NANOMATERIALS

Asymmetry in supramolecular assembly

Photoresponsive organic nanowires connect to gold nanomesh and silicon electrodes

By **Suzette Slim**[1,2] and **Federico Rosei**[1,2]

Like their inorganic counterparts, the optoelectronic properties of organic semiconductors (OSCs) can be tuned by confining charge carriers in nanoscale dimensions. In particular, one-dimensional (1D) nanowires made of conjugated molecules may be formed through supramolecular interactions based on π-stacking. To fully exploit their properties in devices, Zhang *et al.* (*1*) report supramolecular control of OSC nanowire growth. A nanoscale scaffold regulates assembly of nanowires across asymmetric electrodes (gold and silicon), creating p-n junctions that bias current flow. This architecture is then used to demonstrate high-performance photovoltaic device characteristics.

Organic photovoltaics (OPVs) are good candidates for third-generation solar cells because organic synthesis that enables tuning of electronic and optical properties, solution processing, and compatibility with flexible substrates helps reduce manufacturing costs (*2*). Localized excitons (electron-hole pairs) are generated in OPVs when light is absorbed by small molecules or polymers. The power conversion efficiencies of OPVs reached ~11% in laboratory prototypes (*3*), which is well below the 20% target required for commercial devices. Efficiency limitations and long-term stability are two major drawbacks that hinder deployment. To increase efficiency, it is necessary to improve both the absorption and mobility properties of the absorbing OSCs by optimizing the molecular structure of their building blocks, together with their supramolecular ordering.

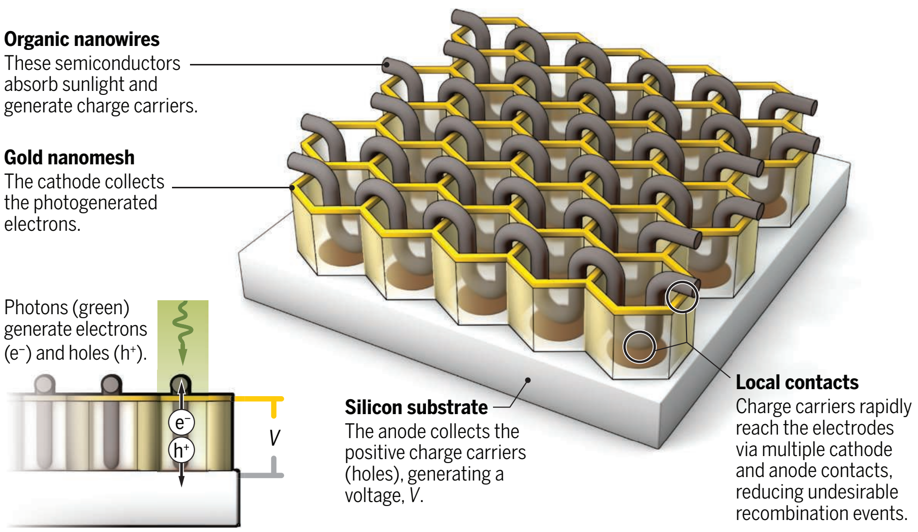
The high surface-to-volume ratio of nanowires facilitates exciton separation by minimizing the diffusion length from the bulk to the surface, where exciton dissociation into free carriers typically occurs (*4*). In addition, the 1D π-stacking in nanowires favors charge transport (*5*). Thus, the high absorption coefficient and remarkable light sensitivity of supramolecular organic nanowires (SMNWs) compared with that of bulk crystals makes them ideal building blocks for optoelectronic technologies (*6*). However, the development of photonic devices based on SMNWs has been hindered by two major challenges. One is the difficulty in wiring them with nanoscale electrodes that have different work functions, which is crucial to harvesting their photogenerated current. The other is the development of approaches that easily and simultaneously connect hundreds of nanowires.

Zhang *et al.* report a general methodology to integrate SMNWs in a hexagonal nanomesh scaffold featuring asymmetric electrodes in order to fabricate a small-molecule OPV cell (see the figure). The nanomesh provides a periodic array of surface templates that guide the growth of SMNWs horizontally, encapsulating them between asymmetric electrodes with different work functions, hence realizing a vertical channel (*7*). Specifically, they assembled nanowires of *N*,*N*′-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) and showed that controlling supramolecular interactions is crucial to obtaining high-performance optoelectronic devices.

The nanomesh is fabricated by using nanosphere lithography, in which a monolayer of hexagonal close-packed nanoscale spheres of polystyrene acts as a mask (*8*). This versatile technique adds materials by deposition and subtracts other materials by selective etching, allowing the fabrication of periodic large-area nanoscale patterns. The gold nanomesh acts as the cathode, and the anode is the n-doped silicon substrate. The anode was modified by functionalizing it with a layer of p-type semiconducting polymer (P3HT) so as to enhance hole selectivity and reduce radiative recombination at the silicon/nanowire interface, facilitating PV response. By connecting hundreds of SMNWs, optimized PTCDI-C8 nanowire solar cells exhibit a signal-to-noise ratio approaching 10^7, a photoresponse time as fast as 10 ns, and an external quantum efficiency exceeding 50%.

Organic nanowire photovoltaics

Illustration showing the high-density array of supramolecular nanowires, assembled by using a vertical channel nanomesh scaffold with asymmetric electrodes fabricated on a silicon substrate.



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Thus, SMNWs have potential applications in high-performance OPVs.

In a broader perspective, the nanomesh scaffold used by Zhang *et al.* is quite versatile and represents a valuable tool for investigating inherent photonic properties of 1D OSCs. By varying geometrical parameters of the mesh, the nanowires, or both, they observed substantial changes in optoelectronic properties. In the vertical direction, the interelectrode distance could be tuned to <100 nm, whereas the device could extend up to a few millimeters laterally. The underlying concept is to optimize charge transport with an ordered array of nanowires that are connected to the same nanoscale electrode.

