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CANCER NANOMEDICINE - FROM THE BENCH TO THE BEDSIDE

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Synthesis and characterization of nanofibers functionalized with nanoparticles with anticancer properties

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Short Term Scientific Mission

Title: **Synthesis and characterization of nanofibers functionalized with nanoparticles with anticancer properties**

Duration of mission: **01/07/2022 to 29/07/2022**

HOME INSTITUTION

Jan Kochanowski University of Kielce

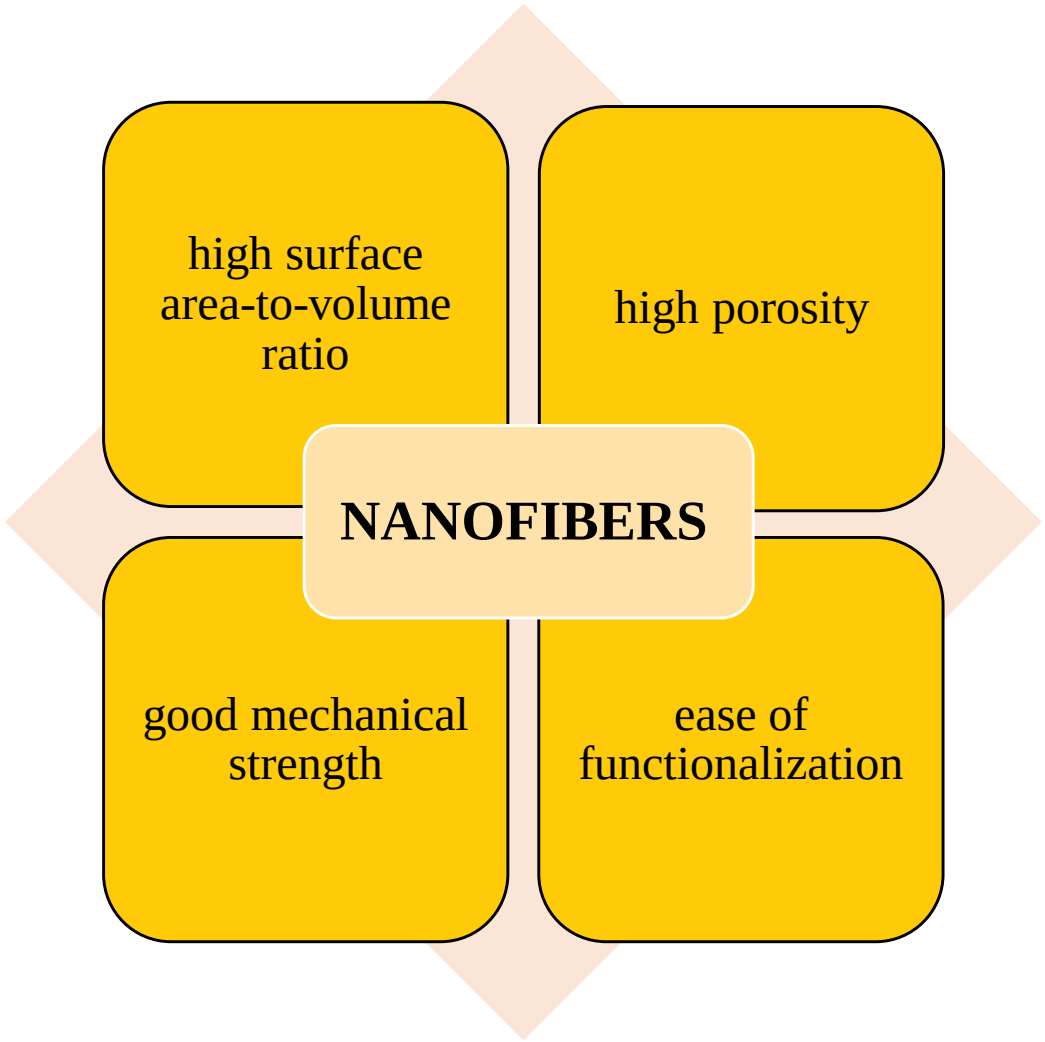
Supervisor: **Dr Karol Ciepluch, Prof. UJK**

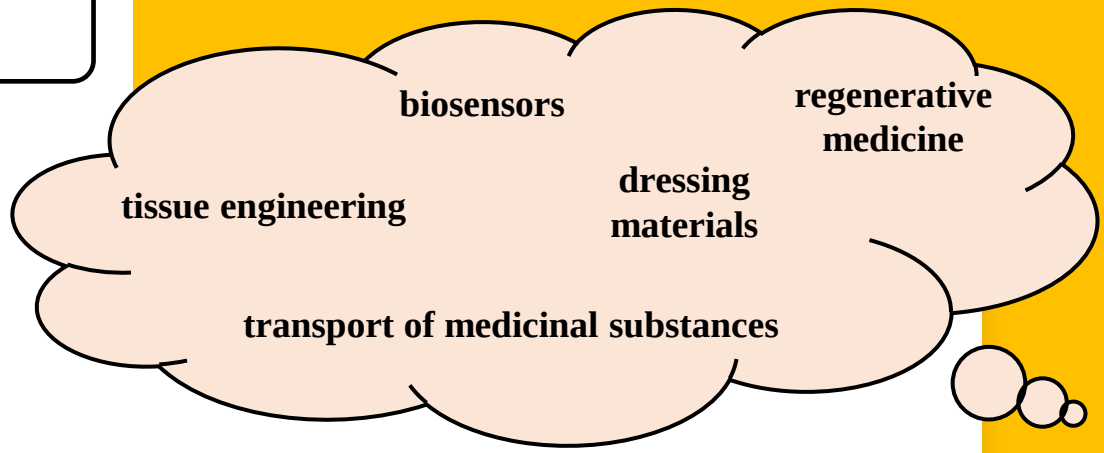
HOST INSTITUTION

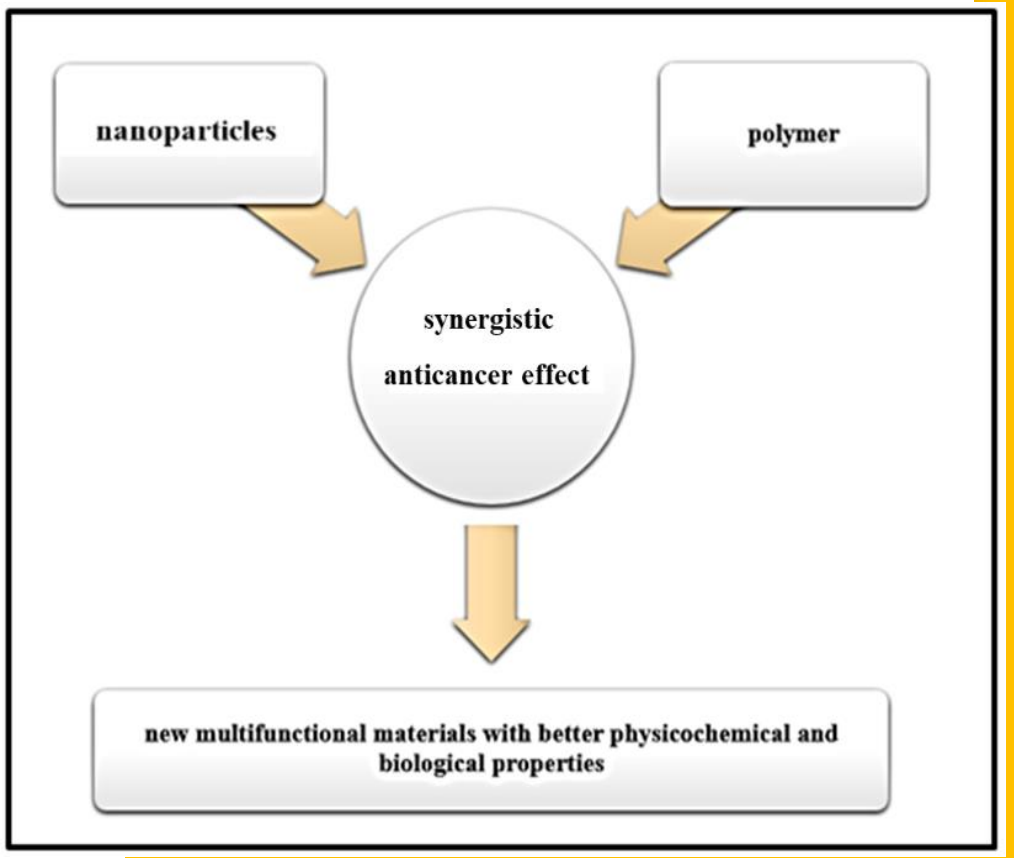
HOCHSCHULE RHEIN-WAAL
Rhine-Waal University of Applied Sciences

