Sekcja Metod Badań Materiałów Komitetu Nauki o Materiałach PAN
oraz
Instytut Metalurgii i Inżynierii Materiałowej PAN

# Characterization of nano-materials with advanced transmission electron microscopy techniques

TEM LAB

Jerzy Morgiel

# TECNAI G2 F20 S-TWIN

## HREM

**Point res.** 0.24 nm

**Inf. Limit** 0.15 nm

## STEM (HAADF)

**Point res.** 0.2 nm

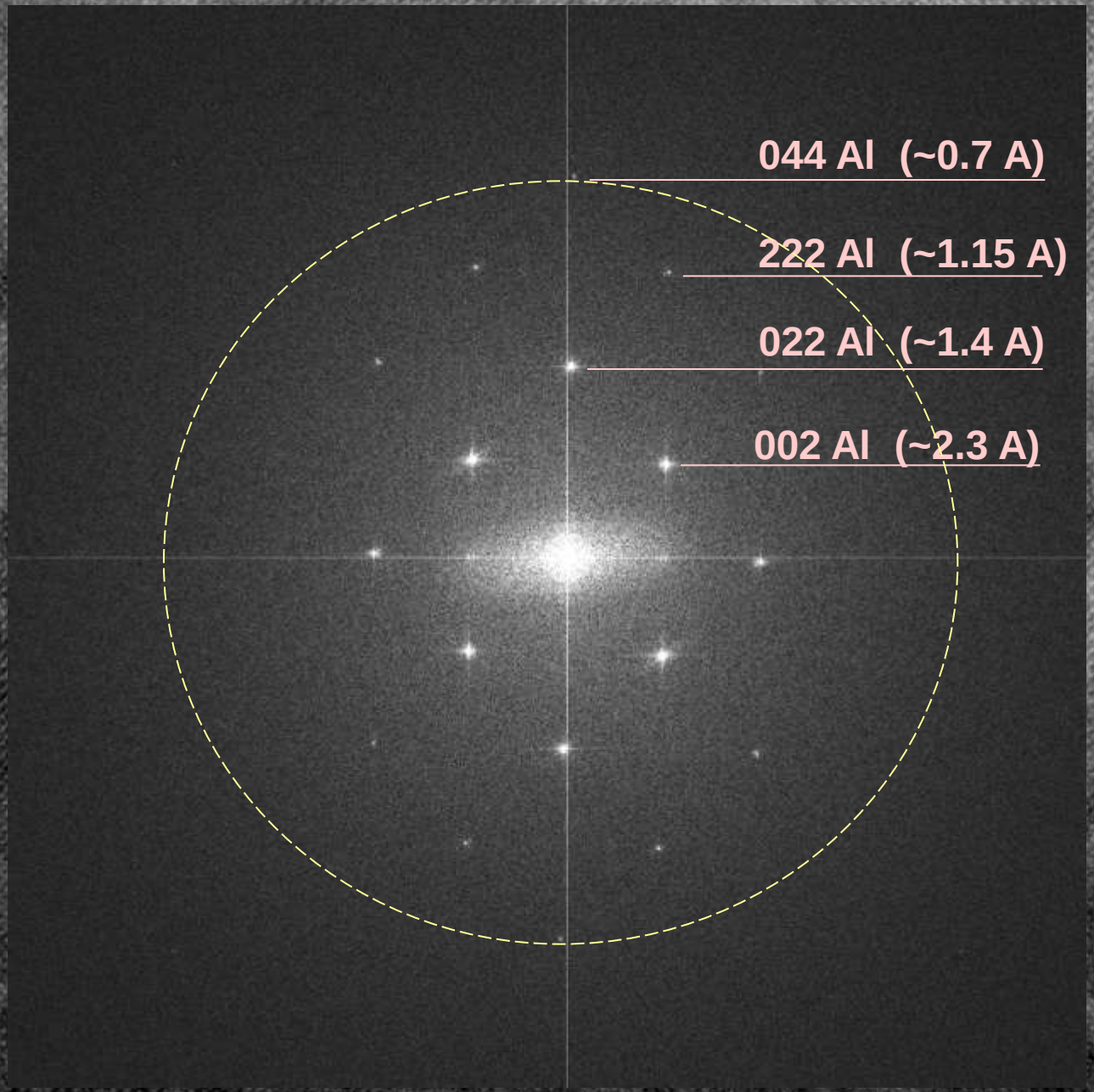
## EDS

**Probe** 0.3 nm/ 0.5nA

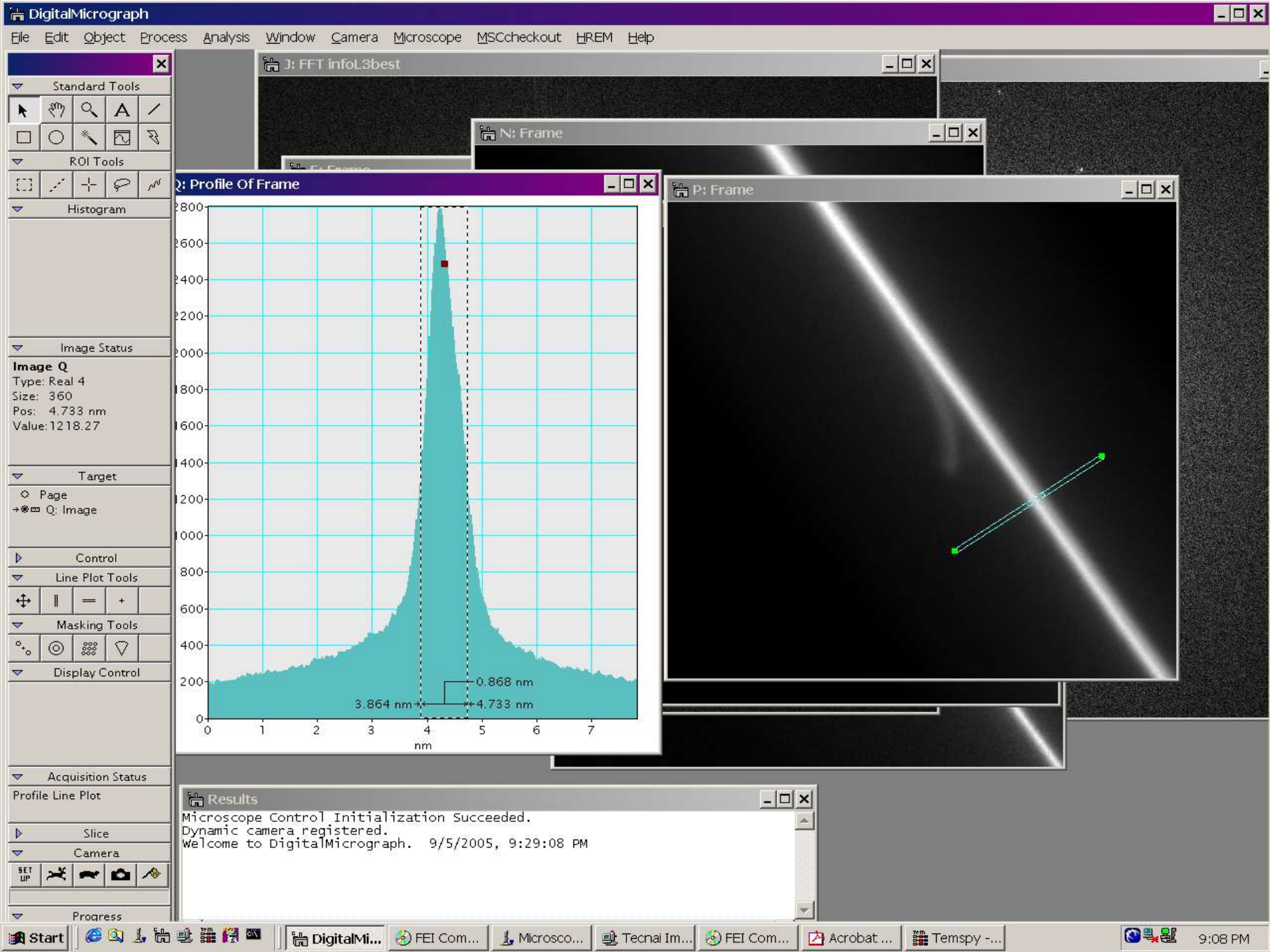
**UTW Si(Li+)** 133eV

*IMIM PAN Kraków - 2005*

HREM [100] Al




5 nm


DigitalMicrograph
File Edit Object Process Analysis Window Camera Microscope MSCcheckout HREM Help
Standard Tools
ROI Tools
Histogram
Image Status
Image Q
Type: Real 4
Size: 360
Pos: 4.733 nm
Value: 1218.27
Target
Page
Q: Image
Control
Line Plot Tools
Masking Tools
Display Control
Acquisition Status
Profile Line Plot
Slice
Camera
Progress
J: FFT infoL3best
N: Frame
Q: Profile Of Frame
2800
2600
2400
2200
2000
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1600
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600
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0
0.868 nm
3.864 nm
4.733 nm
0 1 2 3 4 5 6 7
nm
P: Frame
Results
Microscope Control Initialization Succeeded.
Dynamic camera registered.
Welcome to DigitalMicrograph. 9/5/2005, 9:29:08 PM
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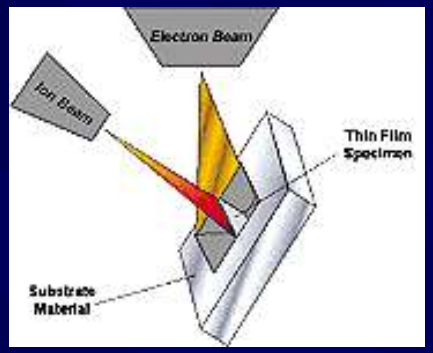
FEI Com...
Microsco...
Tecnai Im...
FEI Com...
Acrobat ...
Temspy -...
9:08 PM




# FIB

**Dual Beam:**

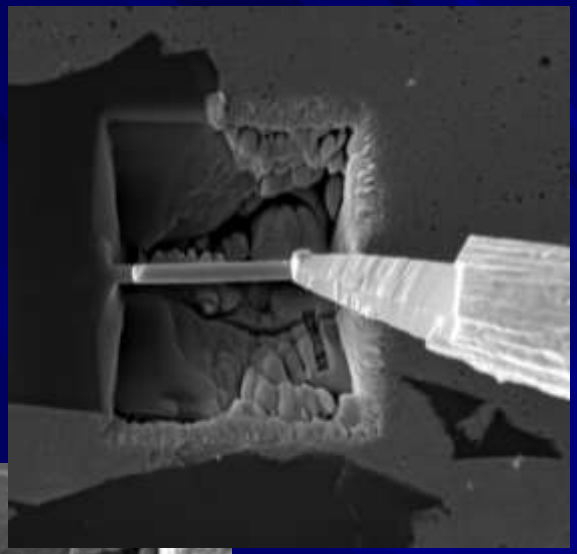
- $e^-$
- $Ga^+$

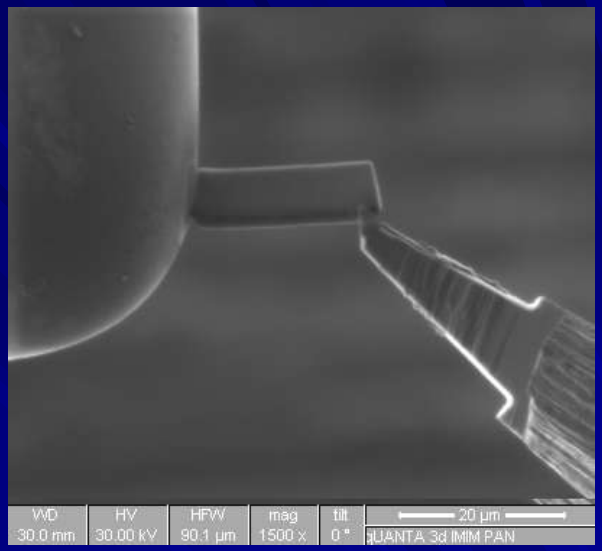
**Plus:**

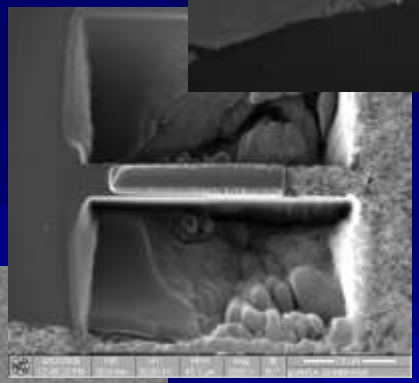
- Pt gun (shadowing)
- W gun
- („welding”)

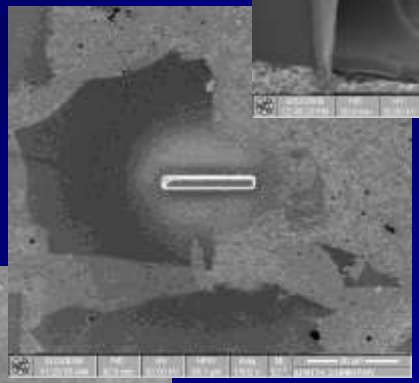
*IMIM PAN Kraków - 2005*

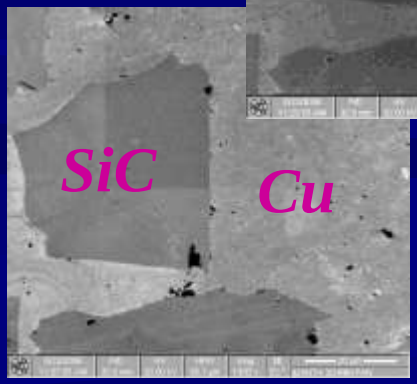
# FIB Omniprobe *lift-out* procedure

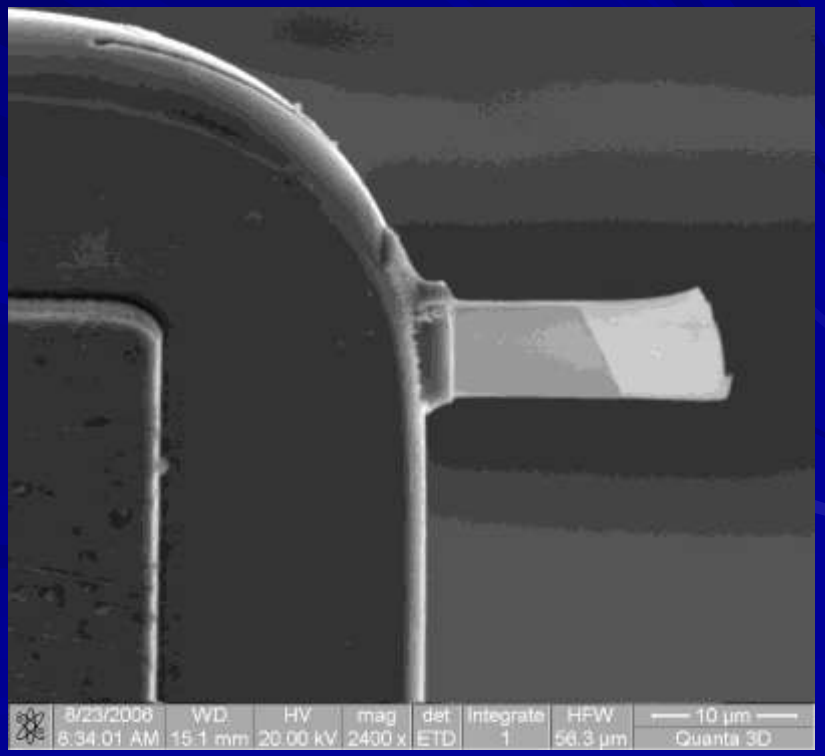








Network of Excellence
Knowledge-based Multicomponent Materials for Durable and Safe Performance
KMM

