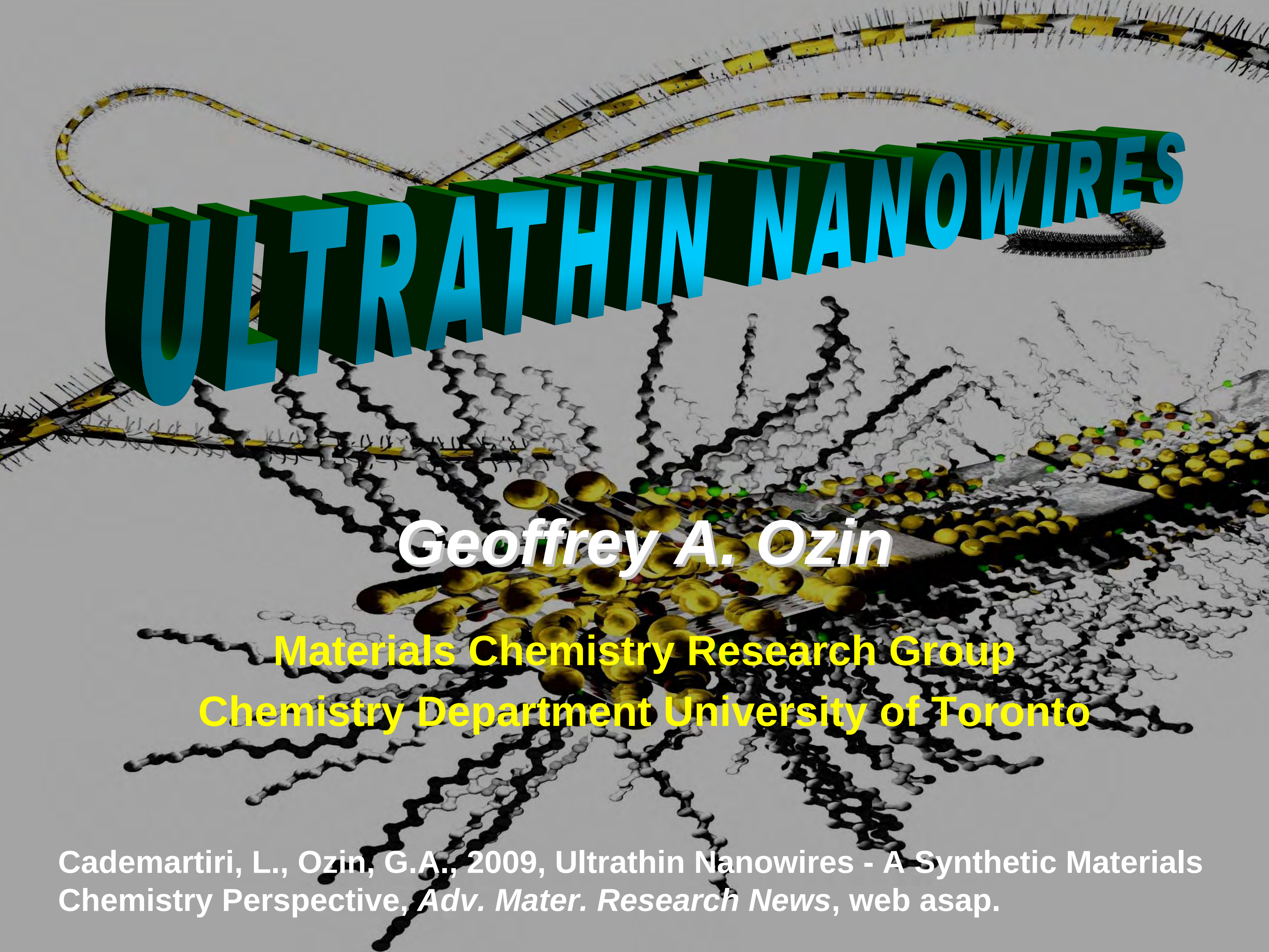

ULTRATHIN NANOWIRES

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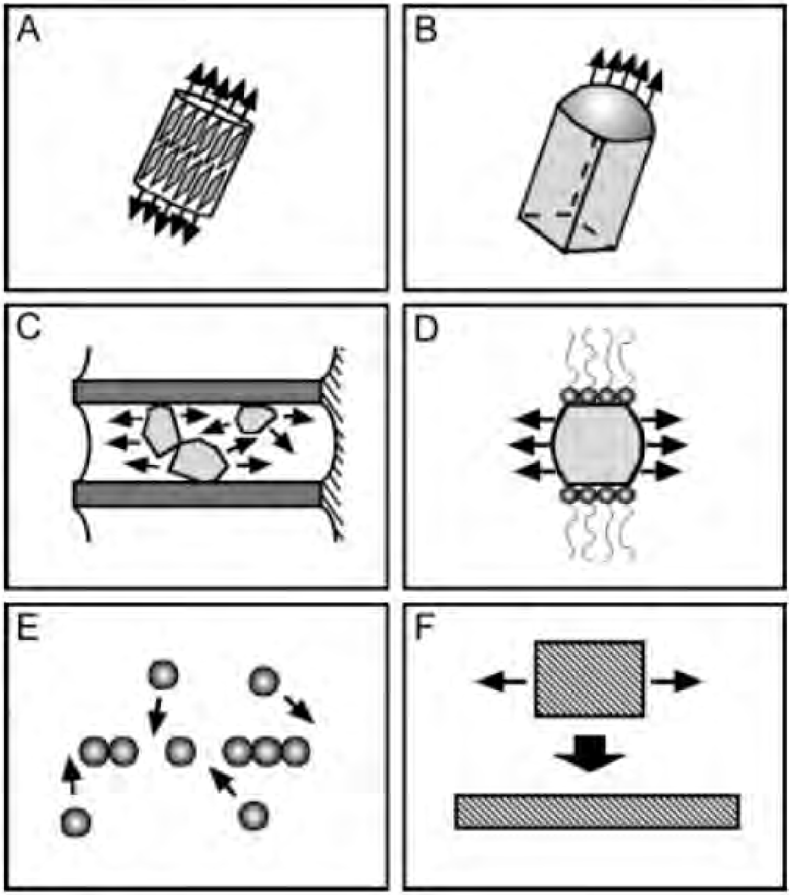
Cademartiri, L., Ozin, G.A., 2009, Ultrathin Nanowires - A Synthetic Materials Chemistry Perspective, *Adv. Mater. Research News*, web asap.

NANOWIRE MOTIVATION

- **QUANTUM AND SPATIAL CONFINEMENT**

- **Nano Electronics - transistors, diodes, interconnects, circuits**
- **Nano Optics - LEDs, Lasers, plasmonics, waveguides, circuits**
- **Nano OptoElectronics – solar cells, photodetectors**
- **Nano Sensors – biological diagnostics, pathogen detection**
- **Nano Memory - phase change, N-NM**
- **Nano Mechanics – UHF 100 MHz oscillators, yg 10^{-24} g mass monitors**
- **Nano Thermoelectrics – solid state refrigeration, power generation**

NANOWIRE GROWTH



- Anisotropic
- VLS
- Template directed
- Ligand controlled
- Oriented attachment
- Size reduction

Choosing a Nanomaterial

Nanotoxicology???

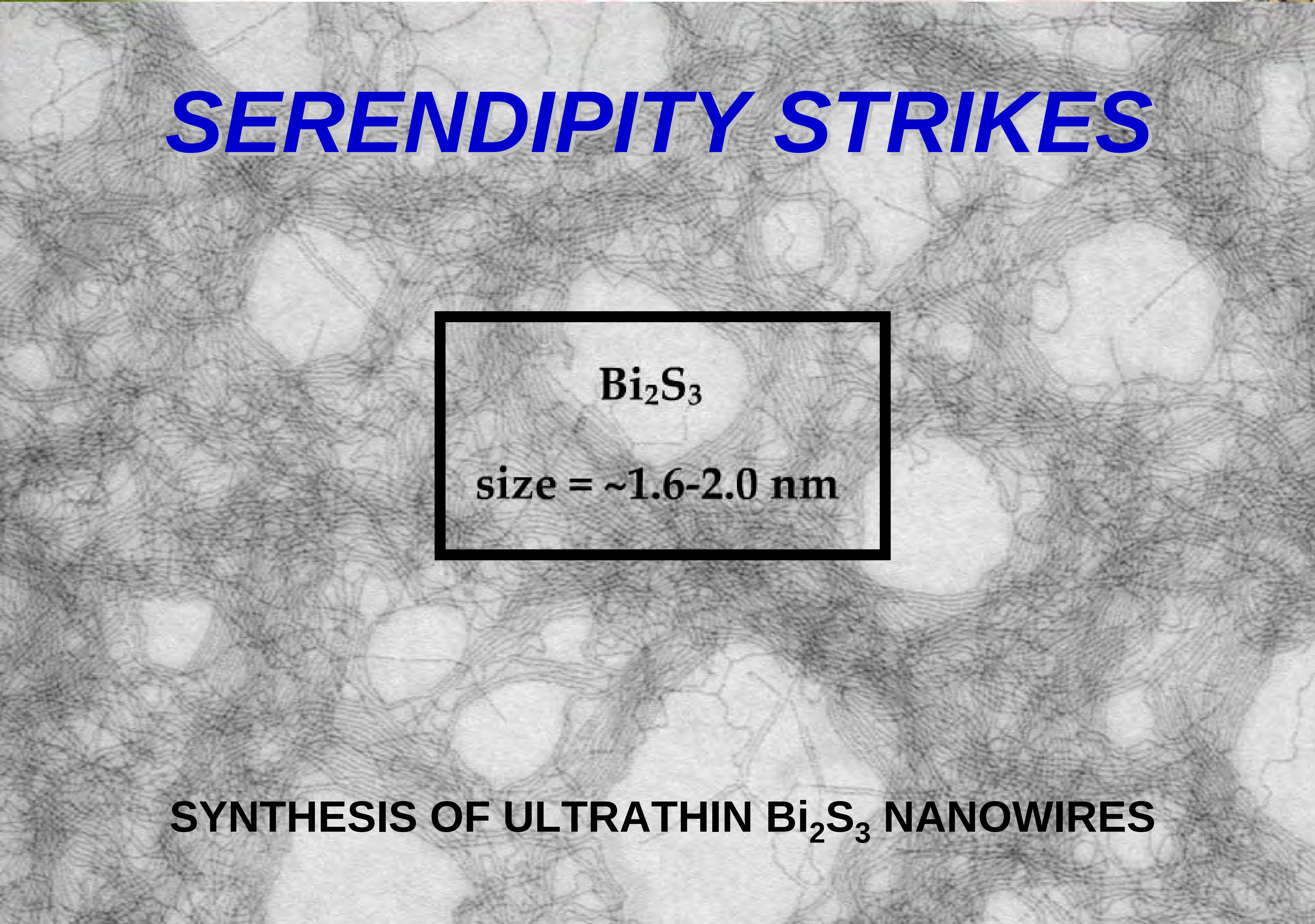
- **Pepto-Bismol®** is an over-the-counter drug produced by the Procter and Gamble company in the United States of America and in Canada to treat minor digestive system upset.

- Its active ingredient is ***Bismuth Salicylate***, which is also responsible for its distinctive pink color.

