Transforming Urban Landscapes with Responsive Materials

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TEXAS A&M UNIVERSITY

Canadian Light Source
Centre canadien de rayonnement synchrotron

Energy & Buildings

- We are in the midst of one of the greatest migrations in the history of mankind
- >50% of the world's population lives in urban areas
- 300M to move to cities in China alone
- 2B m^2 of new construction each year in China, >80% energy inefficient

What do Buildings Cost?

Buildings account for 72 percent of U.S. electricity use and 36 percent of natural gas use

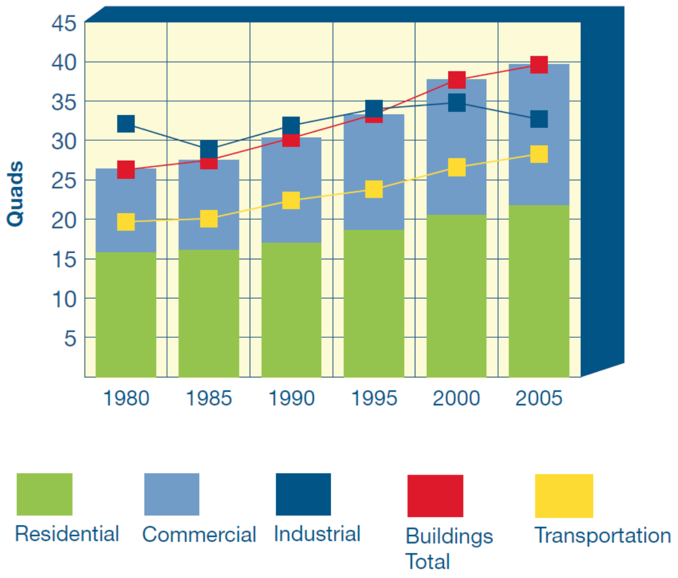


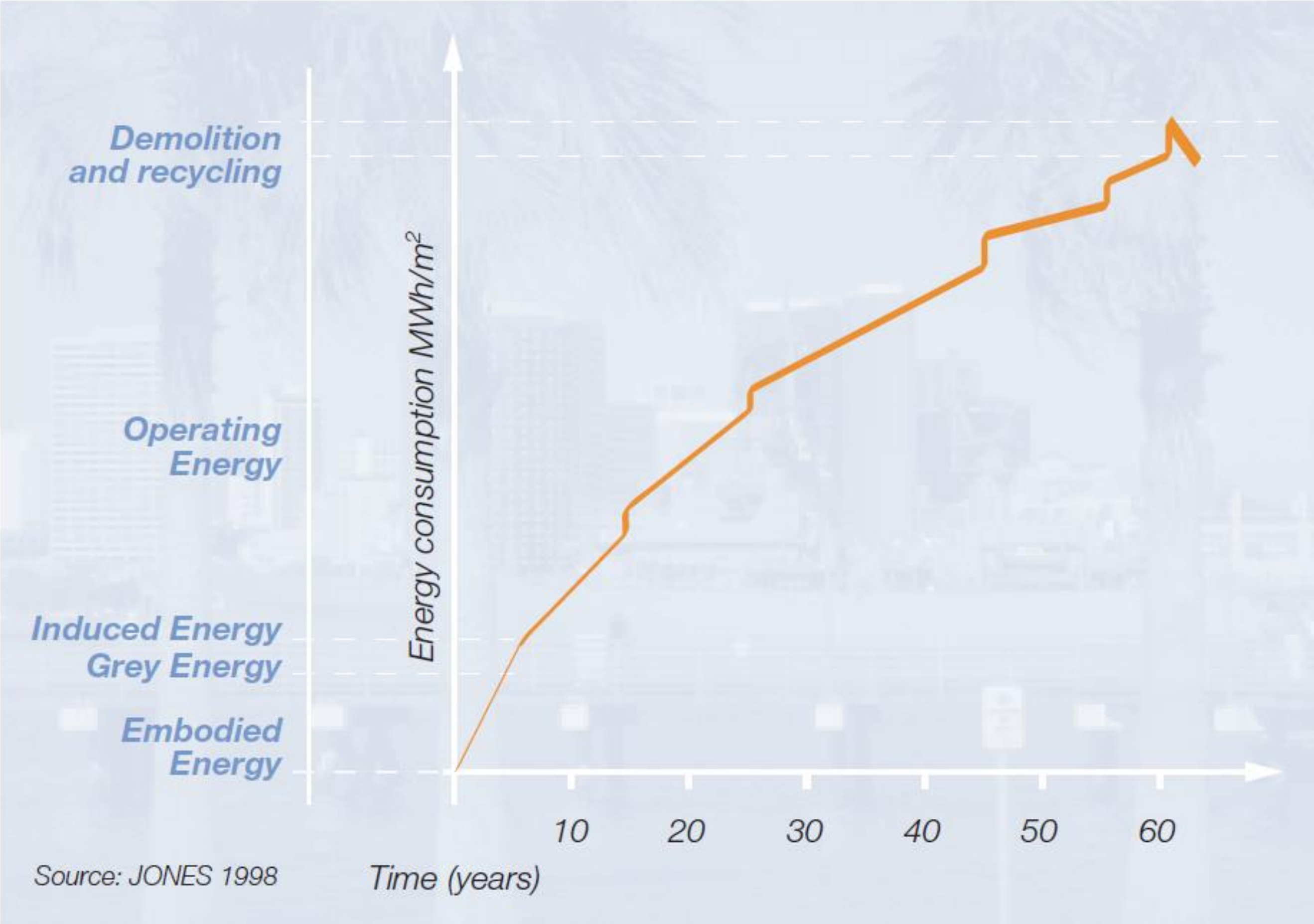
Figure 8
Growth in Buildings Energy Use Relative to Other Sectors

Buildings account for 40 percent of all energy use in the United States. This sector consumes more energy than either industrial or transportation, surpassing industrial as the number one consuming sector in 1998. Both residential and commercial building energy use are growing, and represent an ever-increasing share of U.S. energy consumption. While residential energy consumption exceeds commercial, the latter has been increasing more rapidly, rising from just 14 percent of total U.S. energy consumption in 1980 to 18 percent by 2005, a 70 percent increase.

- 30-40% of energy usage worldwide is from buildings
- Equivalent to 2500 megatons oil equivalent

US Department of Energy, Energy Efficiency Trends in Residential and Commercial Buildings, Washington DC**2008**

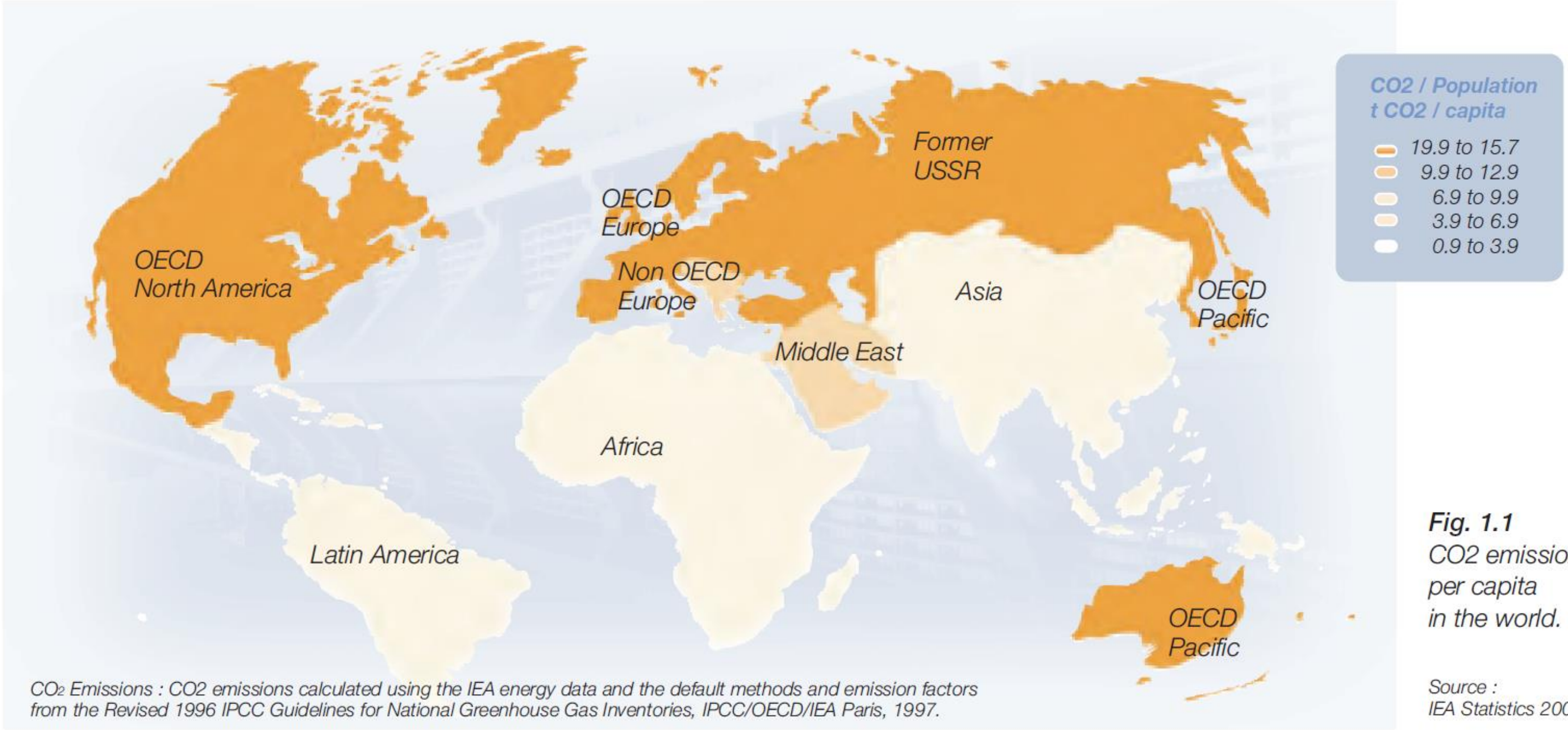
What do Buildings Really Cost?



Source: JONES 1998

- Choices we make now will benefit/haunt us in the decades to come

The Real Costs: CO_2 Emissions



CO_2 Emissions : CO2 emissions calculated using the IEA energy data and the default methods and emission factors from the Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories, IPCC/OECD/IEA Paris, 1997.

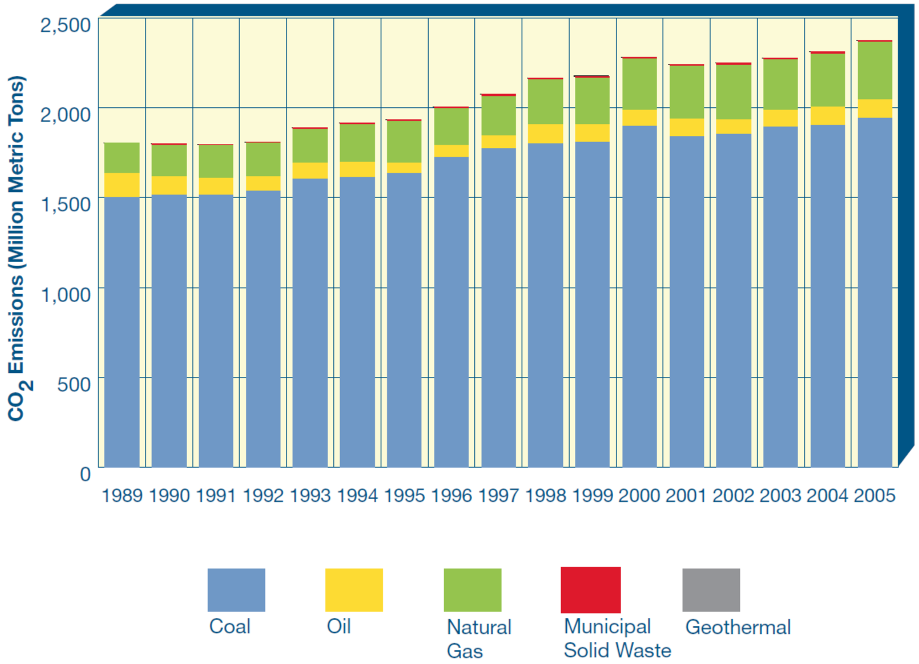
Fig. 1.1
CO2 emissions per capita in the world.

Source :
IEA Statistics 2006

Going up in smoke…

U.S. buildings currently contribute 9 percent of the world's carbon dioxide emissions

Figure 12
Contributors to Electricity CO_2 Emissions



The growth in buildings energy consumption has resulted in carbon dioxide emissions rising from about a third of total U.S. emissions in 1980 to almost 40 percent by 2005. This is a function of the increase in buildings electricity use, 70 percent of which is dependent on fossil fuels. Despite recent efforts to use cleaner coal technologies, the majority of carbon dioxide emissions are still attributable to coal. Both geothermal and municipal solid waste represented negligible amounts of carbon dioxide emissions: 0.4 and 11 million metric tons in 2005, respectively.

US Department of Energy, Energy Efficiency Trends in Residential and Commercial Buildings, Washington DC**2008**

Where does this energy come from? China as a case study

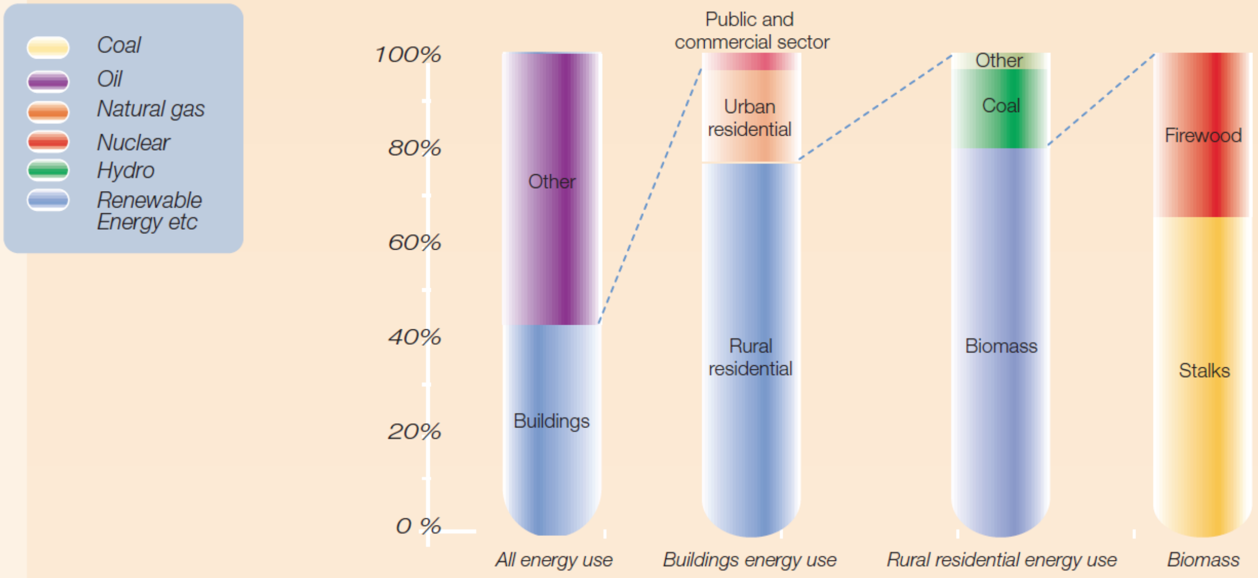


Fig. 2.11
Distribution of Chinese energy use.

Source : Yutaka et al. 2005.

UNEP, Buildings and Climate Change: Status, Challenges, and Opportunities **2007**

Where does the Energy Go?

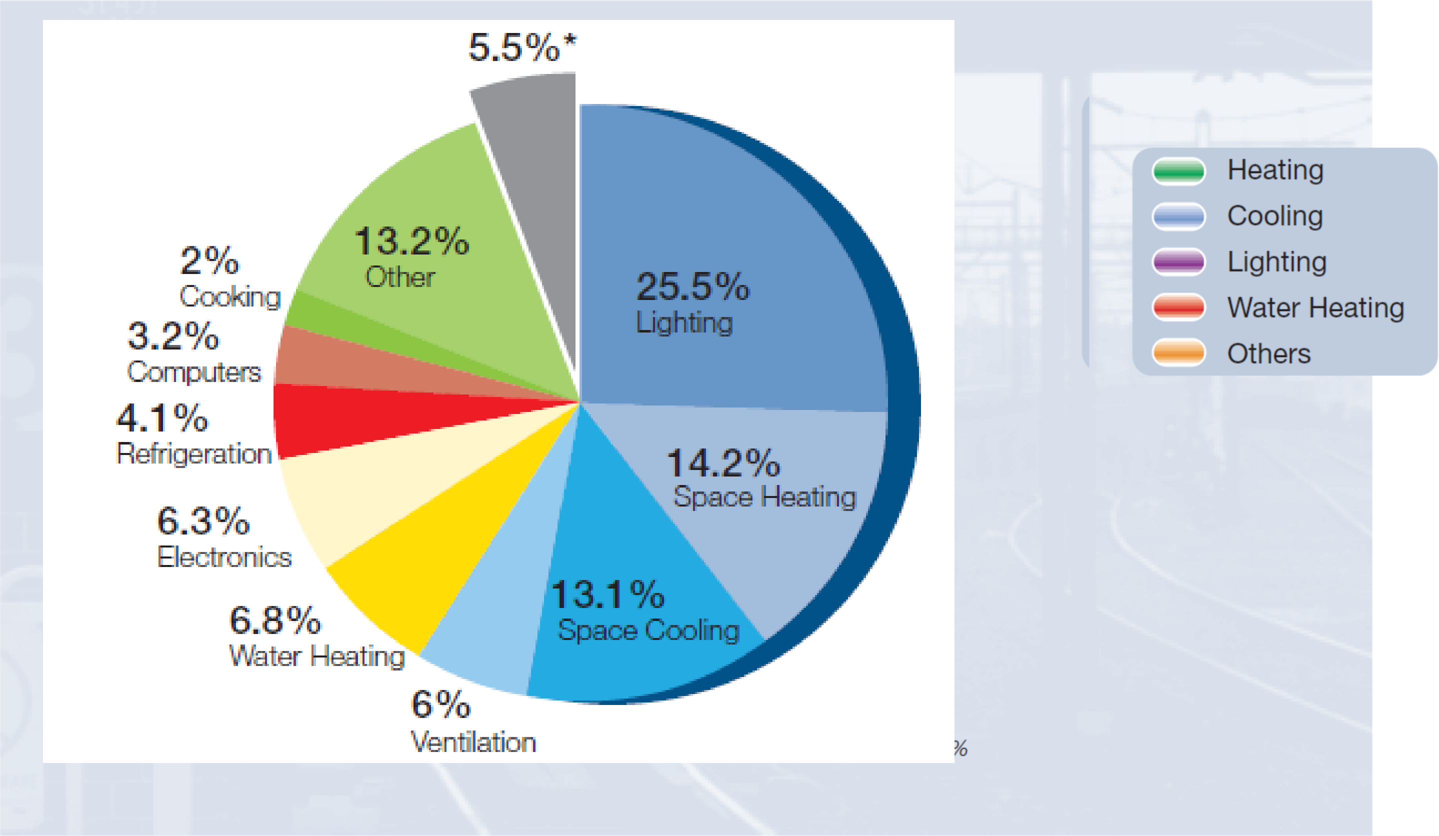


Fig. 2.14
Shares of different energy end-use purposes for residential and commercial buildings in some countries.

Source : Al-Sayed Omar Assem and Al-Ragom 2005, CMIE 2001, Sustainable Energy Authority Victoria 2004, U.S. Department of Energy 2006, Office of Energy Efficiency; Natural Resources Canada 2006.