Prof. Dr Amir Fahmi

NANOFIBERS

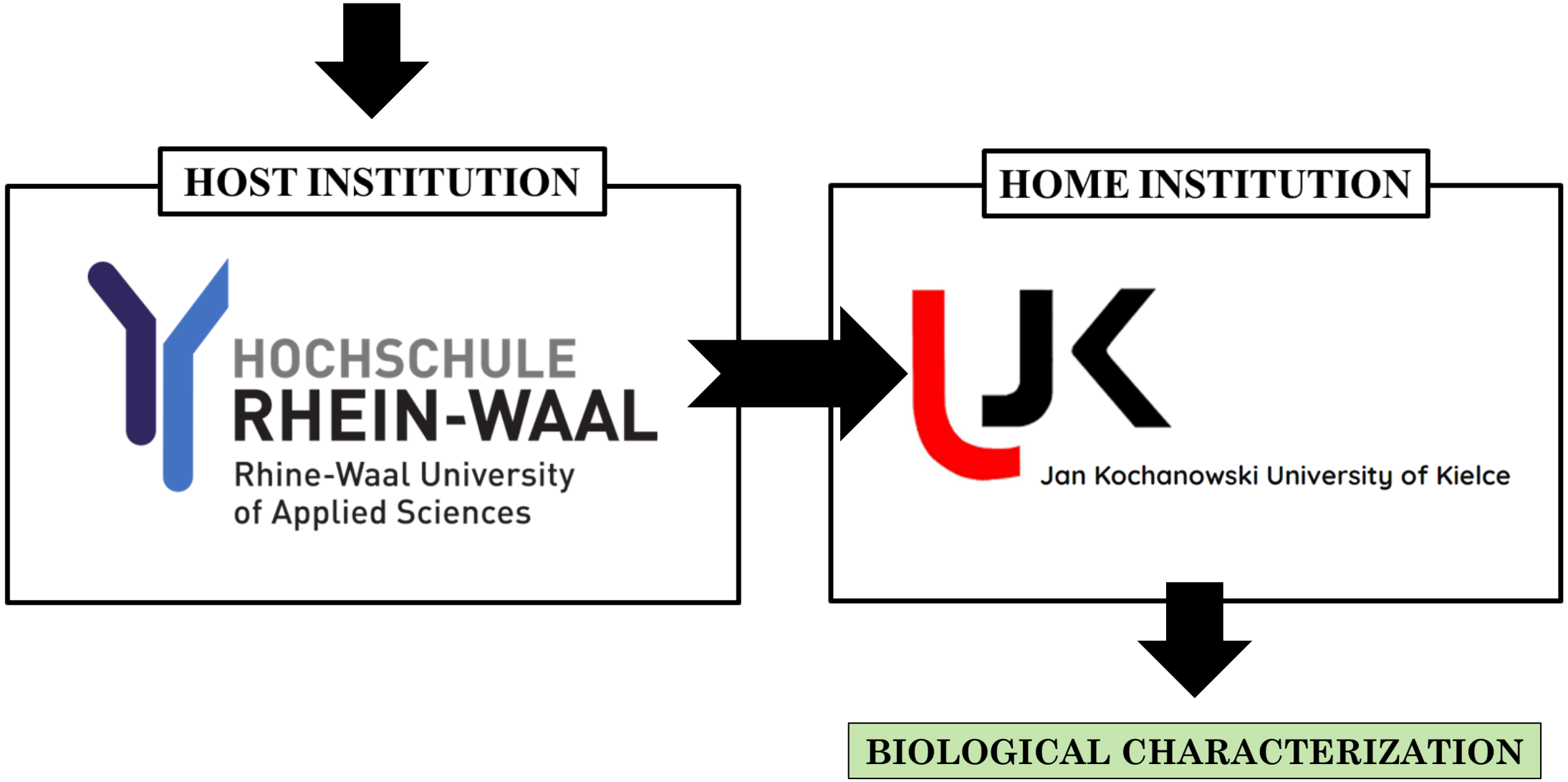

high surface area-to-volume ratio
high porosity
NANOFIBERS
good mechanical strength
ease of functionalization


biosensors
regenerative medicine
tissue engineering
dressing materials
transport of medicinal substances


nanoparticles
polymer
synergistic anticancer effect
new multifunctional materials with better physicochemical and biological properties

Goals of STSM

1. Synthesis of hybrid nanofibers functionalized with different types of nanoparticles.
2. Physicochemical characterization of the fabricated nanofibers.



STSM Research Plan

1.

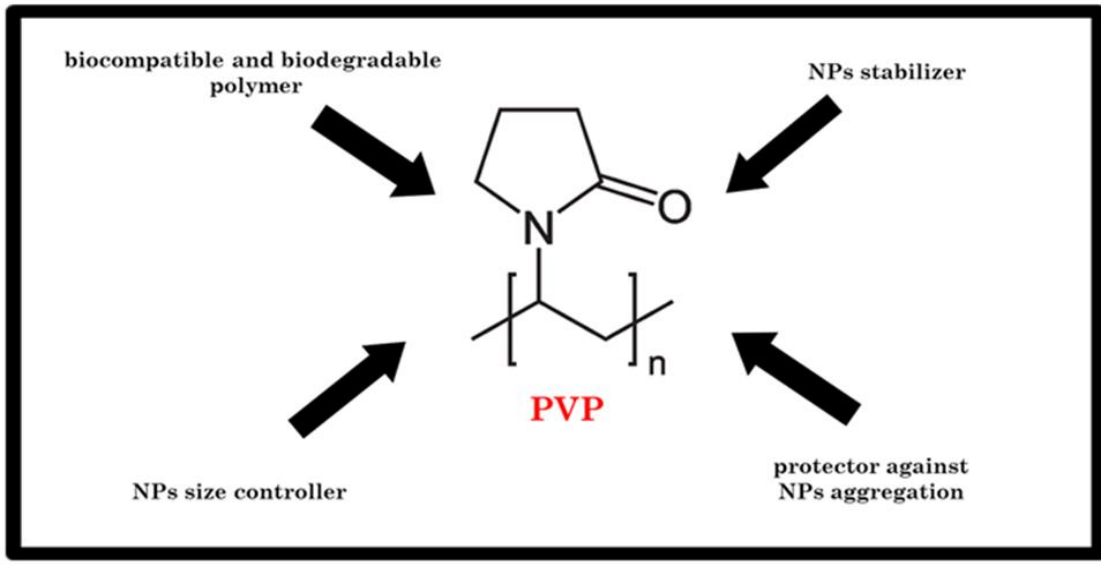
Synthesis of hybrid nanofibers functionalized with nanoparticles - Electrospinning Method

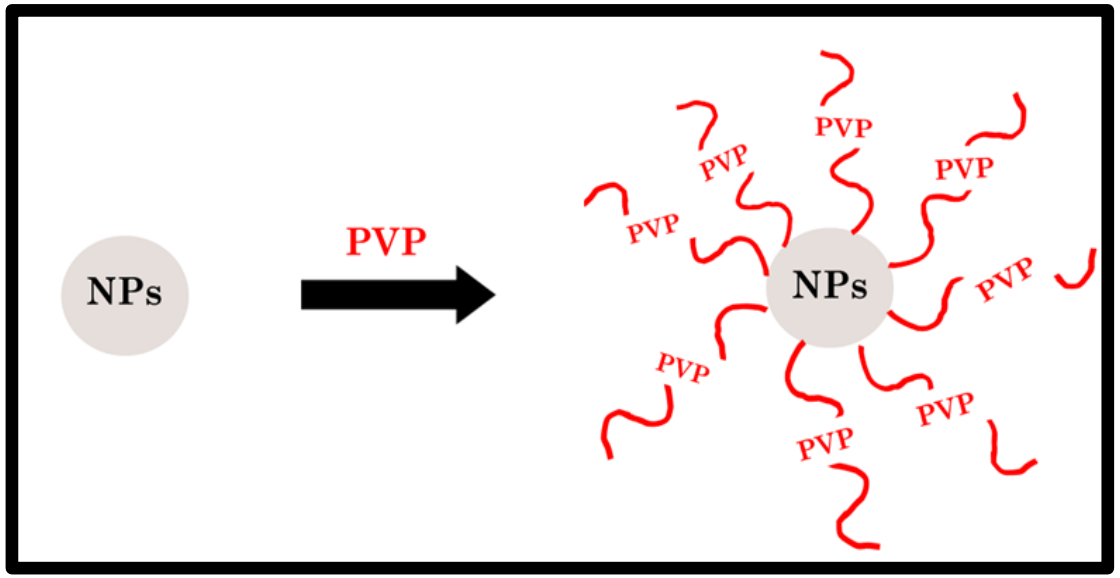
a) PL-b-CL/PVP nanofibers
b) PL-b-CL/PVP+AuNPs nanofibers
c) PL-b-CL/PVP+CdSeNPs nanofibers
d) PL-b-CL/PVP+TaNPs nanofibers

2.

