

Development and application of functional composite surfaces with tunable wettability and photoreactivity

PhD theses

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1. A doktori munka rövid összefoglalója

A fotoreaktív-, valamint az extrém és/vagy szabályozható nedvesedésű felületeket napjainkban fokozódó érdeklődés övezi. Doktori munkám során látható fényben aktív, plazmonikus Ag-TiO₂ fotokatalizátor nanorészecskékből, poliakrilátokból és PDMS-ből kiindulva hoztam létre egyszerre mindkét említett funkcióval rendelkező kompozit felületeket.

Ehhez kapcsolódóan bemutattam, hogy a vizsgált perfluorozott poliakrilátból (FP) készült hidrofób filmek nedvesedési karaktere Ag-TiO₂ fotokatalizátor részecskékkal történő érdesítéssel fokozható. A kapott bevonatok Ag-TiO₂/FP-arány az első említésnél függvényében változó felületi érdességgel és az érdességtől függő nedvesedéssel (és fotoreaktivitással) rendelkeztek a szuperhidrofiltól a szuperhidrofób karakterig terjedő tartományban. A szuperhidrofób nedvesedési karakter eléréséhez szükséges 80 m/m% fotokatalizátor-tartalom megtartása mellett a kompozitok nedvesedésére a mátrix összetétele is hatással volt: poli(2-hidroxietil-akrilát), mint hidrophil mátrixalkotó felhasználásával szuperhidrophil kompozit bevonatokat állítottam elő.

Mivel a mikrofluidika és a folyadékmanipuláció tényérésének köszönhetően egyre nagyobb igény mutatkozik új, stimulus-reszpónzív nedvesedésű funkcionális felületek kialakítása iránt, ezért ennek fényében magneto-, illetve termoreszpónzív nedvesedéssel és fotoreaktivitással rendelkező, PDMS-alapú kompozitokat is létrehoztam, karbonil vas mikrorészecskék és poli(N-izopropil-akrilamid) felhasználásával.

Az extrém nedvesedésű, hierarchikus érdességgel rendelkező felületek gyakorlati alkalmazásának egyik legnagyobb korlátja a felületi képletek sérülékenysége: ennek lehetséges kiküszöbölésére előállításra került egy PDMS-oleogél alapú öngyógyuló fotoreaktív kompozit is, mellyel tartós szuperhidrofób karakter érhető el.

A disszertációmban bemutatott kompozit felületek a jövőben multifunkciós jellegükből fakadóan alkalmasak lehetnek például különböző polaritású szennyezők hatékony fotooxidációs eliminálására, vagy akár összetett folyadékmanipulációs feladatok elvégzésére is.

2. Introduction and aims

The popularity of functional surfaces with extreme wetting properties and liquid manipulation capabilities is rapidly increasing, as they offer new perspectives to various fields, such as microfluidics, analytics, environmental protection, and healthcare. Ranging from the well-known, lotus-inspired superhydrophobic self-cleaning surfaces to superhydrophilic antifogging glasses and mirrors, these materials also offer application possibilities for everyday users.

The elaboration of extreme wetting properties requires not only the right choice surface chemistry, but the presence of hierarchical, micro- and nanoscale surface roughness, as well, which – among many possibilities – can be achieved through enhancing the inherently hydrophobic or hydrophilic surfaces with particulate materials. Depending on the properties of these roughening agents, the resulting composite surfaces may possess additional functionalities, such as magnetism, electric conductivity, optical transparency, or even photocatalytic activity.

In the light of recent years' epidemic and environmental crises, this latter property gained increased attention from both academic and industrial researchers, as semiconductor oxide photocatalysts, such as TiO_2 or ZnO and their modified versions can eliminate harmful organic compounds and microorganisms, without relying on additional chemical treatment, due to their ability to generate reactive oxygen species (such as HO^\bullet , HOO^\bullet or O_2^{2-}) upon ultraviolet or visible light illumination.

