2nd PLASMA NANOTECHNOLOGIES AND BIOAPPLICATIONS WORKSHOP

Scientific Program & Book of Abstracts

Broumov, Czech Republic, October 11–14, 2021

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AND BIOAPPLICATIONS WORKSHOP

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&
BOOK OF ABSTRACTS

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Edited by

Oleksandr Galmiz, Vlasta Štěpánová, Richard Krumpolec, Slavomír Sihelník, Dušan Kováčik

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PREFACE

Dear colleagues,

Almost two years have passed since organizing the 1st workshop focused on *Plasma Nanotechnologies and Bioapplications,* held at the end of 2019 in Telč. At that time, no one had expected a very difficult period ahead of us, requiring strict COVID-19 anti-pandemic measures associated with the restriction of social contacts during several months of the 1st and 2nd wave of the pandemic, which significantly affected our researcher's work process. We had to adapt to new working conditions, restrict laboratory work and, where it was possible, transfer many of our activities to the online space. Many of us have begun to realize that we lack personal contact with colleagues, exchange of opinions and ideas during discussions, participation in conferences and symposia, and travelling, just a usual way of life. Nevertheless, we have successfully managed this challenging period, as evidenced by several new publication outputs, submitted project proposals, but also the new financially supported projects, and last but not least by the successfully defended student's thesis under your supervision.

Therefore, I am glad that despite the ongoing pandemic, thanks to the currently milder measures, we managed to organize the 2nd workshop with personal attendance, outside our workplaces, in the charmful town Broumov with the beautiful surroundings located in northeastern Bohemia. This will be the first scientific forum with personal participation after a very long time for many of us. The workshop participants are the scientists and doctoral students from the Plasma Nanotechnologies and Bioapplications research group at the Department of Physical Electronics (most of them are also members of CEPLANT's centre research team), Faculty of Science, Masaryk University in Brno, and from the Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava.

As can be seen from the submitted abstracts, during the workshop there will be presented interesting and instructive contributions dealing with the current scientific trends in the field of Plasma Physics, Physics of Electrical Discharges and Plasma Chemistry, which correspond to the following thematic topics: *Surface modification, Bioapplications, Flexible and Printed Electronics,* and *New Materials & New Challenges.*

The 2nd workshop will last one day longer, so it was possible to set aside enough time in the afternoons' program for informal discussions, personal meetings, exchange of knowledge and experiences, as well as free-time activities. I believe that thanks to the attractive workshop venue in Hotel Veba with its facilities and services, the historical atmosphere of Broumov town, and the proximity of the Adršpach-Teplice Rocks National nature reserve, each participant will find an own way for relaxing during free time.

In conclusion, I would like to express my wish that this year's workshop would be successful, with lots of fruitful discussions and exchanges of inspiring and supporting ideas for further scientific work!

Dušan Kováčik

SCIENTIFIC PROGRAM

Monday, 11st October 2021

17:00–18:00 Arrival & Check-in and accommodation

18:30–23:00 Welcome party

Tuesday, 12nd October 2021

8:00–9:00 Breakfast

TOPIC 1: SURFACE MODIFICATION – part I Chairman: Dušan Kováčik

9:15–9:30	Opening words
9:30–9:50	**V. Štěpánová:** *Optimisation of the DCSBD roll-to-roll treatment of LLDPE/PA tubular foil using rollers of different electrical resistence*
9:50–10:10	**Z. Kelar Tučeková:** *BOPP foil surface treatment by ambient air volume and coplanar dielectric barrier discharge in roll-to-roll configuration*
10:10–10:30	**J. Kelar:** *Plasma activation of various industrially used materials for UV-digital printing applications*

10:30–11:00 Coffee break

TOPIC 1: SURFACE MODIFICATION – part II Chairman: Oleksandr Galmiz

11:00–11:20	**R. Krumpolec:** - (Title of the lecture is not available to the public)
11:20–11:40	**S. Sihelník:** *Atmospheric plasma treatment of ultra-thin flexible glass for deposition of conductive layers*

11:40–12:00	**J. Feng:** *Surface modification of PTFE by atmospheric pressure plasma*
12:00–12:20	**P. Ghourchi Beigi:** *Surface modification of soda-lime glass with low-pressure glow plasma and gliding arc plasma treatments*

12:30–13:30 Lunch

13:30–15:30 Free time & Informal discussion

15:30–16:00 Coffee break

TOPIC 1: SURFACE MODIFICATION – part III Chairman: Veronika Medvecká

16:00–16:20	**O. Galmiz:** *Measurements of the nanofibers adhesion to the carrier substrates*
16:20–16:40	**D. Pavliňák:** *The effect of plasma on the efficiency of nanofiber filters*
16:40–17:00	**J. Surovčík:** *Effects of plasma treatment on photocatalytic properties of inorganic nanofibers*
17:00–17:20	**M. Stano:** *Plasma-initiated graft polymerization of acrylic acid on microporous polymeric membranes for the use in alkaline water electrolysis cells*
17:20–17:40	**A. Jamaati Kenari:** *Comparative study for investigation of BOPP foil surface treatment by different atmospheric-pressure plasma sources*

18:00–19:30 Dinner

Wednesday, 13rd October 2021

8:00–9:00 Breakfast

TOPIC 2: BIOAPPLICATIONS Chairman: Vlasta Štěpánová

9:30–9:50	**V. Medvecká:** *The decontamination effect of Multi-hollow surface dielectric barrier discharge*
9:50–10:10	**S. Ďurčányová:** *Efficacy comparison of various non-equilibrium plasma sources for surface treatment of soybean seeds*
10:10–10:30	**L. Zahedi:** *Development of functionalized polypropylene wound dressing for betaine hydrochloride controlled drug delivery on diabetic wounds*

10:30–11:00 Coffee break

TOPIC 3: FLEXIBLE AND PRINTED ELECTRONICS Chairman: Richard Krumpolec

11:00–11:20	**T. Homola:** *Recent developments in applications of plasma to the manufacture of flexible solar cells*
11:20–11:40	**V. Kažiková:** *Low temperature plasma treatment of MAPI perovskite*
11:40–12:00	**J. Vida:** *Atmospheric pressure plasma engineering of functional coatings and interfaces*

12:00–13:00 Lunch

13:00–18:00 Free time for visiting Adršpach-Teplice Rocks or other activities & Informal discussion

18:00–19:30 Dinner

Thursday, 14th October 2021

8:00–9:00 Breakfast

TOPIC 4: NEW MATERIALS & NEW CHALLENGES Chairman: Mirko Černák

9:30–9:50	**R. Krumpolec:** *Plasma-triggered reduction-exfoliation of highly porous graphene oxide 3D materials*
9:50–10:10	**M. Pazderka:** *Selection of special dielectric substrates for electrostatic voltage measurement*

GROUP MEETING Chairman: Dušan Kováčik

10:10–11:50	Open discussion related to current projects, research activities, contract research, collaborations, new equipment and future visions
11:50–12:00	Closing words

12:00–13:00 Lunch & Departure

LIST OF ATTENDEES AND CONTRIBUTORS

Masaryk University, Faculty of Science,
Department of Physical Electronics

doc. Mgr. KOVÁČIK Dušan, PhD.

prof. RNDr. ČERNÁK Mirko, CSc.

doc. RNDr. HOMOLA Tomáš, PhD.

doc. Mgr. SLAVÍČEK Pavel, Ph.D.

RNDr. KRUMPOLEC Richard, PhD.

RNDr. KELAR TUČEKOVÁ Zlata, PhD.

Mgr. ŠTĚPÁNOVÁ Vlasta, Ph.D.

Mgr. PAVLIŇÁK David, Ph.D.

Mgr. GALMIZ Oleksandr, Ph.D.

Mgr. KELAR Jakub, Ph.D.

