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DOCTORAL DISSERTATION

H_2O_2-modified TiO_2: Synthesis, Deposition, Properties, and Applications

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Keywords: TiO_2, oxygen-rich groups, sol-gel synthesis, low-pressure cold spray, suspension spraying

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DISSERTATION DETAILS

Title:	**H_2O_2-modified TiO_2: Synthesis, Deposition, Properties, and Applications**
Title (in Polish):	TiO_2 modyfikowany H_2O_2: synteza, osadzanie, właściwości i zastosowania
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Summary:

The presented dissertation consists of a cycle of five scientific articles aiming at developing the synthesis and deposition of H_2O_2-modified TiO_2, which can be applied to the degradation of organic pollutants and bacteria under visible light and in the dark. Selected hydrogen peroxide-based modification is a dopant-free strategy introducing peroxo and superoxo groups which narrows the bandgap energy. The important aspect of the thesis was designing a low-pressure cold spray process for the formation of coatings that maintain the initial characteristics of feedstock materials. The application of feedstock in the form of powder, suspension and aerosolised suspension aimed at investigating the control over the preservation of oxygen-rich groups. The obtained H_2O_2-modified TiO_2 coatings are the results of a synergistic combination of sol-gel synthesis which imparted physicochemical characteristics providing catalytic activity and low-pressure cold spraying that caused thermal drying and offered large-scale technique to produce coatings.

Summary (in Polish):

Na niniejszą rozprawę składa się cykl pięciu artykułów naukowych poświęconych opracowaniu syntezy oraz procesu deponowania TiO_2 modyfikowanego H_2O_2, o potencjale aplikacyjnym do rozkładu zanieczyszczeń organicznych oraz bakterii w świetle widzialnym oraz bez jego udziału. Wybrana modyfikacja oparta na nadtlenku wodoru to strategia niewymagająca domieszkowania, pozwalająca na wprowadzenie do materiału grup nadtlenkowych i ponadtlenkowych, które zmniejszają szerokość pasma wzbronionego. Celem pracy doktorskiej było zaprojektowanie procesu niskociśnieniowego natryskiwania zimnym gazem tak, aby było możliwe wytworzenie powłok o charakterystyce pierwotnych materiałów. Zastosowanie proszków, zawiesin oraz aerozoli zawiesin miało na celu zbadanie wpływu procesu natryskiwania na zachowanie grup bogatych w tlen. Powłoki uzyskane w ten sposób, to synergistyczny efekt syntezy nadającej cechy umożliwiające aktywność katalityczną oraz zastosowanie niskociśnieniowego natryskiwania na zimno jako techniki zapewniającej suszenie oraz obróbkę termiczną uzyskanych materiałów przy zachowaniu skalowalności procesu produkcyjnego.

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CONTENTS

LIST OF ABBREVIATIONS AND ACRONYMS

ANOVA	Analysis of variance
CS	Cold spray
DRS	Diffuse reflectance spectroscopy
DSC	Differential scanning calorimetry
EEA	European Environment Agency
E_g	Bandgap energy [eV]
EPR	Electron paramagnetic resonance
IR	Infrared (radiation)
ISO	International Standards Organisation
IUPAC	International Union of Pure and Applied Chemistry
LPCS	Low-pressure cold spray
MB	Methylene blue
Oxygen-rich groups	Peroxo and superoxo groups
P25	Commercially available crystalline titanium(IV) dioxide (Evonik, Germany, formerly Degussa)
pH_{PZC}	pH of the point of zero charge
PM	Particulate matter
PSA	Particle Size Analysis
ROS	Reactive oxygen species
SA	Surface area [μm^2]
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TIPO	Titanium(IV) isopropoxide
TOC	Total organic carbon [mg/dm^3]
TS	Thermal spray
UV	Ultraviolet light
Vis	Visible light
WUST	Wroclaw University of Science and Technology
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction

LIST OF PUBLICATIONS

This thesis is based on five peer-reviewed articles **[A-E]**.

Table 1 Compilation of metadata of publications

[A]	A. Gibas, A. Baszczuk, M. Jasiorski, M. Winnicki, D. Ociński, **Preparation of visible-light active oxygen-rich TiO_2 coatings using low pressure cold spraying**, Coatings, 31.03.2022, DOI: 10.3390/coatings12040475.	MEiN (2019-2022): 100 IF (2022): 3.4 Quartile: Q2
[B]	A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, **Influence of spraying parameters on microstructure of oxygen-rich TiO_2 coatings deposited using suspension low-pressure cold spray**, Surface & Coatings Technology, 14.02.2023, DOI: 10.1016/j.surfcoat.2023.129321.	MEiN (2023): 100 IF (2023): 5.3 Quartile: Q1
[C]	A. Gibas, A. Baszczuk, M. Jasiorski, A. Lewińska, M. Winnicki, **Low-pressure cold spraying of suspension TiO_2 in a single pass – Process optimization**, Surface & Coatings Technology, 19.08.2023, DOI: 10.1016/j.surfcoat.2023.129933.	MEiN (2023): 100 IF (2023): 5.3 Quartile: Q1
[D]	A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, **Aerosol-assisted low-pressure cold spraying of TiO_2 suspension**, Surface & Coatings Technology, 26.12.2024, DOI: 10.1016/j.surfcoat.2024.131715.	MEiN (2024): 100 IF (2023): 5.4 Quartile: Q1
[E]	A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, **H_2O_2-sensitized titania with activity under visible light and in the dark**, Journal of Environmental Chemical Engineering, 30.08.2024, DOI: 10.1016/j.jece.2024.113975.	MEiN (2024): 100 IF (2023): 7.4 Quartile: Q1

The thesis is further supported by a patent application **[F]**.

[F] **Method of deposition of functional aerosol coatings from the liquid phase**, original title: Sposób nanoszenia funkcjonalnych powłok z aerozolu z fazy ciekłej, signature number P.442330, reported 21.09.2022 by Wroclaw University of Science and Technology, authored by M. Winnicki, A. Gibas, M. Jasiorski, A. Baszczuk.

1 INTRODUCTION

1.1 ENVIRONMENTAL CLEANING

Environmental contamination is a persistent global issue driven by rapid industrialization and urbanization, leading to the release of hazardous chemicals that pose a severe threat to Earth's ecosystems and biodiversity. The European Environment Agency (EEA) highlights significant environmental challenges across Europe. According to Europe's State of Water 2024 [1], only 29% of surface water bodies and 77% of groundwater achieved good chemical status in 2021, as defined under the Water Framework Directive standards. The report identifies that energy generation and agriculture sectors pose the most significant threat to water quality. Priority substances, including pharmaceuticals, brominated flame retardants or polycyclic aromatic hydrocarbons, are challenging to decompose due to their toxicity, and bioaccumulative nature. However, their proper degradation ensures that these substances do not persist in the environment, reducing human health risks and preventing long-term environmental damage.

1.1.1 WATER CLEANING SYSTEMS

The renewal of clean water supplies requires effective water purification processes to meet environmental standards [1]. The comprehensive water purification system consists of various sectors including ultrapure water production, groundwater treatment, air purification, soil remediation, municipal wastewater sludge conditioning, and water and wastewater treatment [2].

Wastewater treatment is a multi-step process with various methods that can be categorised into physical, biological, chemical, and hybrid processes [3]. Physical techniques are used for preliminary wastewater handling [2,3]. Sedimentation, floatation, filtration, etc. focus on the separation of solid waste (sands, metals) or oil media (grease, fats) for their recovery and potential conversion into useful chemicals [2]. Biological methods decompose biodegradable matter including fats, proteins, alcohols, carbohydrates, nitrates and sulphates through aerobic, anaerobic or anoxic procedures. Microbial communities optimized for specific waste types metabolize pollutants converting them into water, carbon dioxide, and, in some systems, bioelectricity [4]. The biological slurry can be then used as biofuels [2]. However, as biological processes depend on living organisms, their activity is time-intensive and constrained by the stability of operational conditions - such as waste composition, pH, and temperature, to prevent bacterial inhibition or death [5–7]. Chemical treatment often yields faster results than biological methods, but it relies on expensive disposable reagents. Techniques such as precipitation, coagulation, flocculation, and disinfection are effective for removing dissolved pollutants (nutrients, pharmaceuticals or organic chemicals). However, produced chemical slurry may contain a variety of chemical compounds requiring different treatment or recycling methods [4,7].

Unlike processes that result in secondary pollution, advanced oxidation processes (AOPs) offer a complete degradation strategy for organic pollutants [6]. Oxidative degradation reactions can be integrated into the degradation process at any stage as pre-, main, and post-treatment [8]. AOPs generate reactive oxygen species (ROS), mainly $^{\bullet}OH$ radicals [7,8]. The non-selective character of radicals causes degradation of target pollutants and intermediates, ultimately leading to complete mineralization into harmless products like CO_2 and H_2O [6]. Depending on the type of pollution, the ROS can be generated using different forms of energy including electromagnetic (photolysis, photocatalysis), thermal (hydrothermal treatment, thermal activation), mechanical (ultrasounds, cavitation), electrical (current, plasma) or chemical (ozonation, peroxide, Fenton) energies [4,7]. To achieve synergistic removal of heavy pollution, several processes are typically combined into hybrid procedures, such as UV/peroxide/ozone or photo-electrocatalysis [4,6–8].

1.1.2 TITANIUM DIOXIDE

Photocatalysts stand out in AOPs for their reusability, as they are not consumed during degradation reactions. The most popular photocatalyst is titanium dioxide [6]. TiO_2 is a versatile semiconductor known for its exceptional optical and electrical activity. When exposed to light with energy larger than its bandgap energy (E_g), the photocatalyst absorbs a photon which excites an electron (e^-) to the conduction band, leaving a hole (h^+) in the valence band. Then the electron participates in reduction reactions, such as converting oxygen (O_2) to superoxide radicals ($O_2^{-\bullet}$), while the hole drives oxidation reactions, such as transforming water (H_2O) into hydroxyl radicals ($^{\bullet}OH$).

Photocatalytic activity depends on several factors, which can be categorized based on their role in the degradation process. Key elements of a photocatalytic pollution degradation system include the pollutant, excitation source and catalyst.

- Pollutant-related catalytic efficiency depends on the physicochemical characteristics of the target pollutants, including solubility, polarity, surface charge, chemical bonding, and concentration which determine the choice of catalyst and decomposition procedure. For example, hydrophobic pollutants (oils, hydrophobic pesticides) require the addition of surfactants or organic solvents [9,10], while water-soluble pollutants (phenolic compounds, pesticides) are readily accessible for degradation in aqueous environments. Non-polar pollutants (oils, aromatic hydrocarbons) primarily undergo degradation through direct oxidation procedures. In contrast, polar pollutants (phenolic compounds, antibiotics) strongly adsorb onto the catalyst surface, allowing degradation via surface-driven reactions [11]. The adsorption is enhanced by the opposite charge of pollutant and catalyst surfaces. As a result, TiO_2 surfaces may adsorb selectively cationic dyes (e.g. methylene blue) and anionic dyes (e.g. congo red), depending on the material's pH-dependent surface charge [11]. Weakly-bonded pollutants (dyes, pharmaceuticals) are easily-degraded in simple procedures while chemically stable pollutants (personal care products, perfluoroalkyl and polyfluoroalkyl substances, microplastic) require hybrid processing [5,7,12]. Degradation of pollution depends also on its concentration. When too high, it can saturate the catalyst's active sites and hinder catalytic efficiency.
- Light-related catalytic efficiency is closely connected to the energy absorption, restricted by the bandgap width of the photocatalyst. Consequently, only a limited range of wavelengths can be absorbed. Suitable light can be delivered from a wide range of sources, including natural (the Sun) and artificial (lamps and diodes) sources. Sunlight, a renewable energy source, contains approximately 7% ultraviolet (UV) radiation, 43% visible light, and 49% infrared radiation [13] and is limited by daylight conditions, weather, seasons and geographic location. Whereas artificial light sources offer constant illumination with tailored spectra and controlled light intensity.
- Catalyst-related catalytic efficiency is determined by the properties of the catalyst including the electron structure, stability, reactivity, surface charge, selectivity, particle size, surface area, morphology, and form. TiO_2-based materials are generally UV-activated photocatalysts and are characterized by high chemical stability, non-toxicity and high resistance to corrosion and light. Particle size is frequently controlled through synthesis because nanomaterials are favoured for

their higher specific surface area-to-mass ratio compared to larger equivalents [10]. Photocatalysts exist in various forms, including fine particles, powders, or granules. They can be used as bulks (unsupported catalysts), membranes or coatings (supported catalysts) [12]. Suspended catalysts exhibit generally higher reactivity than immobilized ones, but their post-process separation is more challenging [10,12]. Because nanomaterials pose ecological and health risks when released into the environment [14], the supported catalysts are preferred.