Besides the effect of photocatalyst content on wetting properties, the effectiveness and mechanism of action of photocatalytic processes is highly influenced by wetting, as well, therefore studying, and influencing the effect of interfacial parameters on the photocatalytic reactions are of high importance. Despite the modifications of photocatalyst particles and the resulting changes in reactivity are already extensively documented, the wettability alterations and their effects on the photocatalytic performance of macroscopic composite surfaces and coatings are less studied.

To fill this vacancy in the literature, the aim of my doctoral work was the preparation and characterization of novel, visible light-active plasmonic Ag- TiO_2 photocatalyst nanoparticle-containing composite coatings with different water wettability and photocatalytic efficiency.

The foundations of this thesis are the previous results of our research group, including the characterization and optimization of plasmonic photocatalysts (such as the applied Ag-TiO₂), regarding their photoreactivity, antibacterial activity and their performance in polyacrylate-based composite coatings.

3. Experimental

During the experimental work, spray-coating and doctor-blade techniques were utilized to prepare composite surfaces with composition-dependent wetting or self-healing ability, consisting of polyacrylate (**Fig. 1 a) and b)**) or poly(dimethyl siloxane) (PDMS) matrices (**Fig. 1 c) and d)**) and visible light-active plasmonic Ag-TiO₂ photocatalyst nanoparticles. To render the silicone-based composites magnetoresponsive (**Fig. 1 c)**), carbonyl iron microparticles were used as magnetizable filler additive, while the thermoresponsive character was achieved upon grafting the PDMS matrix with poly(N-isopropylacrylamide) (pNIPAAm) (**Fig. 1 d)**).

