DEPARTMENT OF SURFACE ENGINEERING F-4

The main activity of our department is tailoring the surface properties of materials using thermodynamically non-equilibrium gas plasma. The basic principle of processing materials with gas plasma is the following: first, we select a suitable gas or gas mixture, and then we create a discharge in the selected gas so that a suitable density of free electrons is reached. Gas molecules, which are close to the ground state under normal conditions and room temperature, are excited to different states with high potential and/or kinetic energy during inelastic collisions with free electrons. Molecules in such energy states then react with the surfaces of the materials. Interactions of molecules in energy states can lead to functionalization, etching or deposition of coatings.

Head:
Prof. Alenka Vesel

Our department's main activity remains the treatment of surfaces of solid materials with thermodynamically non-equilibrium gas plasma. The free electrons in our plasmas have a temperature of about 10,000 K, so they dissociate gas molecules abundantly, which leads to the formation of chemically, highly reactive radicals. Such radicals usually chemically bind to the surfaces of the materials already at room temperature and thereby change their functional properties. Molecular radicals in the gas phase are stable at low pressure, but with increasing pressure, they can combine into stable chemically non-reactive molecules. Due to the loss of radicals at elevated pressure, plasma reactors used in industry for the treatment of material surfaces usually operate at low pressures, typically between 0.1 and 10 mbar. Sometimes, we also want to use gas plasma to process materials at normal air pressure, i.e., around 1000 mbar. This is especially true for biological materials, which typically cannot withstand low-pressure conditions. Maintaining a non-equilibrium plasma with a high degree of dissociation of the H_2O molecules for the treatment of water containing biological material at room temperature represents both a scientific and a technological challenge.

Maintaining a gas plasma in a liquid is, by definition, impossible, but we can create bubbles in the liquid in which we excite the plasma. The bubbles move quickly towards the surface of the liquid water due to buoyancy and are usually too small to accommodate electrodes for plasma excitation. We solved the problem by creating a large, stable bubble in liquid water using hydrodynamic cavitation. The water was forced through a suitably designed nozzle from the container with a slightly elevated pressure into the container at normal pressure. In the limited range of the geometric shapes of the nozzle, a cavitation bubble with a volume of several cubic centimetres was formed behind the nozzle in the direction of the flow of liquid water. The water vapor saturated pressure at room temperature, i.e., around 30 mbar, was sustained in the bubble. At this pressure, we easily maintained a stable gas plasma with a simple DC glow discharge. We protected the innovative solution with a patent application, and in November 2023, the US Office granted a patent US11807555 (B2) [1]. A preferred embodiment is disclosed in Figure 1. Arrows (1) indicate the flow of water between two plates (2, 3). In the area after the narrowing in the direction of the water flow, a stable cavitation bubble (5) appears, in which we installed two electrodes (6, 7). The electrodes were covered with thin insulation (8), which prevented galvanic contact between the water and the electrodes. When a voltage was applied between the electrodes, a gas plasma was maintained in the part of the volume in the cavitation bubble (5) at a saturated water vapor pressure. Since the pressure in the bubble was much lower than the atmospheric pressure, the concentration of OH radicals in the gas phase was large despite a relatively low discharge power. The loss of radicals in the gas phase increases with the square of the pressure so that in a cavitation bubble, it is thousands of times less than it would be in a normal bubble in liquid water. The configuration in Figure 1 has another advantage, i.e., the continuous supply of liquid water to the volume between the bubble (5) and the housing (2). This is very important since the solubility of OH radicals in water is limited. Furthermore, when OH