Mgr. PAZDERKA Michal

Mgr. SIHELNÍK Slavomír

Mgr. VIDA Július

MSc. FENG Jianyu

MSc. JAMAATI KENARI Ali

Mgr. KAŽIKOVÁ Veronika

MSc. ZAHEDI Leila

MSc. GHOURCHI BEIGI Pedram

Mgr. ZAŽÍMAL František

Comenius University in Bratislava,
Faculty of Mathematics, Physics and Informatics,
Department of Experimental Physics

doc. RNDr. ZAHORANOVÁ Anna, PhD.

RNDr. MEDVECKÁ Veronika, PhD.

Mgr. STANO Michal, PhD.

Mgr. SUROVČÍK Juraj

Mgr. ĎURČÁNYOVÁ Sandra

ABSTRACTS

TOPIC 1

SURFACE MODIFICATION – part I

OPTIMISATION OF THE DCSBD ROLL-TO-ROLL TREATMENT OF LLDPE/PA TUBULAR FOIL USING ROLLERS OF DIFFERENT ELECTRICAL RESISTANCE

Vlasta ŠTĚPÁNOVÁ, Slavomír SIHELNÍK, Petra ŠRÁMKOVÁ, Miroslav ZEMÁNEK, Jana JURMANOVÁ, Monika STUPAVSKÁ, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: vstepanova@mail.muni.cz

Abstract

This study aimed to optimise the diffuse coplanar surface barrier discharge (DCSBD) roll-to-roll (R2R) treatment of multi-layer tubular foil using several types of rollers differing in material resistance. Multi-layer tubular foils are used as casings in the meat industry. The effect of ambient air plasma generated by coplanar and volume dielectric barrier discharge on the surface characteristics of tubular foil formed from outside by polyamide had already been studied previously [1]. Subsequently, the influence of R2R plasma treatment on the surface properties of tubular foil's inner layer formed with linear low-density polyethylene (LLDPE) was studied. During the roll-to-roll treatment, the plasma acts from outside of the tubular foil, whereas the inside surface of the tubular foil is affected by plasma as well in dependence on the material of the roller. The utility model “Device for plasma treatment of tubular foils” was registered based on this finding [2]. It has been experimentally verified that a non-conductive roller constructed from plastic does not allow the surface discharge to be superimposed by microfilaments generated perpendicular to the film surface. This finding clarified the different effects of plasma treatment achieved using plastic and metal-rubber roller on the surface properties of LLDPE foil. Applied exposure times of DCSBD treatment were in the range of 0.5–2 seconds. Evident wettability improvement of LLDPE foil surface after the plasma treatment was observed with the naked eye, while the pristine LLDPE foil surface repelled water solution of methylene blue (Fig. 1). The increase in peel resistance in the case of 0.5 s exposure time when comparing plastic and metal-rubber roller was three times higher for the second one. Peel

resistance of untreated LLDPE foil was so low that it was unmeasurable. Best results were obtained for 2 s plasma exposure, where the peel resistance achieved using the metal-rubber roller was 31 % higher than for the plastic roller. The specific electrical resistance of a standard metal roller covered with rubber on the surface corresponds to 238.5 GΩcm^2, whilst the value for an optimised metal-rubber roller is 7.5 MΩcm^2. Significantly better film-to-meat adhesion was observed for the DCSBD plasma unit using a metal-rubber roller with the specific resistance of 7.5 MΩcm^2 than for the metal-rubber roller with the resistance of 238.5 GΩcm^2. This result could be attributed to the low specific resistance of the roller, which means higher conductivity when the surface discharge is superimposed by microfilaments generated perpendicular to the film surface.

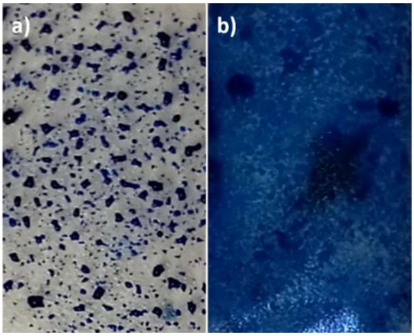

Fig. 1: LLDPE foil surface after soaking in a water solution of methylene blue a) untreated and b) DCSBD treated for 1 s by input power of 400 W.

This research has been supported by the project TG02010067 funded by the Technology Agency of the Czech Republic, and by the project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords: LLDPE/PA tubular foil, roll-to-roll treatment, DCSBD, peel resistance, wettability, film-to-meat adhesion

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BOPP FOIL SURFACE TREATMENT BY AMBIENT AIR VOLUME AND COPLANAR DIELECTRIC BARRIER DISCHARGE IN ROLL-TO-ROLL CONFIGURATION

Zlata KELAR TUČEKOVÁ, Petra ŠRÁMKOVÁ, Michal FLEISCHER, Jakub KELAR, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University,
Kotlářská 2, 611 37 Brno, Czech Republic
e-mail: zlata.tucekova@mail.muni.cz

Abstract

Biaxially oriented polypropylene (BOPP) foils are often used in the packaging industry due to their excellent mechanical and barrier properties. However, the low surface free energy hinders processes such as printing and labelling, where improved wettability and good adhesion are needed. BOPP surface activation was tested using two different low-temperature plasma sources operating in ambient air and capable of in-line operating. The volume dielectric barrier discharge (VDBD) and diffuse coplanar surface barrier discharge (DCSBD) were applied to improve the wettability and adhesion of several seconds (1-10 s) treated surface. The changes in morphology and surface chemistry were analysed by SEM, AFM, WCA, SFE and XPS. The adhesion was estimated by a peel force test, and the ageing of the treatment was monitored for a month. Both plasma sources ensured the stable improvement of surface properties acquired mostly by introducing polar (oxygen-containing) groups onto the surface. However, the VDBD treatment induced structural changes causing undesirable haze and loss of transparency of BOPP foil, which was not observed in the case of DCSBD treatment.

This research has been supported by the project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords: BOPP, VDBD, DCSBD, wettability, oxidation, adhesion, ageing

PLASMA ACTIVATION OF VARIOUS INDUSTRIALLY USED MATERIALS FOR UV-DIGITAL PRINTING APPLICATIONS

Jakub KELAR, Zlata KELAR TUČEKOVÁ, Oleksandr GALMIZ, Michal FLEISCHER, Eva KOSOVÁ, Miroslav ZEMÁNEK, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: jakub.kelar@mail.muni.cz

Abstract

Plasma activation of polymer materials is still one of the hot topics in modern industrial processing. Several applications are eager for enhanced surface properties of materials with excellent bulk properties. One of such fields is UV-digital printing for outdoor applications such as advertisement tables, safety labels, name tags, etc. In our work, we focused on plasma activation of materials commonly used for UV-digital printing, such as polyvinylchloride, polycarbonate, polymethylmethacrylate, and "di-bond" (polyethylene-aluminium composite material). We studied the wetting properties of the treated surface via water contact angle and free surface energy measurements. As expected, all materials reacted to the air plasma activation with a significant increase of the free surface energy. Most notably, the di-bond (PE-Al) material free surface energy value was changed by more than 50 %. In real-life applications, surface adhesion is most important. Thus, we studied the change in adhesion before and after plasma activation by peel test measurements. We confirmed the influence of air plasma on this parameter for all studied materials. We achieved an increase of adhesion on some materials by more than 100 %. Additionally, we analyzed the morphology of treated surfaces. Several air plasma sources have been tested for the potential application and incorporation in the UV-digital printing machine prototype.

This research has been supported by the project FV40114, funded by the Ministry of Industry and Trade of the Czech Republic.

Keywords: polymer plate, adhesion, wettability, ageing, UV-digital printing

TOPIC 1

SURFACE MODIFICATION – part II

ABSTRACT IS NOT AVAILABLE TO THE PUBLIC.

ABSTRACT IS NOT AVAILABLE TO THE PUBLIC.

