BIOTECHNOLOGY OPENS NEW ROUTES TO HIGH-PERFORMANCE MATERIALS FOR IMPROVED PHOTOVOLTAICS, BATTERIES, UNCOOLED IR DETECTORS, FERROELECTRICS AND OPTICAL APPLICATIONS

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ABSTRACT

Biological systems fabricate multifunctional, high-performance materials at low temperatures and near-neutral pH with a precision of three-dimensional nanostructural control that exceeds the capabilities of present human engineering. Using the tools of biotechnology and genetic engineering, we discovered the unanticipated mechanism of simultaneous catalysis and templating governing the nanofabrication of silica in a biological system. We then translated this mechanism to develop a new biologically inspired, low-temperature, low-cost route for the synthesis of silica and a wide range of silicones, organic polymers and nanostructured metal oxide, -hydroxide and -phosphate semiconductor thin films without the use of organic templates. This new synthesis method is generic, yielding more than 30 different inorganic thin films and nanostructured, bimetallic perovskite ferroelectrics. Because kinetic control is achieved at low temperature, thus circumventing the thermodynamic default, many of the inorganic materials made by this process exhibit morphologies and electronic properties not observable in the corresponding products made by conventional high temperature processes. The electronic properties of some of these novel materials suggest strong advantages for high-efficiency photovoltaics, lightweight high power-density 3-D batteries, improved battery safety, uncooled IR detectors and other energy and information storage applications. Because no organics are used, the resulting products exhibit very high purity, making the process fully integrable with MOCVD and other conventional manufacturing methods. Because synthesis occurs from solution, adaptation to roll-to-roll and other high throughput methods may be possible. Transitioning of these developments to Army applications is now beginning. Related efforts now in progress are focused on revolutionary, bio-inspired approaches to optical materials.

1. OVERVIEW AND ARMY SIGNIFICANCE

We discovered the molecular mechanism governing the biological nanofabrication of silica in a group of marine sponges (Shimizu, et al., 1998; Cha et al., 1999; Morse, 1999, 2001; Zhou et al., 1999; Weaver et al., 1999; Aizenberg et al., 2005), and translated this mechanism to a radically new generic method for the low-temperature synthesis of a wide-range of nanostructured semiconductor thin films with properties uniquely advantageous for more efficient energy generation and storage (Schwenzer et al., 2005; Kisailus et al., 2006; Brutchey and Morse, 2006). We have demonstrated that because this method operates at low temperature by kinetically controlled catalysis it yields materials with compositions and properties often not attainable by conventional high-temperature synthesis. The method is widely generic, thus far allowing us to produce more than 30 different nanostructured thin film metal oxides, hydroxides and phosphates - many in forms and with properties not achievable before. We have demonstrated *in situ* conversion of the as-formed materials to the corresponding nitrides, sulfides and phosphides, further extending the range of materials important for energy applications that are accessible by this new method. The kinetic control delivered by this method yields good crystallinity, long minority carrier lifetimes, high dopant densities and high surface areas *all of which are advantageous for more efficient solar energy and lightweight, high power-density 3-d batteries*. Because no organics or biochemicals are used, the method produces very high purity materials that are fully integrable with MOCVD and CMOS fabrication. We have shown the method capable of producing both substrate-supported and free-standing thin films. Because the method operates at low-temperature and near-neutral pH, we have found it uniquely advantageous for growing TiO_2 and ZnO electrode layers on the temperature-sensitive layers of organic polymer photovoltaics being explored by Army Laboratories at ARL and CERDEC for lightweight, flexible, soldier-carried solar energy cells. Because the synthesis method is solution-based, it is potentially adaptable to roll-to-roll and other high-throughput manufacturing methods.

We also found that the new synthesis method we developed can be used with advantage to make highly crystalline bimetallic oxide perovskites, such as $BaTiO_3$, a valuable ferroelectric, piezoelectric and thermoelectric material with useful applications in energy transduction, magnetic information storage, ambient temperature (uncooled) IR detection, and improvements in safety of lithium ion batteries (Brutchey and Morse, 2006). By

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combining the advantages of unique bimetallic precursor molecules with the gentle, low-temperature and vectorially controlled catalysis method we developed, we show that we are able to make novel bimetallic perovskites with never-before achieved control over the stoichiometry and atomic-scale geometry of the two metal centers, without the complications of phase-segregation and degradation of properties typical of high-temperature methods.

2. TRANSLATION FROM BIOLOGY TO SEMICONDUCTOR SYNTHESIS

With a precision of nanostructural control that exceeds present human capabilities, biological systems fabricate 3-D multifunctional high-performance silicon-based materials at low temperatures and near-neutral pH. The fundamental molecular biology of silica production in sponges and diatoms is now being elucidated, and aspects of these processes are being harnessed for industrial and technological processes. Working with the silica needles produced by marine sponges, our laboratory discovered that proteins we named "silicateins" catalyze and structurally direct the polymerization of silica, organically substituted silsesquioxanes (silicones) and organometallic silsesquioxanes from the corresponding silicon alkoxides at neutral pH and low temperature (Shimizu, et al., 1998; Cha et al., 1999; Morse, 1999, 2001; Zhou et al., 1999; Weaver et al., 1999). The silicateins are true enzymes, closely related to a well-known family of hydrolases (Shimizu et al., 1998). Interestingly, we were able to show that these enzymes also catalyze and structurally direct the synthesis of a number of metal oxide semiconductors from the corresponding molecular precursors Sumerel et al., 2003; Kisailus et al., 2005a; Brutchey et al., 2006). These are the first reported examples of enzyme-catalyzed, nanostructure-directed synthesis of semiconductors. Interaction with the template-like protein surface stabilizes polymorphs of these materials (e.g., the anatase form of titanium dioxide and the spinel polymorph of gallium oxide) otherwise not formed at low temperatures. In some cases, interaction between the condensing metallo-oxane and the protein results in preferential alignment of the resulting nanocrystallites, suggesting a pseudo-epitaxial relationship between the mineral crystallite and specific functional groups on the templating protein surface (Kisailus et al., 2005a).

Site-directed mutagenesis of the cloned recombinant DNAs coding for the silicateins confirmed the mechanism of catalysis (Zhou et al.,1999), and has been used to increase the rate of catalysis as well. These studies enabled the synthesis of self-assembling "biomimetics" - peptides, polymers, and self-assembled monolayers on nanoparticles and on planar surfaces - that incorporate the functionalities identified as essential for catalysis, yielding new structure-directing catalysts of polymerization (Cha et al., 2000; Kisailus et al., 2005b, 2006b; Roth et al., 2005). But to achieve the high purity of semiconductors required for most applications, it proved necessary to further translate the advantages of the biomolecular mechanism of synthesis to a method that employs no organic or biochemical molecules, and thus removes that source of contamination from the synthesis pathway.

We now report the successful translation of the underlying principles governing this structure-directing synthesis to a new method capable of the low-temperature nanofabrication of metal oxide semiconductors without the use of any organic or biochemical templates (Schwenzer et al., 2005; Kisailus et al., 2006b; Brutchey and Morse, 2006). We discovered that the fundamental enabling principles responsible for the unique low-temperature biological nanofabrication of silica and semiconductor crystalline materials were two-fold: (1) slow enzymatic catalysis of synthesis from molecular precursors made it possible for kinetic control of the synthesis reactions to circumvent the thermodynamic default, producing in some cases crystal polymorphs of the semiconductors, at low temperature (16 $^{\circ}$C), that otherwise could only be made only at very elevated temperatures (>400 $^{\circ}$C); and (2) this control of polymorph and crystal form was the result of templating imposed by interactions between the growing nanocrystallites and the enzyme (protein) surface - and effect that could be approximated by imposing an alternative means for anisotropically (i.e., vectorially) structuring the crystal-growth environment. As a first proof of principle that we could translate these advantages of the biological synthesis mechanism to a method utilizing no organics, we demonstrated the low-temperature synthesis of a unique, strongly photoconductive cobalt hydroxide- based material, never before achievable through conventional or high-temperature methods, with attractive properties of high dopant density, high carrier density, exceptionally long minority carrier density and strong absorption in the visible, appropriate for photovoltaic applications (Schwenzer et al., 2005).

3. KINETICALLY AND VECTORIALLY CONTROLLED LOW-TEMPERATURE CATALYSIS OF SEMICONDUCTOR NANOFABRICATION

The generic method we developed uses vapor diffusion of ammonia or other catalysts through a gas-liquid interface into a solution of molecular precursor to provide the vectorial control of catalysis, at low-temperature, of synthesis from molecular precursors that require hydrolysis (Schwenzer et al., 2005). The approach proves readily useful with a wide range of catalysts including acids, bases and water (Brutchey and Morse, 2006). The result is a novel, highly generic low-temperature and environmentally benign method for the nanofabrication of a wide range of more than 30 different metal oxide, metal hydroxide and metal phosphate semiconductors, in unique and potentially useful crystal morphologies - some of which could never have been made before - with significantly enhanced electronic performance (Schwenzer et al., 2005; Brutchey and Morse, 2006). The method relies on the integrated tuning of molecular precursors and vectorially controlled catalysis, utilizing only chemical physics and highly purifiable inorganic components, *with no biochemicals, biologicals or organic materials*. In situ conversion to the nitrides, sulfides and phosphides has been shown to extend the range of materials that can be made by this method - many with properties useful for photovoltaic or battery applications. The use of the molecular precursor and its vectorially controlled catalytic hydrolysis provide coordinate kinetic and directional control of semiconductor growth that is not available using conventional high-temperature approaches.

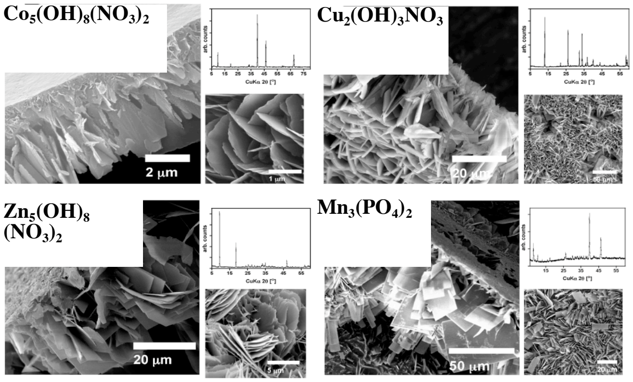

Fig. 1. Representative examples of the nanostructured semiconductor thin films synthesized by the new method described above. Examples shown are cobalt hydroxide, copper hydroxide, zinc hydroxide and manganese phosphate. Insets show the X-ray diffraction patterns of the materials, confirming excellent crystallinity.

By tuning the directionally controlled delivery of the catalyst and the structure of a molecular cobalt-based precursor, for example, the low-temperature solution route described above produces a high surface area array of large single crystal p-type semiconductor plates of $Co(OH)_2$ (ca. 20 nm thick) projecting orthogonally from, and all intimately connected to, a flat and continuous conductive backplane of the same material (Schwenzer et al., 2005). XRD, electronic diffraction, XPS and other physical characterization reveal that the plates are highly doped, high surface area single-crystal $Co(OH)_2$ in the hydrotalcite crystal structure (see figures below). The material is highly doped with anions (dopant density = 3.5 x 10^{20} m^{-3}) intercalated between the crystal plates, facilitating conductivity. X-ray diffraction and electron diffraction results indicate the same structure, demonstrating homogeneity from nanoscale to macroscale dimensions. Electrical measurements show that the material is a p-type semiconductor with good conductance in the semiconductor regime, and that it acts as an efficient photoconductive transducer with high carrier density and long minority carrier half-life. The material exhibits strong absorption in the visible, with a band-gap of 1.9 eV. The work function also has been characterized.

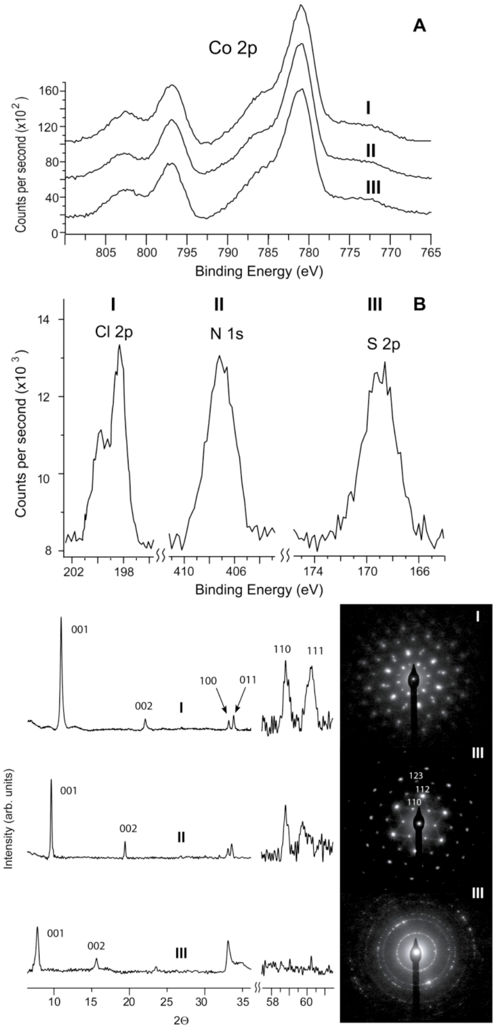

Fig. 2. Figures above: I = chloride-doped; II = nitrate-doped; III = sulfate-doped cobalt hydroxide materials made by the bio-inspired, low-temperature nanostructured catalytic process described above. (See Fig. 1, upper-left quadrant, for illustration of II.)