©NYTimes

- 40% of energy consumed in Mumbai, India goes toward space cooling
- China added 50M home air-conditioning units in 2010
- By 2050, 27% of all global warming will be due to coolant gases

A Deeper Dive…

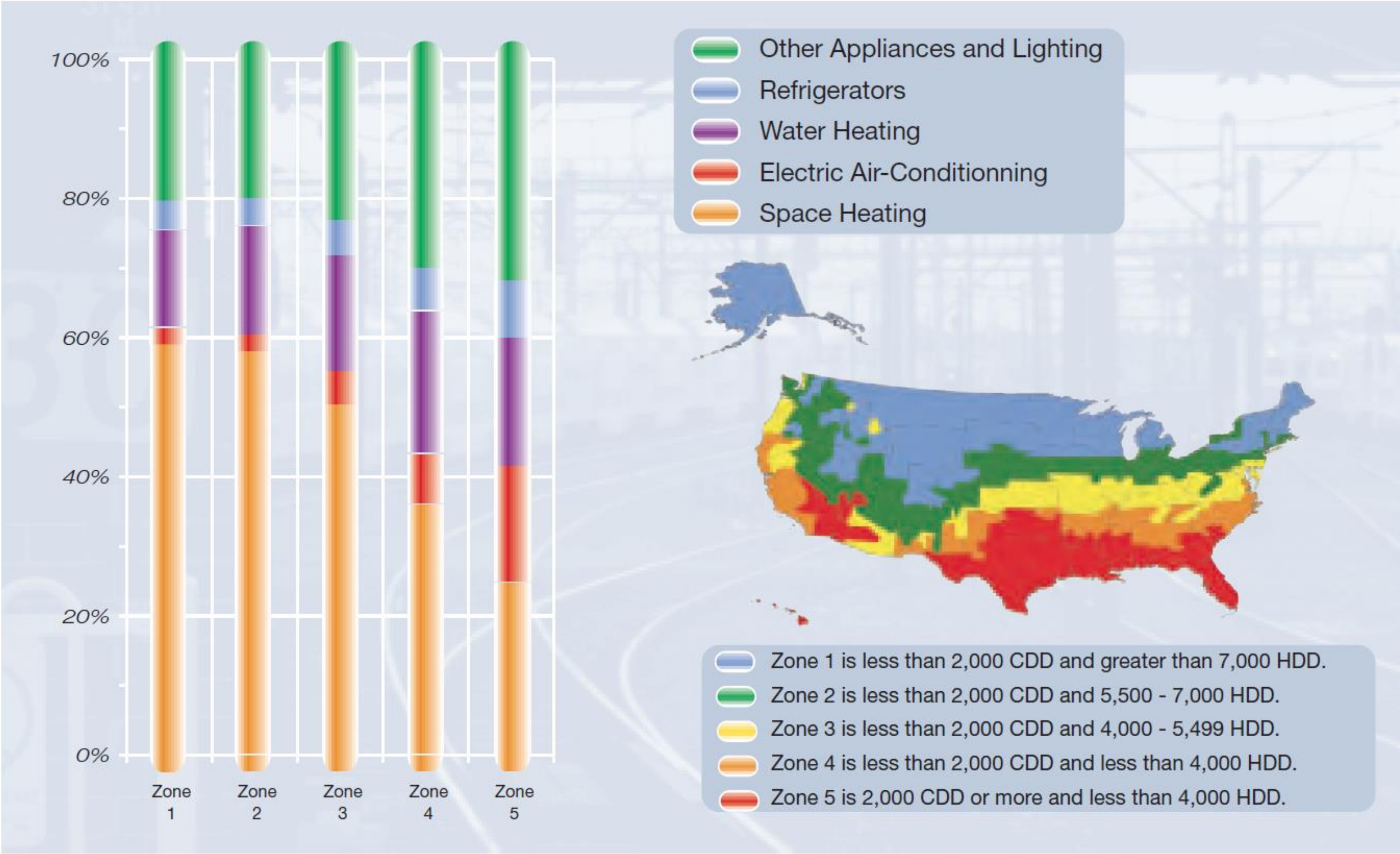
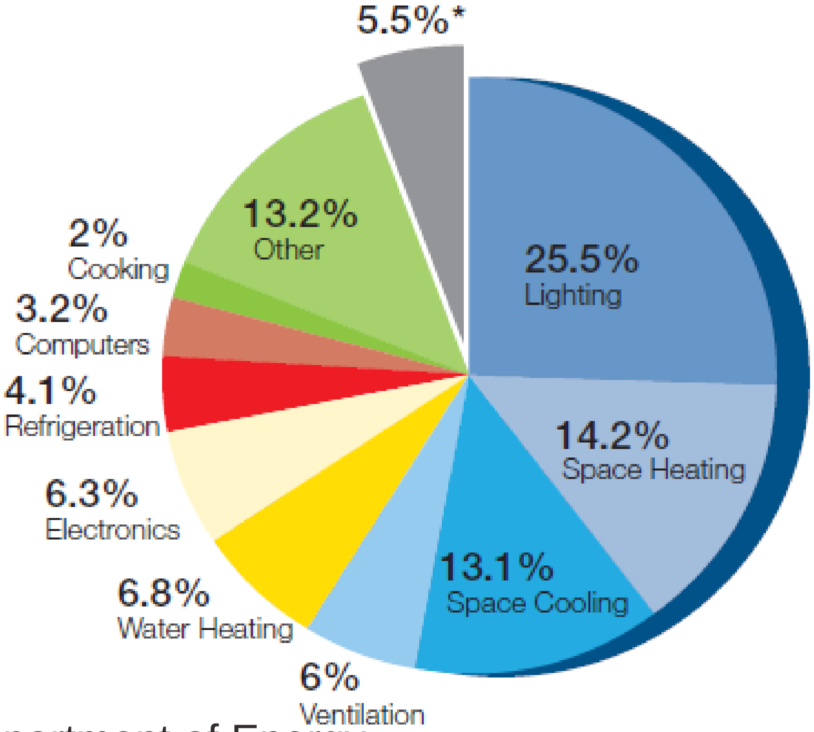


Fig. 2.15
Energy consumption in US residential buildings.

Source : US EIA 2001

The price we pay for our buildings

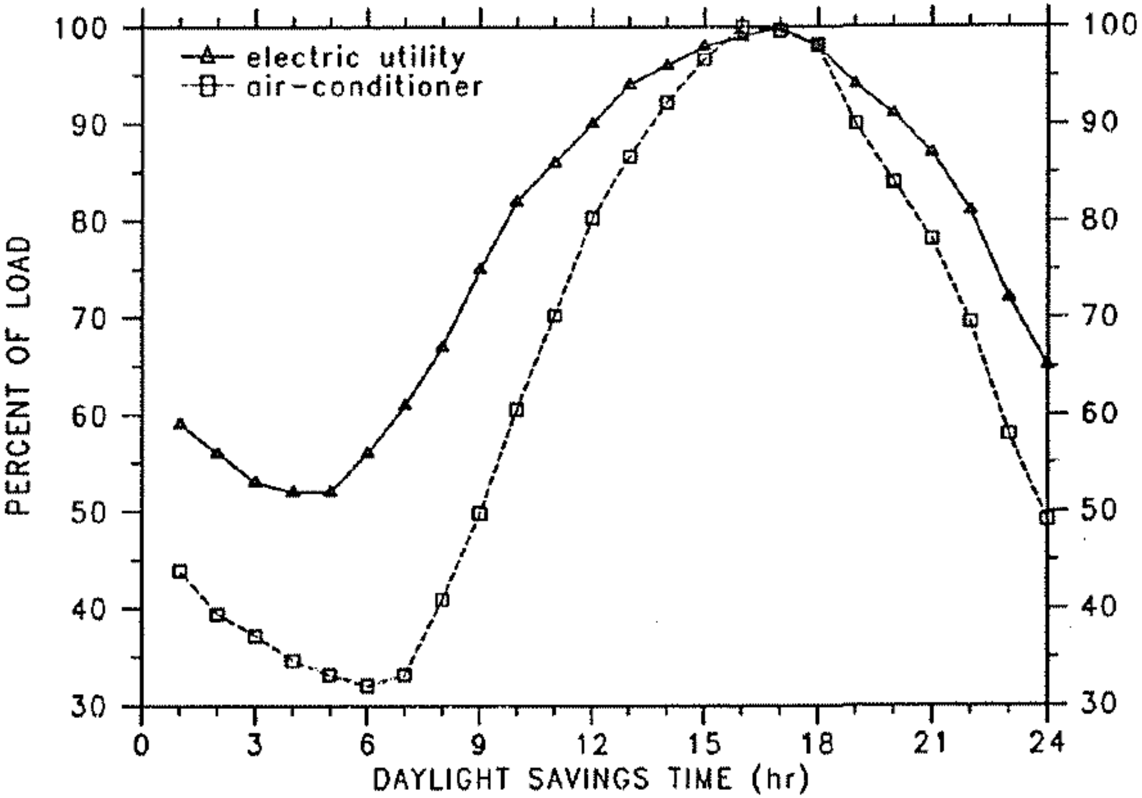


Department of Energy

- ☐ **$15B**
- ☐ **140M metric tons of CO$_2$**

US Department of Energy, Energy Efficiency Trends in Residential and Commercial Buildings, Washington DC**2008**

We live in the grid…



Average peak-summer-day load shape for Florida electric utility and average load shape of 58 residential central air conditioners.

A. F. Rudd, ASHRAE Trans. Research 1997

Conditioned Environments

- 7 Billion Gallons of Gasoline
- 50 Million Metric Tons of CO_2
- Refrigerant Leakage Equivalent to 50 Million Tons of CO_2

The Building Envelope

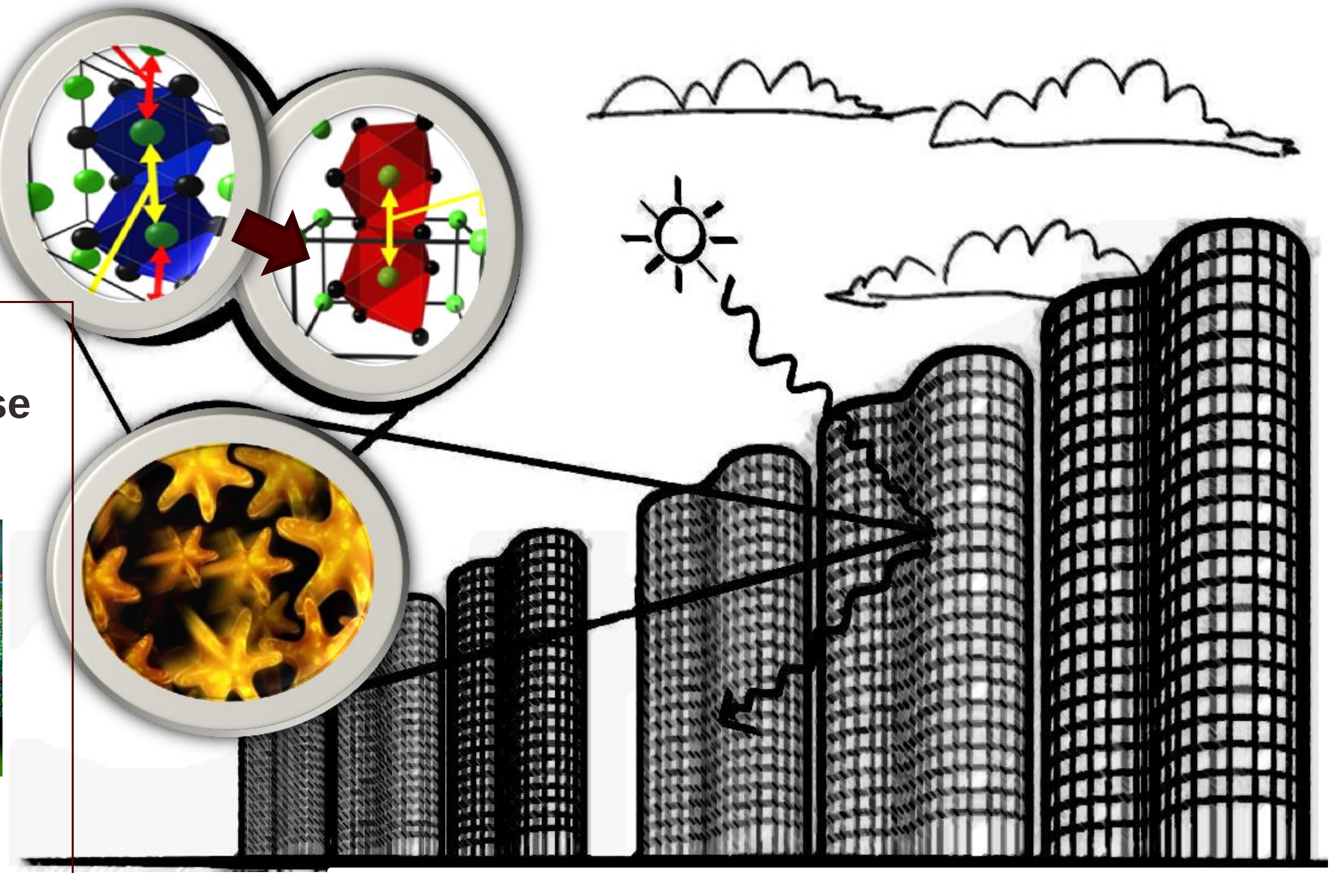
The “building envelope” refers to the external walls, windows, roof, and floor of a building. This barrier between indoors and outdoors is important with regards to ventilation and insulation of a conditioned space.

What does this have to do with physics?

Buildings that change with the climate…

-adaptable to specific climates and to night/day, summer/winter

- Physics and chemistry of phase transformations

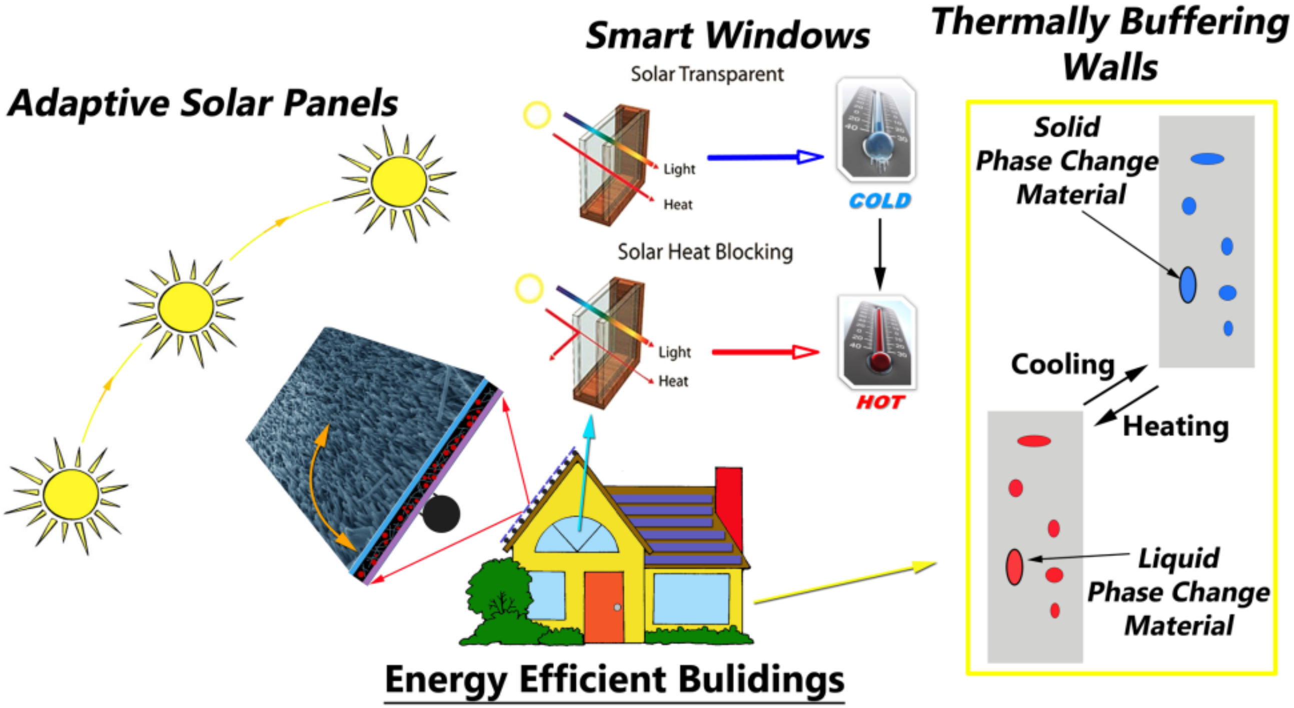


Zero emission buildings that sense and respond to the climate

Can we endow our windows and walls with intelligence?

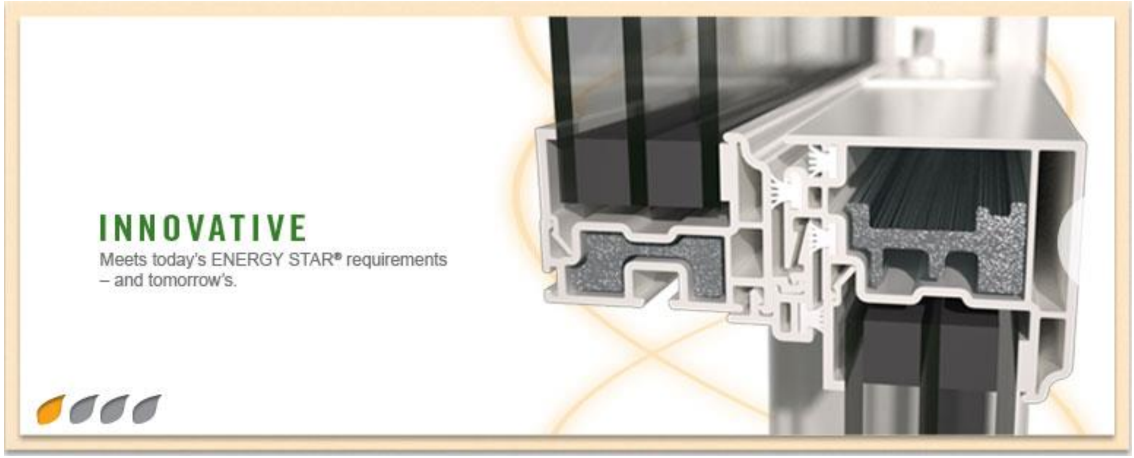
Smart Windows" seen at light and dark settings. | Photo Courtesy of SAGE Electrochromics, Inc., by Susan Fleck Photography

Buildings of the Future: Living and Breathing Constructs

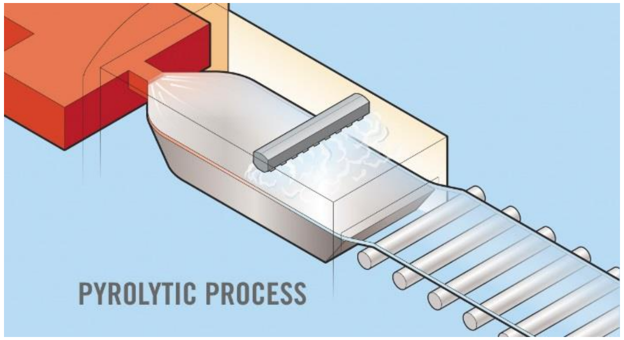


-Local energy conservation
-Distributed energy storage

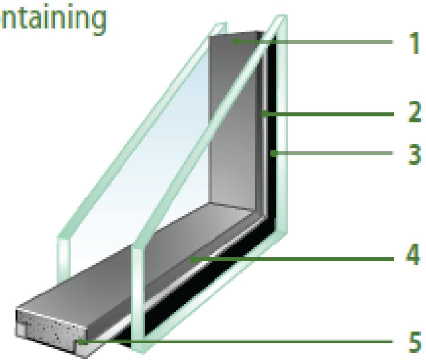
What’s Inside your Windows?

