# Transmission Electron Microscopy: from the principles to the opportunity for analysis of catalytic materials

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# Transmission Electron Microscopy: from the principles to the opportunity for analysis of catalytic materials

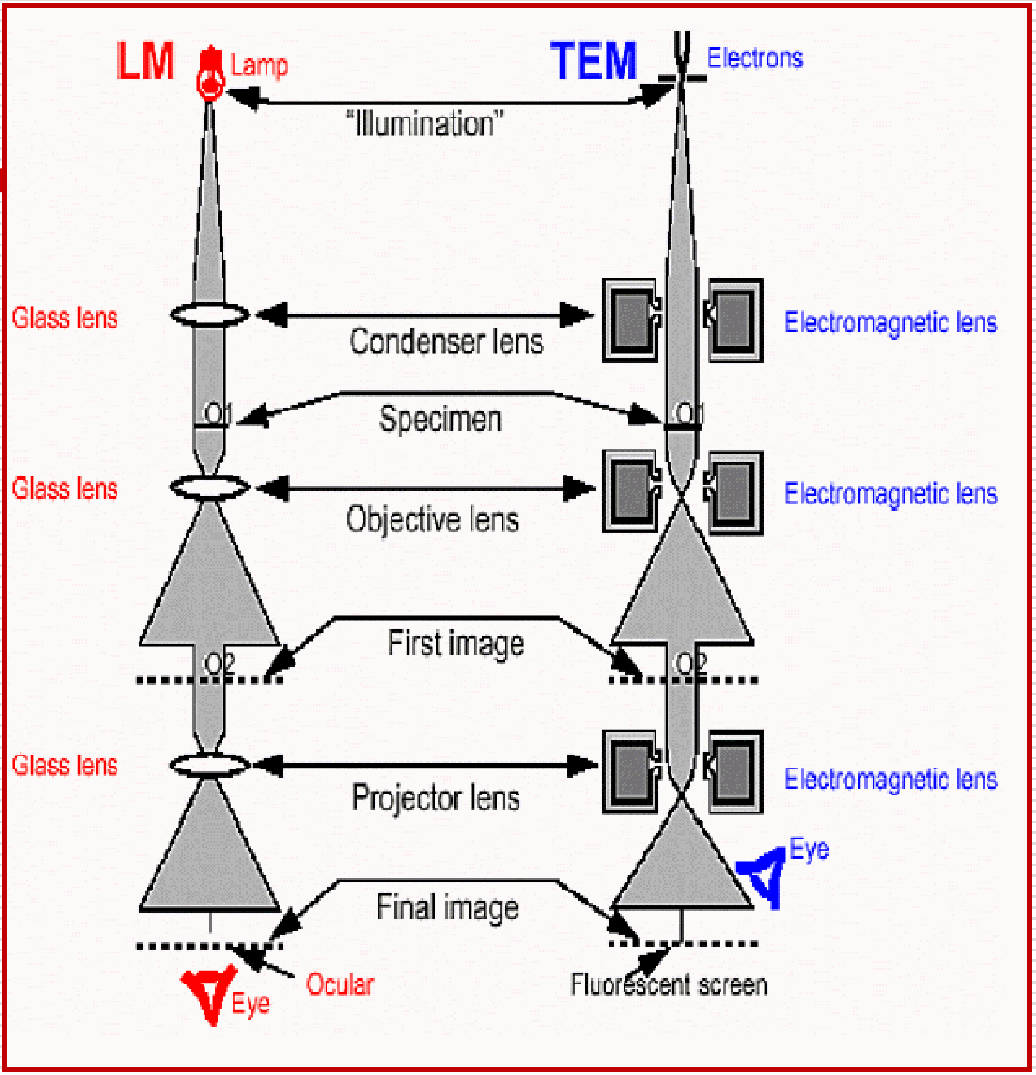
Outline

1. Aim – “Why TEM is useful?”
2. Historical remarks
3. Physical principles of TEM
4. Examples from the practice in LTEM – IOMT&IGIC
5. Examples from references
6. Conclusion

# Transmission Electron Microscopy (TEM) is a modern microscopic technique for visualization of the matter structure at micro- and nano- level down to **atomic resolution**

Simple and complete analogy with optical transmission microscopy except the radiation

- The transmitted electron beam is used to form an image of the sample structure.
- This beam contains information about electron density, phase and periodicity of the structure studied.



# Historical background

1933 – the first transmission electron microscope with magnification greater than that of optical microscopy (around 12 000x) was created by Max Knoll and Ernst Ruska

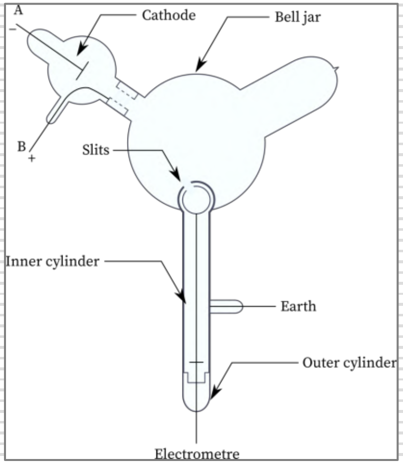
The first practical TEM, now on display at the Deutsches Museum in Munich, Germany

File:Ernst Ruska Electron Microscope - Deutsches Museum - Munich-edit.jpg

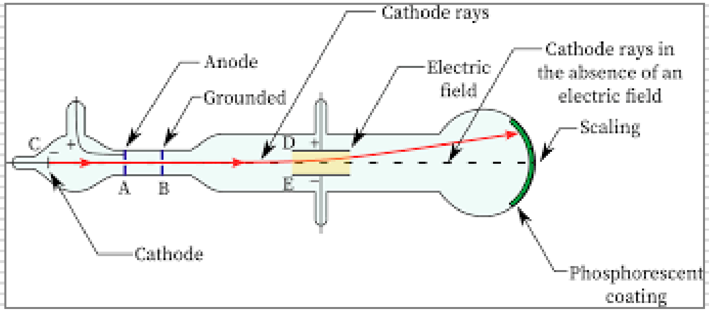
Main prerequisites for this invention:

- Discovery of electrons by J.J.Thomson

(*Sir Joseph John Thomson*) in 1897 in cathode-rays tube (Crookes–Hittorf tube) experiments



Nobel prize in physics 1906



https://chemistrygod.com/cathode-ray-tube-experiments

## Historical background

- second prerequisite

• The proposed by Louis De Broglie in 1924 hypothesis for the wave nature of the electrons, which were considered charged matter particles [*L. Broglie "La nouvelle dynamique des quanta", Électrons et Photons: Rapports et Discussions du Cinquième Conseil de Physique (1928) Solvay.*]

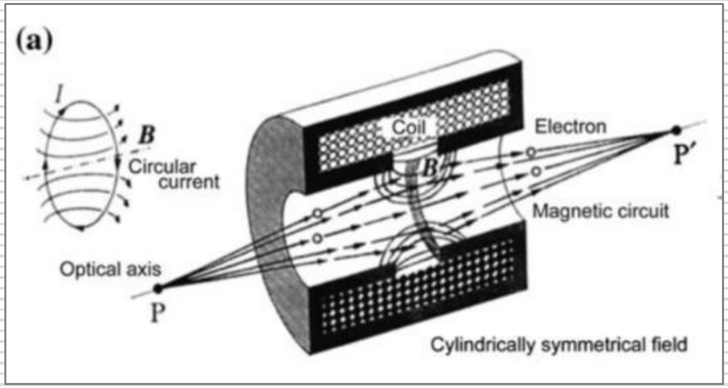
It is an example of wave–particle duality, and forms a central part of the theory of quantum mechanics.

Nobel Prize in Physics
1929

# Historical background

- third prerequisite

- The invention of the electromagnetic lenses in 1926 by Hans Busch. He was a pioneer of electron optics and laid the theoretical basis for the electron microscope.



Patent for electron microscopy in 1928

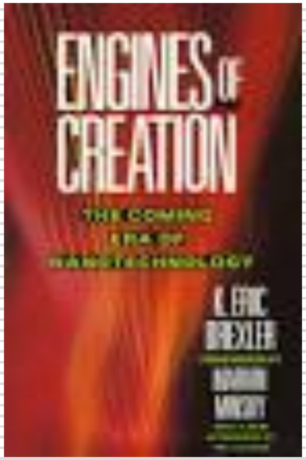
Electron Nano-Imaging: Basics of Imaging and Diffraction for TEM and STEM, Nobuo Tanaka

# Historical background

1986 - Nobel Price in Physics for Ernst Ruska in conjunction with Heinrich Rohrer and Gerd Binnig for the development of the scanning tunneling microscope (STM)

https://www.icollector.com/Ernst-Ruska_i20871160#

In 1986 Kim Eric Drexler used the term "nanotechnology"
in his book *Engines of Creation: The Coming Era of Nanotechnology.*



- up to now – the nanomaterials and nanotechnology have been developed and the importance of TEM has grown continuously
- the TEM microscopes are improved substantially – field emission guns (FEGc), aberration correction, quantitative HAADF STEM, high-energy resolution spectroscopy analysis in STEM
- new, ultra high-speed video cameras
- in-situ experiments – microfluidic devices
- tomography and three-dimensional reconstruction from two-dimensional projected images and the real-time recording

# Laboratory “Transmission Electron Microscopy” (LTEM) – IOMT&IGIC - BAS

## 2009 - JEOL JEM 2100

Main parameters: accelerating voltage: 80 - 200 kV, maximal magnification: 1 500 000x, resolution between two points 0.23 nm

Main regimes: Bright field (BF), Dark field (DF) and High resolution (HR) TEM,

Selected area electron diffraction (SAED), Nano-beam diffraction (NBD) and Converged beam electron diffraction (CBED)

## 2015 – JEOL STEM unit and CCD camera

GATAN Orius 832 under the project BG161PO003-1.2.04-0034-C0001

Increase of magnification to 2 000 000x

The microscopes, optical or electronic possess two important characteristics:

- Magnification – the ratio between the sizes of the image and the object
- Resolution – $d = \lambda/2n\sin\alpha$,

$\lambda$ is the wavelength of the photons that are being used to probe the sample,

$2n\sin\alpha = NA$ numerical aperture of the system (n – refractive index of the medium, $\alpha$ - semi-angle of collection of the magnifying lens)

**De Broglie equation:**

$\lambda = h / p$

$\lambda = h / [2m_0eV (1 + eV/2m_0c^2)]^{1/2}$

Rest mass of an electron: $m_0 = 9.109 \times 10^{-31}$ kg

Speed of light in vacuum: $c = 2.998 \times 10^{8}$ m/s

Planck constant: $h = 6.626 \times 10^{-34}$ J.s

| $V_{acc}$ / kV | Relativistic wavelength / pm | Mass x $m_0$ | Velocity x $10^8$ m/s |
|---|---|---|---|
| 100 | 3.70 | 1.20 | 1.64 |
| 200 | 2.51 | 1.39 | 2.09 |
| 300 | 1.97 | 1.59 | 2.33 |
| 400 | 1.64 | 1.78 | 2.48 |
| 1000 | 0.87 | 2.96 | 2.82 |