The physicochemical characterization of nanofibers

a) SEM *(Scanning Electron Microscopy)*
b) FTIR *(Fourier Transform Infrared Spectroscopy)*
c) TGA *(Thermogravimetric Analysis)*
d) DSC *(Differential Scanning Calorimetry)*





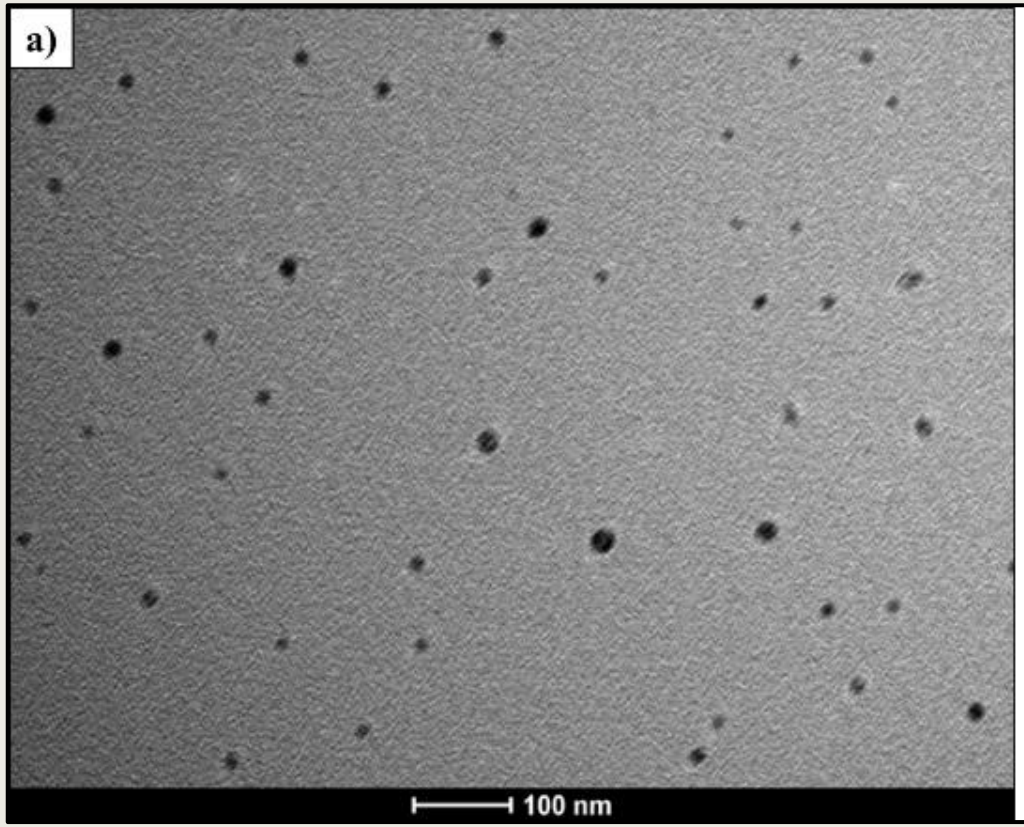
NANOPARTICLES SYNTHESIS

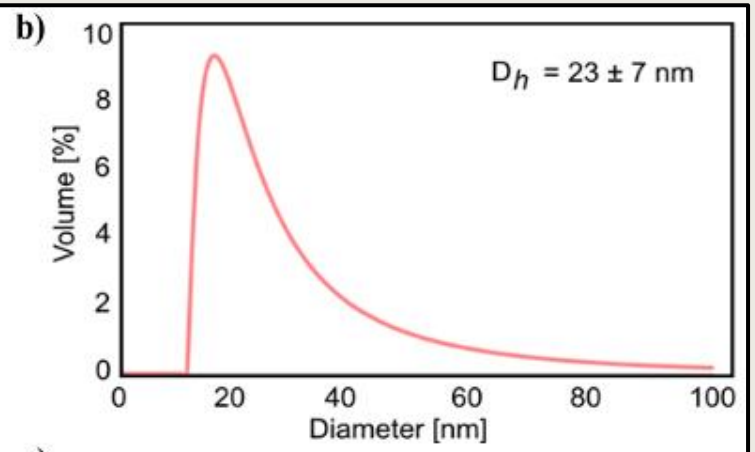
IN SITU PVP
(polyvinylpyrrolidone)

NANOPARTICLES ANALYSIS

	Mean hydrodynamic diameter **
AuNPs	~ 6 nm

	Mean diameter *
TaNPs	12 ± 2 nm



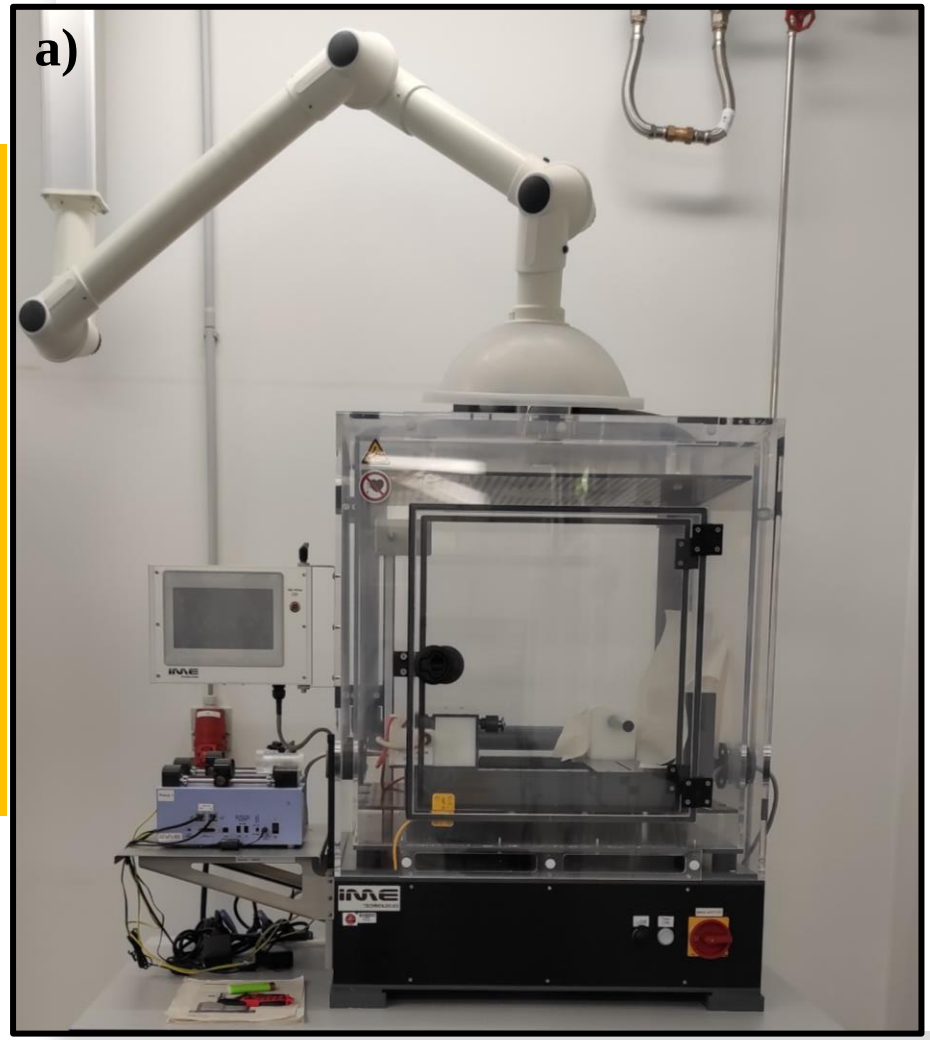


c)

Diameter analysis of CdSeNPs	
Mean diameter*	Mean hydrodynamic diameter **
6 ± 4 nm	23 ± 7 nm

Fig. a) TEM image of CdSe nanoparticles coated with PVP (scale bar = 100 nm); b) DLS graph of CdSeNPs coated with PVP; c) diameter analysis of CdSeNPs coated with PVP. * data based on ImageJ, ** data based on DLS.

Fabrication of nanofibers
Electrospinning Method



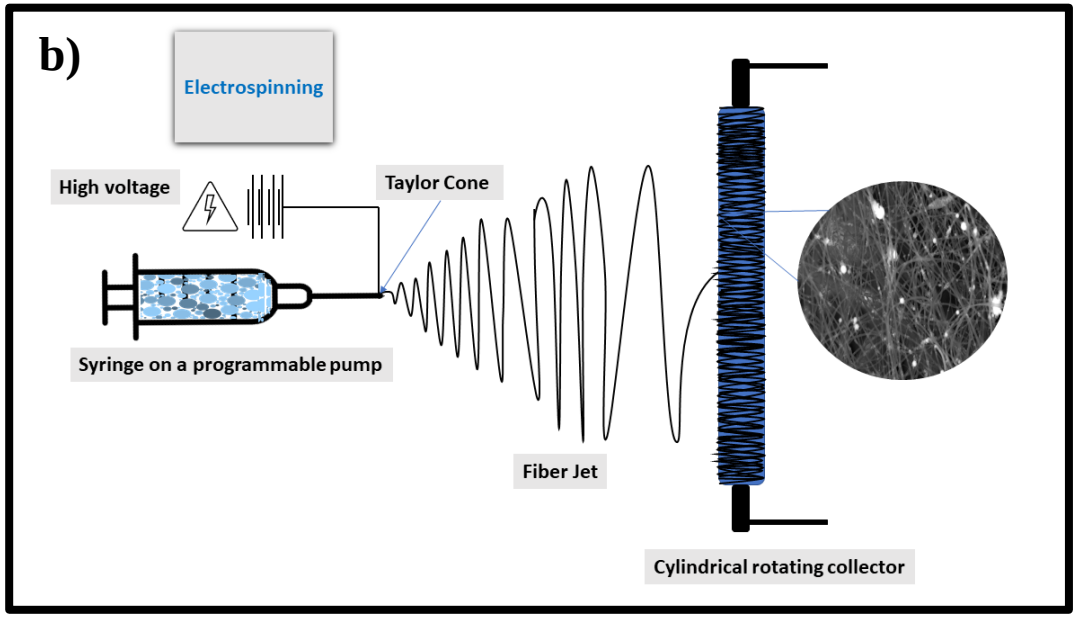


Table 2. The electrospinnig parameters of nanofibers.