(Top two panels): High resolution XPS spectra of (A) Co 2p region for **I**, **II**, and **III** and (B) Cl 2p, N 1s and S 2p regions for **I**, **II**, and **III** respectively.

(Lower three panels and diffraction patterns): Powder XRD and electron diffraction patterns for **I**, **II**, and **III** showing peaks indexing to the brucite structure with $a_{\mathbf{I,II,III}}$ = 3.13; $c_{\mathbf{I}}$ = 8.12; $c_{\mathbf{II}}$ = 9.19; and $c_{\mathbf{III}}$ = 11.26.

Electrical measurements (using an interdigitated electrode array) confirm that material exhibits excellent ohmic conductance (with very low dark sheet dark sheet resistance = 5.9 x 10^{-4} Ω cm), and that it acts as an efficient photoconductive and photovoltaic transducer with a band-gap at 1.9 eV, a high carrier density and long minority carrier half-life. This long minority carrier half-life is a reflection of the high crystallinity and high purity of the material (achieved because our synthesis method, although bio-inspired, uses no organics or biochemicals of any kind). While measured for photoconductive behavior, the long carrier (electron) path-length also indicates an excellent property for high efficiency performance in electrical batteries.

In a project recently begun in collaboration with the U.S. Army's CERDEC and a commercial battery manufacturer, we are exploring the utility of nanostructured cobalt- and iron-based materials made by the bio-inspired low-temperature method described above for potential advantages in 3-dimensional high power-density batteries. Use of the barium titanate nanoparticles made by this method also are being investigated for their potential to quench runaway reactions at battery electrodes by virtue of the material's unique positive thermal coefficient of resistance, to thereby increase the safety of lithium ion batteries.

4. CONCLUSIONS AND PROSPECTS

A new generic, low-cost, low-temperature, biologically inspired method for the synthesis of nanostructured thin-films and nanoparticles of a wide range of metal oxide, hydroxide and phosphate semiconductors and bimetallic perovskites was developed with support from the Army. Advantages of previously unprecedented control over composition and structure offered by this method enables some of these materials to be produced in forms never before achievable, and with electronic properties not previously available. Advantages of performance, purity of the resulting materials (made with no organic contaminants), the simple solution-based synthesis method, integrability with conventional manufacturing and advantages of cost suggest a wide range of applications including higher efficiency photovoltaics, high-power density batteries, improved battery safety, IR detectors, flexible displays, ferroelectric random-access memory (FeRAM) information storage and other optoelectronic applications. Several of these now are under active investigation with the aim of accelerating transition to the Army, in collaborations supported by ARO ARL, CERDEC and DARPA.

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Biotechnology Opens New Routes to High-Performance Materials

for Improved Photovoltaics, Batteries, Uncooled IR Detectors, Ferroelectrics and Optical Applications

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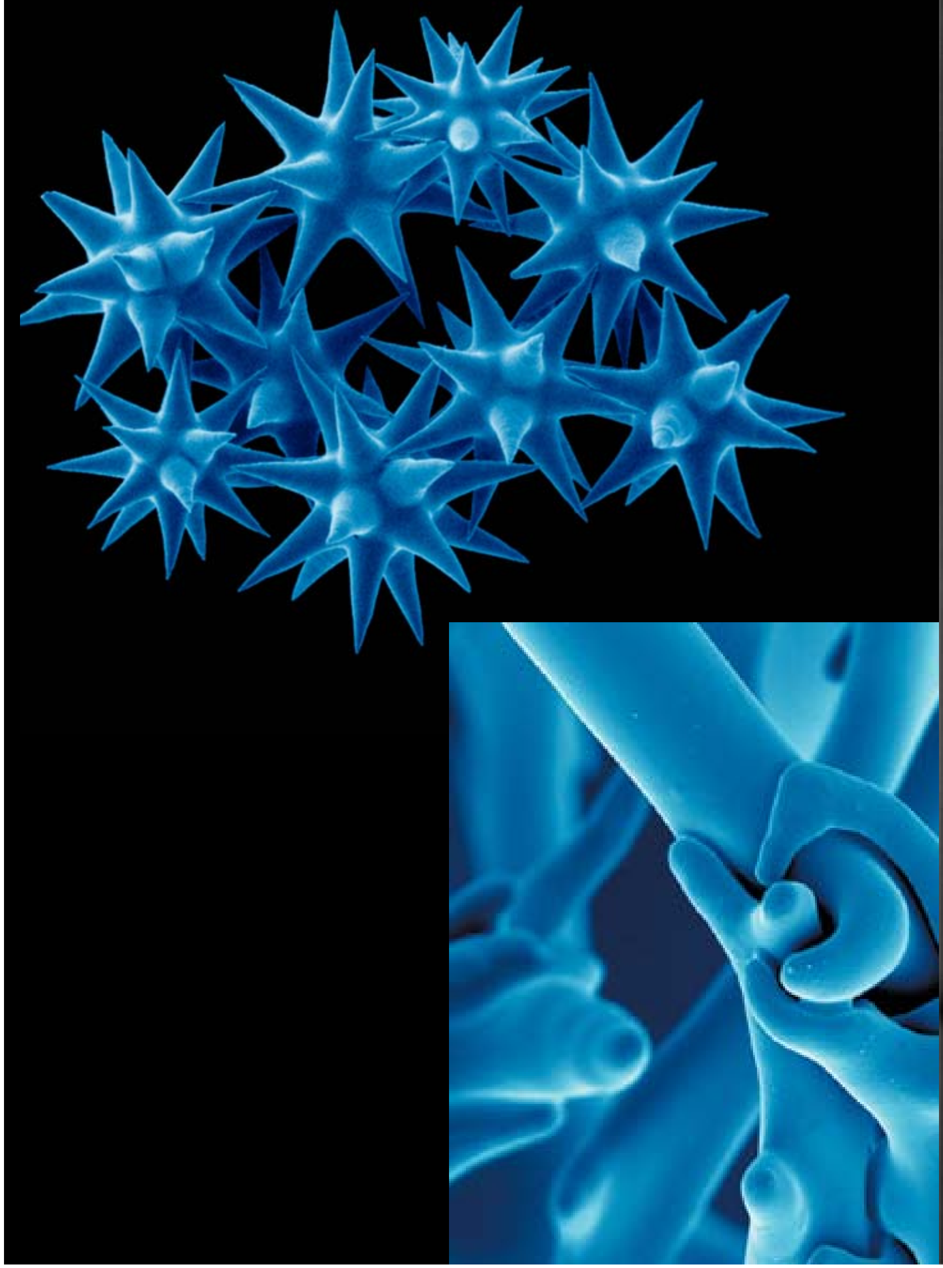
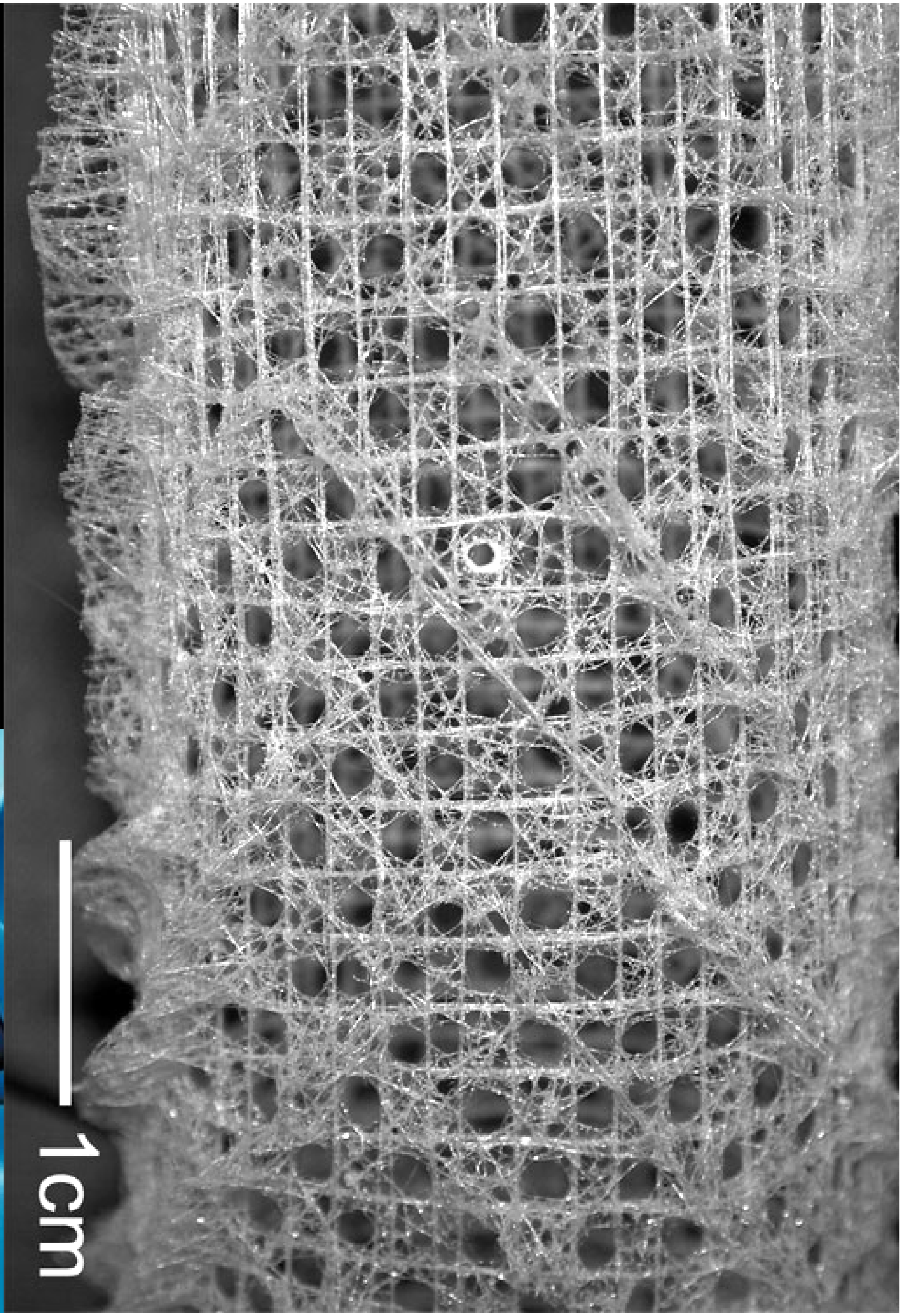
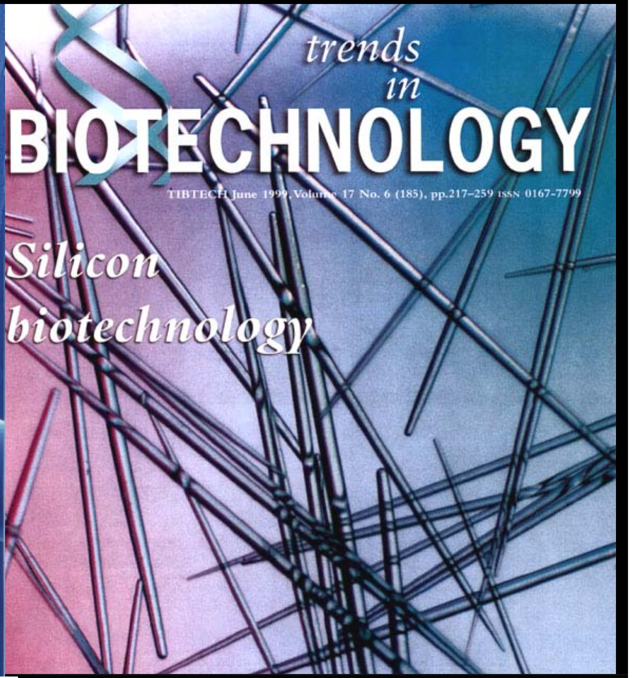
ICB

Remarkable Structures of Bio-silica in Sponges





- Biotechnology revealed previously unsuspected mechanism of low-temp. catalysis & templating
- Developed “Silicon Biotechnology,” leading to $50 M spin-off to Dow Corning and Genencor
- Translated to generic low-T catalytic synthesis of ultrapure semiconductor nanostructured thin films and nanopartiparticles
- Unique advantages for High Power-Density, Safe Batteries and Solar Energy applications




GENETIC ENGINEERING NEWS GEN

Vol. 21, No. 20, November 15, 2001

Silicon Biotechnology

Genencor and Dow Corning Team Up to Make New Products

Carol Potera

Looking for unique opportunities in megatrends, such as biotechnology and materials science, would appear to be a good business strategy in today’s high-tech world. The leaders of **Genencor International, Inc.** (Palo Alto, CA) and **Dow Corning Corp.** (Midland, MI) took that approach and formed a strategic alliance to create a new technology platform, called Silicon Biotechnology™.

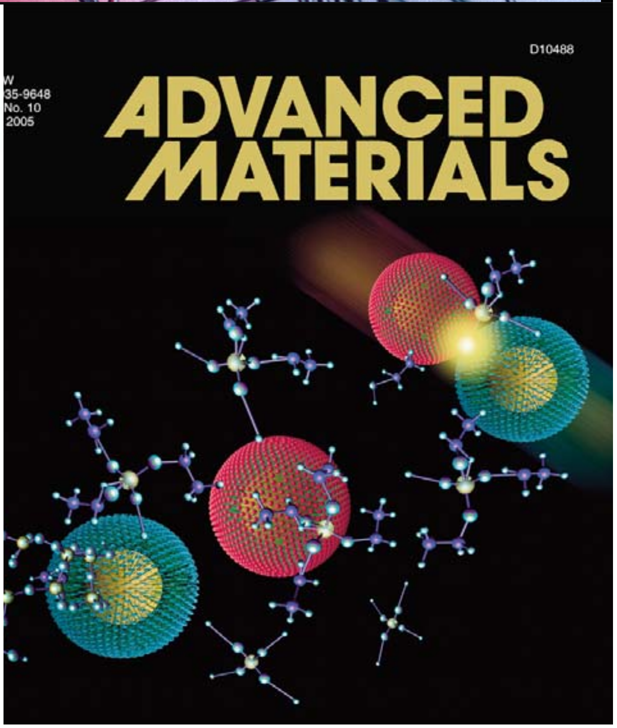
Various forms of silica and silicone: silicon metal, powder, fluids, granules, and pellets in glass beakers.

