Department of Ecology
Faculty of Humanities and Natural Sciences
University of Presov,
Presov, Slovakia

RECENT ADVANCES IN THE GREEN SYNTHESIS OF NANOPARTICLES: PROPERTIES AND APPLICATIONS

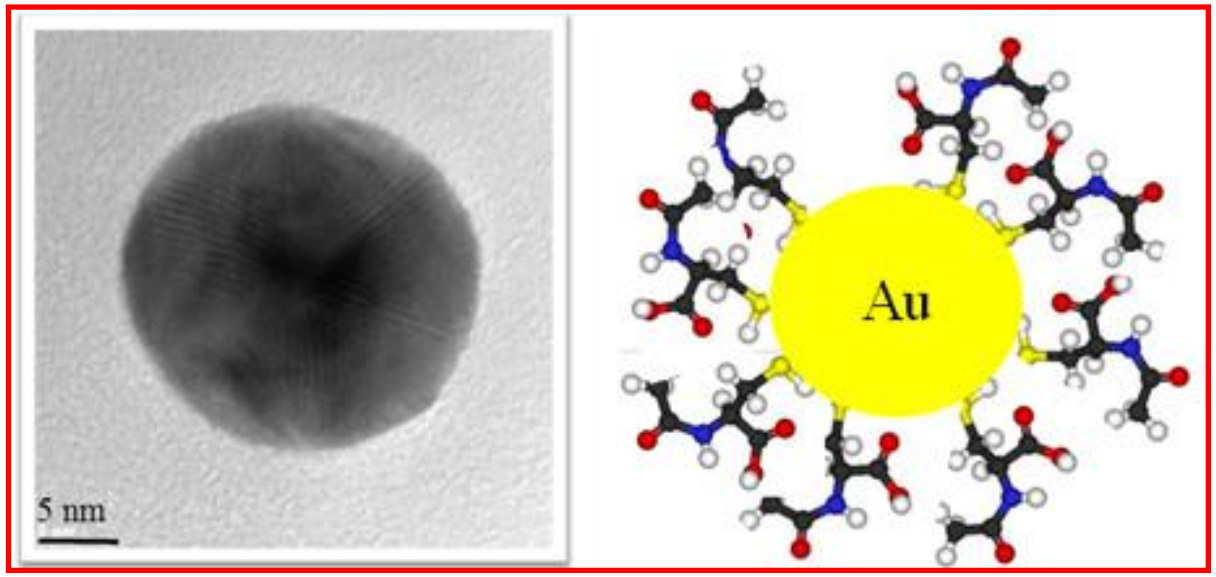
Ruslan Mariychuk

The International Conference
"European Green Dimensions: Fundamental, Applied, and Industrial Aspects"
05-07.06.2025, Mykolaiv, Ukraine

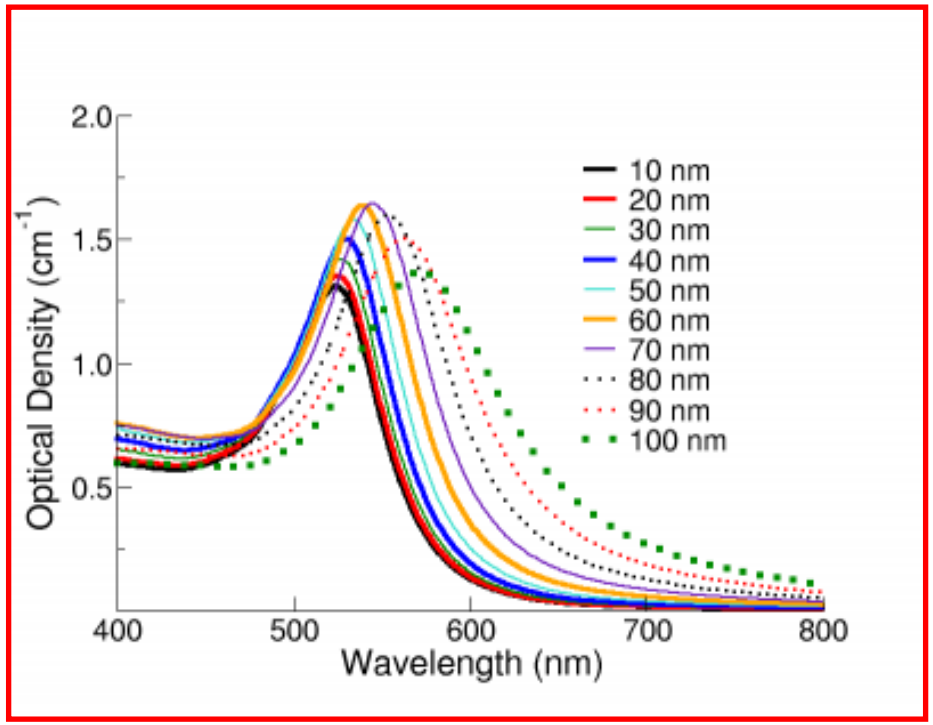
Project topic

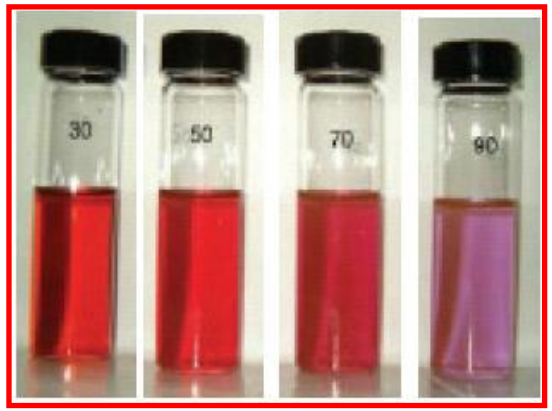
Development of the **green methods** for synthesis of colloidal **nanoparticles** solutions by using aqueous plant extracts:

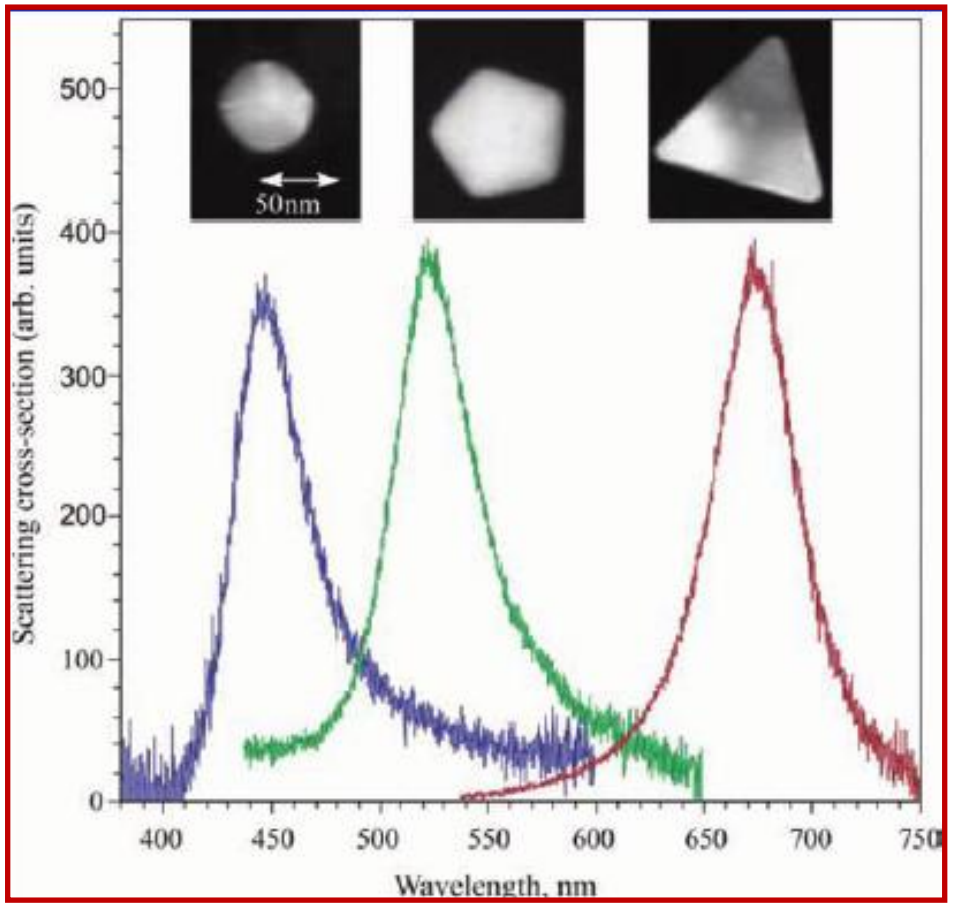
- ***friendly to environment***
- ***cost effectivity***
- ***stability***
- ***shape and size control***
- ***biocompatibility***



