



# MRS Meeting Scene...

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## ICMAT 2011 – International Conference on Materials for Advanced Technologies

Suntec, Singapore  
June 26 - July 1

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The second day of the Sixth International Conference on Materials for Advanced Technologies (ICMAT) in Suntec, Singapore, featured two more Plenary Lectures, the second lunchtime Theme Lecture, and a full slate of technical papers in all the symposia. But in the evening the conference extended beyond the conference center's walls to the National University of Singapore.

Since its founding in 2001, ICMAT has a tradition of reaching beyond the professional science world to hold public lectures in which Nobel Laureates speak to meeting attendees and the general public. On Tuesday evening hundreds gathered at the National University of Singapore to hear Albert Fert, who received the Nobel prize in Physics in 2007, talk about spintronics, and Ada Yonath, who received the Nobel Prize in Chemistry in 2009, speak about "The Amazing Ribosome." In between these lectures, the Institute of Physics, Singapore, held its annual Gold Medal Award to recognize the academic achievements of Singapore high school students who have demonstrated an outstanding grasp of physics at a young age. They must have been thrilled to receive their award from the hands of Nobel Laureate in Physics Albert Fert. Certainly there was at least one future Nobel Laureate in that group of accomplished, promising teenagers.



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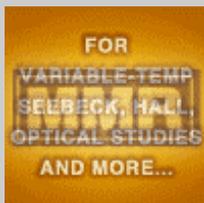
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## ■ Second Plenary Lecture: Joachim Luther

### Transformation of Today's Energy Systems Towards Sustainability -- Challenges for Materials Science



In 1987, the UN defined sustainable energy use as that which meets our present needs without compromising the ability of future generations to meet their's. Joachim Luther, CEO of Solar Energy Renewable Initiative of Singapore, began his plenary lecture with a refresher on the now-common term sustainable energy. He proceeded to lay down a broad overview of the topic, from the pressing need for sustainable energy to the means for achieving it, providing a refreshing perspective on a much-discussed topic.

The motivations Luther cited for replacing fossil-fuels went beyond the obvious: protecting natural life support systems, reducing energy poverty in developing countries, and promoting peace by reducing dependence on regionally concentrated energy resources. By way of perspective, however, he pointed out that all energy sources, including renewables, have secondary impacts, such as the dams required for hydroelectric power and the damage to biodiversity that can accompany biomass energy sources.

The potential for renewable energies is huge. Land-based solar energy alone delivers 30 to 50 times today's energy demands, stated Luther, and the potential for solar harvesting is effectively unlimited. He envisions employing a mix of techniques for solar harvesting, including flat-plate photovoltaics (PVs), optical concentrator PVs, and solar-thermal power plants. For the sake of energy security, he stressed that we should not rely on a single method. The recent growth rates for solar energy are encouraging; Luther cited a 45% increase in world-wide solar power device production since 2000 as cause for optimism. The main obstacle to further growth is simply cost, as solar energy is still at least twice as expensive as non-renewable energies, and often much more. Thus the pressing need to bring down the cost of PVs. To some extent, price reduction will be accomplished by mere scaling. The market-driven approach will only work, however, if market failure can be prevented. Luther recommends monetizing external costs of all energy sources to let market forces work properly, thus lowering the cost of PVs.

In spite of all the technological advances made in recent years, Luther pointed out that Si-wafer PVs still comprise 85% of the market, but he hopes that the development of new materials will

bring more competitive technologies to the market. He opined that the most important challenge to address is developing solar cells that harness the entire solar spectrum, from 0.7 to 3.0 eV. He boiled it down to two most important factors: efficiency and the cost of materials. Presenting a black-box thermodynamic analysis, he pointed to entropic losses as the biggest culprit of low efficiency. In the best laboratory results, the efficiencies are much lower than the theoretical limits, primarily due to the heat generated as excited carriers relax to lower states before collection. By stacking multiple narrow band-gap absorbers, these losses can be minimized and more of the solar spectrum can be utilized. While current multi-band PVs are grown by costly epitaxial processes, the result can also be achieved by mechanical stacking with appropriate interconnects. The next challenge is to collect the carriers efficiently, requiring what Luther terms “semi-permeable membranes,” which are basically materials that permit either holes or electrons to pass, but not both. Here, he entreated the audience of material scientists to focus some of their research efforts on these semi-permeable membrane materials. And of course, all this should be done with ecologically benign, Earth-abundant materials.