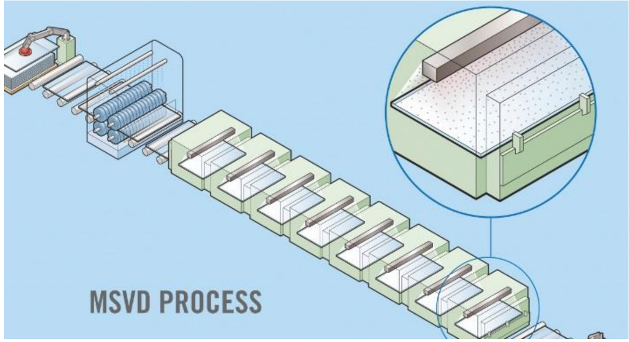


Low-E Glass



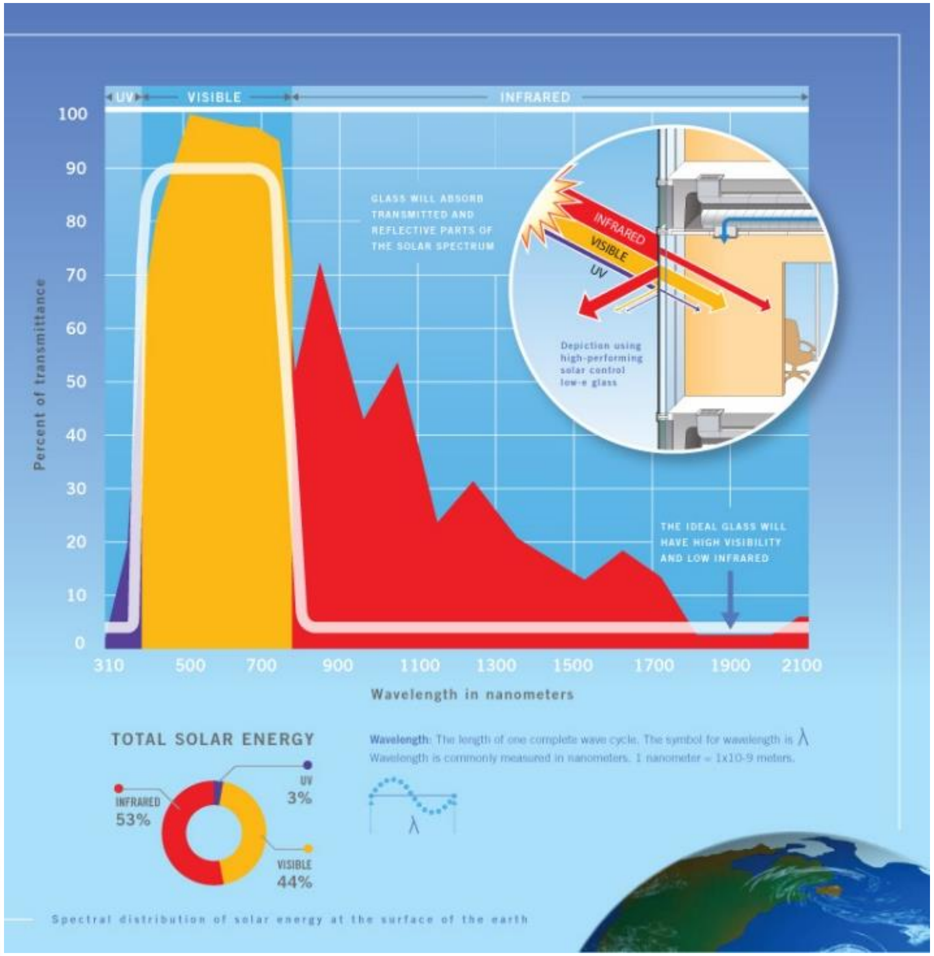
1. Thermoset structural silicone foam containing NO-Metal with integral 3A desiccant
2. PIB primary seal
3. Silicone, Polyurethane, Polysulfide, DSE/DSA's or Hot Melt secondary seal
4. Pressure-sensitive acrylic adhesive
5. Pre-applied advanced multi-layer vapor barrier





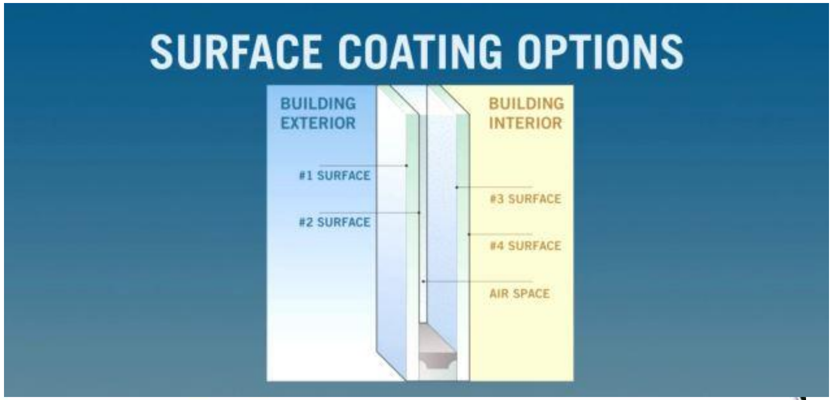
A lot of physics and chemistry!

State-of-the Art: Low-E-Glass



Wavelength: The length of one complete wave cycle. The symbol for wavelength is λ Wavelength is commonly measured in nanometers. 1 nanometer = 1x10-9 meters.

Spectral distribution of solar energy at the surface of the earth



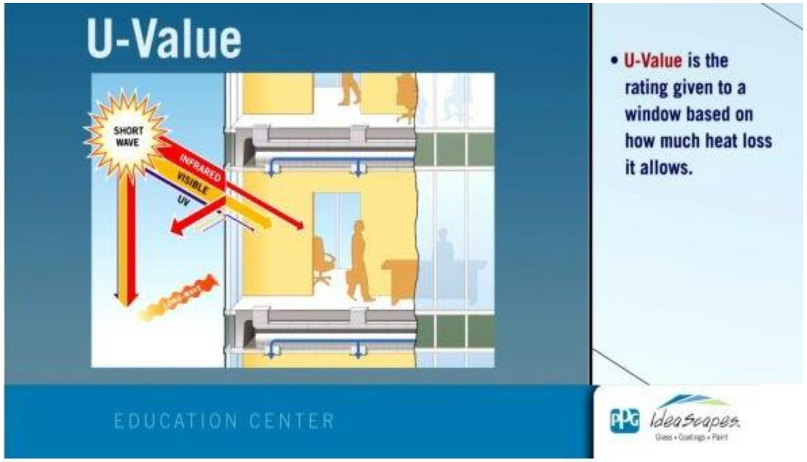
SURFACE COATING OPTIONS

MICROSCOPIC COATINGS

Effective at Reflecting Long-Wavelength IR: “Thermos” Principle

Static · Silver! · High-Vacuum Processing

Measuring up a Window



U-Value

- **U-Value** is the rating given to a window based on how much heat loss it allows.

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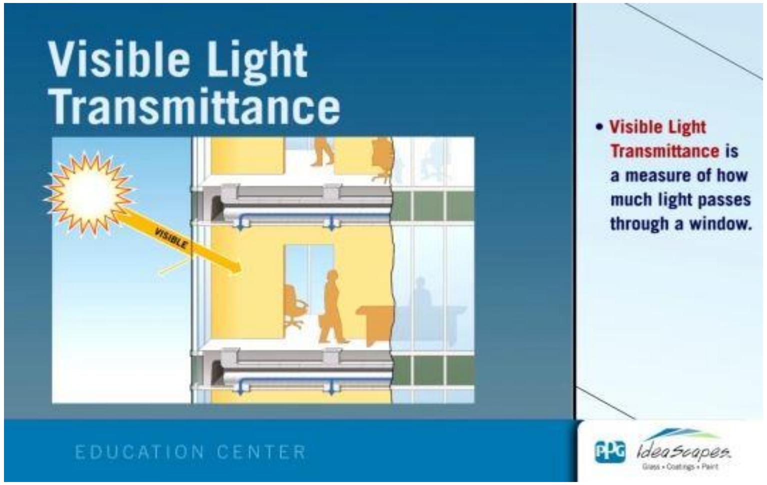

Visible Light Transmittance

- **Visible Light Transmittance** is a measure of how much light passes through a window.

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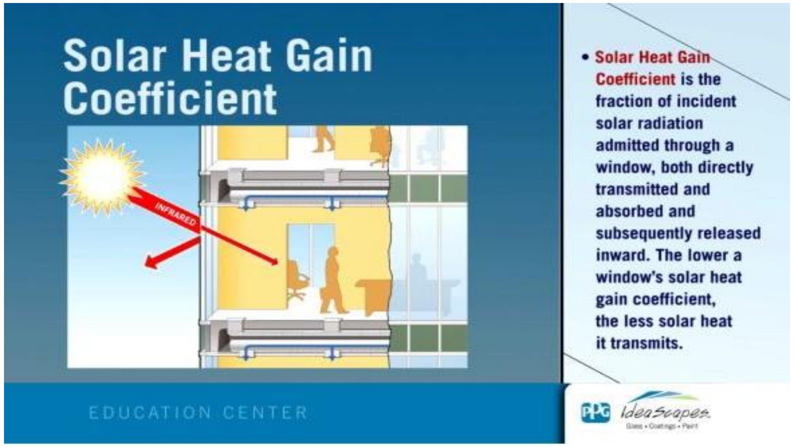

Solar Heat Gain Coefficient

- **Solar Heat Gain Coefficient** is the fraction of incident solar radiation admitted through a window, both directly transmitted and absorbed and subsequently released inward. The lower a window's solar heat gain coefficient, the less solar heat it transmits.

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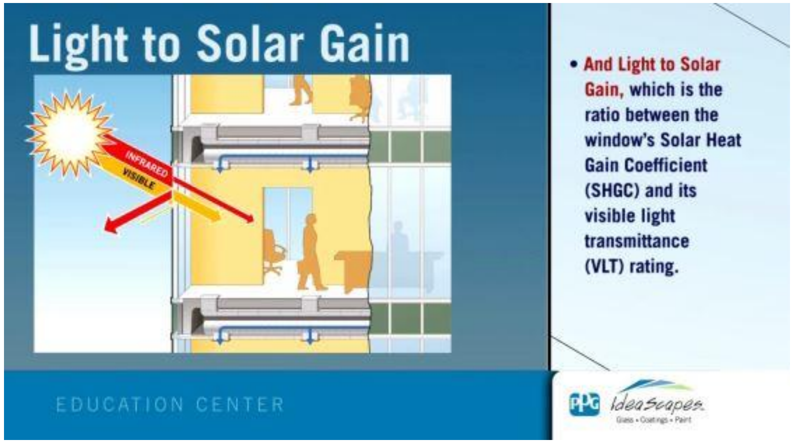

Light to Solar Gain

- **And Light to Solar Gain**, which is the ratio between the window's Solar Heat Gain Coefficient (SHGC) and its visible light transmittance (VLT) rating.

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Graphics courtesy of PPG

Light *versus* Heat

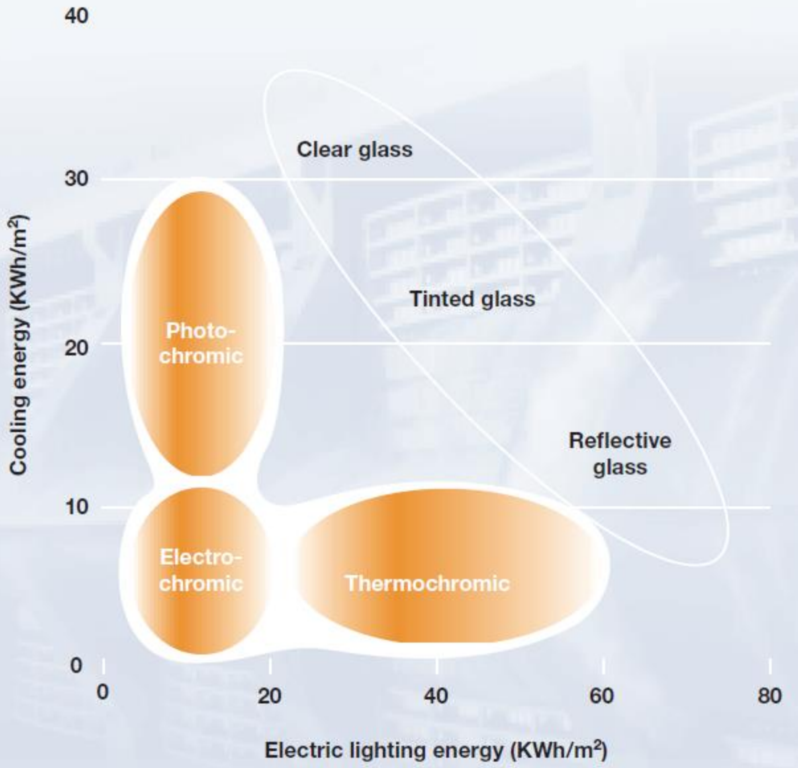


Figure 3.2
Lighting energy versus cooling energy for different glazing types.

UNEP, Buildings and Climate Change: Status, Challenges, and Opportunities **2007**

Adaptive Materials

Respond in a reversible manner to changes in temperature, humidity, or light

-accompanying changes in optical, electronic, or thermal properties allow for modulation of energy consumption within a building

Materials development
Building integration
Efficiency and RoI metrics
Durability
Aesthetic acceptability

Image from Nippon Oil

Responsive Materials for Smart Windows

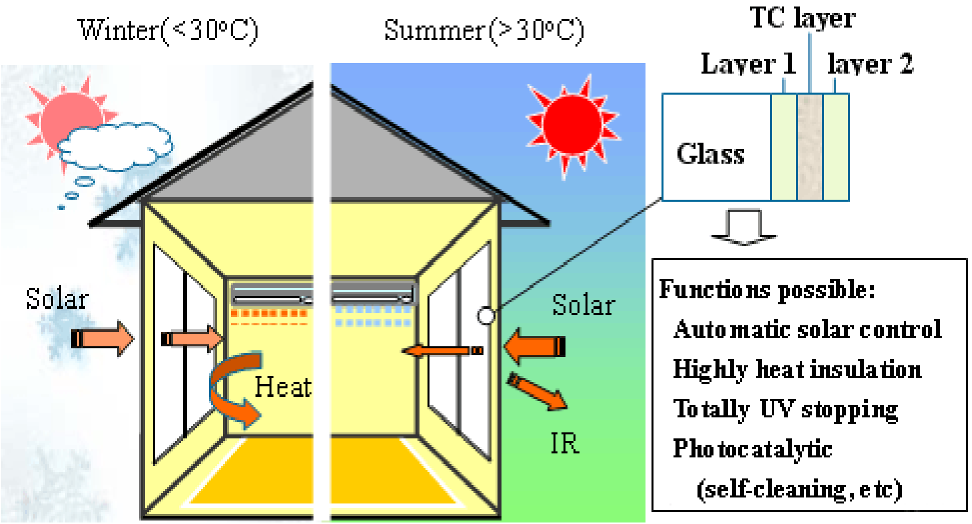
Phase Change Materials: Two or more optical states that can be switched in response to temperature, light, voltage, or humidity

Electronic Crystals: large switching of carrier density induced as a result of electron—phonon or electron—electron interactions

Electrochromics: Changes in redox states or polaronic confinement (inter-valence charge transfer bands)

Phase-Change Materials: Melting or crystalline—amorphous transitions

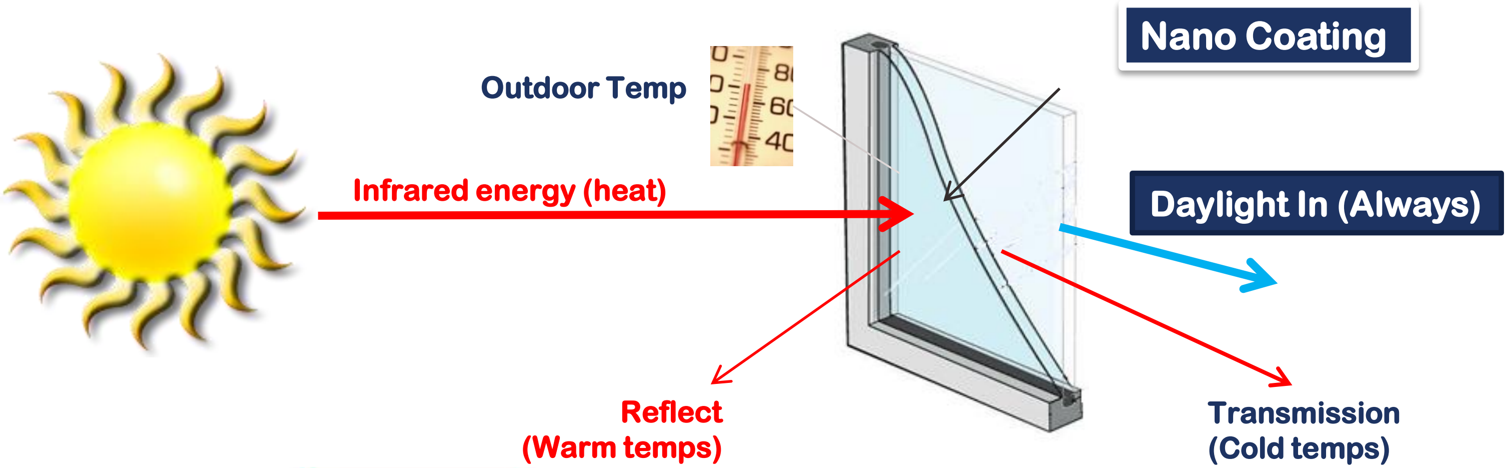
Lyotropic/Thermotropic Transitions: Phase segregation of change in conformation of molecular chains



Thermochromic
Electrochromic
Photochromic
Gasochromic

Image from AIST Japan

Dynamic Windows: Light without Heat?



Nano Coating

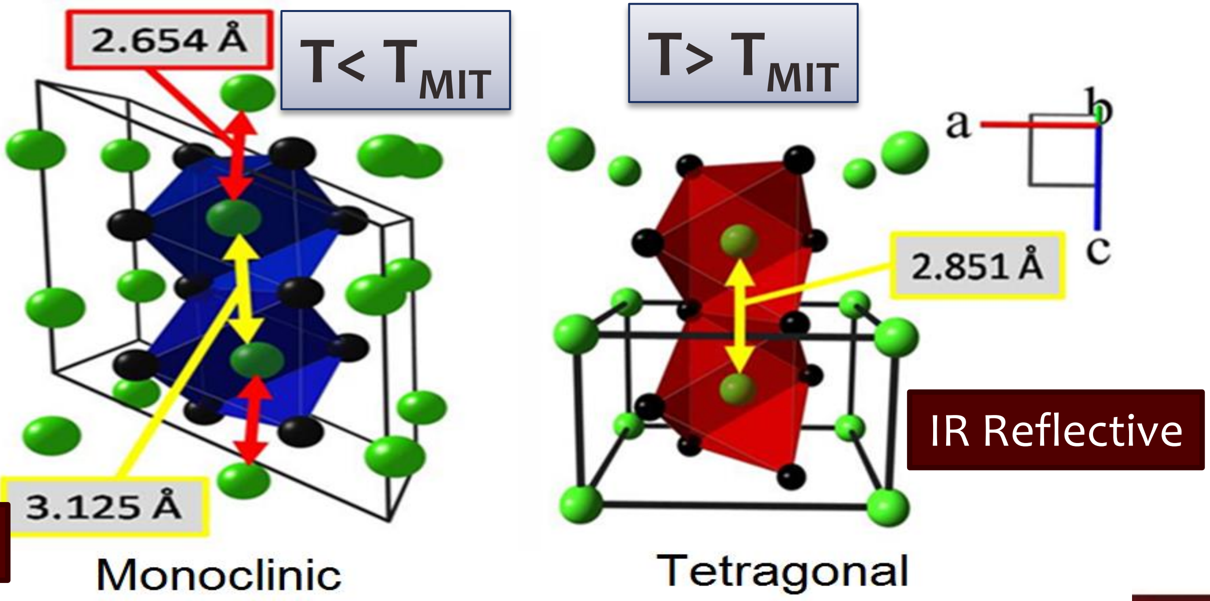
Outdoor Temp

Infrared energy (heat)

Daylight In (Always)

Reflect
(Warm temps)

Transmission
(Cold temps)