Size and shape of nanoparticles

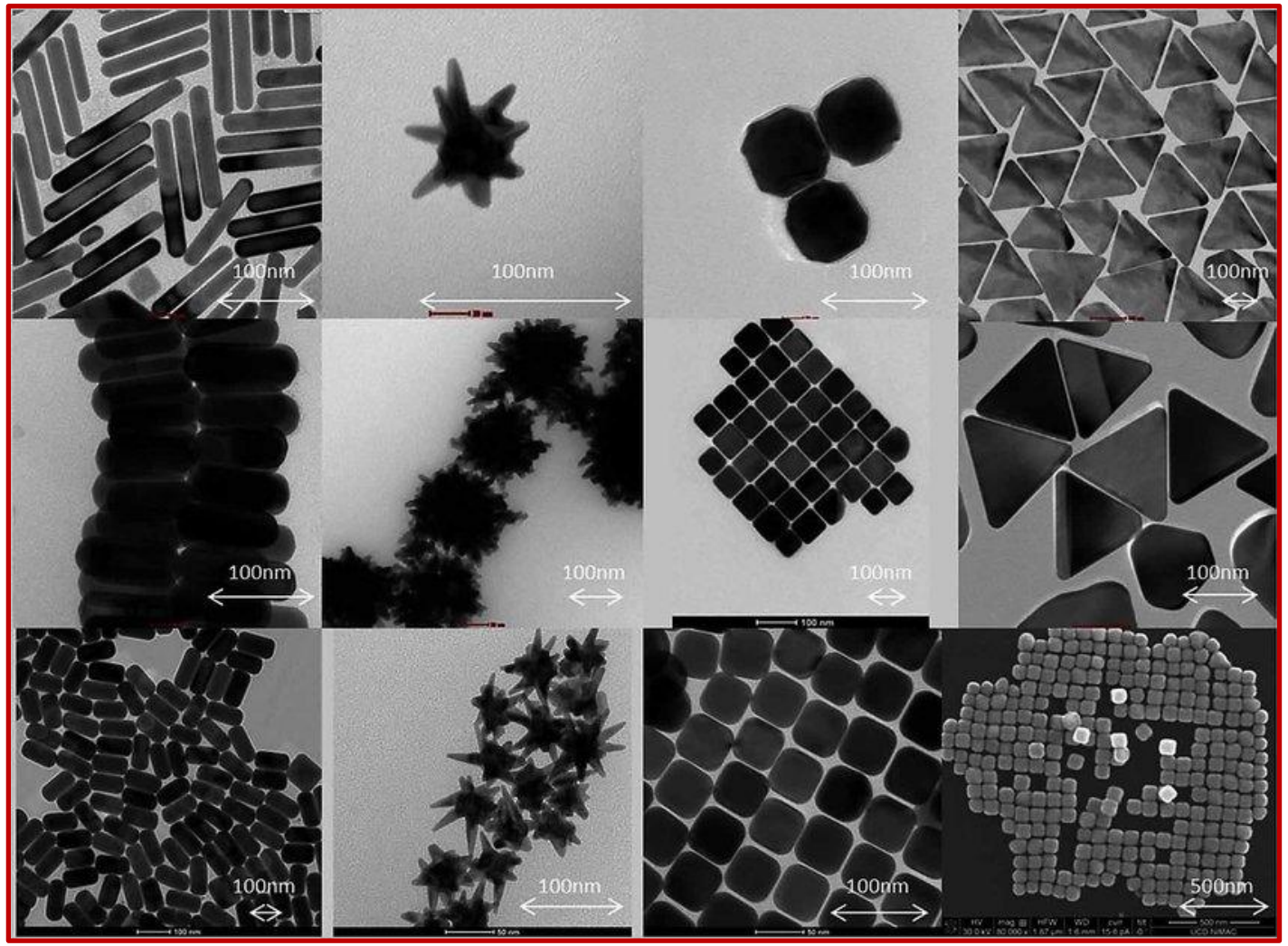






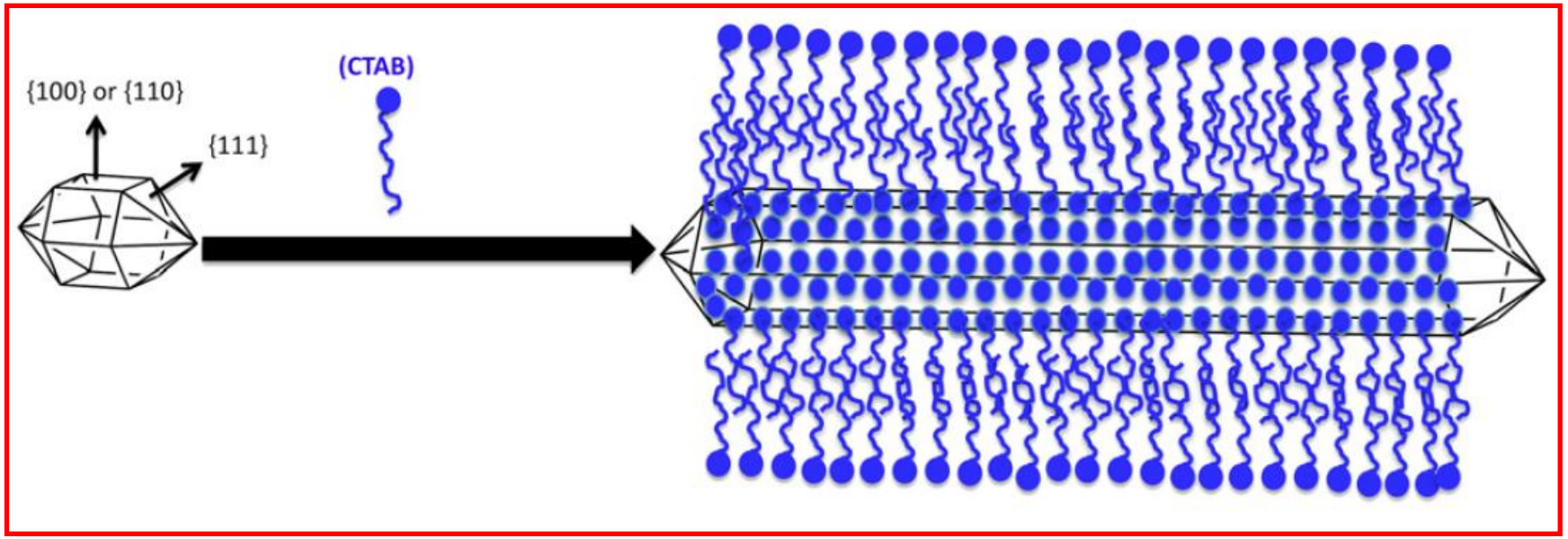
Mock, J.J. et al. (2002) J. Chem. Phys., 116, 6755–6759

Shape management

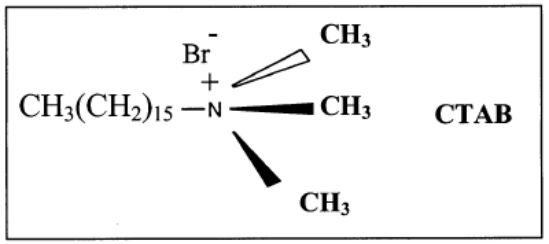


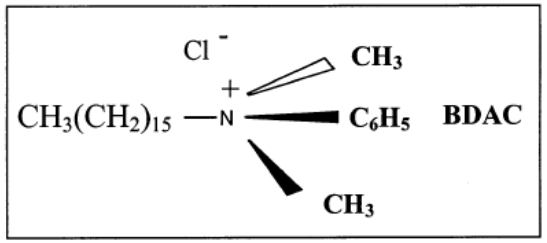
Bouloudenine, M. & Bououdina, M. (2016). Toxic Effects of Engineered Nanoparticles on Living Cells. In M. Bououdina (Ed.), *Emerging Research on Bioinspired Materials Engineering* (pp. 35-68). IGI Global Scientific Publishing. https://doi.org/10.4018/978-1-4666-9811-6.ch002

Seed mediated synthesis of nanorods



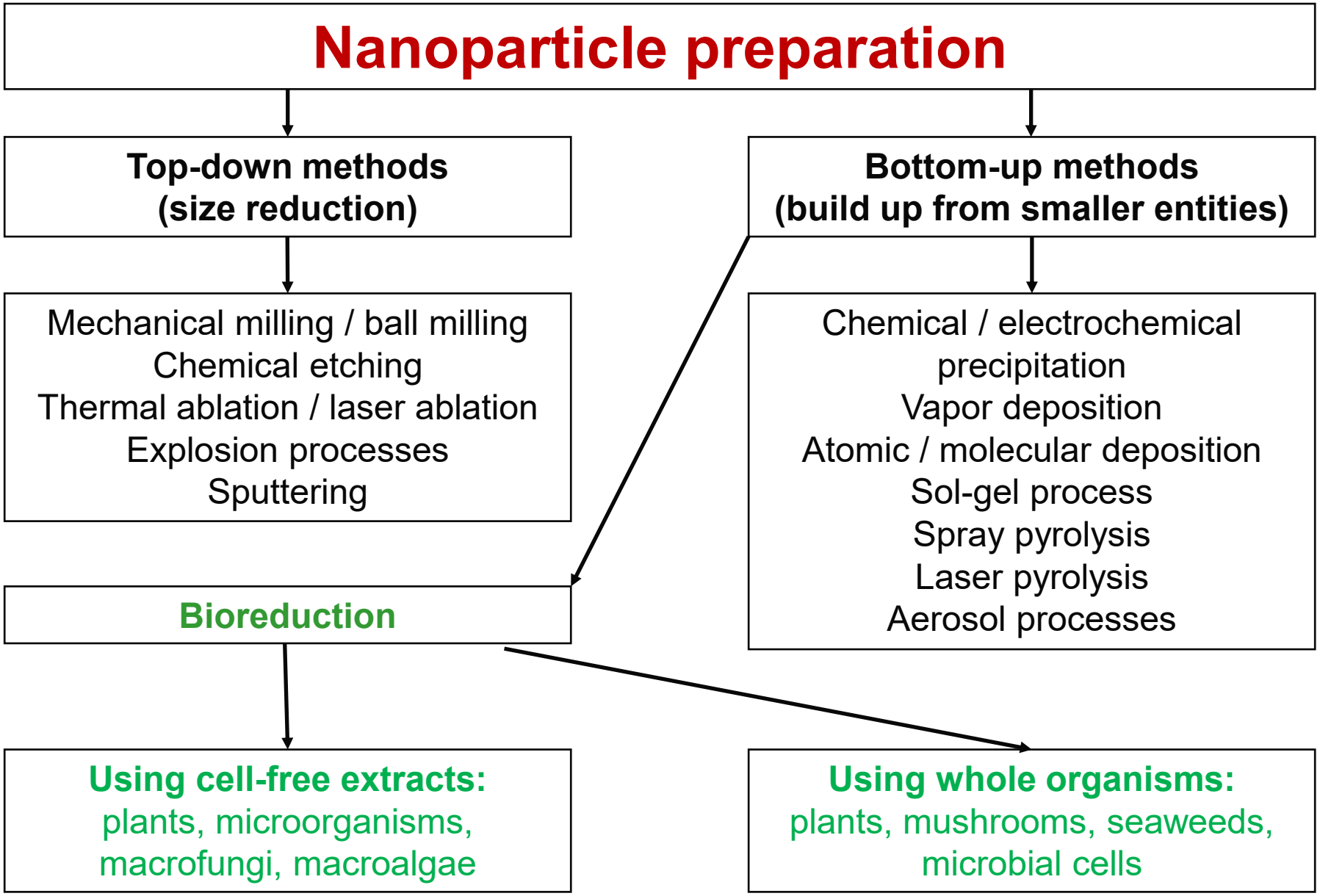
Hexadecyltrimethylammoniumbromide (CTAB) and Benzyldimethylammoniumchloride (BDAC): the Latter Has a Bulkier Head Group





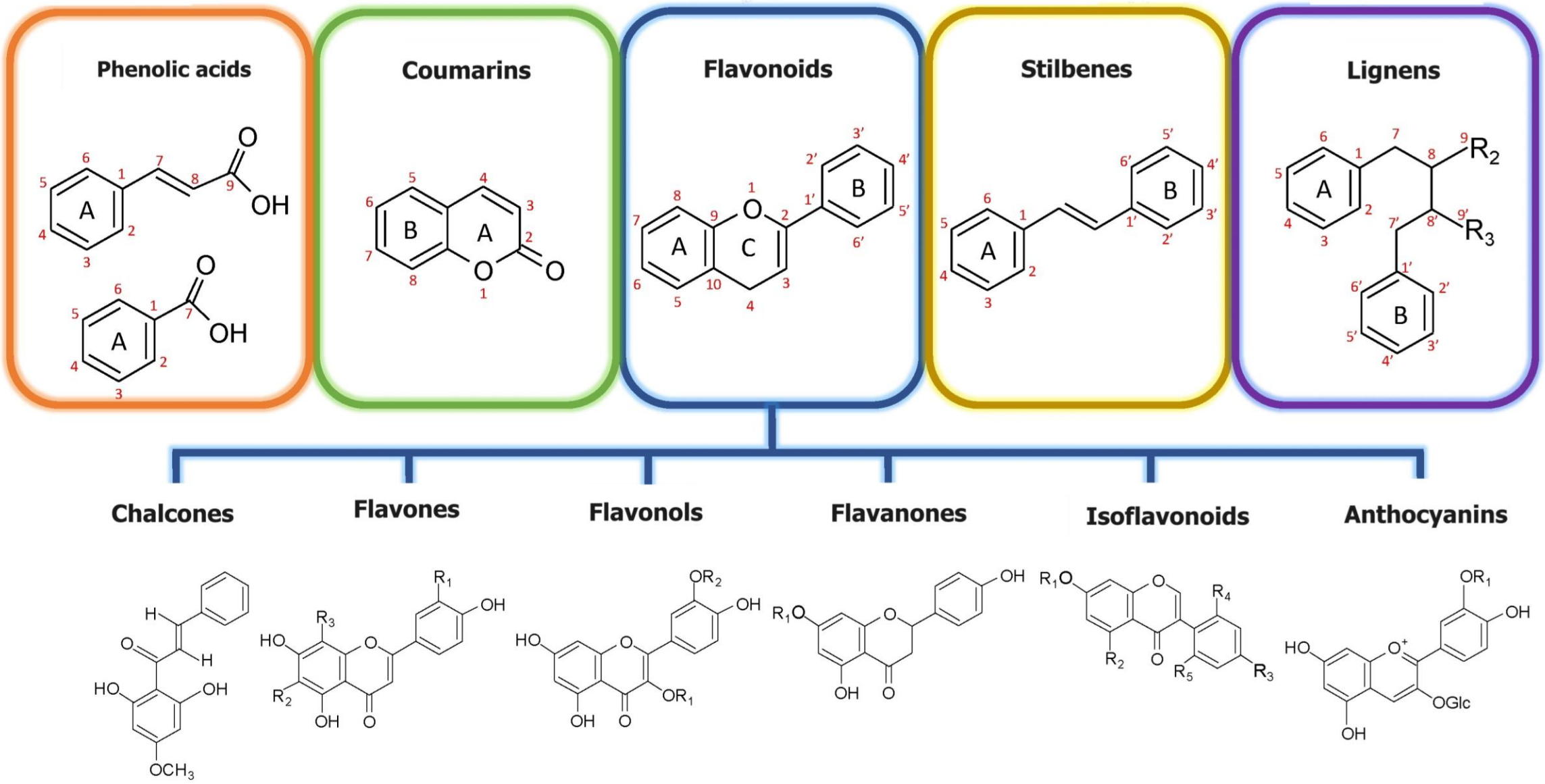
Toxic!