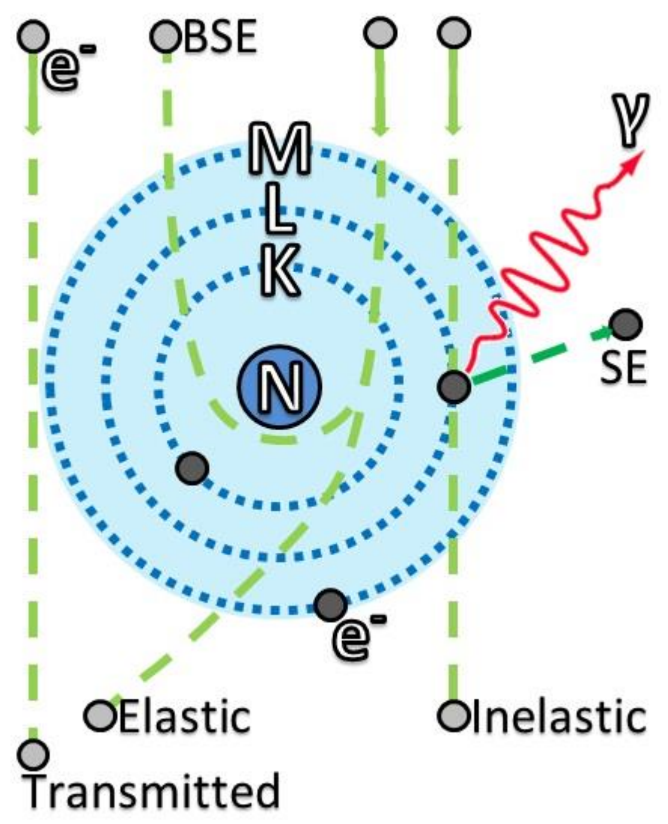
$\lambda = 400 – 700$ nm – visible light

**$d_e/d_{light} = 6.27 \times 10^{-6}$**

# TEM principle: the same as of the light microscope, except that the radiation is different

## electron – matter interraction:

**single atom case**



Elastic scattering of the electron

$\Delta E = 0$

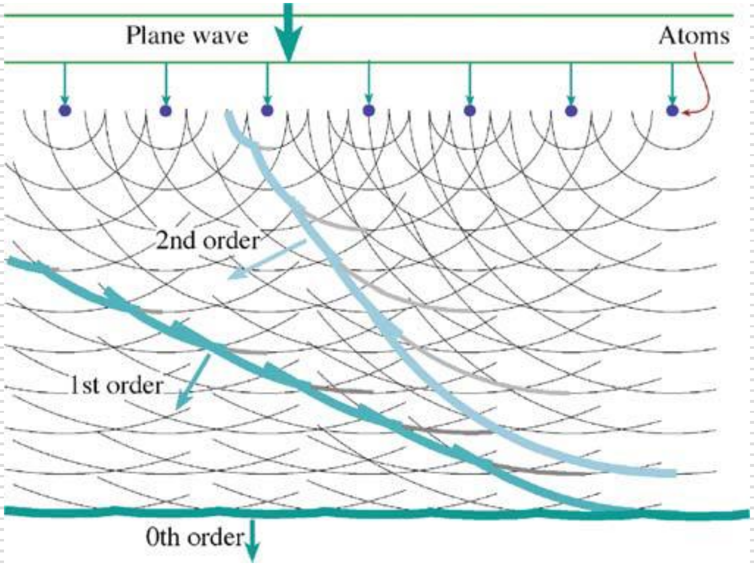
Inelastic scattering of the electron

$\Delta E < 0$

Transmission Electron Microscopy. A Textbook for Materials Science,
David B. Williams and C. Barry Carter
Springer ScienceюBusiness Media, LLC 1996, 2009

# electron – matter interraction:

## **thin foil case**

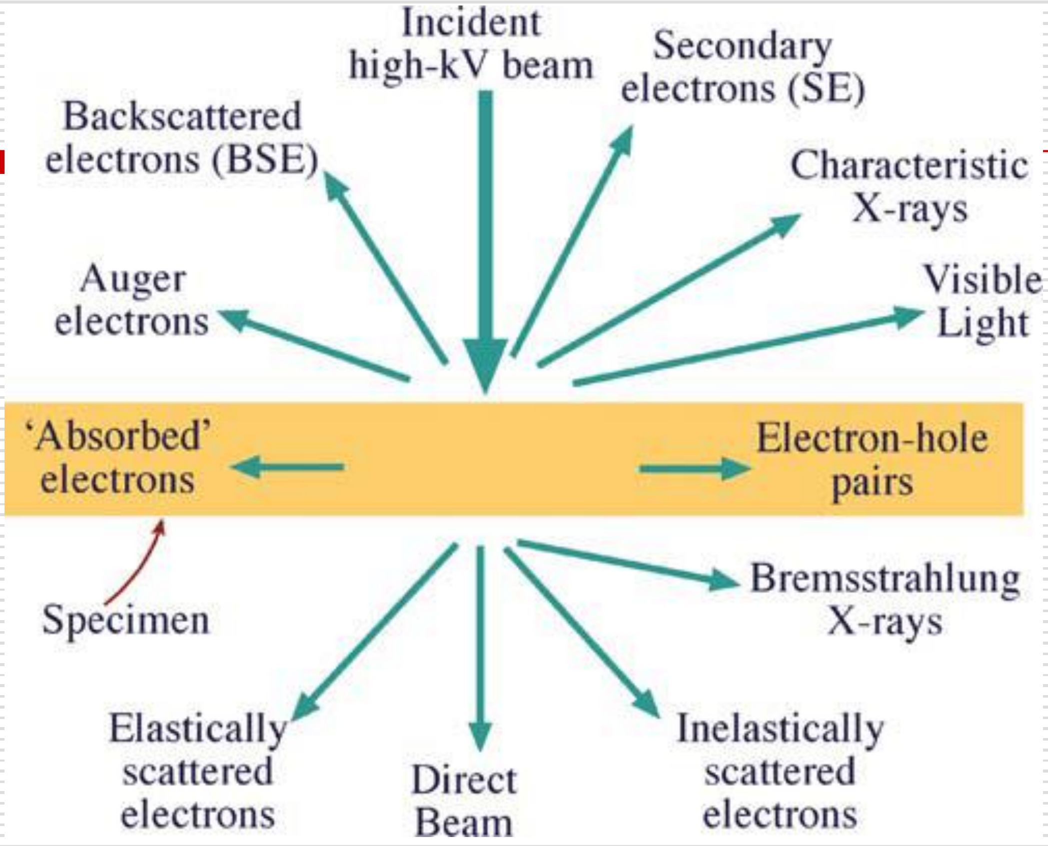


A plane, coherent electron wave generates secondary wavelets from a row of scattering centers (e.g., atoms in the specimen).
The secondary wavelets interfere, resulting in a strong direct (zero order) beam and several (higher order) coherent beams scattered (diffracted) at specific angles.

Transmission Electron Microscopy. A Textbook for Materials Science,
David B. Williams and C. Barry Carter
Springer ScienceюBusiness Media, LLC 1996, 2009

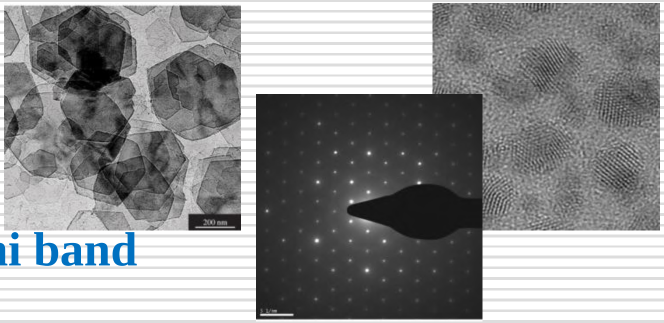
# signals received by

# electron – matter interraction

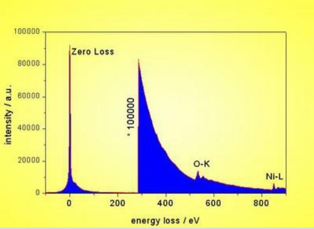


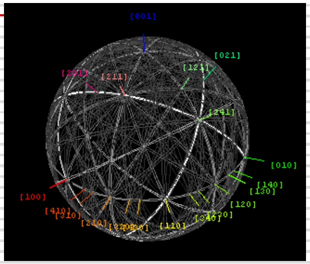
Transmission Electron Microscopy. A Textbook for Materials Science,
David B. Williams and C. Barry Carter
Springer SciencелBusiness Media, LLC 1996, 2009

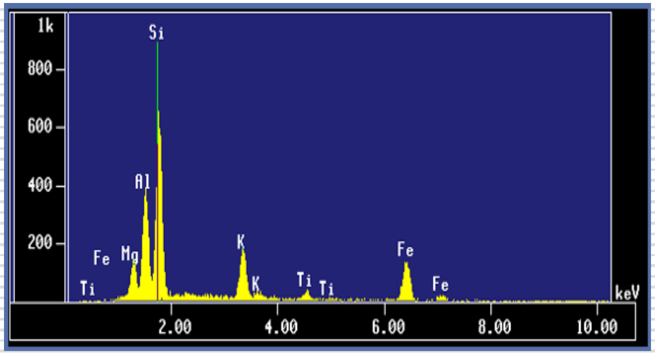
# Use of the signals in EM (TEM, SEM, AEM)

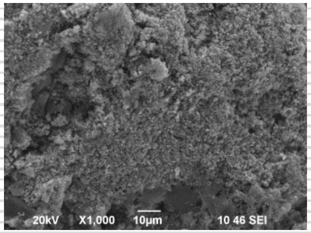


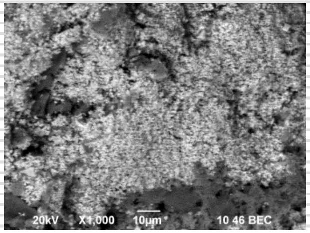
| | |
|---|---|
| thin section | **Unscattered Electrons – BF TEM**<br>**Elasticity Scattered electrons – DF, DP, HRTEM**<br>**Inelastically Scattered Electrons – EELS, Kikuchi band** |
| bulk specimen | **Secondary Electrons – SEM**<br>**Backscattered electrons – SEM, EBSD** |
| analytical tools | **X-rays - EDS**<br>**Auger Electrons - AES** |
| other techniques | Electron-holes creation<br>Cathodoluminescence<br>Interaction with plasmons |
| negative effects | Electron absorption<br>– atom displacement ("knock on")<br>– chemical bound braking<br>– charge collective oscillation excitation (plasmons)<br>– lattice atom vibrations (phonons)<br>– excitation of surface electronic level (transition valence/conduction,…)<br>– Bremsstrahlung radiation |



