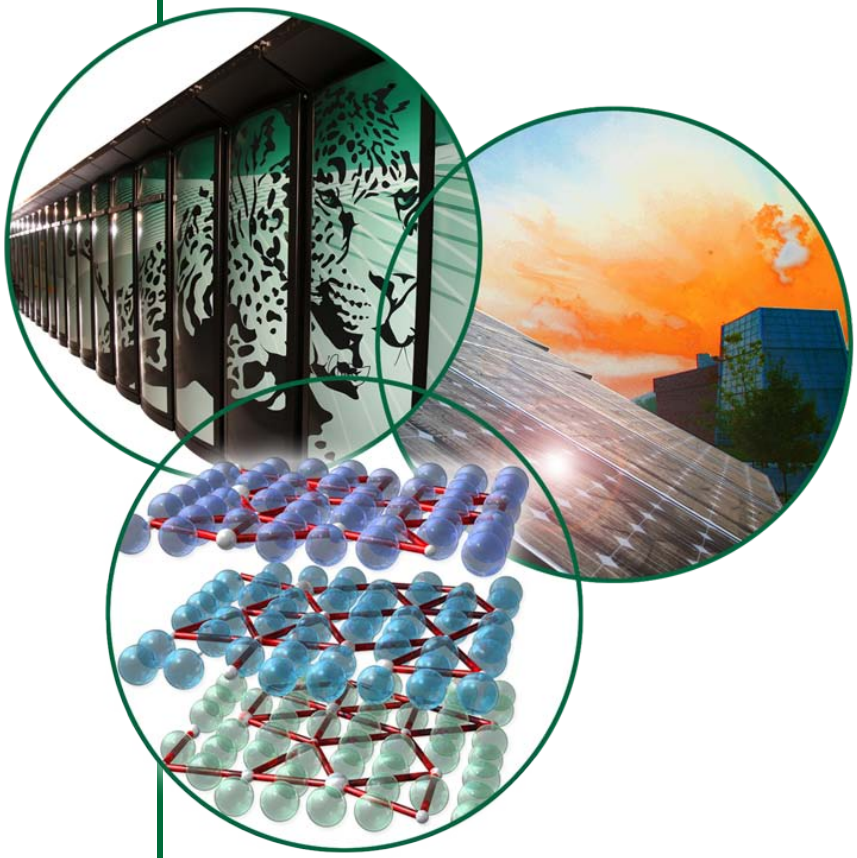
CNMS Theme Research: Multiscale Functionality of Nanostructures

Functional carbon, oxide and hybrid nanostructures



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MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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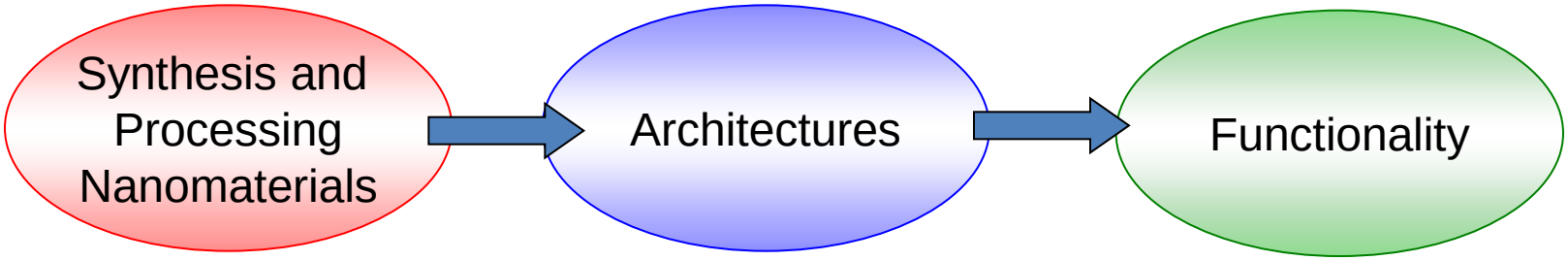
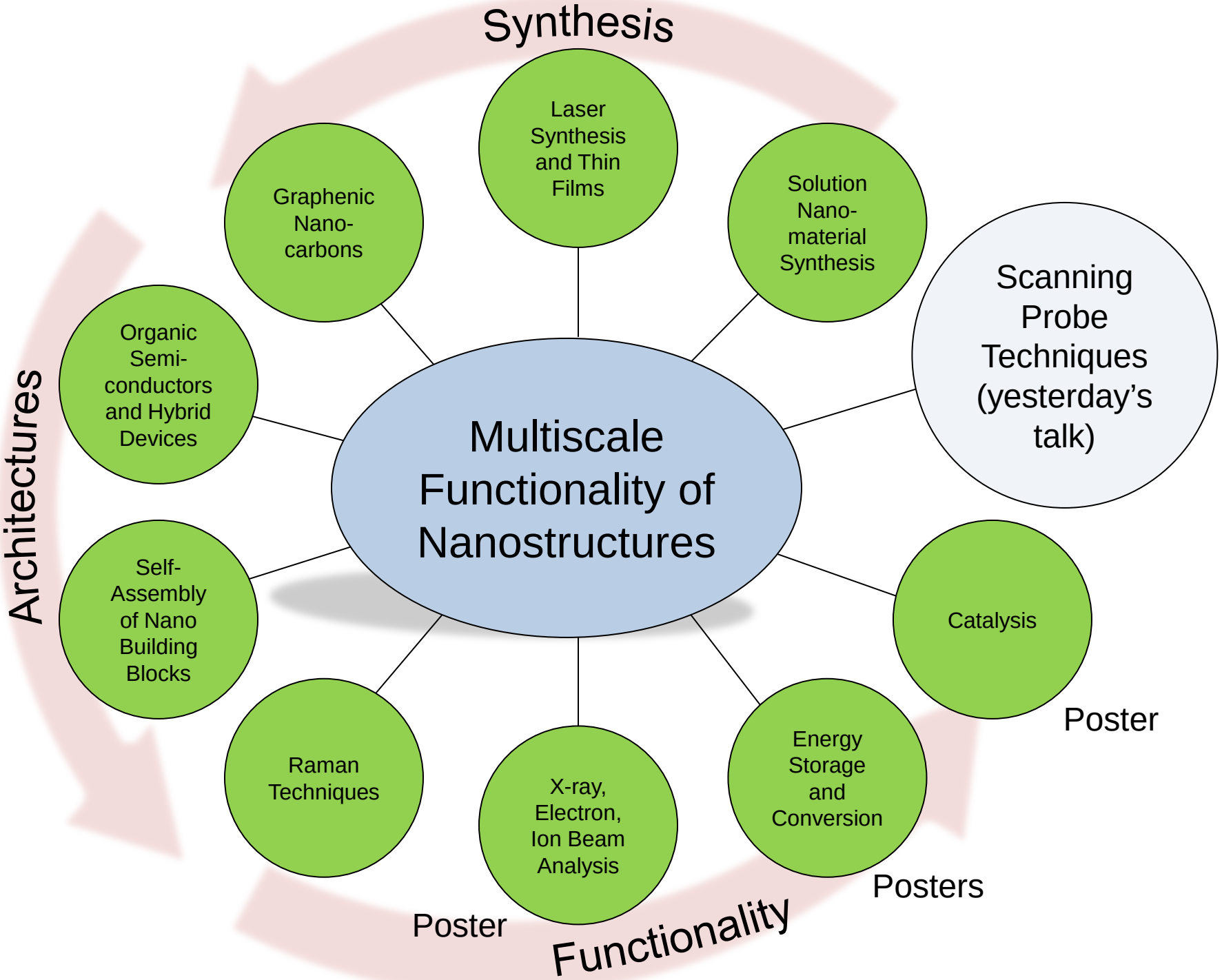
Multiscale Functionality of Nanostructures

Goal: to determine the key phenomena central to functionality at the atomic and molecular scale, at individual interfaces, and between nanoscale objects – then to extend that understanding to collective phenomena at much longer length and time scales.

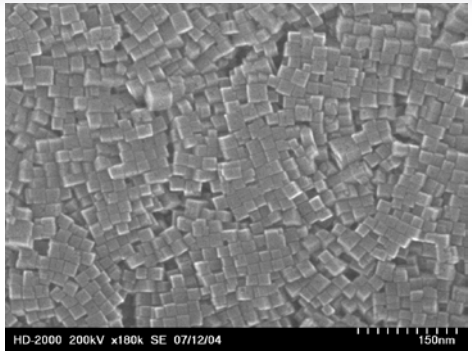
1. Synthesize and characterize nanomaterials and ***interfaces*** at the atomic and molecular scale in order to determine the origins of fundamental phenomena.
   - Nano-carbons, particles, thin-films, wires
2. Understand how ***architectures*** of nanostructures and their interfaces influence collective ***energy transfer*** phenomena to govern ***multiscale functionality***.
   - How percolating networks of nanotubes enhance the photovoltaic and electroluminescence of conducting polymers
   - How decorated edge sites in carbon networks enhance catalytic activity.




Synthesis
Laser Synthesis and Thin Films
Solution Nano-material Synthesis
Scanning Probe Techniques (yesterday's talk)
Catalysis
Poster
Energy Storage and Conversion
Posters
X-ray, Electron, Ion Beam Analysis
Poster
Raman Techniques
Self-Assembly of Nano Building Blocks
Organic Semi-conductors and Hybrid Devices
Graphenic Nano-carbons
Architectures
Multiscale Functionality of Nanostructures
Functionality

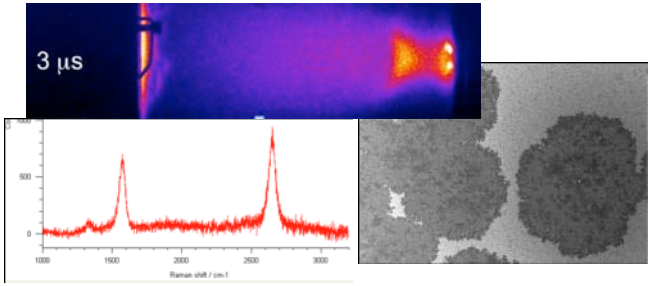
Synthesis
Nanoscale Building Blocks and Interfaces

1. Solution Chemistry – Nanoparticle synthesis using hydrothermal, solvothermal and traditional Schlenck techniques. Studying these processes in situ.