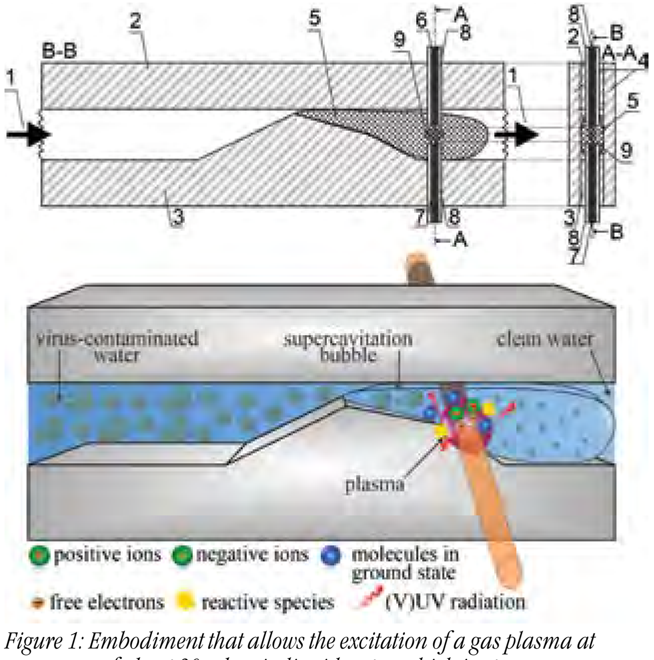

Figure 1: Embodiment that allows the excitation of a gas plasma at a pressure of about 30 mbar in liquid water, which is at a pressure of 1 bar or more [1] (drawing); the principle of operation of plasma cavitation for the inactivation of viruses (illustration).

radicals collide with each other in water, they are very likely to form hydrogen peroxide. The continuous supply of fresh water, therefore, enables an optimal concentration of OH radicals in the liquid water.

The scientific aspects of the innovative technology for supplying a large amount of OH radicals to running water were described in an article published in a reputable journal [2]. The OH radicals are particularly suitable for inactivating viruses because they irreversibly react with any organic material, as illustrated in Figure 1. Biological water pollution is becoming a growing problem even in the developed world, so many groups around the world are developing methods to inactivate micro-organisms in water. The ideal method would work at room temperature (or even lower), should not use chemicals, would consume little energy, and would not change the other properties of the water, such as the natural pH and the appropriate concentration of minerals. The method illustrated in Figure 1 comes very close to the ideal, as only OH radicals are introduced into the water. The radicals quickly react with organic material, and unreacted radicals decay with a half-life that is significantly less than a second. Some OH radicals (especially in excessive concentration in liquid water) form hydrogen peroxide, which also slowly reacts with organic impurities in water. In the scientific article [2] we very convincingly showed that OH radicals inactivate the selected type of virus even before the concentration of hydrogen peroxide becomes too high. The first author of this article received the Golden Emblem of the IJS for her outstanding work in the field of plasma inactivation of viruses. The photograph in Figure 2 shows the winner. On the left-hand side is the head of the programme group (Miran Mozetič), and on the right -hand side is the head of the group in charge of research on plasma inactivation of viruses (Gregor Primc).

We have developed and patented a method for the rapid inactivation of viruses in water

Figure 2: Postdoctoral fellow Arijana Filipić receives the IJS Golden Emblem Prize.

The extremely high oxidation potential of OH radicals is also used for the selective functionalization of synthetic polymers with hydroxyl groups. We studied in detail the kinetics of polystyrene functionalization during a treatment with OH radicals. The source of the radicals was a gas plasma, which was excited in water vapour in a remote plasma at low pressure. To measure the density of these radicals, we used a specially adapted sensor manufactured by our spin-off company Plasmadis Ltd. Figure 3 shows the concentrations of different functional groups versus the dose of OH radicals. At a very low dose of around 6×10^{19} m^{-3}, we observe a plateau on the curve, which corresponds to the surface hydroxyl groups. In the article [3], we presented a model that explains the rapid stabilization of the concentration of hydroxyl functional groups on the surface of polystyrene at low doses. The OH radicals react with a hydrogen atom that is bound to carbon on the surface of polystyrene so that a water molecule is formed. The water molecule quickly desorbs since the pressure in the reaction vessel is much lower than the saturated water-vapor pressure at room temperature. The dangling bond is occupied by the next OH radical that reaches the polymer surface. When the surface is saturated with OH groups, further processing leads to the opening of the aromatic ring and, in the case of larger doses of radicals, to the cleavage of bonds in the polymer chain. Increasing the dose first causes the formation of carbonyl groups, and larger doses also enable the formation of functional groups with more than one oxygen atom bonded to the carbon.