$T < T_{MIT}$

$T > T_{MIT}$

2.654 Å

3.125 Å

2.851 Å

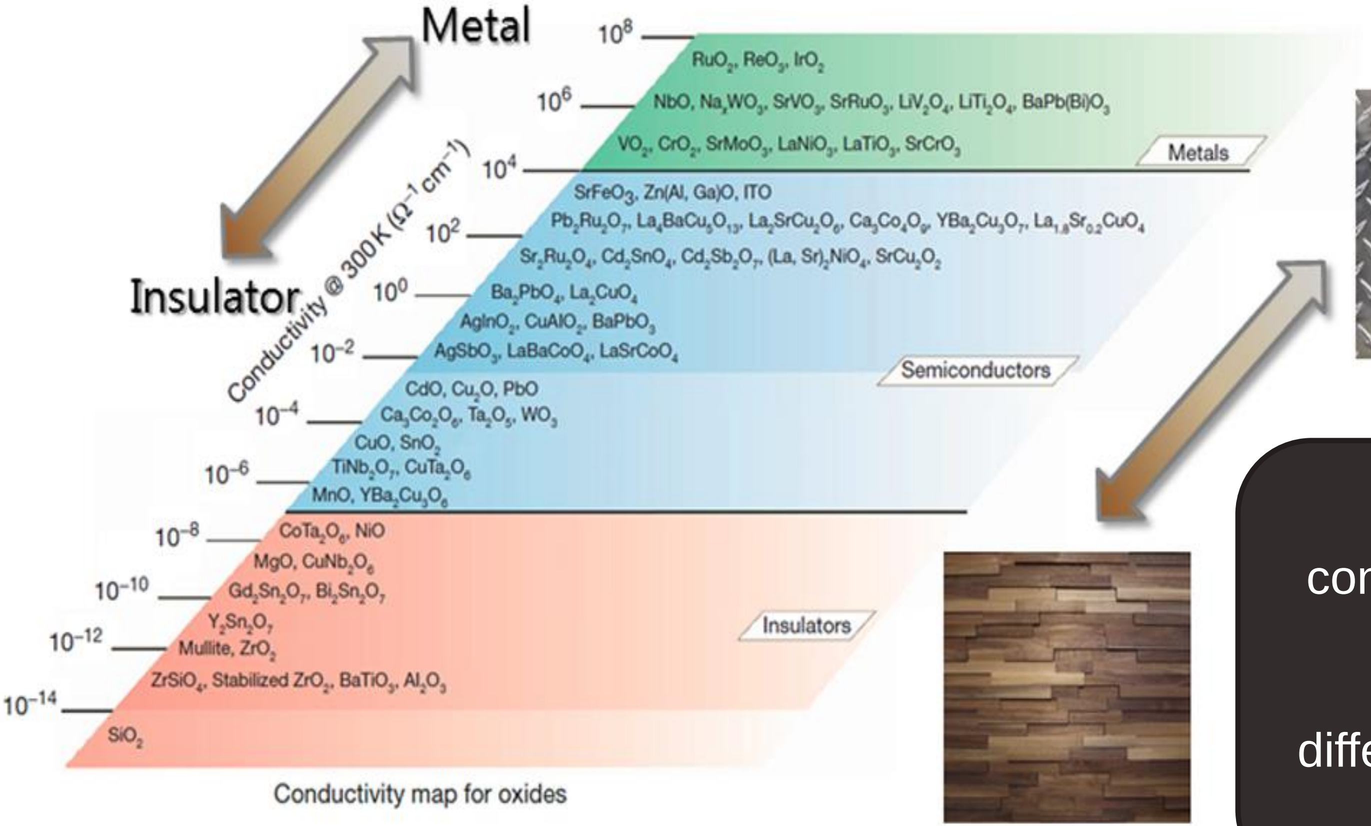
IR transparent

Monoclinic

Tetragonal

IR Reflective

Electronic Phase Transitions

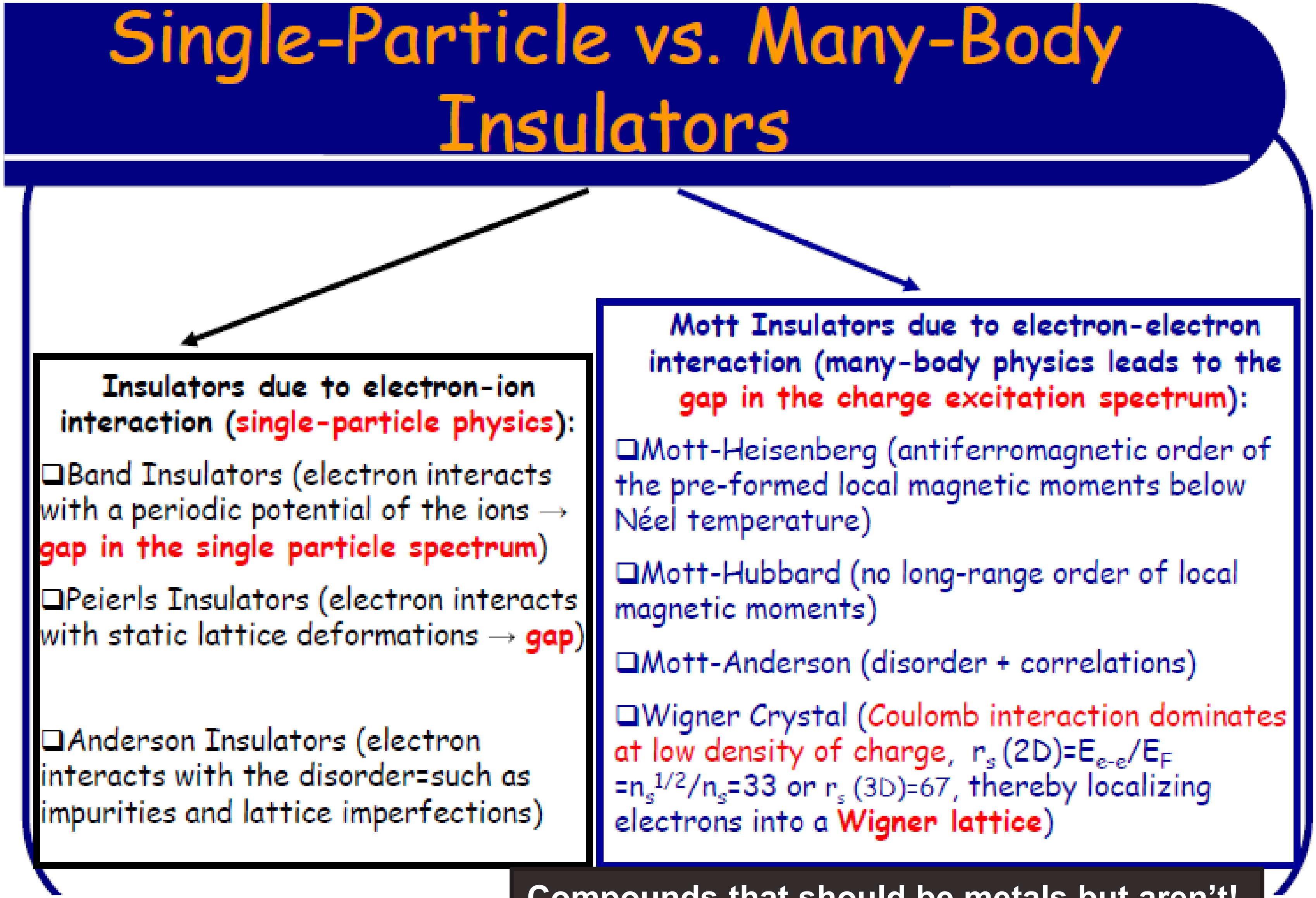


Conductivity map for oxides

Electrical conductivity spans 23 orders of magnitude differences at room temperature

P. M. Marley, G. A. Horrocks, K. E. Pelcher, and S. Banerjee,* Transformers: The Changing Phases of Low-Dimensional Vanadium Oxide Bronzes, Chemical Communications 2015, DOI: 10.1039/C4CC08673B.

P. Edwards, V. Kuznetsov, D. Slocombe and R. Vijayaraghavan, Comprehensive Inorganic Chemistry II, 2013



Single-Particle vs. Many-Body Insulators

Insulators due to electron-ion interaction (single-particle physics):

☐Band Insulators (electron interacts with a periodic potential of the ions → **gap in the single particle spectrum**)

☐Peierls Insulators (electron interacts with static lattice deformations → **gap**)

☐Anderson Insulators (electron interacts with the disorder=such as impurities and lattice imperfections)

Mott Insulators due to electron-electron interaction (many-body physics leads to the gap in the charge excitation spectrum):

☐Mott-Heisenberg (antiferromagnetic order of the pre-formed local magnetic moments below Néel temperature)

☐Mott-Hubbard (no long-range order of local magnetic moments)

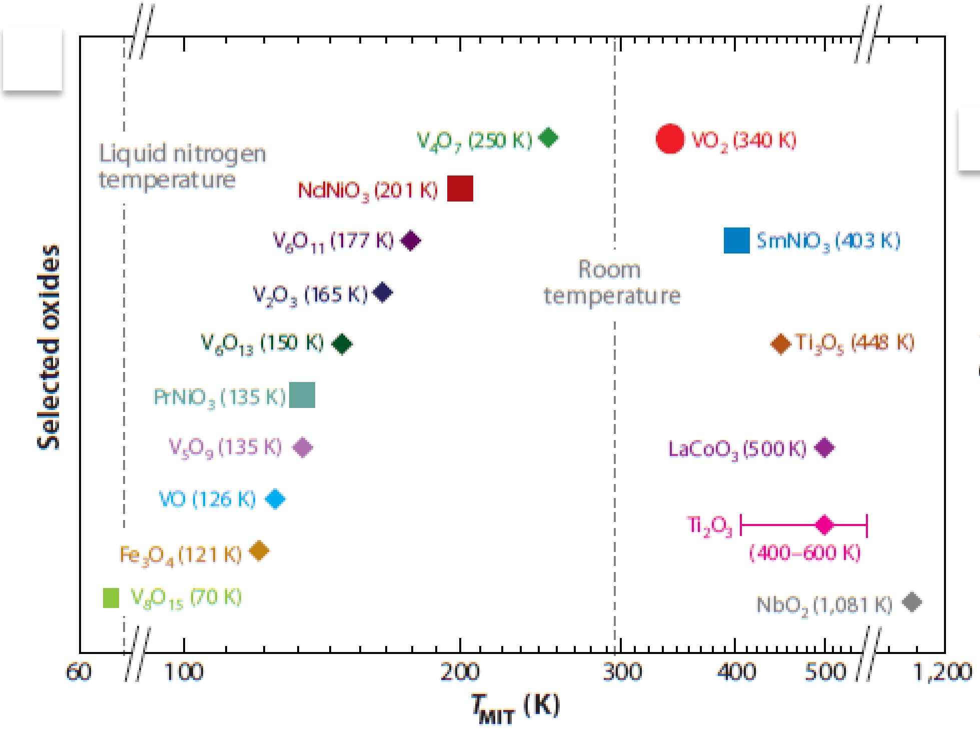
☐Mott-Anderson (disorder + correlations)

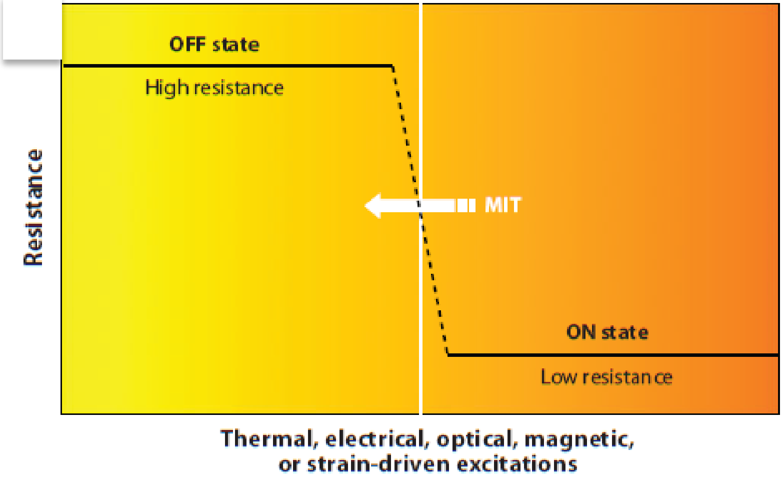
☐Wigner Crystal (Coulomb interaction dominates at low density of charge, $r_s\,(2D)=E_{e\text{-}e}/E_F =n_s^{1/2}/n_s=33$ or $r_s\,(3D)=67$, thereby localizing electrons into a **Wigner lattice**)

Compounds that should be metals but aren't!

Borrowed from lecture notes by Branislav Nikolic, University of Delaware

Metal—Insulator Transitions

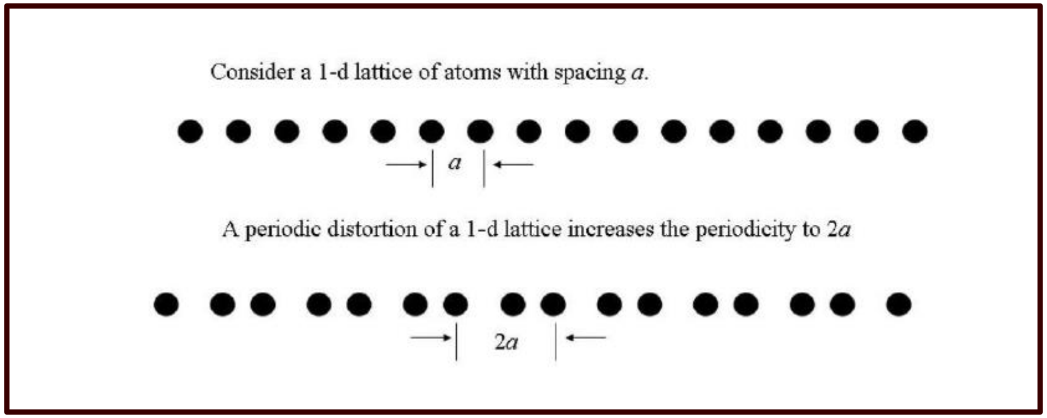




Design of strong electron correlated materials remains one of the “grand challenges” of science

Ramanathan and co-workers, *Annu. Rev. Mater. Res*. **2011**, 41, 337—367.

Electron—Phonon Insulator: Peierl's Insulator

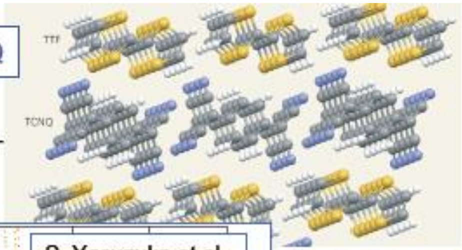


Consider a 1-d lattice of atoms with spacing *a*.

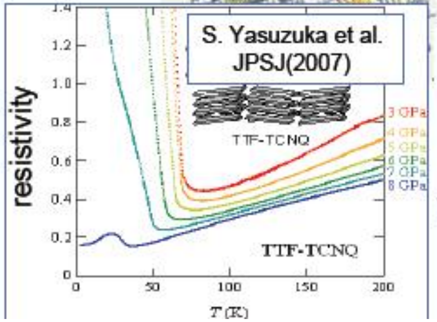
A periodic distortion of a 1-d lattice increases the periodicity to 2*a*

TTF-TCNQ

organic conductor



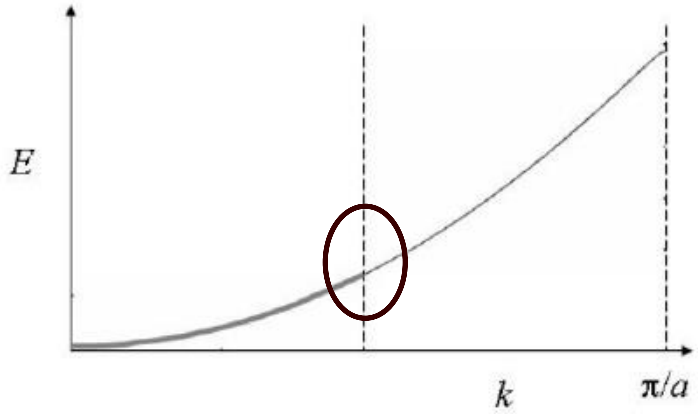
H. Alves et al. Nature Materials

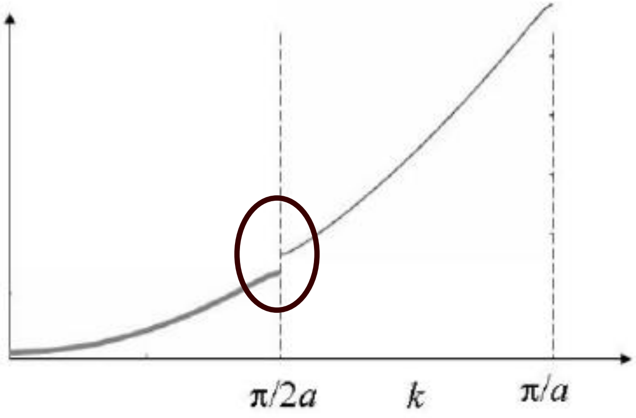


S. Yasuzuka et al. JPSJ(2007)

metal-insulator transition

A gap appears at the end of the filled states: filled states are lowered in energy and unfilled states are raised in energy

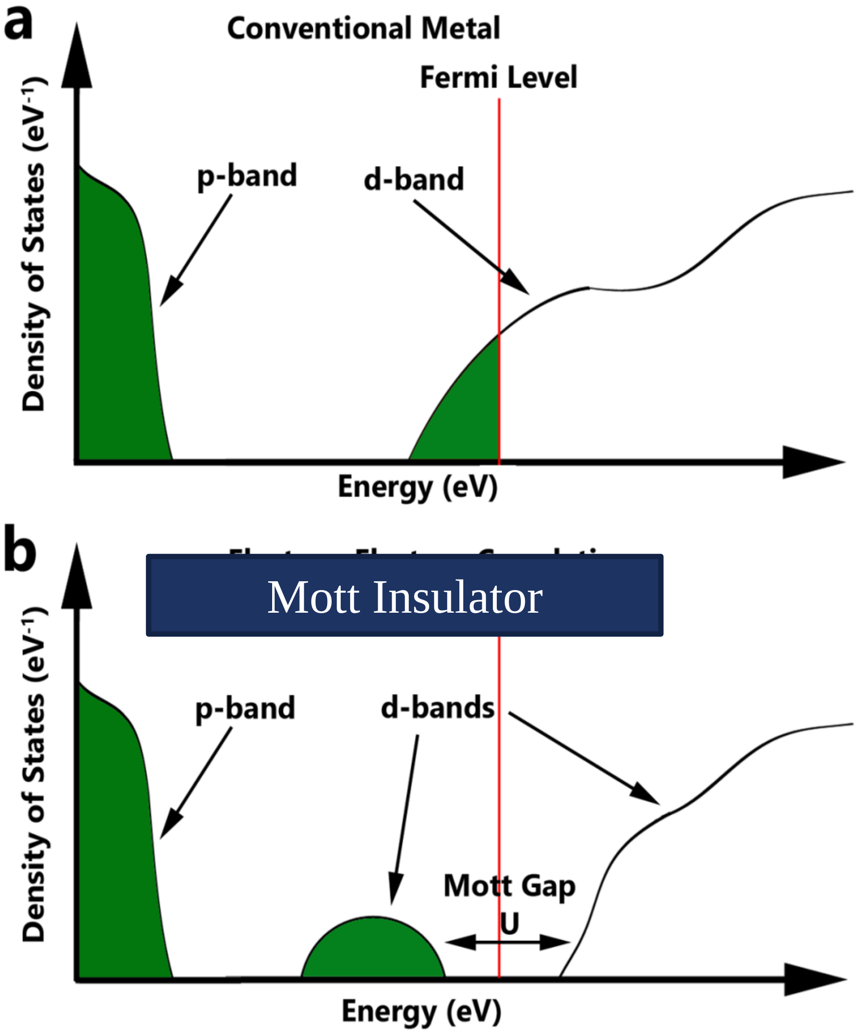




Mott's Initial Idea for Correlation-Induced Gap

- Two electrons localized at a particular site of distance (*d*) will repel each other with an energy, *U* (Mott-Hubbard correlation energy).

- The resulting band is split into Lower and Upper Hubbard Bands (LHB and UHB, respectively) creating a band gap.



