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Building Better Batteries: Raman Spectroscopy – An Essential Tool for Evaluating New Lithium Ion Battery Components

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Presentation Overview

- Lithium-Ion Batteries
  - Why the interest in lithium ion batteries

- Fundamentals of Raman Spectroscopy
  - Overview – What information does it provide
  - Instrumentation (micro and macro)
  - Raman spectroscopy made easy

- Examples of the use of Raman Spectroscopy for the Analysis of Battery Components
  - Cathodes (mixed transition metal spinels)
  - Anodes (carbon allotropes and carbon-hybrid materials)
  - Electrolytes (solid polymer electrolytes)

- Questions and Answers

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Lithium-Ion Batteries – Projected Growth

1970s	1985	1991	2012
Lithium Batteries Proposed	Prototype Lithium Ion Battery Produced (carbon material/ $LiCoO_2$)	First Commercial Lithium-Ion Battery Sony and Ashai Kasei	$11.7 Billion

2012 Global Lithium Ion Battery Revenue $11.7 Billion

(Samsumg SDI predicts a $32 billion lithium ion battery market by 2015)

Predicted Growth: $43 - 61 Billion by 2020

Some Common Uses of Lithium Ion Batteries

- Portable Electronic Devices
  - Laptops
  - Mobile Phones
  - Tablets
  - DVD Players
  - Digital Cameras

- Cordless Tools
  - Drills, Saws, Sanders
- Automobile*
  - Plug-in Hybrid-Electric Vehicles (PHEV)
  - Electric Vehicles

*A substantial growth in lithium ion batteries in transportation is expected $2 billion in 2011 and predicted to grow to $14.6 billion by 2017

Improving Lithium Ion Batteries

- **Capacity**
  - Batteries for Electric Vehicles need greater capacity (miles per charge)
  - Improve from 30-80 miles per charge to 300-400 miles per charge
  - Lighter / Smaller Electronics – longer use

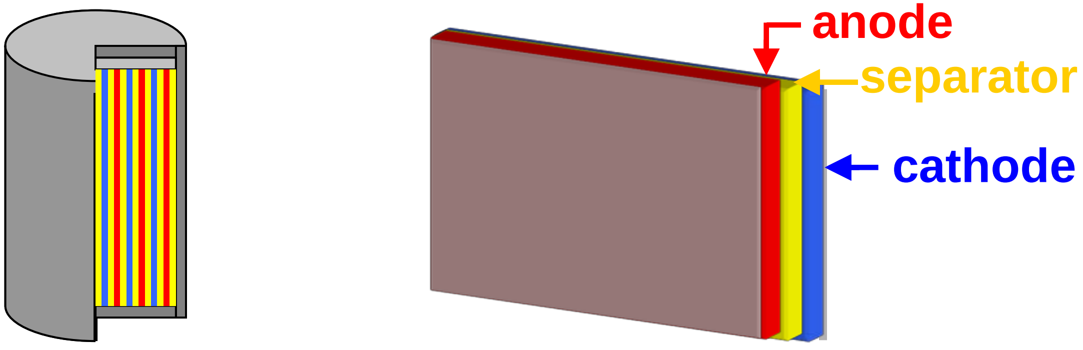
- **Cost**
  - Lithium ion batteries are expensive but costs are decreasing
  - Currently >$1000 per kilowatt hour
  - Goal of about $500 per kilowatt hour by 2017
  - Cycle life (battery replacement costs)

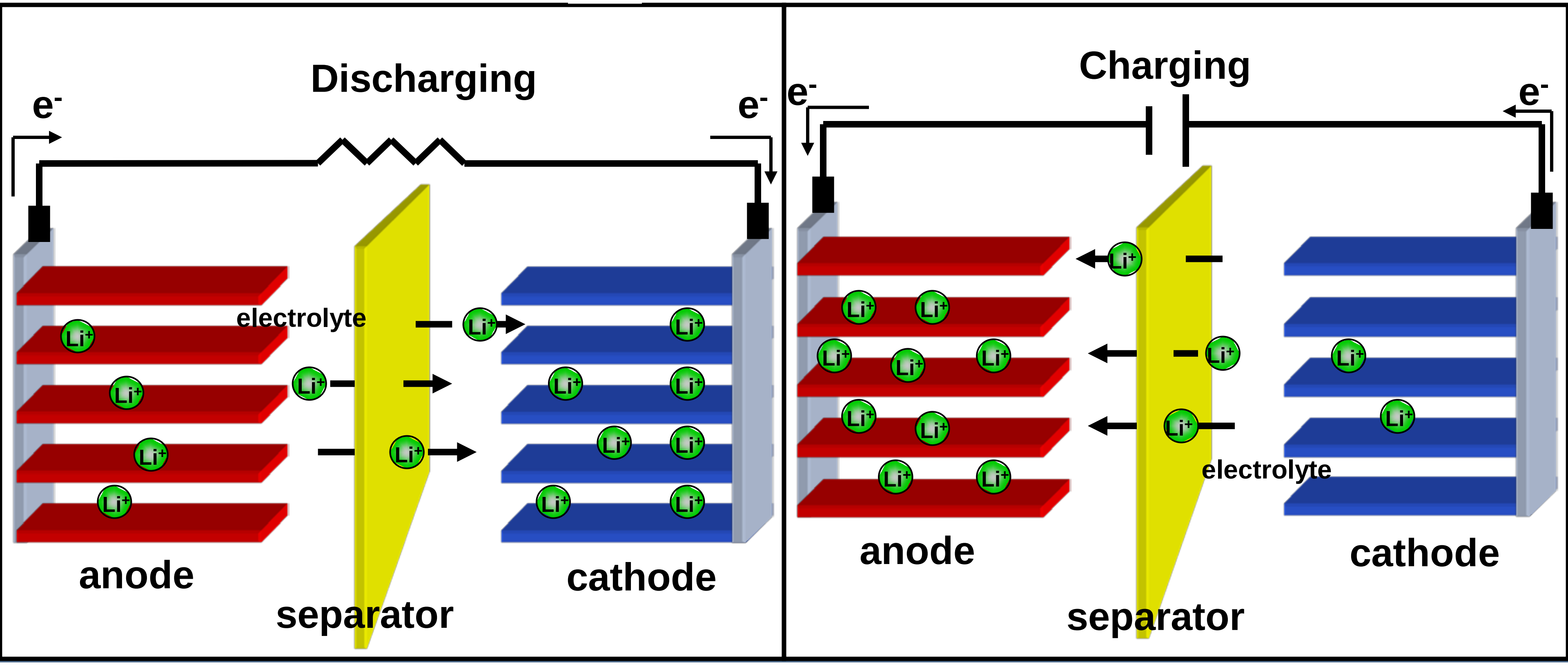
$

- **Performance**
  - Capacity, Voltage, Discharge Rate, Charging Rate, Cycling Lifetime
- **Safety**
  - Example: Boeing 787 Dreamliner – overheating and fire
  - Laptop Battery fires

- **Environmental Impact**
  - More Batteries, Larger Batteries
  - Impact of Used Battery Materials – Recycle, Reuse , Disposal
  - Cycling Lifetime

Major Lithium Ion-Battery Components





Evaluating and Analyzing New Battery Materials

Complex Systems Usually Benefit From a Multifaceted Approach

- Materials Characterization
  - **Raman Spectroscopy**
    - Molecular Structure
    - Chemical Environment
  - Other Complimentary Materials Characterization Techniques
    - DSC, XRD, XPS, EDS, TGA, SEM, TEM, etc.