PL-b-CL weight (g)	PVP weight (g)	Ratio PL-b-CL/PVP	Voltage (kV)	Flow rate (ml/hr^{-1})	Temperature (^{o}C)	Humidity (%)
0.85	0.21	4:1	12	1	16	85

PL-b-CL = L-lactide/ε-caprolactone copolymer

high-strength and flexibility

Fig. **a)** Electrospinning machine used during the synthesis of nanofibers. **b)** Schematic representation of simple electrospinning set up with rotating cylinder collector *(Nirwan, 2022).*

The physicochemical characterization of nanofibers

SEM

FTIR

TGA

DSC

SEM

Scanning Electron Microscopy

- **cylindrical geometry**
- **rough surfaces**

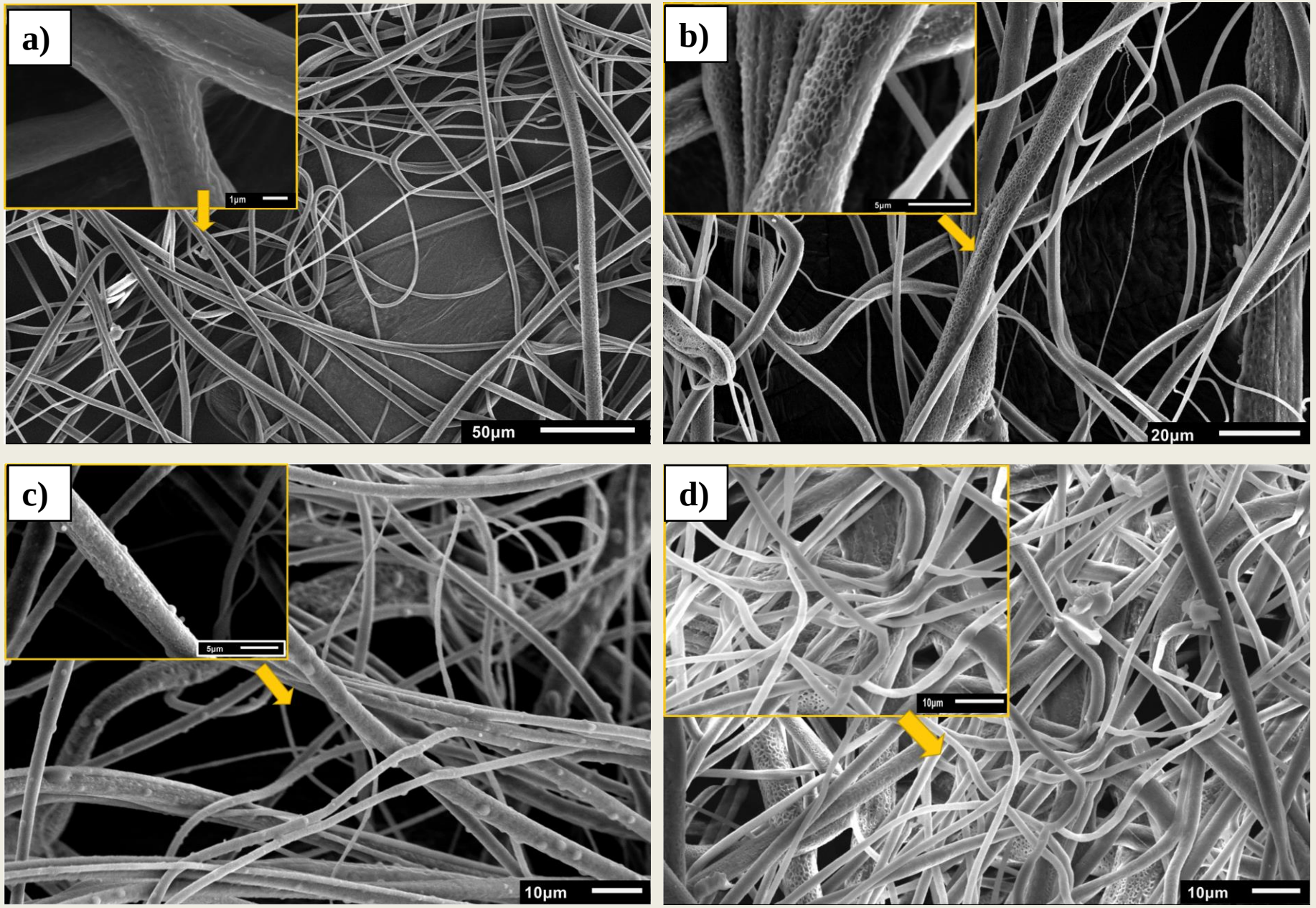


Fig. **SEM images of fabricated nanofibers**: **a)** PL-b-CL/ PVP **b)** CdSe NPs in PL-b-CL/PVP **c)** AuNPs in PL-b-CL/PVP **d)** TaNPs in PL-b-CL/PVP.

SEM

Scanning Electron Microscopy

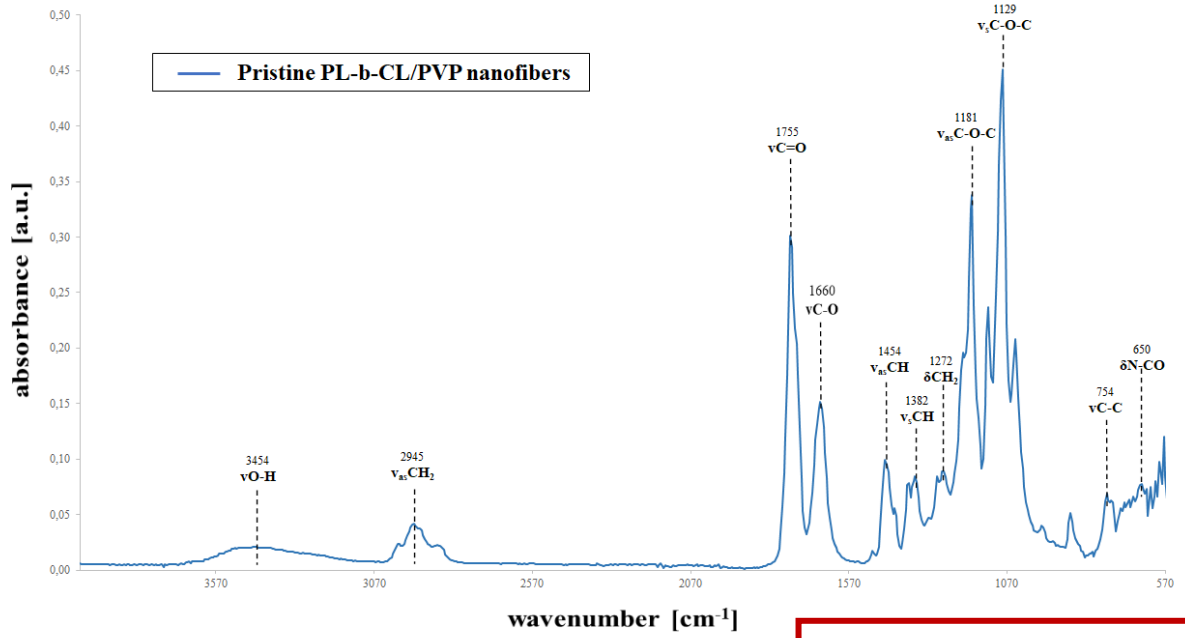
Table 3. Diameter analysis of nanofibers.

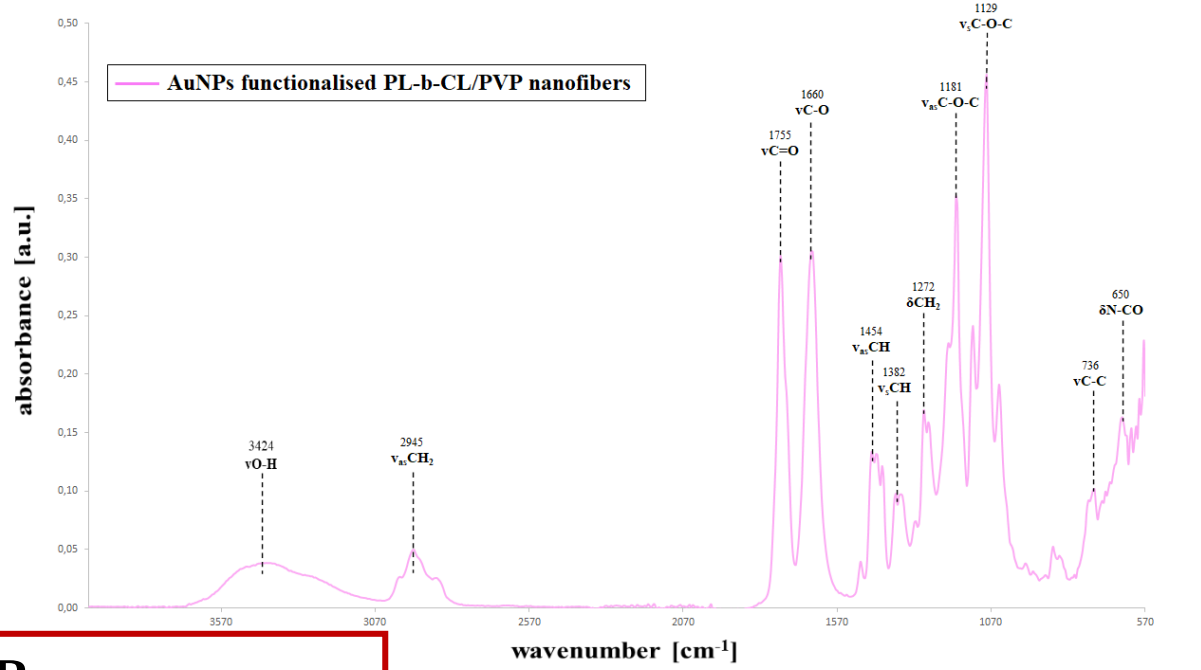
Sample	Mean diameter	Standard deviation
PL-b-CL/ PVP	2.12 μm	1.07 μm
CdSe NPs in PL-b-CL/PVP	1.04 μm	0.7 μm
AuNPs in PL-b-CL/PVP	1.03 μm	0.35 μm
TaNPs in PL-b-CL/PVP	1.64 μm	0.2 μm