SYNTHESIS OF Bi_2S_3 NANOWIRES

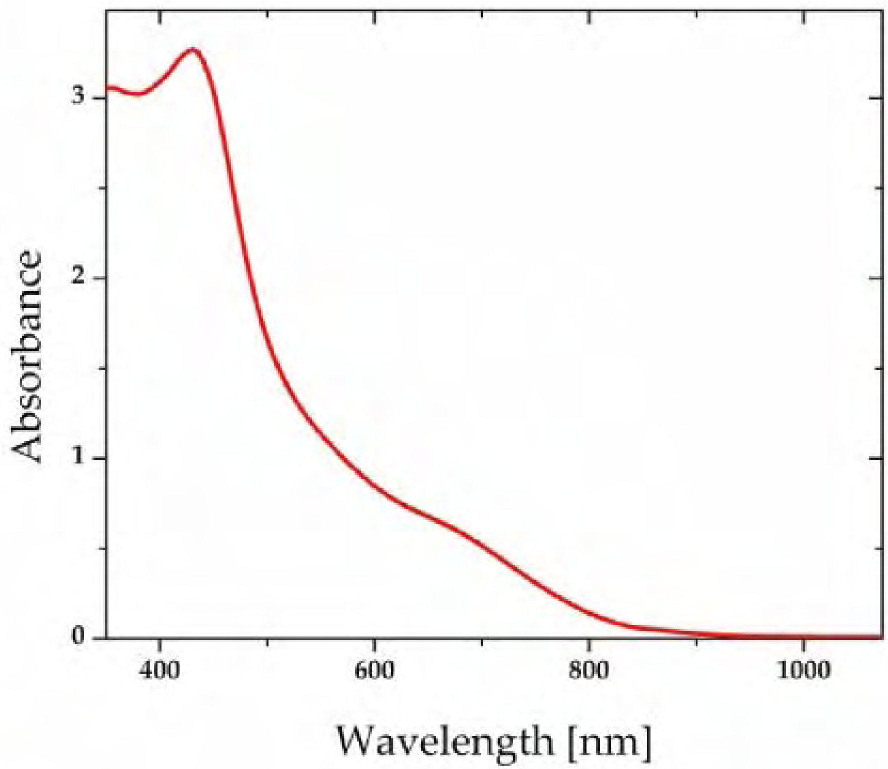
	Bi_2S_3 nanowires
precursors	Bi citrate + S
ligands & solvents	oleylamine or oleylamine + oleic acid
Tinjection	130-200ºC
Tgrowth	100ºC
time	1-30 min
precursor ratio	0.2

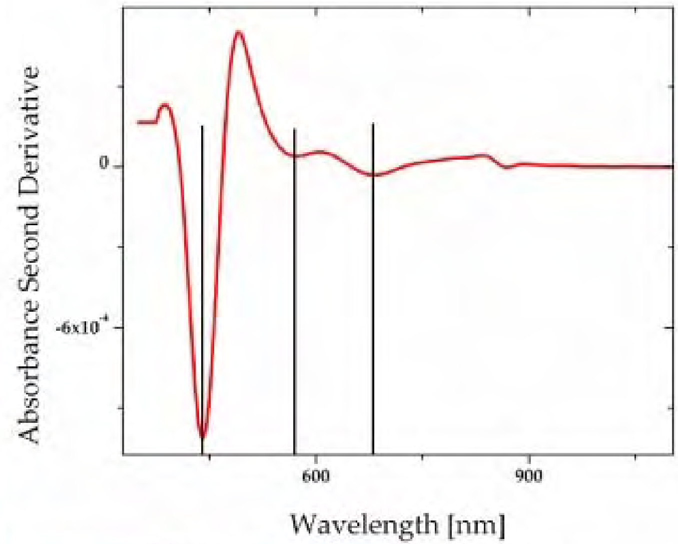
SERENDIPITY STRIKES

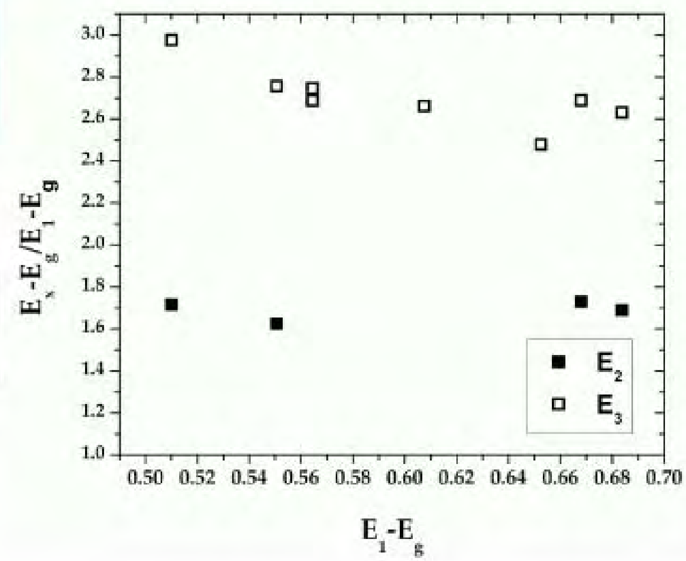


SYNTHESIS OF ULTRATHIN Bi_2S_3 NANOWIRES

Quantum Confinement

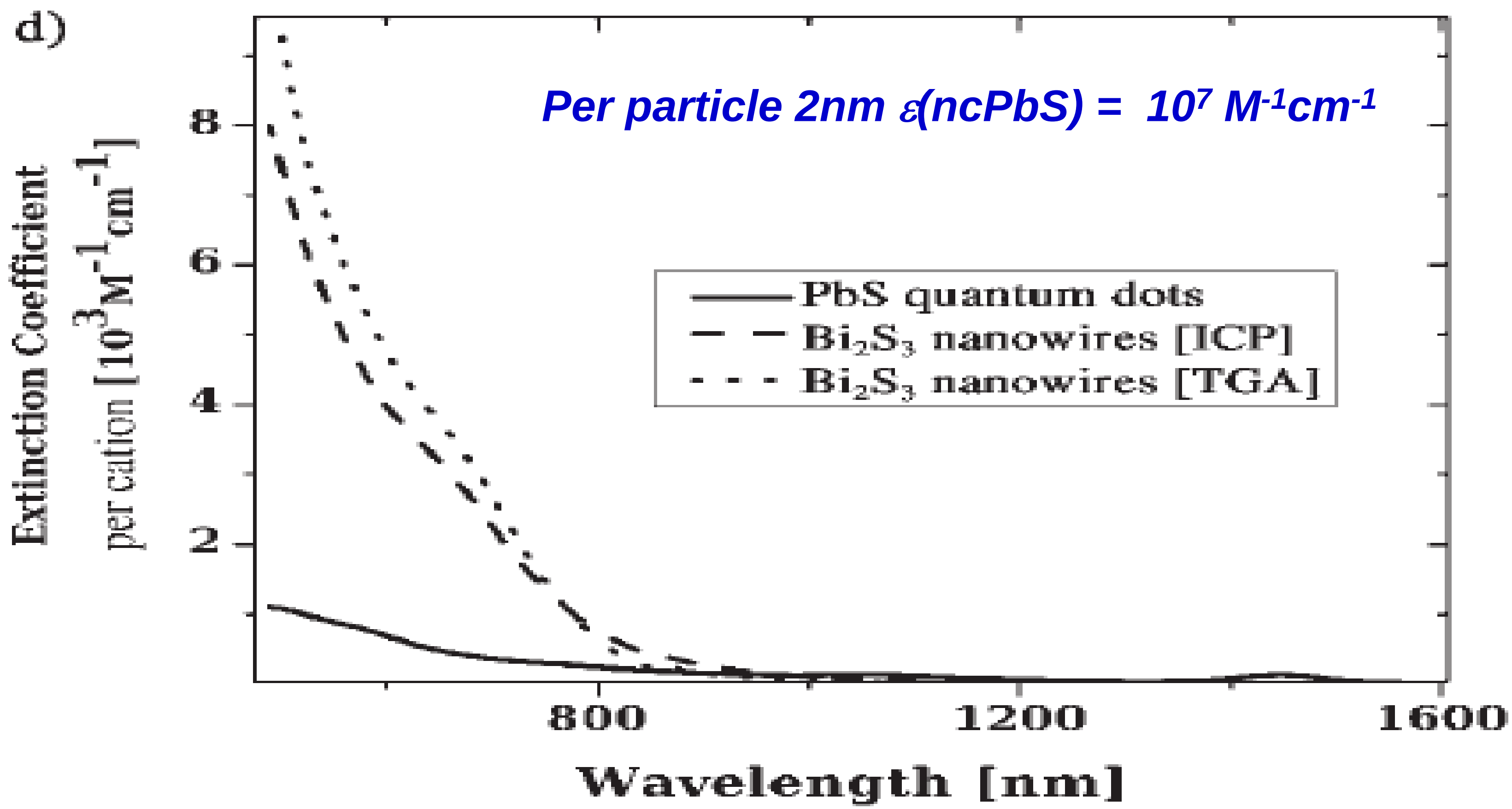






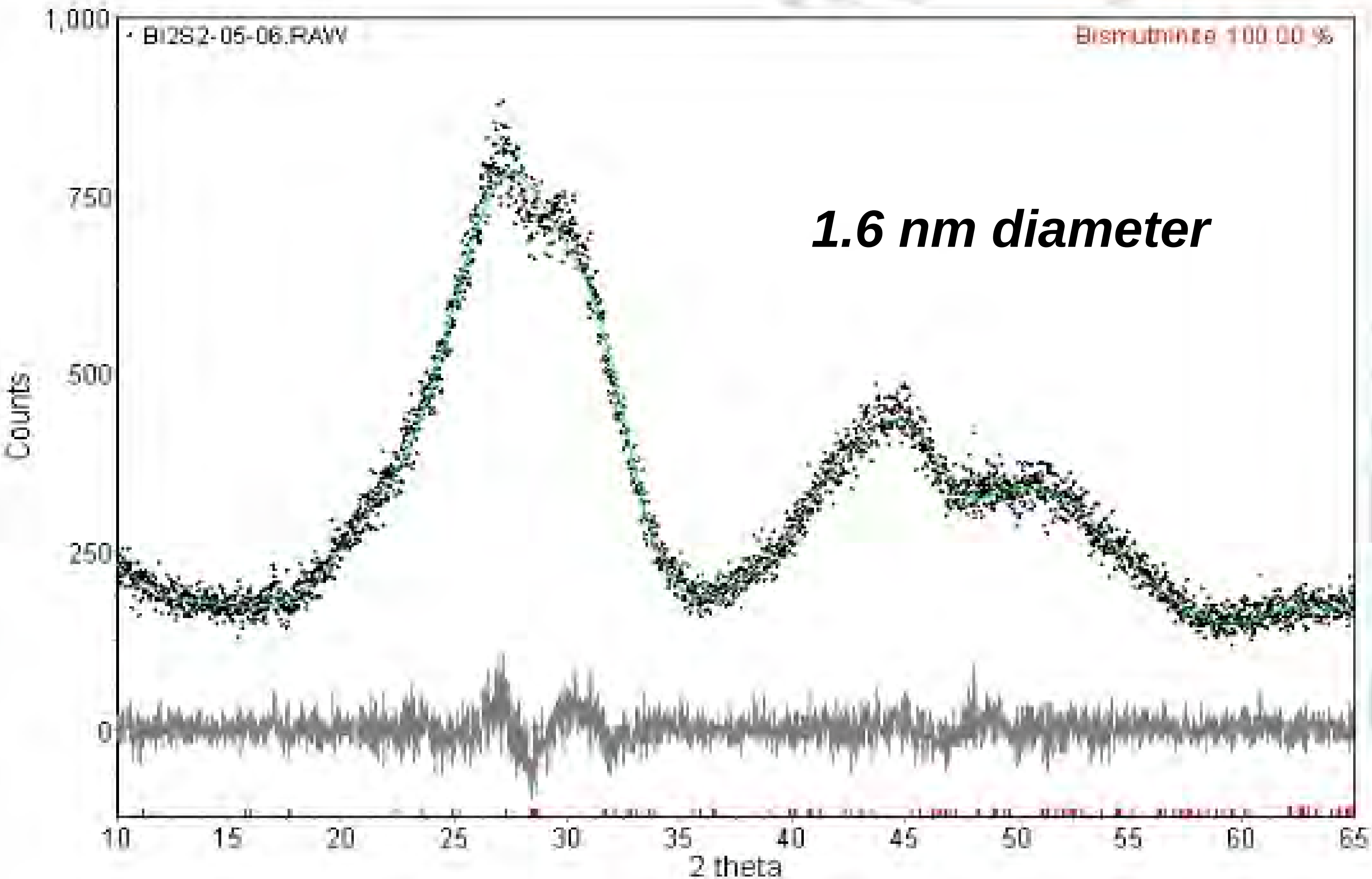
Quantum confinement was demonstrated by Normalized Confinement Energy analysis