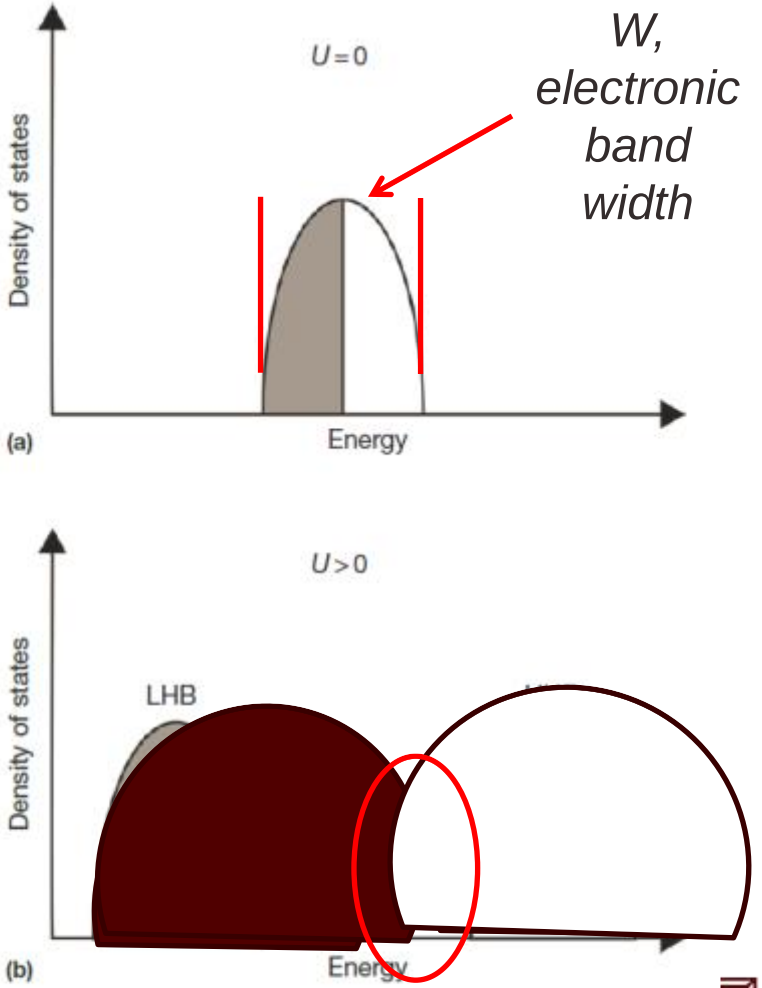
The Mott Metal-Insulator Transition

- *W* = electronic band width
- At a critical ratio of *W*:*U* the bands overlap and metallic behavior sets in.

Mott criterion for MIT:

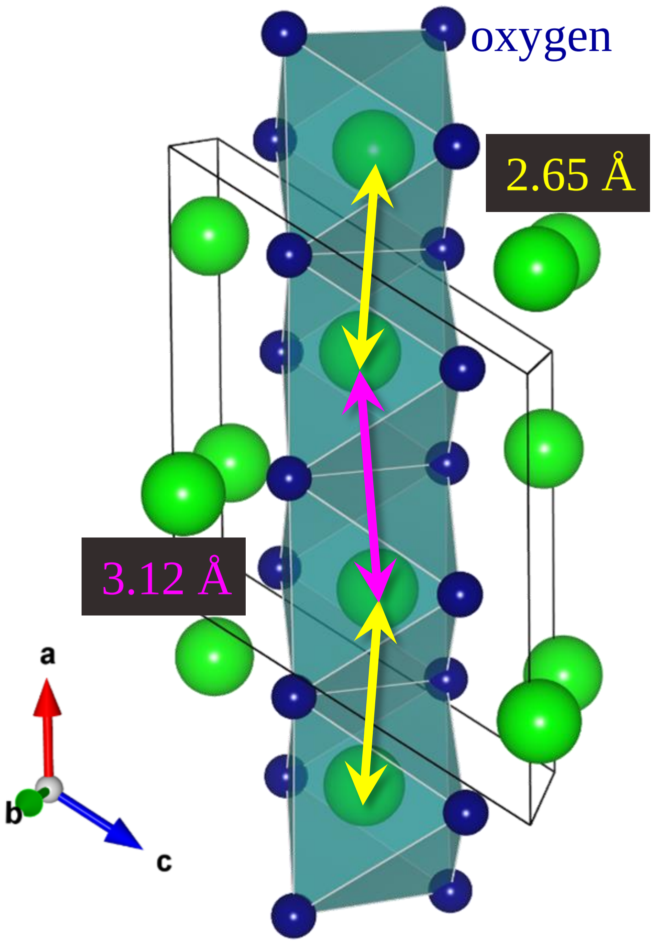
$n_c^{1/3}a^*_h = 0.25$
n_c = critical carrier concentration
a^*_h = Bohr radius of the localized dopant

- **Since the critical distance between dopant centers (d_c) is ~ $n_c^{-1/3}$, the Mot MIT will occur when d_c ~ $4a^*_h$. i.e. when the distance between dopant centers is about four times the Bohr radius of the localized dopant.**

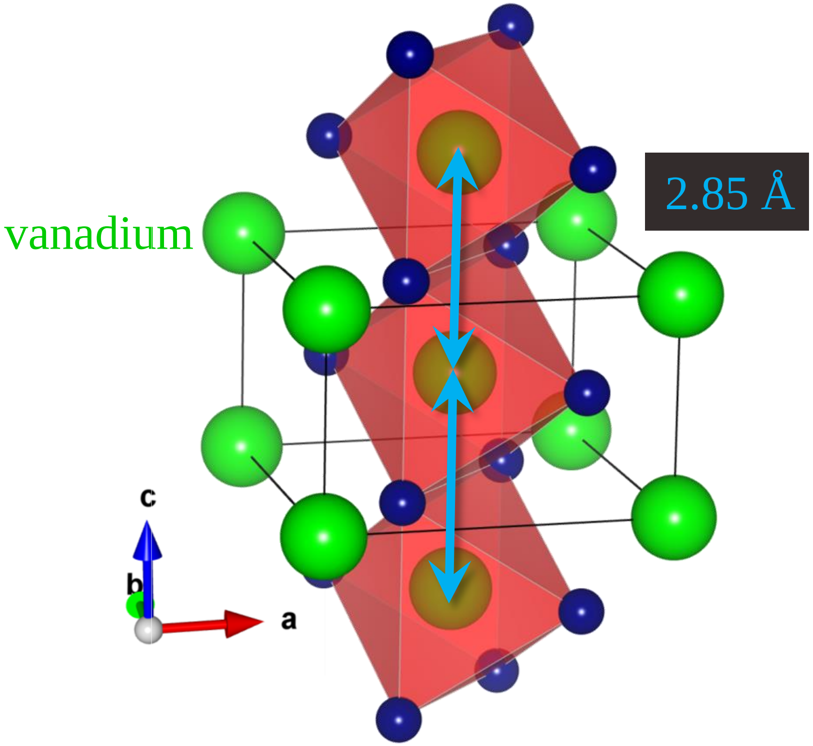


W, electronic band width

Vanadium Oxide



Low Temperature Monoclinic Phase



High Temperature Rutile Phase

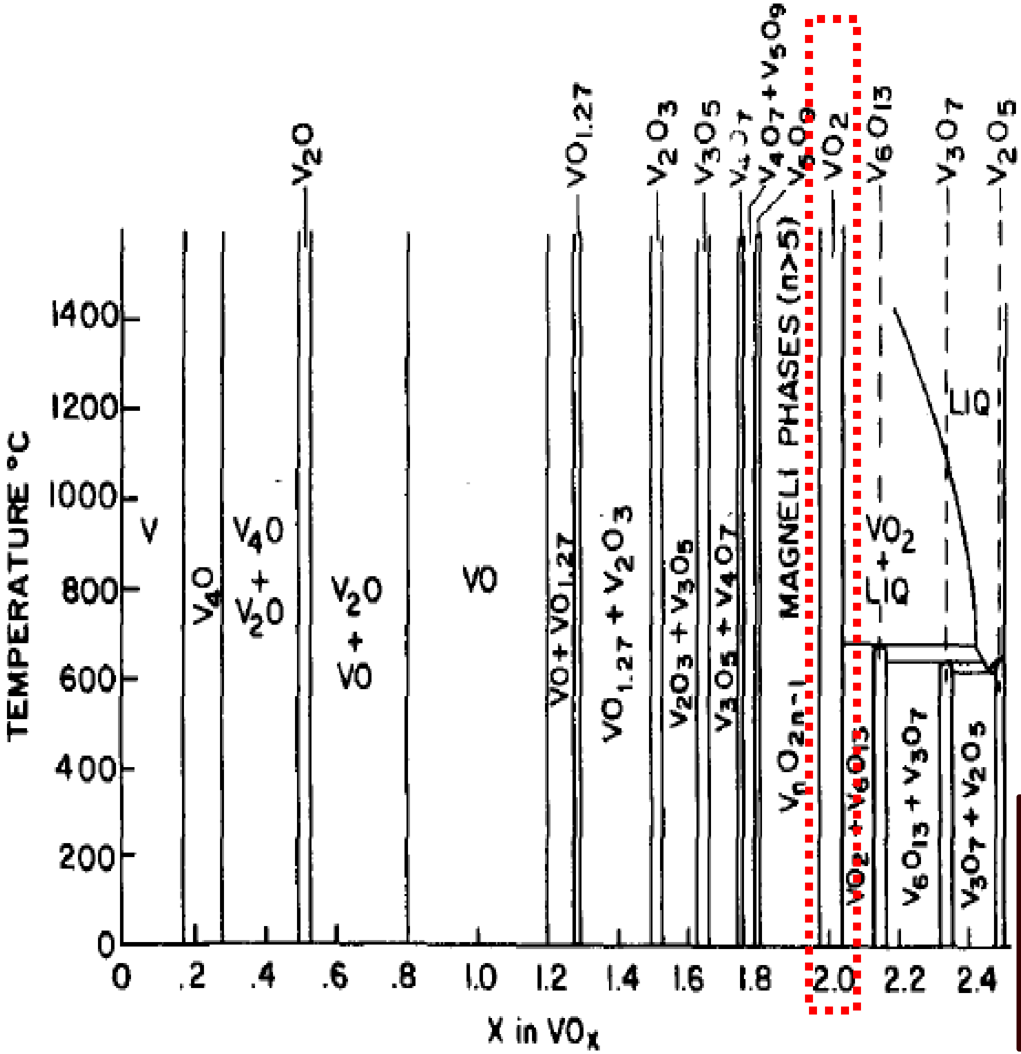
Challenges with VO_2 Windows?

Bulk or thin film VO_2 cracks upon thermal cycling-can’t withstand the thermal stresses upon repeated cycling

The intrinsic metal—insulator transition temperature of 67°C is too high to be useful in a practical window.

Difficult (impossible) to prepare VO_2 with careful control of stoichiometry in large amounts-most “high-quality” VO_2 confined to epitaxial thin films grown under ultra-high-vacuum conditions. No scalable methods to prepare powders

VO_2 as a Synthetic Target



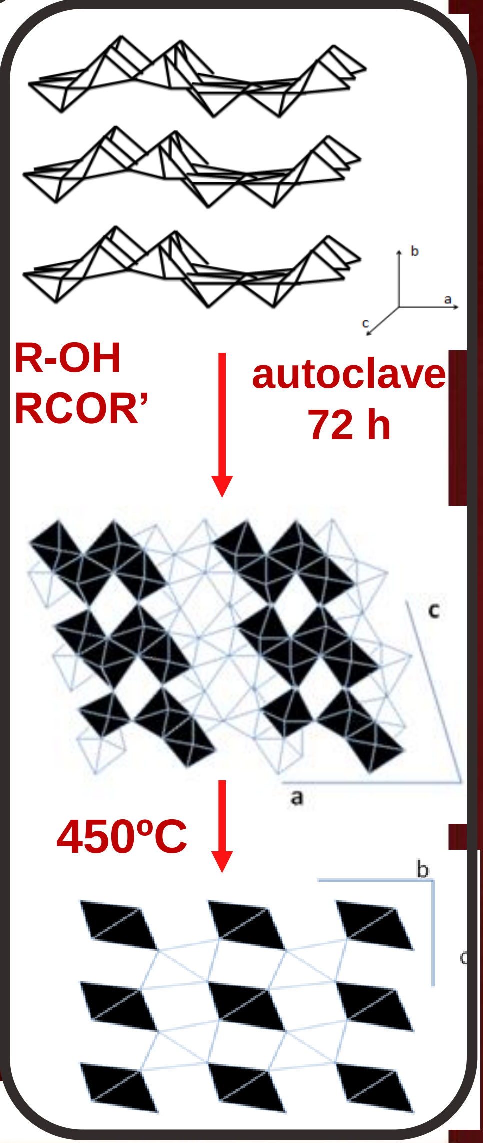
C. H. Griffiths and H. K. Eastwood, Journal of Applied Physics, 1974, **45**, 2201-2206.

V_2O_5

VO2(B)

VO2(R)

VO2(M1)

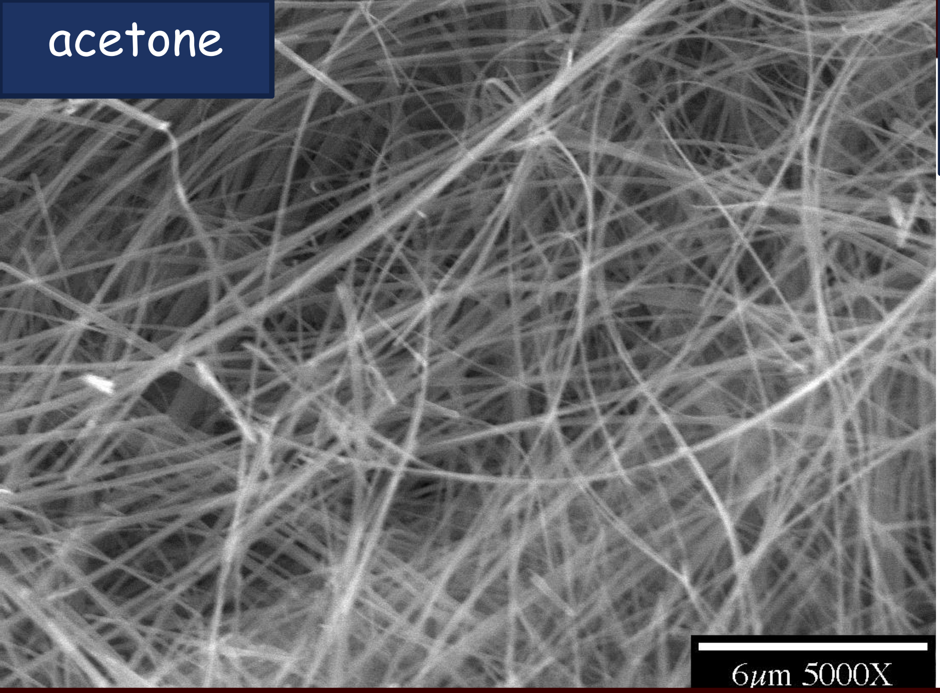


R-OH
RCOR’