ATMOSPHERIC-PRESSURE PLASMA TREATMENT OF ULTRA-THIN FLEXIBLE GLASS FOR DEPOSITION OF CONDUCTIVE LAYERS

Slavomír SIHELNÍK, Richard KRUMPOLEC, Tomáš HOMOLA, Jianyu FENG, Eva KOSOVÁ, Ali Jamaati KENARI, Monika STUPAVSKÁ, Jakub KELAR, Mirko ČERNÁK, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: sihelnik@mail.muni.cz

Abstract

Flexible electronics are nowadays manufactured on substrates that include polymer foils, paper or flexible glass. The various properties of the available materials predestine flexible electronics for applications ranging from biomedicine throughout the electronic industry to energy harvesting. Ultra-thin flexible glass (UTFG) is a novel material with chemical, electrical and optical properties that are attractive for applications in the manufacturing of optoelectronic devices like sensors, filters, displays and photovoltaic cells. UTFG is produced using the down-draw method, which results in different surface properties compared to common float glass. UTFG has relatively low surface free energy, which leads to weak wetting properties of its surface that could hinder coating depositions of liquid precursors. Most studies aimed at flexible conductive layers on glass surfaces were carried out on standard microscopic glass slides. The present research targets practical application of flexible conductive layers on glass and is focused on organic polymer coating deposition on UTFG with respect to implementation into roll-to-roll ink-jet printing systems for large scale electronics production [1].

Cleanness and surface free energy of the surface are important factors for a successful deposition process and the final product quality. Plasma is proposed as an efficient and gentle instrument for treating glass surfaces prior to deposition of conductive layers and appears to be more convenient for the application on UTFG than common

cleaning methods used for standard glass. Diffuse coplanar surface barrier discharge (DCSBD) and industrial corona were used to generate non-thermal plasma in order to compare their efficiency and appropriate optimal conditions. Wettability, chemical and morphological changes of the plasma-treated UTFG surface were analysed with WCA, XPS and AFM measurements. Both applied plasma sources significantly affected surface wettability when the initial value of 68° was reduced after 3 seconds of plasma treatment to 4.6°. However, the effect achieved with DCSBD plasma was more stable in time, with 26° (compared to 34° with industrial corona) after 7 days of storage on ambient air.

Deposition of highly conductive organic polymer PEDOT:PSS was studied to improve the quality of conductive layers made on plasma-treated UTFG. Defects and uniformity of PEDOT:PSS layers were observed with a confocal microscope. Four-point probe resistivity measurements were supplemented with profilometry to determine the electric conductivity of deposited layers. Transparent flexible PEDOT:PSS layers on UTFG could serve in composite structures applied in optoelectronics. Hence, non-thermal plasma treatment could also be involved in the consequent processing of structures prepared on top of or inside a PEDOT:PSS layer [2,3]. The interaction of conductive layer deposited on glass with the DCSBD plasma was also studied in the context of employing plasma in the treatment of PEDOT:PSS layers.

This research has been supported by the projects “R&D centre for plasma and nanotechnology surface modifications (CEPLANT)”, LM2018097 funded by the Ministry of Education, Youth and Sports and project “The improvement of large area UV digital printing quality with the help of atmospheric pressure plasma”, FV40114 funded by the Ministry of Industry and Trade (program TRIO).

Keywords: ultra-thin glass, flexible electronics, conductive layer, DCSBD plasma, industrial corona, cleaning, activation

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SURFACE MODIFICATION OF PTFE BY ATMOSPHERIC PRESSURE PLASMA

Jianyu FENG, Richard KRUMPOLEC, Slavomír SIHELNÍK, Ali JAMAATI KENARI, Monika STUPAVSKÁ, Dušan KOVÁČIK, Mirko ČERNÁK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: jianyufeng@mail.muni.cz

Abstract

Polytetrafluoroethylene (PTFE) is widely used in the engineering field because of its excellent mechanical and chemical properties. However, the lower wettability and poor adhesion greatly limit the application of PTFE, especially in biological field. Researchers are exploring various physical and chemical methods to modify the surface of PTFE to improve these disadvantages. The atmospheric pressure plasma has always been the main force in the field of surface modification due to its unique characteristics [1,2]. The main objective of this work is to modify the surface of the PTFE by Diffuse Coplanar Surface Barrier Discharge (DCSBD) and Multi-hollow Dielectric Barrier Discharge (MHDBD). The PTFE foils were treated by the low-temperature non-equilibrium DCSBD and MHDBD plasma generated in ambient air, oxygen, the mixture of H_2/N_2 (5% volume content of H_2), and argon plasma (only DCSBD). In this work we focused on using standard "safe" gases that requires no special treatment/manipulation and thus we significantly expand the results that have been previously reported for DCSBD plasma modification of PTFE in pure hydrogen plasma [3]. The wettability and aging behavior were measured using See system. The surface chemistry is investigated by X-ray photoelectron spectroscopy (XPS). The results show that the wettability of PTFE can be effectively improved by DCSBD and MHDBD plasma. The mixture of H_2/N_2 plasma was the most effective gas to improve the wettability of PTFE with DCSBD. The plasma-treated PTFE samples, stored in the air for a long time, exhibited only a partial recovery of original WCA values. Furthermore, plasma-treated PTFE tubes were tested for improvement of its adhesion properties. We observed that the plasma can effectively improve the adhesion of glue

joints of the PTFE tubes. Using the MHDBD plasma, we studied the modification of thin PTFE foils and the effects of different experimental parameters, such as power input, working gas flow rate, PTFE foil surface to plasma unit surface gap size. The results show that wettability improvement effect is basically the same when the distance between the PTFE foil and the ceramic surface is in the range 0.1-1 mm. It means that MHDBD can modify slight curved and uneven surfaces to same extent. The XPS analysis show that DCSBD and MHDBD plasma treatment of PTFE results in an increase of oxygen and carbon concentration, decrease of fluorine concentration and changes in presence of polar functional groups. The results of wettability changes of plasma-treated PTFE together with the XPS analysis thus support the observed adhesion improvement of plasma-treated PTFE.

Keywords: surface modification, atmospheric plasma, PTFE, wettability, surface chemistry, adhesion improvement

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SURFACE MODIFICATION OF SODA-LIME GLASS WITH LOW-PRESSURE GLOW PLASMA AND GLIDING ARC PLASMA TREATMENTS

Pedram GHOURCHI BEIGI[1], Mohammad Reza KHANI[1], Babak SHOKRI[1,2]

[1]*Laser and Plasma Research Institute, University of Shahid Beheshti, Tehran, Iran*

[2]*Department of Physics, University of Shahid Beheshti, Tehran, Iran*

e-mail: 518570@mail.muni.cz

Abstract

Surface modification is one of the main steps to improve the adhesion of a wide range of substrates for electronics, photonics, architecture, solar cells, and packaging without facing any poor performance. Soda-Lime Glass, being cheap and amorphous, is a very suitable substrate for preparing films. Since printing on glass is so intolerable, and because of the existing difficulties in activating its surface, we are trying to improve the dyeability, and adhesion properties by using plasma treatments, both atmospheric and low-pressure devices. Plasma treatment is an environmentally friendly method with low energy consumption, which can eliminate chemical primers.

In this research, the glass samples were treated by the gliding arc plasma and low-pressure glow discharge plasma in ambient air at different treatment times and working powers. Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Water Contact Angle (WCA) analyses were performed to study the improvement of the surface. To evaluate the durability of the effect of plasma, the Aging effect was monitored for up to 30 days after the treatment.

Keywords: surface modification, atmospheric plasma, gliding arc, glow discharge, glass

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TOPIC 1

SURFACE MODIFICATION – part III

MEASUREMENTS OF THE NANOFIBERS ADHESION TO THE CARRIER SUBSTRATES

Oleksandr GALMIZ, David PAVLIŇÁK, Michal FLEISCHER, Ali JAMAATI KENARI, Jakub KELAR, Mirko ČERNÁK, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: o.galmiz@mail.muni.cz

Abstract

Filter media containing a nanofiber filter membrane have proven to be an advantageous and economical option for capturing submicron particles. These media can therefore be advantageously used for the production of filters and protective aids with FFP3 filtration efficiency, including protection against viral particles. These nanofiber membranes are made of synthetic polymers mainly by electrospinning technology. This fabrication method which is based on high electrostatic forces to elongation and thinning of flowed polymer fiber is very popular for its simplicity, efficiency, and usability of most industrially expanded polymers.

