Printed Components (from Nanoparticles) and Large Area Capacitors

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ADEPT Metacapacitors

Project funded by Advanced Research Project Agency – Energy
(ARPA-E)
ADEPT Program
(Agile Delivery of Efficient Power Technology)

and City University of New York Energy Institute (CUNY Energy Institute), New York State Energy Research and Development Authority (NYSERDA), Con Edison (Con Ed)

Team Overview: CUNY Energy Institute

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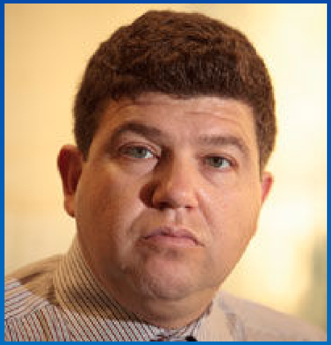
Stephen O'Brien, Associate Prof., Materials Science/ Chemistry

Daniel Steingart, assistant professor ,Chem E/Mat Sci



Alex Couzis, Prof., Chem E

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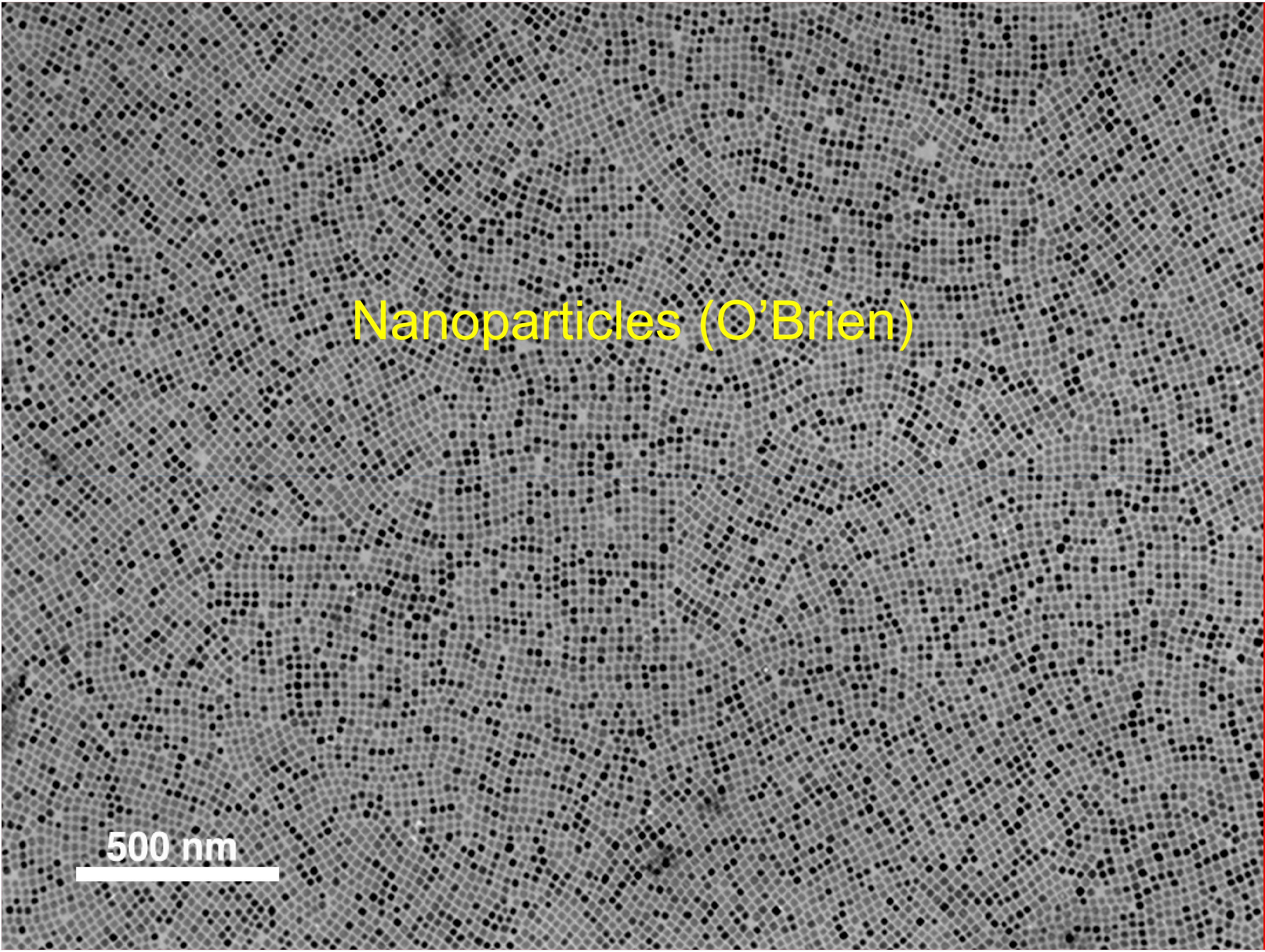
Team Overview: Columbia and UC Berkeley

Ioannis Kymissis is an assistant professor of Electrical Engineering at Columbia University, - Columbia Laboratory for Unconventional Electronics, and a member of the DOE EFRC at Columbia University.

Peter Kinget is an associate professor of Electrical Engineering at Columbia University, - integrated circuit and system integration expertise and keen understanding of analog and RF integrated circuits and signal processing using advanced silicon semiconductor processes.

Seth Sanders is a professor of Electrical Engineering and the University of California, Berkeley. His research interests are in high frequency power conversion circuits and components, in design and control of electric machine systems, and in nonlinear circuit and system theory as related to the power electronics field. - novel designs of switch capacitors topologies



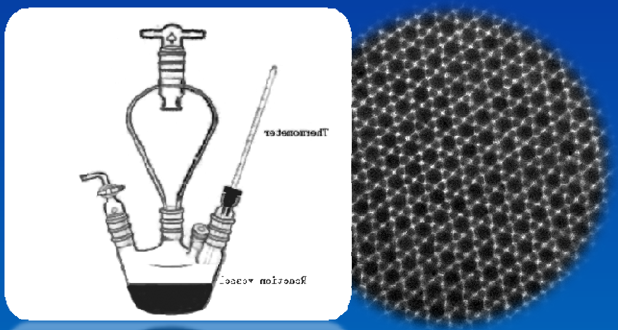
Nanoparticles (O’Brien)

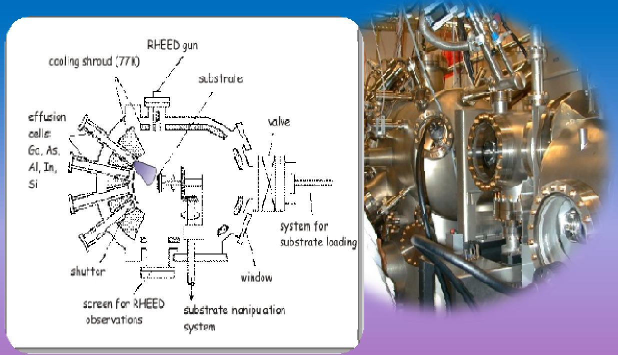
Chemical Approaches to Nanomaterials

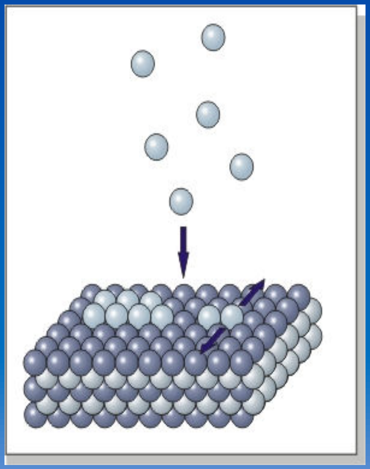
Making Materials Chemistry a Technology

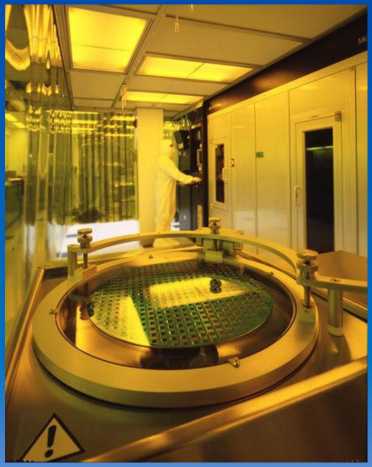
Atomic or molecular units, with well known subatomic structure in isolation, offer the ultimate building blocks for a bottom-up manufacturing synthesis with applications in many industries.

- Can chemistry provide us with a means to produce technologically useful monolayers, thin films and ultimately more complex devices?





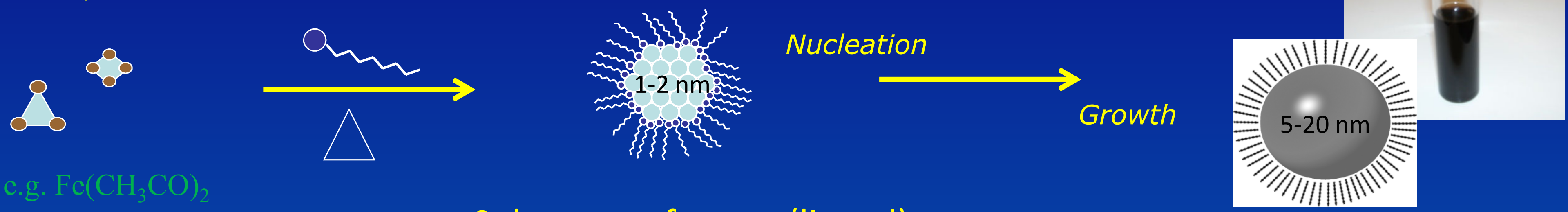




Micro/Nanofabrication (many, many steps)

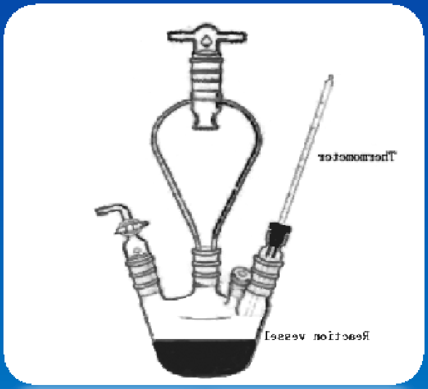
Synthesis of nanocrystals – preparation of nanoscale building blocks

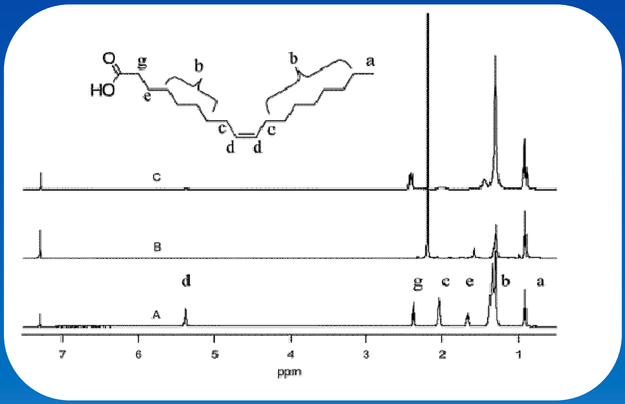
Start with a molecular precursor
(e.g. CVD or MBE precursors
work well)

