# **Energy & Environmental Science**

### www.rsc.org/ees

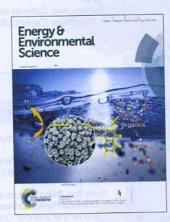
The Royal Society of Chemistry is the world's leading chemistry community. Through our high impact journals and publications we connect the world with the chemical sciences and invest the profits back into the chemistry community.

### IN THIS ISSUE

ISSN 1754-5692 CODEN EESNBY 7(3) 833-1194 (2014)



Cover
See Mitzi et al.,
pp. 1029–1036.
Image reproduced by
permission of David B. Mitzi
from Energy Environ. Sci.,
2014, 7, 1029.



Inside cover See Choi et al., pp. 954–966. Image reproduced by permission of Wonyong Choi from Energy Environ. Sci., 2014, 7, 954.

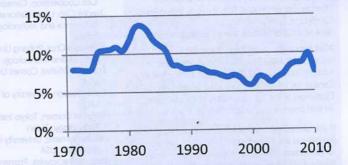
#### OPINION

846

## Solar energy: setting the economic bar from the top-down

E. W. McFarland

Sunlight is thermal radiation from sustained nuclear reactions within our sun. Our challenge is to harness this solar energy at a cost less than 10% of our GDP.



### ANALYSIS

855

## Large scale deployment of polymer solar cells on land, on sea and in the air

Nieves Espinosa, Markus Hösel, Mikkel Jørgensen and Frederik C. Krebs\*

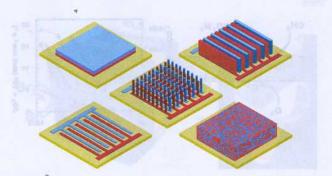
With the development of patterns that connect all cells in series, organic photovoltaics have leapt a step forward being ahead of other solar and even other energy technologies in terms of manufacturing speed, installation speed, ease of deployment and energy pay-back time.



# Capacitive energy storage in micro-scale devices: recent advances in design and fabrication of micro-supercapacitors

Majid Beidaghi and Yury Gogotsi\*

The growing field of micro-supercapacitors is reviewed in this article with a focus on electrode materials and device fabrication methods. The most promising advances and future challenges are identified.

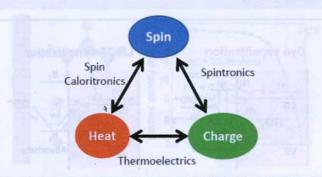


885

#### Spin caloritronics

Stephen R. Boona, Roberto C. Myers and Joseph P. Heremans\*

Spin caloritronics explores the relationship between spin and heat transport in materials. This review provides an in-depth discussion of the physical origins of these transport effects, along with a detailed description of several recent developments in this field, and an overview of some proposed thermal energy conversion applications inspired by these recent discoveries.



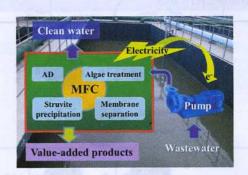
#### **PERSPECTIVES**

911

### Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies

Wen-Wei Li, Han-Qing Yu\* and Zhen He\*

Microbial fuel cells (MFCs) have been conceived and intensively studied as a promising technology to achieve sustainable wastewater treatment.

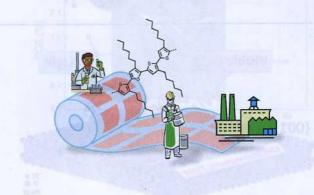


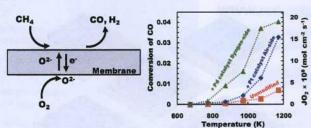
925

### From lab to fab: how must the polymer solar cell materials design change? – an industrial perspective

Riccardo Po,\* Andrea Bernardi, Anna Calabrese, Chiara Carbonera, Gianni Corso and Andrea Pellegrino

The design of materials for efficient large-area printed polymer solar modules beyond the lab-scale research is discussed.





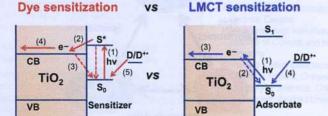
### Interfacial reactions in ceramic membrane reactors for syngas production

A. S. Yu, J. M. Vohs and R. J. Gorte\*

Limitations due to surface reactions in ceramic membrane reactors for syngas production are discussed using insights from solid oxide fuel cell research.

#### MINIREVIEW

954



Alternative way of solar activation of titania

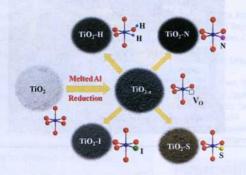
Visible light driven photocatalysis mediated *via* ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania

Guan Zhang, Gonu Kim and Wonyong Choi\*

In this mini-review we summarize the recent advances in the ligand-to-metal charge transfer (LMCT) mediated visible light photocatalysis on  ${\rm TiO_2}$  for environmental and energy applications.