The atmospheric pressure plasma treatment was used for surface activation of polymer textile materials serving as a substrate for electrospun nanofiber (see Fig.1). Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used for nanofiber carriers pre-treatment in continuous mode to improve the adhesion between the produced polyvinylidene fluoride (PVDF) nanofibers and the carrier. As the carrier substrate several commercially used polymers were tested. The increased adhesive forces to carrier substrate were confirmed by two peeling tests.

The results show a weak holding of nanofibers on the reference textile. The manipulation with the untreated carrier of nanofibers is a problem now and requires further processing. Samples that were plasma treated show dependence in increasing adhesion with increasing the exposure time. It was shown that the DCSBD plasma

treatment has an outstanding effect on the adhesion of the spunbond non-woven polypropylene textile and polyester (PES) mesh.

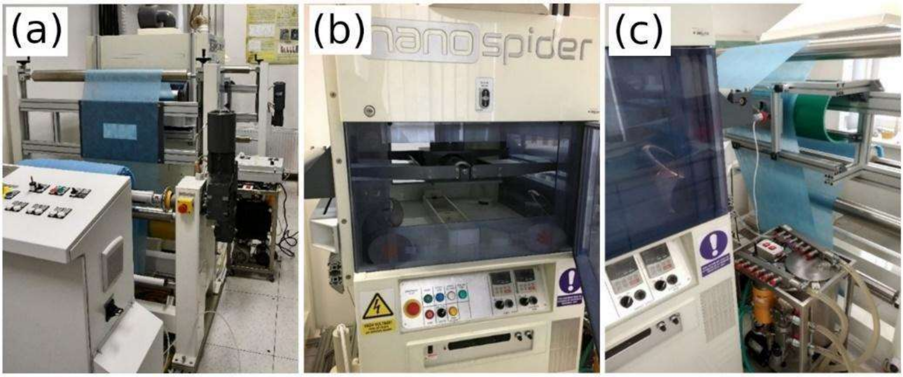

Fig. 1: The line for the carrier plasma pre-treatment and the nanofibers production: a) planar DCSBD electrode, b) the Nanospider NSLAB 500 device, c) curved DCSBD electrode.

This work was supported by project No. E01-14 funded by the ELIIT initiative.

Keywords: PVDF nanofibers, plasma, DCSBD, adhesion, spunbond non-woven polypropylene, PES

THE EFFECT OF PLASMA ON THE EFFICIENCY OF NANOFIBER FILTERS

David PAVLIŇÁK[1], Oleksandr GALMIZ[1], Jakub KELAR[1], Dušan KOVÁČIK[1], Mirko ČERNÁK[1], Michal FLEISCHER[1], Ali JAMAATI KENARI[1], Pavel KOSÍK[1], Jana SVOBODOVÁ[2], Jakub ONDRÁČEK[3]

[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[2]NAFIGATE Corporation a.s., Prosecká 851/641, Prague 190 00, Czech Republic, EU

[3]ICPF CAS, Department of Aerosol Chemistry and Physics, Prague, Czech Republic, EU

e-mail: d.pavlinak@mail.muni.cz

Abstract

Although nanofibers have been known to the scientific community for almost a hundred years, they have long remained on the brink of interest. It was not until the 1990s that there was a renaissance of nanofiber materials research. Thanks to their unique properties, high filtration efficiency, great free surface combined with good breathability, nanofiber materials are directly destined for filtration applications and come to the forefront of industrial interest.[1] At the beginning of the millennium, the last obstacle was solved - the efficient industrial production, and since then nothing has hindered mass commercial production.[2] The recent COVID-19 pandemic, which globally started the mass production of cheap protective devices capable of trapping virus particles, also played a significant role in commercial spreading.[3] The nanofibers fabricated in a thin layer are a very fine material and cannot be easily handled. In practice, this is solved by their application on a carrier substrate, protecting them from damage. Unfortunately, the nanofiber membrane adheres very reluctantly to these substrates, so it must be properly fixed. In industrial production, this is usually solved by a lamination process, which means that the nanofibers are sophisticatedly glued to the substrate with an adhesive and covered with a protective mesh. However, this technique brings several complications and limitations to the useful properties of the resulting material. In addition, the lamination process significantly increases the cost of the production process.[4] Thus, for the production of disposable protective

devices, such as respirators or protective suits, alternative possibilities of attaching nanofibers to the carrier are being sought. A relatively elegant method is the application of plasma to a support substrate, on which nanofibers are subsequently applied. If an atmospheric plasma source is used, this technology can be directly implemented in the in-line production process. It is also possible to apply plasma directly to the nanofiber network, which allows us to modify their chemical and physical properties. In this way, we obtain a functional, inexpensive nanomaterial that we can use for products with high added value. [5, 6] In this work, we focused on the use of dielectric barrier discharges in a coplanar arrangement. These plasma sources are able to generate low temperature energetic plasma over a relatively large area. However, barrier discharges generated at atmospheric pressure also have their disadvantages. From a microscopic point of view, the energy in the plasma is focused into tiny channels called streamers. There is a risk that these energy channels can damage the material during treatment and create small holes inside it. In the case of minor damage to the carrier material, this is not yet a significant problem. However, the perforated nanofiber mesh would of course lose its unique filtering ability. In this work, we mainly focused on the preparation of nanomaterial for air filtration, and we will monitor the positive or adverse effect of plasma on filtration efficiency.

This work was supported by project No. E01-14 funded by the ELIIT initiative.

Keywords: nanofibers, plasma, adhesion, filtration efficiency

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EFFECTS OF PLASMA TREATMENT ON PHOTOCATALYTIC PROPERTIES OF INORGANIC NANOFIBERS

Juraj SUROVČÍK[1], Veronika MEDVECKÁ[1,2], Adam KERDÍK[1], Miroslav ZAHORAN[1], David PAVLIŇÁK[2], Dušan KOVÁČIK[1,2]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovak Republic

[2]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: juraj.surovcik@fmph.uniba.sk

Abstract

In recent years, great focus has been aimed at researching inorganic nanostructures with photocatalytic activity used in wastewater treatment [1]. Hierarchical nanostructures offer high surface/volume ratio, large number of active sites of photocatalytic reactions and high molecular diffusion. These properties contribute to increased photocatalytic performance. We studied two of the popular photocatalysts, titanium (IV) oxide (TiO_2) and zinc (II) oxide (ZnO). These materials have been popular research topics for several years because of their versatility. They are used in various fields, such as medicine, cosmetics, energy production and storage, optoelectronics, and many others. In this work, we use TiO_2 and ZnO in the form of 1D nanofibers, created by combination of low temperature plasma treatment and thermal calcination.

Ceramic TiO_2 and ZnO nanofibers were prepared from metal-organic nanofibers (Polyvinyl pyrrolidone + Titanium tetraisopropoxide and Polyvinyl pyrrolidone + Zinc acetate, respectively), which were produced by needleless electrospinning (Nanospider™). First, as-spun fibers were treated by plasma generated by Diffuse coplanar surface barrier discharge (DCSBD). Low temperature plasma is chemically active environment which is effective in removal of base polymer [2] and might initiate

oxidation process [3]. After plasma treatment, fibers were thermally calcined at elevated temperature for decomposition of organics and formation of oxides. We compared these samples to nanofibers prepared following the same procedure without plasma treatment.

Changes in morphology were investigated using scanning electron microscope (SEM). After plasma treatment, we noticed fibers bonding at intersections, forming harder structure. We observed significant changes in crystallization of plasma treated samples after thermal calcination. Unlike untreated samples, they retained their fiber structure. As a result, treated samples were significantly less brittle in comparison.