1.1.3 STRATEGIES FOR VISIBLE LIGHT AND DARK ACTIVITIES

The photocatalytic potential of titanium dioxide is limited due to a large bandgap energy (3.0 to 3.2 eV, requiring irradiation with ultraviolet light) and the rapid recombination of photo-excited charge carriers. To extend its applicability and overcome limitations associated with UV-only activation, recent efforts focus on reducing the bandgap for visible light activation and improving charge separation.

Several attempts were made thereby to enhance the efficiency of TiO_2, including two basic methodologies: bandgap engineering and junction engineering [13]. Bandgap engineering interferes with band structure by changing the original positions of valence and conduction bands or introducing new midgap states by forming extrinsic defects (metal and nonmetal doping or metal-nonmetal codoping) or intrinsic defects, such as Ti^{3+} or oxygen vacancies [13]. Junction structures are formed by coupling semiconductors, which align their energy bands in a way that enhances charge separation and reduces recombination [13]. However, coupling additive materials or doping various elements to TiO_2 may favour the undesired charge recombination and hamper recyclability.

Hydrogen peroxide-based modification, introducing intrinsic defects, is a dopant-free strategy imparting a characteristic yellow colour as a side-effect [15]. Simple soaking in H_2O_2 may introduce several changes such as diverse oxygen-rich groups (Figure 1), including peroxo and superoxo groups, which provide the photocatalytic activity observed under visible-light radiation [4,16]. Interestingly, the oxygen-rich groups prove advantageous also for the non-light-driven catalytic removal of organic contaminants [17,18]. Apart from the dark degradation of organic pollutants, H_2O_2-modified TiO_2 demonstrates bactericidal properties [19,20].

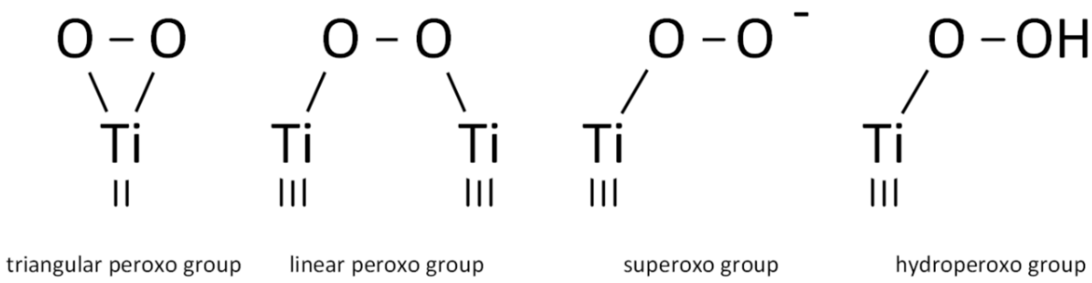

Figure 1 Scheme of the oxygen-rich groups **[E]**

The analysis of recent studies on H_2O_2-modified TiO_2 reveals two key trends. H_2O_2 is an oxidant used for the modification of TiO_2 or in situ pollution degradation **[E]**. The modification process is either part of bottom-up synthesis or the top-down adjustment. Most of the H_2O_2-modified TiO_2 is thermally treated to achieve crystalline phases. The visible-light photocatalytic activity is caused by material modification causing surface hydroxylation, defected structure or the presence of peroxo groups [11,21–24]. In contrast, when H_2O_2 is added in situ, dark activity is often observed, which is explained to be caused by the presence of superoxo groups [17,18,25].

1.2 DESIGN OF THE SUPPORTED CATALYST

1.2.1 SOL-GEL SYNTHESIS

The bottom-up approach for synthesizing oxygen-rich TiO_2 typically involves the aqueous peroxo-titania sol-gel route [11]. Liquid-phase processes offer versatile morphologies, scalable processes and cost-effective solutions, compared to vapour-based and solid-phase methods [14,15,26]. The sol-gel technique offers high control over catalyst-related features, including structure, size and functionality [14,27].

According to the International Union of Pure and Applied Chemistry (IUPAC), the sol-gel route is “a process through which a network is formed from solution by a progressive change of liquid precursor(s) into a sol, to a gel, and in most cases finally to a dry network” [28]. The sol-gel method operates at relatively low temperatures and ambient pressures [29]. The change from solution to sol proceeds via hydrolysis and condensation reactions while from sol to gel through further condensation (Figure 2). Then the wet gel is dried to remove physically adsorbed water and organic solvents and chemically adsorbed hydroxyl groups and precursor residues [29,30]. Drying processes necessitate post-synthesis treatments, including supercritical drying, freeze drying or thermal drying. Thermal drying, such as calcination, is commonly used to achieve the desired crystallinity [30]. Considering wet gels are prone to significant volume shrinkage, heat treatment at inappropriate temperatures and rates may cause cracking [29]. This issue is, however, of lesser importance in the production of powders.

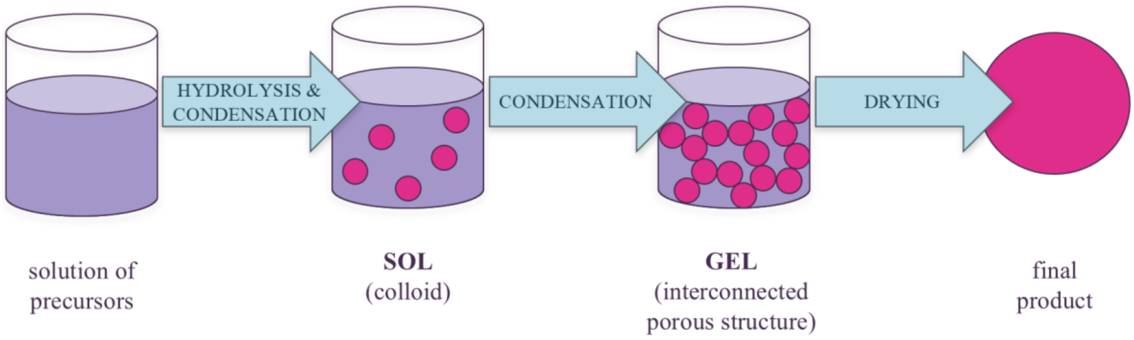

Figure 2 Sol-gel route

1.2.2 THERMAL SPRAYING OF SOL-GEL MATERIALS

From the economical and structural point of view, photocatalyst in the form of coating is more versatile and highly recommended, provided the risk of nanomaterial release is minimized [12]. Unfortunately, coating formation causes the aggregation of the nanomaterials, which reduces the active surface area compared to the suspended particles [14]. Many nanostructured coating formation methods facilitate smooth surfaces only [10,14]. But, unlike them, thermal spraying (TS) uniquely offers a wide range of surface roughness, from coarse to smooth [31] enabling the partial retrieving of initial high surface area-to-mass ratio properties of nanomaterials [10].

Although it is not common, thermal spraying can be coupled with sol-gel synthesis. Sol-gel materials including TiO_2, SiO_2, ZrO_2, Al_2O_3 or hydroxyapatites with tailored chemical composition and functionality may serve as feedstock material for thermal spraying. Whereas thermal spraying can function in two ways. Firstly, it may be used as a thermal drying technique for the removal of the residual solvents, full condensation of the network and removal of synthesis residues. Additional delivered thermal energy is usually consumed on phase transformations [32]. Secondly, thermal spraying offers a scalable method for the production of reproducible coatings.

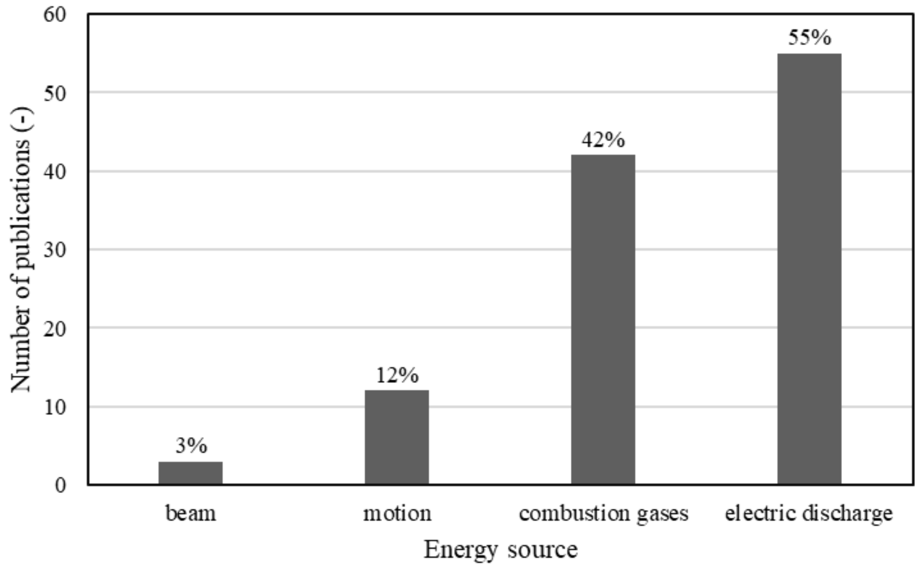

Figure 3 Analysis of current literature on thermal spraying of sol-gel materials based on used energy source for spraying[1]

It is highly convenient that the sol-gel process can be stopped at every step of the synthesis. Sol-gel can be fed in the form of sol-gel solution (precursors or mixture of precursors), suspension (typically powders suspended in the dispersion medium), or powder [14][33] (Figure 2). Solution spraying forms smooth, crack-free structures, while powder spraying provides appropriate porosity and roughness [34,35]. The wet gel is commonly used to form powders and coatings. The powders are mostly produced for catalytic purposes, which require high crystallinity, that can be obtained through high-temperature treatments, such as flame pyrolysis or plasma spraying [36]. Photocatalytic coatings may be produced using flame, plasma, high-velocity oxy-fuel and cold spray [14]. However, the potential uses of coatings extend far beyond photocatalytic activity. Coatings may appear as monolithic, gradient, and multilayer structures. In thermal sprayed multilayers, sol-gel materials play the role of topcoats, interlayers and bond coats deposited on various substrates. Topcoats are used primarily as a sealing agent to decrease porosity. Other applications include increasing the wear, corrosion, or thermal resistance

[1] Based on the analysis of 287 paper found using the inquiry AB=("thermal spray*" OR "flame spray*" OR "detonation spray*" OR "high velocity spray*" OR "high velocity oxy fuel "OR "cold spray*" OR "plasma spray*" OR "laser spray*" OR "laser clad*") AND ALL=("sol-gel*" OR "Sol–gel" OR "sol gel" OR "Sol–gel process" OR "sol-gel process" OR "sol gel process" OR "sol–gel synthesis" OR "sol-gel synthesis" OR "sol gel synthesis") among which 113 was verified to contain the topic of thermal spraying of sol-gel materials

and providing proper roughness and biocompatibility of the outer surface. Interlayers and bond coats usually improve thermal shock resistance and cohesion between layers.

Analysis of current literature on thermal spraying of sol-gel materials conducted for this thesis (Figure 3) shows that the most popular techniques are plasma spraying (55%) and flame pyrolysis (42%). Few papers, investigate laser cladding (3%) and cold spraying (12% of which 7% constitute papers authored by the research team of which the author of this thesis is a member).

1.2.3 COLD SPRAYING OF SOL-GEL MATERIALS

Among thermal spraying techniques, cold spraying is particularly advantageous by operating at lower temperatures, because it may preserve the features of heat-sensitive feedstock materials, which H_2O_2-sensitized TiO_2 surely is [37,38]. Traditionally, the cold spray technique has been used for metal spraying, leveraging the ductility of metals and the advantages of low-temperature deposition to preserve their properties without causing surface oxidation or phase changes [37]. Hard ceramic powders were used preliminary as an admixture to metal powder for reinforcement and densification [37]. However sol-gel materials without thermal treatment may be prone to ductile-like behaviour at the microscale, which enables the formation of coatings due to mechanical interlocking [32,39,40]. Considering the success of the research team to which the doctoral candidate belongs in spraying unmodified TiO_2 [32], cold spraying was chosen to develop oxygen-rich TiO_2 coatings in this thesis.