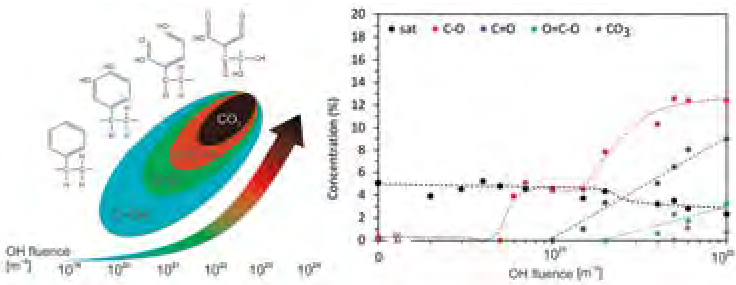

Figure 3: Kinetics of the formation of oxygen functional groups on the surface of polystyrene during treatment with OH radicals [3].

The OH radicals also play an important role in gas conversion, as they chemically react with light hydrocarbons to form alcohols. Even more important is the conversion of nitrogen and hydrogen into ammonia. For a century, the Haber-Bosch process has been used on an industrial level, in which the gas mixture is heated, and ammonia is produced on the surface of the catalyst at high pressure. An alternative to this process is the dissociation of N_2 and H_2 with gas plasma and the binding of atoms into NH_3 molecules. Numerous research groups worldwide are engaged in the plasma synthesis of ammonia, and they use various materials as catalysts for surface reactions. However, the surface synthesis of ammonia is not the only way of binding nitrogen atoms, but the heterogeneous recombination of nitrogen atoms into N_2 molecules also takes place on the surface. A carefully designed experiment made it possible to determine the coefficients for the conversion of nitrogen atoms into ammonia molecules. Atomic nitrogen and hydrogen were synthesized in separate plasmas powered by microwave discharges in the surfatron mode of operation. The atoms were fed into the reaction vessel where they either recombined into parent molecules or formed ammonia. Up to half of the nitrogen atoms are bound into ammonia, which does not disintegrate after the synthesis since we do not have a gas plasma in the reaction vessel, which would otherwise cause dissociation of the ammonia. The research is important not only for the development of small ammonia synthesis reactors but also for determining the rate of conversion of nitrogen to ammonia in future fusion reactors. Some parts of fusion reactors are exposed to large flows of energetic hydrogen ions, which makes it necessary to cool the plasma near the surface. The best way of cooling hydrogen plasma is puffing nitrogen, but some of the nitrogen is converted into ammonia, which has a detrimental effect on the pumps for pumping fusion reactors. The known coefficients reported in the article [4] will enable the optimization of hot plasma cooling in future fusion reactors.

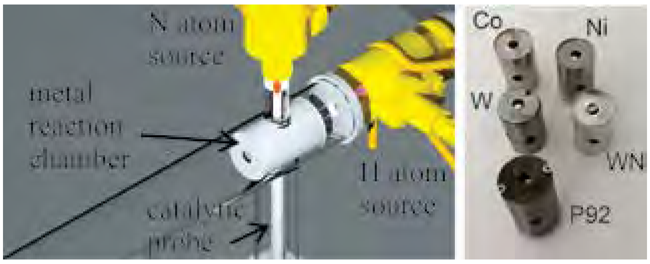

Figure 4: Scheme of the system for determining the coefficient for the conversion of nitrogen atoms into ammonia (left) and reaction sleeves (right) [4].

Hydroxyl surface groups on the surface of polymers enable considerable wettability but will never enable a super-hydrophilic surface finish. Super-wettability is often defined by an immeasurably small angle of a water drop deposited onto a sample surface, as the water spreads over a very large surface due to capillary forces, which are a result of the nanostructured surface and saturation with very polar groups, such as carboxyl groups. This state of the polymer surface is important for the excellent adhesion of the water-soluble coating. We investigated methods for applying a thin layer of water-soluble polysaccharides to the surface of polyvinyl chloride catheters. Polymers containing halogen atoms cannot be adequately hydrophilized using OH or O radicals because the binding energy between the halogen atom and the carbon atom is too large. Treatment with these radicals leads to the breaking of bonds in the polymer chain, but not to the substitution of chlorine with oxygen. To enable the super-wettability of polyvinyl chloride, we used a method that we developed and patented for Teflon years ago. The samples were first treated for a short time with hydrogen plasma and then with oxygen atoms. Hydrogen plasma is a very powerful source of vacuum ultraviolet radiation with a photon energy greater than the binding energy between the chlorine and the carbon in the polymer. As a result, photons cleave the C-Cl bonds in the thin surface layer of the polymer, and atomic hydrogen occupies the free bonds. Treatment with hydrogen plasma, therefore, enables the substitution of chlorine in the surface layer of the polymer with hydrogen. In the next step, we exposed the modified polymer to oxygen atoms and achieved super-wettability. The procedure is described in detail in a scientific article [5]. The upper graph in Figure 5 shows the contact angle of a water droplet on the polymer surface during exposure to oxygen atoms. The smallest achievable angle is around 40°, which is sound to observations reported by other authors. In the same picture, we also show the contact angle of a water droplet on the surface of polyvinyl chloride, which was exposed to hydrogen plasma for 1 second before using oxygen atoms (lower graph). We observed super-wettability (immeasurably small water droplet contact angles), which persists until the treatment time with oxygen atoms is almost a minute. A prolonged treatment with oxygen atoms causes etching of the surface layer of the polymer and, thus, the loss of excellent hydrophilicity, as the contact angle after more than 2 minutes is almost the same as if the polymer was treated with oxygen atoms only.