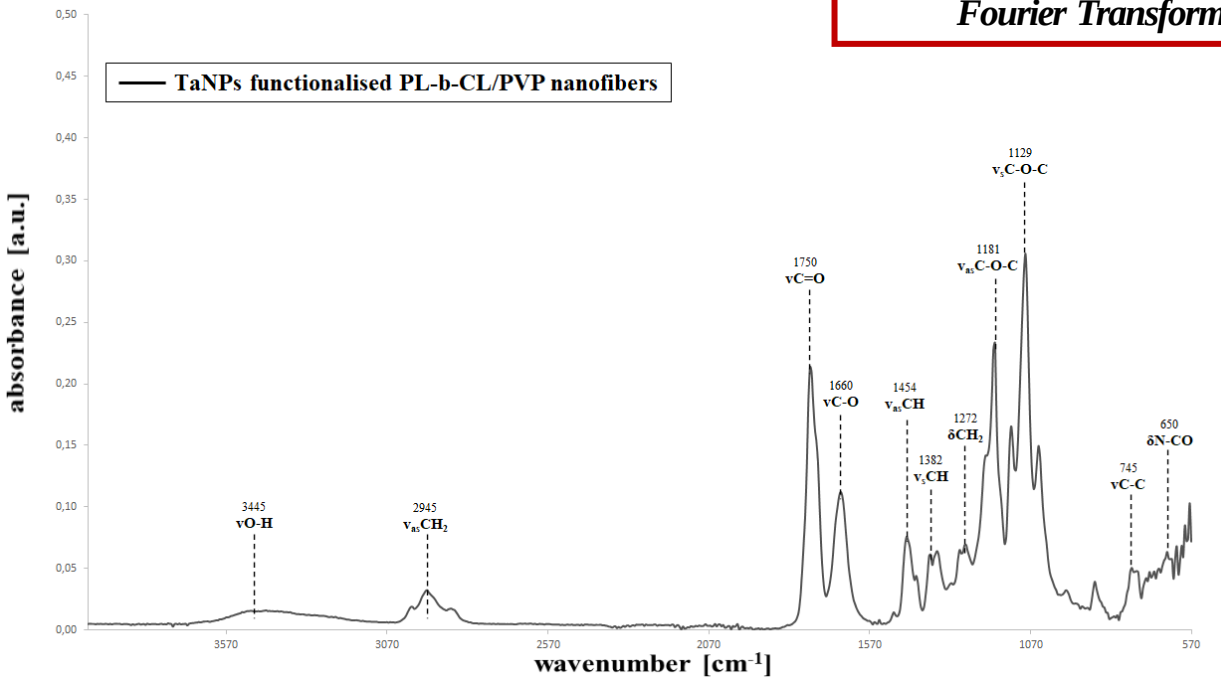
The inclusion of nanoparticles provided relative stability of the electrospinning process.
The presence of NPs can lead to a change in conductivity, viscosity, surface tension, which can result in a change in the size of the diameter.