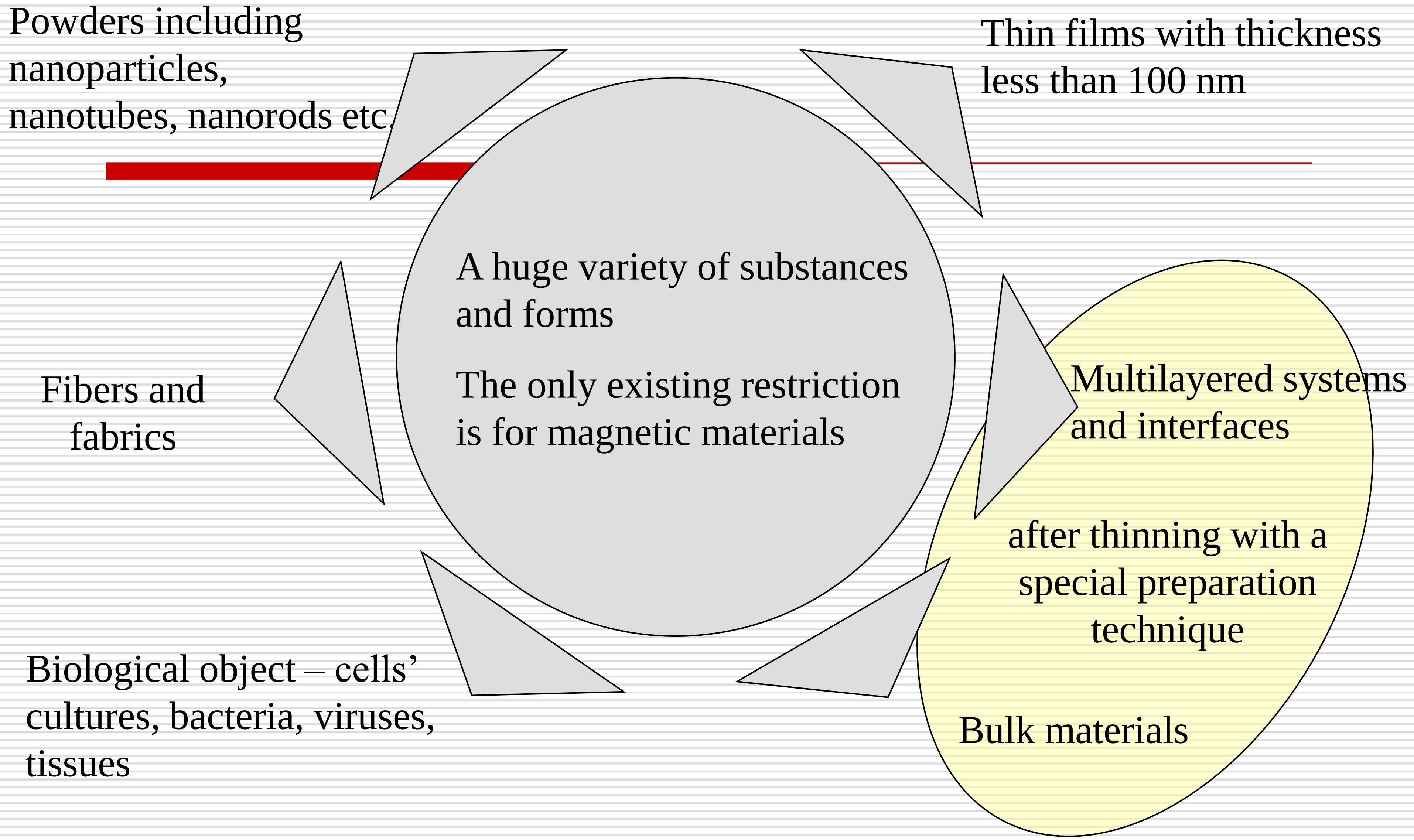








# Possible samples for TEM study



Powders including nanoparticles, nanotubes, nanorods etc.

Thin films with thickness less than 100 nm

A huge variety of substances and forms

The only existing restriction is for magnetic materials

Fibers and fabrics

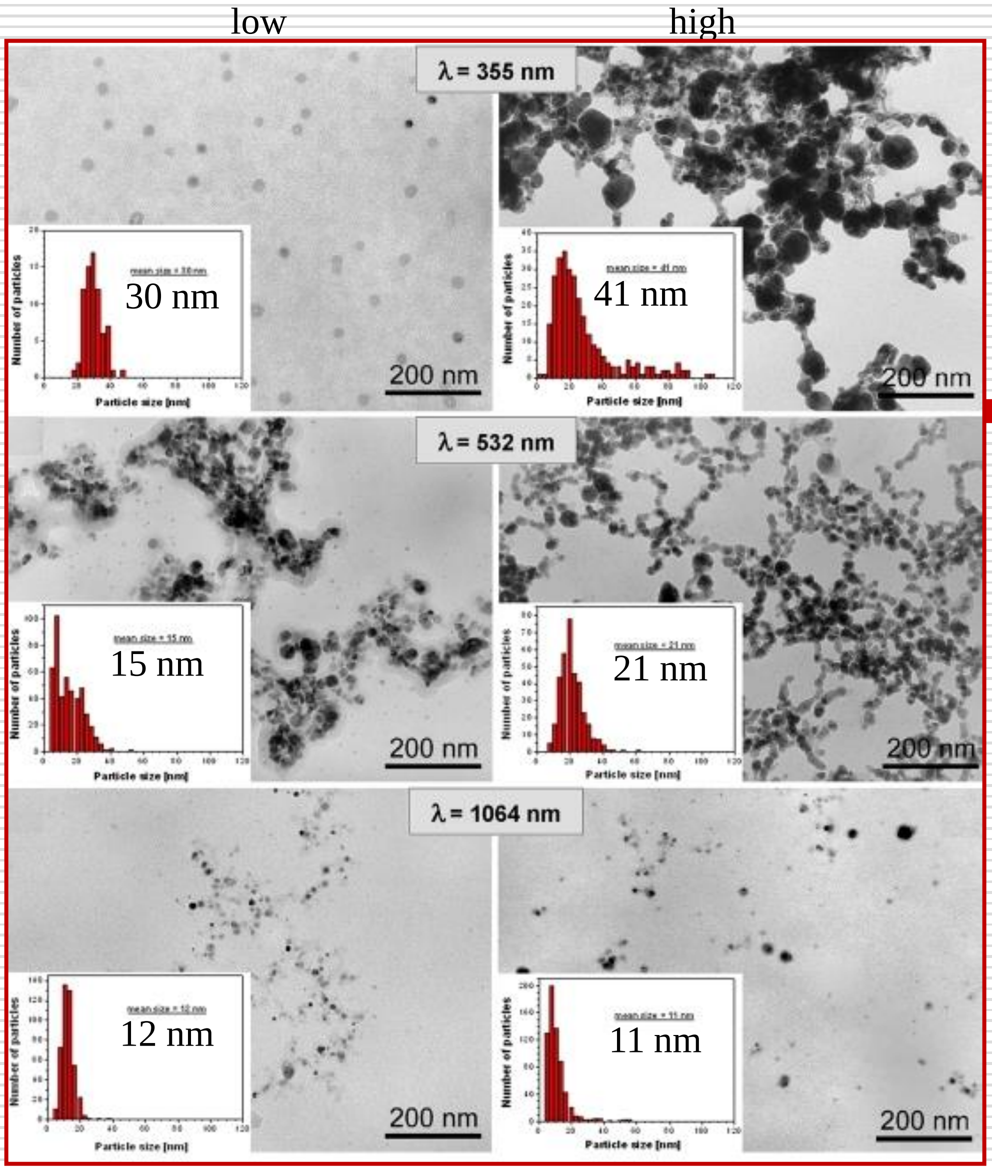
Multilayered systems and interfaces

after thinning with a special preparation technique

Bulk materials

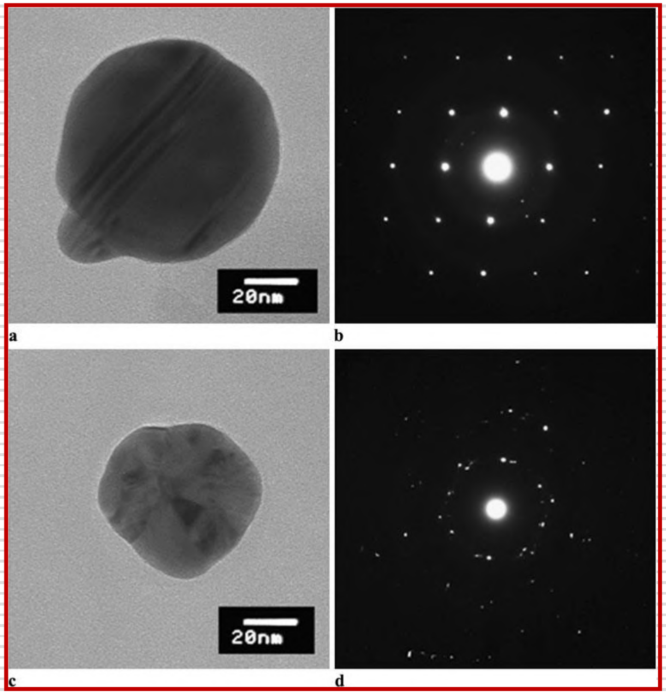
Biological object – cells’ cultures, bacteria, viruses, tissues

# Example 1: Metal and metal alloys nanoparticles and nanostructures



- **Formation of Ag nanosphere or sphere-like nanoparticles by pulse laser ablation (PLA) in water**

TEM micrographs of the colloids prepared at different wavelengths (355, 532 and 1 064 nm) and two values of the laser fluence

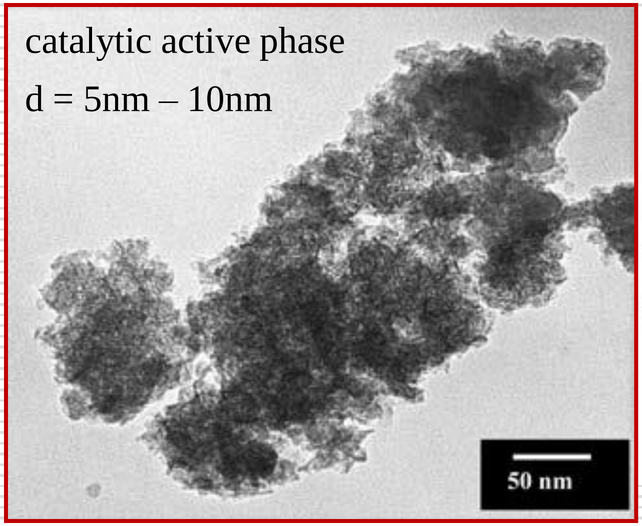


A.S. Nikolov, N.N. Nedyalkov, R.G. Nikov, P.A. Atanasov, M.T. Alexandrov, D.B. Karashanova, “Investigation of Ag nanoparticles produced by nanosecond pulsed laser ablation in water”,
Appl Phys A (2012) 109:315–322 DOI 10.1007/s00339-012-7094-0

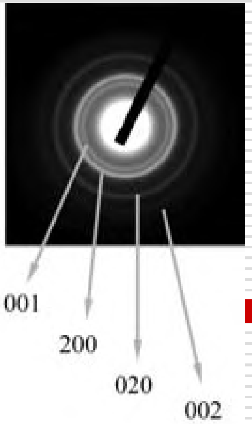
# New catalytic materials for heterogeneous catalysis: supported catalysts and single atom catalysts (SACs) – role of the modern S(TEM)s.

