

Nanostructured Materials for Solar Fuel Production

Presented by: Mostafa Mamdouh

Under the supervision of:

Prof. Adel El-Shabasy

Assoc. Prof. Nageh Allam

Contents

- Background on Energy Challenges
 - Why Water splitting for Hydrogen Production?
 - Introduction to Water Splitting
- Research Plan
- Experimental Work
- Results

Global Energy Challenge

1.2×10^5 TW

at Earth Surface

600 TW

(practical)



HYDROELECTRIC 2TW (Gross)

SOLAR

HYDROELECTRIC
4.6 TW
(Gross)

1.6 TW
(Technically feasible)

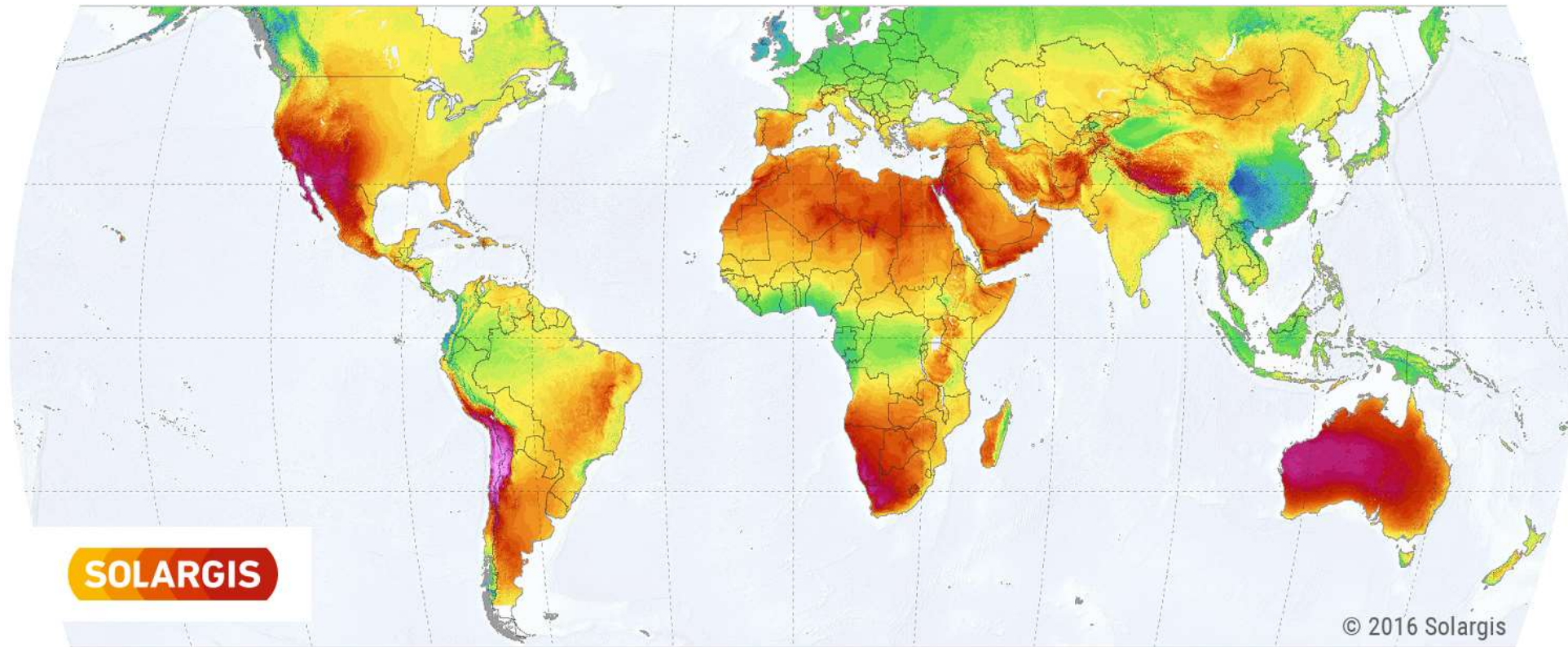
GEOTHERMAL
12 TW
(Gross over land, small fraction recoverable)

NUCLEAR

Waste disposal
60 yr uranium supply !

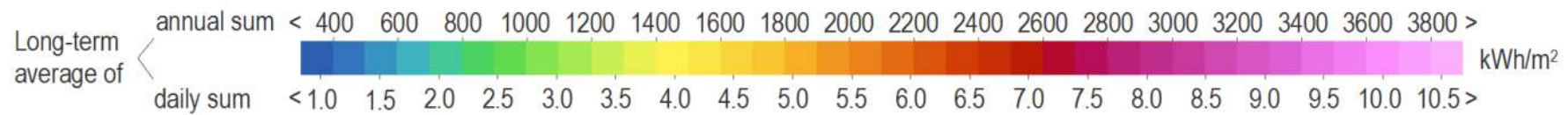
Egypt!

DIRECT NORMAL IRRADIATION



SOLARGIS

© 2016 Solargis



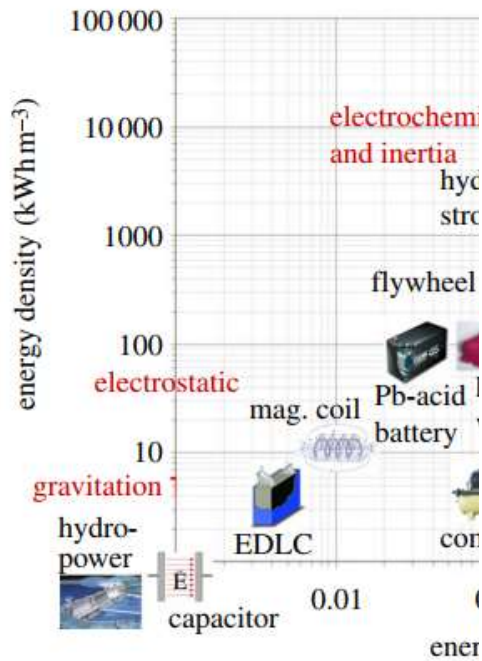
Solar Fuel

- Light is used as an energy source, with solar energy being transduced to *chemical energy* typically by
 - reducing protons to hydrogen
 - or
 - carbon dioxide to organic compounds.
- A solar fuel can be produced and stored for later usage, when sunlight is not available, making it an alternative to fossil fuels.

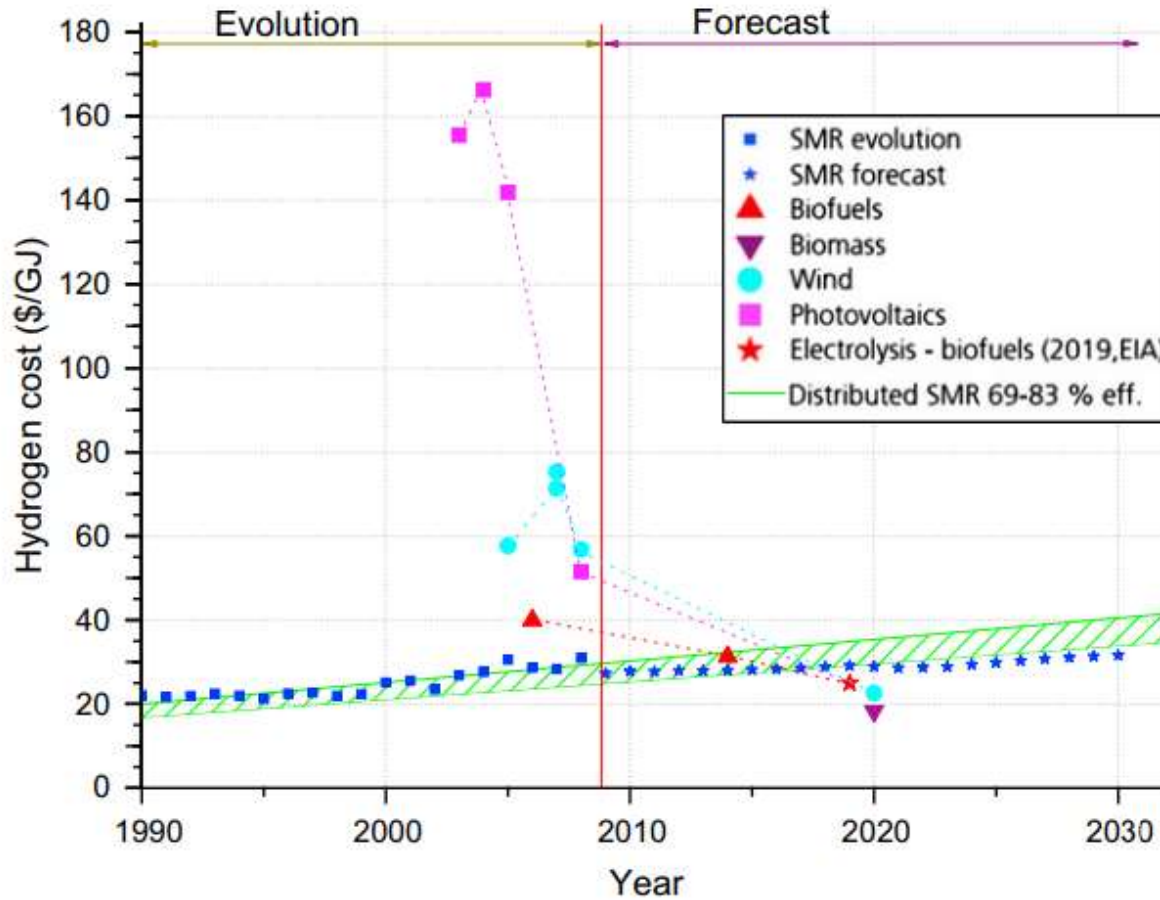
Why Hydrogen?

- Clean – no greenhouse gases
- Energy security – can be produced from abundant sources
- Economic growth demands for energy
- Efficient – fuel cells ~75% efficiency
- Portable: Car tanks, micro fuel cells...

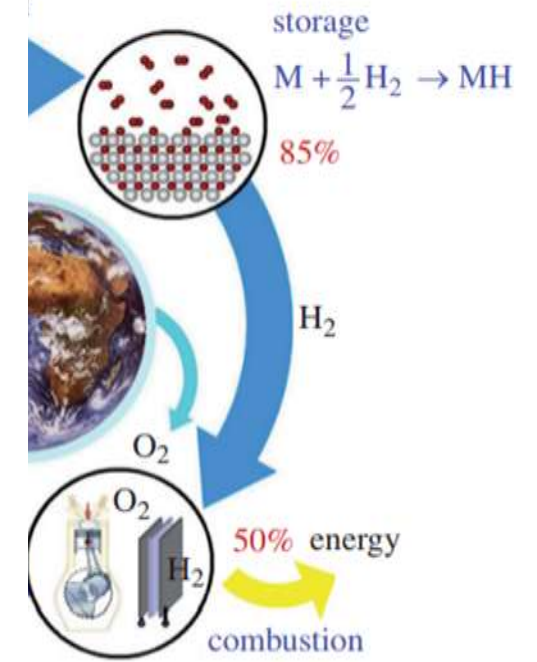
Why Hydrogen?



Volumetric vs. gravimetric energy density of the major energy carriers



Forecast of hydrogen production costs using different technologies.**

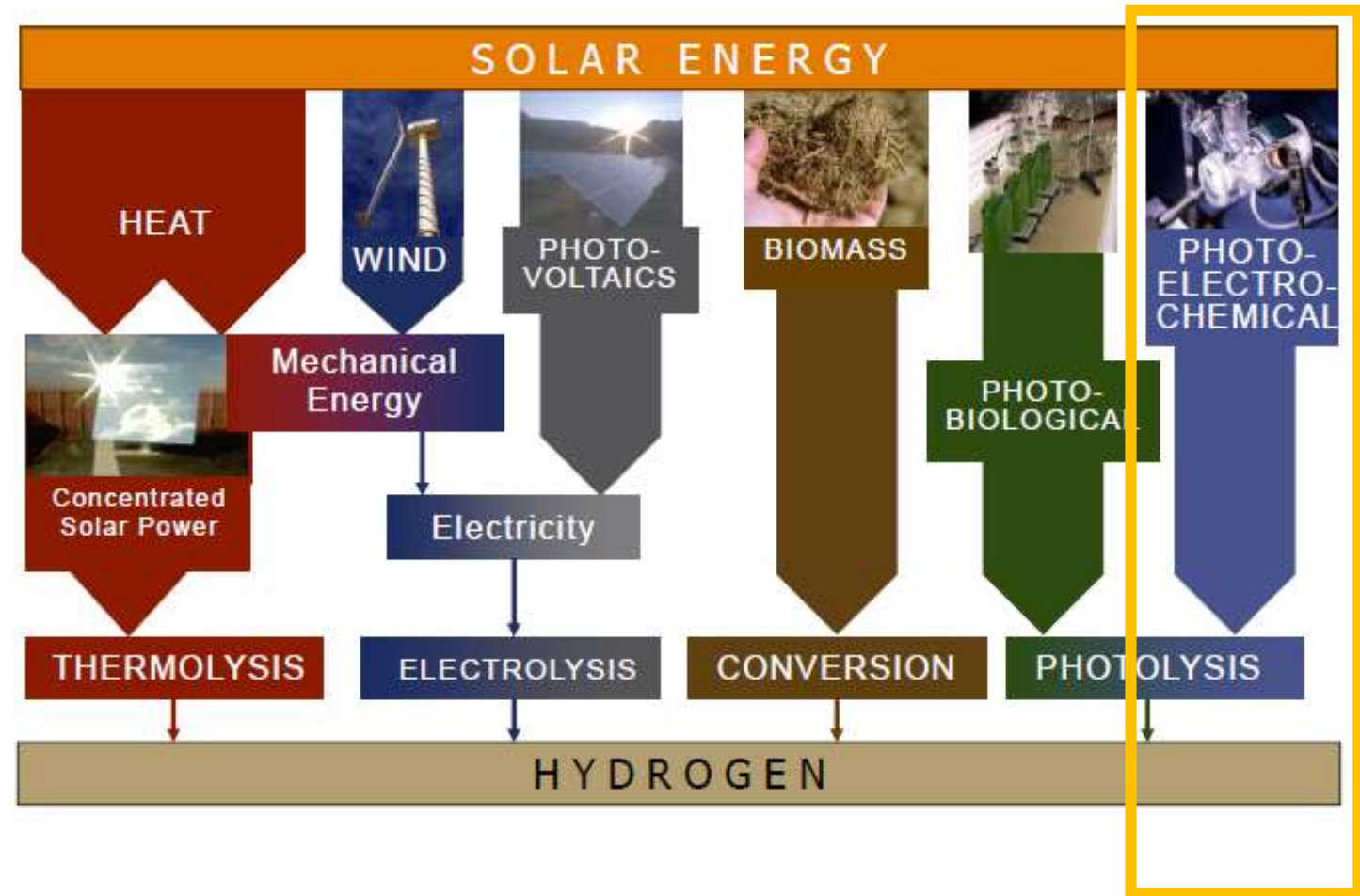


n cycle in nature.*

* Züttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. Hydrogen: The Future Energy Carrier. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2010**, 368 (1923), 3329–3342.

Lemus, R. G.; Duarte, J. M. M. Updated Hydrogen Production Costs and Parities for Conventional and Renewable Technologies. *Int. J. Hydrogen Energy* **2010, 35 (9), 3929–3936.

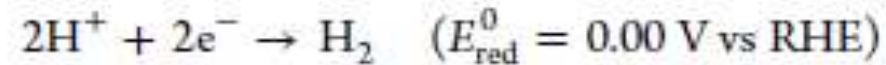
H₂ Production Routes



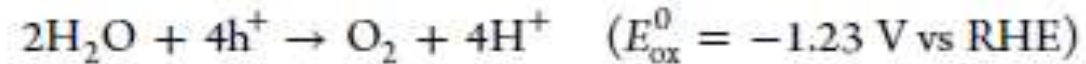
- Our Proposed Solution:
 - Split water with renewable energy sources

Water Splitting Principle

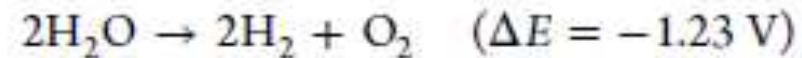
Reduction reaction:



Oxidation reaction:



Overall reaction:

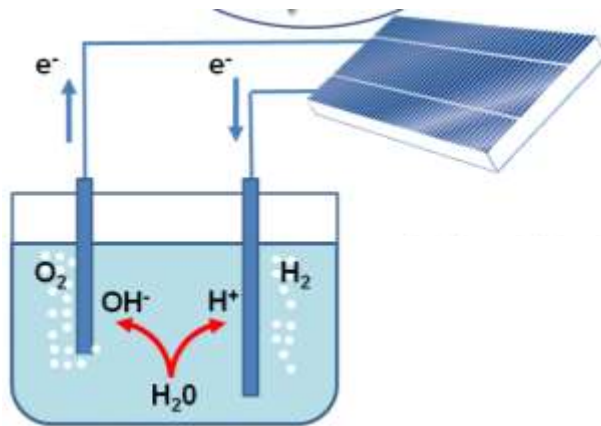


Schematic diagram of water electrolysis process.*

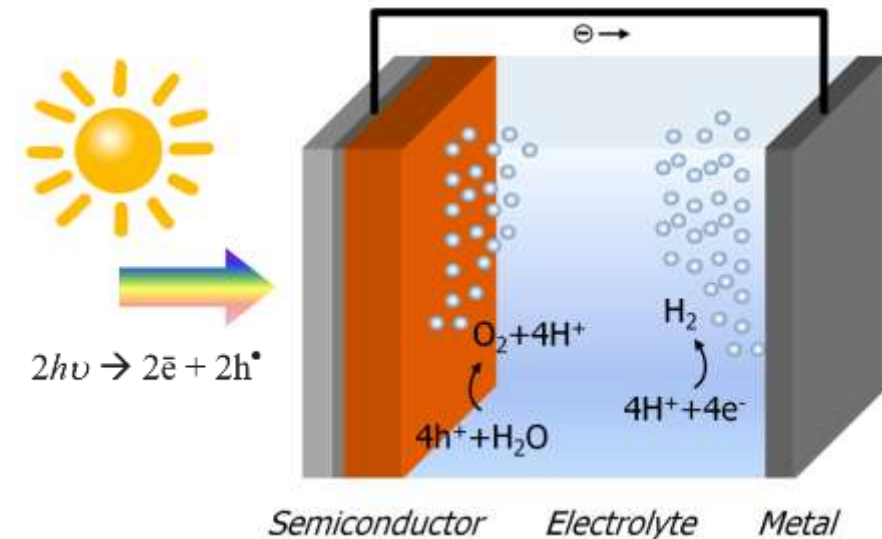
* Züttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. Hydrogen: The Future Energy Carrier. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2010**, 368 (1923), 3329–3342.

Splitting Water *via* Renewable Resources

- Direct PV electrolysis
 - connecting a commercial electrolyser to a PV system.
 - Light harvesting > charge generation > electrolysis > hydrogen and oxygen

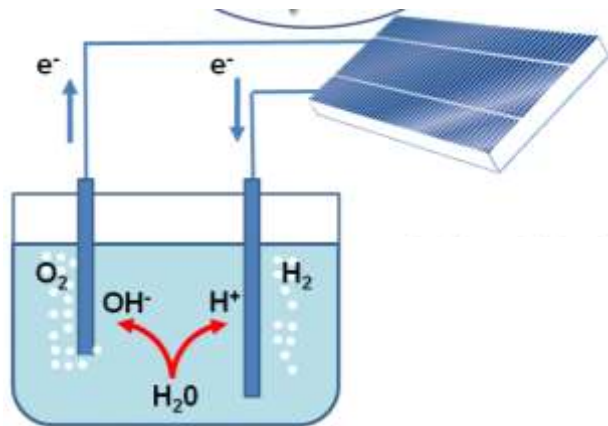


- PEC electrolysis
 - Photoelectrode(s) are immersed into the electrolyte and the photo-generated electron-holes are directly used to reduce and oxidize water.

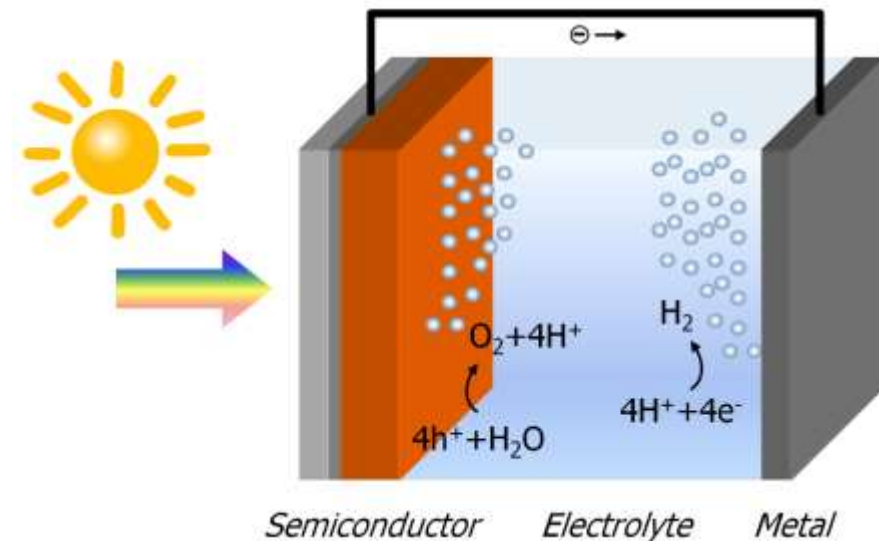


Splitting Water *via* Renewable Resources

- Direct PV electrolysis
 - Expensive?
 - High current densities -> overpotential -> lower efficiency
 - Not compact?



- PEC electrolysis
 - Lower current densities -> higher electrolysis efficiency
 - All in one package: cheap, compact.



PEC first demonstration

- First demonstration in 1972 by Fujishima and Honda,

Electrochemical Photolysis of Water at a Semiconductor Electrode

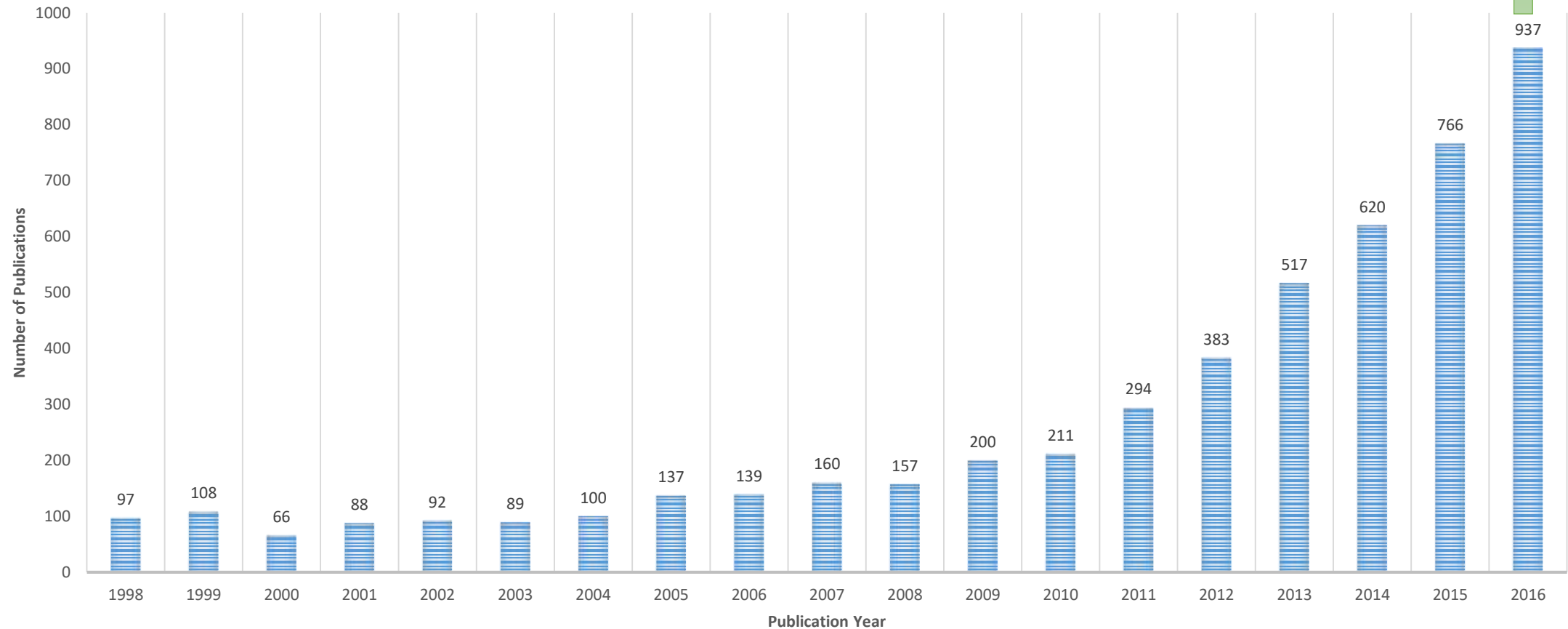
ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled.



Development of the scientific field for Photo-Electrochemical Water Splitting research



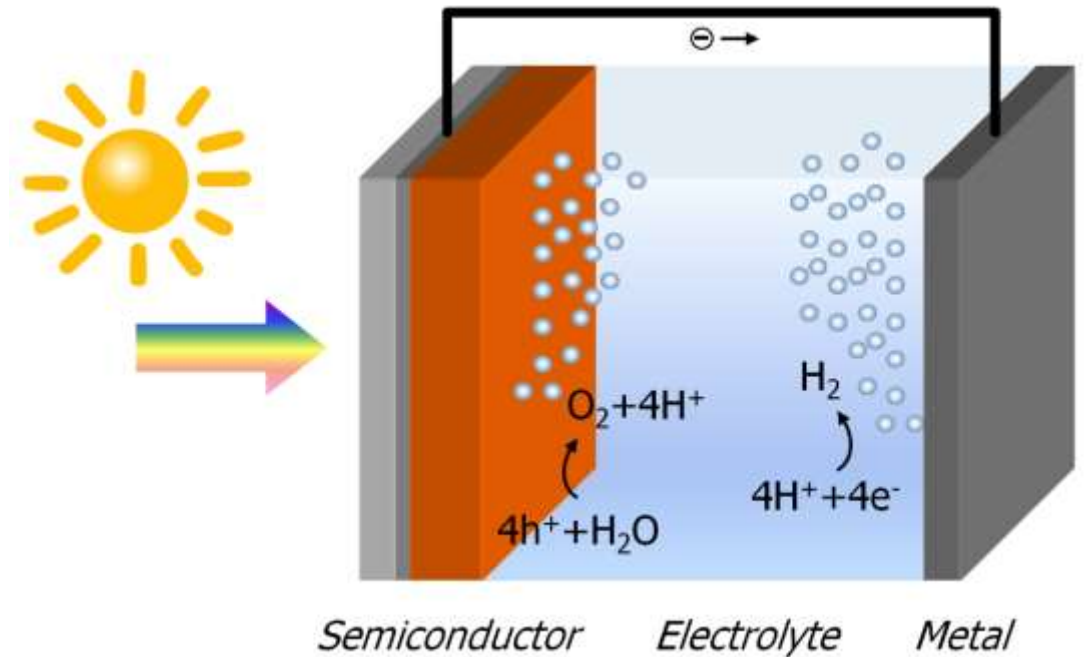
*Based on "Photo-Electrochemical Water Splitting" keyword on Scencedirect.com on 27/8/2016

PEC WS Principle

- It combines the harvesting of solar energy and the electrolysis of water into a single device.
- PEC: Photoelectrochemical
 1. Photo
 2. Electro
 3. Chemical

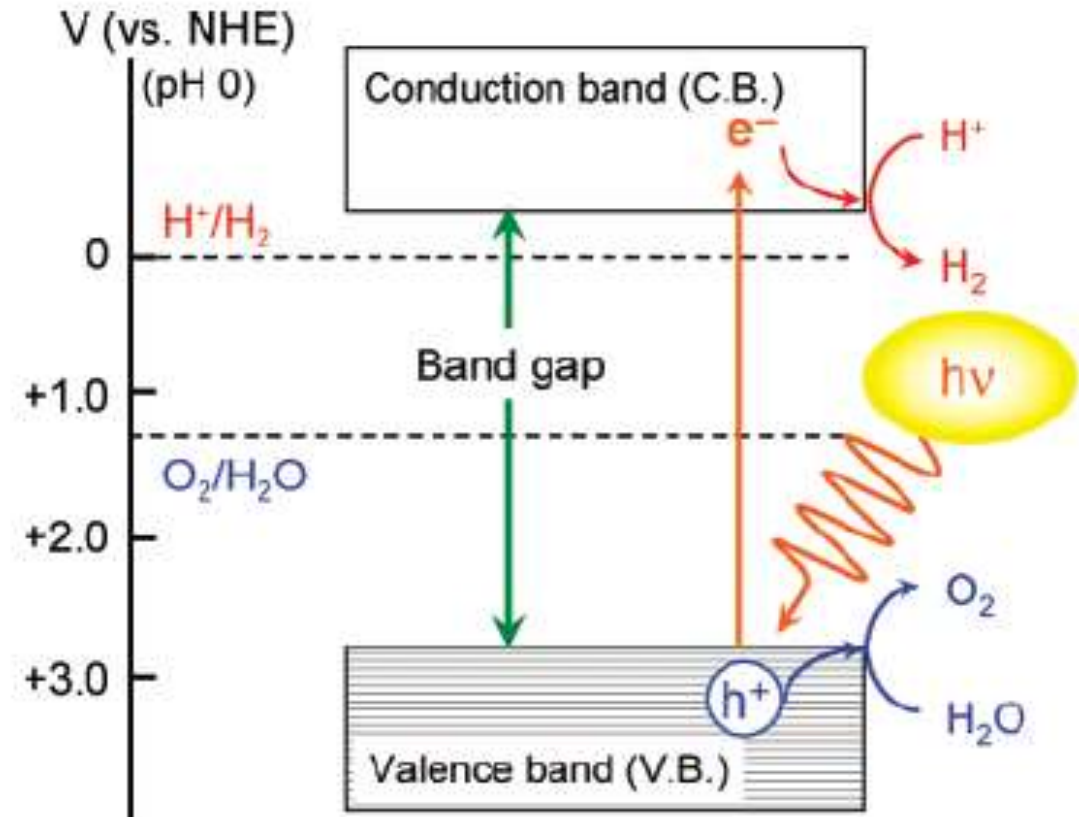
PEC Water Splitting Processes

- Incoming photons ($h\nu$) generate electrons (e^-) and holes (h^+)
 - with an efficiency labeled η_{e^-/h^+}
- The photogenerated electrons and holes then separate and travel through the semiconductor in opposite directions;
 - the efficiency associated with the charge transport process is labeled $\eta_{\text{transport}}$
- The holes drive the Oxygen Evolution Reaction at the surface of the semiconductor working electrode.