2 RESEARCH CONCEPT

The chapter outlines the key research areas related to oxygen-rich TiO_2 materials, focusing on their applications, properties, synthesis and deposition. This thesis specifies 9 research aspects based on current scientific knowledge, complemented by the explicit contributions provided within this thesis, and highlights of potential challenges for future considerations.

2.1 RETHINKING TiO_2 ACTIVITY

When considering the activity of TiO_2-based materials, current trends include photocatalyst activation by visible light, achieving activity in darkness, and the use of amorphous titanium dioxide.

2.1.1 VISIBLE-LIGHT ACTIVITY

TiO_2 has been proven active photocatalyst against over 1000 substances, including pesticide residues, drugs, and hormones, as well as nitrogen oxides, toxic fumes, cigarette smoke, viruses, fungi and bacteria [12,17,18,25,26]. Overcoming UV-only activation that is harmful to living organisms could broaden the applicability of already-developed UV-induced photocatalytic solutions. Visible-light activation is more practical for integration into human environments, as it operates efficiently under natural sunlight and human-neutral artificial lighting. Additionally, it enables clean energy applications, such as solar water splitting for hydrogen production and CO_2 reduction into valuable fuels.

Contribution: The modification of TiO_2 with H_2O_2 is designed to provide visible-light activity against standard organic pollutant (methylene blue) **[A,C,E]**.

Possible issue: The visible-light activity in model pollutant degradation may be caused by the in-situ addition of H_2O_2 [23] dye sensitization [41] or adsorption [24].

2.1.2 DARK ACTIVITY

Recent studies show that TiO_2 can be active in the degradation of organic pollutants and microorganisms for some time after removal of radiation and TiO_2 can be active independently on the delivered light [25]. The dark activity was observed for the oxidised surface of titanium implants [20] or coloured TiO_2, mainly black TiO_2 [18]. Especially interesting is yellow TiO_2 as the addition of H_2O_2 provides dark activity in a facile, room temperature, dopant-free manner (Chapter 1.1.3). Catalysis in the dark holds promise for implant applications (devoiding light) and continuous cleaning processes (not necessarily under continuous illumination), particularly in medical settings, where certain bacteria may persist under photocatalytic conditions and recover in the absence of light [17][18].

Contribution: The modification of TiO_2 with H_2O_2 is designed to provide dark activity against standard organic pollutant (methylene blue) and microbes (*Escherichia coli*, *Enterococcus faecalis*) **[E]**.

Possible issue: Observed dark activity may be partially caused by the exposure to daylight that occurred during synthesis and drying.

2.1.3 ACTIVITY OF AMORPHOUS MATERIALS

Commercially available TiO_2 (P25), a standard photocatalytic material, is composed of anatase, rutile and amorphous particles. Their junction can provide a synergistic effect as anatase is active in oxidative decomposition reactions while rutile - for reductive pathways [42]. Thermal treatment is used to increase crystallinity and get rid of the amorphous phase which is considered inactive [42]. Current research shows, however, that amorphous materials may be active photocatalyst, too [43]. The amorphous phase as the name suggests, is characterized by long-range disorder. Defects may promote charge carrier generation, improve charge separation and transfer efficiency, all of which enhance visible light absorption [13,42]. Additionally, amorphous TiO_2 is a perfect surface adsorbent [44]. What is even more interesting, some researchers observe an even higher photocatalytic activity of amorphous titanium dioxide compared to its commercially available crystalline version, P25 [43,44].

Contribution: The modification of TiO_2 with H_2O_2 is designed to produce an amorphous structure with defects ensuring visible-light activity of the material in the form of powder **[A,E]** and coating **[A,B,C,D]**.

Possible issue: (1) Amorphous TiO_2 is unstable in aqueous media (photo-corrosion) [43]. (2) Defects may serve as recombination centres that limit the activity [13,42].

2.2 DEVELOPMENT OF FEEDSTOCK MATERIALS FOR THE LPCS PROCESS

Developing feedstock materials for LPCS requires a thorough evaluation of their initial functionality, as it directly influences the characteristics of the formed coating. It is also essential to determine whether such materials are suitable for deposition. Moreover, the deposition process may be analysed for its potential to contribute to material preparation which may provide additional features and shorten the production time.

2.2.1 DESIGNING AOP ACTIVITY

Few reports study coatings which underwent top-down H_2O_2-modification [17] probably due to the difficult formation of coatings from H_2O_2-modified TiO_2. Therefore, in designing active feedstock for thermal spraying, analysis of literature on TiO_2 in AOP technologies [15,18] may give useful insights. Generally, H_2O_2 is used as a strong oxidant in UV/H_2O_2 and UV/TiO_2/H_2O_2 systems due to its ability to in-situ generate reactive oxygen species (ROS), including reactive hydroxyl radicals ($^{\bullet}OH$) [41]. Although H_2O_2 decomposition is spontaneous, UV-photolysis can improve and control its decomposition rate [5]. In UV/TiO_2/H_2O_2 systems, the presence of metal ions catalyses the decomposition of H_2O_2 at the TiO_2 interface and enables the formation of different radicals, such as superoxide radicals ($O_2^{-\bullet}$) and hydroperoxyl radicals (radical $^{\bullet}OOH$). Both radicals ($O_2^{-\bullet}$/$^{\bullet}OOH$) can be stabilized on metal oxide surfaces [19] to form metal-dioxygen complexes, called oxygen-rich groups (Figure 1) that can be excited during degradation processes. Apart from oxygen-rich groups, the literature review in **[E]** displays that the common material features providing AOP activity are surface hydroxylation, phase composition, and defects in the structure. Those features can be introduced into the material before the degradation processes. The resulting material structure determines which reactive oxygen species, including $^{\bullet}OH$, $O_2^{-\bullet}$, $^{\bullet}OOH$, or photogenerated intermediates, such as $[\equiv Ti^{IV}-OOH]\bullet$ and $[\equiv Ti^{III}-OOH]^{-}$, are preferentially formed during the test [11].

Contribution: The synthesis of feedstock TiO_2 is followed by the modification with H_2O_2 favouring the formation of oxygen-rich groups, intermediates and radicals to provide visible light and dark activity without relying on in situ addition of H_2O_2 and UV light **[A,E]**.

Possible issue: (1) Excited oxygen-rich groups on TiO_2 may be consumed and fail to regenerate during the degradation processes [11]. Their regeneration may require H_2O_2 treatment [17,24]. (2) Oxygen-rich groups are thermally-sensitive [11] and may not sustain the LPCS process.

2.2.2 IMPARTING DUCTILITY

The principal disadvantage of low pressure cold spaying is the limited range of feedstock materials as this technique was developed for metals which are ductile [37]. It is impossible to plastically deform hard and brittle ceramic materials, such as crystalline TiO_2 [37]. The typical way to embed ductility or deformability of TiO_2 is to combine it with commercially available polymer powder, such as polyvinyl alcohol [37,39]. Some studies show, however, that amorphous oxides such as SiO_2 or Al_2O_3 may exhibit ductile behaviour [45], too. The most effective way to obtain amorphous TiO_2 is to produce it using sol-gel synthesis (Chapter 1.2.1). Apart from promising amorphicity, wet processing gives control over the particle size and agglomeration. Too small particles may be ejected outside the carrier gas stream, so nanoparticles can be deposited using LPCS only in the form of agglomerates [37]. TiO_2 network formed upon sol-gel synthesis encompasses residues of precursors and byproducts like alcohols and adsorbed water. The synthesis residues bind the TiO_2 particles in weakly-bonded agglomerates [32]. Such agglomerates may be then fractured, slipped and compacted to form coatings, which provide so-called ductile-like behaviour [40] ensuring higher deposition efficiency [37]. Hence the heat treatment of the sol-gel TiO_2 may be intentionally omitted to sustain the amorphous structure with the synthesis residues [32]. To maximise further the deposition efficiency of TiO_2 feedstock the substrate material can be selected to be ductile. The evident choice is aluminium, as it tends to jet at the impact of incoming particles enhancing particle attachment [34][40].

Contribution: The synthesis of H_2O_2-modified TiO_2 was conducted using the sol-gel method without following heat treatment to produce an amorphous metal-oxygen network, full of synthesis residues which can act as a binder upon deposition and can be easily anchored on the aluminium substrate **[A]**.

Possible issue: Room-temperature dried TiO_2 may contain irregular shapes and intra-agglomerate pores which may cause the formation of undesired closed porosity that reduces the mechanical properties of the formed coating [39].

2.2.3 PROVIDING THERMAL DRYING

While the sol-gel process begins with a liquid precursor, the final product is a solid. The liquid phase is removed via supercritical, freeze or thermal drying (Figure 2). Apart from the removal of organic residues, thermal treatment is used to change chemical, textural, morphological and crystallographic properties [30,35]. Among thermal post-treatment methods of sol-gel materials, calcination is the standard approach [30,32]. Some attempts have been made to produce sol-gel coatings using air-spraying, but additional calcination is needed to achieve the desired properties [46]. Although this approach remains relatively unknown (Figure 3), instead of traditional long-lasting or energy-consuming heat treatment, thermal spray offers a scalable alternative for thermal drying (Figure 2, Chapter 1.2.2). Either room-dried powders or wet gels can be fed to a spraying gun.

Contribution: LPCS was used as an integrated solution to sol-gel synthesis offering scalability in coating formation and thermal treatment of liquid residues remaining after condensation (wet gel) **[B,C,D]** or room temperature drying **[A]**.

Possible issue: Undried sol-gel materials are characterized by reduced flowability which hinders their transport from the feeder to the spraying gun [47].

2.3 CUSTOMIZATION OF COATINGS THROUGH LPCS PARAMETERS

The final characteristics of the deposited coating can be controlled by adjusting the parameters of deposition. Modifications of the low-pressure cold spray setup can address the limitations of the feedstock materials.

2.3.1 DEPOSITION PARAMETERS-DEPENDENT EFFECTS

Coating quality depends on the deposition parameters. Selecting appropriate parameters is challenging, as there are dozens of possible spraying parameters to consider [48]. The first group of parameters involve feedstock material characteristics, the second contains spraying setup characteristics including carrier gas, manipulator, nozzle and feeding, whereas the third is pre- and post-spraying treatment methods [48]. For LPCS (Chapter 1.2.3), generally, the most important parameters are pressure and temperature as they limit the accessible particle velocities [37]. Increasing delivered thermal energy is crucial for ensuring the homogeneity of the produced coatings and facilitates rough surface development [33,37]. LPCS is generally an air-based technique [39] but for better quality, it can be coupled with inert gases or vacuum [35]. It is worth noting that the continuous coating can be produced in the range of parameters (a window), not a single specific combination (a point) [39].

Contribution: Increasing carrier gas temperature enables coating formation from H_2O_2-modified TiO_2 **[A]**. Partially and fully condensed sol differently react on delivered thermal energy **[B]**. Proper particle size distribution causes sufficient momentum of particles and enables coating formation **[D]**. The formation of discontinuities can be limited using a plan of experiments **[C]**.

Possible issue: (1) Window of deposition for ceramic powders is significantly lower compared to metallic powders [37,39,49]. (2) The currently deposited ceramics LPCS coatings are characterized rather by poor quality (porosity and insufficient particle interlocking) [34,39] (3) Rapid drying of sol-gel materials may cause cracking [29].

2.3.2 COMBATING THERMAL-SENSITIVITY

Although LPCS keeps a low-temperature regime it may cause feedstock material changes, such as an increase in grain size, phase transition or decomposition of O-O species [34]. Given the thermal sensitivity of oxygen-rich complexes [11], their presence and stability in the final product need to be assured by omitting high temperature or pressure post-treatment. To lower the risk of preheating, feedstock material can be used in liquid form [38]. Water and alcohols are the most used solvents in other thermal spraying techniques [33]. Liquid share enables control of the agglomeration of fine particles and their sedimentation [33,38]. In the case of sol-gel material, the synthesized particles may remain suspended in the post-synthesis mixture containing water, unreacted precursors and synthesis by-products which eliminates the need for the application of additional solvents. Additionally, such a wet gel may include a higher solid content compared to a conventional slurry composed of particles and solvent [33]. Thus, the application of H_2O_2-modified TiO_2 wet gels as feedstock material reduces total coating production time by eliminating the drying step (about a week in the room conditions) and repurposes synthesis residues which minimize waste and consumption of chemicals.

Contribution: Suspension spraying leads to the efficient material use and preservation of amorphous TiO_2 with oxygen-rich structures upon spraying **[B,C]**.