[1]Institute for Fundamental and Frontier Science, University of Electronic Science and Technology of China, No. 4, Section 2, North Jianshe Road, Chengdu 610051, China. [2]Centre for Energy, Materials and Telecommunications, INRS, Varennes, Québec J3X 1S2, Canada. Email: rosei@emt.inrs.ca

The use of tailored supramolecular structures for PV applications allows the study of the fundamental physics and chemistry of nanostructured materials through unraveling structure-property relations. The vertical-channel device configuration can be exploited for model studies in spintronics and other applications in optoelectronics such as light-emitting diodes and transistors, which require the optimal combination of asymmetric electrodes with ad hoc work function, nanoscale controlled channel length, and maximal density of active nanostructures. Photovoltaic performance could also be optimized by using SMNWs with higher charge mobility or by introducing a dopant to improve conductivity (*9, 10*). In addition, the gold nanomesh could enhance optical absorption by acting as a plasmonic antenna (*11*), increasing quantum efficiency. The photoresponse could be used to develop ultrafast nanoscale photodetectors, which would be components of future optical quantum computers. Alternative lithographic methods, such as nanoimprint or nanostencil (*12, 13*), could access more complex geometries that are required for specific architectures (such as memory storage devices).

Controlling supramolecular interactions holds the promise of growing highly ordered organic films and nanostructures, which is a prerequisite for the fabrication of high-performance devices (*14*). The device configuration of Zhang *et al.* bridges the gap between bottom-up grown semiconductor nanostructures and macroscopic photonic technologies. We anticipate that it will draw broad interest from the scientific community and affect future developments at the intersection between supramolecular chemistry, nanotechnology, and optoelectronics. ■

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ACKNOWLEDGMENTS

F.R. thanks the Canada Research Chairs program for partial salary support and is grateful to the government of China for a Chang Jiang Chair Professorship.

10.1126/science.aah5571

ECOLOGY

How dams can go with the flow

Small changes to water flow regimes from dams can help to restore river ecosystems

By **N. LeRoy Poff**[1,2] *and* **John C. Schmidt**[3]

The world's rivers are regulated by about 58,000 large dams (more than 15 m high) that provide water supplies for municipalities and irrigation, allow downstream navigation, and enable hydropower production (*1*). New dams are widely seen as sources of green energy. An estimated 75% of the world's potential hydropower capacity is unexploited (*2*), and some 3700 new dams are currently proposed in developing economies (*3*, *4*).

> ***"Managing...rivers to better meet both human and ecosystem needs is a complex societal challenge."***

But dams also cause substantial and often unacknowledged environmental damage. Recent research affords insight into how dams might be strategically operated to partially restore some lost ecosystem functions and services.

Dams transform rivers by creating artificial lakes, fragmenting river networks, and greatly distorting natural patterns of sediment transport and of seasonal variation in water temperature and stream flow (*5*). Impeded upstream-downstream movement of fish and other species and highly altered environmental conditions severely impair downstream ecosystems by modifying productivity and causing species extirpations and replacements (see the figure). Intentional releases of reservoir water can restore some semblance of the predam flow regime. Such environmental flows (*6*) enable recovery of some lost ecosystem functions but carry an economic cost by a dam's operational efficiency.

Many hydropower dams release more water during daytime when societal demand for electricity is greatest. Such hydropeaking creates a fluctuating daily pattern of water flows that typically severely impairs productive, downstream shoreline habitats through repeated wetting and drying. River scientists have long struggled with the conundrum of how to diminish these negative ecological effects in a cost-effective manner, given the strong economic incentive of hydropeaking. A recent study of the Colorado River ecosystem downstream from the hydropeaking Glen Canyon Dam by Kennedy *et al.* (*7*) offers a promising approach (see the figure).

The authors found that the river food web, a fundamental feature of a river's ecological integrity (*8*), lacks large aquatic insects, key species that are common in sections of the Colorado River not strongly influenced by hydropeaking flows. Although aquatic insects spend most of their lifetimes in the water, adults take flight to mate and lay eggs in shallow water near the shoreline. Large aquatic insects firmly cement their eggs just under the water surface on partially exposed boulders. Sudden drops in water level from hydropeaking expose them to the atmosphere and cause extensive mortality.

Using a model that estimates shoreline water-level fluctuations due to hydropeaking throughout the 400 km of river in the Grand Canyon, the authors evaluated egg desiccation risk based on female egg-laying behavior relative to fluctuating water levels. The model predicted that large insects would not occur anywhere in the Grand Canyon. But it also made a second, unexpected prediction: Native, small-bodied insect species would be much more common in two sections of the river where low water levels from the propagating hydropeaking waves occur predictably in the evening, when adults actively fly and lay eggs. These insect species do not cement all eggs on boulders, so some should remain underwater during the entire hydropeaking cycle and thus survive and hatch.

To test these predictions, the researchers turned to the river rafters who camp everywhere throughout the Grand Canyon from late spring to early fall. Over the course of 3 years, hundreds of these citizen scientists captured and preserved more than 2500 individual insect samples during 1 hour beginning at local sunset by attracting flying insects to ultraviolet lamps. The results were striking: Large-bodied insect species were

[1]*Department of Biology, Colorado State University, Fort Collins, CO 80524, USA.* [2]*Institute of Applied Ecology, University of Canberra, ACT 2617, Australia.* [3]*Department of Watershed Sciences, Utah State University, Logan, UT 84322, USA. Email: n.poff@colostate.edu*