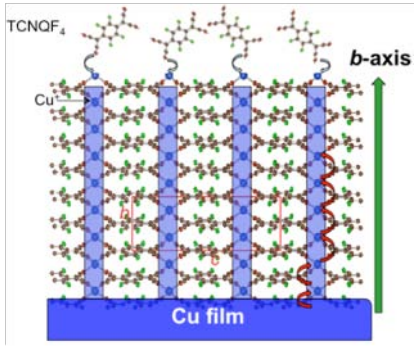


2. Laser and CVD growth with time-resolved in situ diagnostics – for well controlled interfaces in architectures.

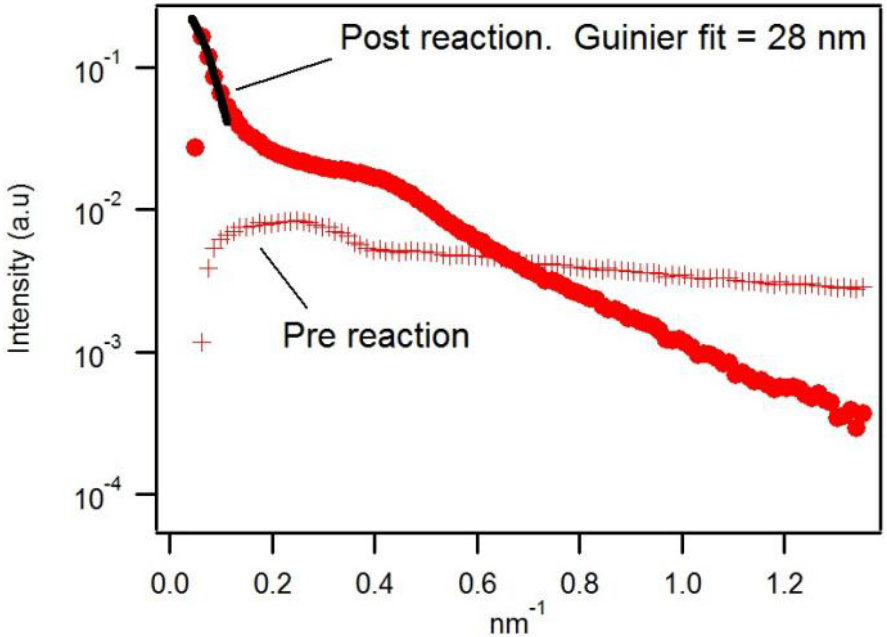
Pulsed CVD of graphene and carbon nanomaterials with laser diagnostics



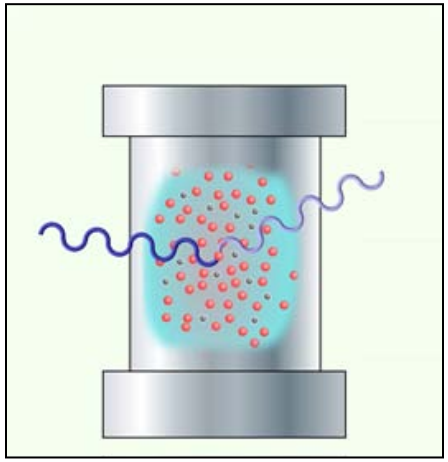
3. Self-assembly – Single crystalline metal-organic nanowires for core-shell donor/acceptor nanowires, hybrid-organic devices, sonospray deposition. How to control the orientation of these in ordered nanoscale morphologies for functional architectures (such as solar cells).



Understanding Solution Synthesis with in situ Scattering

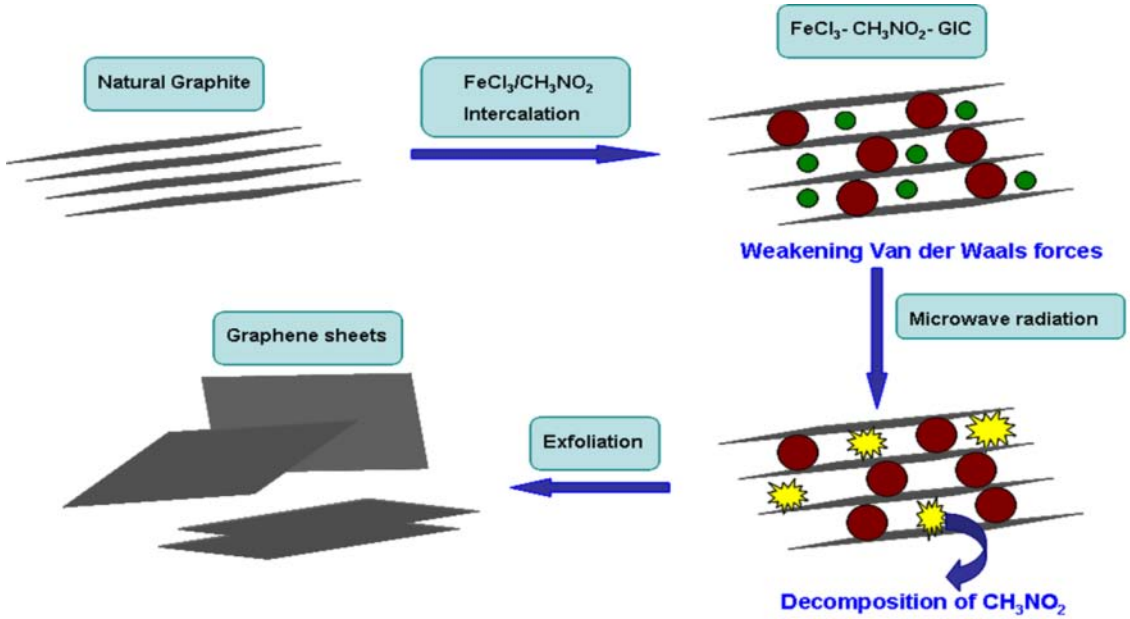


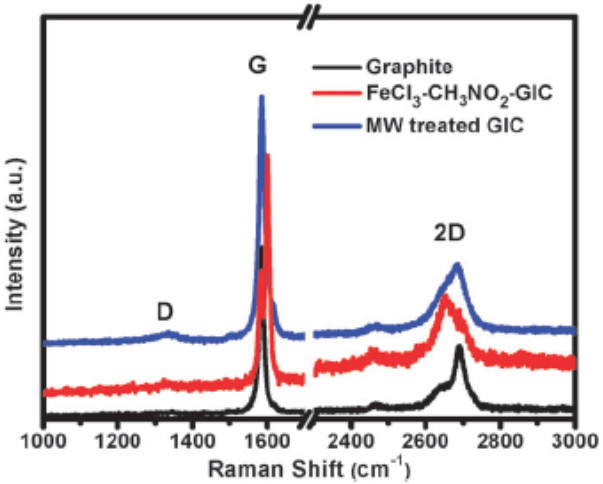
- Solution nanomaterial synthesis is typically Edisonian.
- Temperature and opacity preclude most spectroscopic techniques.
- Extended q-range instruments can probe multiple length scales to capture nucleation, growth and assembly. Size, shape, time resolution in minutes.
- Neutron or x-ray potential.



Low-Temperature Exfoliation of Graphene

- Approach:
  - Synthesis of graphene by intercalation and energetic exfoliation.
- Result:
  - Low T methods yields low defects and functional groups (low Raman D band)
  - Analysis of 2D Raman band suggests five graphene layers.
  - Demonstration of activity for isobutane ODH and correlation with the hybridization character of the carbon atoms.



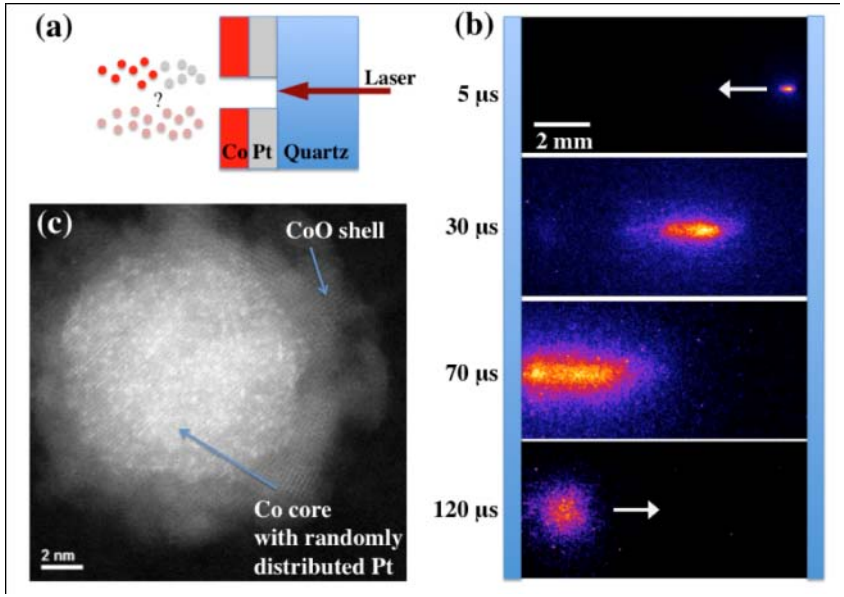


Wujun Fu, Jim Kiggans, Steven H. Overbury, Viviane Schwartz, Chengdu Liang,
Chem. Commun., **2011**, 47, 5265-5267

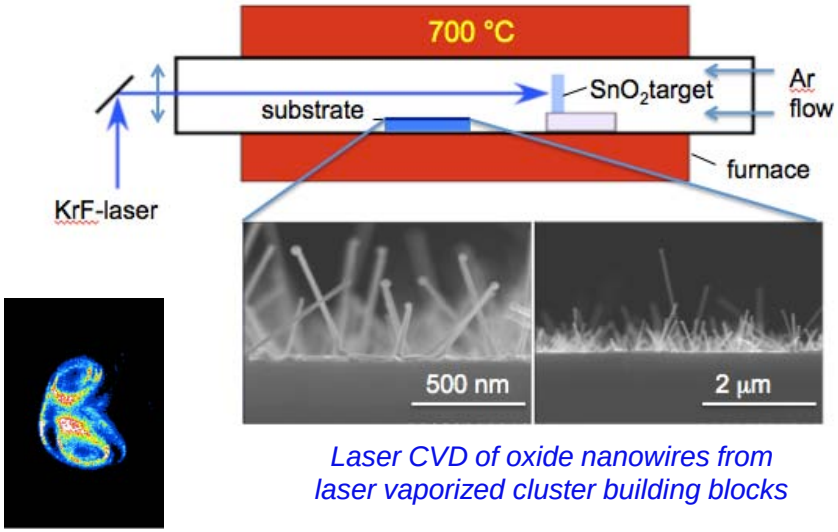
Laser synthesis of nanoparticle building blocks

- Ultrafast (40 fs) laser vaporization of layered thin films can synthesize new building blocks, such as CoPt nanoparticles with finely distributed Pt clusters. The extremely forward-directed packets of nanoparticles in vacuum and background gases are being explored for direct-write of nanoparticles in patterns and architectures.

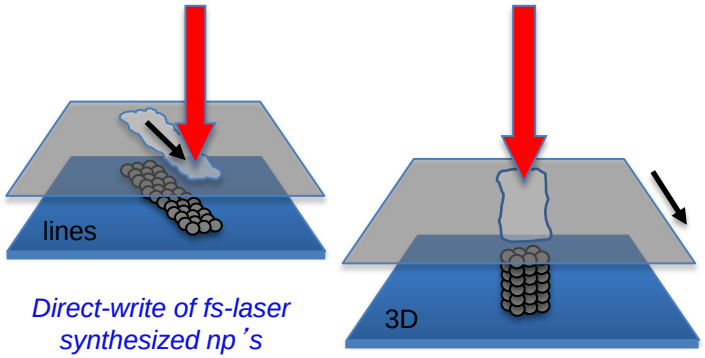
- The condensation and assembly of nanoparticles from laser-vaporized targets into nanowires is being explored.