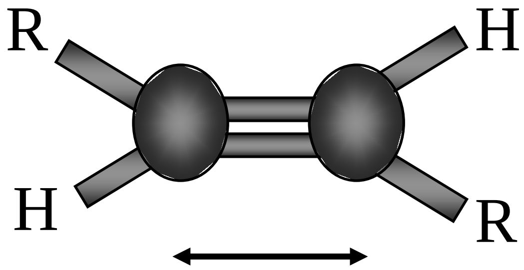
- Electrochemical Characterization
  - Conductivity measurements
  - Electrochemical stability
  - Ion mobility
  - Cell capacity
  - Discharge rates
  - Cycling behavior

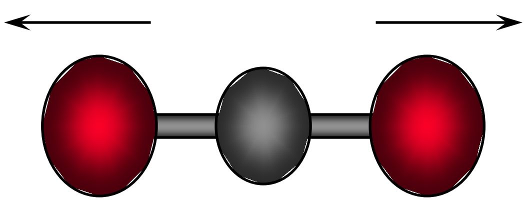
Correlation between Materials Characterization and Electrochemical Properties

Brief Description of Raman Spectroscopy

- Raman spectroscopy is a laser light scattering technique
  - A form of Vibrational Spectroscopy
    - Records vibrations of covalent bonds
    - Provides detailed molecular information

  - Sensitive to even slight changes in bond angle or strength
    - Highly sensitive to geometric structure
    - Highly sensitive to stresses in molecules or modifications which impact bond properties



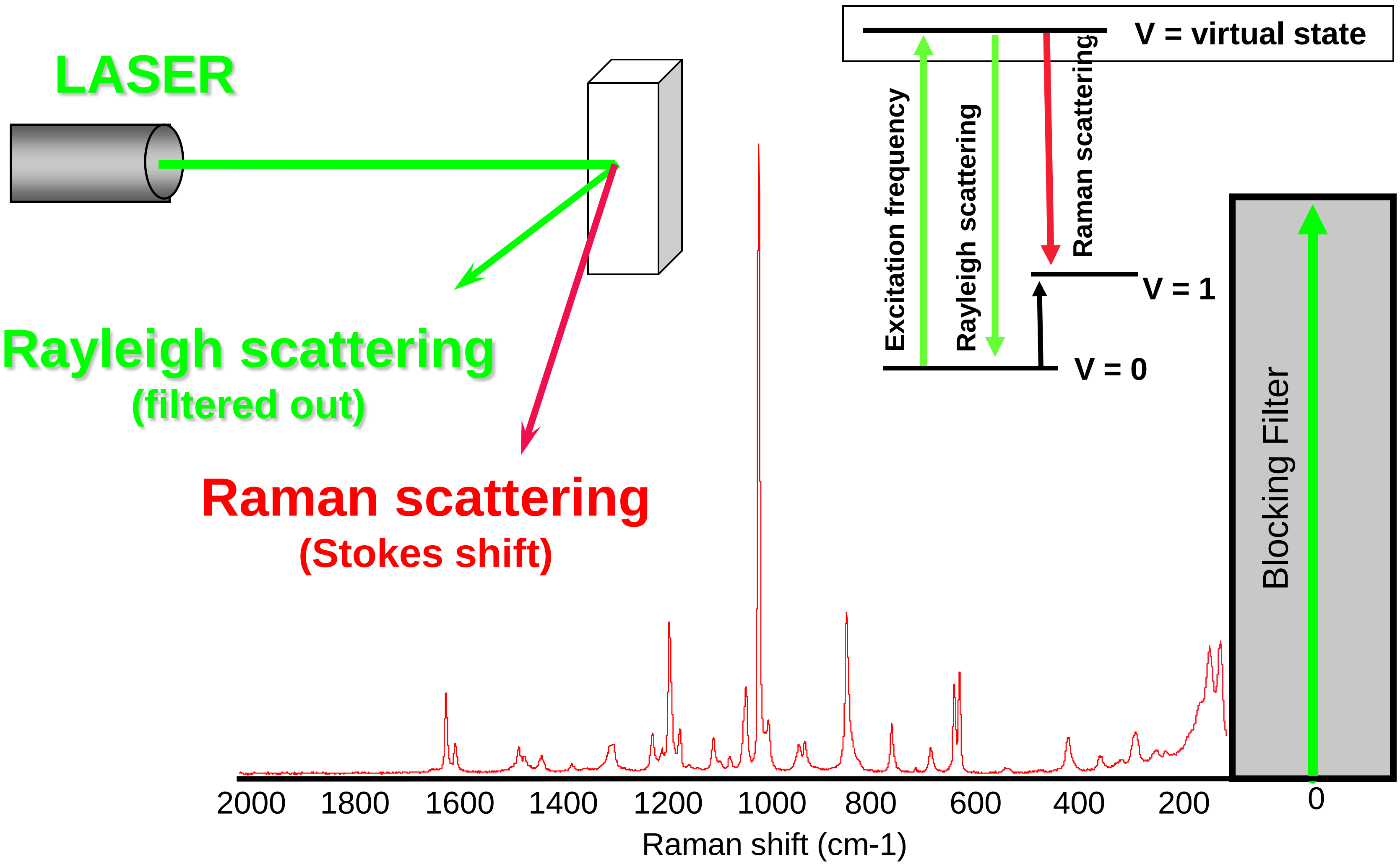


What Information Comes from Raman Spectroscopy?

- Provides information useful for
  - Identifying unknown materials
    - Raman spectrum serves as a “molecular fingerprint”
  - Materials characterization
    - Detect slight differences in materials
    - Understand impact of processing steps
  - Molecular morphology characterization
    - Differentiate material phases
    - Detect and characterize strain effects

Photo courtesy of University of Wisconsin

Raman Spectroscopy Basics



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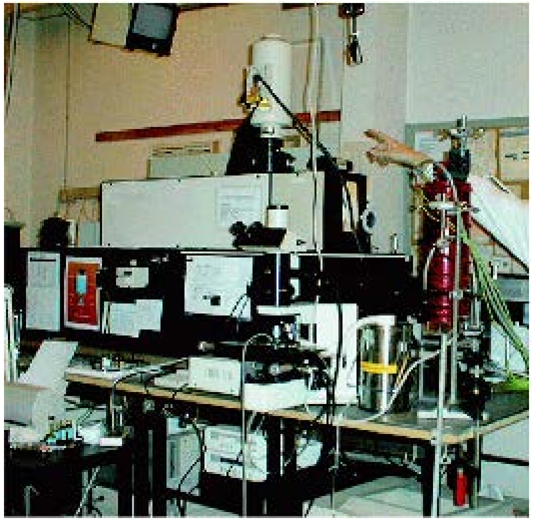
Historical Barriers to Applying Raman

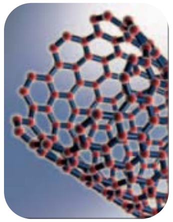
- Instruments required constant maintenance
  - Alignment complex and entirely manual
- Instruments required expert operators
  - Optimizing collection parameters complicated
    - No system intelligence
    - Combination of software settings and manual optimizations
  - Data interpretation difficult
    - Poor calibrations precluded library searching
    - Artifacts were abundant in data
    - Data not intensity corrected making comparison of data between different instruments challenging
    - Few reference libraries existed



Users of Raman Today

- Most researchers buying Raman today are Applied researchers
  - These are people interested in Raman as a tool to further their work rather than Raman as a field of research itself

  - These users value getting results quickly which entails
    - Simplicity of use
    - Fast analysis time
    - Trustworthy data
    - Tools to help get useful information from data


Nanotechnology


Art Restoration


Polymers


Forensics


Pharmaceutical


Geology

Batteries

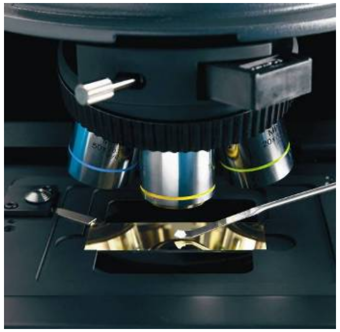

Solar

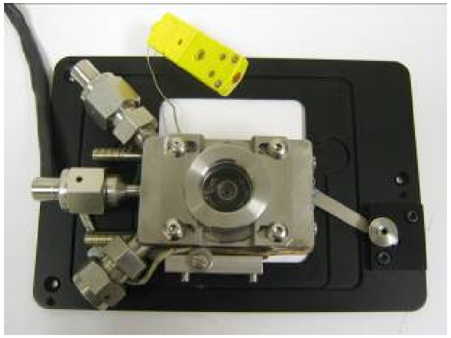
Example of Modern Raman Spectrometers

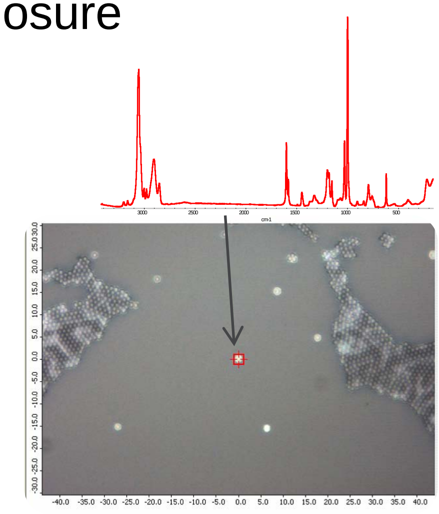
- Simple to operate
- Research grade performance
- Interchangeable lasers, Rayleigh filters, and gratings
- Easily upgraded by user
- Compact, small footprint with Class I laser safe enclosure, suitable for open lab environment
- Automated alignment and calibration routines keep the instrument in optimal working condition
- Advances in software helps select collection parameters and has many time saving functions