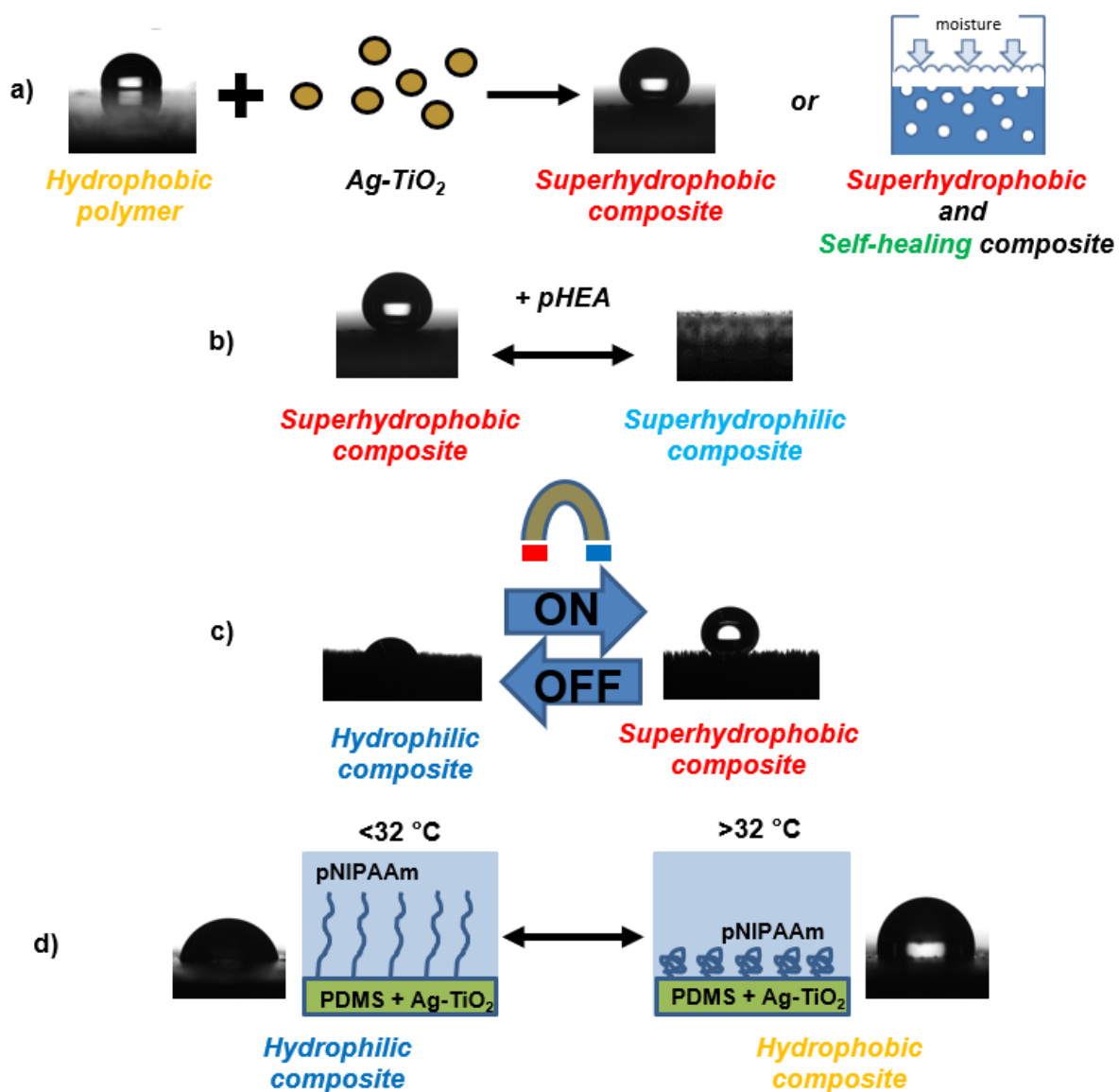


Figure 1. Schematic representation of the prepared photoreactive composites with wetting characters, adjusted by photocatalyst-content **a)**, matrix composition **b)** external magnetic field **c)** and temperature **d)**

The structural properties, wettability, photoreactivity and morphology of the prepared composites were characterized applying the following analytical methods and instruments:

- Scanning electron microscopy (SEM, Hitachi S-4700)
- Energy-dispersive X-ray spectroscopy (EDX, Hitachi S-4700)
- Transmission electron microscopy (TEM, FEI Tecnai G2 20 X-Twin)
- Contact profilometry (Form Talysurf Series 2, Taylor Hobson and Elcometer 224 Digital surface profile gauge)
- X-ray Computed Tomography (μ CT, Skyscan 2211, Bruker)
- Nitrogen adsorption measurements (Gemini Type 2375)
- Oscillatory rheology (Anton Paar Physica MCR 301)
- Thermogravimetry and Differential Scanning Calorimetry (TG & DSC, Mettler-Toledo TGA/SDTA 851e)
- Magnetic flux density measurements (AlphaLab Model GM2 DC)
- Static contact angle and sliding angle measurement (Krüss EasyDrop, TC40-MK2 Peltier Temperature Assembly and a TC3013 Digital Thermometer, custom tilting cradle)
- Dynamic contact angle measurements (Krüss EasyDrop and Krüss K100 force tensiometer)
- UV-Visible diffuse reflectance spectroscopy (UV-VIS DR, USB2000+UV-VIS, Ocean Optics)
- X-ray photoelectron spectroscopy (XPS, SPECS instrument, PHOIBOS 150 MCD 9 hemispherical analyzer)
- Nuclear magnetic resonance spectroscopy (NMR, Bruker DRX 500)
- Raman microscopy (Thermo Scientific DXR)
- Gas chromatography (Shimadzu GC-14B)
- UV-Visible Spectrophotometry (Red Tide SHIMADZU UV-1800)
- Luminometry (SiriusL Single Tube, Titertek Berthold)

T1. Preparation of Ag-TiO₂/fluoropolymer (FP) composite coatings with composition-dependent wettability and photoreactivity, by applying spray-coating technique. The characterization of the composites, regarding their morphology, wettability and photoreactivity at S/G- and S/L-interfaces [1].