Chemical analysis of the samples shows decrease of carbon in the treated samples. This shows that removal of organics is more effective after decomposition was already initiated by low temperature plasma. FTIR measurements exhibit decrease in peaks attributed to PVP after plasma treatment and higher proportion of inorganic TiO_2 and ZnO in the respective samples after plasma assisted calcination.

Effects of plasma pretreatment on photocatalytic activity were demonstrated by degradation of methylene blue solution. Our measurements show improved photocatalytic activity in samples that underwent plasma assisted calcination compared to untreated fibers produced by just thermal calcination.

This study was supported by the Slovak Grant Agency No. 1/0782/19.

Keywords: nanofibers, low temperature plasma, DCSBD, photocatalysis, zinc oxide, titanium dioxide

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PLASMA-INITIATED GRAFT POLYMERIZATION OF ACRYLIC ACID ON MICROPOROUS POLYMERIC MEMBRANES FOR THE USE IN ALKALINE WATER ELECTROLYSIS CELLS

Michal STANO, Ľubomír STAŇO, Martin KUŤKA, Pavol ĎURINA

Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovak Republic

e-mail: michal.stano@fmph.uniba.sk

Abstract

Graft polymerization of a suitable monomer is a convenient method to achieve highly hydrophilic modification of polymer surfaces [1]. Moreover, activation of microporous membranes by plasma can initiate graft polymerization not only on outer surfaces, but also inside the porous structure [2].

This work presents a novel method to prepare inter-electrode separators for alkaline water electrolysis (AWE) cells. The role of the separator is to separate the hydrogen and oxygen produced on the respective electrodes, while posing minimal resistance to - OH^- ions conducting current in the electrolyte. To fulfill this role, the separator has to be mechanically tough, chemically resistant, and highly wettable by aqueous alkaline electrolyte. Some polymers, e.g. polypropylene and polysulfones possess the necessary mechanical strength and chemical resistance, but lack the required wettability. In this work, wettability of polypropylene and polysulfone microporous membranes is achieved by plasma-initiated graft-polymerization of acrylic acid. Two reaction schemes were employed, the hydroperoxide method and the trapped radical method. In the hydroperoxide method, the porous membranes were activated by low-pressure RF discharge in oxygen, resulting in formation of various oxygen-containing functional groups including hydroperoxides. Subsequently, the activated membranes were immersed in aqueous solution of acrylic and heated to 70°C to decompose the hydroperoxides and initiate the graft polymerization [3]. In the trapped radical

method, the membranes were activated by low-pressure RF discharge in argon and immediately flooded with acrylic acid solution without coming in contact with air.

The grafted membranes were characterized by gravimetric grafting degree, critical wetting surface tension (CWST), and scanning electron microscopy (SEM). In addition, the membranes were characterized as separators in AWE cell in terms of electrical resistance and mutual cross-contamination of hydrogen and oxygen produced by the electrolysis cell with the tested membrane used as a separator.

The results indicate that grafting of acrylic acid on microporous membranes strongly improves their performance as separators in AWE cells. While the initial membranes were poorly wettable by the aqueous electrolyte and remained practically non-conductive, the membranes grafted by acrylic acid achieved CWST exceeding 103.8 $mJ.cm^{-2}$ and electrical resistance in the range of 30 – 300 $m\Omega.cm^2$, depending on the initial substrate and the achieved grafting degree. Some of the tested substrates exhibited reducing permeability to gases dissolved in electrolyte with increasing grafting degree, indicating that grafting of acrylic acid notably improves properties of microporous polymeric membranes as separators in AWE cells.

This work was supported by the Slovak grant agency VEGA, project 1/0811/21.

Keywords: graft polymerization, filling polymerization, acrylic acid, water electrolysis, separators

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COMPARATIVE STUDY FOR INVESTIGATION OF BOPP FOIL SURFACE TREATMENT BY DIFFERENT ATMOSPHERIC-PRESSURE PLASMA SOURCES

Ali Jamaati KENARI, Slavomír SIHELNÍK, Jakub KELAR, Dušan KOVÁČIK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: 501897@mail.muni.cz

Abstract

For polymer materials surface treatment, cold atmospheric plasma is widely used [1]. Polypropylene (PP) is a famous type of polyolefin used in a wide variety of applications. Although the biaxially oriented polypropylene (BOPP) films have many advantageous properties, their applications have limitations due to the poor adhesion properties resulting from their non-polar nature and low surface energy [2,3]. In this comparison study, the 25 μm thin BOPP film was treated by plasma generated by three different atmospheric-pressure plasma sources, specifically by diffuse coplanar surface barrier discharge (DCSBD) with the concavely curved electrode installed in the roll-to-roll reactor [4], plasma jet array (Fig. 1) [5], and multi-hollow surface dielectric barrier discharge (MSDBD) [6]. DCSBD was generated in ambient air by supplying the sinusoidal high voltage with the amplitude of 10 kV and the frequency of 15 kHz at the plasma power density of 2.5 W/cm^2 corresponding power 400 W. The plasma jet array was operated in argon used as the working gas. The supplying voltage was of the sinusoidal waveform with 8 kV peak-to-peak value and of 23 kHz frequency at power 12 W. In the case of MSDBD used as a plasma source for the treatment, the voltage amplitude was 7 kV, and the frequency was 27 kHz at 30 W power. During the plasma treatment, the following distances between treated BOPP film and plasma sources were kept: 0.3 mm from the curved ceramics of DCSBD, 50 mm from the plasma jet nozzle, and 0.3 mm from the perforated ceramics of MSDBD. The samples were treated by plasma for the exposure times 1 s, 3 s, 5 s, 10 s.

The surface wettability of BOPP film treated by all plasma sources was investigated by measuring the water contact angle (WCA) immediately after treatment, and for DCSBD and plasma jet treatment also after 1 and 3 weeks later to study the stability of the treatment and the possible ageing behavior. Furthermore, Attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) for characterization of the plasma-induced chemical groups changes on the surface, the profilometer/roughness gauge for roughness measurement, and scanning electron microscopy (SEM) for BOPP film surface morphology investigation were used and the results were compared. The best WCA values immediately after treatment were shown for the treatment by plasma jet with 10 s exposure time. However, the most stable treatment was confirmed for DCSBD plasma treatment with the 5 second exposure time. The results of SEM and roughness measurement of the BOPP film surface after DCSBD and plasma jet treatments were very similar.

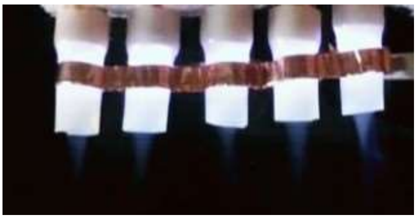

Fig. 1: The photo of the plasma jet array.

Keywords: BOPP foil, DCSBD, plasma jet array, Multi-hollow surface dielectric barrier discharge

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RF PLASMA NOZZLE FOR ANALYTICAL CHEMISTRY

Pavel SLAVÍČEK[1], Aleš HRDLIČKA[2], Magda DVOŘÁKOVÁ[2], Lukáš NOVOSAD[2], Viktor KANICKÝ[2]

[1]*Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[2]*Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
e-mail: ps94@physics.muni.cz

Abstract

Different plasma sources were used for chemical analysis – inductively coupled plasma, glow discharges, capacitively coupled plasma and microwave sources. Discharges at atmospheric pressure were used in most cases. Our study was aimed to rf plasma nozzle (plasma pencil) at atmospheric pressure as an alternative excitation source for analytical chemistry. Plasma pencil had been a capacitively coupled plasma rf jet discharge, operated typically in argon at atmospheric pressure. The experimental arrangement is shown in Fig. 1. The plasma was boosted by a Cesar 136 rf generator at 13.56 MHz frequency, and the correct feedback was driven by a laboratory-made matching unit keeping the reflected power close to zero. It was enclosed in a 250 mm long quartz tube (o.d. 4 mm, i.d. 2 mm). The position 6.5 cm corresponds to the ground electrode, 0 cm is the position of the sample inlet, and the power electrode is on position -1.5 cm. The main argon stream was dosed with a mass flow controller. The aerosol sample introduction system employed a peristaltic pump, and a double pass Scott spray chamber with a pneumatic concentric nebulizer. The created aerosol was transported by the carrier gas perpendicularly into the main discharge argon stream. The analytical profit of this plasma source had been shown during the determination of Li, Na, Mg, Ca, Cu and Zn in aqueous solutions as representatives of alkali, alkali-earth and transition metals [1-3]. The parameters of the plasma nozzle (rotational and excitation temperature) were calculated by optical emission spectroscopy (OES) [4]. The advantage of the tested plasma source had been lower operational costs

compared with conventional inductively coupled plasma or microwave plasma excitation sources for chemical analysis.

