



Finally, pores were generated in the graphene membranes by oxidative etching on exposure to ultraviolet light. The molecular selectivity of these membranes was then demonstrated by the observation that δ decreases two orders of magnitude more rapidly as compared with nonporous graphene for small gas molecules such as H_2 and CO_2 , while the rate

remains largely unchanged for Ar and gas molecules with a larger kinetic diameter.

In graphene membranes that have larger pores, faster leak rates were measured using a mechanical resonance method which again demonstrated size-selective leak rates, but this time for molecules above and below the size of SF_6 .

“Our results are consistent with theo-

retical models based on effusion through Ångstrom-sized pores,” stated group leader J. Scott Bunch, “and represent an important step toward the realization of macroscopic, size-selective porous graphene barriers.”

Rich Louie

Energy Focus

Energy harvesting in electronic displays enabled by fluorescent-dye-cascade linear polarizer

As anyone with a smart phone or tablet knows, battery life is the key to a useful mobile device. Recently, luminescent solar concentrators (LSCs) have gained attention as a possible energy-harvesting technique to extend mobile battery life. When integrated into a display, LSCs steer incoming light that would otherwise be wasted (sunlight, room lights, or the internal backlight) to small photovoltaics placed inside the device perimeter. However, current LSCs reduce display quality and therefore remain impractical. Now, A.M. Velázquez and colleagues at the Massachusetts Institute of Technology have demonstrated an LSC based on cascading fluorescence that may eliminate this problem by shifting reemitted light into the infrared. They reported their findings in the October 25, 2012 online edition of *Energy & Environmental Science* (DOI: 10.1039/c2ee23265k).

LSCs studied to date have been based on luminescent dye molecules placed

in a glass sandwich waveguide. These molecules can be aligned within a liquid crystal host, making the system into a linear polarizer, which could potentially replace the standard linear polarizers used in display technology. However, photons that result from the dye fluorescence can escape from the waveguide and be reemitted from the surface, contaminating the display image. The researchers hypothesized that they could overcome this problem by combining four different fluorescent dyes, with emission and absorption spectra that overlap to cover the optical spectrum all the way to the infrared. The final emission of this cascade could therefore be filtered out by a standard infrared filter.

The researchers prepared the device by first dissolving four dyes in chloroform, mixing them with a nematic liquid-crystal host at 60°C for five minutes and desiccating the mixture for 12 hours. Next, they used capillary action to fill a 5- μ m-gap liquid-crystal cell with the mixture, heating the materials to 70°C and slow-cooling them to ensure good alignment on the rubbed polyamide surfaces of the cell. The dyes chosen were (in wt% in the final device) coumarin 6

(0.3%), DCM2 (0.3%), Nile Red (0.6%), and a squaraine dye (0.2%).

Using an integrating sphere to make optical measurements, the researchers found that the final device exhibits good optical quantum efficiency: approximately 20% of incident photons at the peak absorption wavelengths are steered to the perimeter, which is in good agreement with theory. This suggests that the cascade of multiple dyes undergoes Förster resonant energy transfer with approximately unity efficiency. The combination of dyes selected also ensured that the photoluminescence of the dye cascade peaks in the near-infrared, meaning that light escaping the waveguide could be easily filtered without affecting display quality. If used in a standard crossed-polarizer display, the researchers estimate that the device could generate over 10 μ W/cm² indoors and as much as 1–10 mW/cm² outdoors.

These results suggest that displays on mobile devices may someday do double duty, providing information for the user while also generating electrical power for the device.

Colin McCormick

Bio Focus

Bioinspired polymeric carbon nitride nanospheres dramatically improve photoredox catalysis

Many attempts have been made to create synthetic analogues of the natural photosynthesis system. However, the ability to mimic the spatial

organization of this system, where the thylakoid membrane acts as a photosynthetic scaffold that captures and distributes light, and separates the oxidative from reductive species, remains a significant challenge. As reported in the October 16, 2012 online edition of *Nature Communications* (DOI: 10.1038/ncomms2152), X. Wang and co-researchers at Fuzhou University, China,

and M. Antonietti at the Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, have addressed this challenge by employing polymerized hollow nanospheres as analogues of the thylakoid membrane of a chloroplast. These hollow carbon nitride nanospheres (HCNSs) were used as a light-harvesting platform for catalyzing hydrogen evolution under visible light



irradiation, achieving a 7.5% overall apparent quantum yield.

The hollow nanospheres were fabricated using 220-nm-silica spheres coated with 20–100 nm mesoporous silica shells as templates. The particle size was selected such that it was similar to the optical bandgap of the carbon nitride semiconductor (less than 430 nm). Light harvesting from inner reflections and photonic effects within the nanostructures is therefore maximized. After loading cyanide into the porous shells and annealing to give graphitic- C_3N_4 -silica nanocomposites, the silica was then removed with NH_4HF_2

to leave hollow carbon nitride vesicles. Extensive characterization confirmed the generation of graphitic C_3N_4 nanostructures.