- Heterogeneous catalytic reactions occur primarily on the surface and interface.
- When the size of the nanoparticles dispersed on support materials decreases, this increases the exposed surface and could provide more active sites for catalytic reactions.
- The dispersion of active material under the form of nanomaterial reduces the amount of costly materials being used, bringing economic benefits.
- In the case of supported catalysts XRD method usually can’t provide an information for the active phases, because of their small dimensions and quantities and du to the method limitations.

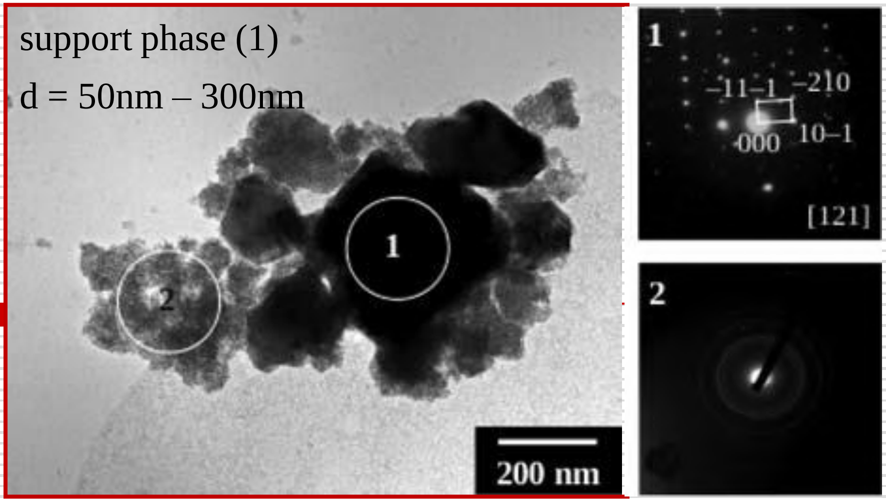
# Example 2: Catalist: NiOx/ZrO2 for oxidation of phenol


catalytic active phase

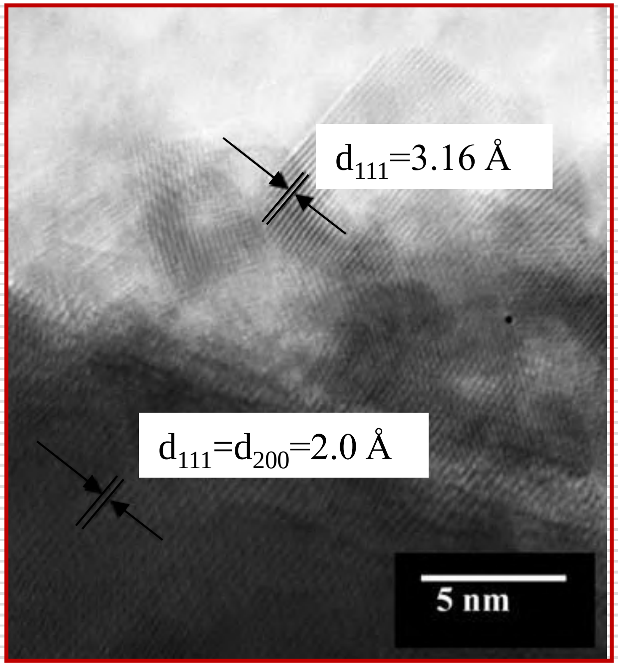
d = 5nm – 10nm



monoclinic $Ni_{15}O_{16}$ phase [PDF 72-1464]


support phase (1)

d = 50nm – 300nm



TEM micrograph of the fresh catalytic system $NiO_x/ZrO_2$ and the corresponding SAED for the two areas

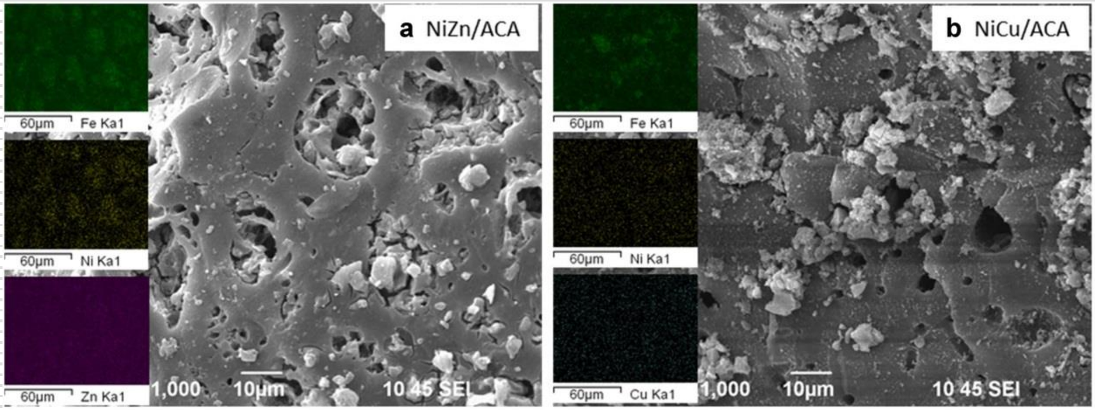
(1) Monoclinic $ZrO_2$ [PDF 37–1484], directed to the zone axis [121]

(2) Monoclinic $Ni_{15}O_{16}$ [PDF 72-1464]

Authors have been guided by the main requirements for low-temperature environmental catalysts for complete oxidation of organic compounds under ambient conditions.

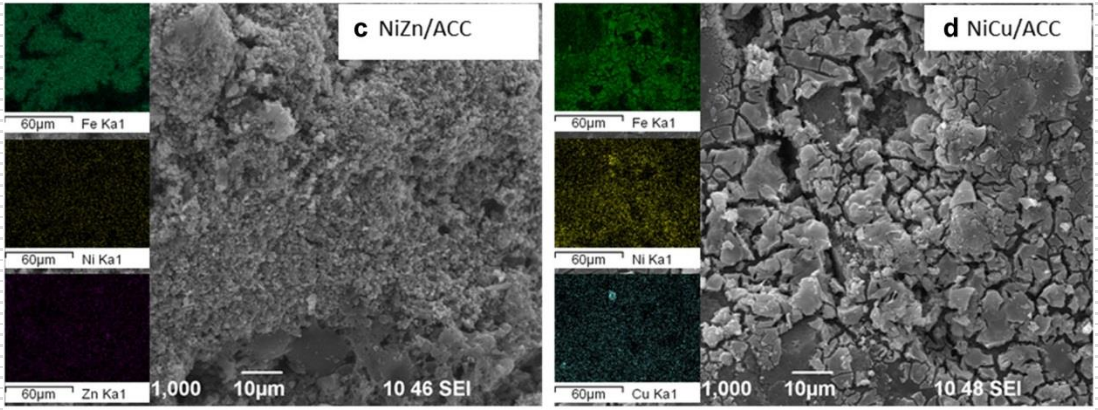
D.Petrov, S.Christoskova, M.Stoyanova,V.Ivanova and D.Karashanova, “Preparation, Characterization and Catalytic Activity of NiOx and $NiO_x/ZrO_2$ for Oxidation of Phenol in Aqueous Solution”, *Acta Chim. Slov.* 2014, *61*, 759–770

# Example 3: Catalist: $Ni_{0.5}M_{0.5}$(M=Cu, Zn)Ferite/AC for hydrogen production



| Element | Fe | Ni | Zn | O | C |
|---|---|---|---|---|---|
| Weight | 21.47 | 6.27 | 7.20 | 20.61 | 44.46 |

| Element | Fe | Ni | Cu | O | C |
|---|---|---|---|---|---|
| Weight | 31.24 | 3.24 | 1.64 | 17.58 | 45.89 |



| Element | Fe | Ni | Zn | O | C |
|---|---|---|---|---|---|
| Weight | 38.93 | 1.91 | 4.28 | 27.90 | 26.99 |

| Element | Fe | Ni | Cu | O | C |
|---|---|---|---|---|---|
| Weight | 20.98 | 4.08 | 5.94 | 25.13 | 43.33 |

- SEM micrographs of NiZn/ACA (**a**), NiCu/ACA (**b**), NiZn/ACC (**c**) and NiCu/ACC (**d**) samples.

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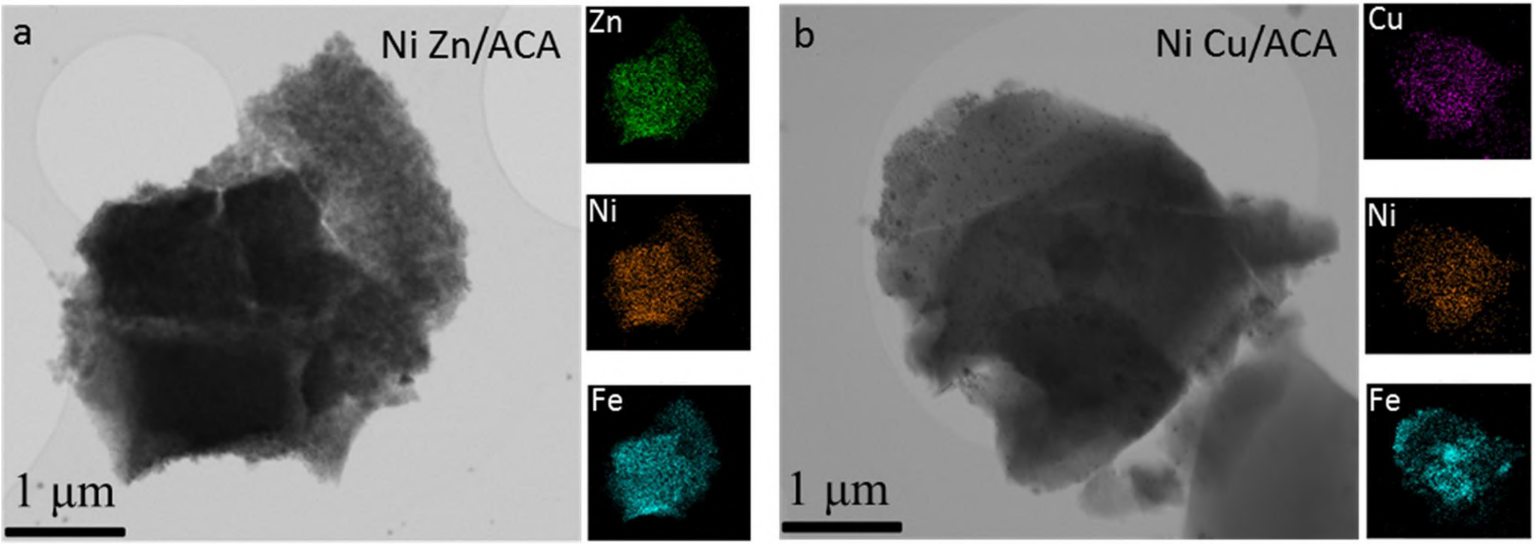
- Elemental mappings for Fe, Zn, Ni and Cu in different colors
- Elemental composition