We have developed a method to achieve the super-wettability of polyvinyl chloride

Radicals from oxygen plasma are important not only for the functionalization and improvement of surface wettability, but also for nanostructuring and the growth of oxide layers. The combination of low-pressure gas plasma, hydrothermal treatment, or electrochemical anodization allows the formation of biomimetic surfaces that have been shown to have a selective biological response. We have shown that the combination of gas plasma treatment

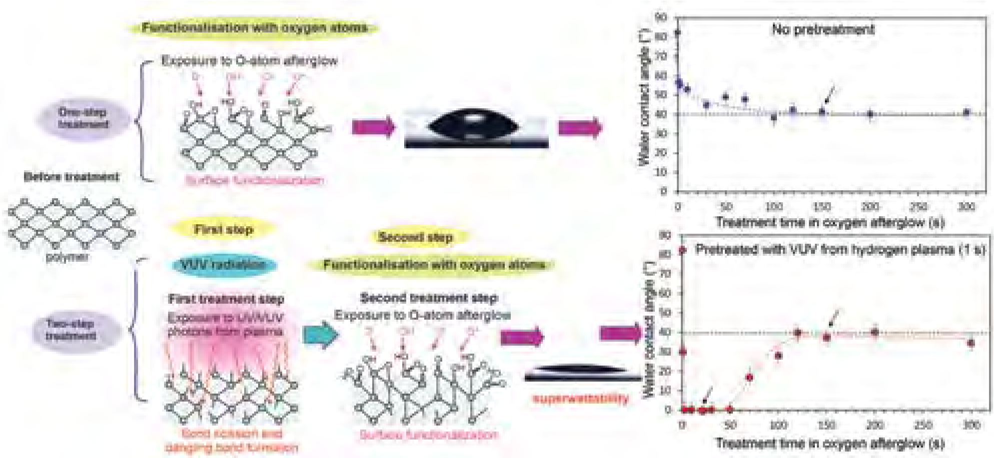

Figure 5: (left) Illustration of the method for achieving superhydrophilicity of the surface; (right) The water contact angle on the polyvinyl chloride surface versus the treatment time with atomic oxygen. The upper graph shows the wettability after treatment with only oxygen atoms, and the lower graph after treatment with hydrogen plasma and oxygen atoms.

and hydrothermal techniques increases the proliferation of human coronary artery endothelial cells (HCAECs), and the cells appear to interconnect with so-called tunnelling nanotubes (TNTs) strongly. These nanotubes are green in Figure 6. TNTs are membrane nanotubes that enable the direct connection of neighbouring cells and thus enable intercellular communication. TNTs contain actin filaments that begin to grow as filopodia (Figure 6). On the other hand, for HCASMCs (Primary Coronary Artery Smooth Muscle Cells), we observed a significant reduction in proliferation in the case of plasma-modified samples. These scientific results, published in the article [6], give great hope for the development of biomimetic surfaces of vascular implants, where the surface topography and chemistry can be fine-tuned to achieve a specific biological response important for the prevention of restenosis (uncontrolled proliferation of smooth muscle cells) and at the same time improving endothelialization.