DXR Raman Microscope: Micro-Sampling

- Integrating a Raman spectrometer and a visible light microscope
- Micro-spectroscopy sampling options
- Spatial Resolution ≤1 micron - Small laser spot sizes achieved with optical design and high brightness lasers
- Confocal microscope design
  - Excellent Depth Profiling
- Class I Laser-Safe enclosure







1-µm polystyrene bead

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DXR SMARTRaman – Macro Sampling

- Multiple Sampling Options
  - Universal Platform Sampling Accessory
    - Universal plate
    - Tablet holder
    - Bottle holder
    - Well plates
  - Variable Dynamic Point Sampling
    - area up to 5 mm x 5 mm
- 180 degree refractive sampling option
- Carousel autosampler

Examples of Raman Spectroscopy Applied to the Study of Lithium Ion Battery Components

Cathodes, Anodes, & Electrolytes

Cathode Materials

- $LiCoO_2$
  - Classical Lithium Ion Battery Cathode Material
  - Expensive (low abundance of cobalt)
  - Environmental Impact of Cobalt
    - Essential element (vitamin B12)
    - Higher doses cause health issues
    - Insufficient data
- $LiMn_2O_4$
  - Used in some commercial lithium ion cells
  - Manganese less expensive (3rd most abundant transition metal)
  - Essential element but also toxic at high doses
  - Cathodes suffer from capacity fade over time.
    - Disproportionation reaction of Mn(III) at high potentials
    - Doping with other transition metals to suppress this disproportionation

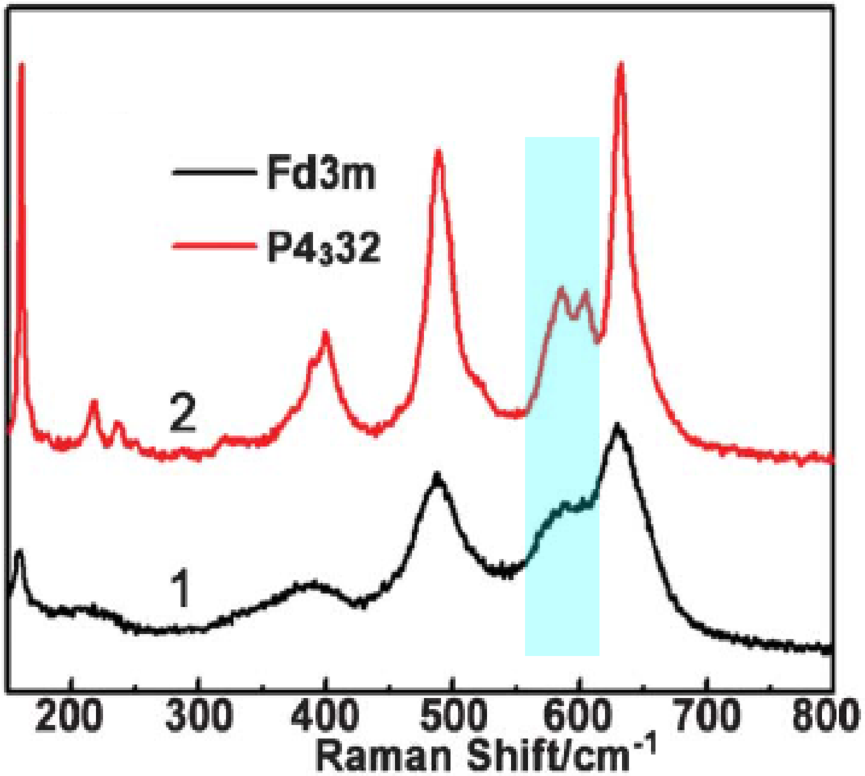
Transition Metal Doped $LiMn_2O_4$ Spinel

- $LiNi_{0.5}Mn_{1.5}O_4$
  - Different synthesis conditions can produce different structures
  - Space groups **$P4_332$** (ordered) and **Fd3m** (disordered, normal)
  - Higher temperatures favor the ordered structure
  - **Different phases can be identified from the Raman spectra**
  - Fd3m (normal) phase has higher conductivity than the ordered phase ($P4_332$)

- $LiNi_{0.5-x}Mn_{1.5-y}M_{x+y}O_4$ (M = Cr, Al, Zr)
  - Doping with other transition metals can effect the structural preference
  - Doping with Cr favors the Fd3m structure
  - Doping with Al favors the $P4_332$ structure
  - Doping with Zr is most consistent with the $P4_332$ structure

Si Hyoung Oh, Kyung Yoon Chung, Sang Hoon Jeon, Chang Sam Kim, Won Il Cho, Byung Won Cho, *Journal of Alloys and Compounds*, 2009, **469**, 244-250
Battery Research Center, Korea Institute of Science and Technology

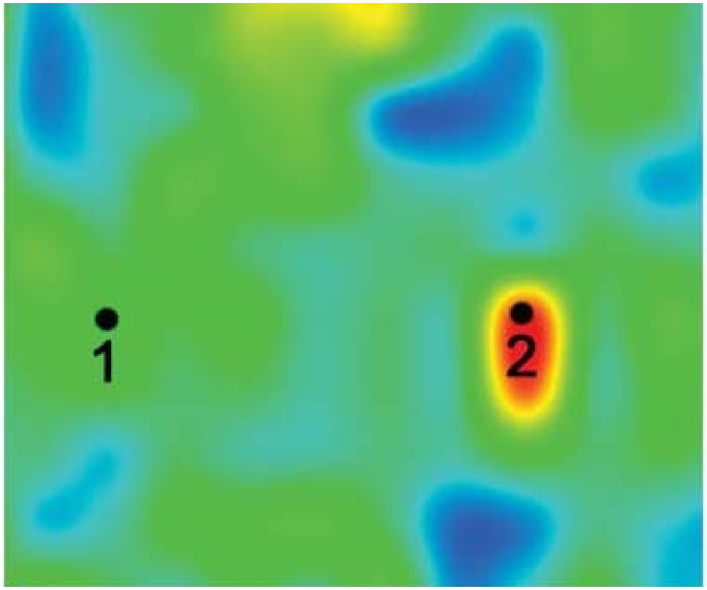
Raman Spectra of the Two Phases of $LiNi_{0.5}Mn_{1.5}O_4$



- $P4_332$
  - Spinel structure with Ni and Mn in ordered octahedral positions in the structure
  - Sharper more intense peaks
  - Split in the peak at 580-600 cm^{-1}
- Fd3m
  - Spinel structure with Ni/Mn occupying the octahedral sites in the structure.
  - Broader less intense peaks
  - Single peak at 580-600 cm^{-1}

Xiaolong Zhang, Fangyi Cheng, Kai Zhang, Yanliang Liang, Siqi Yang, Jing Liang, Jun Chen,
RSC Advances, 2012, 2, 5669-5675
Key Laboratory of Advanced Energy Materials Chemistry, College of Chemistry, Nankai University

Spatial Distribution of Phases



- Raman Mapping Data
  - Mapping area 10 x 10 μm^2
  - 1 μm resolution
  - Colors based on spectral differences
  - Shows spatial distribution of phases
  - Red spot indicates $P4_332$ phase
  - Blue and Green typical of Fd3m