EXTINCTION COEFFICIENT

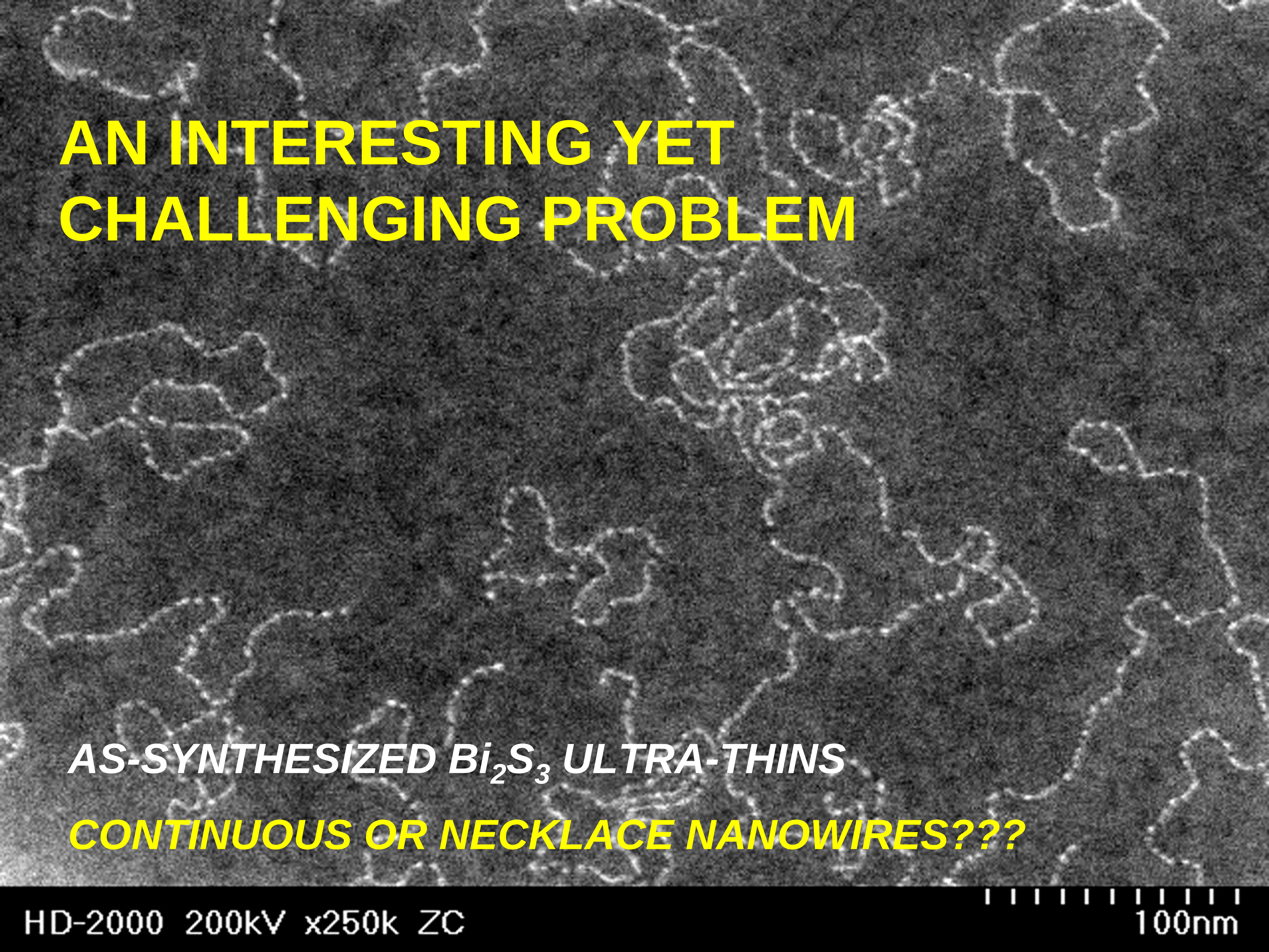


per cation extinction coefficients of PbS quantum dots and Bi_2S_3 nanowires measured by ICP and TGA

RIETVELD PXRD FULL PROFILE STRUCTURE REFINEMENT OF ULTRATHIN Bi_2S_3 NANOCRYSTAL NANOWIRES

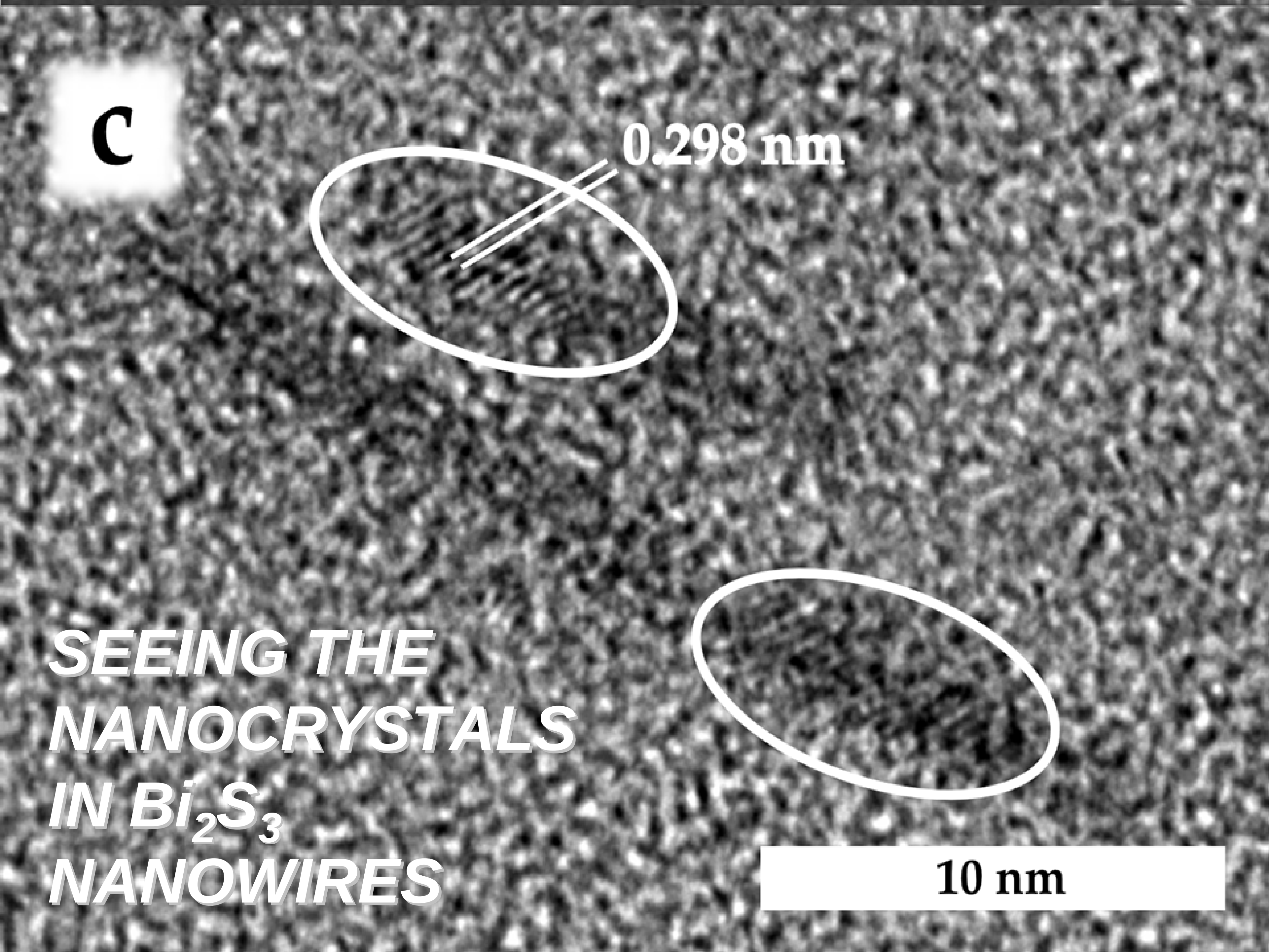


AN INTERESTING YET CHALLENGING PROBLEM



AS-SYNTHESIZED Bi_2S_3 ULTRA-THINS

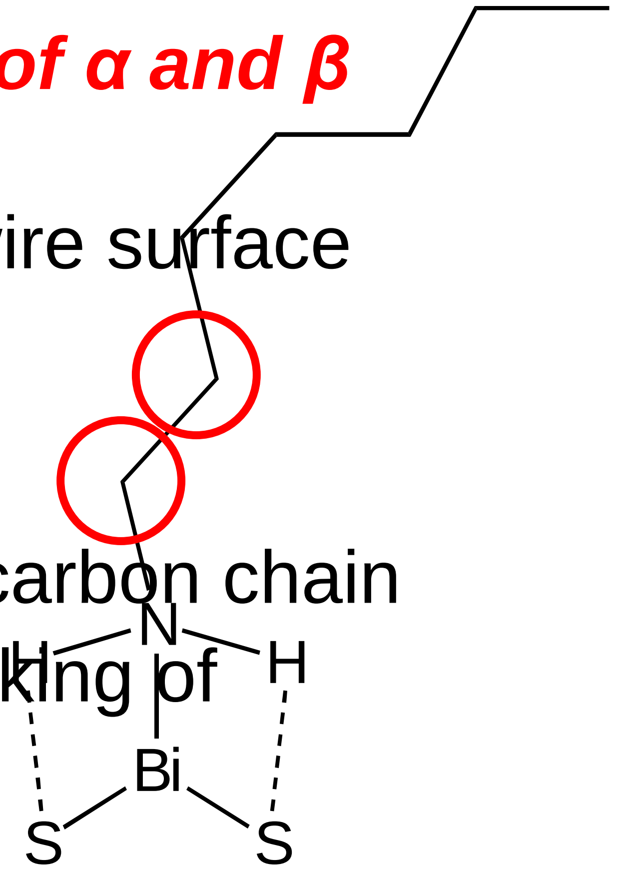
CONTINUOUS OR NECKLACE NANOWIRES???


c
0.298 nm
SEEING THE NANOCRYSTALS IN Bi_2S_3 NANOWIRES
10 nm

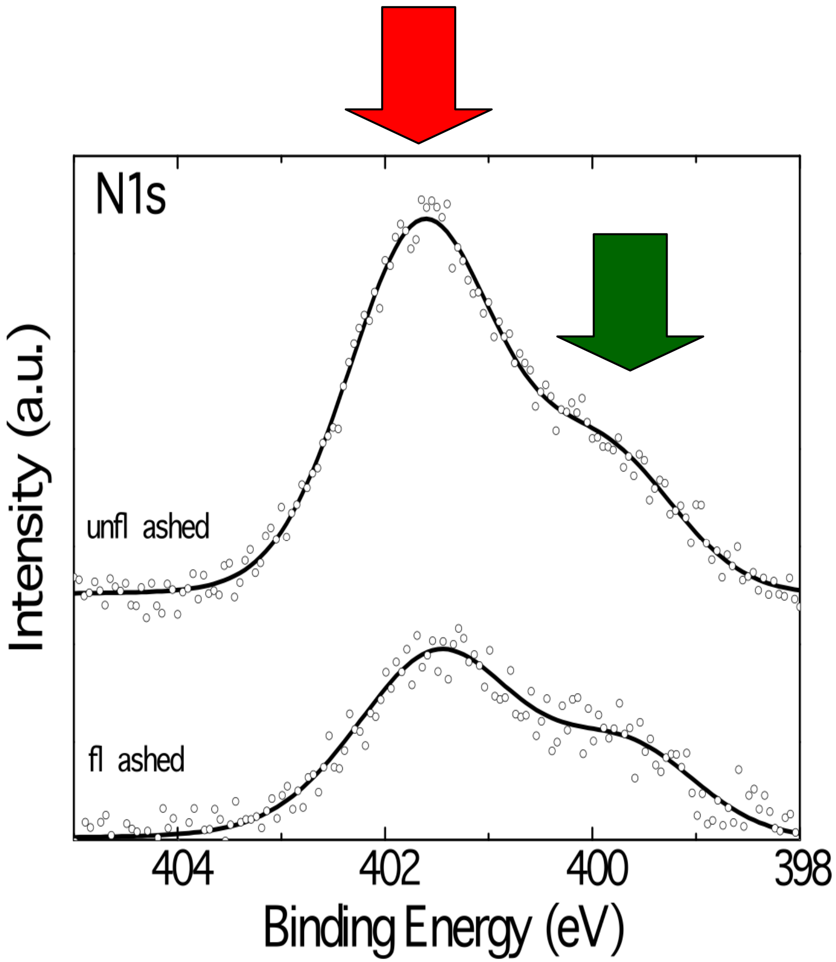
^{1}H NMR - Ligand Capping

- HDA exchanged nanowires
- ***Large ^{1}H NMR downfield shift of α and β hydrogen's***
- Indicating a strong ligand-nanowire surface interaction

- ***^{1}H NMR peaks are sharp***
- Indicating rotational freedom of carbon chain
- Likely results from imperfect packing of alkylamine chains