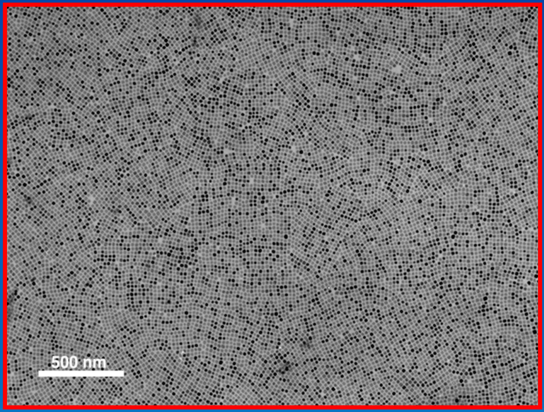


e.g. $Fe(CH_3CO)_2$

Solvent, surfactant (ligand), e.g.
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH)$

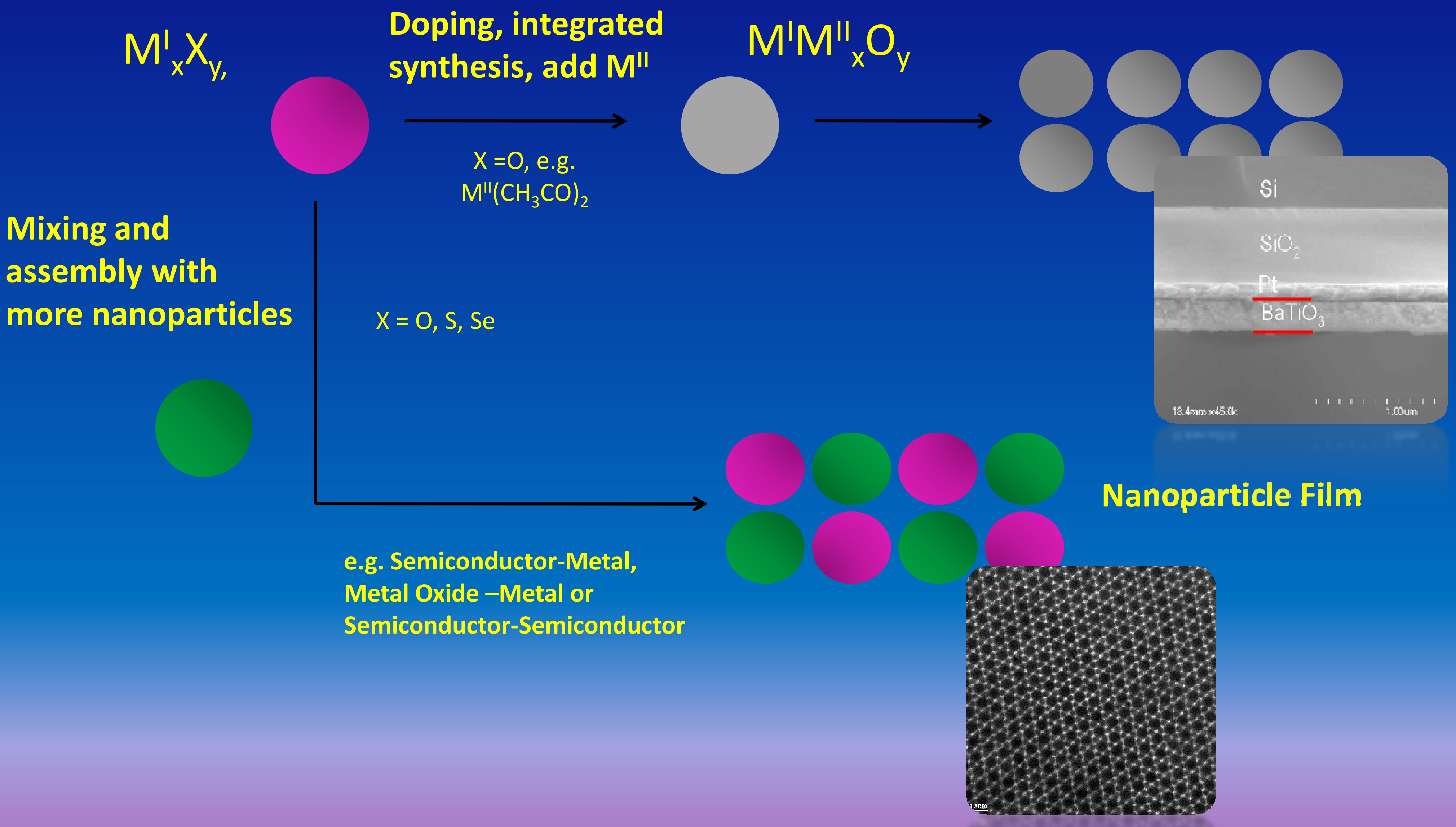






1. Willis, A. L.; Chen, Z.; He, J.; Zhu, Y.; Turro, N. J.; O'Brien, S. *Journal of Nanomaterials,* **2007**, doi:10.1155/2007/14858; 2. Yin, M.; Chen, Z.; Deegan, B.; O'Brien, S. *Journal of Materials Research* **2007**, *vol.22,* 7, 1987-1995; 3. Andelman, T.; Gong, Y.; Neumark, G.; O'Brien, S. *Journal of Nanomaterials,* **2007**, doi:10.1155/2007/73824; 4. White, B.; Yin, M.; Hall, A.; Le, D.; Stolbov, S.; Rahman, T.; Turro, N.; O'Brien, S. *Nano Letters* **2006**, 6, 2095-2098; 5. Chen, Z.; Huang, L.; He, J.; Zhu, Y.; O'Brien, S. *Journal of Materials Research* **2006**, 21, 3187-3195. 6. Yin, M.; Willis, A.; Redl, F.; Turro, N. J.; O'Brien, S. P. *Journal of Materials Research*, **2004**, 19(4), 1208-1215.; 7. Redl, F. X., Black; C. T.; Papaefthymiou, G. C.; Sandstrom, R. L.; Yin, M.; Zeng, H.; Murray, C. B. O'Brien, S. P. *J. Am. Chem. Soc.,* **2004,** 126(44); 14583-14599.

Obrien Nanoparticle Film Strategy: Increasing Complexity: towards enhancing properties – collective properties



$M^{I}{}_{x}X_{y,}$

Doping, integrated synthesis, add M^{II}

$M^{I}M^{II}{}_{x}O_{y}$

X =O, e.g. $M^{II}(CH_3CO)_2$

Mixing and assembly with more nanoparticles

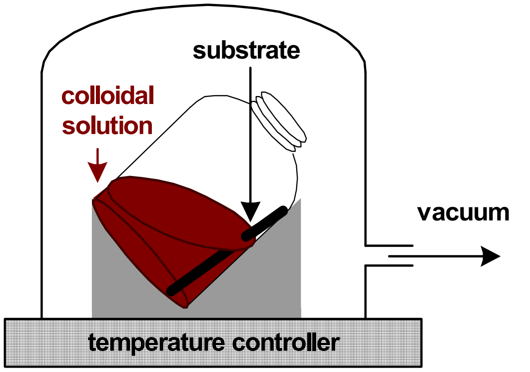
X = O, S, Se

Nanoparticle Film

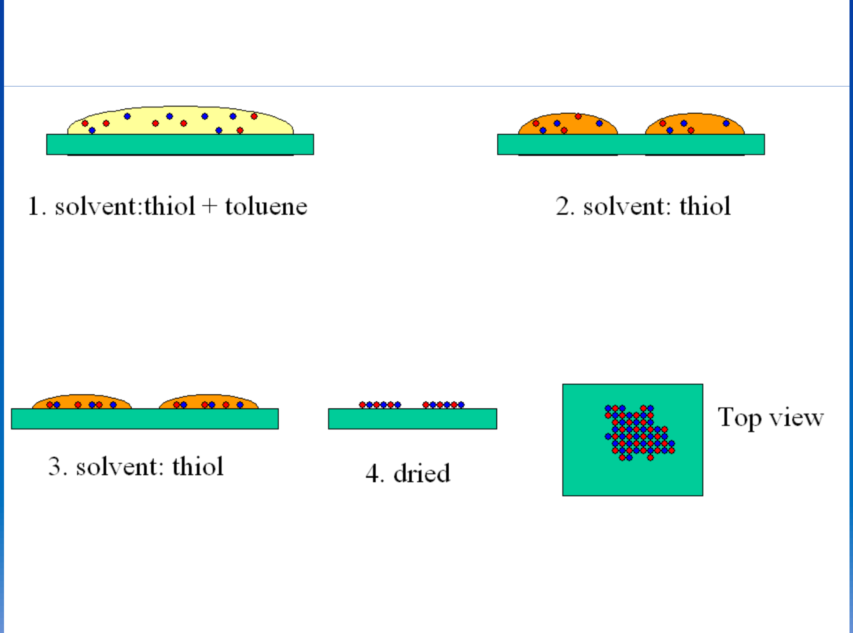
e.g. Semiconductor-Metal, Metal Oxide –Metal or Semiconductor-Semiconductor

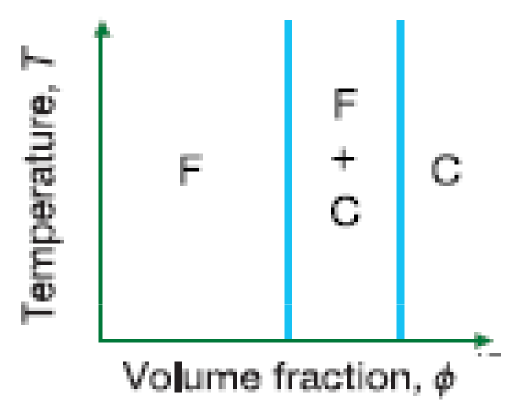
Formation of Binary Nanoparticle Superlattices (BNSLs)

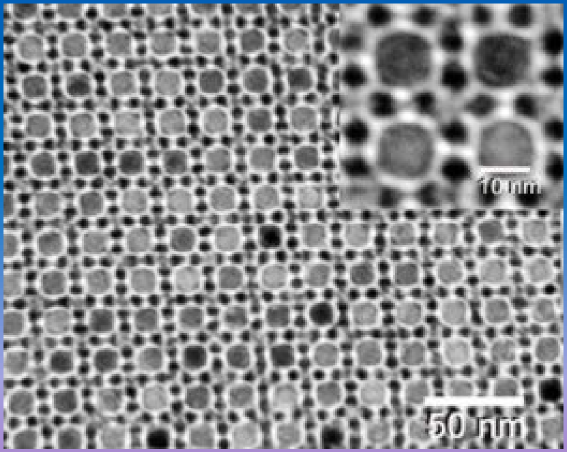
Evaporation Driven Assembly.



