

Study of photocatalytic systems based on polymer and metal nanoparticles for hydrogen production

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Zásady pro vypracování

Produkce vodíku ve fotokatalytické reakci ze slunečního záření má zásadní význam při ekologicky čisté tvorbě energie a jejím uskladnění. Většina solárních panelů současnosti je založena na monokrystalickém křemíku, který je však poměrně drahý vzhledem k jeho využití při výrobě elektronických čipů. Hlavním posláním této diplomové práce bude najít náhradu za křemík v podobě levnějšího polymerního substrátu, který by byl vhodný pro nanosení kovových nanočástic (např. Au, Ag, Ga) a grafenu tak, aby jej bylo možné použít při fotokatalytické produkci vodíku při vhodném ozáření z oblasti UV, případně VIS. Samotný mechanismus produkce vodíku může využívat polovodičový efekt tvorby páru elektron-díra a plazmonické zesílení pole, jak je popsáno v článku Bartošík et. al.

Dílčí cíle:

- Připravte rešerši uvedené problematiky s ohledem na diskuzi vhodných polymerů a výběr kovových nanočástic.
- Provedte přípravu vhodných polymerních substrátů na základě výsledků rešerše a zkušeností pracoviště.
- Provedte depozici kovových nanočástic (z koloidu nebo napařovacími technologiemi), které následně zakryjte grafenem, pro efektivní elektronické propojení částic.
- Analyzujte povrch vhodnými technikami (např. AFM, SEM, XPS, Ramanova spektroskopie).
- Provedte fotokatalytické experimenty a vyhodnoťte produkci vodíku.
- Diskutujte získané výsledky.

Forma zpracování diplomové práce: **tištěná/elektronická**
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ABSTRAKT

Tato práce si klade za cíl prozkoumat možnost použití vhodného polymerního substrátu jako nosiče fotokatalytických nanočástic na bázi oxidu galia/galia nanesených metodou fyzikální depozice z plynné fáze a následně zhodnotit efektivitu takového systému měřením množství vodíku vzniklého při fotokatalytickém štěpením vody na těchto substrátech. Dále byla zkoumána možnost modifikace povrchových vlastností substrátů pomocí metody breath figures, přičemž byla pro tento účel sestrojena atmosférická komora vybavena senzorovou jednotkou na bázi Arduina pro zajištění definovaných experimentálních podmínek. Celkem byly použity dva typy polymerních substrátů: polykaprolaktonový film s udělenou porozitou a polyetheretherketonové pláty hodící se pro vyšší depoziční teploty. Nanesené nanočástice oxidu galia/galia byly úspěšně detekovány pomocí vysokorozlišovací rastrovací elektronové mikroskopie umožněné nanesením vrstvy grafenu pro účinnou disipaci náboje. Fotokatalytické experimenty ukázaly, že značné množství vodíku vzniká z nativních polymerních vzorků (bez přítomného fotokatalyzátoru) ve vodném roztoku methanolu, a to pravděpodobně v důsledku fotodegradace polymerního povrchu vyvolané UV zářením. Dále bylo zjištěno, že příspěvek naneseného oxidu galia/galia k výtěžku vodíku byl v porovnání s čistými polymerními substráty pouze minimální.

Klíčová slova: fotokatalýza, oxid galia, breath figures, grafen, polykaprolakton, polyetheretherketon

ABSTRACT

This thesis aims to investigate the feasibility of employing a suitable polymer substrate as a carrier for photocatalytic gallium oxide/gallium nanoparticles deposited via physical vapour deposition, and to evaluate the photocatalytic performance of such a system by measuring hydrogen gas yields during the photocatalytic water splitting reaction. Furthermore, the study examined the possibility of tailoring the substrate's surface properties via breath figures patterning in a custom atmospheric chamber equipped with an Arduino-based sensor unit to ensure defined experimental conditions. Two types of polymer substrates were employed: a breath figures patterned polycaprolactone film and polyetheretherketone sheets suitable for higher deposition temperatures. The deposited gallium oxide/gallium nanoparticles were successfully detected using high-resolution SEM imaging facilitated by a graphene monolayer for effective charge dissipation. Photocatalytic experiments revealed substantial hydrogen evolution from native, photocatalyst-free polymer samples in an aqueous methanol solution, likely due to the UV-induced photodegradation of the polymer surface. In comparison, the contribution of the deposited gallium oxide/gallium nanoparticles to overall photocatalytic performance was found to be minimal.

Keywords: photocatalysis, gallium oxide, breath figures, graphene, polycaprolactone, polyetheretherketone

I would like to thank doc. Ing. Miroslav Bartošík, Ph.D. for the mentorship, patience and availability throughout the preparation of this thesis.

I hereby declare that the print version of Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

“A man who dares to waste one hour of time has not discovered the value of life.”

