the assembly by design and optimization according to performance (i.e., engineering) of complex π -conjugated structures.

Photochemistry

D. P. Nair, N. B. Cramer, J. C. Gaipa,
M. K. McBride, E. M. Matherly,
R. R. McLeod, R. Shandas,
C. N. Bowman*1502–1510

Two-Stage Reactive Polymer Network Forming Systems

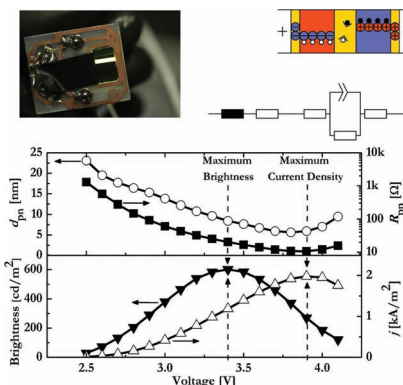


Within two-stage reactive polymer systems, the stage 1 reaction is a self-limiting “click” Michael addition between multifunctional thiols and acrylate monomers with excess of acrylate functional groups. It results in a loosely crosslinked, low modulus polymer with idealized properties for intermediate polymer processing. The stage 2 reaction is a photoinduced acrylate polymerization that rapidly achieves a highly crosslinked high modulus polymer.

Electrochemistry

A. Munar, A. Sandström, S. Tang,
L. Edman*1511–1517

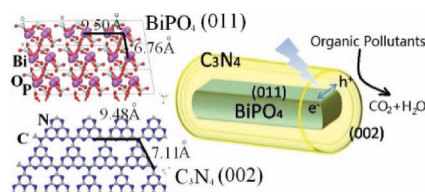
Shedding Light on the Operation of Polymer Light-Emitting Electrochemical Cells Using Impedance Spectroscopy



The formation of electric double layers (EDLs) and an emissive p-n junction in light-emitting electrochemical cells are studied. At low applied voltage, EDLs with a thickness of ≈ 2 –3 nm form at the electrode interfaces, and at voltages exceeding the bandgap potential of the emissive conjugated polymer, a light-emitting p-n junction forms in situ, with a steady-state structure that depends strongly on the applied voltage.

FULL PAPERS

A $\text{C}_3\text{N}_4/\text{BiPO}_4$ core/shell structured photocatalyst is synthesized via a facile ultrasonic dispersion method. The match of the lattice and energy levels between C_3N_4 and BiPO_4 facilitates the separation and transfer of photogenerated electron–hole pairs at the heterojunction interfaces so that it significantly enhances UV light photocatalytic activity and visible light photocatalytic activity.

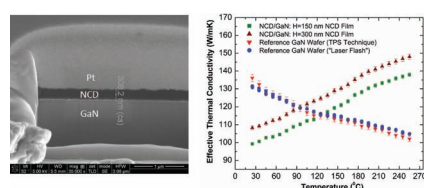


Self-Assembly

C. Pan, J. Xu, Y. Wang, D. Li, Y. F. Zhu* 1518–1524

Dramatic Activity of $\text{C}_3\text{N}_4/\text{BiPO}_4$ Photocatalyst with Core/Shell Structure Formed by Self-Assembly

A direct method to integrate nanocrystalline diamond (NCD) with gallium nitride (GaN) is demonstrated by tuning growth conditions to form nanocrystalline diamond thin films with grain sizes of 100–200 nm on GaN substrates at low temperature (450 °C), which is essential for maintaining the structural integrity of GaN. The thermal conductivity of the composite NCD/GaN wafer is higher than that of GaN substrates at temperatures characteristic for GaN electronics.

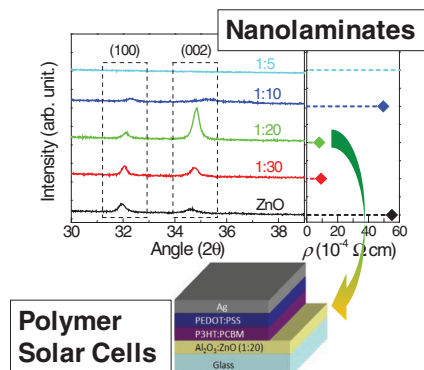


Thin Films

V. Goyal, A. V. Sumant,* D. Teweldebrhan, A. A. Balandin* 1525–1530

Direct Low-Temperature Integration of Nanocrystalline Diamond with GaN Substrates for Improved Thermal Management of High-Power Electronics

The structural, electrical, and optical properties of $\text{Al}_2\text{O}_3:\text{ZnO}(1:x)$ nanolaminates synthesized by atomic layer deposition are evaluated as a function of the relative number of cycles x . $\text{Al}_2\text{O}_3:\text{ZnO}(1:20)$ nanolaminates exhibit a seven-fold increase in electrical conductivity compared with neat ZnO films, which is attributed to changes in the crystal structure of the films and doping effects. Efficient poly(3-hexylthiophene) (P3HT):phenyl- C_{61} -butyric acid methyl ester (PCBM) polymer-based inverted solar cells utilizing $\text{Al}_2\text{O}_3:\text{ZnO}(1:20)$ nanolaminate electron-selective electrodes are demonstrated.



Solar Cells

H. Cheun, C. Fuentes-Hernandez, J. Shim, Y. Fang, Y. Cai, H. Li, A. K. Sigdel, J. Meyer, J. Maibach, A. Dindar, Y. Zhou, J. J. Berry, J.-L. Bredas, A. Kahn, K. H. Sandhage, B. Kippelen* 1531–1538

Oriented Growth of $\text{Al}_2\text{O}_3:\text{ZnO}$ Nanolaminates for Use as Electron-Selective Electrodes in Inverted Polymer Solar Cells