Prepare by co-evaporation

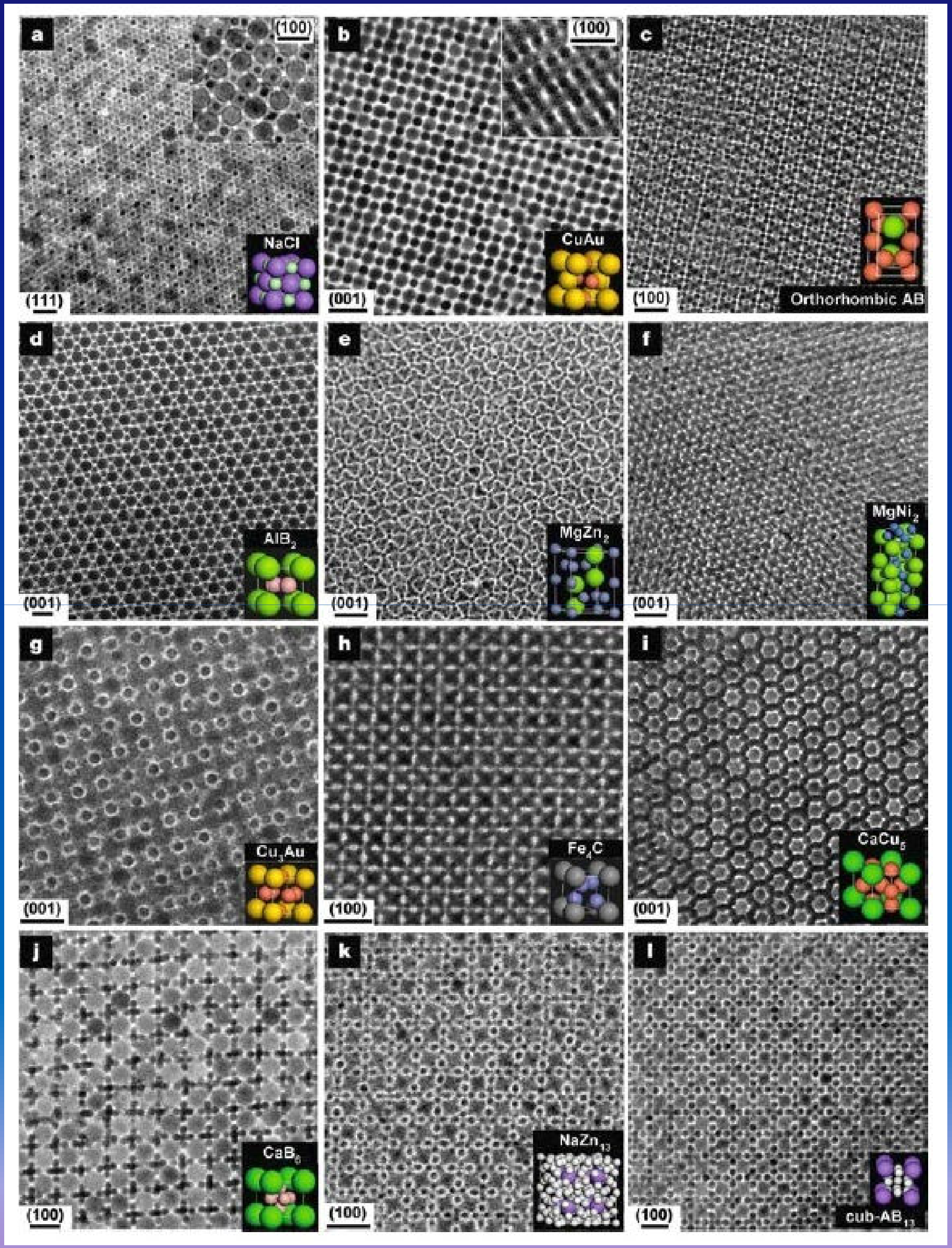






Structural Characterization

Structural diversity in binary nanoparticle superlattices

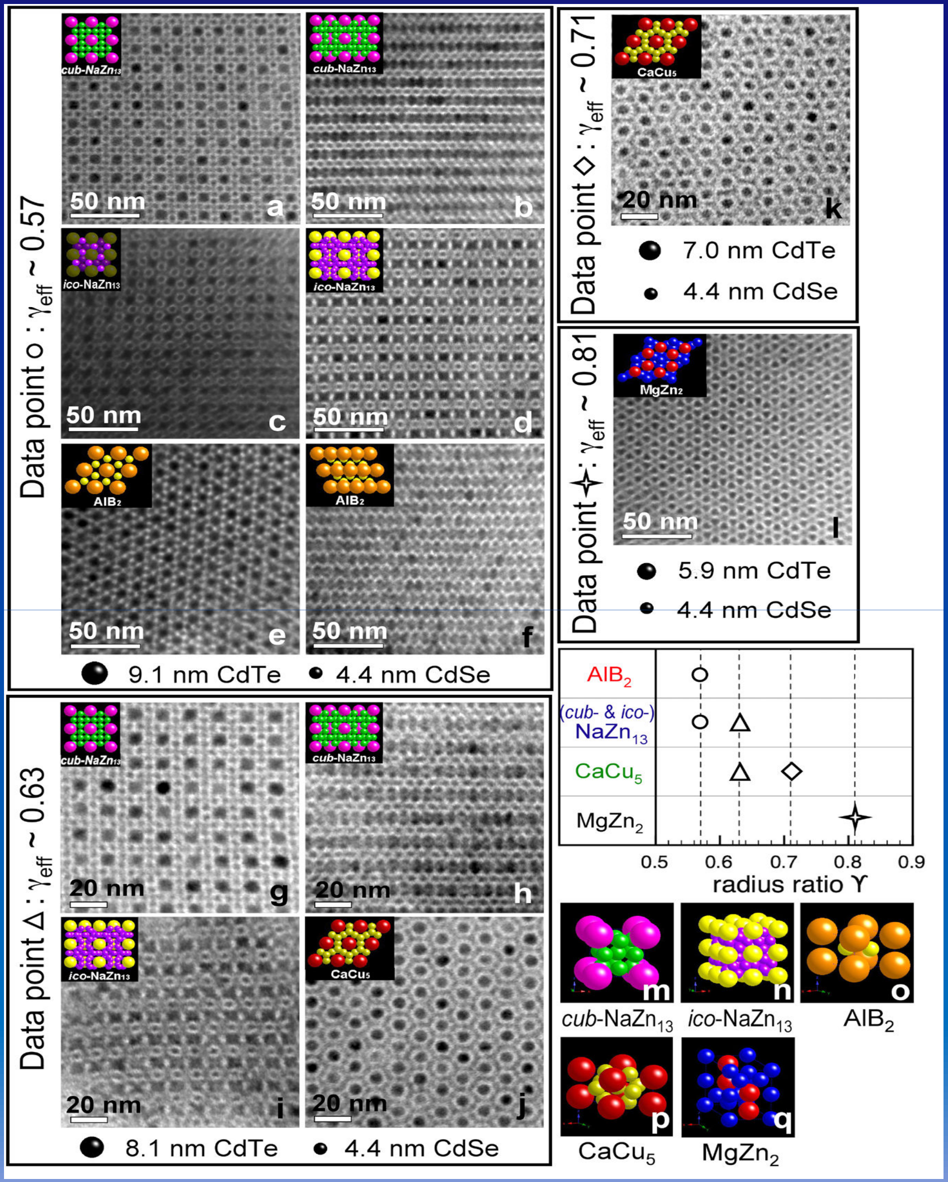


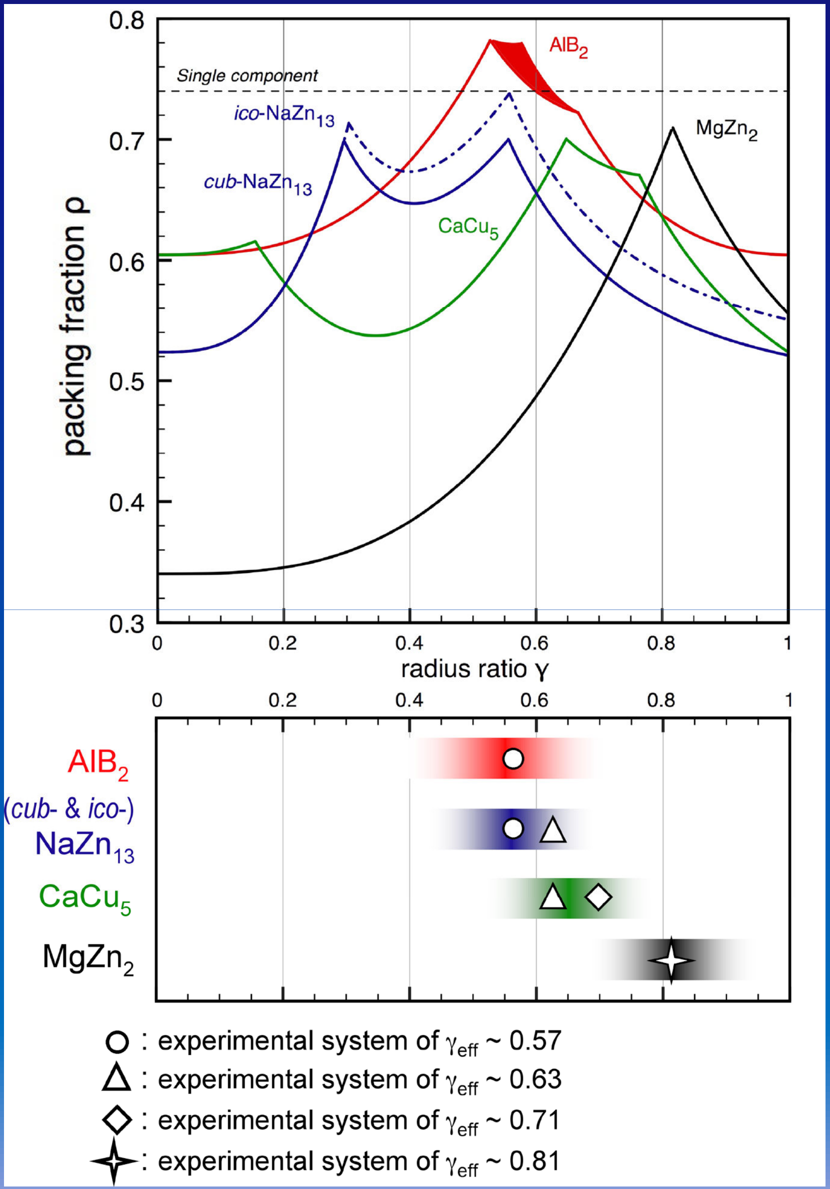
Made from Pairs of Nanoparticles of Ag, Pd, Au, PbSe, Fe_2O_3.

e.g. (a) 13.4 nm Fe_2O_3 and 5nm Au

Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, 439, 55-59.