Dow Corning Corp.

This merger of silicon chemistry and biotechnology represents “Genencor’s theme of pushing the boundaries of biotechnology,” says Thomas Mitchell, president and CEO of Genencor. In fact, the concept of Silicon Biotechnology is so new that he knows of no other company designing products that intersect both disciplines. “That’s what makes it so exciting,” adds Mitchell, who envisions revolutionary new products that will benefit both industrial and health-care-based customers.

Dow Corning is the world’s largest manufacturer of silicon materials, which are found in cosmetics, personal care items, detergents, computer chips, plastics, and textiles.

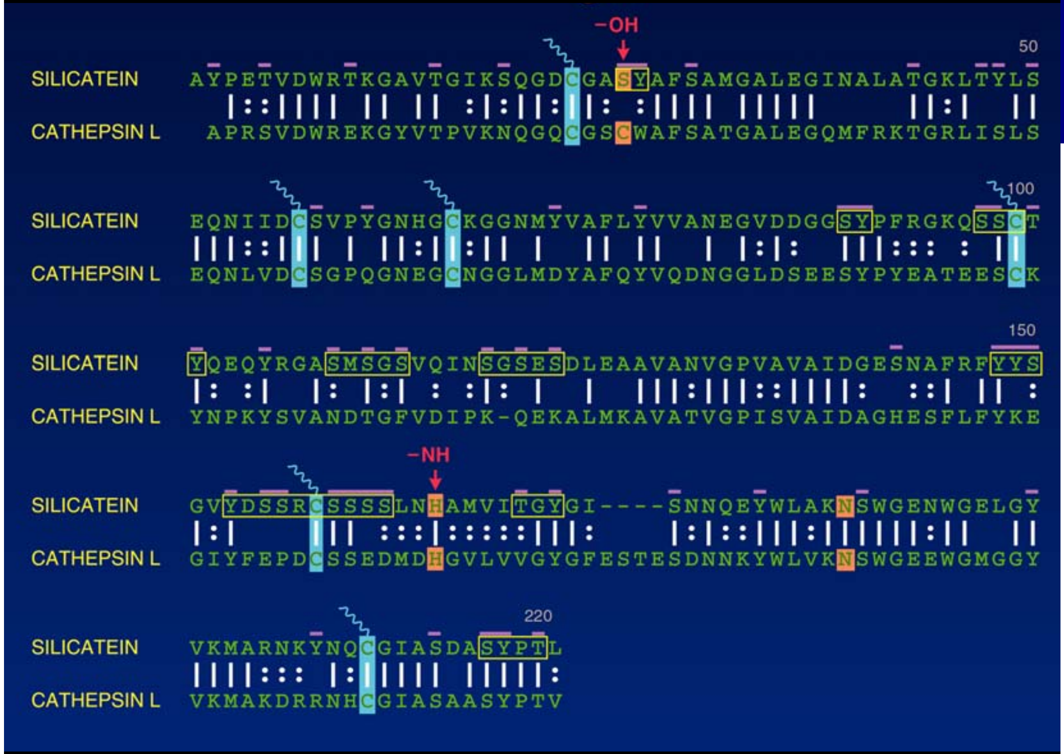
“We believe that biotechnology is one of the most

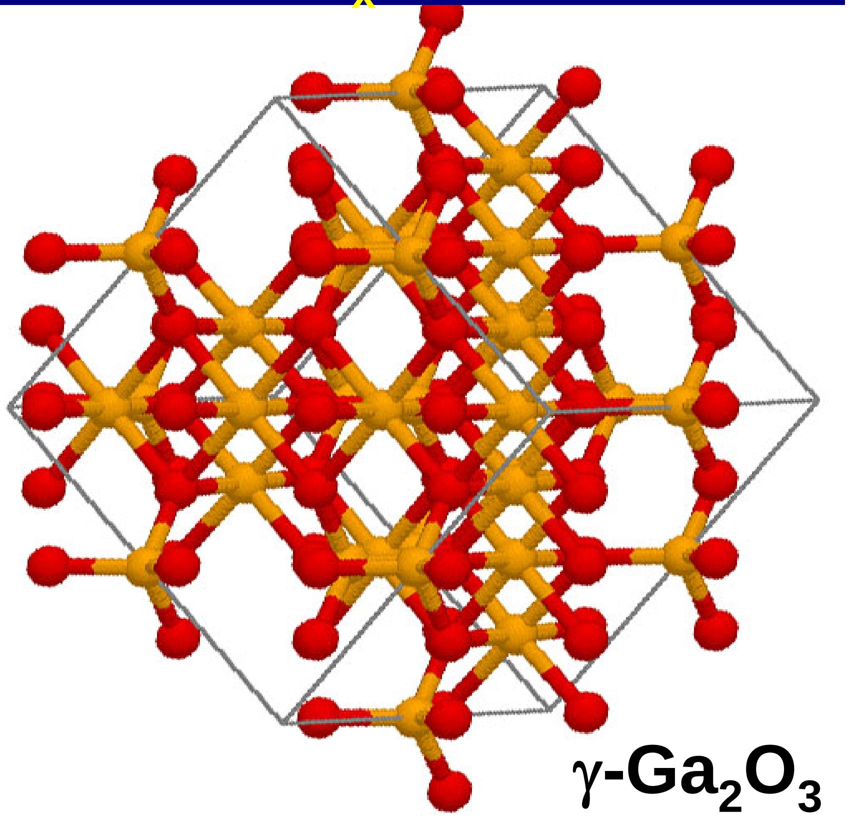


Cloning reveals:
Protein template
is an <u>enzyme catalyst</u>:

Enzyme that catalyzes & templates synthesis of silica at low temperature also makes semiconductors from molecular precursors:

TiO_2 , Ga_2O_3, ZnO, CoO, RuO_x

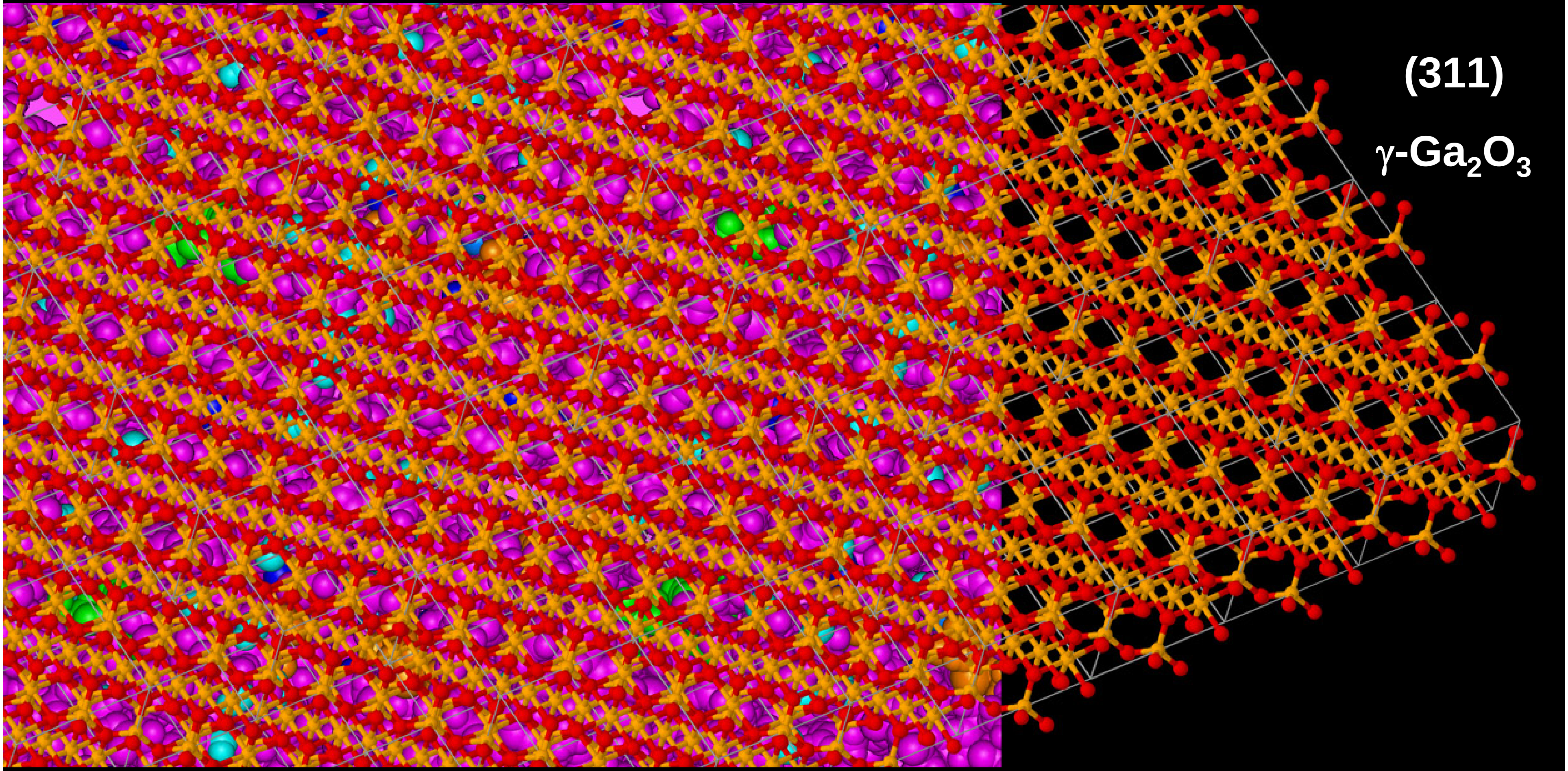




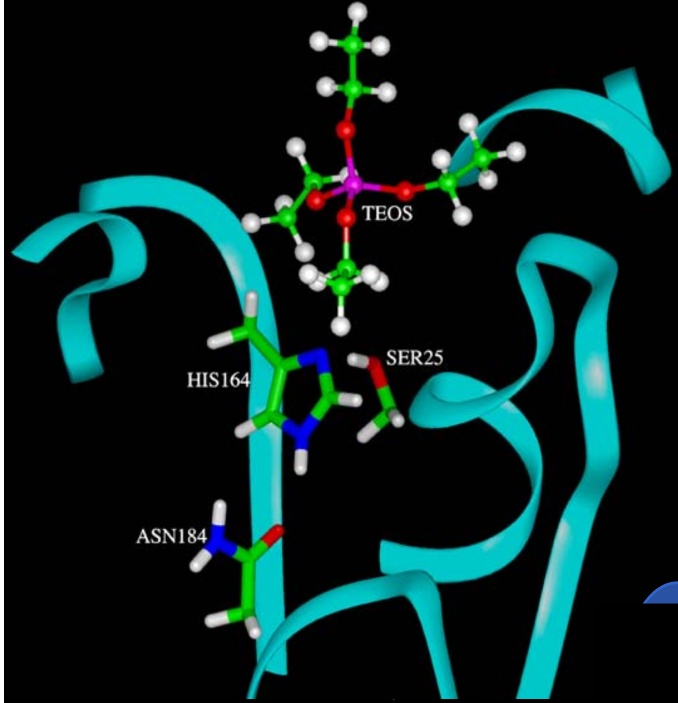
γ-Ga_2O_3

Low-temperature *catalysis & templating* of semiconductor synthesis

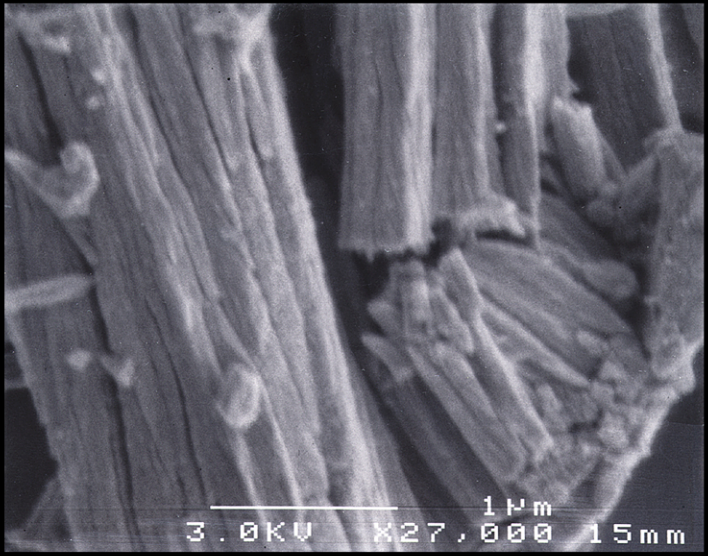
The catalyst IS the template!