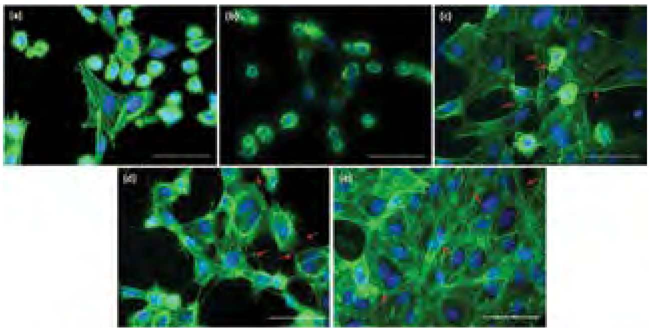

Figure 6: HCAEC on the surface of (a) untreated Ti6Al4V, (b) Ti6Al4V + P, (c) HT, (d) HT + P and (e) P + HT determined by immunofluorescence microscopy. F-actin is shown in green (FITC-phalloidin). Nuclei are visualized with DAPI (blue colour). The scale bar is 25 μm. The P designation means plasma treated, and the HT designation means hydrothermal treatment.

An important department activity with numerous projects, including two EU projects, is plasma agriculture. In 2023 we completed the CRP project: "The possibility of improving productivity and reducing dependence on the use of chemical fungicides in agriculture using gas plasma" in cooperation with the Agricultural Institute of Slovenia and the company Interkorn. The most important result of the project was the development of a low-pressure plasma approach for i) removing toxins from the surface of seeds, especially corn and wheat, ii) an approach to reduce blueberry infections by Drosophila suzukii and iii) systematic analysis of seed biochemistry, morphology, and physiology, which we published in a scientific article [7], where we observed differences in plasma treatment on different varieties of wheat. In the article [7] we reported that the plasma treatment of common buckwheat seeds does not change the ability of zinc uptake when soaking in an aqueous solution of zinc chloride. We also found that plasma treatment of buckwheat seeds caused a decrease in the concentration of Zn in the sprouts. The benefits of cold plasma treatment need to be tested in further studies, where it may be necessary to optimize the soaking time of the grains to produce Zn-enriched sprouts. However, further optimization of the use of gas plasma in agriculture is still needed. So far, it seems that the removal of toxins is the most important. We performed systematic research on the plasma-stimulated decomposition of toxins in the framework of much larger projects than the completed CRP project and filed several patent applications. The Slovenian office published one of our patents on toxin decomposition with gas plasma [8]. In this patent we showed that even a short-term treatment of seeds with gas plasma, which operates within a limited range of parameters, reduces the concentration of toxins below the detection limit of the analytical technique.

Our department is equipped with modern instruments for surface and thin-film characterization, such as X-ray photoelectron spectroscopy (XPS), secondary-ion mass spectrometry (ToF-SIMS), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). These instruments enable the determination of the chemical composition, molecular structure of surfaces, oxidation states of elements, various compounds, and electronic properties, and the surface morphology is analysed at the nanometre level. With the help of ion etching, we can remove surface layers in a controlled manner and measure XPS and SIMS depth profiles of the chemical composition in the area below the surface and in thin-layer structures. Our analyses help to understand phenomena in various fields, such as advanced surface treatments, catalysis, corrosion, nanomaterials, hard coatings, photovoltaic layers, microelectronics elements, tribology, biological materials and batteries.Our analytical methods are available to other departments of our institute, other Slovenian research and academic organizations, and Slovenian industrial partners. In cooperation with the Institute of Chemistry and other research groups, we investigated in detail the surfaces of catalytic materials made of thin nano-structured layers of TiO_xN_y, into which we embedded small clusters of Ir atoms. We prepared this type of structure using an innovative process. Due to the small amount of incorporated Ir, which is of limited availability and is an expensive raw material, such catalysts are very promising for use in hydrogen production. We reported results in a scientific article [9]. Catalytic layers were prepared by ion sputtering from a target made of a Ti-Ir alloy. The deposited layers were first anodically oxidized into an amorphous TiO_2-Ir phase and then heated in a nitrogen atmosphere to form a stable oxy-nitride layer with a large specific surface area and embedded clusters of Ir atoms. The catalyst showed excellent properties for the release of oxygen in an acidic medium, which is important for the development of new electro-catalysts. Apart from other analytical methods for the characterization of the catalytic layer, we also used XPS

