

Editor's Note: In keeping with the European setting of the 203rd ECS Meeting we thought it would be interesting to gather perspectives from some of the speakers at this gathering in advance of the meeting. Excerpted below are comments from three invited speakers in the A2-Nanotechnology Symposium in Paris. In the next issue of Interface, we will present more comments from this symposium. PRASHANT KAMAT, a co-organizer of this symposium (which is sponsored by all the Divisions) and the current chairman of the Fullerenes, Nanotubes, and Carbon Nanostructures Division, is thanked for his assistance in coordinating the following submissions.

Surface Science in Nanotechnology

by Marie-Isabelle Baraton

Nanotechnology originates from the ability of researchers to manipulate matter at the nanometer scale and has resulted in materials with novel and significantly improved physical, chemical, and biological properties. Nanotechnology implies the control of matter at the atomic and molecular level and is requiring researchers to work across boundaries of classical disciplines, including social sciences and education.^{1,2} Figure 1 gives a very basic scheme of the interdisciplinary character of nanotechnology by showing the overlaps between nanotechnology and fields of applications. This scheme should however be regarded as a three dimensional construction because all these fields also overlap each other.

Strong hopes are now put on nanomaterials and nanotechnology and are resulting in a sort of dream in which nanotechnology will solve all the current problems in any scientific field from electronics, optoelectronics, and photonics to energy storage or to medicine and biology. Many proposed approaches can in principle bring ultimate solutions and successful demonstrations have been made in laboratories throughout the world. In Fig. 1, some applications, which have already been proved to benefit from nanotechnology, are mentioned in each classical field. But, a very important point to address is certainly the integration of nanotechnology in current industrial processes. Although big companies, such as IBM, HP, Hitachi, Dow, 3M, Corning, and Motorola, to name a few, are devoting an important part of their R&D budget to nanotechnology, this field of research is still considered as highly risky by investors who do not expect a return on investment before 5-7 or even 12 years. Nevertheless, the National Scientific Foundation (NSF, USA) has estimated that the total market for products and services related to nanotechnology should reach 1,000 billion U.S. dollars by 2015.

To achieve systems at the nanometer size, researchers are actually following two parallel ways known as the "top-down" and "bottom-up" approaches. The main drawback of the "top down" approach (basically an extension of the existing processes, such as microlithography), to reduce the size of systems, is that the cost for constructing new fabrication lines ensuring sub 10 nm resolution become highly prohibitive. In the "bottom-up" approach, the controlled assembly of atoms, molecules, and

building blocks into the desired component is highly problematic and there are no established mass production techniques for obtaining devices on a commercial basis. Obviously, the ultimate nanodevices will emerge from the balance between these two complementary nanofabrication approaches.

One of the major problems that researchers are facing when working in nanotechnology is that matter at the nanometer scale can no longer be considered as a bulk entity.

Nanoparticles, for example, should be regarded as surfaces in 3 dimensions.³ The role played by surfaces and interfaces becomes preponderant and the properties of the material are determined by surface effects. Indeed, if one considers a cube with a size around 3 nm, 50% of the total number of atoms are surface atoms. As a consequence, adsorbates and surface contaminants play a major role. As the chemical species adsorbed on the surface continuously evolve with the environmental conditions, it becomes extremely difficult

to define intrinsic properties of the materials at the nanometer scale.⁴

The part played by the surface in nanomaterial properties is far from being clearly evaluated. First, it is not always straightforward to discriminate surface effects from size effects. For example, the size of a particle influences the surface reactivity and therefore both the nature of the adsorbates and the strength of the interactions, whereas the surface adsorbates influence the work function and the space charge region of a semiconductor and therefore the electronic properties. Second, in the case of nanomaterials and nanosized particles, the techniques for surface characterization do not always allow one to adequately probe the very first atomic layers independently from the bulk.

Because surface effects play the dominant role, specific properties can be obtained by modifying, adjusting, and tailoring the surface chemical composition and the surface reactivity of the considered nanomaterial. Surface functionalization thus becomes an essential asset to design nanomaterials exactly suited for a particular application.⁵ In the case of nanoparticles, controlling the surface chemical composition and mastering its modification at the nanometer scale are critical issues for high-added value applications.⁶ As a result, control of the surface