#### COMMUNICATIONS

967

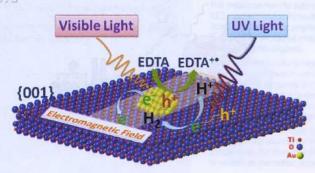


## Effective nonmetal incorporation in black titania with enhanced solar energy utilization

Tianquan Lin, Chongyin Yang, Zhou Wang, Hao Yin, Xujie Lü, Fuqiang Huang,\* Jianhua Lin, Xiaoming Xie and Mianheng Jiang

Heavy nonmetal-doped black titania with a unique crystalline core/amorphous shell structure is achieved to boost visible-light photocatalysis.

973



# Gold-plasmon enhanced solar-to-hydrogen conversion on the {001} facets of anatase TiO<sub>2</sub> nanosheets

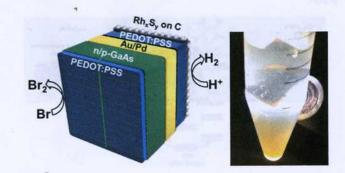
Jinlin Long,\* Hongjin Chang, Quan Gu, Jie Xu, Lizhou Fan, Shuchao Wang, Yangen Zhou, Wei Wei, Ling Huang,\* Xuxu Wang, Ping Liu and Wei Huang\*

A 64-fold improved efficiency of solar-to-hydrogen conversion was achieved via exposing Au nanoparticles on the  $\{001\}$  facets of anatase  $TiO_2$  nanosheets.

# Stable electrocatalysts for autonomous photoelectrolysis of hydrobromic acid using single-junction solar cells

N. Singh, S. Mubeen, J. Lee, H. Metiu, M. Moskovits and E. W. McFarland\*

Here we demonstrate the use of a metal sulfide catalyst to extend the lifetime of a photoelectrochemical cell for electrolysis of HBr using only sunlight.

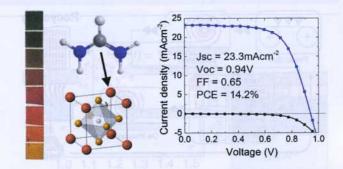


982

# Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells

Giles E. Eperon, Samuel D. Stranks, Christopher Menelaou, Michael B. Johnston, Laura M. Herz and Henry J. Snaith\*

A new perovskite, formamidinium lead trihalide, shows bandgap tunability between 2.23 eV and 1.48 eV. When incorporated into planar heterojunction perovskite solar cells, it is able to generate high short-circuit currents of >23 mA cm<sup>-2</sup>, resulting in efficiencies of up to 14.2%.

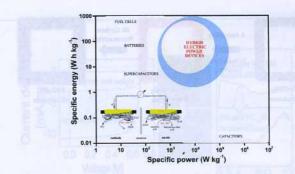


989

### A hybrid electric power device for simultaneous generation and storage of electric energy

Dmitry Pankratov, Peter Falkman, Zoltan Blum and Sergey Shleev\*

Hybrid electric power devices, simultaneously generating electric power and capacitively storing electric energy within a singular contrivance, were fabricated.

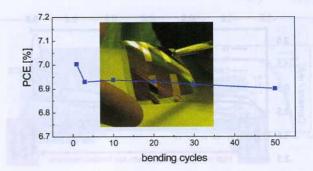


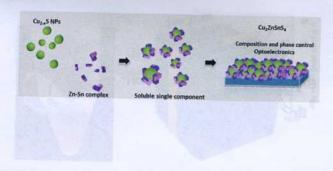
994

### Flexible high efficiency perovskite solar cells

Cristina Roldán-Carmona, Olga Malinkiewicz, Alejandra Soriano, Guillermo Mínguez Espallargas, Ana Garcia, Patrick Reinecke, Thomas Kroyer, M. Ibrahim Dar, Mohammad Khaja Nazeeruddin and Henk J. Bolink\*

High efficiency flexible methylammonium lead iodide perovskite based solar cells are compatible with roll to roll processing.