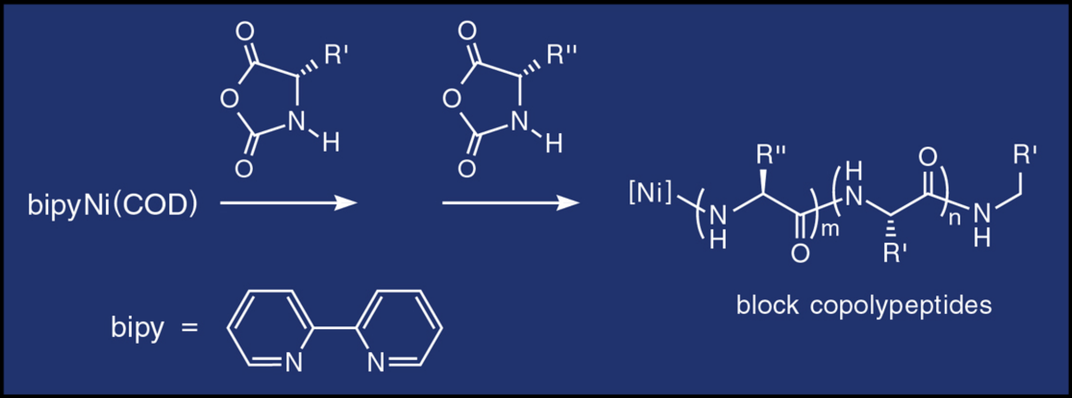


Translating the Enzymatic Mechanism to “Biomimetic” Materials Synthetics



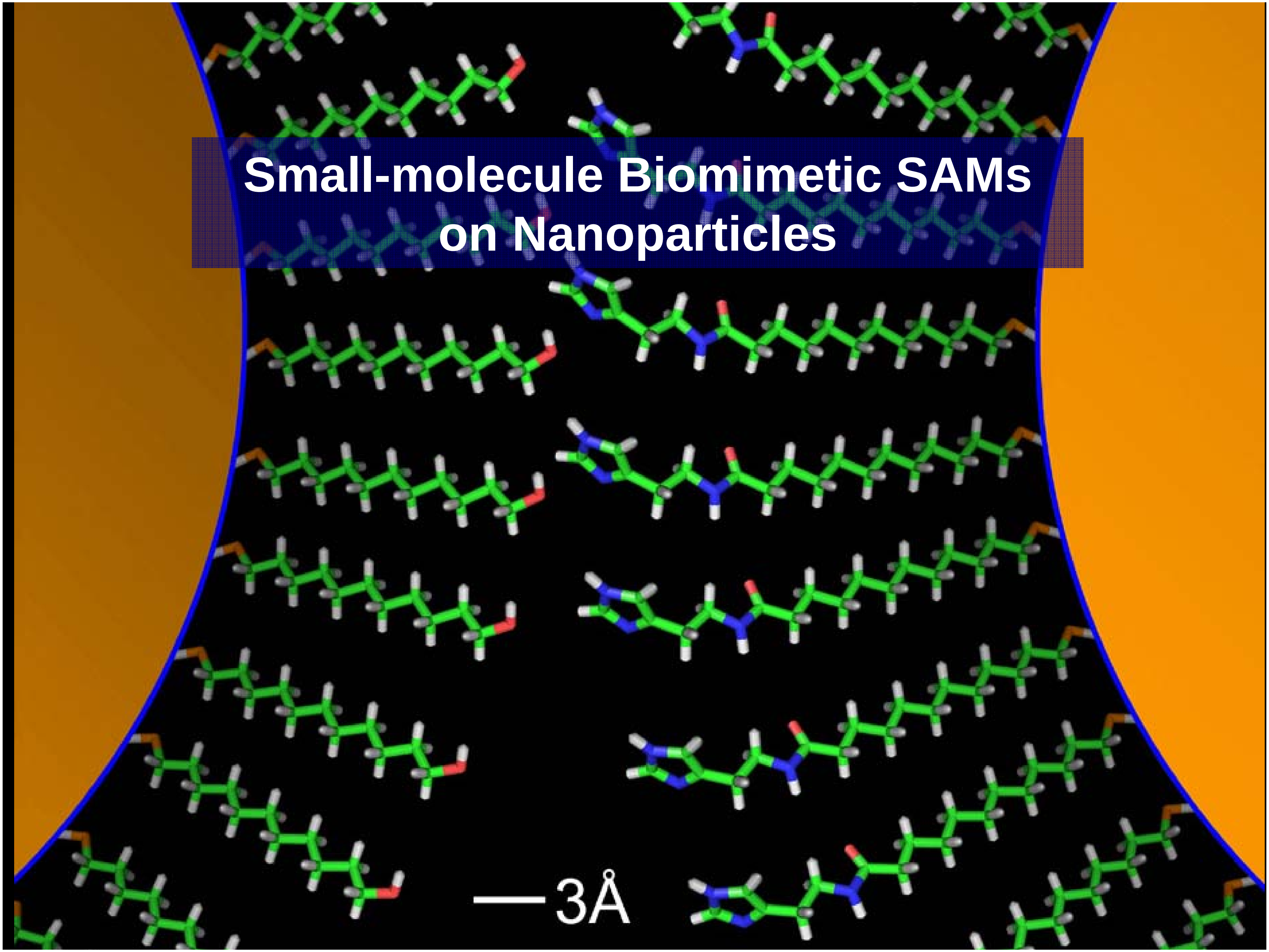
Catalytic & Structure-Directing Peptides and Polymers!

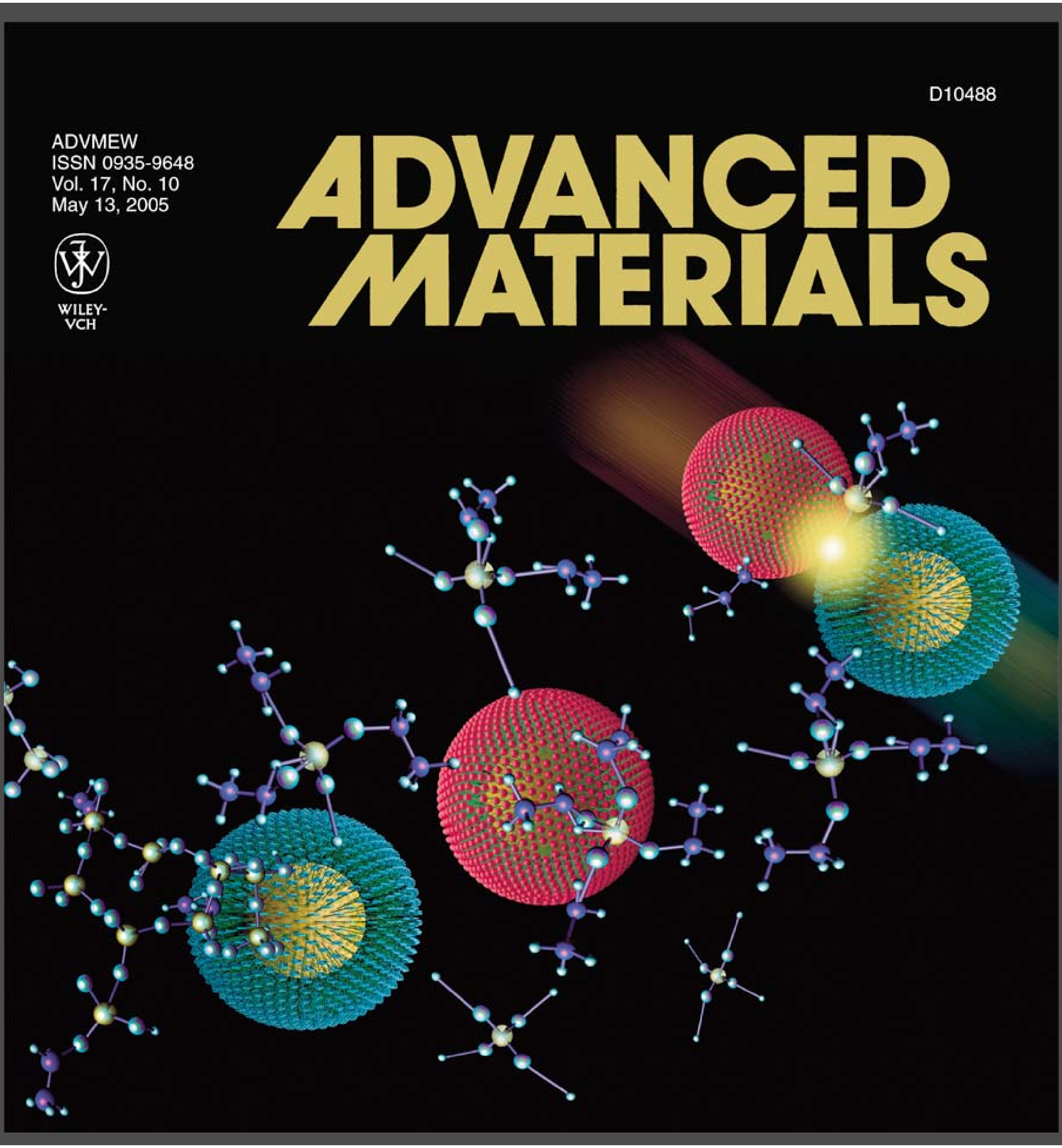




Cha, Stucky, Morse & Deming
Nature 403: 289 (2000)

Small-molecule Biomimetic SAMs on Nanoparticles





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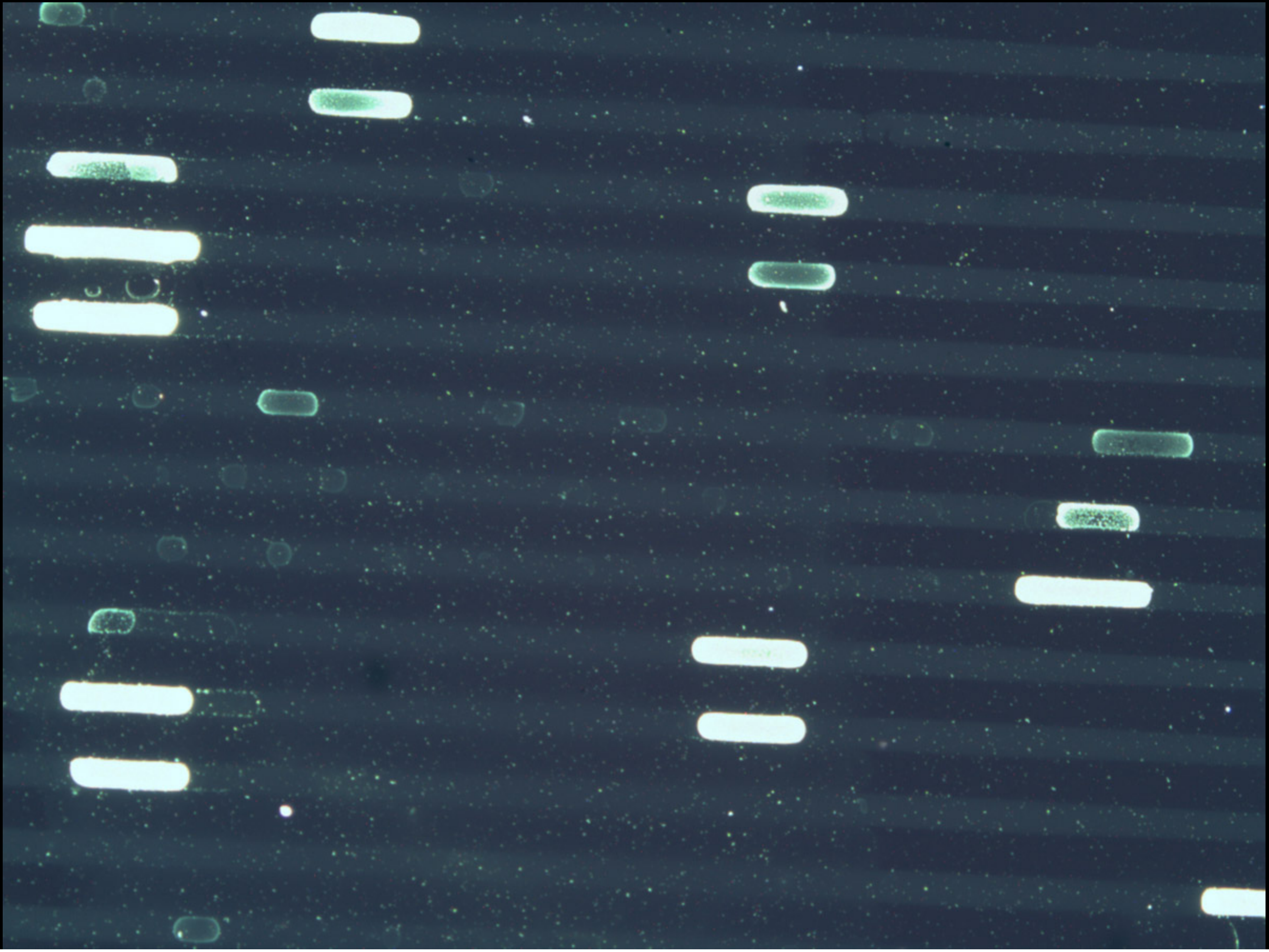
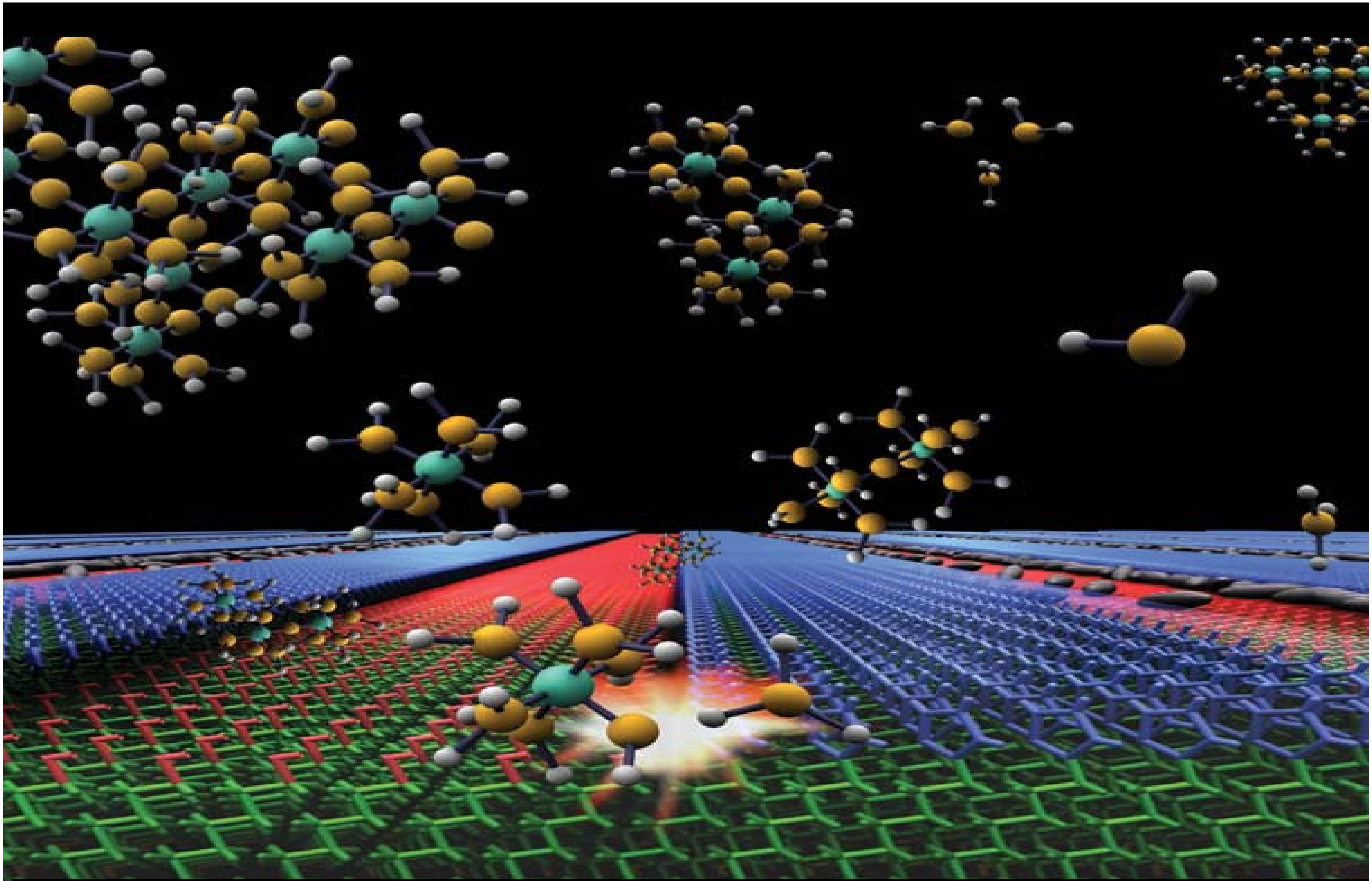
ADVANCED MATERIALS