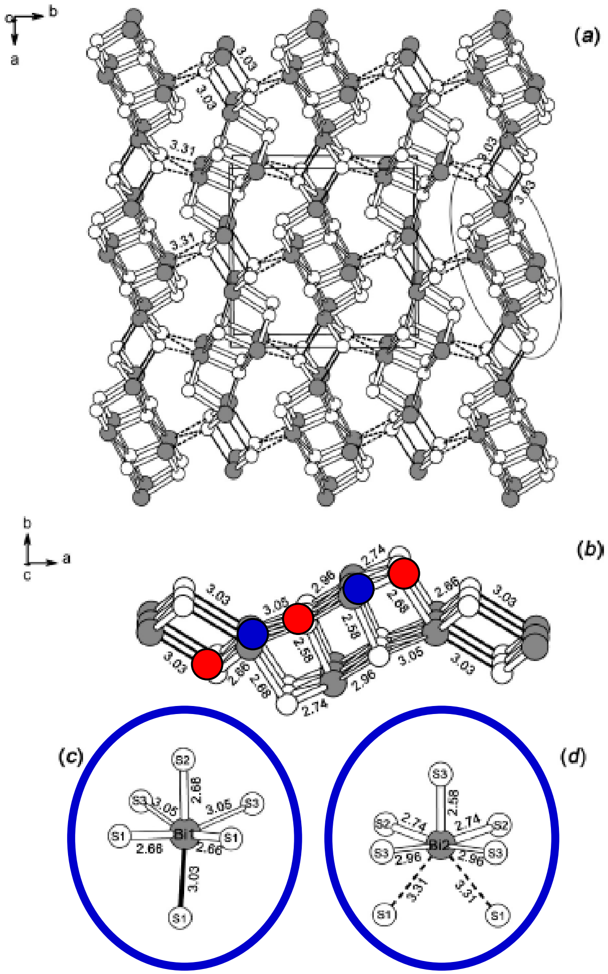
XPS – Ligand Capping



Alkylamines found at 399.5 eV and protonated alkylammonium at 401.5 eV

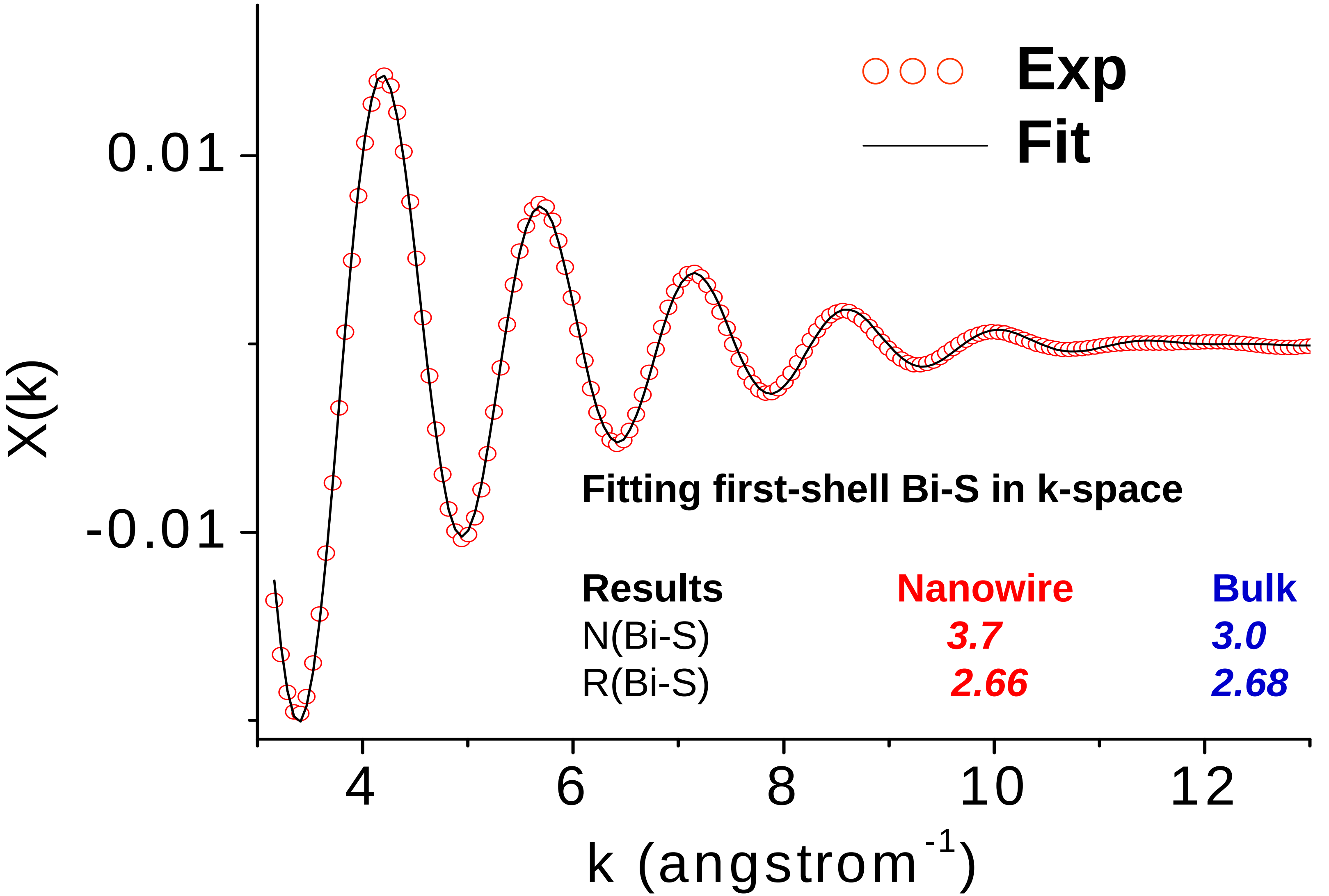
N1s spectrum shows peak at 401.5 eV corresponding to Bi-N bond and shoulder at 399.5 eV to free or weakly bound oleylamine

SCXRD Bi_2S_3



- Ribbon structure
- Chains along 001
- ***Two Bi(III) crystal sites***
- Short Bi-S 2.58-2.78 Å
- Long Bi-S 3.03-3.31 Å
- ***First BiS coordination shell***
- **N = 3**
- **R = 2.68 Å**

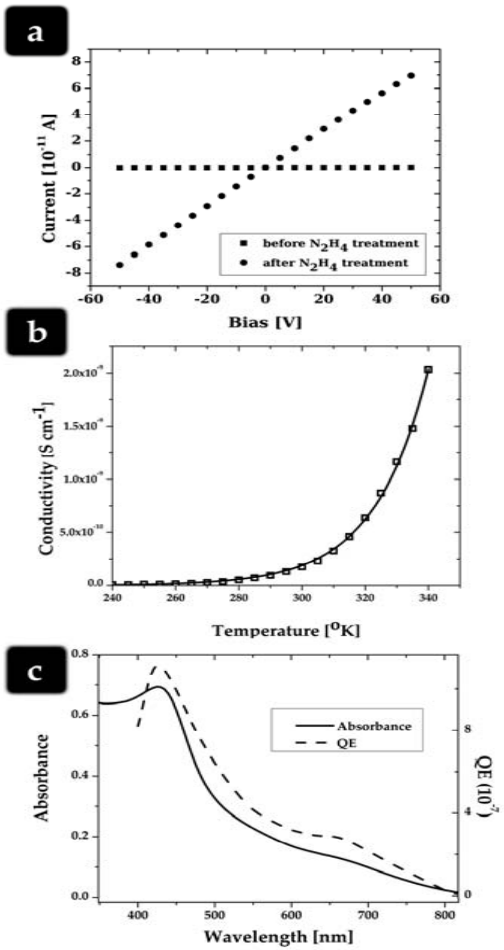
EXAFS : Bi-S Local Structure



1.6 nm Diameter Nanowires!!!

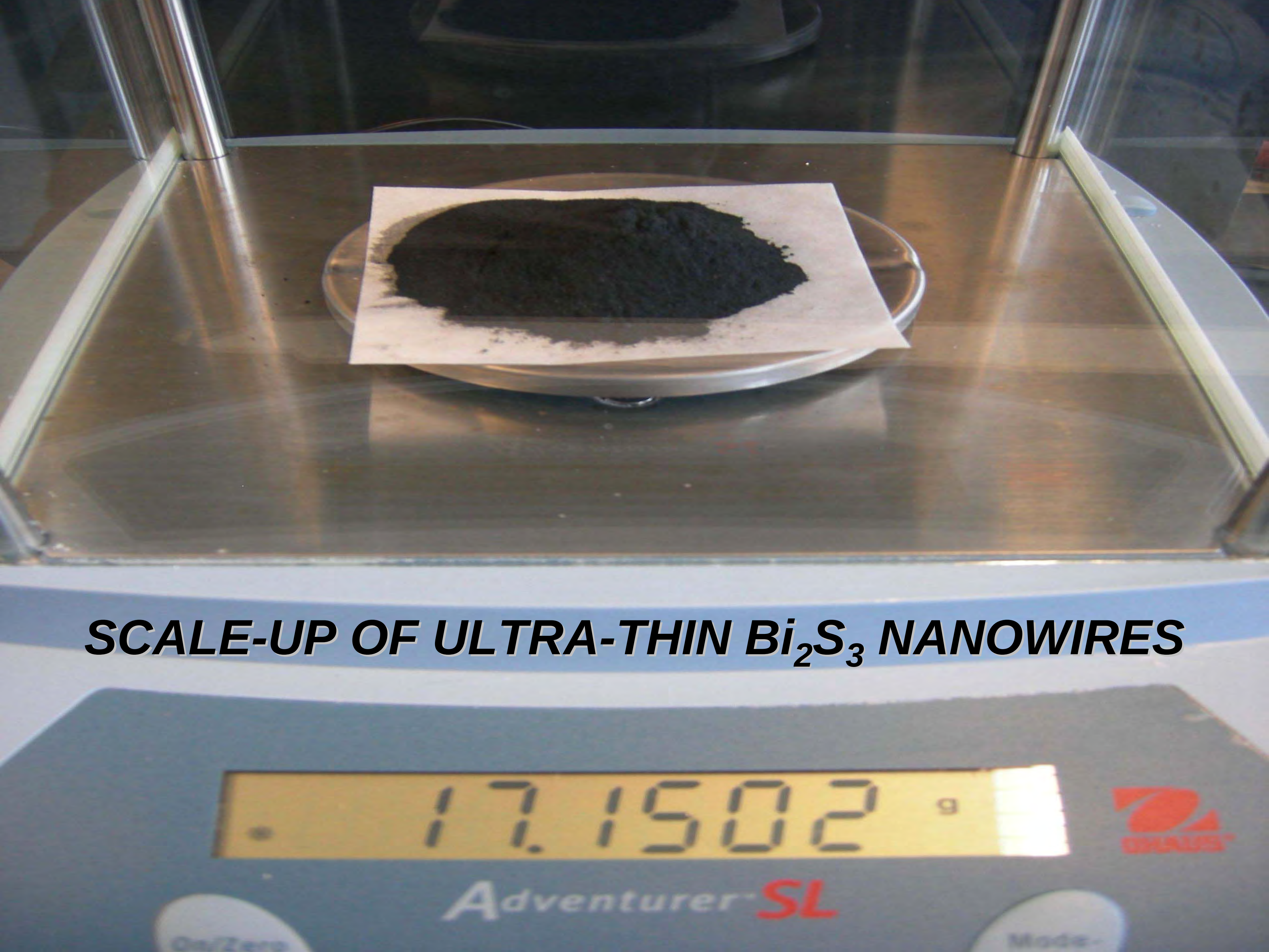
- **Proposed structure for the Bi_2S_3 nanowires**
- **Yellow are the Bi atoms, red are the S atom**
- **Size driven reconstruction**
- ***More than half the bismuths reside at the nanowire surface!!!***

ELECTRICAL, OPTICAL AND PHOTOCONDUCTIVITY OF ULTRATHIN NANOWIRES

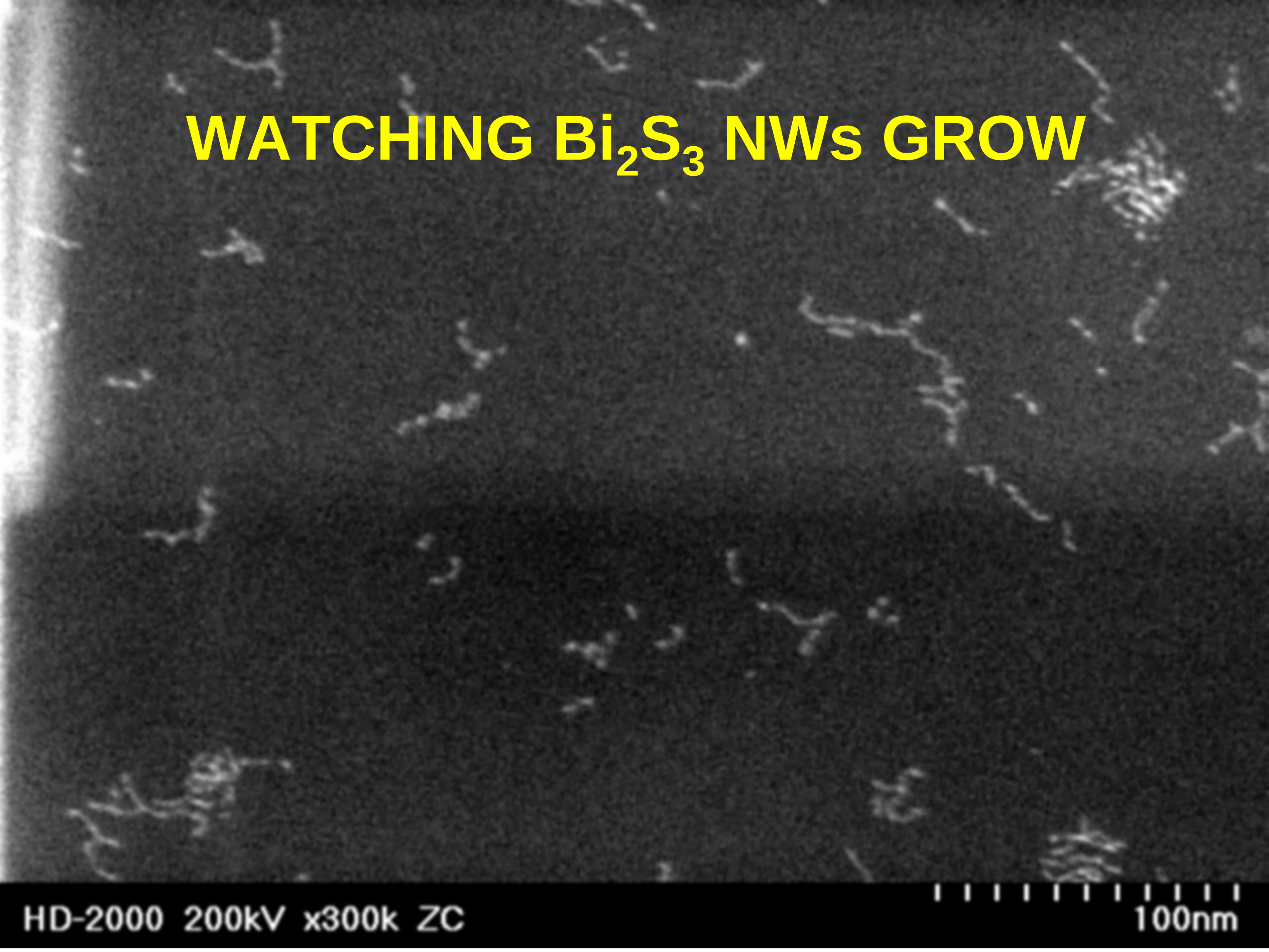


- a) two probe IV curves of alkylamine capped Bi_2S_3 nanowire films with Al contacts - before and after hydrazine treatment
- a) increase of 3 orders of magnitude in the conductivity is due to the reduction of the distance between the wires caused by the exchange of the original long chain capping amine ligand with short hydrazine molecules
- b) temperature dependence of conductivity showing semiconductor behavior
- c) spectral response of photoconductivity (dashed line action spectrum) compared to absorbance spectrum (solid line)

