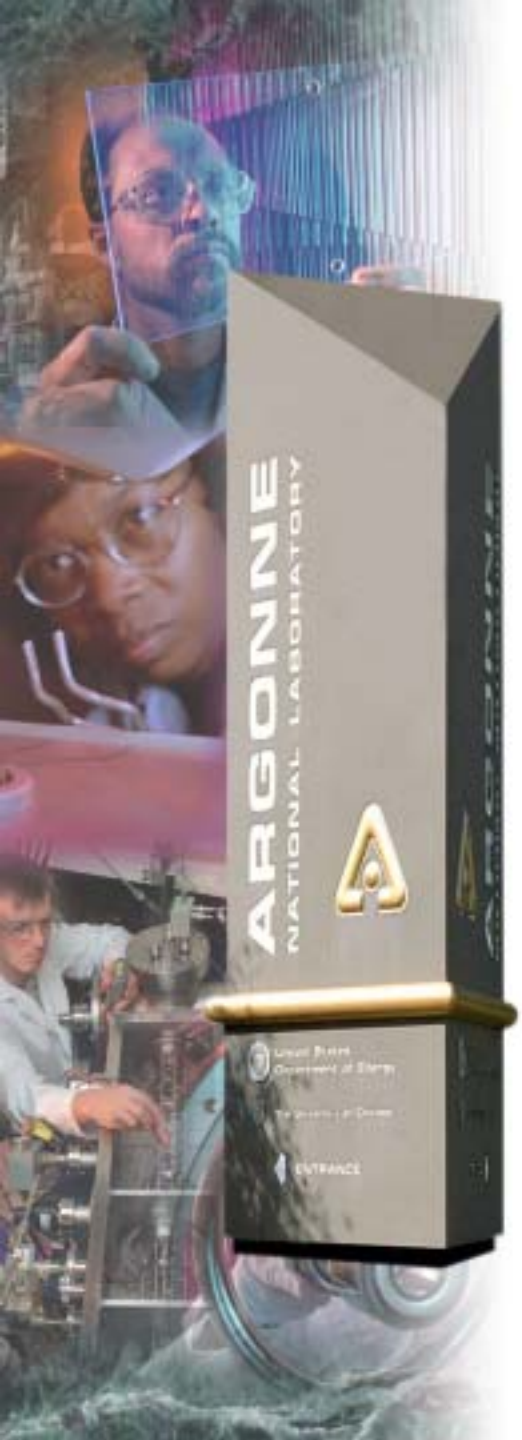

Time-Resolved X-ray Excited Optical Luminescence from Nanoscaled Systems and Related Phenomena

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Argonne National Laboratory

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Outline

- **Introduction**
- **Technique**
- **Illustrations**
- **Prospects**

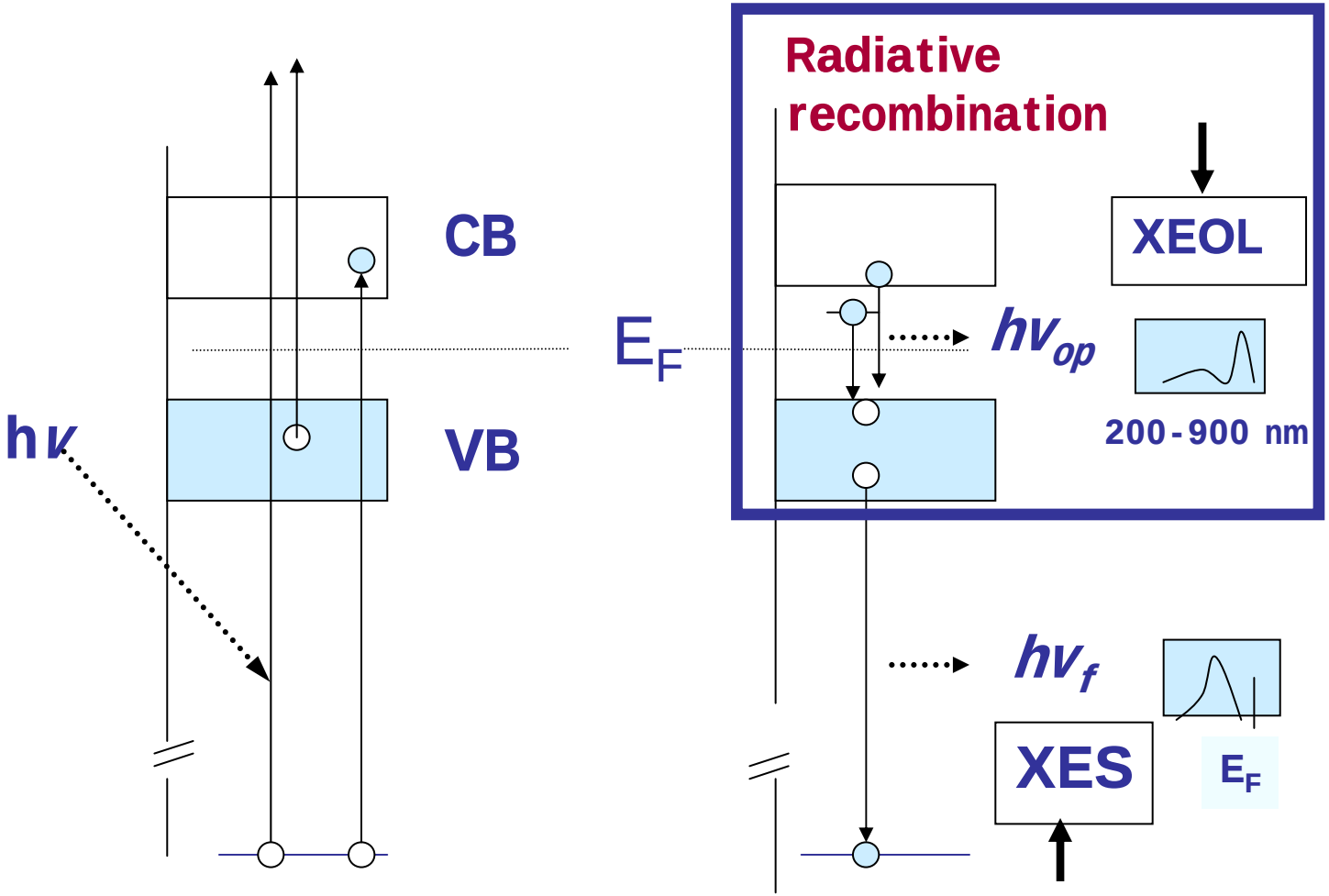
What is XEOL? What is TRXEOL?

X-ray scintillation → **X-ray Excited Optical Luminescence** → **Time-Resolved X-ray Excited Optical Luminescence**

Pre-synchrotron ↘ *Energy Domain* ↓ *Time Domain* ↙

X-ray photon-in optical photon-out

Photon-in Photon-out Spectroscopy



Excitation

Radiative core hole decay

What is a nanoscaled system?

Materials comprise crystallites of the size of nanometers or confined in one, two or all three dimensions in space to the size of nanometers

→

quantum well,
quantum wire,
quantum dot,
quantum sponge, etc.

XEOL and nano systems, what is the connection?

Nanomaterials exhibit properties that differ significantly from that of the bulk

- Bulk **Si** is not a light emitter but porous silicon emits visible light strongly due to the effect of **"quantum confinement"**
- Compound semiconductors nano-dots (CdS, CdTe, etc.) exhibits **size dependent** band gap luminescence
- **Au nanoparticles** are found to exhibit photoluminescence !

Light emitters → ***XEOL & TRXEOL*** study

Techniques

Energy Domain

XEOL: Fix excitation energy, scan optical mono

Optical XAFS: Monitor the absorption across an edge with the optical signal (mono set at a selected wavelength)

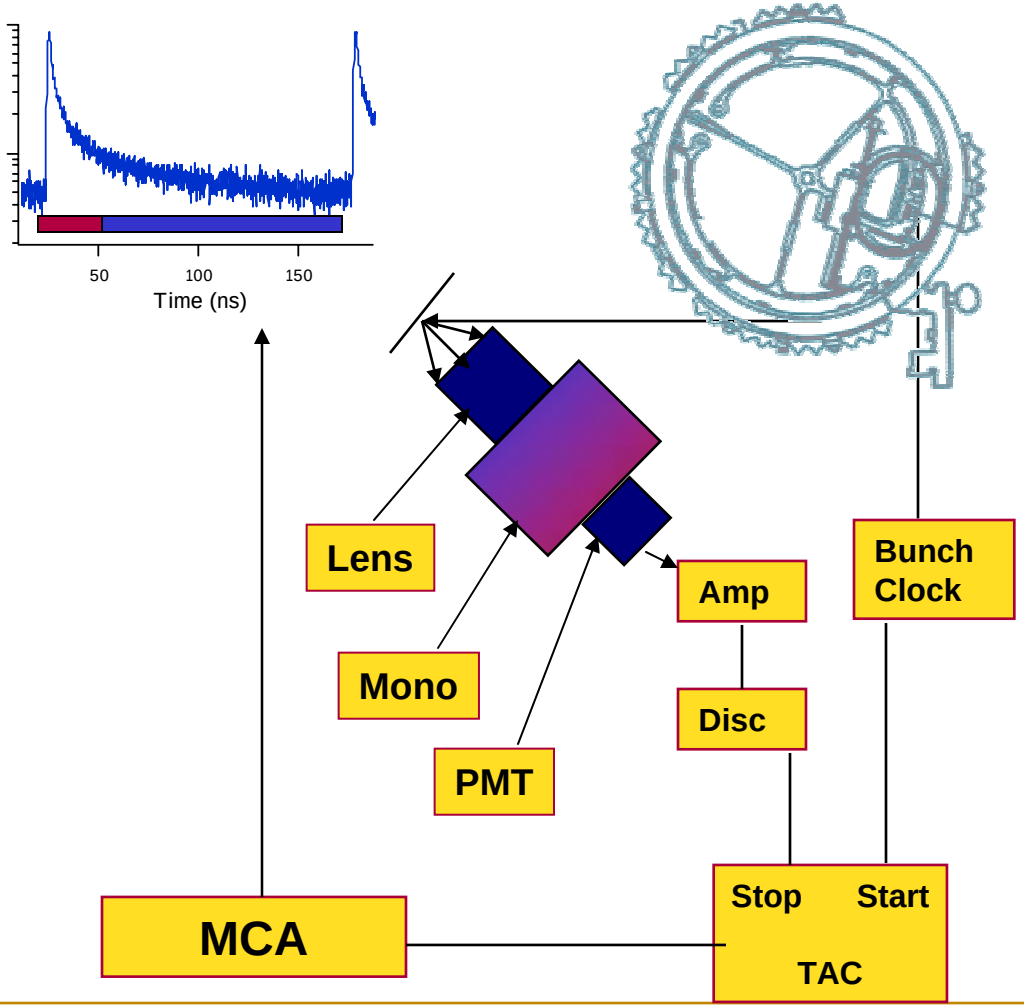
Time Domain

Life time: Use the synchrotron pulse as the start

Time-gated XEOL: Record luminescence within a selected time window of the decay curve

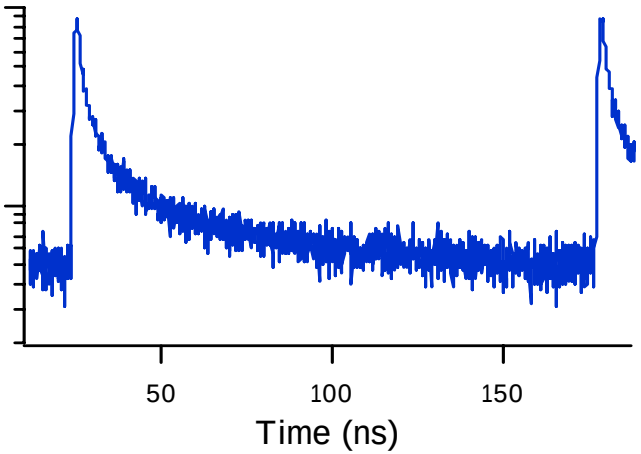
Time-gated Optical XAFS: Record luminescence within a selected time window of the decay curve

Time - Layout

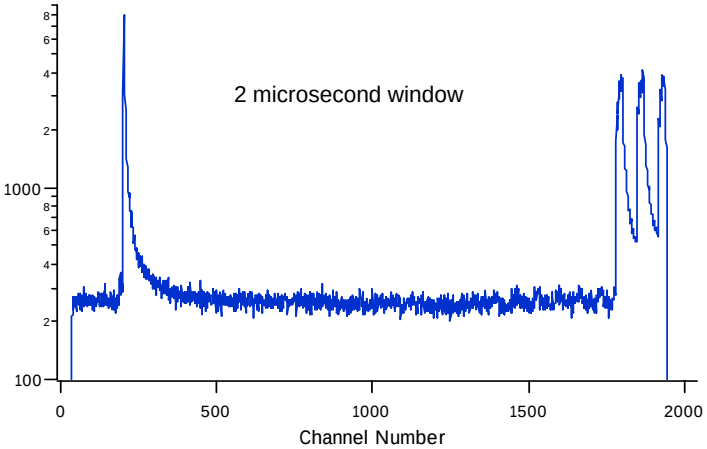

50
100
150
Time (ns)
Lens
Mono
PMT
Amp
Disc
Bunch Clock
MCA
Stop
Start
TAC

APS Timing Modes

- **Normal**: **24** equally spaced bunches (**153 ns** period)