Laser CVD of oxide nanowires from laser vaporized cluster building blocks



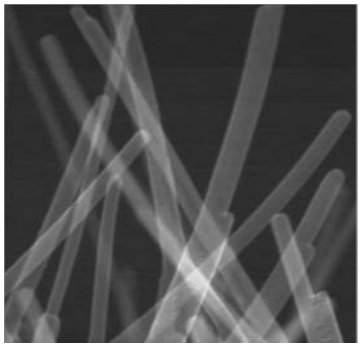
Laser CVD of oxide nanowires from laser vaporized cluster building blocks

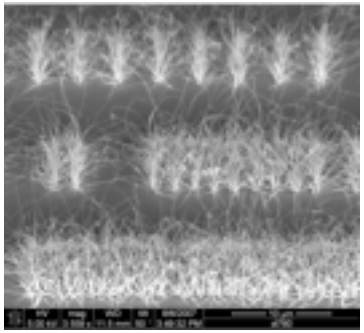


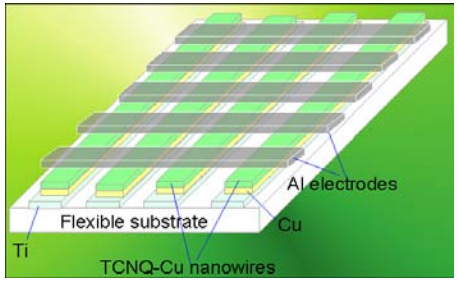
Direct-write of fs-laser synthesized np´s

Single-Crystalline Organic Nanowires – Unraveling their growth mechanism

Deterministic growth of organic crystalline nanowires using vapor-solid chemical reaction (VSCR) method



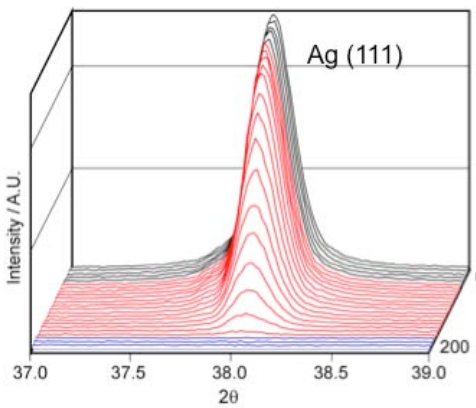


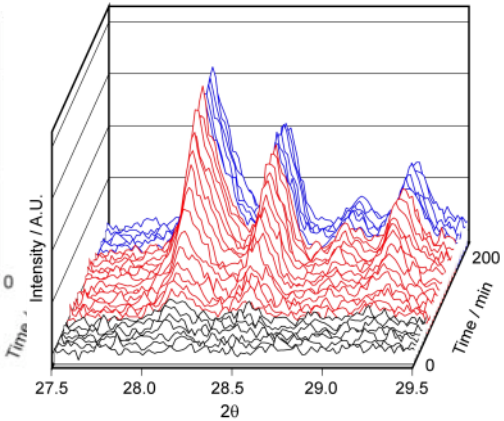


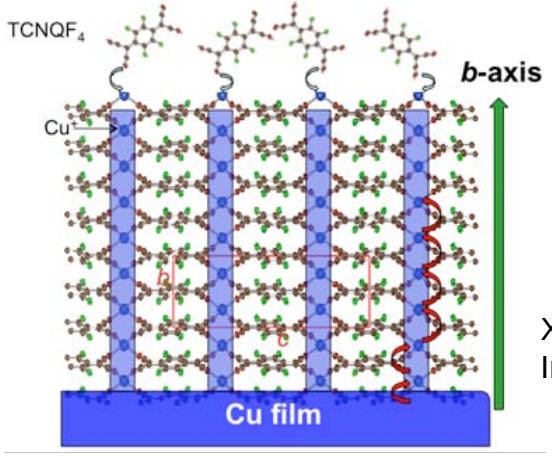
Flexible cross-point memory devices

Xiao, K.; et al. *Chemistry Materials,* **21**, 4275 (2009).
Xiao, K. et al *Angewandte Chemie International Edition,* **46,** 2650 (2007)

In-situ XRD: The new interfacial growth mechanisms- 1D ion diffusion tip growth





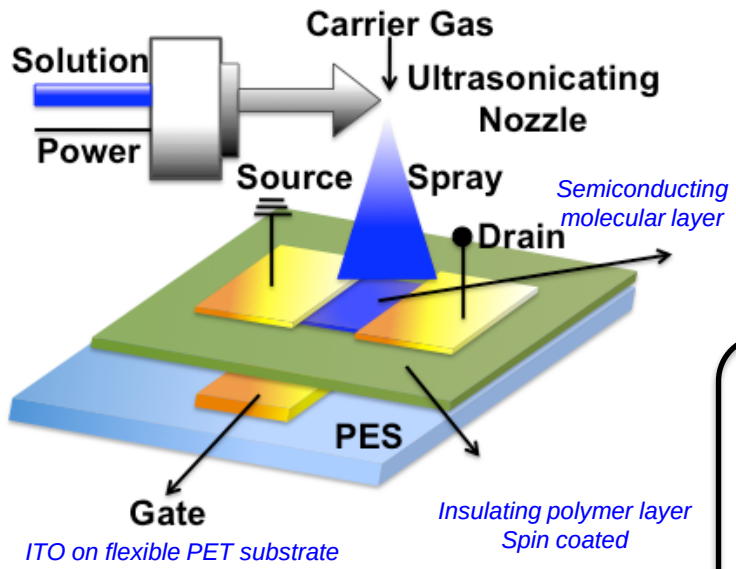


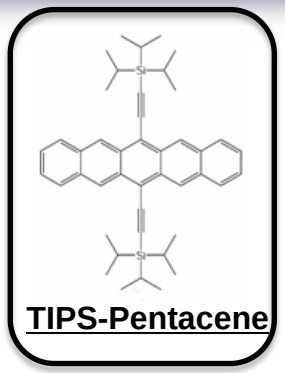
Xiao, K.; et al.
In preparation

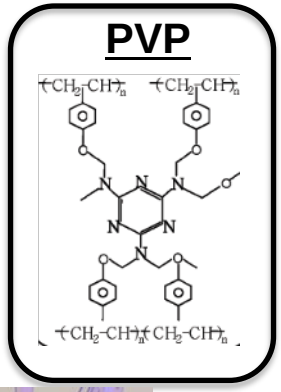
Fundamental understanding of how the metals direct small molecules to assemble into organic crystalline nanowires (CONs), and what determines the selectivity of a metal for an organic vapor reactant in the selective and deterministic growth of VSCR process is important for synthesis and functionality of novel optoelectronic nanomaterials

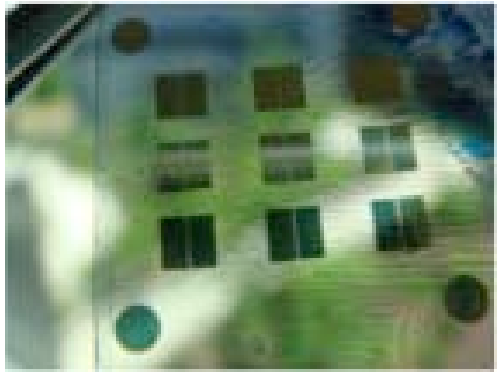
Flexible Organic Field-Effect Transistors by Spray Printing

- Sonospray deposition of organic molecules, nanoparticles, nanotubes, and quantum dots is being developed to develop hybrid organic electronic architectures.
- Flexible organic field effect transistors were demonstrated. (unpublished results).
- Spray printing may be potentially integrated with plastic electronic components.

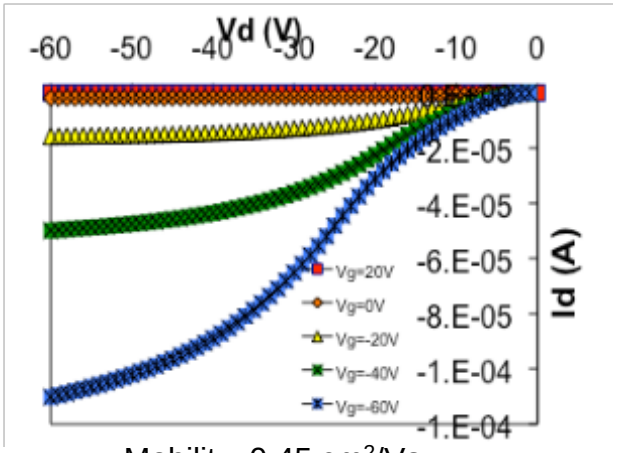




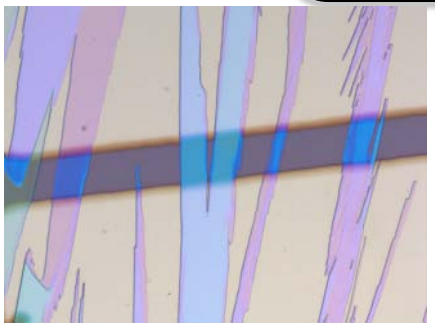




Printed, flexible organic thin film transistors



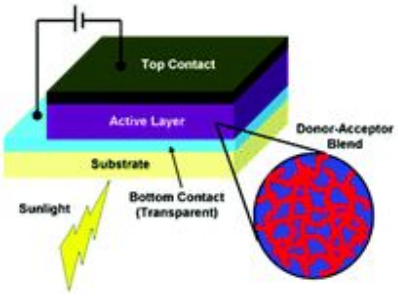
Mobility: 0.45 cm^2/Vs
On/off: 100

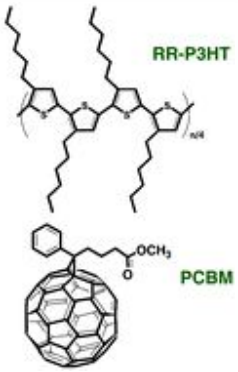


TIPS-Pentacene crystals on ITO gate

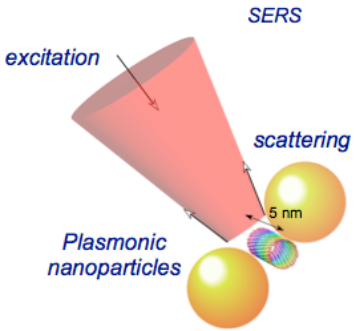
How Architectures Lead to Functionality

1. *Organic electronics*
   - *Architectures for photovoltaics*
   - *Understanding principles of molecular alignment at interfaces*

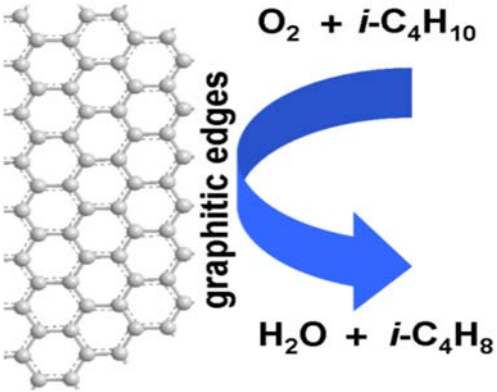




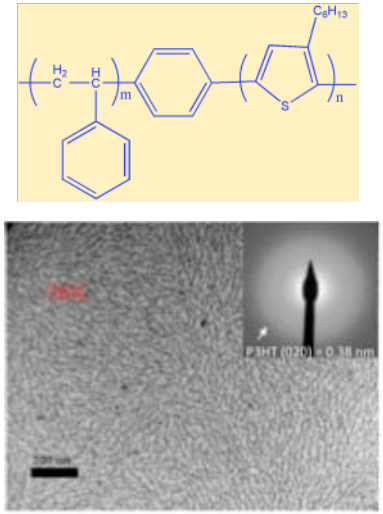
2. *Studying Interfacial Phenomena using Raman*
   - *Understand SERS enhancement*
   - *Monolayer characterization*



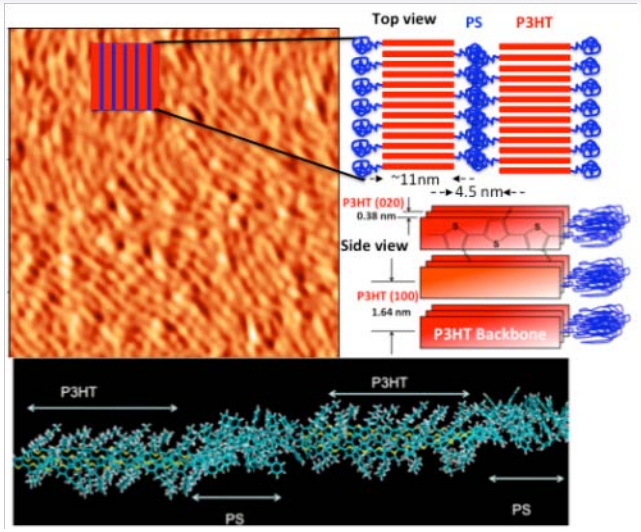
3. *Catalysis*
   - *Oxide-supported nanostructures*
   - *Carbon edge functionality*
   - *Structure-function relationship*