Tanya Tsoncheva, Ivanka Spassova, Gloria Issa, Radostina Ivanova, Daniela Kovacheva, Daniela Paneva, Daniela Karashanova, Nikolay Velinov, Boiko Tsyntsarski, Biliana Georgieva, Momtchil Dimitrov, Nartzislav Petrov, “Ni0.5M0.5Fe2O4 (M = Cu, Zn) Ferrites Hosted in Nanoporous Carbon from Waste Materials as Catalysts for Hydrogen Production”,

Waste and Biomass Valorization

https://doi.org/10.1007/s12649-020-01094-2

## Example 3: Catalist: $Ni_{0.5}M_{0.5}$(M=Cu, Zn)Ferite/AC for hydrogen production

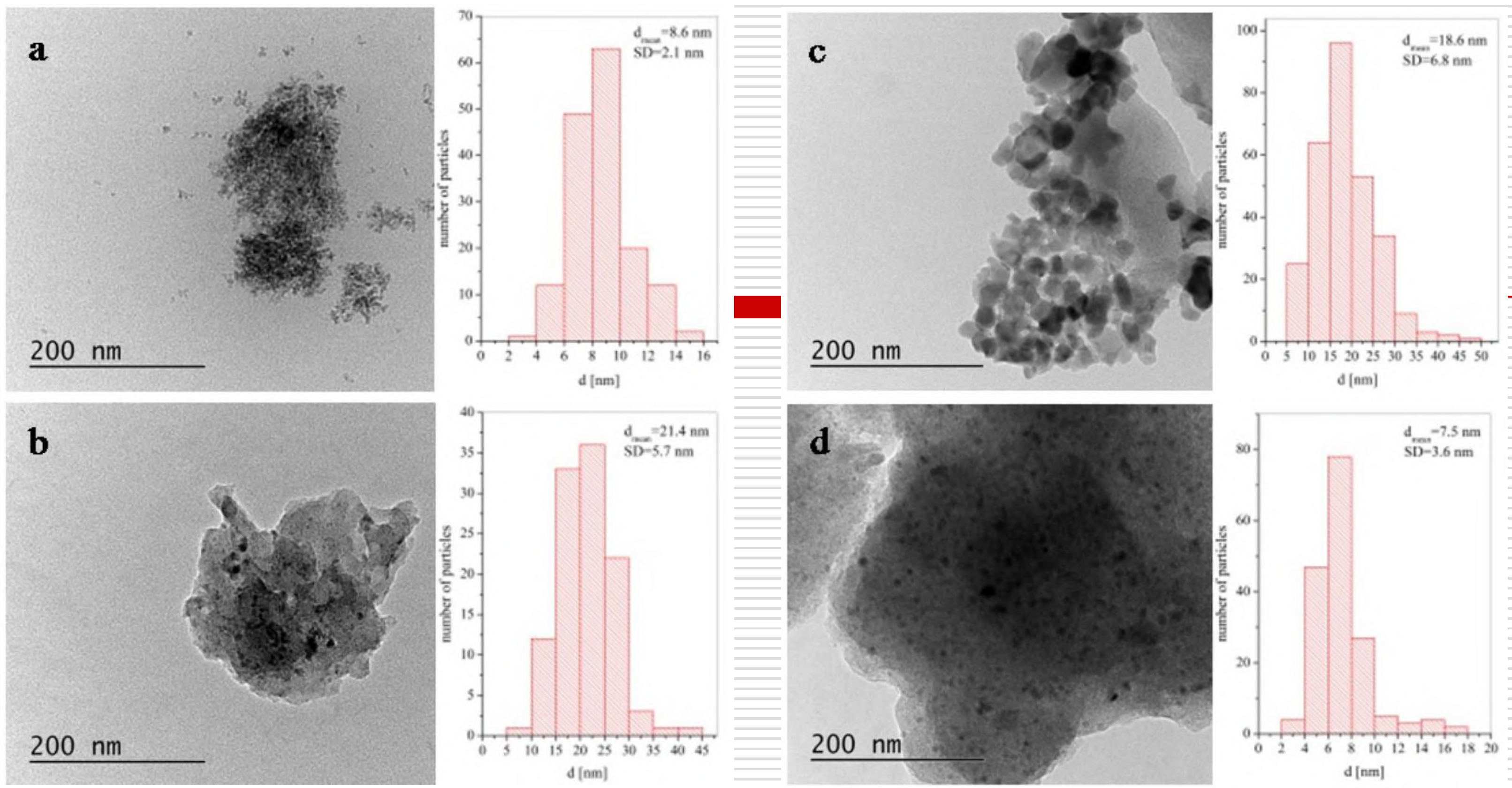


| Element | O | Fe | Ni | Zn |
|---|---|---|---|---|
| Weight % | 25.39 | 43.31 | 13.95 | 17.35 |

| Element | O | Fe | Ni | Cu |
|---|---|---|---|---|
| Weight % | 39.3 | 39 | 10.59 | 11.1 |

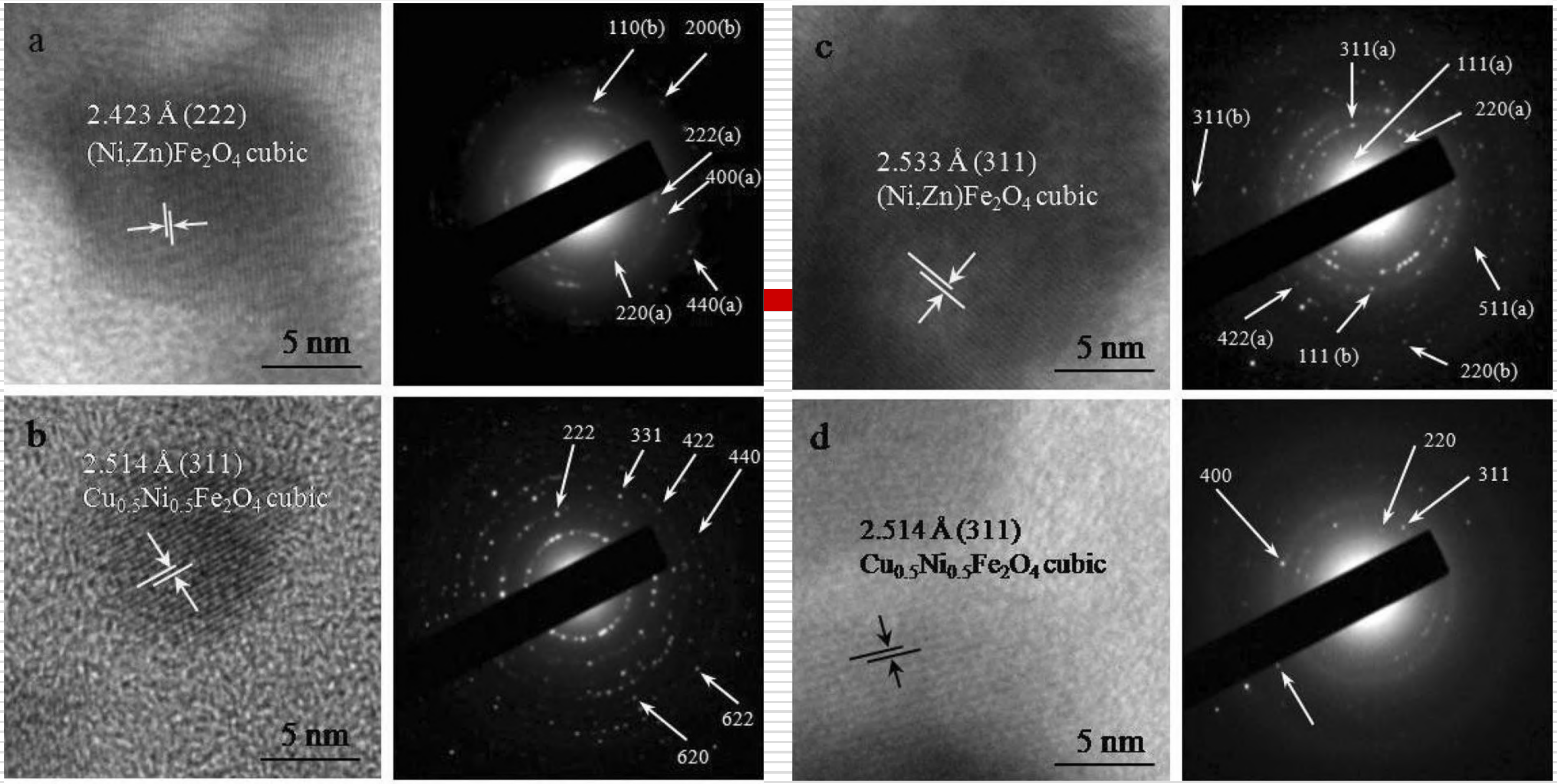
- TEM micrographs of NiZn/ACA (**a**), NiCu/ACA (**b**) samples.
- Elemental mappings for Fe, Zn, Ni and Cu in different colors
- Elemental composition

## Example 3: **Catalist: $Ni_{0.5}M_{0.5}$(M=Cu, Zn)Ferite/AC for hydrogen production**



Bright field TEM images and corresponding particles size distribution histograms for NiZn/ACA (**a**), NiCu/ACA (**b**), NiZn/ACC (**c**) and NiCu/ACC (**d**) samples.