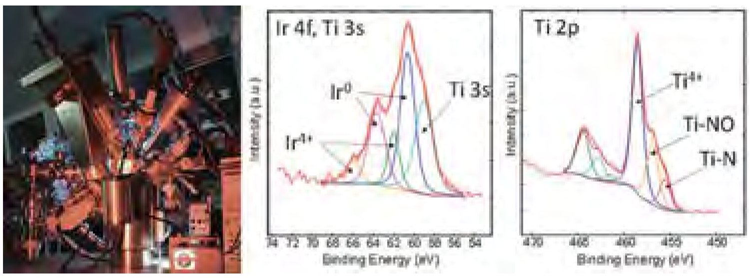

Figure 7: (left) XPS spectrometer enabling the identification of chemical bonds and examples of high-resolution XPS spectra of iridium Ir 4f (middle image) and titanium Ti 2p (right) from a TiOxNy-Ir catalyst showing oxidation states of Ir(0), Ir(4+), Ti(4+) and Ti-NO and Ti-N chemical bonds.

and ToF-SIMS. Using the XPS, the oxidation states of the elements Ir(0), Ir(4+), Ti(4+) and the chemical bonds Ti-NO and Ti-N in the thin layer were determined from the spectra of Ir 4f, Ti 2p, O 1s and N 1s catalyst as shown in Figure 7. ToF-SIMS depth profiles of the distribution of elements in thin layers helped to understand the growth mechanism of thin layers of the catalyst in the form of a porous Ti-N-O-Ir structure.

Patent granted

1. Primc, Gregor, Zaplotnik, Rok, Mozetič, Miran, Filipić, Arijana, Gutiérrez-Aguirre, Ion, Dobnik, David, Dular, Matevž, Petkovšek, Martin, Method and device for disinfection of liquid, US11807555 (B2), United States Patent and Trademark Office, 7. 11. 2023

INTERNATIONAL PROJECTS

1. COST CA19110; Plasma Applications for Smart and Sustainable Agriculture
   Asst. Prof. Gregor Primc
   COST Association Aisbl
2. COST CA20114; PlasTHER - Therapeutical Action of Cold Atmospheric Plasmas
   Prof. Ita Junkar
   COST Association Aisbl
3. H2020 - ATHENA; Implementing Gender Equality Plans to Unlock Research Potential of RPOs and RFOs in Europe
   Prof. Ita Junkar
   European Commission
4. Promising Eco-Sterilization of Pathogenic Fungi on Seeds Using Reactive Species in Gaseous Plasma
   Prof. Miran Mozetič
   Slovenian Research Agency
5. Facile Preparation of Superhydrophobic Cellulose Nanofibers and Compounding with PLA for Packaging
   Prof. Miran Mozetič
   Slovenian Research Agency
6. Characterization of Oxygen Plasma Sustained with Powerful Discharges
   Prof. Miran Mozetič
   Slovenian Research Agency
7. Catalytic Probes for Characterization of Hydrogen Plasma
   Asst. Prof. Gregor Primc
   Slovenian Research Agency
8. Sustainable Food Processing for Tomorrow – Implementing Plasma on Multiple Levels
   Prof. Ita Junkar
   Slovenian Research Agency
9. Synthesis and characterizatiom of catalytic materials with interactive substrates based on doped titanium dioxide nanoparticles of various shapes for fuel cells
   Prof. Janez Kovač
   Slovenian Research Agency
10. HE - EUROfusion; WP05: PWIE-1,2,3,_HE-FU, PWIE-4-Accelerator
    Prof. Janez Kovač
    European Commission
11. HE - AgroServ; Integrated SERvices supporting a sustainable AGROecological transition
    Prof. Miran Mozetič
    European Commission