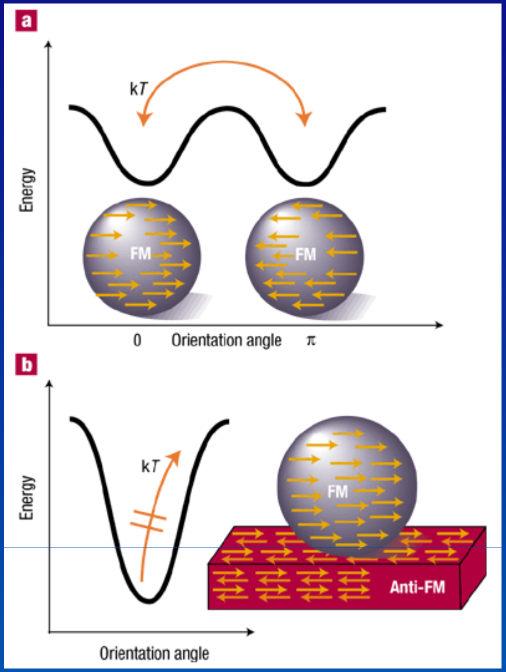
Binary nanoparticle superlattices

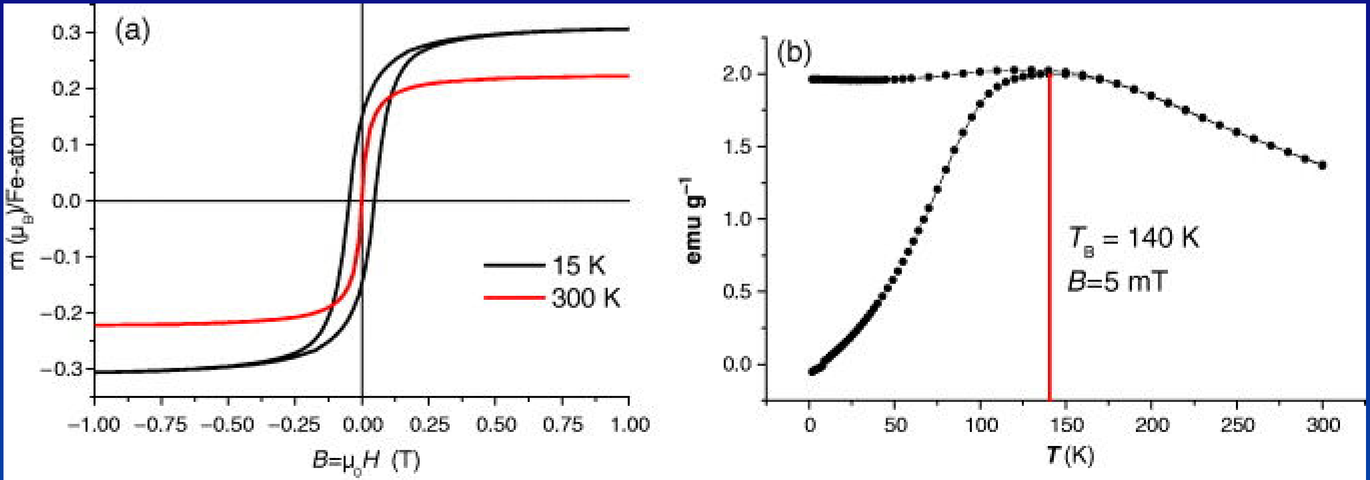




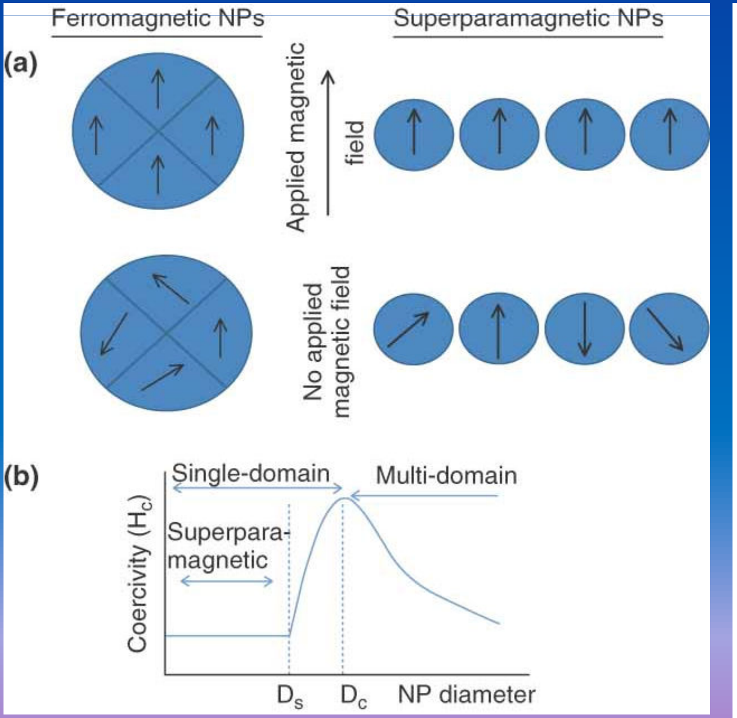
"Structure Direction of II-IV Semiconductor Quantum Dot Superlattices by Tuning Radius ratio", *ACS Nano*, **2008**, 2(6), 1219-1229.

Superparamagnetic Nanoparticles



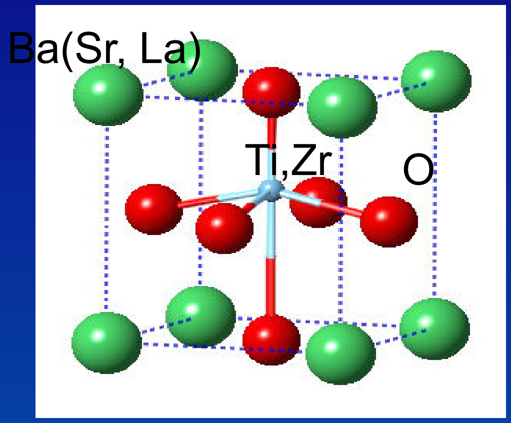


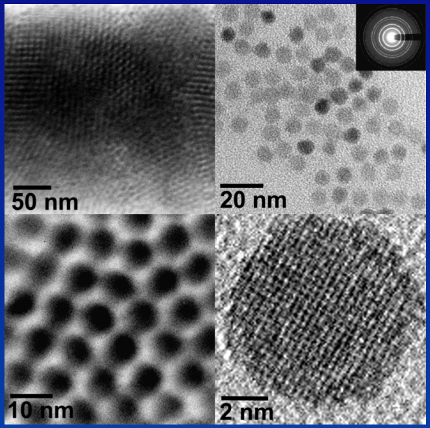
$$T_B = \frac{KV}{k_B \ln\left(\frac{\tau_m}{\tau_0}\right)}$$



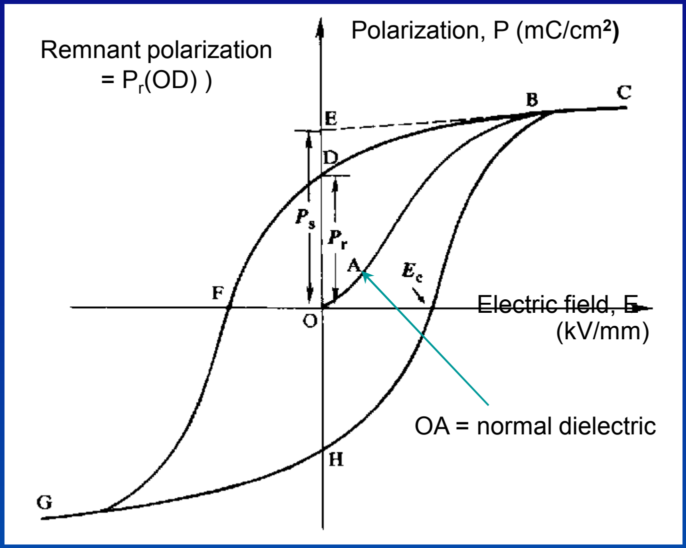
1. Magnetic nanostructures: Overcoming thermal fluctuations, Johannes Eisenmenger and Ivan K. Schuller, *Nature Materials* 2, 437 - 438 (2003); 2. Wiki (superparamagnetism); 3. **Monodisperse magnetic nanoparticles for biodetection, imaging, and drug delivery: a versatile and evolving technology,** SHIVANG R. DAVE,XIAOHU GAO. ; 4. New J. Phys. **11** (2009) 033034 doi:10.1088/1367-2630/11/3/033034**Structural and magnetic deconvolution of FePt/FeO$_x$-nanoparticles using x-ray magnetic circular dichroism** D Nolle[1], E Goering[1,4], T Tietze[1], G Schütz[1], A Figuerola[2,3] and L Manna

Scaling Barium Titanate ($BaTiO_3$) and the Ferroelectric Phase Transition





O'Brien, S.; Brus, L.; Murray, C. B. *Journal of the American Chemical Society* **2001**, 123, 12085-12086.



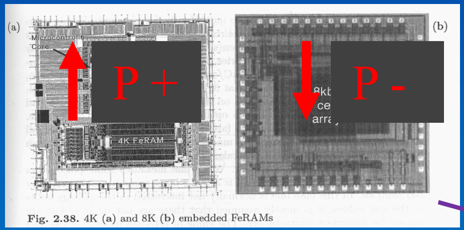
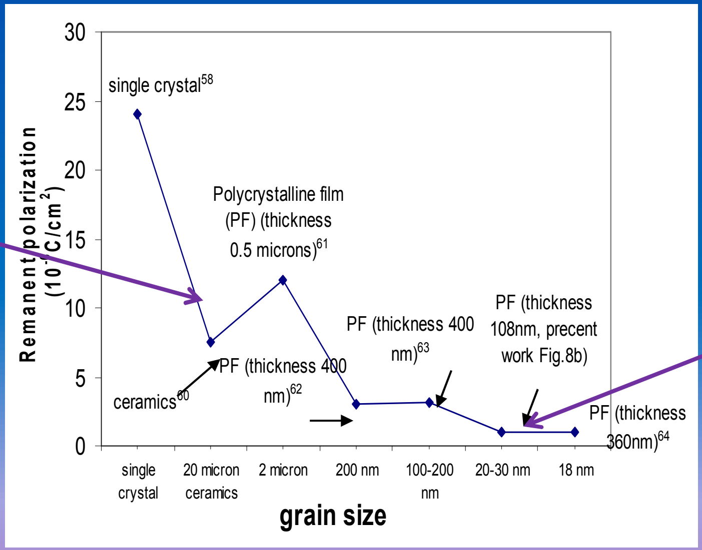
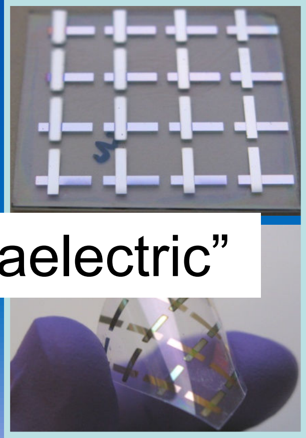


Fig. 2.38. 4K (a) and 8K (b) embedded FeRAMs

FRAM: Non - Volatile Memory





“Superparaelectric”

Capacitors?

Huang, L.; Chen, Z.; Wilson, J. D.; Banerjee, S.; Robinson, R. D.; Herman, I. P.; Laibowitz, R.; O'Brien, S. *Journal of Applied Physics* **2006**, 100, 034316.

Complex Oxide Nanocrystal Synthesis with Applications in Flexible/Printable Thin Film Technologies

BaTi alkoxide

- •Ba(BaO) + Ti(iPr)$_4$
- •BaTi ethylhexano-isoproxide
- •Ba(iPr)$_2$ + Ti(iPr)$_4$

+

Alcohol

- •ethanol, ethanol with controlled amount of water(5-20wt%)
- •isopropanol
- •ethanol +isopropanol

solvothermal: 200-220°C, 1-4 ds

Individual BaTiO$_3$ nanocrystals → stable suspension

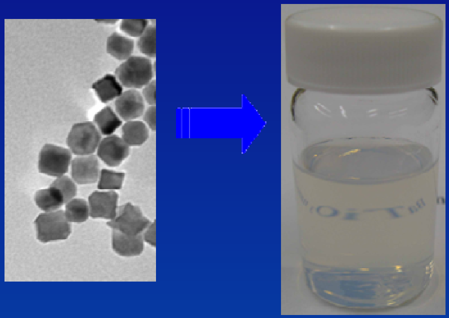
hydrophilic surface: ethanol, DMF as solvents
hydrophobic surface (oleic acid coating): hexane, toluene as solvents

adding polymer (optional)

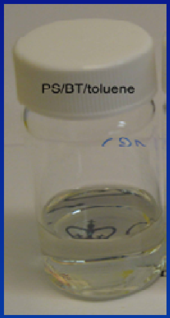
low T processing (spin-coating)

thin film of BaTiO$_3$ nanocrystals or polymer/BaTiO$_3$ nanocomposites

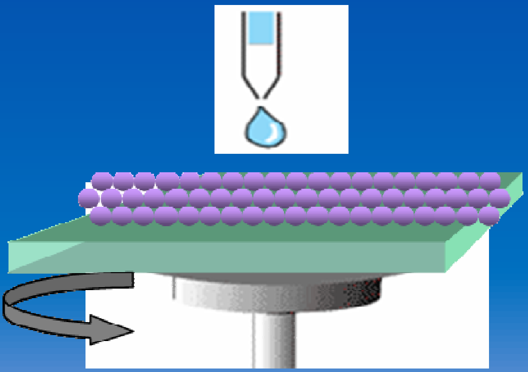
solvothermal process: BaTi alkoxide+ alcohol/water