## **Example 3:** **Catalist: $Ni_{0.5}M_{0.5}$(M=Cu, Zn)Ferite/AC for hydrogen production**



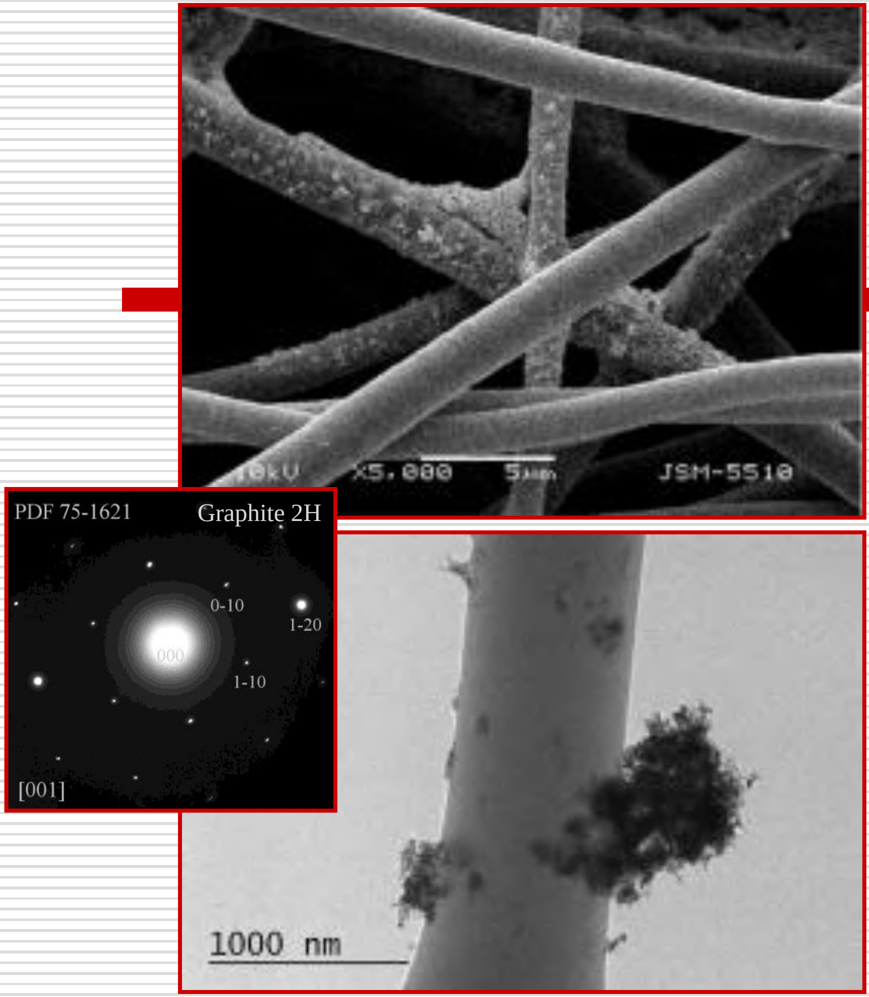
HRTEM images and corresponding SAED patterns for NiZn/ACA (a), NiCu/ACA (b), NiZn/ACC (c) and NiCu/ACC (d) samples.

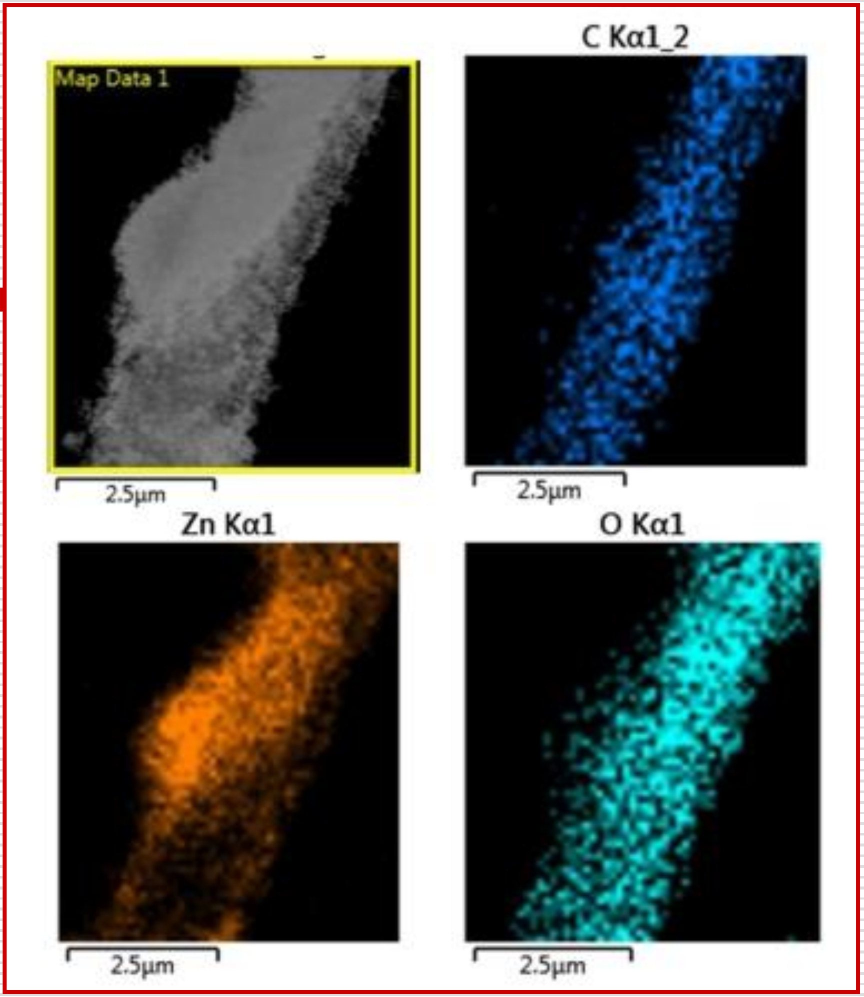
In SAED pattern a, the indices (a) are for (Ni, Zn)$Fe_2O_4$ phase and (b) are for Fe phase.

In SAED pattern c, the indices (a) are for (Ni, Zn)$Fe_2O_4$ and (b) are for NiFe alloy.

The $Ni_{0.5}Zn_{0.5}Fe_2O_4$ modifications demonstrate higher potential as catalysts for hydrogen production via methanol decomposition.

## **Example 4**: PLL fibers + ($ZnO_2$+Expanded graphite)NPs





EDX: Elemental mapping

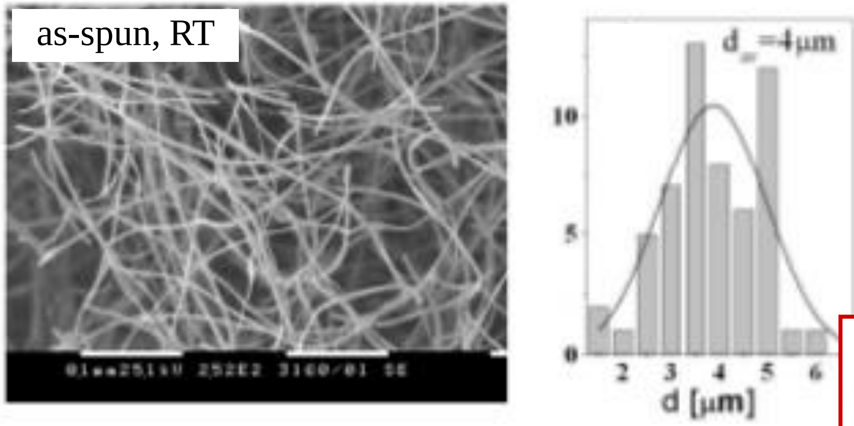
D.Virovska, D.Paneva, N.Manolova, I.Rashkov, D.Karashanova, "Photocatalytic self-cleaning poly(L-lactide) materials based on a hybrid between nanosized zinc oxide and expanded graphite or fullerene", Materials Science and Engineering C 60 (2016) 184–194

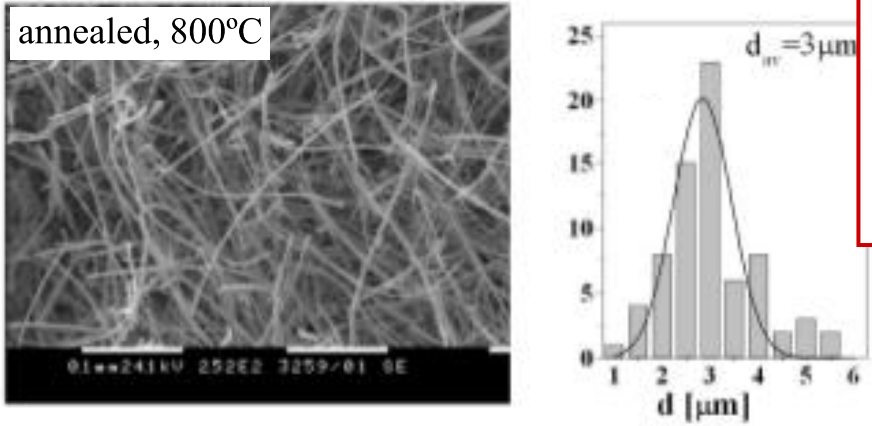
# Example 5: Fibers – inorganic materials

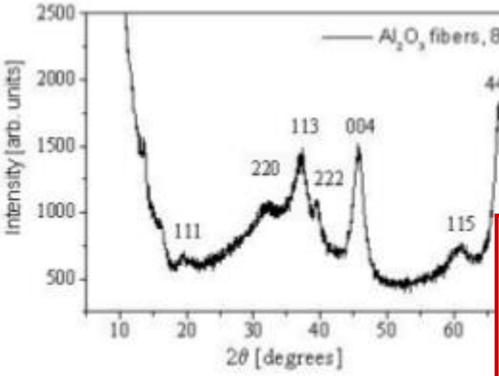
$Al_2O_3$ fibers produced by the method of electrospinning, applied electric field strength E>1 kV.cm$^{-1}$ (applied voltage 15 kV, distance needle – collector 10 cm)

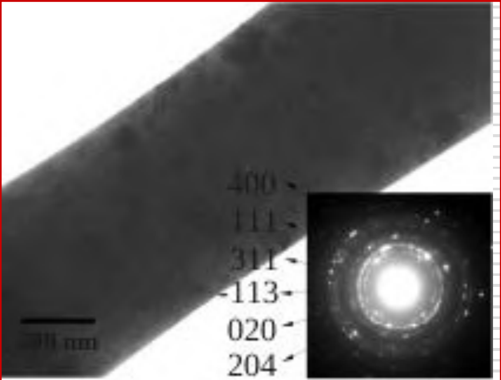
aluminum sec-butoxide (Al(OCH[CH3]C2H5)3): butanol (CH3(CH2)3OH = 5:1

monoclinic θ-$Al_2O_3$ with crystalline structure, characterized by lattice parameters a=11,79Å, b=2,91 Å, c=5,62 Å, ß=103,79°


as-spun, RT


annealed, 800ºC





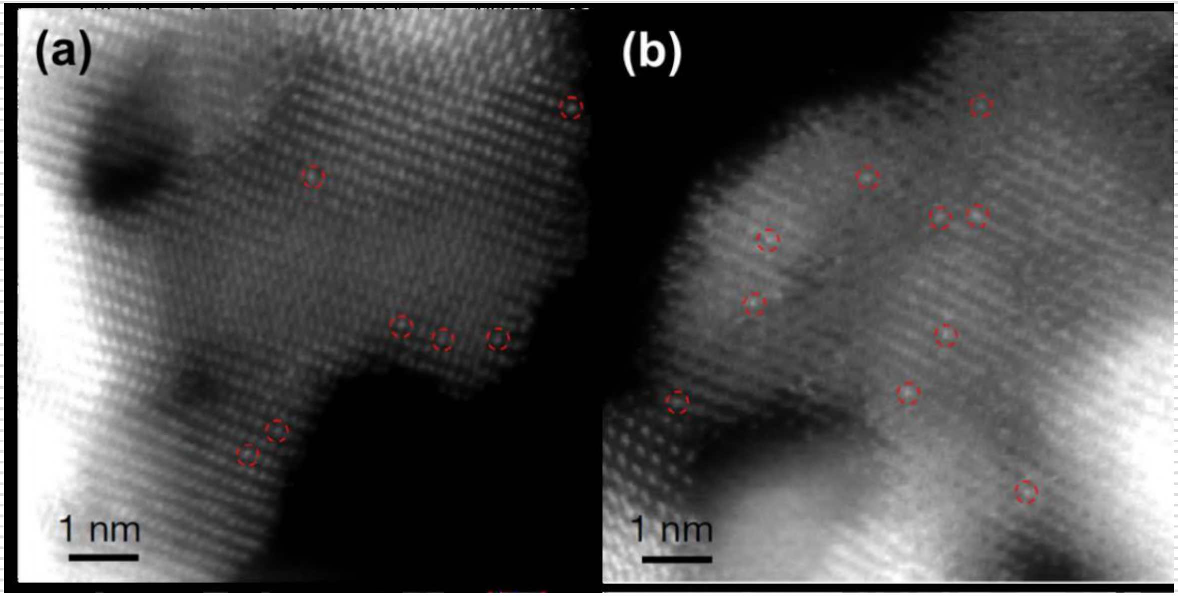
M.M. Dimitrova, E.D. Krumov, D.B. Karashanova, “Simplified procedure for Al2O3 microfibers preparation by the method of electrospinning”, Bulgarian Chemical Communications 45, Special Issue B (2013) 94-98