WPI „Intermetalics”
(J. Dutkiewicz)

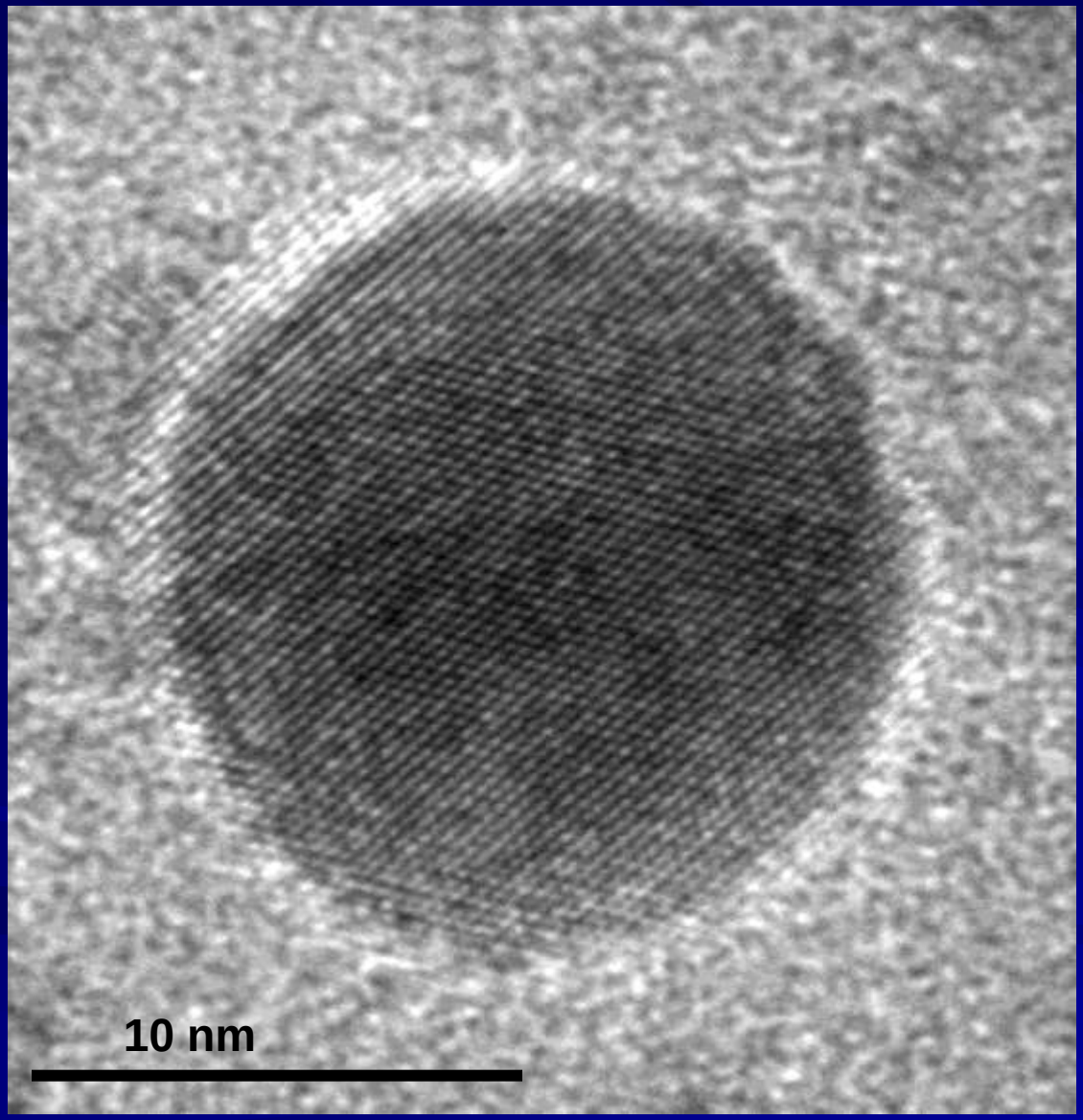
WPII „Composites”
(J. Morgiel)

WPIII „Coatings + FGM”
(B. Major)

**Ł. Major, J. Grzonka, M. Pomorska, A.M. Janus, Ł. Rogal**

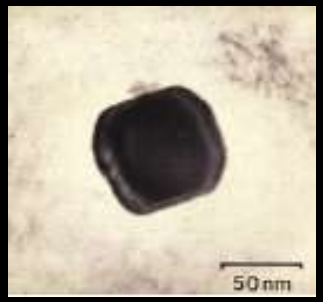
- IPPT - Institute Fundamental Technological Research, Polish Academy of Sciences
- TUD - Technische Universität Darmstadt
- FHG - Fraunhofer-Gesellschaft zur Föerderung der angewandten Forschung e.V.
- TUV - Vienna University of Technology
- ONERA - Office National d'Etudes et de Recherches Aérospatiales
- UM - Université de Metz
- POLIMI - Politecnico di Milano
- UNIPAD - Università degli Studi di Padova
- UWC - University of Wales Cardiff
- IMBAS - Institute of Mechanics, Bulgarian Academy of Sciences
- AGH - AGH University of Science and Technology
- IMIM - Institute of Metallurgy and Materials Science, Polish Academy of Science
- NETCOM - NetComposites
- ITC - Instituto de Tecnología Cerámica - AICE
- IMPER - Imperial College
- UH - University of Hertfordshire
- LMT - Ecole Normale Supérieure de Cachan
- POLITO - Politecnico di Torino
- UNIVPM - Università Politecnica delle Marche
- CIDETEC - Fundacion CIDETEC
- ICASAS - Institute of Construction and Architecture, Slovak Academy of Sciences
- IMRSAS - Institute of Materials Research of Slovak Academy of Sciences
- CUT - Cracow University of Technology
- WUT - Warsaw University of Technology
- IPSUA - Institute for Problems of Strength, National Academy of Sciences
- MCL - Werkstoff-Kompetenzzentrum- (Materials Centre Leoben)
- INASMET - Fundación Inasmet
- MERL - Materials Engineering Research Laboratory Ltd
- ATECA - ATECA
- IFM - Institute for Ferrous Metallurgy
- PZL - Wytwornia Sprzetu Komunikacyjnego 'PZL-Swidnik' S.A.
- EADSG - EADS Deutschland GmbH - Corporate Research Center Germany
- EADSF - EADS CCR
- SNECMA - Snecma Moteurs
- FIAT - Centro Ricerche Fiat S.C.p.A.
- ALENIA - Alenia Aeronautica S.P.A

# Cz. I. Metalic nano-crystalline (Au, Ag, Cu) in amorphous matrix ($SiO_{2)}$

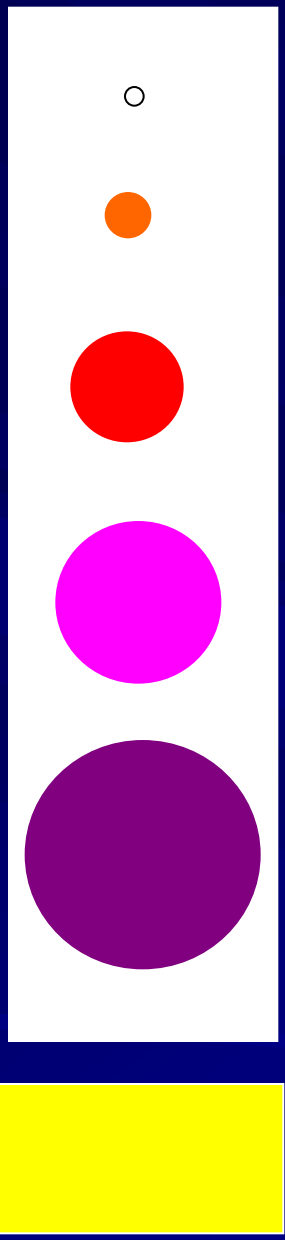



in collaboration with
prof..Monika Ferraris
Politechnic of Torrino
(POLITO)

British
Museum
IV th Cent.
A.D.




***Lycurgus Cup is the only complete example of a dichroic type of glass, which changes colour when held up to the light. The opaque green cup turns to a glowing translucent red when light is shone through it. The glass contains tiny amounts of colloidal gold and silver***



*Paul Mulvaney, MRS Bulletin, Dec. 2001, p.1009*

**Au Atom: ~0,1 nm (1A), colorless**

**Au clasters: < 1nm, nonmetalic, orange**

**Au nanocrystallites: 3 - 30 nm, metalic, transparent / red**

**Au particles: 30 - 500 nm, metalic, transparent / turbid**

**crimson -> blue**

*M. Faraday, Philos. Trans. R. Soc. London, 147 (1857) 145-181*

Gold leaf can be beaten to thicknesses of 1/278000 of an inch (around 90 nm). Such films are continuous and green in transmission. Further thinning with KCN gives ruby red films.

Chemical means to finely divided gold. Also deflagration of gold wires to produce ruby red particles. Chemically indistinguishable from gold.

**Au bulk: golden color!**

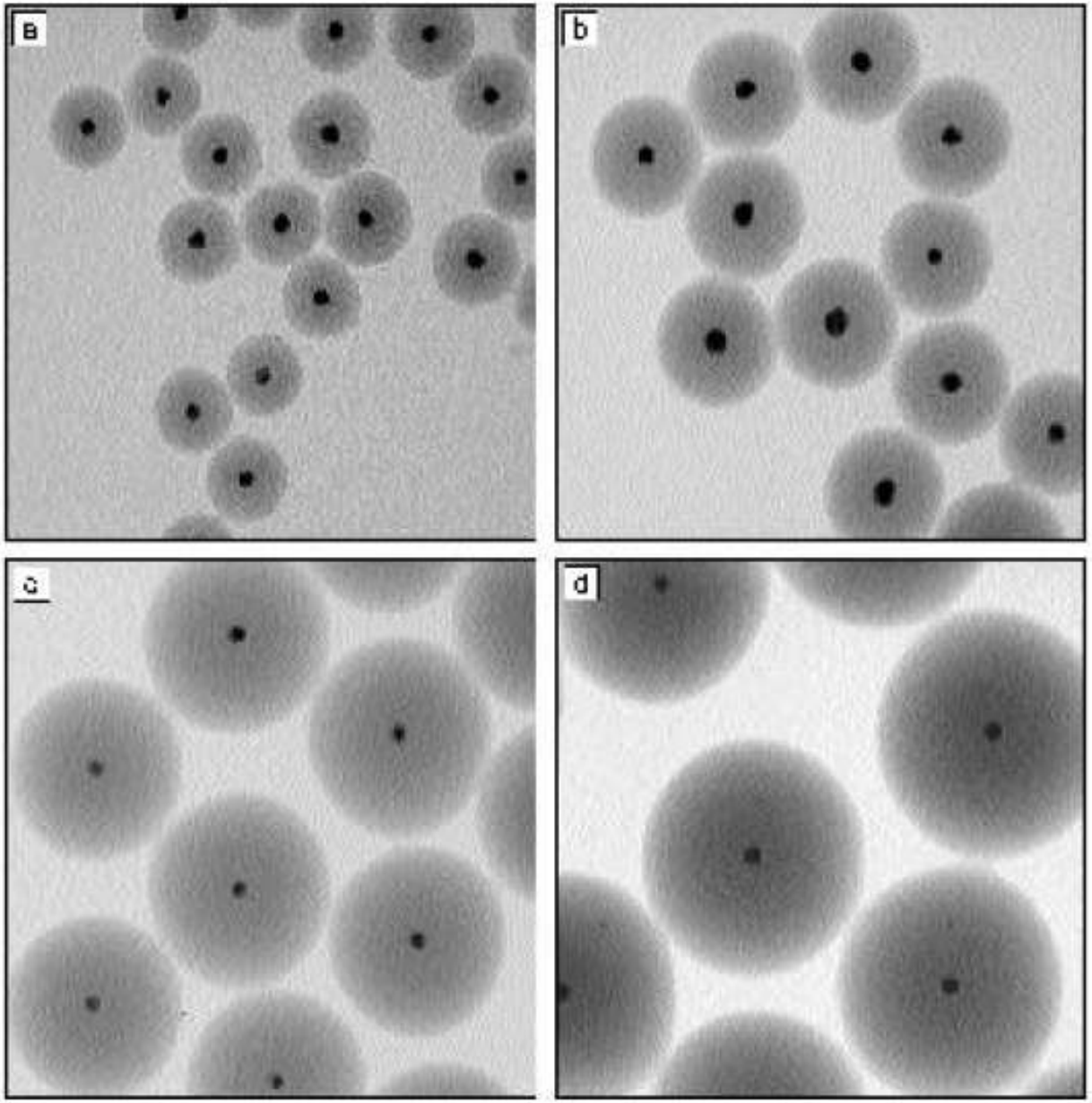
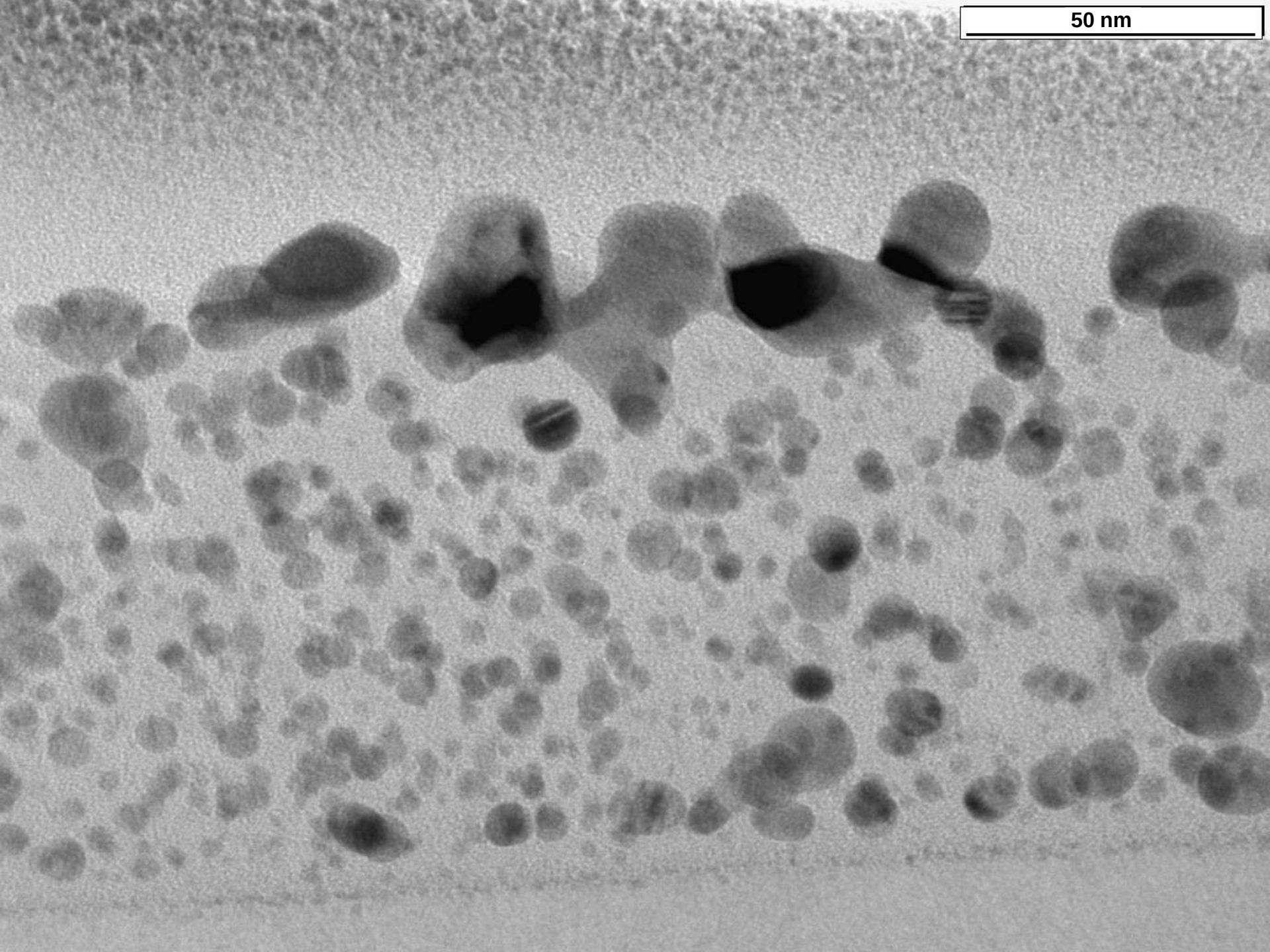
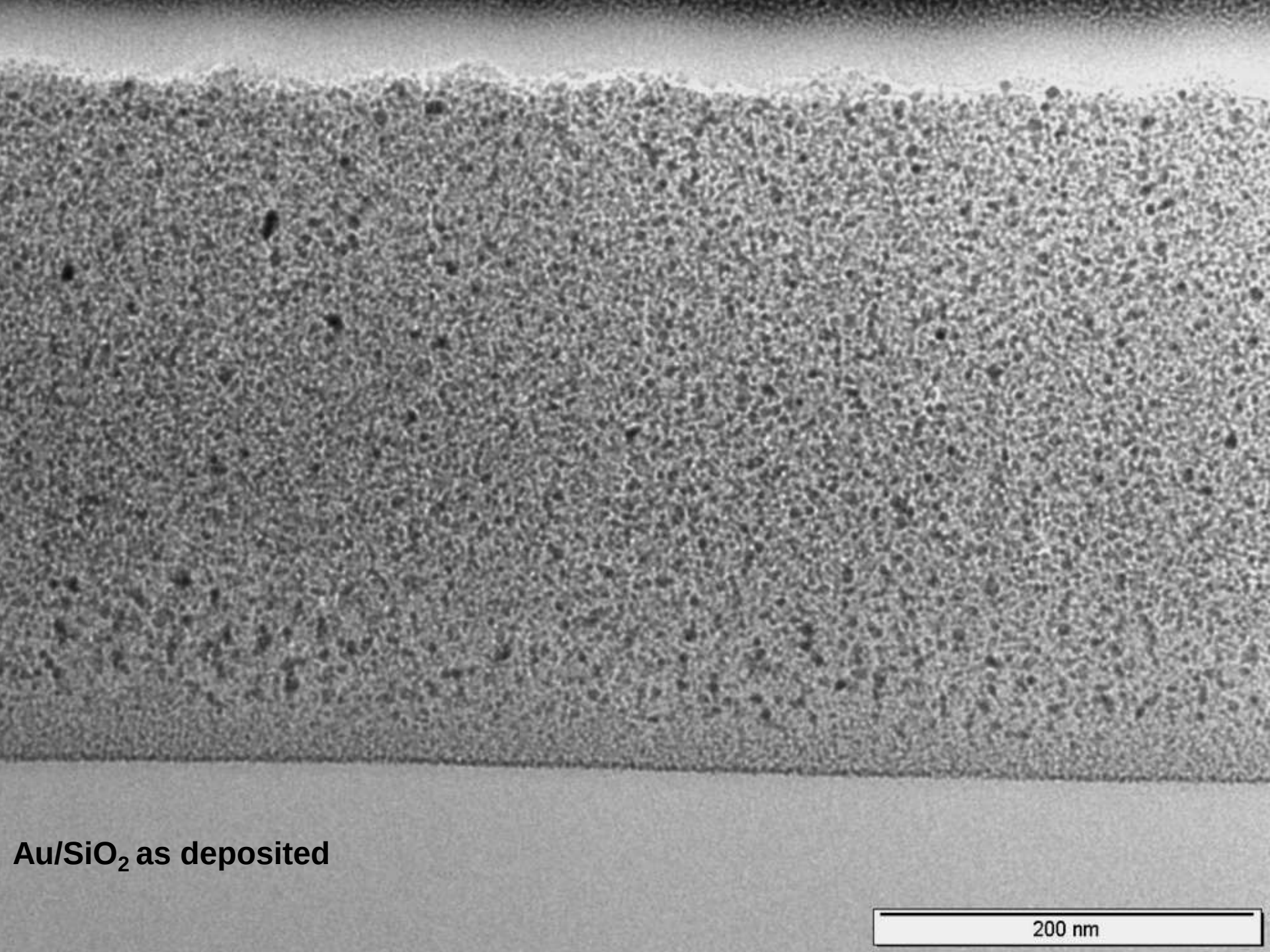


