DEPARTMENT OF SURFACE ENGINEERING AND OPTOELECTRONICS F-4

The Department of Surface Engineering conducts interdisciplinary research on designing the surface properties of various materials. We use advanced techniques for surface and thin-film characterization, in particular with our XPS, AES, SIMS and AFM instruments. The scientific activities are focused on surfaces and coatings, gaseous discharges, thermodynamically non-equilibrium plasma and the interaction of reactive plasma species with organic and inorganic materials. Patent applications protect innovative solutions for industry, medicine, biotechnology and agriculture.

Head:
Prof. Miran Mozetič

The scientific activities of our research team are in line with the priorities of the Slovenian Strategy of Smart Specialization (S4), which represents the roadmap for the transition to a modern society according to the European Smart Specialisation Strategy (S3). An important task within S4 is the introduction of plasma technologies in agriculture praxis. The plasma techniques have already been approved for specific segments of the food chain, from farm to fork, but the science is still in its infancy. The shortage of appropriate literature encouraged us to prepare a comprehensive monography [1]. The book comprises almost 200 pages and introduces the basic science of non-equilibrium gaseous plasma when interacting with agricultural products. The authors then focus on the influence of plasma processing on an autochthonic Slovenian variety of garlic. The plasma treatment stimulates the germination and growth of these plants, and ultimately better crops. There is a limited range of useful parameters indicating the complex behaviour of the organic matter upon exposure to gaseous plasma. The best treatment conditions are recommended and explained by the effects of neutral plasma radicals, charged particles and radiation in the ultraviolet and vacuum ultraviolet range of wavelengths. The cover page of the monography is shown in Figure 1.

Plasma techniques for virus inactivation were critically evaluated [2]

While the treatment of agricultural products provides an efficient solution for better crops, the plants can suffer from inadequate water quality used for irrigation. Water scarcity remains a global problem, and contamination of the water with microbes that infect plants is a major concern, especially in modern vegetable-production methods such as hydroponics and aeroponics. The plasma treatment of contaminated water represents a powerful microbe-inactivation technique, but an obstacle is the limited applicability at atmospheric pressure. Namely, the plasma radicals' lifetime is limited by the three-body recombination in the gas phase, whose frequency increases with the square of the pressure. Gaseous bubbles in liquid water always assume the ambient pressure, typically slightly above 1 bar. The introduction of hydrodynamic cavitation overcomes this natural obstacle. The liquid water passes a narrow orifice, and the hydrodynamic effect causes the formation of a bubble of water vapour with a pressure close to the water-vapour saturation pressure, which is about 0.03 bar at room temperature. The lifetime of the plasma radicals is thus about 1000-times longer than at atmospheric pressure. This effect was found to be beneficial for sustaining a glow discharge in the bubble inside liquid water. The discharge enabled the formation of stable plasma with a high concentration of radicals and a significant radiation in the virucidal range. Both effects caused the rapid inactivation of the viruses in water. The research group was awarded the first prize for innovation with the highest commercial potential by international judges at the 13th International Technology Transfer Conference. Figure 2 shows the innovators with a prototype of the innovative device.

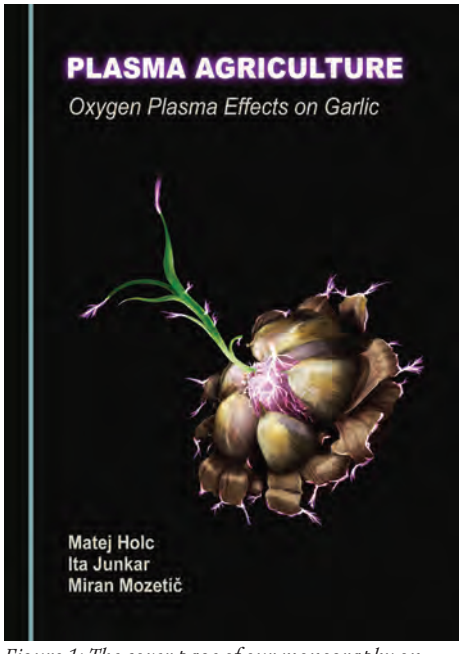

Figure 1: The cover page of our monography on plasma agriculture.