# **Example 6: Unveiling the structure of heterogeneous catalysts at the atomic scale**

## 6.1 Platinum (Pt)/α-MoC catalysts for low temperature hydrogen production.

Lin L L, Zhou W, Gao R, Yao S Y, Zhang X, Xu W Q, Zheng S J, Jiang Z, Yu Q L, Li Y W, Shi C, Wen X D and Ma D 2017 Nature 544 80

The best catalytic activity is demonstrated by Pt/α-MoC catalyst loading 0.2% Pt and owing a single Pt atom dispersion on α-MoC support.

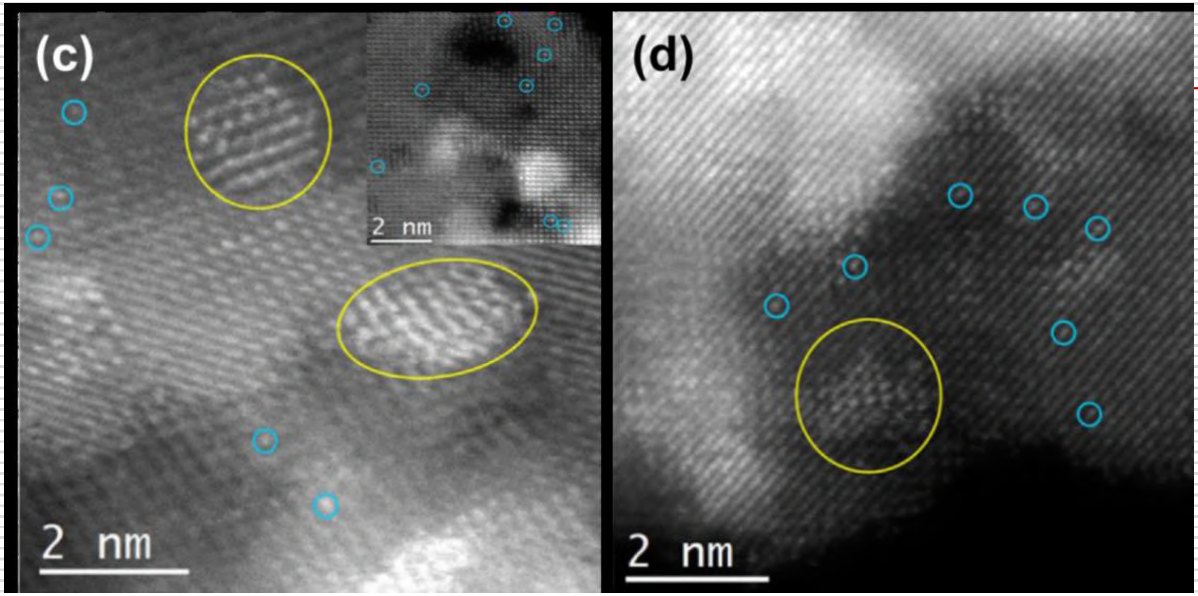


Atomic-resolution STEM-HAADF images verified the fact that Pt metal disperses atomically on the α-MoC surface, as highlighted in red in (a).
On the spent catalyst, the atomic dispersion of Pt was well retained (b).

High-resolution STEM-HAADF images of fresh 0.2% Pt/α-MoC (a) and used 0.2% Pt/α-MoC catalysts (b)

# **Example 7: Unveiling the structure of heterogeneous catalysts at the atomic scale**

## 6.2 (Au)/α-MoC catalysts for water-gas shift (WGS) reaction in low temperature hydrogen production.

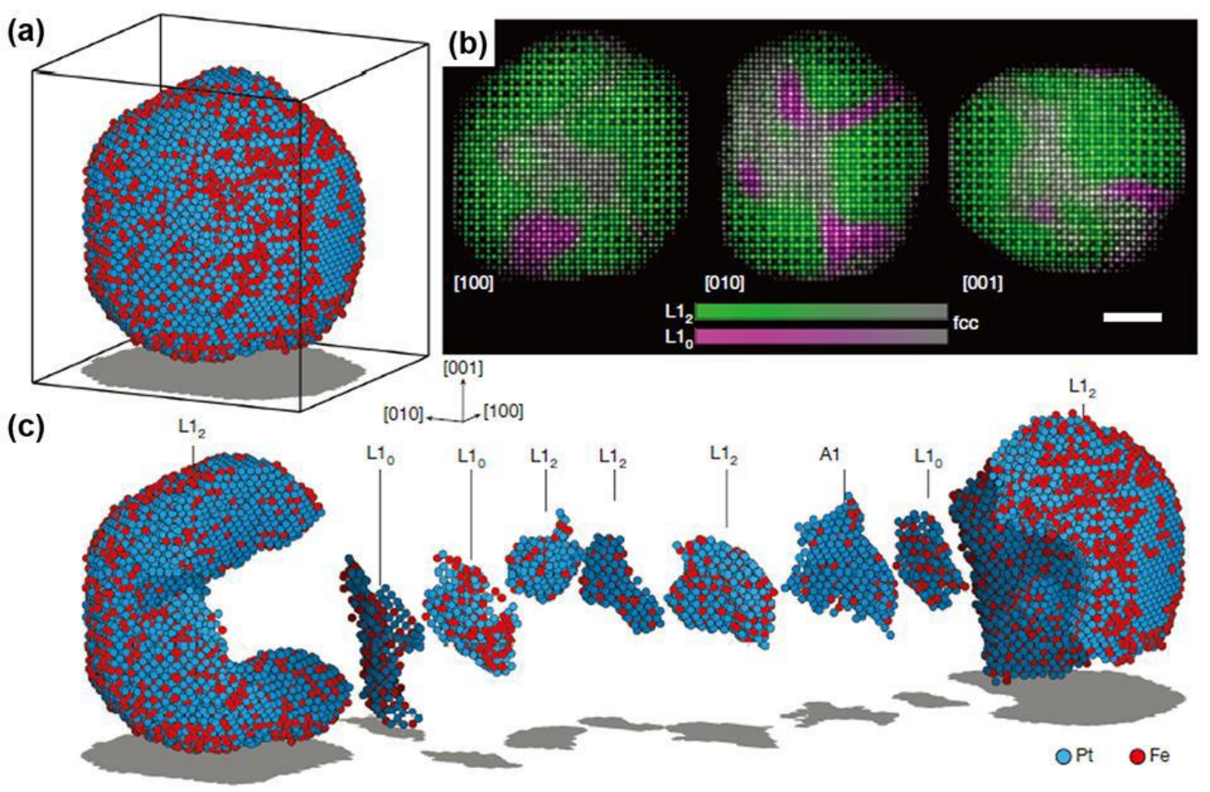


High-resolution STEM-HAADF images of fresh 2% Au/α-MoC (c) and used 2% Au/α-MoC catalysts (d), and the NaCN-leached specimen (inset in (c))

STEM-HAADF imaging was again the key for revealing the atomic structure of the active species in this novel catalyst. It shows that there are two different Au configurations on the α-MoC surface: individually dispersed Au atoms and Au layered clusters (labeled by blue and yellow in (c), respectively). After catalytic testing, both configurations maintained (d), which contributed to the good stability during catalytic process.

Yao S Y, Zhang X, Zhou W, et al. 2017 Science 357 389

# Example 7: 3D reconstruction for the study of heterogeneous catalysts

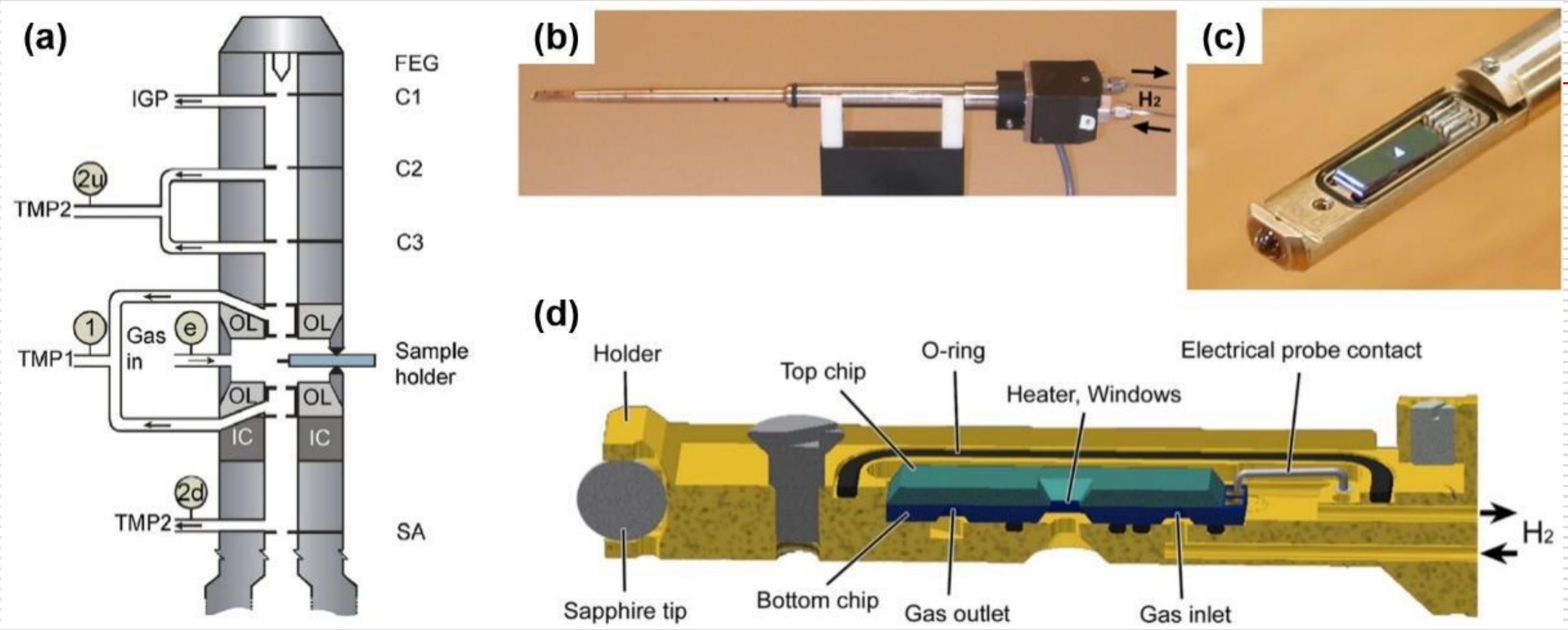


(a) The 3D positions of individual atoms of Fe and Pt. (b) Multislice images through the reconstructed 3D atomic model along the [100], [010] and [001] directions. Color bars indicate the degree of ordering, varying between pure L12/L10 and chemically disordered fcc. Scale bar, 2 nm. (c) The nanoparticle consists of two large $L1_2$ grains, three small $L1_2$ grains, three small $L1_0$ grains and a Pt-rich A1 grain.