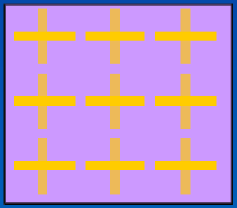
ethanol suspension of BaTiO$_3$ nanocrystals



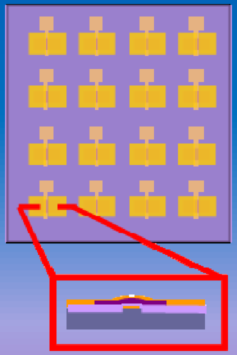
toluene suspension of polymer/nanocrystal nanocomposite



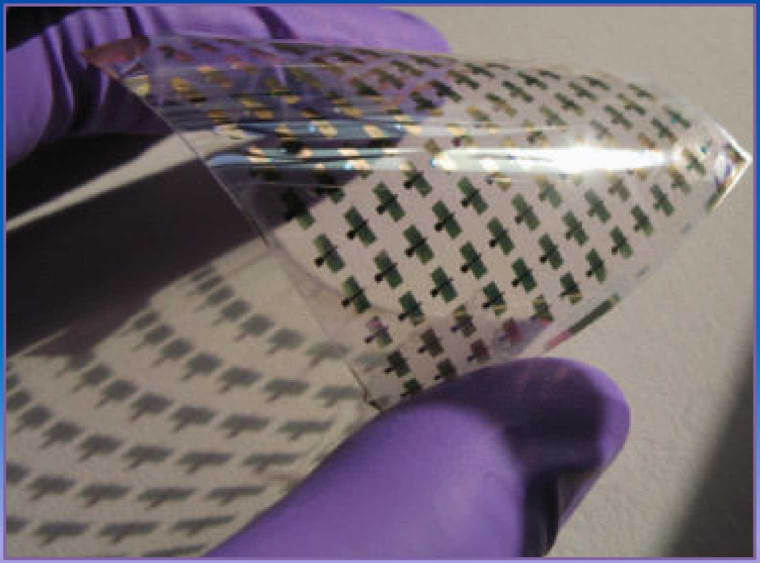
low temperature processing: Individual, well crystallized Nanocrystals as building blocks