Possible issue: The residues containing H_2O_2 which are trapped in the coating cause coating disintegration due to H_2O_2-containing bubble collapse **[B,C]**. Poorly evaporated liquid increases thermal shock and causes cracking [46].

2.3.3 RESIDUES EVAPORATION

Excess liquid can lead to inefficient material use due to overspray and increased coating defects due to cracking [46]. The obvious solution is to increase thermal energy, but increasing energy can cause changes in the composition and hence is not suitable for heat-sensitive materials. Another solution for enhanced liquid evaporation is better control of the droplets that can be provided using non-continuous feeding systems – aerosolization of the feedstock suspension. Liquid aerosol formation can be done using an atomizer, including pneumatic, hydraulic and sonic atomizers [33]. The atomizer breaks the suspension into separate droplets. The formation of mist gives control over the diameter of liquid particles [50]. The high kinetic energy of carrier gas in cold spraying may induce evaporation [50]. The final structure of the coating depends on the droplet flattening [50]. The behaviour of large liquid droplets is similar to the behaviour of solid particles of adequate size [33]. In other thermal spraying techniques, usually liquid evaporates before reaching the substrate material [51].

Contribution: The aerosolization of feedstock suspension enhances the complete removal of residual H_2O_2-containing liquid and hence retains coating integrity **[D]**.

Possible issue: Rare commercial spraying guns for liquid injection are not designed for cold spraying [33].

3 AIMS OF RESEARCH

The thesis aims at the development of oxygen-rich TiO_2 coatings deposited using low pressure cold spraying of sol-gel synthesized TiO_2 modified with H_2O_2. This dissertation addresses gaining a better understanding of the spraying parameters on TiO_2 embedding and preserving oxygen-rich structures. Produced coatings are meant to demonstrate visible-light activity. Additionally, the dark activity of powders is investigated.

The main aims can be summed up with regard to each study:

Table 2 Compilation of main aims

[A]	The oxygen-rich powder is designed using an aqueous peroxo-titania sol-gel route. The effects of H_2O_2 modification are confirmed by the presence of oxygen-rich groups and the reduction of the bandgap width. Feeding as-synthesized amorphous powder without thermal treatment provides ductile-like behaviour during spraying. The maximum range of carrier gas temperature is used to show wide deposition widow. The dye degradation test verifies visible-light activity.
[B]	The oxygen-rich suspension is used instead of powder to combat the thermal sensitivity of feedstock (retain the chemical and structural changes) and reduce the total production time (no drying step). Relatively high carrier gas temperature is used but deposition is controlled additionally by manipulator movement.
[C]	The oxygen-rich suspension is sprayed with parameters of ranges selected based on **[B]** to provide the same chemical and optical structure as powders **[A]**. The spraying parameters are optimized for bandgap energies and surface area to reduce the number of performed photocatalytic tests. The dye degradation test verifies the visible-light activity of the coating sprayed with optimal parameters.
[D]	The oxygen-rich suspension is atomized for spraying to improve the removal of residual H_2O_2-containing liquid and improve coating integrity. The influence of the preparation of suspension is investigated with respect to the formed coating.
[E]	The oxygen-rich, H_2O_2-modified powder **[A]** is compared with unmodified TiO_2 and P25 to investigate the factors contributing to its visible-light and dark activity verified in dye degradation and bacteria-killing tests.

4 METHODOLOGICAL CONSIDERATIONS

This thesis analyses H_2O_2-modified TiO_2 (coloured blocks in Figure 4) in various forms.

- The **coating** is produced by the spraying of feedstock material in the form of powder, suspension (wet gel formed via the sol-gel reactions without consecutive drying) and aerosol of suspension.
- The **powder** is obtained by ambient drying of suspensions at room temperature.

Unmodified sol-gel synthesised TiO_2 and typical commercial TiO_2, P25, were investigated for comparison (white blocks in Figure 4).

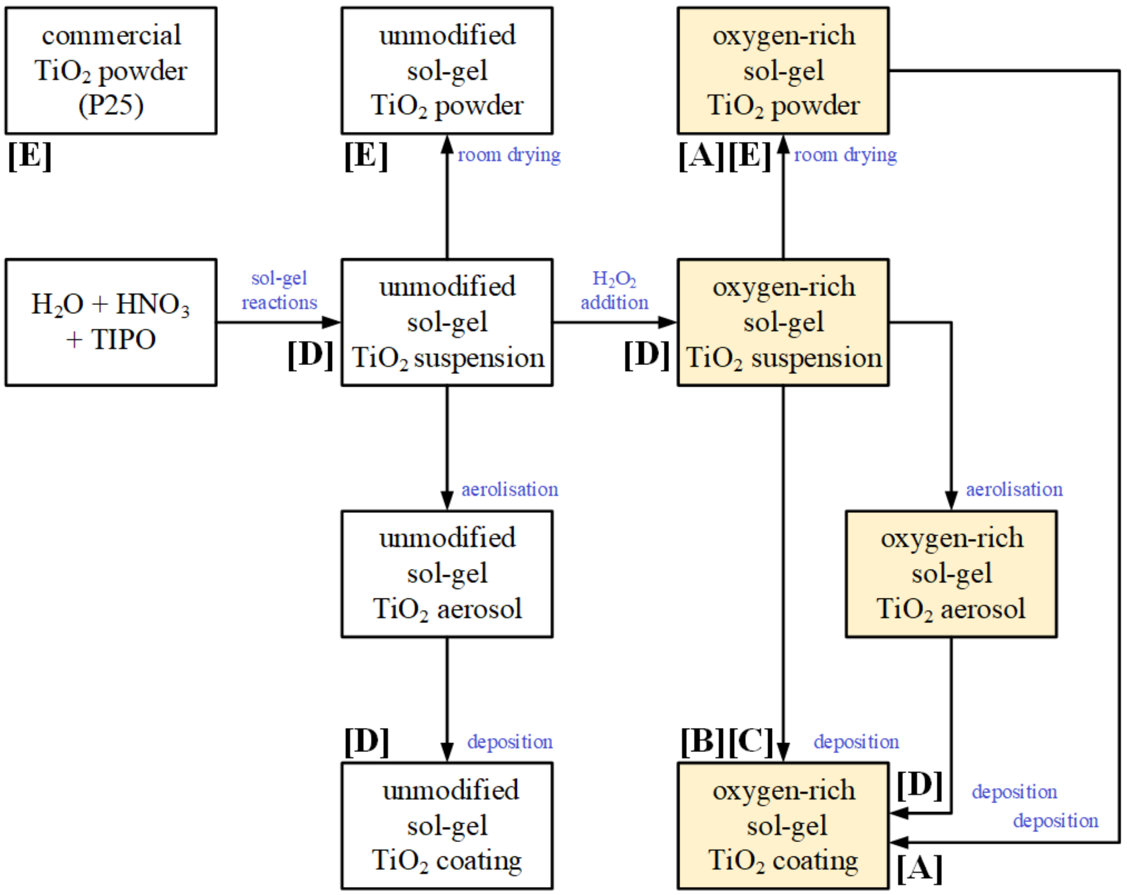

Figure 4 Thematic correlation between the papers that constitute the scientific achievement. Coloured blocks denote TiO_2 materials modified with H_2O_2, and white blocks represent TiO_2 without H_2O_2 modification and commercial P25 powder. Process flow labels indicate the transformations occurring between each step. Citations are included to specify which papers studied each material type.

4.1 SOL-GEL SYNTHESIS

TiO_2 was synthesised via single-pot sol-gel method (Figure 5). Titanium dioxide was formed from titanium(IV) isopropoxide (TIPO) used as a precursor, distilled water and nitric acid. The sol-gel reactions result in formation of metal-oxygen network with residual isopropoxide groups or partially hydrolysed species. Upon the contact of H_2O_2, oxygen-rich groups are formed on the surface of the titania [21,23]. The colour of reaction mixture changes instantly and ranges from red, through orange to yellow depending on the type of the peroxo groups (linear Ti-OOH, Ti-O-O-Ti, and triangular TiO_2), superoxo groups and their concentrations [21]. The colour of the dried H_2O_2-treated TiO_2 appear yellow to the naked eye. In other research oxygen-rich groups serve most commonly as an essential intermediate step to achieve hydrated crystalline TiO_2 phases which is obtained through heat treatment which transform oxygen-rich group to hydroxy groups [24]. In this research, resigning from thermal treatment aimed to preserve oxygen-rich groups (possible issue 2.2.1).

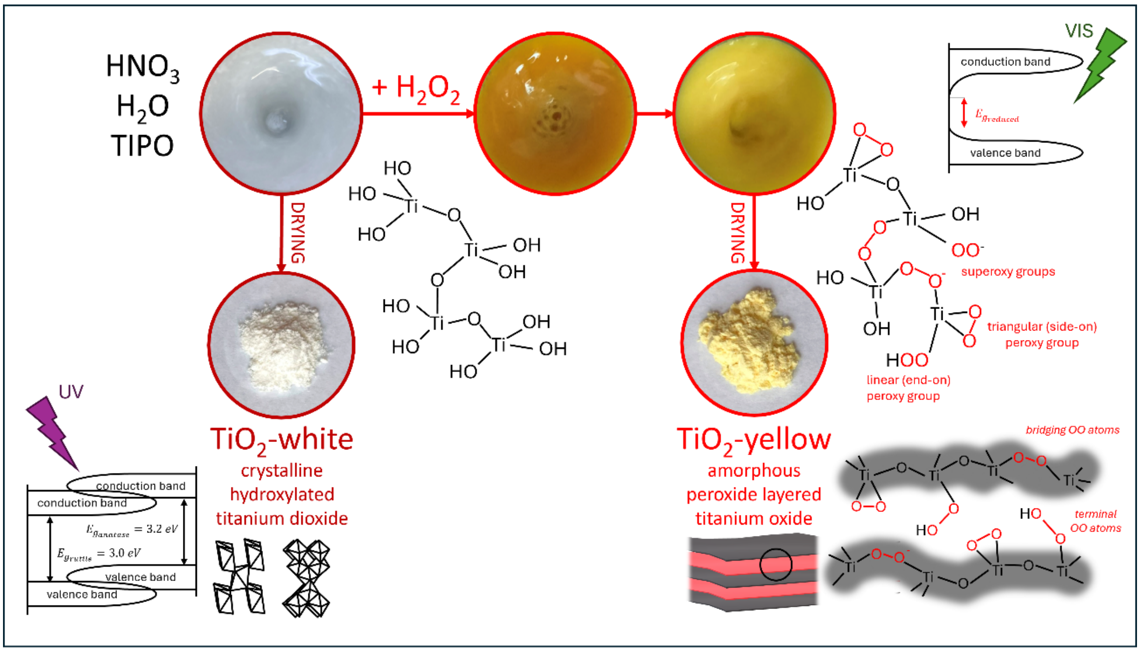

Figure 5 Scheme of sol-gel synthesis of H_2O_2-modified and unmodified TiO_2 supplemented with a graphic illustration depicting the differences in the chemical composition **[E]**

In this thesis, the same recipe is used to synthesize:

- powders (oxygen-rich TiO_2 **[A, E]** and unmodified **[E]**)
- suspensions (oxygen-rich TiO_2 **[B,C,D]** and unmodified **[D]**).

4.2 LOW-PRESSURE COLD SPRAYING

The coatings were deposited on the aluminium AW-1050A H14/H24 (min. 99.5 wt.% of Al) substrates with dimensions of 20 mm × 20 mm × 4 mm. Aluminium naturally passivates (Al_2O_3) in humid or aqueous environments which provides water and corrosion resistance. Compared to other corrosion-resistant metals, such as stainless steel or titanium, aluminium is significantly more affordable. Its low density (approximately one-third that of steel) makes it exceptionally lightweight without compromising structural integrity. This property is particularly beneficial in complex assemblies where minimizing weight is crucial, such as in aerospace, automotive, architectural applications or photocatalytic reactors with replaceable inserts. Aluminium is also a highly ductile metal, allowing it to be easily shaped, textured, or micro-patterned. During cold spraying, aluminium enhances coating build-up due to its impact characteristics [34,40]. Roughening provides an additional point of contact with surface and valleys that facilitate the anchoring of particles due to shear instabilities [32,34,40]. Typical techniques for topography modification include grit and sand blasting, grinding, and laser texturing [39]. In this thesis, before the LPSC process, all substrates were grit-blasted using corundum (Al_2O_3, mesh 45).