Charles Darwin

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INTRODUCTION

In recent decades, there has been an incentive to search for alternative energy sources, fuelled by the demand for sustainable technology providing not only clean and affordable energy, but also the possibility of efficient and long-term energy storage. Based on these requirements, hydrogen-based solutions seem the most promising, as they deliver clean energy free of harmful byproducts while allowing indefinite storage in tanks for use when needed.

Apart from traditional hydrogen production methods like steam methane reforming and electrolysis (including solar electrolysis), the focus has recently shifted towards photocatalytic systems that produce hydrogen through oxidation-reduction reactions, facilitated by electron-hole pairs generated in a semiconductor-type catalyst upon exposure to electromagnetic irradiation (preferably solar). Such systems enable direct energy conversion and minimise energy losses, bypassing the need for an external electrical circuit, as is required in conventional solar electrolysis, which relies on generated electrical current to split water into oxygen and hydrogen. Furthermore, the minimal external energy input could reduce the cost of hydrogen, making it a competitive energy source with current options. If these systems prove viable and capable of large-scale manufacturing, they could decrease the demand for silicon in photovoltaic panels. This would allow greater diversification of material dependencies and reallocation of silicon resources primarily to the semiconductor manufacturing industry.

The theoretical part of this thesis presents recent findings in the field of photocatalytic systems designed for hydrogen production and aims to describe the basic principles of photocatalysis, stemming from solid state physics, photonics and physical chemistry. It also describes approaches for preparing such systems and fundamentally explores the possibility of employing a polymer material as a substrate in a nanoparticle-based photocatalytic system.

The experimental part whether a polymer material could act as a carrier of photocatalytic gallium oxide/gallium nanoparticles deposited via the physical vapour deposition, for which two polymer materials – porous polycaprolactone film and polyetheretherketone sheets – were employed. The possibility of modifying polymer surfaces via breath figures patterning was investigated using a custom atmospheric chamber characterised in terms of its process condition parameters. Ultimately, the photocatalytic performance of systems is evaluated.

I THEORETICAL PART

1 BAND THEORY OF SOLIDS

When matter forms a solid state, the originally discrete energy levels of atoms are split into continuous energy bands, which can overlap (in metals) or exist separately (in semiconductors or insulators). Energy gaps that separate these bands, also referred to as forbidden bands, represent the energy ranges that do not correspond to any allowed electron state. The highest energy band filled with electrons at absolute zero is called the valence band (VB), while the lowest unoccupied energy band is called the conduction band (CB). The forbidden energy band between the lowest point of VB and the highest point of CB is called the bandgap. [1], [2].

If the allowed energy bands are either fully occupied or empty, the material behaves as an insulator, as electrons cannot move freely under an electric field (Figure 1). If one or more bands are partially filled, the material behaves as a metal, with electrons available for conduction. If one or two bands are nearly full or nearly empty, the material behaves as a semiconductor or a semimetal. Whereas a semiconductor becomes an insulator at absolute zero, a semimetal retains some conductivity due to slight band overlap [1].

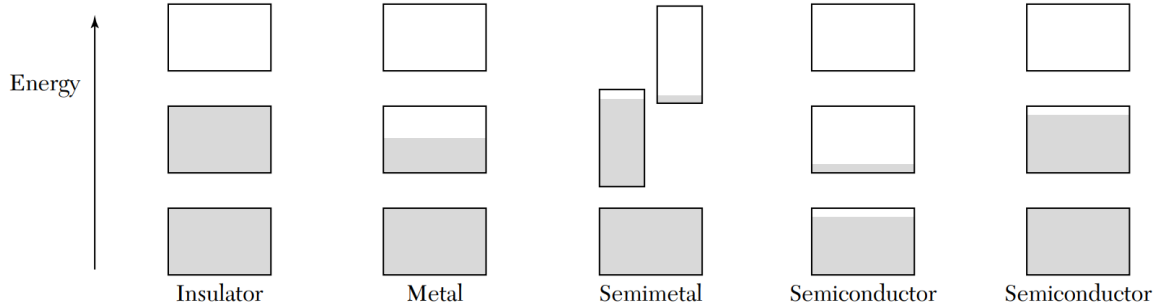


Figure 1 – Electron occupancy of allowed energy bands for an insulator, metal, semimetal and semiconductor [1].

1.1 Fermi-Dirac distribution

At absolute zero, a solid's electrons fill the lowest energy levels in the ground state. Rising temperature causes thermal excitation, enabling electrons to reach higher energy states, with their distribution governed by the Fermi-Dirac distribution function:

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \quad (1)$$

where E is the energy state, relative to the Fermi level E_F divided by the thermal energy of the Boltzmann constant k_B times temperature T . The Fermi level represents the energy at which the probability of finding an electron is 50% at thermodynamic equilibrium; the value of the Fermi level at absolute zero is referred to as the Fermi energy [1], [3].