T1.1. As a new scientific result, I presented that spray-coated composite coatings with composition-dependent roughness ($R_q=5.2\pm1.5-15.2\pm1.2\ \mu\text{m}$) and wetting properties ($0^\circ<\Theta<150.9^\circ$) can be prepared on the basis of visible light-active plasmonic Ag-TiO₂ photocatalyst nanoparticles ($d_{\text{primer}}\sim 50\ \text{nm}$) and the solid content of the commercial Capstone ST-110 fluoropolymer aqueous latex dispersion (FP). According to the results of contact angle measurements, the initially hydrophobic ($\Theta=105.0^\circ$) and smooth ($R_q=3.7\pm0.9\ \mu\text{m}$) layers of the FP matrix became rough and superhydrophobic ($R_q=15.2\pm1.2\ \mu\text{m}$; $\Theta=150.9^\circ$) upon the addition of 80 wt.% photocatalyst (r-FP layer). As the photocatalyst-loading was increased over 90 wt.%, the composites showed superhydrophilic character ($\Theta\sim 0^\circ$), which is also characteristic to the pure photocatalyst.

T1.1.2. SEM images evidenced that these extreme wetting characters are the results of the hierarchical surface roughness, formed during the spray-coating process: while the nanoroughness can be attributed to the primer catalyst particles, the microtexture with spherical protrusions is the result of their aggregation. The effect of roughness on the surface free energy was examined through dynamic contact angle measurements (Wilhelmy method): the surface free energy value of the pure, smooth FP surface was calculated to be $27.3\ \text{mJ/m}^2$, while in the case of the superhydrophobic r-FP layer it was even lower ($13.0\ \text{mJ/m}^2$).

According to the results of x-ray micro- computer tomography measurements, the porosity of the r-FP coatings was 74.8%, which was in good accordance with the porosity value (78.9%), obtained as a result of calculations, based on layer thickness measurements and the densities of the components. This high porosity may be beneficial in future photocatalytic applications.

T1.1.3. It was also presented, that the visible light-photoreactivity ($\lambda=405\ \text{nm}$; $t=1\ \text{h}$; $\text{EtOH } c_0=0.36\ \text{mM}$) of the composites at the S/G-interface was composition- and therefore wetting-dependent. The higher Ag-TiO₂ loading and increased hydrophobic character resulted in higher EtOH(g)- degradation efficiencies (0.4-68.1%), however, the achieved degradation efficiencies still could not exceed the efficiency of the pure photocatalyst (95.7%).

At the S/L-interface, the apolar Sudan IV dye was adsorbed and photodegraded (0.92 mg dye/ cm², 90 min irradiation time) on the surface of the superhydrophobic, 80 wt.% Ag-TiO₂-containing film, while the non-wetting properties of aqueous methylene-blue (MB) solution hindered the photooxidation of the hydrophilic dye.

T2. Preparation of Ag-TiO₂/fluoropolymer+poly(2-hydroxyethyl acrylate) (Ag-TiO₂/FP+pHEA) composite coatings by applying spray-coating. The morphological-, wettability- and photoreactivity characterization of the composites at S/G and S/L interfaces [2].

T2.1. As a new scientific result, I prepared and characterized Ag-TiO₂/FP+pHEA composite coatings. Besides keeping the 80 wt.% photocatalyst loading (previously proven to be required for extreme wetting characteristics; **T1.**), the wettability of these composites was adjusted from superhydrophilic to superhydrophobic ($\Theta=0-150.9^\circ$) by changing the ratio of the hydrophilic/hydrophobic polymeric matrix components (0-100 wt.% FP-content). The extreme wetting properties were also evidenced by dynamic contact angle measurements and the concomitant surface free energy calculations ($\gamma_s^{\text{tot}}=6.5-72.91 \text{ mJ/m}^2$).

T2.2. The recorded SEM images showed hierarchical micro- and nanoroughness, which could be attributed to the spherical aggregates of the primer particles, and to the unique, primer particles, respectively. The microroughness was also evidenced during profilometry measurements: in the case of pure pHEA matrix (r-pHEA coating), the roughening effect of the photocatalyst resulted in an R_q value of $11.7 \pm 2.2 \text{ }\mu\text{m}$.