All coatings are prepared using a Dymet 413 unit (Obninsk Center for Powder Spraying, Obninsk, Russia) coupled with a computer-controlled manipulator (BZT Maschinenbau GmbH, Leopoldshöhe, Germany). Dymet systems are considered a benchmark for low-pressure cold spraying [39,52]. The integration with a computer-controlled manipulator provides precise movement and positioning, ensuring operator safety, uniform coating thickness, and customizable layer designs. Additionally, it enables flexible coating patterns and efficient application on complex geometries.

Only one nozzle design is used throughout the study. The feedstock material is delivered to the nozzle (internal feed system, Figure 6a and Figure 8a) or bypassing the nozzle (external feed system, Figure 7a and Figure 8a).

4.2.1 POWDER FEED LPCS SYSTEM **[A]**

Dymet system is equipped with a standard vibrational hopper feeder designed for metallic powders with particles ranging from 5-50 μm [37,52]. In the case of low-density soft-phase powders with wide particle size distribution, the vibrations cause powder tamping and clogging of the hopper outlet [39](possible issue 2.2.3). That is why instead of a hopper, an aerosol powder feeder RBG 1000 SD (Palas GmbH, Karlsruhe, Germany) was applied [53]. According to producer information, the particle size range is larger (0.1-100 µm) [53]. The powder is filled into a feedstock powder compartment whose size is controlled by the programmable movement of the piston. The powder is delivered into the dispersion head with a rotating precision brush. Then due to the application of carrier gas (nitrogen, 0.1 MPa), the loose powder is transferred to the dispersion unit outlet.

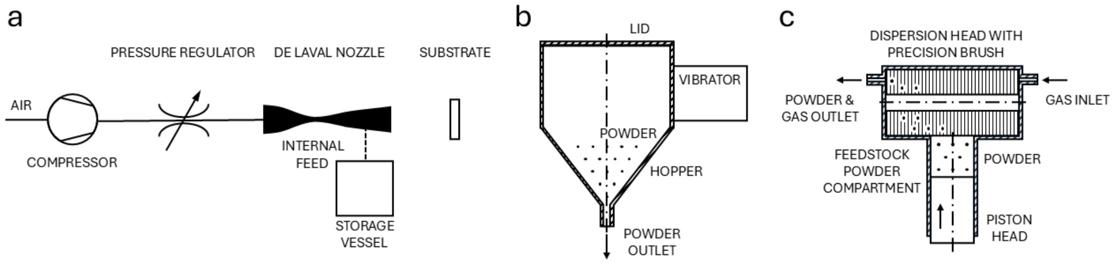

Figure 6 (a) Scheme of low-pressure cold spraying system with powder feeder, (b) with a detailed view of the standard hopper feeder, and (c) Palas aerosol generator based on producer data [53]

4.2.2 SUSPENSION FEED LPCS SYSTEM **[B,C]**

Suspension spraying is an effective heat-protection technique. The liquid phase reduces thermal energy delivered to the particles by consuming it partially for evaporation. The system for suspension feed needs to be leakproof. Traditional syringe pumps are used in thermal spraying procedures [33]. For spraying of H_2O_2-modified TiO_2 suspension, different construction was developed (Figure 7b,c). The carrier gas is supplied to the

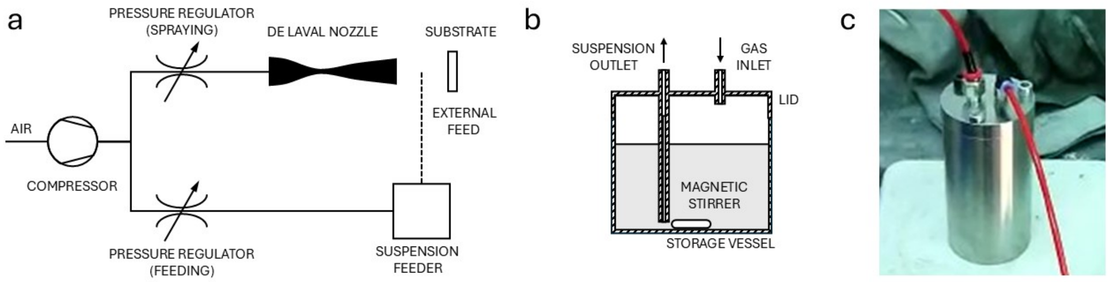

Figure 7 (a) Scheme of low-pressure cold spraying system with suspension feeder, (b) with a detailed view of the suspension feeder, and (c) the photograph of the suspension feeder on the magnetic stirrer storage vessel and pushes the suspension. The suspension is homogenized by constant stirring. To enable proper stirrer operation, austenitic stainless steel (non-magnetic) was used for construction. Its corrosion resistance reduces vessel degradation in contact with H_2O_2-containing substances. The important part of the storage vessel is the pressure relief valve, as the decomposition of H_2O_2 is exothermic which may lead to explosions.

The volume of the suspension delivered to the substrate is controlled by the gas pressure and the diameter of the feeder outlet. Small diameters cause nozzle clogging. Too high a feed rate may cause problems with the evaporation of the liquid part which is required for H_2O_2-containing structures **[B,C]**. This is especially important for cold spraying in which the distance from the nozzle to the substrate is generally lower than for other thermal spraying techniques [33,35].

4.2.3 AEROSOL FEED LPCS SYSTEM **[D]**

The application of a non-continuous suspension feeding system facilitates the rapid evaporation of liquid. The most important effect of this research is that it may provide full evaporation of H_2O_2-containing suspension. The construction of the atomizer was also developed for this research. It consists of a specially designed 3-D printed storage vessel and a vacuum generator mounted inside (Figure 8b,c) [54][F]. The suspension is supplied in a batch process and to provide homogeneity it is under continuous mixing with a magnetic stirrer. For aerosolization, gas flows through the vacuum generator which creates a negative pressure that draws the liquid from the chamber to the aerosol outlet. Then the aerosol of suspension is introduced either at the diverging section of the de Laval nozzle or externally in the middle of the distance between the nozzle end and the substrate material.

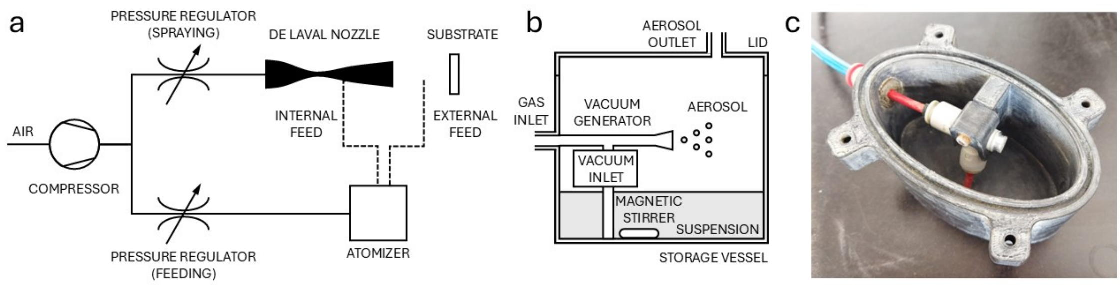

Figure 8 (a) Scheme of the low-pressure cold spraying system with suspension atomizer, (b) a with detailed view of the atomizer, and (c) the photograph of the atomizer with the lid removed **[D]**

4.2.4 SPRAYING PARAMETERS SUMMARY

To reach the various aims of research (Chapter 3), different combinations of spraying parameters were selected (Table 3).

Table 3 Compilation of spraying parameters

[A]	The modified spraying parameters: – carrier gas temperature (200, 600 °C). Other spraying parameters: – feedstock material: oxygen-rich TiO_2 **powder** – carrier gas: type: air, pressure: 0.5 MPa, – nozzle: circular with 2.5 mm throat and 5 mm outlet, – manipulator: traverse speed: 2.5 mm/s, stand-off distance: 10 mm, scanning step: 2 mm, – feeding: feeding rate: 61 g/h, powder feed: internal.
[B]	The modified spraying parameters: – scanning step (1, 2, 3 mm), – standoff distance (10, 20, 30 mm), – traverse speed (75, 150, 300 mm/min) – temperature of carrier gas (400 and 600 °C). Other spraying parameters: – feedstock material: oxygen-rich TiO_2 **suspension** – carrier gas: type: air, pressure: 0.5 MPa, – nozzle: circular with 2.5 mm throat and 5 mm outlet, – feeding: feeding rate: 28.6 µL/s, suspension feed: external, in the middle of standoff distance, skewed 20° relative to nozzle axis.
[C]	The modified spraying parameters: – scanning step (2, 3, 4 mm) – traverse speed (150, 300, 450 mm/min) – temperature of carrier gas (200, 400, 600 °C). Other spraying parameters: – feedstock material: oxygen-rich TiO_2 **suspension** – carrier gas: type: air, pressure: 0.5 MPa, – nozzle: circular with 2.5 mm throat and 5 mm outlet,

	– manipulator: standoff distance: 30 mm, scanning step: 2 mm, – feeding: feeding rate: 28.6 μL/s, suspension feed: external, in the middle of standoff distance, skewed 20° relative to nozzle axis.
[D]	The modified spraying parameters: – suspension feed (downstream injection or external injection (in the middle of standoff distance, skewed 20° relative to nozzle axis)). – feedstock material (oxygen-rich TiO_2 **aerosol of suspension** or unmodified TiO_2 **aerosol of suspension**). Other spraying parameters: – carrier gas: type: air, pressure: 0.5 MPa, – nozzle: circular with 2.5 mm throat and 5 mm outlet, – manipulator: standoff distance: 10 and 30 mm, scanning step: 2 mm, traverse speed: 300 mm/min, temperature of carrier gas: 600 °C, – feeding: feeding rate: 28.6 μL/s, suspension feed: internal, and external, in the middle of standoff distance, skewed 20° relative to nozzle axis.
[E]	No coating[2]

[2] No coatings. The paper provides an in-depth analysis of the powders utilized in **[A]**.

4.3 CHARACTERIZATION METHODS

This section presents the most relevant techniques for the examination of H_2O_2-modified TiO_2 powders, suspensions and coatings.

4.3.1 X-RAY DIFFRACTION **[A,D,E]**

X-ray diffraction is widely used for the investigation of phase composition, degree of crystallinity, and structural defects. In this thesis, it was primarily used to detect whether LPCS deposition caused phase transition from amorphous phase to anatase [32].

4.3.2 RAMAN **[A,B,C,D,E]** AND INFRARED SPECTROSCOPY **[E]**

Raman spectroscopy confirms phase composition changes and recognises oxygen-rich groups. Raman bands are assigned based on the literature review which is presented in **[A]**. Infrared spectroscopy is more specific for distinguishing their different geometries, including triangular or linear groups [11].

4.3.3 ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY **[C,E]**

Interaction of TiO_2 with H_2O_2 causes the formation of paramagnetic defects. In this research, electron paramagnetic resonance spectroscopy excluded the presence of most popularly detected oxygen vacancies and Ti^{3+} defects [11,21] and enabled the identification of superoxide radical anion (O_2^{-}) in the powders **[C]** and coatings **[E]** before and after catalytic activity tests.

4.3.4 X-RAY PHOTOELECTRON SPECTROSCOPY **[E]**

X-ray photoelectron spectroscopy confirms primarily the oxidation states of titanium (Ti^{4+}) and provides information about Ti−O bonding, including the existence of surface hydroxy groups, oxygen-rich groups, and adsorbed water [11,21].

4.3.5 SURFACE CHARGE **[E]**

The point of zero charge (pH_{PZC}) is critical for understanding the adsorption processes of pollutants on the catalyst surface. The drift method [55] is a simple and inexpensive approach to assess at which pH negative and positive charges are equal. This means that at pH lower than pH_{PZC} the positively charged surface of TiO_2 attracts anions (including condo red), while at pH higher than pH_{PZC} negatively charged surface attracts cations (such as methylene blue) [11].

4.3.6 SEDIMENTATION TEST **[D]**

To maintain constant feed, homogeneity, and prevent defects in the coating, the stability and settling behaviour of suspension should be examined. To avoid interactions between glass and titanium precursors, polymeric cylinders are used instead of standard glass cylinders for the sedimentation test.

4.3.7 DIFFUSE REFLECTANCE SPECTROSCOPY **[A,B,C,D,E]**

The Kubelka-Munk function is used to determine the optical bandgap width, which represents the energy gap between the valence and conduction bands of semiconductors. Additionally, the method provides information about localized electronic midgap states which are caused by the disorder and defects and may be observed as the Urbach tail [56]. Thanks to sub-bandgap absorption, which allows absorbing photons of energy lower than the bandgap, H_2O_2-modified TiO_2 is a promising material for visible-light applications.