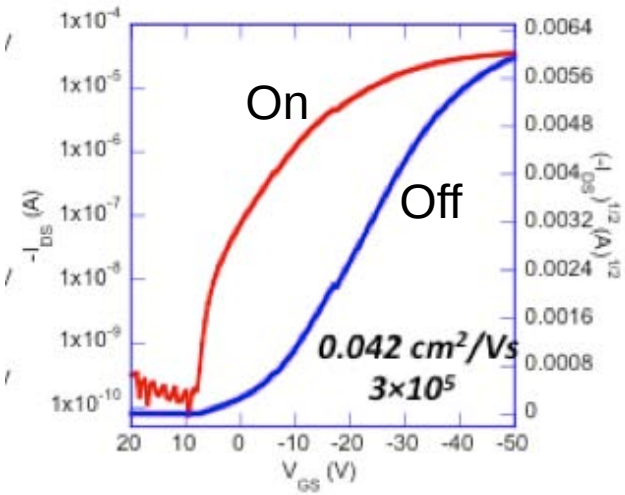
Using molecular self-assembly to improve the functionality of conjugated polymers



Molecular structure and TEM image of PS-*b*-P3HT block copolymer



Lamellar structure of self-assembled PS-*b*-P3HT copolymer



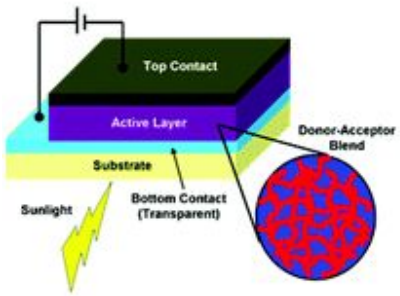
Field-effect mobility of PS-*b*-P3HT block copolymer

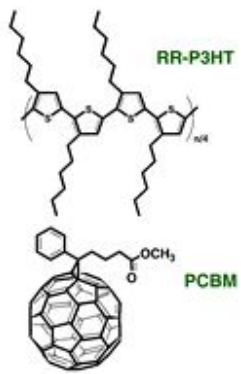
PS-b-P3HT diblock copolymers with different block ratios form different different nanoscale domain morphologies with different crystallinity and alignment to the substrate (e.g. π-π stacking), allowing improvements to the transport properties of the conjugated polymer and environmental stability – demonstrated OFETs with high ON/OFF ratio and good mobility.

Joint project across multiple groups and themes

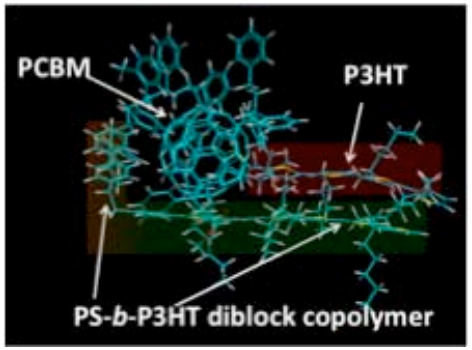
"High-Performance Field-Effect Transistors Based on Polystyrene-b-Poly(3-hexylthiophene) Diblock Copolymers,"
Yu, X.; Xiao, K.; Chen, J.; Lavrik, N. V.; Hong, K.; Sumpter, B.G.; Geohegan, D. B., *ACS Nano*, 2011, 5, 3559.

Controlling molecular ordering, morphology and phase-separation through addition of the ternary phase



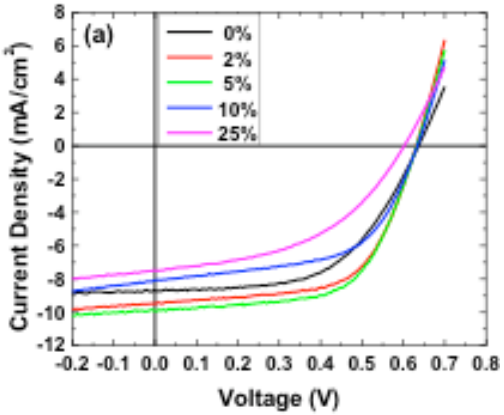


AFM image of a well-ordered polymer blend film



QDFT calculation: copolymer acts like plasticizer by diffusing to the P3HT/PCBM interface

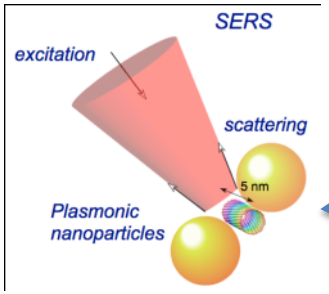
- OPV power conversion efficiency was enhanced from 3% to 4.2% by adding 5% copolymer as compatibilizer.
- Molecular ordering, orientation and crystallinity of polymer blend were improved with 5% copolymers, evidenced by AFM, GISAXS.
- Neutron Reflectivity data demonstrates the buried interfacial structure in blend film - the addition of 5% copolymer drive PCBM to the film surface.

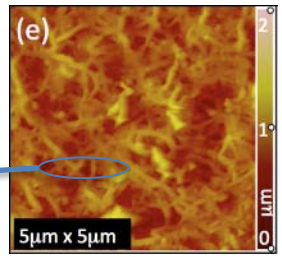


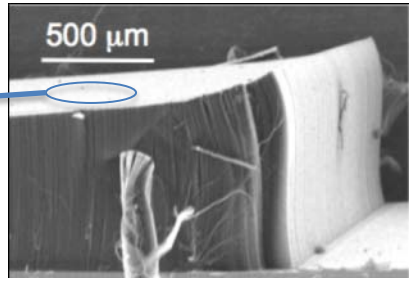
Device Performance of polymer PVs

Z. Sun, K. Xiao, X. Yu, K. Hong, J. K. Keum, I. Ivanov, J. Chen, D. Li, B. Sumpter, A. Payzant, C. Rouleau, D. Geohegan , **"PS-*b*-P3HT Copolymers as P3HT/PCBM Interfacial Compatibilizers for High Efficiency Photovoltaics**", 2011, *submitted*

Discovery of Low-Frequency Resonances in SERS spectra of Single Wall Carbon Nanotubes

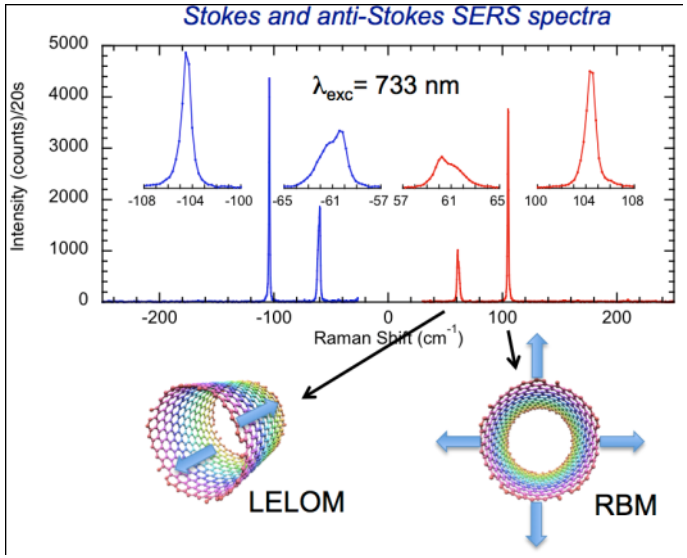






- Gold deposited atop nanotube array formed a unique SERS matrix exhibiting distinct hot spots. Where do they come from?

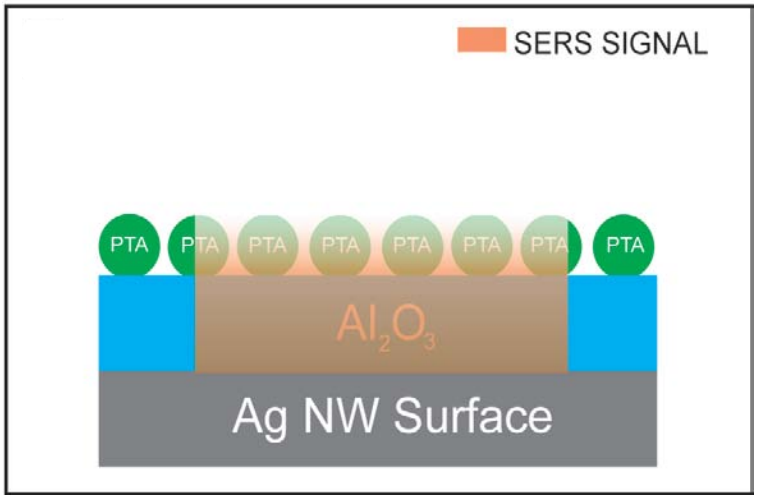
- Narrow and intense Raman scattering resonances - *10 times narrower than previously measured* - arise from small, defect-free regions of individual SWNTs
- Permitting first exploration of Raman spectra in the very low frequency region (10-100 cm^{-1}) of nanotubes.
- Radial breathing modes (RBMs) of large-diameter nanotubes, weak ring modes (RMs), and low-energy longitudinal optical modes (LELOMs) were observed.
- RBM's of large-diameter SWNTs were studied for the first time.



Narrow and intense resonances in the low-frequency region of surface-enhanced Raman spectra of single-wall carbon nanotubes
A. A. Puretzky, D. B. Geohegan, C. M. Rouleau, *Phys. Rev. B* **82**, 245402 (2010)

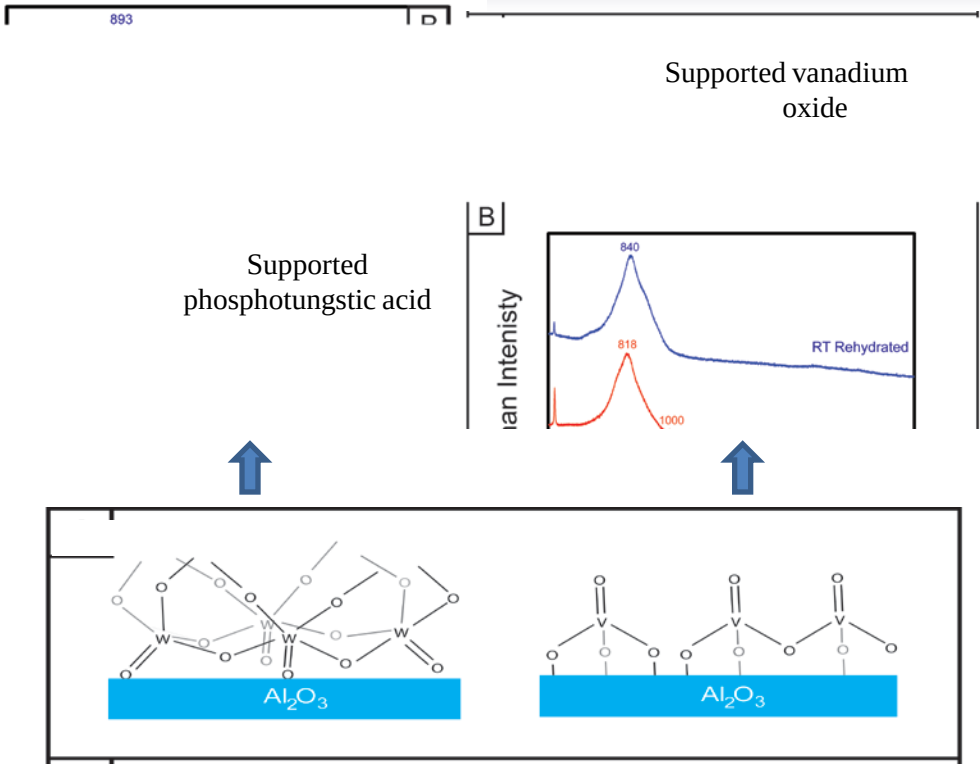
In situ SERS for Catalysis

Illustration of SERS substrate as catalyst support



SEM image of SERS substrate

High temp SERS of catalysts



Significance:

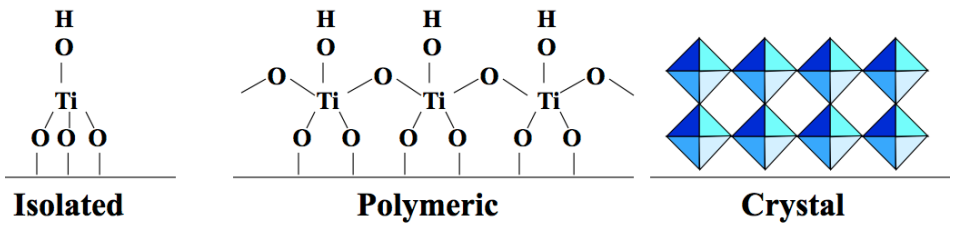
- Thermally robust SERS substrate
- First SERS study of catalyst structure
- Selective detection of interface structure that is catalytically active center

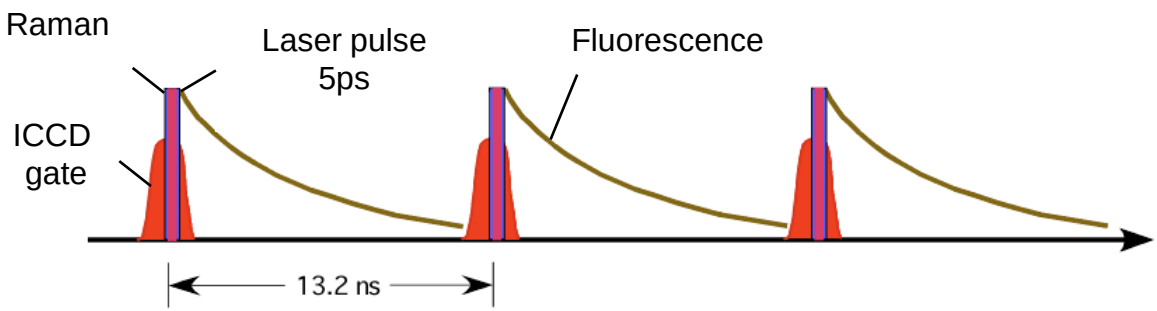
Formo, Wu, Dai, J. Phys. Chem. C, 2011, 115, 9068

2. Energy Transfer at Interfaces –*In situ* photoluminescence and Raman spectroscopy

Understanding functional properties and growth mechanisms of nanostructures using in situ optical diagnostics

TiO_2 domains





Examples:

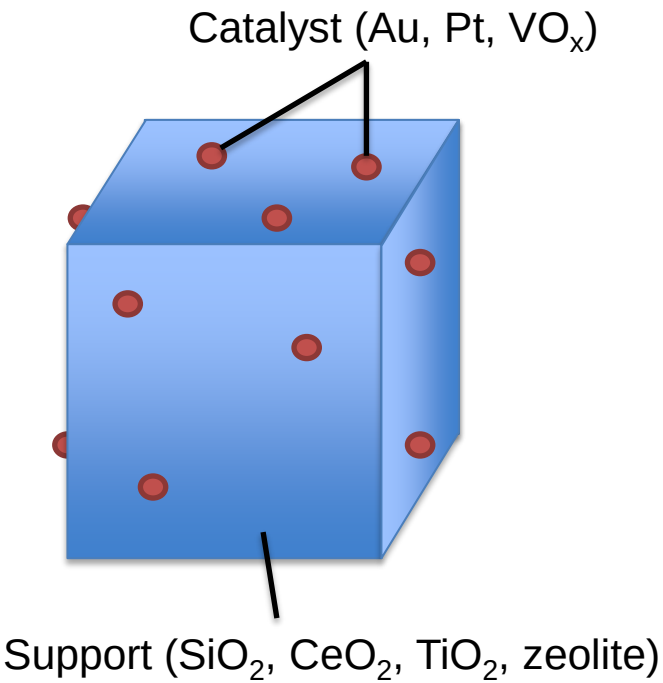
- *In situ* photoluminescence lifetime measurements of well defined TiO_2 domains on SiO_2 support
  - correlation with water splitting efficiency.
  - the isolated TiO_4 sites - most active for photocatalysis.
  - direct relationship between slow PL lifetime, electron-hole recombination time, and high photocatalytic activity.
  - beneficial for future studies of the rational design of novel photocatalyts for H_2O splitting.

C. A. Roberts, A. A. Puretzky, S. P. Phivilay, I. E. Wachs

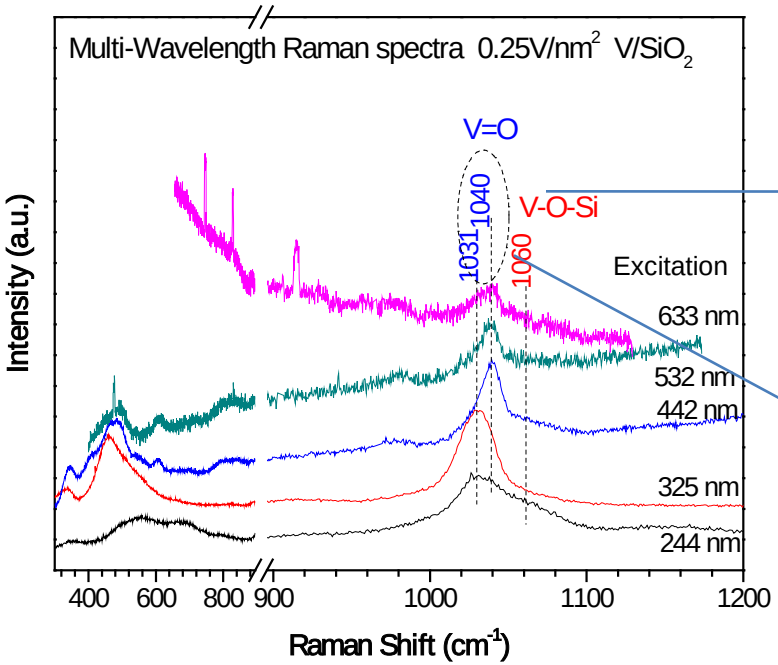
Nanostructured oxide catalysts

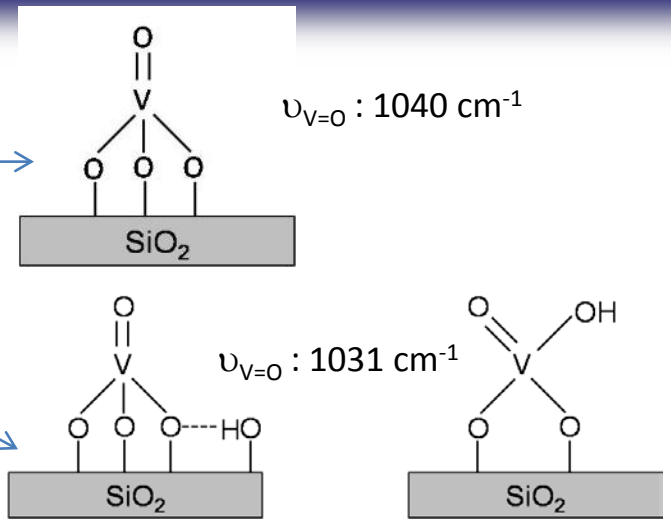
Large class of supported nano-catalysts

- Metal or oxide cluster of active material, supported by a more inert oxide.
- Nano-dimension provides activity that doesn't exist in bulk, and support provides separation, mechanical integrity and sometimes reactants like oxygen.
- What is the molecular structure of surface metal oxide clusters and how do they function under reaction conditions?
- What is the nature of the catalyst-support interaction and how does the support impact catalysis?

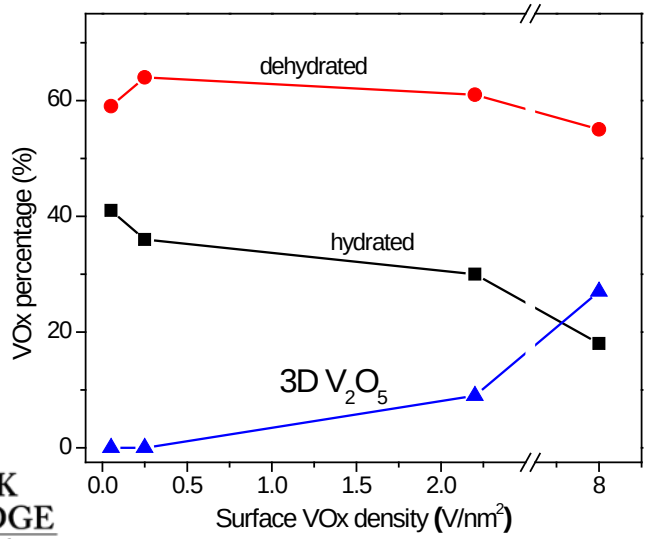


Structural identification of supported vanadium oxide clusters





- Identification and distribution of various oxide clusters by multi-excitations.
- Resonance enhancement facilitates assignments
- Overtone analysis provide bond strengths