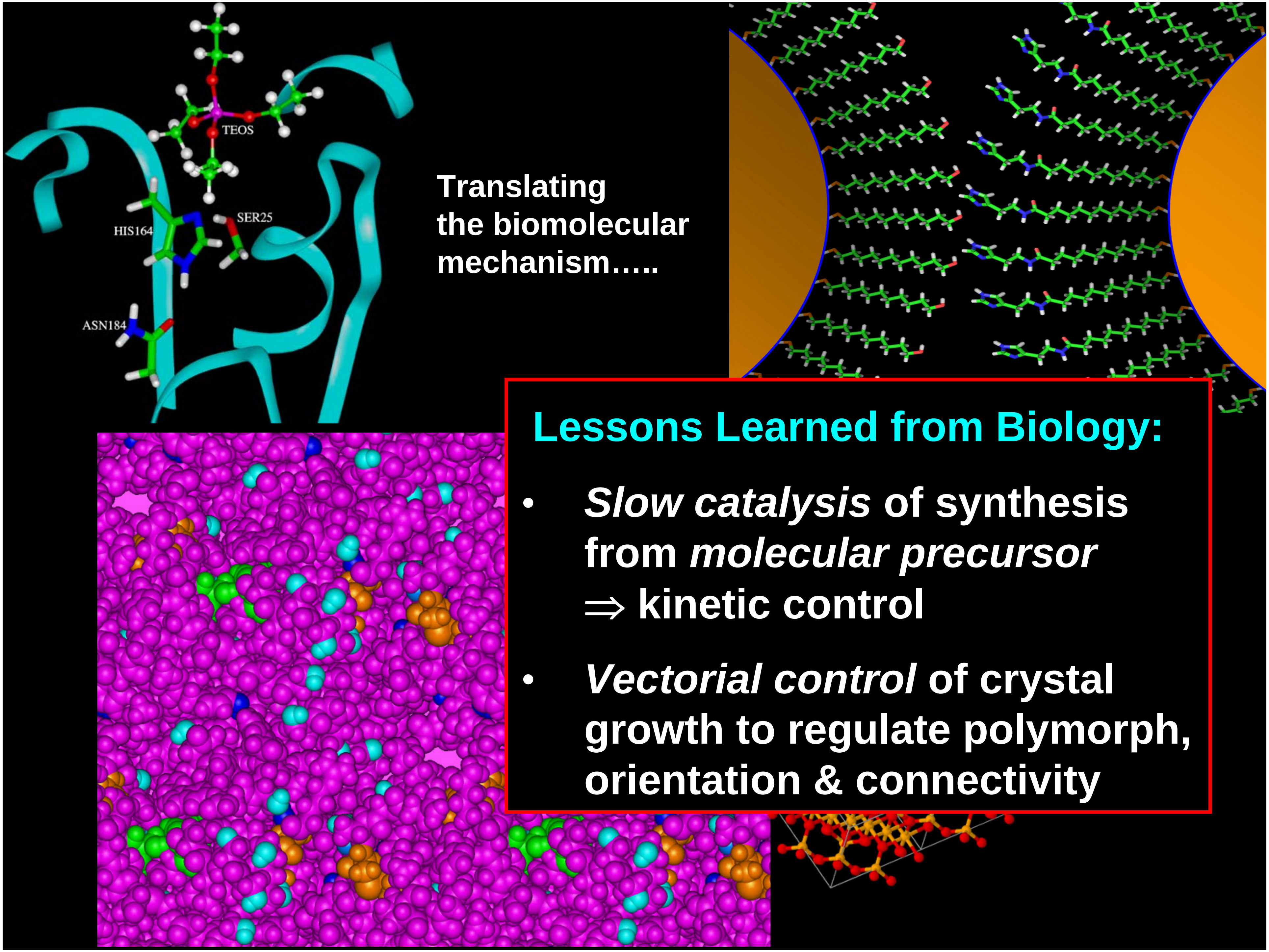
Biomimetic SAM Writes Nanoscale Pattern of Semiconductors on Silicon Chip





…..a low-temperature, bio*catalytic* counterpart to MOCVD!

But: can we do this ***with no organics***?

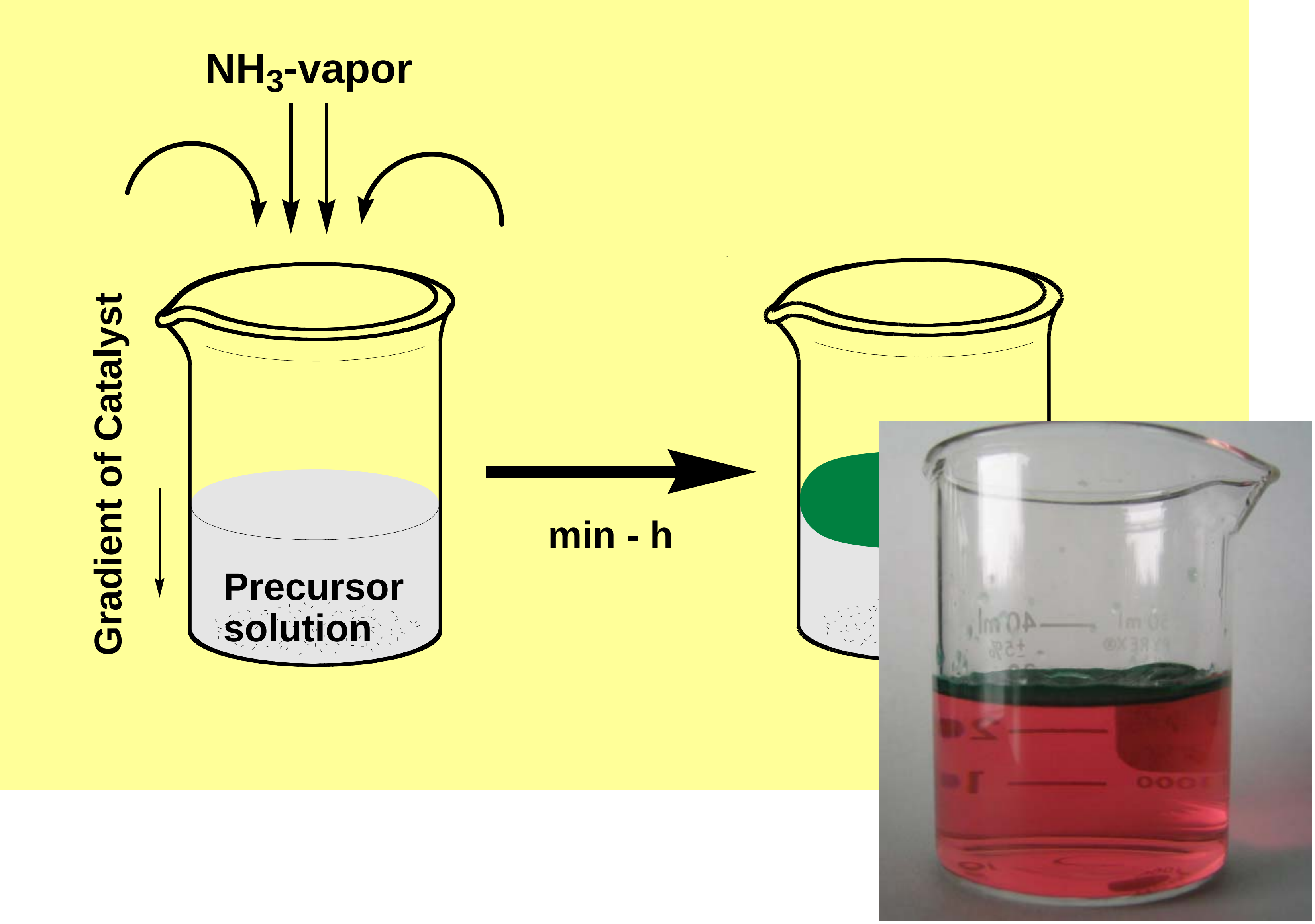


Translating the biomolecular mechanism…..

Lessons Learned from Biology:

- *Slow catalysis* of synthesis from *molecular precursor* ⇒ kinetic control
- *Vectorial control* of crystal growth to regulate polymorph, orientation & connectivity

Kinetically Controlled Growth of Template -free Nanostructured Films - *with No Organics*