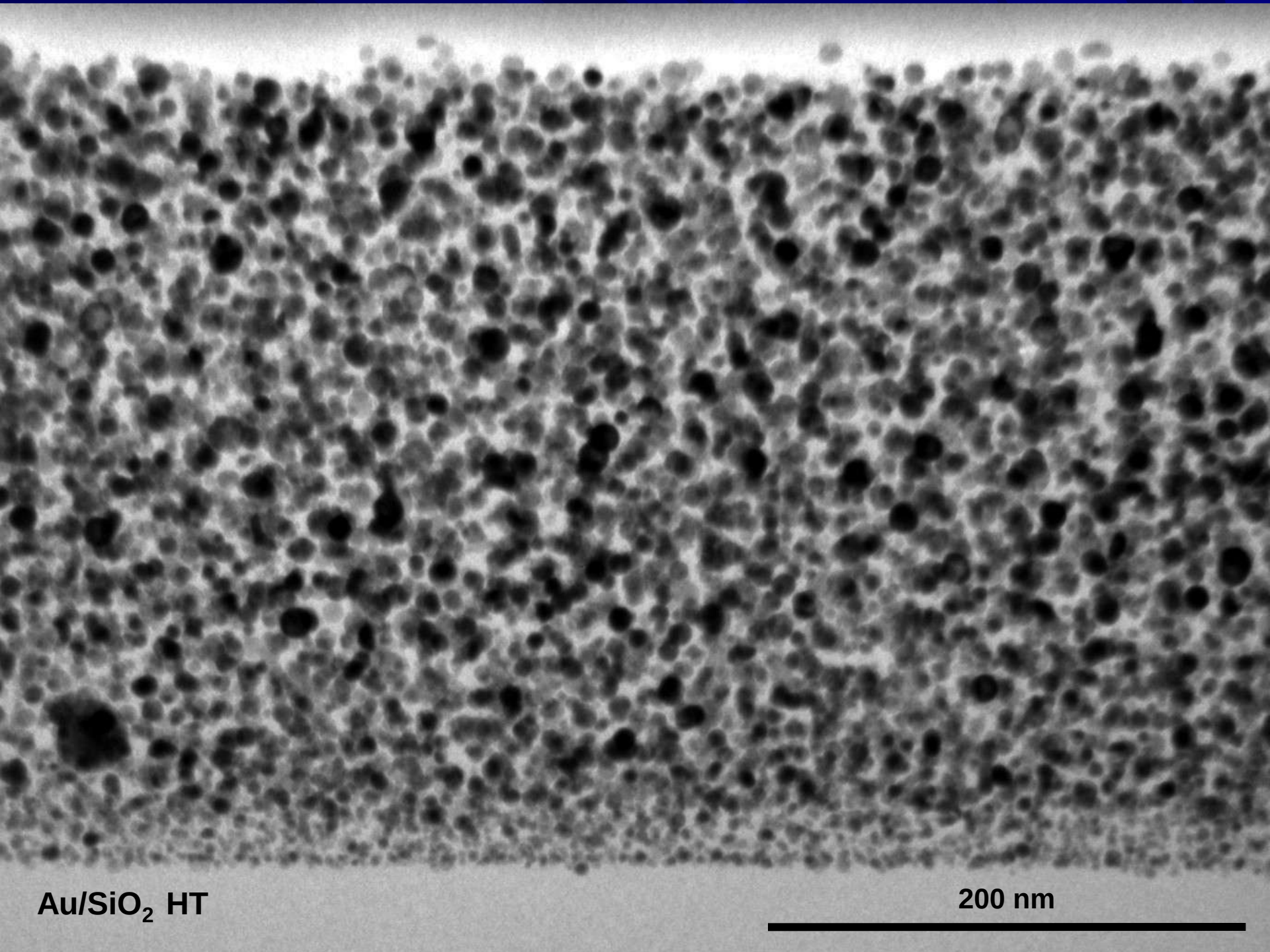

Figure4.(a)–(d) Electron micrographs of silica-coated 15-nm gold particles with various shell thicknesses.

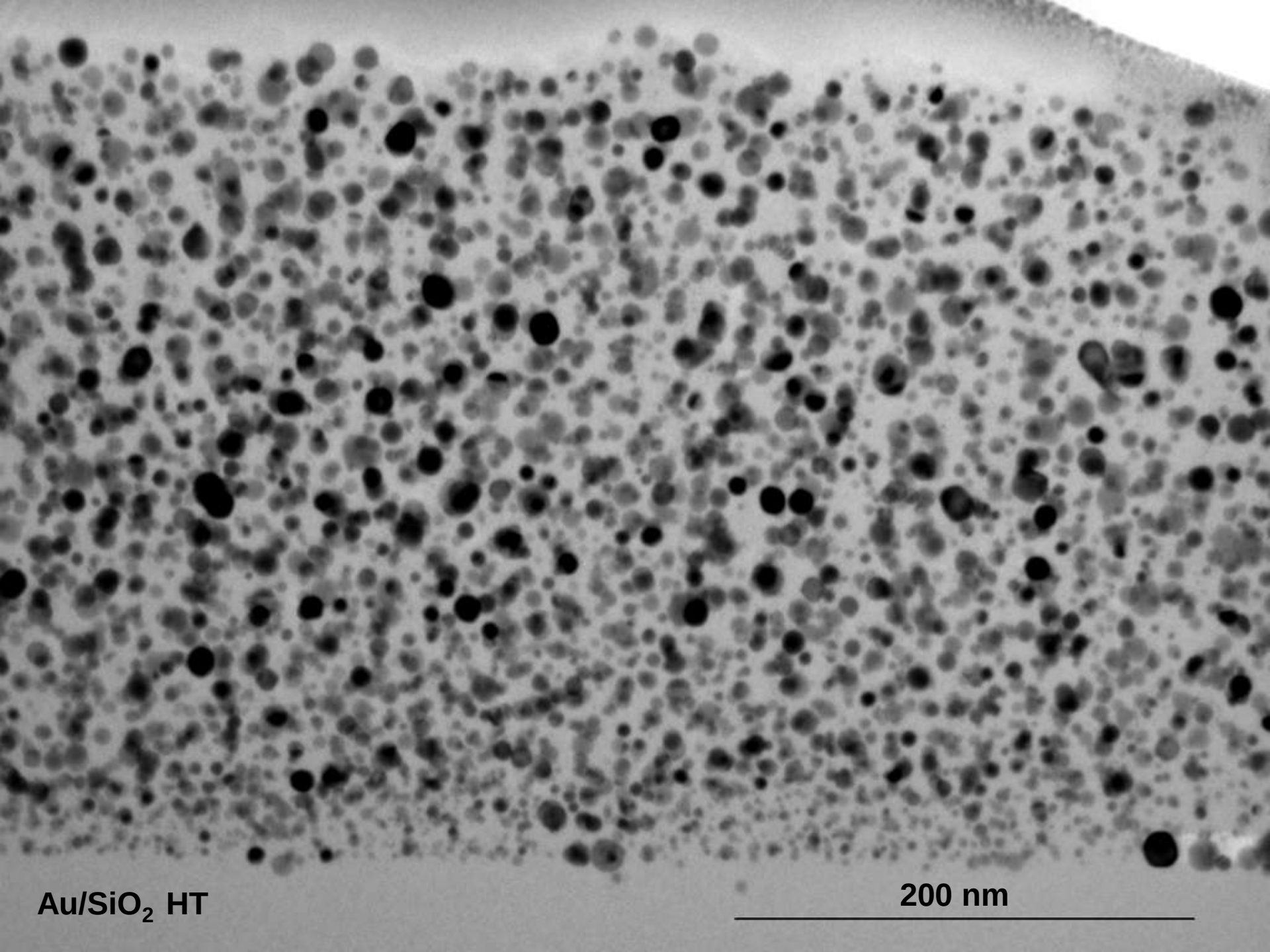
*Paul Mulvaney, MRS Bulletin, Dec. 2001, p.1009*

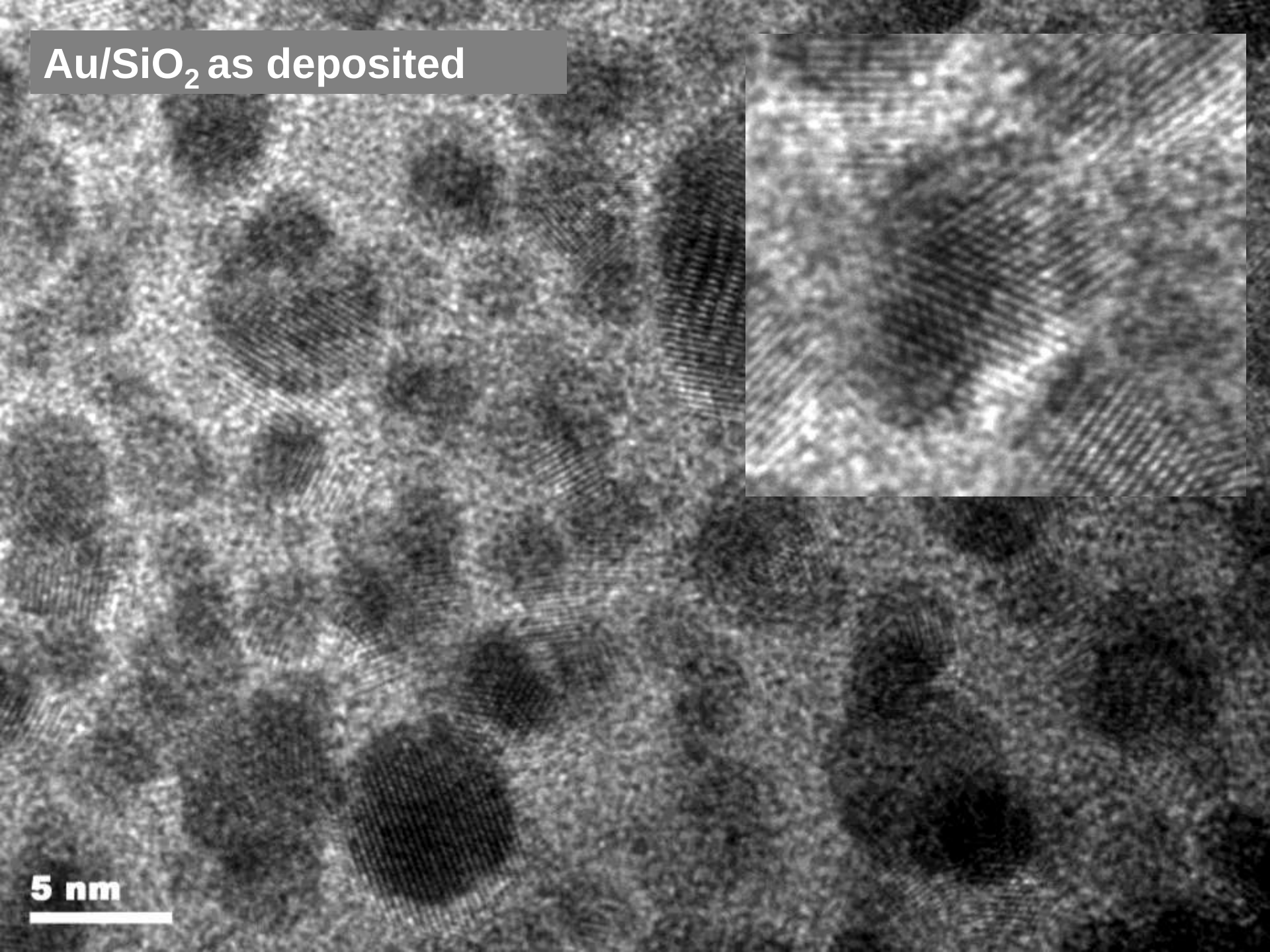
**in the limit of very small spacings and a gold volume fraction 50%, the film spectrum is almost identical to that of the bulk gold thin film**