The virucidal efficiency of gaseous plasma is a hot topic of interdisciplinary research. Many research groups worldwide have tackled this challenge and reported promising results. Different groups used plasma sustained by various discharges and configurations, so the results are difficult to compare. Our research team prepared a review paper to summarise the results and enlighten a few aspects of plasma-virus interaction. The interdisciplinary group of plasma scientists and virologists explained the interaction between the combination of plasma radicals and radiation and viruses. The exact inactivation mechanisms depend on the properties of plasma and virus peculiarities. However, the key mechanisms involved are the irreversible oxidation of virus receptors by plasma radicals of high oxidation potential and bond cleavage in genetic material due to the absorption of plasma radiation. The review paper [2] represents guidance for future scientific work on virus-inactivation mechanisms upon treatment with

gaseous plasma. This scientific niche is expected to burst in the next future due to the limitations of currently available virucidal methods and the pandemic with SARS-CoV-2. An illustration of the plasma effects on viruses is shown in Figure 3.

Another prospective field of plasma technologies is in medicine. Standard materials commonly employed in body implants do not provide a desired biological response, mainly because they lack the appropriate surface properties. The interaction of proteins and biological cells with the surface is crucial for the long life-span of all implantable devices. Depending on the implant function and position in the body, the surface has to be appropriately conditioned to provide the desired biological response. In the case of vascular implants, the proliferation of endothelial cells is desired. These cells otherwise represent the uppermost layer on the inner side of our natural blood vessels. Furthermore, the adhesion and aggregation of blood platelets should be prevented, as these effects can cause thrombosis. Moreover, in the case of vascular stents, the prevention of the uncontrolled proliferation of smooth muscle cells should be considered, as this could cause restenosis. When blood vessels are badly damaged, they have to be replaced with synthetic ones, often made from knitted polymer (Dacron). The haemo-compatibility of such vascular grafts is inadequate, so various groups worldwide have probed methods for suppressing reactions between the blood constituents and polymeric vascular grafts. An optimal solution would be a heparin coating on the grafts. For decades, heparin has been known as the best anti-coagulant, but the covalent bonding of this substance on the polymer surface has remained a technological challenge. We managed to overcome this by grafting amino groups onto the polymer matrix. The afterglow of ammonia plasma was a source of -NH_2 radicals. Within a limited range of processing parameters, the radicals formed a sub-monolayer film of amino groups, which enabled the covalent grafting of about a monolayer of heparin. Such a surface finish prevented the activation of blood platelets on vascular grafts and thus assured optimal haemocompatibility. The procedure is disclosed in a recently granted EU patent [3].

Figure 2: The interdisciplinary research group gained an award for an innovative technique for water disinfection.

Technology for optimal surface finish of vascular grafts was approved [3]

When blood vessels are not so severely damaged, the vascular stent can be employed to restore the blood flow through an affected vessel. Mostly metallic materials like nitinol, stainless steel, titanium and cobalt-chromium are used for vascular stents. Although these materials provide the desired mechanical stability, their surface features are still far from optimal. Various types of coatings have to be used to prevent thrombosis and restenosis. Our group developed a novel approach based on the surface modification of a NiTi alloy using highly reactive hydrogen and oxygen species. Using this approach, the surface of the NiTi alloy is altered so that a rather thick nanostructured titanium oxide layer is formed on the surface. This layer significantly reduces the adhesion and aggregation of platelets on the surface and reduces surface-induced thrombosis. Our recent studies also showed that the release of toxic Ni ions from the NiTi alloy in the biological environment was reduced. Moreover, the proliferation of endothelial cells was improved, while the proliferation of smooth muscle cells on the surface was reduced. A European patent entitled "Method for treatment medical devices made from nickel-titanium (NiTi) alloys" has been filed. The invention was presented at an international virtual meeting, and we were awarded the "Innovation of the Year" award at the entrepreneurship fair. A picture from the announcement of the winners is in Figure 4.