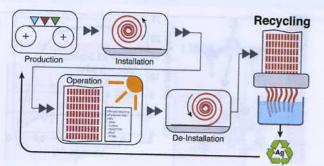


# Facile single-component precursor for Cu<sub>2</sub>ZnSnS<sub>4</sub> with enhanced phase and composition controllability

Huanping Zhou, Hsin-Sheng Duan, Wenbing Yang, Qi Chen, Chia-Jung Hsu, Wan-Ching Hsu, Chun-Chao Chen and Yang Yang\*

We report a facile, quantitative and clean fabrication of kesterite  $Cu_2ZnSnS_4$  film from a single-component precursor, crystalline  $Cu_{2-x}S$  capped with multi-metal chacolgenide ligands, Zn-Sn complex, and demonstrate its optoelectronic performance.

1006

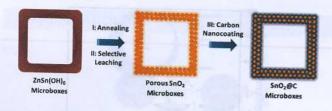


# Efficient decommissioning and recycling of polymer solar cells: justification for use of silver

Roar R. Søndergaard, Nieves Espinosa, Mikkel Jørgensen and Frederik C. Krebs\*

The use of silver in fully printed polymer solar cells is justified through efficient recovery and recycling.

1013

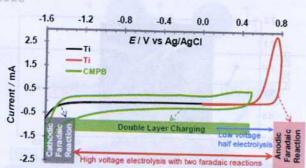


# Formation of porous SnO<sub>2</sub> microboxes *via* selective leaching for highly reversible lithium storage

Lei Zhang, Hao Bin Wu, Bin Liu\* and Xiong Wen (David) Lou\*

Porous carbon-coated  $SnO_2$  microboxes with high uniformity are prepared via a novel selective leaching strategy, and exhibit excellent electrochemical performance as anode materials for lithium-ion batteries.

1018



## Achieving low voltage half electrolysis with a supercapacitor electrode

Chuang Peng,\* Di Hu and George Z. Chen\*

Half electrolysis consists of one faradaic reaction and a supercapacitor double layer charging process. In such a configuration, the product of the electrolysis is only generated in the vicinity of one electrode. Furthermore the electrolysis voltage and electric energy consumption are significantly reduced.

#### COMMUNICATIONS

1023

### Double superexchange in quantum dot mesomaterials

Huashan Li, Zhigang Wu, Tianlei Zhou, Alan Sellinger\* and Mark T. Lusk

A new optoelectronic mesomaterial is proposed in which a network of quantum dots is covalently connected *via* organic molecules.



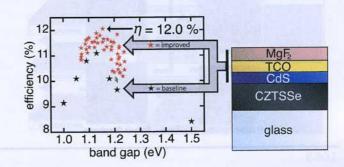
#### PAPERS

1020

## Optical designs that improve the efficiency of Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> solar cells

Mark T. Winkler, Wei Wang, Oki Gunawan, Harold J. Hovel, Teodor K. Todorov and David B. Mitzi\*

The world-record efficiency of a Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> solar cell has been improved to 12.0% via improved photon management.

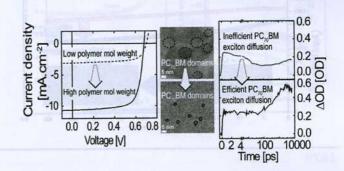


202

## Towards optimisation of photocurrent from fullerene excitons in organic solar cells

Stoichko D. Dimitrov, Zhenggang Huang, Florent Deledalle, Christian B. Nielsen, Bob C. Schroeder, Raja Shahid Ashraf, Safa Shoaee, Iain McCulloch and James R. Durrant\*

Photocurrent from fullerene excitons in polymer–fullerene solar cells is optimised by employing a series of low bandgap diketopyrrolopyrrole-containing polymers with differing molecular weights.

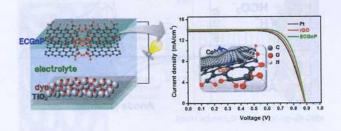


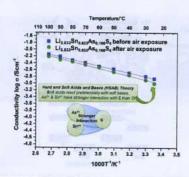
1044

# Edge-carboxylated graphene nanoplatelets as oxygen-rich metal-free cathodes for organic dyesensitized solar cells

M. J. Ju, I-Y. Jeon, K. Lim, J. C. Kim, H-J. Choi, I. T. Choi, Y. K. Eom, Y. J. Kwon, J. Ko,\* J-J. Lee,\* J-B. Baek\* and H. K. Kim\*

Edge-carboxylated graphene nanoplatelets (ECGnPs) prepared by the dry ball-milling of graphite showed lower charge-transfer resistance ( $R_{\rm CT}$ ) and better electrochemical stability for the JK-303-based solar cell with Co(bpy)<sub>3</sub><sup>2+/3+</sup> redox couple.