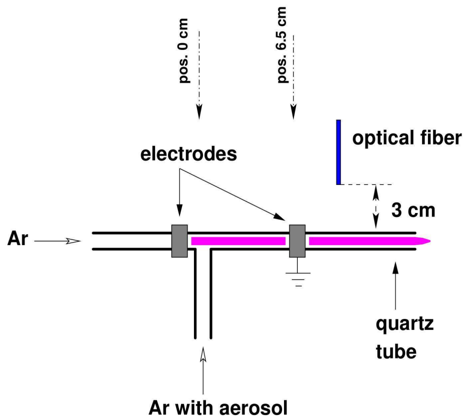

Fig. 1: Experimental arrangement of the discharge [4].

Keywords: plasma nozzle, atmospheric pressure plasma, OES, chemical analysis

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TOPIC 2

BIOAPPLICATIONS

THE DECONTAMINATION EFFECT OF MULTI-HOLLOW SURFACE DIELECTRIC BARRIER DISCHARGE

Veronika MEDVECKÁ[1], Silvia MOŠOVSKÁ[2], Anna MIKULAJOVÁ[2], Anna ZAHORANOVÁ[1]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovak Republic

[2]Department of Nutrition and Food Quality Assessment, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 811 07 Bratislava, Slovak Republic

e-mail: medvecka3@uniba.sk

Abstract

The decontamination effect of low-temperature plasma generated by Multihollow Surface Dielectric Barrier Discharge (MSDBD) was investigated on *Salmonella* Enteritidis, *Escherichia coli*, and *Bacillus subtilis* inoculated on the surface of nutrient-agar plates [1,2]. The effect of MSDBD plasma treatment was studied in dependence on applied working gas (ambient air, oxygen and nitrogen) and treatment time from 3 s to 180 s.

Ambient air plasma showed the strongest antimicrobial effect against tested microorganisms. The inactivation of about 5.04 log CFU/g and 3.69 log CFU/g was achieved after 15 s plasma treatment for *E. coli* and *S.* Enteritidis, respectively. After 30 s of plasma application, vegetative cells of *B. subtilis* were decreased by 3.74 log. In case of oxygen and nitrogen plasma application, a higher treatment times were needed to decontamination of tested microorganism compared to ambient air plasma. The highest inactivation of 4.23 log after 120 s of oxygen plasma treatment was achieved for *E. coli.* After 180 s of nitrogen plasma exposure an inactivation of 4.47 log for *E. coli* and 4.32 for *B. subtilis* was reached.

The composition of plasma generated in different working gases was analyzed by Optical Emission Spectroscopy and Fourier Transform Infrared Spectroscopy. The strong inhibition effect of MSDBD plasma in ambient air compared to oxygen and nitrogen was attributed to more variety of active RONS produced in plasma.

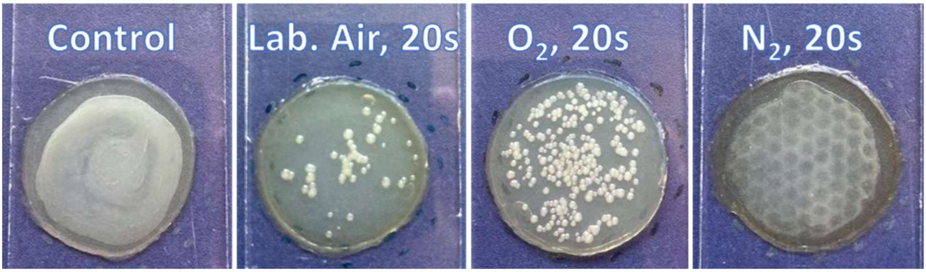

Fig. 1: Decrease of vegetative cells of *S. Enteritidis* inoculated on nutrient-agar plates after treatment by MSDBD for 20s in different working gases.

This study was supported by the Slovak Research and Development Agency under the contract No. APVV-16-0216.

Keywords: Multihollow Surface DBD, decontamination effect, OES, FTIR analysis

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EFFICACY COMPARISON OF VARIOUS NON-EQUILIBRIUM PLASMA SOURCES FOR SURFACE TREATMENT OF SOYBEAN SEEDS

Sandra ĎURČÁNYOVÁ[1], Matej KLAS[1], Ľudmila SLOVÁKOVÁ[2], Dušan KOVÁČIK[1], Anna ZAHORANOVÁ[1]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovakia

[2]Department of Plant Physiology, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia

e-mail: sandra.durcanyova@fmph.uniba.sk

Abstract

Using non-thermal plasma for surface treatment of biological materials, namely plant seeds, in order to improve their growth, is an increasingly relevant topic [1]. In this work, we studied the efficacy of various sources of non-thermal plasma for surface treatment of soybean seeds (*Glycine max* L.) at atmospheric pressure. We compared three types of plasma treatments: direct treatment with plasma generated by a diffuse coplanar surface barrier discharge (DCSBD), direct treatment with plasma generated by a multi-hollow surface dielectric barrier discharge (MSDBD), and indirect treatment with the gaseous products of plasma generated by a plasma jet. Characteristics of the plasma sources were determined by electrical measurements and the chemical composition of their gaseous products, measured with FTIR spectroscopy. Parameters of plasma treatments in various working gases were optimized in order to improve the germination and growth dynamic of soybeans. Plasma-treated seeds were examined with water contact angle measurements, imbibition measurements, ATR-FTIR spectroscopy and SEM surface analysis. ATR-FTIR surface analysis showed minor changes in the chemical bonds on the surface of plasma-treated seeds, which suggest the presence of polar oxygen and nitrogen groups on the surface [2], and also led to an increase in wettability and imbibition. SEM analysis confirmed that plasma treatment is non-invasive and does not leave changes in the morphology of the seeds'

surface. The importance of optimizing plasma treatment parameters for a specific plant seed variety has been demonstrated. We also introduced a new type of plasma device construction optimized for surface treatment of plant seeds consisting of two DCSBD plasma units. This prototype is suitable for direct application to seed surface treatment and will be the next subject of our research in this field.

This work has been supported by the Slovak Research and Development Agency under the contract No. APVV-16-0216.

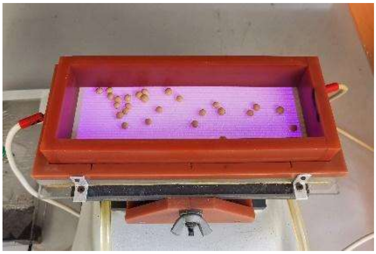

Fig. 1: DCSBD plasma treatment of soybean seeds.