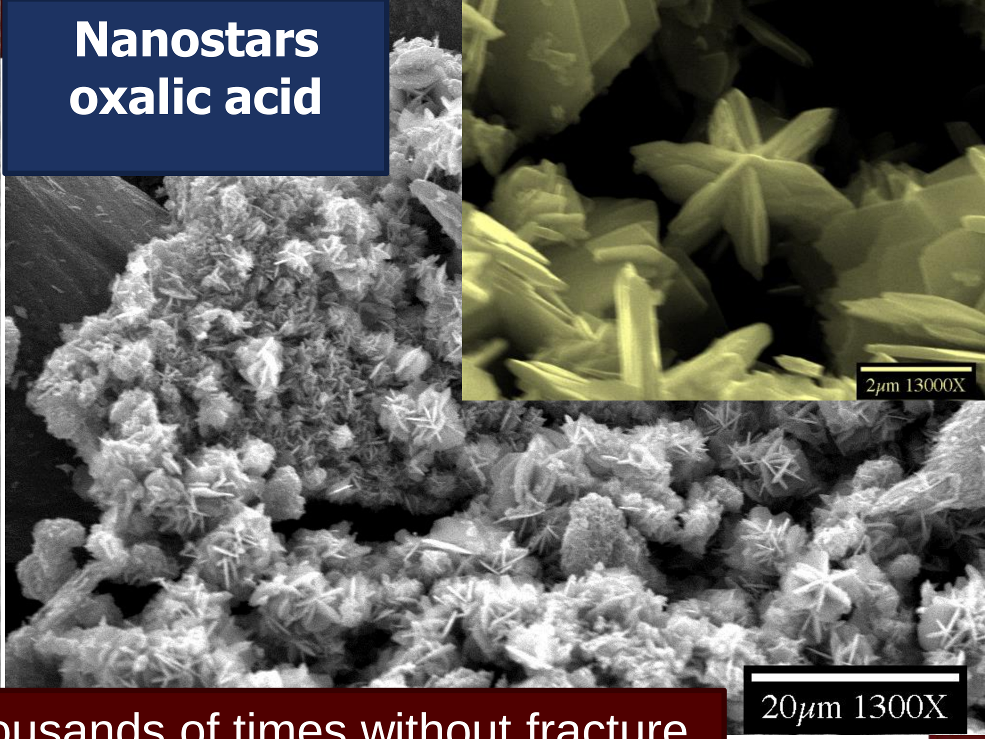
autoclave
72 h

450ºC

acetone

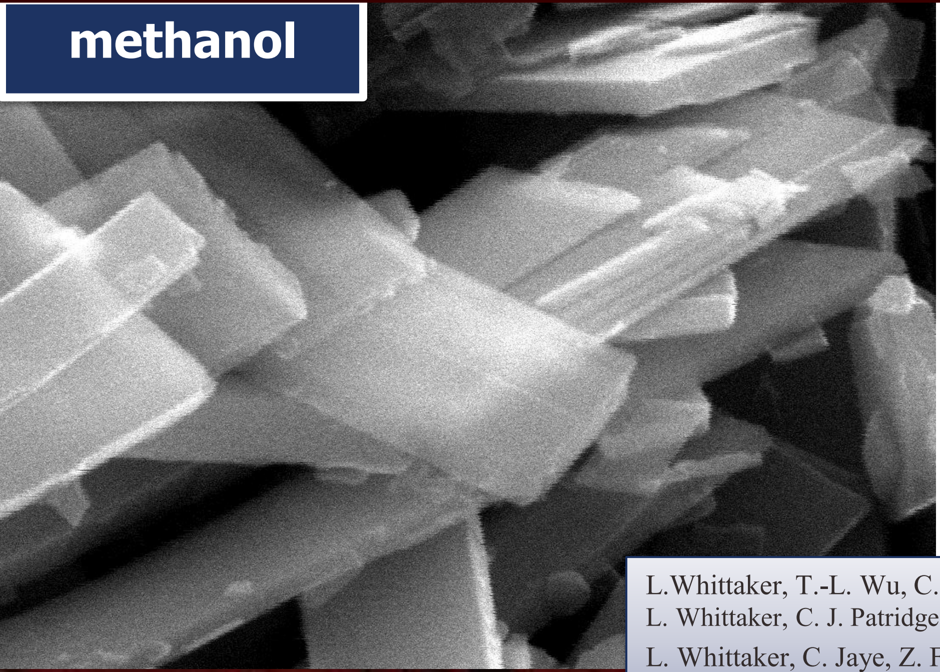


Nanostars oxalic acid

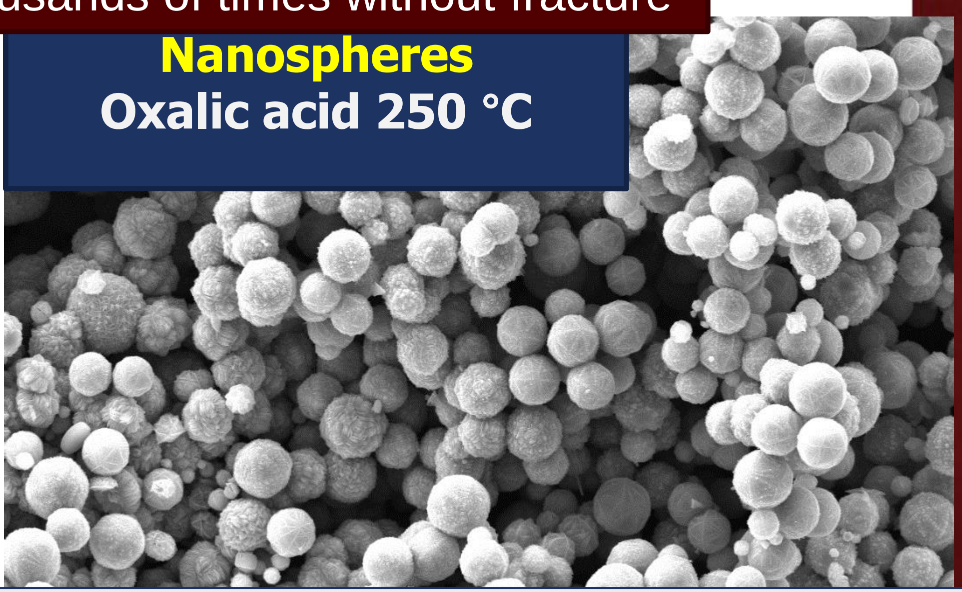


Nano and microstructures can be cycled thousands of times without fracture

methanol

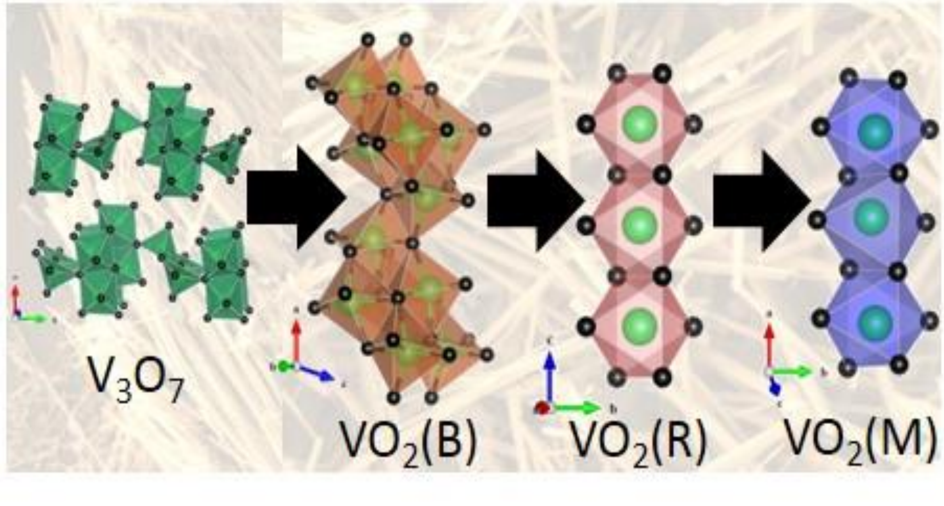


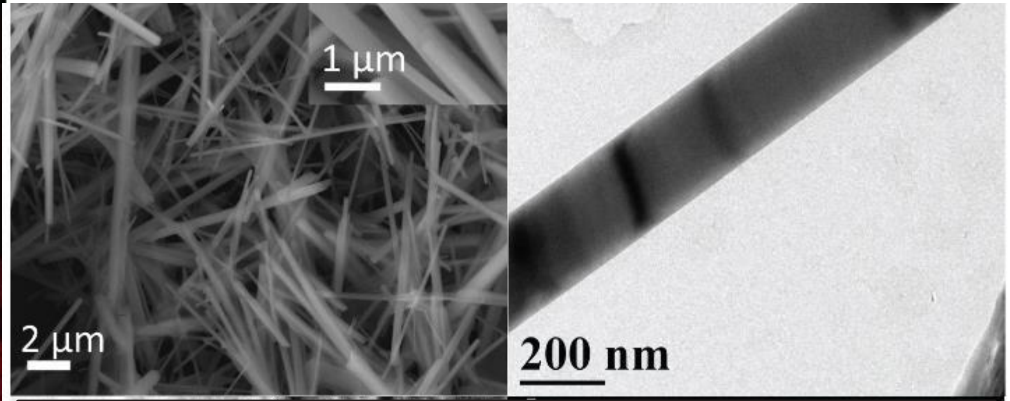
Nanospheres
Oxalic acid 250 °C

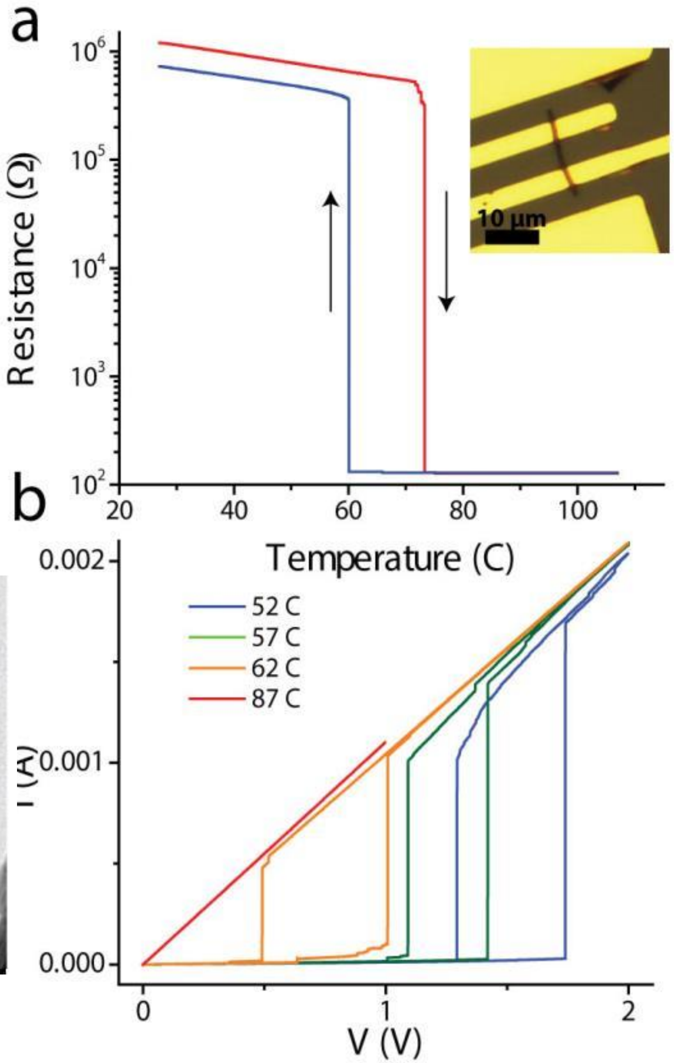


L.Whittaker, T.-L. Wu, C. J. Patridge, G. Sambandamurthy, and S. Banerjee, *J. Mater. Chem.* **2011**, *21*, 5580.
L. Whittaker, C. J. Patridge, and S. Banerjee, *J. Phys. Chem. Lett.* **2011**, *2,* 745-758
L. Whittaker, C. Jaye, Z. Fu, D. A. Fischer, and S. Banerjee,. *J. Am. Chem. Soc.* **2009,** *131*, 8884-8894.

Phase Transitions in VO_2



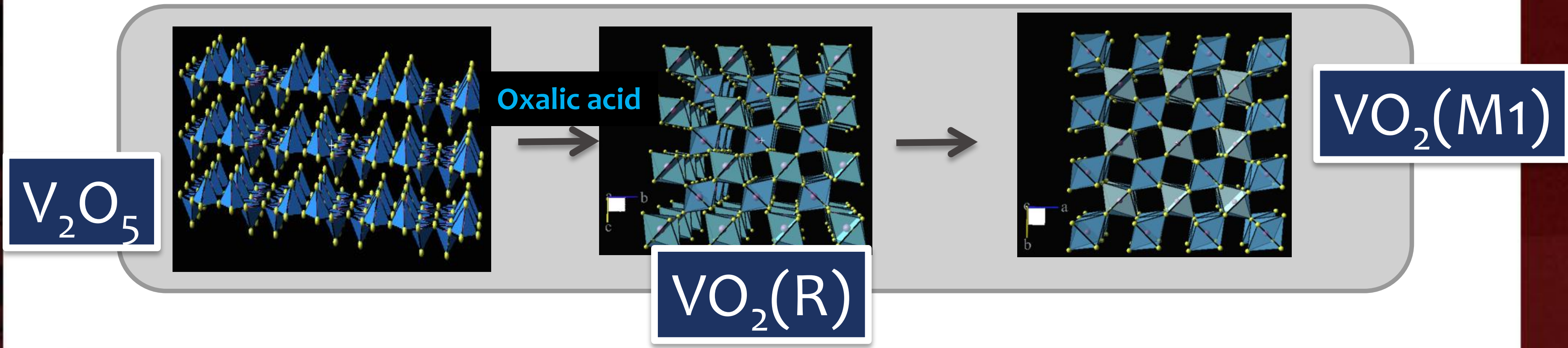




- Almost four orders of magnitude MIT: reproducible across different nanowires and syntheses

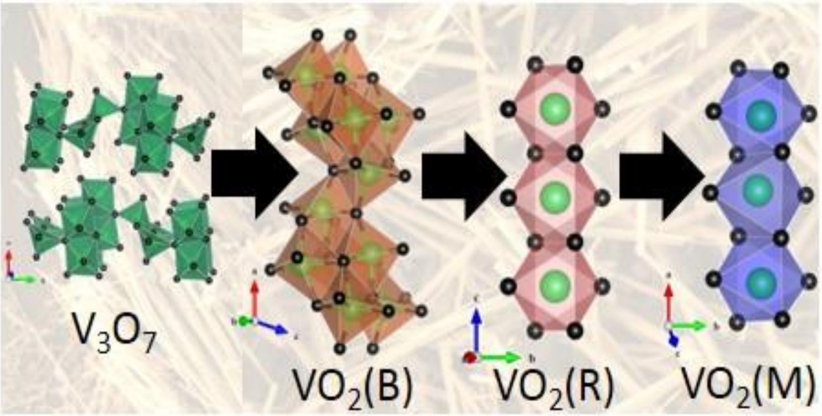
G. A. Horrocks, S. K. Singh, M. F. Likely, G. Sambandamurthy, and S. Banerjee,, *ACS Applied Materials and Interfaces*, **2014**, *6*, 15726–15732.

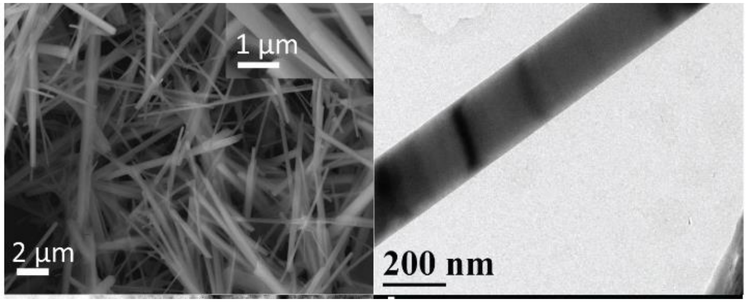
Synthesis & Scale-Up



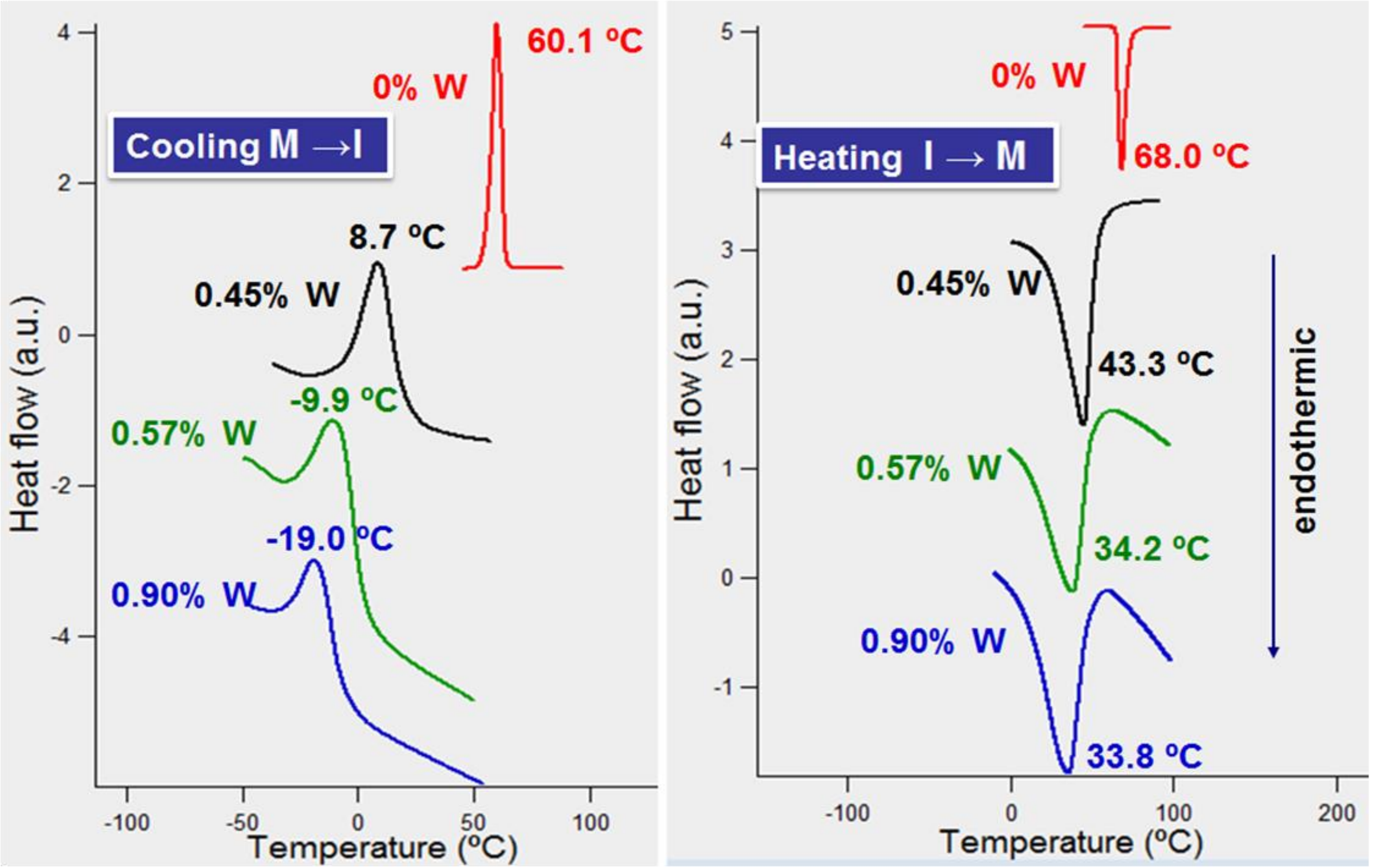
1. High-pressure route: One step, allows for introduction of W or Mo dopants

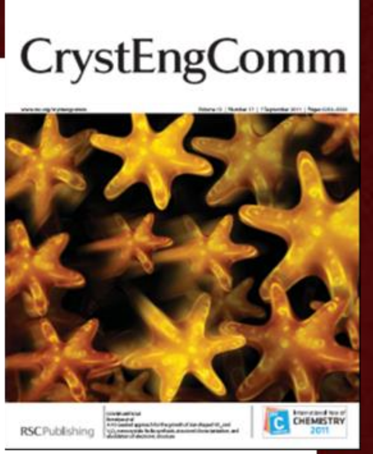
2. Low-pressure route: Two steps, can introduce dopants, high-quality materials

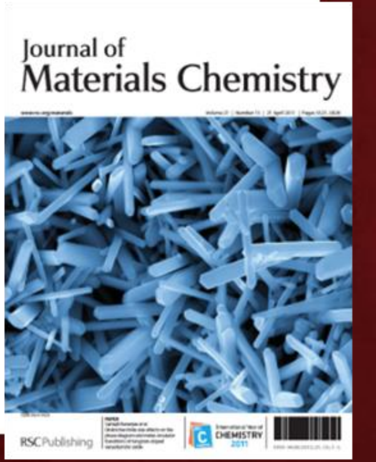




Depressing the Phase Transition



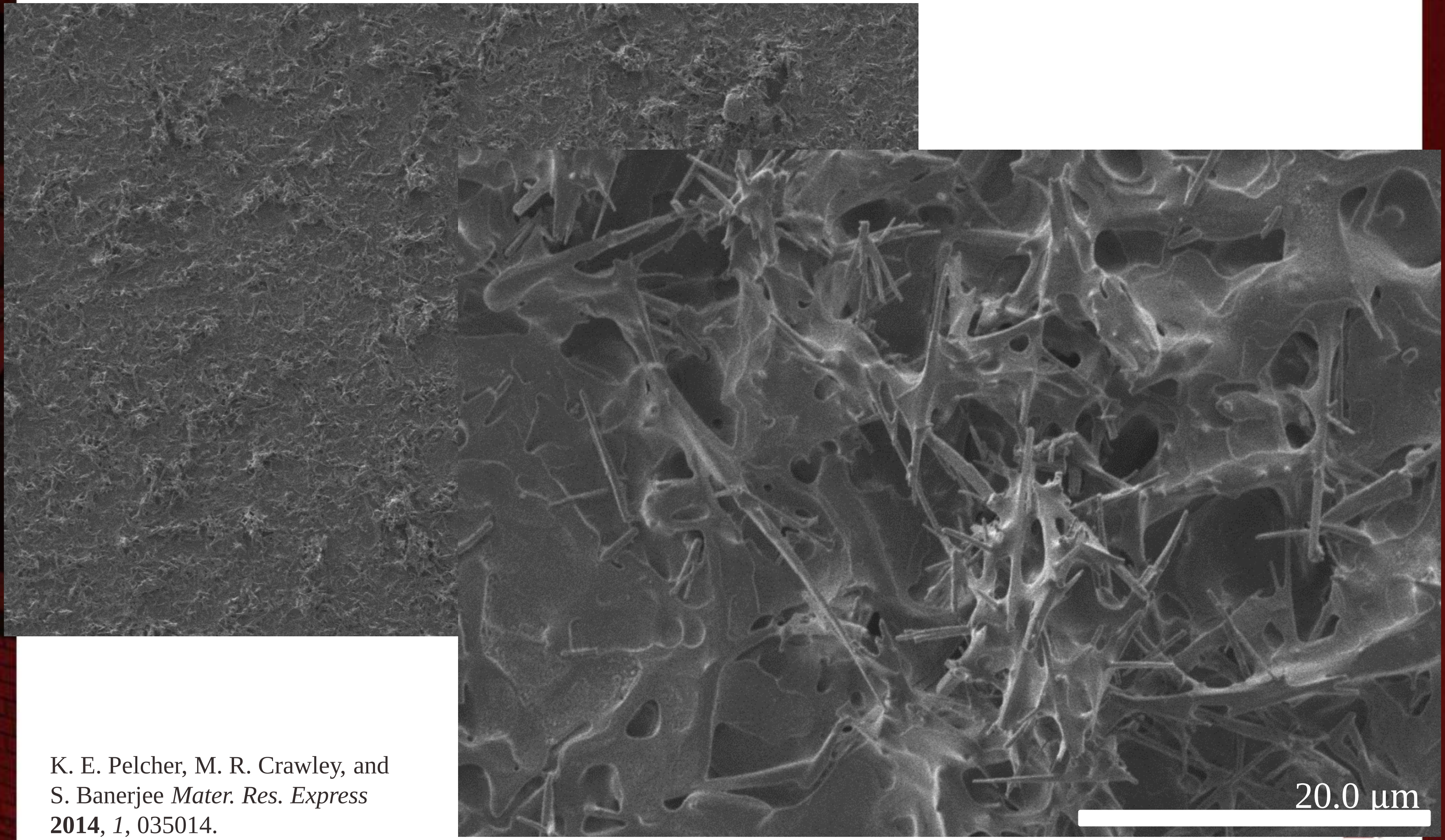




Customizable to different climates

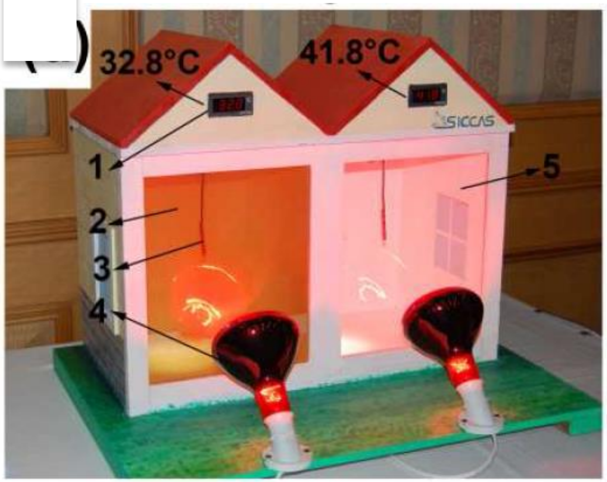
L.Whittaker, T.-L. Wu, C. J. Patridge, G. Sambandamurthy, and S. Banerjee, *J. Mater. Chem.* **2011**, *21*, 5580.
L. Whittaker, T.-L. Wu, A. Stabile, G. Sambandamurthy, S. Banerjee, *ACS Nano* **2011**, 8861–8867

