1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Development of multi-instrumental approach for analysis of human fingerprints and its application in forensic science

1.1. Project goals aimed at development of multi-instrumental approach for the analysis of human fingerprints.

Analysis of fingerprints is a key element in study of the crime scenes as well as forensic investigations. However, it is challenged by limitations of analytical techniques since fingerprints have complex chemical composition consisting of lipids, fatty acids, sebum compounds, sweat metabolites. Therefore, the aim of the study is to develop multi-instrumental approach for comprehensive study of human fingerprints. Low molecular weight metabolites (in both sebaceous and sweat fingerprints) will be targeted aiming at revealing individual's lifestyle, differentiation between several groups, which potentially can narrow the search of suspects. Spectroscopic and spectrometric techniques will be applied for targeted search and chemical profiling of fingerprints.

1.2. Outline

Spectroscopic and spectrometric techniques allow for direct profiling of fingerprints without the need of extraction and separation prior to analysis. This advantage allows for facile chemical profiling of fingerprints directly deposited on the substrate. Substrates assisted with nanomaterials may provide intense analytical signals, when used in spectroscopic and spectrometric techniques such as FTIR, Raman and LDI. Optical properties of nanomaterials are determined by size and morphology, as well as method of synthesis and deposition. Wet chemical methods are simple in use, however deposition of colloidal solution onto the substrate lead to formation of the "coffee ring" effect (Hu, Chen, and Urban 2013), thus challenging reproducible measurements. Bottom-up methods such as chemical vapor deposition and atomic layer deposition allow for synthesis of nanomaterials with well-controlled size and morphology (Piszczek and Radtke 2018). This benefits to reproducibility of measurements, as well as optical properties of resulting nanostructures. In addition, clean decomposition of the precursor provides clean chemical background, thus preventing interference with studied analytes.

Furthermore, one of the main advantages of utilization of nano-assisted substrates in research of fingerprints is versatility. Due to compatibility of substrates with spectrometric and spectroscopic

techniques, synthesis of nano-assisted substrates for comprehensive research of fingerprints will be performed in a cost-effective manner. Analytical techniques assisted with nanostructures are surface enhanced Raman spectroscopy (SERS), surface enhanced IR analysis (SEIRA) and nano-assisted laser desorption ionization (NALDI).

Precious-metal nanostructures are of the most attractive candidates for preparation of nano-assisted substrates for application in SERS, SEIRA and NALDI due to excellent UV-absorbance, optimal light-to-heat conversion properties. Occurrence of localized surface plasmon resonances (LSPRs), which are collective oscillations of free electrons (Brown et al. 2016), which are excited upon laser irradiation, leads to enhancement and/or intense analytical signal. Thus, these techniques are suitable for samples with trace amount of the analyte, which can be beneficial in forensic science and crime investigations.

Silver nanostructured substrates (Sagandykova et al. 2022), synthesized with chemical vapor deposition (CVD) showed sensitivity towards low molecular weight compounds at nano- and picomolar level. Occurrence of ionization of small sized molecules in ion-negative mode was suggested as evidence of occurrence of LSPR hot electrons (Li et al. 2018). Rhodium nanostructures have not yet been reported as LDI substrates previously, however several papers reported ultra-violet plasmonic properties (Watson et al. 2015) and utilization in SERS (Koya et al. 2021; Kumar and Soni 2022), which shows great perspective for utilization as nano-assisted substrate in development of multi-instrumental approach. Furthermore, rhodium has only one stable isotope, which is beneficial due to absence of interference in low mass region (< *m/z* 500).

1.3. Work plan will be realized according to main research tasks:

- Development of *nano*-assisted substrates based on Ag and Rh nanostructures based on chemical vapor deposition and atomic layer deposition techniques (optimization of deposition conditions)
- Characterization of nano-assisted substrates using instrumental techniques such as SEM, AFM, XPS, SAXS, UV-Vis-DRS,
- Application of substrates for analysis of low molecular weight compounds in human fingerprints using nano- and complemented with matrix-assisted laser desorption/ionization mass spectrometry to reveal individual's lifestyle,
- Application of substrates for analysis of low molecular weight compounds using FTIR, Raman spectroscopy and chemometric analysis aiming at differentiation,

- Application of substrates for mass spectrometry imaging (MSI) for analysis of spatial distribution of low molecular weight analytes in fingerprints.