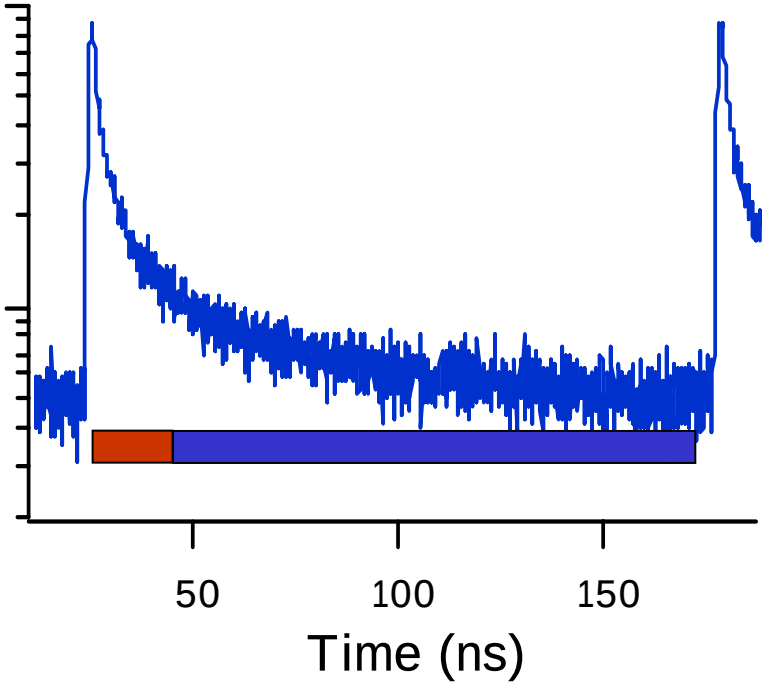


- **Special Timing Mode**: A single bunch containing a maximum of **5 mA** isolated from the remaining bunches by symmetrical **1.59 μs** gaps.



Time-Gated Spectroscopy

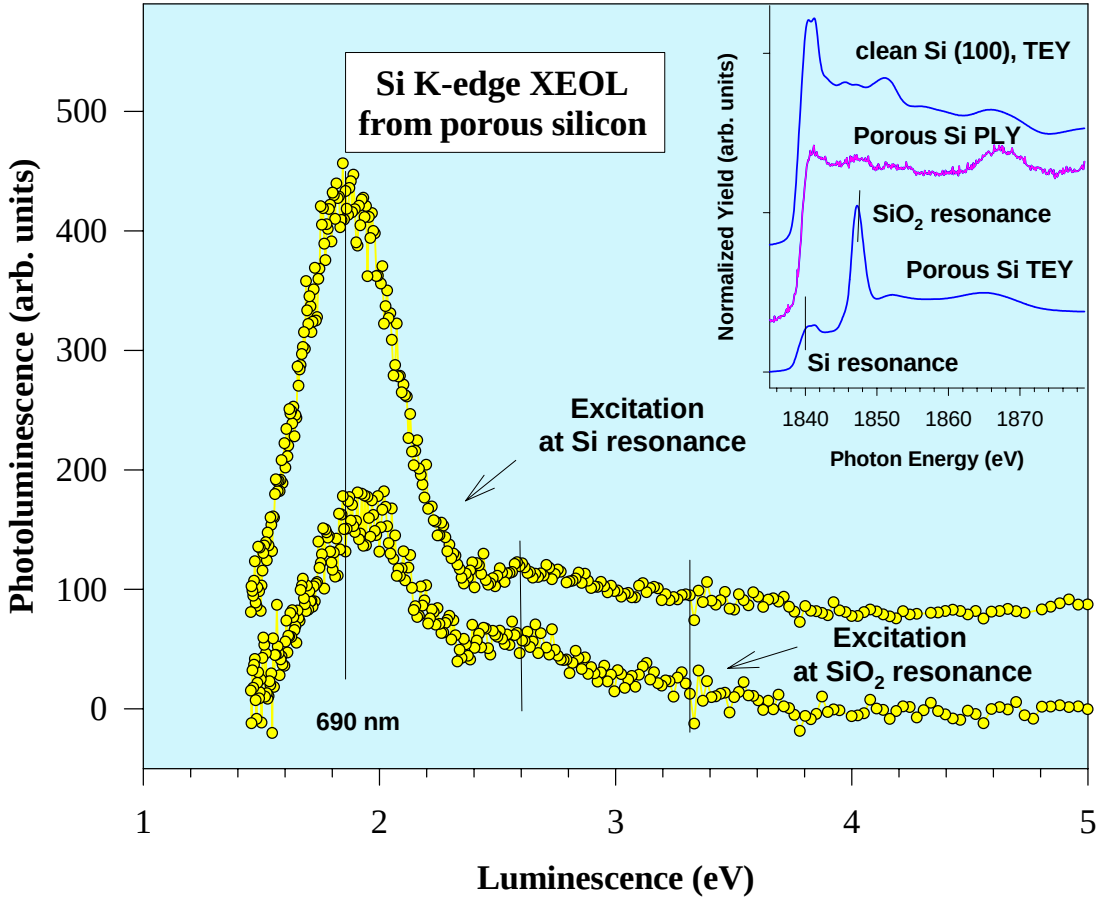
- Select time window(s)
- Obtain spectra/yields of photons arriving within that window
- Powerful tool for delineation of spectral features and origin of luminescence



The XEOL & TRXEOL Advantages

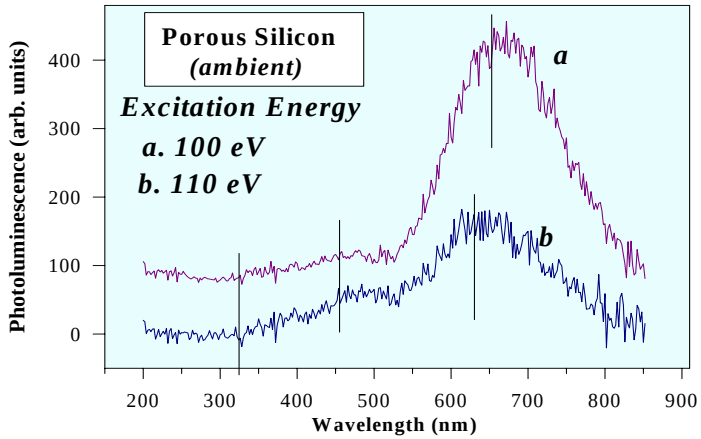
- XEOL spectra reveal the states involved in the radiative de-excitation process and can be site and excitation channel specific when excited in the x- ray absorption near edge (XANES) region.
- XANES reveals the local structure and bonding of the absorbing atom; XANES recorded with optical yield reveals the origin of the luminescence.
- Lifetime and time-gated measurements, when combined with the above, can reveal the temporal and chemical nature of the fluorescent sites.
- Even in the absence of localized excitation, time-resolved XEOL is still a powerful diagnostic when combined with other techniques (x- ray absorption, photoelectron spectroscopy).

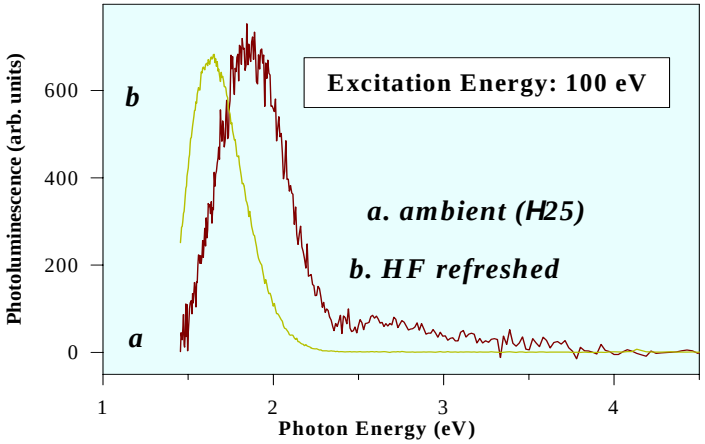
E.g.: Porous Si (Si K-edge excitation)

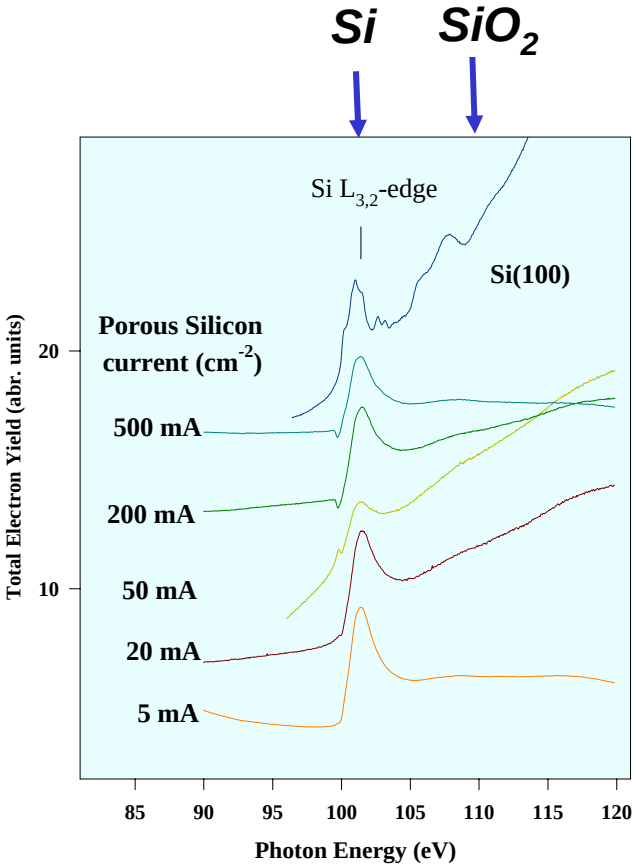


I. Coulthard Ph.D. Thesis, University of Western Ontario 1998

E.g.: Porous Si (Si L-edge excitation)

