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SPIE International Technical Group on Nanotechnology

The SPIE Nanotechnology Group, launched in Seattle two years ago and already over 270 strong, had a packed and lively meeting at the 49th Annual Meeting of SPIE on 5 August 2004. We had two special presentations: one technical, and one on the ethical and practical implications of nanotechnology as discussed in a new Royal Society report. Both were followed by lively discussion.

First, in a fascinating survey entitled *Trends in Thin Film Modeling*, Dr Talat Rahman[1] from Kansas State University described the considerable intricacies that arise in representing processes such as nucleation, diffusion, and island formation. At the atomic level, the nature or meaning of a conventional diffusion coefficient is something of a mystery: not least because of the diversity of units (single atoms, dimers, trimers etc.) that can move around.

A critical island size, judging from scanning tunneling microscope experiments, often seems to be a dimer. Illustrating her exposition with results from a variety of systems, Dr Rahman showed how island shapes and growth morphology are influenced by a host of factors including the substrate structure. Fractal formations are often observed at low temperatures, especially on the (111) face of a face-centered-cubic lattice. Under other conditions, dendritic structures form: though often an extremely marginal change in conditions can completely alter the growth morphology. The dependence on temperature, in particular, is non-trivial: it has an indirect influence on other system parameters such as the form of potential energy surfaces and vibrational modes. Dr Rahman's talk prompted a highly stimulating discussion.

The second half of the meeting began with a presentation by Dr Akhlesh Lahktakia[2] from Pennsylvania State University, summarizing the Royal Society and Royal Academy of Engineering report *Nanoscience and Nanotechnologies: Opportunities and Uncertainties*,[3] published the previous week. The ensuing discussion session on the societal value and ethics of nanotechnology drew the audience into a wide-ranging and highly thought-provoking debate. Many participants flagged the need for nanotechnology practitioners to better educate the general public on the real issues for concern.

The scale of this task was highlighted by several who pointed to the generally low level of science comprehension—there are some members of public who believe nanoparticles are smaller than atoms! It was pointed out that molecules are smaller than nanoparticles, and that we have learned to work with them. Moreover, in dealing with other risks such as chemical toxins, biohazards, and radioactive materials, scientists ands technologists have put in place all the necessary protocols. What is required is to implement them appropriately for nanoparticles, at least until it can be shown that the risk for any particular particle is insignificant. Importantly, this extends to proper waste management. It was generally agreed that—as with other areas of science—it is best practice to treat nanoparticles as potentially dangerous until proven otherwise.

It was also noted that the media often drives public concern more effectively than expert view. Nanoparticles already exist in the everyday world in places where the public might not expect to find them: in cigarette smoke, for example, and in the dust released by sanding down paintwork. In terms of atmospheric ingestion, one redeeming feature of nanoparticles is their tendency to aggregate, though the larger, micron-sized particles in smoke certainly represent significant health risk. It is helpful to delineate a distinction between nanoscience (which might involve studies on maybe just one particle), nanotechnology, and nanomaterials. In considering the possible health impact on students and others involved—the welfare of those making or using materials such as nanodots, for example—a possible threshold for concern might be the milligram level.

At any event, it is necessary to build all necessary safeguards and establish full confidence. Is it not better that those who are experts engage in these matters, rather than let politicians or lawyers to make the decisions? The clear consensus of the meeting was that those who are involved in nanotechnology in its broadest sense need to recognize their responsibility to establish all necessary safeguards, and to cultivate a sense of ownership to responsibly inform the public.

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Fluctuation-enhanced sensing: electronic dog nose identifies odors and counts molecules

Chemical sensing classically involves the measurement of the value of a physical quantity in the sensing medium. Such methods are many orders of magnitude less sensitive than are the noses of dogs or even humans.

So, how do biological noses do the job? They contain a large array of olfactory neurons which communicate stochastic voltage spikes to the brain. When odor molecules are adsorbed by a number of neurons, the statistical properties of these stochastic spikes change. The brain decodes the changes in statistics and matches the result with an odor database in memory.