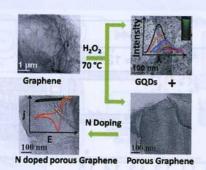


## Air-stable, high-conduction solid electrolytes of arsenic-substituted Li<sub>4</sub>SnS<sub>4</sub>

Gayatri Sahu, Zhan Lin, Juchuan Li, Zengcai Liu, Nancy Dudney and Chengdu Liang\*

HSAB theory predicts the design of air-stable, high-conduction sulfide based solid electrolytes.

1059

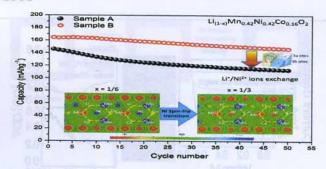


Nanoporous graphene by quantum dots removal from graphene and its conversion to a potential oxygen reduction electrocatalyst *via* nitrogen doping

Thangavelu Palaniselvam, Manila Ozhukil Valappil, Rajith Illathvalappil and Sreekumar Kurungot\*

Photoluminescent graphene quantum dots and nitrogendoped porous graphene are formed through a sequential process and their characteristic properties are evaluated.

1068

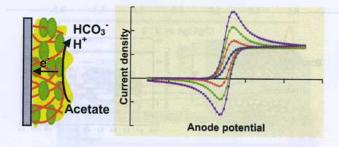


Study of the lithium/nickel ions exchange in the layered LiNi<sub>0.42</sub>Mn<sub>0.42</sub>Co<sub>0.16</sub>O<sub>2</sub> cathode material for lithium ion batteries: experimental and first-principles calculations

Haijun Yu, Yumin Qian, Minoru Otani, Daiming Tang, Shaohua Guo, Yanbei Zhu and Haoshen Zhou\*

Experimental and first-principles calculations of the Li $^+$ /Ni $^2$ + ions exchange in the LiNi $_{0.42}$ Mn $_{0.42}$ Co $_{0.16}$ O $_2$  materials are reported in this work.

1079



## A theoretical model of transient cyclic voltammetry for electroactive biofilms

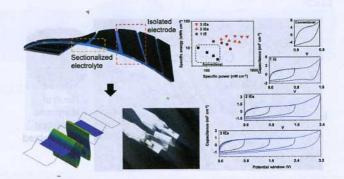
Raphael Rousseau, Marie-Line Délia and Alain Bergel\*

Relationships of the transient peak currents with the potential scan rate are enlarged beyond the conventional 0.5 and 1 exponent-laws.

### All-solid-state, origami-type foldable supercapacitor chips with integrated series circuit analogues

Inho Nam, Gil-Pyo Kim, Soomin Park, Jeong Woo Han and Jongheop Yi\*

Origami-type stretchable supercapacitors permit energy and power to be simultaneously increased and accommodate stable stretching with integrated series circuit analogues.

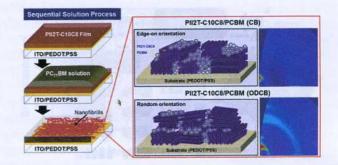


1103

## Sequentially solution-processed, nanostructured polymer photovoltaics using selective solvents

Do Hwan Kim, Jianguo Mei, Alexander L. Ayzner, Kristin Schmidt, Gaurav Giri, Anthony L. Appleton, Michael F. Toney and Zhenan Bao\*

High-performance sequentially solution-processed organic photovoltaics have been achieved by controlling the swelling and intermixing processes of the layer with various processing solvents during deposition of the fullerene.

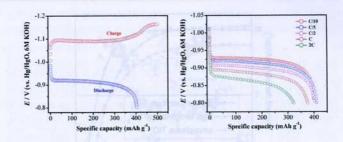


1110

### An in situ carbon-grafted alkaline iron electrode for iron-based accumulators

Aravamuthan Sundar Rajan, Srinivasan Sampath and Ashok Kumar Shukla\*

A carbon-grafted iron electrode prepared from the active material obtained by decomposing the  $\alpha\text{-FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}-$  PVA composite exhibits improved performance and high-rate capability.

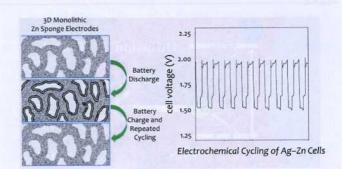


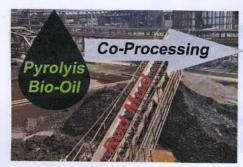
1117

## Wiring zinc in three dimensions re-writes battery performance—dendrite-free cycling

Joseph F. Parker, Christopher N. Chervin, Eric S. Nelson, Debra R. Rolison\* and Jeffrey W. Long\*

Zinc-based replacements for Li-ion batteries are now feasible by using 3D-interconnected Zn sponges that suppress dendrite formation when cycled.