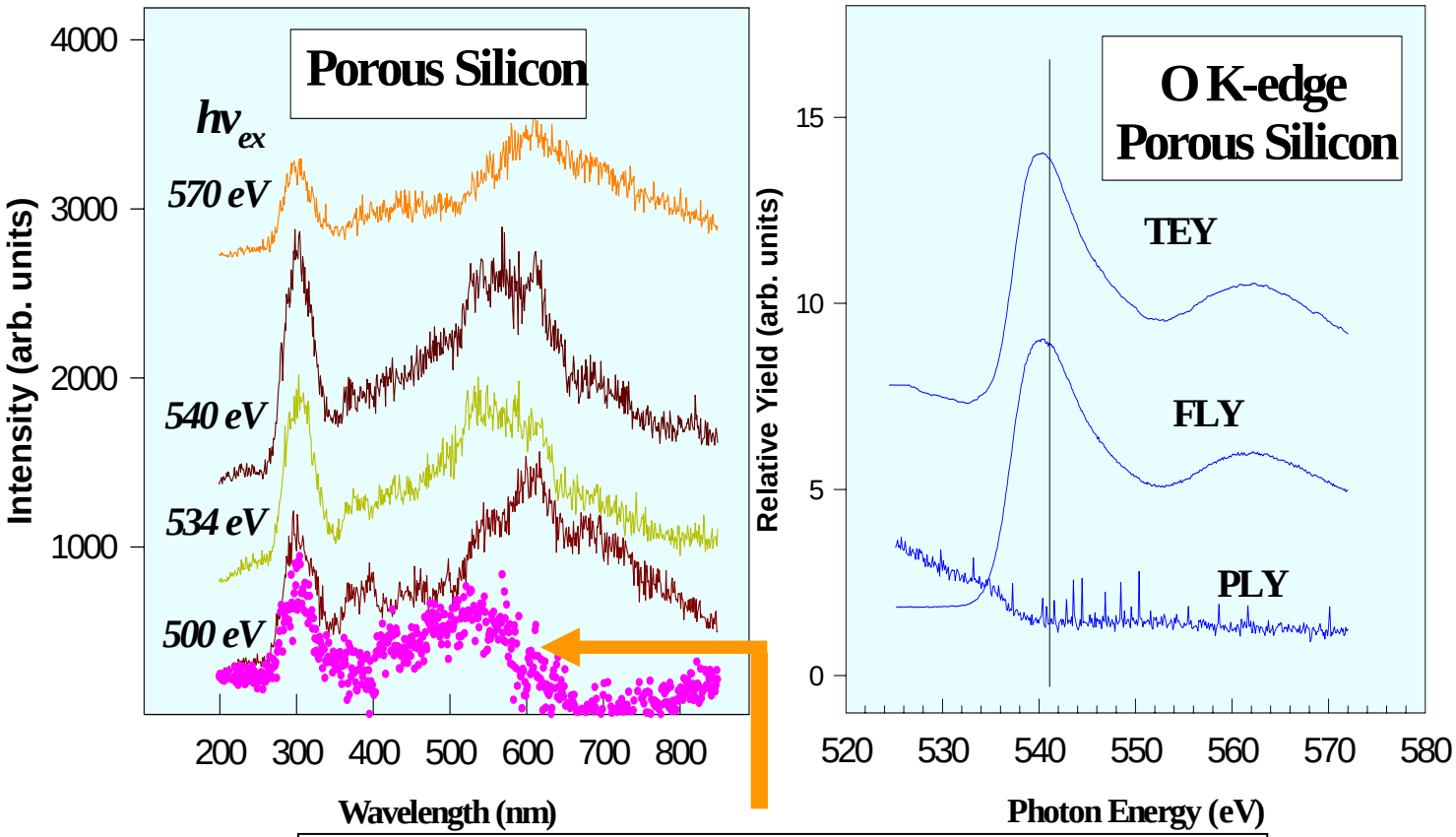






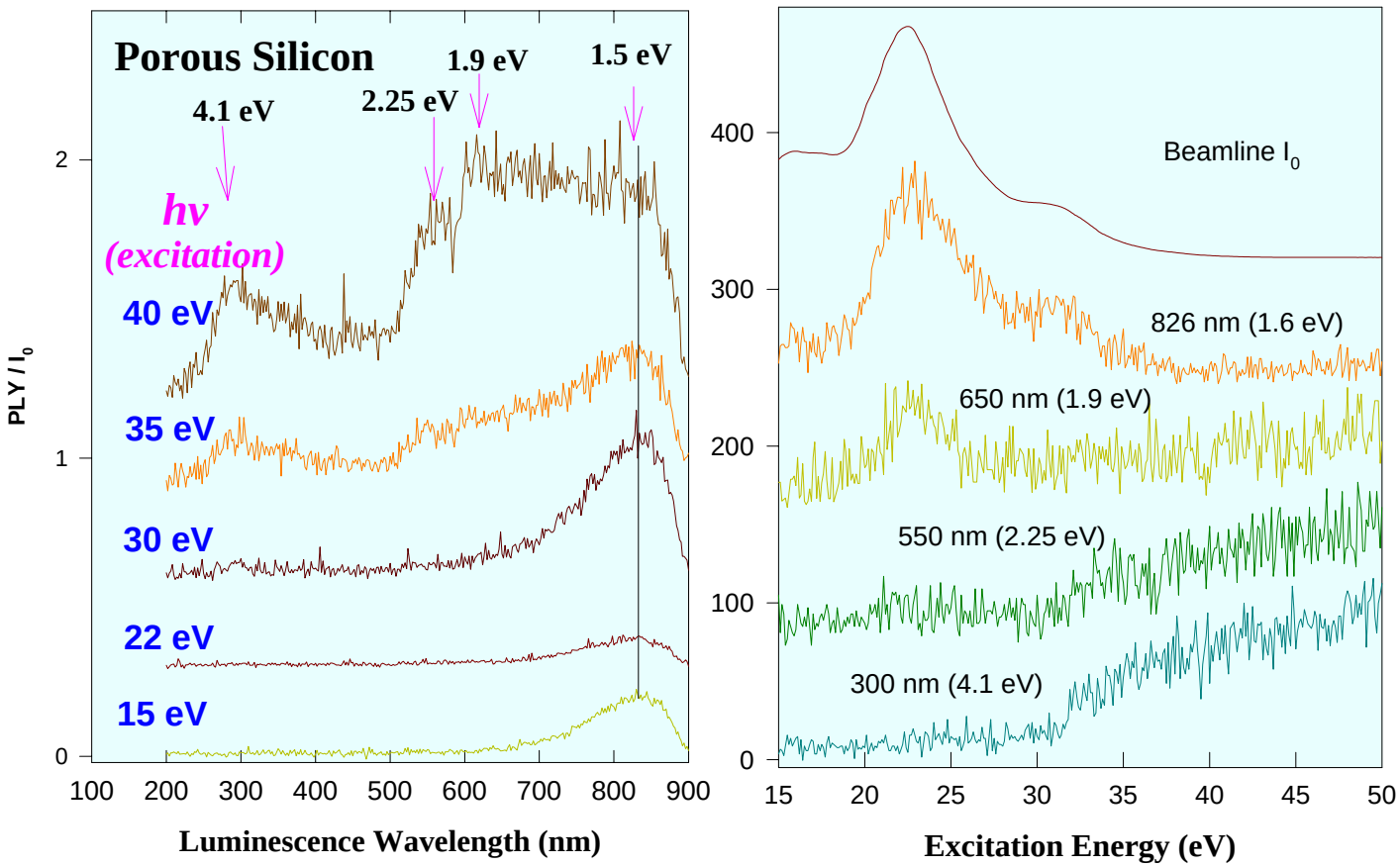
Coulthard et.al, Solid State Comm., 110, 203(1999)

E.g.: Porous Si (O K-edge excitation)



Difference curve above & below the O K-edge

E.g.: Porous Si (Inner valence excitation)



Morphology of Silicon Nanowires (SiNW)

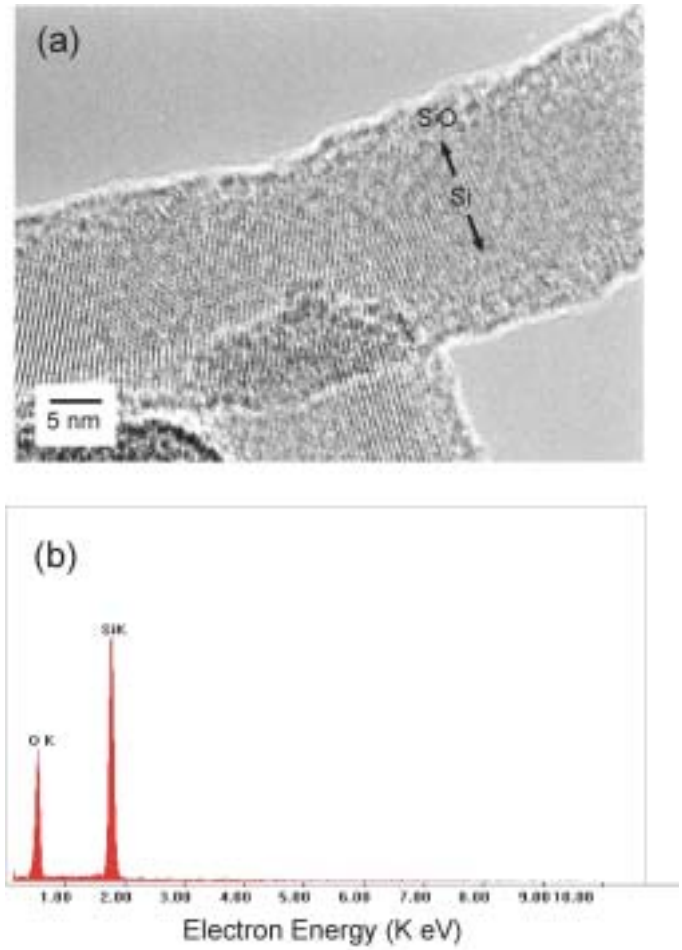


Fig. 1(a) The TEM image and (b) EDS result of as-prepared SiNWs

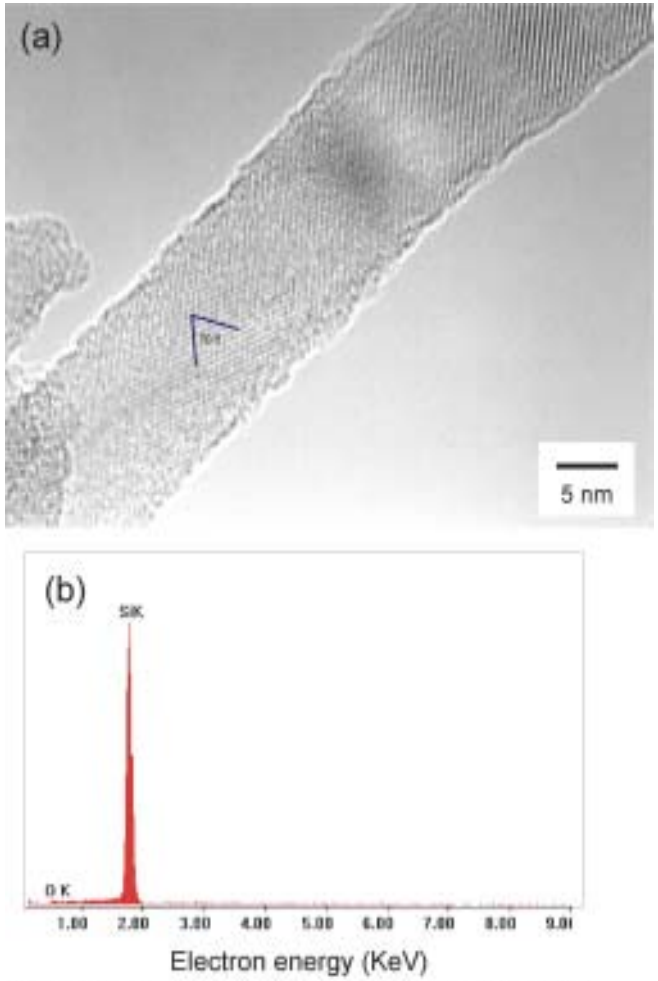
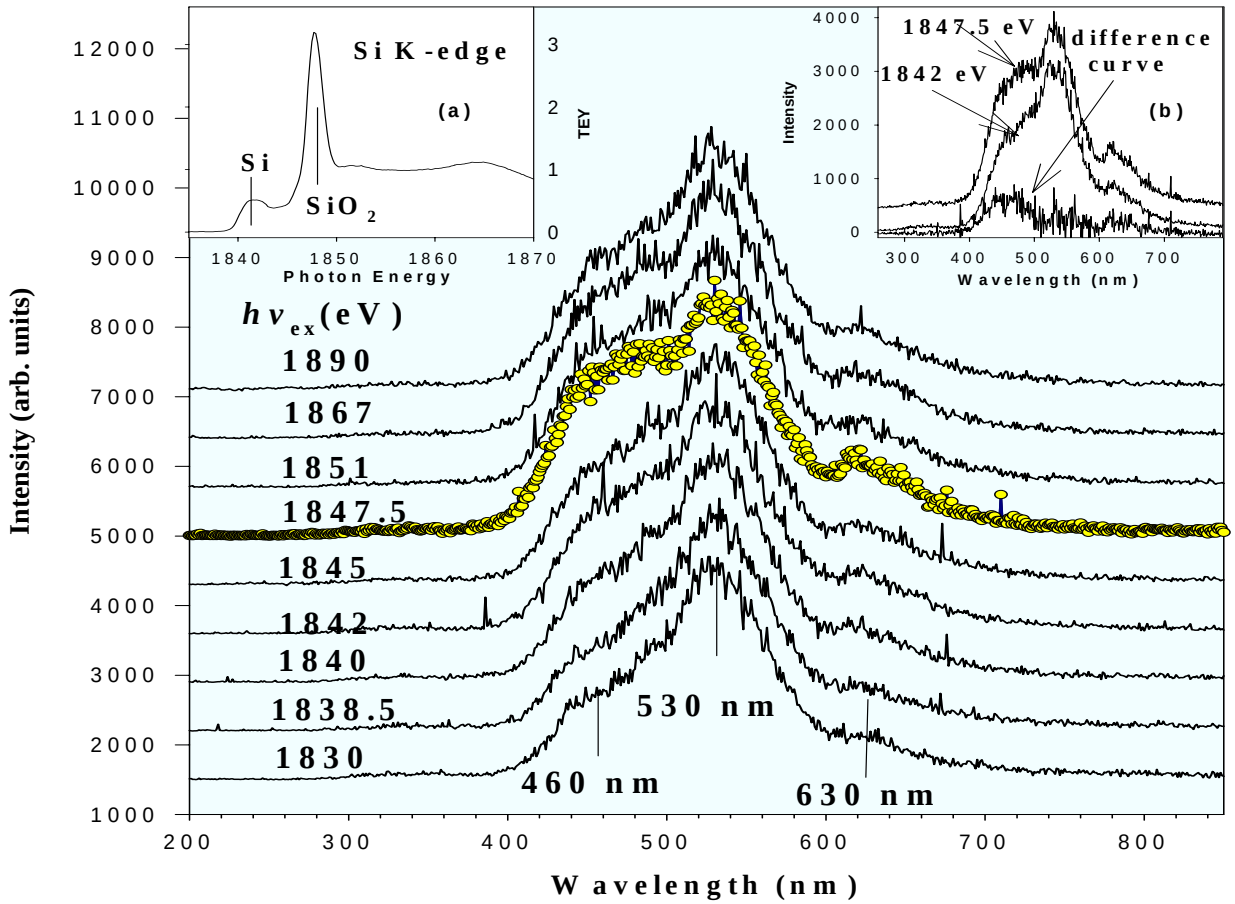