Yang Y, Chen C C, Scott M C, Ophus C, Xu R, Pryor A, Wu L, Sun F, Theis W, Zhou J, Eisenbach M, Kent P R, Sabirianov R F, Zeng H, Ercius P and Miao J 2017 Nature 542 75

## Example 8.1: In-situ characterization of heterogeneous catalysts

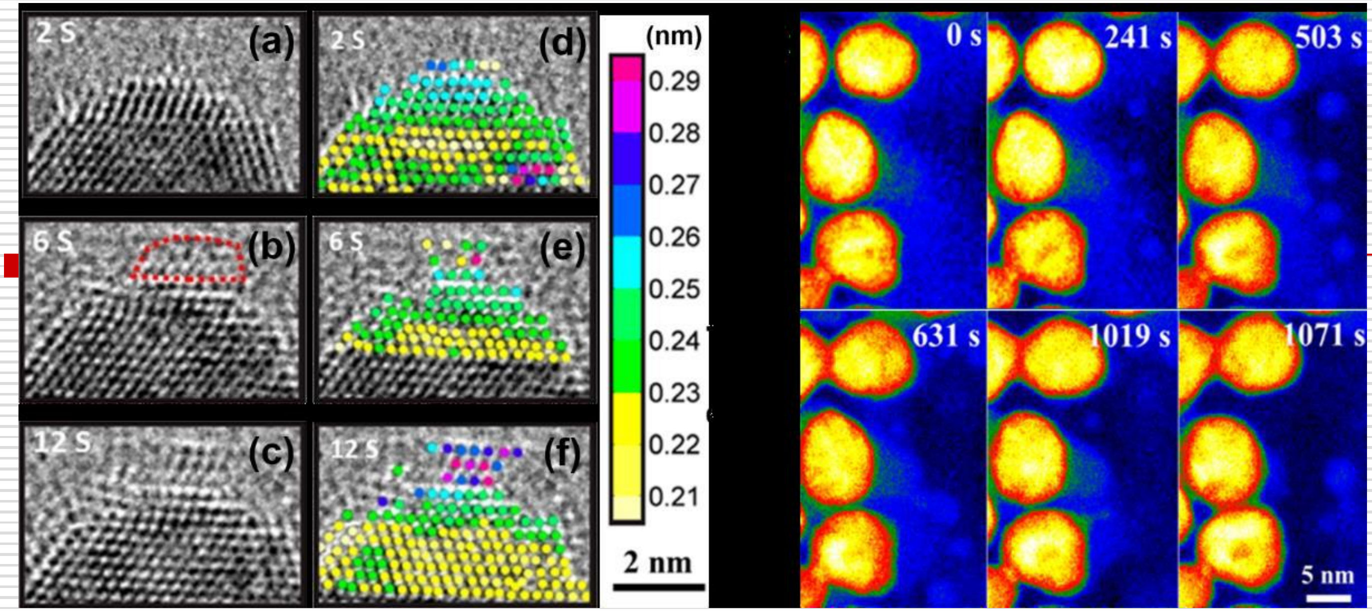
In-situ (S)TEM techniques have been developed to identify the intermediate structures and to capture structural evolution with atomic resolution under gas and heating conditions that mimic those in real catalytic reactions.



Two different approaches for in-situ experiments using either ETEM or micro-electromechanical system (MEMS)-based functional holders. (a) Schematic of a differential pumping system in ETEM. (b-d) Configuration of nanoreactors in the in-situ sample holder.

Jinschek J and Helveg S 2012 Micron 43 1156
Gai P L, Kourtakis K and Ziemecki S 2000 Microsc. Microanal. 6 335

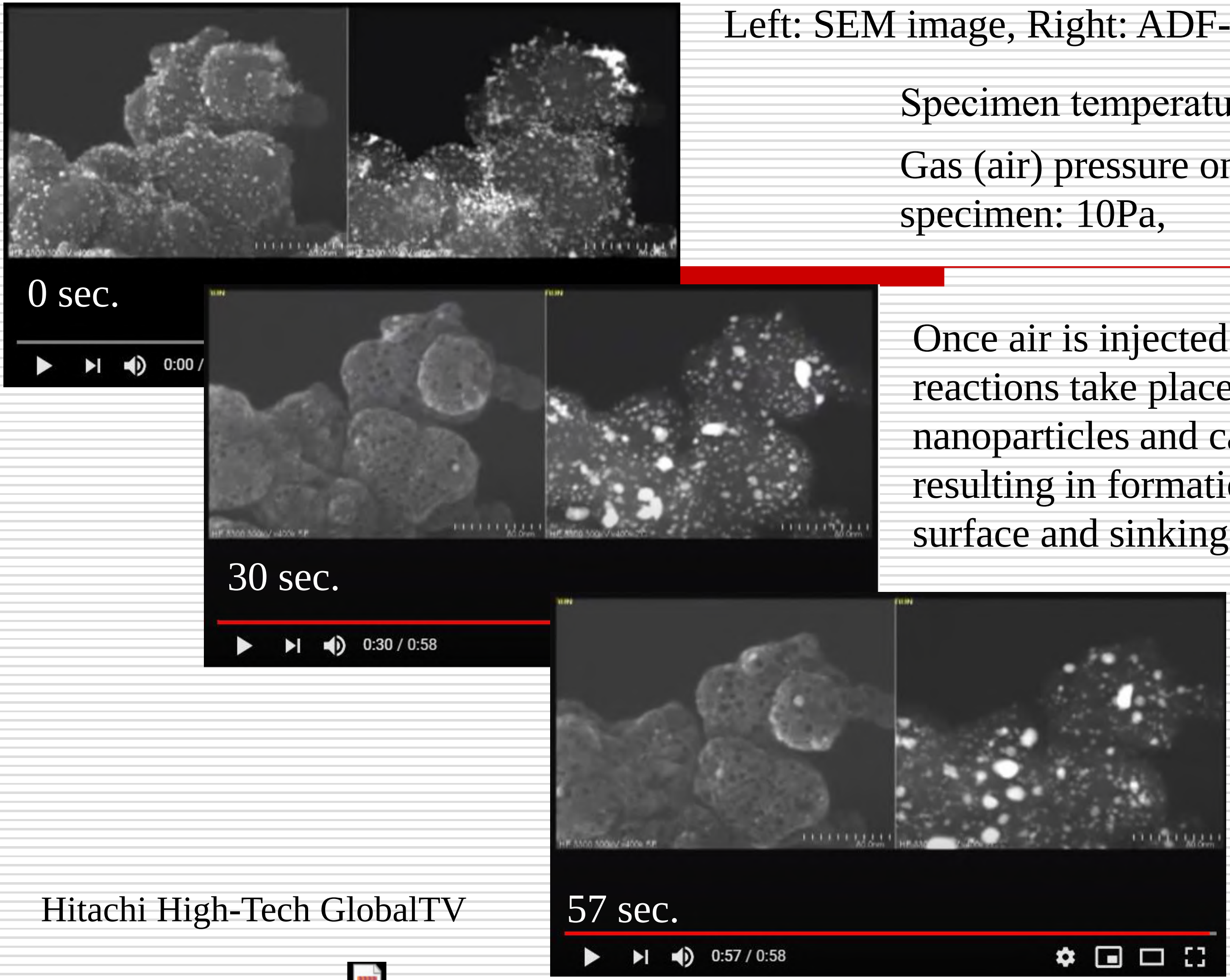
# Example 8.2: In-situ characterization of heterogeneous catalysts



In-situ characterization of Pt0.5Co0.5 nanocrystals during oxidation and reduction reactions. HRTEM images showing the CoO-island forming behavior in a Pt0.5Co0.5 nanocrystal under 0.1 mbar O2 and 250 °C at 2 s (a), 6 s (b) and 12 s (c), and the corresponding lattice spacing as measured from the HRTEM images (d-f). (g) STEM-LAADF images for the in-situ reduction of oxidized Pt-Co nanoparticles under H2 at 400 °C (CoO in blue and the metallic core in yellow).

Xin H L, Alayoglu S, Tao R Z, Genc A, Wang C M, Kovarik L, Stach E A, Wang L W, Salmeron M, Somorjai G A and Zheng H M 2014 Nano Lett. 14 3203

# Example 9 (video): Pt/C catalyst working in oxygen atmosphere



Left: SEM image, Right: ADF-STEM image

Specimen temperature: 200°C

Gas (air) pressure on specimen: 10Pa,

Once air is injected to the specimen area, reactions take place between Pt nanoparticles and carbon support, resulting in formation of holes on carbon surface and sinking of nanoparticles.

Hitachi High-Tech GlobalTV

300 kV in situ SEMSTEM observation of PtC catalysts using a Hitachi HF-3300 microscope_.mp4

# CONCLUSIONS

- Transmission electron microscopy (TEM) is a modern and intensively developing technique for visualization of the structure at micro-, nano- and atomic level.
- Almost all signals received in TEM microscope, due to the interaction of the accelerated electrons with the matter are well exploited and give rise of a large variety of analytical tools (EDS, EELS, AES), giving information for phase and chemical composition in the frame of single nanoparticle and single atom.
- Precise crystallographic information could be received by TEM for individual crystal lattice, thus supporting Electron Crystallography research.
- In-situ experiments in TEM open infinite horizons to study and design new materials and reactions, especially in the fields as catalysis, electrochemistry and batteries.
- remarque: It is highly recommended to combine TEM investigation of materials with other structure methods, especially XRD analysis, which have to be made previously.

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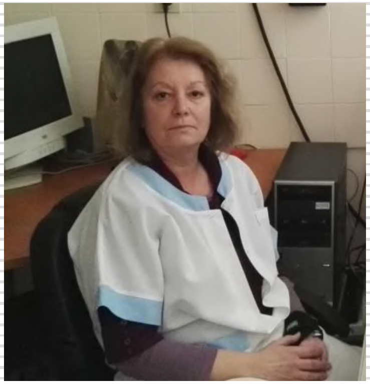

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# Thank you for your attention!

I hope we will be able to travel again soon and to meet in Bulgaria in live!