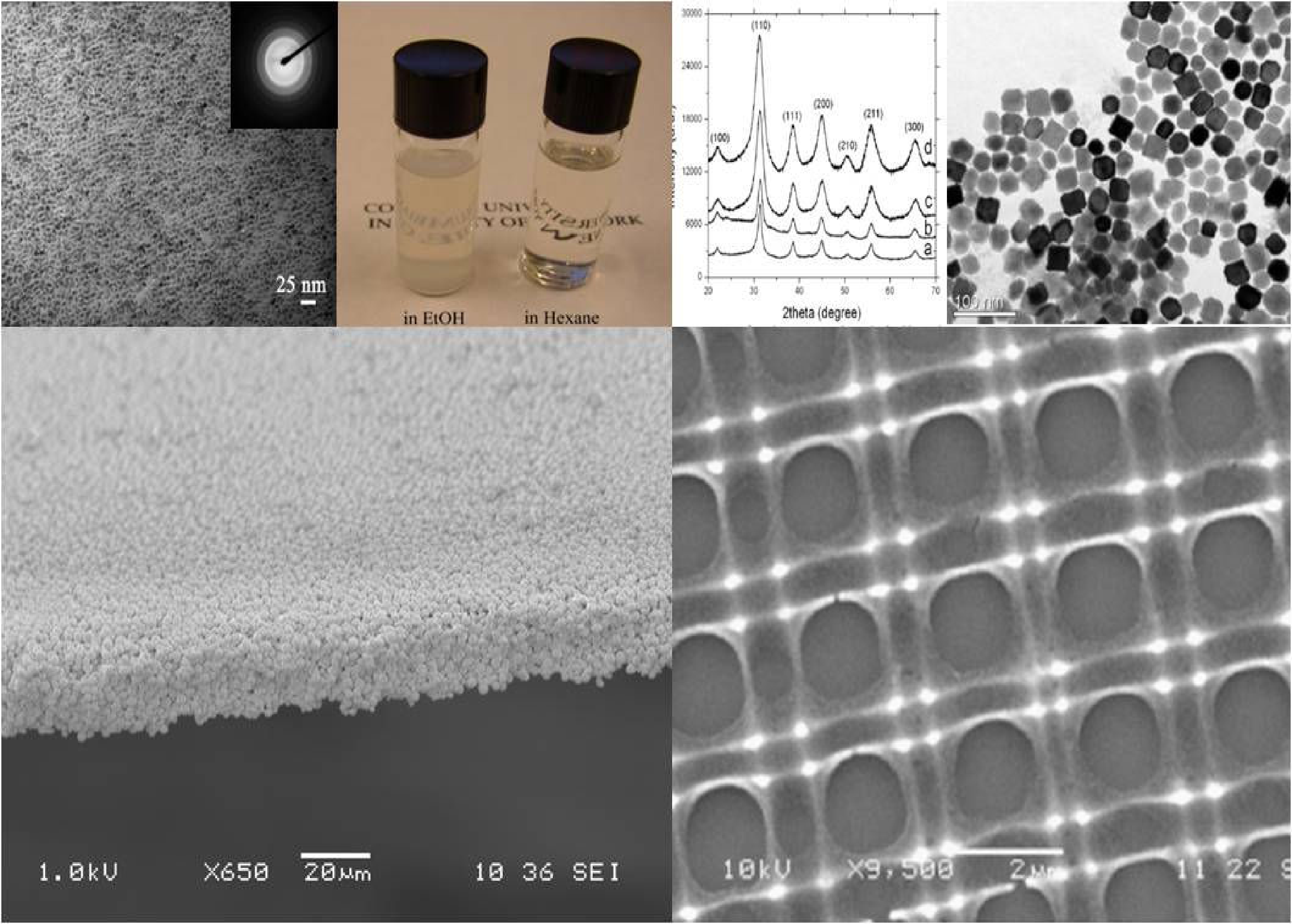
capacitor structure



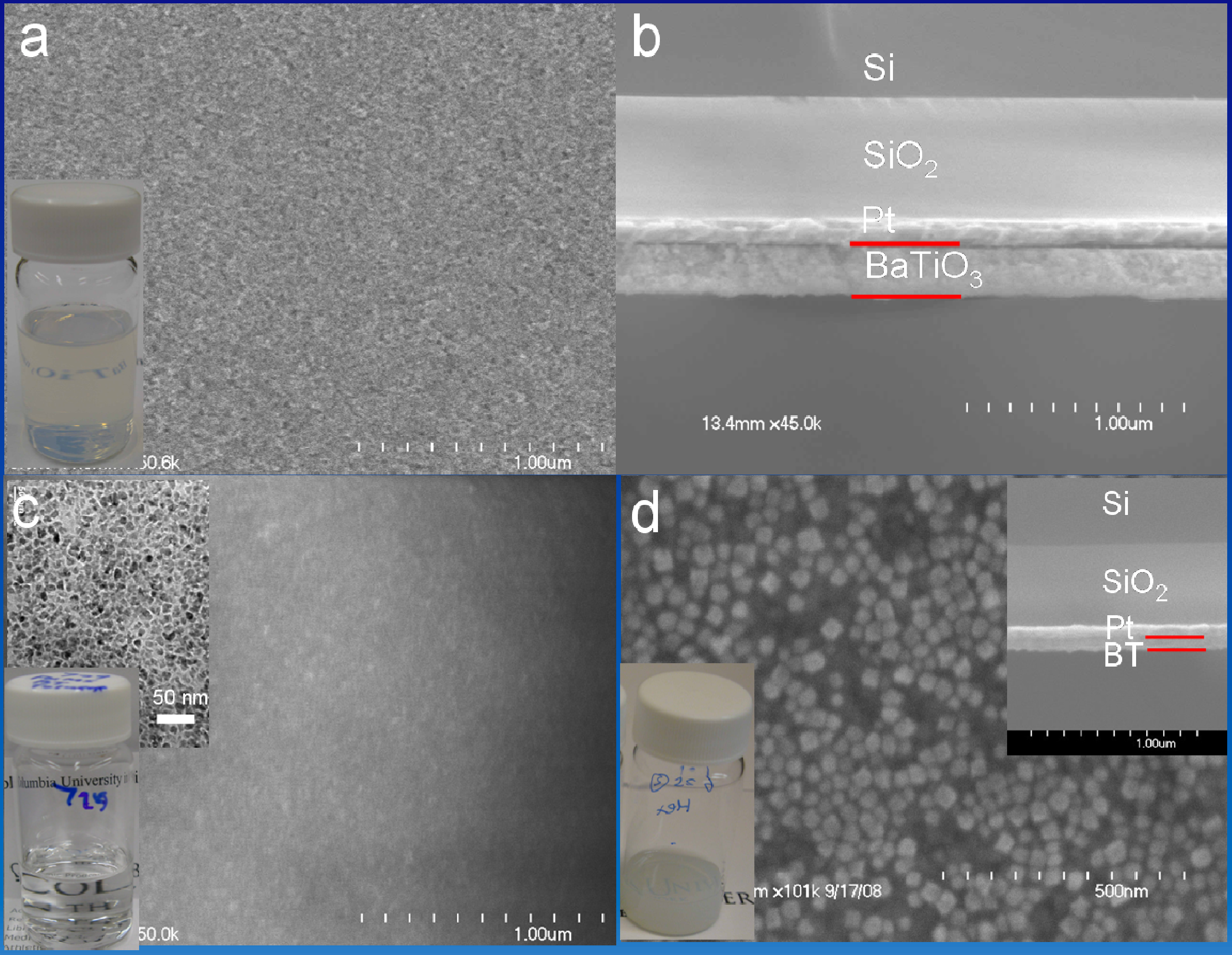
pentacene transistors



Free Standing Films

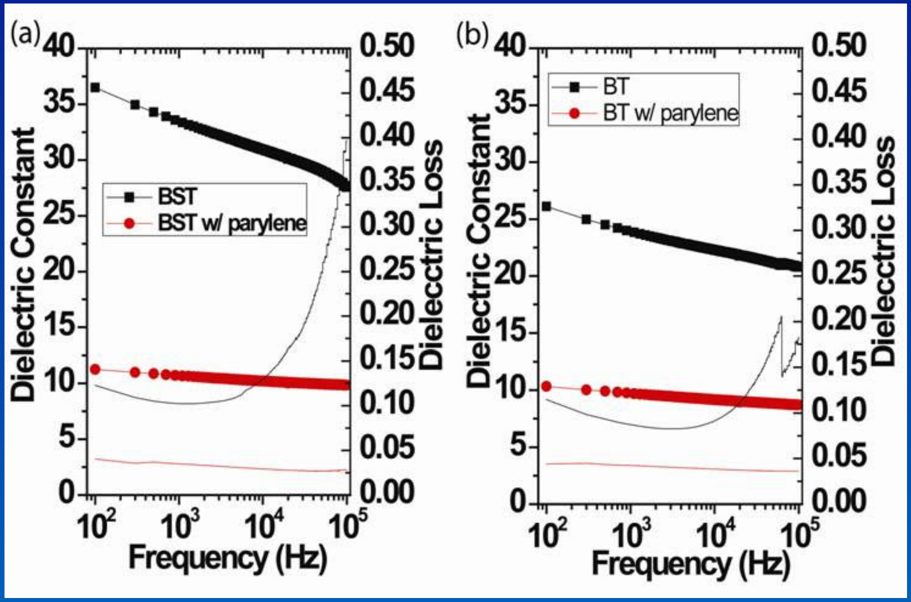


Barium Titanate Nanocrystal Thin Films and Polymer Composite Films

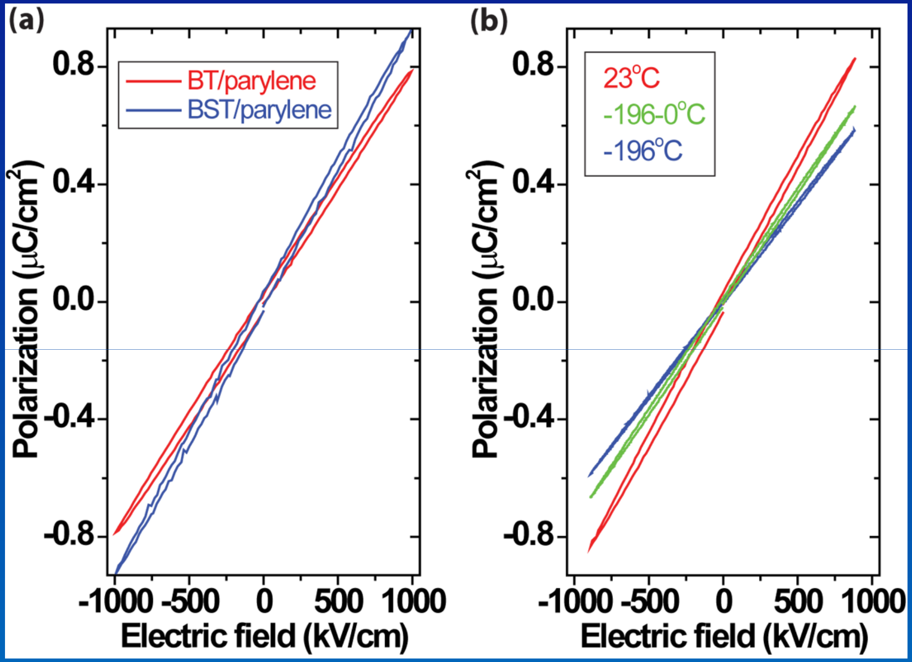


a) SEM images of a $BaTiO_3$ nanocrystal thin film (8nm), top view. (inset) a photo image of a homogeneous ethanol suspension of $BaTiO_3$ nanocrystals (~20 mg/ml); (b) cross-sectional view of the film; (c) SEM image of poly(alpha-methylstyrene)/$BaTiO_3$ nanocomposite thin film, top view. (inset) a photo image of a transparent poly(a-methyl styrene)/$BaTiO_3$ nanocomposite solution (~ 20 mg/ml, 8 nm, weight ratio of polymer/$BaTiO_3$ = 1), and a TEM image of the uniform polymer/$BaTiO_3$ nanocomposite; (d) SEM image of poly(alpha-methylstyrene)/$BaTiO_3$ nanocomposite thin film, top view. (inset) a cross-section view of the uniform polymer/$BaTiO_3$ nanocomposite thin film and a photo image of a semitransparent $BaTiO_3$ nanocrystal solution (~ 20 mg/ml, 25 nm).

BT and BST Thin Film Capacitors



Thin film sample	*Crystal size (nm)*	*Dielectric constant (measured at 100kHz)*
$BaTiO_3$	8-12	22-25
$BaTiO_3$/parylene	25-30	34
$Ba_{0.7}Sr_{0.3}TiO_3$	8-12	10
$Ba_{0.7}Sr_{0.3}TiO_3$/parylene	25-30	13
	8-12	27
	25-30	47
	8-12	12
	25-30	16

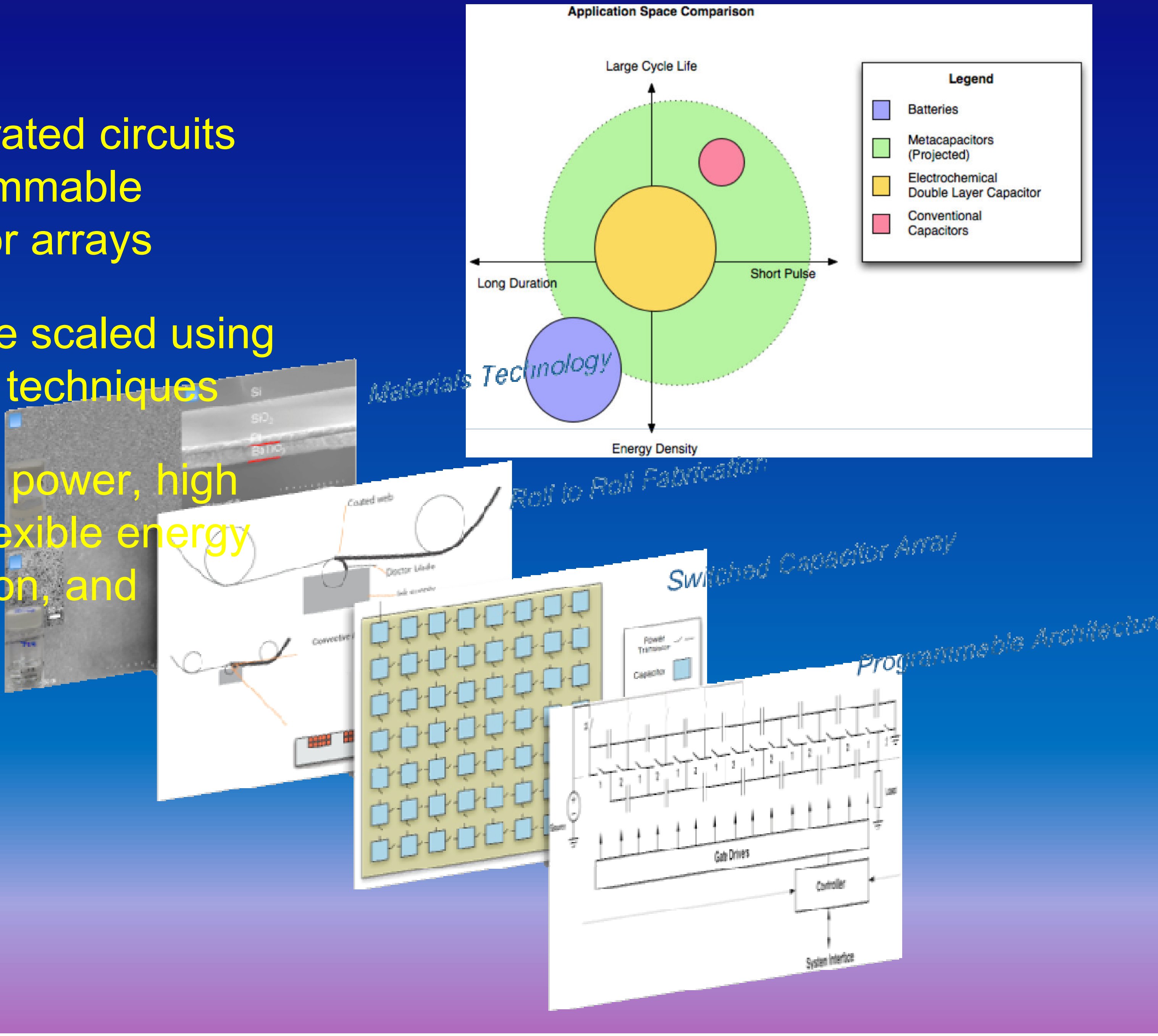


Ferroelectric measurements of assembled nanocrystal thin films of BT and BST in Sawyer Tower configuration under conditions of (a) demoisturized films with an evaporated film of parylene, dried at 60 °C (b) RT and immersed in liquid N_2 for the BT/parylene thin film.

1. Huang, L.; Zhang, J.; Kymissis, I.; O'Brien, S. "High K thin films built from uniform Barium Titanate Nanocrystals in the Superparaelectric Limit" *Adv. Func. Mater.* **2010,** 20**,** 554-560.

Concept: Metacapacitors™

- Goals:
- In-structure integrated circuits can make programmable switched capacitor arrays
- Processing can be scaled using roll-to-roll coating techniques
- long lifetime, high power, high energy density, flexible energy storage, conversion, and conditioning



Switched Capacitor Design

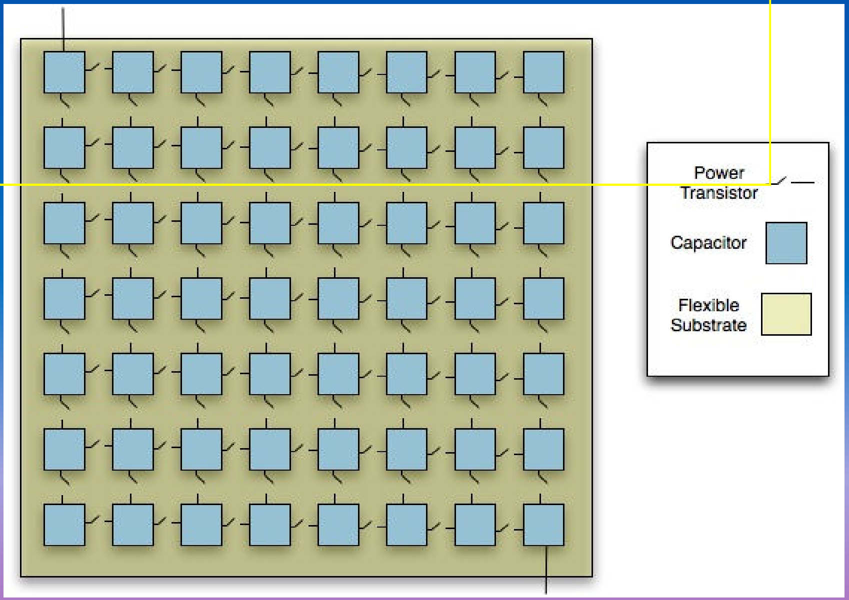
Magnetic-based power converters are currently the common solution for higher power applications (1W and above)

The use of switched-capacitor (SC) DC/DC conversion circuits (a.k.a. charge pumps) has been limited to very low power levels.

For practical switching frequencies, the power levels of SC designs can only be increased by using larger capacitors.

SC designs have a number of important advantages as long as cheap and dense capacitors are available and they can outperform magnetic-based converters for medium to high conversion ratios.

Project to make switched-capacitor DC/DC converter amenable to address a wide range of new applications in power conversion.



Novel Power Conversion Circuit Topologies

The circuit architectures to be exploited in the Metacapacitor program rely on switched capacitor dc-dc and multi-level inverter conversion topologies. Switched capacitor dc-dc converter topologies have been the poor step-sister technology to the industry dominating magnetic-based power conversion topologies due to many factors. Some of these pertain to sunken investments and mature design strategies built on standardized designs for key components: switch technologies (eg. Si MOSFET and IGBTs); ferrite, powdered-metal, and laminated metal magnetic cores;_and CMOS based analog and digital PWM controllers.