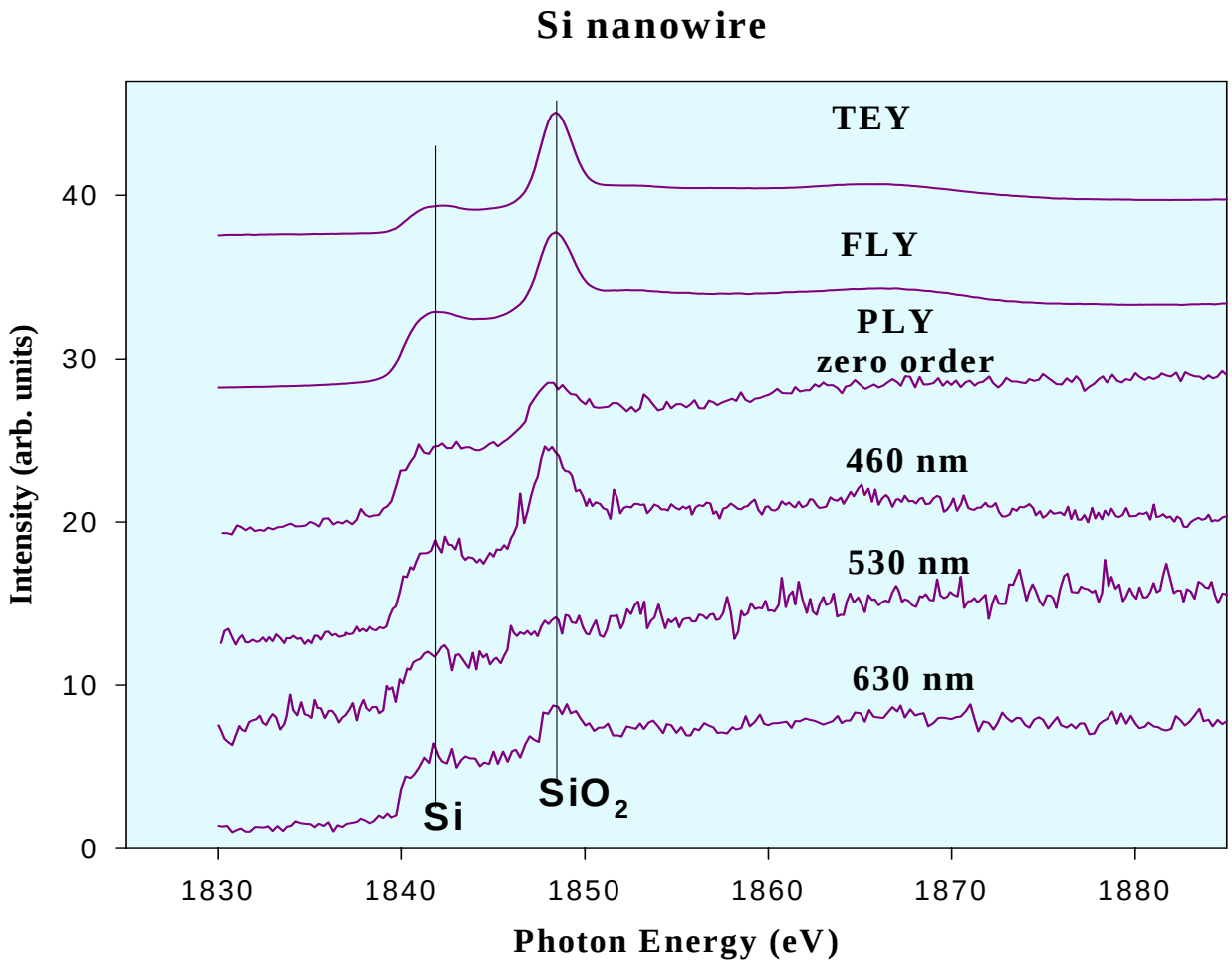
Fig. 2 The TEM image (a) and EDS result (b) of HF etched SiNWs

Si K-edge XEOL of silicon nanowires

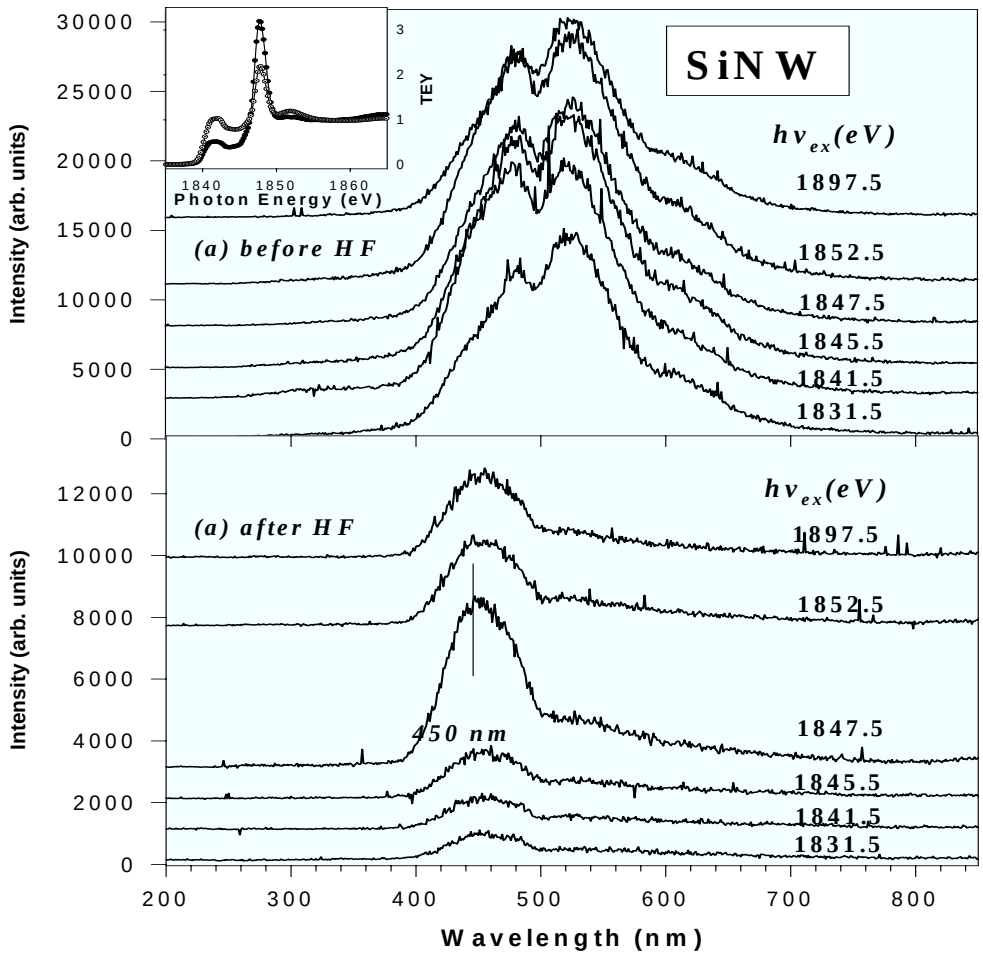


Sham et al. Phys. Rev. B 70, 045313 (2004)