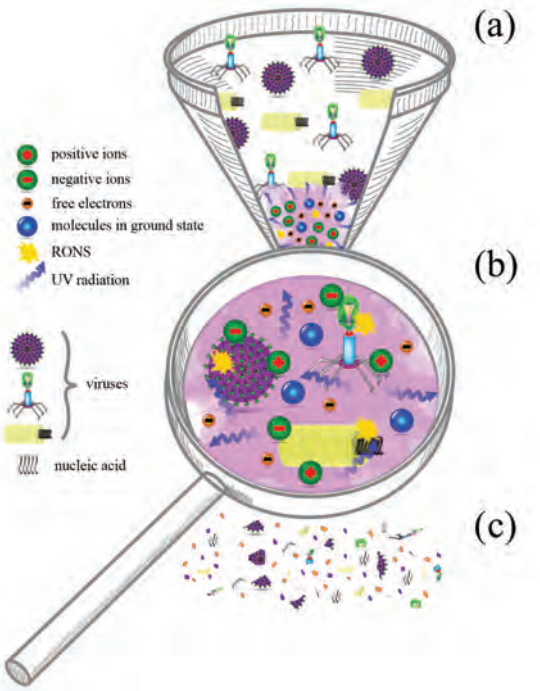

Figure 3: Illustration of plasma-virus interaction. Reprinted from [2].

Our research team is renowned worldwide for its expertise in surface and applied surface sciences. Our expertise provides the characterisation of various materials and the interpretation of the observed surface composition and structure. These activities are often performed in collaboration with other research groups in Slovenia and abroad. The results are usually published in prominent journals. Recently, we have provided expertise in the surface chemistry of Pt catalysts on nanotubular titanium oxynitride-supports [4], fluorinated polymer materials [5], nano-carbon polymer composites [6] and nitrogen-doped graphene-like materials [7].

The research team is among the most innovative groups in Slovenia. In 2020 alone, researchers filed eight patent applications protecting intellectual property rights in different niches of plasma technologies. A team member, Prof. Alenka Vesel, won a medal for the most innovative Slovenian researcher. The medal was granted by the International Intellectual Property Organization (WIPO), based in Geneva, Switzerland. This organisation was founded by the United Nations in 1967. Its mission is to develop and continuously upgrade a balanced and effective system for the protection of intellectual property globally. An international jury consisting of Jeff Skinner, London School of Business (UK), Jon Wulff Petersen, Plougmann Vingtoft (Denmark) and Alojz Barlič, Slovenian Intellectual Property Office, awarded the medal for outstanding results. Alenka Vesel has co-authored seven patents granted by offices that provide a full examination of the innovativeness of a patented solution in the past 10 years. Furthermore, she is also a co-founder of our spin-off company Plasmadis d.o.o., which markets innovative products and services.

Figure 4: Announcement of the "Innovation of the Year" at the 2020 regional fair of innovation and entrepreneurship.

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Awards and Appointments

1. Asst. Prof. Dr Ita Junkar, Dr Metka Benčina, Prof. Dr Janez Kovač, Prof. Dr Miran Mozetič, Asst. Prof. Dr Rok Zaplotnik: Innovation of the Year, virtual, Regional Virtual Fair on Innovation and Entrepreneurship "Sarajevo 2020", "Method for treatment medical devices made from nickel-titanium (NiTi) alloys".
2. Asst. Prof. Dr Ita Junkar: Excellent in Science 2020 Achievement (Odlični v znanosti 2020), Ljubljana, Scientific Council of Slovenian Research Agency (ARRS), "Method of treatment of tools used for isolation of microvesicles, nanovesicles and exosomes".
3. Asst. Prof. Dr Gregor Primc, Prof. Dr Miran Mozetič, Asst. Prof. Dr Rok Zaplotnik (Jožef Stefan Institute), in collaboration with David Dobnik, Matevž Dular, Arijana Filipić, Ion Gutierrez-Aguirre and Martin Petkovšek: Prize for the Best Innovation with Commercial Potential in 2020, Ljubljana, 13th International Technology Transfer Conference for the innovation, "A scalable method for eco-benign destruction of waterborne microorganisms".
4. Pia Starič, Asst. Prof. Dr Ita Junkar, Prof. Dr Miran Mozetič, Prof. Dr Katarina Vogel-Mikuš: Best Paper Award, virtual, Sciforum, The 1st International Conference on "Green" Polymer Materials 2020, "Bio-Polymers in the World of Plasma: Effects of Cold Plasma on Seed Surface".
5. Prof. Dr Alenka Vesel: WIPO medal for inventors, Ljubljana, Slovenian Intellectual Property Office and the World Intellectual Property Organization.