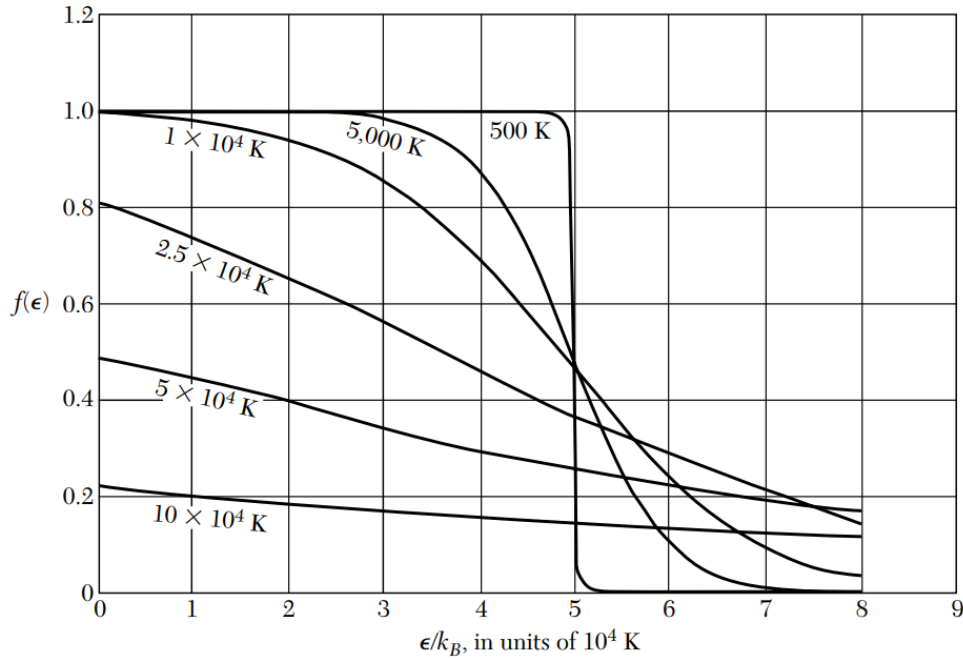


Figure 2 – Fermi-Dirac distribution function at the various temperatures [1].

With decreasing temperatures, the Fermi-Dirac distribution function becomes steeper (see Figure 2), approaching a step function at $T = 0$, where all states below E_F are fully occupied and all states above E_F are empty [1].

1.2 Intrinsic and extrinsic semiconductors

Thermally generated electrons in the CB and holes in the VB are intrinsic charge carriers, contributing to intrinsic conductivity. In an intrinsic semiconductor, the number of electrons equals the number of holes, as each thermally excited electron leaves one hole in the VB,

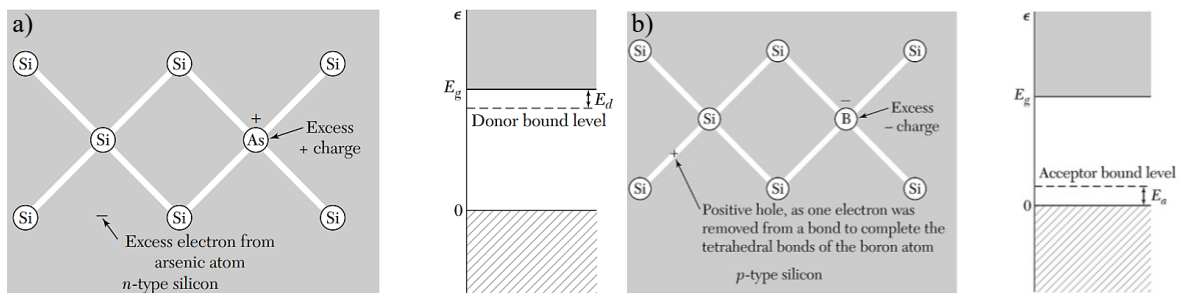


Figure 3 – doping; (a) arsenic impurity in silicon (n-type doping), (b) boron impurity in silicon (p-type doping) [1].

positioning the Fermi level at the bandgap's midpoint. However, doping (deliberate addition of impurities) can alter a semiconductor's electrical properties. Doping introduces additional charge carriers: donors, like arsenic, provide extra electrons, forming n-type silicon, while acceptors, like boron, create additional holes, forming p-type silicon. In n-type doping, extra electrons populate the CB, shifting the Fermi level toward the CB (Figure 3a). Conversely, in p-type doping, additional holes from acceptors shift the Fermi level toward the VB (Figure 3 b) [1].