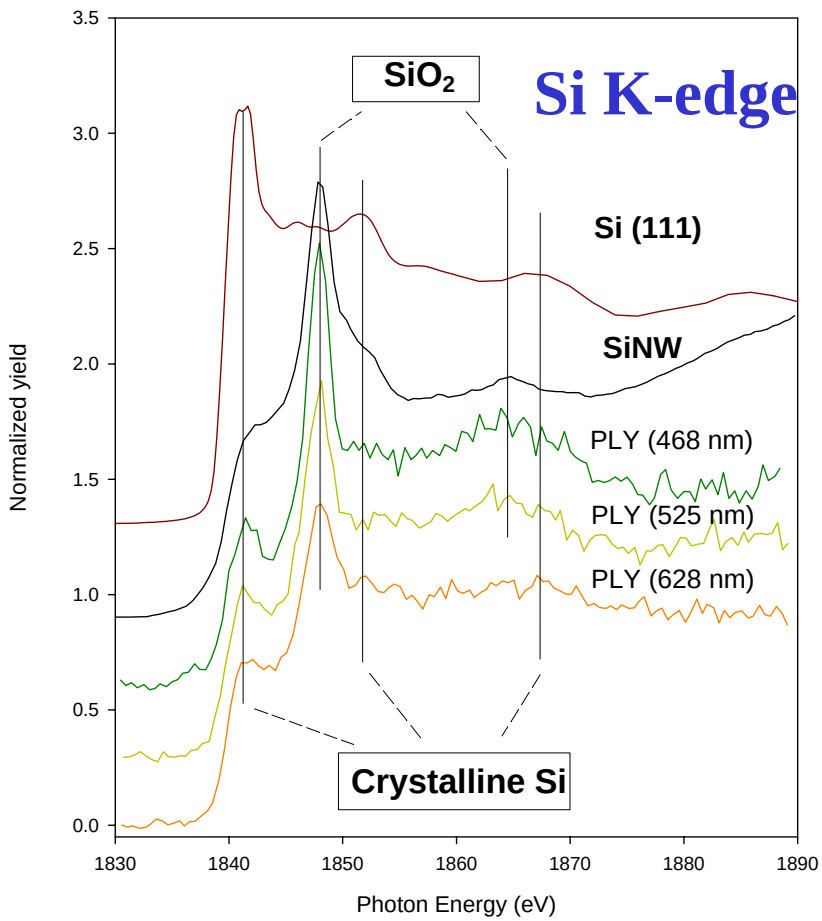
Photoluminescence: Si K-edge

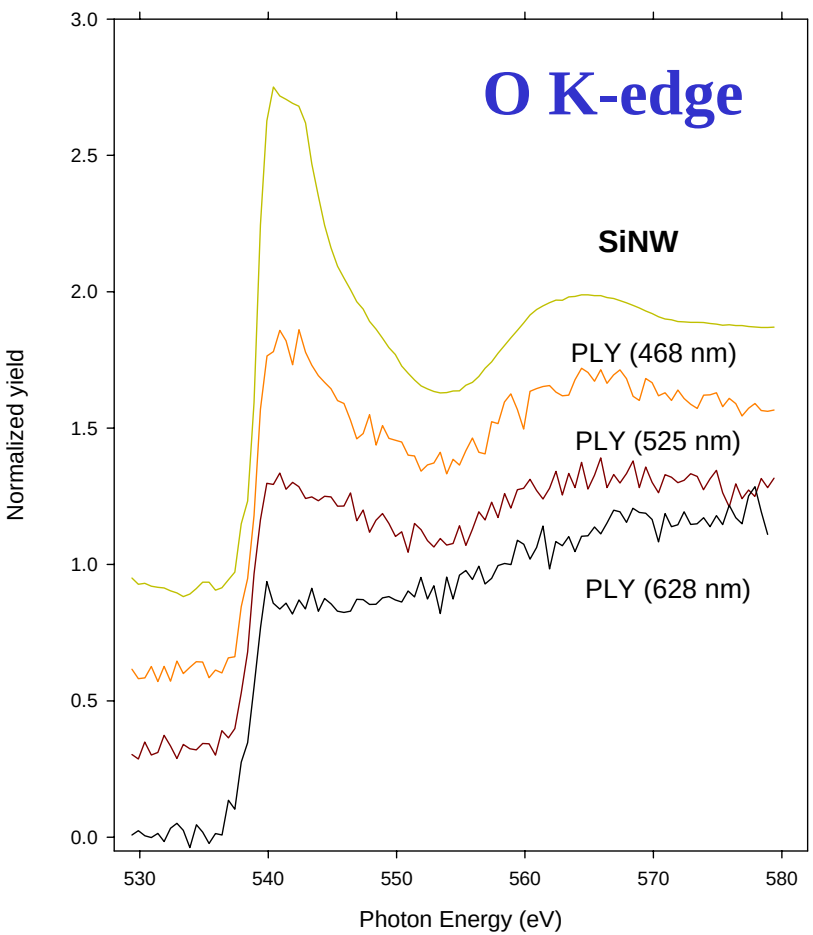


XEOL and chemistry of SiNW

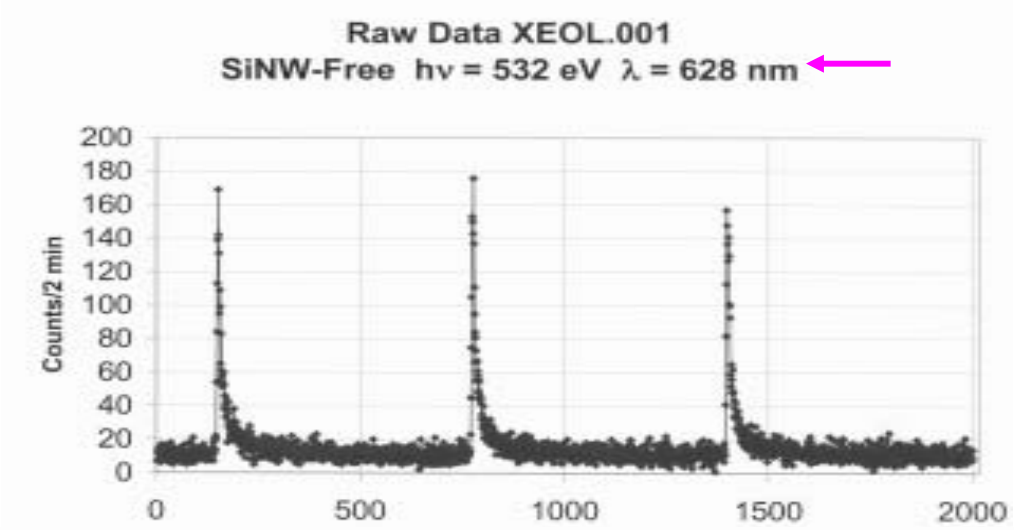


SiNW XEOL and chemical specificity in



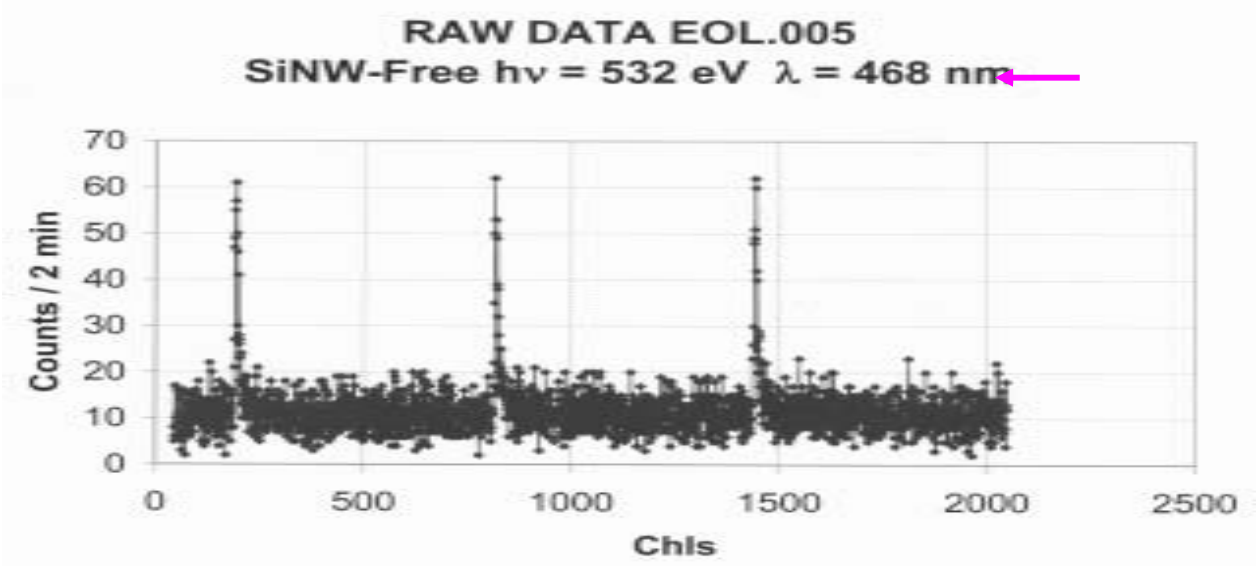


TRXEOL: lifetime measurements



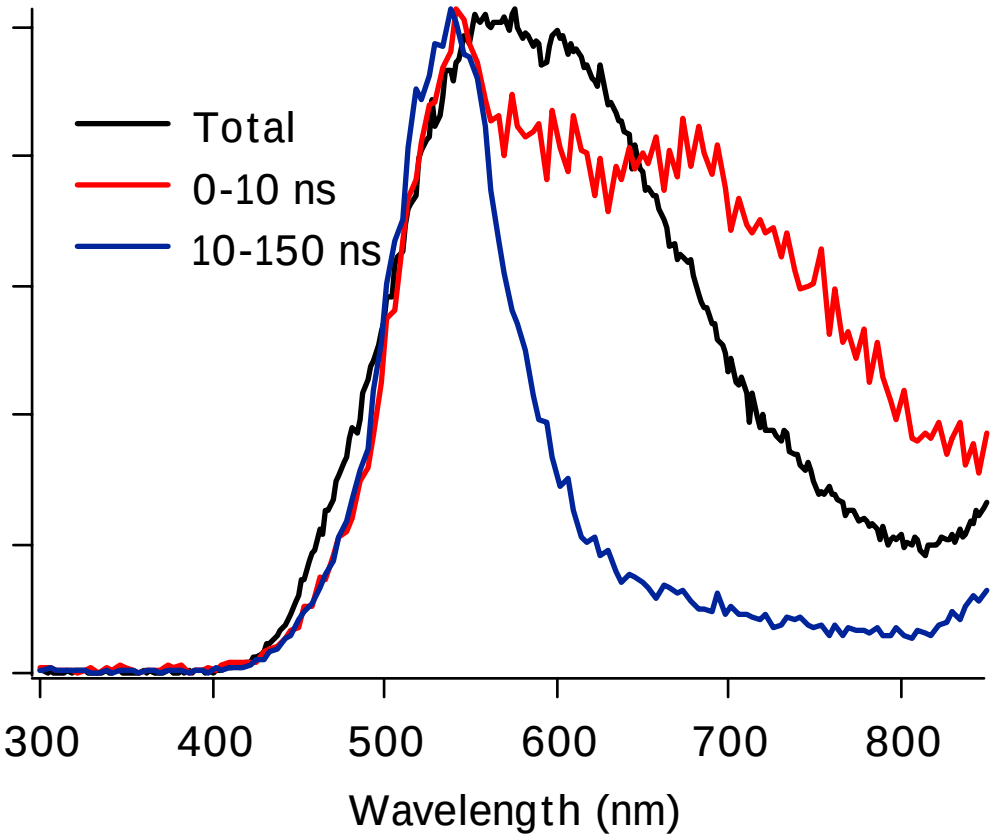
O K-edge

$h\nu_{ex}$ = 532 eV



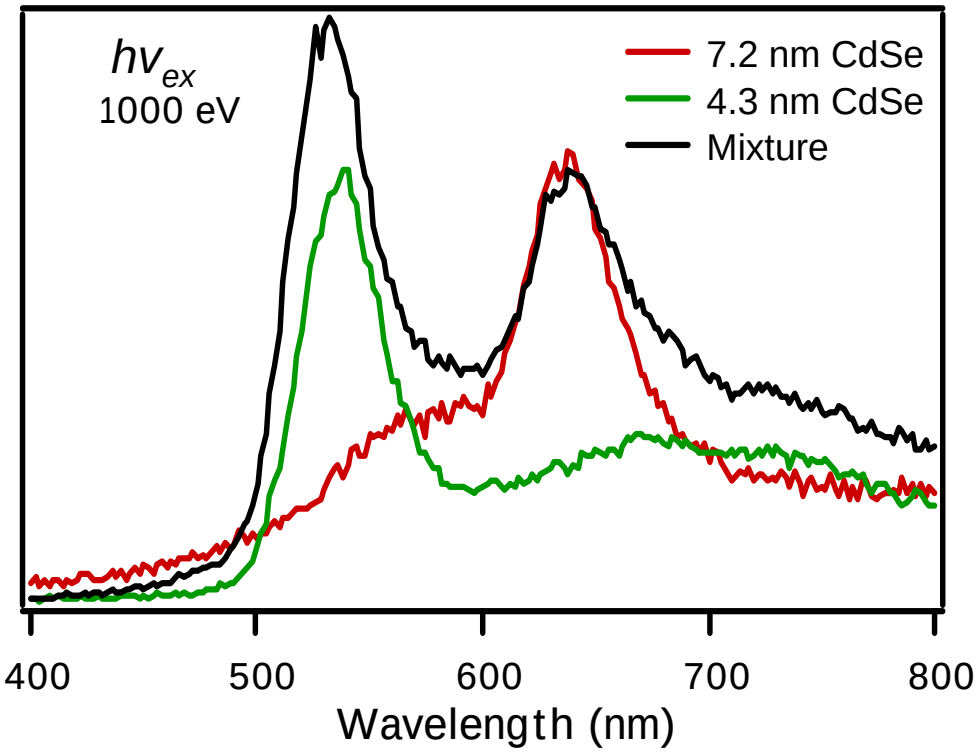
Time-gated XEOL of SiNW

$h\nu_{ex}$ = 1000 eV



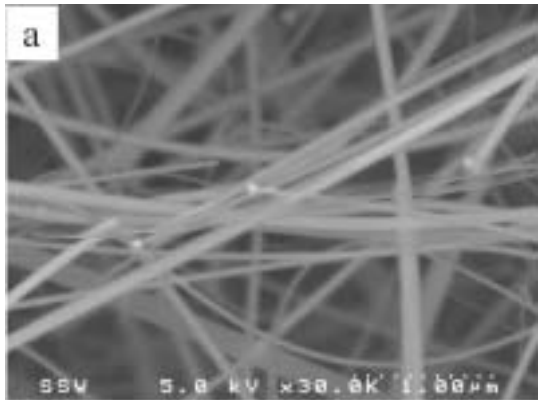
Nanoscience Applications: CdSe nano dots

- The luminescence of nanoparticles is often dominated by quantum size effects.
- Luminescence can yield size as well as chemical information

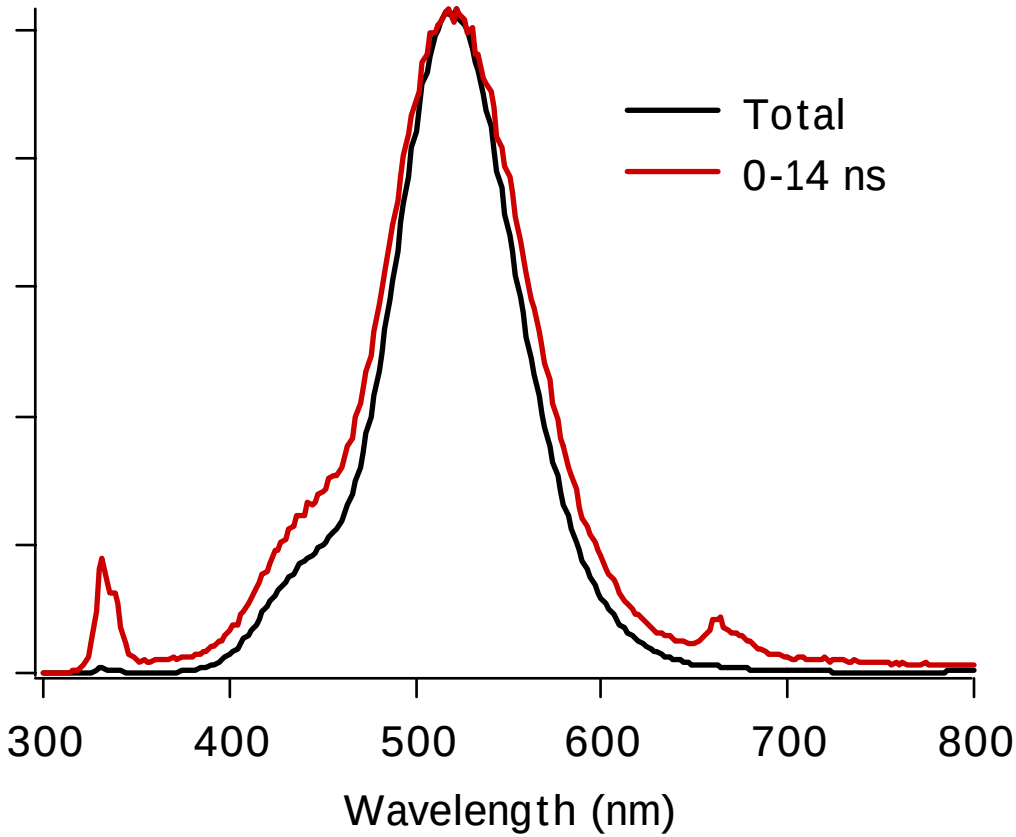


Quantum confinement: The smaller the size, the larger the band gap (shortening the dimension of a 1-D particle in a box)