The reflectance measurement is, however, influenced by multiple factors, including surface characteristics [57]. This aspect was used in **[C]** where bandgap energy underestimation in coatings with the same chemical characteristics resulted from the presence of coating discontinuities. Detection of defective coatings facilitated the optimisation of spraying parameters for the development of crack-free surfaces.

4.3.8 TRANSMISSION ELECTRON MICROSCOPY **[E]**

Electron microscopy provides information about the morphology of the powders. Selected-area electron diffraction offers observation of diffraction patterns at different orientations directly on the transmission electron images which confirms the presence of crystalline phases at atomic level. This technique is particularly useful for heterogenous materials and nanostructures of low-crystallinity.

4.3.9 SURFACE FEATURES **[A,B,C]**

There are two technical approaches to determining the specific surface area of TiO_2 coatings: detaching the coating or measuring it in situ without detachment. The first option is impractical, as TiO_2 coatings lack sufficient mechanical integrity to be removed without damaging their structure. In the second option, mercury porosimetry or nitrogen adsorption to access specific surface area are limited to detecting only open porosity. Additionally, such analysis relies on comparing the mass of the sample and the substrate. For thin coatings with low mass (on the order of a few milligrams), this can lead to significant measurement errors due to the small mass difference.

To overcome these challenges, optical image profilometry is used. This optical technique generates a three-dimensional surface profile by scanning multiple focal planes along the z-axis, allowing for the calculation of surface area and roughness. Its resolution is limited by the nature of light, preventing the detection of features smaller than approximately 200 nm, as well as complex topologies such as step edges and undercuts [17]. But optical image profilometry (as used in **[B,C]**) is more suitable for analysing thin coatings compared to tactile profilometry (as used in **[A]**), which may damage brittle surfaces.

4.3.10 SURFACE AND CROSS-SECTION IMAGING **[A,B,C,D]**

The morphology of surface and cross sections is investigated using a scanning electron microscope equipped with secondary electrons and backscattered electrons detectors. The limitation of backscatter images includes low contrast (because of the relatively close atomic number of titanium (Z=22) and aluminium (Z=13)) and reduced resolution due to image distortion caused by the lack of conductivity of TiO_2 layers. To reduce charging without carbon or gold sputtering, the low vacuum mode is used.

4.3.11 CROSSCUT TEST **[D]**

To assess the adhesion strength of thermal sprayed coatings, the standard method typically used is the pull-off test (ASTM C633). However, for very thin and smooth coatings, the scratch test (ASTM C1624) is often employed. In our study, the coatings were too thin (with a thickness below 380 μm) to apply the ASTM C633 standard and too rough to utilize the ASTM C1624 standard. As a result, the adhesion was assessed strength using the cross-cut method, in accordance with the ISO 2409 standard, which is suitable for coatings with the characteristics observed in this study.

4.3.12 STATISTICAL ANALYSIS **[C]**

Photocatalytic activity testing is time-consuming. Taguchi's orthogonal design approach reduces the number of experimental test runs. The method was developed for the industry but currently is applied also scientific research of various processes, including coating preparation processes using thermal spraying [48]. This means that the photocatalytic activity test in **[C]** has been performed only for selected samples.

4.3.13 MB DEGRADATION **[A,C,E]**

Dyes degradation test coupled with UV-VIS spectroscopy is a simple, cheap, reliable and reproducible mean to assess real-time photocatalytic activity. Several standardised methods for dye degradation in aqueous solution using UV light have been developed, including ISO 10678:2010, and the newest ISO 10678:2024 standards. Visible light can, however, excite dye molecules (possible issue 2.1.1). To exclude dye sensitization, it is essential to use an irradiation source with wavelengths shorter than the maximum absorption of methylene blue (600–700 nm, Figure 9a). Consequently, a source with maximum emission within the range of 420–500 nm was used (Figure 9b) or an appropriate cut-off filter (Figure 9c).

The spectroscopic method is based on measuring the decreasing concentration of MB. To exclude the effect of dye adsorption (possible issue 2.1.3), total organic carbon measurements were carried out to provide a quantitative value for degraded dye **[E]**.

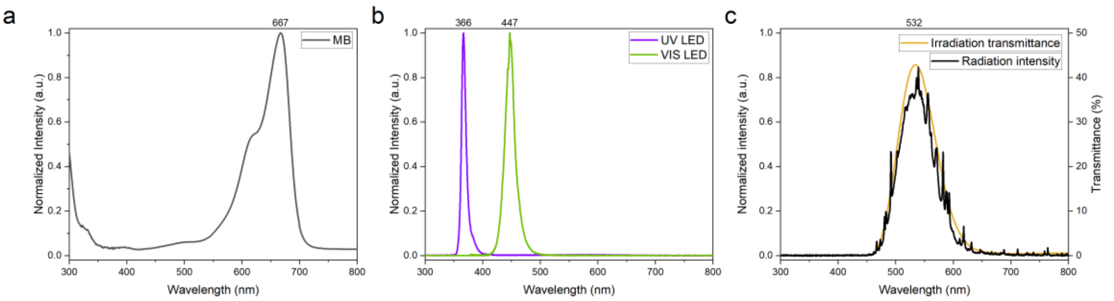

Figure 9 (a) UV-Vis absorption spectrum of methylene blue and spectral characteristics of (b) UV and Vis diodes **[E]** and (c) Xe lamp with the UV cut-off filter **[A,C]**

4.3.14 BACTERIA KILLING **[E]**

The bactericidal effects of TiO_2 against both Gram-positive (*Enterococcus faecalis*) and Gram-negative (*Escherichia coli*) bacteria were evaluated under solar-like illumination and in darkness to observe dose-dependent effects. Bacterial viability was quantified by counting colony-forming units on agar plates. Although a cooling system was used, the XENON lamp often caused a temperature rise, potentially influencing bacterial viability.

Additionally, the XENON lamp emitted a mixture of UV and visible light, complicating the interpretation of light-specific effects. No standard substances active under visible light or in darkness were used for comparison of antimicrobial activity as there are currently none popularly used.

4.3.15 LIST OF CHARACTERIZATION METHODS

The overview of all characterization methods is presented in Table 4.

Table 4 Compilation of methods used for characterization of prepared materials

[A]	Particle size (particle size analysis), surface topography and cross-section morphology (scanning electron microscopy), surface roughness (tactile profilometry), phase composition (X-ray diffraction), chemical composition (Raman spectroscopy), optical bandgap width (diffuse reflectance spectroscopy), MB degradation (UV-Vis spectroscopy)
[B]	Surface topography and cross-section morphology (scanning electron microscopy), surface roughness (optical profilometry), chemical composition (Raman spectroscopy)
[C]	Surface topography and cross-section morphology (scanning electron microscopy), surface roughness (optical profilometer), chemical composition (Raman, electron paramagnetic resonance spectroscopy), MB degradation (UV-Vis spectroscopy)
[D]	Particle aggregation in feedstock suspensions (particle size analysis), suspension stability (sedimentation test), surface topography and cross-section morphology (scanning electron microscopy), phase composition (X-ray diffraction), chemical composition (Raman spectroscopy), mechanical integrity (cross-cut test)
[E]	Phase composition (X-ray diffraction), morphology (transmission electron microscopy), particle size (particle size analysis), thermal stability of oxygen-rich groups (differential scanning calorimetry and thermogravimetric analysis), optical bandgap width (diffuse reflectance spectroscopy), chemical composition (X-ray photoelectron, electron paramagnetic resonance, infrared, and Raman spectroscopy), net charge (pH_{PZC}), MB degradation (UV-Vis spectroscopy, total organic carbon), bacteria-killing (colony forming unit assay)

5 KEY FINDINGS

The concluding remarks include the investigated results of TiO_2 modification with H_2O_2, the development of low-pressure cold spraying strategies for the deposition of oxygen-rich TiO_2 and careful examination of the influence of delivered thermal energy on deposited sol-gel materials.

5.1 INFLUENCE OF H_2O_2 MODIFICATION

In this thesis, different impacts of TiO_2 modification with H_2O_2 on its structure and activity are observed. The effects of oxygen-rich groups include:

- Narrowing the optical bandgap energy of the TiO_2 by forming midgap states (Urbach tail) so TiO_2 can be potentially activated by visible light.
- Blocking the formation of 3D structures (during bottom-up synthesis) which inhibits crystallization and may lead to the formation of the layered structure (2D).
- Improving the adsorption process through the formation of an oppositely charged TiO_2 surface, which attracts pollution.
- Creating an oxidative environment for the oxidation of pollutants or bacteria (ROS analysis) which provides the activity in the darkness.
- Depending on the type, promoting short-term activity (superoxo groups) or long-term activity (peroxo groups).

5.2 INNOVATIVE APPROACHES TO OXYGEN-RICH COATINGS

The other key aspect of this thesis is to provide the procedure for oxygen-rich coating formation using low-pressure cold spraying with feedstock in various forms.

- Spraying of sol-gel powder is possible without an inert atmosphere or vacuum. Changing spraying parameters may reduce unwanted phase transformations and enable the preservation of oxygen-rich groups (possible issue 2.2.1). Application of appropriate feeder excludes clogging of feeding system (possible issue 2.2.3)
- Spraying of sol-gel suspension may be beneficial. The liquid phase in the wet gel consumes excessive thermal energy on liquid evaporation so oxygen-rich groups can be preserved (possible issue 2.2.1)
- Spraying of aerosolised sol-gel suspension may improve liquid evaporation which combats coating disintegration caused by trapping residual H_2O_2 in the coating

(possible issue 2.3.2), providing coating homogeneity and presence of oxygen-rich groups (possible issue 2.2.1).

5.3 THERMAL DRYING OF SOL-GEL MATERIAL BY LPCS

The spraying temperature does indeed influence TiO_2 particle bonding and the resulting coating microstructure. Discussion of the thermal energy effects on coatings sprayed from sol-gel materials relies on liquid evaporation **[B]**.

The suggested mechanism (Figure 10) was developed because wet gels differ from the most commonly used particle-solvent systems. The sol-gel particle consists of a condensed core and a partially condensed shell which behave differently in the gas stream. The dense particles result in dense coating with a well-developed profile while the porous shells can be preserved to form multi-tier roughness on generally flatter coatings.

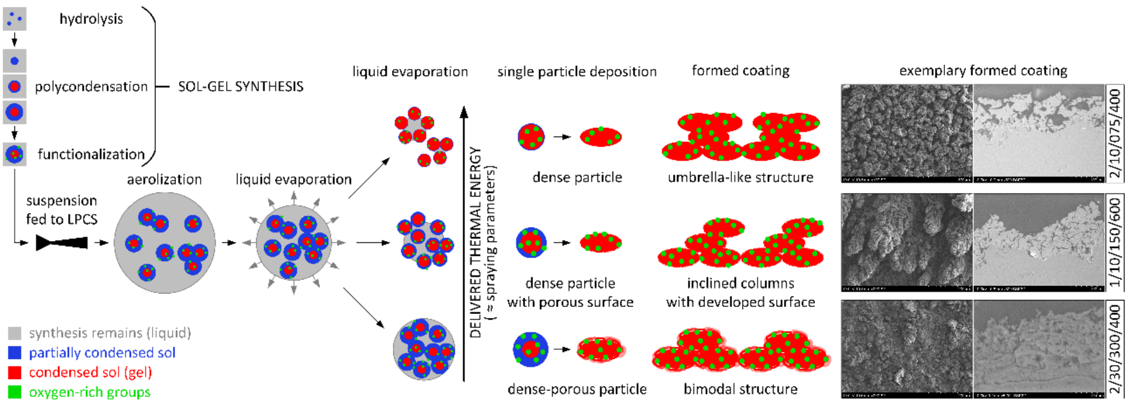

Figure 10 Scheme of the proposed mechanism for suspension low-pressure cold spraying of oxygen-rich TiO_2 **[B]**

Insufficient thermal energy in coatings sprayed from aerosolized suspension **[D]** resulted in pancake-like coatings, while higher energy improved particle bonding and coating density. Coatings applied using the internal feed system exhibited uniform bonding due to the rapid evaporation of the liquid phase, causing mechanical interlocking of the particles. In contrast, the external feed system produced thicker coatings, which reduced the influence of the underlying grit-blasting texture. While increased thermal energy promoted densification, it also led to the formation of network-like cracks within the coatings.