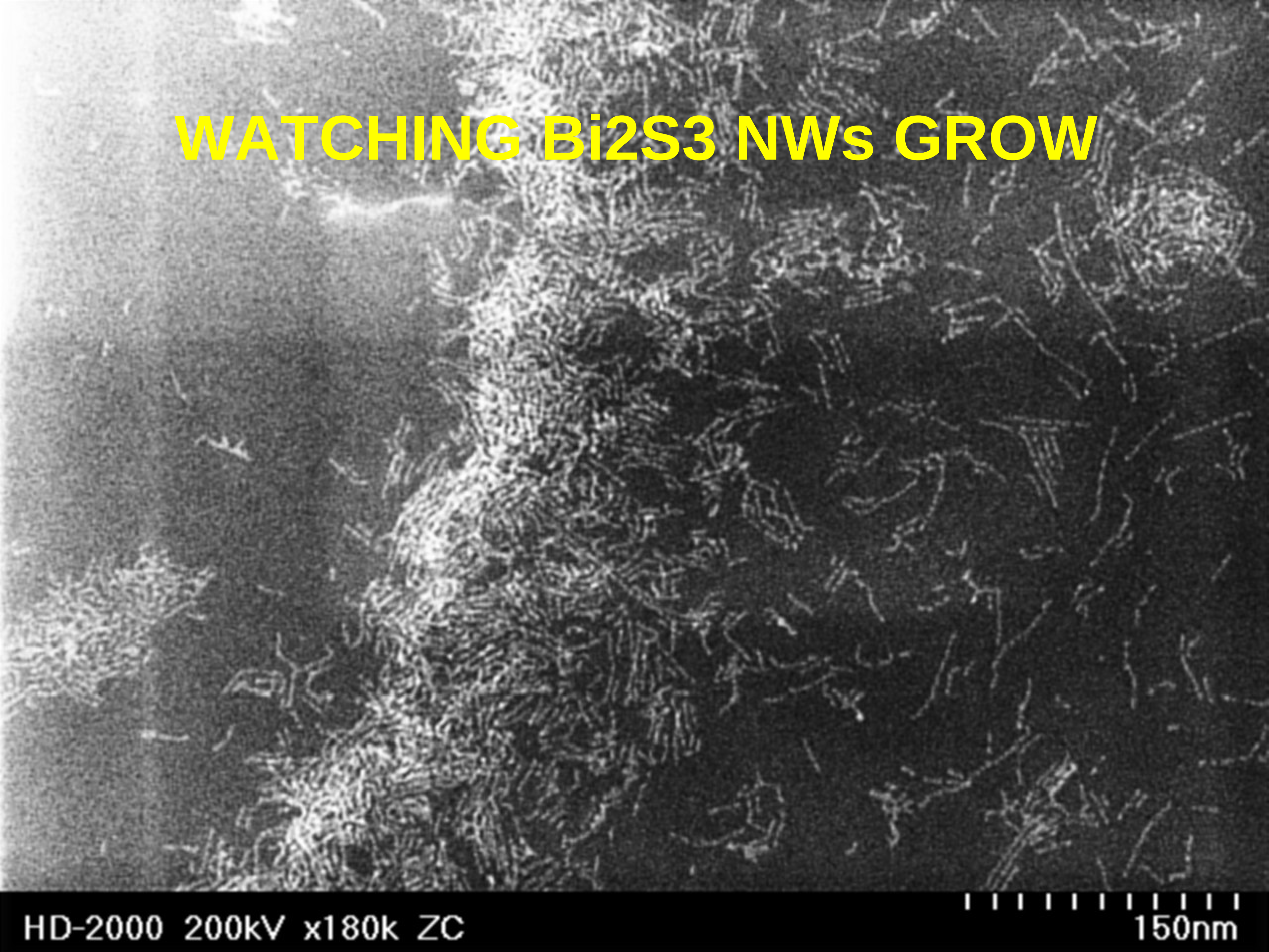
SCALE-UP OF ULTRA-THIN Bi_2S_3 NANOWIRES