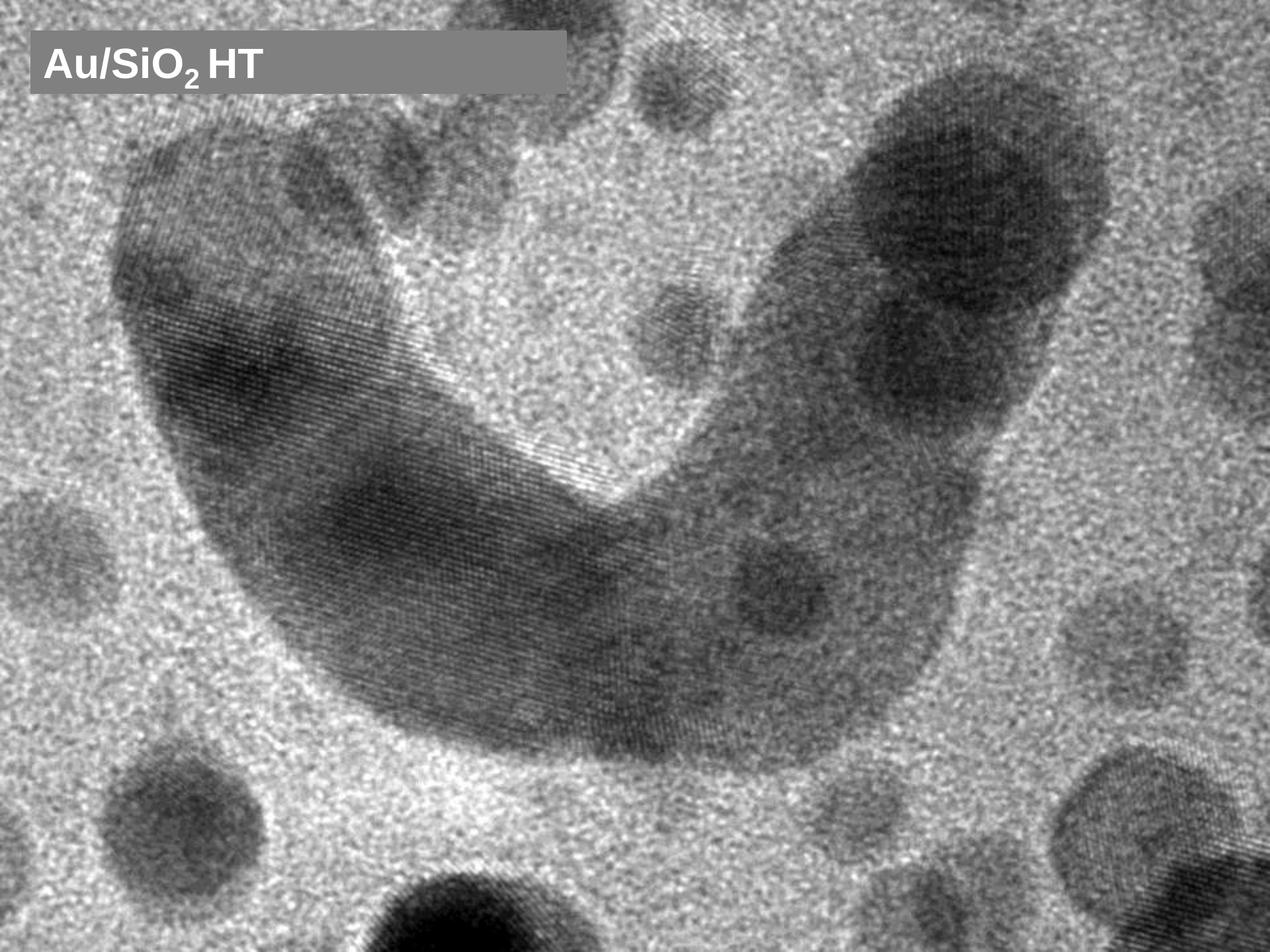

50 nm

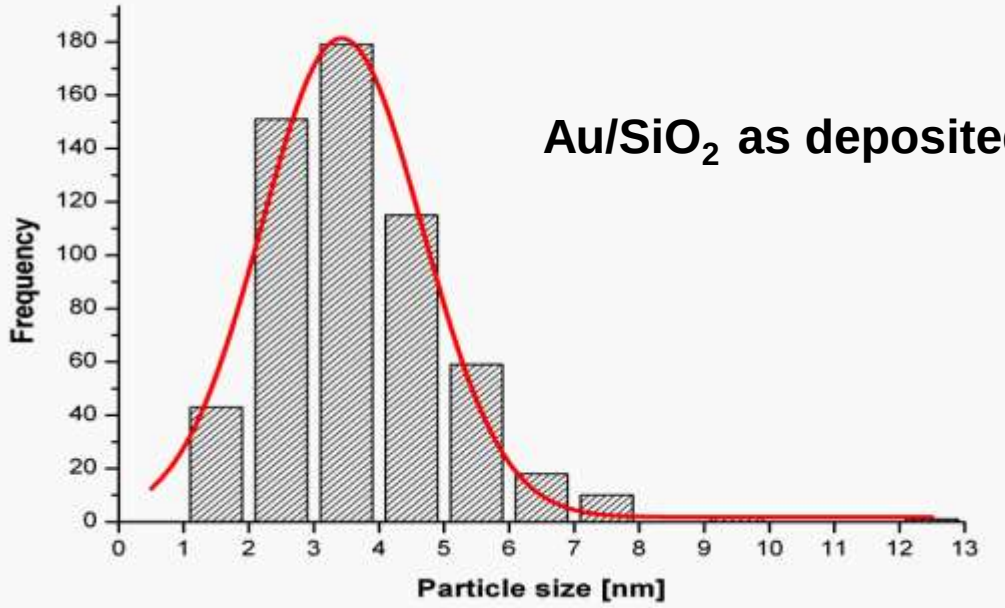

Au/SiO2 as deposited
200 nm


Au/SiO2 HT
200 nm

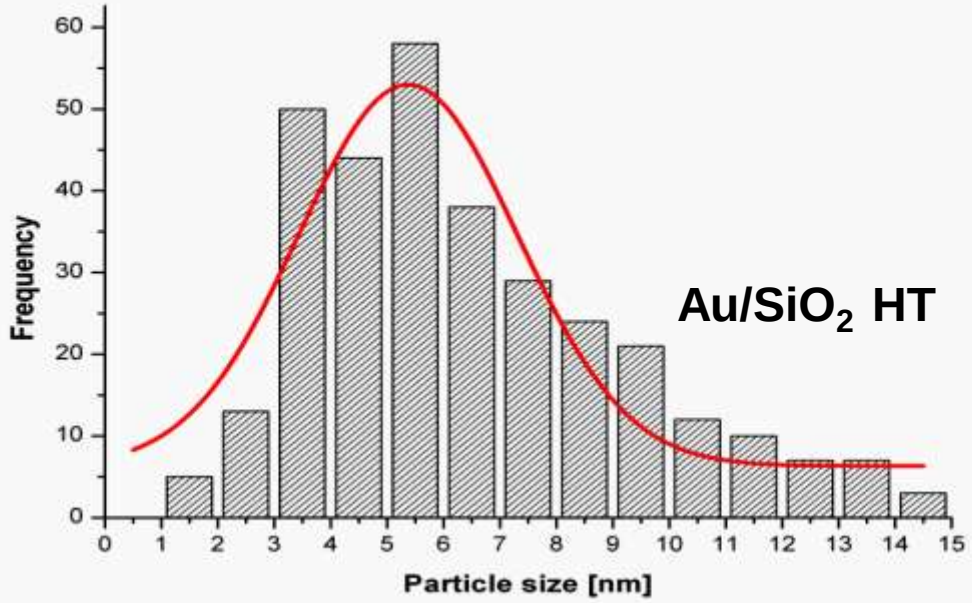

Au/SiO2 HT
200 nm


Au/SiO2 as deposited
5 nm


Au/SiO2 HT

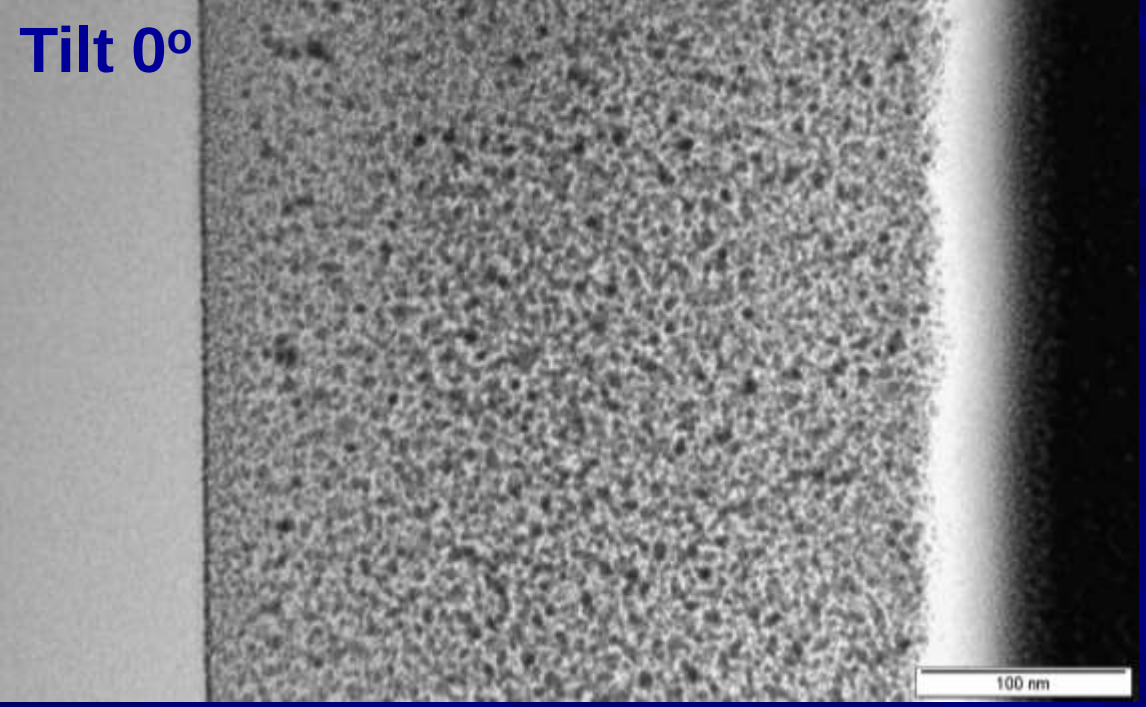



**$Au/SiO_2$ as deposited**

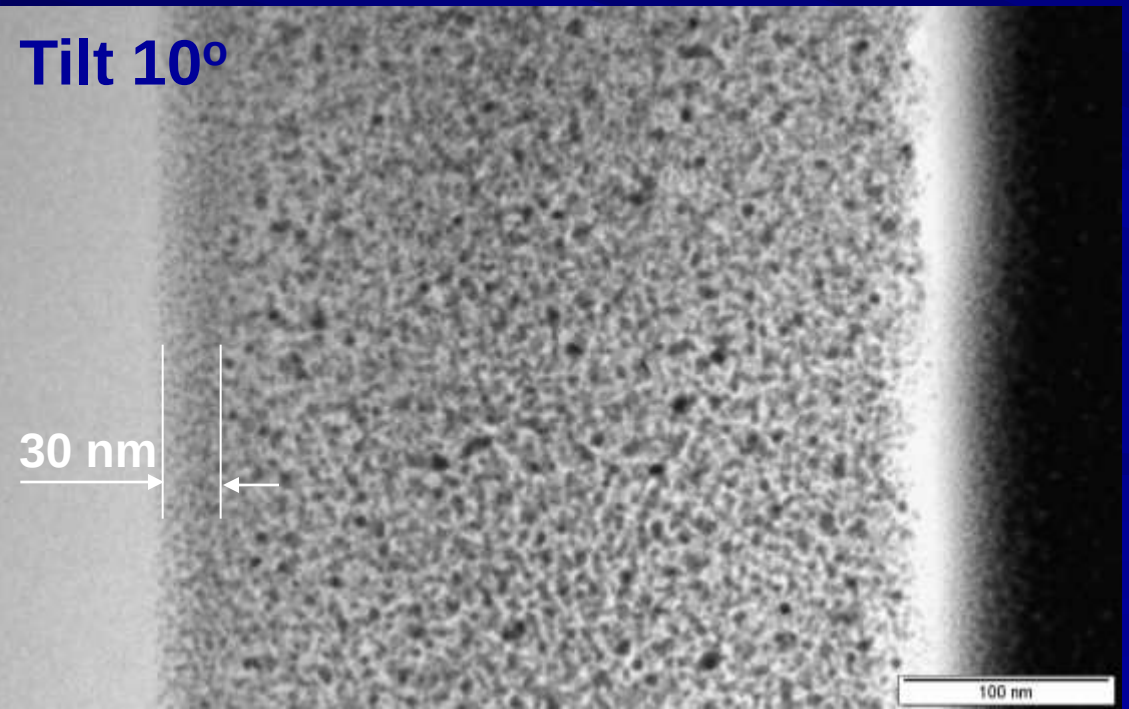



**$Au/SiO_2$ HT**

Tilt 0°




Tilt 10°




thin foil thickness ~170 nm

# Cz. I. Au nano-crystallites: summary

**Problems solved:**

- **The microstructure of Au-nanocrystallites was described in as-deposited (AD) and heat treated state (HT).**
- **The performed measurements indicated that the size of nano-crystallites agrees with normal distribution and that the they average increases from 3 to 5,5 nm for AD and HT respectively**