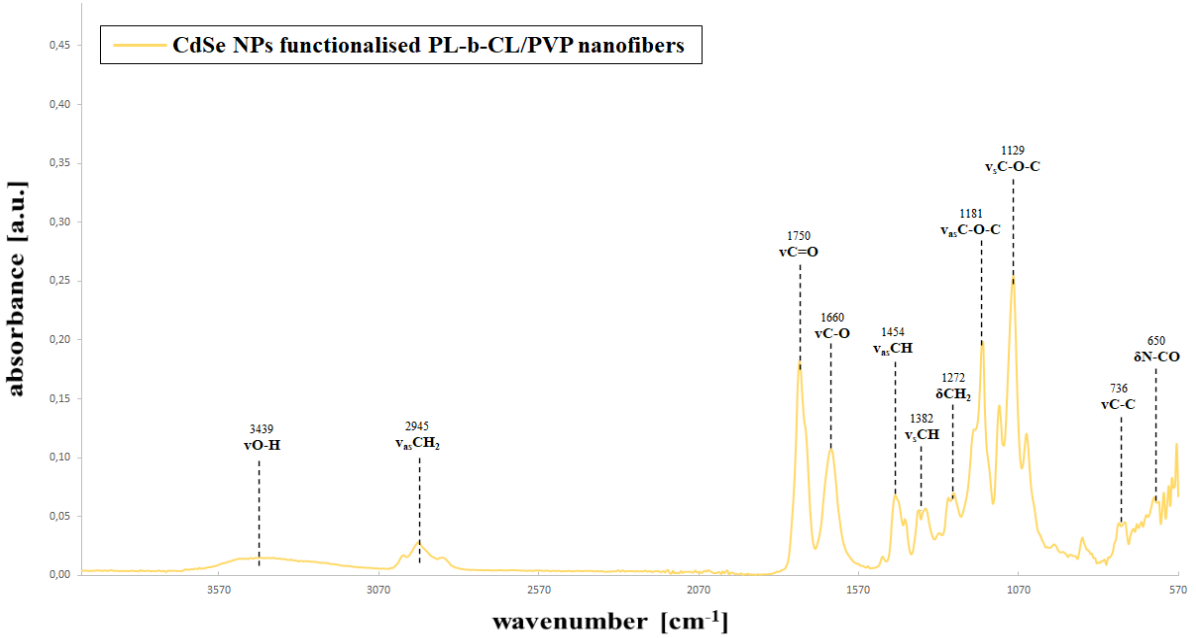
FTIR

Fourier Transform Infrared Spectroscopy





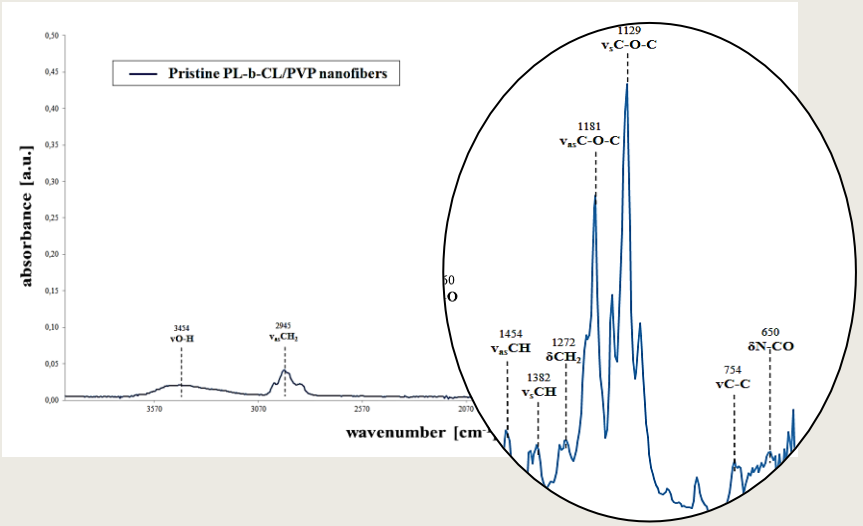


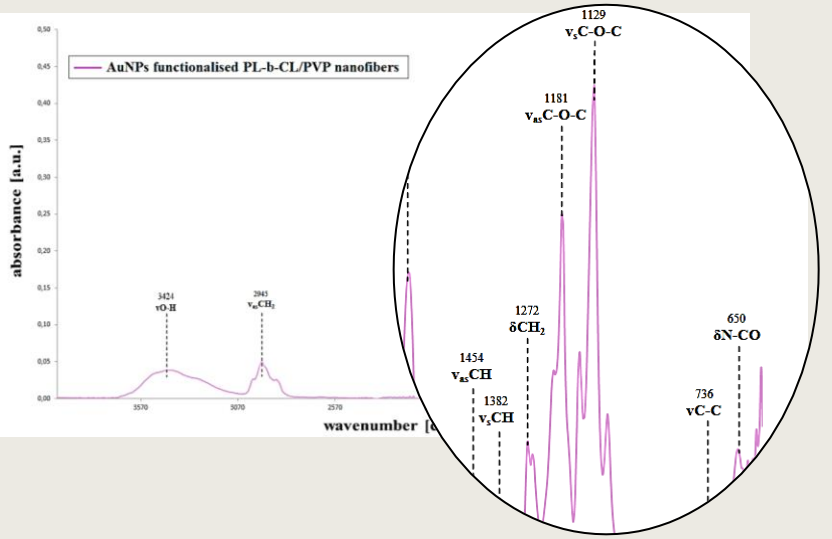


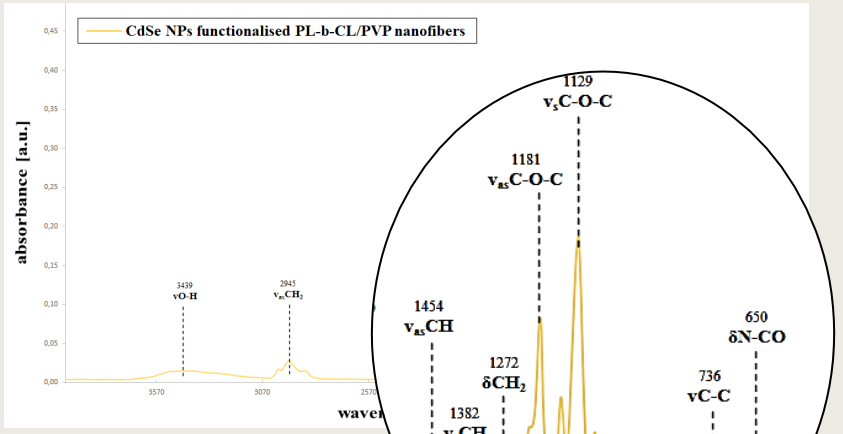
FTIR

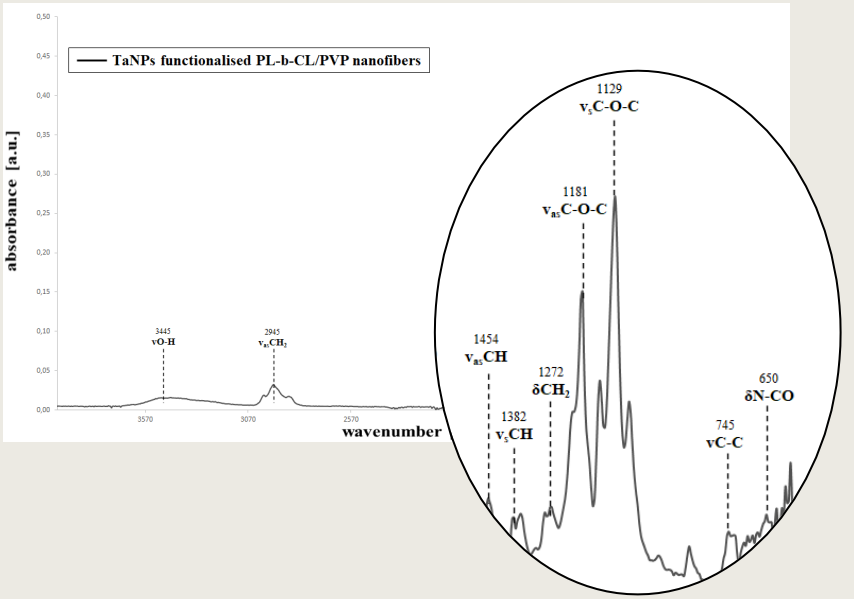
Fourier Transform Infrared Spectroscopy

- FTIR analysis showed slight changes between the absorption spectra of the produced nanofibers.
- The occurring peak shifts (vC-C) may indicate the interaction of PVP-coated nanoparticles and PL-b-CL/PVP matrices.
- The characteristic fingerprint region of polymers used for fabrication of nanofibers, remained unchanged before and after the inclusion of NPs.









The inclusion of NPs favors weak interactions between organic and inorganic moieties.

TGA

Thermogravimetric analysis

- The nanofiber samples showed a 3-stage degradation profile, indicating a multicomponent electrospinning formulation.
- Degradation occurred at 280°C, which was the onset degradation temperature for nanofibers with CdSeNPs.

CdSeNPs inside the nanofibers acting as heat spots, leading to a lower degradation temperature

- Fibers containing NPs were characterized by a lower percentage weight loss.

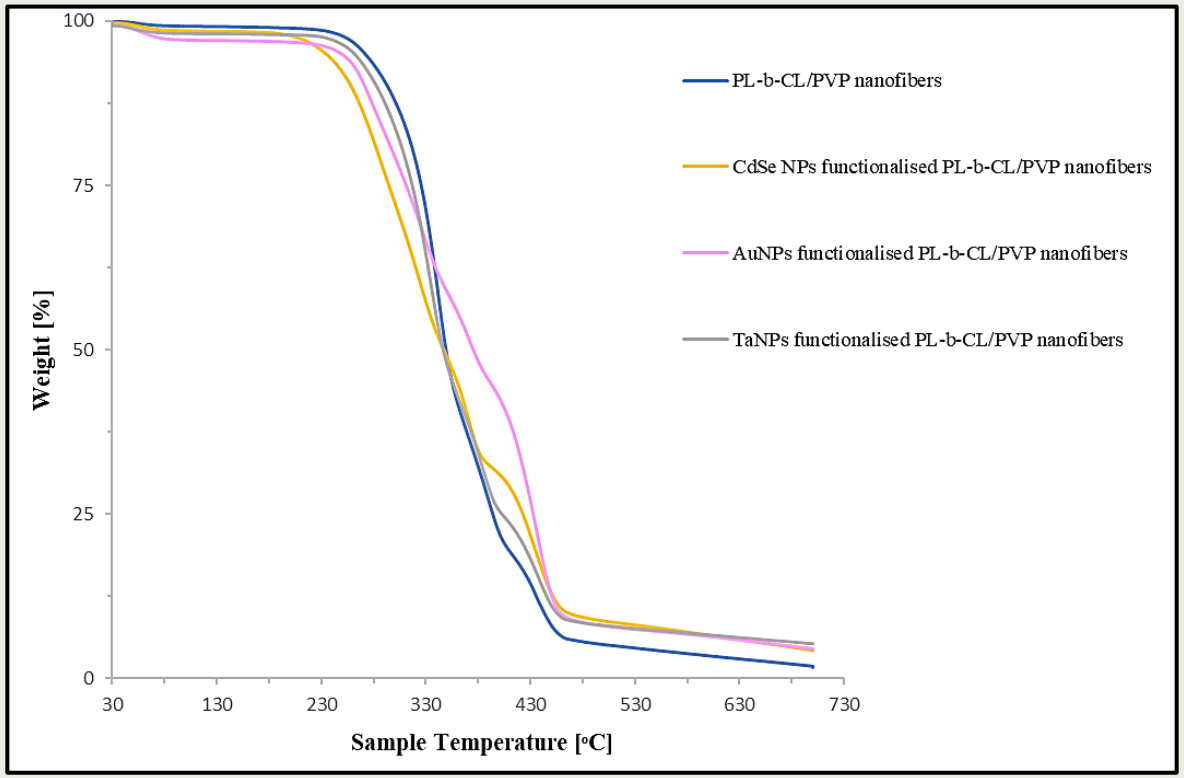


Fig. Thermogravimetric analysis of nanofibers.

Table 4. Data obtained after TGA analysis of nanofibers.

Sample	Onset [°C]	End [°C]	Total Weight Loss [%]
PL-b-CL/ PVP	304	384	98.3
CdSe NPs in PL-b-CL/PVP	280	429	91.6
AuNPs in PL-b-CL/PVP	345	457	95.7
TaNPs in PL-b-CL/PVP	294	389	94.8

DSC

Differential Scanning Calorimetry

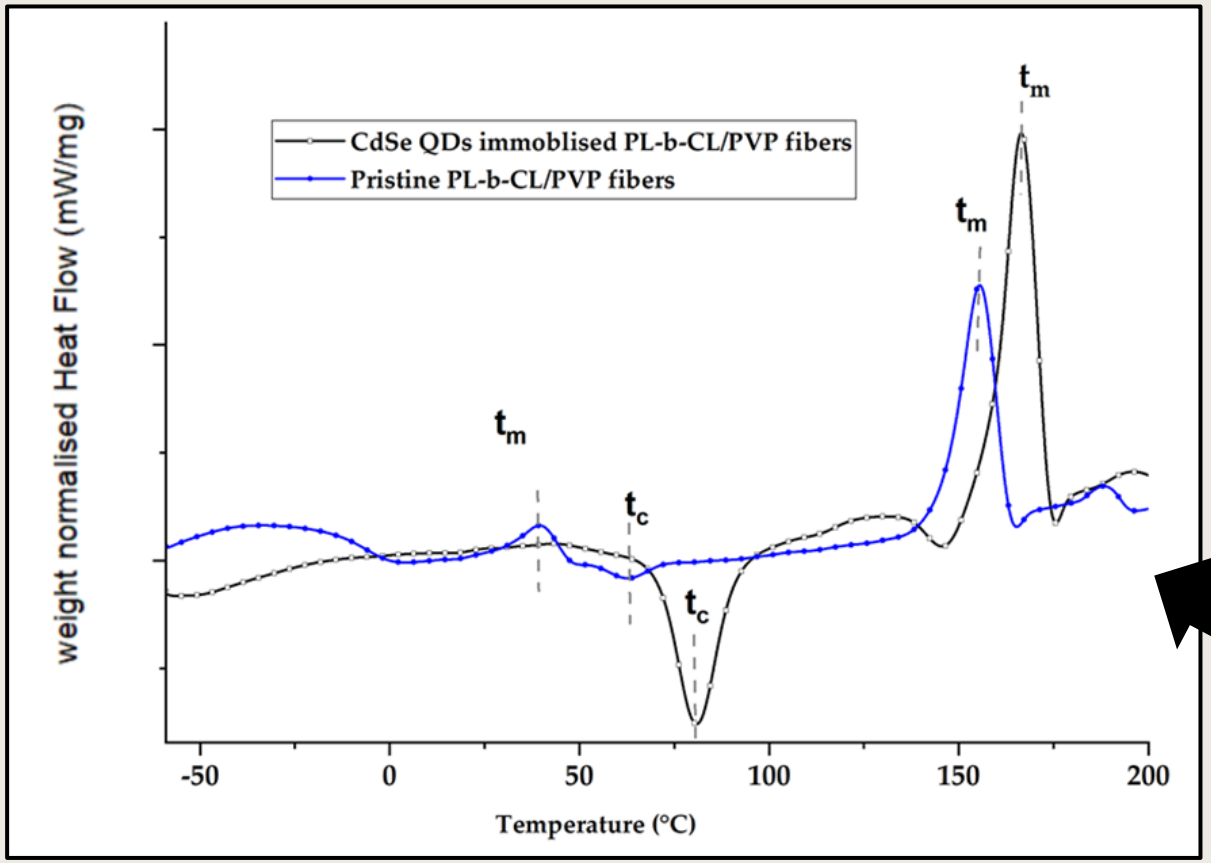
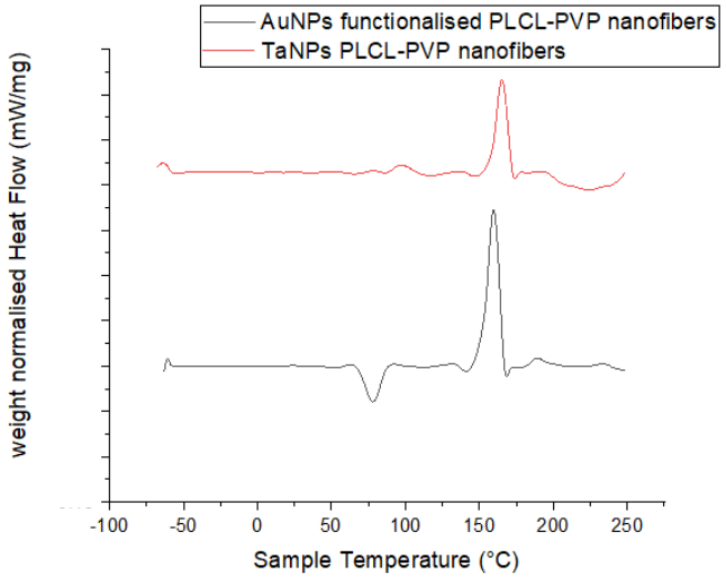