1.3 p-n junction

A p-n junction is formed within a single crystal on the interface of two distinct regions: a p-type area doped with acceptor impurities, where holes as the primary charge carriers and an n-type area doped with donor impurities, with electrons as the major charge carriers. Far from the junction, the negatively charged ionised acceptor atoms on the p-side are balanced by an equivalent number of free holes, with the positively charged ionised donor atoms on the n-side matched by an equivalent concentration of free electrons. Thus, holes predominate on the p-side and electrons on the n-side (Figure 4a). Due to the tendency to achieve the equilibrium state and uniform charge distribution across the crystal, the holes on the p-side tend to diffuse towards the n-side and electrons on the n-side similarly seek to diffuse towards the p-side. A slight charge transfer, however, results in an excess of negatively charged ionised acceptors on the p-side and positively charged ionised donors on the n-side. This forms a charge double layer with a local electric field (from n-side to p-side) opposing further diffusion and thereby preserving the separation of charge carriers. The electrostatic potential undergoes a sharp change across the double layer (Figure 4b) [1].

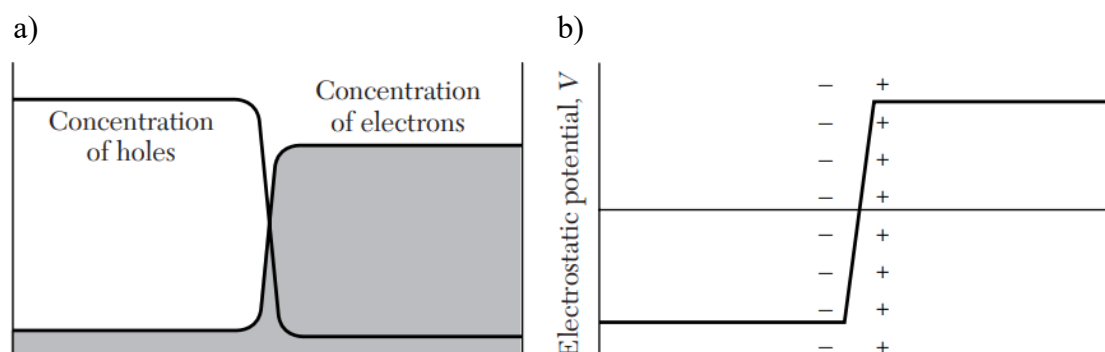


Figure 4 – Unbiased p-n junction; (a) variation of charge carrier concentration, (b) electrostatic potential formed by acceptor (–) and donor (+) ions near the junction [1].

A p-n junction exhibits rectifying behaviour: when a forward bias is applied, a significant current passes through the junction. The reverse bias, however, allows only a minimal current. A p-n junction therefore allows the current to flow predominantly in one direction. In solar cells, the p-n junction facilitates the photovoltaic effect, where photons excite electrons from the valence band to the conduction band, creating an electron-hole pair that is separated by the junction's electric field, driving electrons to the n-type region and holes to the p-type region, generating electrical current [1].

1.4 Schottky barrier

The Schottky barrier is a layer formed at the semiconductor-metal interface, where mobile charge carriers are significantly depleted. Its formation is depicted in Figure 5, showing an n-type semiconductor brought into contact with a metal. Initially, the n-type semiconductor, rich in electrons, has a Fermi level near the conduction band. Upon contact, the differing Fermi levels of the semiconductor and metal align: electrons flow from the n-type semiconductor's CB into the metal, where the Fermi level is lower. Once the Fermi level equilibrates, the electron transfer is stopped. This electron departure creates a depletion region near the metal-semiconductor interface, populated by positively charged donor ions, with excess electrons accumulating in the metal. Similarly to the p-n junction, this charge separation generates an electric field, forming a potential barrier (the Schottky barrier) across the depletion region [1].

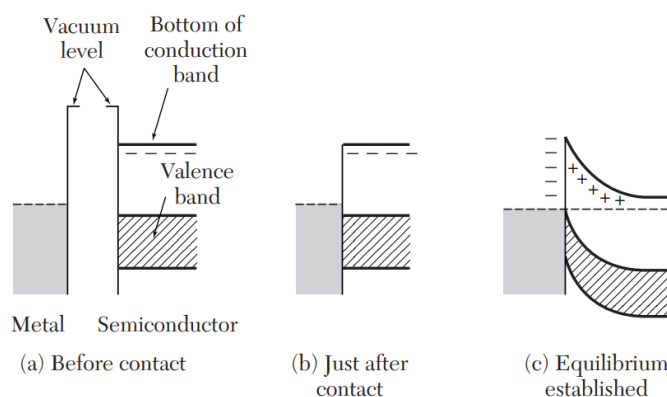


Figure 5 – Schottky barrier on the n-type semiconductor-metal interface with the Fermi level shown as an intermittent line [1].

The Schottky barrier not only enables rectifying behaviour but also enhances the efficiency of charge carrier separation (electrons from holes), thereby reducing their recombination, which is commonly utilised in photocatalytic systems by combining semiconductor materials with metal cocatalysts. [1], [4].