5.4 MAIN CONCLUSIONS

The major results can be summed up with regard to each study:

Table 5 Compilation of main findings

[A]	The oxygen-rich TiO_2 powder produced using the aqueous peroxo-titania sol-gel route without thermal treatment is characterized by narrowed bandgap width through the formation of midgap states (2.2 eV) and lack of powder annealing sustains it in an amorphous state. The characteristic of oxygen-rich TiO_2 coatings produced from oxygen-rich TiO_2 powder using low-pressure cold spray depends on carrier gas temperature: – With 600 °C: 25–50 µm thick, porous anatase coating, rough at the surface, weighting 35 ± 9 mg, with bandgap energy 3.1 eV was formed. – With 200 °C: 2–3 µm thin, discontinuous amorphous coating weighing less than 1 mg with bandgap energy 2.8 eV was formed. Both coatings exhibit visible light activity in methylene blue degradation (17 % and 3.1 % degradation in 6 h for coating sprayed using carrier gas preheated to 600 °C and 200 °C). Feedstock powder changes upon spraying. Structure crystallization and only partial preservation of oxygen-rich groups in coatings are observed.
[B]	Application of liquid feedstock for spraying oxygen-rich TiO_2 coatings using low-pressure cold spray reduces the material changes upon spraying: – In most of the coatings, the oxygen-rich structure is preserved. – For coatings sprayed with the scanning step of 1 mm, the standoff distance of 10 mm, the traverse speed of 150 mm/min and the carrier gas temperature of 600 °C, delivered thermal energy-induced partial crystallization but despite this oxygen-rich groups are partially preserved. 50 µm thick coatings can be deposited in a single pass. The most uniform coatings are produced using the standoff distance of 30 mm.

	Application of sol-gel materials (consisting of partially condensed sol and condensed gel) produces complex structures after deposition. The residues containing H_2O_2 which are trapped in the coating cause coating disintegration shortly after coating deposition due to H_2O_2-containing bubble collapse.
[C]	The spraying of oxygen-rich TiO_2 suspension with parameters preserving oxygen-rich amorphous structure selected based on **[B]** is reproducible and provides the same chemical and optical properties of coating as of powders **[A]**. Experimenting with spraying oxygen-rich TiO_2 coatings according to plan (Taguchi method) provides: – The process parameters for spraying optimal E_g and SA values (the scanning step of 2 mm, the traverse speed of 150 mm/min and the carrier gas temperature of 600 °C). – ANOVA showed that the most influential spraying parameter is carrier gas temperature with an effect of 53.81 % and 56.62 % on the E_g and SA values, respectively. The least significant parameter is traverse speed with a contribution of 15.69 % on E_g. The coating prepared with optimal parameters (thickness 5–25 μm, mass 3.4 mg) possesses the expected characteristics (E_g and SA of the optimal coating were 2.39 eV and 2 553 369 μm^2, respectively). It exhibits visible light activity (14.1 % degradation in 6 h). The residues containing H_2O_2 which are trapped in the coating cause coating disintegration shortly after coating deposition due to H_2O_2-containing bubble collapse.
[D]	The spraying of aerosolized oxygen-rich TiO_2 suspension causes full evaporation of H_2O_2-containing synthesis residues which preserve the structure of coatings. The oxygen-rich TiO_2 coatings produced from oxygen-rich TiO_2 aerosolised suspension using low-pressure cold spray retain an oxygen-rich structure and form thick coatings (20 to 80 μm).

- The internal feed enhances liquid evaporation and causes loosely bound particles to be observed on the coating similar to **[A]**.
- The external feed provides surface uniformity.

Coating deposition in a single pass contributes to maintaining amorphous structure, while 3 passes cause partial crystallisation to anatase.

The initial characteristics of suspension changed with respect to mixing times of suspension before and after modification:

- The addition of H_2O_2 to TiO_2 suspension mixed for 48 h causes the formation of a jelly-like structure, not possible to be aerosolised.
- Prolonged mixing after the addition of H_2O_2 causes the decomposition of oxygen-rich groups.

[E] More detailed research on oxygen-rich TiO_2 powder, as in [A], shows that:

- Chemical and structural changes in the titania composition are introduced by the incorporation of additional oxygen in the whole volume.
- Modifications narrows the bandgap width through the formation of midgap states (2.2 eV).
- Lack of powder annealing sustains the produced powder in an amorphous state, which can be used for low-temperature low-energy deposition techniques (such as low-pressure cold spray described in [A-D]).

H_2O_2-modified TiO_2 showed visible light photo-activity and dark activity for methylene blue oxidation and bacteria killing:

- The adsorption is facilitated by the low pH_{pzc} of the material (3.2).
- The visible light activity is caused by photocatalytic oxidation and photocatalysis leading to degradation of 75% of MB in 8 h in zero-order kinetics, k = 0.027 (mg/L) min^{-1}, and bacteria ($MBC_{enteroccocus}$ = 750 µg/mL, MBC_{coli} = 375 µg/mL (6 log_{10} CFU/mL removal)).
- Dark activity resulted from the unique chemical composition of the studied material (presence of superoxo groups) which enabled the oxidation of pollutants degrading 36% of MB in 8 h in zero-order kinetics, k = 0.014 (mg/L) min^{-1}, and bacteria ($MBC_{enteroccocus}$ > 1500 µg/mL, MBC_{coli} = 1500 µg/mL (6 log_{10} CFU/mL removal)).

6 OUTLOOK

Modern photocatalytic materials are meant to provide multi-faceted activity. The presented research can be extended with new types of pollution including antibiotics, microplastics or personal care products. Additionally, the degradation of air pollution may be addressed, so that an integrated environmental strategy can be developed.

Because in dark degradation processes, oxygen-rich groups were partially consumed, the regeneration strategies with H_2O_2 or laser may be investigated. Such procedures may be studied particularly for coatings because the application of a supported catalyst offers easy separation.

Electron paramagnetic resonance spectroscopy may be employed for in-situ detection of free radicals and reactive oxygen species (•OH, O_2^{-}•, •OOH) during degradation reactions, which are popular for the specification of degradation pathways [18][19].

Microstructures obtained from low pressure cold spraying of aerosolised suspensions may be promising for depositing other materials. For instance, bone-like structures obtained in **[E]** can be beneficial in the process of formation of hydroxyapatite coatings.

In-flight particle characteristics can be studied more extensively, too. Information about the exact temperature and velocity could improve the deposition efficiency of powders, suspensions and aerosolised suspensions, and provide data to understand the spraying of partially condensed sol-gel materials. Computational fluid dynamics modelling would require more detailed materials information which can be accessed from density functional theory.

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8 LIST OF TABLES AND FIGURES

9 SCIENTIFIC ACHIEVEMENTS

9.1 SUMMARY OF SCIENTIFIC ACHIEVEMENTS

9.1.1 OTHER ARTICLES

The skills and techniques used to develop this work were also valuable in preparing 10 published and 2 currently proceeded scientific publications (Table 6).

Table 6 Compilation of metadata of other scientific articles

[1]	K. Płatek, L. Łatka, **A. Gibas**, A. Lewińska, M. Michalska, P. Sokołowski, Deposition of defect-rich titanium oxide coatings using Ar/H_2 powered suspension plasma spraying, submitted for peer-review, 2025
[2]	**A. Gibas**, A. Baszczuk, M. Jasiorski, M. Winnicki, W. Seremak, Alloying of composite Cu-Al cold sprayed coatings by near-infrared radiation, submitted for peer-review, 2025
[3]	A. Szukalska, A. Żak, E. Chrzumnicka, **A. Gibas**, A. Baszczuk, J. Myśliwiec, Crystallization-driven tuneable lasing of perylene doped into the nematic liquid crystal, Giant, 2024, DOI: 10.1016/j.giant.2024.100279, IF: 5.4 (2023)
[4]	E. Kociołek-Balawejder, **A. Gibas**, A. Baszczuk, M. Jasiorski, I. Jacukowicz-Sobala, Transformation of CuO and Cu_2O particles into Cu_xS within the polymeric matrix of anion exchangers, and its structural and morphological implications, Reactive & Functional Polymers, 2023, DOI: 10.1016/j.reactfunctpolym.2023.105734, IF: 4.5 (2023)
[5]	M. Winnicki, A. Baszczuk, **A. Gibas**, M. Jasiorski, Experimental study on aluminium bronze coatings fabricated by low pressure cold spraying and subsequent heat treatment, Surface & Coatings Technology, 2023, DOI: 10.1016/j.surfcoat.2023.129260, IF: 5.3 (2023)
[6]	I. Jacukowicz-Sobala, A. Ciechanowska, E. Kociołek-Balawejder, **A. Gibas**, A. Zakrzewski, Photocatalytically-assisted oxidative adsorption of As(III) using sustainable multifunctional composite material – Cu_2O doped anion exchanger, Journal of Hazardous Materials, 2022, DOI: 10.1016/j.jhazmat.2022.128529, IF: 13.6 (2022)
[7]	W. Seremak, A. Baszczuk, M. Jasiorski, **A. Gibas**, M. Winnicki, Photocatalytic activity enhancement of low-pressure cold sprayed TiO_2 coatings induced by

	long-term water vapour exposure, Journal of Thermal Spray Technology, 2021, DOI: 10.1007/s11666-021-01244-5, IF: 2.8 (2021)
[8]	**A. Gibas**, J. Gąsiorek, Perspective of sol-gel hydrophobic silica deposited using low-pressure cold spray and ultrasonic atomizing for automotive coatings, Journal of TransLogistics, ISSN 2450-5870, 2021, DOI: 10/JoT2021_08
[9]	M. Winnicki, **A. Gibas**, A. Baszczuk, M. Jasiorski, Low pressure cold spraying of TiO_2 on acrylonitrile butadiene styrene (ABS), Surface & Coatings Technology, 2021, DOI: 10.1016/j.surfcoat.2020.126717, IF: 4.9 (2021)
[10]	**A. Gibas**, A. Baszczuk, M. Jasiorski, M. Winnicki, Prospects of low-pressure cold spray for superhydrophobic coatings, Coatings, 2019, DOI: 10.3390/coatings9120829, IF: 2.4 (2019)
[11]	**A. Gibas**, M. Gnych, Tlenkowe materiały proszkowe otrzymywane metodą zol-żel jako atrakcyjny substrat do nanoszenia powłok techniką niskociśnieniowego natryskiwania na zimno, Wydawnictwo Naukowe TYGIEL, 2019, ISBN: 978-83-65932-70-9, http://bc.wydawnictwo-tygiel.pl/publikacja/B748B37A-5C63-7A37-CE6D-B000648E2D2E
[12]	V. Hoppe, **A. Gibas**, W. Grzegorczyk, M. Małecki, M. Hasiak, Experimental study of Fe-Ni-Ti-Cr system, Interdisciplinary Journal of Engineering Sciences, 2019, http://ijes.pwr.wroc.pl/Vol-VII/No-1/VII-p1-9_Hoppe.pdf

9.1.2 CONFERENCE CONTRIBUTIONS

The research presented in the thesis was also supported by 10 contributions (6 oral presentations and 4 posters) related to the thesis delivered at 8 international and 2 domestic scientific conferences (Table 7).

Table 7 Compilation of conference presentations

[a]	ORAL PRESENTATION: **A. Gibas**, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, Peroxide gel route: photocatalytic activity of TiO_2 in visible light and darkness, International Sol-Gel Conference, https://premc.org/solgel2024, Berlin, Germany, 1-6.09.2024.
[b]	ORAL PRESENTATION: **A. Gibas**, M. Winnicki, A. Baszczuk, Aerosol-assisted low-pressure cold spraying of TiO_2 suspension, Les Rencontres

Internationales de la Projection Thermique: 11 RIPT, https://go.fzj.de/ript2024, Jülich, Germany, 5-7.06.2024.

[c] POSTER: **A. Gibas**, W. Seremak, Thermal spraying of sol-gel materials, Les Rencontres Internationales de la Projection Thermique: 11 RIPT, https://go.fzj.de/ript2024, Jülich, Germany, 5-7.06.2024.

[d] ORAL PRESENTATION: **A. Gibas**, A. Baszczuk, All the shades of H_2O_2-sensitized TiO_2, Interdisciplinary Doctoral Symposium: Rajd Doktoranta 2024, Przesieka, Poland, 17-19.05.2024.

[e] ORAL PRESENTATION: **A. Gibas**, I. Jacukowicz-Sobala, A. Baszczuk, M. Jasiorski, A. Ciechanowska, E. Dworniczek, A. Seniuk, A. Lewińska, Photocatalytic and antibacterial properties of H_2O_2-sensitized TiO_2, 2nd International Conference an Advanced Materials for Bio-Related Applications, AMBRA 2024, https://ambra.pwr.edu.pl, Wroclaw, Poland, 19-23.05.2024.