NH_3-vapor

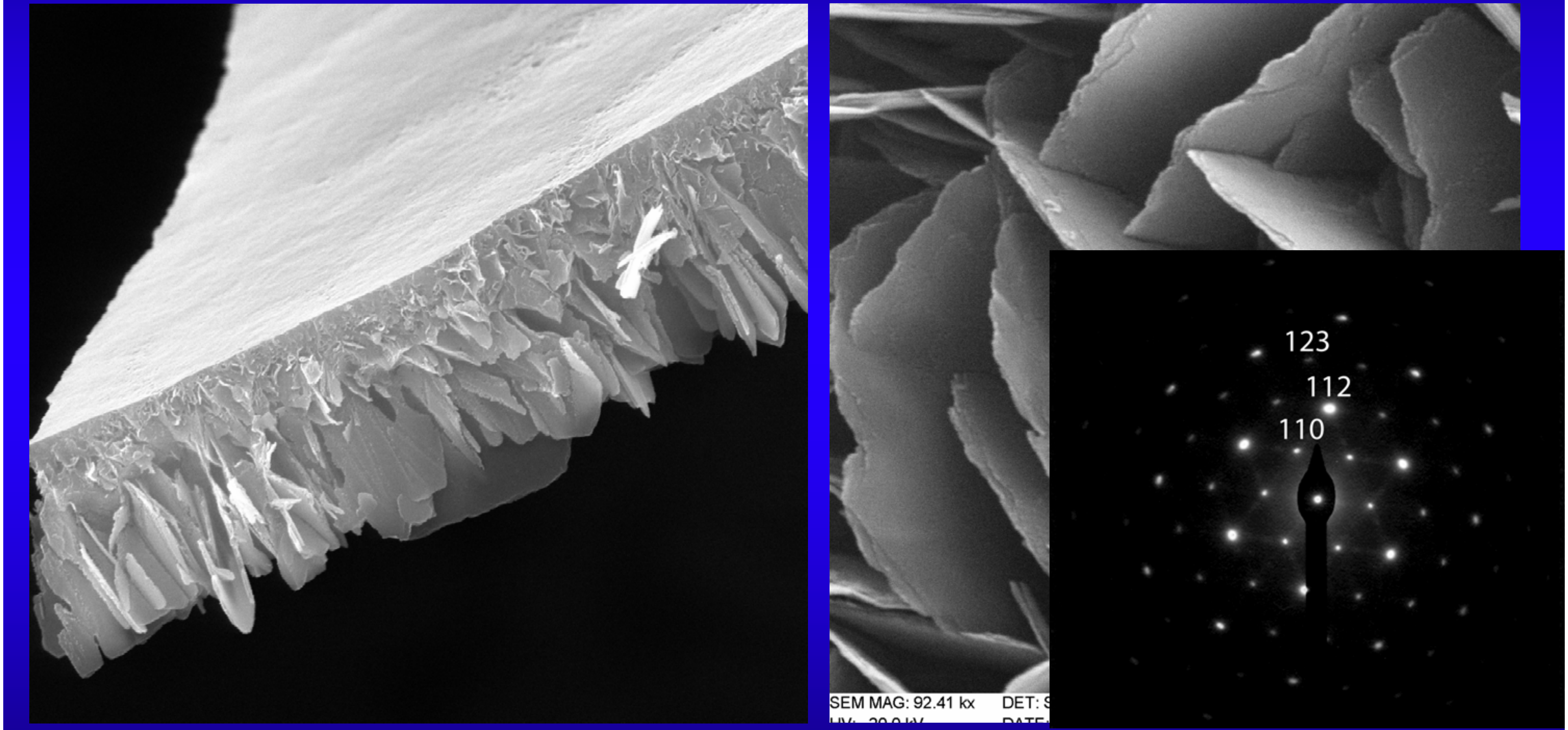
Gradient of Catalyst

Precursor solution

min - h

Bio-inspired, Low-Temperature Synthesis of Nanostructured Electronic Materials

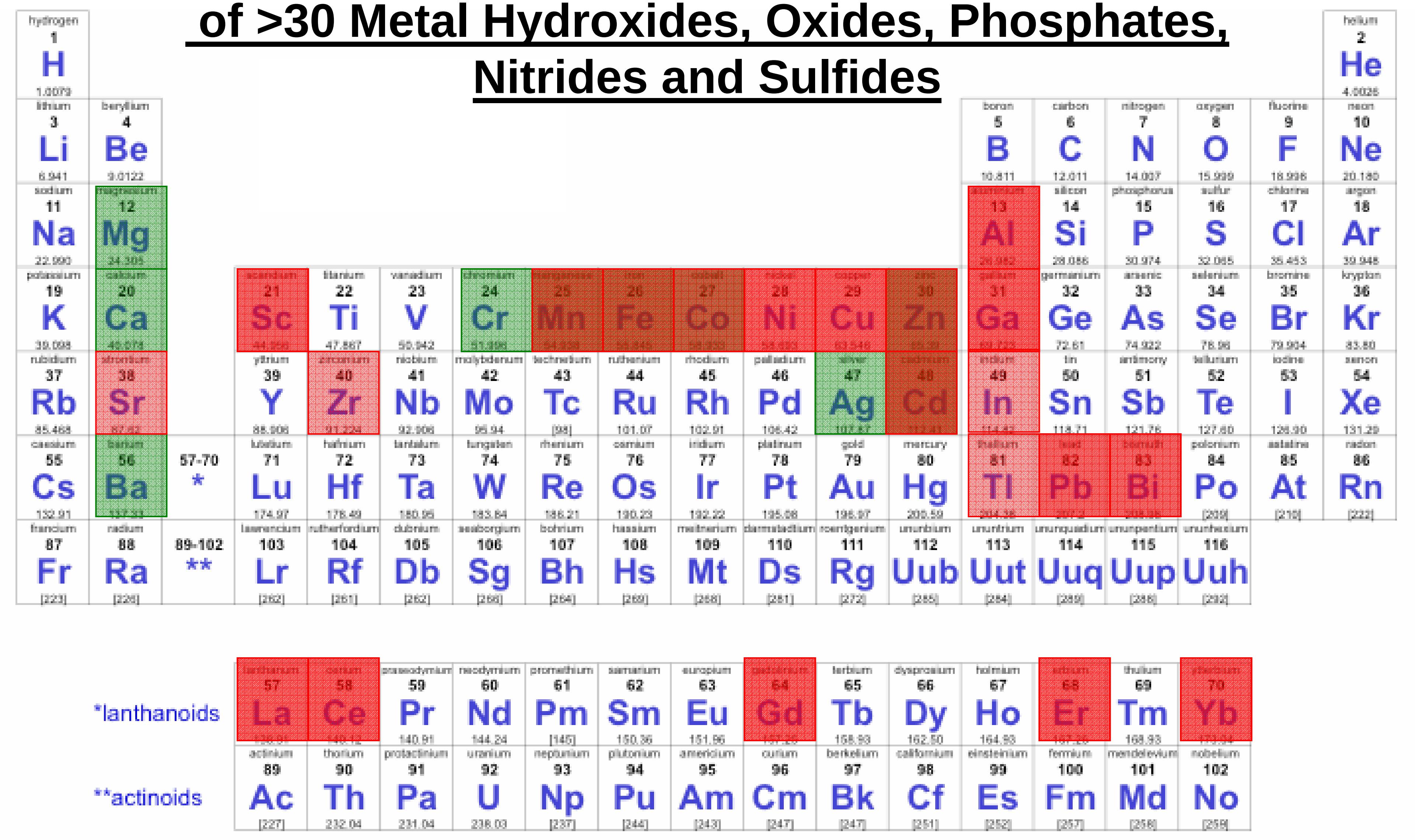
- with no biochemicals or organics!



Single-crystal Co(OH)$_2$ plates connected to flat conductive backplane

➲ *Many Novel Materials that Can't Be Made by Conventional Methods!*

The Method is Generic for Nanostructured Thin-Films of >30 Metal Hydroxides, Oxides, Phosphates, Nitrides and Sulfides



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	🟩 magnesium 12 Mg 24.305												🟥 aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	🟩 calcium 20 Ca 40.078		🟥 scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	🟩 chromium 24 Cr 51.996	🟥 manganese 25 Mn 54.938	🟥 iron 26 Fe 55.845	🟥 cobalt 27 Co 58.933	🟥 nickel 28 Ni 58.693	🟥 copper 29 Cu 63.546	🟥 zinc 30 Zn 65.39	🟥 gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	🟥 strontium 38 Sr 87.62		yttrium 39 Y 88.906	🟥 zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	🟩 silver 47 Ag 107.87	🟥 cadmium 48 Cd 112.41	🟥 indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	🟩 barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	🟥 thallium 81 Tl 204.38	🟥 lead 82 Pb 207.2	🟥 bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [272]	ununbium 112 Uub [285]	ununtrium 113 Uut [284]	ununquadium 114 Uuq [289]	ununpentium 115 Uup [288]	ununhexium 116 Uuh [292]		

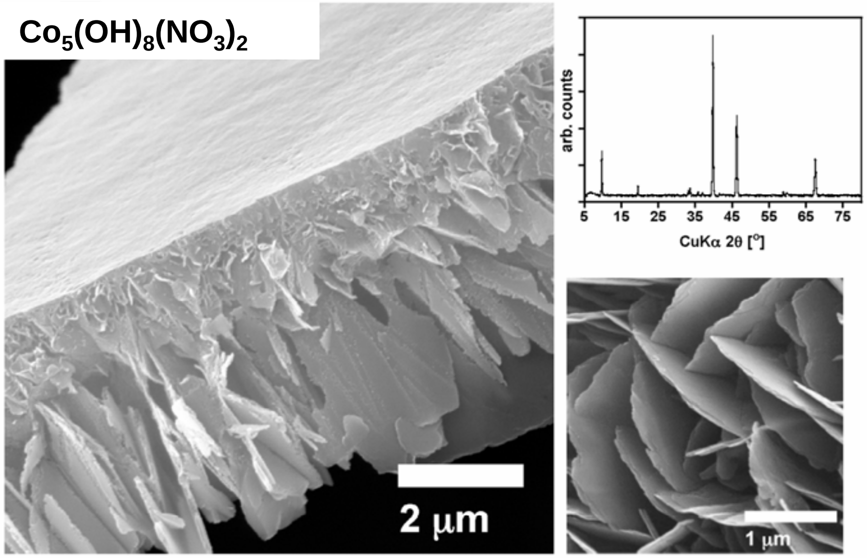
*lanthanoids	🟥 lanthanum 57 La 138.91	🟥 cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	🟥 gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	🟥 erbium 68 Er 167.26	thulium 69 Tm 168.93	🟥 ytterbium 70 Yb 173.04
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

🟥 Hydroxide films

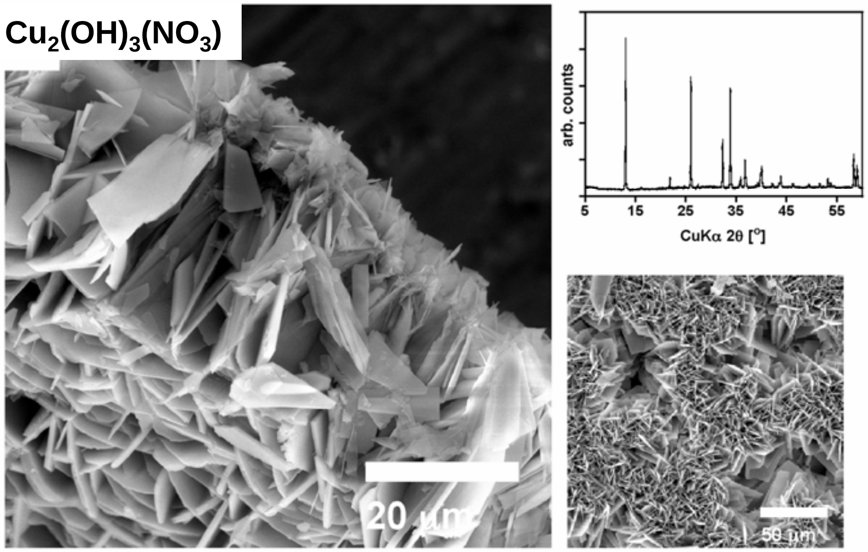
🟩 Phosphate films

Generic Synthesis of Template-free Nanostructured Films

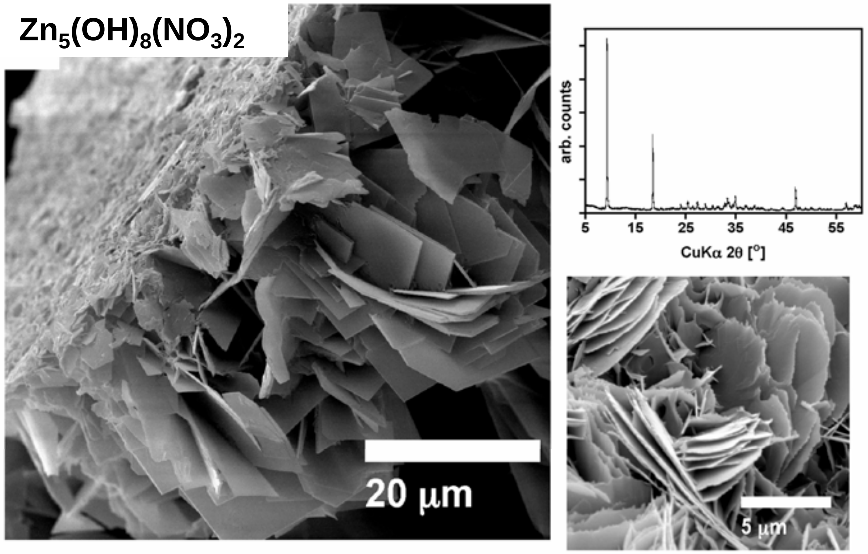
$Co_5(OH)_8(NO_3)_2$



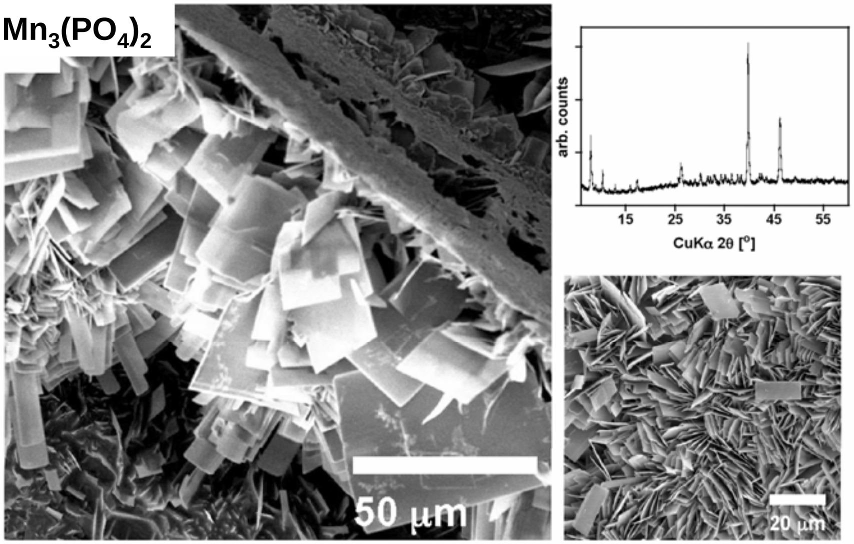
$Cu_2(OH)_3(NO_3)$



$Zn_5(OH)_8(NO_3)_2$

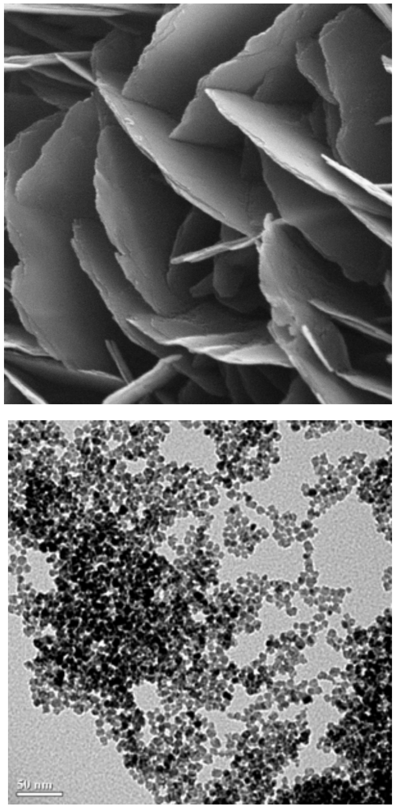


$Mn_3(PO_4)_2$



Strong Transitioning with Army, DoD & Industry Partners

Discovered Molecular Mechanism of Biological Nanofabrication of Silica



Translated to New Bio-inspired, Low-temperature Synthesis of Nanostructured Semiconductor Thin-films and Nanoparticles

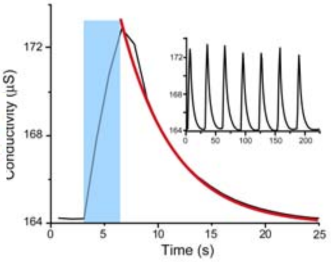
- Novel Structures; Uniquely Useful Properties!

