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P.S.I.C.5.

Femtosecond laser nanostructuring of MXene films

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MXenes, two-dimensional transition metal carbides or carbonitride nanomaterials, generally with the formula of Mn+1XnTx (n = 1, 2, or 3; M = transition metal, *e.g.* Ti, V, Nb, Mo; X = C and/or N; T = surface termination, *e.g.* –OH, =O, –F), have earned significant attention since their discovery1, owing to their remarkable and widely tunable properties. MXenes manifest a captivating combination of high electronic conductivity, hydrophilicity, and chemical stability. The stability and reliability of MXene films, when applied in moist or wet environments, could be altered by their hydrophilicity. The capability to switch between hydrophilicity and hydrophobicity of materials could pave the way for self-cleaning surfaces, self-assembly of particles, drug delivery, and lab-on-a-chip devices.
Laser-induced periodic surface structures (LIPSS) is an intriguing phenomenon which arises when femtosecond laser pulses generate periodic nanoscale modifications of materials. The LIPSS formation mechanism is commonly attributed to the interference of incident laser light with a surface plasmon-polariton wave propagating at the surface, resulting in a periodic intensity modulation that is imprinted onto the surface.
In this work, we used a fs-laser to generate LIPSS on MXene films. The experiments were performed in both, a single pulse mode and multi-pulse laser ablation regime, on Ti3C2 MXene multilayer films deposited on a Si substrate. An Yb:KGW laser was used emitting linearly polarized light with a pulse duration of 266 fs at 1030 nm wavelength. Efficient LIPPS formation was observed. We demonstrate that the presence of LI1PSS on MXene films significantly changes wetting properties. The laser-treated surface became hydrophilic with a much lower contact angle compared to untreated films.

Reference

1. Naguib, M. et al. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2. Adv. Mater. 23, 4248–4253 (2011)

P.S.I.D.6.

The effect of various preparation procedures of metal phenoxides on the activity and selectivity of phenol carboxylation

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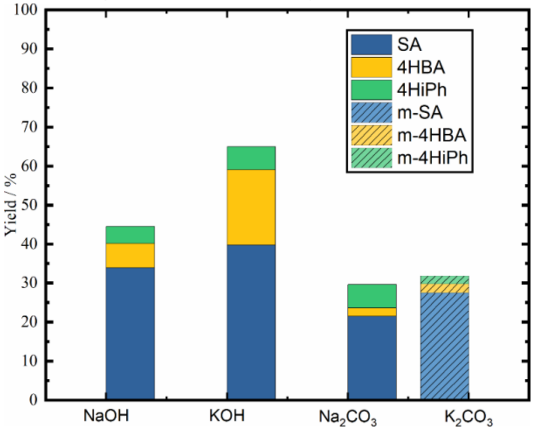
Carbon dioxide as a readily available, renewable, inexpensive, non-toxic and non-flammable compound represents one of the most promising C1 carbon sources. Through the carbon capture and utilization (CCU) practices the usage of CO_2 for various reactions in research and chemical industry have been incentivized. The CO_2 fixation reactions with carbon dioxide as a reactant for formation of new C-C bonds is considered more advantageous due to higher atom and energy efficiency, resulted by the higher energy density. Most of the research involving the carboxylation reactions has been devoted to dialkyl carbonate or carbamates synthesis, while the carboxylation of aromatics has been marginalized. Carboxylic acids as one of the most abundant and most important class of compounds are used in various applications, while also finding their role as a promising raw material for synthesis of other value-added chemicals.



Salicylic acid is one of the most important aromatic carboxylic acids. It is a highly valuable ingredient as it finds its use in various medicinal and cosmetic products, and most importantly, as a precursor to acetyl-salicylic acid (Aspirin). This work will show various preparation procedures involving the 2-step procedure of Kolbe-Schmitt and a single step Marasse method, and their effect on activity and selectivity towards the production of salicylic acid (SA), 4-hydroxybenzoic acid (4HBA), and 4-hydroxyisophthalic acid (4HiPh).

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P.S.II.A.6.

Imaging of high power impulse magnetron sputtering plasma by high-speed camera

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Magnetron sputtering is a widely used deposition technique for the preparation of high-quality thin films. It utilizes high-density plasma to sputter target material. Over the years, it has been demonstrated that plasma is non-homogenous over the racetrack area. Imaging and other plasma diagnostic techniques have shown that plasma is localized in dense regions called spokes. These structures form periodic or quasi-periodic patterns, have triangular shape and rotate with velocities of several km/s. The presence of spokes in magnetron plasmas is observed for all types of magnetron operation regimes: continuous DC magnetron sputtering [1], pulsed high power impulse magnetron sputtering (HiPIMS) [2] and oscillatory RF magnetron sputtering [3].
In this work, we imaged individual pulses of HiPIMS plasma by a high-speed camera and correlated its dynamics to the current and voltage characteristic of the discharge. The plasma was investigated for a range of working gas pressures (0.25-2 Pa) and peak discharge currents (10-400 A). Experiments show that plasma self-organization undergoes a complex reorganization as the discharge current increases. In the initial stages, after the discharge ignition, the plasma forms spoke patterns similar to the ones observed in DCMS regime. During this period, spokes rotate in the direction opposite to drifting electrons. As discharge current increases above a certain threshold (around 30 A), a chaotic re-organization of plasma occurs. After this period, stable patterns start to form with typically triangular shape of spokes. In this stage, spokes rotate in the same direction as drifting electrons. The plasma evolution is reproducible if the current waveforms are comparable from pulse to pulse.