Keywords: DCSBD, MSDBD, plasma jet, non-thermal plasma, surface treatment, soybean

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DEVELOPMENT OF FUNCTIONALIZED POLYPROPYLENE WOUND DRESSING FOR BETAINE HYDROCHLORIDE CONTROLLED DRUG DELIVERY ON DIABETIC WOUNDS

Leila ZAHEDI[1], Pedram GHOURCHI BEIGI[1], Mojtaba SHAFIEE[1], Fatemeh ZARE[2], Hamed MAHDIKIA[1], Majid ABDOUSS[3], Mohammad-Amin ABDOLLAHIFAR[2], Babak SHOKRI[1,4]

[1]Laser and Plasma Research Institute, Shahid Beheshti University, G.C, Velenjak Avenue, Tehran, Iran

[2]Department of Biology and Anatomical Sciences, School of Medicine, Shahid Beheshti University of Medical Science, Evin, Tehran, 1985717443, Iran

[3]Department of Chemistry, Amirkabir University of Technology, 424 Hafez Avenue, P.O. Box 15857-4413, Tehran, Iran

[4]Department of Physics, Shahid Beheshti University, G.C, Velenjak Avenue, Tehran, Iran

e-mail: 518571@mail.muni.cz

Abstract

Diabetes Mellitus is one of the most worrying issues among illnesses, and its chronic subsequences almost refer to inflammations and infections. The loading and local release of antioxidants to wounds may decrease inflammations. However, the low wettability of Polypropylene (PP) restricts the drug from loading. So, to increase the adhesion of PP for loading an optimum amount of Betaine Hydrochloride (BET), a low-pressure glow discharge plasma source and Plasma-Enhanced Chemical Vapor Deposition (PECVD) generated by RF (56.13 MHz) have been applied in two steps of functionalization and polymerization, respectively, which has been confirmed with FE-SEM, ATR-FTIR, and EDX. The new chemistry of surface led to almost 80% of BET loaded. The drug-releasing ratio studied by HPLC approved the presence of a PEG-like layer, which was coated by polymerization of tetraglyme. To evaluate the wound healing potential of the application of the PP meshes treated by plasma, 72 Wistar rats were subdivided into four groups. The skin injury site was removed and underwent

biomechanical tests, stereological analysis, and RNA extraction. The results showed a significant improvement in the polymerized scaffold containing BET for skin injury. The present study suggests that the use of a modified PP mesh can induce tissue regeneration and accelerate wound healing at the skin injury site.

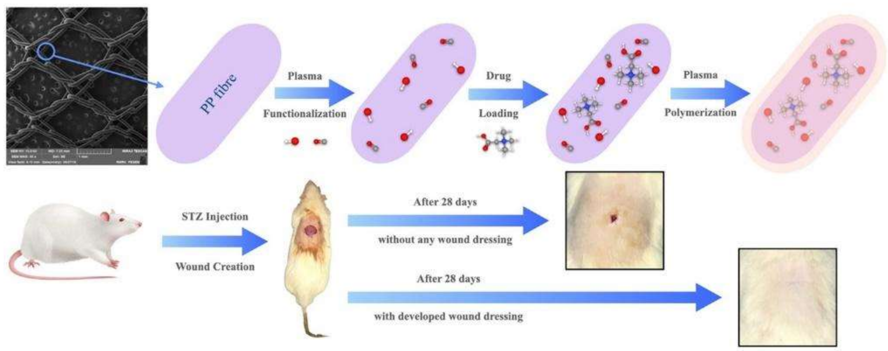

Fig. 1: The graphical representation of the research.

Keywords: low-pressure plasma, diabetes, drug delivery, wound healing, polypropylene meshes, betaine hydrochloride

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TOPIC 3

FLEXIBLE AND PRINTED ELECTRONICS

RECENT DEVELOPMENTS IN APPLICATIONS OF PLASMA TO THE MANUFACTURE OF FLEXIBLE SOLAR CELLS

Tomáš HOMOLA [1], Július VIDA [1], Jan POSPÍŠIL [2], Petr DZIK [2]

[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[2] Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

e-mail: tomas.homola@mail.muni.cz

Abstract

The current photovoltaic technologies based on c-Si do not meet the requirements for economical fabrication steps, which have recently come to involve sheet-to-sheet (S2S) and roll-to-roll (R2R) and manufacturing and require flexible substrates and fast processing technologies. S2S and R2R manufacturing combines low-cost materials with high manufacturing speeds and enables the manufacture of various devices on a large scale. The implementation of low-temperature processes, particularly low-temperature plasma, into S2S and R2R manufacturing is essential for successful commercialization also in other industrial sectors, all combined in flexible and printed electronics.

In this contribution we summarize the recent developments of plasma applications to the manufacture of flexible perovskite solar cells.

Keywords: photovoltaics, perovskite solar cells, plasma treatment, surfaces and interfaces

LOW TEMPERATURE PLASMA TREATMENT OF MAPI PEROVSKITE

Veronika KAŽIKOVÁ[1], Július VIDA[1], Aleš VLKAL[2], Martin LEDINSKÝ[2], Anna ARTEMENKO[2], Tomáš HOMOLA[1]

[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[2]Department of Thin Films and Nanostructures, Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague 8

e-mail: 517378@mail.muni.cz

Abstract

Methylammonium-lead-iodide (MAPI) perovskite, as one of the most promising light-absorbing material in solar cells, have been spin-coated on glass substrates and treated with a low temperature plasma. Plasma treatment have already been used to other parts of perovskite solar cells (PSC), such as electron/hole transport layers or electrodes, in order to achieve more suitable connection of interfaces, lower the charge recombination rate and obtain higher power conversion efficiencies (PCE). [1] However little is known about the effect of different plasmas used directly on the perovskite surface. As a plasma source, diffuse coplanar surface barrier discharge (DCSBD) has been used, placed directly into a glovebox with nitrogen atmosphere together with a photoluminescence (PL) measurement setup to exclude contact of samples with ambient air during and directly after treatments. PL measurements have revealed intriguing behavior dependent on a length of a plasma treatment. Chemical composition of a surface after treatment has been determined by an X-ray photoelectron spectroscopy.

Keywords: perovskite, plasma treatment, solar cells, photoluminescence, XPS

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ATMOSPHERIC PRESSURE PLASMA ENGINEERING OF FUNCTIONAL COATINGS AND INTERFACES

Július VIDA[1], Pavol GEMEINER[2], Jan POSPÍŠIL[3], Veronika KAŽIKOVÁ[1], Tomáš HOMOLA[1]

[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[2]Department of Graphical Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia

[3]Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

e-mail: jvida@mail.muni.cz

Abstract

Atmospheric pressure plasma has become a standard tool for treatment of various surfaces. Due to the complex nature of the interactions between plasma and surface the applications of plasma treatment are very diverse, ranging from pretreatment of polymeric foils for better wettability and adhesion of inks, through etching of surfaces and disinfection of surfaces to improved germination of plant seeds [1].

Recently a new field of applications for atmospheric pressure plasma has emerged in post-deposition processing of printed functional coatings for flexible and printed electronics [2, 3]. The effects of plasma on coatings can include oxidation, or reduction of surfaces, passivation of defects on the interfaces, formation of multiple material composites, sintering of nanoparticles. Due to the possibility of igniting plasma in diffuse coplanar surface barrier discharge (DCSBD) in various gases including air, nitrogen, oxygen, hydrogen and argon, the process of plasma treatment of functional coating can be tuned to achieve the desired result.

In this contribution we present a recent progress in atmospheric pressure, low temperature plasma treatment of functional coatings for

a) oxidation of printed MXene coatings in oxygen plasma and formation of TiO_2/MXene composite with possible applications as electron transport layer in perovskite solar cells or in photocatalysis,

b) passivation of interfacial defects of mesoporous TiO_2 electron transport layer in perovskite solar cells by hydrogen plasma for improved band alignment and charge transfer across the interface.