Nanoscience Applications: ZnS nano ribbons

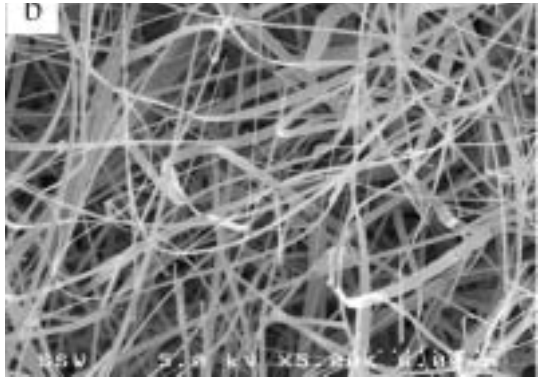


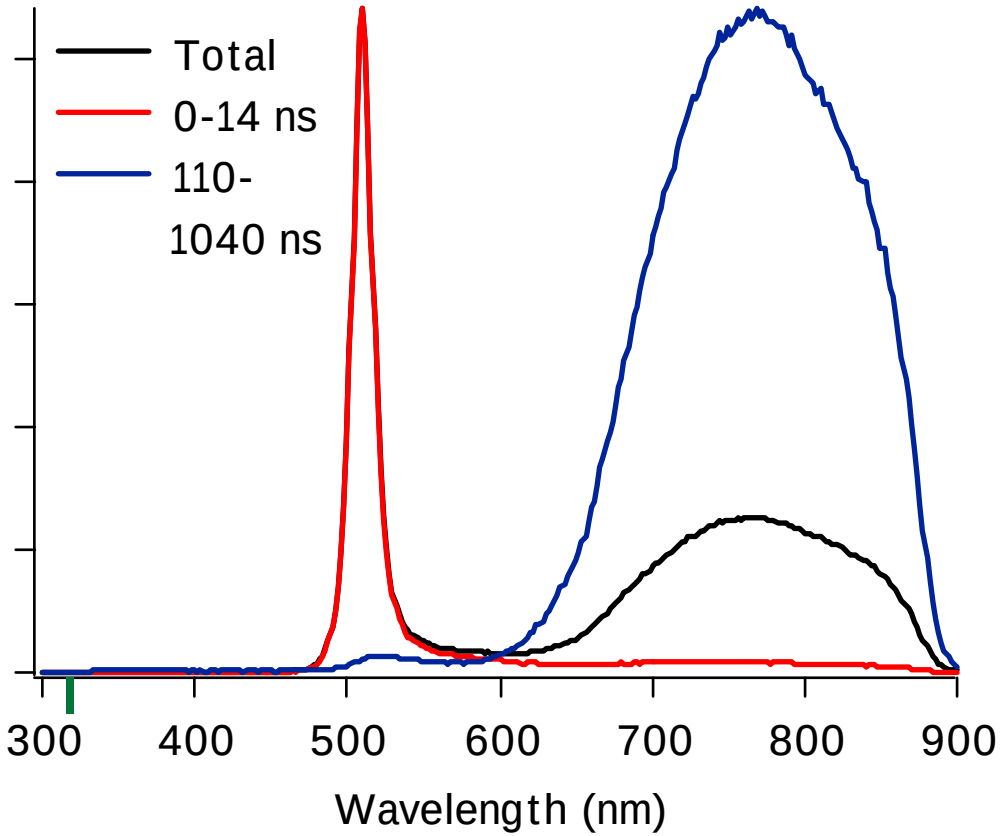
$h\nu_{ex}$ = 1000 eV



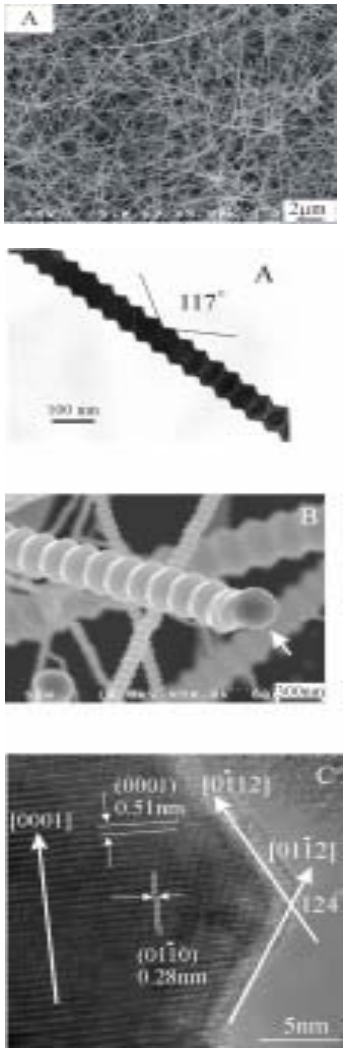
Nanoscience Applications: CdS nano ribbons

$h\nu_{ex}$ = 1000 eV

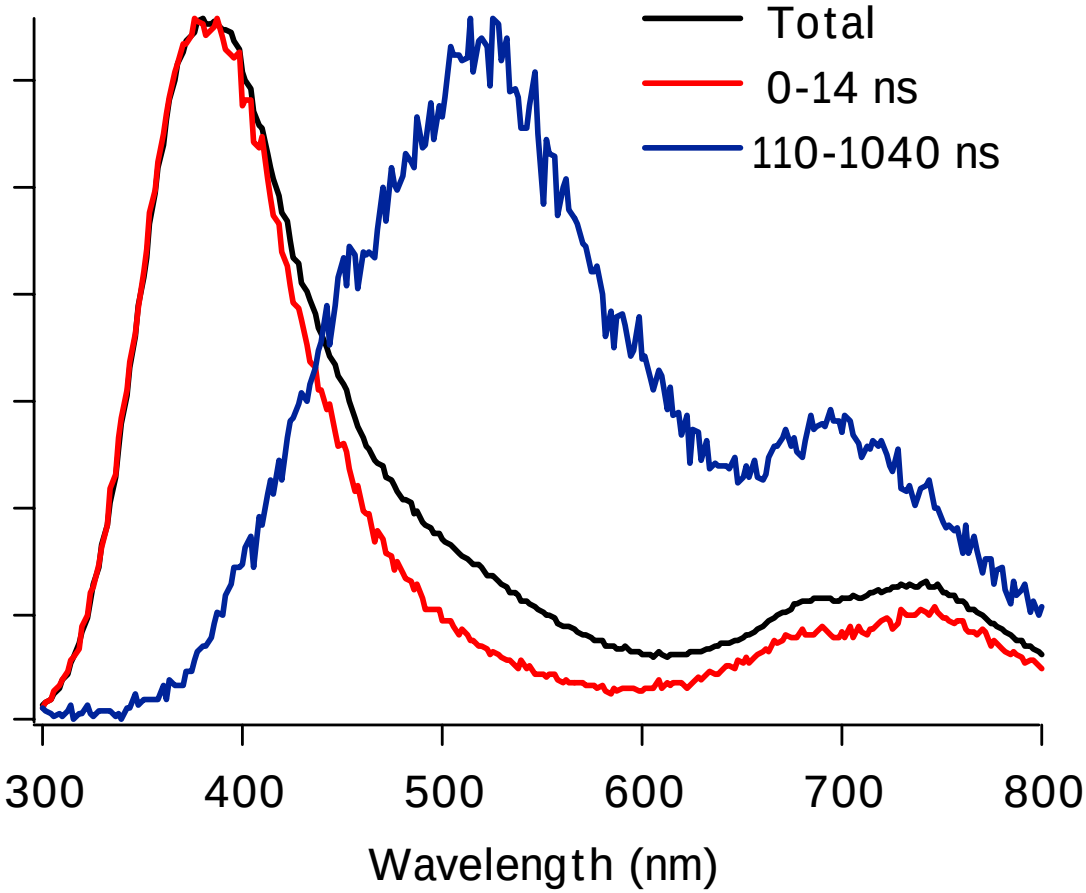




Nanoscience Applications: GaN nanowires

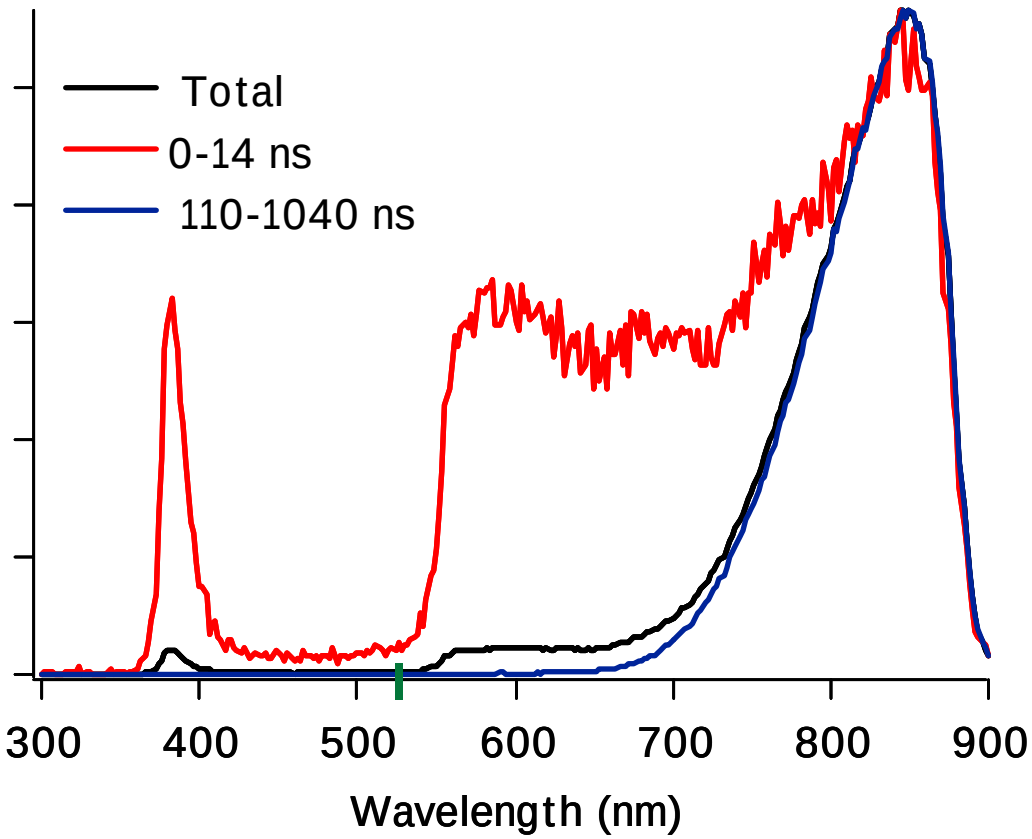


$h\nu_{ex}$ = 1000 eV

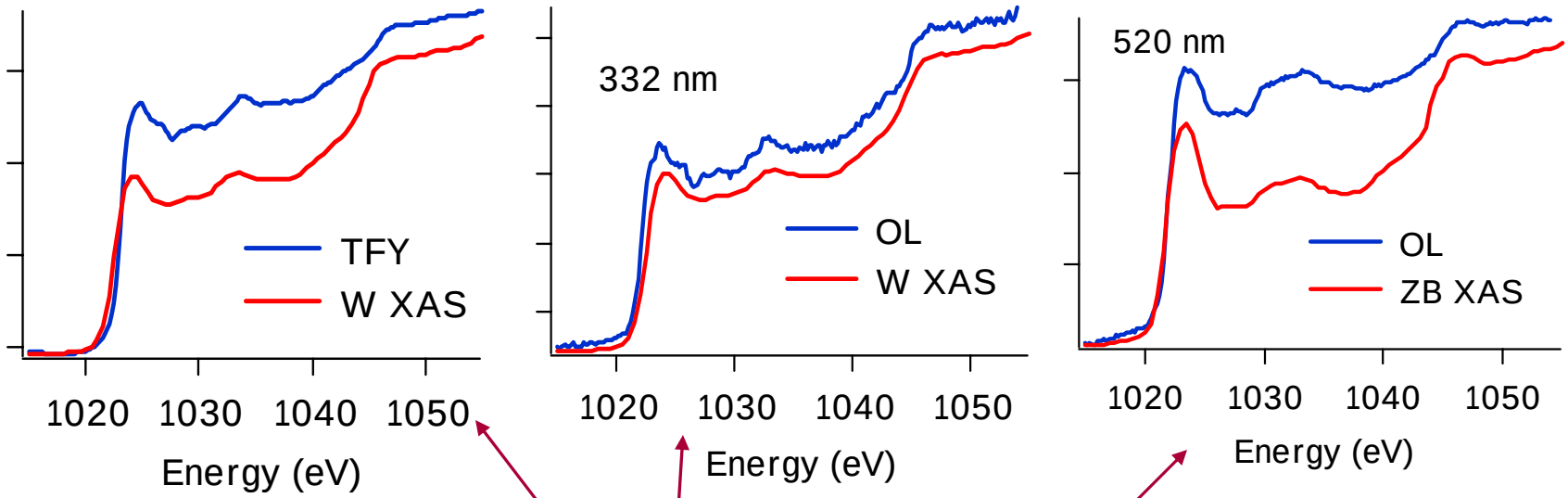


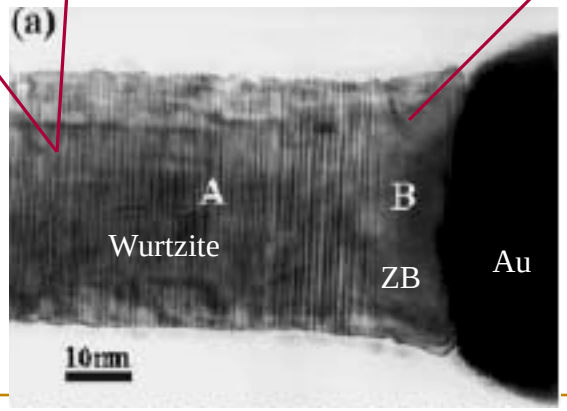
Nanoscience Applications: ZeTe nano dots