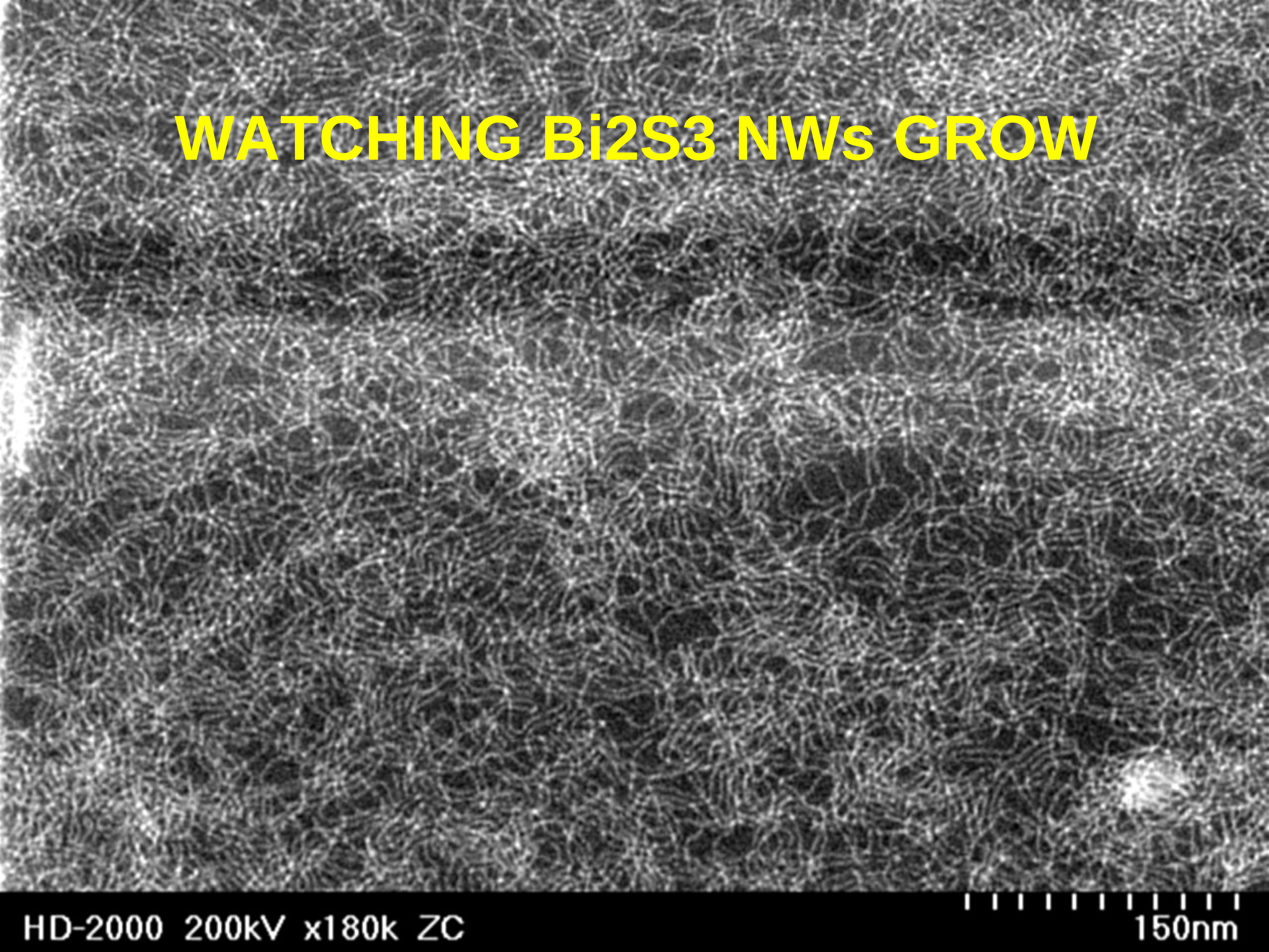


WATCHING Bi_2S_3 NWs GROW



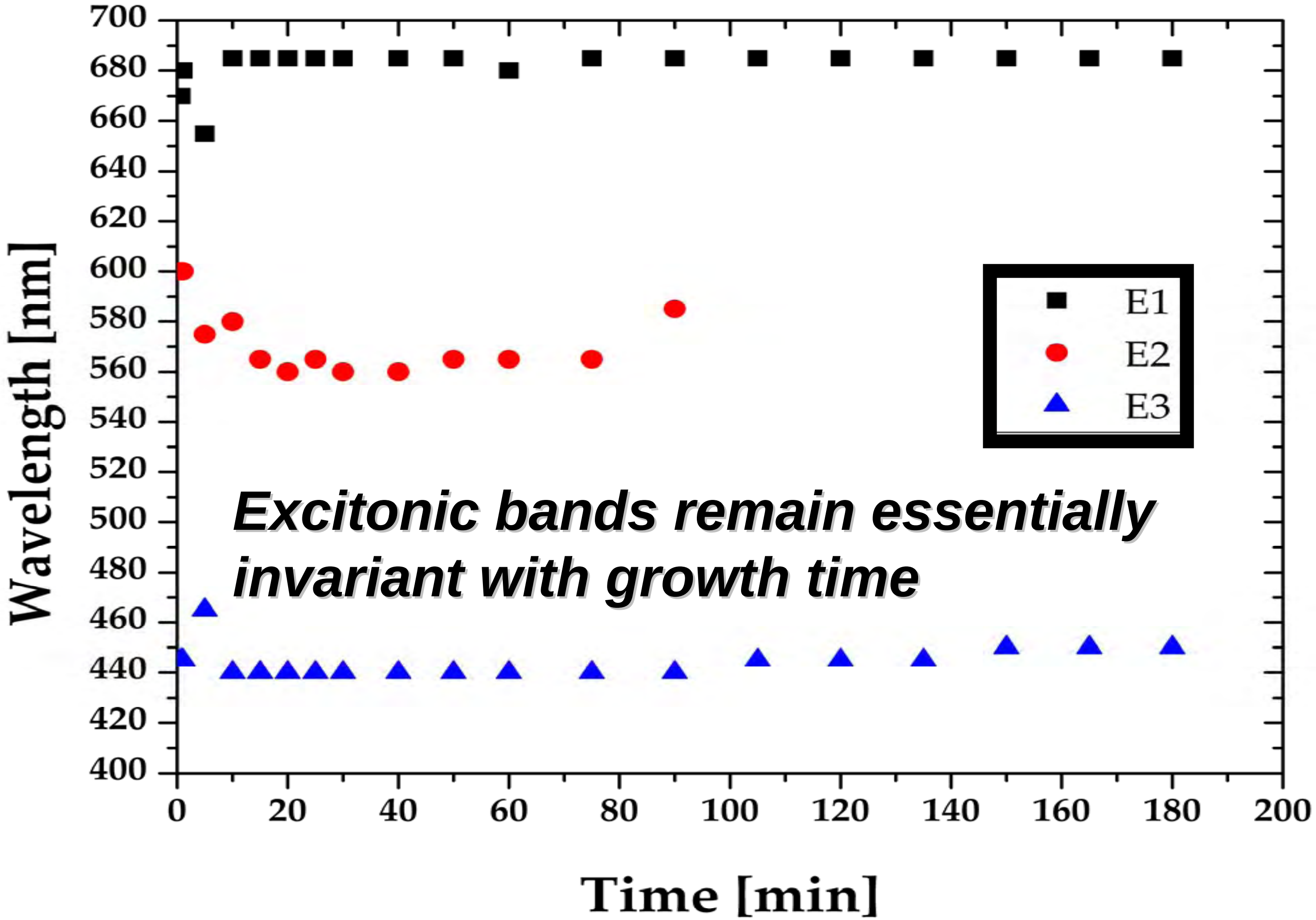
WATCHING Bi2S3 NWs GROW




WATCHING Bi2S3 NWs GROW
HD-2000 200kV x180k ZC
150nm

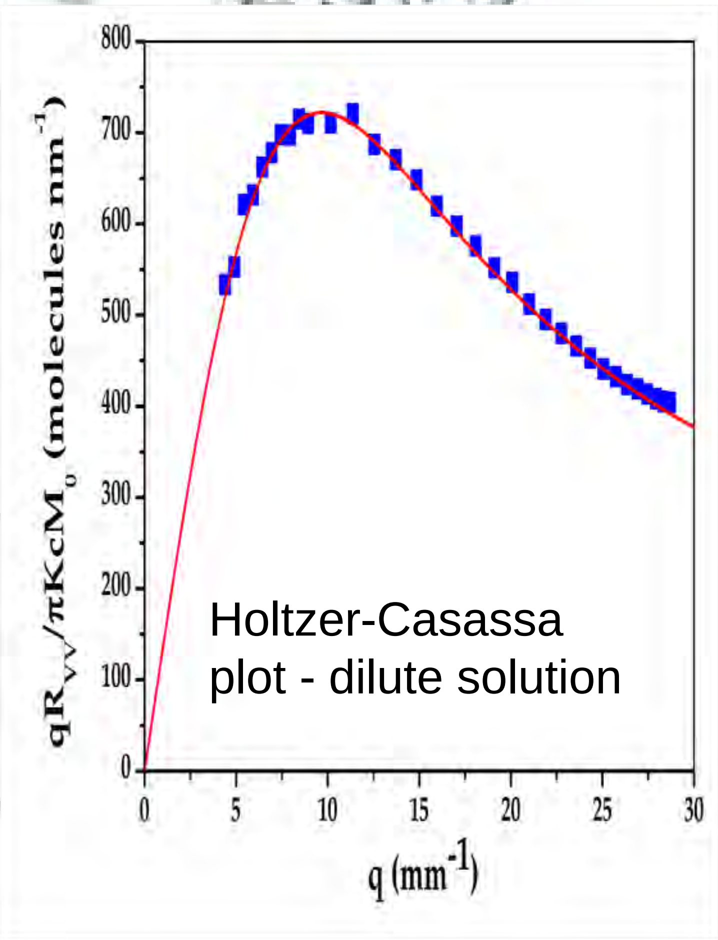

WATCHING Bi2S3 NWs GROW
HD-2000 200kV x150k ZC
200nm

Bi_2S_3 NW GROWTH – INCREASING LENGTH WITH CONSTANT WIDTH



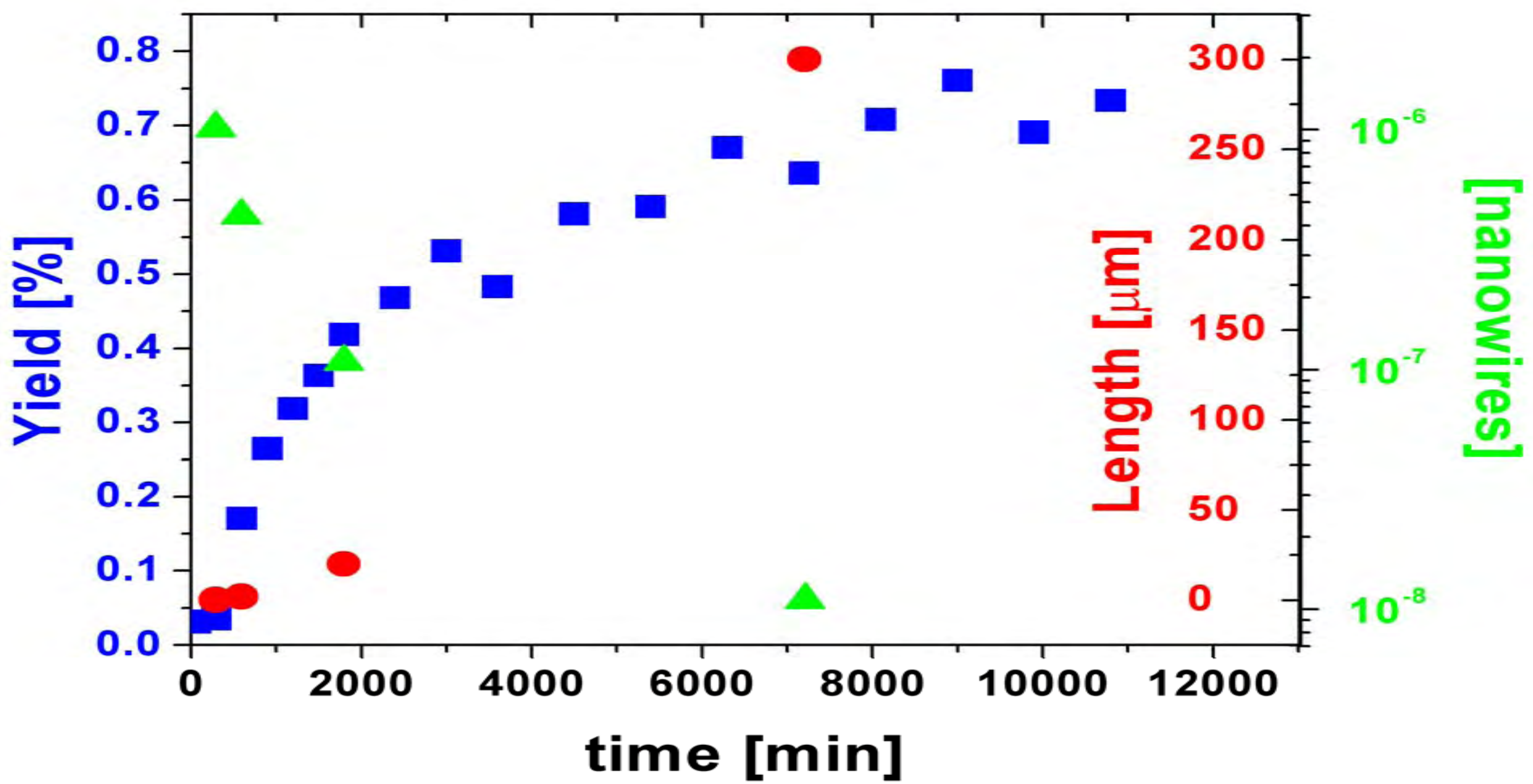
Excitonic bands remain essentially invariant with growth time

DLS: EMERGENT POLYMER-LIKE BEHAVIOR IN INORGANIC NANOWIRES



- **Kojyiama worm-like chain (continuously flexible smoothly curved isotropic rod)**
- **Weight average $M_w = 2.2 \times 10^8$ g/mol**
- **Contour (extended) chain length 3.5 μm**
- **Persistence length (polymer segments behaving like flexible elastic rod) 80 nm**
- **Nanowire contains ~ 45 segments**
- **Linear aggregation number 123 Bi_2S_3 units per nm of nanowires**
- **Radius of gyration (dimension of polymer chain) Rg = 152 nm**

How do ultrathin nanowires grow?



From yield at 2h growth each ml of solution contains ~2 million kilometers of ultrathin nanowires - moon and back 2.5 times

The decreasing number of nanowires comes from yield based total length divided by length obtained by DLS

Preliminary kinetic model for exploring nanowire growth

Assumptions:

1. Induction period t_0 before growth time t_g
2. N_0 nanowires at t_0 and N_g at t_g
3. Addition of Bi happens at the tips of nanowires
4. Grow with constant cross-sectional surface area A
5. Aggregation happens exclusively at nanowire tips
6. Branching not observed

Kinetic Model

- **Growth kinetics**

1) $$\frac{dBi}{dt} = -k_{growth} A_{tot} = -2k_{growth} AN$$ for $t > t_g$

- **Aggregation kinetics**

2) $$\frac{dN}{dt} = -k_{attachment} N^2$$ $N(t_g) = N_g$

3) $$N(t) = \frac{N_g}{1 + k_{attachment} N_g (t - t_g)}$$

- ***Substitution of N(t) into growth equation leads to:***

$$\frac{dBi}{dt} = -\frac{2k_{growth}AN_g}{1 + k_{attachment}N_g(t - t_g)}$$

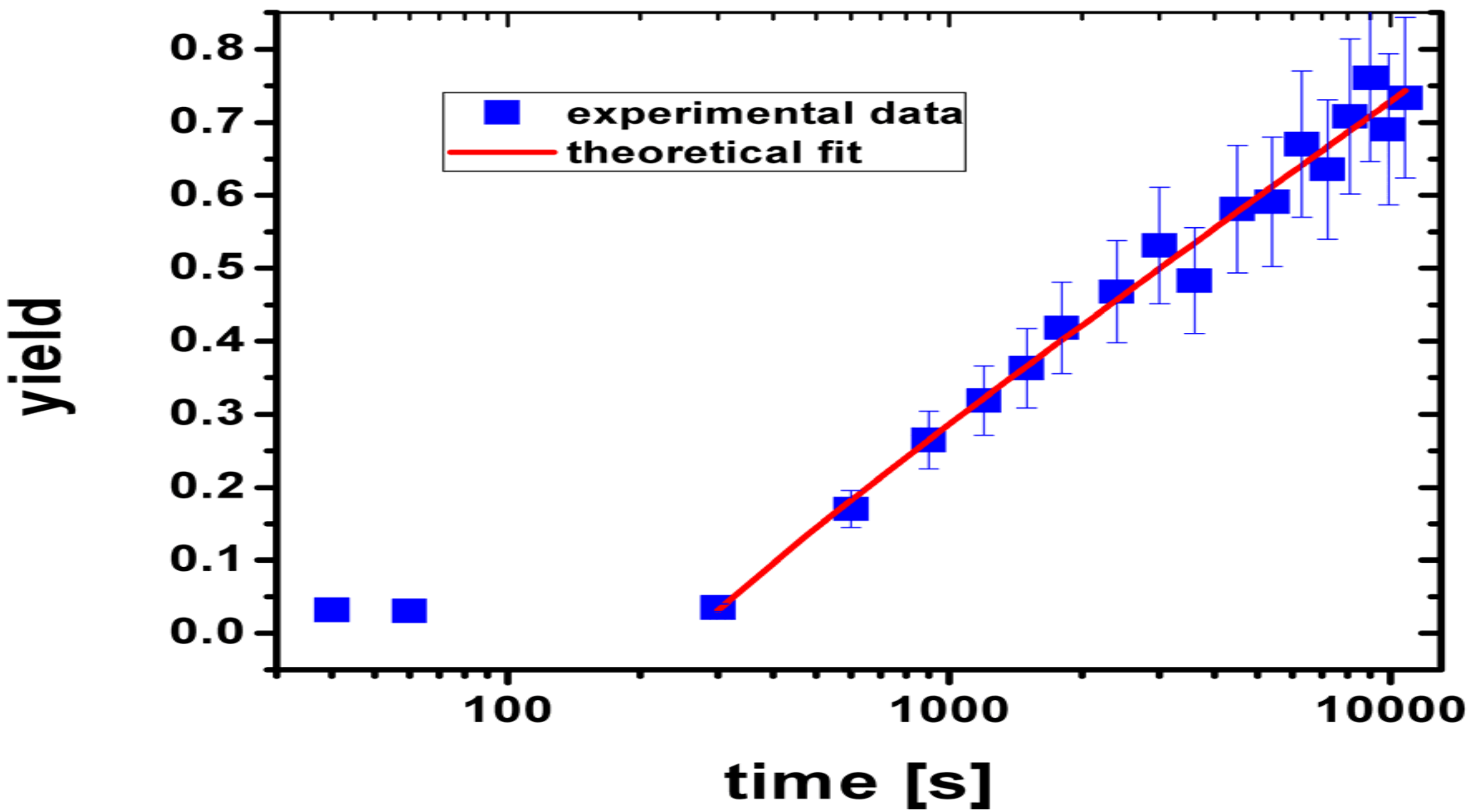
Bi corresponds to bismuth not in the nanowires

- ***Integration leads to:***

$$Bi_g - Bi = \frac{2k_{growth}A}{k_{attachment}}\ln(1 + k_{attachment}N_g(t - t_g))$$

- …*which, in terms of yield becomes*

$$Y(t) - Y_g = \frac{Bi_g - Bi}{Bi_g} = 2\frac{k_{growth} A}{k_{attachment} Bi_g} \ln(1 + k_{attachment} N_g (t - t_g))$$