Material criteria to be met

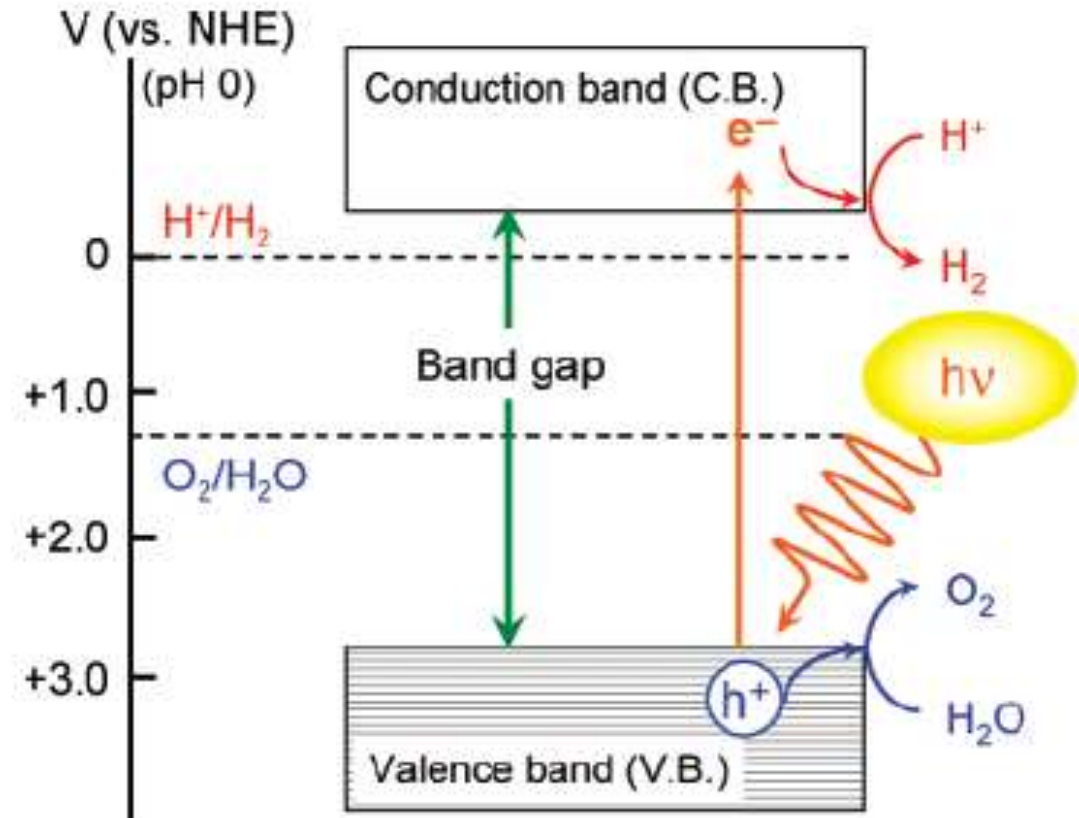
- The semiconductor system must generate sufficient voltage upon irradiation to split water
 - Or an external bias needs to be applied.
- The bulk band gap must be small enough to absorb a significant portion of the solar spectrum
- The band edge potentials at the surfaces must straddle the hydrogen and oxygen redox potentials



Domen et al. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem.* 2007

Material criteria to be met

- The system must exhibit long-term stability against corrosion in aqueous electrolytes
 - Metal oxides: Charge transfer kinetics > anodic decomposition rate
 - Non-oxides: thin oxide layer formation, dissolving.
- The charge transfer from the surface of the semiconductor to the solution must be facile to minimize energy losses due to kinetic overpotential



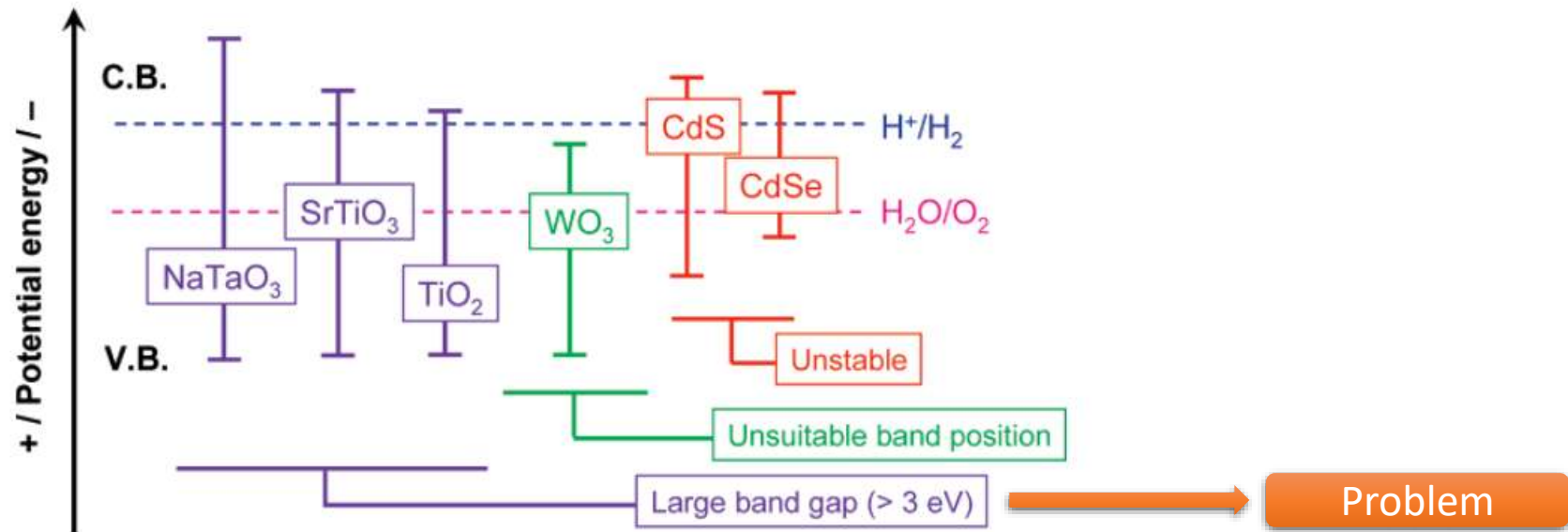
Domen et al. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem.* 2007

Target

- Band gap greater than 1.23 eV* but low enough to absorb visible light
- Band edge straddling
- High stability
- Fast charge transfer
- Low cost

Current Challenge

- As far as we know, no cost-effective materials system satisfies all of the technical requirements listed above for practical hydrogen production.
- Schematic illustration of band structures of several semiconductor



Domen et al. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem.* 2007

Possible Solutions

- Materials Engineering
 - Introducing elements to reduce BG (Doping/Alloying)
 - e.g.: N₂
 - Since N replaces O in certain positions, providing a smaller band gap.
- Nanostructuring
 - Increasing surface area
 - Tuning electronic properties
- Different annealing conditions

Why NTs?

- In 1991, Iijima reported on the formation of carbon nanotubes
 - Milestone in MSE
 - Then transition to MOs
- quantum size and dimensionality may fully be effective on physical and chemical properties, such as electron mobility, optical band gap, and surface reactivity.
- NTs attracts tremendous interest due to specific advantages:
 - Geometric Factors:
 - High surface area
 - Size exclusion effects
 - Diffusion behavior
 - Biological Interactions
 - Directional Charge and Ion transport

*Lee, Kiyong, Anca Mazare, and Patrik Schmuki. "One-dimensional titanium dioxide nanomaterials: nanotubes." *Chemical reviews* 114.19 (2014): 9385-9454.

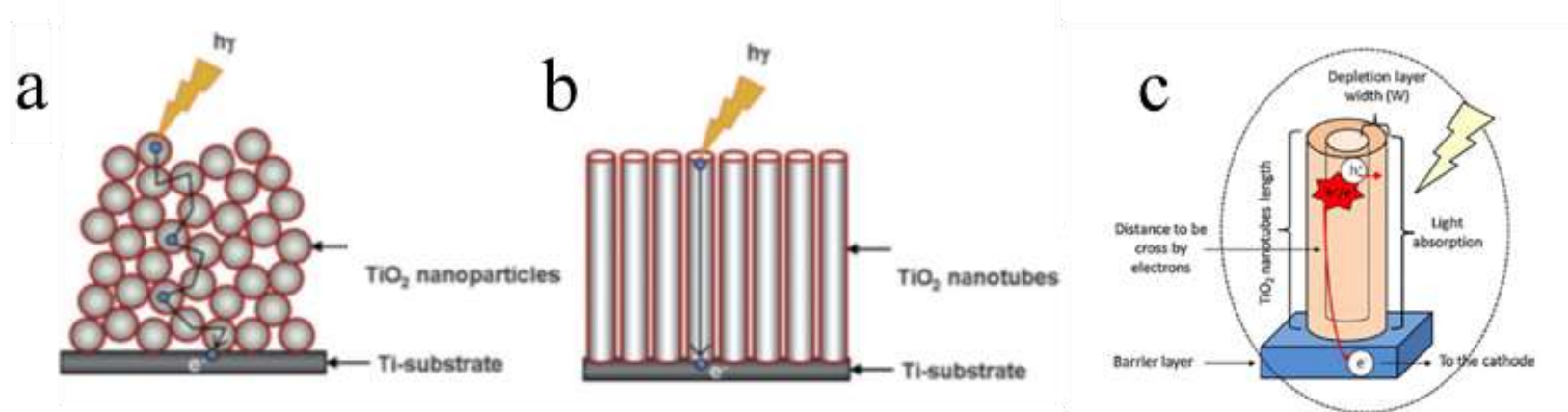
Why NTs?

- Classical 1D quantum size effects:
 - Reduced e- scattering (ballistic transport)
 - Extreme surface curvature (Modified physical and chemical properties)
 - Diffusion length of holes lies within the range of tube wall thickness
 - Orthogonal carrier separation:
 - Hole to the wall
 - E- to the back contact
 - Core shell Structures (Carrier Separation)
 - Decoration of wall ability
 - Nano test-tubes (high observation length)
- IPCE in NT \gg NP layers
 - Since high current collection efficiency
 - Since (τ_{av} NT) (transport time constant) $>$ NPs
 - Since surface recombination NT $<$ NPs

*Lee, Kiyong, Anca Mazare, and Patrik Schmuki. "One-dimensional titanium dioxide nanomaterials: nanotubes." *Chemical reviews* 114.19 (2014): 9385-9454.

Why NTs?

- High surface area allows for increased photon absorption
 - Twice the surface area/unit volume compared to NPs and NRs with the same outer diameter
- NTs perpendicular to the substrate surface, reduce e^- diffusion path to the external circuit



Why Ti?

- This is due to a broad set of outstanding properties that this class of materials has to offer.

TiO₂ application

Photocatalysis

Self-cleaning, wetting

Solar cell

Catalysis

Gas sensing

Doping

Biomedical

Ceramics

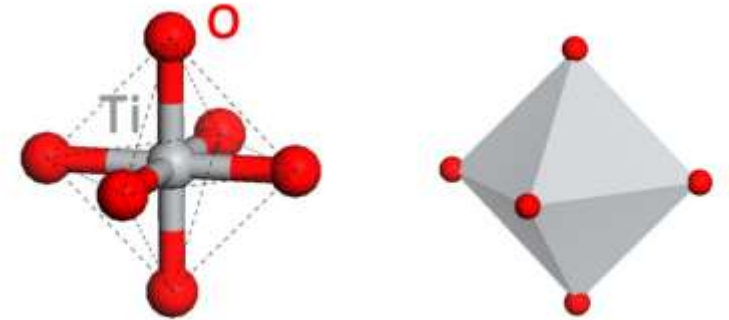
Interference coating, optical devices

Macak, J. M., et al. "TiO₂ nanotubes: self-organized electrochemical formation, properties and applications." *Current Opinion in Solid State and Materials Science* 11.1 (2007)

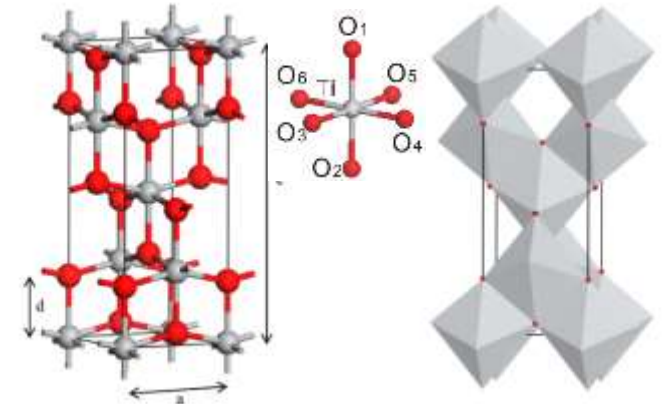
Why TiO₂?

- TiO₂ has shown to be an excellent photocatalyst
 - long-term stability, low-cost preparation and a strong enough oxidizing power to be useful for the decomposition of unwanted organic compounds
- The anatase form of TiO₂ shows the highest solar energy conversion efficiency

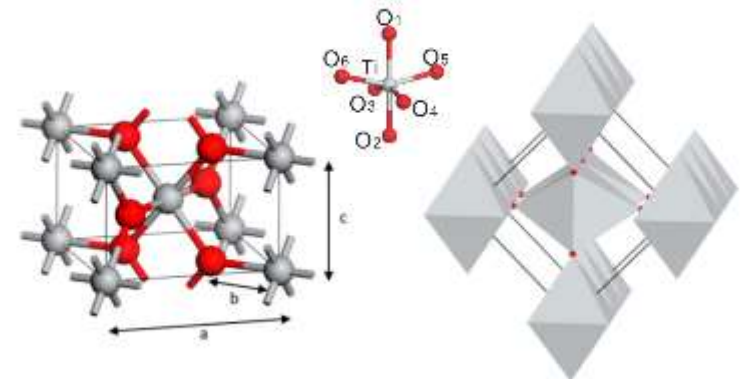
Main TiO_2 Crystal Structures



Anatase



Rutile



Why TNTs?

- Enhanced properties
- Cost-effective construction,
- higher surface-to-volume ratio
- Due to its photocatalytic property

Proposed Material

- Ti 3510
 - (Ti-35Zr-10Nb)
- Why?
 - The fabricated Ti-Nb-Zr-O nanotubes showed a 17.5% increase in the photoelectrochemical water oxidation efficiency as compared to that measured for pure TiO₂ nanotubes under UV illumination.
 - Nb, Zr alloying
 - shifts absorption band edges towards visible region
 - Enhances charge transfer

Objective

- Fabrication of a complex metal oxide NTs and tuning its morphology for an efficient water splitting performance.
- Investigating the formation and growth of the NTs.
- Assessing the PEC performance of the fabricated NTs.

Research Plan

- Literature Review on Water Splitting and different requirement for materials used.
- Selection of Material/Alloy.
- Material Preparation and Synthesis.
- Material Processing by Annealing at different temperatures and in different atmospheres.
- Studying the effect of different annealing conditions on the structure and properties of the material.
- Material characterization and assessment of the required properties for Water splitting.

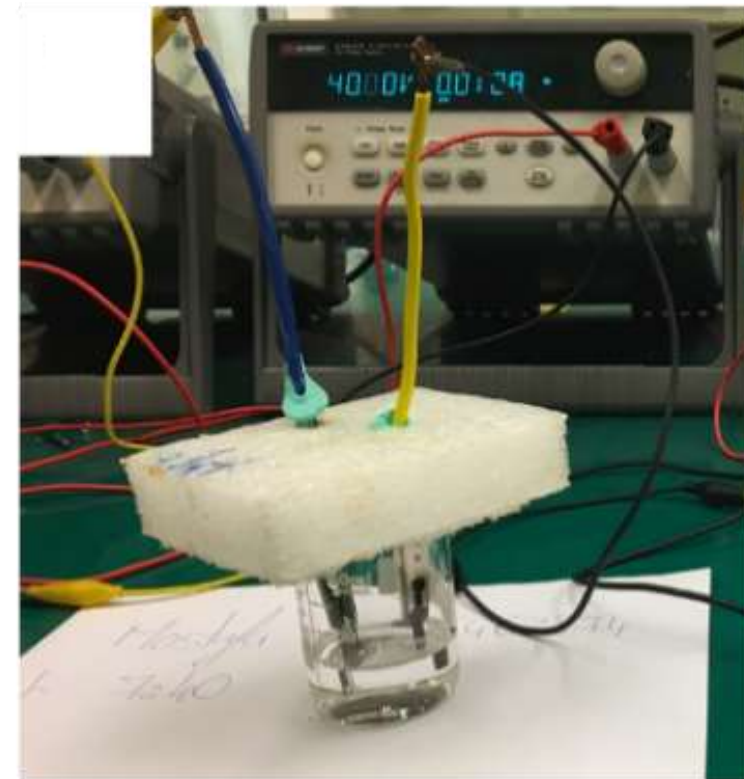
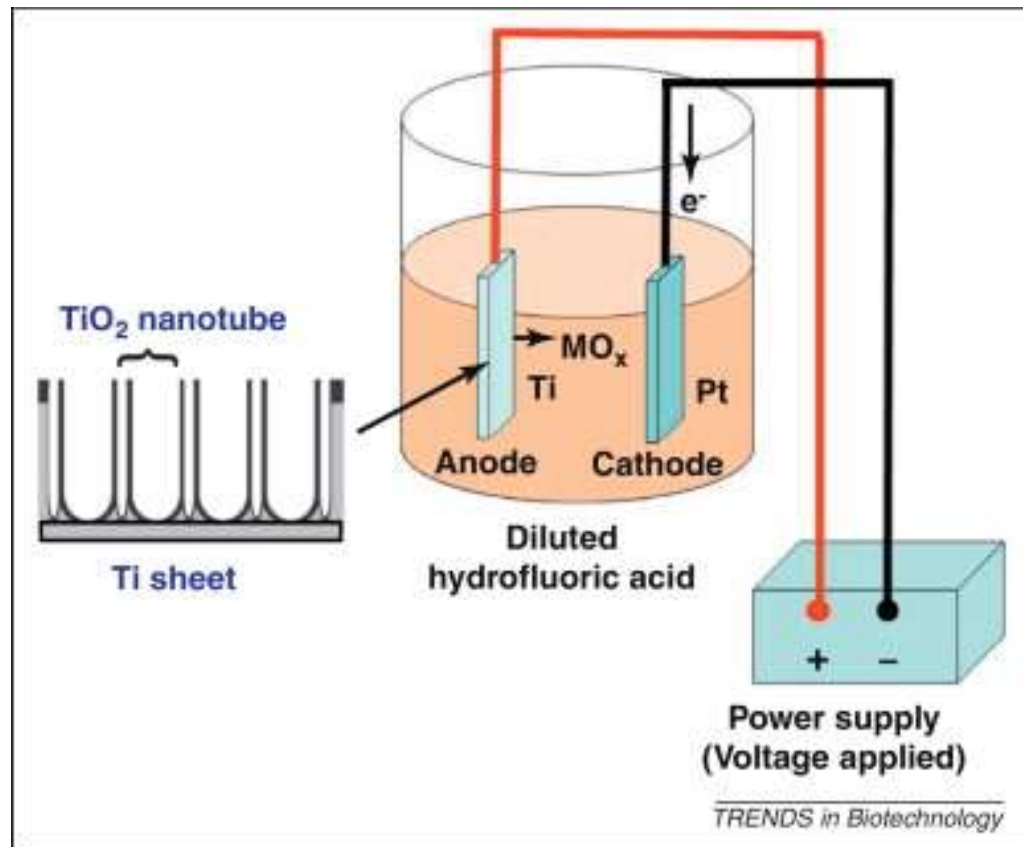
Experimental Methods

Main Phases

1. NTs Synthesis
 - *Via Anodization*
 - Optimization of anodization parameters
2. Morphology Investigation
 1. Studying effect of time
 2. Studying effect of Anodization Potential
 3. Selection of the most promising condition
3. Characterization

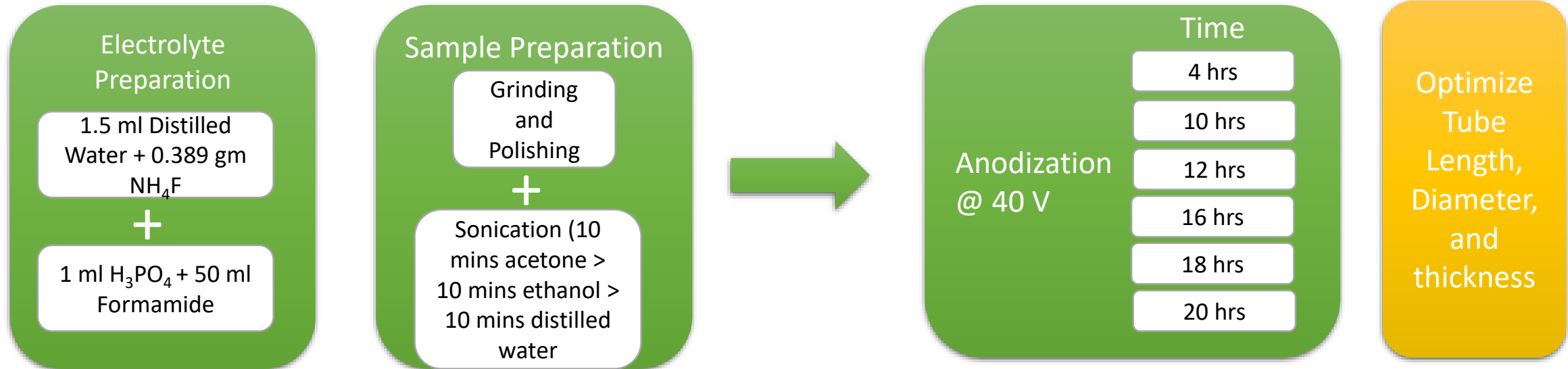
I. NTs Synthesis

- Via Anodization



Experimental Work

- Anodization



Anodization Conditions

Sample Preparation	Time	Voltage
Grinded	0.5 h	40 V
	1 h	
Polished	2 h	
	4 h	
	6 h	
	8 h	
	10 h	
	12 h	
	14 h	
	16 h	
	18 h	
	20 h	

Anodization Conditions

Sample Preparation	Time	Voltage
Grinded	2 hrs	10 V
	4 hrs	20 V
Polished	8 hrs	30 V
	14 hrs	40 V
		50 V
		60 V
		80 V
		100 V

		Anodization Time			
		2 hrs	4 hrs	8 hrs	14 hrs
Anodization Potential	10 V				
	20 V				
	30 V				
	40 V				
	50 V				
	60 V				
	80 V				
	100 V				

Annealing Conditions

Atmospheres

H₂

Air

Temp.

500 °C

Ramp rate

1 °C/min



Temp.