References
[1] M. Panjan *et al. Plasma Sources Sci. Technol.*,**24** (2015) 065010
[2] A. Anders et al. *J. Appl. Phys.* **111** (2012) 053304
[3] M. Panjan *J. Appl. Phys.* **125** (2019) 203303

P.S.II.B.16.

Recent developments in applications of deep eutectic solvents in separation science

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Deep eutectic solvents (DES) are a novel type of materials with high potential in separation science. These materials have significantly lower melting point comparing to its pure components. This property makes them useful as a new liquid state materials for several applications [1-2].
This paper presents recent developments in real application of DESs as stationary phases for gas chromatography (GC), extractants for analytical chemistry as well as materials that tune properties of membranes for pervaporation process. Presented solutions revealed high selectivity for designed separation processes as well as improved properties of developed applications. In case of GC stationary phases DESs revealed to offer unusual selectivity towards sepration of volatile organic compounds (VOCs). Their applications in microextraction systems allows to minimize usage of organic solvents, as well as to increase recovery in respect to target analytes ans selectivity towards matrix componets. Incorporation of DESs in non-porous membranes allows to increase selectivity of such materials and their productivity for pervaporation applications. DESs due to possibility of their formation from chemical compounds having different polarity and sorptive interactions provide a wide variety of configurations that allows to design a fit-to-the-purpose separation systems.

References

1. A.R. Harifi-Mood *et al.* Solvent dependency of carbon dioxide Henry's constant in aqueous solutions of choline chloride-ethylene glycol based deep eutectic solvent, *Journal of Molecular Liquids* **319**(2020) 114173
2. M. Momotko *et al.* First deep eutectic solvent-based (DES) stationary phase for gas chromatography and future perspectives for DES application in separation techniques, (2021) *Journal of Chromatography A* **1635** (2021) 461701

Y.PL.S.III.1.

Sculpting of 2D materials: From pores and nanoporous membranes to sequencing and water desalination

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Introducing atomic-scale defects and holes in 2D materials changes their electrical and optical properties. When 2D materials are suspended, vacancies make the membranes permeable to ions and molecules in liquid or gas phases, allowing transport studies at atomic scales. Angstrom-size holes allow the passage of water molecules but block the larger hydrated salt ions and can effectively desalinate water. Raman peak shifts combined with TEM, provide a comprehensive approach to characterize the holes and transport through them. When molecules are driven through 2D nanopores in solution, they can perturb the ion current flow through the pore, from which molecule's physical and chemical properties can be inferred. DNA other biomolecules can be detected in this way. Thanks to advanced materials, device designs and custom electronics, the temporal and spatial resolution for their detection has been rapidly improving.

References:

1. Marija Drndić, *Nature Review Physics* **3**, 606, 2021.
2. Joshua Chen, Adrian Balan, Paul Masih Das, Jothi Priyanka Thiruraman, Marija Drndić, *Ultramicroscopy*, 113249, 2021.
3. *Yung-Chien Chou, Joshua Chen, Chih-Yuan Lin, Marija Drndić, Journal of Chemical Physics* **154**, 105012, 2021.
4. Jothi Priyanka Thiruraman, Paul Masih Das and Marija Drndić, *ACS Nano* **14**, 11831, 2020.

P.S.III.C.16.

Upscaling the manufacture of MAX phases and MXenes synthesis

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A large class of 2D transition metal carbides and/or nitrides MXenes has numerous applications in different fields - electrical engineering, composites, energy storage, biomedicine and etc. Availability of MAX phase precursors and production cost are the key factors on the way to scaled up manufacturing and application of MXene nanomaterials in industry. Their low-cost synthesis and safe use is potentially possible, the transition from the laboratory level to the industrial scale can be implemented and is expected in nearest future due to increased interest to MXenes.
Initial material MAX phase should have specific composition intended for obtaining high quality MXene with proven controlled stable properties that is the critical point in research and further industrial use. Here we assumed different MAX phase sintering technologies and appropriate equipment, including promising low cost SHS technology and SHS reactor of our own design. This poster also will address the transition to safe laboratory synthesis of MXenes in 100-g quantities by selective etching in various acidic etchants in MXene reactors of our proprietary design, the evolution of designed and manufactured reactor equipment and potential scaling up of proposed technology to industrial scale.