### ■ Third Plenary Lecture: Susumu Kitagawa

#### New Generation of Porous Materials—Soft Porous Crystals



“Gas science and technology is very important for the future,” began Susumu Kitagawa of Kyoto University in his plenary lecture on Tuesday. “Because they are crucial components of energy, life forms, and the environment, we must be able to separate gases and store them for conversion.” He and his colleagues have developed soft porous crystals (SPCs) based on porous coordination polymers (PCPs) (also known as metal-organic frameworks) to handle difficult gas separations, among other applications. SPCs are defined as solids possessing both a highly ordered framework and structural transformability. The technique uses what Kitagawa called “very simple chemistry” to produce flexible nanoscale frameworks with channel densities up to 1 million per  $\mu\text{m}^2$  in a matter of minutes. Think of the controlled pore structure of a zeolite with flexibility added to its properties. One of the PCPs they developed is 26 times more selective for adsorbing  $\text{C}_2\text{H}_2$  than  $\text{CO}_2$ —

demonstrating success in a separation that was previously difficult to achieve because of the molecules’ size similarity.

The chemistry involves metal atoms, such as zinc, and a wide range of organic ligands from which the researchers can tailor the channel size of a single crystal to accept one molecule and reject others. Flexibility comes from the organic ligands. The sizes and shapes of the various ligands give them a complete toolkit from which to create porous crystals having the desired channel diameters. The researchers can form stacked layers, flexible pillars, or interpenetrating stiff frameworks that can move independently to impart flexibility to the structure. The frameworks are single crystalline, but are not rigid. Instead, they can be squeezed or stretched, and can even undulate. As such, the channels can “evolve.”

Ligands such as  $\text{Co}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4$  and  $[\text{Cu}_2(\text{dhbc})_2(\text{bpy})]_n$  are just a couple of the many ligands that Kitagawa and others have investigated. The former has a high selectivity for adsorbing carbon dioxide, while the latter can transform from a closed to an open pore morphology when a threshold gas pressure is reached. Other PCPs depend upon charge differences to separate gases. For instance,  $[\text{Zn}(\text{TCNQ-TCNQ})\text{bpy}] \cdot 1.5$  benzene adsorbs  $\text{O}_2$  from a gas mixture but not  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ , or  $\text{N}_2$ , based on the partial negative charge that  $\text{O}_2$  possesses in this complex.

Besides selectively adsorbing gases, these SPCS can be used as miniature reactor systems: reactive open shell atoms (ROSAs) can hold a molecule for on-demand photoactivation. The channels can also act as proton exchange materials under non-humid conditions. Kitagawa said that possible applications for PCPs include gas storage, reaction capabilities, hydrophilicity, and size selectivity.

## Second Theme Lecture: D.D. Sarma

### Semiconductor Nanocrystals: How Do They Grow and Why Do They Glow?



Semiconductor nanocrystals (commonly called quantum dots) are an interesting class of materials because their electromagnetic absorption and emission spectra can be tuned by many synthetic routes. Ever since Bawendi's group displayed size-dependent optical properties and brilliant colors from these quantum dots, there has been an intimate relationship between the way they grow and the way they glow. D. D. Sarma of the Indian Institute of Technology carefully walked the audience through this deceptively simple synthesis and optical property.

In general, quantum dots form due to basic crystal nucleation theory and grow due to ripening. However, like any nanomaterial, things are not so simple. For example, simple defects in the crystal structure or surface morphology due to the capping agent can cause unexpected shifts in the optical emission spectra and ruin device utility. Some simple solutions, such as intentionally introducing defects by doping or coating the core material with a different material can negate and even eliminate most of these problems. Essentially, to make stable quantum dots, one merely needs material, a capping agent, temperature, and time. Mix them all in the right amounts, and you get stable quantum dots.

They glow because they are stable semiconductors with a band gap on the order of several eV (UV-visible) light. That means that ultraviolet or simple light from the sun can excite an electron from the valence band to the conduction band, creating an electron-hole pair. Upon de-excitation and recombination of the electron-hole pair, light is emitted, which we can see with the naked eye or a spectrometer. Tuning the materials or the morphology of the quantum dots gives rise to tunable band gaps and thus tunable absorption and emission spectra. Essentially, this photoluminescence is the equivalent of metal nanoparticles' surface plasmon resonance, and many of the growth mechanisms and electromagnetic interactions can be viewed in a similar light.