3-D Batteries

CERDEC, Qualllion

Solar Energy

DARPA



Uncooled IR

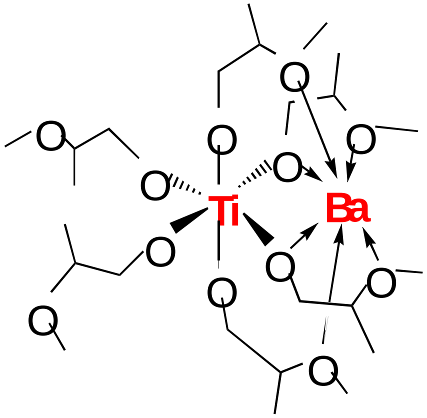
ARL, Aerospace

Flexible Displays

ARL, Aerospace

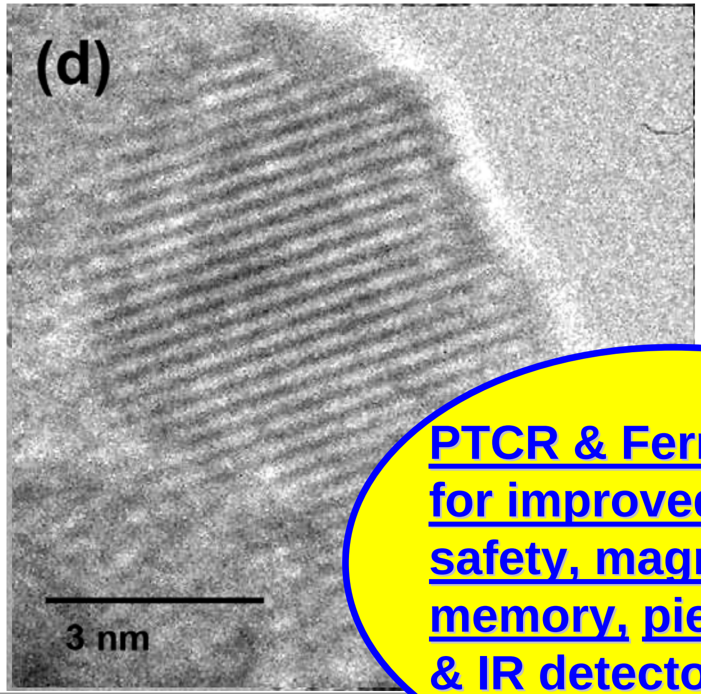
Bimetallic Perovskites:

Nano-crystalline $BaTiO_3$ at 20 ºC! – Typically requires extreme T or pH.



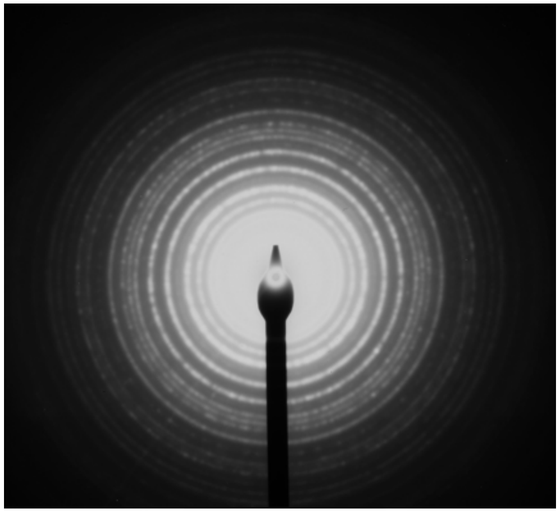
Gentle, bio-inspired catalysis preserves atomic-scale geometry of bimetallic precursor

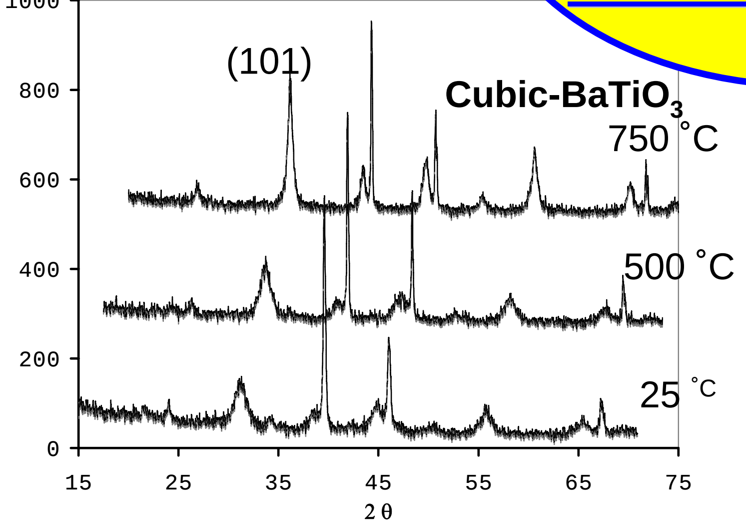
- with no phase-segregation!



6 nm, ultrapure

PTCR & Ferroelectric: for improved battery safety, magnetic memory, piezoelectric & IR detectors





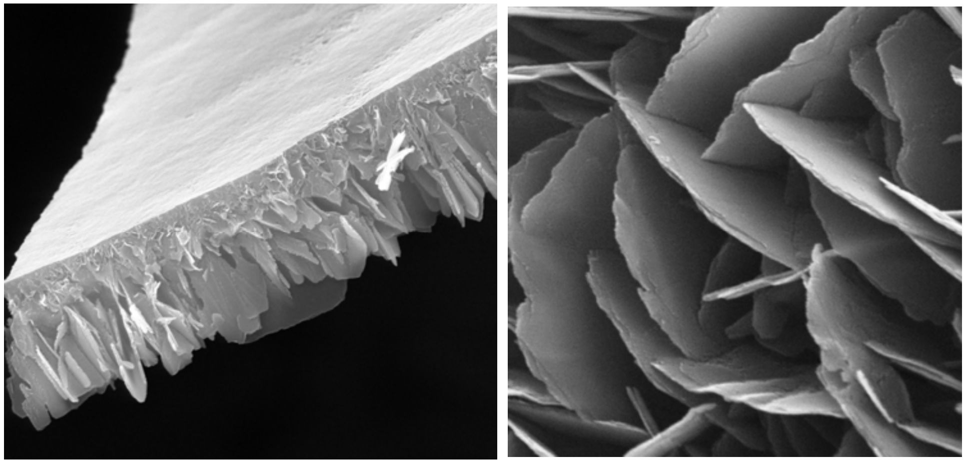
Angewandte Chemie (in press, 2006).

Exceptional Advantages for Lightweight Portable Energy

Lightweight high power-density 3-d batteries (with CERDEC and Quallion, Inc.):

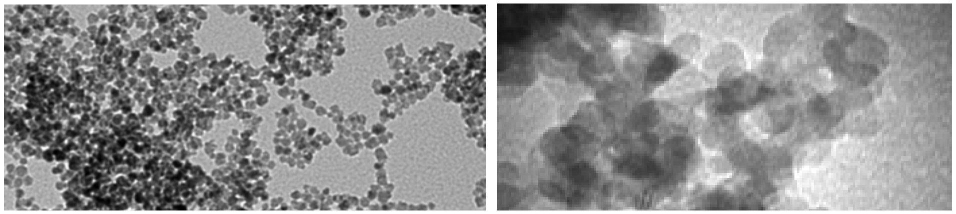
Nanostructured cobalt oxide and iron phosphate for true 3-d high power-density Li-ion batteries

(*J.Mater. Chem.* 16: 401 - 407, 2006)



$BaTiO_3$ nanoparticle coatings for electrodes for first explosion-proof rechargeable Li-ion batteries (protection resulting from Positive Thermal Coefficient of Resistance)

(Angewandte Chemie in press, 2006)



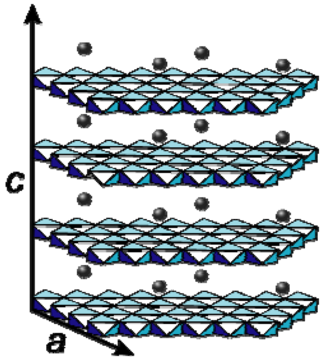
The New York Times

SONY, DELL & Apple Recall 6 Million Batteries Because of Fire Threat

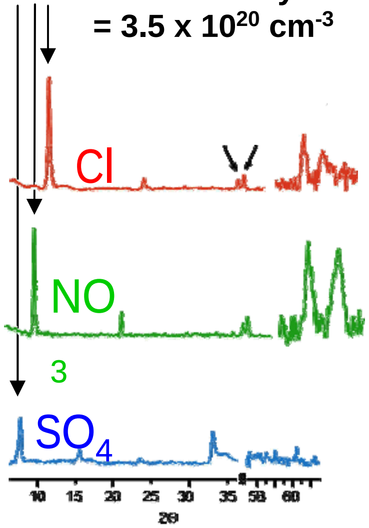
New Materials for Energy Applications:

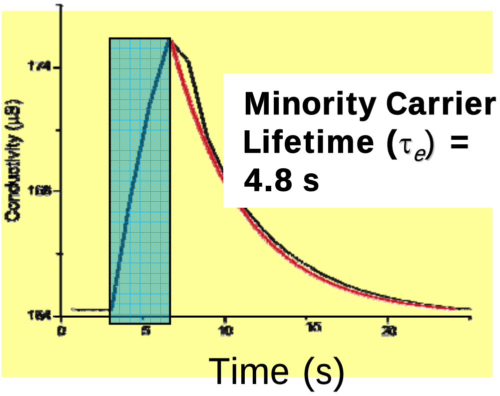
High-efficiency photovoltaics

Novel cobalt hydroxide nanostructured thin-films:

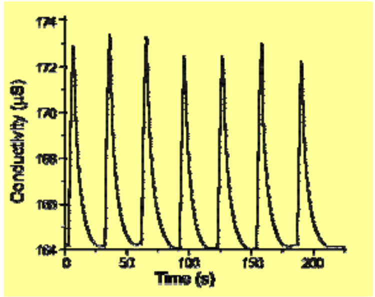


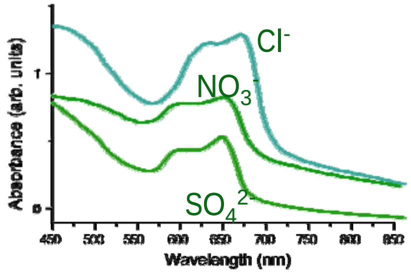
Counterion density = 3.5×10^{20} cm^{-3}



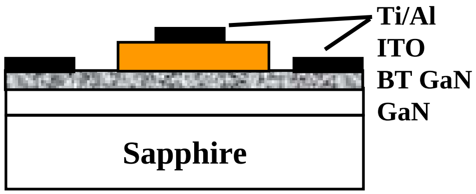


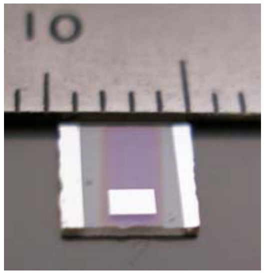
Minority Carrier Lifetime (τ_e) = 4.8 s

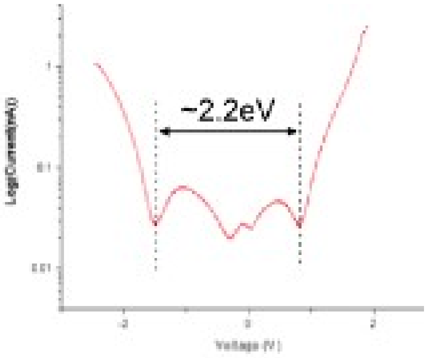


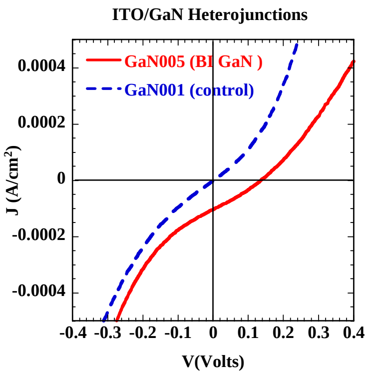


Low-cost Gallium Nitride thin-films:





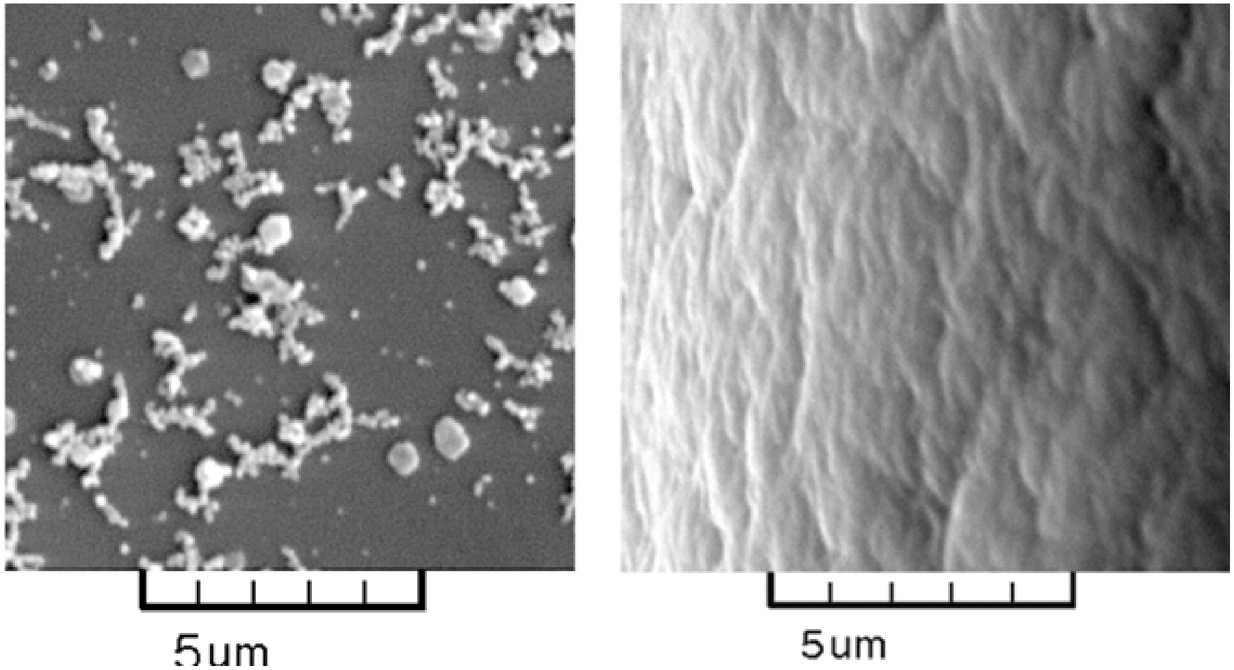




New Materials for Energy Applications:

Lightweight flexible photovoltaics

Low-Temperature Growth of Thin-film Electrodes on Organic Polymer Photovoltaics: more intimate connection of TiO_2 electrode with organic polymer photovoltaic:



Discontinuous particulate TiO_2 film made by conventional sol-gel method (*l.*)
and the continuous TiO_2 thin-film made by ICB's kinetically controlled (low-temp) method (*r.*)

Summary and Advantages

- **Generic low-temperature method for kinetically controlled synthesis of >30 nanostructured crystalline inorganic thin films, many with morphologies not possible with conventional methods**
- **Conversion to Nitrides, Phosphides and Sulfides demonstrated**
- **Kinetic control yields good crystallinity, long minority carrier lifetimes, high dopant densities and high surface areas *advantageous for more efficient solar energy and lightweight, high power-density batteries!***
- **High purity materials containing no organics**
- **Methods & materials fully integrable with MOCVD and CMOS fabrication**
- **Supported and free-standing thin films; readily amenable to electrochemical measurements ⇒ previously unknown properties**
- **Potentially adaptable to roll-to-roll and other high-throughput methods**

Adaptive Optical Materials

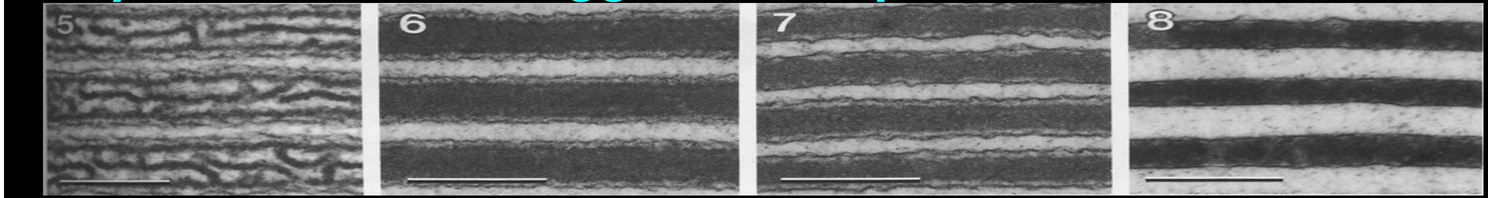

R. Hanlon

Our Approach:

Identify the Mechanism, and Translate
to Practical Materials Synthesis and Engineering

We recently identified the molecular switch.
- This discovery can guide new materials design!

Signal-dependent changes in the density, thickness & spacing of protein-based Bragg reflector plates determine reflectivity & color:

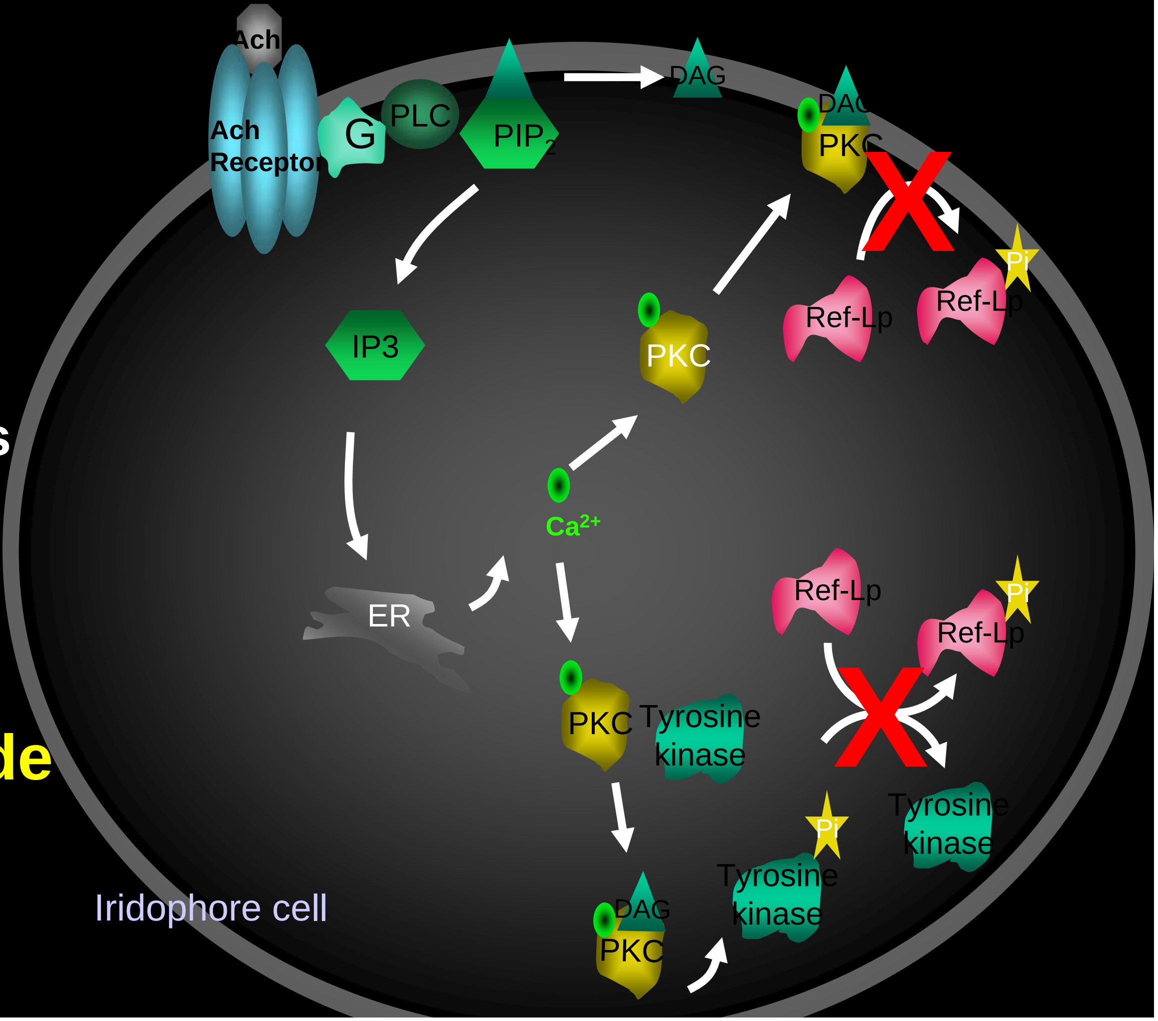


Non-reflecting Red Gold/Green Blue

Recent discovery: the molecular switch

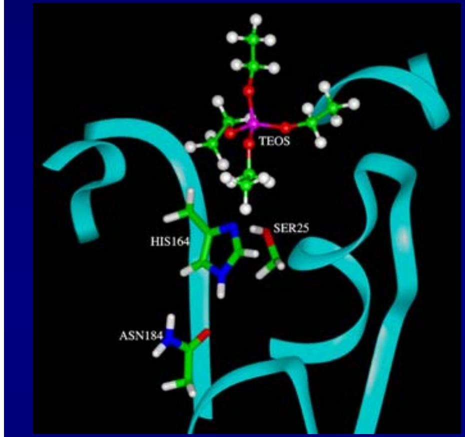
Catalytic phosphorylation controls optical properties of the protein-based Bragg Reflectors.

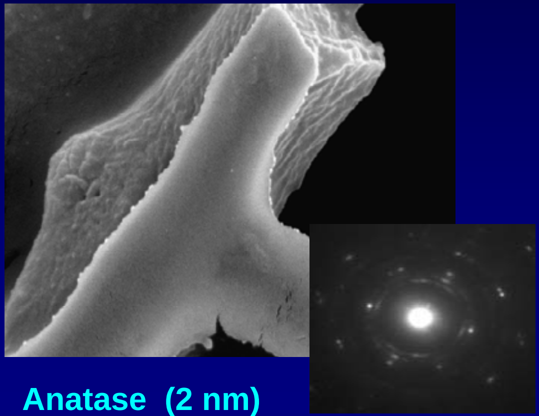
This discovery will guide path to new materials!



Bio-inspired, Low-Temperature Generic Synthesis of Nanostructured Semiconductor Thin-Films for Energy

Genetic engineering identified mechanism of catalysis



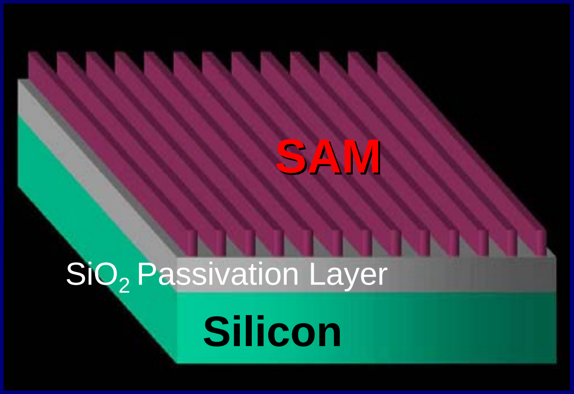


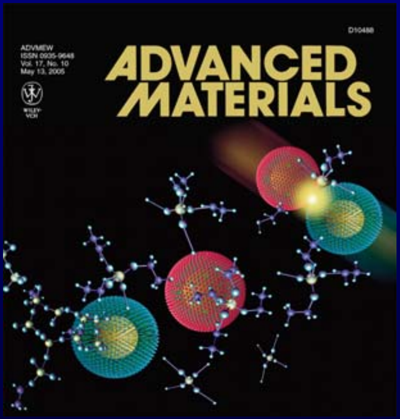
Anatase (2 nm)

Oriented $\gamma\text{–}Ga_2O_3$

Electron diffraction and XRD revealed molecular mechanism of templating

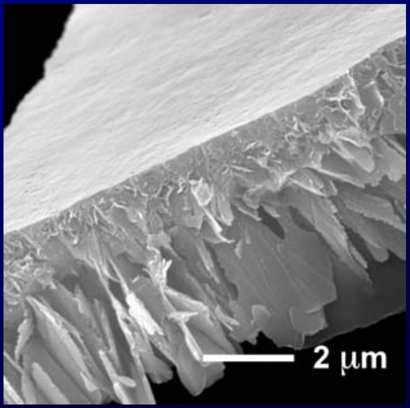
…that we translated to low-temperature biocatalytic counterpart to MOCVD

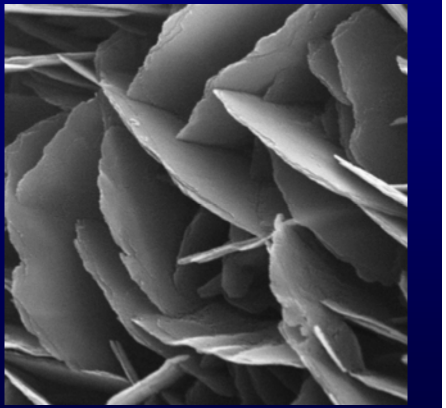




… a paradigm shift:

Kinetically controlled vapor-diffusion synthesis of inorganic films - using no organics!





This new understanding led to…