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. Alternative approaches to assuring guality and security of buckwheat grain microbiome
   Prof. Miran Mozetič
2. Investigation of two-way interactions during plasma treatment of solid wood
   Prof. Janez Kovač
3. Cell membrane uptake of bacteria, virions and anorganic particles controlled by membrane mechanics and topology
   Prof. Ita Junkar
4. Removal of selected antimicrobials by plasma-cavitation hybrid technology from water matrices of varying complexity (Causma)
   Asst. Prof. Gregor Primc
5. Self-organization of plasma in magnetron sputtering discharges
   Prof. Miran Mozetič
6. New startegies for fabrication of biomimetic vascular implants
   Prof. Ita Junkar
7. Innovative procedures for advanced surface properties of medical stainless steel
   Dr. Metka Benčina
8. Novel Surface Modification of Dental Prosthetic Replacements by Gaseous Plasma
   Dr. Metka Benčina
9. Nanoparticle-reinforced new metal matrix composites manufactured by selective laser melting for tooling industry
   Prof. Miran Mozetič
10. A Novel High-strength Aluminium Alloy developed for Selective Laser Melting and Lightweight Applications
    Prof. Miran Mozetič
11. Hybrid SLM/DED Additive Manufacturing of Ti6Al4V Advanced Fuel System Components for Aerospace Industry
    Prof. Ita Junkar
12. Miniature fiber-optics sensors for free-radical detection in plasma assisted processe
    Asst. Prof. Rok Zaplotnik
13. Nanocellulose from eco-farms for optimal enforcement of bioplastics
    Asst. Prof. Gregor Primc
14. Selected area functionalization of polymeric components by gaseous plasma
    Prof. Miran Mozetič
15. Innovative method for purification of wastewater
    Asst. Prof. Gregor Primc
16. Development of safe multifunctional surfaces for catheters to combat biofilms (DemoCat)
    Prof. Alenka Vesel
17. Waterborne virus inactivation efficiency of a prototype device combining non-equilibrium plasma and hydrodynamic cavitation
    Asst. Prof. Rok Zaplotnik
18. Plasma VUV and UV radiation – a method for successful deactivation of Aflatoxins
    Dr. Nina Recek
19. Non-equilibrium plasma processing for superior composite magnets
    Prof. Miran Mozetič
20. Supercapacitors with graphene nanowalls synthesized from waste plastics
    Prof. Alenka Vesel
21. Nanostructured high entropy alloy coatings for tooling applications
    Asst. Prof. Gregor Primc
22. Use of gaseous plasma for higher yields and lower use of antifungal agents in agriculture
    Prof. Ita Junkar
23. Fusion technologies
    Asst. Prof. Rok Zaplotnik
    Slovenian Research Agency
24. Use of gaseous plasma for higher yields and lower use of antifungal agents in agriculture
    Prof. Ita Junkar
    Ministry of Agriculture, Forestry and Food
25. 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
26. EVT770_Mozetič_CNW2_Reimbursement of the Costs for Patent; Income from Coowners of Invention for Reimbursement of Costs for IP Protection in the Case of EVT770_Mozetič_CNW2
    Prof. Miran Mozetič
    Nagoya University
27. CKPN LAPTP; Center for the analysis of surfaces and thin layers
    prof. Janez Kovač
    Slovenian Research Agency

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.
3. Development of safe multifunctional surfaces for catheters to combat biofilms (DemoCat)
   Prof. Alenka Vesel
   Tik d. o. o.
4. Waterborne virus inactivation efficiency of a prototype device combining non-equilibrium plasma and hydrodynamic cavitation
   Asst. Prof. Rok Zaplotnik
   Kolektor Group d. o. o.
5. Co-financing L2-50052 Supercapacitors with graphene nanowalls synthesized from waste plastics
   Prof. Alenka Vesel
   Iskra, d. o. o.

VISITORS FROM ABROAD

1. Prof. Katsuhisa Kitano, Takashi Kunizawa, Osaka University, Osaka, Japan, 23.2.2023
2. Prof. Dr Tomoyuki Murakami, Seikei University, Tokyo, Japan, Prof. Dr. Kinga Kutasi, Budapest, Hungary, 13.5.2023
3. Prof. Jacek Jagielski, Łukasz Kurpaska, National Centre for Nuclear Research, Warsaw, Poland, 26.9.2023
4. Assis. Dr Lenka Zajičkova, Central European Institute of Technology (CEITEC), Brno, Czech Republic, 21.12.2023

STAFF

Researchers
1. Dr. Metka Benčina
2. Asst. Prof. Ita Junkar
3. Prof. Janez Kovač
4. Prof. Miran Mozetič
5. Asst. Prof. Gregor Primc
6. Dr. Nina Recek
7. **Prof. Alenka Vesel, Head**
8. Asst. Prof. Rok Zaplotnik

Postdoctoral associate
9. Dr. Parameswaram Ganji

Postgraduates
10. Jernej Ekar, B. Sc.
11. Domen Paul, B. Sc.
12. *Pia Starič, B. Sc., left 16.08.23*
13. Mark Zver, M. Sc.

Technical officers
14. Tatjana Filipič, B. Sc.
15. Maja Šukarov, B. Sc.

Technical and administrative staff
16. Janez Trtnik