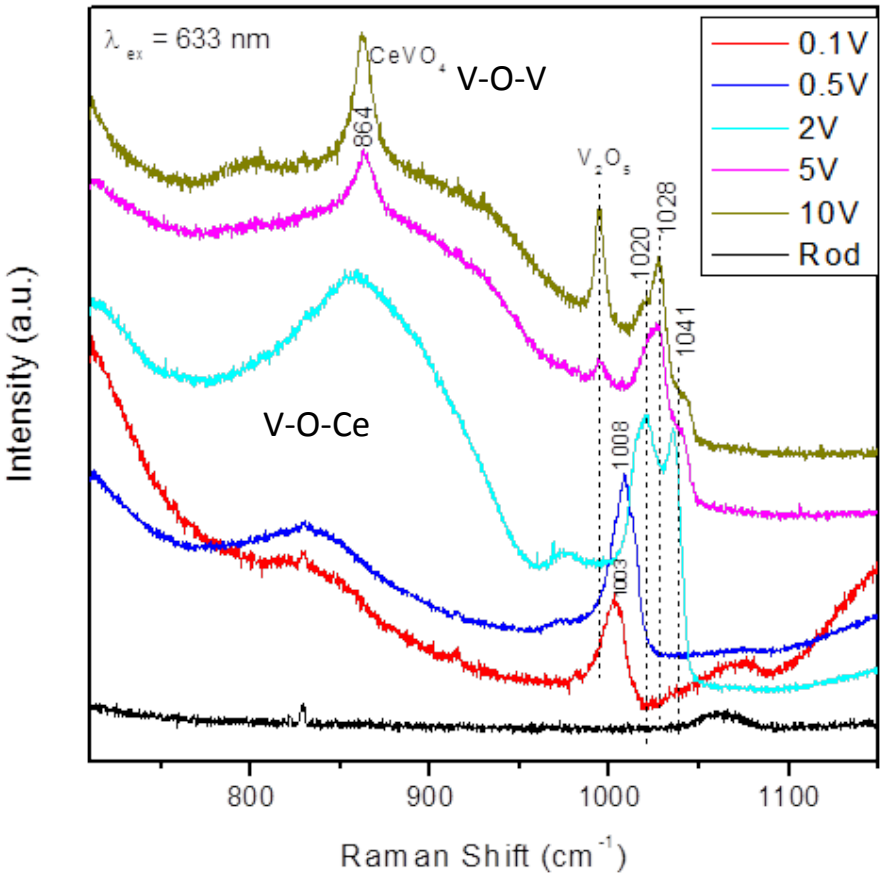


Multi-wavelength excitation Raman differentiates hydrated and dehydrated VO_x

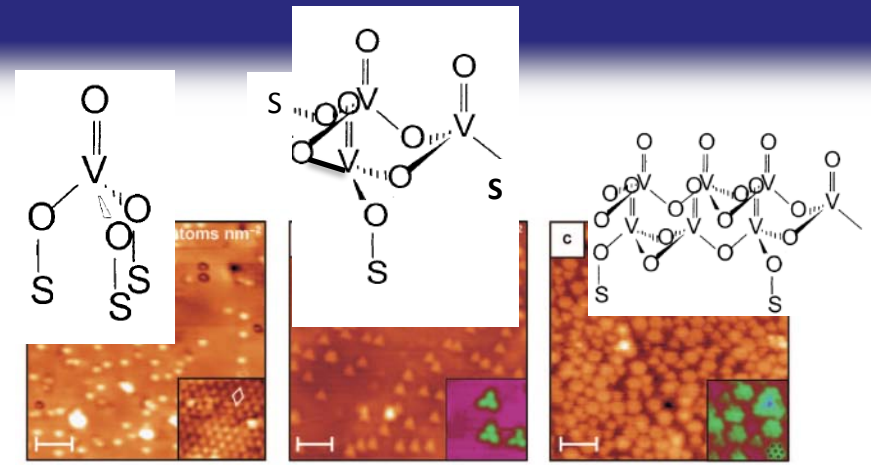
Wu, Dai, Overbury, J. Phys. Chem. C, 2010, 114, 412.

Structural identification of supported metal oxide clusters – VO_x/CeO_2

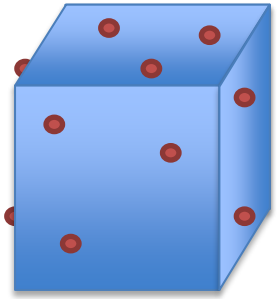
Dehydrated VOx/CeO_2-rods

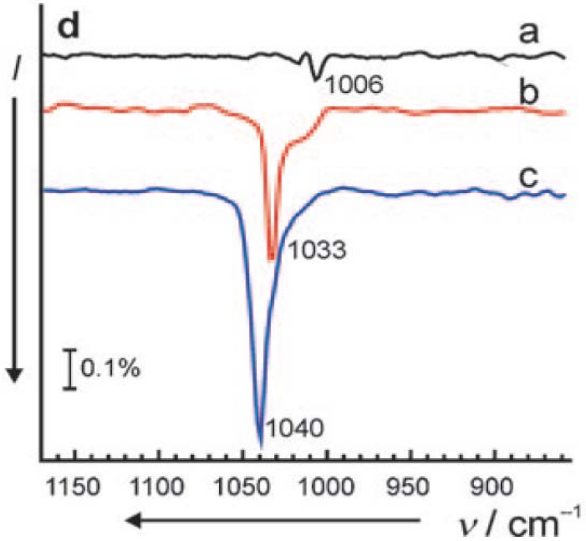


Wu, etc., J. Phys. Chem. C, 2011, submitted



Baron *et al.*, *Angew Chem 2009, 48, 8006*



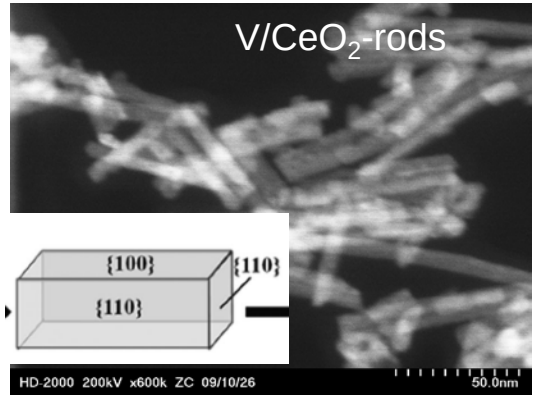


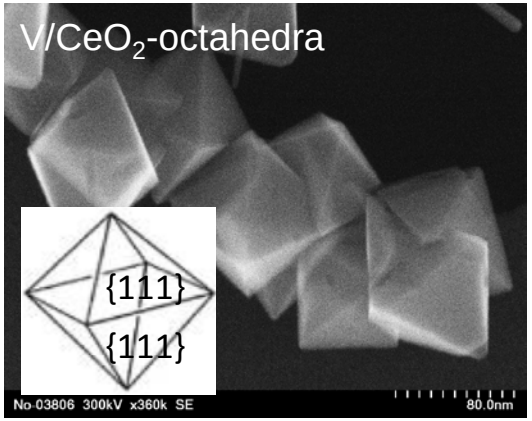
First detailed structure evolution information on real catalyst:

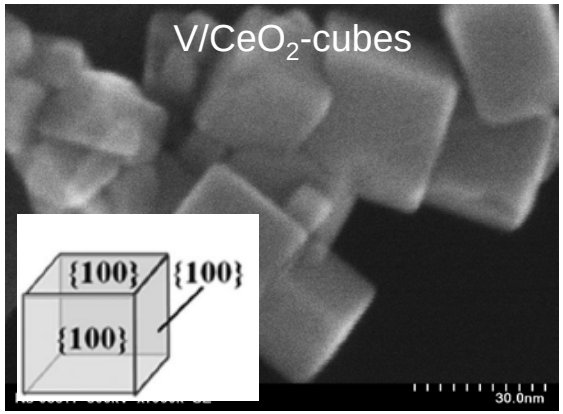
monomer → dimer, trimer → polymer → V_2O_5, $CeVO_4$

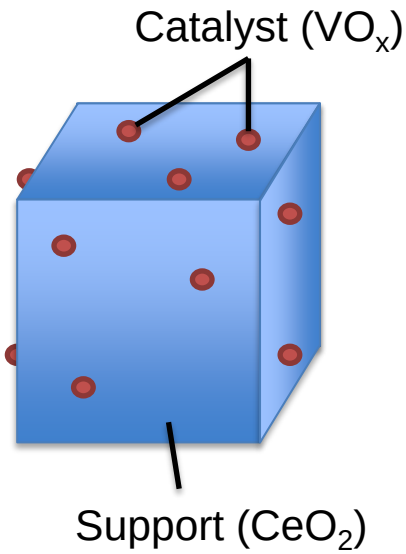
Support effect in metal oxide catalysis: crystal plane effect

-What is the relationship between the structure of supported oxide clusters and their catalytic properties?





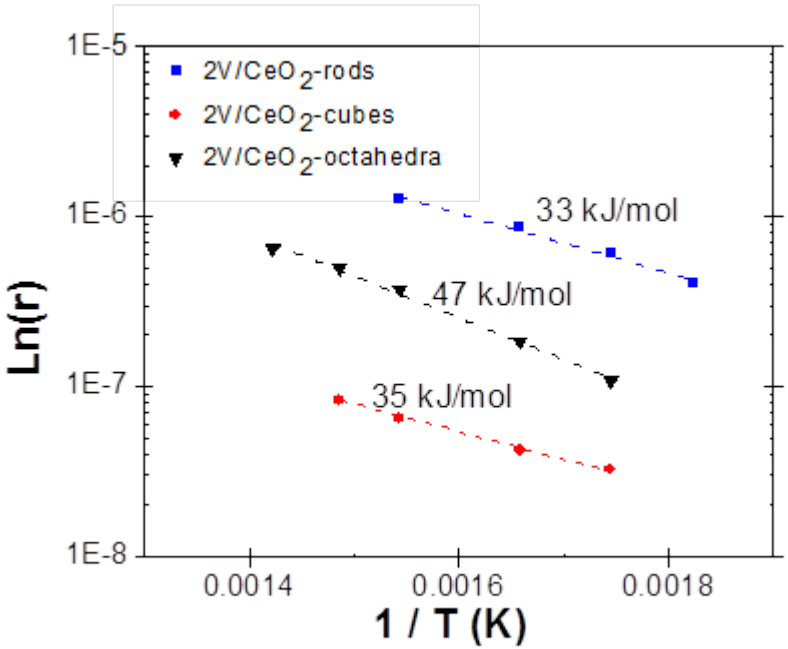


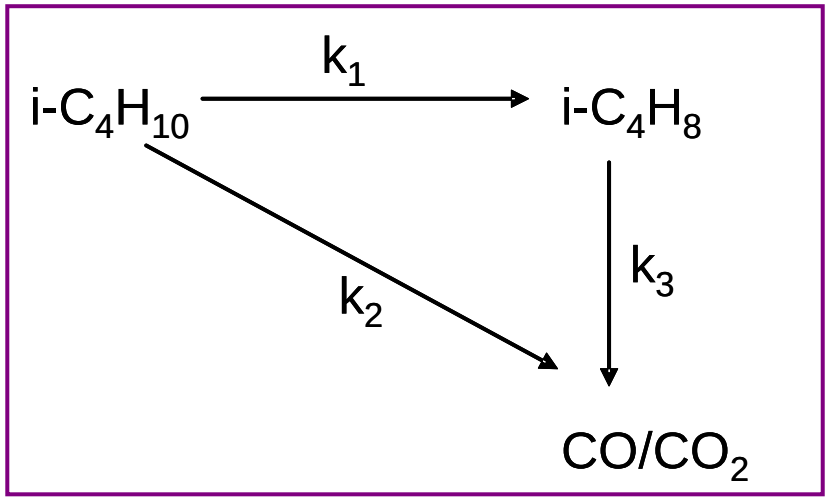


- *Ordinarily, we think of nanomaterials as the active material. Here, we utilize a nanomaterial's high surface area and directed expression of one crystal face as a tool to study a broader effect.*

Wu, Schwartz, Overbury, 2011, to be submitted

Support effect in metal oxide catalysis: crystal plane effect





Catalyst	Ea (kJ/mol)	Selectivity, % at 320°C $i\text{-}C_4H_8$
2V on NPs	68	19.1
5V on NPs	70	12.7
10V on NPs	86	18.5
2V on rods	48	79.7
5V on rods	56	66.3
10V on rods	58	77.9

Theoretical Activation energy:

- $2V/CeO_2$-rods $\leq$ $2V/CeO_2$-cubes < $2V/CeO_2$-octs,
- Catalysis performance correlates to surface oxygen vacancy formation energy of ceria nanocrystals.