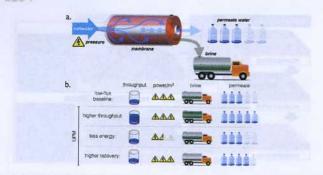
- Neutral
- Magnetic
- Reduced
- Carbonized

# Optimization of the neutralization of Red Mud by pyrolysis bio-oil using a design of experiments approach

Véronique Jollet, Christopher Gissane and Marcel Schlaf\*

Co-processing alkaline Red Mud (bauxite residue) with acidic pyrolysis bio-oil yields a gray pH-neutral solid containing  $\sim\!\!30\%$  (w/w) biomass derived carbon and magnetic iron suboxides.

1134

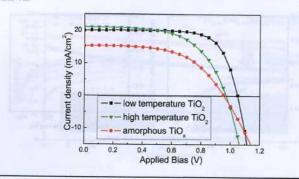


## Quantifying the potential of ultra-permeable membranes for water desalination

David Cohen-Tanugi, Ronan K. McGovern, Shreya H. Dave, John H. Lienhard and Jeffrey C. Grossman\*

In light of recent advances in membrane materials for water desalination by reverse osmosis (RO), we assess the potential of ultra-permeable membranes to improve the performance and cost of RO.

1142

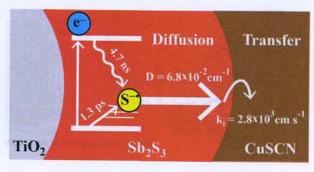


## Sub-150 °C processed meso-superstructured perovskite solar cells with enhanced efficiency

Konrad Wojciechowski, Michael Saliba, Tomas Leijtens, Antonio Abate and Henry J. Snaith\*

Fabrication of highly efficient mixed halide perovskite solar cells in an entirely low temperature process (sub-150 °C).

1148



### Rate limiting interfacial hole transfer in Sb<sub>2</sub>S<sub>3</sub> solidstate solar cells

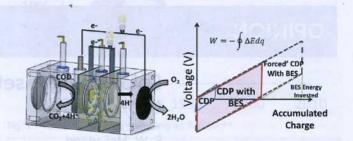
Jeffrey A. Christians, David T. Leighton Jr. and Prashant V. Kamat\*

The hole diffusion coefficient and diffusion length in  $Sb_2S_3$  is measured. Hole transfer from  $Sb_2S_3$  to CuSCN is found to be predominately limited by transfer across the  $Sb_2S_3$ -CuSCN interface

# Capacitive mixing power production from salinity gradient energy enhanced through exoelectrogengenerated ionic currents

Marta C. Hatzell, Roland D. Cusick and Bruce E. Logan\*

Immersion of capacitive electrodes into a multiple-chamber bioelectrochemical reactor substantially increased energy capture from synthetic river water and seawater.

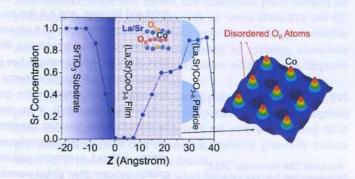


1166

# Revealing the atomic structure and strontium distribution in nanometer-thick $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ grown on (001)-oriented SrTiO<sub>3</sub>

Zhenxing Feng, Yizhak Yacoby, Wesley T. Hong, Hua Zhou, Michael D. Biegalski, Hans M. Christen and Yang Shao-Horn\*

Surface segregation in metal oxides can greatly influence the oxygen transport and surface oxygen exchange kinetics critical to the performance of solid-state devices such as oxygen permeation membranes and solid oxide fuel/electrolytic cell electrodes.



1171

# Modeling of internal conversion in photoexcited conjugated molecular donors used in organic photovoltaics

N. Oldani, S. Tretiak,\* G. Bazan and S. Fernandez-Alberti\*

Using the Non-Adiabatic Excited States Molecular Dynamics (NA-ESMD) approach, we investigate the ultrafast electronic relaxation in a recently synthesized small molecule donor, p-DTS(PTTh<sub>2</sub>)<sub>2</sub>, which belongs to the dithienosilole-pyridylthiadiazole family of chromophores.



1185

# Enhanced thermal conductivity of phase change materials with ultrathin-graphite foams for thermal energy storage

Hengxing Ji, Daniel P. Sellan, Michael T. Pettes, Xianghua Kong, Junyi Ji, Li Shi\* and Rodney S. Ruoff\*

Embedding continuous ultrathin-graphite foams (UGFs) with volume fractions as low as 0.8–1.2 vol% in a phase change material (PCM) can increase the effective thermal conductivity by up to 18 times, with negligible change in the melting temperature or mass specific heat of fusion.