[f] POSTER: **A. Gibas**, M. Winnicki, Towards sustainable coatings: cold spray additive manufacturing, The Fourth International Conference on Intelligent Systems in Production Engineering and Maintenance, ISPEM 2023, https://ispem.pwr.edu.pl, Wroclaw, Poland, 13-15.09.2023.

[g] POSTER: **A. Gibas**, A. Baszczuk, Effect of modification of TiO_2 powders using H_2O_2 on photocatalytic activity, original title: Wpływ modyfikacji proszków TiO_2 używając H_2O_2 na aktywność fotokatalityczną, XVI Kopernikańskie Seminarium Doktoranckie, Wydział Chemii Uniwersytet Mikołaja Kopernika w Toruniu, Toruń, 29-30.06.2023

[h] ORAL PRESETNATION: **A. Gibas**, M. Winnicki, A. Baszczuk, M. Jasiorski, Low pressure cold sprayed TiO_2 suspension coatings for visible-light photocatalytic applications, 6th International Thermal Spraying and Hardfacing Conference, ITSHC 2022: progress, application and modern technologies, https://www.itshc.pwr.edu.pl, Wroclaw, Poland, 22-23.09.2022.

[i] ORAL PRESENTATION: **A. Gibas**, A. Baszczuk, M. Jasiorski, M. Winnicki, Morphology and structure of selected low-pressure cold sprayed TiO_2 coatings analysed for working as photocatalysts, 10th edition of Les Rencontres Internationales de la Projection Thermique, 10 RIPT, https://www.fz-juelich.de/en/iek/iek-1/news/news/10ript-2022-from-june-1st-to-3rd-in-julich, Jülich, Germany, 1-3.06.2022.

[j] POSTER: **A. Gibas**, J. Gąsiorek, Ultrasonic atomizing as a feasible method of sol-gel coatings fabrication, 7th ISGS Online Summer School: Hybrid Materials: cutting edge applications, Castelló de la Plana, Spain, 2-3.09.2020.

9.1.3 OTHER SCIENTIFIC EVENTS

The author of this thesis actively participated in organizing international scientific events:

- Conference secretary and editor of the book of abstract for the 2nd International Conference on Advanced Materials for Bio-Related Applications (AMBRA2024)
  Contribution: event coordination, communications with keynote speakers, organizing conference materials, registration and participant management, organizing committee management, developing promotional materials, on-site support, best poster and best short communication contest management

- Organizing committee member for the 6th International Thermal Spraying and Hardfacing Conference (ITSHC2022)
  Contribution: registration and participant management, on-site support, entertainment organization, developing promotional materials

9.1.4 GRANTS

The author of this thesis contributed to the following scientific projects:

- Sonic Jet - a precision printer for producing flexible electronics (in Polish: Sonic Jet - precyzyjna drukarka do wytwarzania elastycznej elektroniki), Lider 013/L/0009/20, grant type: NCBR, budget: 1 498 875.00 PLN, grant manager: dr. hab. inż. Marcin Winnicki
  Contribution: Atomic force microscope analysis of silver traces

- Multi-scale numerical modeling of condensation and mechanical properties of organosilica-based aerogels, grant type: OPUS-LAP, NCN, budget: 1 243 624.00 PLN, grant manager: Leader: dr hab. inż. Jakub Maksymilian Gac, Warsaw University of Technology, Partner: mgr. inż. Bartosz Babiarczuk, Wroclaw University of Science and Technology, Foreign partner: prof. Barbara Milow, The German Aerospace Center
  Contribution: Raman spectroscopy analysis of silica aerogel formation

9.2 SCIENTIFIC CONTRIBUTIONS

9.2.1 AUTHOR CONTRIBUTION

The author of this thesis made a significant impact on the research, which included the following contributions:

- **Conceptualization:** Proposing the research idea and framework, formulating hypotheses and establishing experimental objectives.
- **Methodology:** Proposing methods and tools for conducting research. Designing and carrying out syntheses and modification procedures. Refining the coating preparation setup for spraying powders, suspensions and aerosolized suspensions. Selecting key parameters for the spraying process.
- **Formal analysis:** Interpreting all analysed data in the context of the study. Support in the statistical analysis.
- **Investigation:** Conducting experiments to generate primary data, XRD, Raman and IR spectroscopies, DRS, PSA, sedimentation, SEM, optical profilometry, cross-cut test, DSC/TGA, UV-Vis spectroscopy during dye degradation. Managing laboratory activities.
- **Resources:** Acquiring materials and small laboratory equipment. Managing access to datasets, computational tools, or relevant facilities.
- **Writing – Original Draft:** Drafting all initial manuscripts.
- **Writing – Review & Editing:** Revising the manuscript in response to feedback from coauthors and reviewers, polishing language, structuring and formatting.
- **Visualization:** Creating illustrations and schematics to explain concepts or methodologies, and generating figures, graphs, and tables to present data.
- **Project Administration:** Coordinating tasks, timelines, and responsibilities among coauthors. Managing communication.
- **Funding Acquisition:** Receiving an internal research grant for EPR and XPS measurements, precursors and substrates (Internal mini-grant for PhD students).

9.2.2 COAUTHORS' STATEMENTS

The statements of the coauthors are included on the following pages.

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DECLARATION OF THE COAUTHOR OF DOCTORAL CANDIDATE

Oświadczam, że w niniejszych publikacjach:
I declare that in the publications:

[A] A. Gibas, A. Baszczuk, M. Jasiorski, M. Winnicki, D. Ociński, Preparation of visible-light active oxygen-rich TiO_2 coatings using low pressure cold spraying, Coatings. (31.03.2022), https://doi.org/10.3390/coatings12040475.

[B] A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, Influence of spraying parameters on microstructure of oxygen-rich TiO_2 coatings deposited using suspension low-pressure cold spray, Surf. Coatings Technol. (14.02.2023), https://doi.org/10.1016/j.surfcoat.2023.129321.

[C] A. Gibas, A. Baszczuk, M. Jasiorski, A. Lewińska, M. Winnicki, Low-pressure cold spraying of suspension TiO_2 in a single pass – Process optimization, Surf. Coatings Technol. (19.08.2023), https://doi.org/10.1016/j.surfcoat.2023.129933.

[D] A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, Aerosol-assisted low-pressure cold spraying of TiO_2 suspension, Surf. Coatings Technol. (26.12.2024), https://doi.org/10.1016/j.surfcoat.2024.131715.

[E] A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, H_2O_2-sensitized titania with activity under visible light and in the dark, J. Environ. Chem. Eng. (30.08.2024), https://doi.org/10.1016/j.jece.2024.113975.

mój udział polegał na nadzorowaniu prac badawczych, analizie, dyskusji wszystkich wyników i końcowej wersji manuskryptów oraz prac redakcyjnych.
my contribution involved supervising the research work, analyzing and discussing all results, as well as reviewing the final version of the manuscripts and editorial work.

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mój udział polegał na deponowaniu powłok.
my contribution involved depositing coatings.

[B] A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, Influence of spraying parameters on microstructure of oxygen-rich TiO_2 coatings deposited using suspension low-pressure cold spray, Surf. Coatings Technol. (14.02.2023), https://doi.org/10.1016/j.surfcoat.2023.129321.

mój udział polegał na deponowaniu powłok oraz przygotowaniu stanowiska do natrysku zawiesin we współpracy z Doktorantką.
my contribution involved depositing coatings and preparing the setup for suspension spraying in collaboration with the Doctoral Candidate.

[C] A. Gibas, A. Baszczuk, M. Jasiorski, A. Lewińska, M. Winnicki, Low-pressure cold spraying of suspension TiO_2 in a single pass – Process optimization, Surf. Coatings Technol. (19.08.2023), https://doi.org/10.1016/j.surfcoat.2023.129933.

mój udział polegał na deponowaniu powłok i statystycznej analizie danych.
my contribution involved depositing coatings and performing statistical data analysis.

[D] A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, Aerosol-assisted low-pressure cold spraying of TiO_2 suspension, Surf. Coatings Technol. (26.12.2024), https://doi.org/10.1016/j.surfcoat.2024.131715.

mój udział polegał na deponowaniu powłok oraz przygotowaniu stanowiska do natrysku aerozoli zawiesin we współpracy z Doktorantką.
my contribution involved depositing coatings and preparing the setup for aerosol suspension spraying in collaboration with the Doctoral Candidate.

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[D] A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, Aerosol-assisted low-pressure cold spraying of TiO_2 suspension, Surf. Coatings Technol. (26.12.2024), https://doi.org/10.1016/j.surfcoat.2024.131715.

[E] A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, H_2O_2-sensitized titania with activity under visible light and in the dark, J. Environ. Chem. Eng. (30.08.2024), https://doi.org/10.1016/j.jece.2024.113975.

mój udział polegał na wykonaniu pomiarów przekrojów powłok przy użyciu skaningowego mikroskopu elektronowego.
my contribution involved performing cross-section measurements of coatings using a scanning electron microscope.

Wrocław 03.03.2025
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I declare that in the publication:

[A] A. Gibas, A. Baszczuk, M. Jasiorski, M. Winnicki, D. Ociński, Preparation of visible-light active oxygen-rich TiO_2 coatings using low pressure cold spraying, Coatings. (31.03.2022), https://doi.org/10.3390/coatings12040475.

mój udział polegał wykonaniu pomiarów DRS i przygotowaniu stanowiska do pomiarów fotokatalitycznych.
my contribution involved performing DRS measurements and preparing the setup for photocatalytic measurements.

Wrocław, 06.03.25
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mój udział polegał na analizie testów fotokatalitycznych i dyskusji wyników w kontekście możliwych mechanizmów rozkładu błękitu metylenowego. Ponadto brałam udział w przygotowaniu tekstu artykułu.
my contribution involved analyzing photocatalytic tests and discussing the results in the context of possible methylene blue degradation mechanisms. Additionally, I participated in the preparation of the text of manuscript

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mój udział polegał na wykonywaniu części pomiarów fotokatalitycznych.
my contribution involved performing part of the photocatalytic measurements.

Wrocław
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[C] A. Gibas, A. Baszczuk, M. Jasiorski, A. Lewińska, M. Winnicki, Low-pressure cold spraying of suspension TiO_2 in a single pass – Process optimization, Surf. Coatings Technol. (19.08.2023), https://doi.org/10.1016/j.surfcoat.2023.129933.

[E] A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, H_2O_2-sensitized titania with activity under visible light and in the dark, J. Environ. Chem. Eng. (30.08.2024), https://doi.org/10.1016/j.jece.2024.113975.

mój udział polegał na zarejestrowaniu oraz symulacji widm EPR.
my contribution involved recording and simulating EPR spectra.

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[E] A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, H_2O_2-sensitized titania with activity under visible light and in the dark, J. Environ. Chem. Eng. (30.08.2024), https://doi.org/10.1016/j.jece.2024.113975.

mój udział polegał na zaplanowaniu testów inaktywacji bakterii i dyskusji wyników.
my contribution involved planning bacterial inactivation tests and discussing the results.

Wrocław 21/02/2025
(miejscowość, data / place, date)

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mój udział polegał na wykonaniu testów inaktywacji bakterii oraz analizie wykonanych pomiarów.
my contribution involved performing bacterial inactivation tests and analyzing the measurements.

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10 REPRINTS

This section provides the appended publications.

[A]	A. Gibas, A. Baszczuk, M. Jasiorski, M. Winnicki, D. Ociński, **Preparation of visible-light active oxygen-rich TiO_2 coatings using low pressure cold spraying**, Coatings, 31.03.2022, DOI: 10.3390/coatings12040475.
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[D]	A. Gibas, M. Winnicki, A. Baszczuk, M. Jasiorski, **Aerosol-assisted low-pressure cold spraying of TiO_2 suspension**, Surface & Coatings Technology, 26.12.2024, DOI: 10.1016/j.surfcoat.2024.131715.
[E]	A. Gibas, A. Baszczuk, I. Jacukowicz-Sobala, A. Ciechanowska, M. Jasiorski, E. Dworniczek, A. Seniuk, A. Lewińska, **H_2O_2-sensitized titania with activity under visible light and in the dark**, Journal of Environmental Chemical Engineering, 30.08.2024, DOI: 10.1016/j.jece.2024.113975. + Supplementary materials 1 + Supplementary materials 2