Fig. DSC curve of nanofibers. t_c –crystallization temperature; t_m – melting temperature.



The inclusion of CdSeNPs into nanofibers matrix, increased their amorphosity.

The nanofibers with CdSeNPs had a sharp crystallization peak at 80°C and also had a high melting peak at 166°C.

TGA and DSC analyzes showed that **the inclusion of NPs allows to obtain nanofibers with satisfactory thermal stability**.

The biological characterization of nanofibers

BEAS-2B cells *(human non-cancerous lung epithelial cells)*
A549 cells *(human lung cancer epithelial cells)*

Microscopic observations of cell growth and proliferation in the presence of nanofibers

- **The nanofibers inhibit the growth of BEAS-2B and A549 cells.**
- **PL-b-CL/PVP + CdSeNPs nanofibers clearly inhibit the growth of BEAS-2B and A549 cells.**

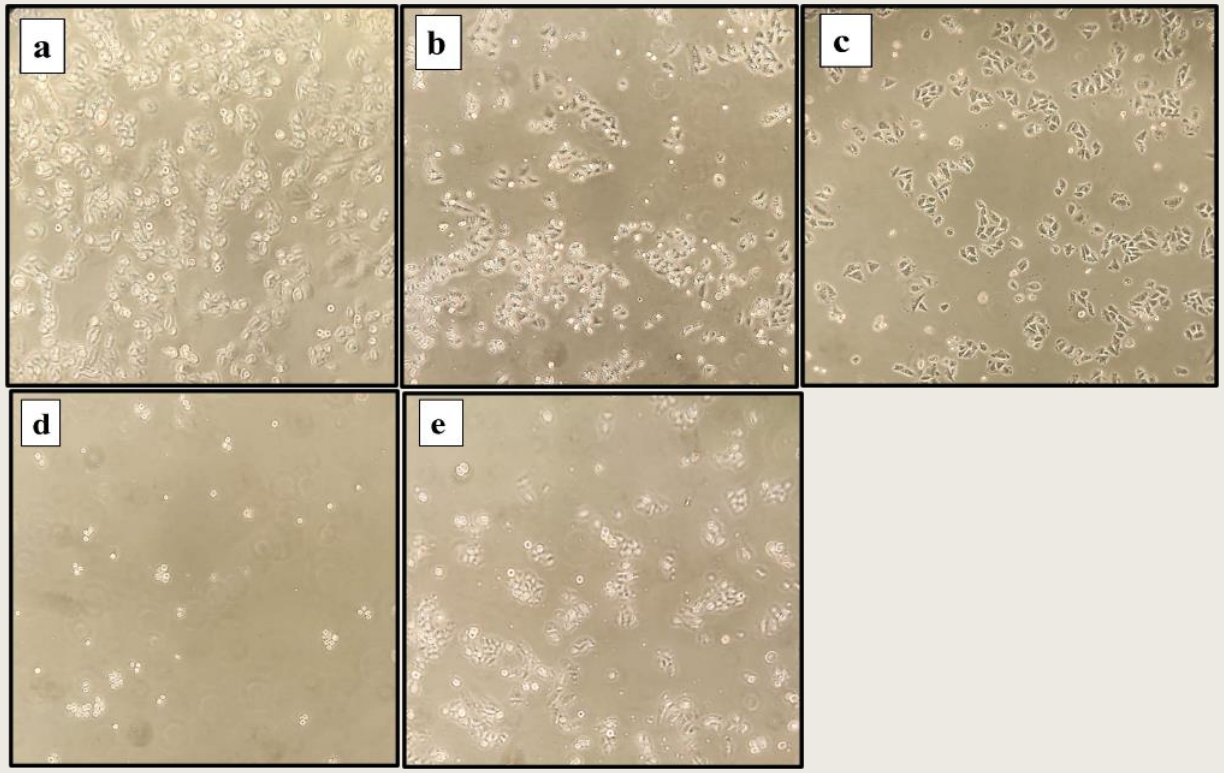


Fig. A549 cells culture after 72h incubation with various types of nanofibers. Untreated A549 cells were used as control **(a)**. Cells cultured in the presence PL-b-CL/PVP **(b)**, PL-b-CL /PVP + AuNPs **(c)**, PL-b-CL/PVP + CdSeNPs **(d)**, PL-b-CL/PVP + TaNPs **(e)**. The culturing was carried out in 6-well plates. The pictures from an optical microscope (x64).

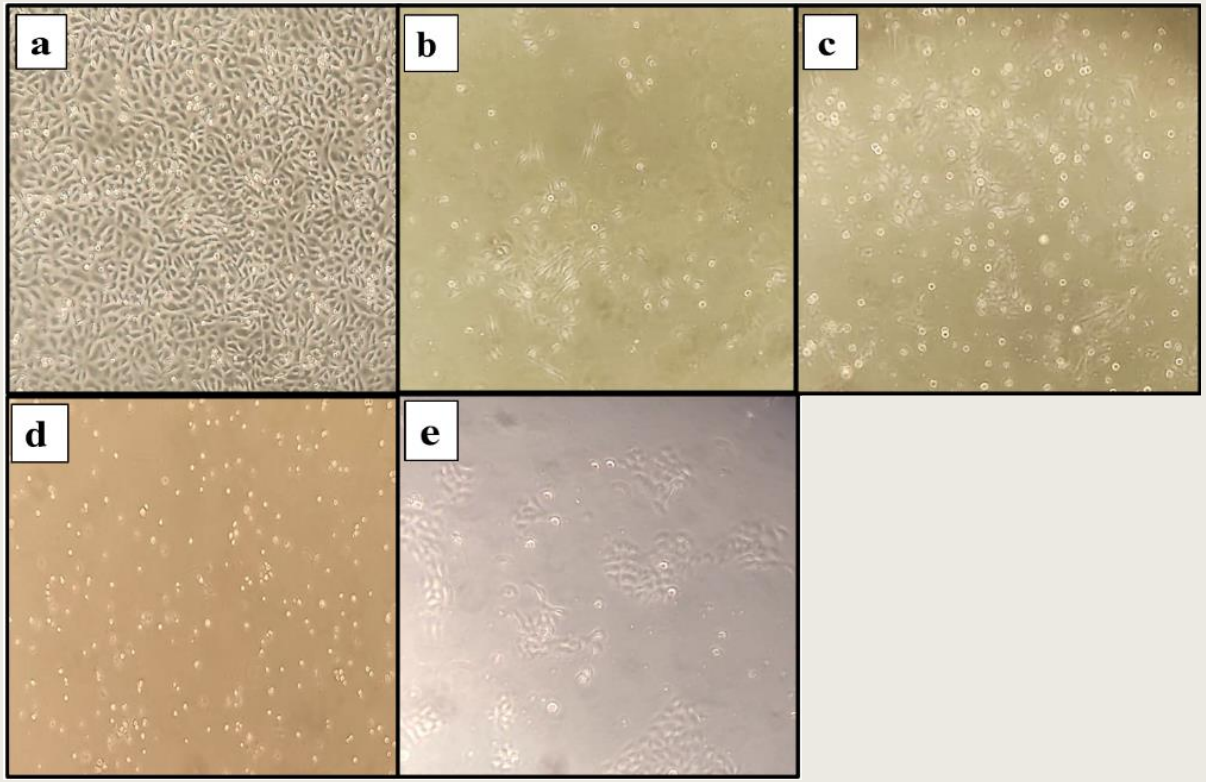


Fig. BEAS-2B cells culture after 72h incubation with various types of nanofibers. Untreated BEAS-2B cells were used as control (a). Cells cultured in the presence PL-b-CL/PVP (b), PL-b-CL/PVP + AuNPs (c), PL-b-CL/PVP + CdSeNPs (d), PL-b-CL/PVP + TaNPs (e). The culturing was carried out in 6-well plates. The pictures from an optical microscope (x64).