C.J. Murphy et al. / Current Opinion in Colloid & Interface Science 16 (2011) 128–134

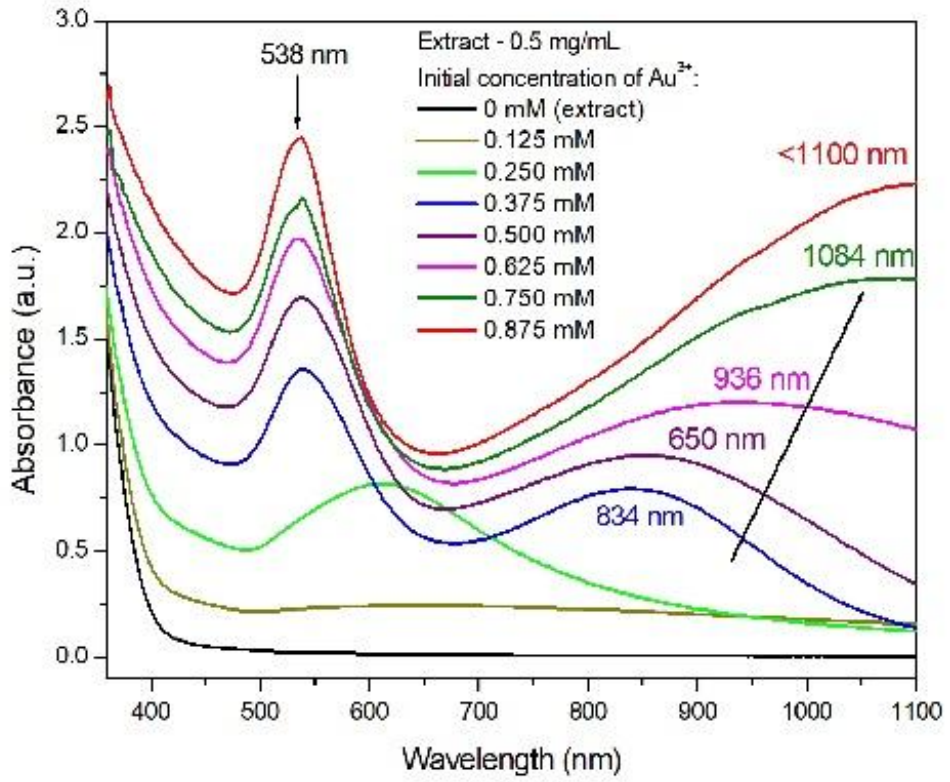


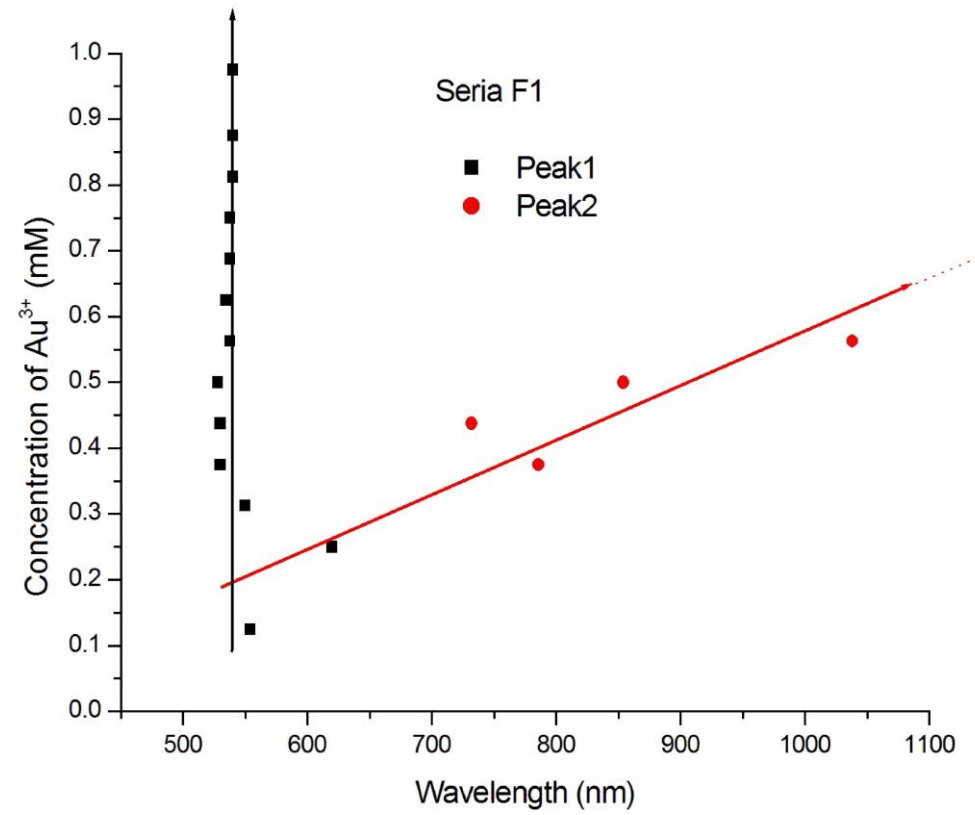
Hypothesis: The use of medicinal plant extracts will lead to the production of biocompatible nanoparticles.

Plant polyphenols



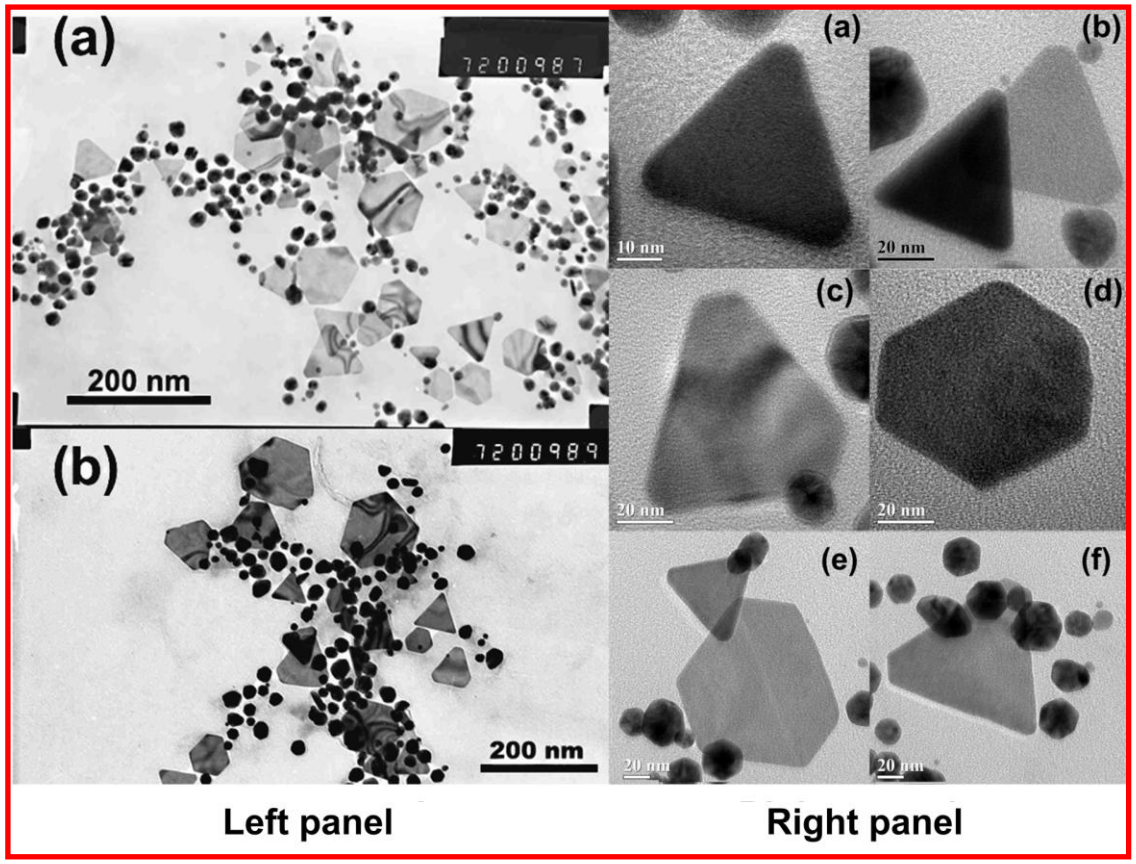
Synthesis of AuNPs using aqueous peppermint extract (*Mentha* x *piperita*)

