OPTOELECTRONICS

Combining chemical worlds

Using self-assembly and electrodeposition, complementary organic and inorganic building blocks are combined to form a lamellar hybrid that is an efficient photoconductor.

Alejandro L. Briseno and Peidong Yang

A goal of molecular materials chemistry is to develop synthetic strategies for the precise placement of molecular building blocks at nano- and mesoscale levels. If the building blocks comprise both organic and inorganic moieties, the resultant hybrid composites have the advantage of combining complementary strengths from two different chemical worlds. By piecing together a judicious choice of these components in a controlled manner, the complexity and functionality of the crystalline framework can be considerably enhanced[1]. These materials, with properties that are difficult or impossible to achieve in a conventional solid lattice, may have far-reaching implications for a number of areas such as photovoltaics, magnetism and superconductivity.

A classic example of these hybrid materials is intercalated compounds[2]. Many layered materials, such as graphite and clay, occur naturally. When the space between the crystalline sheets is occupied by selected ions or molecules, intercalated crystalline solids with tunable electronic and optical properties are produced. For example, layered organic–inorganic perovskites have been successfully used for flexible, light-emitting devices as well as field-effect transistors[3,4]. The inability to design and synthesize organic–inorganic hybrid materials in which the precise placement of molecular building blocks can be controlled, however, remains a problem. On page 68 of this issue, Samuel Stupp and co-workers take up this challenge and report a strategy for synthesizing well-ordered, alternating lamellar layers of electronically active, hybrid nanomaterials[5].

One possible strategy towards functional optoelectronic composites is to use an organic material that can efficiently harness photons from light and convert them to useful energy through a highly conducting inorganic material[6]. Until now, this has been achieved by incorporating structure-directing insulating organic materials to template-ordered nanoscale patterns of inorganic semiconductors, followed by removal of the organic component and infiltration with a functional organic

material[7]. This approach, however, does not further improve the nanoscale ordering nor does it take part in the crystallization process of self-assembly.

The nanocomposites made by Stupp and colleagues[5] are composed of conjugated organic semiconductors and inorganic ZnO. The layers are deposited in one simple step directly onto the surface of an electrode, resulting in the fabrication of a photoconductor device. This remarkable hybrid system incorporates the spectral tunability of conjugated organic semiconductors and the highly conducting nature of ZnO to produce an air-stable photoconductor with unprecedented performance (Fig. 1).

In general terms and in Stupp's hybrid system, the principle of operation of an organic–inorganic photoconductor is based on light absorption by the organic species. When a photon strikes the conjugated organic molecule, it excites an electron, which gets dumped into the electron-accepting inorganic lattice. This generates a flow of electrons that cause an

increase in conductivity, which is detected as a 'boost' in photocurrent. In essence, the device has the ability of converting light into either current or voltage.

Stupp and colleagues make their organic semiconductor–ZnO hybrid material in one step by using molecular self-assembly and electrochemistry. The electrodeposition is directly carried out within a solution of zinc precursor and selected conjugated organic molecules, such as the dicarboxylic acid 3-methyl-quinquethiophene. The various organic semiconductors incorporated into the hybrid system by the Northwestern University group are intelligently designed with functional groups serving specific purposes. The molecules have carboxylic acid end groups that provide chemical bonding to the ZnO lattice and alkyl linkers, which impart solubility and regulate spacing. The conjugated organic framework has a two-fold contribution: it serves as the optoelectronic element for absorbing light and also as the architectural stabilizer for lamellar formation by way of π–π interactions.
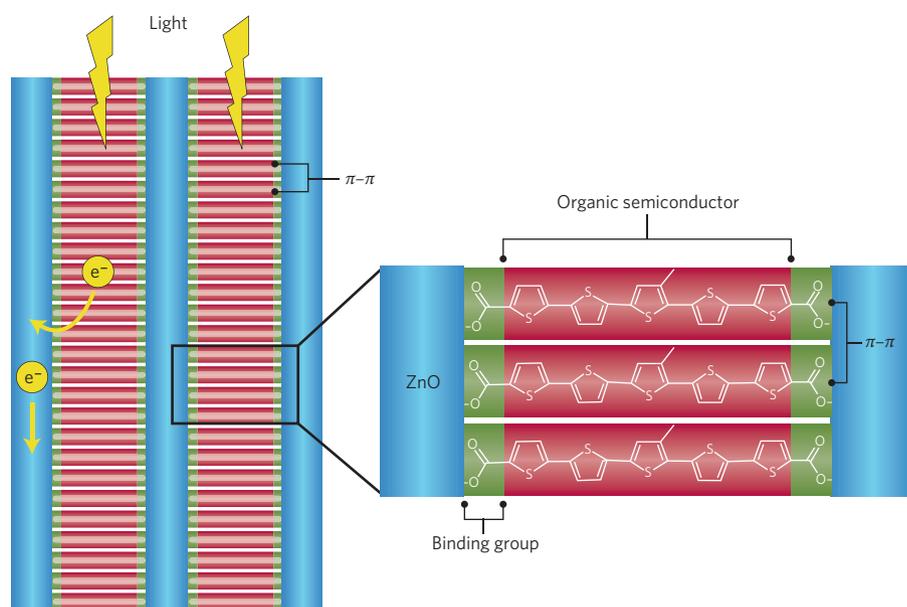

Figure 1 | Schematic of nanoscale lamellar ordering of polycrystalline ZnO layers and π-stacked layers of a dicarboxylic quinquethiophene organic semiconductor. On absorbing photons, the organic semiconductor injects 'excited' electrons into the ZnO lattice. The flow of electrons produces a photocurrent.