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References:
1. M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, Y. Gogotsi, *Chemistry of Materials* **29 (18**) (2017) 7633-76445.
2. C.E. Shuck, M. Han, K. Maleski, K. Hantanasirisakul, S.J. Kim, J. Choi, W.E.B. Reil, Y. Gogotsi, *ACS Appl. Nano Mater* **2** (2019) 3368-3376
3. Shuck, C.E., Sarycheva, A., Anayee, M., Levitt, A., Zhu, Y., Uzun, S., Balitskiy, V., Zahorodna, V., Gogotsi, O., Gogotsi, Y. Scalable, *Adv. Eng. Mater*. **22** (2020) 1901241.
4. M. Pogorielov, K. Smyrnova, S. Kyrylenko, O. Gogotsi, V. Zahorodna, A. Pogrebnjak. Nanomaterials **11(12)** (2021) 3412.
5. V. Balitskyi, C. Shuck, Y. Gogotsi, O. Gogotsi, V. Zahorodna, *Scalable synthesis of Ti_3C2Tx MXene and a reactor design for MXene synthesis*, Book of abstracts, *Conference MXene at the Frontier of the 2D Materials World. Beilstein Nanotechnology Symposium* 2019. October 15–17, 2019 Mainz / Germany
6. C. E. Shuck and Y. Gogotsi, *Chemical Engineering Journal* **401** (2020) 125786,

VIRTUAL POSTER PRESENTATION

V.P.S.2.

The use of Drava river sediments in the construction sector

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Dravske elektrarne Maribor (DEM) operates eight hydroelectric power plants on the Drava River. Each year, up to 40,000 m3 of sediment accumulates behind the dams (1). The limited space in the Drava valley and regulations require new sediment management concepts (2). The sediment of the Drava River is influenced by several Pb-Zn mines located in the upper part of the river that were active in the past (3). Despite elevated Pb, Zn and Cd content, the measured heavy metal concentrations allow their use for the production of construction materials (1). The READY4USE project aims to improve the use of river sediments and reduce their landfilling by developing new value-added products. For instance, the clay industry tends to replace natural clay with suitable complementary materials in order to conserve natural resources. River sediments from the Drava River have successfully replaced up to 30 wt.% clay in brick manufacturing, which has been demonstrated both in the laboratory and on an industrial scale. Another successful application was their incorporation in alkali activated materials (AAMs). The reactivity of the sediments in AAMs was improved by their calcination. The sediments were added into clay brick raw mixture or used as AAM precursor, in different proportions. The differences in bending/compressive strength can be attributed to the variation in chemical properties, mineralogy and microstructure. The study confirmed the suitability of river sediments for the production of bricks and AAMs and contributed to industrial symbiosis and the implementation of the circular economy.

1. Ducman, V., Fifer Bizjak, K., Likar, B., Kolar, M., Robba, A., Imperl, J., Božič, M., Gregorc, B.. Evaluation of sediments from the river Drava and their potential for further use in building sector, Materials, 2022, 15(12): 4303.
2. (Basson, G.R., Sedimentation and Sustainable Use of Reservoirs and River Systems, Draft Icold Bull. 187 ST-Sedimentation and Sustainable Use of Res, 2009.
3. Šajn, R., Halamić, J., Peh, Z., Galović, L., Alijagić, J. Assessment of the natural and anthropogenic sources of chemical elements in alluvial soils from the Drava River using multivariate statistical methods, J. Geo-chemical Explor., 2011, 110, 278–289.

P.S.I.C.1.

Investigation of 3D printing and thermomechanical properties of free-radical resin filled with TiO_2 nanoparticles

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Additive manufacturing provides an easy way to produce prototypes at a small scale with the possibility of complex-shaped 3D prints, which cannot be prepared by conventional subtracting methods. Specifically, stereolithography (SLA) 3D printing uses UV light to cure a photosensitive resin point by point (or layer by layer in case of masked-SLA) to produce a 3D object. The wide commercial availability of 3D printing generally requires further improvements and new technologies implemented in additive manufacturing. For example, SLA 3D prints are usually stiff and very brittle. Therefore, the desire is to make them tougher by either 3D printing using different monomers/oligomers or by mixing other particles/nanoparticles into a free-radical resin.
In our study, we prepared SLA nanocomposites by mixing titanium dioxide (TiO_2) nanoparticles (NPs) in two forms (anatase and rutile) into a free-radical resin. Radical resin prepared at our laboratories was used with varying loadings of NPs. The focus was placed on the investigation of the printing parameters of the mixtures, the comparison of SLA (point-by point) and masked-SLA (layer-by-layer) printing techniques, and the post-curing process that affects the thermal properties and mechanical performance. Jacob's working curves have shown a higher critical energy to cure a layer for resin mixtures with increasing loading of TiO_2 NPs. It has become clear that the nanoparticles in resin interact with UV curing light during 3D printing causing scattering of the UV light and lowering the light penetration depth, which reduces the overall curing degree of the exposed resin. Nanoparticle-curing light interactions have been shown to also be important for post-curing process. 3D prints from pure free-radical resin possessed a higher glass transition temperature and a greater storage modulus with increasing post-curing time. On the other hand, this effect was less pronounced for free-radical resin/TiO_2 nanocomposites.

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