T2.3. The composites showed composition- and wetting-dependent photoreactivity at both the S/G- and S/L-interfaces. During the photodegradation of EtOH(g) ($\lambda=405 \text{ nm}$; $t=1.5 \text{ h}$; $c_0=0.36 \text{ mM}$), the photodegradation efficiency increased with increasing FP-content, (51.3-88.3%), while during luminometry measurements at the S/L-interface, the more hydrophobic composites produced reactive oxygen species in lower concentrations (0.80-3.81 mM H₂O₂-equivalent radical concentration). The composites with purely pHEA and FP matrices showed different behaviours during the photodegradation of methylene blue (MB; in aqueous solution) and Sudan IV (in abs. EtOH) dyes: while the superhydrophilic r-pHEA composite was proven to be effective against MB in aqueous solution (100% degradation efficiency; $t_{\text{illum.}}=1.5 \text{ h}$), its degradation efficiency against Sudan IV in EtOH was significantly lower (9.2%). On the

contrary, the superhydrophobic r-FP coating was proven to be more effective against Sudan IV (77.5%), while its MB-degradation efficiency was slightly lower (17.3%). These results indicate that the composites are more capable of degrading pollutants in a medium which provides good wetting.

T3. Preparation of Ag-TiO₂+cFe/PDMS composites with external magnetic field-dependent wetting and photoreactivity by applying a magnetic field-directed spray-coating method. The characterization of the composites, regarding their morphology, wettability and S/L-photoreactivity [3].

T3.1. As a new scientific result, I prepared elastic grass composites with adjustable morphology on the basis of Ag-TiO₂ photocatalyst nanoparticles ($d_{\text{primer}} = \sim 50$ nm), carbony iron (cFe) microparticles ($d = 0.5\text{--}4$ μm) and a two-component commercial poly(dimethyl siloxane) (PDMS). During the preparation process, the dispersions of the components (cFe : PDMS : toluene = 4,5 : 3 : 9; m : m : m) were sprayed on plain glass substrates, placed next to permanent magnets (0.30 T or 0.35 T) to promote grass-like self-assembly. The Ag-TiO₂ loading of the composites was maximized at 16.7 wt.% to preserve mechanical integrity, while the grass height was set to 3 mm for the sake of objective comparison of wettability. In the case of photocatalytic tests, the specific mass of the grasses was uniformized and set to 63.3 ± 1.6 mg/cm².

T3.2. According to the results of contact angle and sliding angle (s.a.) measurements, the composite grass coatings possessed photocatalyst loading- and external magnetic field-dependent wettability. As it was proven by SEM images, the increased photocatalyst content (0-16 wt.%) enhanced the surface roughness of the grass strands, which resulted in increasing hydrophobicity ($\Theta = 139.4^\circ \rightarrow 155.2^\circ$) when the grass was stiffened by the help of an external magnetic field, perpendicular to the glass substrate. This surface roughness also provided near-superhydrophobic character even when the grass strands were aligned parallelly to the substrate ($\Theta = 136.1^\circ \rightarrow 144.6^\circ$). Without an external magnetic field, the grass had random orientation, which allows the penetration of water droplets and the formation of larger contact area, which resulted in higher adhesion and an apparently more hydrophilic character. This difference between the wettability of randomly oriented and stiffened grasses can be utilized in liquid manipulation scenarios, as the composites were able to pick up water droplets without a magnetic field, and were able to release them upon the introduction of a magnet.

T3.3. As it was proven during MB photodegradation tests, the composite grass with 16.7 wt.% Ag-TiO₂ possessed magnetic field-dependent photoreactivity, as well: without magnetic field, the LED irradiation ($\lambda=405$ nm; $t=5$ h) of the randomly oriented grass photodegraded $42.1\pm3.5\%$ of the initial MB concentration ($6.25\ \mu\text{M}$), while in the more hydrophobic stiffened state, this degradation efficiency was only $22.4\pm3.3\%$.

T4. Preparation of Ag-TiO₂/PDMS-gr-pNIPAAm composite coating with thermoresponsive wetting and photoreactivity by applying spray-coating and doctor-blade techniques. Characterization of the composites regarding their morphology, wettability and photoreactivity at the S/L-interface [4].