Xiaolong Zhang, Fangyi Cheng, Kai Zhang, Yanliang Liang, Siqi Yang, Jing Liang, Jun Chen,
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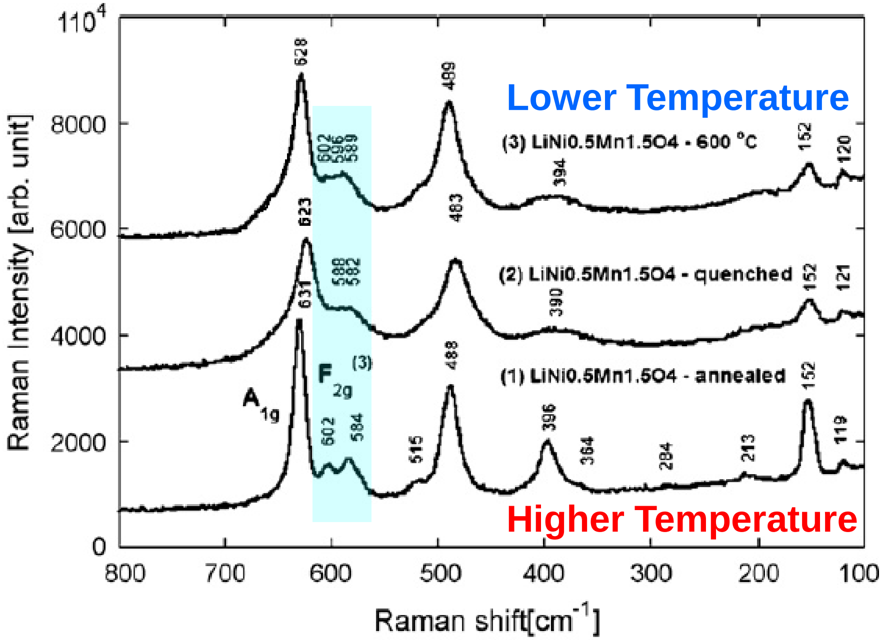
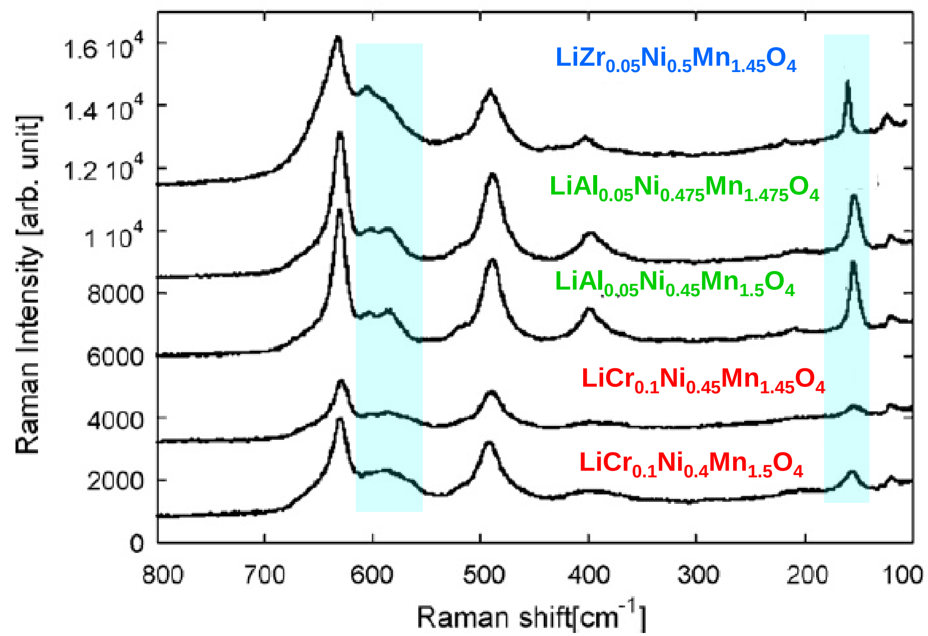
Key Laboratory of Advanced Energy Materials Chemistry, College of Chemistry, Nankai University

The Effect of Reaction Conditions and Doping





_Fd3m_

Lower Temperature Synthesis
Cr doped
Higher Conductivity

$P4_332$

Higher Temperature Synthesis
Al and Zr Doped
Lower Conductivity

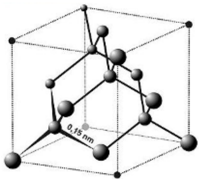
Si Hyoung Oh, Kyung Yoon Chung, Sang Hoon Jeon, Chang Sam Kim, Won Il Cho, Byung Won Cho, *Journal of Alloys and Compounds*, 2009, **469**, 244-250
Battery Research Center, Korea Institute of Science and Technology

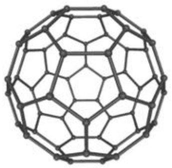
Anode Materials

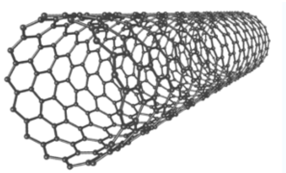
- Graphite is an example of a classical anode material for lithium ion batteries
- Graphite shows a reversible electrochemical intercalation of lithium ions
- Other allotropes of carbon and hybrid materials as new anode materials
  - Graphene
  - Carbon nanotubes (SWCNT, MWCNT)
    - One of the first carbon nanotube applications marketed by Showa Denko were as additives for lithium ion battery electrodes
    - Showa Denko: Current capacity of carbon nanotubes 500 tons/year
  - Fullerenes
  - Coatings and Hybrid Materials

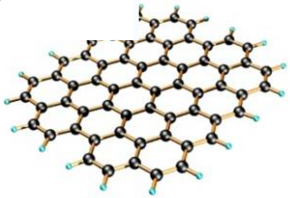
Raman Spectroscopy – Benefits for Carbon Analysis

- High information content - specific molecular information
  - Superior differentiation between different allotropes of carbon
    - graphite, diamond, carbon nanotubes (single or multi-walled), C60, graphene

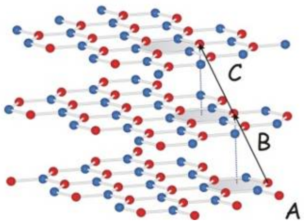








  - Additional Structural Information
    - Graphene layer thickness (single or multi-layered)
    - Evaluation of the quality of the graphene – defects
    - Graphene domain size
    - Strain in graphene
    - Evaluating diameters of single walled carbon nanotubes
    - Chemical modification



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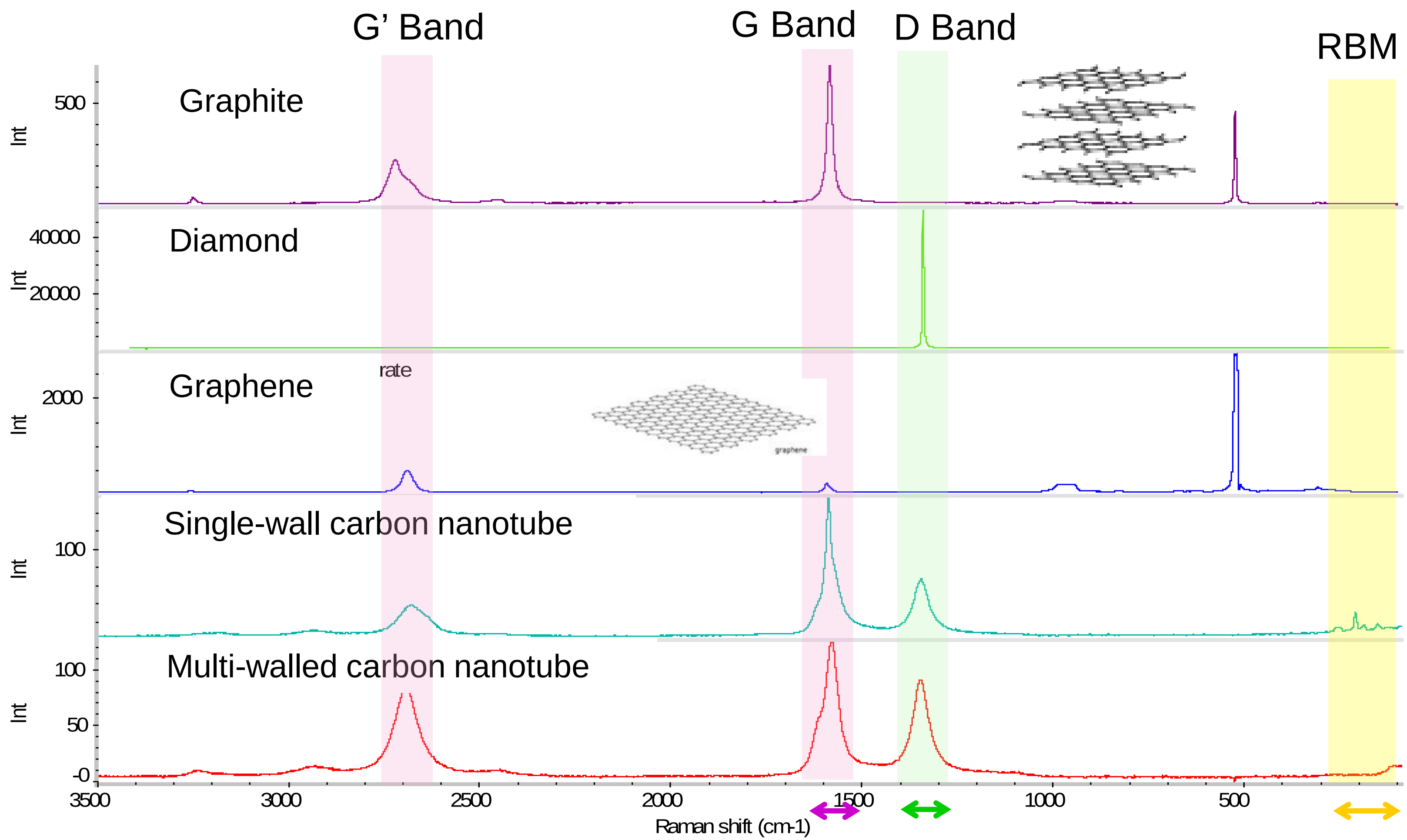
Raman in Carbon Nanotechnology

