

tion technique based on post-growth thermal diffusion of Fe in polycrystalline ZnSe.

As reported in the January 1st issue of *Optics Letters* (DOI:10.1364/OL.36.000094; p. 94), the researchers investigated Er:Cr:YSGG laser-pumped Fe:ZnSe lasing in a Fabry–Perot cavity in the temperature range of 236–300 K. Thermal diffusion of Fe was carried out in sealed quartz ampoules at  $10^{-5}$  Torr for

14 days at 1000°C, which resulted in a highly concentrated (Fe concentration  $2 \times 10^{19} \text{ cm}^{-3}$ ) gain element. High gain in the developed active medium ensured reduced oscillation build-up time, improved temporal overlap of the pump pulse (20 ns) and output oscillation (15 ns), and effective absorption of the pump pulse, leading to increased output energy. A fourfold increase in the output energy of the gain-switched Fe:ZnSe

laser was obtained. The maximum laser output energy was 4.7 mJ at 4.3  $\mu\text{m}$  and 236 K, and 3.6 mJ at 4.37  $\mu\text{m}$  and 300 K (limited by available pump energy) with maximum obtained power of 0.3 MW at 4.3  $\mu\text{m}$ . The researchers said that additional improvements can be achieved by further optimization of the laser cavity and also by using a pump with higher energy.

**Mousumi Mani Biswas**

### Energy Focus

#### ZnO nanoforest delivers high-efficiency solar cell

Inspired by the network of branches that trees use to gather sunlight, an innovative team of researchers recently grew a “nanoforest” of light-absorbing nanowires to ramp up productivity in dye-sensitized solar cells (DSSC). As detailed in the January 5th online edition of *Nano Letters* (DOI: 10.1021/nl1037962), S.H. Ko and co-workers at the Korea Advanced Institute of Science and Technology and University of California, Berkeley developed a multi-stage seeded growth process to grow intricately branched structures of ZnO nanowires that resemble a tightly packed forest of pine trees. The team then fabricated the nanoforests into a DSSC and demonstrated a significant jump in the solar cell’s efficiency.

In a DSSC, a wide-bandgap semiconductor works in conjunction with a sensitizing dye to absorb incident sunlight and convert it to electrical energy. ZnO is

an effective semiconductor for this purpose and is appealing due to the ease with which it can be grown, but the resulting solar cells suffer from low efficiencies. However, this nanoforest approach could be the crucial step to making ZnO a viable DSSC component.

To achieve the forest-like structure, the researchers first grow nanowires by a hydrothermal growth process, depositing seed particles (ZnO quantum dots) on a substrate and immersing it in a solution containing zinc nitrate hydrate and the polymers hexamethylenetetramine (HMTA) and polyethylenimine (PEI). Then they wash off the polymer, bake the sample, and deposit a new layer of seed particles over the pillar-like nanowires. Next they repeat the hydrothermal growth step, which now causes nanowires to form along the length of the original wires, like branches on a tree. They perform additional cycles to create higher orders of branching, leading to a dense network of hierarchically branched nanowires.

The team demonstrated that both the “trunk” and the “branches” of ZnO are crystalline and grow along the wurtzite *c*-axis. The trunks are 40–50  $\mu\text{m}$  long with an aspect ratio greater than 100, while the branches are 2–10  $\mu\text{m}$  in length.

To test the usefulness of these novel structures, the researchers fabricated DSSCs by sandwiching a dye-sensitized ZnO nanoforest between electrodes. The measured current–voltage characteristics show a light-induced current that increases with trunk length and the degree of branching. Ko and the research team report efficiencies of 2.6% for their devices, which is an increase of 350–500% over devices made with regular, non-branched ZnO nanowires. The team cites the increased surface area as the primary cause for improvement, as it allows for greater dye-loading and photon absorption. They also said that the complex network of overlapping branches allows for better electron transport to the collection electrodes.

**Alison Hatt**

### Nano Focus

#### Functionalization of graphene leads to enhanced hydrogen adsorption

The on-board, high-capacity, facile, and reversible storage of hydrogen fuel is one of several significant challenges for hydrogen-fueled vehicles. While gas-adsorbant metal-organic framework structures display high  $\text{H}_2$  uptake, the volume of  $\text{H}_2$  they can hold

is insufficient due to the material’s low density. The densities of carbon materials are sufficiently high but their capacity for  $\text{H}_2$  adsorption is low. Strategies for increasing the  $\text{H}_2$ -uptake capacity of carbon materials include surface modification with heteroatoms or functional groups in order to polarize the  $\text{H}_2$  molecules. Pillared graphene’s potential for  $\text{H}_2$  storage has been demonstrated with theoretical calculations. In addition, recent experiments show that  $\text{H}_2$  uptake

by thermally exfoliated graphene (TEG) increases linearly with surface area. Recently, C. Kittrell and J.M. Tour of Rice University, K.J. O’Neill of the National Renewable Energy Laboratory (NREL), and co-researchers hypothesized that  $\text{H}_2$  uptake in TEG could be improved by engineering nanospaces; carbon scaffolds could be created by insertion of molecular spacers between graphene sheets.