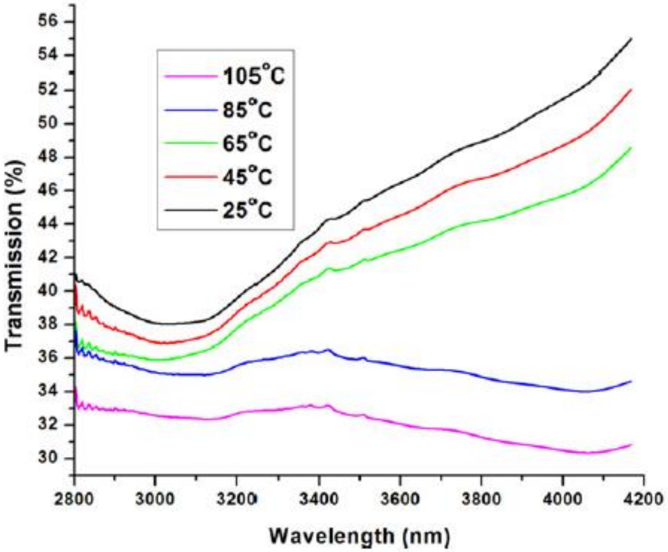
Adhering VO_2 to Glass: $VO_2@SiO_2$



K. E. Pelcher, M. R. Crawley, and S. Banerjee *Mater. Res. Express* **2014**, *1*, 035014.

Optical Studies





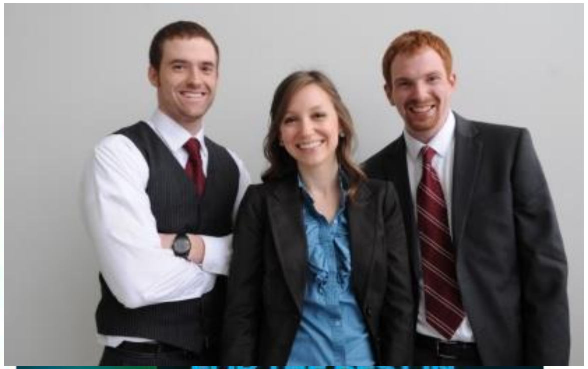
Panasci winners capitalize on high-tech coating

Entrepreneurs take top prize in UB's Panasci competition

***By Matt Glynn** | News Business Reporter*
on April 23, 2013 - 6:00 PM, updated April 23, 2013 at 11:50 PM

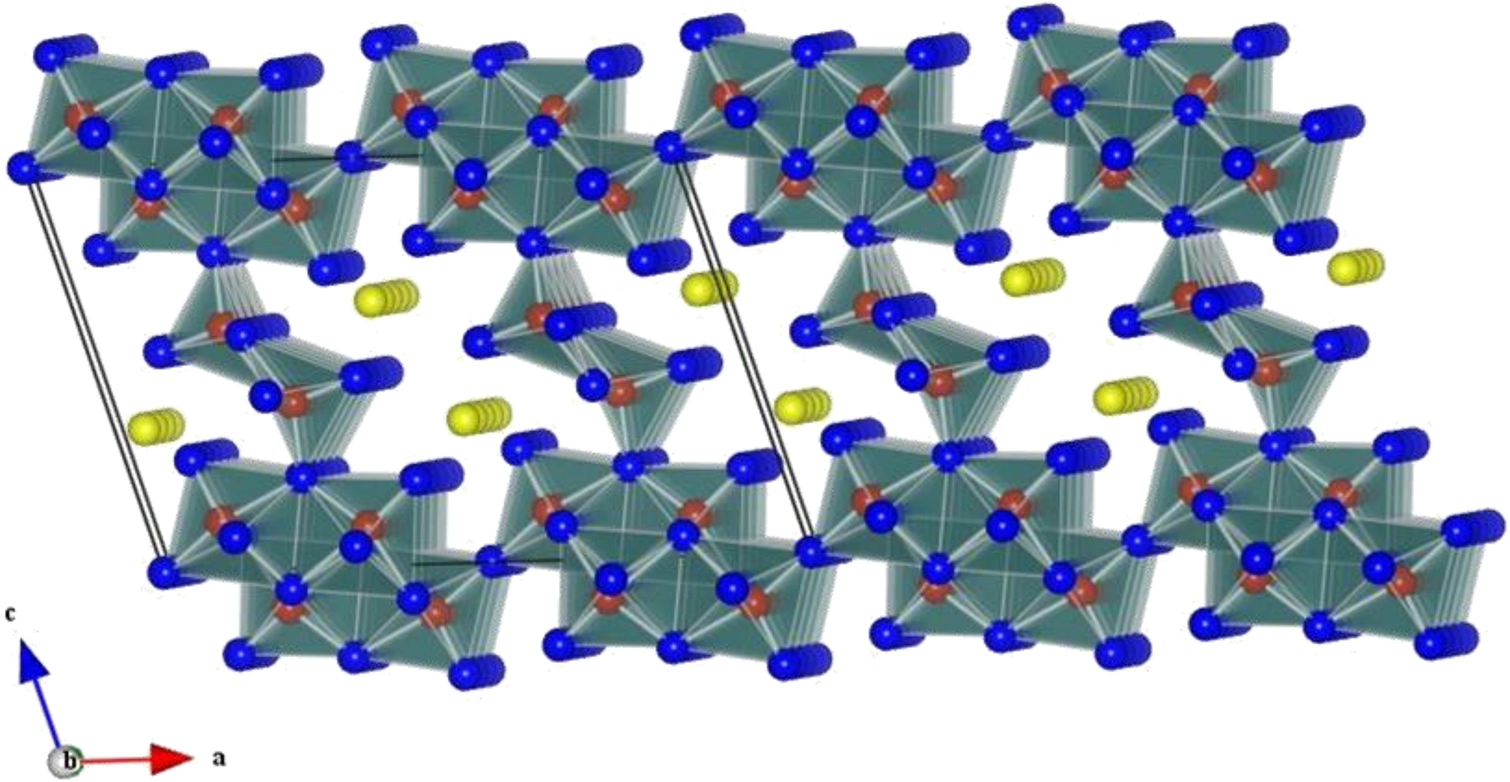
The winning team in a University at Buffalo entrepreneurial competition pitched a plan to make a material coating that can regulate heat from the sun in a building, creating "smart" surfaces or windows.

Ann Brozek, Peter Marley and Brian Schultz won $25,000 in start-up funding for their business, diMien LLC, in the Henry A. Panasci Jr. Technology Entrepreneurship Competition. A panel of judges selected the winners from five teams of finalists.



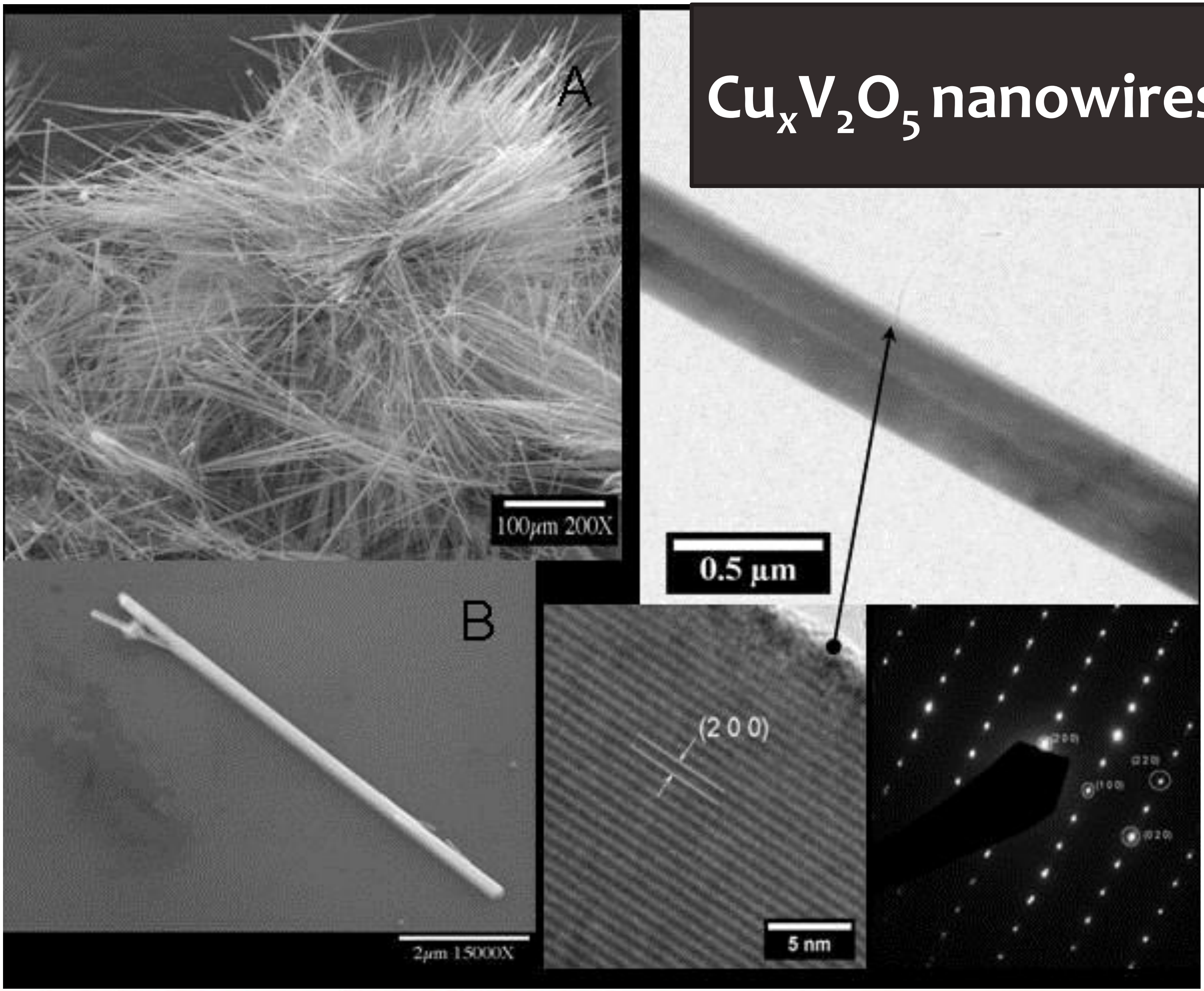
Peter Marley, Ph.D. '15
Ann Brozek, MBA. '14
Brian J. Schultz, Ph.D. '13

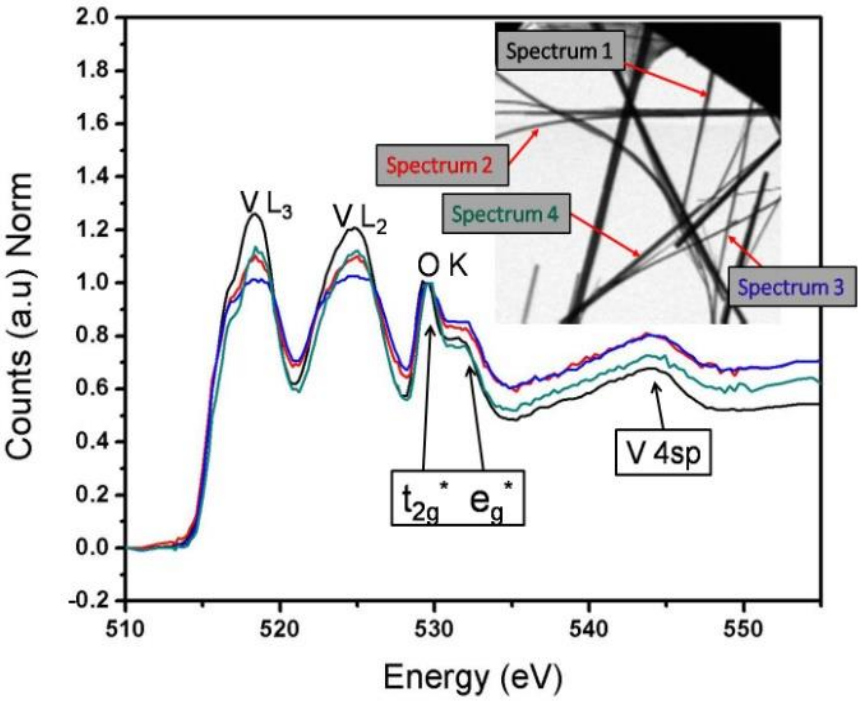
Life Beyond VO_2: β'-$Cu_xV_2O_5$

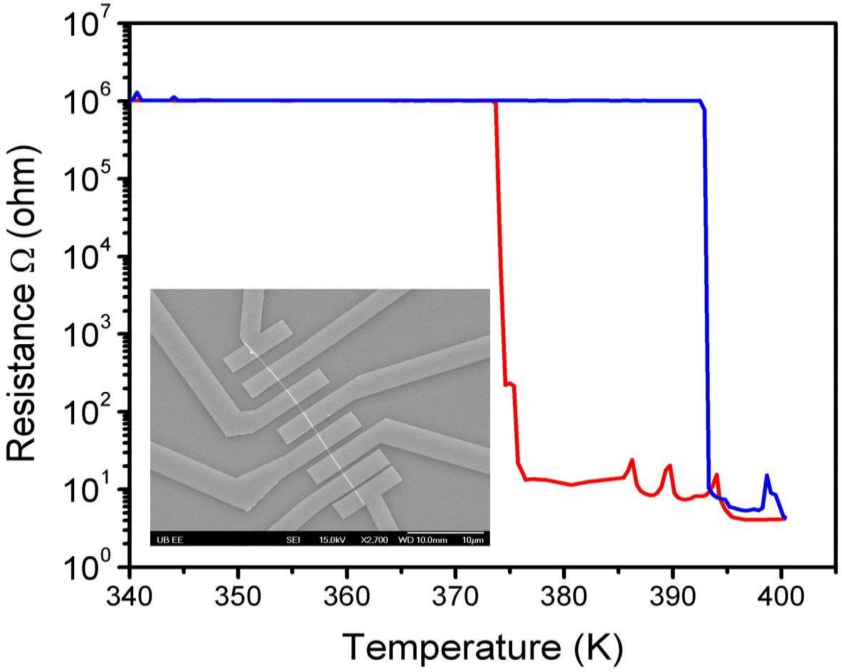


C. J. Patridge, C. Jaye, H. Zhang, A. C. Marschilok, D. A. Fischer, E. S. Takeuchi, and S. Banerjee, *Inorg. Chem.* **2009**, *48*, 3145-3152

$Cu_xV_2O_5$ nanowires







Colossal Metal—Insulator Transition in a Sienko-Wadsley Tunnel Bronze
MIT Temperature and Magnitude Depend on Cu concentration in $Cu_xV_2O_5$

C. J. Patridge, C. Jaye, H. Zhang, A. C. Marschilok, D. A. Fischer, E. S. Takeuchi, and S. Banerjee, *Inorg. Chem.* **2009**, *48*, 3145-3152.

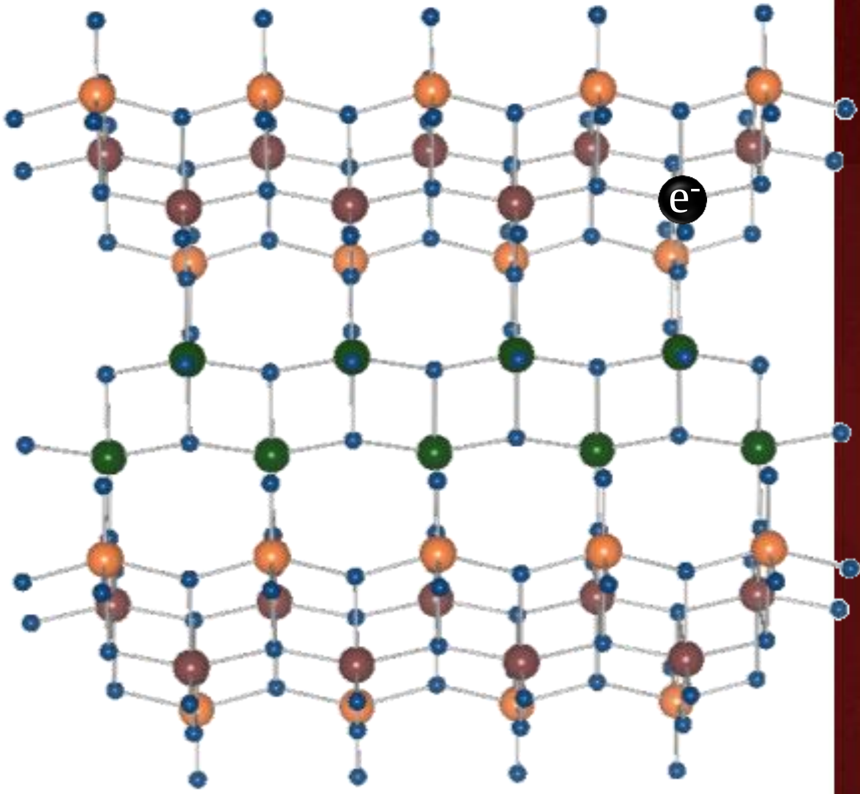
C. J. Patridge, T.-L. Wu, G. Sambandamurthy, and S. Banerjee, *Chem. Commun.* **2011**, *47*, 4484-4486.

Some Mechanistic Ideas

In the insulating state localized V^{4+} (d^1 electrons) alternate with V^{5+} (d^0) cations along the vanadium oxide framework.

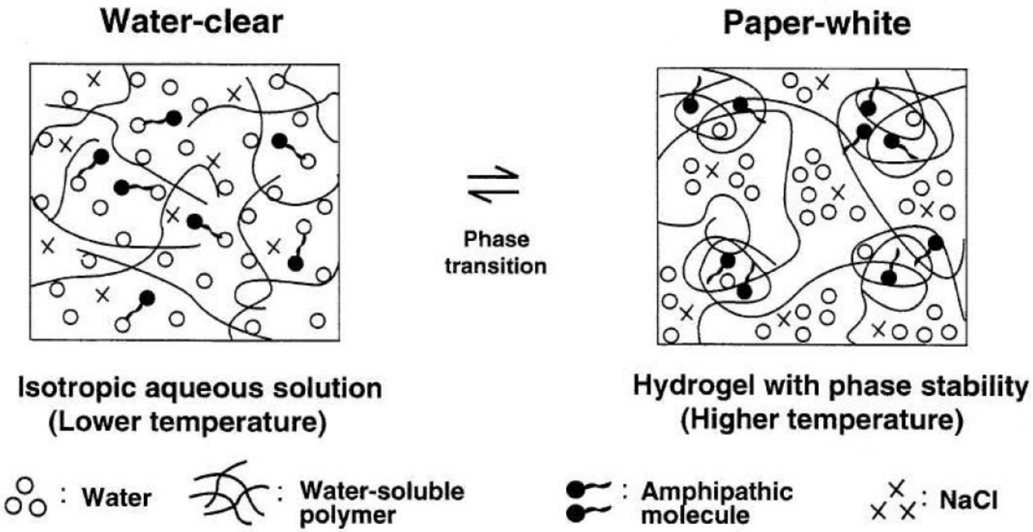
The specific mode of localization depends on the crystal structure and stoichiometry

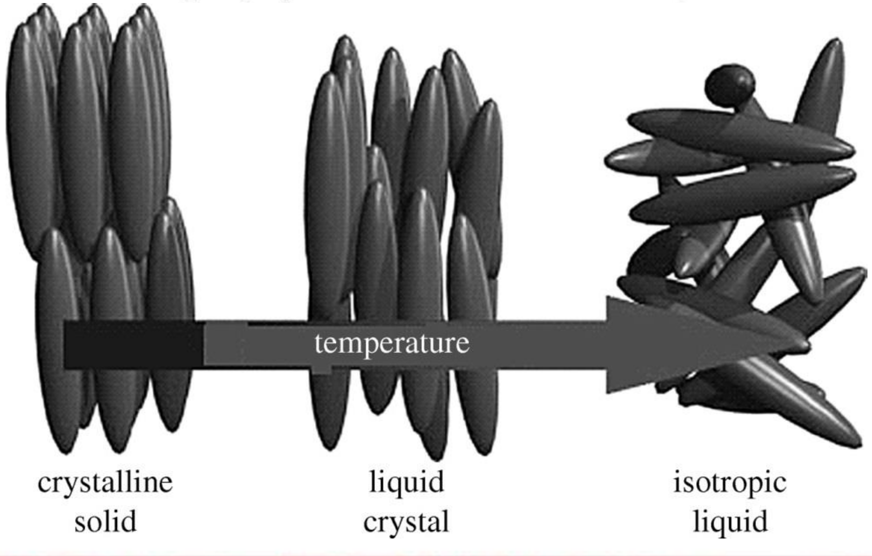
Application of external stimuli results in reaching the Mott criterion and leads to a MIT.