500°C

4 hours Soaking

Heating 1°C/min

Natural Cooling

Time

3. Different Characterization Techniques Used

- Surface/Morphology:
 - SEM
- Structural:
 - X-ray Diffraction - XRD
- Elemental:
 - Energy-dispersive X-ray spectroscopy - EDX
 - X-ray photoelectron spectroscopy - XPS
- Optical:
 - UV-Vis Spectroscopy
 - Raman Spectroscopy
- Electrochemical:
 - LSV
 - I-t

Results

I. NTs Fabrication

1. NTs Layer Adhesion



Good Adhesion



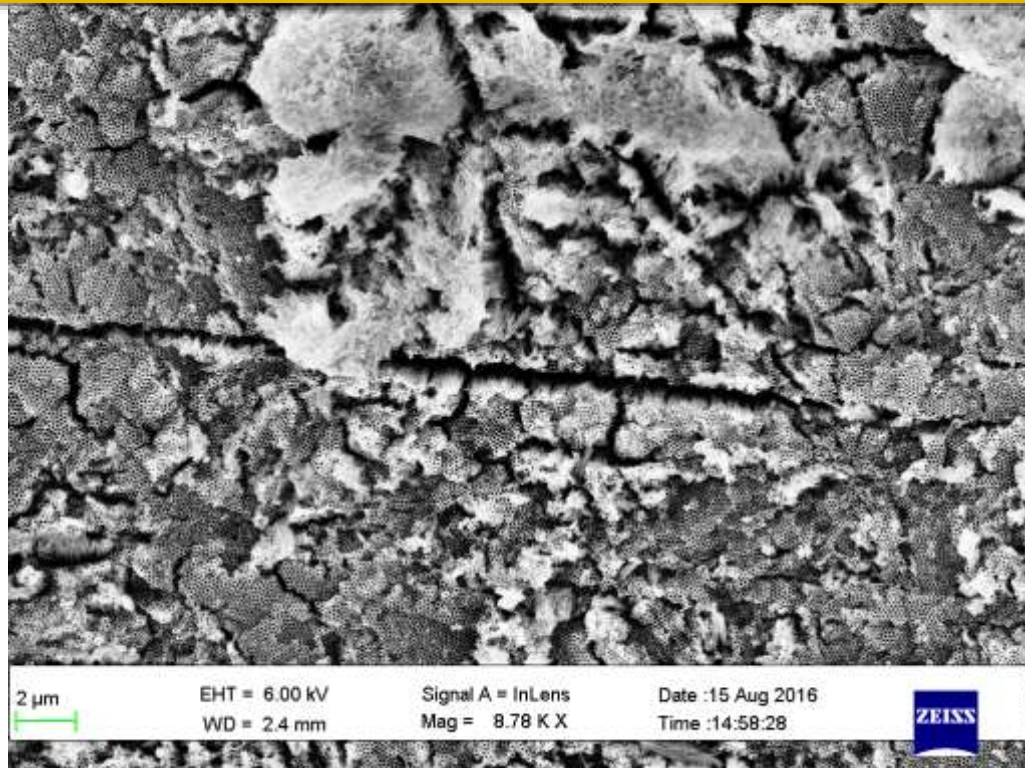
Poor Adhesion



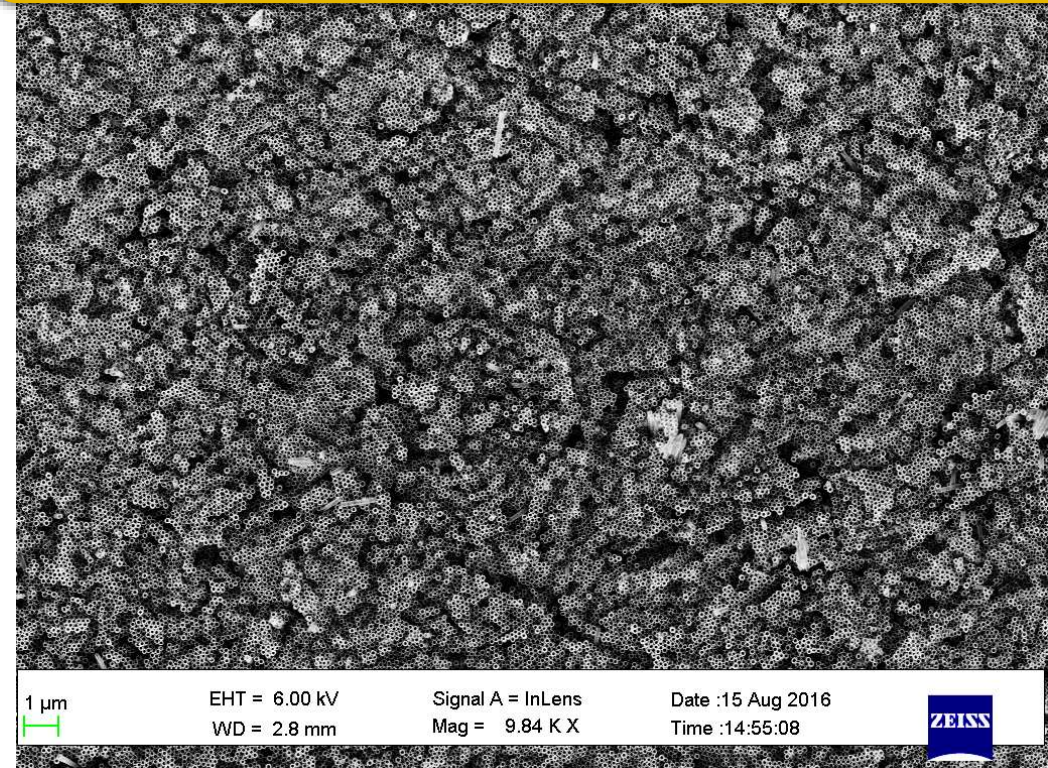
~ No Adhesion

2. Effect of Surface roughness

18 hrs grinded

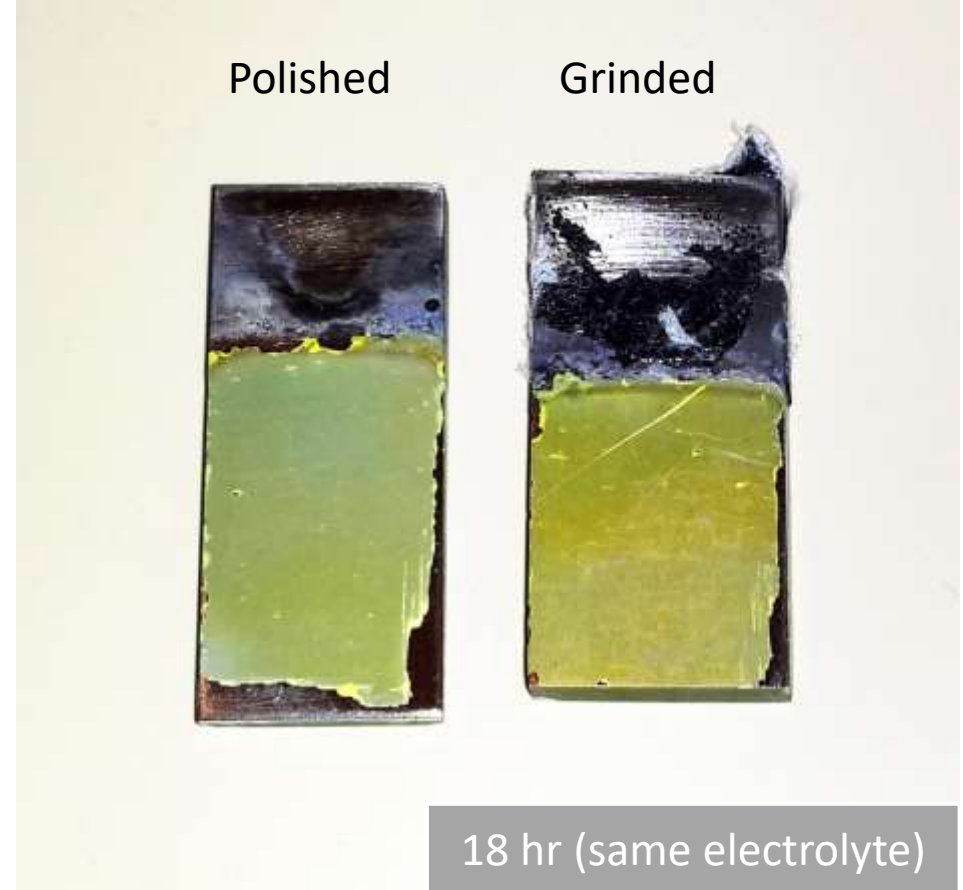


18 hrs Polished

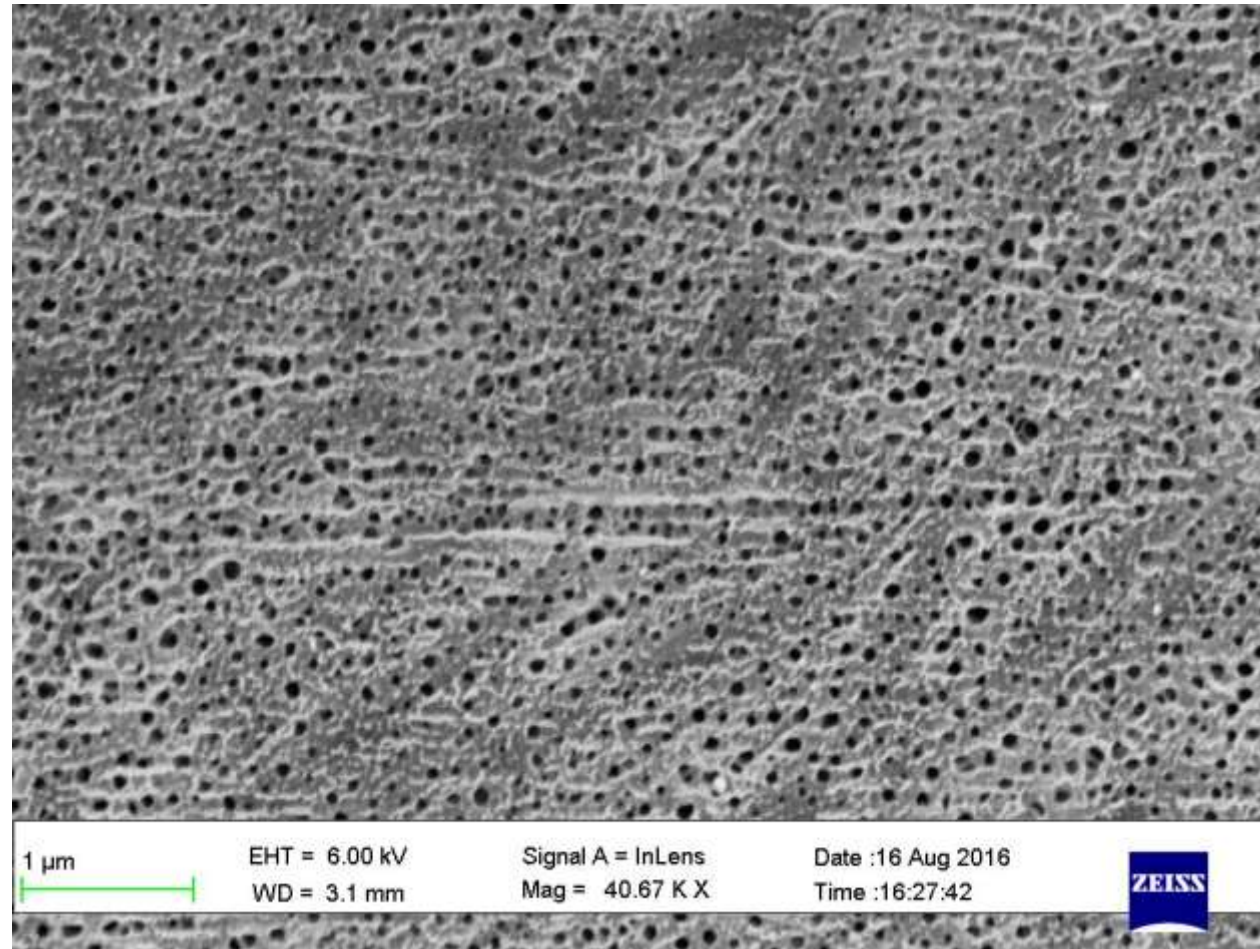


Potential causes

- ~~Electrolyte~~
 - Using same electrolyte
- ~~Grinding / Polishing~~
 - Almost same conditions
- Sonication?
 - Pealed off even when drying under air stream!
- Fluorine rich layer?
 - Existed on both long and short times



Porous Layer instead of NTs!



Effect of time and Anodization Potential

Effect of Anodization Potential on the Morphology

10 V

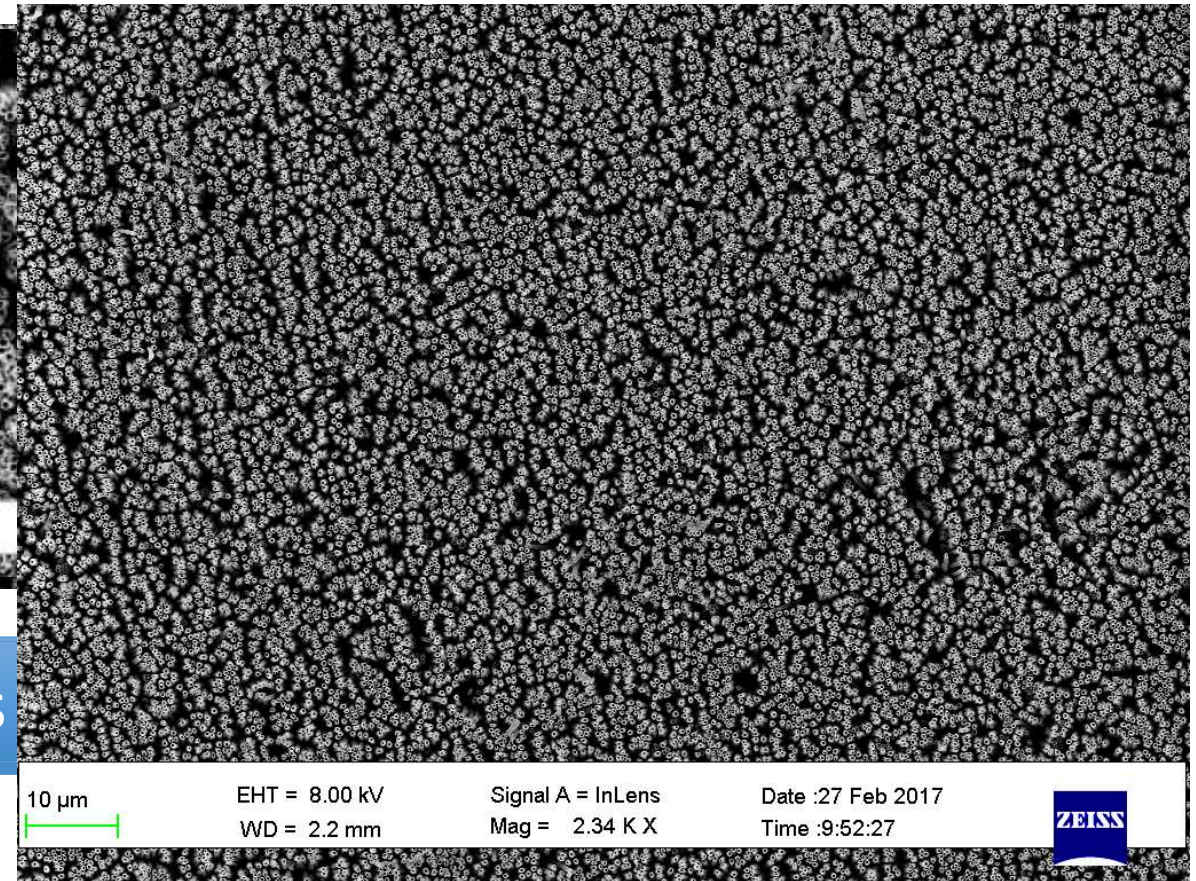
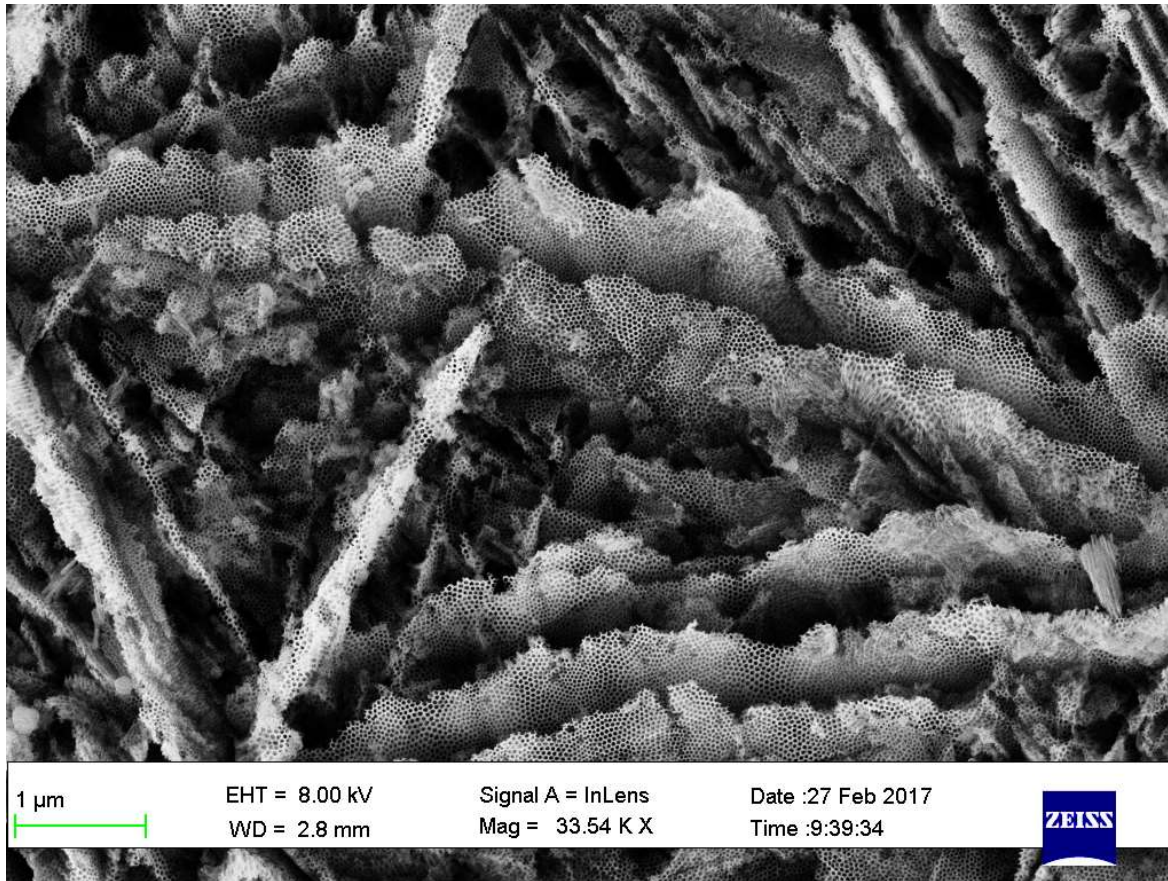
30 V

50 V

60 V

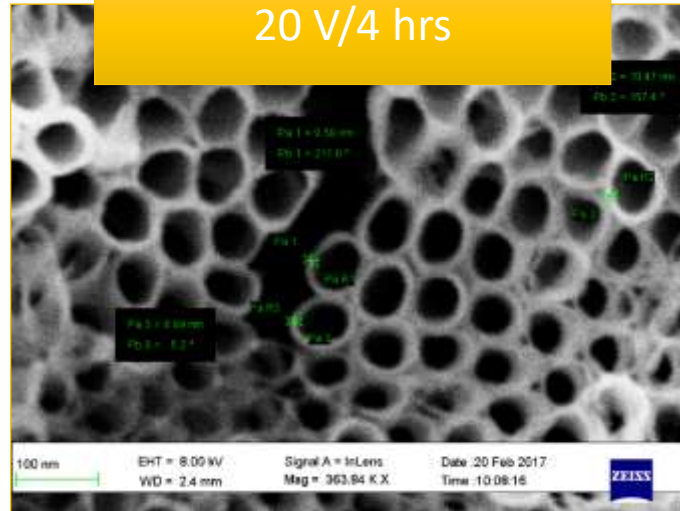
80 V

100V

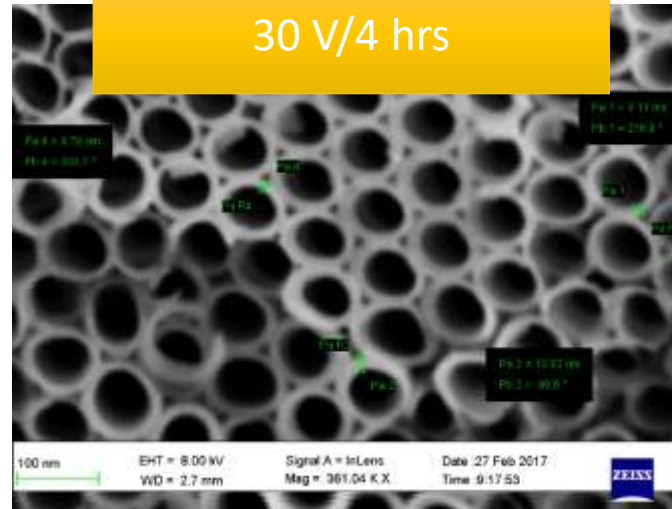


Effect of Anodization Potential on the NTs Top pore

20 V/4 hrs



30 V/4 hrs



40 V/4 hrs



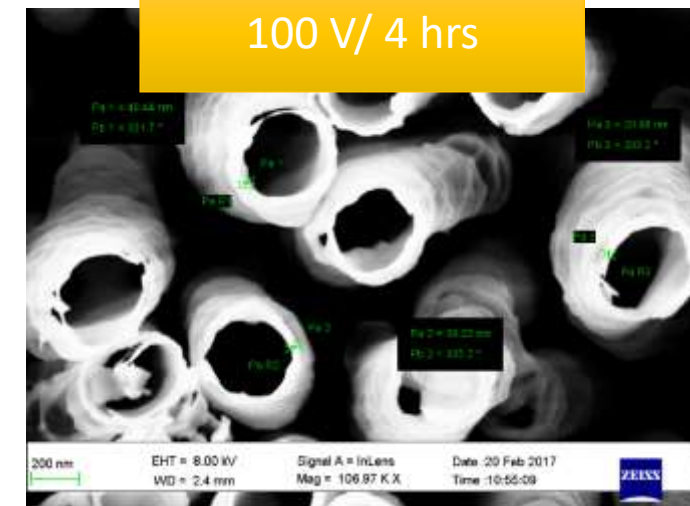
50 V/4 hrs



80 V/4 hrs



100 V/4 hrs



Effect of Anodization Time on the Morphology

10 V

20 V

30 V

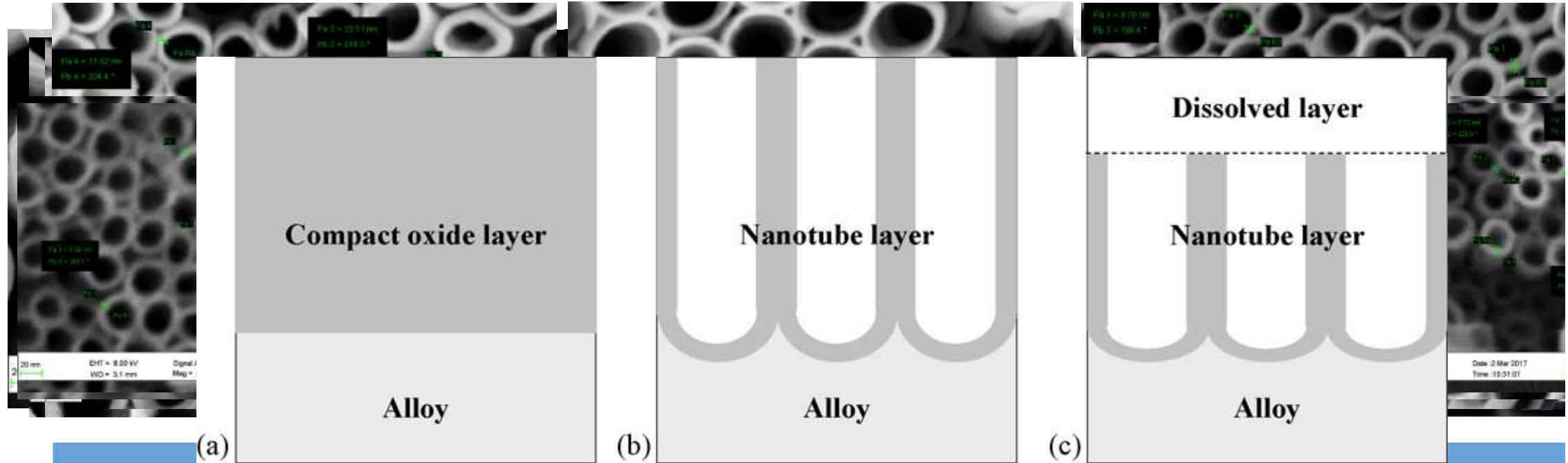
40 V

50 V

60 V

80 V

100 V



(a)

2 hrs

(b)

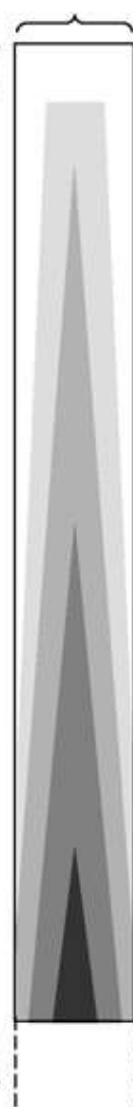
4 hrs

4 hrs

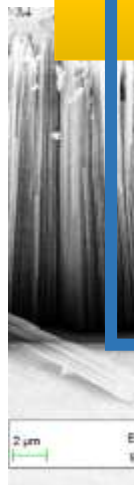
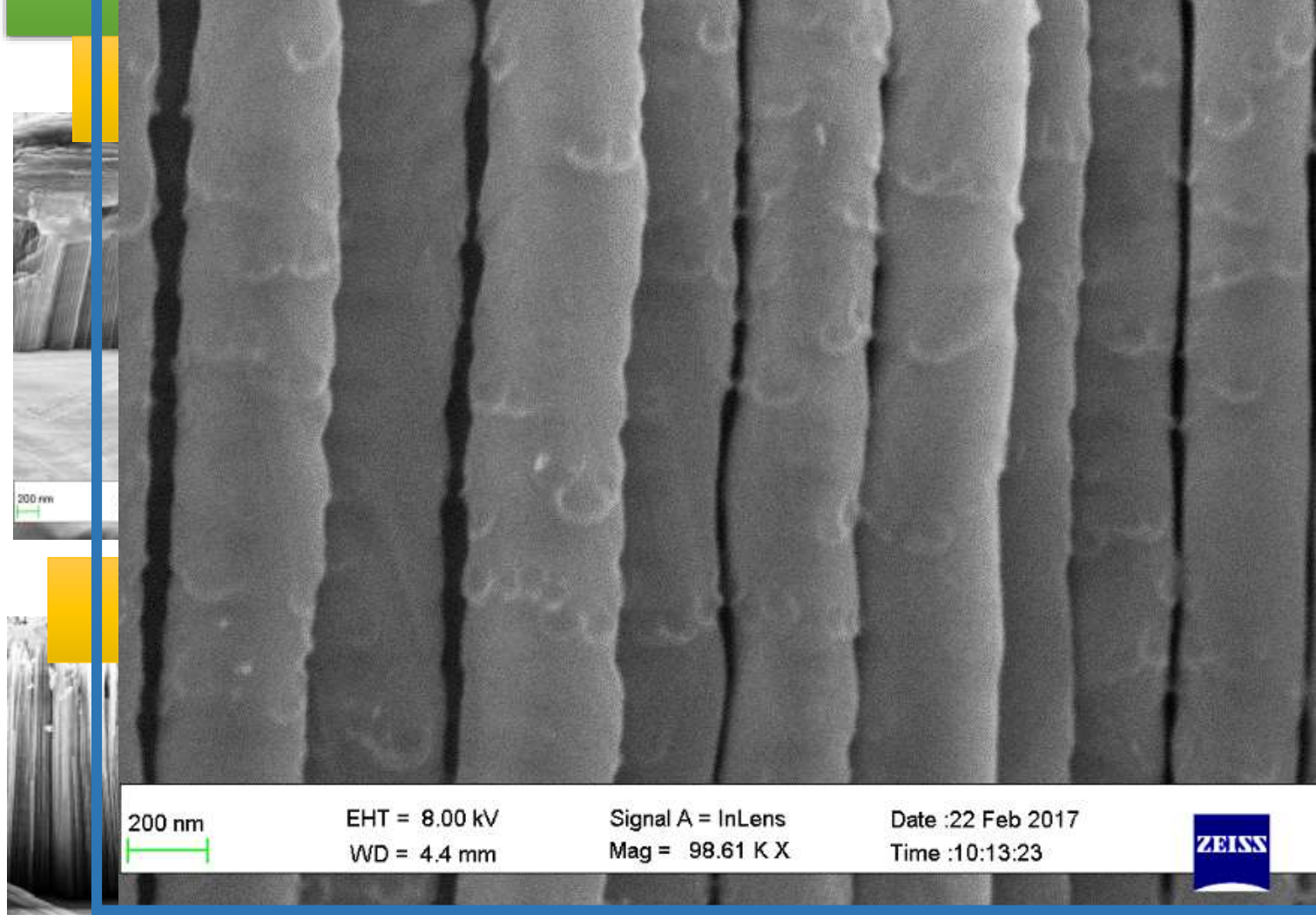
(c)