As reported in the February 22nd issue of *Chemistry of Materials* (DOI: 10.1021/

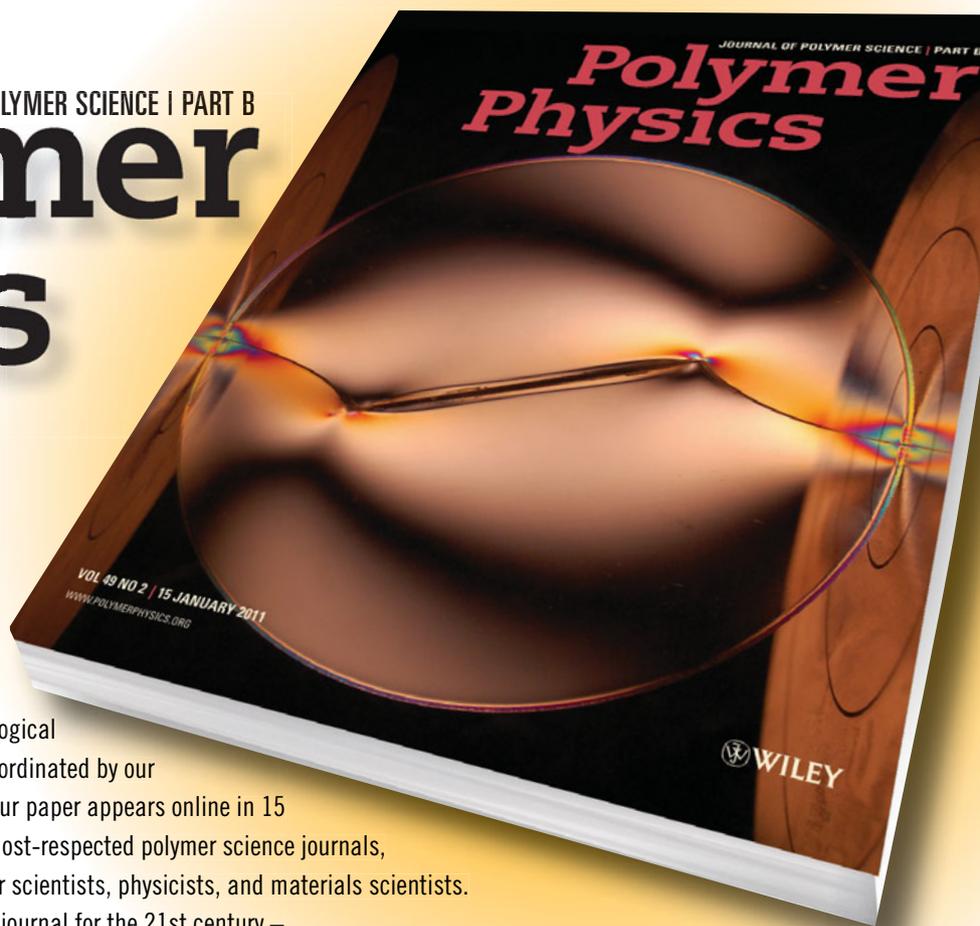
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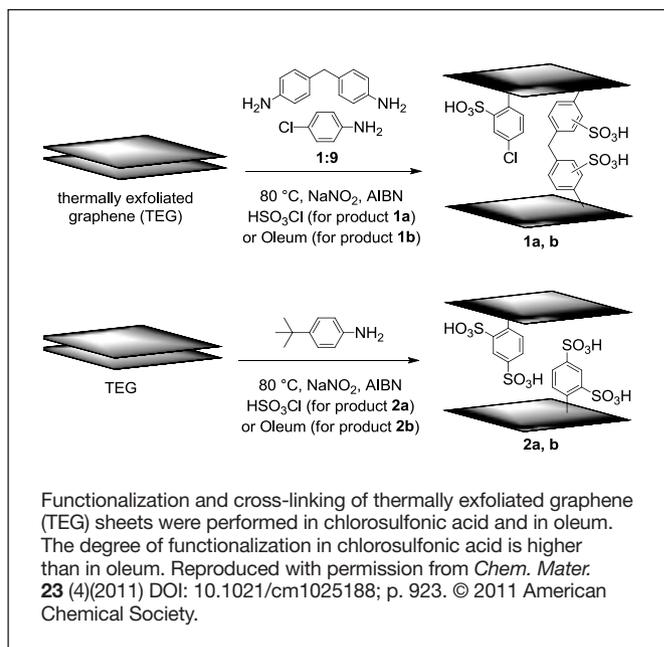
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cm1025188; p. 923), the researchers used a modified procedure to make the TEG, in which most of the oxygen was removed by reduction at elevated temperature. Dispersion and functionalization of the graphene sheets were achieved by reaction with either a diazonium compound or *t*-butylaniline in the super acids chlorosulfonic acid or oleum (see Scheme). Cross-links between the graphene sheets were obtained with the diazonium reaction in oleum (see Scheme).