**Problems to be investigated/determined:**

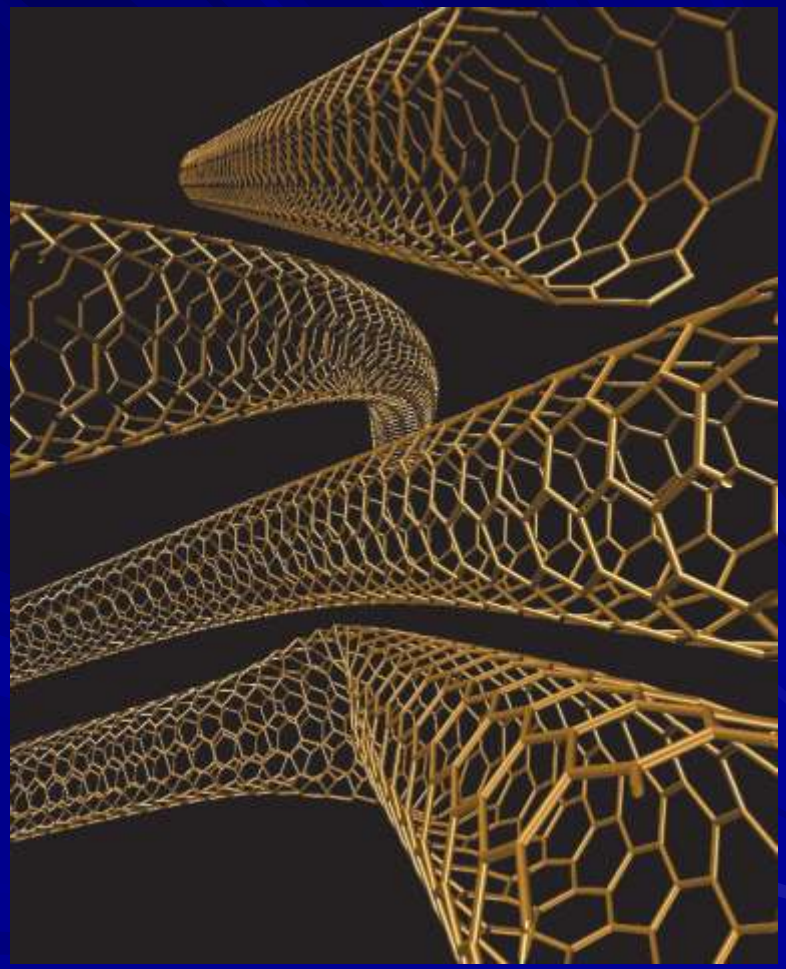
- **Nano-crystallites density**
- **Minimum size of nano-crystallites**
- **Minimum size of defected nano-crystallites**

# Cz. II. Nano-composites: ceramic + CNT

**Increased conductivity:**

*(CNT~1GA/cm$^2$, Cu ~1MA/cm$^2$)*

- **$ZrO_2$ + CNT**
  ***(Jan Dusza IMR SAS, Koszyce)***



**Increased strength:**

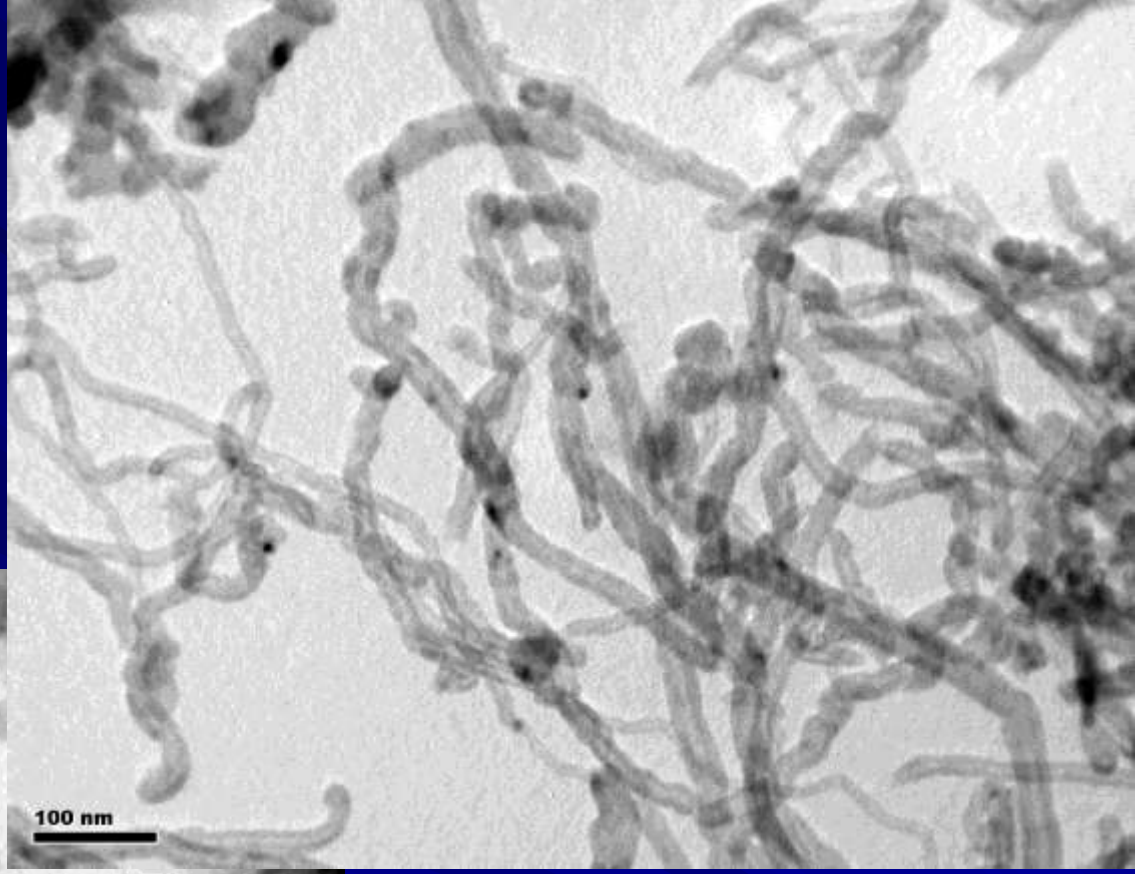
*(CNT ~45GPa, stal <2GPa)*

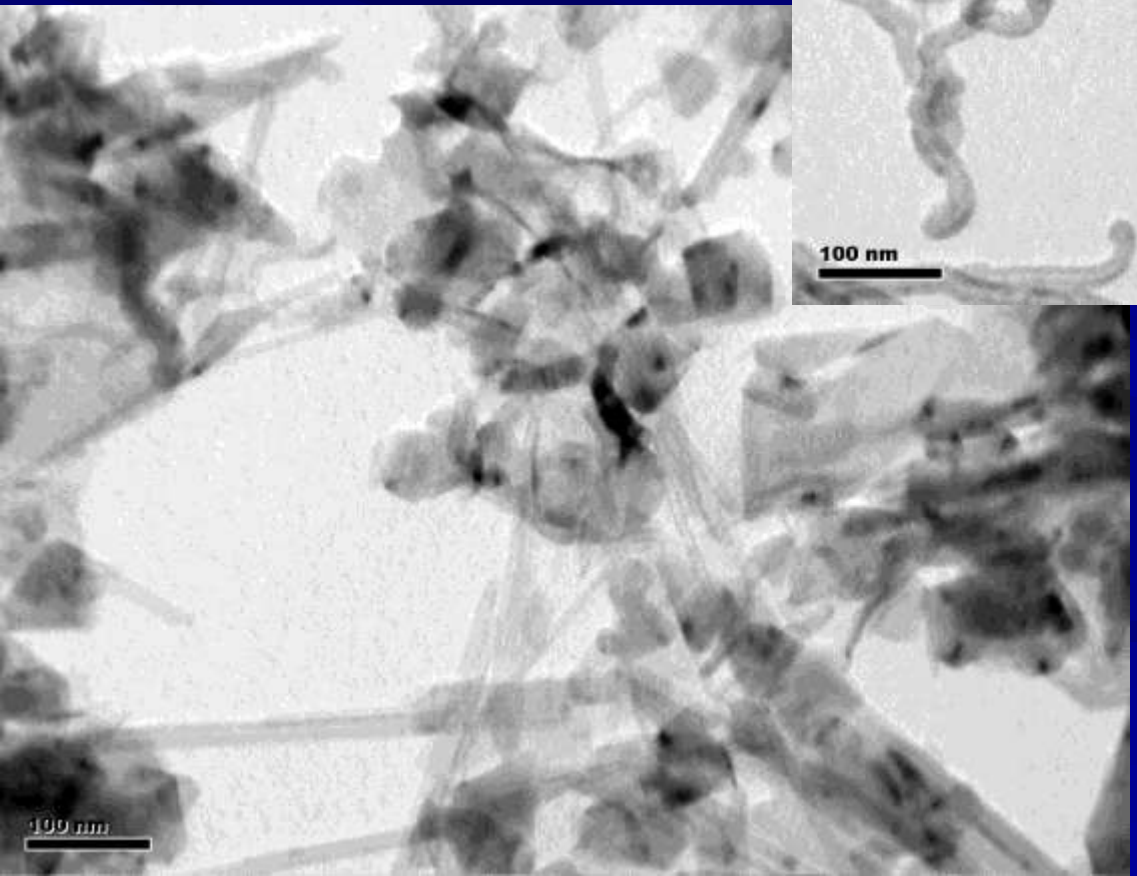
**$(Zr,Ti)O_2$ + CNT**
***(Waldemar Pyda, AGH)***