1.5 Direct and indirect absorption process

In addition to thermal excitation of electrons from the valence band (VB) to the conduction band (CB), an electron can be excited by absorbing a photon with energy $h\nu$ equal to or greater than the bandgap energy E_g :

$$h\nu \geq E_g \quad (2)$$

The process of optical absorption in semiconductors depends on whether the bandgap is direct or indirect, resulting in either direct or indirect absorption. Direct optical absorption occurs when the CB minimum and the VB maximum are at the same k -vector in the Brillouin zone (the primitive unit cell in wavevector space). The photon with a threshold energy of:

$$h\nu = E_g \quad (3)$$

excites an electron from VB to CB without a change in the electron's momentum. In indirect optical absorption, the CB minimum and VB maximum are at different k -vectors in the Brillouin zone and thus, a photon alone cannot excite an electron to the CB. The k -vector represents the electron's momentum in the crystal's reciprocal lattice as:

$$\vec{p} = \hbar \vec{k} \quad (4)$$

where $\vec{p}$ is the crystal momentum of an electron and $\hbar$ is reduced Planck's constant. The transition, during which a change in momentum occurs, requires interaction with a phonon (lattice vibration) that matches the k -vector difference between the CB minimum and VB maximum. The absorption threshold energy is therefore greater than the true bandgap:

$$h\nu = E_g + \hbar\Omega \quad (5)$$

where Ω is the frequency of the phonon. At higher temperatures, the phonons can already be present, and the photon is absorbed together with the phonon:

$$h\nu = E_g - \hbar\Omega \quad (6)$$

It is also necessary to define the k -vector as the wavevector of a Bloch wave with magnitude:

$$k = |\vec{k}| = \frac{2\pi}{\lambda} \quad (7)$$

where λ is the wavelength. Both the direct and indirect transition is illustrated in Figure 6 on the following page [1].

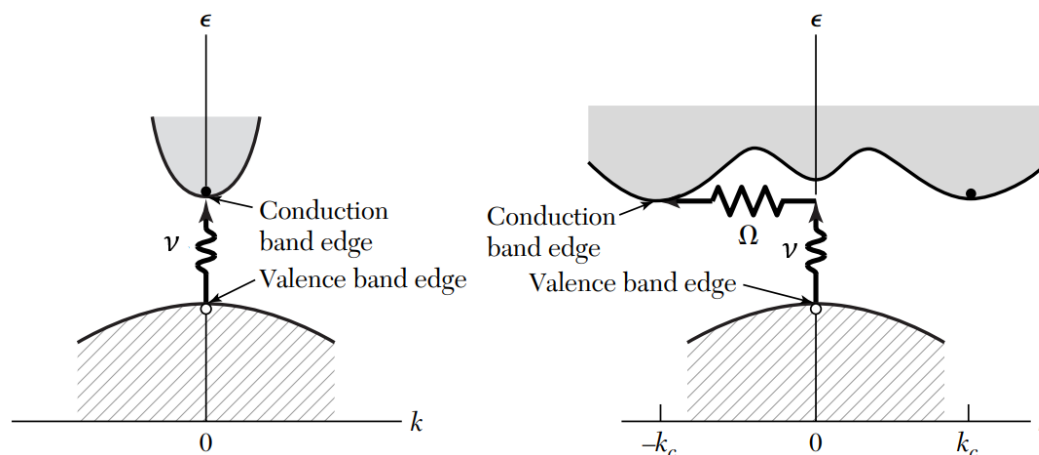


Figure 6 – Energy of electron states in a crystal as a function of the k -vector in reciprocal space (dispersion relation); (a) direct optical absorption; (b) indirect optical absorption. Adapted from [1].

1.6 Semiconductors by bandgap

Based on the size of the bandgap energy, the semiconductors can be classified into three categories: wide-bandgap, intermediate-bandgap and short-bandgap semiconductors. Examples in each category (mainly those used in photocatalytic water splitting), along with their corresponding bandgap energy ranges, are presented as reported by Villa et al, 2021 [5]:

1.6.1 Wide-bandgap semiconductors; $E_g > 3$ eV

Materials in this category exhibit photochemical stability and reusability. With a bandgap higher than 3 eV, absorption occurs at wavelengths smaller than 413 nm, which limits their capacity to capture the full range of solar irradiation. Examples include TiO_2 (titanium dioxide), zinc oxide (ZnO), zinc sulfide (ZnS), SrTiO_3 (strontium titanate) and Ga_2O_3 (gallium oxide) with a bandgap of 4.8 eV, which is utilised as a semiconductor photocatalyst in this thesis [5], [6].

1.6.2 Intermediate-band gap semiconductors; $3.0 \text{ eV} \geq E_g \geq 2.2 \text{ eV}$

Absorption in the range of approximately 413-563 nm, corresponding to the visible spectrum (VIS), makes these suitable for solar water splitting. This includes CdS (cadmium sulfide), SiC (silicon carbide), TaON (Tantalum (oxy-)nitride), g- C_3N_4 (graphitic carbon nitride) [5].