Recently, a new method[1-6] has been discovered and developed that mimics biological smelling. The first step is similar to the classical sensing method: the value of a physical quantity in the sensing medium is measured (the output voltage of a chemical sensor, for example). Then the microscopic spontaneous fluctuations of these measurements are strongly amplified (typically 1-100 million) and the statistical properties of these fluctuations are analyzed. These fluctuations are due to the dynamically changing molecular-level interactions between the odor molecules and sensing media, thus they contain the chemical signature of the odor. The results are compared with a statistical pattern database to identify the odor. The new method has been called *fluctuation-enhanced* sensing.

Fluctuation-enhanced sensing has outstanding properties compared to classical chemical sensing, because:

1. It provides significantly more chemical information about the odor.[1,2] Even a single sensor produces a complete pattern[1-3] corresponding to the chemical and its concentration, see Figure 1. (It is important to note that the results in Figure 1 were obtained by a commercial, off-the-shelf sensor designed for nitric oxide detection). These patterns can be stored in a database and may be used to identify the chemicals belonging to subsequently-measured patterns.[4]
2. The relative mean-square fluctuations scale inversely with the active surface of the sensor.[1] Therefore, the smaller the sensor, the greater the sensitivity of this method. Figure 1 was obtained by a large sensor with an active surface of a few square millimeters. Using the same kind of sensor material with submicron size, the estimated sensitivity is in the sub parts-per-billion concentration range.

To count individual molecules,[5,6] sensors at the nanometer scale are required. Figure 2 shows the result of computer simulations[5] of the output signal of a nanoscale MOSFET (metal-oxide-semiconductor field-effect transistor) sensor. Instead of spectral-statistical measures, this method uses amplitude-density measures[5] of a single-molecule occupation of sub-spaces in a submicron-sized sensor with surface diffusion.

Though fluctuation-enhanced sensing has been proven to be superior to classical methods, many important questions have to be solved before the method can be industrialized. These include signal separation of simultaneously-present chemicals, selection of the most appropriate sensor materials, optimal sensor geometries, and so forth.

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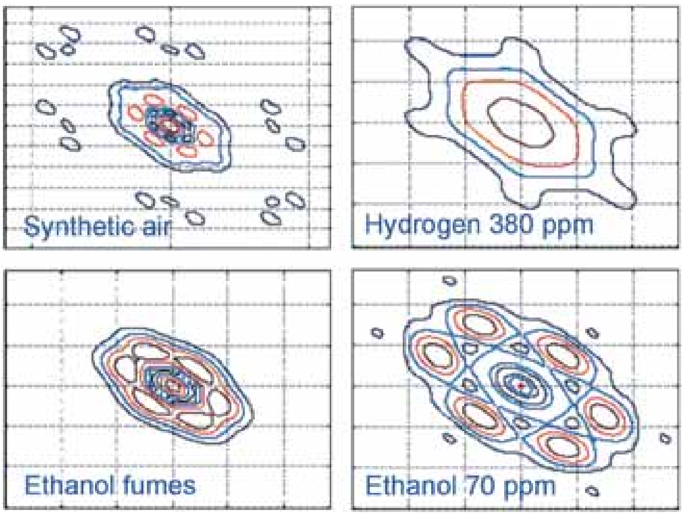

Figure 1. Bi-spectra signatures of chemicals recorded with a commercial nitric-oxide sensor of surface area of the order of square millimeters. Because the normalized fluctuations scale linearly with area, a micron-sized sensor would allow sub parts-per-billion sensitivity.

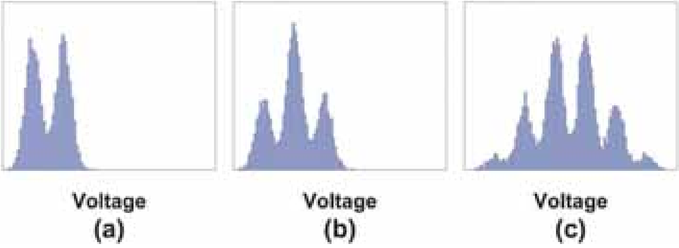

Figure 2. Amplitude density of the output voltage of a molecular counter arrangement with a submicron MOSFET (metal-oxide-semiconductor field-effect transistor) sensor with surface diffusion: (a) one molecule; (b) two molecules; and (c) five molecules.