8 hrs

14 hrs

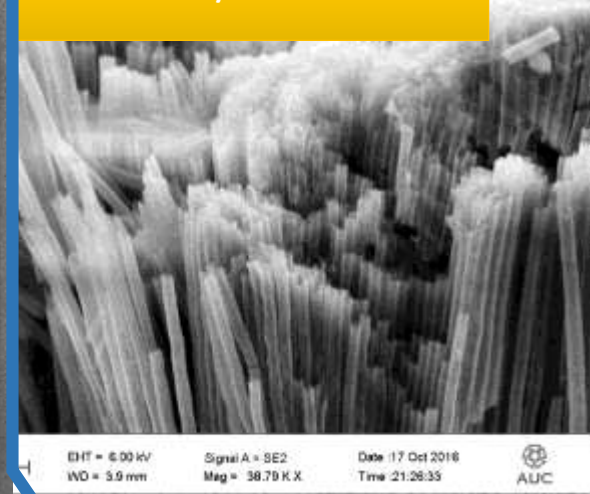


Effect of Time on the Tube Walls



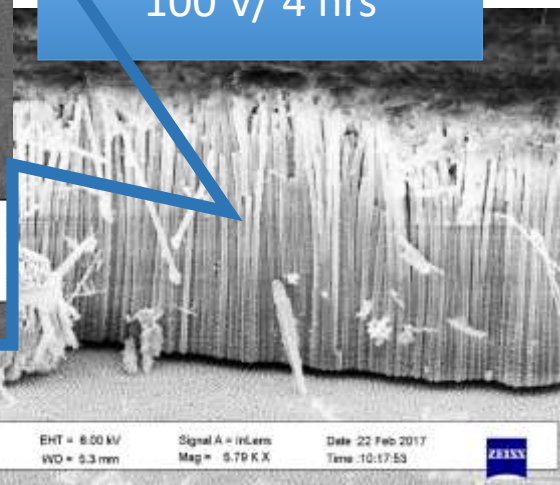
200 nm EHT = 8.00 kV Signal A = InLens Date :22 Feb 2017
WD = 4.4 mm Mag = 98.61 K X Time :10:13:23

40 V/2 hrs



EHT = 8.00 kV Signal A = SE2 Date :17 Oct 2016
WD = 5.9 mm Mag = 38.79 K X Time :21:26:35

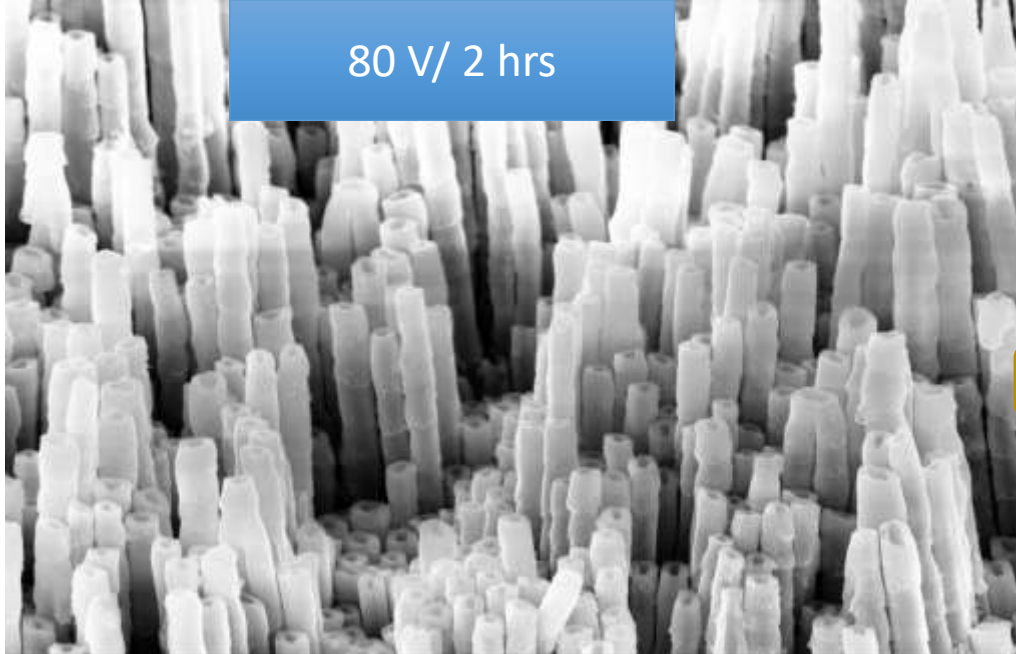
100 V/ 4 hrs



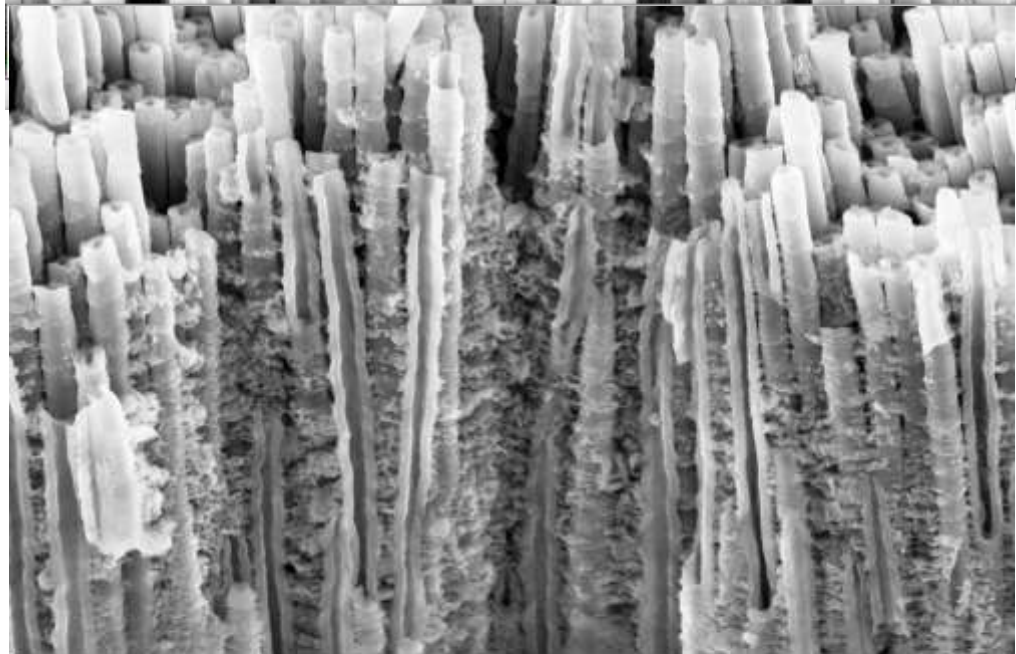
200 nm EHT = 8.00 kV Signal A = InLens Date :22 Feb 2017
WD = 5.3 mm Mag = 5.79 K X Time :10:17:53

200 nm EHT = 8.00 kV Signal A = InLens Date :16 Mar 2017
WD = 2.4 mm Mag = 4.03 K X Time :9:10:49

80 V/ 2 hrs



Top

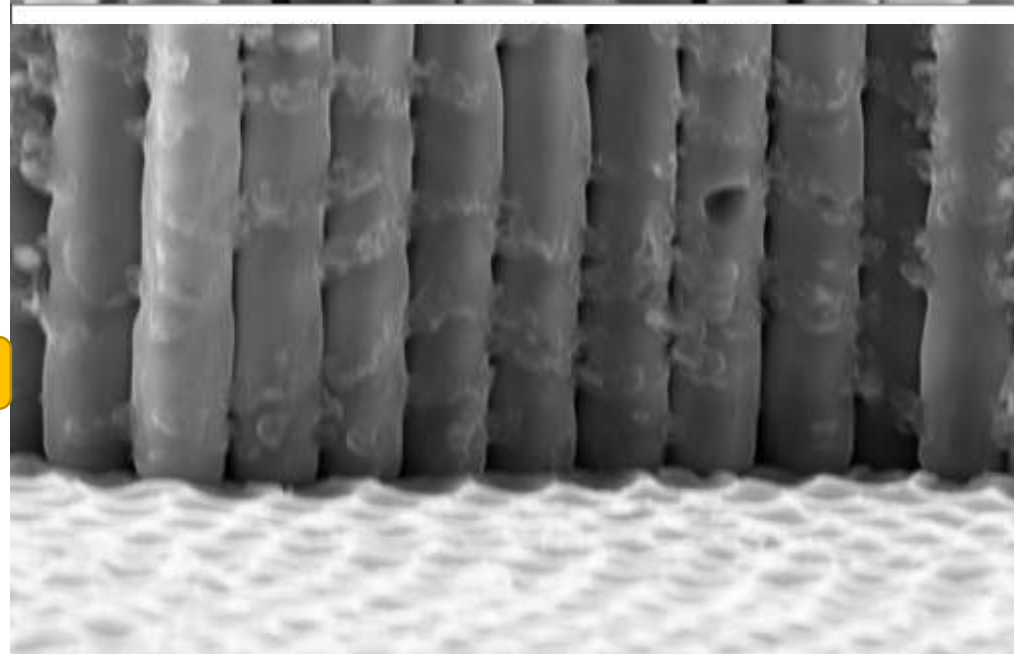
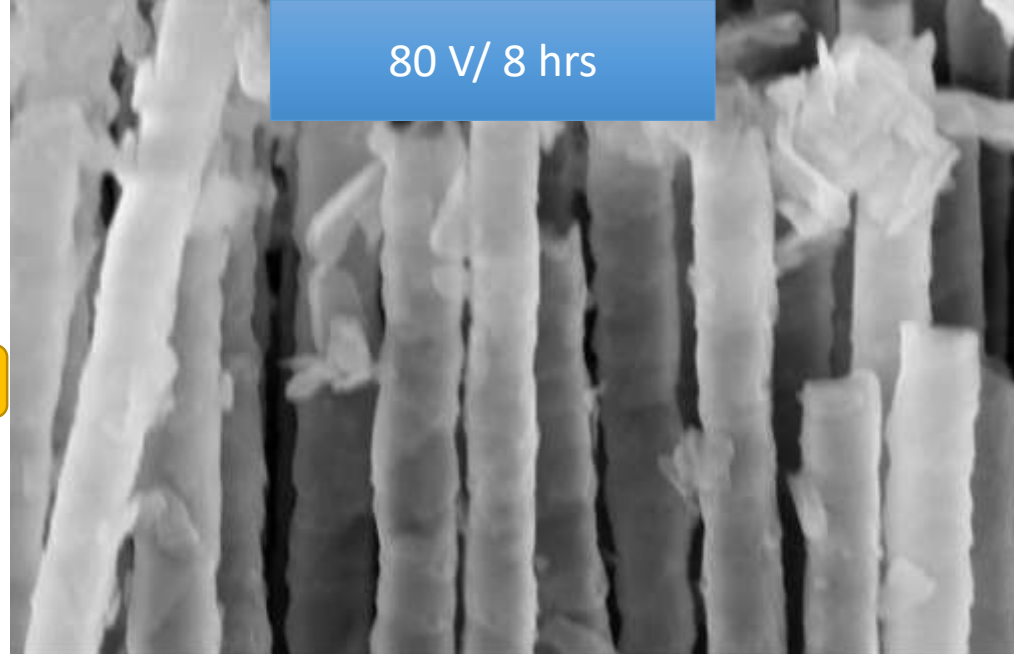


Base

1 μ m EHT = 10.00 kV Signal A = InLens Date :3 Apr 2017
WD = 2.4 mm Mag = 20.28 K X Time :11:28:04

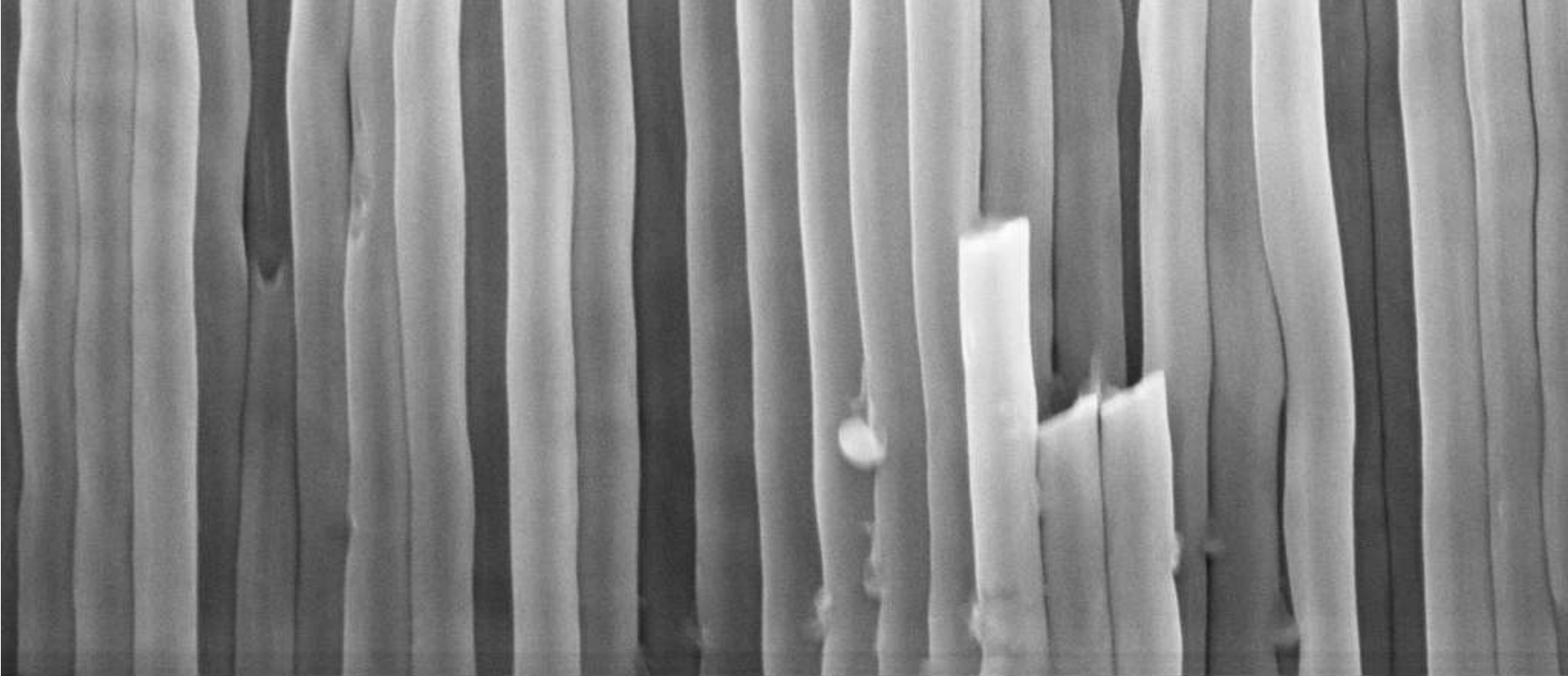


80 V/ 8 hrs



200 nm EHT = 10.00 kV Signal A = InLens Date :3 Apr 2017
WD = 2.7 mm Mag = 51.87 K X Time :11:39:55





60 V/ 8 hrs

200 nm


EHT = 10.00 kV
WD = 3.1 mm

Signal A = InLens
Mag = 35.24 K X

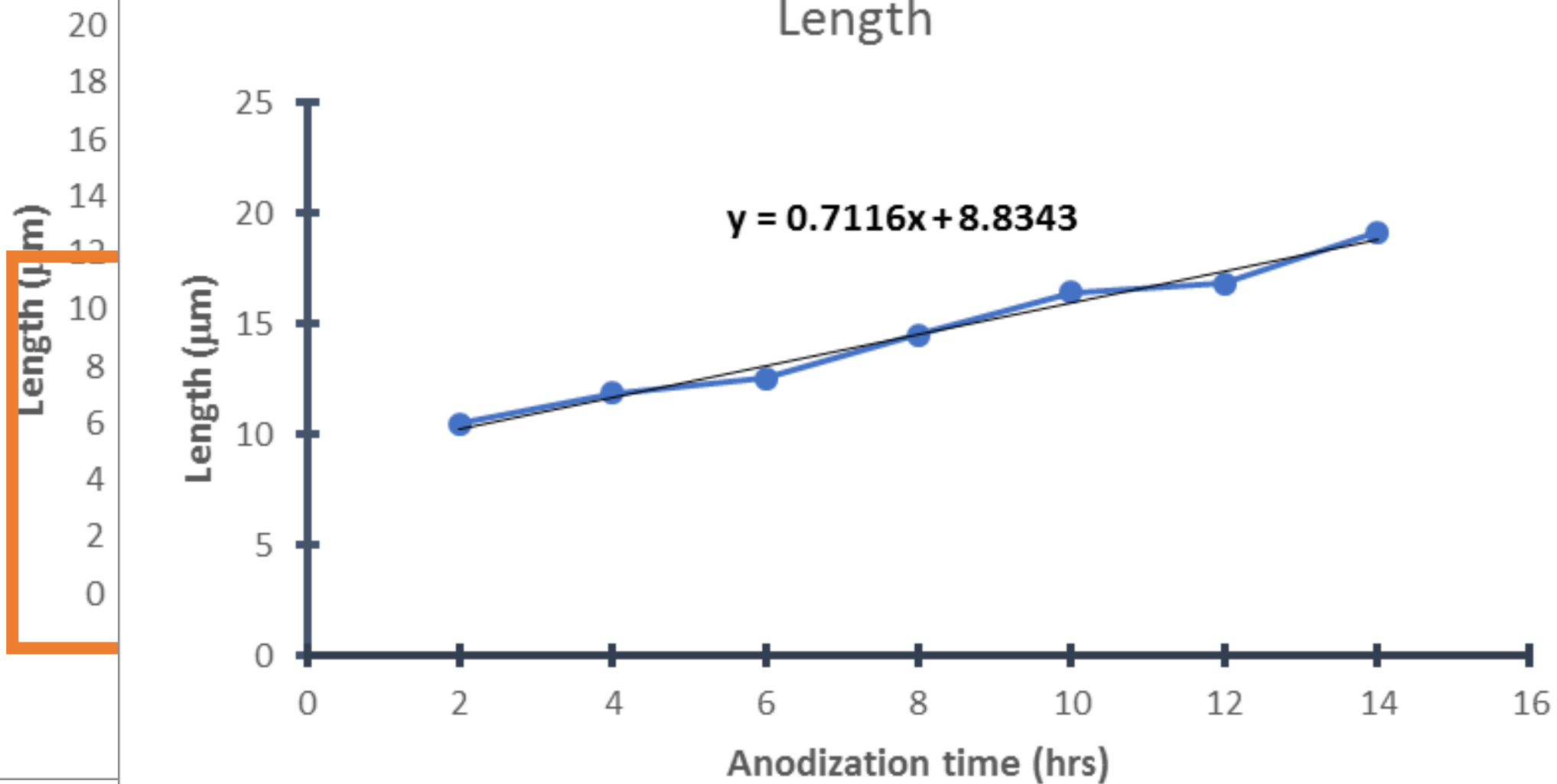
Date :3 Apr 2017
Time :11:47:00



Ti3510 @ 40 V

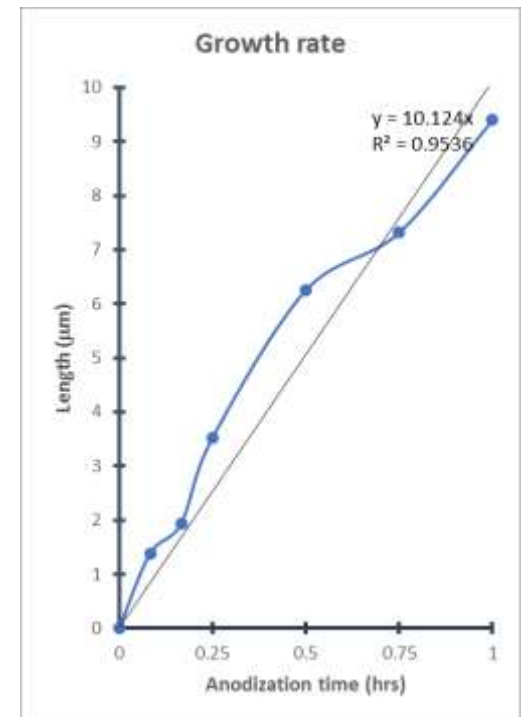
Growth rate

Length



Growth rates

- Initial Growth Rate) $_{40V} = \frac{9.4 \times 10^3 \text{ (nm)}}{1 \times 60 \times 60 \text{ (s)}} = 2.61 \text{ nm/sec}$
- Steady State Growth rate) $_{40V} = 0.198 \text{ nm/s}$



Initial Growth Stage

5 min



10 min



15 min



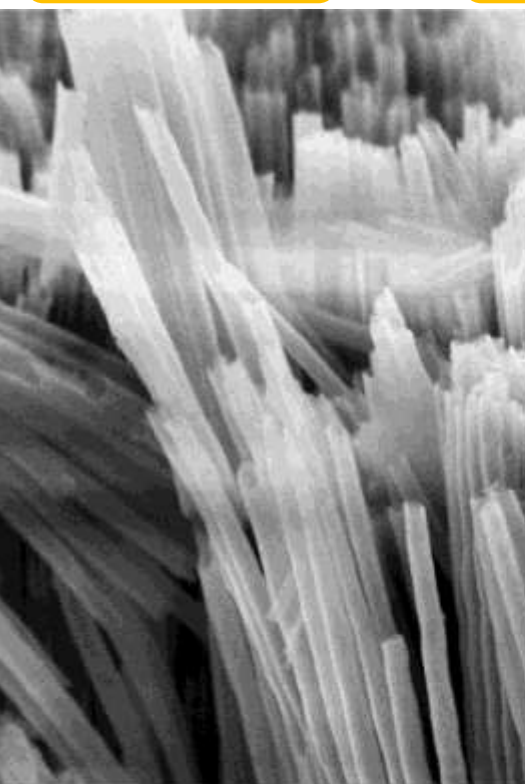
30 min



1 hrs.



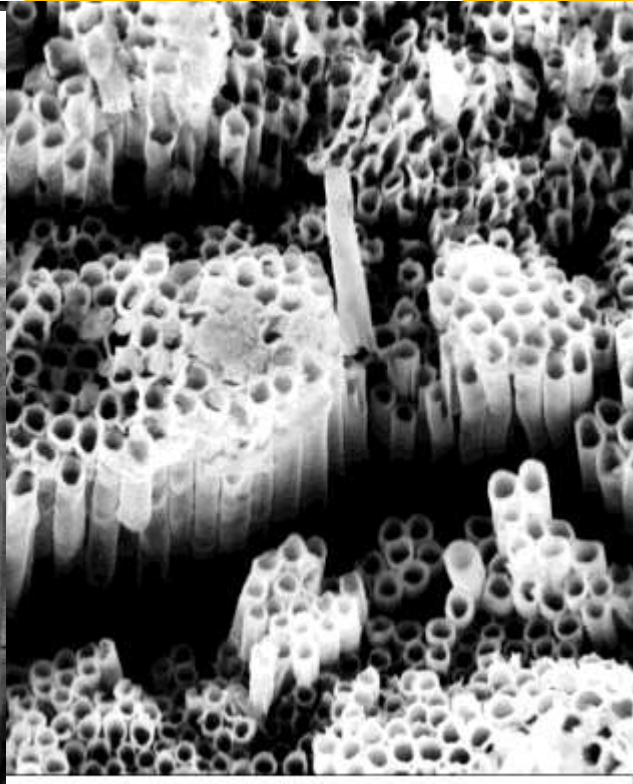
2 hrs.



1 μ m
EHT = 6.00 kV
WD = 3.9 mm
Signal A = SE2
Mag = 12.75 K X

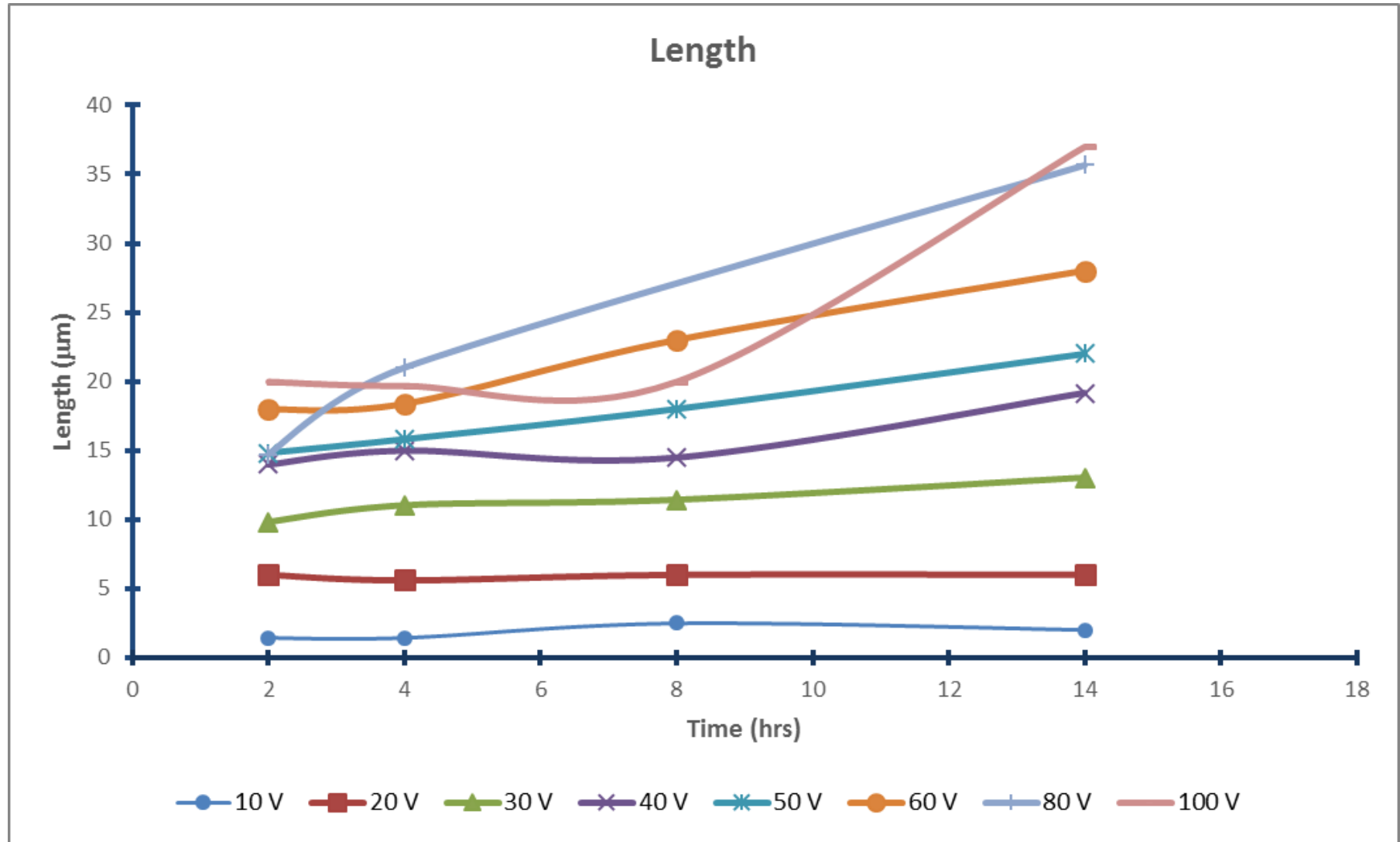


2 μ m
EHT = 6.00 kV
WD = 3.9 mm
Signal A = SE2
Mag = 12.75 K X
Date :17 Oct 2016
Time :21:22:31
AUC