Not only did Sarma walk through the fundamentals of semiconducting quantum dots, he used numerous examples from his own research and alluded to some of the remaining big questions in the field today. It was refreshing to see a true expert give a surprisingly complex discussion that was enjoyable and understandable to novice and master alike.

## Public Lectures at the National University of Singapore



### Research and Applications: from the Spin of Electrons to our Computers and Telephones

Albert Fert of the Unité Mixte de Physique CNRS/Thales and the



Université Paris-Sud (Orsay) delivered a revised version of the plenary lecture he gave on Monday, with several slides added to explain difficult concepts to the general public. He explained spintronics and giant magnetoresistance (GMR), which won him the Nobel prize and led to major advances in the read heads of hard disks, making iPods and computer tablets possible. Fert also talked about tunneling magnetoresistance (TMR), which may supplant GMR in the future by increasing data density and reducing energy consumption. Of particular interest to the audience was his description of "memristors," which are neuromimetic components with synaptic plasticity, which could be hardwired in to the brain in the future, creating the ultimate man-machine interface. A

more complete description of this lecture can be found in yesterday's issue of the Meeting Scene.

### The Amazing Ribosome



Ada Yonath of the Weizmann Institute in Israel followed up with a heartfelt talk on the joys of the "amazing ribosome," to which she has dedicated her working life. "A ribosome is a universal factory that produces proteins continuously by decoding the genetic information in all living cells," Yonath explained. The millions of ribosomes in each living cell can make 15 to 40 peptide bonds in one second with only one mistake in a million attempts. Messenger RNA (mRNA) carries the genetic code, and many ribosomes run along side it, working together as polysomes. Then transfer RNA (tRNA) connects to the mRNA and enters the first part of the ribosome, called the small ribosome sub-unit. Each ribosome is composed of two structures: the small ribosome subunit and the large ribosome subunit. The small subunit consists of one RNA chain about 1,600 nucleotides long; the large subunit

consists of two RNA chains with approximately 3,000 nucleotides. The subunits come together to translate the information coming in on the tRNA into proteins. The newly formed proteins then exit through a tunnel in the ribosome, and eventually the small and large subunits separate. Yonath showed a brief movie clip detailing this fascinating process.

With the basics explained, Yonath delved into higher level concepts, such as the discovery of the existence in modern ribosomes of a semi-symmetrical region called the proto-ribosome that is left over from the early stages of the evolution of life. This proto-ribosome makes up only 3-4% of our modern ribosome, but it still performs its function. "Nature devised a way to take a lousy protein machine and turn it into an excellent protein machine," Yonath said. The proto-ribosome is highly conserved—98% of it has been conserved throughout the course of evolution. "It's above evolution," she said.

Yonath ended her talk by describing how antibiotics work by binding to functional sites on the ribosomes. Each antibiotic works by a different mechanism, one blocking the entrance of the small ribosome subunit's, another block the protein tunnel's exit. Bacteria become resistant antibiotics when changes occur in the tunnel wall. Yonath considers antibiotic resistance to be a major concern, but she isn't optimistic about ever conquering it completely. "I don't think there will ever be no resistance," she said, "because bacteria want to live, and they will find a way to live."



A good time for a coffee break

## ■ Technical Talks

### Symposium F: Toxicology of Engineered Nanomaterials

#### *Preparation and Nanotoxicity Study of Monodisperse Ag Nanoparticles*

Silver nanoparticles have seen an explosion of research and regulation because they are being engineered into consumer products, often without knowing the impact on humans or the environment, because they have natural antibacterial and antifungal properties. Silver itself possesses this property, as silver containers have been used to disinfect water, and dilute silver nitrate solutions have been used as eye droplets in newborns to prevent blindness due to infection. However, little regulation exists because the cytotoxicity is poorly understood.

Qiangban Wang of the Chinese Academy of Sciences performed systematic studies of silver nanoparticle toxicity to determine some key principles. First, the passivating agent protecting the silver nanoparticle plays an important role. Second, the size of the particle has a significant effect: the larger sized particle exhibits higher toxicity. Third, when comparing concentration, it needs to be defined clearly whether particle or mass is used as the baseline for concentration. Wang recommends mass, as he found it is possible to compare different silver nanoparticles' toxicity if performed on a mass concentration basis. This may seem trivial, but it sets a strong basis for comparative toxicological evaluations of an overused and unregulated substance in consumer products: silver.