1.4. Literature

Brown, Ana M., Ravishankar Sundararaman, Prineha Narang, William A. Goddard, and Harry A. Atwater. 2016. "Nonradiative Plasmon Decay and Hot Carrier Dynamics: Effects of Phonons, Surfaces, and Geometry." *ACS Nano* 10(1):957–66.

Hu, Jie Bi, Yu Chie Chen, and Pawel L. Urban. 2013. "Coffee-Ring Effects in Laser Desorption/Ionization Mass Spectrometry." *Analytica Chimica Acta* 766:77–82.

Koya, Alemayehu Nana, Xiangchao Zhu, Nareg Ohannesian, A. Ali Yanik, Alessandro Alabastri, Remo Proietti Zaccaria, Roman Krahne, Wei Chuan Shih, and Denis Garoli. 2021. "Nanoporous Metals: From Plasmonic Properties to Applications in Enhanced Spectroscopy and Photocatalysis." *ACS Nano* 15(4):6038–60.

Kumar, Govind, and Ravi Kant Soni. 2022. "Rhodium Concave Nanocubes and Nanoplates as Deep-UV Resonant SERS Platform." *Journal of Raman Spectroscopy* 53(11):1890–1903.

Li, Yafeng, Xiaohua Cao, Lingpeng Zhan, Jingjuan Xue, Jiyun Wang, Caiqiao Xiong, and Zongxiu Nie. 2018. "Hot Electron Transfer Promotes Ion Production in Plasmonic Metal Nanostructure Assisted Laser Desorption Ionization Mass Spectrometry." *Chemical Communications* 54:10905–8.

Piszczek, Piotr, and Aleksandra Radtke. 2018. "Silver Nanoparticles Fabricated Using Chemical Vapor Deposition and Atomic Layer Deposition Techniques: Properties, Applications and Perspectives: Review." Pp. 187–213 in *Noble and Precious Metals - Properties, Nanoscale Effects and Applications*. InTech.

Sagandykova, Gulyaim, Piotr Piszczek, Aleksandra Radtke, Radik Mametov, Oleksandra Pryshchepa, Dorota Gabryś, Mateusz Kolankowski, and Paweł Pomastowski. 2022. "Silver Nanostructured Substrates in LDI-MS of Low Molecular Weight Compounds." *Materials* 15(4660):1–12.

Watson, Anne M., Xiao Zhang, Rodrigo Alcaraz De La Osa, Juan Marcos Sanz, Francisco González, Fernando Moreno, Gleb Finkelstein, Jie Liu, and Henry O. Everitt. 2015. "Rhodium Nanoparticles for Ultraviolet Plasmonics." *Nano Letters* 15(2):1095–1100.

1.5. Required initial knowledge and skills of the PhD candidate

PhD candidate should be familiar with instrumental techniques such as FTIR, Raman spectroscopy and laser desorption/ionization mass spectrometry (LDI-MS). Candidate should show interest in forensic science, and knowledge of instrumental approaches applied in analysis of human fingerprints will be highly appreciated. Experience/basic knowledge in the field of materials science, i.e. synthesis and characterization of nanomaterials, is required.

1.6. Expected development of the PhD candidate's knowledge and skills

PhD candidate will gain knowledge and skills in field of materials, forensic science and analytical chemistry. Candidate will gain specialized knowledge in instrumental analytical techniques, materials science and synthesis of nanostructured substrates and their characterization.

Candidate is expected to deepen his/her knowledge in synthesis of nanomaterials with utilization of chemical vapor deposition and atomic layer deposition. He/she is also expected to gain skills on reporting and dissemination of research results in form of high-impact factor publications, conference oral and poster presentations.