The researchers monitored the degree of functionalization with x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. Scanning electron micrographs of the functionalized TEG show that the aryl groups serve as spacers, and open up nanometer-sized interstitial gaps between the graphene planes where H<sub>2</sub> can adsorb, in contrast to the original TEG sheets, which appear as disordered, fluffy conglomerates.

Another factor leading to increased H<sub>2</sub> adsorption is the charge transfer

generated by the sulfonic acid groups. The H<sub>2</sub> uptake and surface areas were measured for TEG and functionalized TEG with a custom-built, high-precision system at NREL. The H<sub>2</sub> uptake (measured as a weight-percent per 500 m<sup>2</sup>/g at 77 K and 2 bar) for the functionalized TEG samples were higher than the H<sub>2</sub> uptake for TEG by 60%, 40%, 40%, and 10% for 1a, 1b, 2a, and 2b, respectively (see Scheme). The researchers said that they expect the H<sub>2</sub> uptake by the functionalized TEGs to be substantially higher at higher pressures, and that the “hydrogen uptake enhancement of TEG by organic cross-linking



demonstrates a possible route to further increase the hydrogen storage capacity of graphene materials.”

**Steven Trohalaki**

### Energy Focus

#### Study on energy transfer in CdSe/CdS nanocrystals uncovers role of particle morphology

Semiconductor heterostructures that have large absorption cross sections, high stability, and quantum yields as well as size-tunable electronic structures are good candidates for light-harvesting and energy conversion applications. Nanoscale CdSe/CdS heterostructures have been reported to exhibit either Type I behavior, in which a photogenerated electron–hole pair remains in one of the materials, or Type II behavior in which the electron and hole separate between the materials. This distinction in carrier migration behavior determines for which applications a structure may be used, light emission (Type I) versus photovoltaics (Type II) for example. A detailed understanding of the origin of the electronic structure of such heterojunctions is not only crucial for engineering particles

for the desired application, but can also lead to the ability to fine-tune the material for optimal performance. N.J. Borys and M.J. Walter from the University of Utah, J. Huang and D.V. Talapin from the University of Chicago, and J.M. Lupton from the University of Utah and the Universität Regensburg, Germany, report on the morphological effects of CdSe/CdS nanocrystals on interfacial energy transfer properties as published in the December 3, 2010 issue of *Science* (DOI: 10.1126/science.1198070; p. 1371).

The researchers used single-particle light-harvesting action spectroscopy on a range of CdSe/CdS heterostructures to probe the electronic structure of the heterojunctions. Specifically they measured photoluminescence excitation (PLE) of absorbing CdS through emission from CdSe. The single-particle approach enables the detection of properties that might be obscured in ensemble measurements. Typically nanoscale CdS exhibits a peak in its PLE spectrum due to the quantum-confined exciton state.

Intriguingly, results from single-particle spectroscopy showed this peak only occurred in some fraction of the spectra collected from tetrapods, a CdSe core connecting four arms of CdS.

By studying other particle morphologies, including rods and spheres, the researchers were able to isolate structural features that seemed to control the presence or absence of the peak. A crucial part of this study was developing a method to correlate the single particle PLE with scanning electronic microscope images of the same particle to unambiguously show the connection to particle shape. Notably, spheres and rods with a bulbous coating around the CdSe particles did not show a peak. The researchers said that non-uniform diameter in the arms of the tetrapods or overgrowth of the CdS shell around the central core broadens quantum confinement effects and is responsible for the distinct spectra observed in the tetrapod population.

By spectrally resolving the emis-