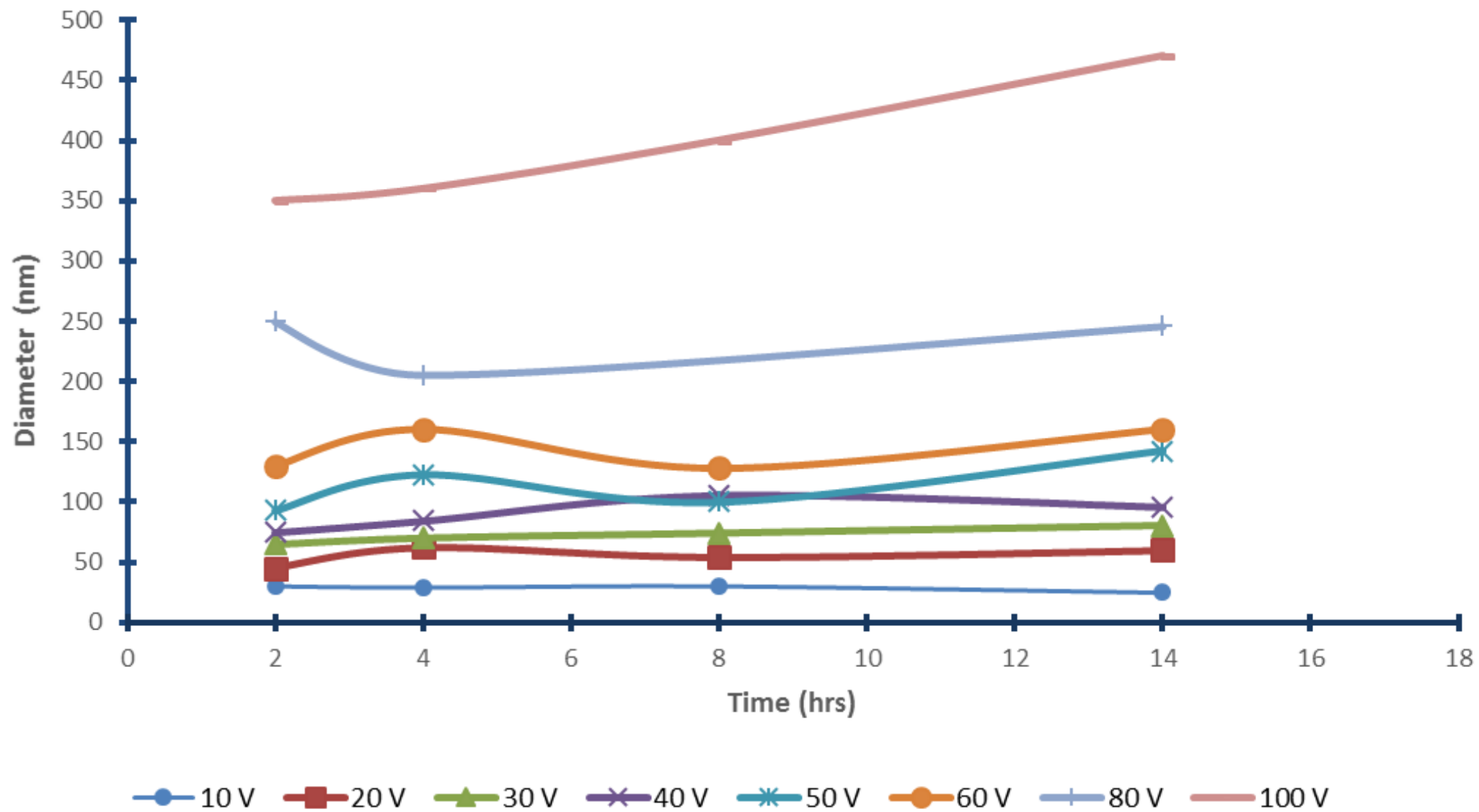


A = InLens
49.79 K X
Date :17 Oct 2016
Time :21:31:34
AUC

NTs Geometry Analysis

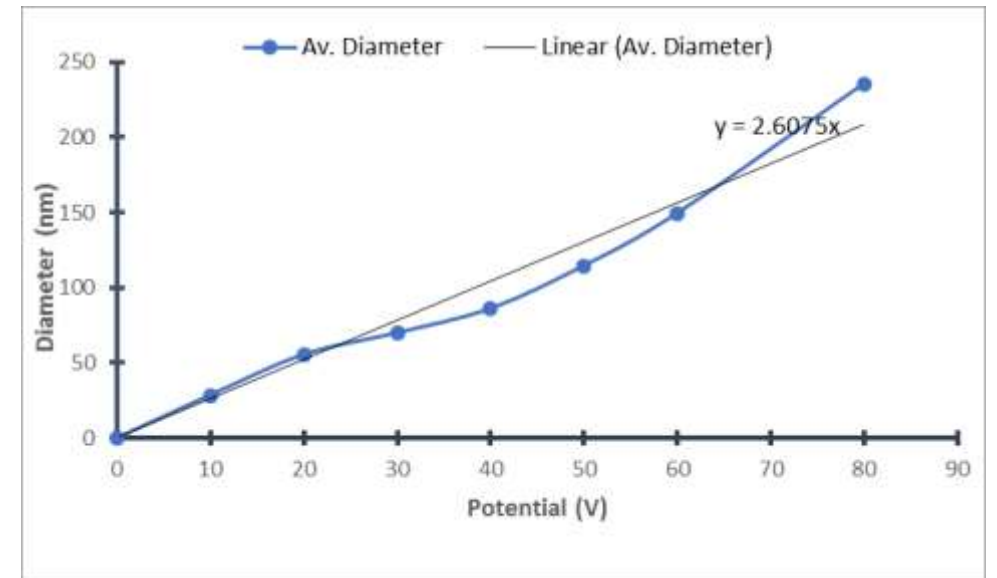
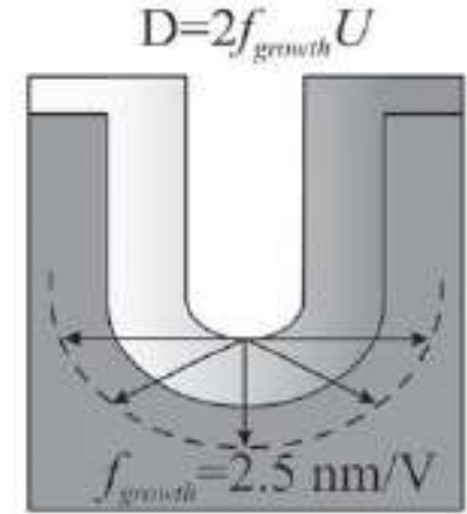


Diameter

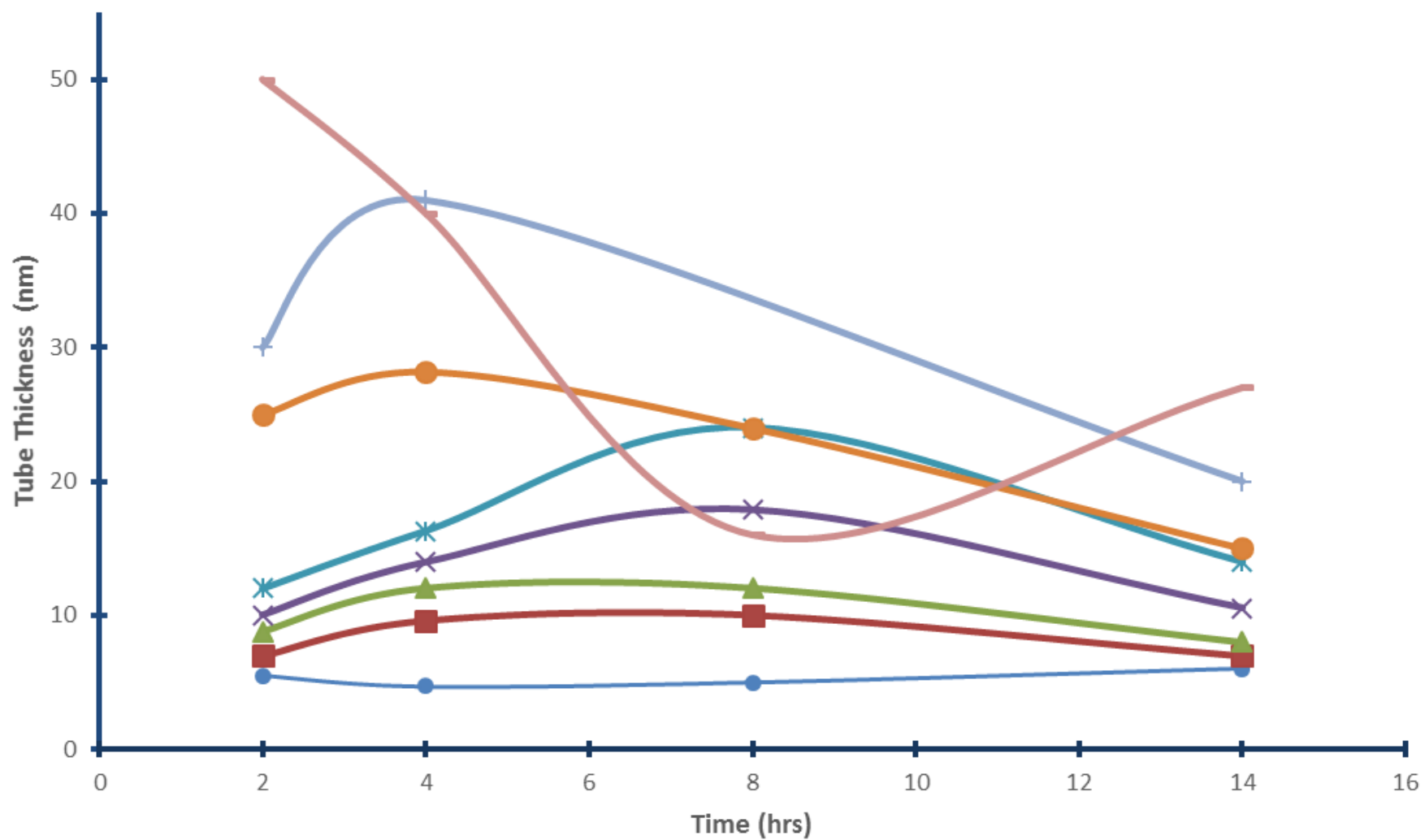


Anodic Growth Factor (f_g)

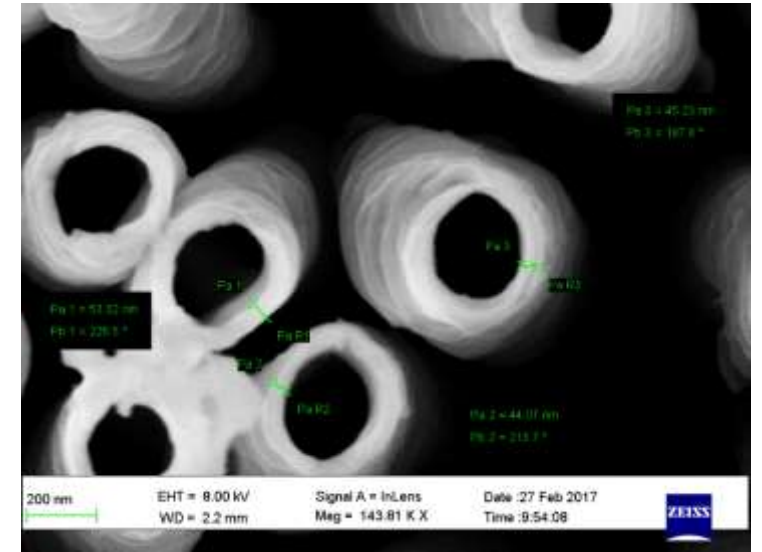
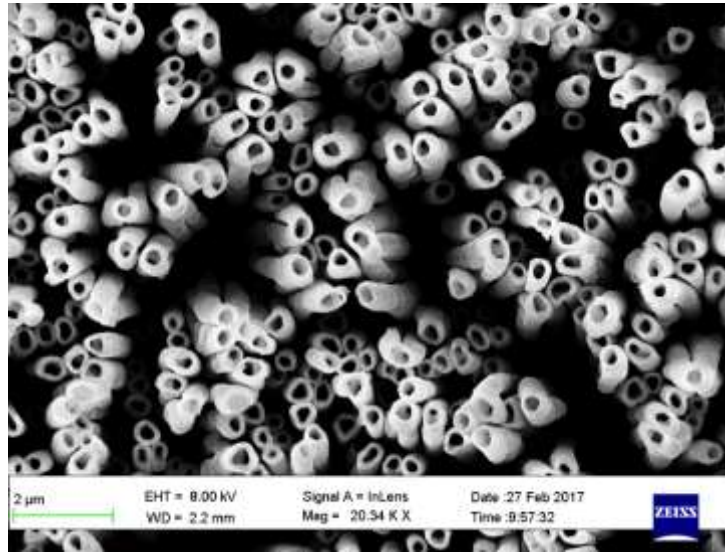
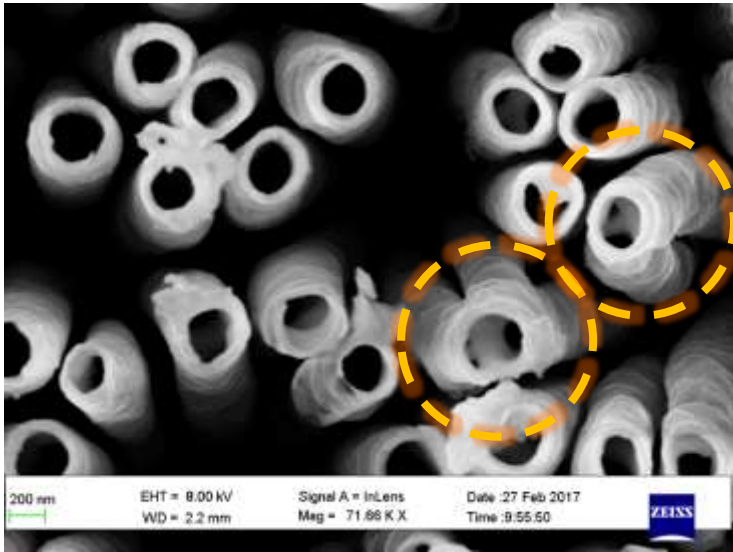
- Migration of ions expressed as the max. radius of the oxide per applied potential
- $D=2f_g V$
- $\therefore f_g)_{\text{Ti310}} = 2.6 \text{ nm/V}$
 - Compared to 2.5 nm/V for TiO_2



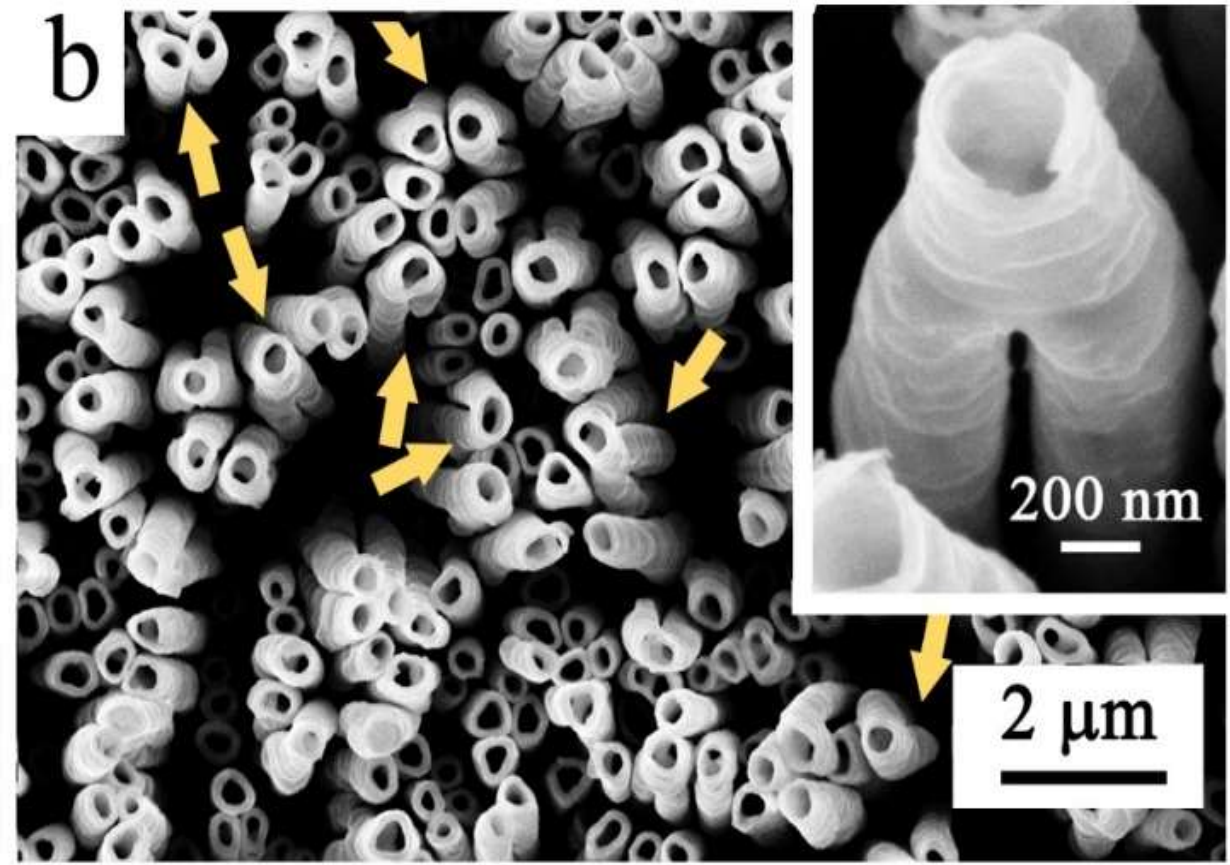
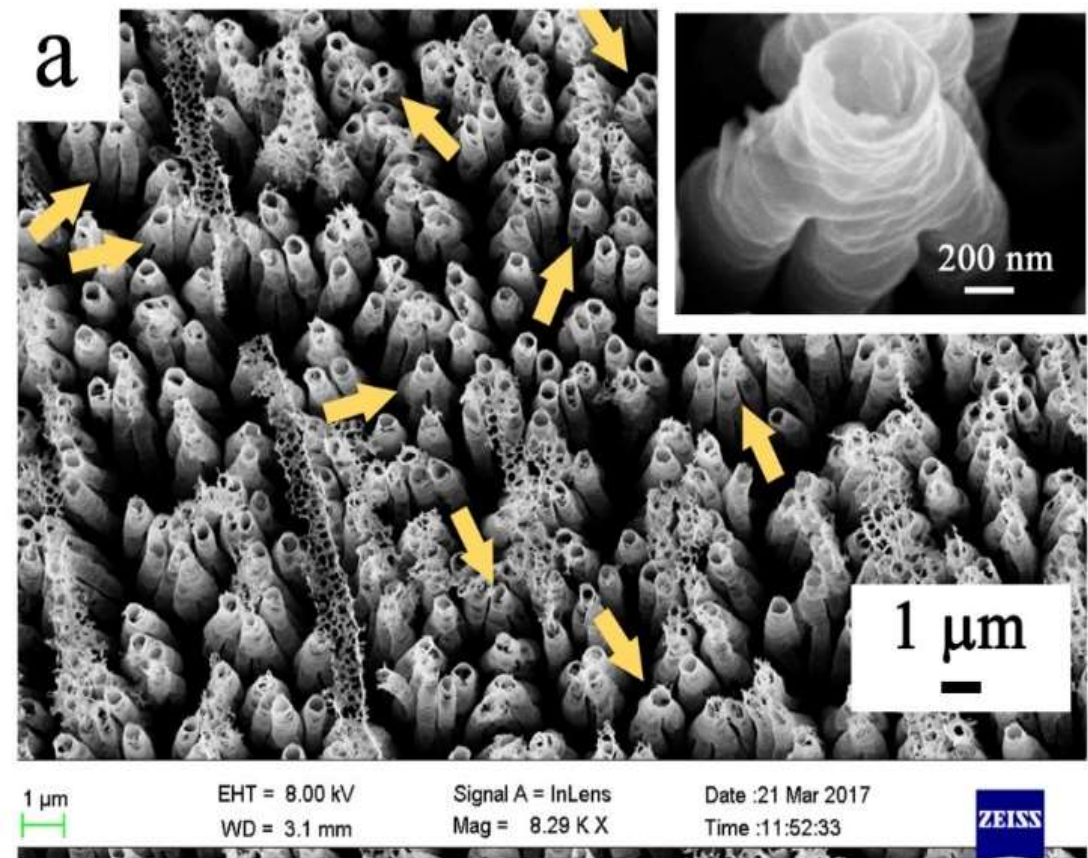
Thickness

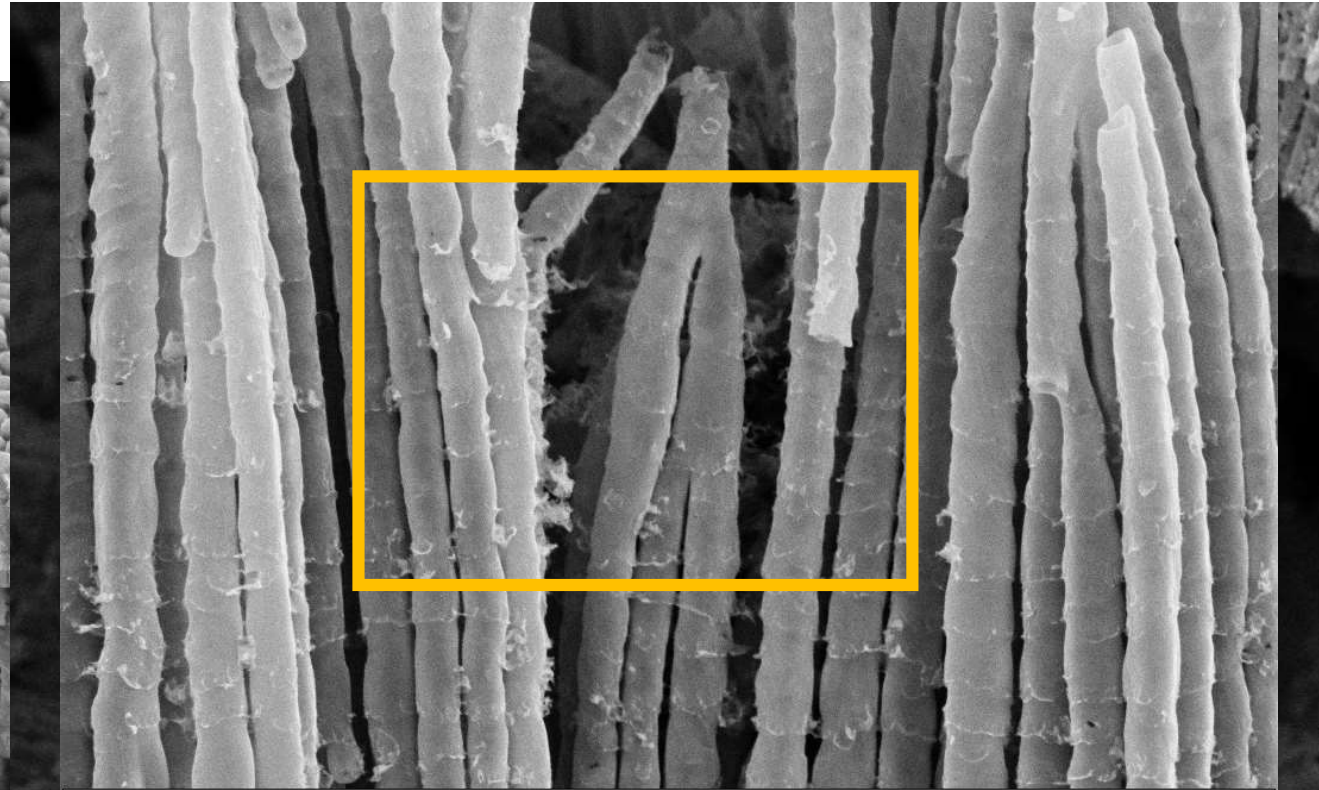


4. 2,3 tubes -1 pore!