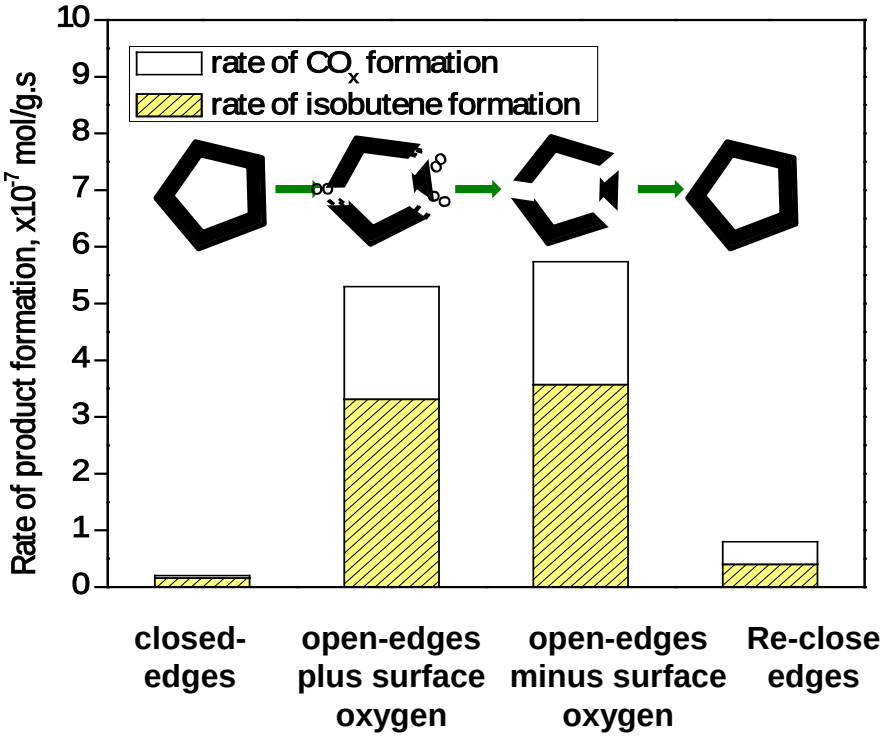
Support surface oxygen also participates in catalysis.

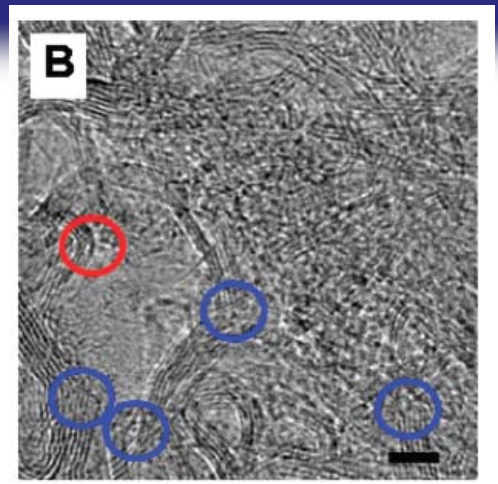
J. Phys. Chem. C, 2010, 114, 412-422

Oak Ridge National Laboratory
CNMS Center for Nanophase Materials Sciences

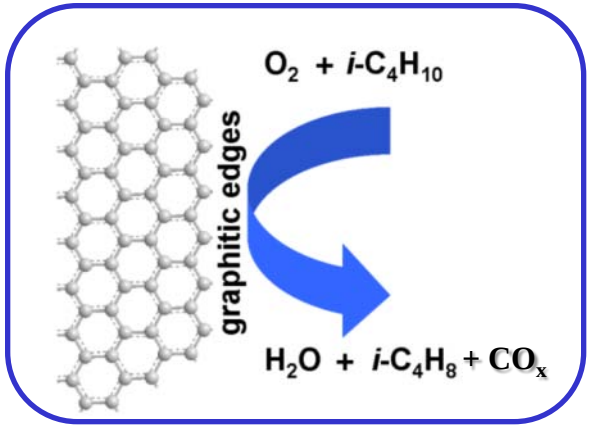
Carbons as Catalysts

- Graphitic carbons are catalytically active
- Negligible activity if no open-edge sites; high activity for catalysts with open-edge sites
- No significant differences were found when surface oxygen groups were created on the carbons





synthesis of graphitic mesoporous carbon with cages that can be opened and closed

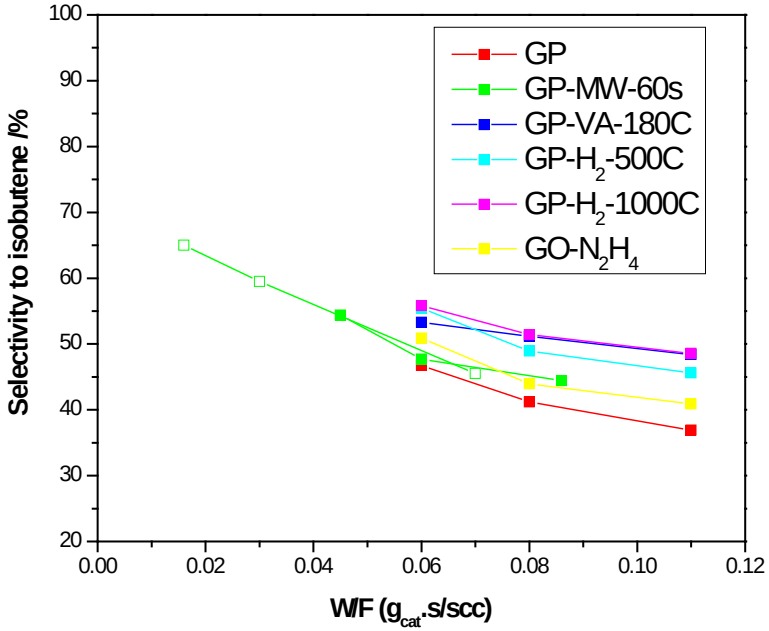


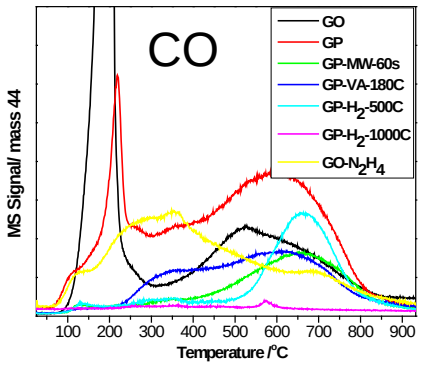
Open-edge sites are the active sites

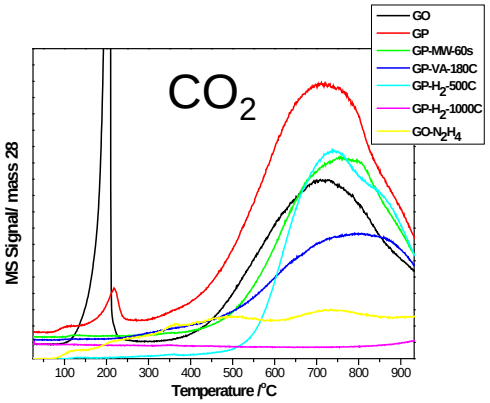
Liang et al. J. Am. Chem. Soc. **2009,** 131,*7735.*

Effect of oxygen functional groups

- Distinguish oxygen types from TPD of CO and CO_2
- Selectivity and reactivity little affected and not correlated with O functionality





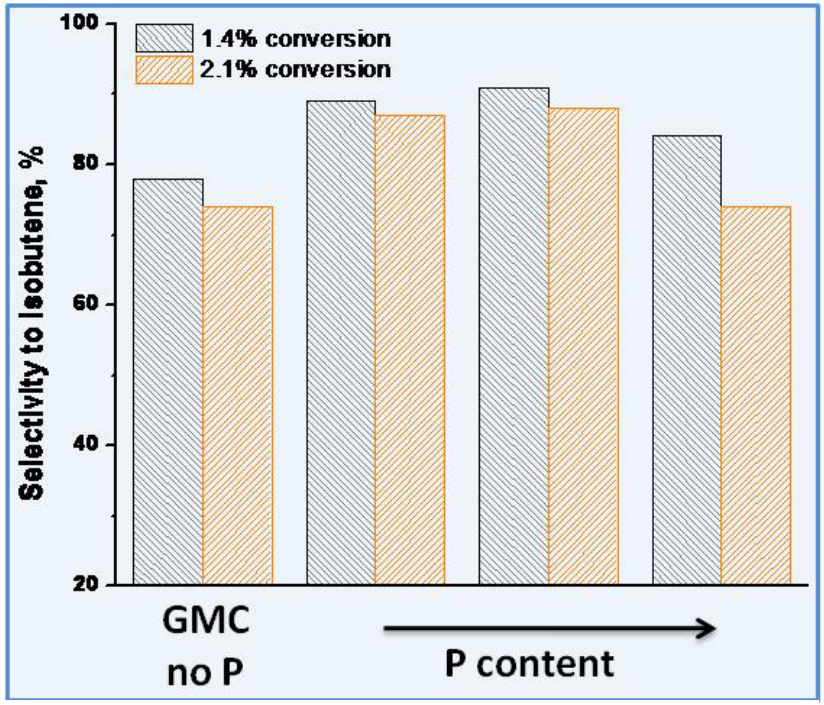


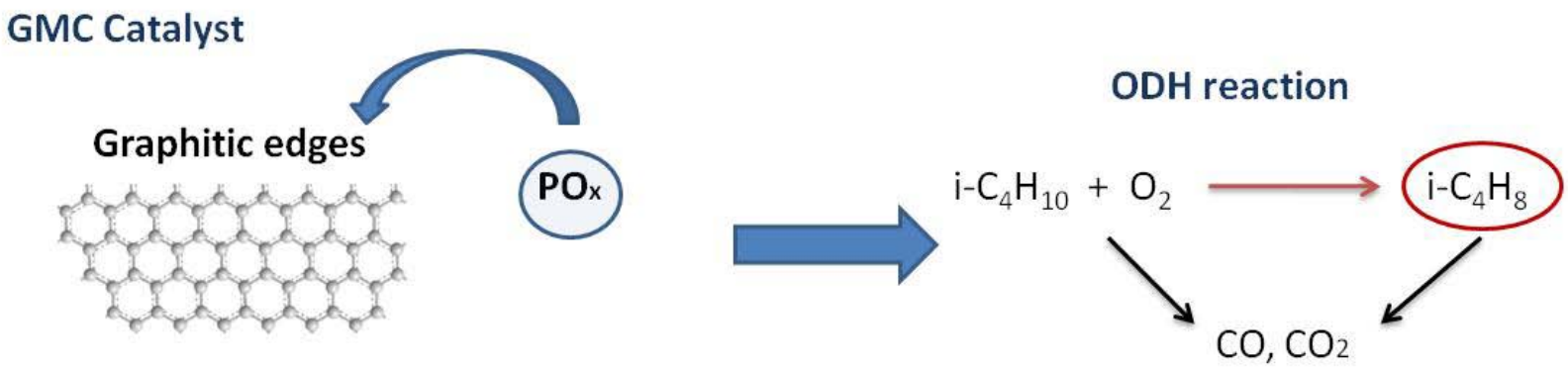
Catalyst	amount of O (μmoles/g)			
	CHNOS	XPS	TPD	TPD (area after 400C)
GO	29836	36291	28003	6742
GP	12212	17644	16254	13245
GP-MW-60s	8546	10550	10405	9392
GP-VA-180C	10089	10169	8855	7559
GP-H_2-500C	7228	13398	10381	9530
GP-H_2-1000C	267	1489	159	159
GO-N_2H_4	6150	5899	8776	5926

Surface oxygen (e.g. quinones) play little role in conversion of i-butane to i-butene

Effect of phosphorous functional groups

- Approach:
  - Modification of oxygen functional groups on graphitic mesoporous carbon by reaction with variable amounts of phosphoric acid in order to understand effect on selectivity
- Scientific result:
  - P-doping blocks the undesired direct combustion pathway, but the selectivity is concentration dependent pointing to an optimum amount of P-groups addition.