What about nanowire lengths…

$$\frac{dL_{tot}}{dt} = \frac{\nu}{A}\frac{dBi}{dt}$$

$L_{tot} = L(t)N(t)$

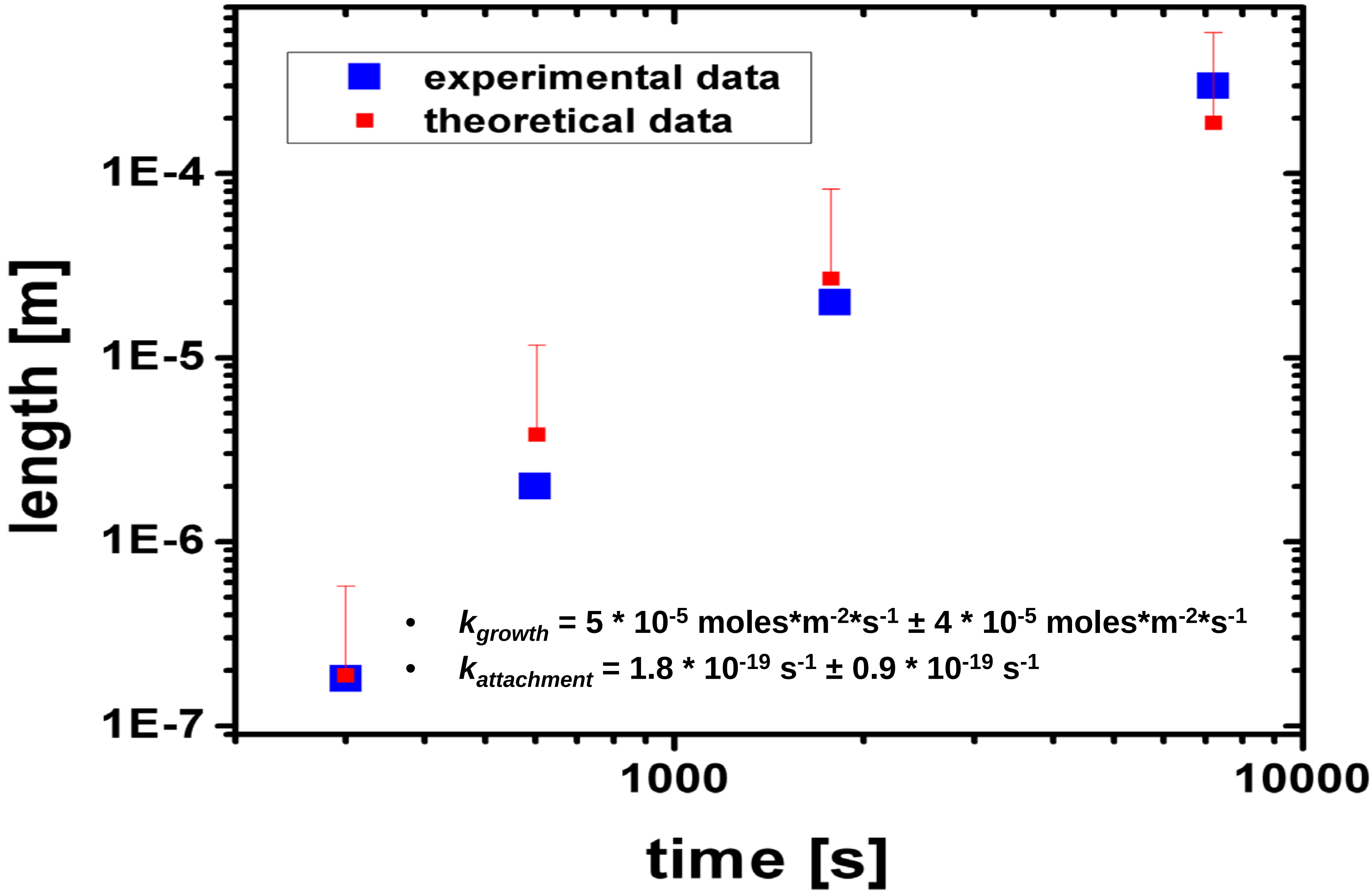
$L_{tot,g} = L_g Ng$

- ***Can be integrated to give***

$$L_{tot} - L_{tot,g} = -\frac{\nu}{A}(Bi - Bi_g) = \frac{\nu Bi_g}{A}(Y - Y_g)$$

$$L(t) = \left(2\frac{\nu k_{growth}}{k_{attachment}N_g}\ln(1 + k_{attachment}N_g(t - t_g)) + L_g\right)\left(1 + k_{attachment}N_g(t - t_g)\right)$$

$\nu = 75.83 * 10^{-6}$ m^3/mole, $MW(Bi_2S_3) = 514.16$, $\rho(Bi_2S_3) = 6.78$ g/ml

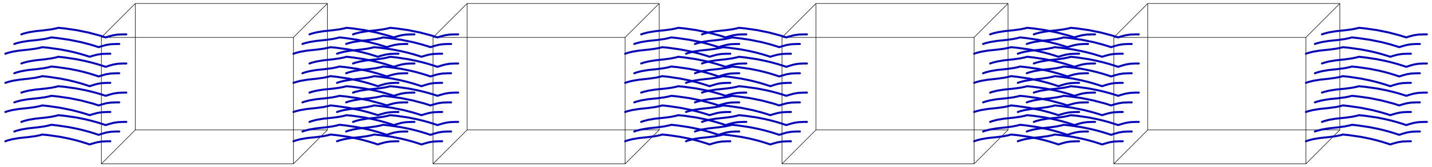


experimental data
theoretical data
1E-4
1E-5
1E-6
1E-7
length [m]
1000
10000
time [s]
• k_{growth} = 5 * 10^-5 moles*m^-2*s^-1 ± 4 * 10^-5 moles*m^-2*s^-1
• $k_{attachment}$ = 1.8 * 10^-19 s^-1 ± 0.9 * 10^-19 s^-1

What did we learn from the kinetics of ultrathin nanowire nucleation and growth ?

- nucleation followed by growth
- growth happens on ends with equal probability
- termination and fracture can be disregarded???
- attachment not strongly length dependent
- nucleation can be disregarded after t_g

MECHANISM OF NANOWIRE GROWTH



Interdigitation driven oriented attachment ???

ULTRATHIN NANOWIRE OVERVIEW

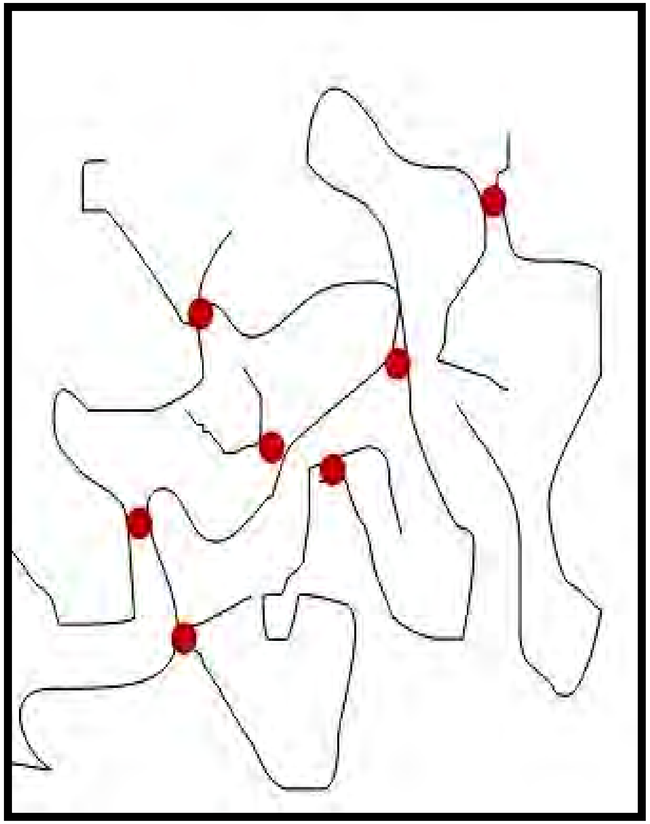
- **Hot injection method works for synthesizing ultrathin nanowires**
- **Colloidal stability for months in solution after purification**
- **Proof-of-concept for scaling synthesis demonstrated**
- **Bulk and surface structure investigated**
- **Thermal properties delineated**
- **Evidence for quantum confinement, electrical and photoconductivity, and redox activity established**
- **Preliminary model for growth kinetics explored**

POLYMER-LIKE
ULTRATHIN NANOWIRES

WHAT IS NEXT?