T4.1. As a new scientific result, I prepared composites with thermoresponsive wetting and photoreactivity, on the basis of Ag-TiO₂ photocatalyst nanoparticles ($d_{\text{primer}} \sim 50$ nm), and poly(N-isopropyl acrylamide)-grafted (pNIPAAm) PDMS matrices, applying spray-coating and doctor-blade techniques. The grafting reaction was implemented applying Activators ReGenerated by Electron Transfer - Atomic Transfer Radical Polymerization (ARGET-ATRP). Preceding the composite preparation, the influence of the ATRP-initiator molecule (10-undecenyl 2-bromoisobutyrate or INI) on the elasticity of PDMS was studied during oscillatory rheology measurements: according to the obtained storage- and loss moduli, the INI-content was maximized at 4.3 wt.% in the PDMS matrix to avoid viscous behaviour. The successfulness of PDMS and INI copolymerization was evidenced by XPS measurements (Br 3d peak at 70.22 eV), while the successfulness of the grafting process was evidenced by Raman- and EDX measurements. While in the case of Raman spectra, the successful grafting was evidenced by the disappearance of bands, related to double bonds (at $1622\ \text{cm}^{-1}$) and the presence of isopropyl groups (appearance of a high intensity peak at $2958\ \text{cm}^{-1}$) on the surface, the EDX mapping of the grafted surfaces indicated the presence of nitrogen in 12-17.5 at.%. The Ag-TiO₂-content of the photoreactive composites was maximized at 15 wt.% to avoid mechanical instability.

T4.2. As it was evidenced by the results of contact angle measurements, both the photocatalyst-free and photocatalyst-containing coatings possessed composition- and thermoresponsive wetting properties. At $25\ ^\circ\text{C}$ a more hydrophilic character ($48.0^\circ < \Theta < 108.7^\circ$) could be

experienced, however, at 40 °C, the coatings showed a more hydrophobic ($93.5^\circ < \Theta < 117.5^\circ$) character due to the surface presence of thermoresponsive NIPAAm macromolecule chains. Upon increasing the grafting NIPAAm monomer concentration (0-10 M), the hydrophobicity gradually diminished at both temperatures. An indirect proof of the presence of surface-bound pNIPAAm chains was the gradual spreading (and contact angle decline) of water droplets on the surfaces below the LCST, however, this phenomenon was absent over the LCST ($\sim 34^\circ\text{C}$). The thermoresponsive wettability of Ag-TiO₂/PDMS-gr-PNIPAAm (5 M NIPAAm; 1.2 wt.% INI) composites was also proved by the conducted advancing- and receding contact angle measurements and the concomittant surface free energy calculations (γ_s^{tot} : $42.12 \pm 5.75 \text{ mJ/m}^2$ at 25 °C and $8.22 \pm 1.25 \text{ mJ/m}^2$ at 50 °C).

T4.3. The thermoresponsive photoreactivity of Ag-TiO₂/PDMS-gr-PNIPAAm (5 M NIPAAm; 1.2 wt.% INI) composites was evidenced by the conducted MB photodegradation ($\lambda=405 \text{ nm}$; $t=5 \text{ h}$) tests. While at 25 °C, 36.6% of the dye was decomposed by the help of the composite (efficiency of direct photolysis was 21.1%), at 40 °C, the achieved degradation efficiency (36.4%) was nearly equal to the efficiency of direct photolysis (35.2%). These results clearly indicated a suppressed photoreactivity over the LCST. According to the auxiliary photometry measurements, the previously obtained results were not influenced by the thermal degradation of MB as it was proven to be negligible.

T5. Preparation of self-healing superhydrophobic and photoreactive Ag-TiO₂/PDMS-oleogel composite surfaces by applying spray-caoting and their characterization, regarding wettability, self-healing, morphology and photoreactivity at S/G-interface [1].