1.6.3 Short-band gap semiconductors $2.2 \text{ eV} > E_g \geq 1.3 \text{ eV}$

These absorb wavelengths between approximately 563 nm to 954 nm (near-IR region) and include Cu_2O (cuprous oxide), WS_2 (tungsten disulfide), MoS_2 (molybdenum disulfide) [5].

1.7 Band structure of graphene

Graphene is a two-dimensional allotrope of carbon, a monolayer of carbon atoms arranged into a honeycomb grid. The sp^2 hybridisation of carbon atoms forms three σ -bonds with neighbouring carbon atoms, leading to a trigonal planar structure. The remaining unhybridized p_z orbitals are then oriented perpendicularly to the graphene's plane, which overlap to create a delocalised π -bonding system below and above the plane of carbon atoms [7]. The honeycomb arrangement of carbon atoms is shown in Figure 7 (b).

The structure can be described in a triangular Bravais lattice with a two-atom basis per unit cell (A and B) with lattice vectors [7]:

$$a_1 = \frac{a}{2}(3, \sqrt{3}), \quad a_2 = \frac{a}{2}(3, -\sqrt{3}) \quad (8)$$

where $a \approx 1.42 \text{ \AA}$ is the distance between carbon atoms. The reciprocal lattice vectors are defined as:

$$b_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad b_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (9)$$

with $\delta_1, \delta_2, \delta_3$ resembling the nearest-neighbour vectors:

$$\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = -a(1, 0) \quad (10)$$

The unique properties of graphene stem from charge carriers that mimic the behaviour of relativistic particles and can be described with the Dirac equation rather than the conventional Schrödinger equation used for electrons in most solids. The interaction of charge carriers (electrons and holes) with a periodic potential of graphene's lattice then leads to the Dirac fermions, indicating particles of matter with the same linear dispersion as relativistic quasiparticles with zero mass [8].

Graphene's first Brillouin zone (a reciprocal space reflecting the lattice symmetry) hosts the K and K' points at its vertices, where the VB and CB meet at a Dirac point, thus rendering graphene a semimetal with bandgap energy $E_g = 0$. This is shown in Figure 7 (a), (b), where VB and CB, represented by Dirac cones, touch at a single point [7].

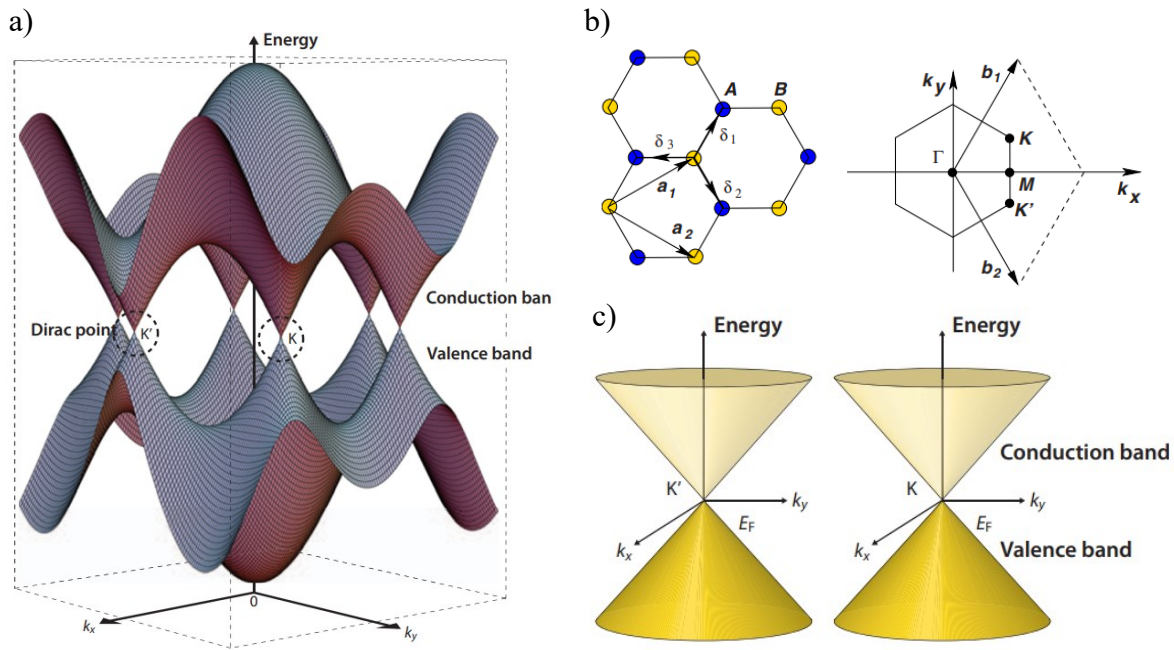


Figure 7 – (a) dispersion relation of graphene, VB and CB cross at K and K' points; (b) graphene's lattice and its Brillouin zone; (c) conic energy bands close to K and K' points. Adapted from [7], [9].