- **Bioglass + CNT**
  ***(Aldo Boccaccini/ Imperial College London)***

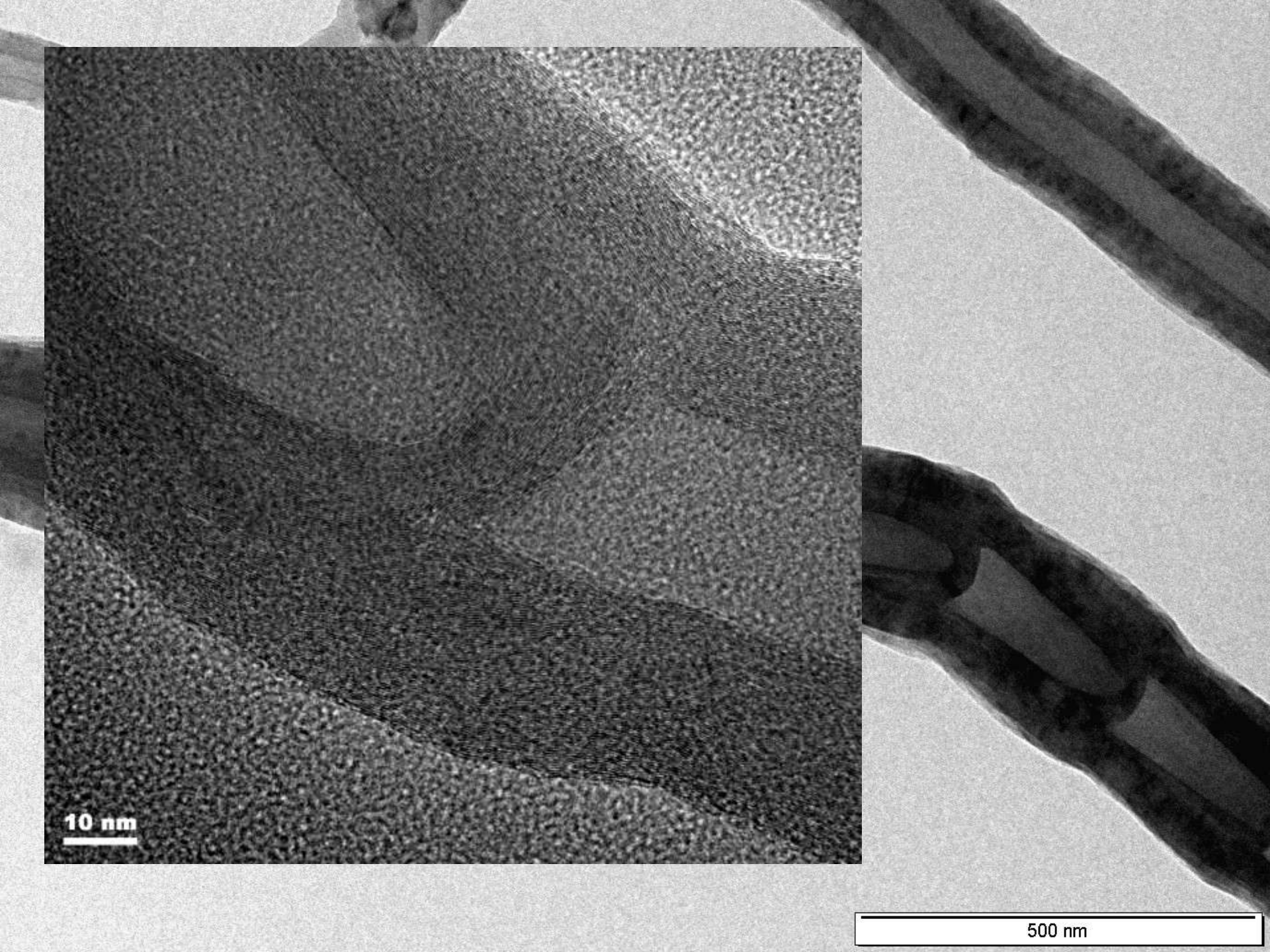
**CNT**

*Prof.. Stanisław Błażewicz,*
*Kathedra of Biomaterials*
*AGH*

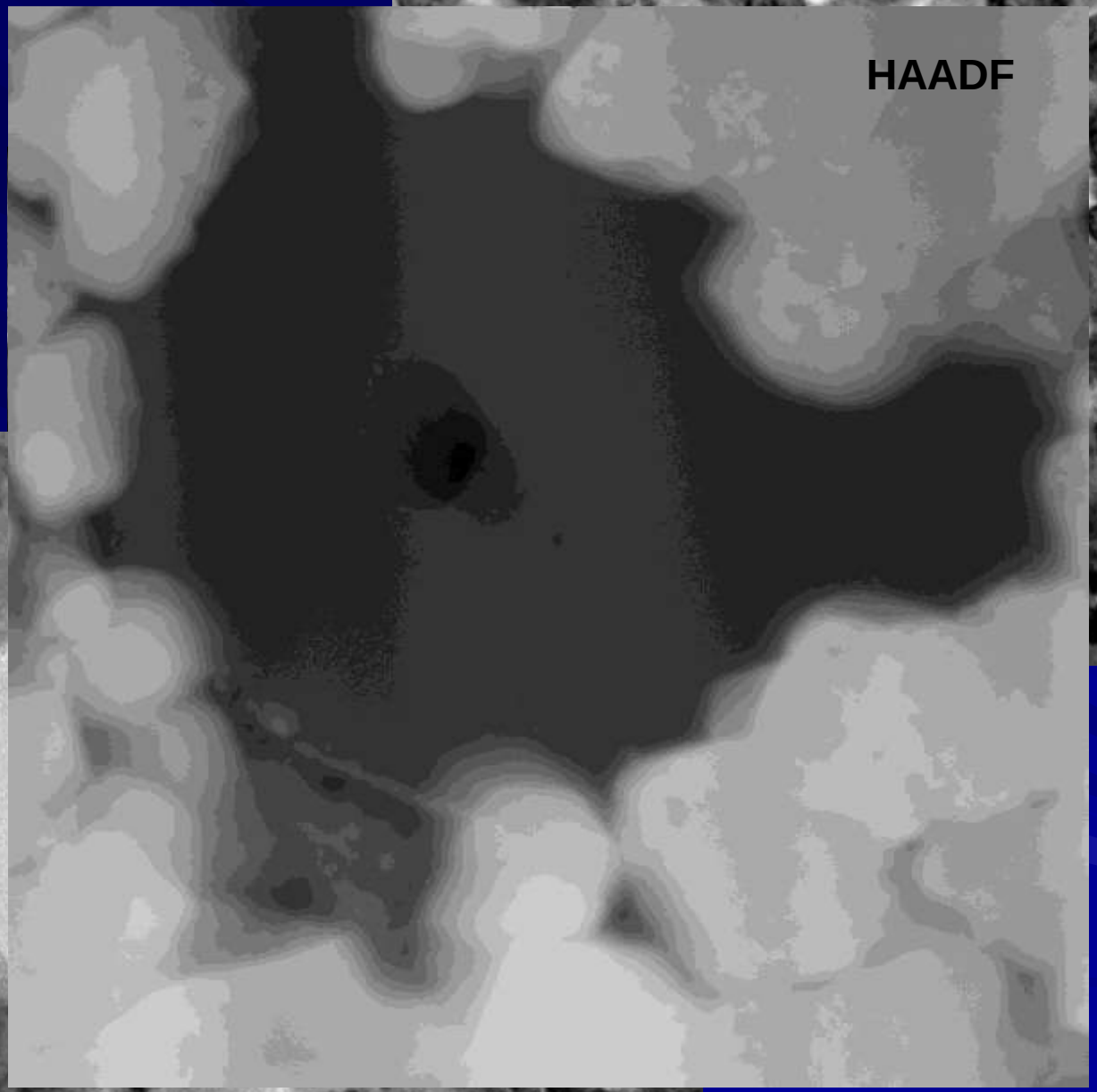


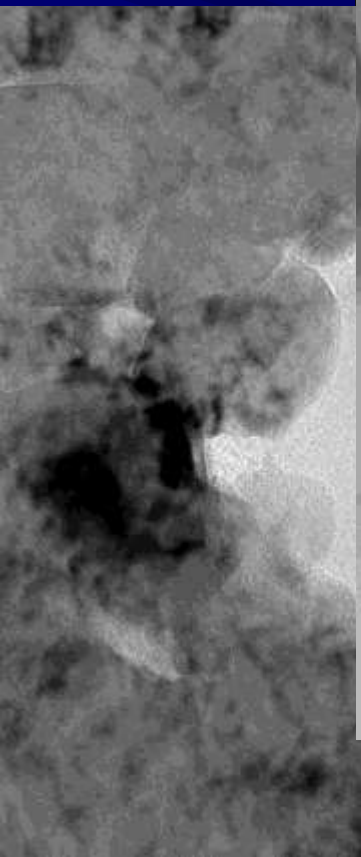




*Prof. Aldo Boccaccini,*
*Imperial College, Londyn*

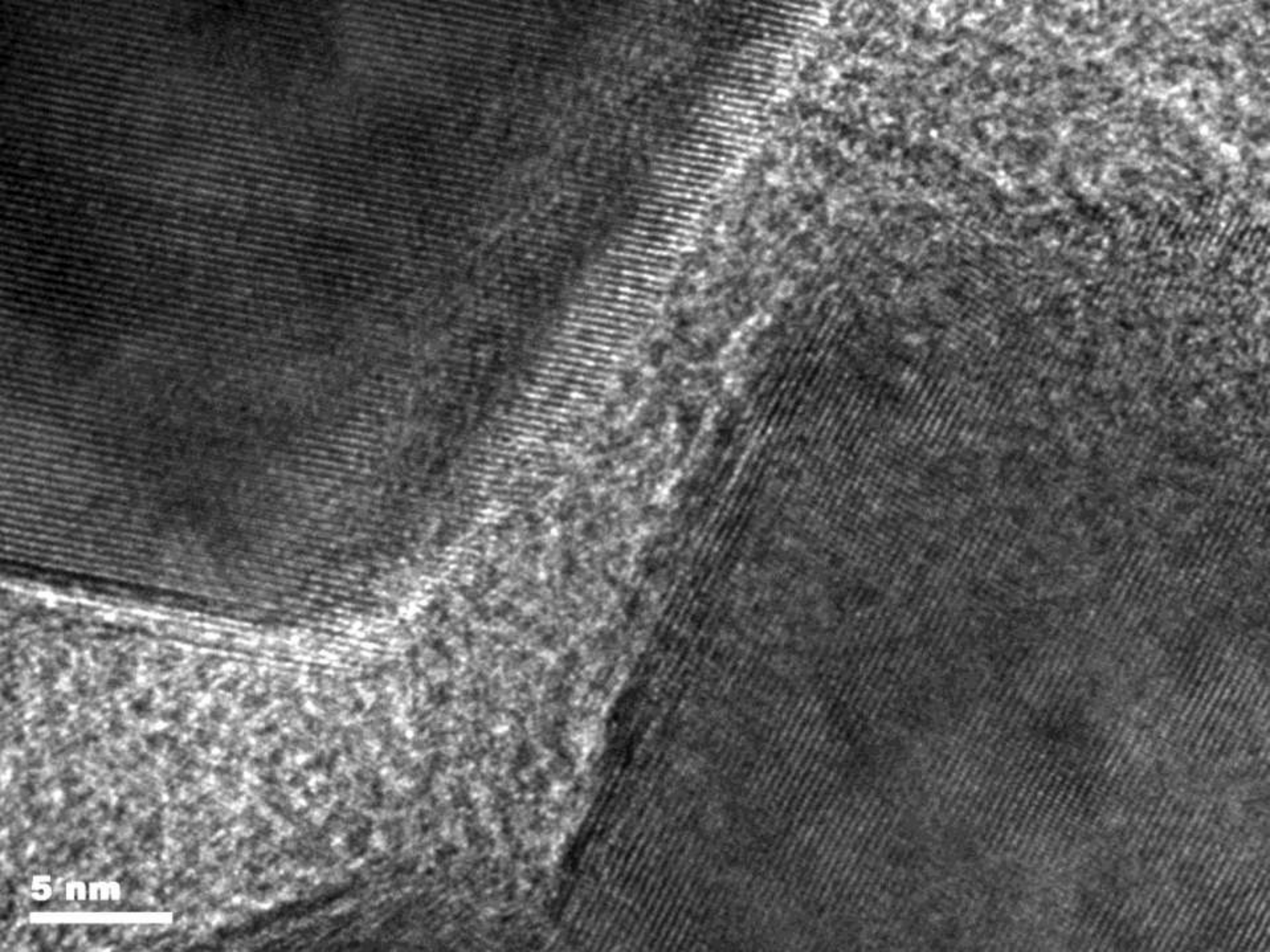

10 nm
500 nm

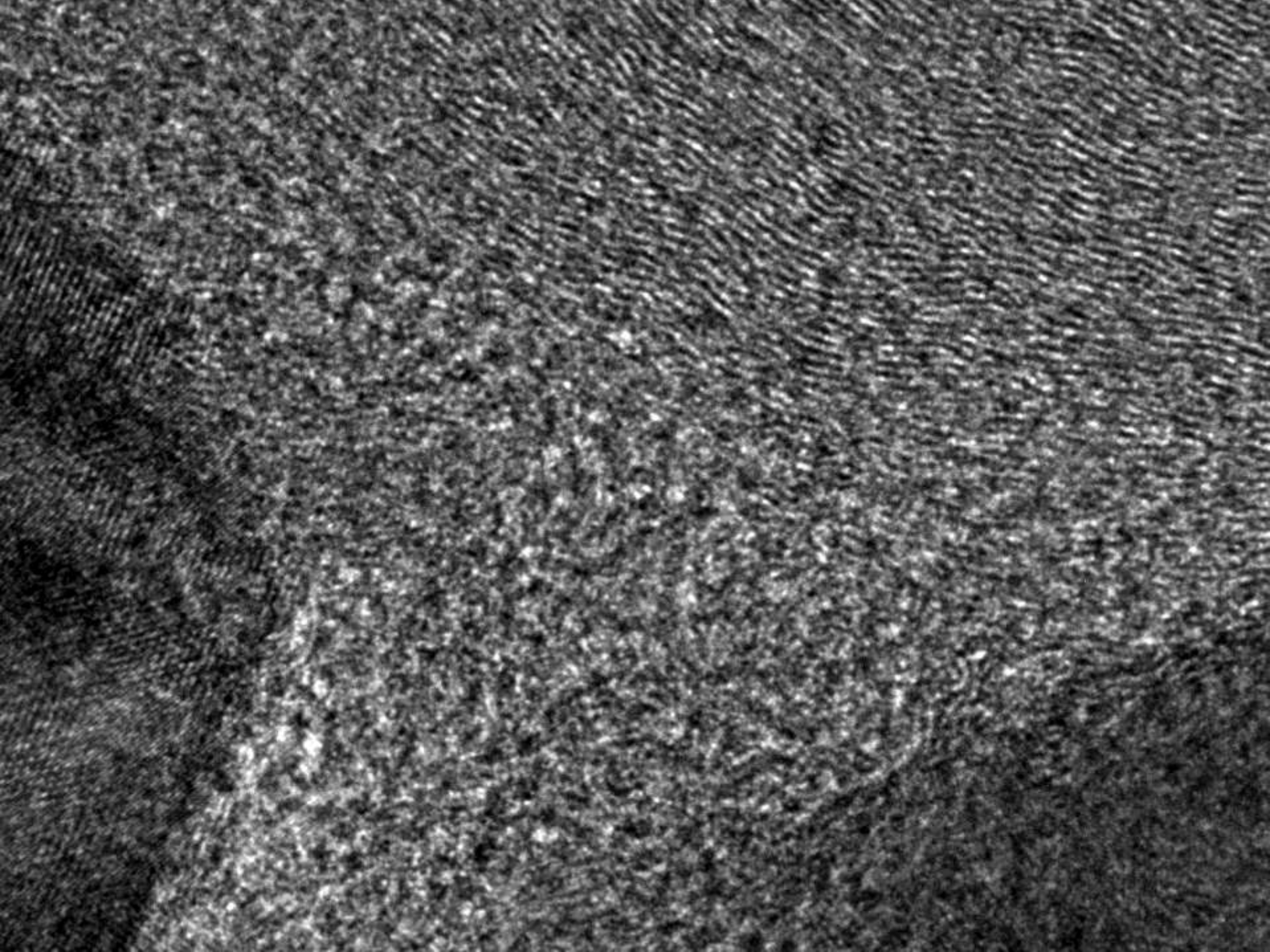
# $ZrO_2$ + CNT

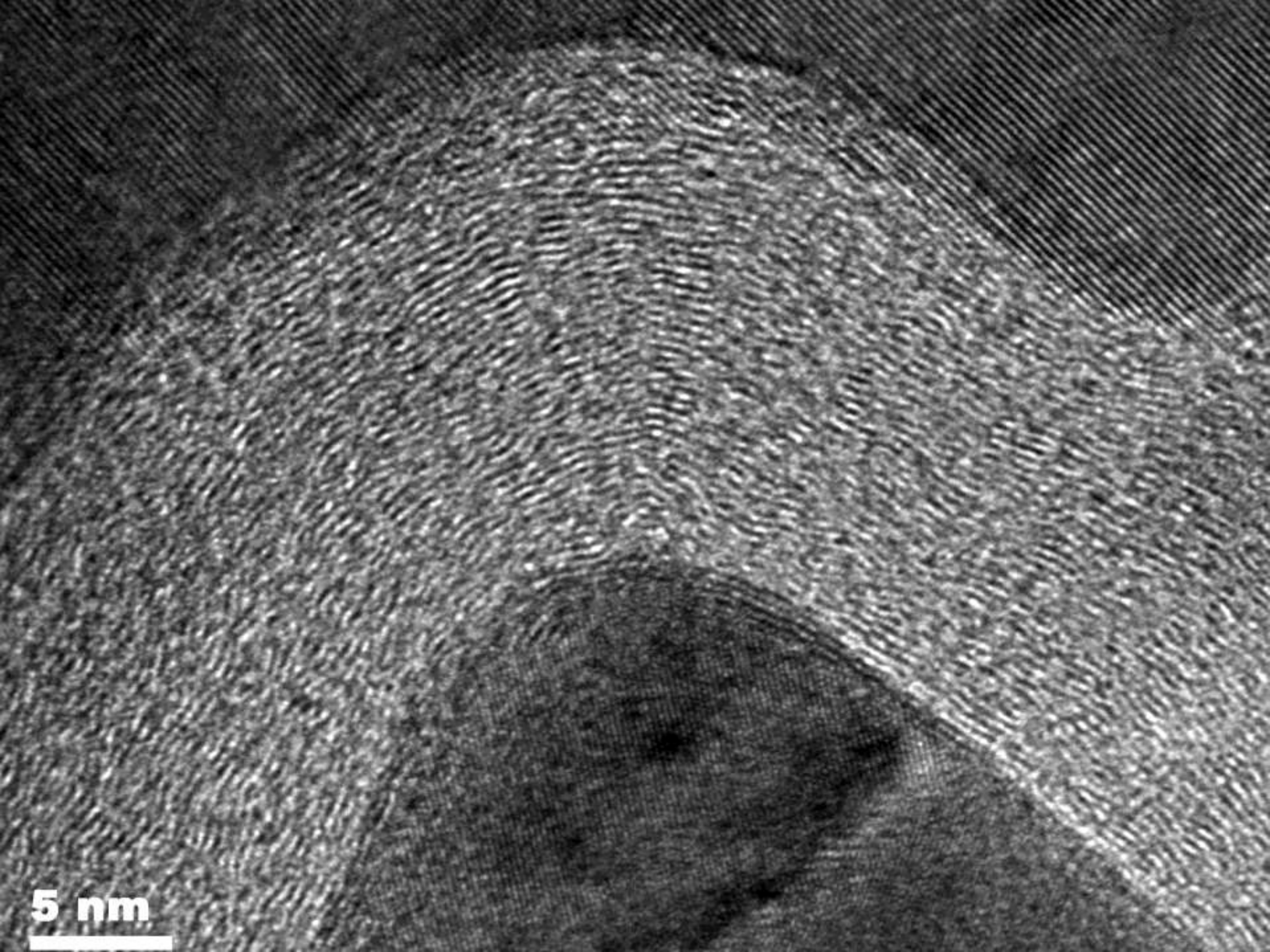






5 nm




5 nm

Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 58 (2008) 520–523
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

# Zirconia/carbon nanofiber composite

Annamária Duszová,[a] Ján Dusza,[b,*] Karel Tomášek,[a] Jerzy Morgiel,[c] Gurdial Blugan[d] and Jakob Kuebler[d]

[a] *Technical University of Košice, Faculty of Metallurgy, Letná 9, 042 00 Košice, Slovak Republic*
[b] *Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04353 Košice, Slovak Republic*
[c] *Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Reymonta 25, 30 059 Krakow, Poland*
[d] *Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, 8600 Duebendorf, Switzerland*