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The influence of a well-ordered lamellar nanostructure on photoconduction is one of the key aspects of the system of Stupp and colleagues. Electron microscopy verified that the lamellar network consists of alternating organic and inorganic components with periodicities dependent on the organic molecule being used. It is the intricate lamellar architecture that enables their devices to generate extremely large spectral responsivities efficiently. This is probably a consequence of the high loading density of organic chromophores bound to the polycrystalline ZnO network, which, of course, are responsible for harnessing photons from light. In fact, the loading density is roughly one organic molecule per atom of Zn, and this stoichiometry is among the largest reported so far. Finally, the ~1-nm-wide polycrystalline ZnO nanostructures provide a highly conducting pathway for transporting electrons to the electrodes. The resulting photoconductor sensitivity, the minimum amount of optical signal that can be detected, is among the best for organic and composite photoconductors[8],

and is even comparable to the best value reported for amorphous silicon photoconductors[9]. There is, however, still room for improvement, such as reducing the background noise and dark current in the device.

> **Using this methodology to construct hybrid materials could produce a new class of high-performance solar cells.**

The hybrid organic–inorganic photoconductors of Stupp and co-workers have several appealing features. They are comparatively easy to process, cheap, mechanically flexible and are potentially compatible with different cost-effective, roll-to-roll patterning technologies, such as screen-printing, ink-jet printing and nano-imprinting. The photoconductor device constructed from the hybrid material greatly resembles the operation of a solar cell; one can anticipate future devices being fabricated from analogues of this

electronic material. Synthesis of organic semiconductors with wider absorption ranges incorporated into such materials with the above methodology may very well enable the production of a new class of high-performance solar cells. ❐

Alejandro L. Briseno and Peidong Yang are in the Department of Chemistry, University of California, Berkeley, California 94720, USA.
e-mail: p_yang@berkeley.edu

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QUANTUM DOTS

Squeeze or stretch?

In semiconductor quantum dots, the electronic wave functions are squeezed into small areas. Stretching them in a controllable yet simple way profoundly affects their properties and can give them characteristics important for practical applications.

Jacek Kossut

Semiconductor quantum dots are materials systems in which the electron motion is confined in all spatial directions. This confinement gives rise to a discreet energy spectrum for the electrons similar to that of atoms; hence the term 'artificial atoms' is often used to refer to quantum dots, even if they actually consist of thousands, or even tens-of-thousands, of atoms. Quantum dots are undoubtedly one of the most studied systems in materials science: they can be used as models for fundamental studies of the quantum properties of electrons; they also have strong potential for diverse applications, ranging from electronic devices to biomedical imaging. There are several methods of quantum-dot fabrication, of which wet chemistry is probably the cheapest and therefore the most interesting in terms of wide-scale application[1–3]. Because of their typical size (a few nanometres in diameter), quantum

dots obtained in this way are typically referred to as 'nanocrystals'.

A common approach to strengthen confinement in a quantum dot, as well as improve its optical properties, is to enclose the nanocrystal in a layer of a different material (usually with a wider bandgap), effectively creating a core–shell structure. On page 35 of this issue, Bussian and colleagues report on such a core–shell structure in which the shell is used to stretch the electronic wavefunction rather than squeeze it even more[4]. The quantum dots they examined consist of ZnSe cores doped with Mn and enclosed in a CdSe shell. The addition of magnetic atoms actually transforms the quantum dots in the nanoscale analogues of bulk-diluted magnetic semiconductors (DMSs) — the workhorse materials of emerging spintronics. Each Mn atom carries a large magnetic moment, S, and through an exchange interaction with the electron

spin it influences the energy spectrum of the electrons[5]. In particular, it can induce the so-called 'giant spin splitting' of the energy levels, which corresponds under favourable conditions to a g-factor of several hundred.

Bussian *et al.* used a CdSe shell with a narrower gap than the ZnSe core. The effect of this unusual design is that although the electrons in the conduction band are still confined in the core, those in the valence band — and therefore any optically excited hole — have a wavefunction peaked in the shell and in proximity to the core–shell interface (Fig. 1). The degree to which the valence electrons are pulled out depends on the thickness of the outer shell and may be precisely controlled during preparation of the nanocrystals. On the other hand, introducing Mn ions into nanocrystals occurs only during the early stages of growth, so they tend to be buried in ZnSe. The fact that the valence electrons reside in the outer shell, rather than in the core,