Multipodal NTs Formation Mechanism





1 μ m

EHT = 8.00 kV
WD = 2.9 mm

Signal A = InLens
Mag = 19.46 K X

Date :7 Aug 2017
Time :9:31:19



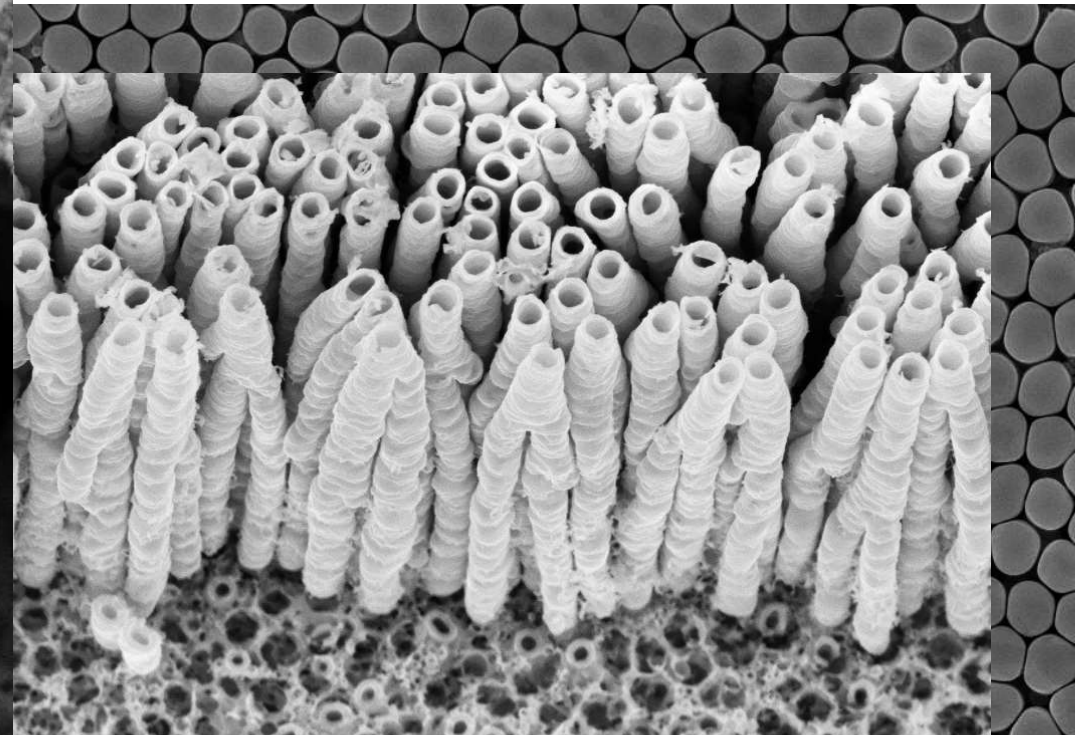
2 μ m

2 μ m

WD = 2.9 mm

Mag = 6.40 K X

Time :9:29:25



EHT = 8.00 kV
WD = 5.1 mm

Signal A = InLens
Mag = 18.34 K X

Date :7 Aug 2017
Time :9:55:59



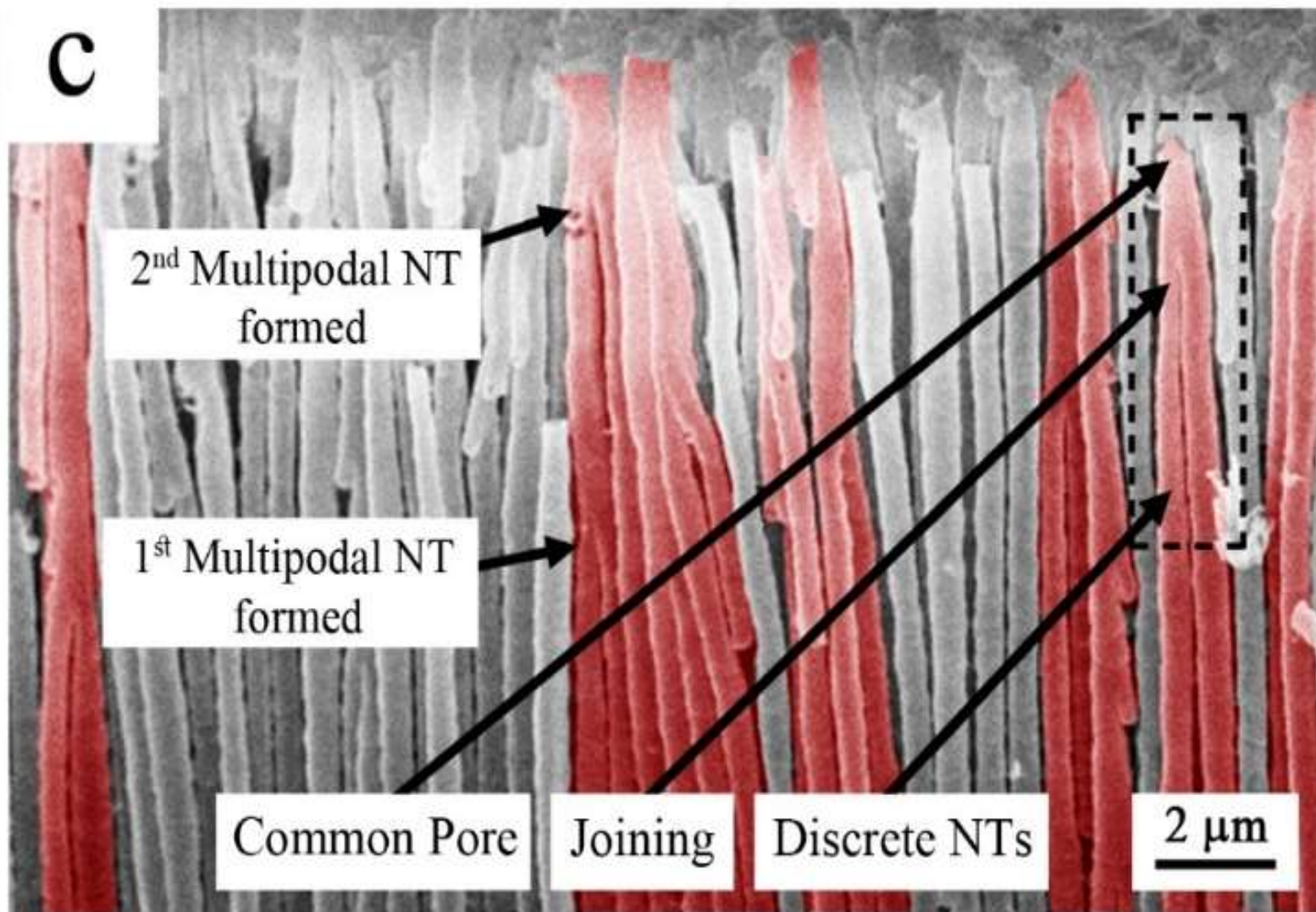
WD = 3.3 mm

Mag = 19.72 K X

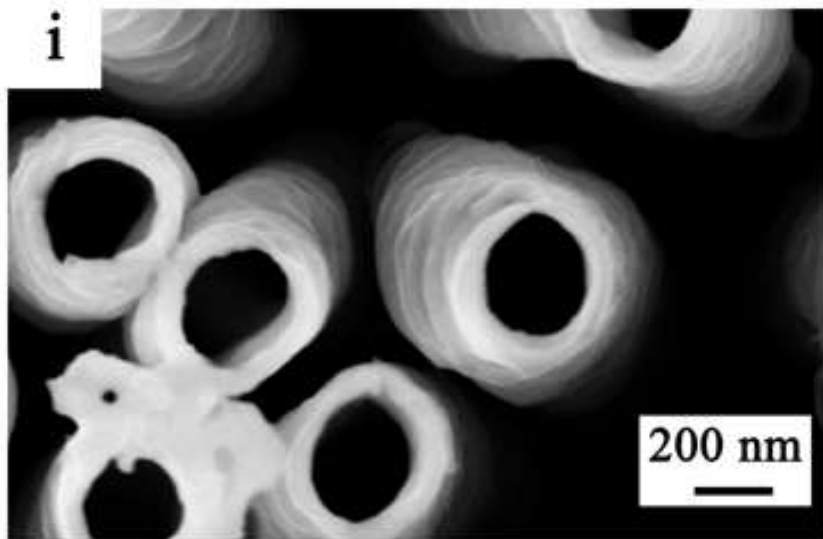
Time :10:20:14



C

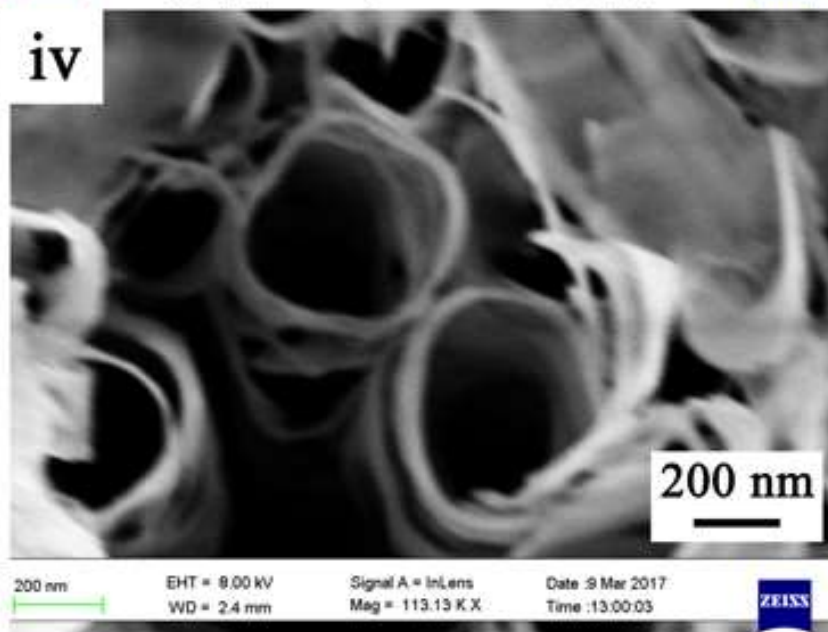
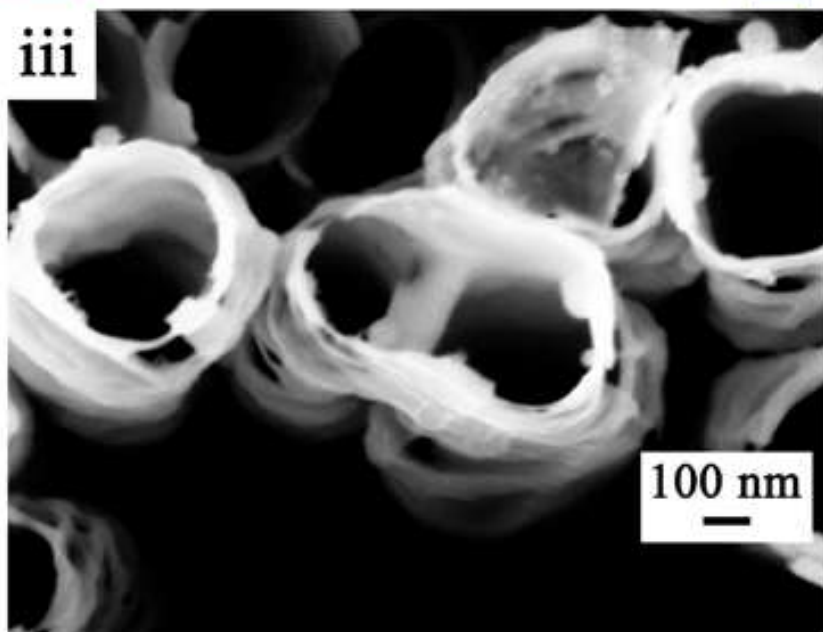


2 hrs



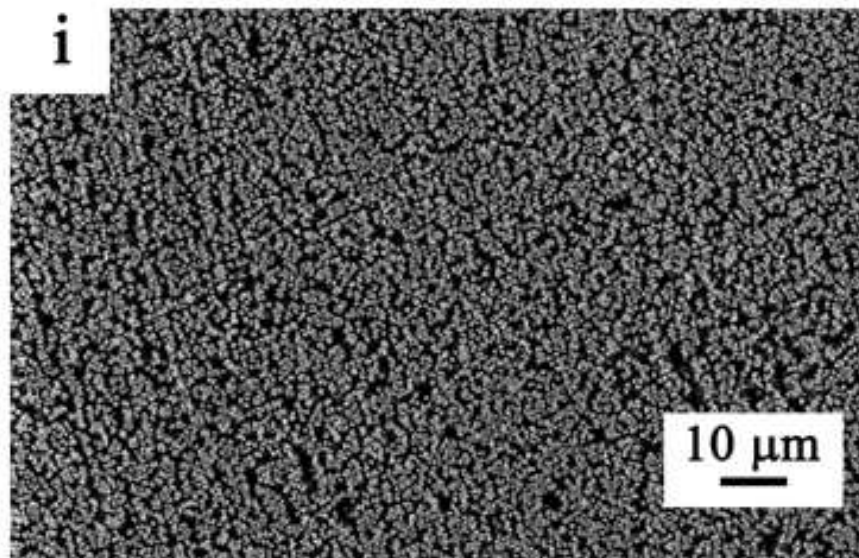
4 hrs

8 hrs

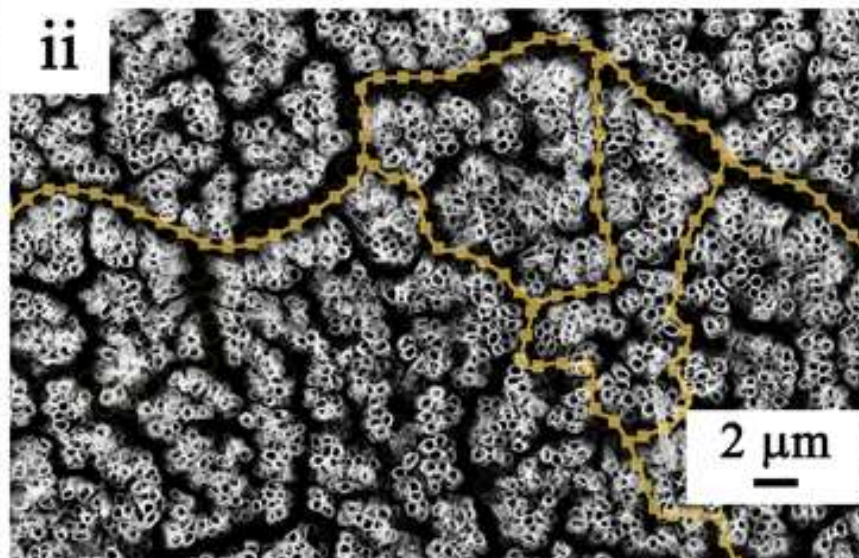


14 hrs

2 hrs



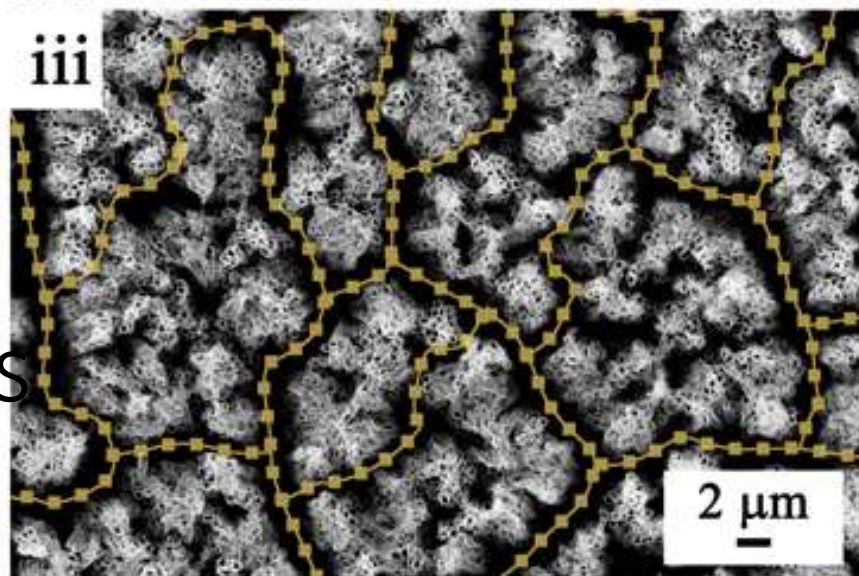
10 μm EHT = 8.00 kV Signal A = InLens Date :27 Feb 2017
WD = 2.2 mm Mag = 2.34 K X Time :9:52:27 ZEISS



2 μm EHT = 8.00 kV Signal A = InLens Date :16 Mar 2017
WD = 2.3 mm Mag = 5.79 K X Time :8:42:34 ZEISS

4 hrs

8 hrs



2 μm EHT = 8.00 kV Signal A = InLens Date :9 Mar 2017
WD = 2.4 mm Mag = 4.41 K X Time :12:58:29 ZEISS

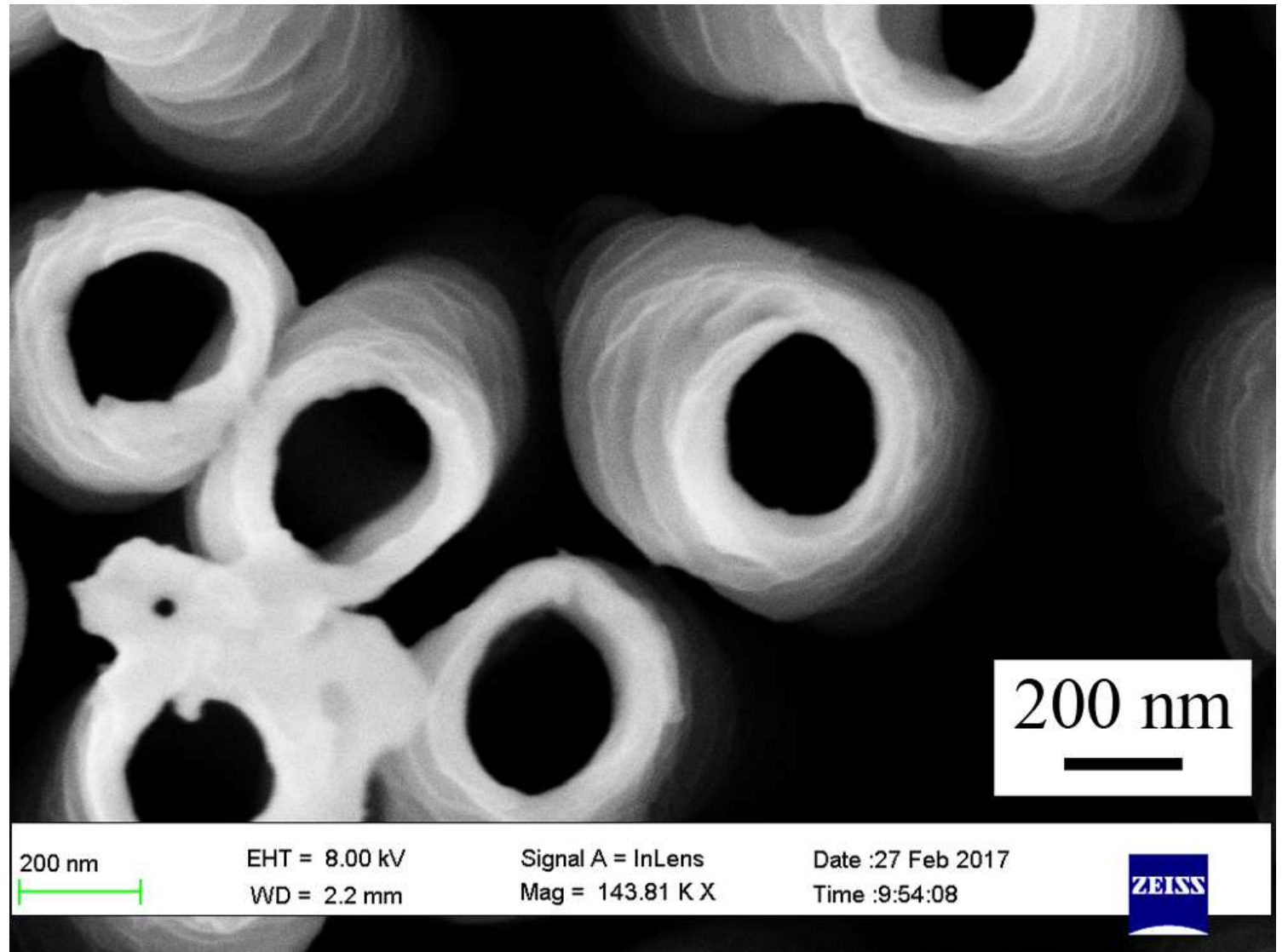
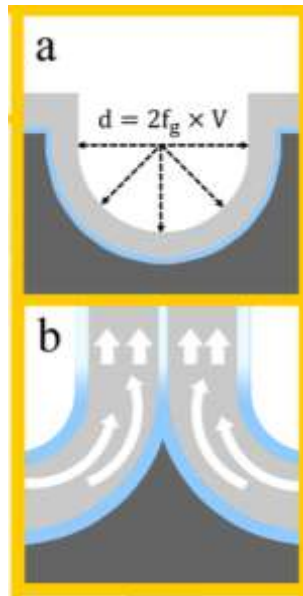


1 μm EHT = 10.00 kV Signal A = InLens Date :3 Apr 2017
WD = 2.8 mm Mag = 25.40 K X Time :11:03:06 ZEISS

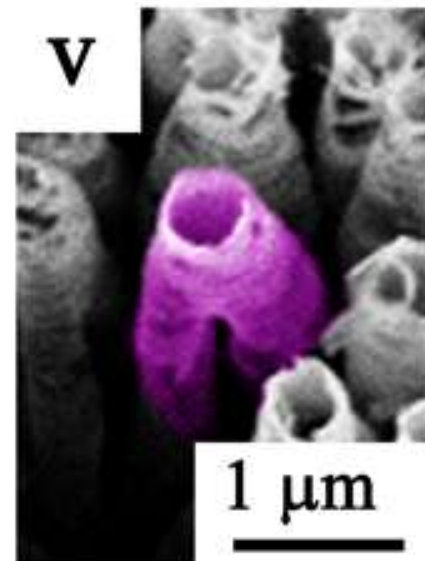
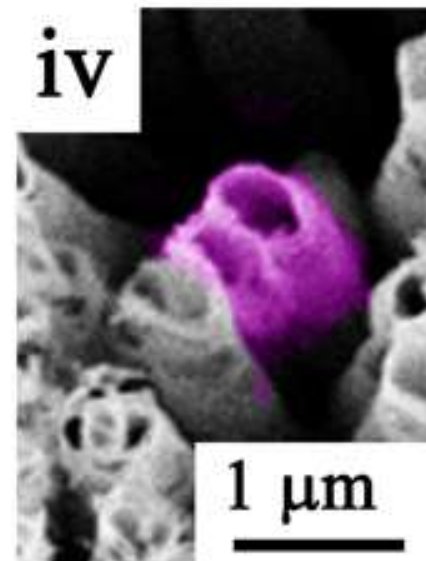
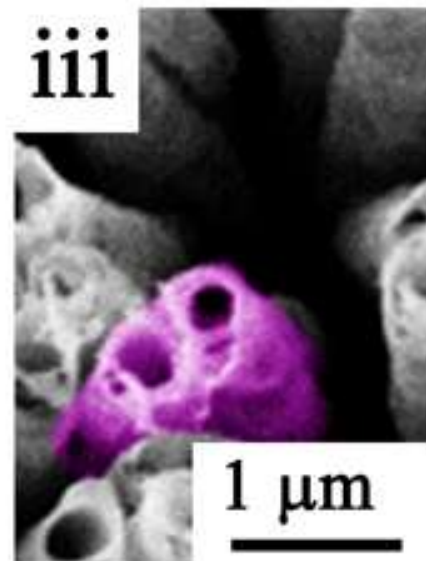
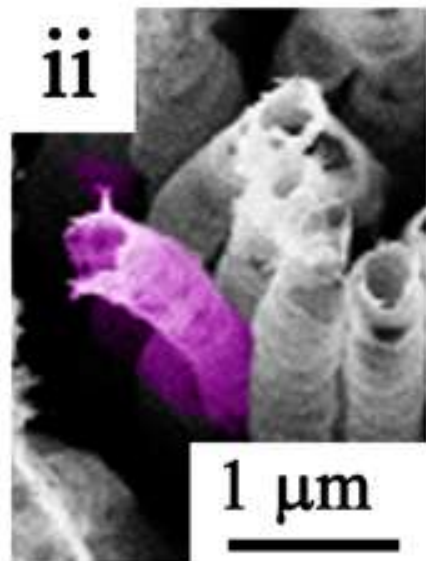
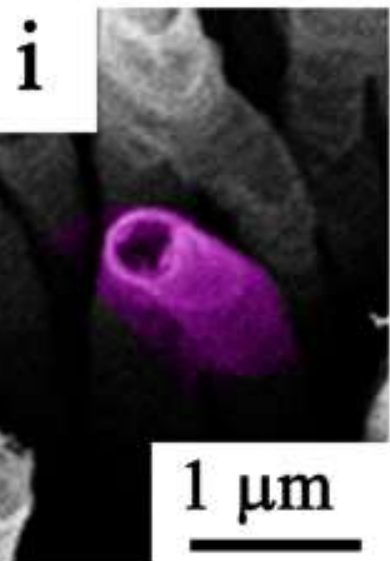
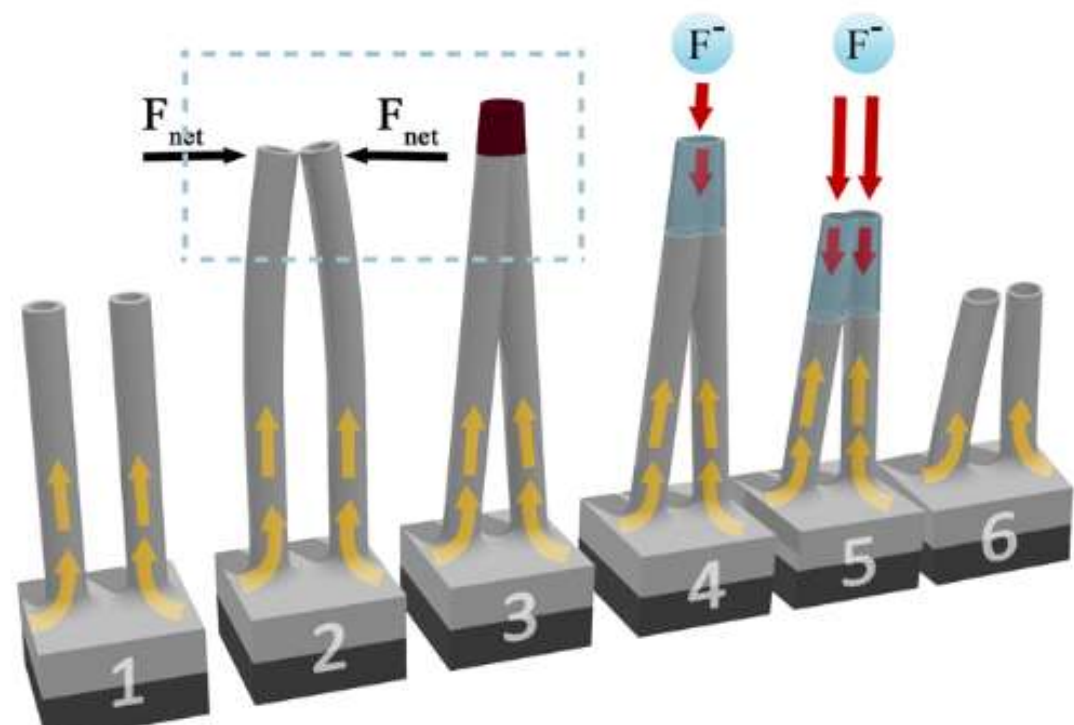
Taper Shape

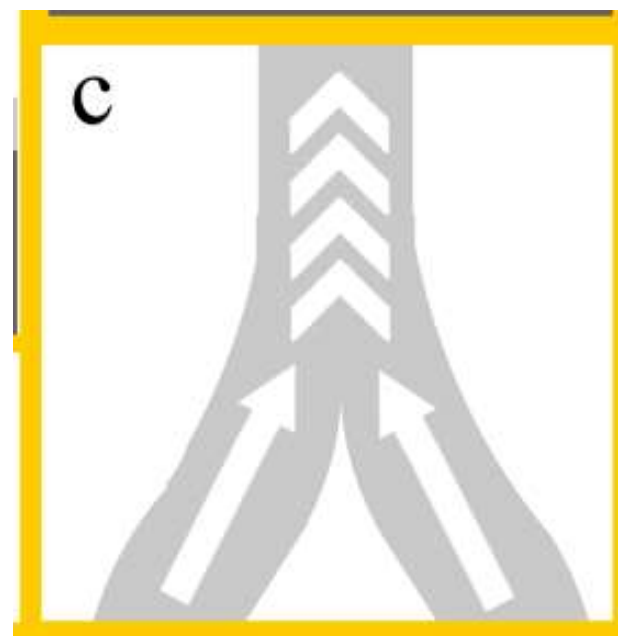
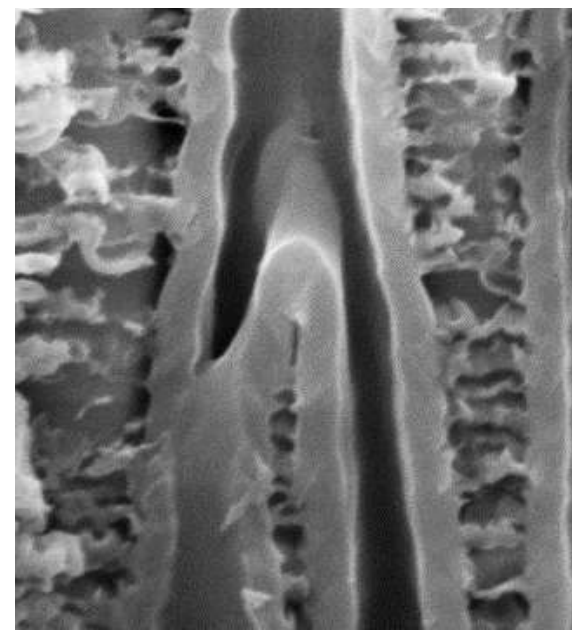
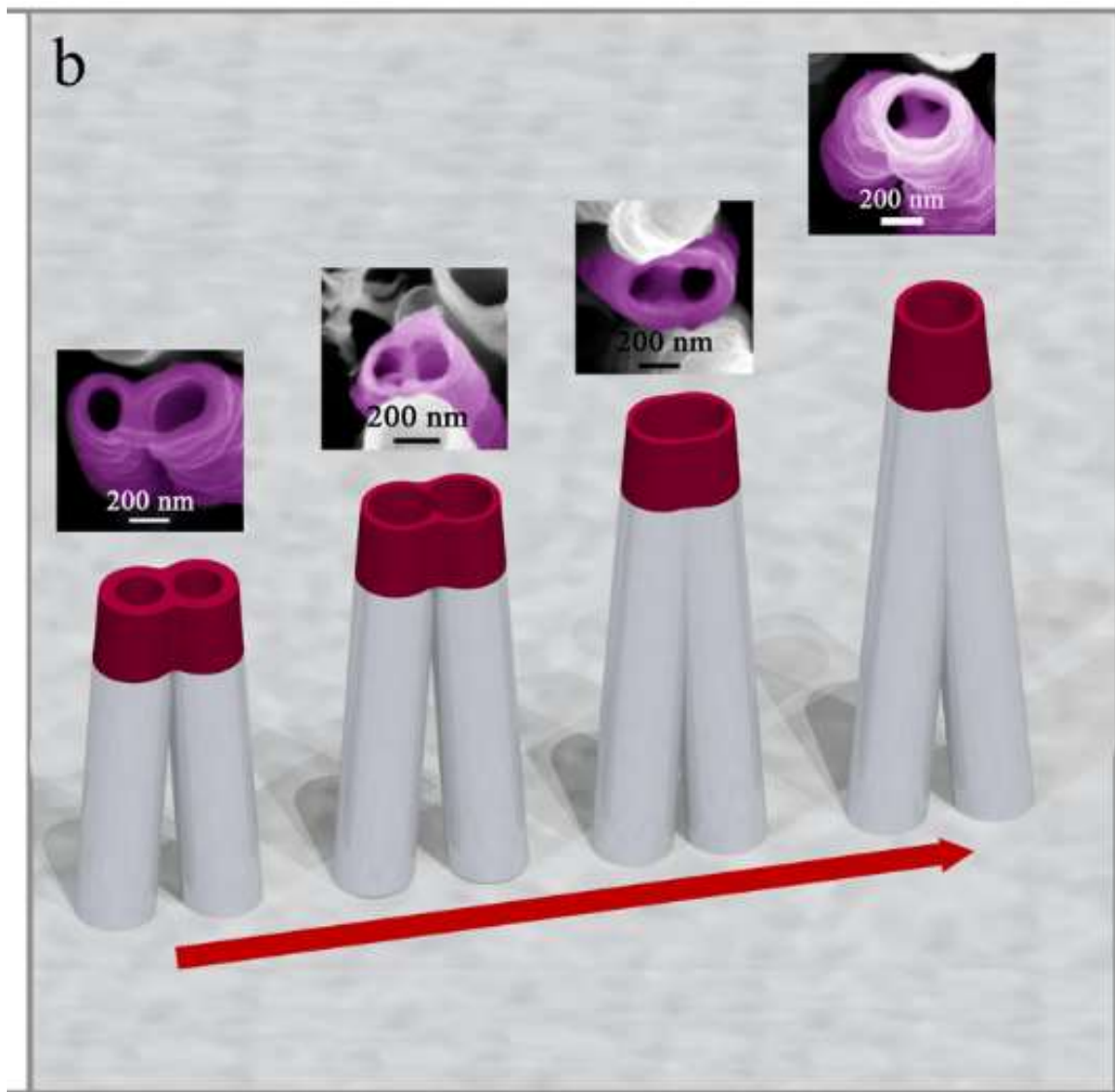
$$d = 2f_g \times V$$