- Carbon materials are well characterized by Raman



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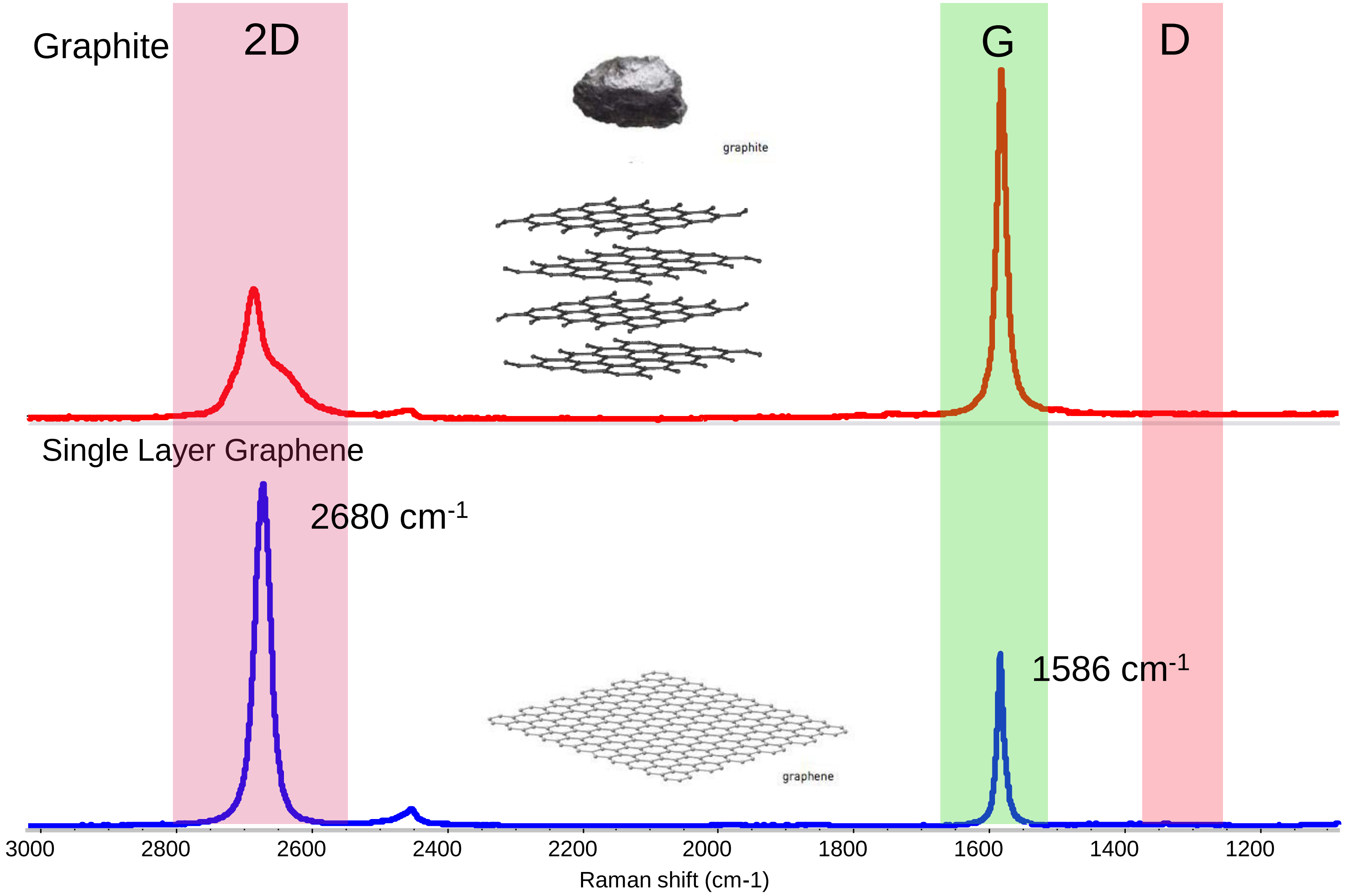
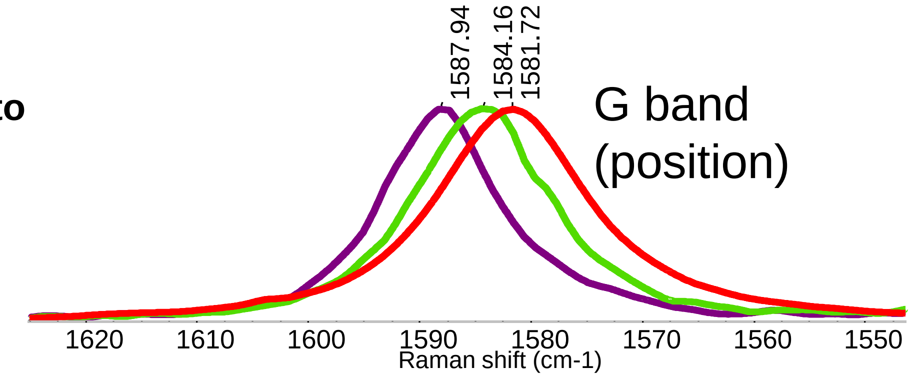
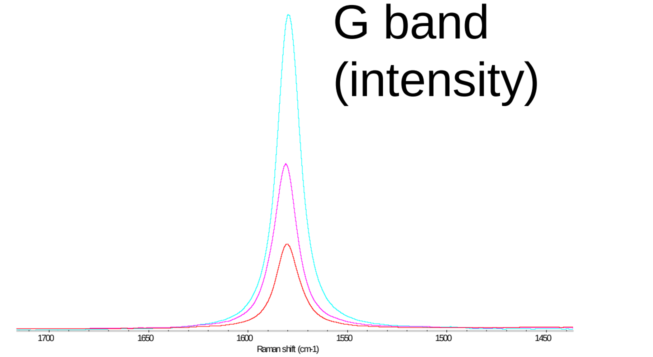
Raman Provides Additional Structural Information



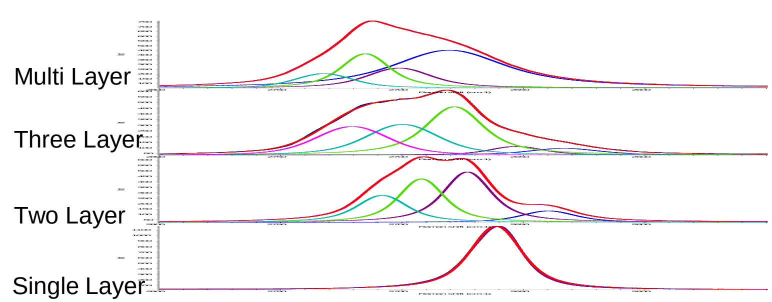
Raman Spectrum of Graphene – Principle Bands

- **G band**
  - **Peak position and relative intensity is sensitive to**
    - **Layer thickness**
    - **Doping**
    - **Strain**
- **D band**
  - **Peak intensity is sensitive to**
    - **Presence of defects or disorder**
    - **Sampling in proximity of an edge**
    - **Chemical modification**
      - **Increase of sp^3 hybridized C bonding at the expense sp^2 hybridized C bonding**
- **2D band**
  - **Peak position, band shape, and intensity sensitive**
    - **Layer thickness and interlayer orientation**
    - **Excitation frequency**
    - **Strain**