The existence of a free-standing atomic monolayer was not expected until the discovery of graphene in 2004 by A. Geim and K. Novoselov, due to the argument that such one-atom-thick structures would be thermodynamically unstable as the thermal vibrations would shatter the lattice. However, experimental observations showed that the gentle warping of the lattice in the third dimension suppresses these vibrations, minimising the system's free energy [8], [10].

Due to its unique nature, graphene exhibits properties like quantum Hall effect, high mobility of charge carriers $\mu = 15\,000\text{ cm}^2/\text{V}\cdot\text{s}$, Young's modulus of 1 TPa and thermal conductivity ranging from 3 000-6 000 W/m·K [8], [11]. Graphene finds its use in energy storage devices, transistors, solar cells and other graphene-based electronics, biomedicine or water filtration technologies [12].

2 HYDROGEN AS AN ENERGY CARRIER

Hydrogen (H_2) is an energy carrier with a low volumetric energy density but a high gravimetric energy density of 120 MJ/kg, approximately three times that of gasoline [13], [14]. Due to its ability to act as a fuel source in fuel cells or direct combustion while producing little to no byproducts commonly associated with fossil fuel use (carbon dioxide, nitrogen oxides, sulphur oxides), hydrogen is considered a promising clean and sustainable energy carrier of the near future [14]. Despite various production routes and technologies at different stages of development, the widespread adoption of hydrogen as an energy carrier is constrained by relatively high costs [14].

Hydrogen gas is utilised in the metallurgical industry sector, transportation, production of ammonia for fertilisers, the petroleum refining industry or food industry [15], [16]. While the global hydrogen output accounted for 70 Mt in 2019 [16], the amount of hydrogen produced has reached 97 Mt in 2023 [17]. Due to the increasingly growing demand, global hydrogen production was estimated to reach 100 Mt by the end of 2024 [17].

Current hydrogen production routes are dominated by the steam reforming of natural gas (steam methane reforming) responsible for over 60 % of the world's total hydrogen production, followed by the 20 % generated by coal gasification and with 15 % being a byproduct in the petrochemical industry. The current global leaders in hydrogen production are China (with approx. 30 % of total hydrogen produced), United States and Middle East (accounting for 14 % each) [17]. The share of hydrogen production is further illustrated in Figure 8.

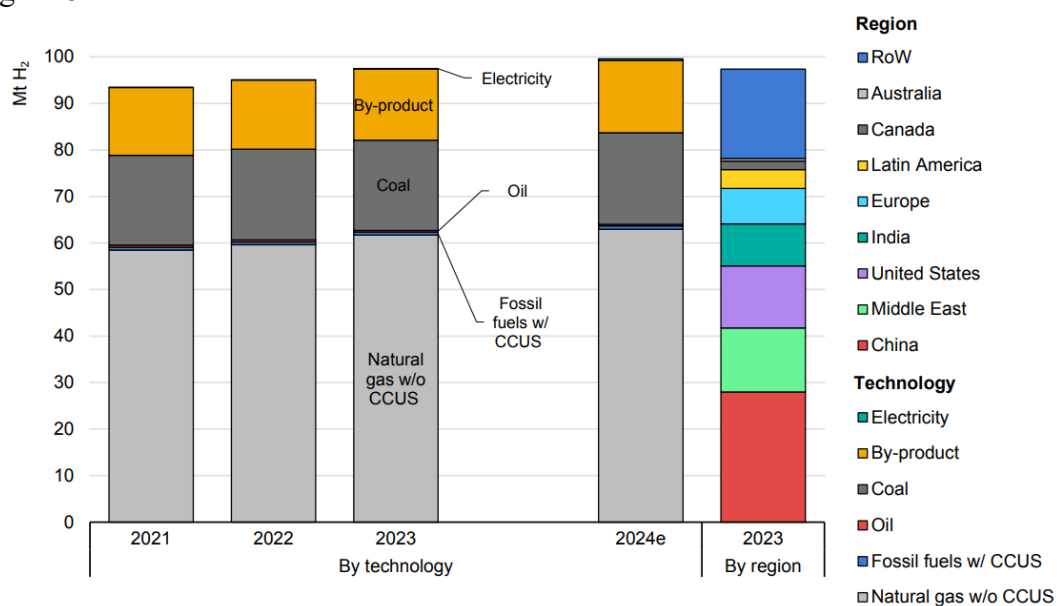


Figure 8 – Hydrogen production by technology and by region, 2021-2024 [17].

Out of total global hydrogen production, low-emission hydrogen accounts for less than 1%, with the majority produced from fossil fuels with CCUS (Carbon Capture, Utilisation, and Storage) and only a minuscule amount produced via electrolysis. While hydrogen serves as a zero-emission energy carrier, the CO₂ emissions associated with its production reached 900 Mt in 2022 and 920 Mt in 2023 [17]. It has therefore been established as a general goal to increase low-emission hydrogen production and reduce reliance on fossil fuel-based technologies, with electrolysis expected to play a major role by 2030 [17]. Although renewable hydrogen costs up to six times more than fossil fuel-based hydrogen, its price is expected to drop significantly by the 2030s as renewable energy prices decline [17], [18].