MTS

Assessment of nanofibers cytotoxicity

- **PL-b-CL/PVP + CdSeNPs nanofibers were the most cytotoxic to BEAS-2B and A549 cells.**
- **PL-b-CL/PVP + CdSeNPs nanofibers reduced the viability of BEAS-2B and A549 cells to ~ 20%.**

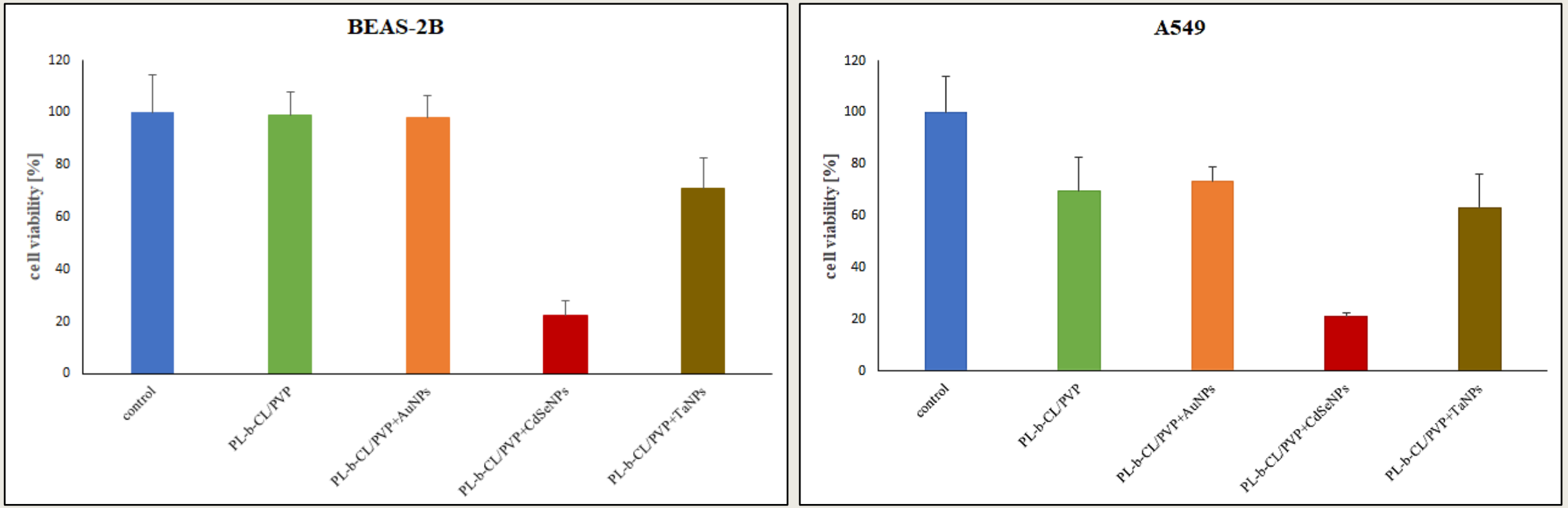
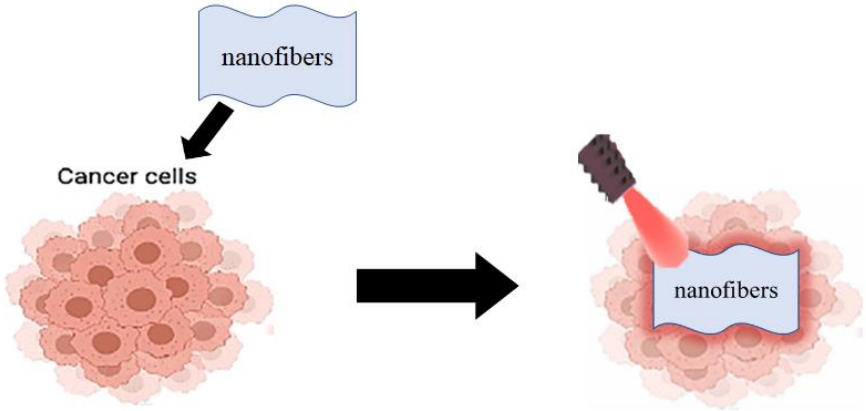


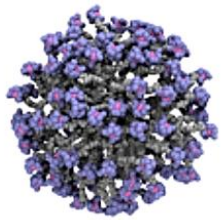
Fig. The cell viability of BEAS-2B and A549 cells treated with nanofibers. Untreated cells were used as control. Experiments were performed in triplicate and results are presented as percentage of control.

PL-b-CL/PVP + CdSeNPs nanofibers

toxic to BEAS-2B cells ⟷ toxic to A549 cells (cancer cells)

THE ANTICANCER AGENTS IN THE LOCAL TREATMENT OF CANCER
(e.g. in photodynamic therapy)





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CANCER NANOMEDICINE - FROM THE BENCH TO THE BEDSIDE

nanomaterials

MDPI

Article

Hybrid Nanomat: Copolymer Template CdSe Quantum Dots In Situ Stabilized and Immobilized within Nanofiber Matrix

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Abstract: Fabrication and characterization of hybrid nanomats containing quantum dots can play a prominent role in the development of advanced biosensors and bio-based semiconductors. Owing to their size-dependent properties and controlled nanostructures, quantum dots (QDs) exhibit distinct optical and electronic characteristics. However, QDs include heavy metals and often require stabilizing agents which are toxic for biological applications. Here, to mitigate the use of toxic ligands, cadmium selenide quantum dots (CdSe QDs) were synthesized in situ with polyvinylpyrrolidone (PVP) at room temperature. The addition of PVP polymer provided size regulation, stability, and control over size distribution of CdSe QDs. The characterization of the optical properties of the CdSe QDs was performed using fluorescence and ultraviolet–visible (UV-Vis) spectroscopy. CdSe QDs exhibited a typical absorbance peak at 280 nm and a photoluminescence emission peak at 580 nm. Transmission electron microscopy (TEM) micrographs demonstrated that CdSe QDs having an average size of 6±4 nm were obtained via wet chemistry method. CdSe QDs were immobilized in a blend of PVP and poly(L-lactide-co-ε-caprolactone) (PL-b-CL) copolymer that was electrospun to produce nanofibers. Scanning electron microscopy (SEM), thermal analyses and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) were used to characterize properties of fabricated nanofibers. Both pristine and hybrid nanofibers possessed cylindrical geometry and rough surface features, facilitating increased surface area. Infrared absorption spectra showed a slight shift in absorbance peaks due to interaction of PVP-coated CdSe QDs and nanofiber matrix. The presence of CdSe QDs influenced the fiber diameter and their thermal stability. Further, in vitro biological analyses of hybrid nanofibers showed promising antibacterial effect and decline in cancer cell viability. This study offers a simple approach to obtain hybrid nanomats immobilized with size-controlled PVP-coated CdSe QDs, which have potential applications as biosensors and antibacterial and anticancer cell agents.

Citation: Nirwan, V.P.; Lasak, M.; Ciepluch, K.; Fahmi, A. Hybrid Nanomat: Copolymer Template CdSe Quantum Dots In Situ Stabilized and Immobilized within Nanofiber Matrix. *Nanomaterials* **2023**, *13*, 630. https://doi.org/10.3390/nano13040630

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References

- Khalil AM, Hassan ML, Ward AA. Novel nanofibrillated cellulose/polyvinylpyrrolidone/silver nanoparticles films with electrical conductivity properties. *Carbohydrate Polymers*. 2016; 157:503–511.
- https://www.brookhaveninstruments.com/molecular-weight-of-pvp-with-the-bi-mwa/
- Nirwan VP, Kowalczyk T, Bar J, Buzgo M, Filová E, Fahmi A. Advances in Electrospun Hybrid Nanofibers for Biomedical Applications. *Nanomaterials*. 2022; 12(11):1829.
- Abadi B, Goshtasbi N, Bolourian S, Tahsili J, Adeli-Sardou M, Forootanfar H. Electrospun hybrid nanofibers: Fabrication, characterization, and biomedical applications. *Frontiers in Bioengineering and Biotechnology*. 2022; 10.
- Contreras-Cáceres R, Cabeza L, Perazzoli G, Díaz A, López-Romero JM, Melguizo C, Prados J. Electrospun Nanofibers: Recent Applications in Drug Delivery and Cancer Therapy. *Nanomaterials*. 2019; 9(4):656.
- Koczkur KM, Mourdikoudis S, Polavarapu L, Skrabalak SE. Polyvinylpyrrolidone (PVP) in nanoparticle synthesis. *Dalton Transactions*. 2015;44(41):17883–905.
- Kim G-M, Le KHT, Giannitelli SM, et al. Electrospinning of PCL/PVP blends for tissue engineering scaffolds. *J Mater Sci Mater Med Mater Med*. 2013; 24: 1425–1442
- Trotsiuk L, Antanovich A, Lizunova A, Kulakovich O. Direct synthesis of amphiphilic polyvinylpyrrolidone-capped gold nanoparticles in chloroform. *Colloid and Interface Science Communications*. 2020;37:100289.