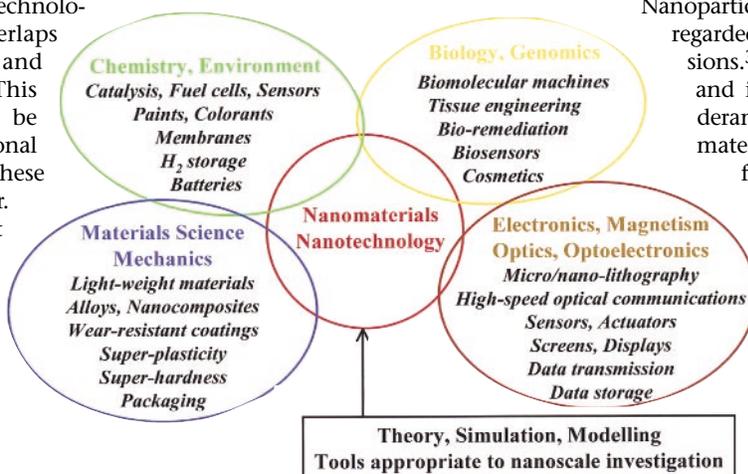


Fig. 1. Basic scheme of the overlaps between nanotechnology and classical disciplines.

chemical composition and the monitoring of the chemical reactions leading to surface modifications are prerequisites to reliability and reproducibility of nanoparticle and nanomaterial performance. ■

References

1. N. Lane, *J. Nanopart. Research*, 3 (2-3), 95 (2001).
2. M. C. Roco and W. S. Bainbridge, *J. Nanopart. Research*, 4 (4), 281 (2002).
3. G. A. Somorjai, *MRS Bulletin*, 23 (5), pp. 11 (1998).
4. R. K. Cavin III, D. J. C. Herr, and V. V. Zhirnov, *J. Nanopart. Research*, 2 (3), 213 (2000).
5. *Synthesis, Functionalization, and Surface Treatment of Nanoparticles*, M.-I. Baraton Editor, American Scientific Publishers, Stevenson Ranch (CA, USA), 2002.

6. K. E. Gonsalves, M.-I. Baraton, R. Singh, H. Hofmann, J. X. Chen, and J. A. Akkara (eds.), in *Surface Controlled Nanoscale Materials for High-Added-Value Applications*, Proceedings of the Materials Research Society, Vol. 501, Warrendale, PA, USA (1998).

About the Author

M.-I. BARATON is with SPCTS-UMR 6638 CNRS, University of Limoges in France. She can be reached via e-mail at baraton@unilim.fr.

Squeezing Light Through Tiny Holes

by T. W. Ebbesen

Materials structured on the nanometer scale can lead to improved and sometimes surprising properties. Metals are no exception to this rule. Metal particles display colors which vary with their size. The color results from the coupling of light with the free electrons of the metal particle to form surface plasmons.

Several years ago it was discovered that the reverse structures, *i.e.* holes in a metal film, display extraordinary optical properties that also involve surface plasmons.¹ Optically thick metal films perforated with subwavelength hole arrays as shown in Fig. 1 transmit light with an efficiency 100 times greater than what is predicted for single holes. Perhaps even more surprising is that the efficiency is greater than the area occupied by the holes. In other words even some of light impinging on the metal between the holes is transmitted, the periodic structure acting much like an antenna at optical wavelengths. This is possible because the incident light couples to surface plasmon of the film. The transmission spectra contain peaks that correspond to surface plasmon modes, which depend on the symmetry and period of the hole array.¹⁻³ By simply changing the period (*i.e.* the distance between the holes), the transmission peaks move leading very different apparent colors as illustrated in Fig. 1.

The hole diameter being smaller than half the wavelength of the transmitted light, light cannot propagate through the holes. Instead the transmission process involves evanescent tunneling from the input side to the output side. The surface plasmon modes on the output side then couple back to light which propagates away from the surface.⁴

In general a flat metal surface cannot trap light in the form of surface plasmons due to momentum mismatch. This problem is overcome in the presence of a periodic structure, such as the hole array, which allows momentum conservation. Hence one would expect that single

apertures in a metal film surrounded by a periodic corrugation also display enhanced transmission and indeed this is the case.⁵ For example, a subwavelength hole in bull's eye structure as shown in Fig. 2 give rise to highly efficient enhanced transmission.

If the film surrounding the hole on the output side is smooth, then the light diffracts in all directions as expected from standard optics. Hence the emerging light spot size increases and its intensity decreases rapidly away from the surface. Recently we have shown that this problem can be overcome by adding a period corrugation on the output surface.⁶ The emerging light is then directed in a well defined beam with a relatively small optical divergence (ca. 6°). Such structures can

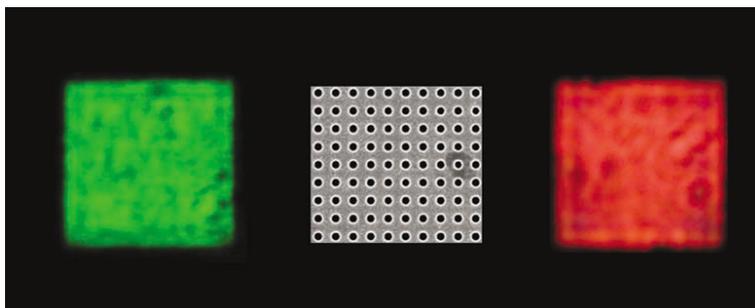


Photo courtesy of A. Degiron

FIG. 1. Center is SEM image of a hole array in Ag (hole diameter ca. 200nm). Right and left are far field images of the transmitted light, the colored being tuned by the period of the hole array.