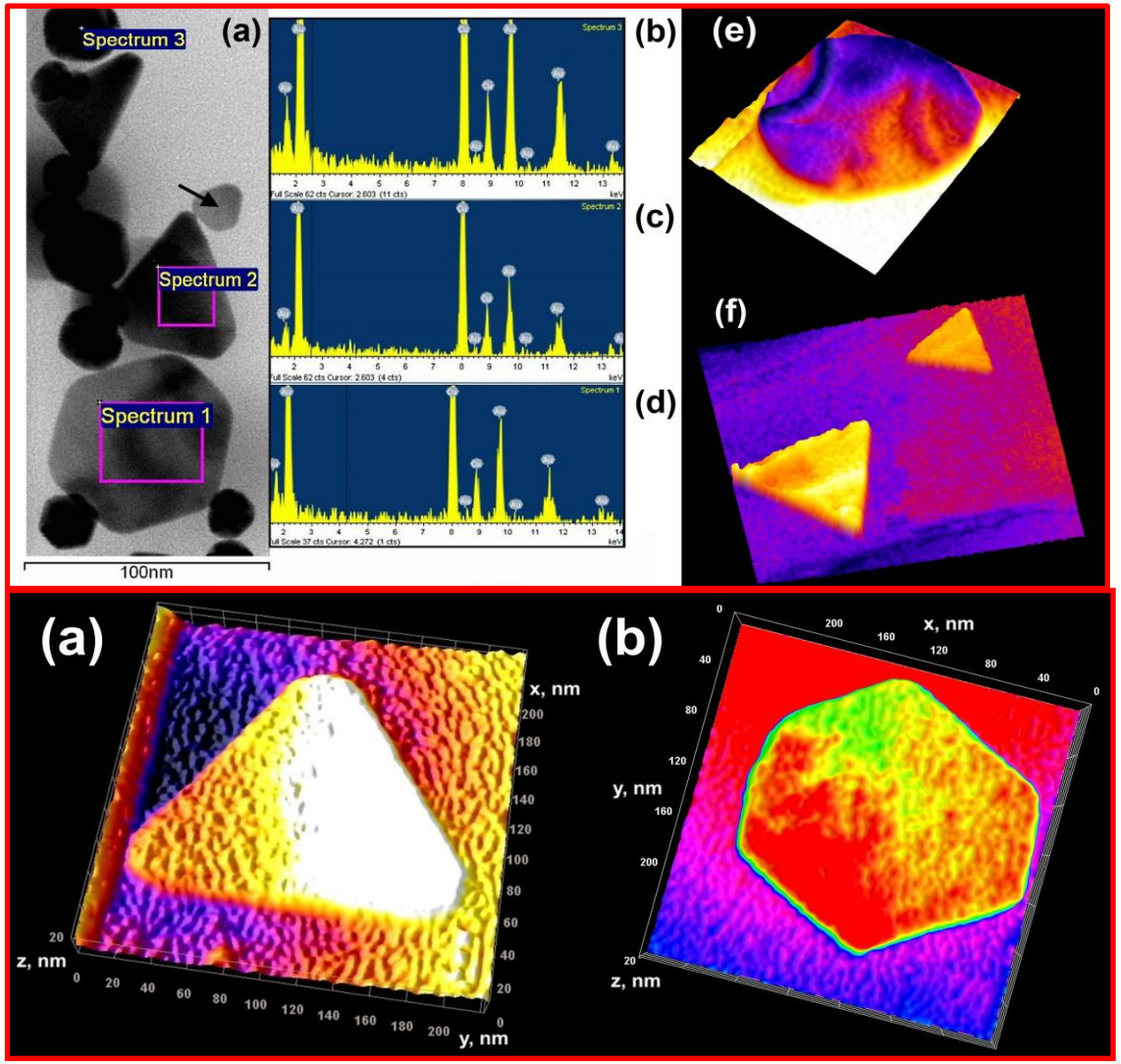




Mariychuk, R., Smolková, R. et al. The regularities of the ***Mentha piperita*** L. extract mediated synthesis of gold nanoparticles with a response in the infrared range (2022) Applied Nanoscience, 12 (4), pp. 1071-1083. DOI: 10.1007/s13204-021-01740-8

Synthesis of AuNPs using aqueous peppermint extract (*Mentha* x *piperita*)





Mariychuk, R., Smolková, R. et al. The regularities of the ***Mentha piperita*** L. extract mediated synthesis of gold nanoparticles with a response in the infrared range (2022) Applied Nanoscience, 12 (4), pp. 1071-1083. DOI: 10.1007/s13204-021-01740-8

Conclusions

Silver nanoparticles (AgNPs) typically inhibit microbial growth, with resistance levels varying across strains. The *Pseudomonas putida* USM4 strain demonstrated inhibited biomass accumulation in the presence of AgNPs, but the cells remained viable

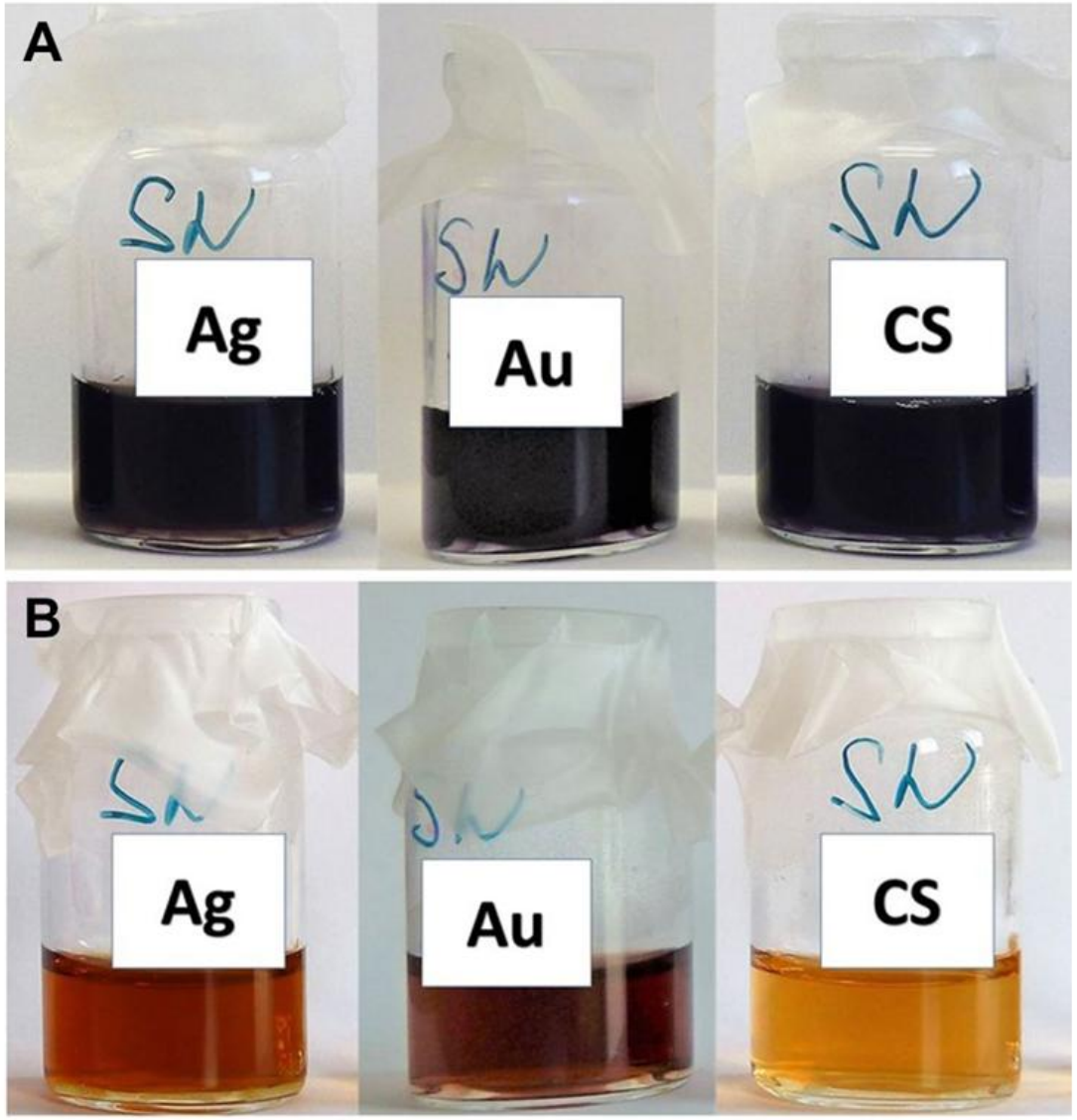
Similarly, the *Pseudarthrobacter oxydans* USM2 strain showed resistance to AgNPs at 0.125 mM, while biomass accumulation was inhibited at 0.25 mM without causing complete cell death.

In *Brevundimonas vesicularis* USM1, initial growth was followed by cell lysis; the strain exhibited the ability to interact with and precipitate silver, highlighting its potential for environmental biotechnology applications.

Regarding **gold nanoparticles (AuNPs)**, the strains *Pseudomonas putida* USM4 and *Pseudarthrobacter oxydans* USM2 showed no significant inhibition, while *Brevundimonas vesicularis* USM1 also precipitated gold, likely through organic ligand decomposition, consistent with the known minimal impact of AuNPs on microorganisms.

These results are promising for further studies on the interaction pathways between microorganisms and metal nanoparticles.

Reaction mixtures prepared with polyphenolic fraction of the elderberry extract

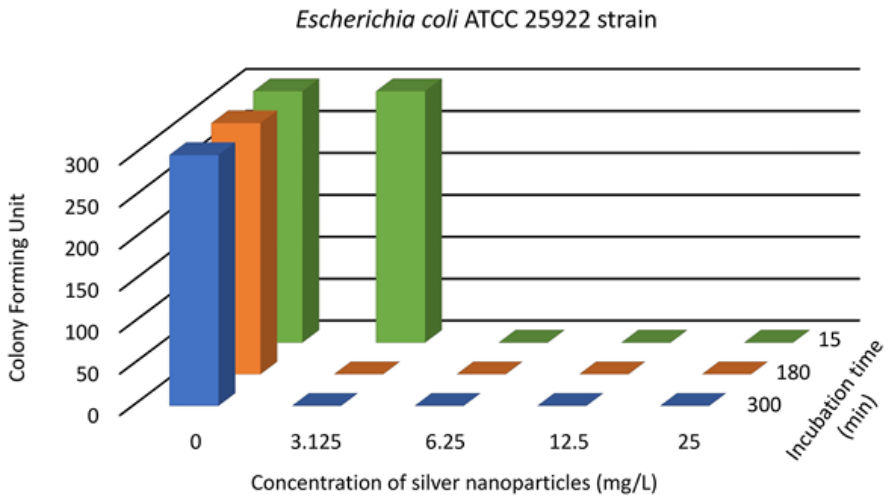


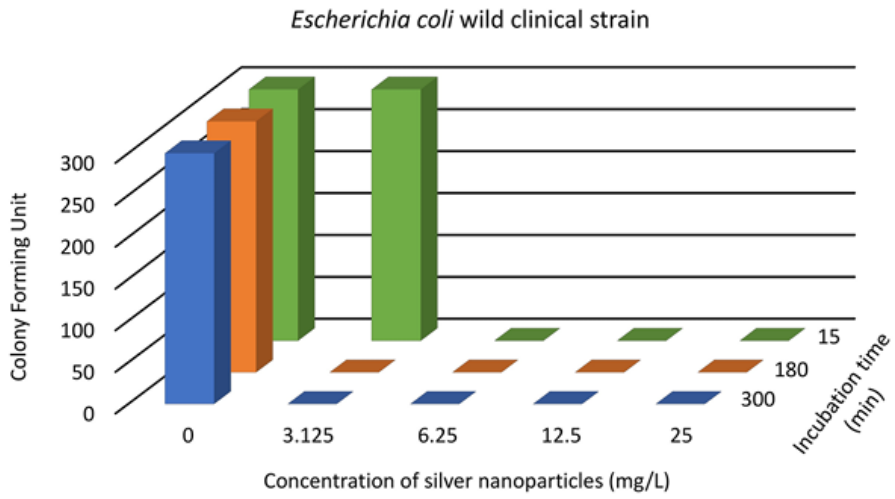
(A) at the beginning of the synthesis (A) and (B) after 24 h of heating at 65 °C

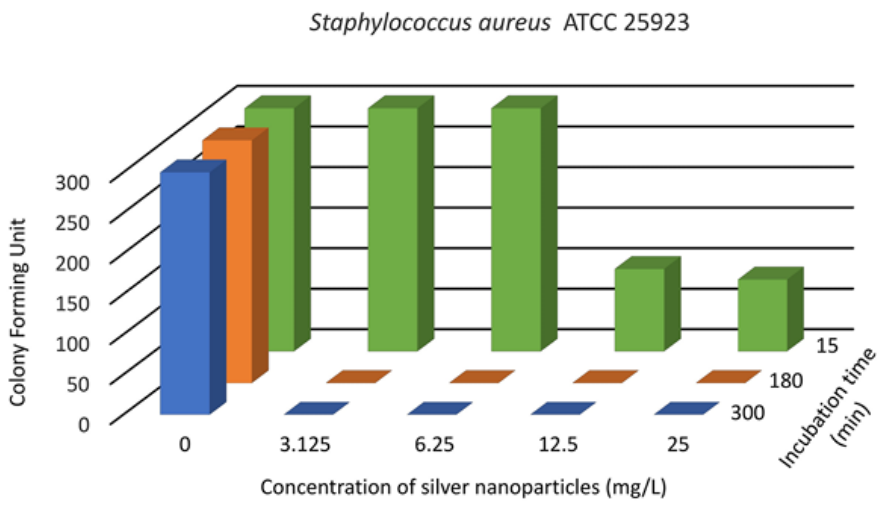
Ag: sample of silver solution,
Au: sample of gold solution,
CS: control sample (extract without metal salt precursor)