Silica-gold nanoparticle clusters as chemical sensors

In recent years, inorganic nanomaterials have been increasingly used as components in chemical sensors. Inorganic nanoparticles are well suited to chemical sensing applications because their physical properties often depend sensitively on the chemical environment of the particle. Molecules or ions that adsorb to the surface of the particle are often able to perturb the electronic structure, causing a change of a physical property (magnetism, color, conductivity) that is then analyzed in the sensor. Living systems, on the other hand, have developed a different sensing mechanism. Here, the binding of a molecule or a cell often causes a structural or conformational change in the receptor. This structural change is then converted into a change of the reactivity or another property of the sensor.

Using inorganic materials, we have constructed a sensor that adopts this biological-sensing principle. Instead of directly causing a change of a physical property of the sensing material, the binding of a molecule initiates an analyte-specific structural reorganization of it, which then leads to a characteristic change of the optical properties of the sensor.

The sensor consists of silica particles (diameter 470±40nm) that carry ~1800 gold nanoparticles (9.7±1.0nm) on their surfaces (see Figure 1).[1] These 'nanoparticle clusters' are supported by electrostatic attractions between negatively-charged citrate groups on the surface of the gold particles, and positively-charged 3-ammoniumpropylsilyl groups on the surface of the silica particles. Because the negatively-charged gold particles repulse each other, they maintain an average separation of 17nm. The sensor particles are synthesized easily and at high yield by mixing aqueous dispersions of silica nanoparticles with an excess of gold, followed by centrifuge separation.

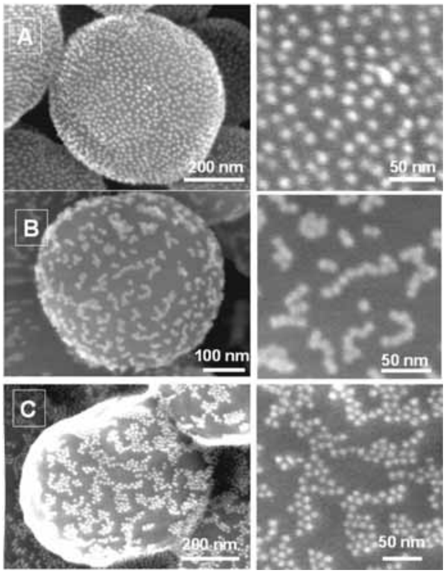

Figure 1. Scanning-electron micrographs of silica-gold nanoparticle clusters. A: As synthesized. B: After reaction with ethanethiol, which leads to chains of gold nanoparticles. C: After reaction with octadecanethiol. In this case, hexagonally-ordered islands of gold nanoparticles form. The spacing between particles in these islands is larger than in B.

When exposed to solutions of alkane thiols in methanol, the sensor particles undergo an isomerization process that leads to the structures shown in Figure 1b and 1c. Within seconds of the exposure, chain-like aggregates—small two-dimensional islands—of gold nanoparticles form by diffusion on the surface of the silica spheres. This structural rearrangement is triggered by the binding of the thiols to the gold particles and by displacement of the charged citrate groups from the gold surfaces. As neutral particles, the thiol-monolayer-coated gold nanoparticles are only weakly-bonded to the silica surfaces and thus become capable of diffusion at room temperature.

In the islands, the distances between gold nanoparticles are determined by the lengths of the alkyl groups of the thiols which range between 0.54nm (ethanethiol) and 2.93nm (octadecanethiol) in their stretched conformations. The reduced average distance between gold particles causes a shift of the gold plasmon band absorption from 540nm to 540-640nm for the thiol-reacted particles and, as a result, the sensors adopt colors ranging from purple to blue (see Figure 2). We plotted the absorption maxima of the optical spectra of the thiol-reated sensor particles against the lengths of the alkane groups of the thiols. What we observed was an inverse relationship between the length of the thiol-alkyl group and the wavelength of the absorption maximum of the sensor particle (see Figure 3). It was thus possible to identify an alkanethiol from the color change of the sensor particle.