#### *Environmental Fate Evaluation of Silver Nanoparticles Released to the Soil*

Following the lecture on nanotoxicity of silver, Soomin Park filled in for his advisor, Jongheop Yi of Seoul National University, to speak about the environmental fate of nanoparticles in soil. He started off by showing a curious commercial device called Samsung's SilverCare Washing Machine which uses silver nanoparticles to disinfect clothes during the wash cycle.

Briefly, a standard silver nanoparticle suspension from ABC Nanotech Korea was introduced into a test tube containing soil. The test tubes were then agitated to mix the soil and nanoparticles. The resultant product was centrifuged and the resulting supernatant was analyzed with ICP-AES to determine the silver content. Two key properties were found: (1) below pH 4, adsorption of silver is negligible, and (2) silver nanoparticles adsorb better than silver ions. The reverse process of silver desorption from soil was also studied, with the results showing the same general trend, namely that larger particles desorb faster than ions. These two results are directly related to the fact that silver ions dissolve quite readily and are dilutely absorbed or desorbed, whereas nanoparticles carry large amounts of silver ions to specific sites in the soil. Nanoparticles can also precipitate out of solution and down into the soil, causing increased silver concentration in the soil and negligible amounts in the supernatant.



Trying to get the poster just...right!

### Symposium J: Nanoscale Patterning, Assembly, and Surface Modification

#### *Charge Transport Through Gold Nanoparticle Assemblies*

A large research theme for nanoparticles is the arrangement of individually conducting nanoparticles into an assembly that can conduct electricity as a single entity. Naturally, this requires measurement of the current from one point to another, which can be extremely challenging. With a bulk metallic wire, the charge transport occurs simply with free electrons, however, in a nanowire or linear array of metal nanoparticles, charge transport is more complex. Does charge hop from particle to particle, does it tunnel, or something else?

These questions are fundamentally interesting because nanoscale devices can exhibit single electron transitions at room temperature, making nanoelectronics very practical. However, basic studies of nanoscale electron transport are still lacking. Ulrich Simon and coworkers at RWTH Aachen University are trying to bridge the gap. Experiments were presented in which electron tunneling was shown to occur in 1D chains of gold nanoparticles and also in isolated single nanoparticles sandwiched between electrodes. The experimental design consisted of lithographically fabricated metallic contacts in a field emission scanning electron microscope. The experiments were performed at low temperature (~4 K). It was shown that even the shape of a nanoparticle (icosahedral vs. decahedral) can cause a significant change in the conductance and tunneling of electrons through a nanoparticle structure.

#### *The Role of Halide Ions in Seed-mediated Growth of Anisotropic Au Nanostructures*

It is a little-known secret in the gold nanorod community: be careful where you buy your chemicals. The most common technique for growing nanorods, developed by Catherine Murphy's group, involves preferentially growing a long rod of material from a small seed particle's crystal plane. However, nanorods were exceedingly difficult to reproducibly synthesize with this method, because as Brian Korgel's group pointed out 7 years later, if you bought one of the main chemicals, CTAB, from 10 different companies you would obtain 10 different types of particles.

According to W. David Wei of the University of Florida, trace amounts of iodide ions ( $I^-$ ) are to blame. In fact, the research group performed a deceptively simple experiment to show this to be the case. The researchers extensively purified CTAB from different manufacturers and obtained identical nanorod solutions. They then repeated the synthesis and added "impurities" in the form of  $I^-$  and found that they arrived back where they started: irreproducible, poor quality nanorods. Thus the addition of a halogen ( $I^-$ ,  $Br^-$ ,  $Cl^-$ ,  $F^-$ ) to CTAB can cause significant deviation in the resulting synthesized nanorods. In fact, by changing the halogen one can change the crystal plane (i.e., 100 vs. 111) on which the nanorods will grow. This means that adding excess bromide will cause particles to grow on the 100 face, instead of iodide's ability to cause growth on the 111 surface. This is a quite startling yet important discovery: if you try to make nanorods and buy your chemicals from various vendors, expect to obtain spheres, plates, and prisms as well.