$h\nu_{ex}$ = 1000 eV



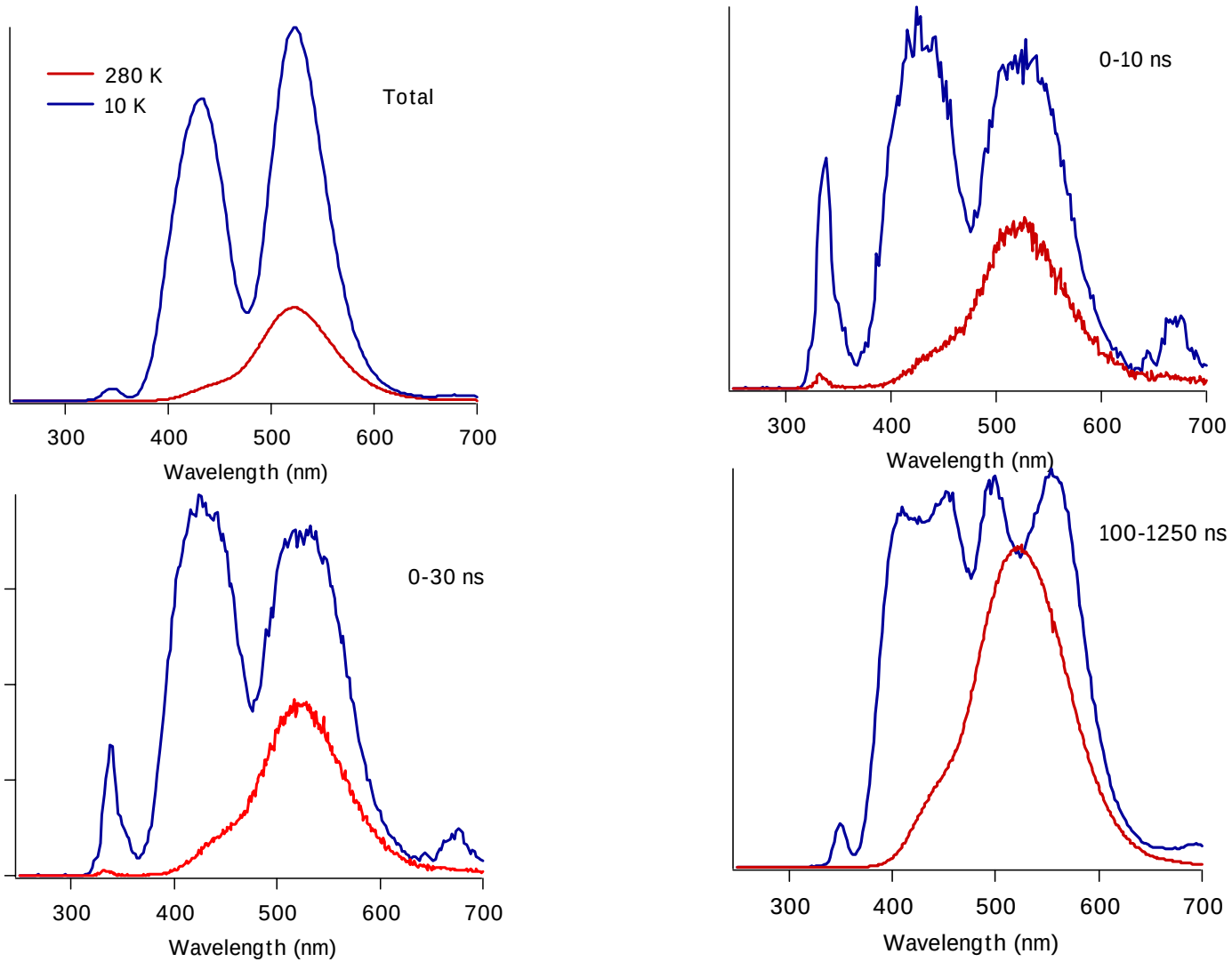
Zn L-edge excitation spectra



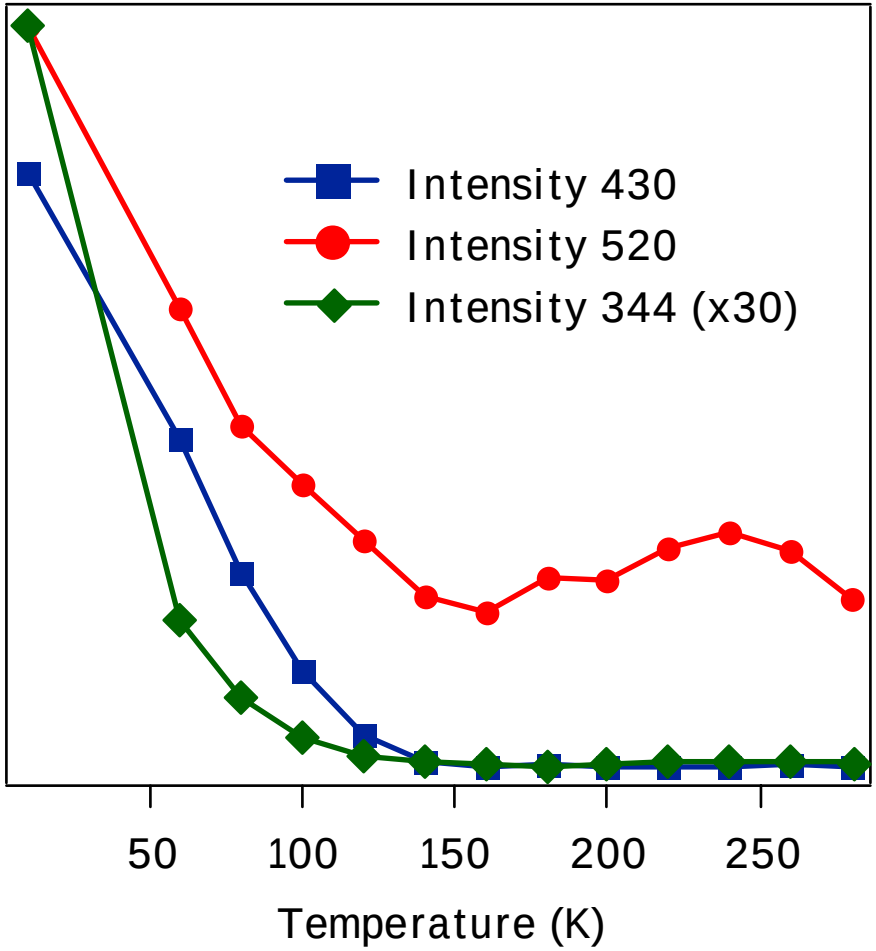


XAS Data: B. Gilbert et al, Phys. Rev. B 66, 245205 (2002).

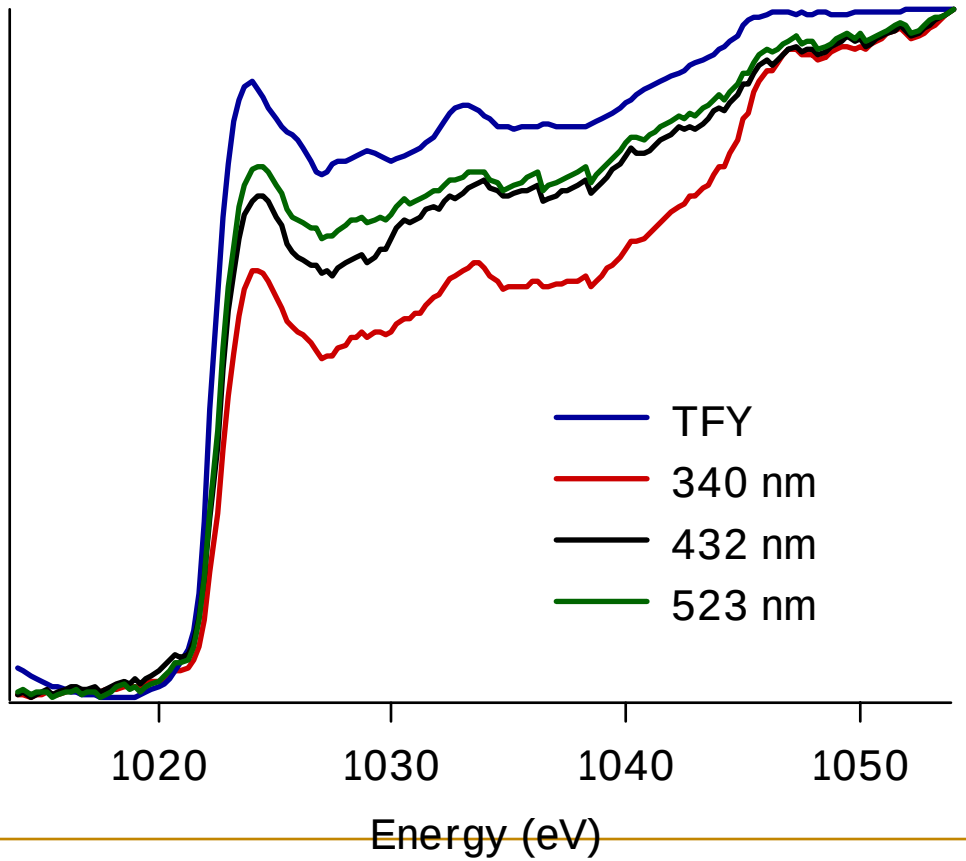
ZnS Nanowires, f(T)



ZnS Nanowires, f(T)



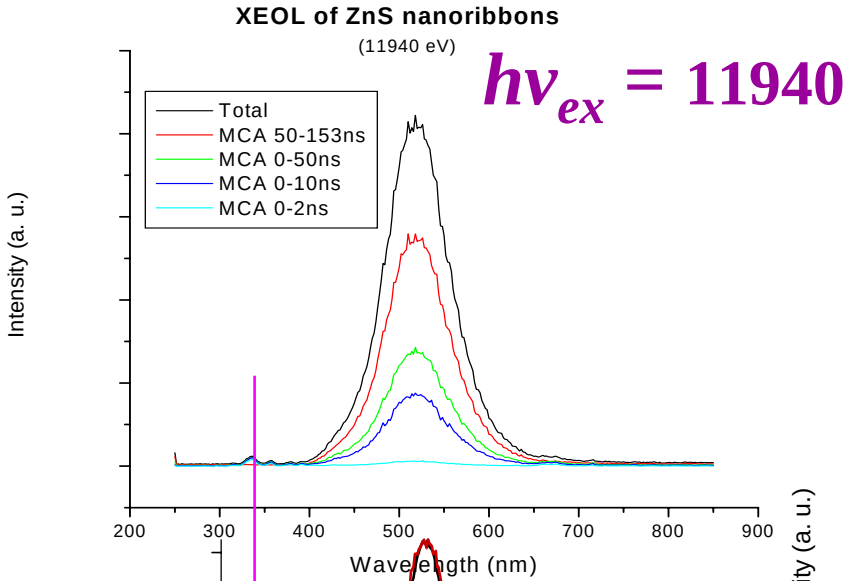
ZnS Zn L-edge Absorption at 10 K



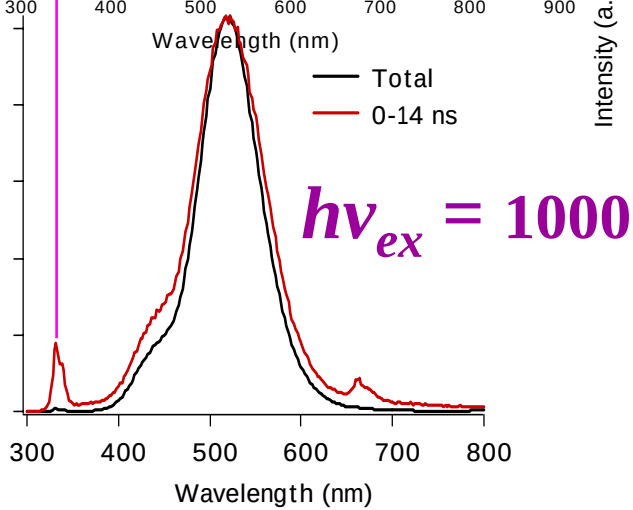
TRXEOL: The hard x-ray advantage

- Can access deeper core levels and are more site specific
- Does not require an UHV environment and in fact measurement can be conducted in any environment
- Can be applied to study liquids
- Utilization of the X- ray microbeam