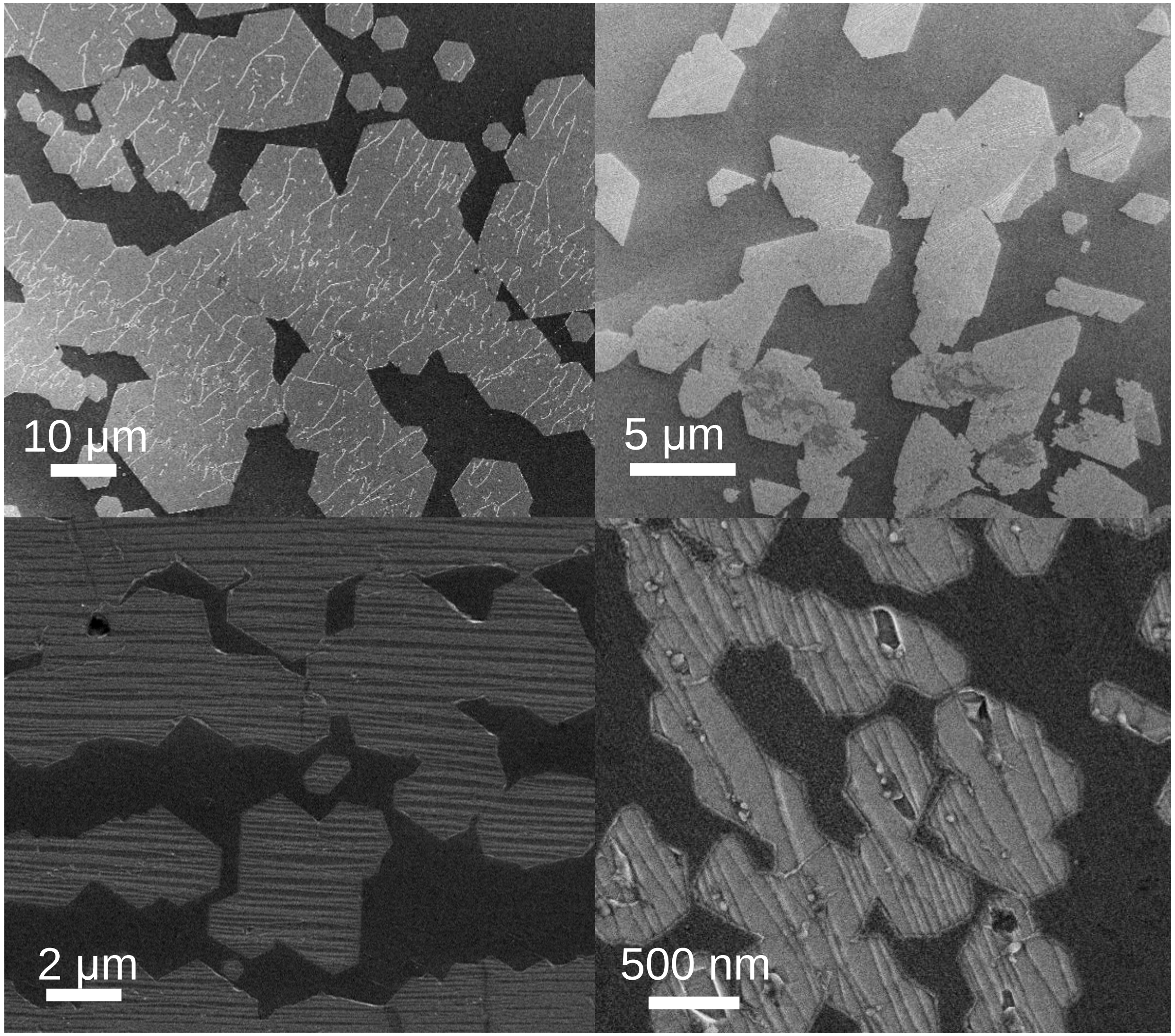


2D Band Shape Analysis



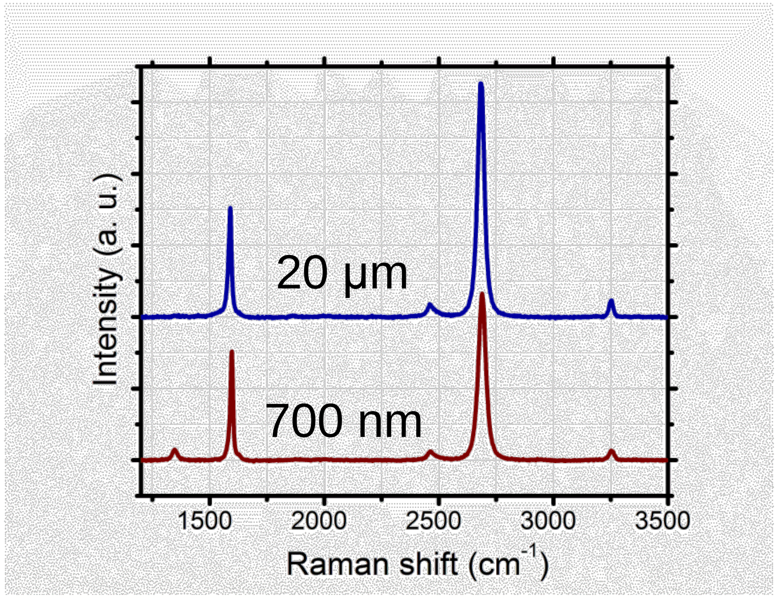
Growth of Graphene with Controlled Grain Size

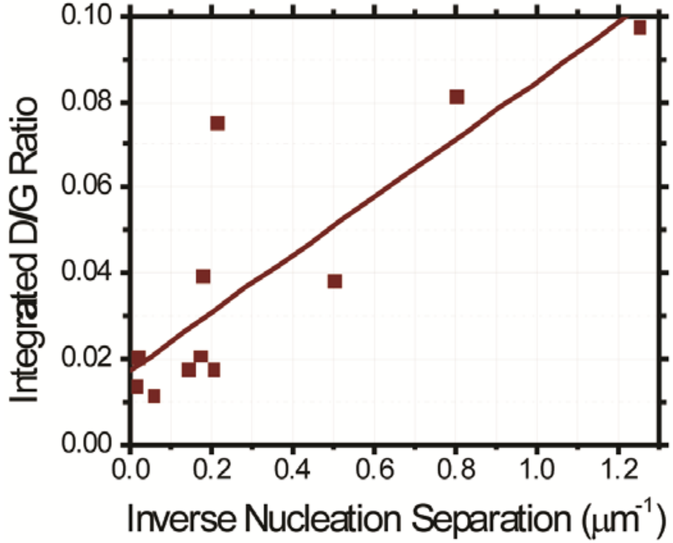
- Graphene was grown with different grain sizes
- Achieved through control of nucleation density
- Full monolayers can be grown
- Raman spectroscopy can be used to assess defects from the grain boundaries



Growth of Graphene with Controlled Grain Size

- Larger domain graphene shows:
  - Larger 2D/G
  - Smaller D-band
- D-band intensity follows linear trend with inverse domain size
  - Caused mainly by defects at the grain boundaries
- Defects (edges and vacancies) in graphene have been shown to be advantageous for anode materials
  - Additional reversible storage sites for lithium ions
  - Improves capacity and cycling stability





Carbon Coating and Hybrid Anode Materials

- **Silicon**
  - Attractive Material for Anode Materials
  - High Theoretical Capacity (4200 mAh/g)
  - Large Volume Changes during Cycling
    - Mechanical degradation
  - Attempt to improve solid electrolyte interface (SEI)
  - Plasma assisted thermal evaporation with different precursors
    - C60 (fullerene)
    - Boron doped C60
  - Plasma enhanced chemical vapor deposition
    - Acetylene (producing DLC films)
  - Carbon coating silicon anodes improved the cycling stability and reversible capacity
  - Raman Spectroscopy used to determine I_D/I_G ratio

Series of Papers: Arenst Andreas Arie, Joong Kee Lee, et.al. Advanced Energy Materials Processing Laboratory, Battery Research Center, Korea Institute of Science and Technology