Figure 5: Prof. Alenka Vesel was awarded a WIPO medal

Patents granted

1. Gregor Primc, Miran Mozetič, Rok Zaplotnik, Alenka Vesel, Maja Ravnikar, Jana Žel, Nataša Mehle, Ion Gutiérrez-Aguirre, Arijana Filipić, David Dobnik, Procedure for inactivating virus in water, SI25811 (A), Urad RS za intelektualno lastnino, 30. 09. 2020.
2. Joško Valentinčič, Izidor Sabotin, Matic Resnik, Pavel Drešar, Nejc Matjaž, Marko Jerman, Andrej Lebar, Matej Pleterski, Apparatus and method for cutting an electrically conductive tube, EP3603866 (B1), European Patent Office, 30. 12. 2020.
3. Metod Kolar, Miran Mozetič, Ita Junkar, Alenka Vesel, Martina Modic, Karin Stana-Kleinschek, Method for immobilization of heparin on a polymeric material, EP2997984 (B1), European Patent Office, 03. 06. 2020.
4. Alenka Vesel, Miran Mozetič, Rok Zaplotnik, Gregor Primc, Nina Recek, Procedure for increasing the hydrophilicity of a polymer containing fluorine, SI25862 (A), Urad RS za intelektualno lastnino, 31. 12. 2020.

INTERNATIONAL PROJECTS

1. Small Services
   Prof. Janez Kovač
2. COST CA19110; Plasma Applications for Smart and Sustainable Agriculture
   Asst. Prof. Gregor Primc
   Cost Association Aisbl
3. H2020 - EUROfusion; Education-ED-FU
   Prof. Miran Mozetič
   European Commission
4. H2020 - EUROfusion; WPPFC-PEX-FU, WPPFC-PEX-FU, EUROfusion
   Asst. Prof. Rok Zaplotnik
   European Commission
5. Catalytic Probes for Characterization of Hydrogen Plasma
   Asst. Prof. Gregor Primc
   Slovenian Research Agency
6. Control of Chemical Composition of Thin Films by High Resolution Mass Spectrometry of Secondary Ions
   Prof. Janez Kovač
   Slovenian Research Agency
7. Advanced Catalysts based on Multilayered Vertically Oriented Graphene Nanostructures
   Prof. Alenka Vesel
   Slovenian Research Agency
8. Characterization of Oxygen Plasma Sustained with Powerful Gaseous Discharges
   Prof. Miran Mozetič
   Slovenian Research Agency
9. Low Temperature Plasma Diagnostics and its Applications for Seed Treatment
   Prof. Miran Mozetič
   Slovenian Research Agency
10. Functionalization of Ti-Based Surfaces Using Energy Beams and Plasma for Biomedical Applications
    Asst. Prof. Gregor Primc
    Slovenian Research Agency

RESEARCH PROGRAMMES

1. Thin film structures and plasma surface engineering
   Prof. Miran Mozetič
2. Fusion technologies
   Asst. Prof. Rok Zaplotnik