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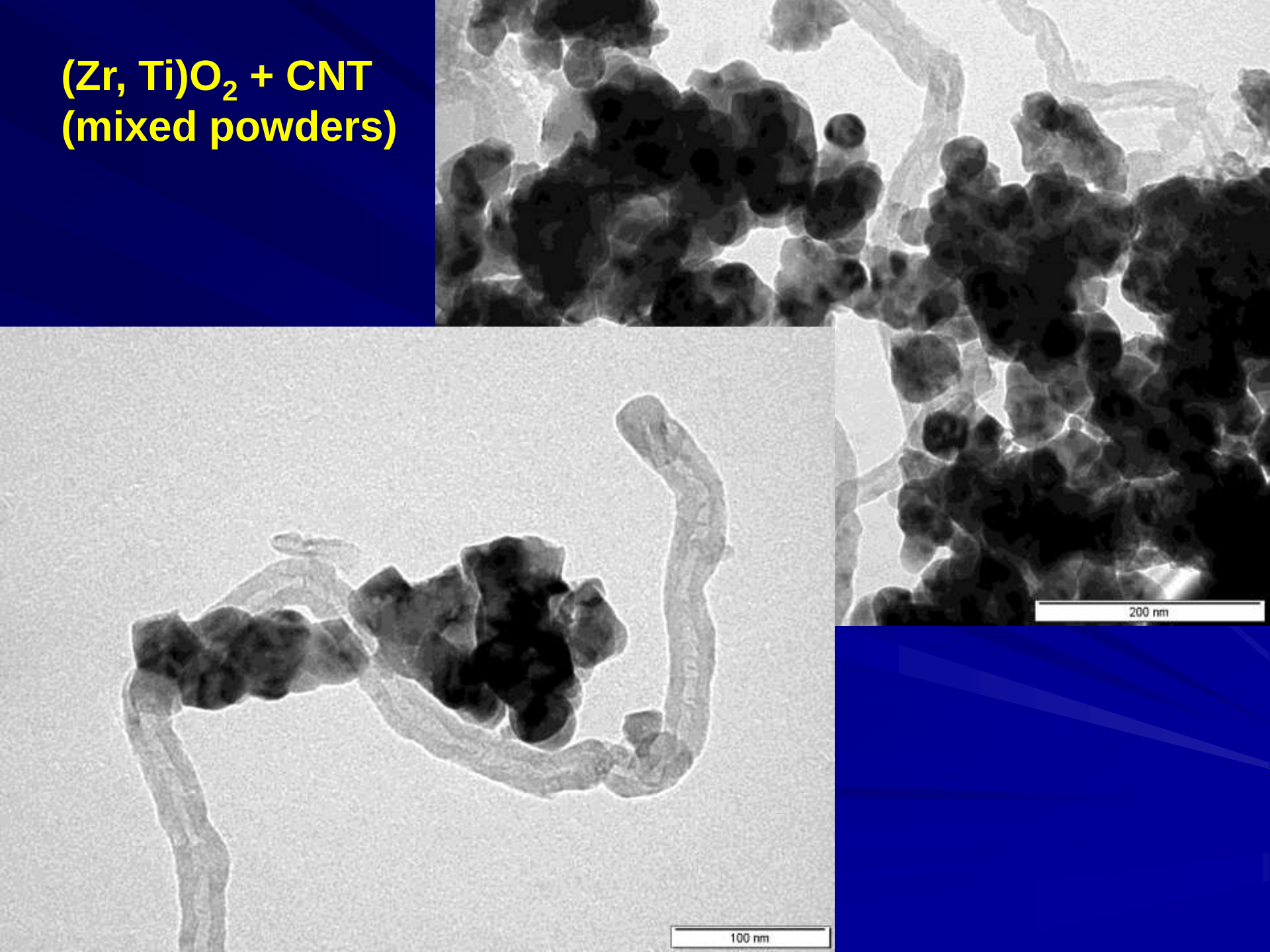
Available online 3 December 2007

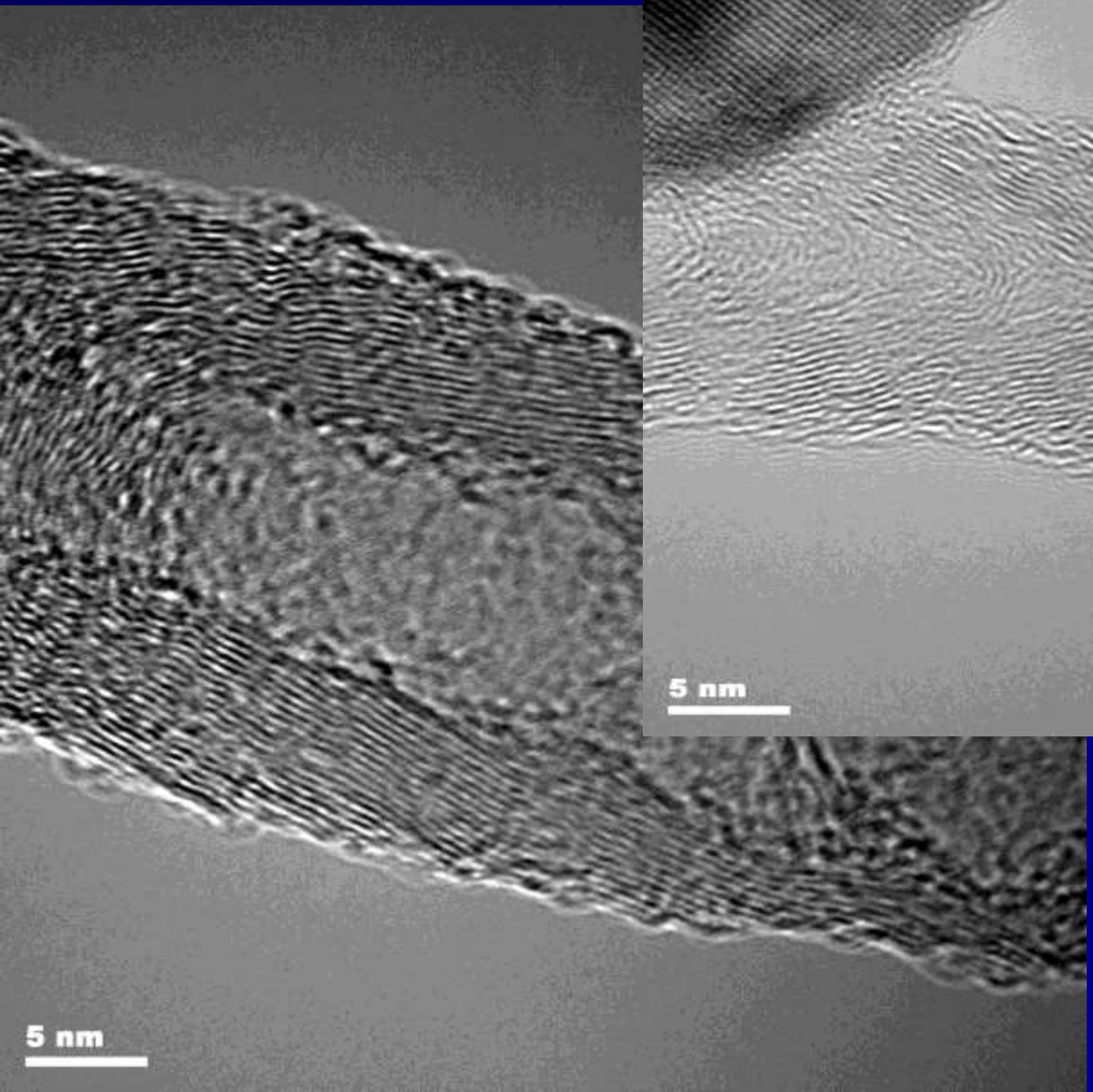
The effect of the addition of carbon nanofibers (CNFs) on the microstructure, fracture/mechanical and electrical properties of the CNF/zirconia composite has been investigated. The microstructure of both $ZrO_2$ and $ZrO_2$–CNF composites consists of a very low grain sized matrix (approximately 160 nm) with relatively well dispersed carbon nanofibers in the composite. The mechanical properties slightly decreased after the addition of CNFs to the $ZrO_2$ but the electrical resistivity decreased significantly, exhibiting approximately 0.1 Ω cm.

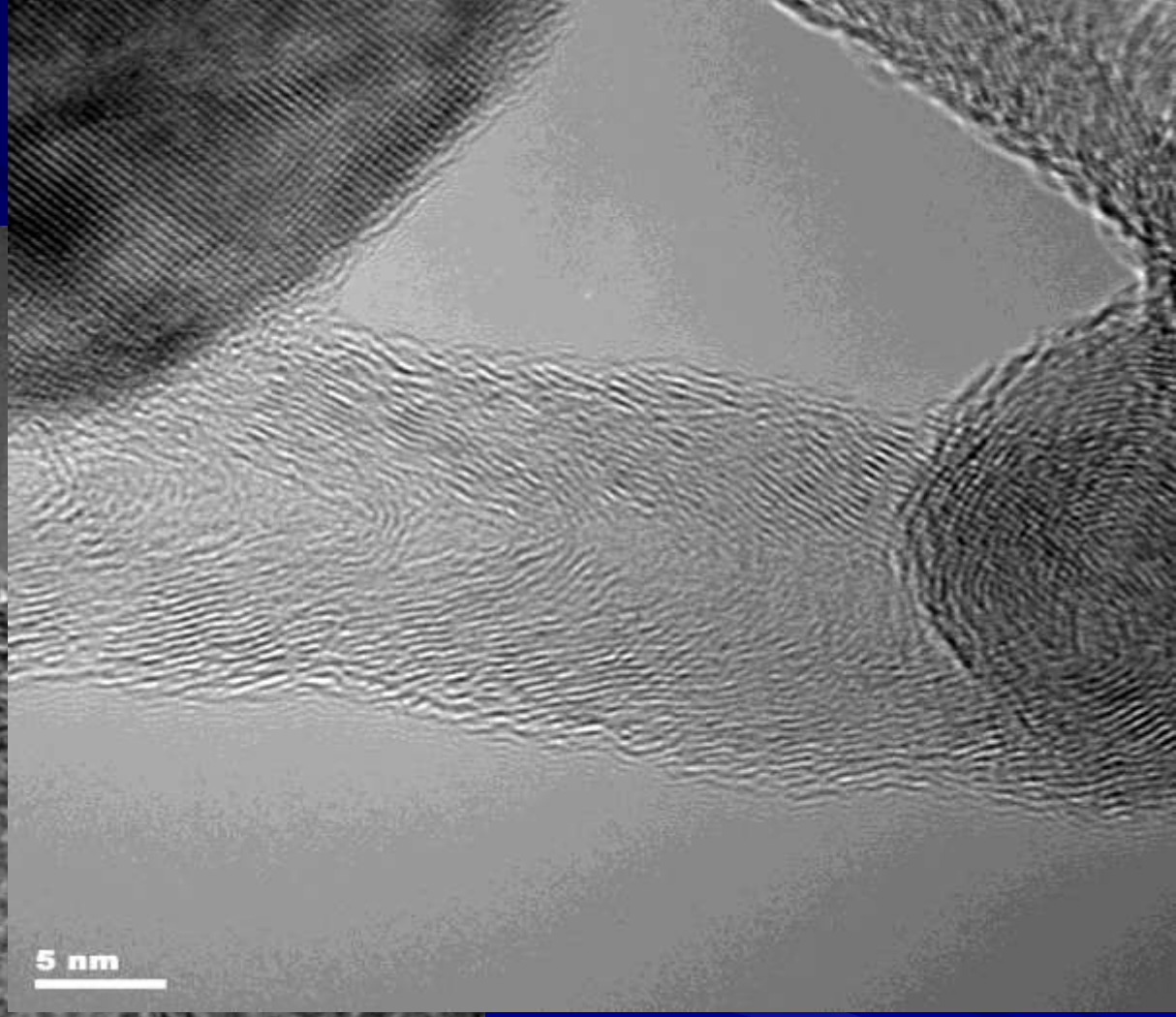

*Keywords:* 3Y-TZP; Carbon nanofiber; Microstructure; Fracture; Electrical resistivity