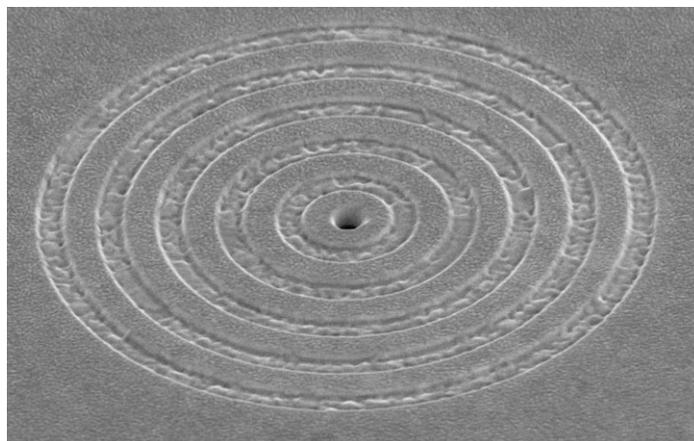


Photo courtesy of A. Degiron

FIG. 2. Subwavelength hole (diameter ca. 200 nm) in a bull's eye corrugation in Au. Such structure gives rise to enhanced transmission and beaming of the light exiting the hole.

also be used to disperse light according to wavelength much like a miniature prism.

These findings, and those of other groups, demonstrate the possibility of making miniature novel optical devices using surface plasmons. Surface plasmon photonics is presently being tested for applications in areas such as optomagnetic data storage, quantum cryptography, near-field microscopy, sensors, and optical circuitry. Modern nanofabrication techniques are allowing us to tailor the structure of metals and thereby the properties of surface plasmons offering a multitude of possibilities to explore. ■

References

1. T. W. Ebbesen et al., *Nature*, 391, 667 (1998).

2. Ghaemi et al., *Phys. Rev. B*, 58, 6779 (1998).

3. Kim et al., *Optics Letters*, 24, 256 (1999).

4. Grupp et al., *Adv. Mater.*, 11, 860 (1999).

5. Martin-Moreno et al., *Phys. Rev. Lett.*, 86, 1114 (2001).

6. Lezec et al., *Science*, 297, 820 (2002).

About the Author

T. W. EBBESEN is at ISIS, Université Louis Pasteur in Strasbourg, France. He can be reached at: ebbesen@isis-ulp.org.

Nanocomposite-Based "Plastic" Solar Cells

by Niyazi Serder Sariciftci

Hybrid materials combine the unique properties of one or more kinds of nanoparticles with the film forming properties of polymers. Most of the polymers can be processed from solution at room temperature, enabling the manufacturing of large area, flexible, and light weight devices. In solar cells based on pristine semiconducting polymers (Fig. 1), charge collection requires that the neutral excited states produced by photo excitation can be separated into free charge carriers first, the so called exciton dissociation. The generated free charges are then transported through the device to the electrodes. The charge collection is dependent on how the carriers can reach the electrodes without recombining with oppositely charged carriers in the photoactive layer. Exciton dissociation is known to occur very efficiently at interfaces between the two organic semiconductors mixed together in a composite thin film such as a conjugated polymer and fullerene mixtures. In this interconnected network structure, blending an electron accepting and a hole accepting material can result in the formation of domains close to the desired 20 nm exciton diffusion length scale. Replacing the flat interface by an interconnected network structure of *p*- and *n*-type materials leads to a high surface area in the whole volume for charge separation, *i.e.*, the bulk heterojunction.^{1,2} Based on interconnected networks of hole conducting polymers (*p*-type) with percolating electron con-

ducting Buckminsterfullerene (C₆₀) derivatives (*n*-type), recently more than 2.5 % solar power conversion efficiency has been achieved (Fig. 2).⁴ In bulk heterojunction cells, nanoscopic morphology of the composite layers play a fundamental role for efficient solar cell performance.

Another strategy is to fabricate blends of nanocrystals of inorganic semiconductors with semiconductive polymers as a bulk heterojunction photovoltaic layer. The classical inorganic semiconductor materials for photovoltaic applications can have a high absorbance coefficient and photoconductivity. For a reasonable morphology of the blends, nanoscale inorganic particles should be used. To give an idea, the fullerene molecules embedded in the polymer are about <1 nm in diameter, the cluster size, however, is heavily dependent on the processing conditions. It has been shown that composite films cast from chlorobenzene have grain sizes fullerene below 50 nm.