The reaction of these particles with thiols is also very sensitive. Micromolar concentrations of hexanethiol still produce a color change that can be observed with the bare eye, and as little as 2nmol of hexanethiol can be detected this way. However, a drawback of the sensor system is that the structural and optical changes induced by the thiols are not reversible. Also, the system only detects thiols, which are known to have a strong binding-affinity to gold. However, using surface-engineered gold nanoparticles, it might be possible to overcome these limitations. The result could be nanoparticle-based materials, with comparable structural flexibility, that could be used as chemical sensors or as reversible chemical switches.

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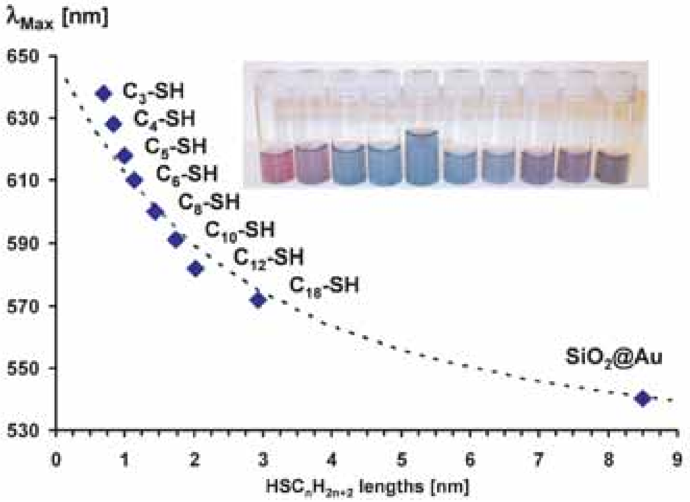

Figure 2. Dependence of the absorption maxima of the sensor particles on the lengths of the alkyl groups in the thiols. Insert: Photograph of dispersions of the particles after reaction with thiols.

Direct measurement of the picosecond, photoelectric response time of bacteriorhodopsin

Bacteriorhodopsin (BR) is a protein found in the cell membrane wall of a micro-organism called *Halobacterium salinarum*, where it functions as a light-driven proton pump.[1,2] Its extreme light sensitivity, polarization sensitivity, and robustness make this protein an attractive material for applications involving agile photoreception. These include high-speed tracking, motion and edge detection, high-resolution image detection, and so forth.[3-6] In order to be able to predict the full potential of BR in high-speed optoelectronic applications, it is necessary to understand and characterize the molecular dynamics of BR upon photoexcita-tion and, in particular, the initial photovoltage transient.

BR spans the 5nm thickness of the purple membrane (PM) of *Halobacterium salinarum* and is arranged as trimers in a two-dimensional crystalline hexagonal lattice (lattice constant ~6nm). The light-absorbing chromophore of BR carries a positive charge, which interacts electrostatically with charged amino acids in the protein and establishes an overall electrostatic and photochemical equilibrium. Upon absorption of light, there is a shift of electron density by ~2.6 Å. This shift interacts with negative-charge residue in the protein, which induces a rotation around double-bond carbon atoms and generates a torsional distortion (bending) ofthe chain. This is the so-called photoisomeriza-tion process.

Photoisomerization of the chromophore causes a movement of the protonated Schiff base away from its negative counter ion on the opsin, and conversion of BR to the virtual, excited J state. Photoisomerization also causes a charge separation perpendicular to the membrane as the protein relaxes from the J to the K state. This generates a transient photoelectric signal.