Carbon Coating and Hybrid Anode Materials

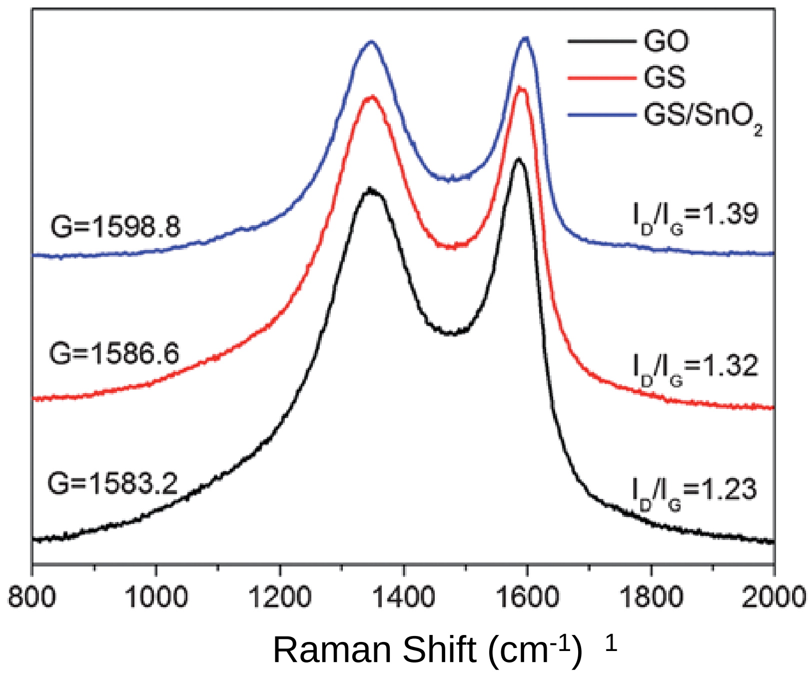
- **SnO_2 and SnS_2**
  - Attractive Materials for Anode Materials
  - High Theoretical Capacities (782 mAh/g, 990 mAh/g)
  - Large Volume Changes during Cycling
    - Mechanical degradation

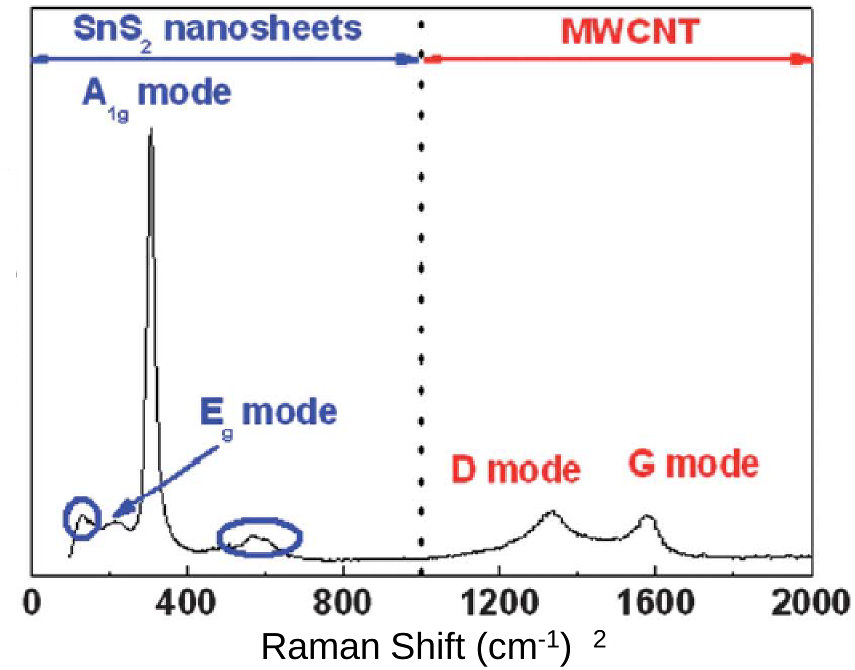
- **Hybrid Materials**
  - SnO_2 nanorods dispersed on graphene [1]
  - SnS_2 / MWCNT nanosheets [2]
  - Improved electrochemical properties over non-hybrid materials

1) Chaohe Xu, Jing Sun, Lian Gao, J. Mater. Chem., 2012, 22, 975-979

2) Jin-Gu Kang, Gwang-Hee Lee, Kyung-Soo Park, Sang-Ok Kim, Sungjun Lee, Dong-Wan Kim, Jae-Gwan Park J. Mater. Chem. 2012, 22, 9330-9337

Raman Analysis of the Hybrid Materials



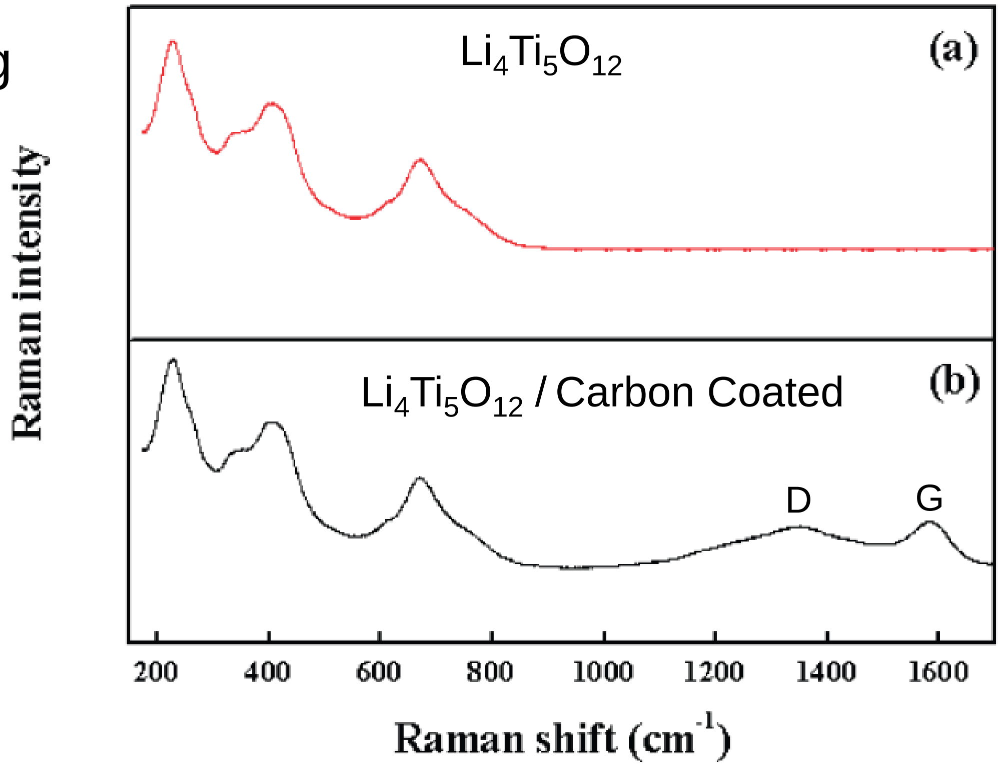


1) Chaohe Xu, Jing Sun, Lian Gao, J. Mater. Chem., 2012, 22, 975-979

2) Jin-Gu Kang, Gwang-Hee Lee, Kyung-Soo Park, Sang-Ok Kim, Sungjun Lee, Dong-Wan Kim, Jae-Gwan Park J. Mater. Chem. 2012, 22, 9330-9337

Carbon Coated $Li_4Ti_5O_{12}$

- Zero Strain Insertion Material
  - Small expansion and contraction during cycling
  - Good cycling stability
- Theoretical Capacity - 175 mAh/g
- Low Conductivity
  - Initial capacity loss
  - Poor rate capacity
- Carbon Coated $Li_4Ti_5O_{12}$
  - Improved discharge capacity
  - Improved cycling capacity



Ju Bin Kim, Domg Jin Kim, Kyung Toon Chung, Dongjin Byun, Byung Won Cho, Phys. Sci. 2010, T139, 1-4

Electrolytes / Solvents

- No Ideal Electrolyte
  - $LiPF_6$
    - potentially corrosive
  - $LiAsF_6$
    - toxic
  - $LiSO_3CF_3$
    - low conductivity
  - $LiBF_4$
    - reacts at electrode surfaces
- Cost, Performance, Safety, Environmental Impact

Solid Polymer Electrolytes (SPE)

- Electrolytes in a polymer matrix (example: poly(ethylene oxide) (PEO))