# $(Zr, Ti)O_2$ + CNT (mixed powders)

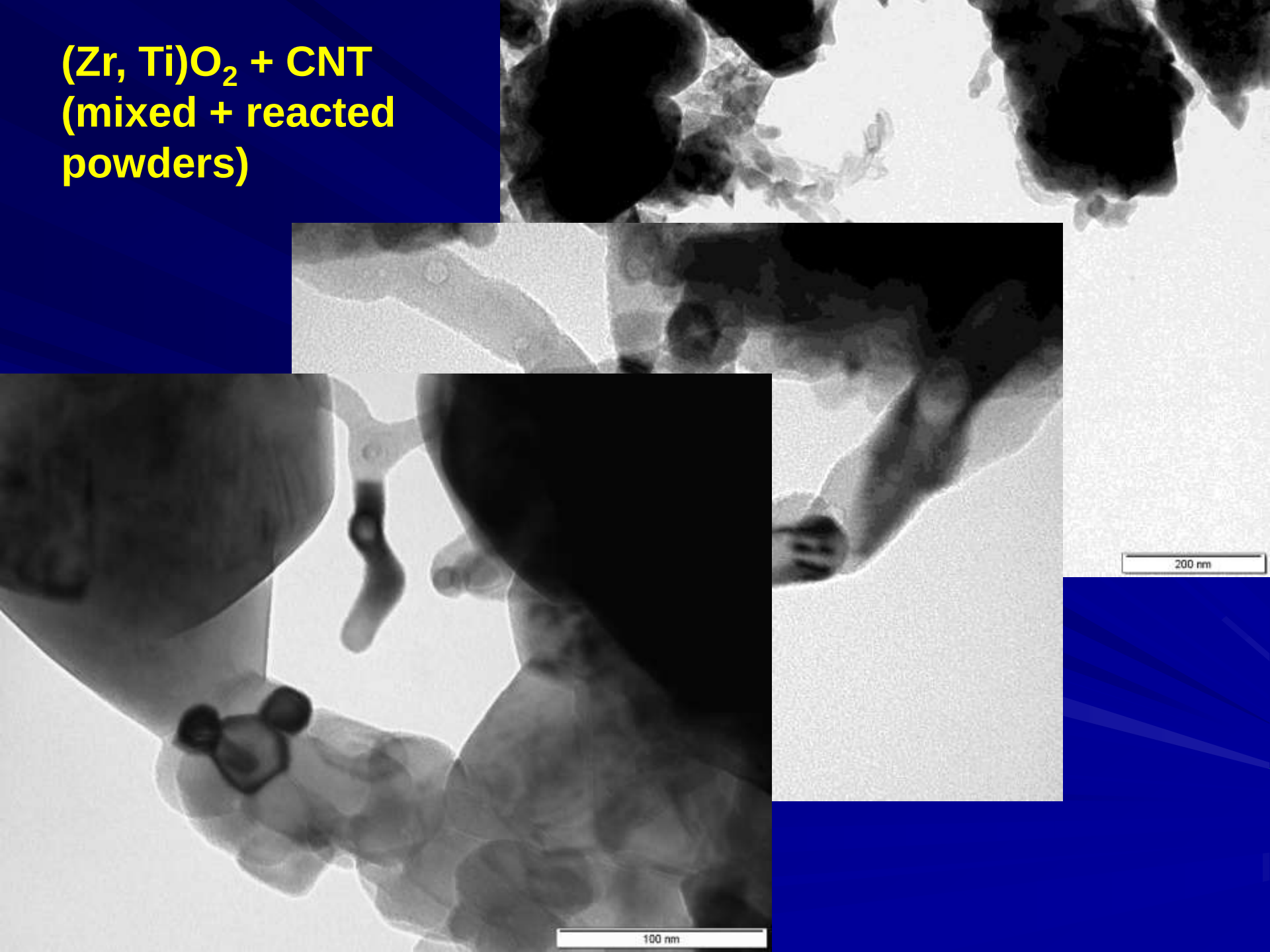


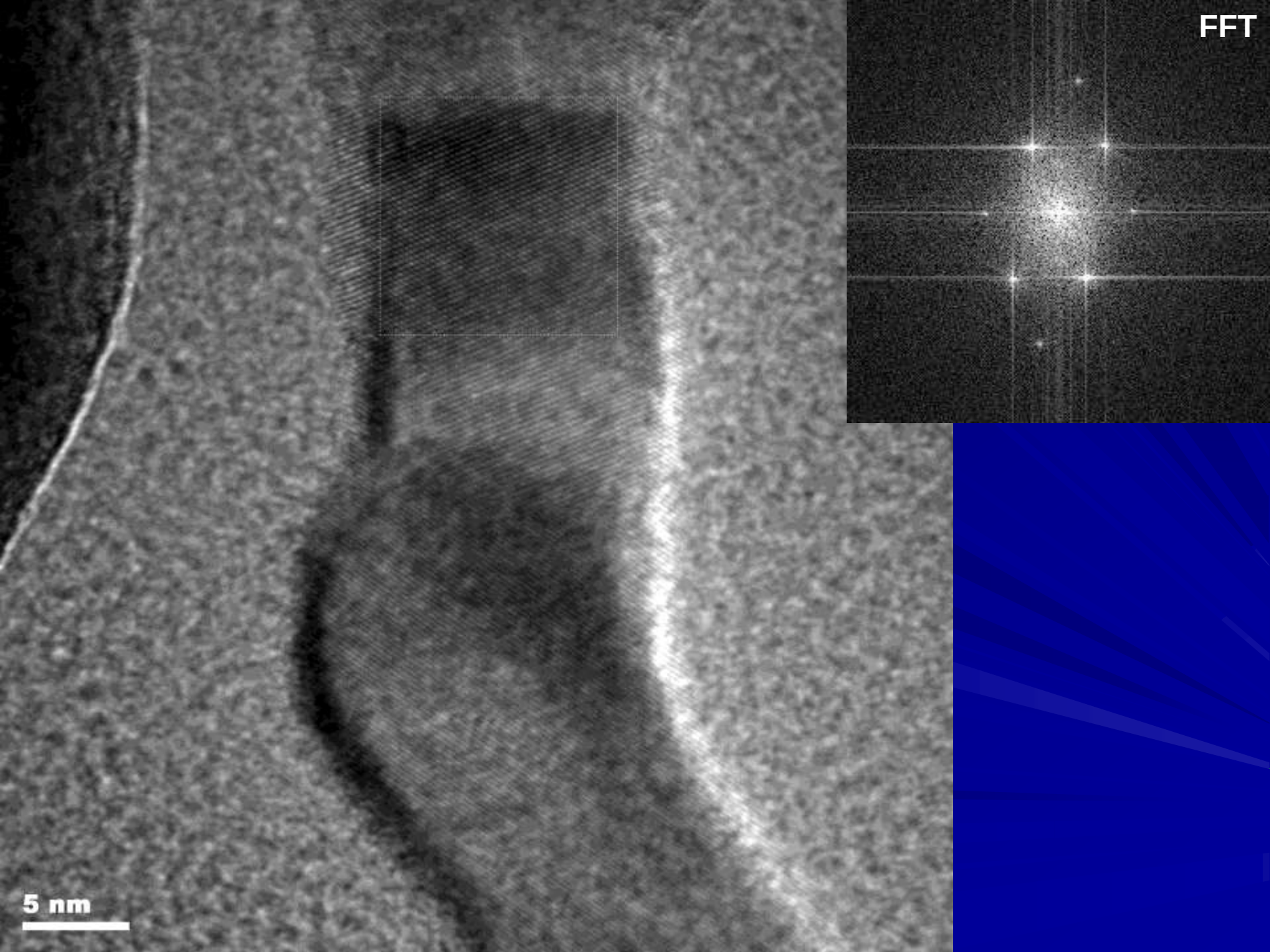
# $(Zr, Ti)O_2$ + CNT (mixed powders)

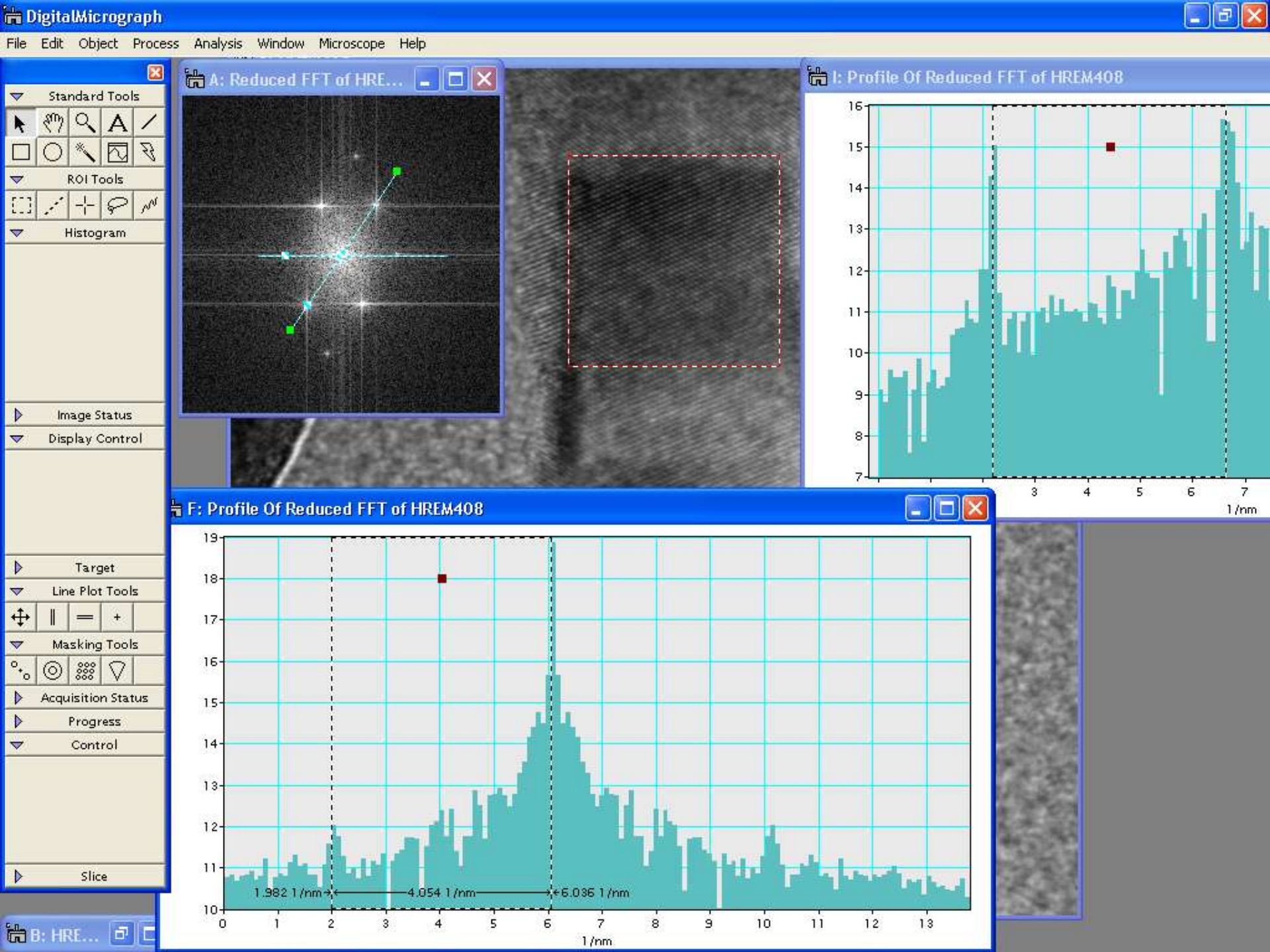


# $(Zr, Ti)O_2$ + CNT (mixed + reacted powders)




FFT
5 nm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Target
Line Plot Tools
Masking Tools
Acquisition Status
Progress
Control
Slice
A: Reduced FFT of HRE...
I: Profile Of Reduced FFT of HREM408
1/nm
F: Profile Of Reduced FFT of HREM408
1.982 1/nm
4.054 1/nm
6.036 1/nm
1/nm
B: HRE...

CaRIne 3.0

File Edit Cell hkl/uvw Calcul. Specials Crystal View Window ?

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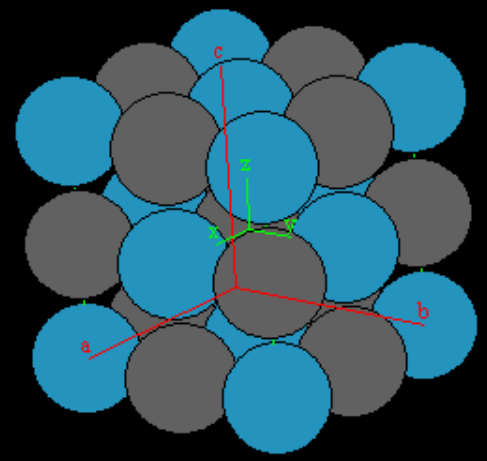


x'n 137.30 y'n 126.65 z'n 108.77 Cmd None Nb 8 a 4.3 b 4.3 c 4.3 α 90.0 β 90.0 γ 90.0 Sy

## Identification of Planes

V : (kV)

λ : (Å)

L : (cm)

K : (cm.Å)

r1 (cm)

r2 (cm)

d1 2.5 (Å)

d2 : 2.27 (Å)

α 56.2 (°)

| (hkl)#1 | (hkl)#2 | dhkl1 | dhkl2 | Angle(°) | E(%) | Zone axis |
|---|---|---|---|---|---|---|
| 1,-1,1 | 2,0,0 | 2.49 | 2.16 | 54.74 | 7.8 | 0,1,1 |
| 1,1,1 | 2,0,0 | 2.49 | 2.16 | 54.74 | 7.8 | 0,1,-1 |
| 1,-1,1 | 0,0,2 | 2.49 | 2.16 | 54.74 | 7.8 | 1,1,0 |
| 1,-1,-1 | 2,0,0 | 2.49 | 2.16 | 54.74 | 7.8 | 0,-1,1 |
| 1,1,1 | 0,0,2 | 2.49 | 2.16 | 54.74 | 7.8 | 1,-1,0 |
| 1,1,1 | 0,2,0 | 2.49 | 2.16 | 54.74 | 7.8 | -1,0,1 |
| 1,1,-1 | 0,2,0 | 2.49 | 2.16 | 54.74 | 7.8 | 1,0,1 |
| 1,1,-1 | 2,0,0 | 2.49 | 2.16 | 54.74 | 7.8 | 0,1,1 |
| 0,2,0 | 1,1,-1 | 2.16 | 2.49 | 54.74 | 26.1 | 1,0,1 |
| 2,0,0 | 1,1,1 | 2.16 | 2.49 | 54.74 | 26.1 | 0,-1,1 |
| 2,0,0 | 1,-1,1 | 2.16 | 2.49 | 54.74 | 26.1 | 0,1,1 |
| 2,0,0 | 1,-1,-1 | 2.16 | 2.49 | 54.74 | 26.1 | 0,1,-1 |
| 2,0,0 | 1,1,-1 | 2.16 | 2.49 | 54.74 | 26.1 | 0,1,1 |
| 0,0,2 | 1,1,1 | 2.16 | 2.49 | 54.74 | 26.1 | -1,1,0 |
| 0,2,0 | 1,1,1 | 2.16 | 2.49 | 54.74 | 26.1 | 1,0,-1 |
| 0,0,2 | 1,-1,1 | 2.16 | 2.49 | 54.74 | 26.1 | 1,1,0 |

Compute Print -> ASCII Help Close

Crystal

Rotations

Keyboar Control

Ster. Proj

ES Vision - Jurek - [Acquisition Window (1) - E:\JM_TECNAI\2007_KMM-NoE\AGH_C-tube+n-cryst_powder\ZrO2+CNT_reacted\STEM\STEM1+.emi]

File Edit View Display Acquire Process Tools Window Help

Normal Image Display

Markers

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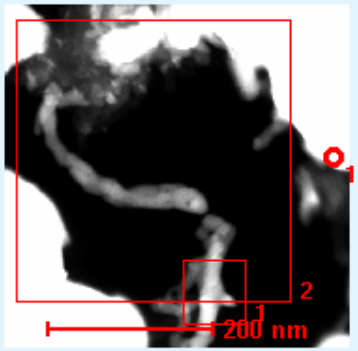
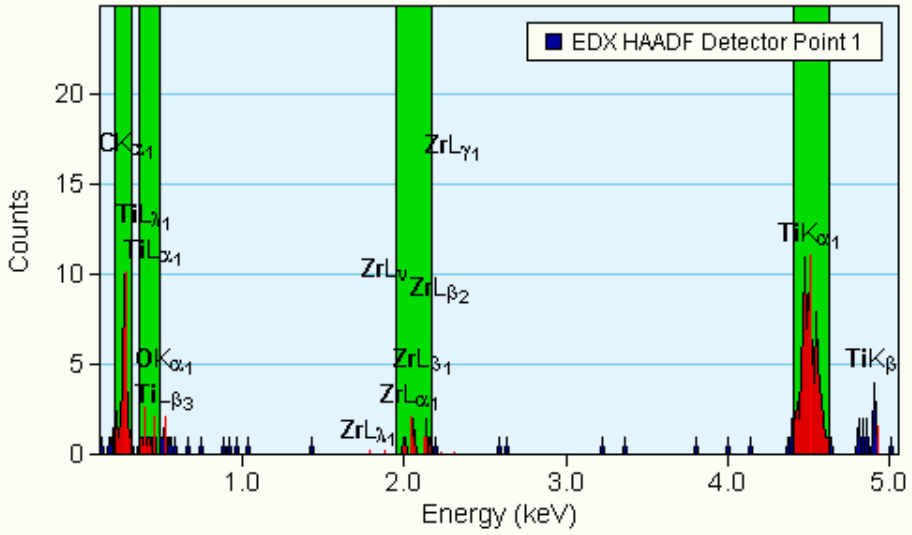
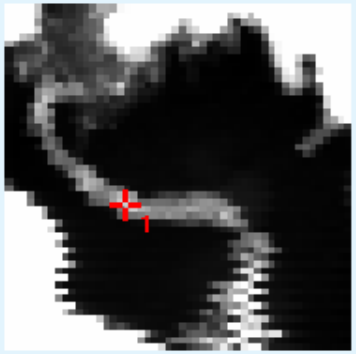
HAADF Detector



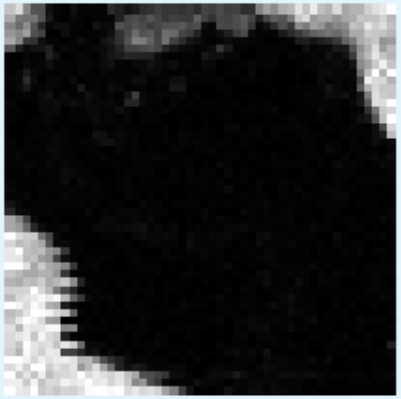

EDX HAADF Detector Point 1



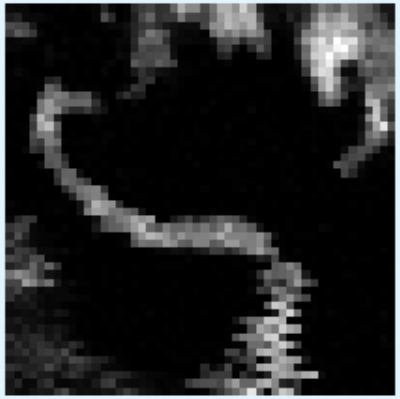

STEM HAADF Detector




Zr_La

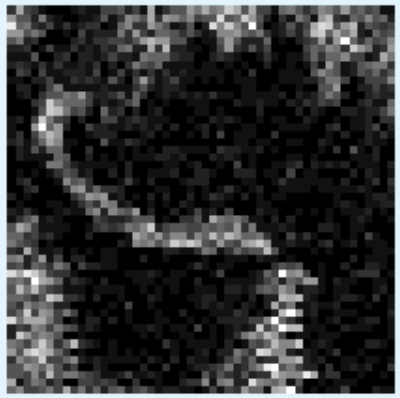


Ti_Ka



C_Ka

O_Ka + Ti_La



Ready