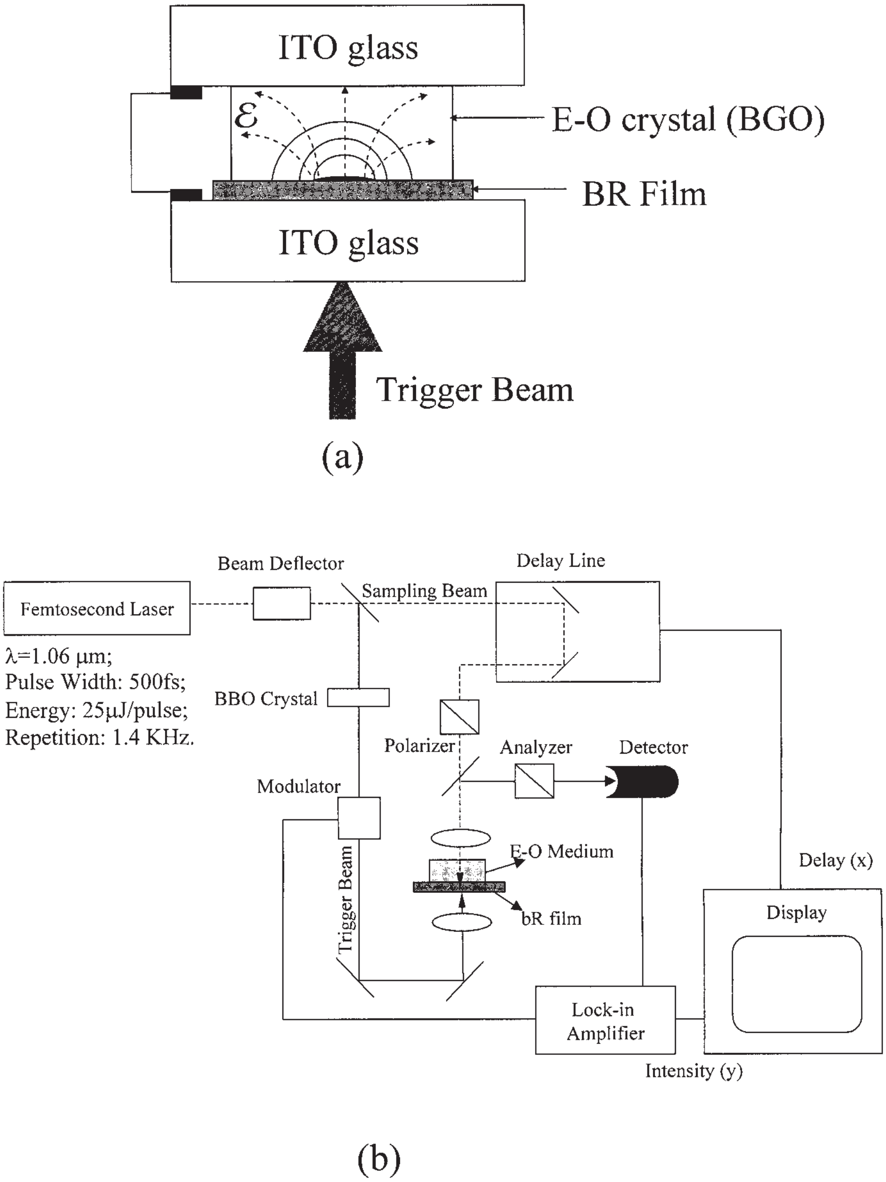

Figure 1. (a) Schematic of the induced birefringence in the electro-optic crystal by the electric field of the photo-pumped bacteriorhodopsin (BR) film. (b) Schematic diagram of the electro-optical measurement system used to observe the ultrafast photoelectric response of BR.

We used an ultrafast electro-optic (E-O) sampling technique[7] where the photoinduced electric field in the BR is directly probed to exactly measure the transient photoresponse characteristics (see Figure 1). A 10μm-thick BR film was placed in contact with a bismuth-germanium-oxide (BGO) Crystal that was 100μm thick and had a surface area of 10×10mm^2 normal to the <001> direction. The BGO crystal has cubic symmetry (23), a refractive index of 2.55 at λ=1.06μm, a quasistatic relative permittivity of 40, and a linear electro-optic coefficient of 3.4×10^{12}m/V. A coating that is highly-reflective at both wavelengths 1064nm and 532nm was placed on the protein-contacting side of the BGO crystal, which was then sandwiched between two indium-tin-oxide-(ITO-) coated glass plates (see Figure 1a). Measurements were made with a passively mode-locked, 1.06μm regenerative amplifier delivering 500fs, 0.025mJ pulses with a repetition rate of 1.4kHz. A separate pump beam at 532nm was generated with a non-linear BBO crystal (Beta-Barium-Borate). The 1.06μm probe beam was passed through a variable delay line and the sample was placed between a crossed polarizer and an analyzer. The transmitted probe signal was detected with a cooled InGaAs photodiode and lock-in technique for high sensitivity.