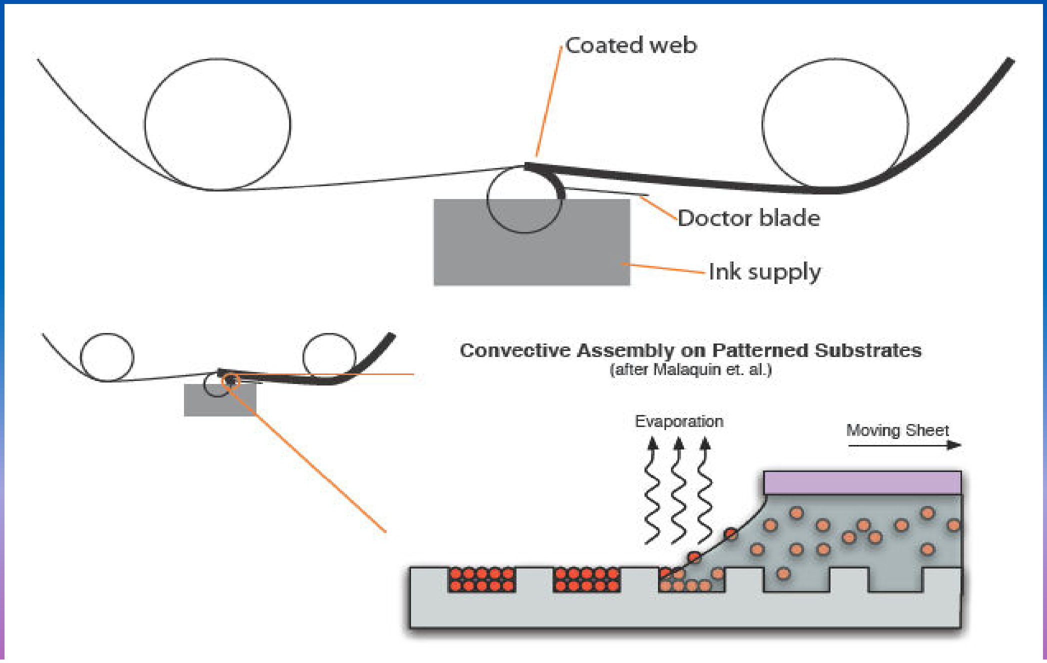
However***, the all capacitor approach is especially effective due to the higher energy density of many capacitor technologies in comparison to compact magnetic devices. Given the exceptional energy densities of the capacitors being developed in this Metacapacitor program, the advantage of the all capacitor topologies is further accentuated.***

Application example: PV inverter topology - single PV panel (eg. ~30 Vdc @ 200 W) with a local stabilizing Metacapacitor (20-100 mF for 120 Hz ripple filtering) and a power MOSFET H-bridge to form a single submodule.

Printed/Spin Coated Thin Film Capacitors

The key requirement in the formation of the BST nanoparticle based capacitors is the consolidation of the nanoparticles into dense interconnected structures upon deposition onto a flexible conductively coated substrate. Requirements emerge from this approach:

(i) that the particle form dense monolayer clusters;
(ii) that multilayers can be deposited with appropriate registry
(iii) that the coating approach provides appropriate lateral position control
(iv) the process must be scalable, materials agnostic, and economically viable. Gravure and rotogravure printing of nano-colloid inks is a process that satisfies these requirements and provides a direct path to process scalability and lost cost.
(v) Preparation of Multilayer Capacitors is possible



Collaboration and Acknowledgements

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Brian Tull
(Columbia)
Lev Sviridov
(Energy Institute)

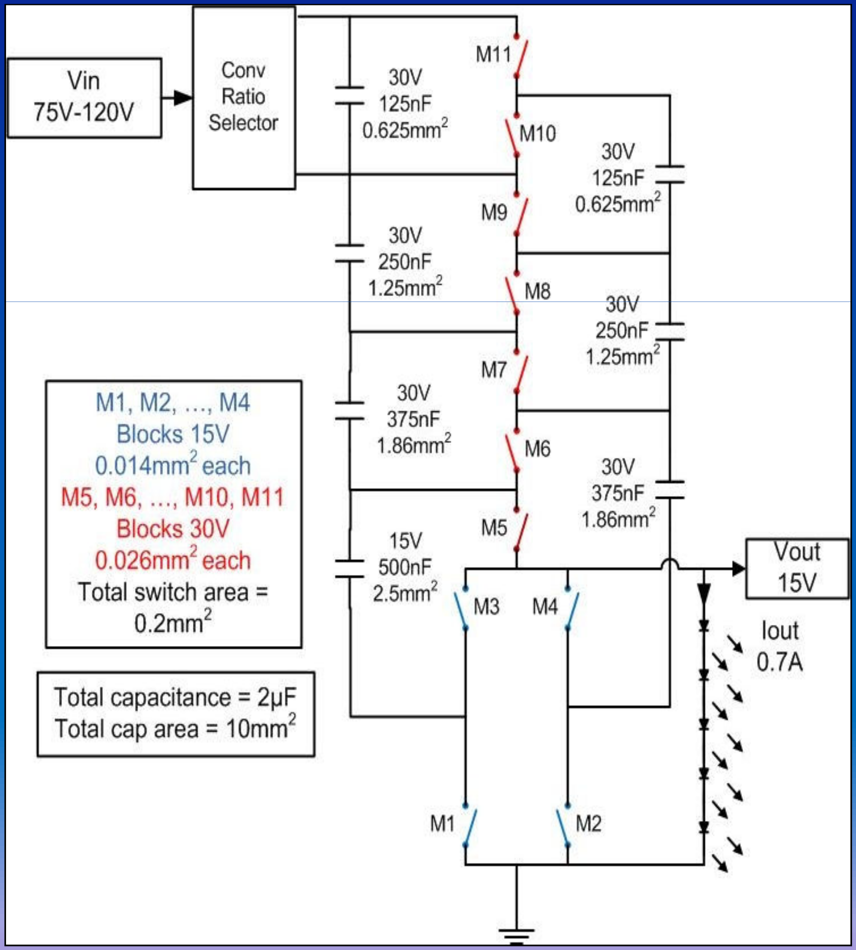
Novel Power Conversion Circuit Topologies

2. LED Driver Topology (ADEPT)

A Metacapacitor solid-state LED driver topology is illustrated in Figure 8. Possible target applications are single-unit screw-in Edison replacement lamp devices rated at about 15 W, as well as higher power commercial lighting fixtures.

A bulk storage capacitor in the range of 25-100 uF, rated for 200 Vdc, is convenient for the dc bus to handle 120 Hz ripple. The controls and switches can be implemented on a single CMOS IC with devices rated for handling voltages indicated, and junction isolation to provide for the overall voltage stand-offs to the substrate.

The switched capacitor approach enables graceful low power operation by simply reducing clock rate, thus enabling a wide range of dimming without sacrificing efficiency.

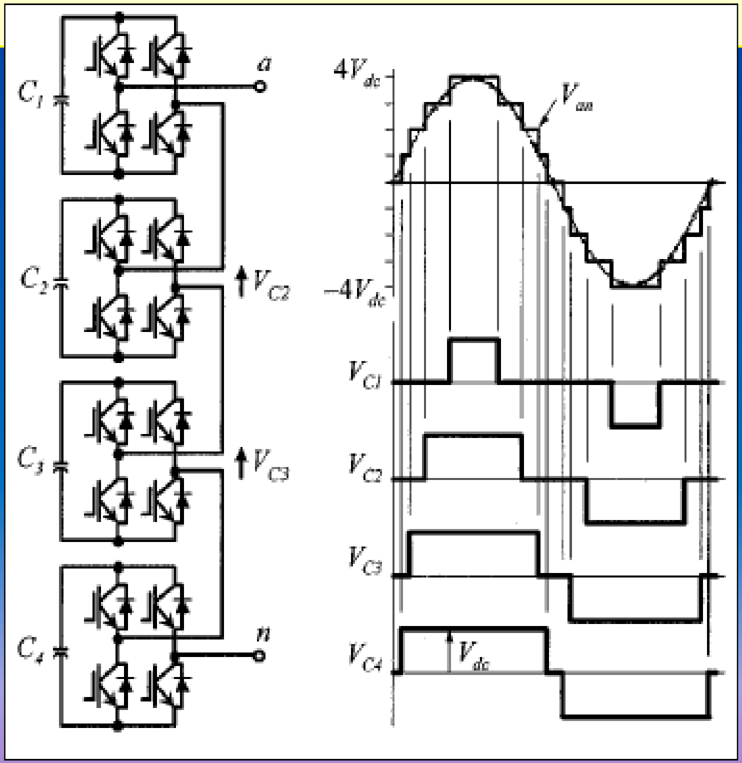


Novel Power Conversion Circuit Topologies

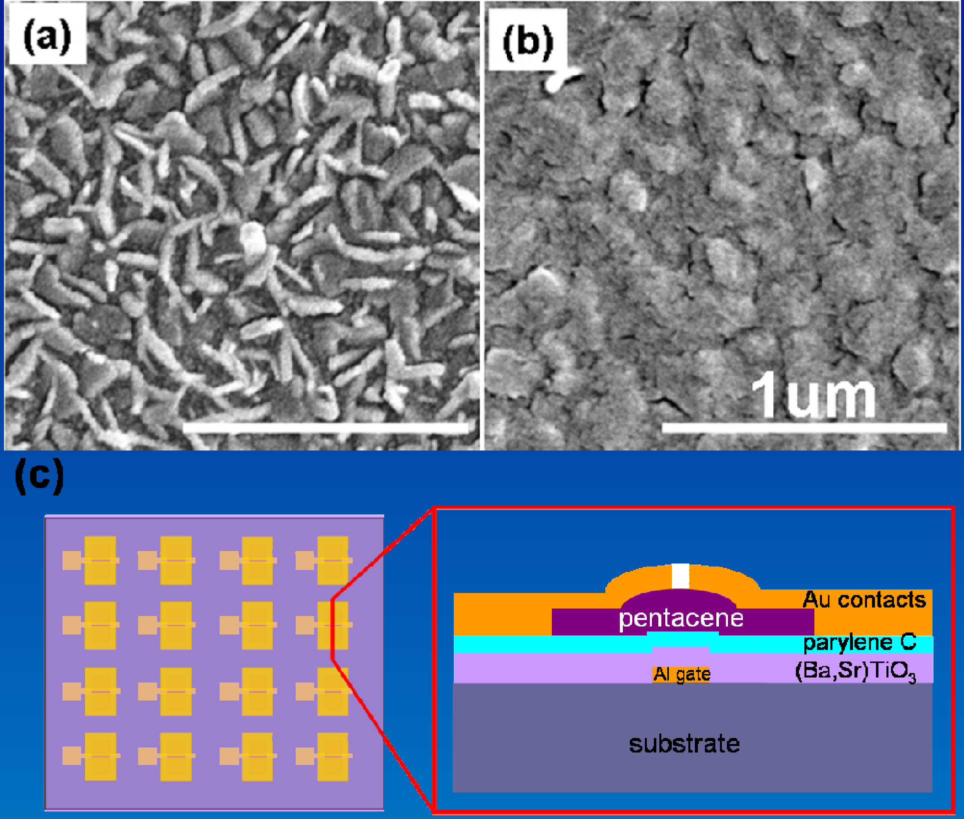
1. PV Inverter (Not Part of ADEPT Scope)