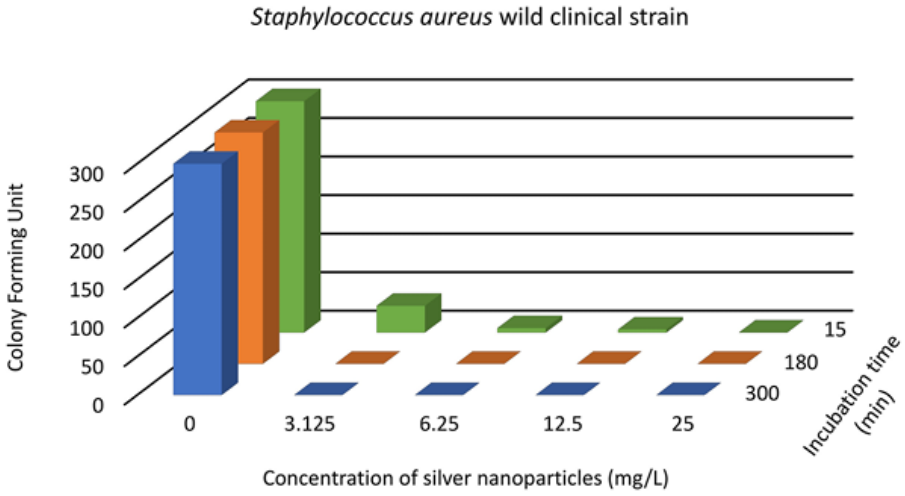
Mariychuk, R., Porubská, J., Ostafin, M. *et al.* *Appl Nanosci* **10**, 4545–4558 (2020). https://doi.org/10.1007/s13204-020-01324-y

Growth inhibition of the tested bacterial strains by varying AgNPs concentrations







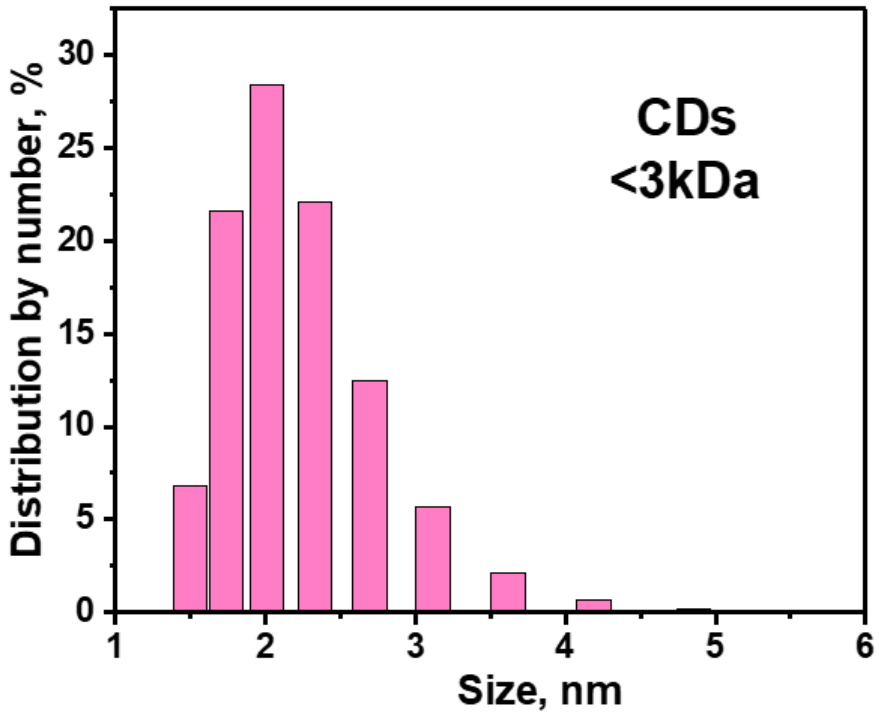


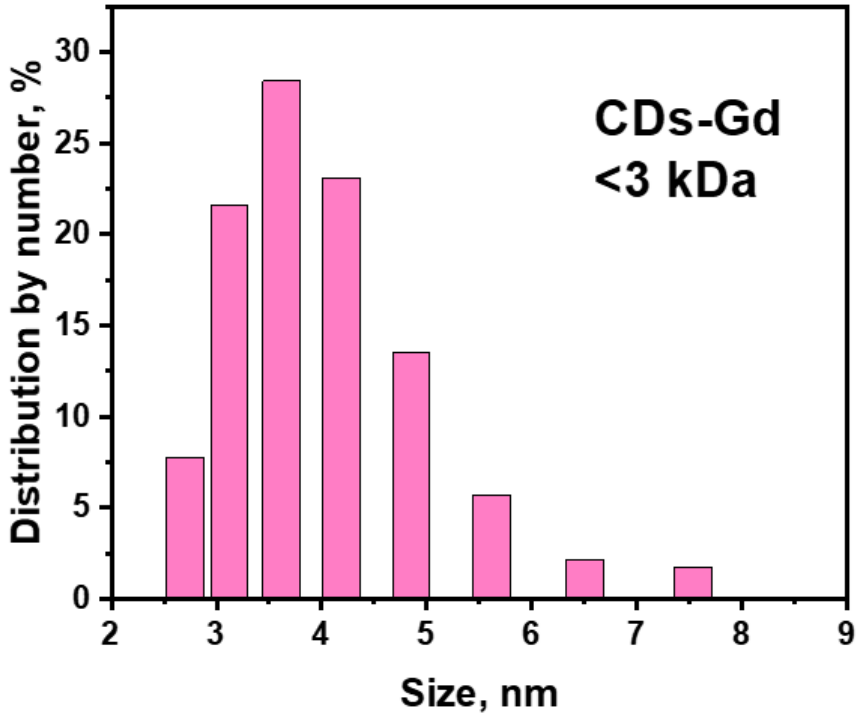
Mariychuk, R., Porubská, J., Ostafin, M. *et al.* *Appl Nanosci* **10**, 4545–4558 (2020). https://doi.org/10.1007/s13204-020-01324-y

Carbon dots

Nobel Prize in Chemistry 2023
for the discovery and development of quantum dots
Carbon dots - 2004

Synthesis. Gd^{3+}-free and Gd^{3+}-doped carbon dots were synthesized by one-step **solvothermal method** using ***urea, citric acid***, and ***3-(trifluoromethyl)aniline*** as precursors (DMFA solvent).

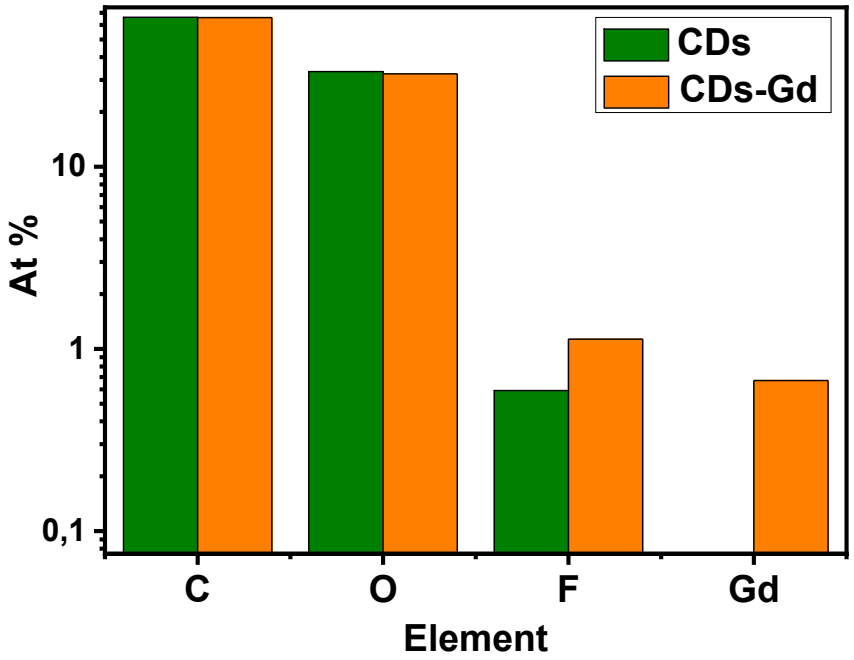




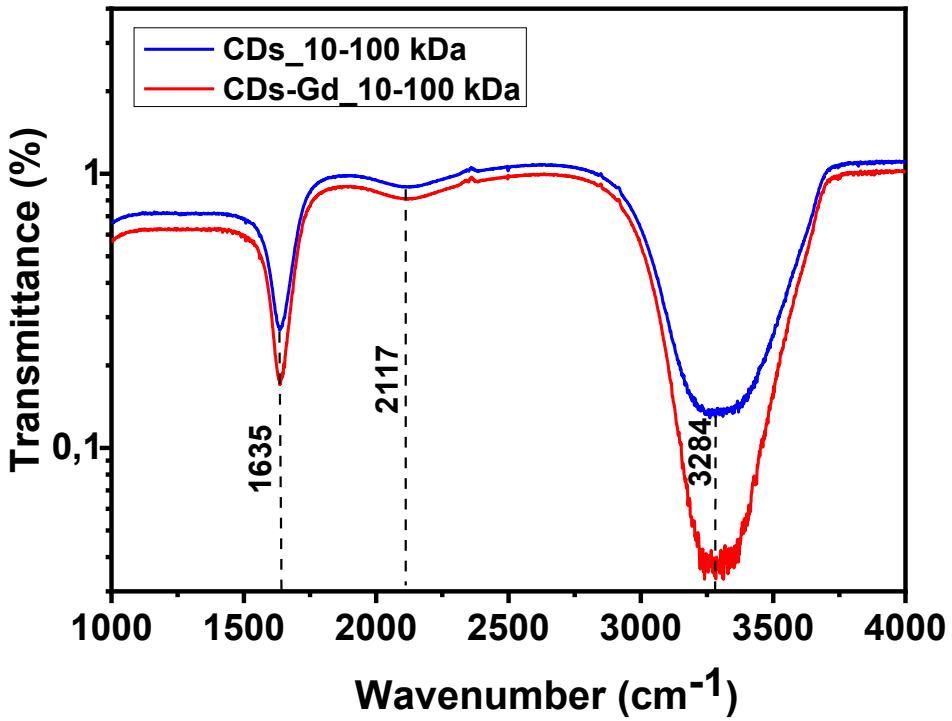
Zhylkybayeva N. et al. (2024) *Scientific Reports*, 14 (1), 27812.
DOI: 10.1038/s41598-024-76500-z