Nanoscience Applications: ZnS nano ribbons

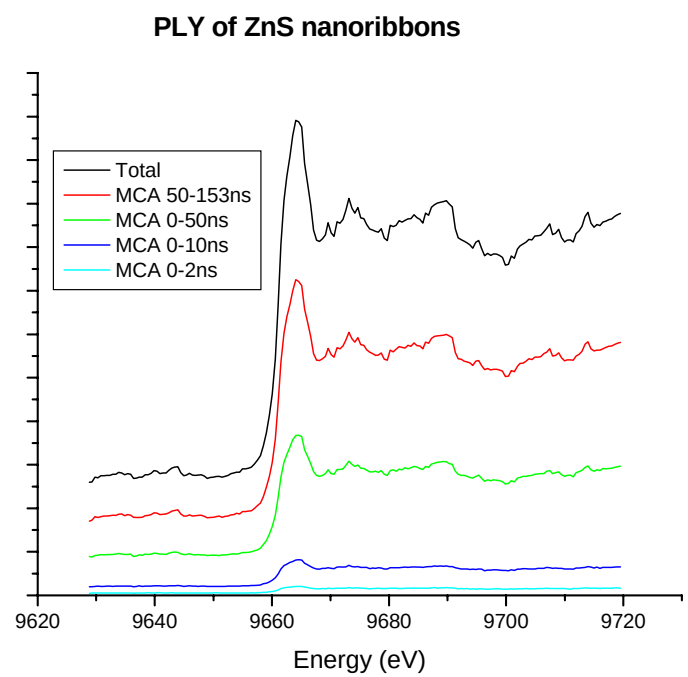


$h\nu_{ex}$ = 11940 eV

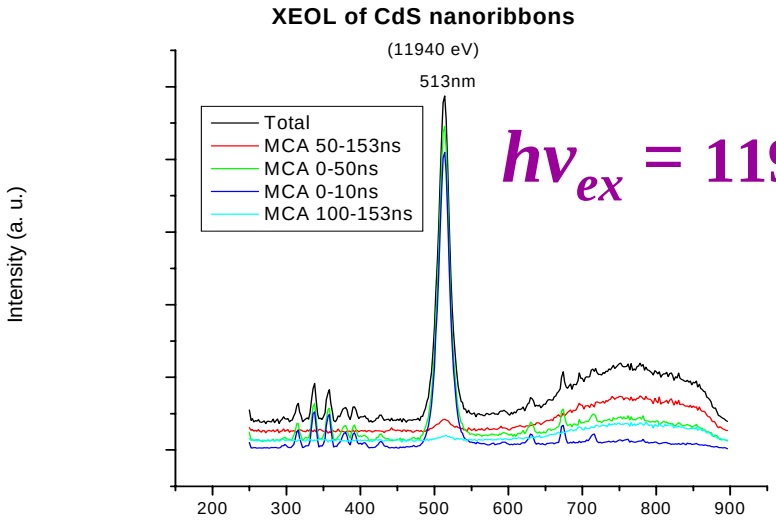


$h\nu_{ex}$ = 1000 eV

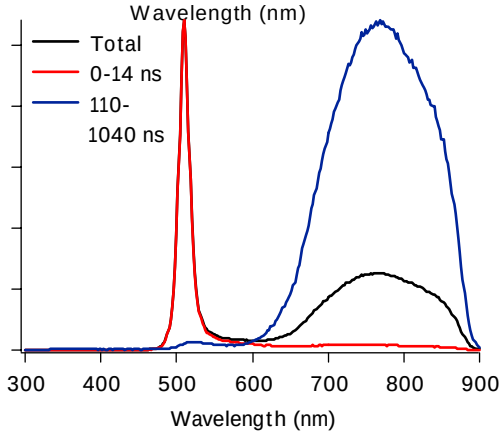
Zn K-edge XANES (time-gated PLY)



Nanoscience Applications: ZnS nano ribbons

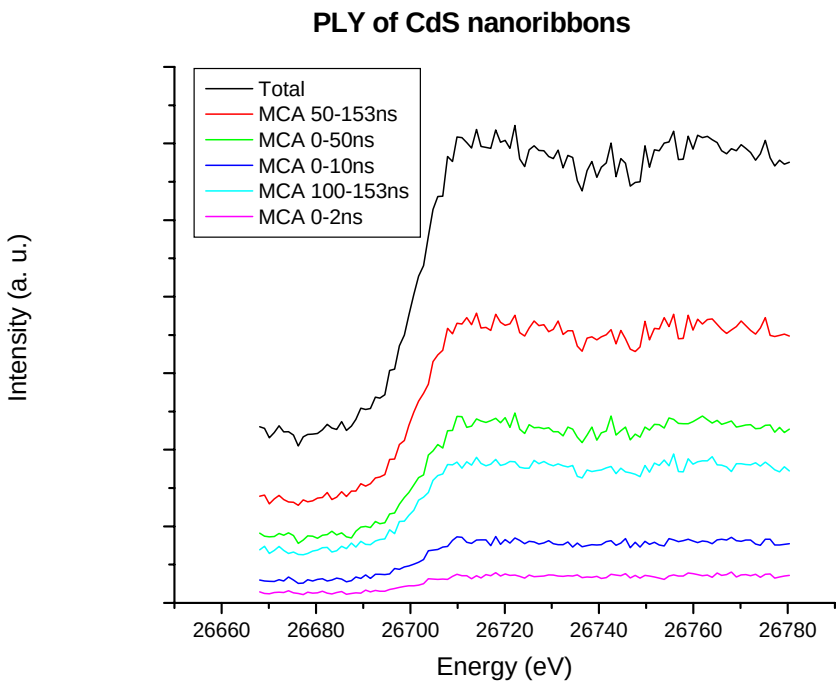


$h\nu_{ex}$ = 11940 eV

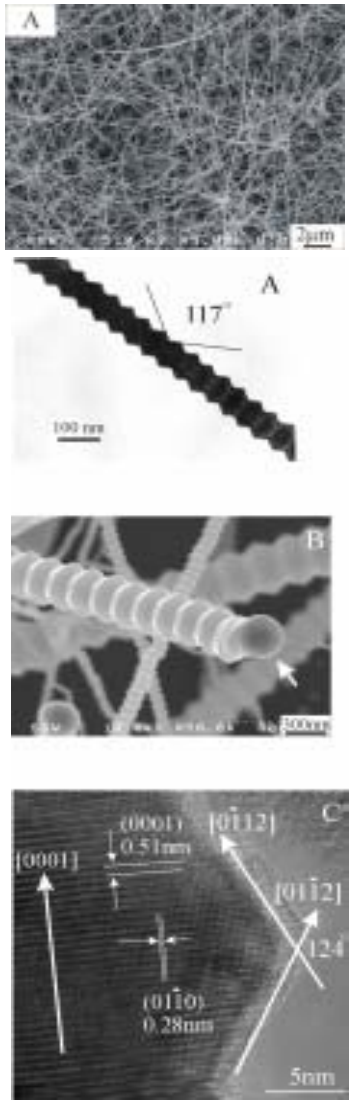


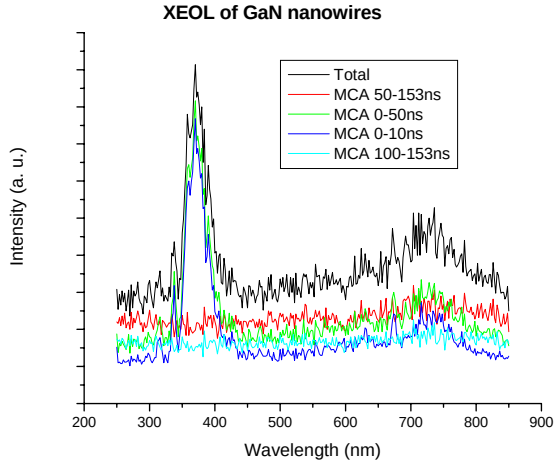
$h\nu_{ex}$ = 1000 eV

Cd K-edge XANES (time-gated PLY)



Nanoscience Applications: GaN nanowires

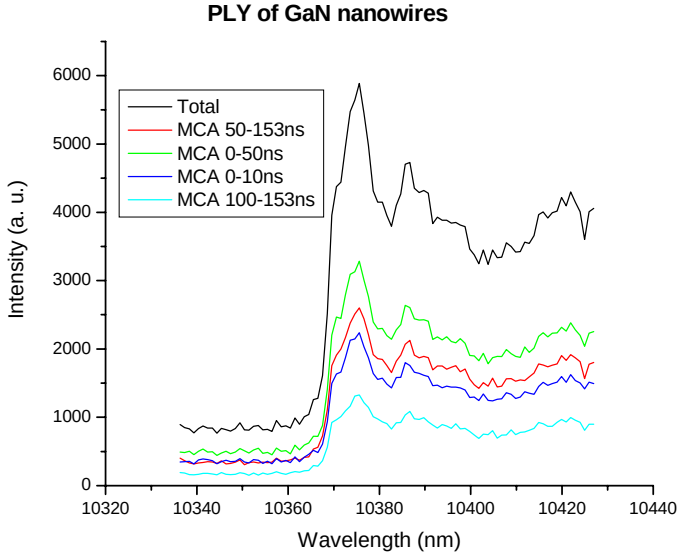




Time-gated XEOL

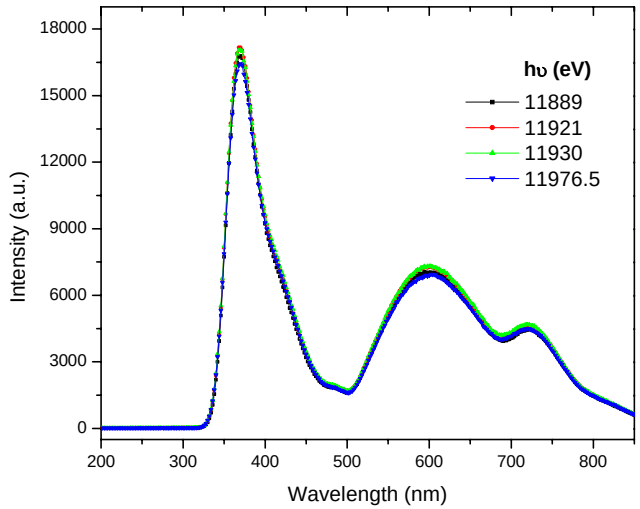
slow

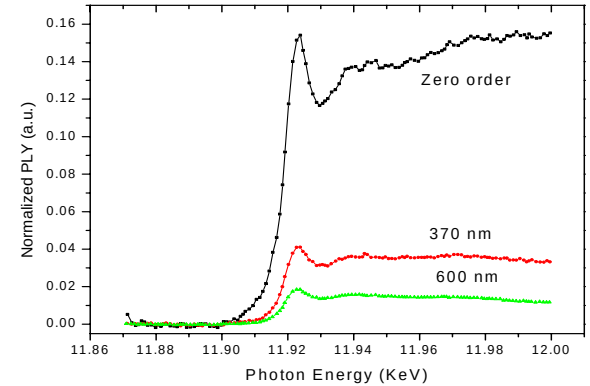
fast

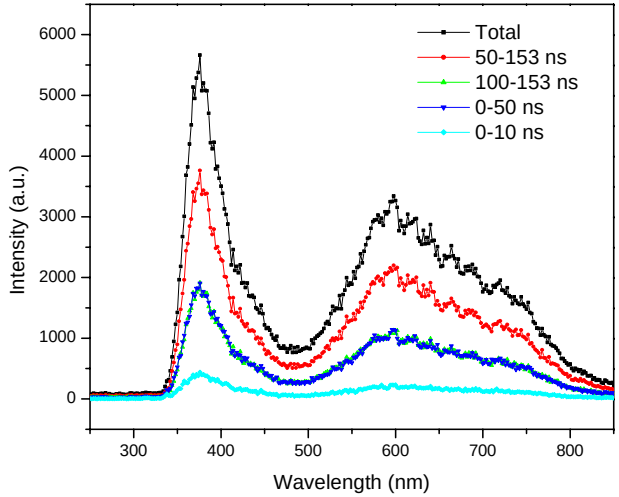


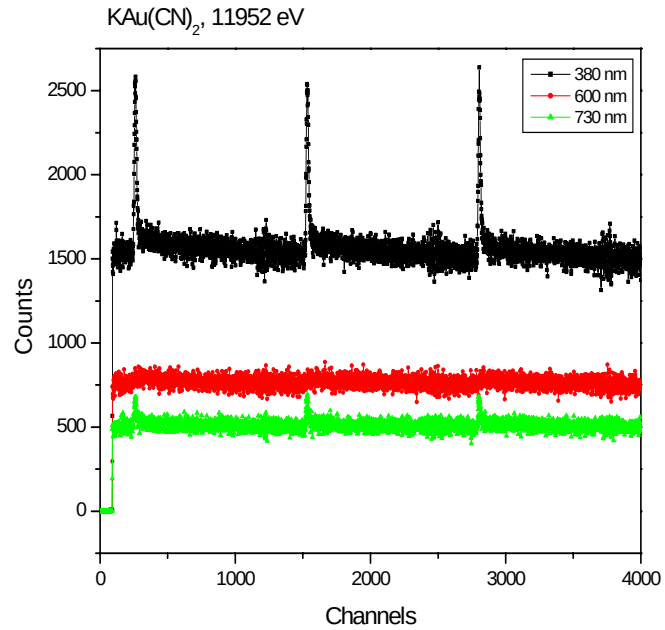
Ga K-edge XANES (time-gated PLY)

Related Applications: TRXEOL from $KAu(CN)_2$









Prospects

- **Correlation** of luminescence in both energy and time domain with other measurements (e.g. electronic, magnetic and transport properties).
- **Dynamics of energy transfer** in nanostructure and assembly of nanostructures.
- **Temperature dependence** of luminescence, lifetimes and time-gated spectroscopy.
- Magnetically doped nanostructures, luminescence **dichroism, opto-magnetic phenomena.**
- **Imaging with a micro x-ray beam** in both energy and time domain and time-dependent microspectroscopy (e.g. molecular beacon tagged proteins)

Acknowledgements

- **University of Western Ontario**
  - P.-S. G. Kim, X.-T. Zhou
- **Canadian Synchrotron Radiation Facility**
  - F. Heigl, Y.-F. Hu
- **Advanced Photon Source**
  - J. Freeland, D. Keavney, S. Head, D, Brewe, R. Gordon