The photophysics of the HCNSs was investigated using a light-induced H_2 -evolution assay, employing 3 wt% Pt as the co-catalyst. While all HCNS samples exhibited enhanced photocatalytic activity over bulk Pt/graphitic- C_3N_4 , the HCNSs with the thickest shells of 85 nm displayed the highest H_2 -evolution rate of $224 \mu\text{mol h}^{-1}$. This is a factor of 25 higher than that of bulk Pt/graphitic- C_3N_4 , and is comparable to benchmark inorganic photocatalysts under UV-light

irradiation and outperforms those under visible light irradiation.

The researchers said, “Hybrid nano-architectures based on finely tuned polymeric carbon nitride capsules provide a valuable platform for constructing highly organized photosynthetic systems for the efficient and sustained utilization of solar radiation after the controlled deposition of a co-catalyst onto the exterior and/or interior surfaces and the construction of a dyadic layer to promote exciton dissociation.”

Steven Trohalaki

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- A Film Silicon Science and Technology
- B Organic and Hybrid Photovoltaic Materials and Devices
- C Thin-Film Compound Semiconductor Photovoltaics
- D From Molecules to Materials—
Pathways to Artificial Photosynthesis
- E Materials and Integration Challenges for Energy Generation
and Storage in Mobile Electronic Devices
- F Materials for Vehicular and Grid Energy Storage
- G Electrochemical Interfaces for Energy Storage and Conversion—
Fundamental Insights from Experiments and Computations
- H Nanoscale Thermoelectrics—
Materials and Transport Phenomena II
- I Materials for Solid-State Refrigeration
- J *In-Situ* Characterization Methods in Energy Materials Research
- K Materials for Sustainable Development

NANOMATERIALS

- L Nanoparticle Manufacturing, Functionalization, Assembly,
and Integration
- M Solution Synthesis of Inorganic Functional Materials—
Films, Nanoparticles, and Nanocomposites
- N Nanomaterials in the Subnanometer-Size Range
- O Beyond Graphene—2D Atomic Layers from Layered Materials
- P Graphene and Related Carbon Nanomaterials
- Q Surfaces of Nanoscale Semiconductors
- R Nanostructured Semiconductors and Nanotechnology
- S Nanostructured Metal Oxides for Advanced Applications
- T Electrical Contacts to Nanomaterials and Nanodevices
- U Measurements of Atomic Arrangements and Local Vibrations
in Nanostructured Materials
- V Nanoscale Heat Transport—From Fundamentals to Devices
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for Imaging Functionality on the Nanoscale
- Z Nanotechnology and Sustainability

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Materials, Processes, and Reliability
- BB Evolutions in Planarization—
Equipment, Materials, Techniques, and Applications
- CC Gate Stack Technology for End-of-Roadmap Devices
in Logic, Power, and Memory
- DD Emerging Materials and Devices
for Future Nonvolatile Memories
- EE Phase-Change Materials for Memory, Reconfigurable
Electronics, and Cognitive Applications
- FF Compound Semiconductors for Generating, Emitting,
and Manipulating Energy II
- GG Single-Dopant Semiconductor Optoelectronics
- HH Materials for High-Performance Photonics II
- II Resonant Optics in Metallic and Dielectric Structures—
Fundamentals and Applications
- JJ Fundamental Processes in Organic Electronics
- KK Charge and Spin Transport
in Organic Semiconductor Materials

BIOMATERIALS

- LL Hybrid Inorganic-Biological Materials
- MM New Tools for Cancer Using Nanomaterials,
Nanostructures, and Nanodevices
- NN Multifunctional Biomaterials
- OO Design of Cell-Instructive Materials
- PP Adaptive Soft Matter through Molecular Networks
- QQ Conjugated Polymers in Sensing and Biomedical Applications
- RR Lanthanide Nanomaterials for Imaging, Sensing,
and Optoelectronics
- SS Bioelectronics—Materials, Interfaces, and Applications
- TT Materials and Processes for Electronic Skins

GENERAL

- UU Plasma and Low-Energy Ion-Beam-assisted Processing
and Synthesis of Energy-related Materials
- VV Materials Applications of Ionic Liquids
- WW Nuclear Radiation Detection Materials
- XX Oxide Thin Films and Heterostructures
for Advanced Information and Energy Technologies
- YY Titanium Dioxide—Fundamentals and Applications
- ZZ Carbon Functional Interfaces II
- AAA Superconducting Materials—
From Basic Science to Deployment
- BBB Size-Dependent and Coupled Properties of Materials
- CCC Novel Functionality by Reversible Phase Transformation
- DDD Extreme Environments—A Route to Novel Materials
- EEE Materials Education—Toward a Lab-to-Classroom Initiative

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