Carbon dots

Energy Dispersive X-ray Spectroscopy



Fourier transform infrared spectroscopy spectra

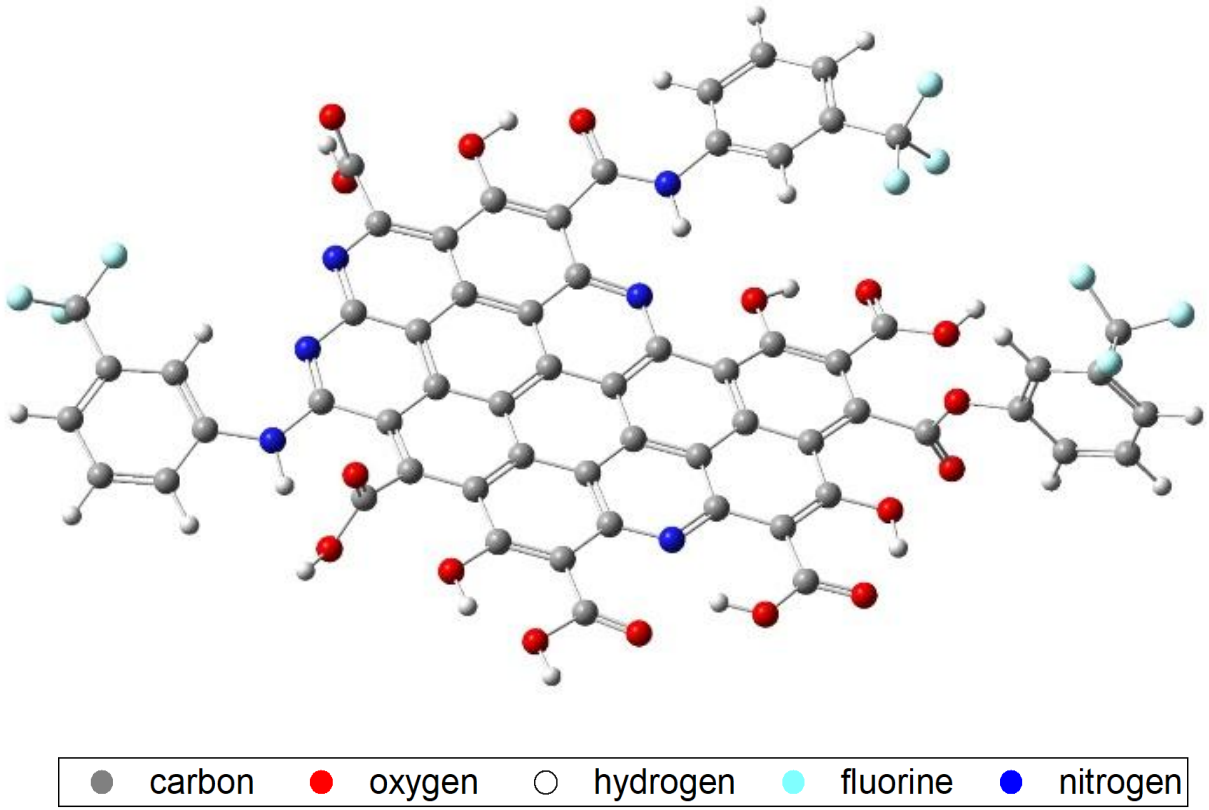


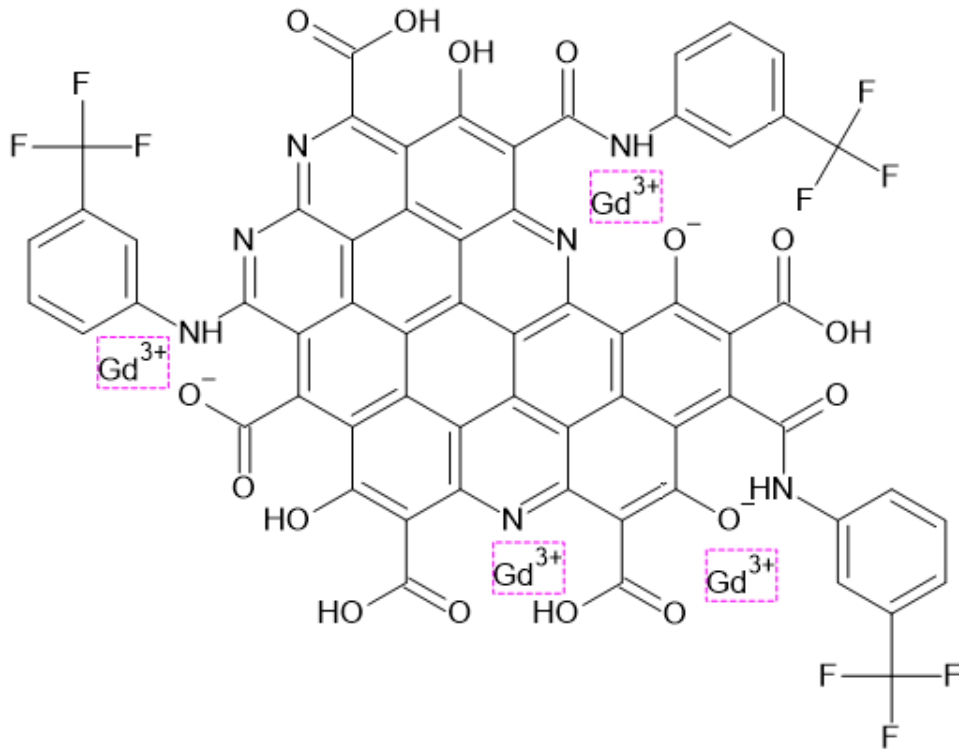
Specifically, a peak at 1635 cm^{-1}, indicates the presence of C–NH_2 (amine) bonds. Moreover, a peak around 2117 cm^{-1} is attributed to C=N=C (cyanate) bonds.

Zhylkybayeva N. et al. (2024) *Scientific Reports*, 14 (1), 27812.
DOI: 10.1038/s41598-024-76500-z

Carbon dots

Schematic structure of Gd^{3+}-free carbon dots

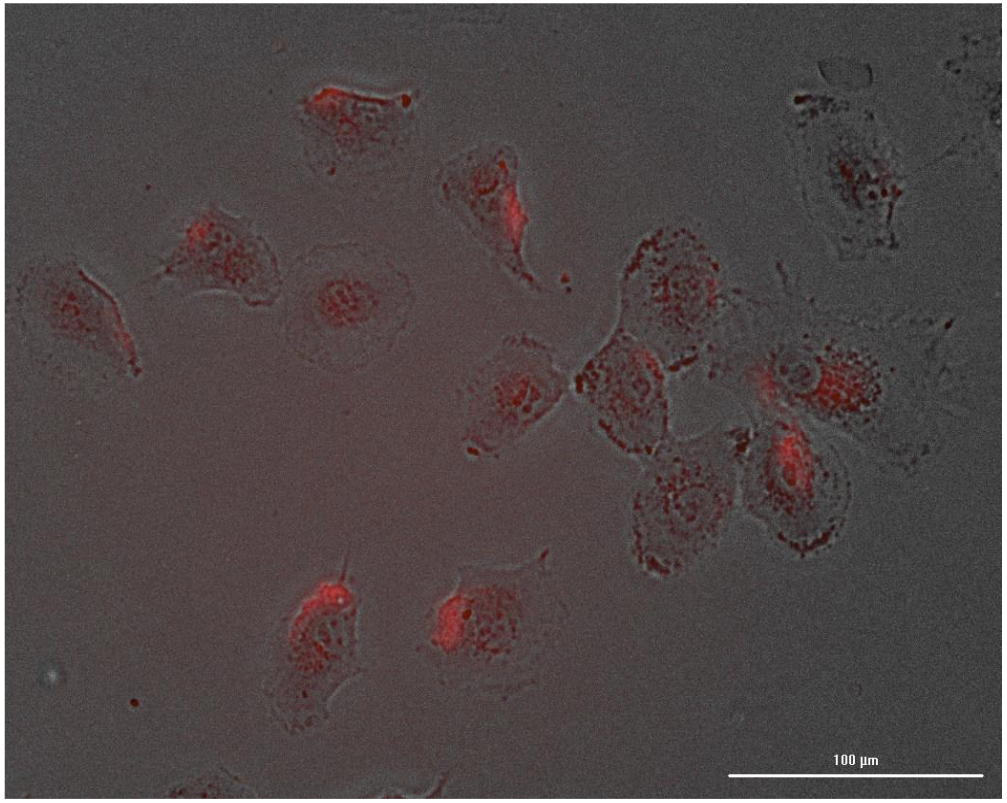


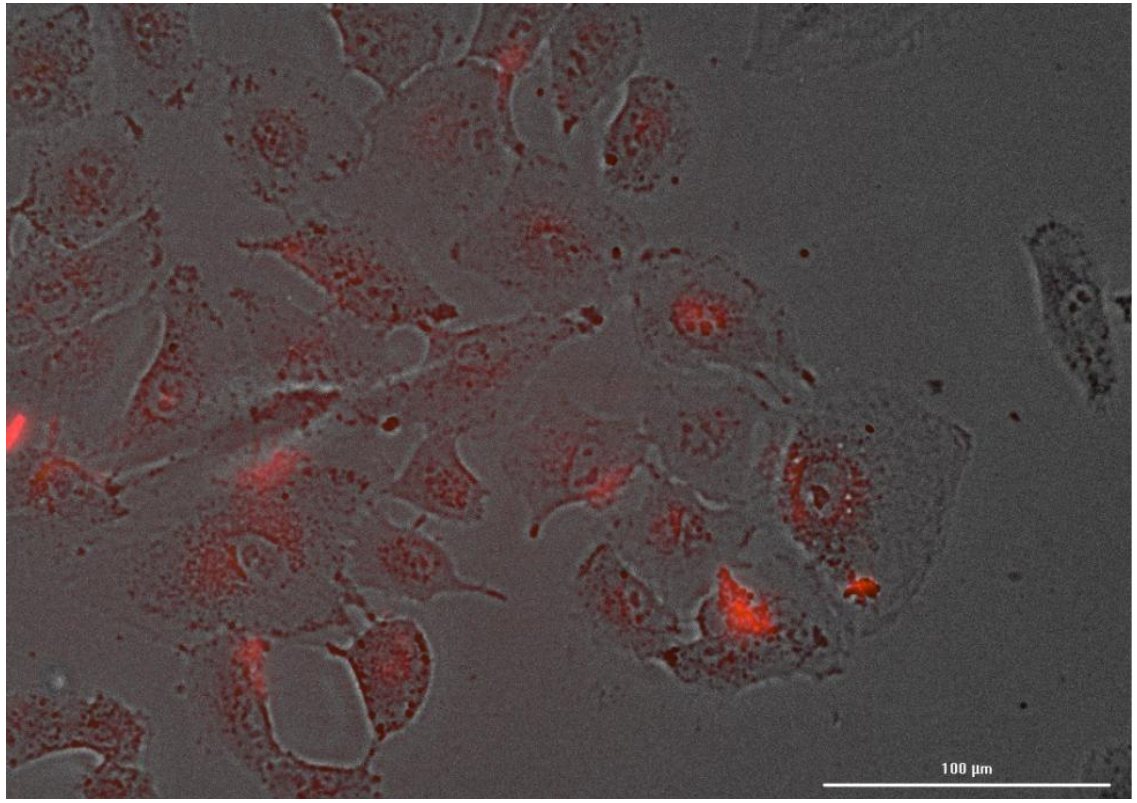


Zhylkybayeva N. et al. (2024) *Scientific Reports*, 14 (1), 27812.
DOI: 10.1038/s41598-024-76500-z

Carbon dots

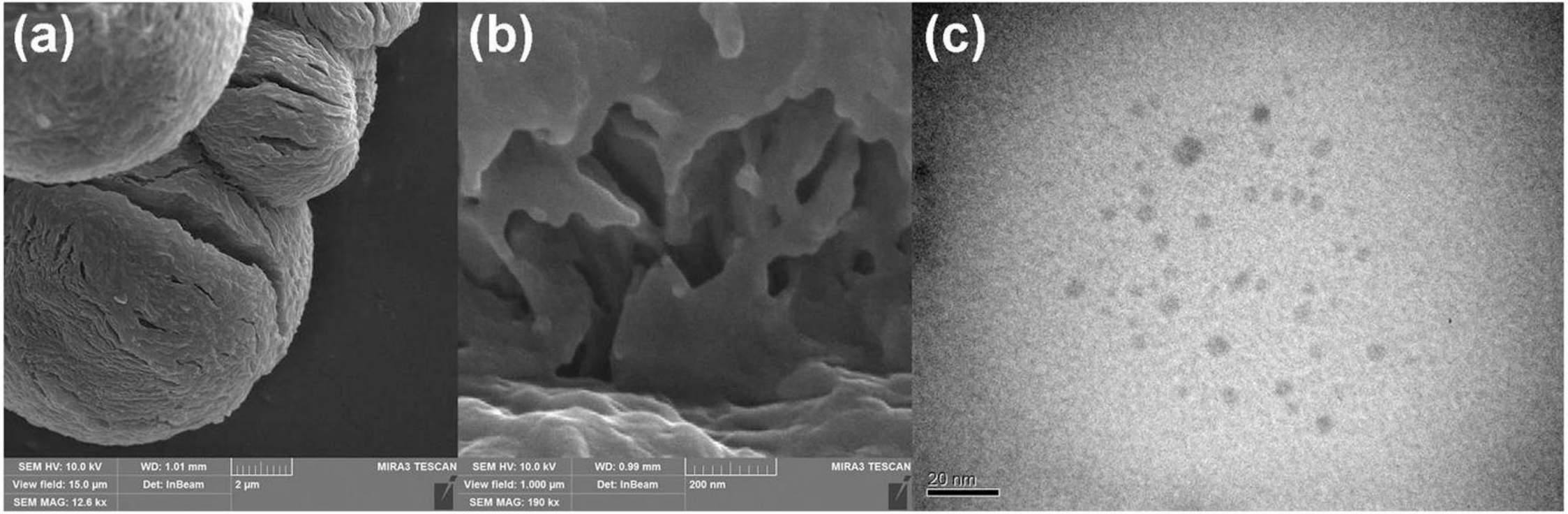
Fluorescent microscopy images of human carcinoma A549 cells labeled with Gd^{3+}- doped CDs at different concentrations: (a) 5 µg/mL; (b) 10 µg/mL.