- Safety
  - Leakage less likely
    - mitigates toxicity and corrosive issues
  - No volatile organic solvents
    - vapor pressure – rupture

- Low Ionic Conductivity
  - Crystallinity of the polymer matrix can reduce conductivity
  - Additives to suppress the crystallinity and improve mechanical properties

- Poor transport of lithium ions
  - Additives to partially immobilize anions and thus improve cation charge transfer

Some Applications of Raman Spectroscopy to SPEs

- Characterization and Distribution of Additives
  - Ceramic materials
    - Disrupt crystallinity of the polymer matrix (PEO)
    - Aluminia & titania
    - Surface modifications of fillers
  - Supramolecular additives
    - Partially Immobilizing anions – improving lithium transfer
    - Example: Calix[4]arene derivatives

- Spatial Distribution of Components in SPE Membranes
  - Crystalline vs. Amorphous Matrix
    - Polymer matrix (PEO)
  - Distribution of Additives
    - Supramolecular additives
  - Distribution of Electrolytes
    - Example: $LiCF_3SO_3$

- Determination of Ionic Associations
  - Free ions, Ion Pairs, Triplets
  - Effects conductivity

Example: PEO Matrix with Supramolecular Additive

<u>Additive(Cx2)</u>

5,11,17,23-tetra-p-tetra-butyl-25, 27-bis(((N-p-nitrophenylureido)butyl)oxy)-26, 28-dipropylcalix[4]arene

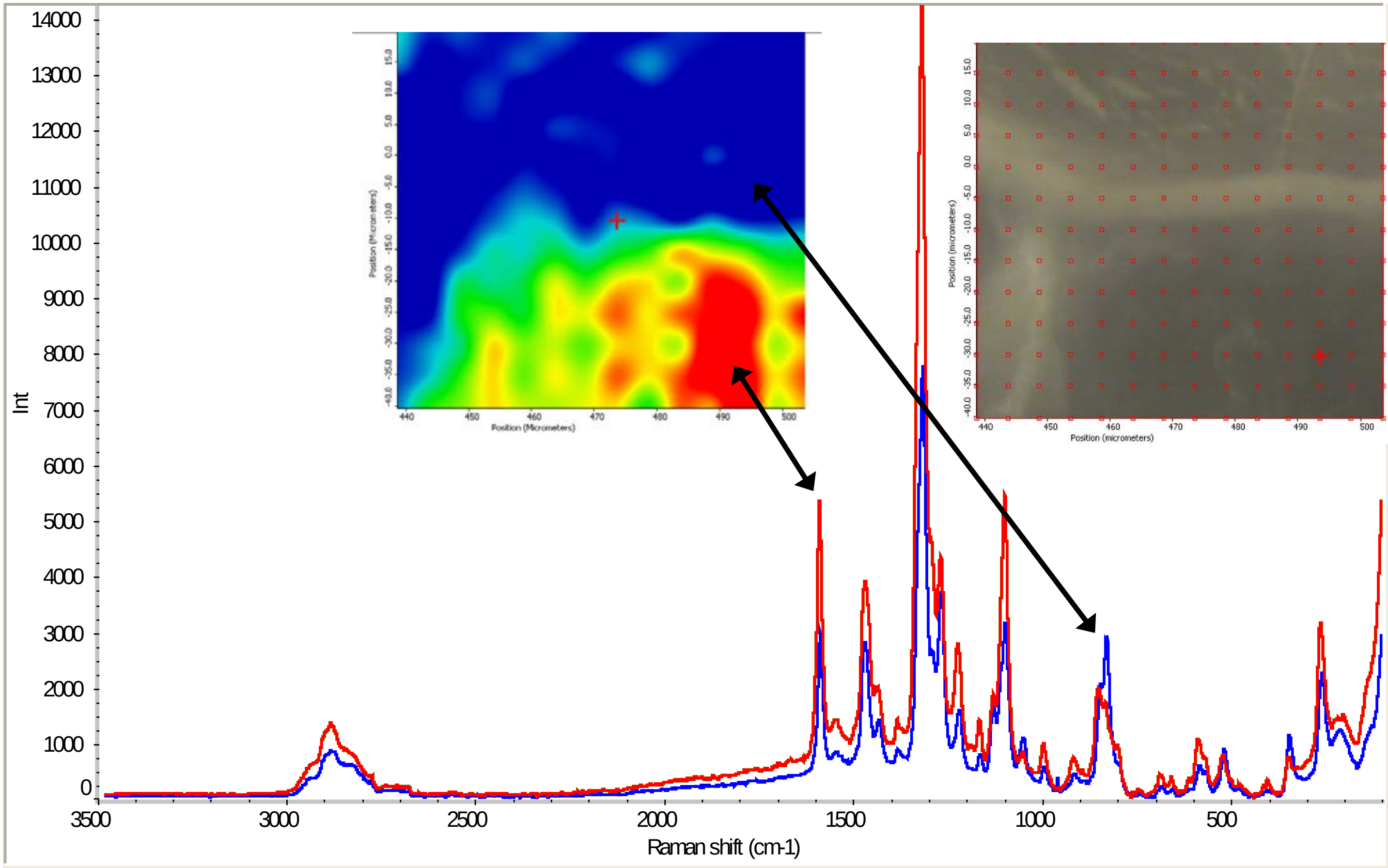
Matrix
Poly(ethylene oxide)

<u>Raman Image</u>

Ratio of 1600 cm^{-1} peak of Cx2 to 840 cm^{-1} peak of crystalline PEO

Red indicates greater relative concentration of Cx2

Blue indicates lower relative concentration of Cx2



This data was supplied by Dr. Grazyna Zukowska, Warsaw University of Technology, Faculty of Chemistry

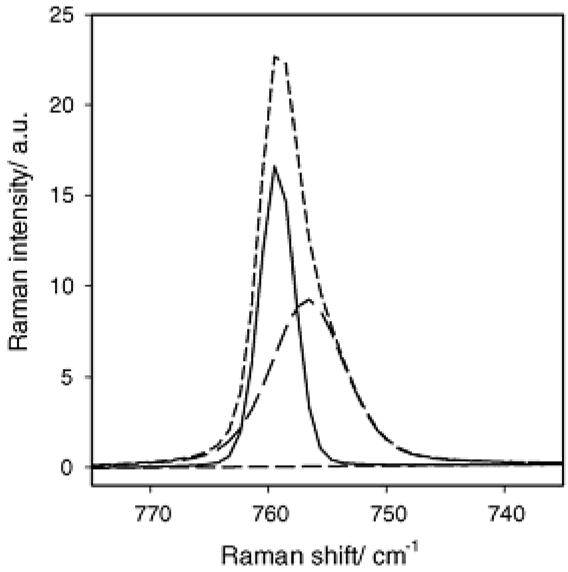
Example: Degree of Ionic Associations using Raman

Association of Ions Lowers the Conductivity

(M^+) (X^-) ⇄ $(M^+ X^-)$ ⇄ $(M^+ X^- M^+)$ (X^-)

Free Ions — Ion Pairs — Triplet

$(LiCF_3SO_3)$ – PEO System



- Peak at 759 cm^{-1}
  - CF_3 peak
  - Free ions & ion pairs
- Deconvolution
- Peak at 756 cm^{-1}
  - Free ions (42%)
- Peak at 759 cm^{-1}
  - Ion pairs (52%)

M.Pawlowska, G.Z.Zukowska, W. Kalita, A. Solgala, P. Parzuchowski, M. Siekierski, J. Power Sources, 2007, 173, 755-764.

Summary

- Significant growth in the use of lithium ion batteries is expected to continue

- Building Better Batteries - advances in the battery technology will be required to meet growing demands (improved battery components)

- Raman Spectroscopy is a very useful technique for the characterization of materials
  - Provides Molecular Structure Information
  - Sensitive to Chemical Environment
  - Modern Commercial Instruments like the DXR Raman Microscope have been designed to be easy to use but still provide high quality results.

- Raman Spectroscopy has been shown to be a valuable tool for advancing the research and development of a variety of new battery components.

Additional Resources

Raman Resources

- Learn about the Thermo Scientific DXR Raman products at www.thermoscientific.com/dxr
- Check www.thermoscientific.com/ramanwebinars for upcoming and on demand webinars at any time.

General Molecular Spectroscopy Resources

- Find our listing of molecular spectroscopy webinar offerings at www.thermoscientific.com/spectroscopywebinars

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