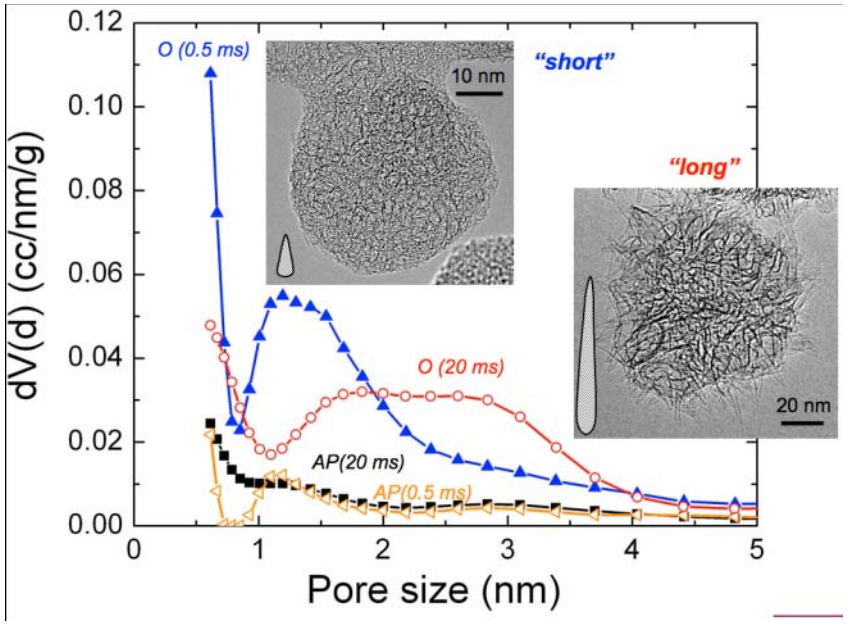


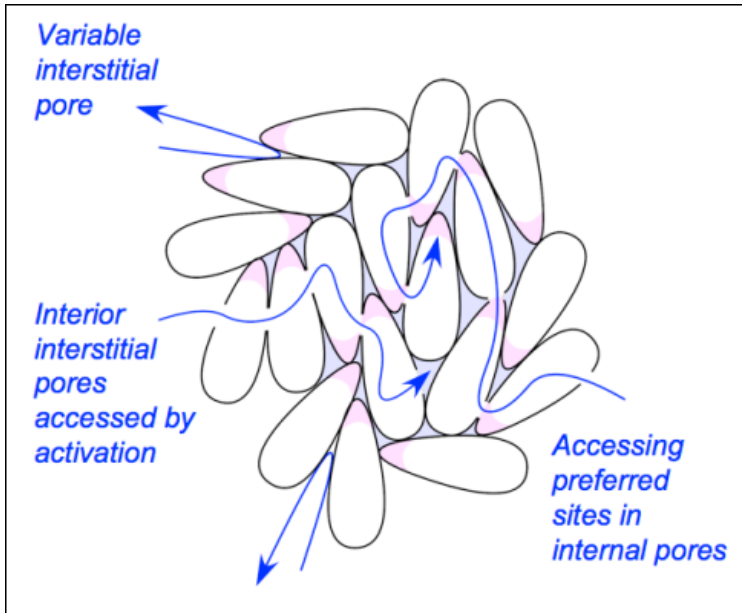


Schwartz et al.; Oxidative Dehydrogenation of Isobutane on Phosphorous-Modified Graphitic Mesoporous Carbon, *Carbon* **2010,** *49*, 659-668.

Single-wall carbon nanohorns – Self-assembled graphene architectures for carbon catalysis

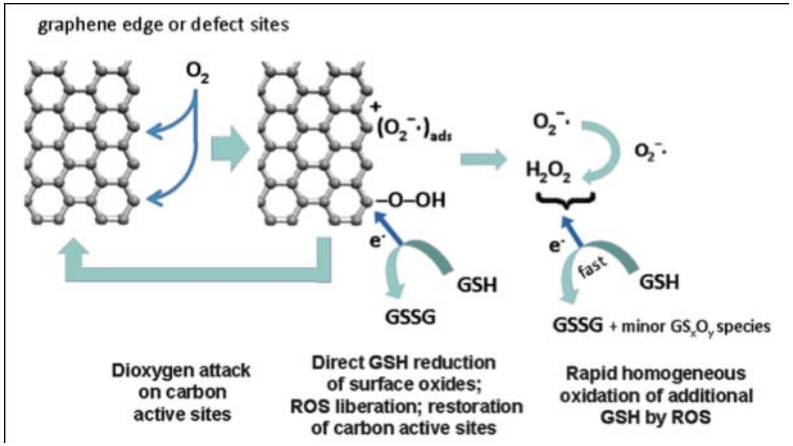
- SWNHs are formed by laser vaporization of pure carbon, and form high surface area porous architectures.
- The individual nanohorns form tightly-bound, spherical aggregates where their internal and interstitial pore size is tunable during synthesis and post-processing
- The synthesis process is being studied, as it is akin to substrateless graphene growth. The functionality of the doped and decorated nanomaterials are being explored for fuel cell applications, hydrogen storage, or biological imaging.

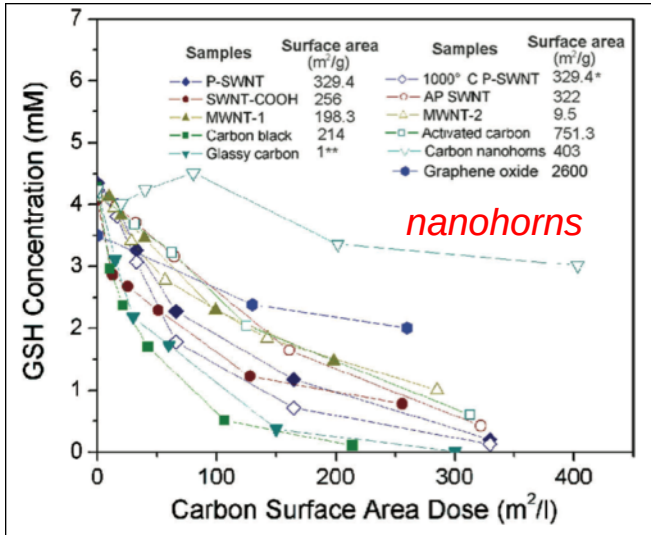




Antioxidant Deactivation on Graphenic Nanocarbon Surfaces

- What function do carbon nanomaterials play in nanotoxicity?
- They deplete antioxidants. How?
- Using well-characterized nanomaterials (SWNTs, MWNTs, graphene, carbon nanohorns), it appears that carbon nanomaterial edges react with oxygen molecules to produce reactive surface-bound oxygen intermediates (shown) and free reactive oxygen species (such as O_2^- and H_2O_2) which deplete key physiological antioxidants (here glutathione, GSH) by producing oxidized byproducts (here, the oxidized dimer GSSG).
- Carbon nanohorns are unusual, in that their sealed structure presents few edges, leading to a lack of reactivity with oxygen and generally non-reactive with antioxidants.



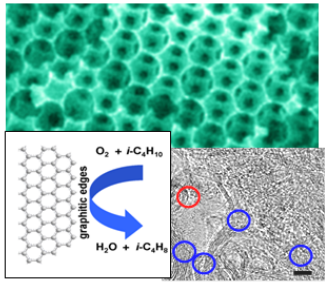


Antioxidant deactivation on graphenic nanocarbon surfaces X. Liu, S Sen, J. Liu, I. Kulaots, D. Geohegan, A. Kane, A. A. Puretzky, C. M. Rouleau, K. L. More, G. T. R. Palmore, R. H. Hurt *Small* Aug. 5, 2011. DOI: 10.1002/smll.201100651

Chemical Functionality

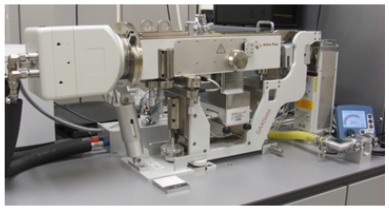
Scientific Focus

- Understand energy flow in nanoscale architectures and how macroscale functionality is determined - focusing on synthesis, structure, catalysis and energy storage.
- Develop novel methods to synthesize, process, and characterize inorganic/organic nanoscale building blocks with well defined structure, interfaces and architectures.
- Utilize coordinated chemical and physical probes to understand functional mechanisms of nanostructures.



Nanostructure Synthesis

- Template- and surfactant-mediated synthesis of mesoporous oxides and carbons for catalysts and functional supports
- Chemical, hydrothermal, solvothermal routes for nanoparticle synthesis
- Surface functionalization of oxides and carbon
- Atomic layer deposition (ALD) and surface sol-gel processing (SSG) for conformal functionalization of support surfaces
- Graphitization and carbonization



Characterization and Functional Testing

- Electron microscopy (TEM, SEM, STEM) including soft-matter, EELS, EDX, Cryo-TEM and energy-filtered imaging for soft-materials
  - Sub-angstrom resolution through SHaRE
- X-ray diffraction and small-angle scattering at temperature and pressure
  - Powder, thin-film
  - SAXS with grazing-incidence, humidity control, temperature, capillary, powders
- Operando, in situ characterization of reaction intermediates, surface species, and catalytic nanostructure: Raman, IR, DRIFTS, XRD
- Thermogravimetric and sorption measurements
- Cells, environments and collaborations for neutron scattering experiments
- Structural characterization of oxide and metal nanomaterials, surface and bulk structure
- Catalyst performance characterization including gas and condensed phase reactivity and selectivity
- High precision measurements of battery performance with controlled temperature
- Battery diagnoses through impedance measurements
  - Drybox for cell construction
- Elemental analysis with X-ray fluorescence and CHNS-O analyzer

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Functional Hybrid Nanostructures

Scientific Focus

- Develop novel methods to synthesize, process, and characterize primarily inorganic nanoscale building blocks with well defined structure, interfaces and architectures.
- Utilize coordinated multiscale probes to understand energy flow in nanoscale architectures and how functionality emerges at multiple length scales.

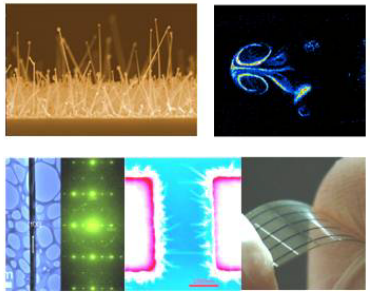
Hybrid nanomaterials synthesis facility

Characterization and Functional Testing

- Optoelectronic characterization and functional testing (UV-Vis-NIR, PL, Raman)
- Calibrated, OLED, PV, and OFET testing
- Tunable ultrafast laser spectroscopy (Raman, confocal micro-Raman, pump-probe)
- Electrical transport, semiconductor parameter analysis, four-point-probe, AC-impedance measurements.
- Ferroelectric and R-T measurements
- Thin film XRD at temperature and pressure

Nanostructure Synthesis

- Synthesis with time-resolved, in situ spectroscopic diagnostics and growth kinetics
- Carbon nanomaterials: SWNTs, SWNHs, MWNTs, VANTAs, graphene, by PVD and CVD
- Oxide thin films and heterostructures
- Crystalline organic nanowires by PVD
- Nanoparticles and nanowires by PLV, LA-CVD
- Sonospray patterning and large area deposition
- Inert-atmosphere glovebox processing for inorganic/organic hybrid electronics
- Nanoparticles by ultrafast laser vaporization and surface nanostructuring



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Center for Nanophase Materials Sciences

Synthesis and Processing Nanomaterials → Architectures → Functionality