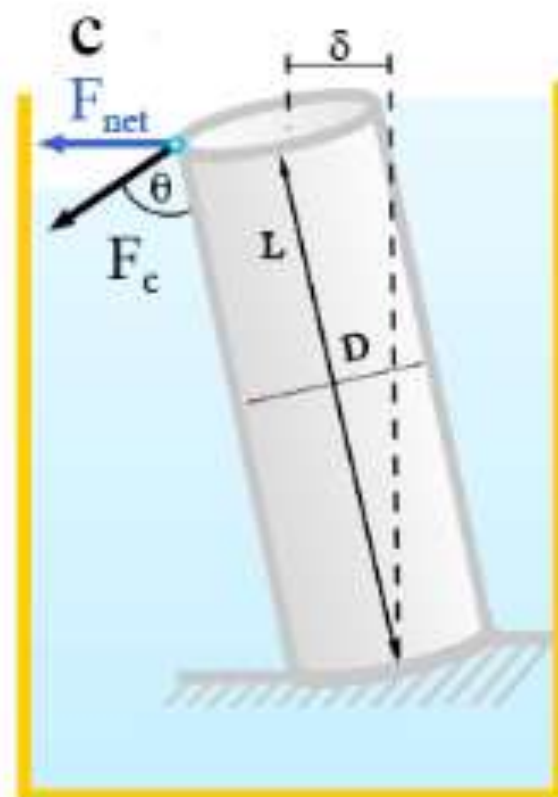
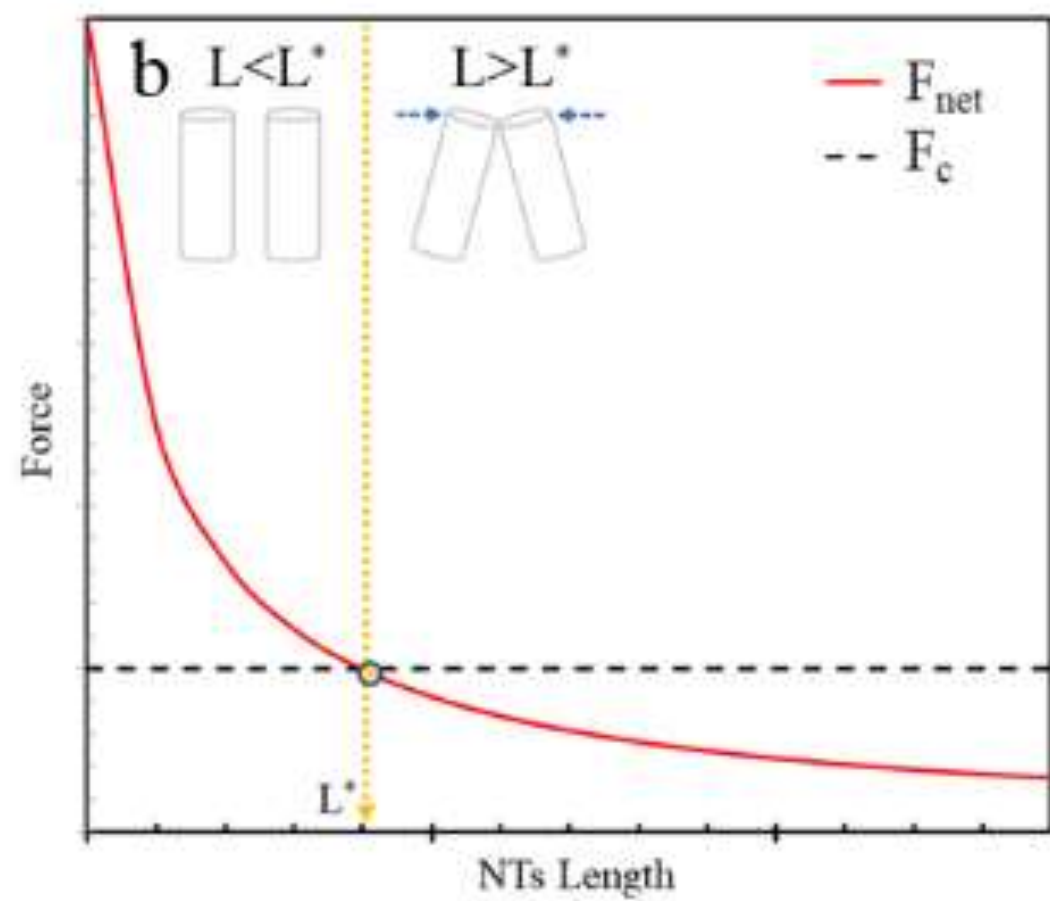
$$E = \frac{(V_{\text{applied}} - IR_{\Omega})}{d}$$



a





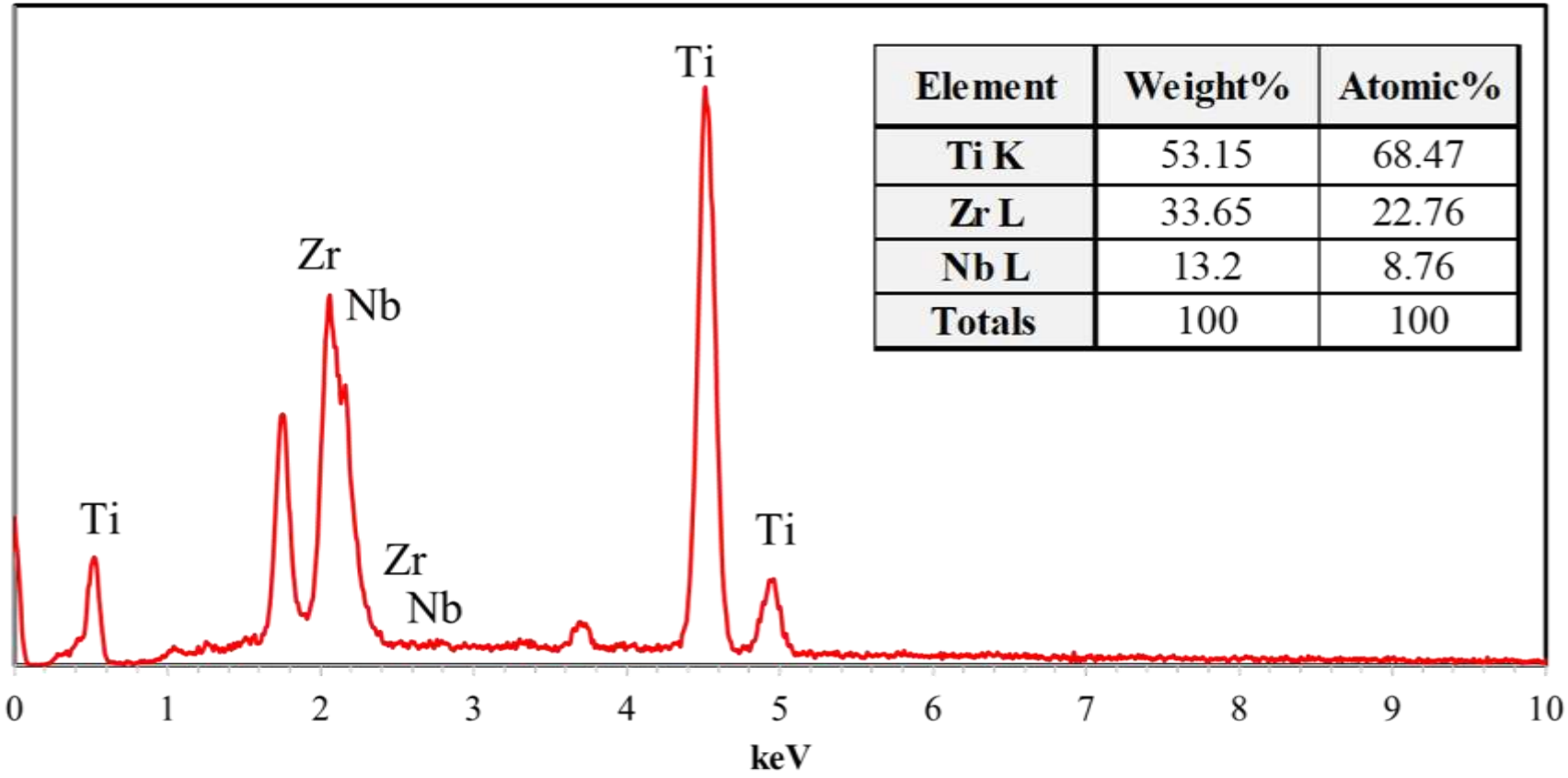


III. Characterization

Material Characterization

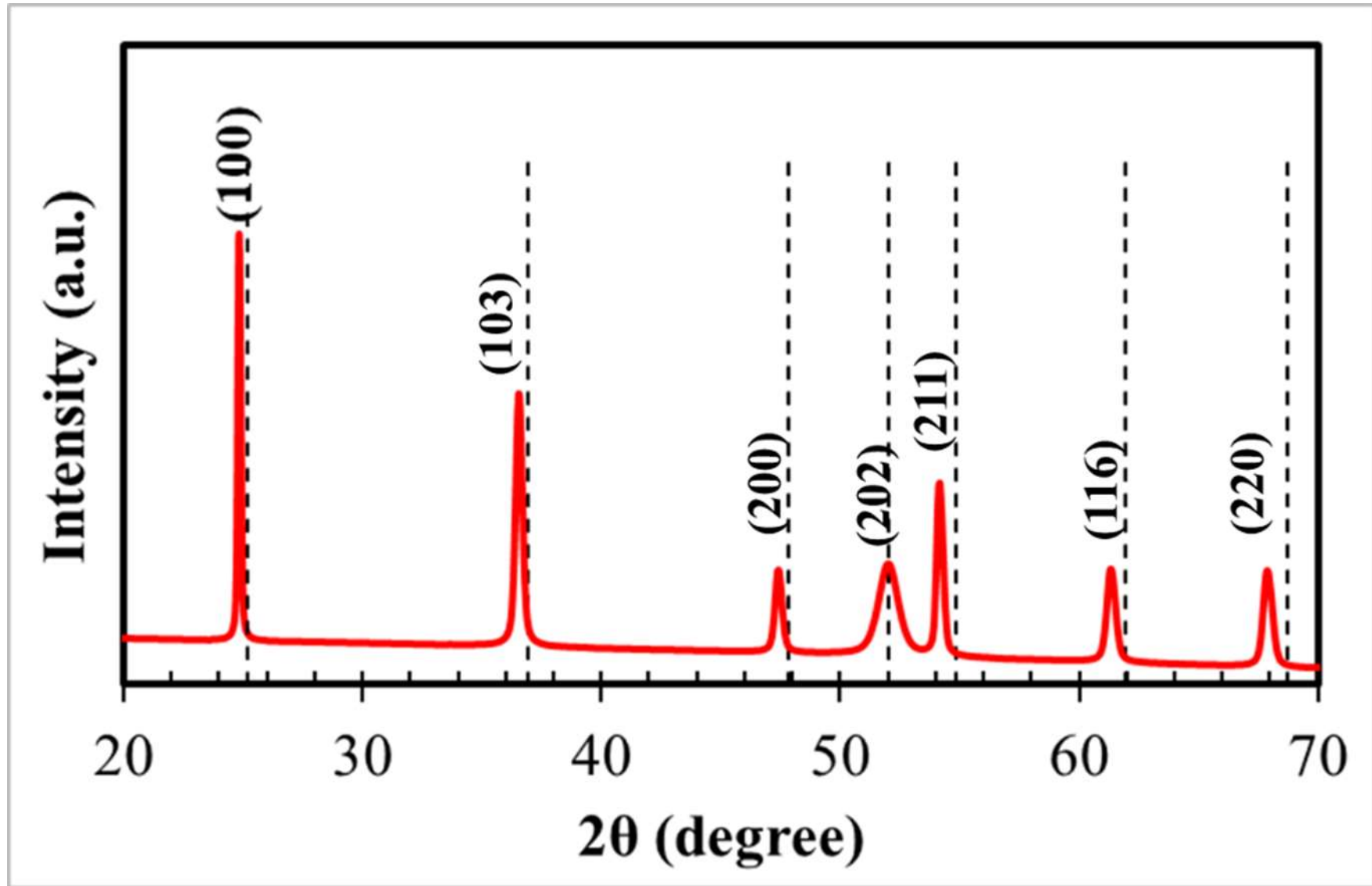
- Structural
- Optical
- PEC

EDX



EDX spectra of the metal alloy before anodization

XRD

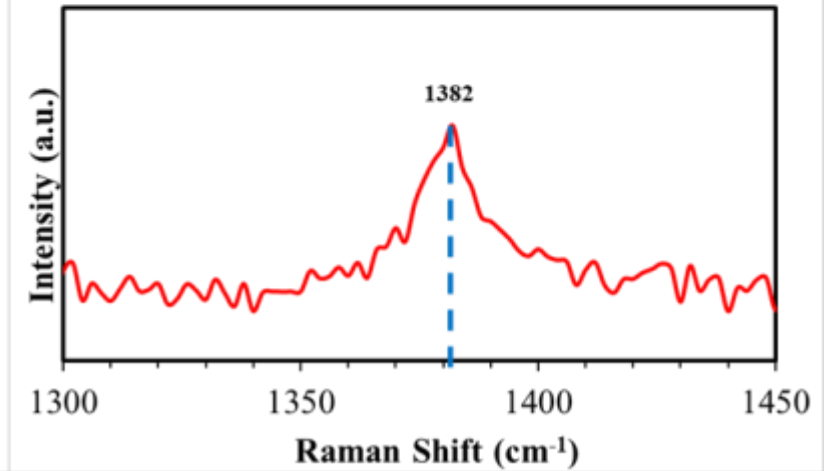
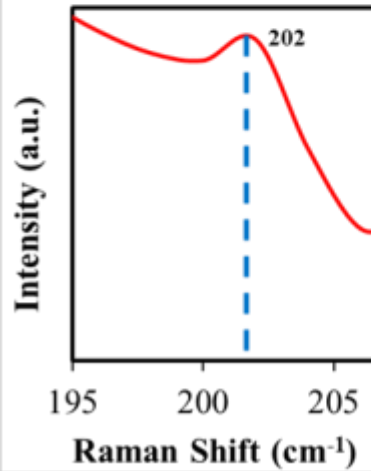
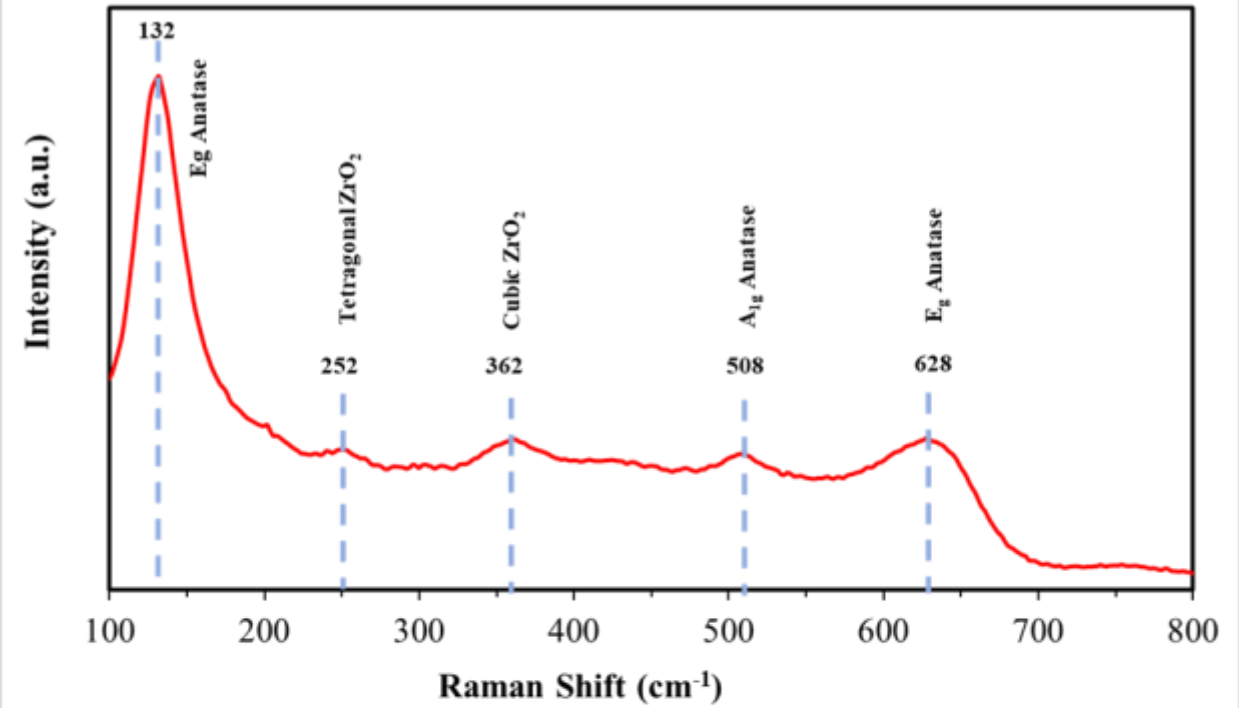


XRD diffraction patterns of the air-annealed sample. (Vertical lines indicated the positions of the nominal anatase peaks (Ref. code: 01-075-2545))

XRD

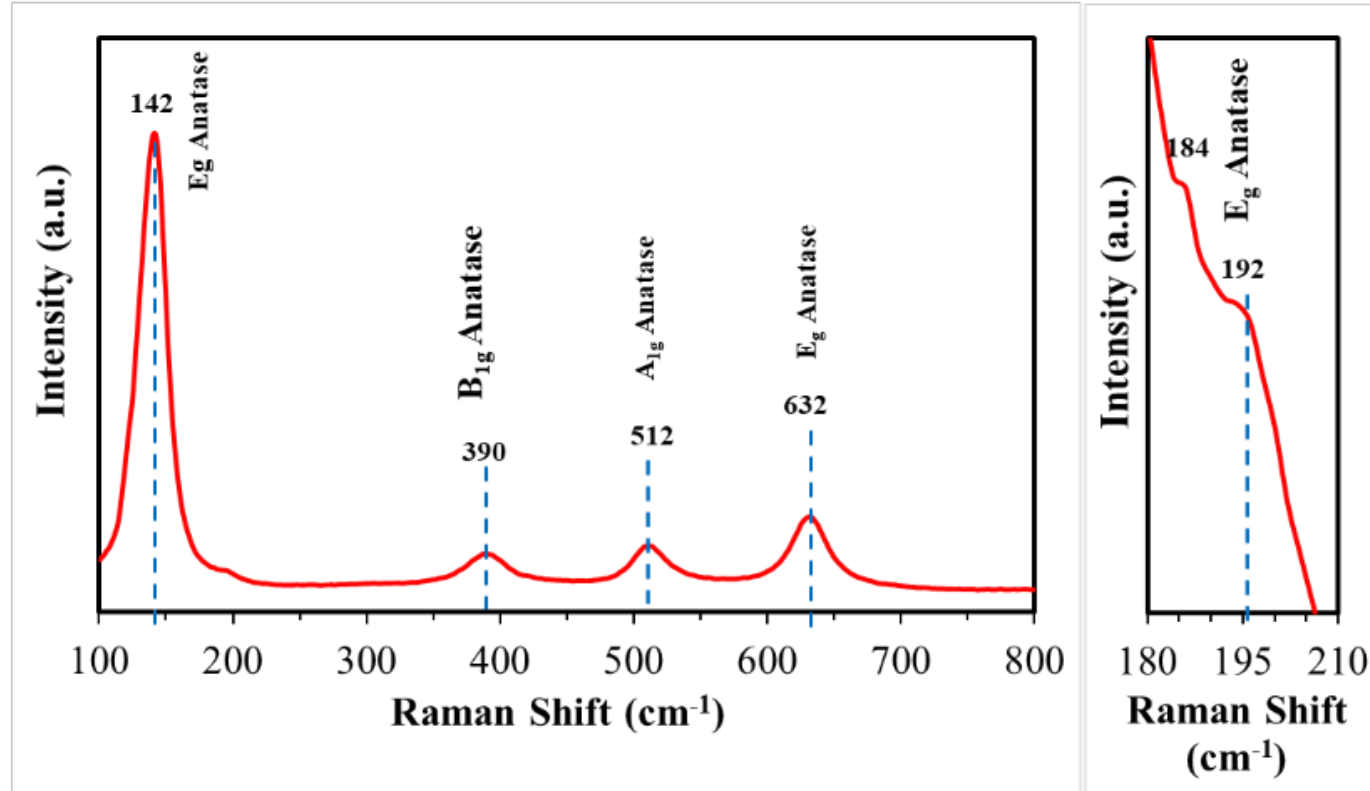
(2θ) Air Annealed	(2θ) Std Anatase Peaks	Shift
24.84°	25.22°	-0.38°
36.53°	36.9°	-0.37°
47.37°	47.85°	-0.48°
51.96°	52.05°	-0.09°
54.12°	54.85°	-0.73°
61.28°	61.92°	-0.64°
67.82°	68.71°	-0.89°

Raman Spectroscopy



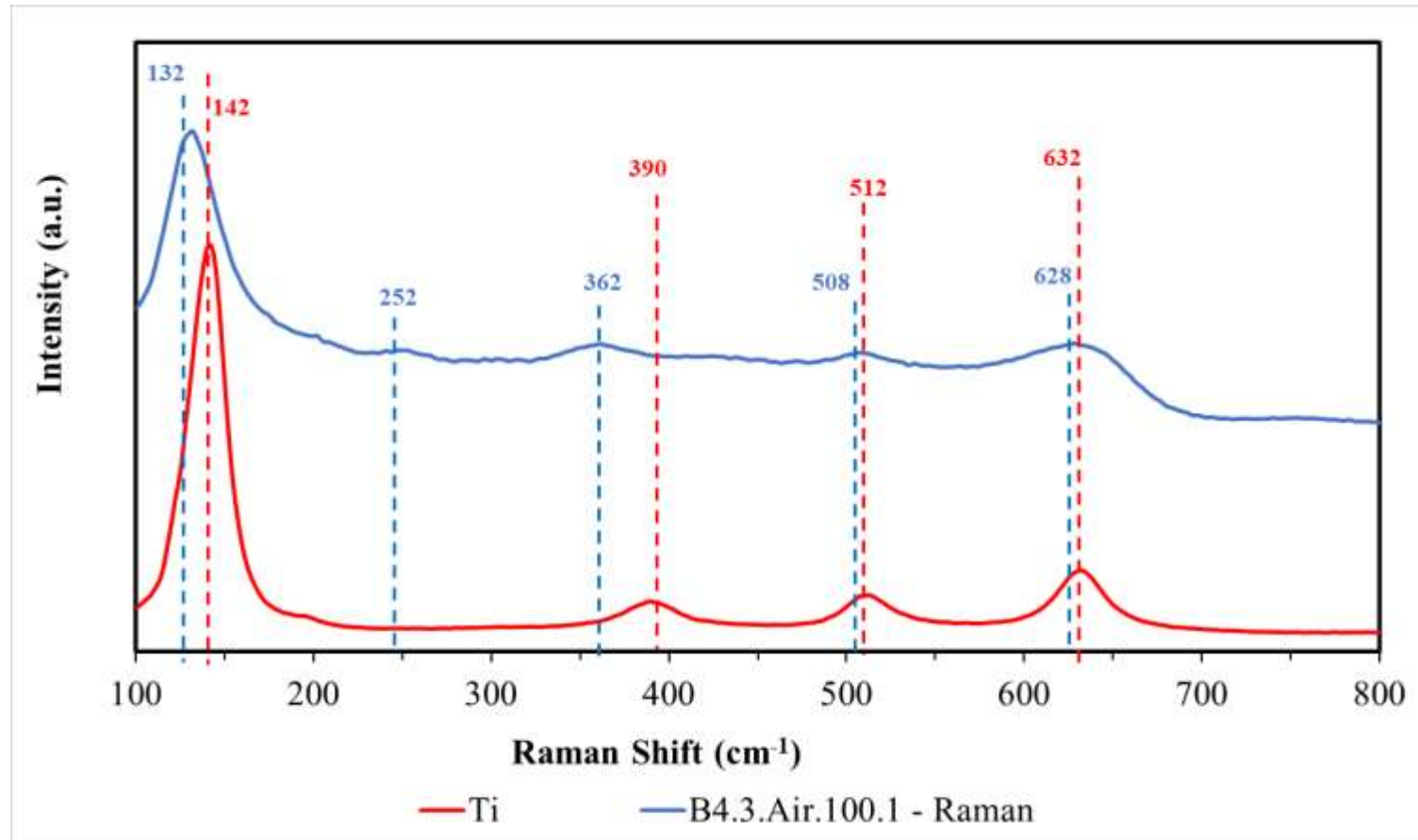
Raman spectra of a 4 hour annealed samples.