Keywords: functional coatings, plasma, DCSBD, MXene, mesoporous TiO_2, flexible and printed electronics

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MAGNETIC LAYERS FOR APPLICATIONS IN PRINTED ELECTRONICS

František ZAŽÍMAL[1,2], Tomáš SVOBODA[3], Petr Dzik[3], Yvonna Jirásková[2], Tomáš HOMOLA[1]

[1]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[2]Institute of Physics of Materials AS CR, v. v. i., Žižkova 513/22, 616 00 Brno, Czech Republic

[3]Brno University of Technology, Faculty of Chemistry, Purkyňova 464, 612 00 Brno, Czech Republic

e-mail: fzazimal@mail.muni.cz

Abstract

Fe_2O_3 and Fe_3O_4 nanoparticles were used for the preparation of magnetic inks and applied for the deposition of nanocomposite layers by 2D inkjet printing technology under ambient conditions. The structural and magnetic properties of samples in all forms - powder, ink, layer - were investigated by means of wide portfolio of structural and surface analysis methods. The results have shown the applicability of 2D inkjet printing for preparation of magnetic layers and, slight differences in structural properties with respect to magnetic material used, and little worse magnetic properties of coatings based on Fe_2O_3 ink. The main aim was to obtain a set of complex data for the production of printed magnetic layers applicable in electronic devices, e.g. in magnetic core with eight printed layers of Fe_3O_4 ink on flexible PET substrate. The core has been tested as an induction magnetic sensor illustrated by Fig. 1. The relative permeability was 2, which is about 1 magnitude higher than values reported by other authors [1].

Fig. 1: Prototype of inkjet printed magnetic field sensor.

Keywords: inkjet printing, printed magnetic layers, magnetic ink, nanoparticles, printed magnetic field sensor

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TOPIC 4

NEW MATERIALS & NEW CHALLENGES

PLASMA-TRIGGERED REDUCTION-EXFOLIATION OF HIGHLY POROUS GRAPHENE OXIDE 3D MATERIALS

Richard KRUMPOLEC, František ZELENÁK, Mirko ČERNÁK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
e-mail: krumpolec@mail.muni.cz

Abstract

Simple, cheap, and fast mass-production of graphene-derived materials like graphene oxide (GO) and reduced graphene oxide (rGO), together with a direct application of GO/rGO materials with extraordinary properties exceeding the state-of-the-art solution, is a crucial to reach its widespread commercial success.

We are working on fast, low-cost, scalable, chemical-free fabrication method [1] of rGO-based sheets, 3D rGO aerogel-like “cakes” and composites using an electrical plasma-triggered reduction-exfoliation process of highly porous GO materials and GO-based composites that are fabricated using our custom method.

We have found that atmospheric Diffuse Coplanar Surface Dielectric Barrier Discharge (DCSBD) plasma generated in nitrogen is capable to trigger a fast ($\ll$1 s), self-propagating reduction-exfoliation of GO into rGO [2] associated with a significant improvement (~ 10^5 fold) of electrical properties of plasma-treated material. Typically, plasma-reduced GO sheets (Fig 1a-b) and 3D aerogel-like cakes (Fig.1c), after rolling press to a thin films of thickness 20-100 µm possess sheet resistance ~ 10 $\Omega.sq^{-1}$ and sheet conductivity reaching 2000 $S.m^{-1}$.

Despite of standard thin effective thickness of DCSBD plasma of 0.3 mm, the nitrogen DCSBD plasma trigger the modification process even in whole volume of porous GO samples of thickness of several mm. From the point of view of plasma physics and interaction of studied GO-based porous material with DCSBD plasma, we have observed a strong influence of the electrode geometry of diffuse coplanar surface barrier discharge on the properties of plasma triggered reduction-exfoliation process.

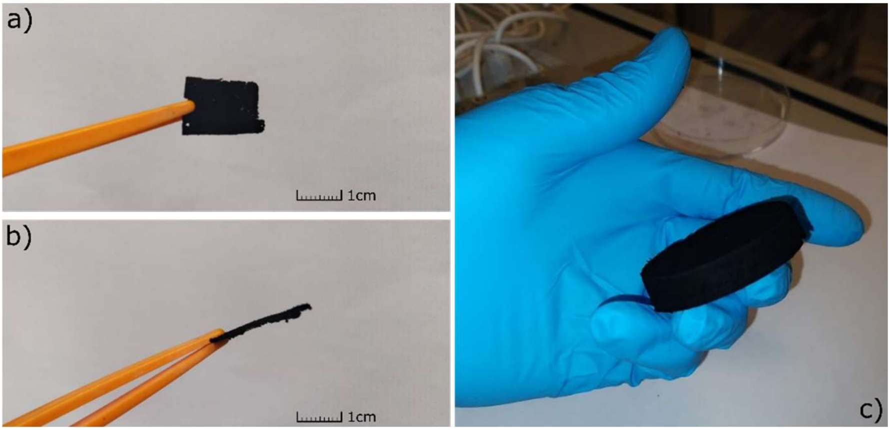

Fig. 1: Free-standing rGO sheet (a,b) and 3D rGO aerogel-like cake (c).

We will present two applications that we are currently working on: a) free-standing rGO aerogel-like sheet as a supporting electrode for Li-based batteries and b) plasma-reduced rGO layer on PES nonwoven as a potential membrane for water treatment applications.

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Keywords: graphene oxide, reduced graphene oxide, atmospheric plasma, reduction-exfoliation, 3D GO composites, electrical conductivity

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SELECTION OF SPECIAL DIELECTRIC SUBSTRATES FOR ELECTROSTATIC VOLTAGE MEASUREMENT

Michal PAZDERKA, Lucia ŠVANDOVÁ, Roman PŘIBYL, Jakub KELAR, Zlata KELAR TUČEKOVÁ, Miroslav ZEMÁNEK and Mirko ČERNÁK

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

e-mail: michpa@mail.muni.cz

Abstract

The recently developed method [1] for measurement of ignition voltage turned out to be a great tool for investigating properties of new dielectric barrier materials, e.g. Mg dopped alumina [2]. The main advantage of this method is its safety and production of large statistical datasets due to the repetitive discharge ignition. In other words, the applied voltage periodically changes, and the discharge is turned on for time t_1 and turned off for time t_2 (relaxation).

The variation of times t_1 and t_2, however, can lead to interesting results. Such data can be seen in Fig. 1, where an evolution for every relaxation time is shown for three different materials as the average over 20 individual measurements. Tested materials are widely used 96 % Alumina and pure Alumina dopped with 3 vol.% and 5 vol.% of Cr. We varied the relaxation time t_2 from 7 s to 247 s, while the discharge time t_1 remained fixed at 57s. The plot shows normalized voltage, where data for every barrier has been normalized by their maximum value (Elceram 5,4 kV, 3Cr 6,5 kV and 5Cr 66,3 kV).

The first explanation for such behaviour could be thermal effects. However, the measured time evolution of the cooling does not show any significant differences between ceramics. Moreover, in the simplest approximation the ignition voltage of the discharge is a function of instantaneous temperature [3]. Therefore, thermal effects cannot be the only explanation of tendency in Fig 1.

It is known that after the discharge phase, a remaining surface charge can be present on the surface of the ceramics [4], which now seems to be the best candidate to explain shown behaviour of the ignition voltage. In such a case, the charge trapping properties of Cr-dopped Alumina ceramics would be proven. Moreover, the study repetitive discharge ignition on various barrier materials could be an alternative for direct potential measurement using a sensitive electrostatic voltmeter.

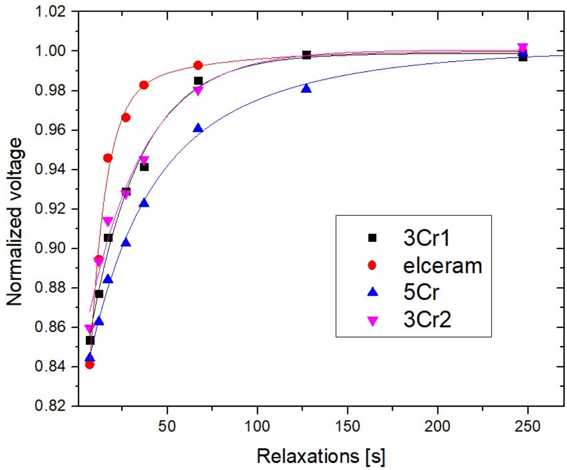

Fig. 1: The evolution of average normalized ignition voltage for three different materials depending on the relaxation time.

Keywords: ignition voltage, charge traps and surface charge

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R&D Centre for Plasma and Nanotechnology Surface Modifications

Faculty of Science | Masaryk University

Kotlářská 267/2
611 37 Brno
Czech Republic

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