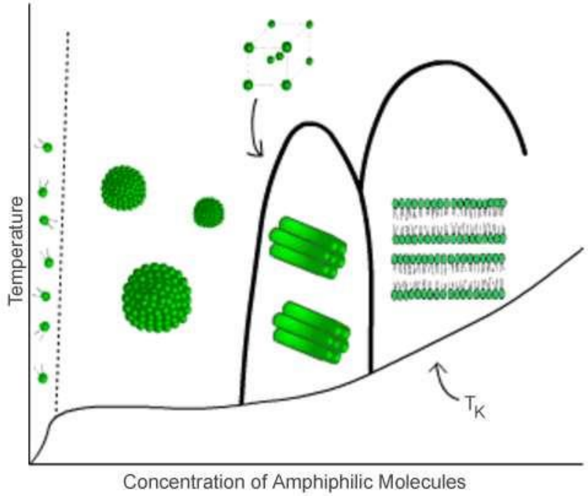


Thermotropic and Lyotropic Transitions

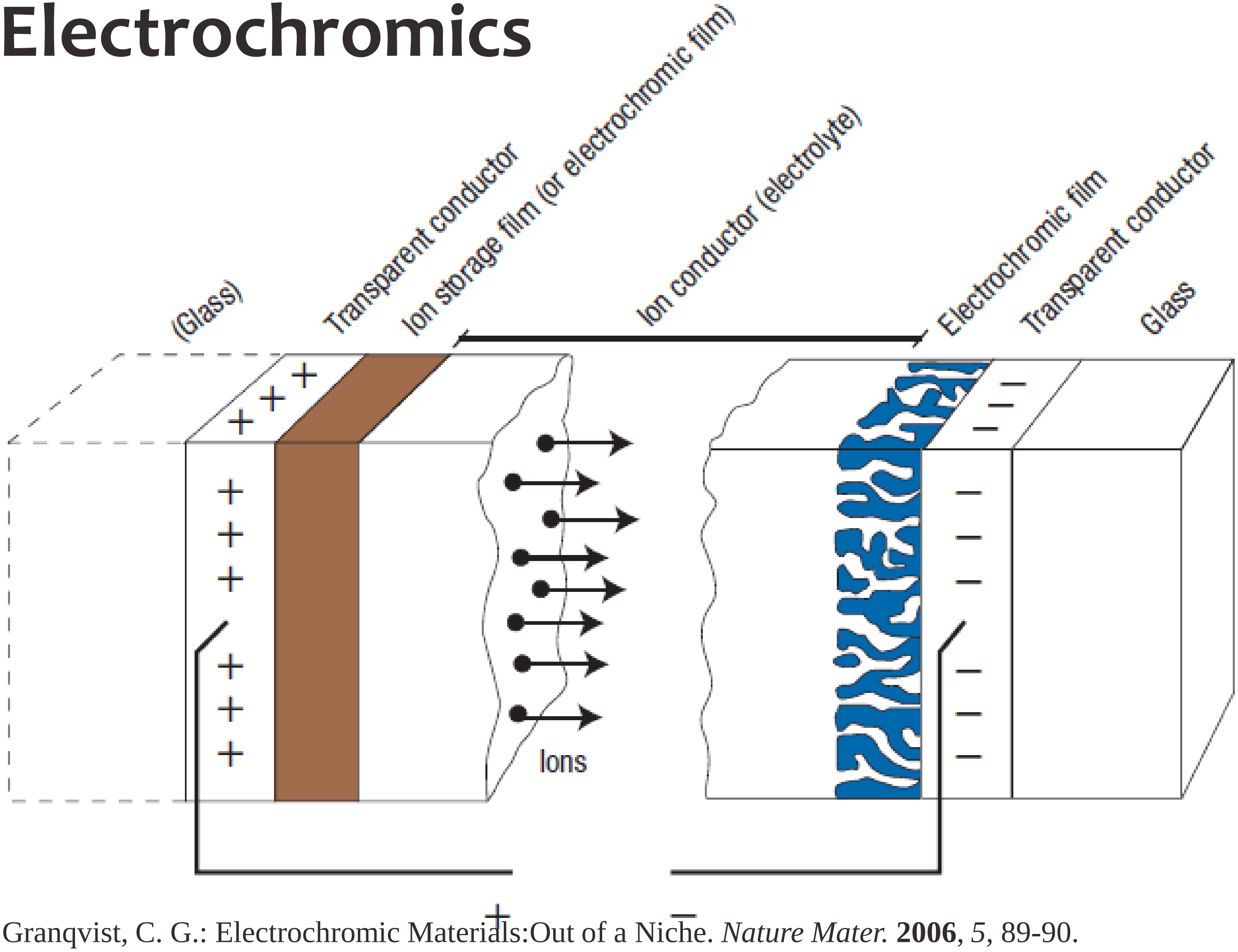
Phase segregation or change in assembly mode vastly alters refractive index





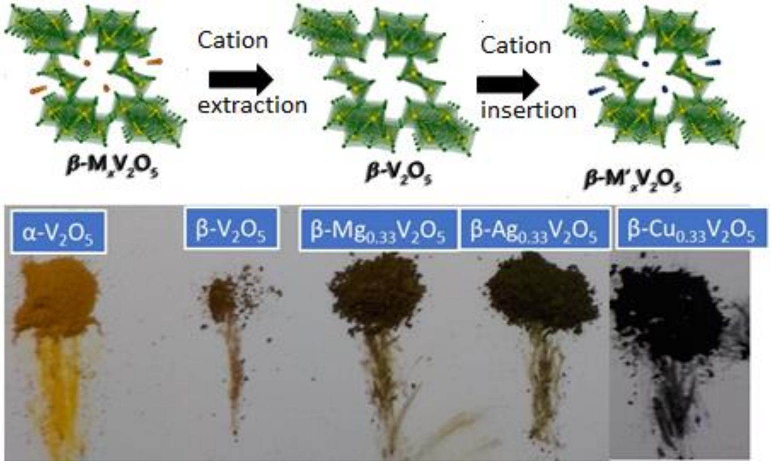


Electrochromics



Granqvist, C. G.: Electrochromic Materials:Out of a Niche. *Nature Mater.* **2006**, *5*, 89-90.

Redox changes in active layers constituted of transition metal oxides: WO_3, MoO_3, V_2O_5

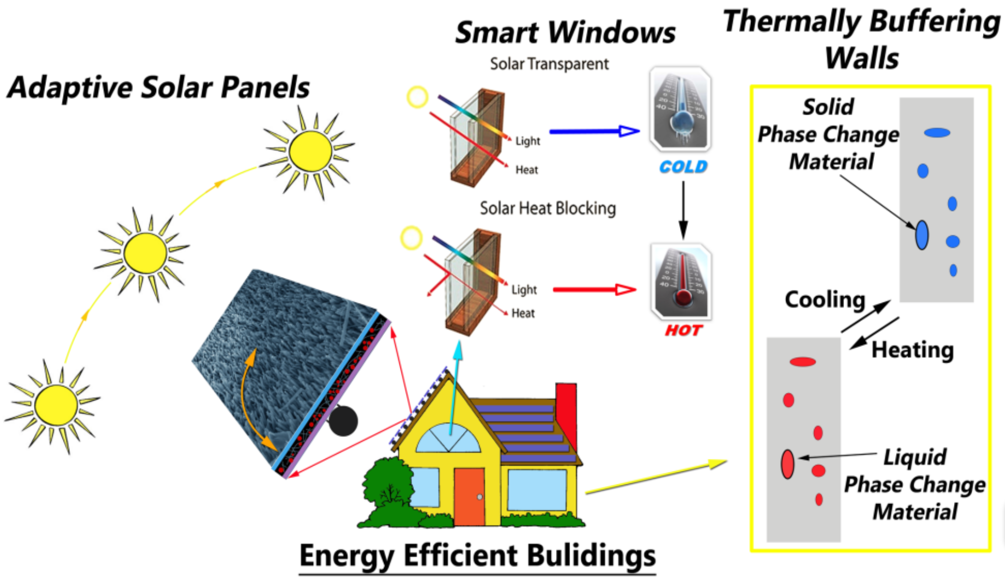


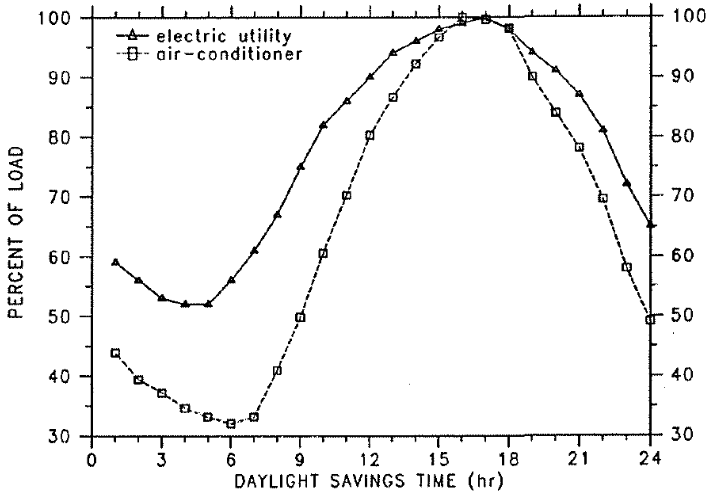
Granqvist, C. G.: Electrochromic Materials:Out of a Niche. *Nature Mater.* **2006**, *5*, 89-90.

Not just windows…

Nairobi, Ke

Buffering Heat Within Wallboards

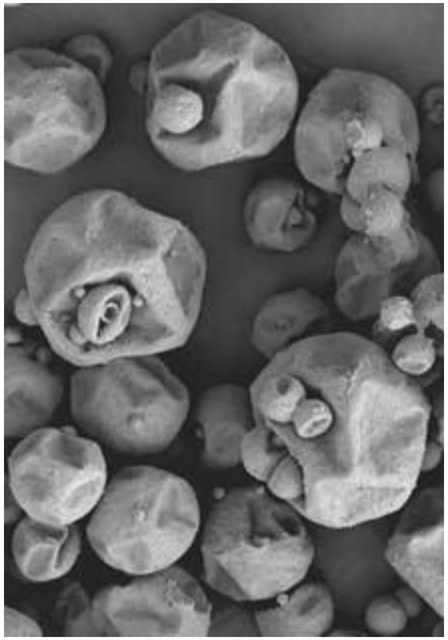


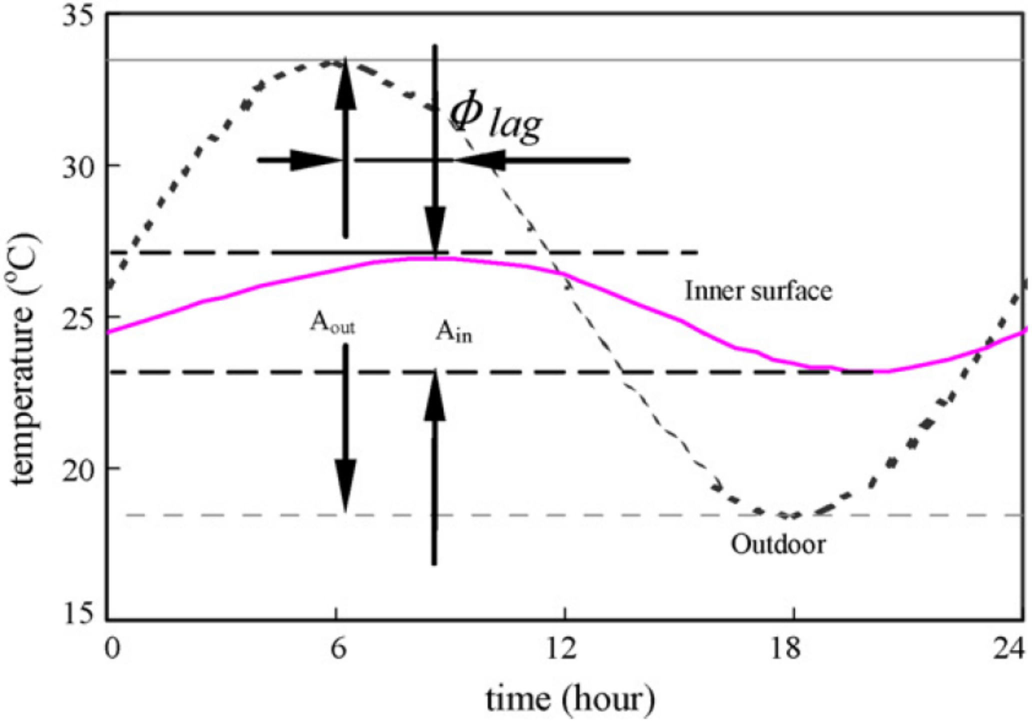


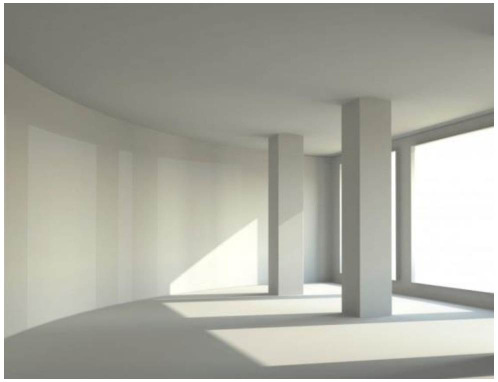
Average peak-summer-day load shape for Florida electric utility and average load shape of 58 residential central air conditioners.

Melting of paraffins or salt hydrates allows for storage of thermal energy within walls

Phase Lag and Modulation







Energy and Buildings 40 (2008) 1771–1779

Image: Acrylic microcapsules from BASF
Phase change drywall from Universidad Politécnica de Madrid

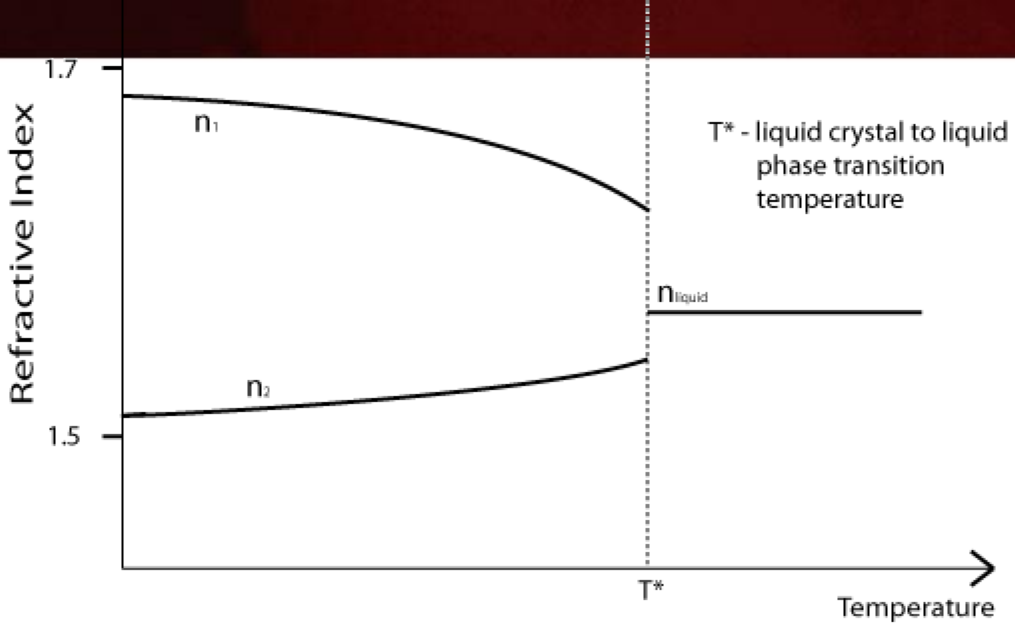
Conclusions

Designing responsive materials for building envelopes represents an underexplored opportunity: tremendous scope for phase-change materials (and for the scientists that like to play with them!)

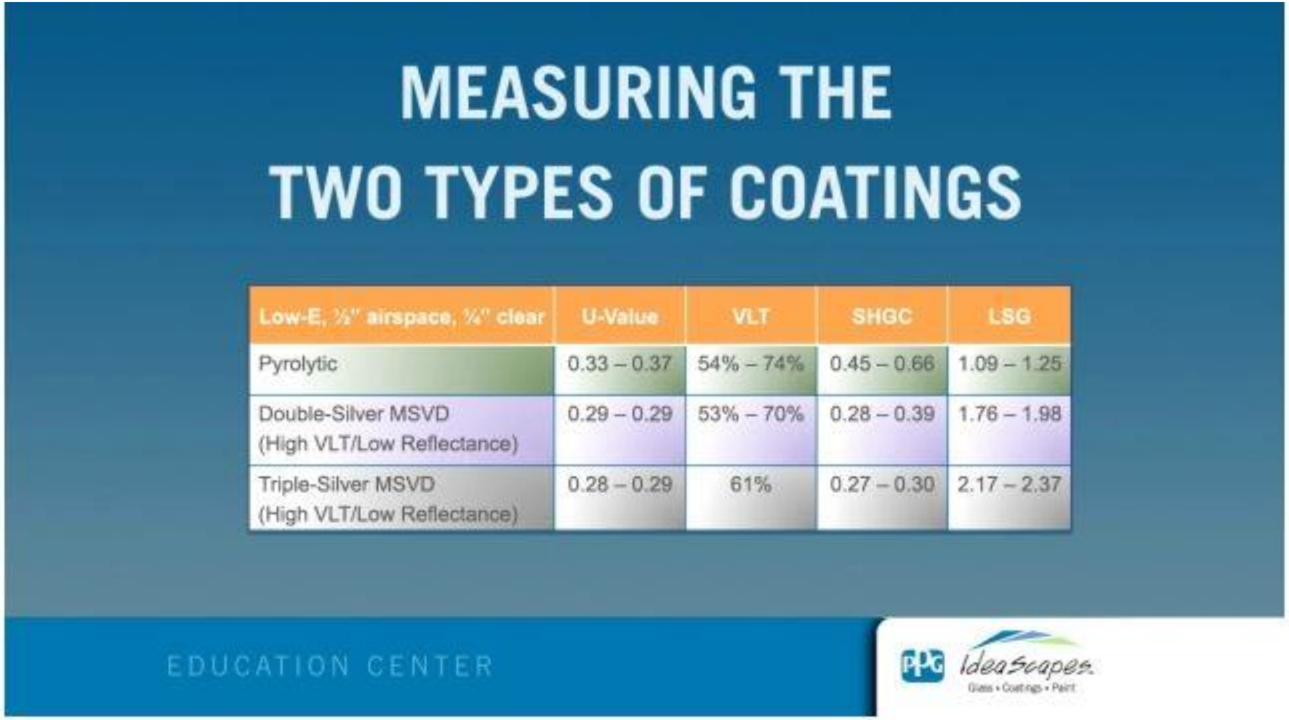
Advances required in materials development, stability, building integration, and accurate stochastic modeling

Stakes are tremendously high from both energy efficiency and climate change perspective!

Quanex building products
intel
NSF



T* - liquid crystal to liquid phase transition temperature



MEASURING THE TWO TYPES OF COATINGS

Low-E, ½" airspace, ¼" clear	U-Value	VLT	SHGC	LSG
Pyrolytic	0.33 – 0.37	54% – 74%	0.45 – 0.66	1.09 – 1.25
Double-Silver MSVD (High VLT/Low Reflectance)	0.29 – 0.29	53% – 70%	0.28 – 0.39	1.76 – 1.98
Triple-Silver MSVD (High VLT/Low Reflectance)	0.28 – 0.29	61%	0.27 – 0.30	2.17 – 2.37

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