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### Symposium M: Nanonets and Nanomaterials for Energy Harnessing & Storage

#### *Model Investigations for Catalysis in Electrochemical Energy Conversion*

Most efforts to improve the reactivity of electrochemical fuel cells focus on the chemical composition of the catalysts, according to Holger Wolfschmidt. That overlooks a host of other parameters; Wolfschmidt presented research that attempts to tackle the problem with other approaches. In particular, he has studied the impact of the size and distribution of catalyst particles on their reactivity for hydrogen reduction. He fabricates nanoparticles of Pt using an electrochemical pulse technique or a jump-to-contact technique in which Pt is transferred from an STM tip to a Au or diamond substrate, creating dots a few nanometers wide and one to two monolayers thick. Wolfschmidt points out that systems of Pt on diamond and Au are not ever intended for use in fuel cells, but rather provide a well-defined model system with which to understand catalytic process. Measuring the single-particle reactivity of the Pt nanoparticles via the hydrogen oxidation current at an STM tip, he finds some surprising results. Namely, the exchange current density (a measure of the reactivity) increases as the Pt coverage is reduced, contrary to intuition.

These surprising results are understood in terms of lattice strain imparted by the mismatch between the substrate and the nanoparticle. Tensile strain reduces the width of the Pt  $d$ -band and raises the Fermi level, which increases the binding energy of hydrogen, a condition favorable to reduction. Thicker nanoparticles are less strained, and so have lower reactivity. The model is supported by observation of the reverse trend for Pt on Cu substrates, which creates compressive rather than tensile strain. Through these kinds of detailed studies, Wolfschmidt hopes to better understand the conditions relevant to catalysis, and thereby design more efficient fuel cells.

#### *Dragon Fruit Dye as Natural Sensitizer and Titanium Dioxide Paste for Dye -- Sensitized Solar Cell Application*

In Malaysia, where sunlight and tropical fruit are abundant, solar cells made with fruit-based dyes are an attractive prospect. With this in mind, Riyaz Ahmad of Universiti Tun Hussein Onn Malaysia, is studying dye-sensitized solar cells (DSSC) fabricated with dye from the dragon fruit. Ahmad shared his results in a standing-room-only afternoon session devoted to DSSCs. He prepares the dragon-fruit dye by blending the fruit with water and separating the solids in a centrifuge. UV-vis spectroscopy shows an absorption peak at 535 nm, and FTIR analysis identifies anthocyanin, a water-soluble pigment. Both results are promising for DSSC application. Indeed, Ahmad incorporated the dragon-fruit dye in DSSCs, using  $\text{TiO}_2$  films made cheaply and simply from paste, and measured modest solar conversion efficiencies of 0.22%. He pointed out that, while they still want to improve efficiencies, the benefit of using cheaply available and environmentally friendly ingredients could offset some of the drawbacks of low efficiency.



Getting new sales leads!



## Symposium II: Computational Science of Transport Phenomena in Materials: Methods and Applications

### *The Dynamics of Liquid Drops during Vapor-Liquid-Solid Nanowire Growth*

First developed in the 1960's, vapor-liquid-solid growth of nanowires is now a fairly routine process, wherein crystalline whiskers form at the solid-liquid interface of a liquid alloy droplet. Many questions still exist, however, regarding the growth process. Why, for example, does the liquid droplet remain on the whisker tip instead of sliding down and forming a ring, or annulus, leading to kinked or branched nanowires? Peter Voorhees, of Northwestern University, USA, tackled this question by simulating the kinetic growth process in three-dimensional models of droplets on nanowires. As he discussed in today's symposium, Voorhees and coworkers model the system using phase field methods, simulating a three-phase, two-component alloy. Under an incident flux of silicon, they find that dewetting of the wire to form a droplet occurs in a mere 3 microseconds, compared to the microsecond time-scale of wire growth. They find that the speed of dewetting is a function of the huge pressure inside the droplet, on the order of  $10^7$  to  $10^8$  Pa.

To address the stability of a droplet versus an annulus, the researchers perturb a droplet artificially and evolve the system. Previous non-kinetic calculations identified the stability range of a droplet versus an annulus as a function of droplet-to-wire aspect ratios. In the studies shown by Voorhees, they found that in the region of droplet stability, an annulus configuration returns to being a droplet in a swift 60 nanoseconds. By inflicting much larger perturbations, they found they could access the metastable annulus configuration, but the results help explain why nanowires grown from vapor-liquid-solid techniques are so rarely kinked or branched.

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### Scanning the Meeting



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