Raman Spectroscopy



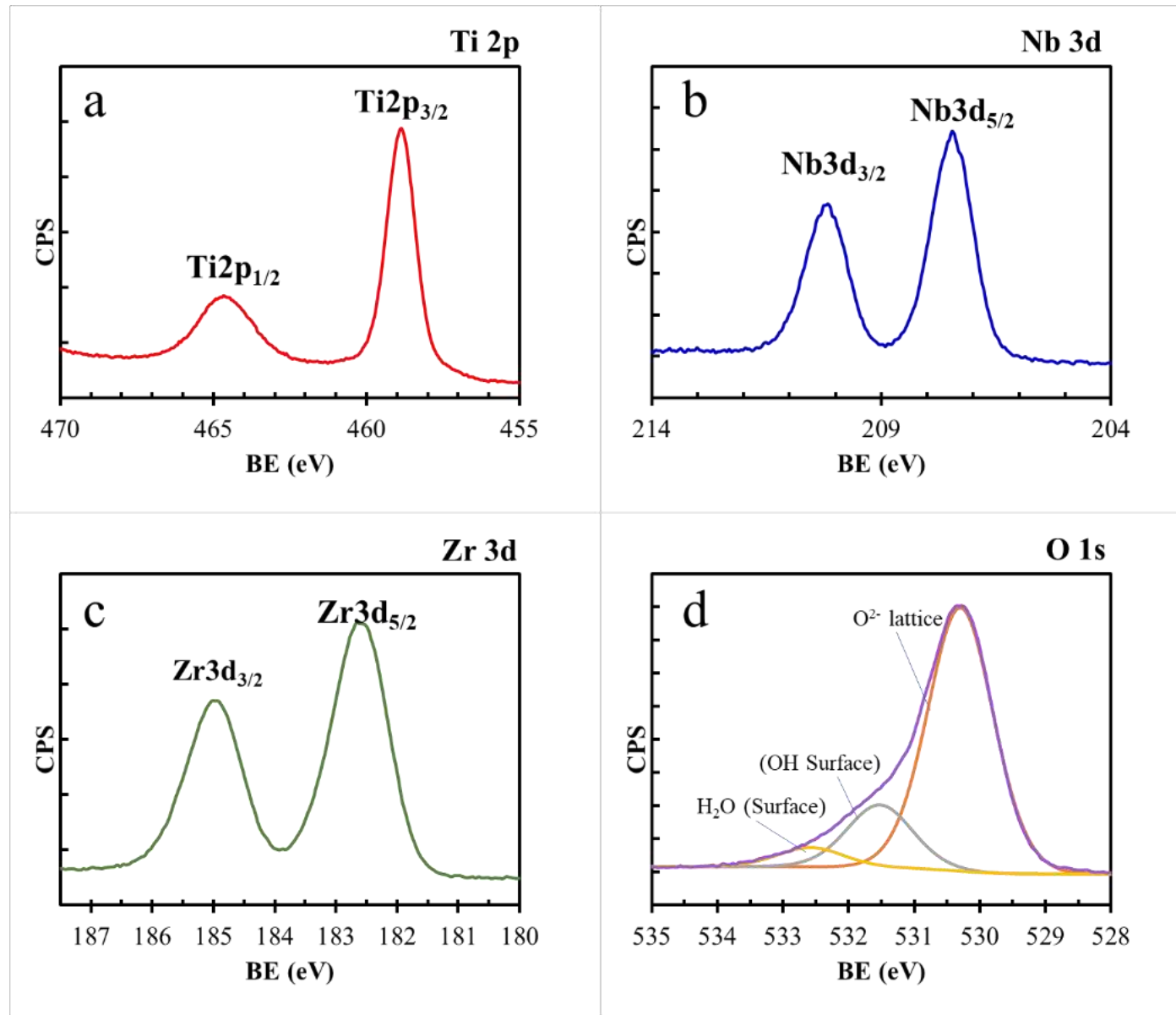
Pure Ti annealed synthesized at the same conditions of the alloy.

Raman Spectroscopy



The Raman peaks of pure titanium and the air-annealed alloy showing the shift resulting from the alloying effect.

XPS

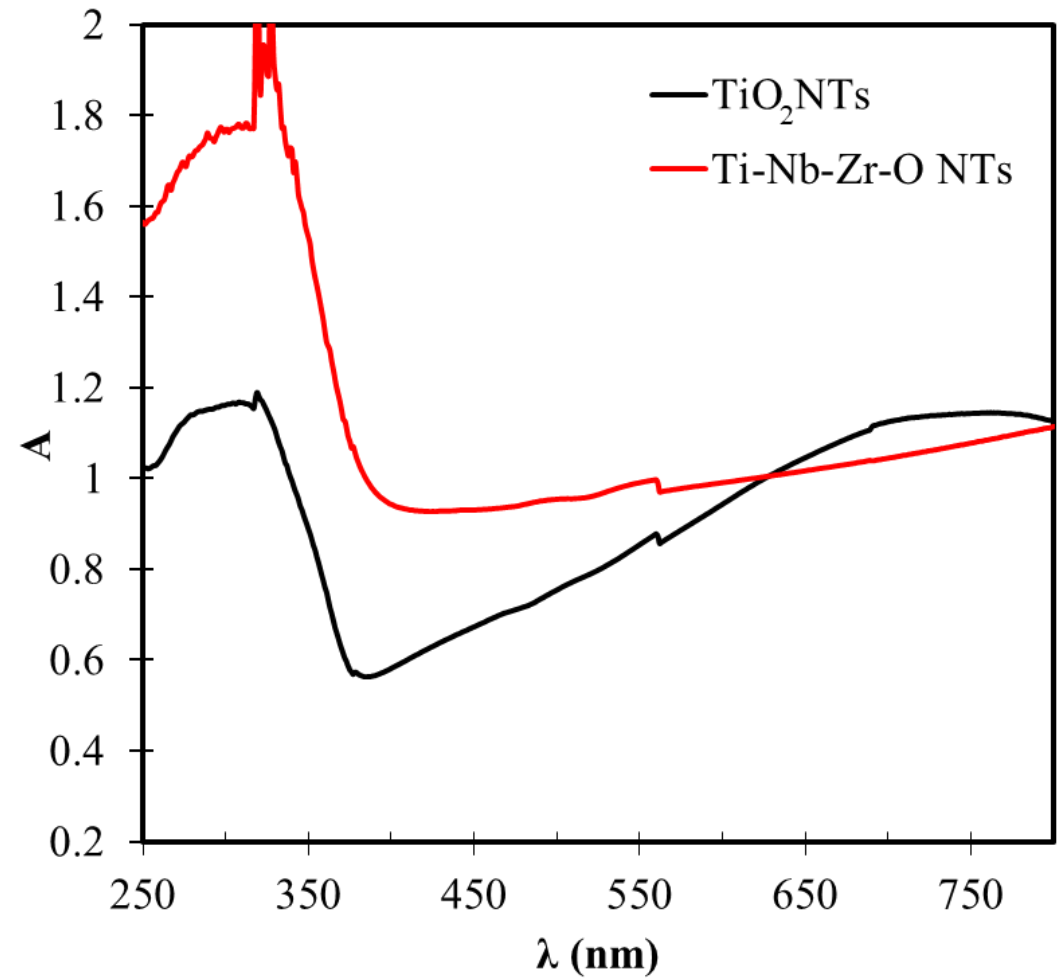


XPS spectra of (a) Ti, (b) Nb, (c) Zr, and (d) O.

Material Characterization

- Structural
- Optical
- PEC

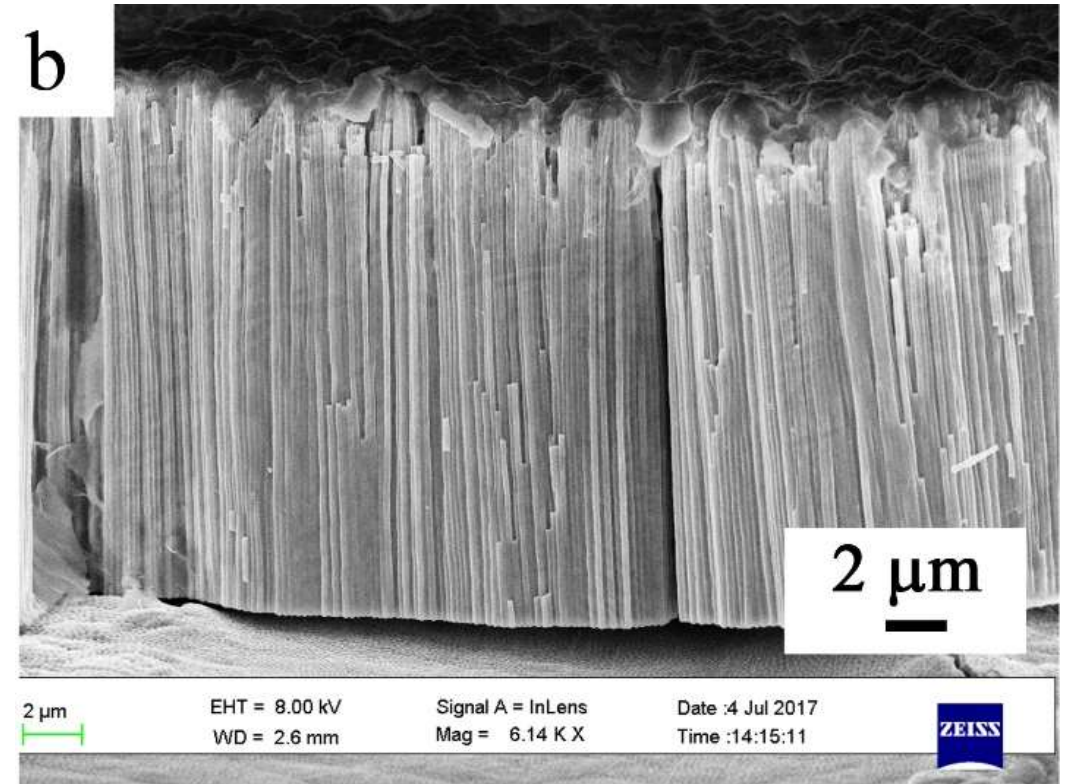
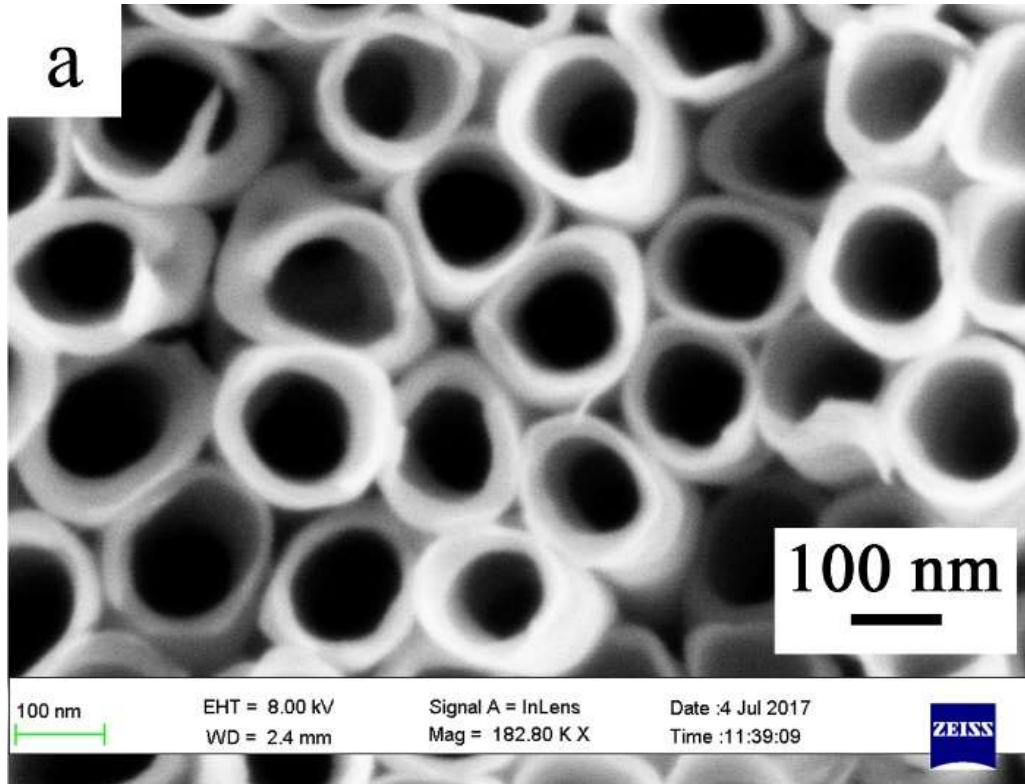
Absorbance



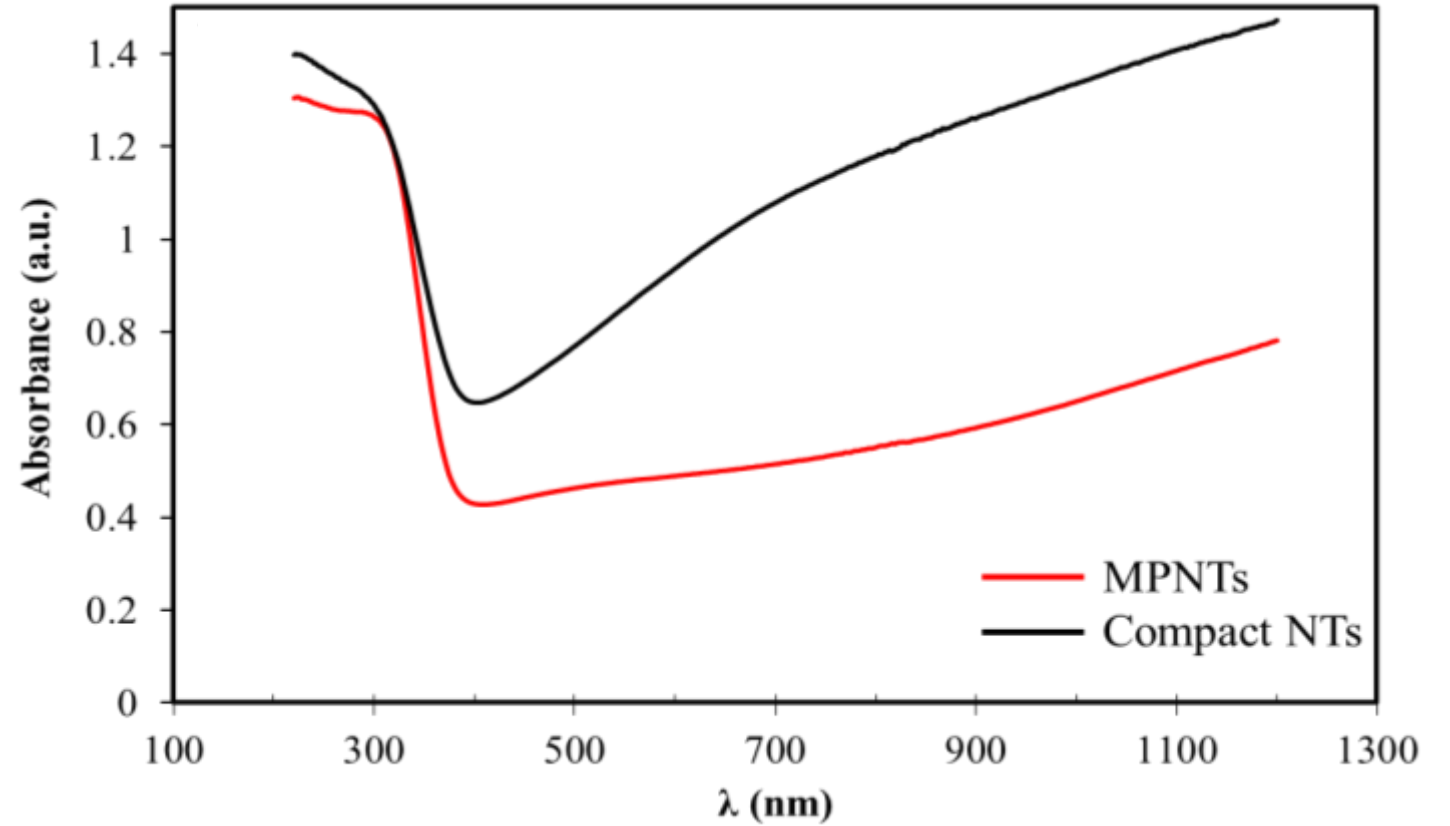
Absorbance of the TiO₂ compared to the formed oxide

Studying Multipodality Effect

Vs. Compact NTs



Absorbance

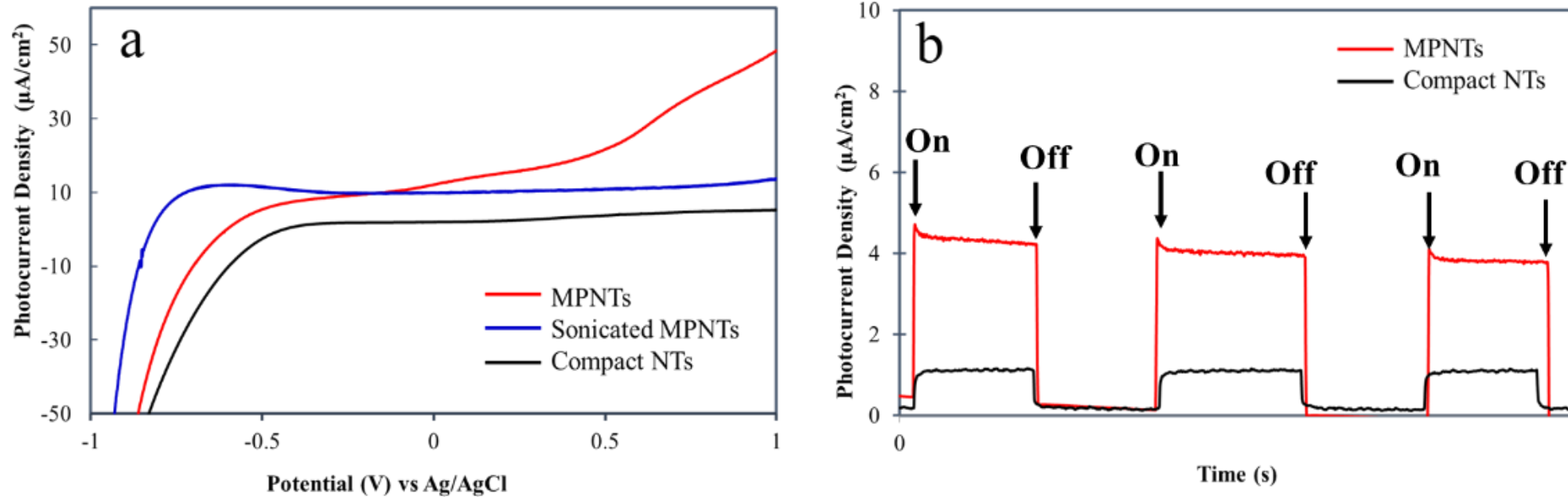


Absorbance spectra of MPNTs and compact NTs

Material Characterization

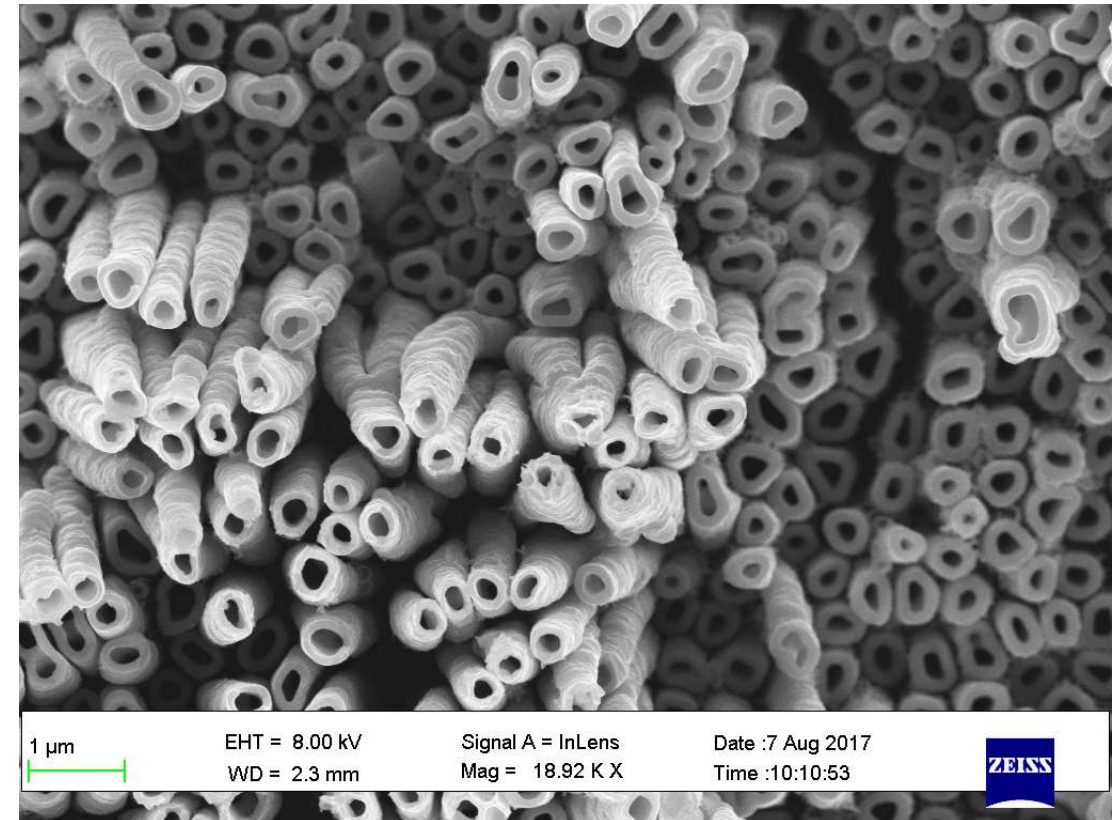
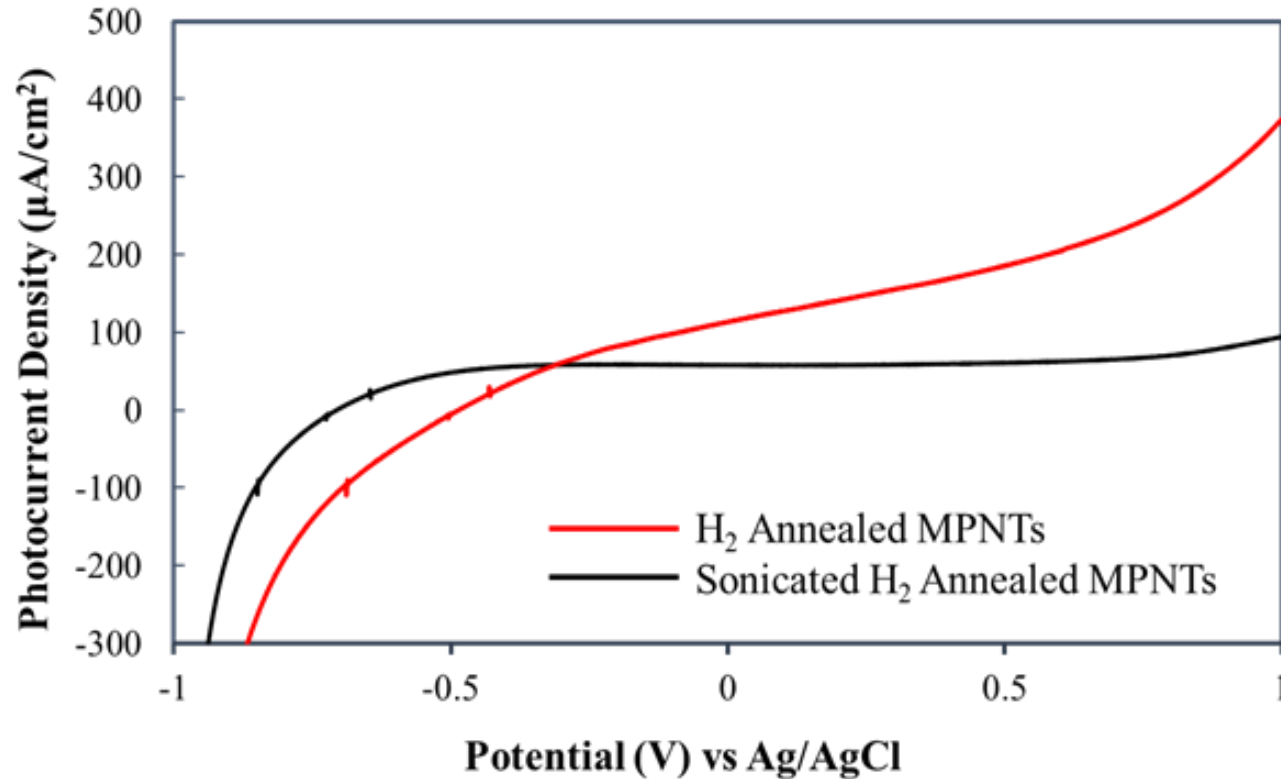
- Structural
- Optical
- PEC

Linear Sweep Voltammetry

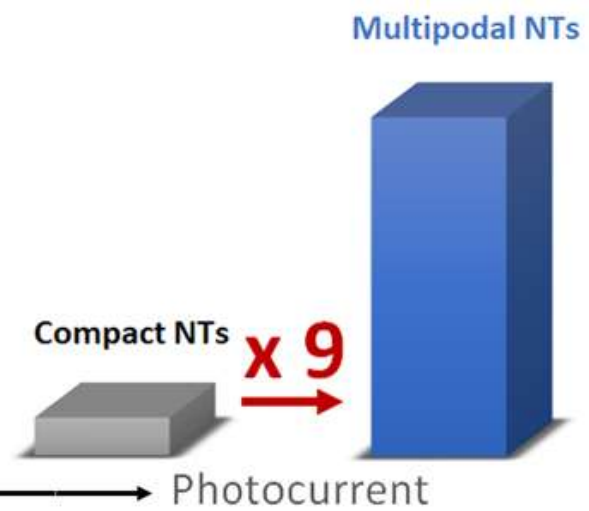
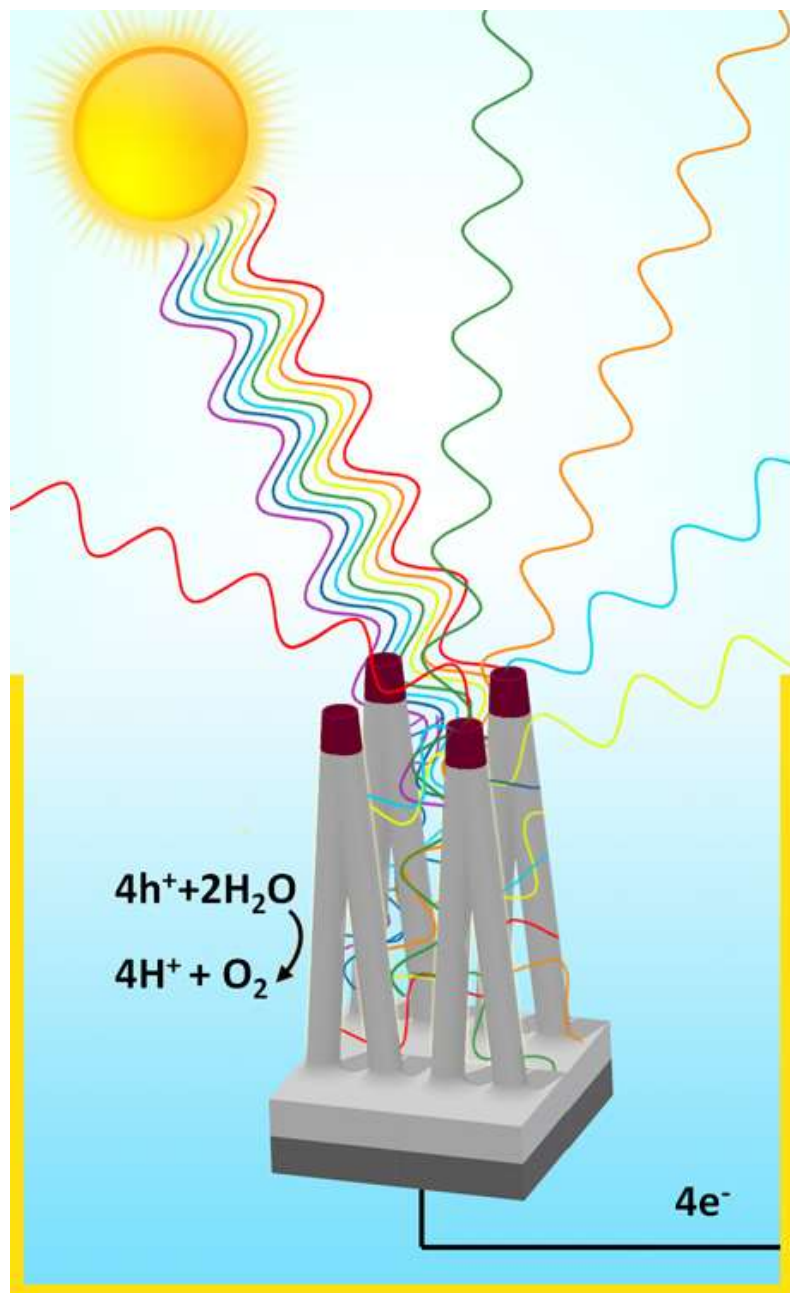


Photoelectrochemical performance of MPNTs and compact NTs: (a) LSV, (b) normalized Chronoamperometric measurements conducted at 0.5 V.

H₂ annealing confirming the Multipodal Effect



Conclusions



Thank You