R & D GRANTS AND CONTRACTS

1. Structural and surface properties of fibrous membranes for purification and chromatographic separation of biomacromolecules
   Asst. Prof. Ita Junkar
2. Ecologically friendly in-situ synthesis of ZnO nanoparticles for the development of protective textiles
   Asst. Prof. Gregor Primc
3. Initial stages in surface functionalization of polymers by plasma radicals
   Prof. Janez Kovač
4. Advanced surface finishing technologies for antibacterial properties of patient specific 3D printed implantable materials
   Asst. Prof. Ita Junkar
5. Hybrid and Reengineered Nanocatalysts for New Purification Routes
   Prof. Janez Kovač
6. Self-organization of plasma in magnetron sputtering discharges
   Prof. Miran Mozetič
7. New startegies for fabrication of biomimetic vascular implants
   Asst. Prof. Ita Junkar
8. Development of new, environment-friendly approaches for plant and human virus inactivation in waters
   Asst. Prof. Gregor Primc
9. Innovative sensors for real-time monitoring of deposition rates in plasma-enhnced chemical vapour deposition (PECVD) systems
   Asst. Prof. Rok Zaplotnik
10. Nanoparticle-reinforced new metal matrix composites manufactured by selective laser melting for tooling industry
    Prof. Miran Mozetič
11. Evaluation of the range of plasma parameters suitable for nanostructuring of polymers on industrial scale
    Prof. Miran Mozetič
12. Selective plasma oxidation of FeCrAl alloys for extended-lifetime of glow plugs for diesel engines
    Prof. Janez Kovač
13. Innovative configuration of inductively coupled gaseous plasma sources for up-scaling to industrial-size reactors
    Prof. Miran Mozetič
14. Carbon nanowalls for future supercapacitors
    Prof. Alenka Vesel
15. Selected area functionalization of polymeric components by gaseous plasma
    Prof. Miran Mozetič
16. Innovative method for purification of wastewater
    Asst. Prof. Gregor Primc
17. Use of gaseous plasma for higher yields and lower use of antifungal agents in agriculture
    Asst. Prof. Ita Junkar
18. Food for future - F4F
    Prof. Alenka Vesel
    Ministry of Education, Science and Sport
19. Potential of biomass for development of advanced materials and bio-based products
    Asst. Prof. Ita Junkar
    Ministry of Education, Science and Sport
20. Innovative ECO plasma seed treatment (for sowing and for human and animal diet/nutrition
    Dr. Nina Recek
    Ministry of Education, Science and Sport
21. Building blocks, tools and systems for the Factories of the Future – GOSTOP
    Prof. Miran Mozetič
    Ministry of Education, Science and Sport
22. Development of nanostructured biosensors for diagnosis/treatment of cancer and surfaces with antibacterial
    Dr. Metka Benčina
    Ministry of Education, Science and Sport
23. Strategic Research & Innovation Partnership Factories of the Future (SRIP FoF)
    Prof. Miran Mozetič
    Ministry of Economic Development and Technology
24. Method for preparation of bacteriostatic surfaces on 3D printed medical implants
    Dr. Matic Resnik
    Ministry of Education, Science and Sport
25. Reimbursement of costs of scientific publications in golden open access for 2019, 2020
    Prof. Miran Mozetič
    Slovenian Research Agency
26. Use of gaseous plasma for higher yields and lower use of antifungal agents in agriculture

Asst. Prof. Ita Junkar
Ministry of Agriculture, Forestry and Food
27. Income from Coowners of Invention for Reimbursement of Costs for IP Protection in the Case of EVT140_Mozetič_Carbon Nanowall
Prof. Miran Mozetič
Nagoya University

NEW CONTRACTS

1. L-project co-financing: Innovative method for purification of wastewater
Asst. Prof. Gregor Primc
Induktio d. o. o.
2. L-project co-financing: Selected area functionalization of polymeric components by gaseous plasma
Prof. Miran Mozetič
Elvez, d. o. o.

VISITOR FROM ABROAD

1. Prof. Dr Petr Špatenka, Czech Technical University in Prague, Prague, the Czech Republic, 25 February 2020

STAFF

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20. Maja Šukarov, B. Sc.
21. Janez Trtnik

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Original Article

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7. Dane Lojen, Rok Zaplotnik, Gregor Primc, Miran Mozetič, Alenka Vesel, "Effect of VUV radiation and reactive hydrogen atoms on depletion of fluorine from polytetrafluoroethylene surface", *Applied Surface Science*, 2020, **533**, 147356.
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10. Živa Marinko, Luka Suhadolnik, Zoran Samardžija, Janez Kovač, Miran Čeh, "The influence of a surface treatment of metallic titanium on the photocatalytic properties of TiO_2 nanotubes grown by anodic oxidation", *Catalysts*, 2020, **10**, 7, 803.
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20. Veronika Kralj-Iglič *et al.* (34 authors), "From extracellular vesicles to global environment: a cosmopolite Sars-Cov-2 Virus", *International journal of clinical studies and medical case reports*, 2020, **4**, 1, 4.
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