Zhylkybayeva N. et al. (2024) *Scientific Reports*, 14 (1), 27812.
DOI: 10.1038/s41598-024-76500-z

Carbon dots

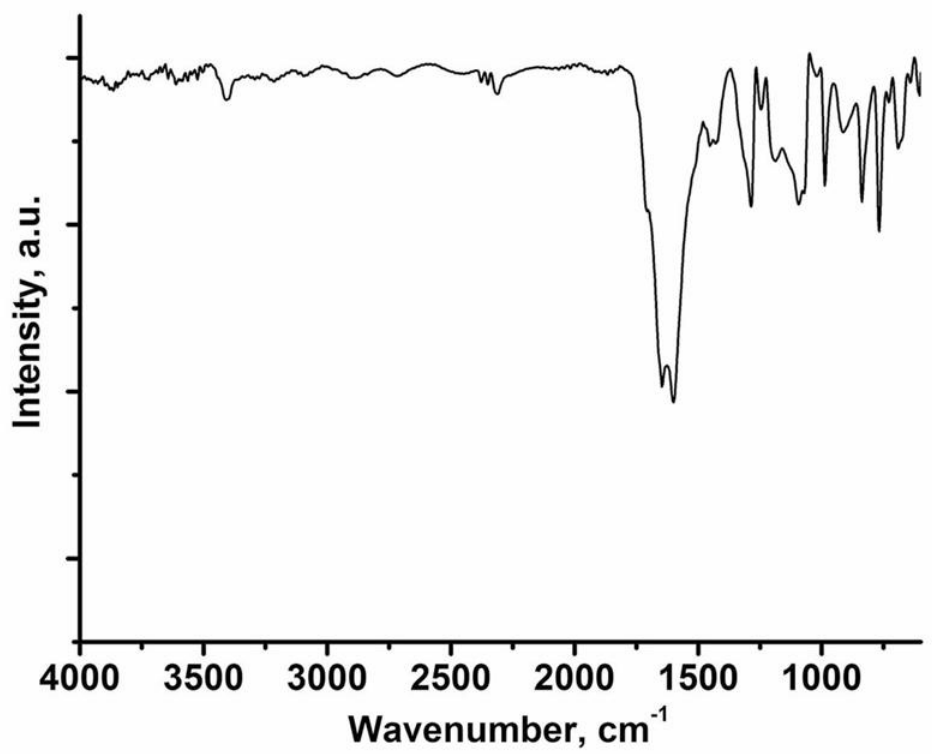


SEM (a, b) images of a solid sample of CNPs and TEM (c) images of carbon nanoparticles.

Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Carbon dots

ATR-FTIR spectrum of a solid sample of CNPs.

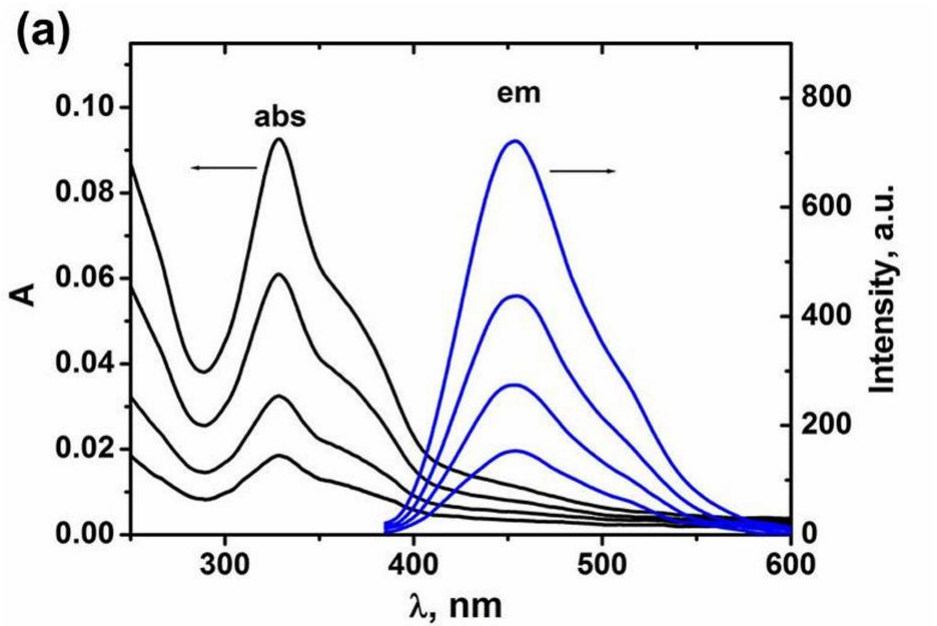


The band with maxima at 1646 and 1600 cm^{-1} corresponds to vibrations of C=O bonds.
The low-intensity band at 1438cm^{-1} corresponds to vibrations of C–N bonds in amino groups.
The more intense band at 1286cm^{-1} probably corresponds to vibrations of C–O bonds in the composition of phenolic and alcohol groups.
A broad band in the range of 1200–1070cm^{-1} covers the region characteristic of in-plane vibrations of =C–H bonds.
Two bands at 988 and 915cm^{-1} may correspond to vibrations of –C–OH bonds in carboxyl groups.
The bands at 840 and 767cm^{-1} probably correspond to out- of-plane vibrations of C–H bonds and ring vibrations of C–H bonds.

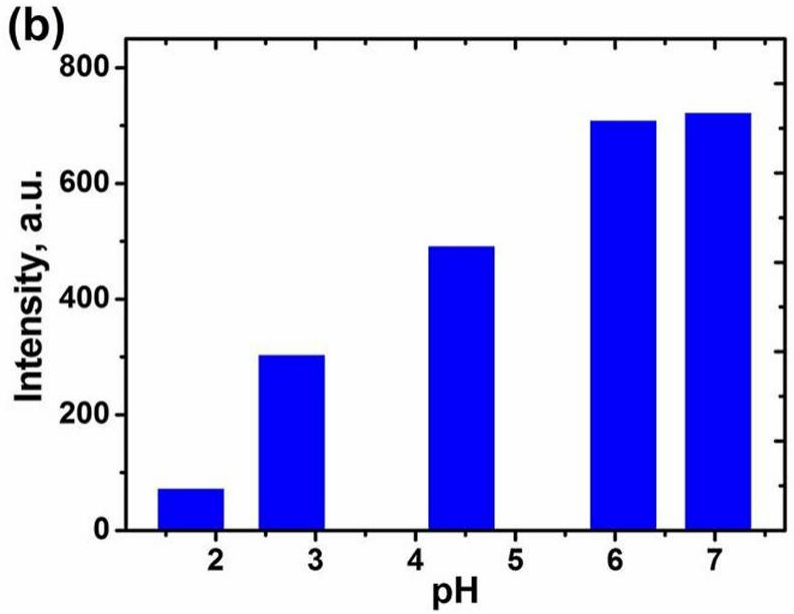
Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Carbon dots

(a) **Optical absorption** (abs) and **PL emission** (em) spectra of aqueous solutions of CNPs (C= 0.5-10 (wt/v, %), C increases with a fixed step size from bottom to top). pH = 7.00, k_{ex} = 360nm, l=1.00cm



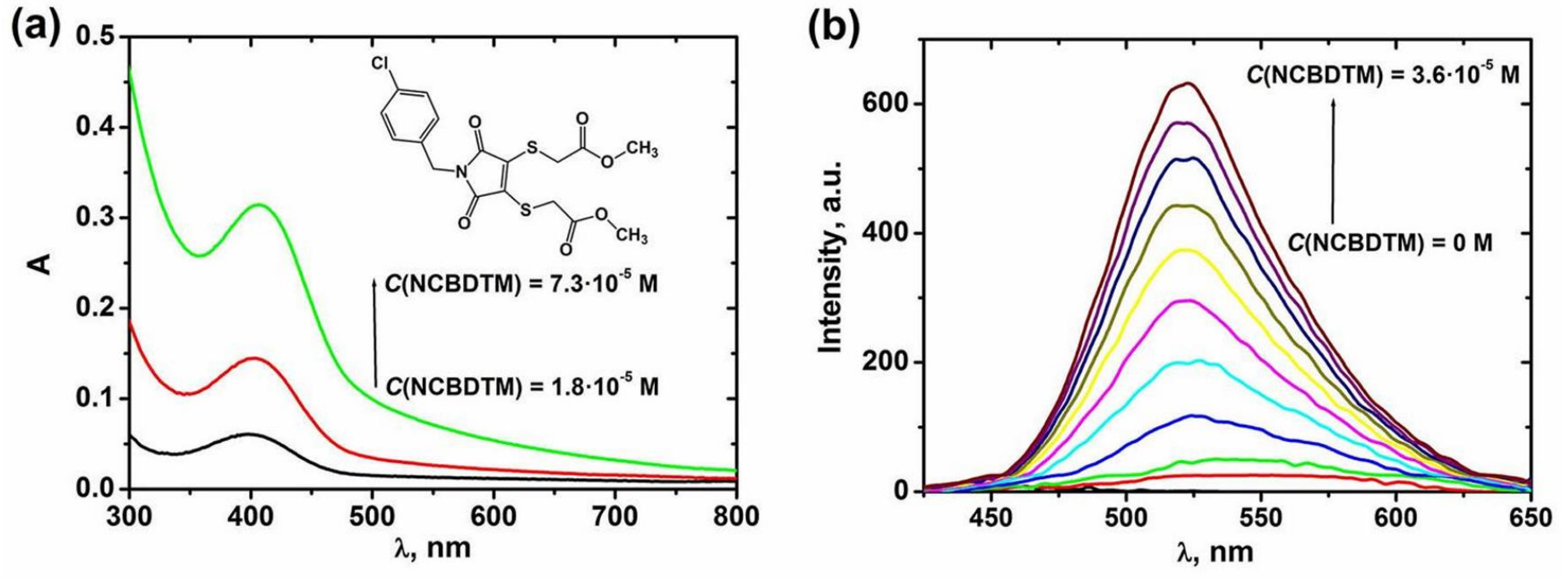
(b) **Dependence of the PL emission intensity** of CNPs on the pH of the solution.
k_{ex} = 360nm, k_{em} =450nm, and l=1.00cm.



Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Carbon dots

New fluorophore molecule:
N-chlorobenzyl dithiomaleimide dimethyl diacetate (NCBDTM)

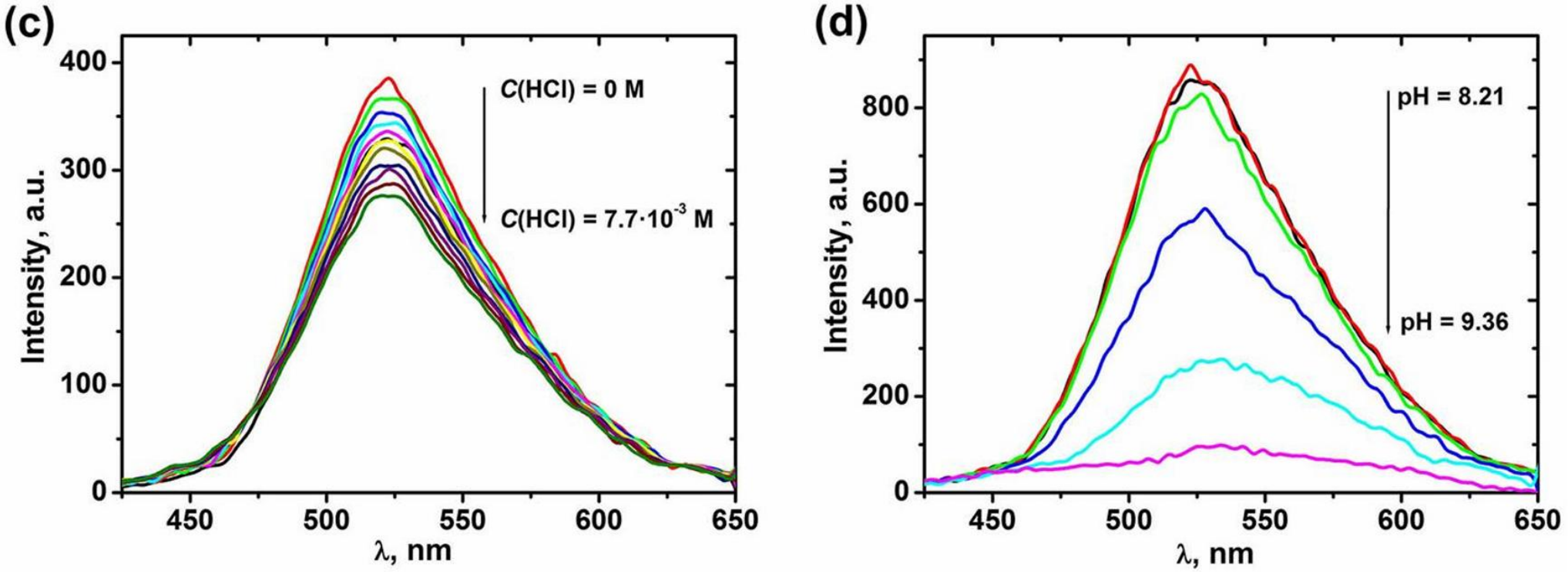


(a) **Absorption spectra of NCBDTM aqueous solutions** at different reagent concentrations.
(b, c) **PL spectra of NCBDTM aqueous solutions** at **different (b) NCBDTM and (c) acid concentrations** and (d) **in an alkaline medium in the range of pH of 8.21–9.36**.

Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Carbon dots

New fluorophore molecule:
N-chlorobenzyl dithiomaleimide dimethyl diacetate (NCBDTM)

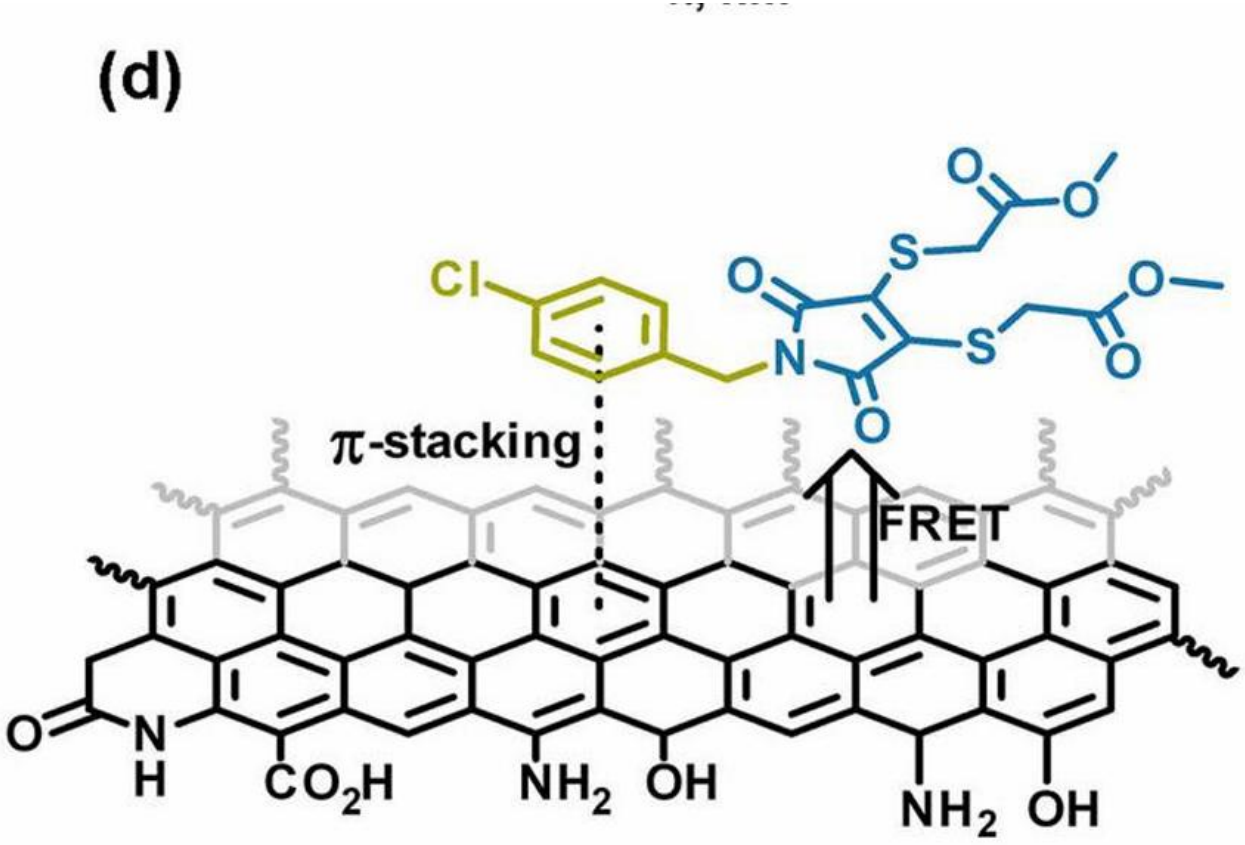


(a) **Absorption spectra of NCBDTM aqueous solutions** at different reagent concentrations.
(b, c) **PL spectra of NCBDTM aqueous solutions** at **different (b) NCBDTM and (c) acid concentrations** and (d) **in an alkaline medium in the range of pH of 8.21–9.36**.

Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

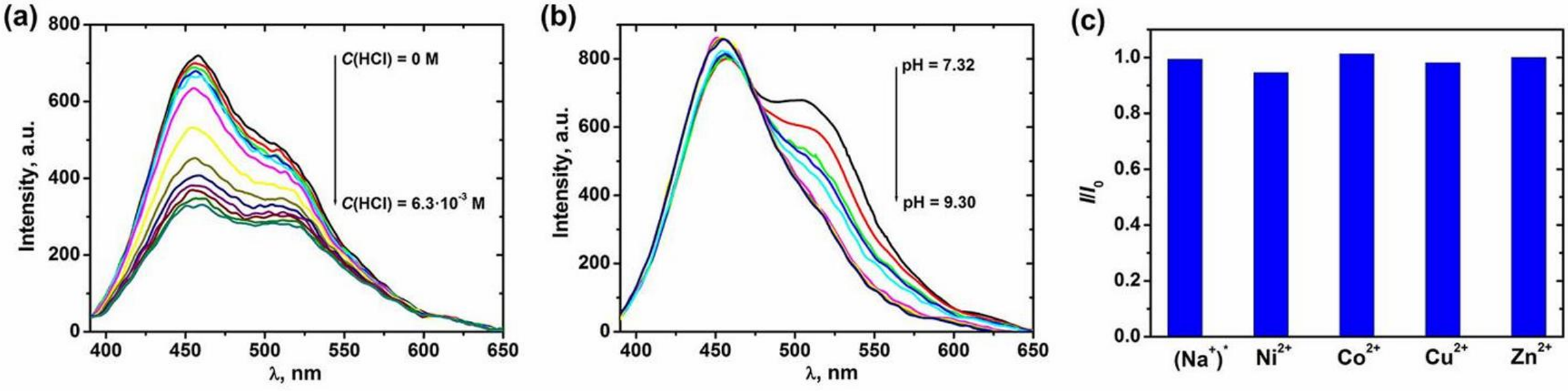
Carbon dots

Scheme of FRET between CNPs and NCBDTM.



Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Carbon dots



(a) **PL spectra** of aqueous solutions of a mixture of CNPs and NCBDTM at (a) **different acidity** and (b) **pH**
(c) **change in the PL intensity** of aqueous solutions of CNPs and NCBDTM mixture, composed as in (a, b) at **different concentrations** of metal cations (Na^+ and M^{2+} = Ni, Co, Cu, and Zn).

Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Conclusions

The developed aromatic system of the CNPs is responsible for the intense blue luminescence of their aqueous solutions, as well as the quantum yield Q of the CNPs in neutral and slightly alkaline aqueous solutions. NCBDTM is characterized by a green-yellow luminescence in aqueous solution and a quantum yield Q of 3.1%. In contrast, a moder ate decrease in the PL intensity of NCBDTM was observed in an acidic environment. Instead, a sharp and irreversible decrease in the PL intensity of NCBDTM is observed in alkaline aqueous solutions at pH > 8.7, which is associated with the opening of the fluorophore cycle. With the combined presence of CNPs and NCBDTM in an aqueous solution, a phenomenon of non-radiative energy transfer from CNPs to NCBDTM by the FRET mechanism is observed, which increases the emission of the organic molecule as acceptor at the excitation wavelength of the donor. The FRET process of the CNPs– NCBDTM system confirms the possible intermolecular interactions and the retention of the analytical response to the acidity of the solution allows the further use of the system with a significant Stokes shift (Dk¼170nm) for the visualization of pH-dependent processes in the green-yellow range of visible light.

Diyuk, N. V. *et al*. 2024. Photoluminescence of Carbon Nanoparticles–Dithiomaleimide System. Mol. Cryst. Liq. Cryst 768 (9): 251–60. doi:10.1080/15421406.2024.2348205.

Acknowledgements:

University of Prešov
Dr. Romana SMOLKOVA, PhD.
Dr. Adriana ELIASOVA, PhD.
Mgr. Viktoria BARTASOVA

Claude Bernard University of Lyon, France
Dr. Vladimir LYSENKO, PhD.

Taras Shevchenko National University of Kyiv, Ukraine
Dr. Vladyslav LISNYAK, DrSc.
Dr. Lyudmyla GRISCHENKO, PhD.
Prof. Valeriy SKRYSHEVSKY, DrSc.
Ivan LYSENKO
Nadiia DIYUK
Dr. Tetiana KEDA
Dr. Alexander ZADERKO

Al-Farabi Kazakh National University, Almaty, Kazakhstan
Dr. Gauhar MUSSABEK, PhD.

University of Opole, Poland
Prof. Oleksandr TASHYREV, DrSc.
Prof. Ewa MOLISZEWSKA, PhD
Dr. Vira HOVORUKHA, PhD

The study is supported by project VEGA 1/0836/25 "Irregularly shaped noble metal nanoparticles for photothermal and sensing applications".

Thank you for your attention!