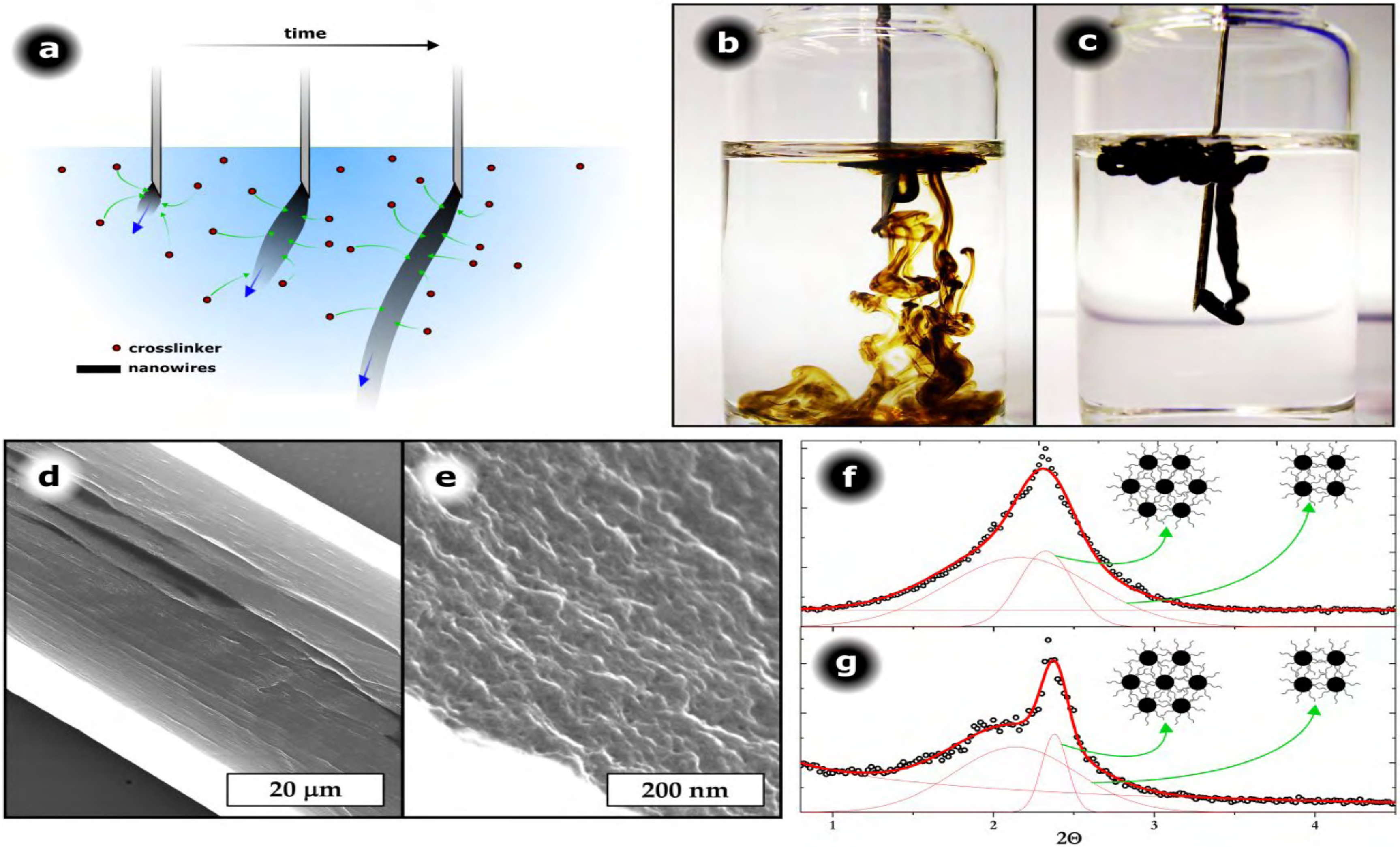
CROSSLINKING POLYMER-LIKE NANOWIRES

POLYMER GELS, FIBERS, MESHES

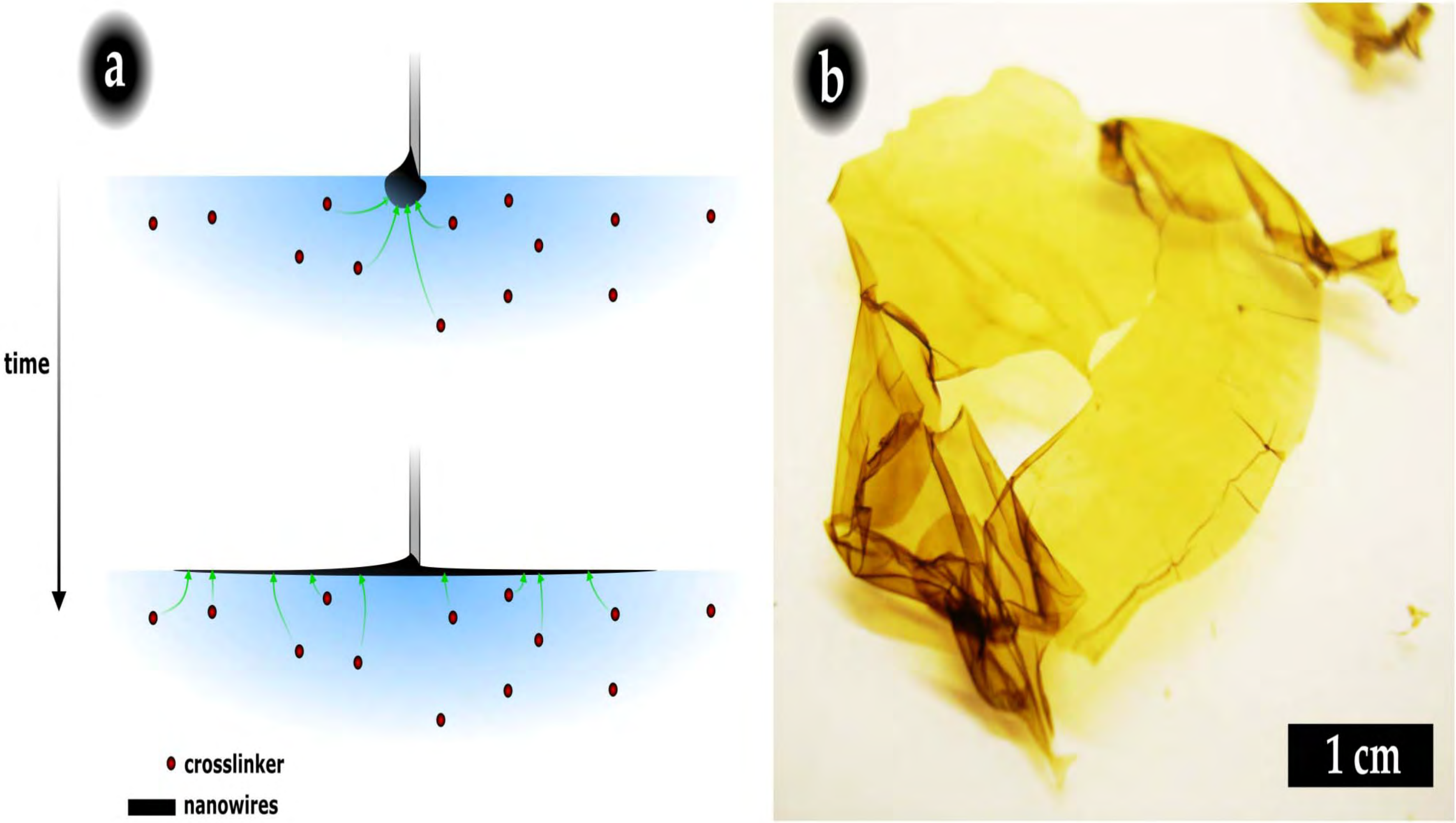


- As-synthesized nanowires - monodentate OLA capping ligands
- OLA alkane chain interdigitation crosslinking
- Ligand replacement with poly-dentate amines
- Crosslinker control of nanowire network morphology and properties
- Insulating and conducting crosslinkers
- Short and long crosslinkers
- Rigid and non-rigid crosslinkers

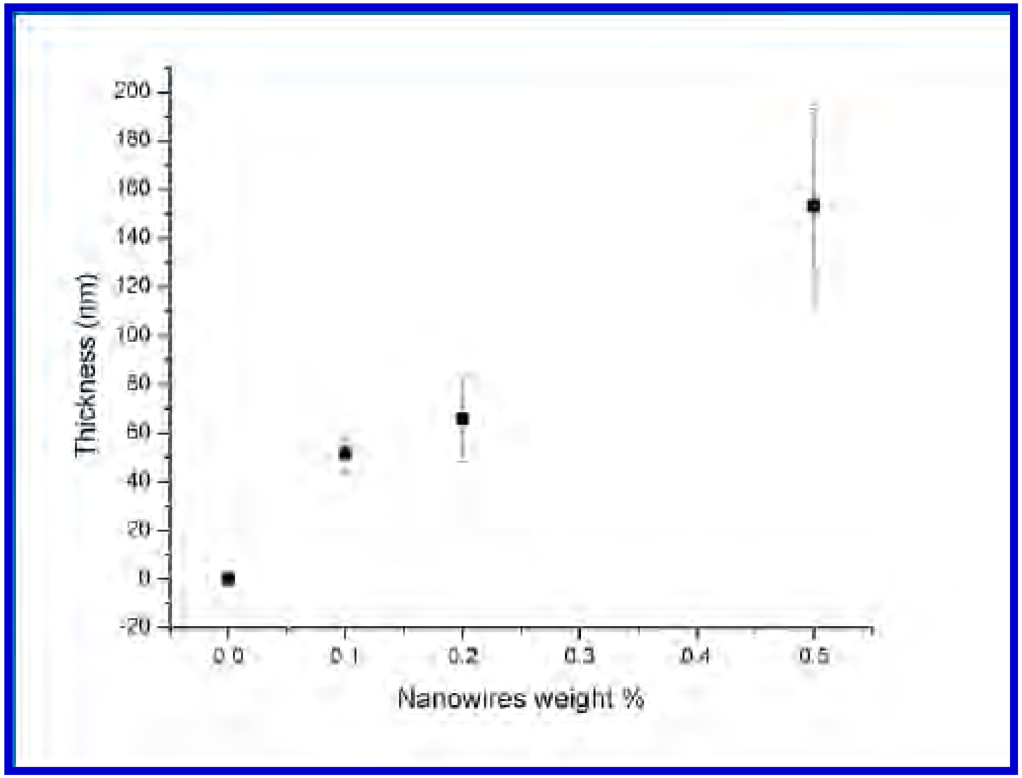
ChemoSpinning Oriented Polymer-Like Nanowire Fibers



Interfacial Cross-linking of Polymer-Like Nanowire Meshes



Control of Mesh Thickness



Images of a mesh made with 0.1w% of nanowires with the optical microscope (Transmission Bright Field)

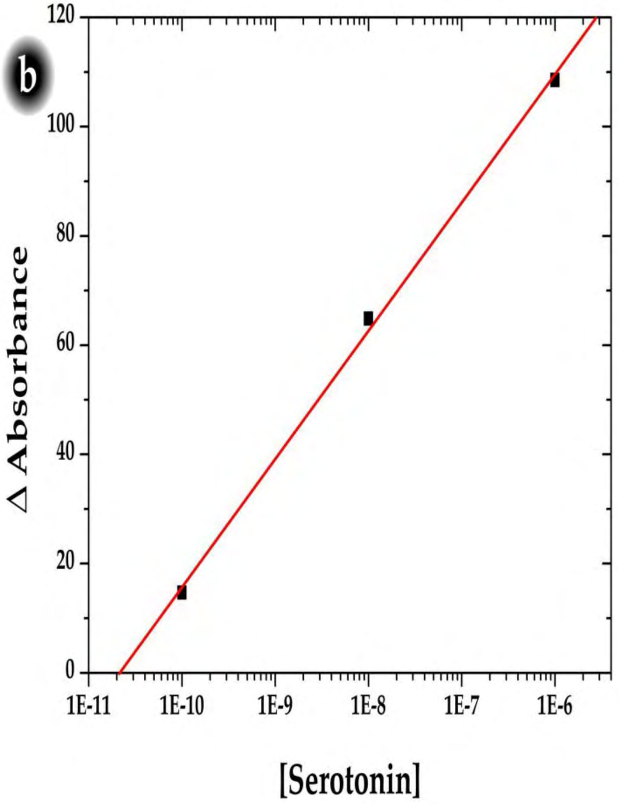
With different weight percentages of Bi_2S_3 nanowires in Toluene, it is possible to have smooth meshes with different thicknesses (using a solution of $5x10^{-7}$ of Ethylenediamine in THF).

Ultrahigh surface area controlled thickness nanowire meshes for sequestration of toxic heavy metals and organics pollutants

MAKING USE OF NANOWIRE CROSSLINKING

HIGH SENSITIVITY COLORIMETRIC DETECTION OF BIOLOGICALLY RELEVANT AMINES

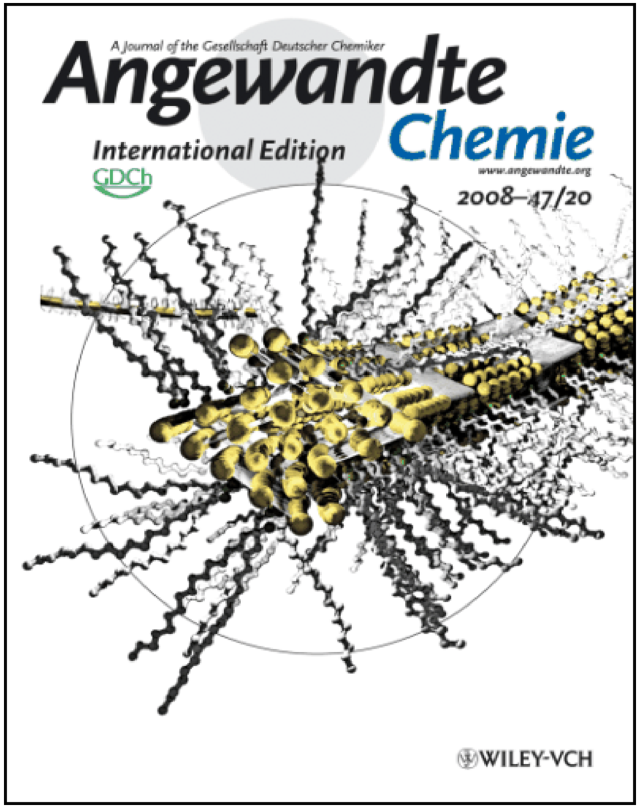
Left: Bi_2S_3 nanowires in THF/Water. Right: Bi2S3 nanowires in THF/Water + serotonin.



Serotonin 5-hydroxytryptamine a monoamine neurotransmitter synthesized in serotonergic neurons in the central nervous system

Easy to detect picomoles !!!

FUTURE OF POLYMER-LIKE INORGANIC NANOWIRES



- ***New nanocomposites with organic polymers, DNA, proteins, enzymes, fullerene, carbon nanotubes, quantum dots***
- ***Electrically conducting chemically and physically driven swellable-shrinkable gels***
- ***Nanothermoelectrics – high performance refrigeration and power generation***
- ***Nanomedicine – diagnostics, therapy and high contrast CT imaging***
- ***Nanowire flash lithography***


Follow your nose!
curiosity driven nanochemistry research
NSERC Funding
Ludovico Cademartiri
CIC Doctoral Prize, NSERC PDF, DIC ACS Young Investigator Award, DIC
CIC Young Investigator Award, Governor General Medal
Cademartiri, Ozin and Coworkers
Nature Materials, Nature Photonics, JACS, AM, NL, JPC, JMC, AC, Small, ACR, AMRN 2009- 2006

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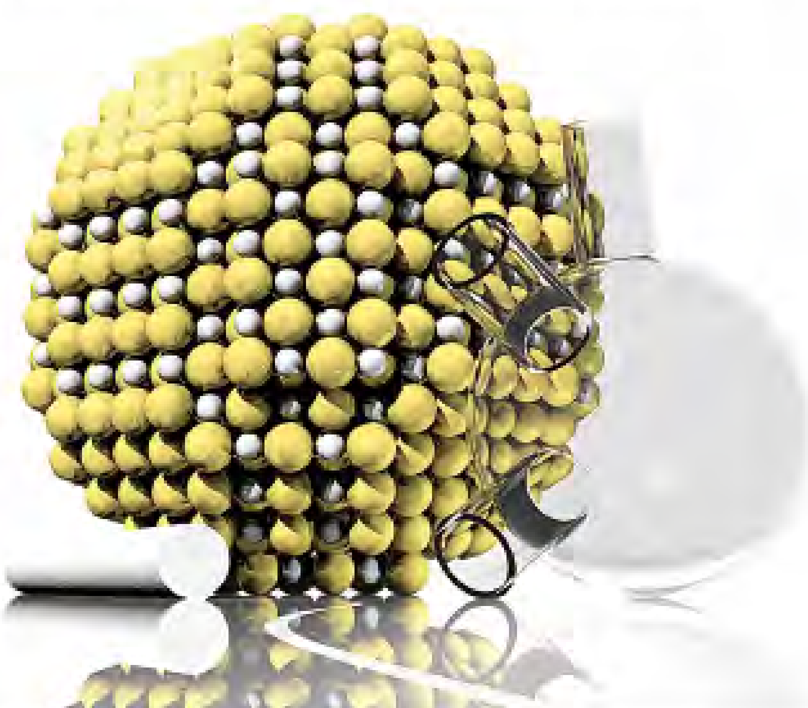

RSC Publishing

Foreword by Chad A Mirkin

Ludovico Cademartiri and Geoffrey A. Ozin

WILEY-VCH

Concepts of Nanochemistry

With a Foreword by Jean-Marie Lehn

Following Ludo's Nose

What was that weird stuff Ludo discovered?

Thank you for the invitation and thank you for listening

Jordan Thompson

NSERC Graduate Scholar