The time-resolved electro-optic measurements were carried out with an incident (average) maximum pump-beam intensity of 50mW/cm^2 (~35μJ/cm^2 pulse energy density) and (average) maximum probe beam intensity of 300mW/cm^2 (~200μJ/cm^2 pulse energy density). The transmitted probe light detected with lock-in amplification is plotted against delay time. Figure 2 shows the normalized BR photoelectric temporal response. The observed negatively-increasing photoelectric response has a time constant of 4.5ps, which provides an upper limit for the response speed of BR-based photodetectors. The picosecond response time is expected to be highly significant in nanophotonics and bionanotechnology.

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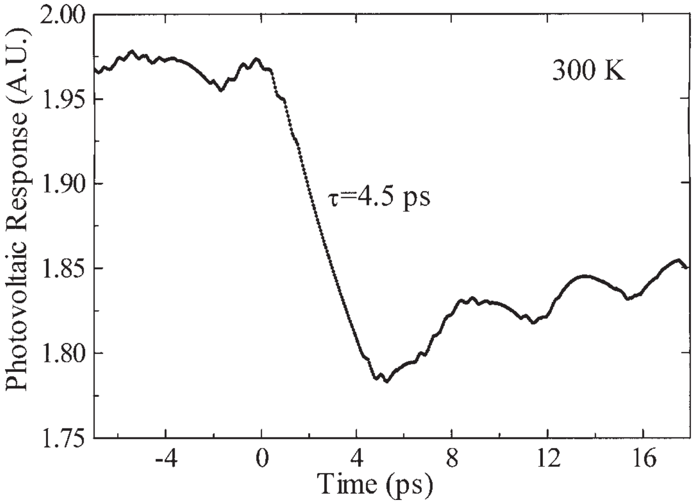

Figure 2. Time-resolved temporal measurement of the initial photoelectric response of the oriented bacteriorhodopsin film. The rise time of the photoelectric signal was measured to be 4.5ps.

BOOK REVIEW

Nanobiotechnology: Concepts, Applications and Perspectives

Edited by **C. M. Niemeyer and C. A. Mirkin**

Published by John Wiley & Sons, Weinheim, 2004
ISBN: 3527306587, pp. 491, $180

Nanobiotechnology could be the next big thing, and curing cancer the killer application. At least, the US National Cancer Institute seems to agree with that statement and held a series of 'roadshows' throughout the US to discuss the state of the art and future directions for funding. However, the participants seemed to be challenged in defining what research and development activities can be reasonably labeled nanobiotechnology, and the formulation of a proper definition of the field was cited as one of the critical tasks.

In this situation, the publication of *Nanobiotechnology* is a milestone, since it provides, in 27 chapters written by leading scientists, the first overview of, "Concepts, applications, and perspectives," of the field, as the imaginative subtitle of the book already suggests. Christof Niemeyer and Chad Mirkin, the editors and eminent authorities, define nanobiotechnology as, "A field that concerns the utilization of biological components…to fabricate functional nanostructured and mesoscopic architectures comprised of organic and inorganic materials," and the application of nanotechnologies to the study of biology. But by following the ideas laid out in this book by nanobiotech's practitioners, the reader can gain a deeper, more implicit understanding of the diversity of the field. The range of the experimental and theoretical approaches is impressive, and each of the chapters covers a distinct topic in depth.

Niemeyer and Mirkin provide only a minimal preface, which does not elaborate much on their personal vision. Given the pace of progress and the fluidity of the boundaries of this field, this understated approach to editing may be a wise choice. Their target audience is clearly the advanced student or experienced scientist who desires an up-to-date text rich in detail, but is herself or himself capable of placing the material in a larger context.

While a particular strength of the book is the choice of outstanding contributors from the US, Europe, and India, the complete absence of Japanese authors was surprising to me, given the large Japanese presence in nanotechnology in general.

In summary, I would rate the book a 'strong buy'. It is a high-quality text—well illustrated, and extensively referenced—that provides the first authoritative overview of this emerging field.

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