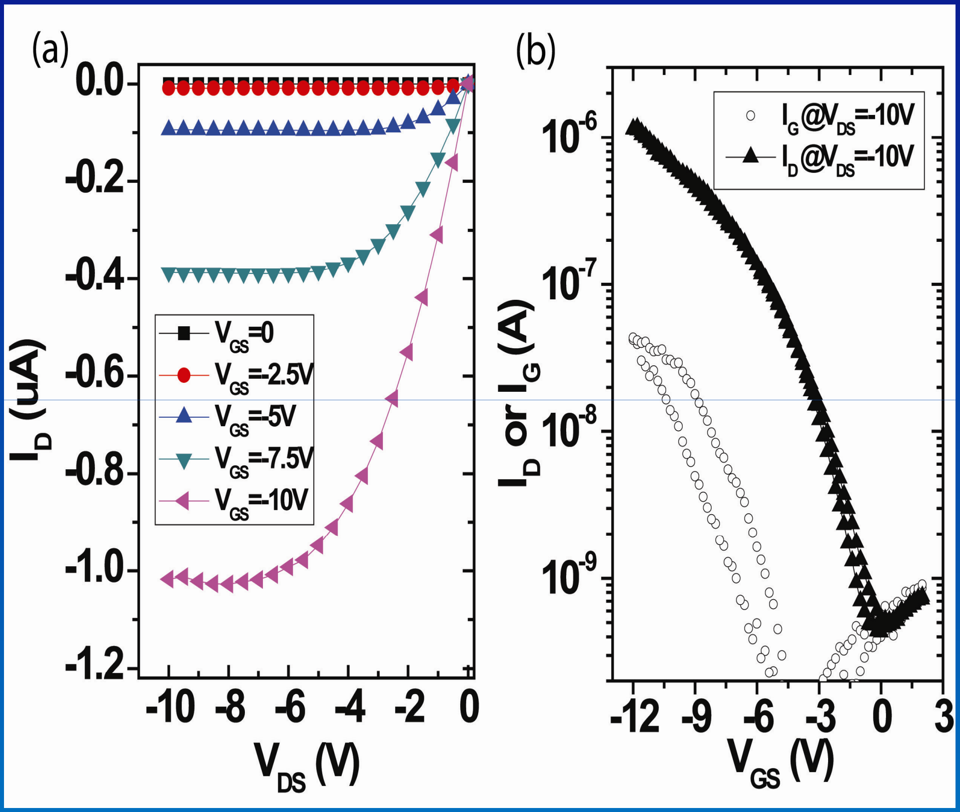
PV inverter topology is conceptually illustrated merges a single PV panel (eg. ~30 Vdc @ 200 W) with a local stabilizing Metacapacitor (20-100 mF for 120 Hz ripple filtering) and a power MOSFET H-bridge to form a single submodule. The diagram of only four submodules which enable nine-level modulation at the inverter output, a representative rooftop installation rated for 3 kW might be comprised of 15 submodules. An array of 15 such submodules would allow a peak output voltage capability of roughly 450 Vdc, making an interface with a 220 Vrms line quite convenient.

This proposed architecture provides all the best features required for a highly reliable distributed PV line interface. These include peak power tracking on a panel by panel basis (i.e. "micro-inverter" functionality), no use of electrolytic capacitors, no substantial use of magnetic devices, highest possible panel efficiency, very low electromagnetic interference (EMI), fault tolerance and high safety potential.



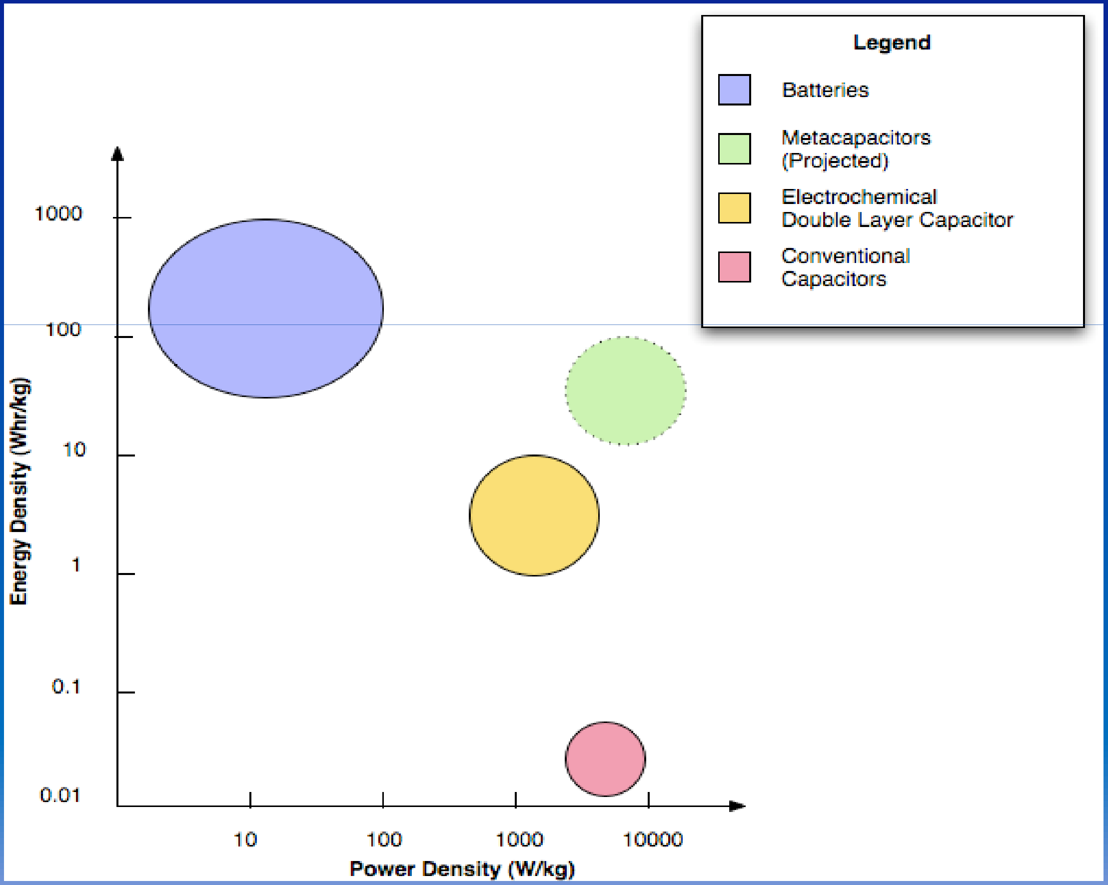
Gate Dielectric: Thin Film TFTs on Flexible Substrates Using Nanocrystal Films of BT/BST (Collaborator Ioannis (John) Kymissis





Transport characteristics of OFETs on flexible PEN substrate, with 200 nm BST and 53 nm parylene C as the gate dielectric (effective dielectric constant is 11.3). (a) is the drain IV curves under different gate biases. The device has an on/off ratio 10^4 and mobility 0.25 $cm^2/(Vs)$ in the saturation region fitted using the data from (b). Leakage characteristics: (9–12 nA/cm^2, measured at 5Vdc for a 1mm^2 area

High k materials - capacitors Innovation in Core Technologies for Power Conversion and Energy Storage



Metacapacitors

City College of New York/Columbia University
Metacapacitors^{TM} , Stephen O'Brien, Dan Steingart, Ioannis Kymissis, Peter Kinget, Alex Couzis

STATUS QUO

Currently there exists a fundamental tradeoff between chemical storage and charge separation

- *Chemical bonds store energy, but kinetically limit pow*
- *Charge separation quick power, but cannot stora temporally or spatially a chemical bonds*

PROPOSED GOAL(S):

Through the combination of a proven, low T materials synthesis and a novel approach to device fabrication, we will make large capacitors with compelling energy density and power density.

	Batteries	Ultracapacitors	Metacapacitors
Programmable	No	No	Yes
Energy Density Range (Wh/kg)	10-500	1-10	1-100
Power Density Range (W/kg)	10-500	1000-8000	1000-20000
Cycle Life	500-3000	> 1,000,000	> 1,000,000
Whr/kg over life	50,000 to 900,000	1,000,000 – 10,000,000	1,000,000 – 100,000,000
Market Saturation?	Mature	Moderate	Nascent

outperforms conventional capacitors while maintaining excellent power density

ASSUMPTIONS AND LIMITATIONS:

- We assume we can create a system with an effective dielectric constant of 50
- We assume we can manufacturing such capacitors in a large scale roll-to-roll process

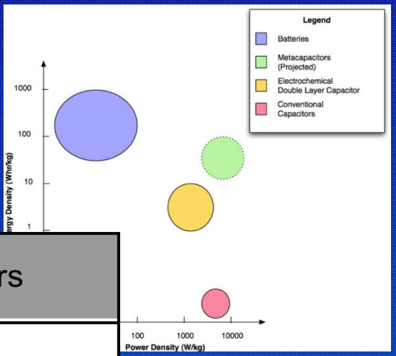
NEW INSIGHTS

Self Assembled Na complex oxide Film dielectric properties by paraelectric effect

Barium Titanate Nanoparticles exhibit excellent dielectric properties

Through low temperature processing such particles can be assembled into devices with exceptional energy density *and* power density

ATIVE IMPACT



als production will be ed to allow for large pacitor production.

apacitors will be printed h a roll-to-roll process

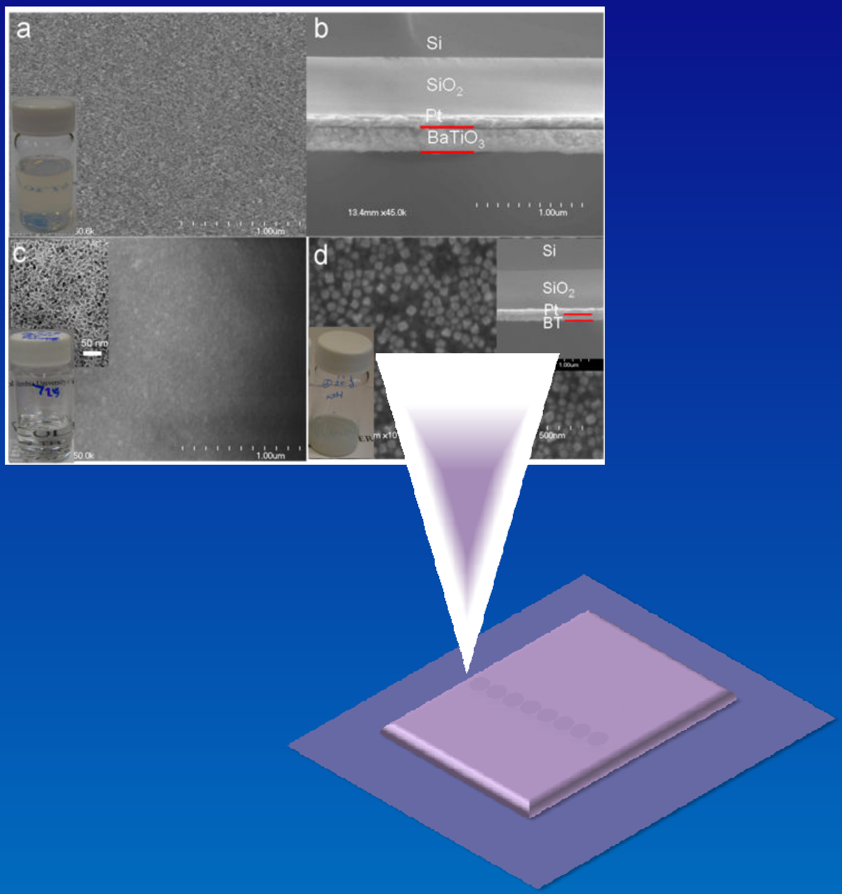
fully functional metacapacitor prototype

END-OF-PHAS

Demonstration of long term charge retention at or above EDLC capacity, with the power density of a capacitor

Metacapacitors^{TM}: Background

- We have a new process for making high *k* dielectric films at room temperature based on solution control processing.
- We have demonstrated high value/low hysteresis capacitors with high voltage tolerance.
- The substrate and device design allows full integrated device manufacture.
- The principal of $E = CV^2$: The energy stored scales with the square of the voltage. We propose a "metacapacitor" – the energy density of a battery or ultracapacitor but the discharge and lifetime of a ceramic capacitor



Homogeneous solvent suspensions of BaTiO3 nanocrystals (inks) are deposited as thin films through evaporative driven self assembly. Alternatively facile incorporation into a range of high k/ low k polymers can generate a series of nanocomposites.