T5.1. As a new scientific result, oleogel composites were prepared on the basis of Ag-TiO₂, PDMS, silicone oil and dodecyl trichlorosilane (DDSiCl₃) by applying spray-coating and bulk-phase moulding. The composite surfaces were proven to be superhydrophobic ($\Theta=151.6^\circ$) and hierarchically rough ($R_q=13.8 \pm 1.4 \text{ }\mu\text{m}$). To preserve the gelous character, the Ag-TiO₂ loading was maximized at 25 wt.%.

T5.2. The self-healing character of the bulk-phase oleogels was evidenced during the regular complete removal and regrowth of the surfacial siloxane layer, which formed as a result of DDSiCl₃ hydrolysis and condensation under humid atmosphere. According to the conducted

UV-VIS diffuse reflectance spectroscopy measurements, the formation of the surfacial siloxane layer takes approximately 6 hours at 25 °C and 100% relative humidity.

T5.3. According to the conducted gas chromatography measurements, the Ag-TiO₂/PDMS-oleogel composites showed considerable photoreactivity at the S/G-interface during EtOH(g) photodegradation ($\lambda=405$ nm; $t=90$ min; $c_0=0.36$ mM; 50.8 % degradation efficiency).

10. List of Publications

Hungarian Scientific Bibliography (MTMT) identifier: 10064997

Original research articles related to the PhD dissertation:

[1] **Mérai L**, Varga N, Deák Á, Sebők D, Szenti I, Kukovecz Á, Kónya Z, Dékány I, Janovák L. *Preparation of photocatalytic thin films with composition dependent wetting properties and self-healing ability*. Catal Today 2019;328:85–90. <https://doi.org/10.1016/j.cattod.2018.10.015>
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<https://doi.org/10.3144/expresspolymlett.2018.93>
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[3] **Mérai L**, Deák Á, Sebők D, Kukovecz Á, Dékány I, Janovák L. *A Stimulus-Responsive Polymer Composite Surface with Magnetic Field- Governed Wetting and Photocatalytic Properties*. Polymers 2020;12:1890. <https://doi.org/10.3390/polym12091890>
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[4] **Mérai L**, Deák Á, Szalai B, Samu GF, Katona G, Janovák L. *Visible light-photoreactive composite surfaces with thermoresponsive wetting and photocatalytic properties*. Express Polym Lett 2022;16:34–51. <https://doi.org/10.3144/expresspolymlett.2022.4>
IF=3.952

Related original research Σ IF=17.031

Other publications:

[5] **Mérai L**, Imre-Deák Á, Dékány I, Janovák L. *Utilization of Solid/ Liquid Phase Boundary Interactions on functional surfaces: Fundamentals, Recent Advances and General Considerations – A Unifying Approach*. Adv Colloid Interface Sci 2022;303:102657.
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Other publications ΣIF=56.142

All publications: ΣIF=73.173

Patents:

2021: „Készítmény és eljárás szuperhidrofób és fotokatalitikus hatással rendelkező bifunkciós vékonyrétegek kialakítására - COMPOSITION AND PROCESS FOR THE PREPARATION OF BIFUNCTIONAL THIN LAYERS WITH SUPERHYDROPHOBIC AND PHOTOCATALYTIC EFFECTS” (under provisional patent protection).

Inventors: Dr. Janovák László (50%), Dr. Dékány Imre (20%), Deák Ágota (10%), **Mérai László (10%)**, Varga Norbert (10%).

Patent application number: P2100009/11

Oral presentations:

(1) **Mérai L**, Frank É. *Farmakológailag aktív 17-exo-pirazolin- 5'-onok mikrohullámú szintézise az androsztán sorban* A Szegedi Ifjú Szerves Kémikusok Támogatásáért Alapítvány 15. tudományos előadóülése, Szeged, Hungary, 12.5.2016.

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(1) Baji Á, Frank É, Kovács D, **Mérai L** *Microwave-assisted access to novel steroidal 17 β -3'-pirazole-5'-ones IX*. Joint Meeting in Medicinal Chemistry, Athens, Greece, 7-10.6.2015.

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with controlled structures 3rd International Conference on Polycarboxylate Superplasticizers (PCE 2019), Munich, Germany, 24-25.09.2019.

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