Photovoltaic characteristics of CdSe and CdS core/shell particles have been most extensively explored by the group of Alivisatos, et al.^{3,4} Arici, et al. investigated blends of poly (2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) and of regioregular poly (3-hexylthiophene) (P3HT) with copper indium diselenide (CISE) and copper indium disulfide (CIS) nanocrystals.⁵

Recent efforts in dye-sensitized nanocrystalline TiO₂ solar cell research are more

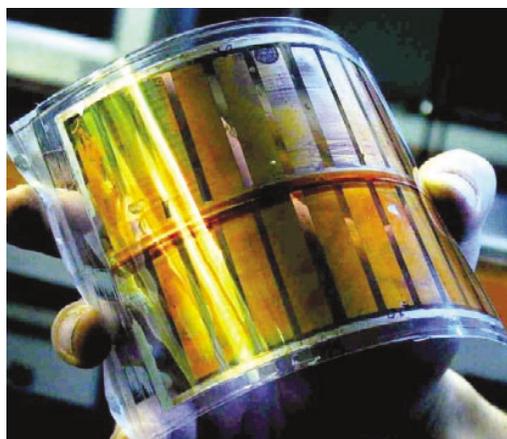


Fig. 1. A Nanocomposite-based plastic solar cell.

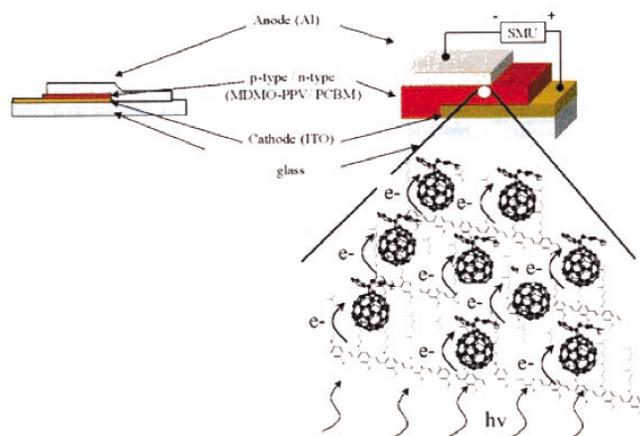


Fig. 2. Schematic of a polymer-C₆₀ based plastic solar cell.

focused on replacing the liquid electrolyte with solid-state analogs to eliminate problems with sealing and degradation.⁶⁻⁸ Early work focused on the use of solid state *p*-type semiconductors CuI and CuSCN. Cells made in this way gave solar efficiencies of several percent. Various procedures have been employed in the fabrication of solid-state dye-sensitized TiO₂ solar cells with *p*-type organic materials, that accept holes from the Ru-bipyridyl-based dye cation.⁷ For an efficient cell, organic materials placed on the top of the working electrode should penetrate into the nanoporous TiO₂ and should form a good contact to the adsorbed dye. Crystallization of the organic material is undesirable, as it would impair the formation of a good contact between the electrode and the hole conductor. Semiconducting polymers in this sense are good candidates due to their mainly amorphous character. Such hybrid solar cells based on nanocrystalline TiO₂ electrodes with semiconducting polymers are investigated in many groups worldwide.^{7,8}

Research efforts over the last decade have led to a number of new strategies for the preparation of organic/organic as well as organic/inorganic nanocomposite solar cells. A number of major scientific and technological advances in the construction of bulk heterojunction hybrid solar cells have occurred recently and many more are expected. It is envisioned that future application potential of photovoltaics will depend on optimising the production technologies for large

area/large scale, low cost products. In this manner, the nanocomposite materials displayed here have an edge due to their production and processing advantages. ■

References

1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science*, **258**, 1474 (1992).
2. C. Brabec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Func. Mat.*, **11**, 15 (2001).
3. W. U. Huynh, W. W. Dittmer, and A. P. Alivisatos, *Science*, **295**, 2425, (2002).
4. A. P. Alivisatos, *Science*, **21.7**, 933 (1996).
5. Elif Arici, N. S. Sariciftci, and D. Meissner, *Adv. Func. Mater.*, In press.
6. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).
7. M. Grätzel, *Nature*, **414**, 338 (2001).
8. D. Gebeyehu, C. J. Brabec, N. S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F. Kienberger, and H. Schindler, *Synth. Met.*, **125**, 279 (2002).

About the Author

N. S. SARICIFTCI is at the Johannes Kepler University in Linz, Austria. He can be reached at: serder.sariciftci@jku.at.