Photocatalytic water splitting, though currently regarded as an immature technology, remains a subject of study and interest as it aligns with low-emission production methods [17].

2.1 Colours of hydrogen

In both the industrial sector and scientific community, hydrogen is commonly classified into categories with colours assigned based on its production method and energy source. The following table presents an overview of these types with the corresponding production route.

Table 1 – Colours of hydrogen. Data source from [13].

Hydrogen type	Production technology
Green	Electrolysis of water (electricity from renewable energy sources), photocatalysis
Pink, Purple, Red	Electrolysis of water (electricity from a nuclear power plant)
Yellow	Electrolysis of water (electricity from the energy grid)
Grey	Steam methane reforming, partial oxidation
Turquoise	Pyrolysis of methane
Brown, Black	Coal gasification
Blue	Production from fossil fuels with CCUS
Aqua	Extraction from oil sands
White	Naturally occurring

For a given technology, hydrogen production costs fluctuate with factors such as weather conditions, supply chain disruptions, feedstock and energy prices, and other variables. The price ranges for currently established manufacturing methods are as follows: grey hydrogen from natural gas spans from \$0.67–1.31/kg; brown and black hydrogen derived from coal

range from \$1.2–2\$/kg [13], and green hydrogen from renewable-powered electrolysis reaches \$2.28–7.39\$/kg [13]. As noted, declining renewable energy prices are expected to significantly reduce the cost of green hydrogen in the coming years, making it one of the most promising solutions for lowering the energy sector's carbon footprint with environmentally friendly and sustainable technology that produces only a negligible amount of greenhouse gas emissions [14].

2.2 Solar to hydrogen (STH) efficiency

The solar to hydrogen (STH) conversion efficiency is a standardised and widely used parameter that enables performance comparison of systems producing hydrogen by harnessing solar energy, regardless of whether photocatalysis is the primary mechanism in a given production pathway [19]. The STH efficiency is defined as a ratio of the amount of chemical energy produced to the incident solar energy:

$$STH = \frac{\text{Chemical energy produced}}{\text{Solar energy input}} = \frac{\text{Rate of } H_2 \text{ production} \cdot \Delta G}{\text{Total incident solar power} \cdot \text{Area}} \quad (11)$$

where ΔG is the Gibbs free energy change for the water-splitting reaction [19].

2.3 Photocatalytic (PC) and photoelectrochemical (PEC) water splitting

Photocatalysis (PC) is a process in which an electron-hole pair is generated within a semiconductor catalyst upon the absorption of a photon with energy equal to or greater than the semiconductor's bandgap. This pair further participates in the redox reaction, ultimately resulting in the splitting of water into oxygen and hydrogen [13]. This process was first reported in 1972 by Fujishima and Honda [20] who utilised TiO_2 as an n-type semiconductor catalyst generating electron-hole pairs upon UV irradiation to match TiO_2 bandgap of 3.0–3.2 eV [20], [21]. Although the water splitting process is driven by photocatalysis facilitated by semiconductor upon its illumination, the experimental setup presented by Fujishima and Honda also required external bias voltage that facilitated electron flow through external circuit from TiO_2 photoanode to platinum cathode, where water was reduced to produce hydrogen (thus oxidised on TiO_2 photoanode to produce oxygen) [20].

In this approach, known as photoelectrochemical (PEC) water splitting, a photoanode and cathode are immersed in an electrolyte and connected via an external circuit. By integrating photocatalysis with an electric field, this method significantly improves the efficiency of the water splitting process compared to solely photocatalytic systems. High rates of electron-

hole recombination, which are an inherent part of any photocatalytic reaction, are effectively reduced by the electric field [5], [20], [22].

Although being more complex and still in development, PEC systems have achieved STH efficiency up to 20 % [5], making them competitive with the solar electrolysis approach which can reach efficiency up to 28 % [23]. Current PC systems achieve STH efficiency close to 1 % [5], making them inefficient and currently non-competitive. To be considered economically viable, this approach requires STH efficiency of at least 10 % [5]. PC systems, however, offer simple setup, mild reaction conditions, scalability, and enable straightforward, direct conversion of solar energy without the need for external bias [5].

Villa et. Al., 2021 [5] identified key criteria for selecting suitable semiconductor materials in photocatalytic water splitting:

- Redox potential – conduction band (CB) must be negative enough to reduce protons to hydrogen and valence band must be positive enough to oxidise water to oxygen (more than 1,23 V which is the minimal potential value needed for oxidation of water to O₂)
- Broad wavelength absorption – material should absorb visible and near-infrared light, as UV light represents just 5 % of the solar radiation at the Earth's surface
- STH efficiency at least 10 % to achieve economic viability, as the current STH efficiency values of photocatalytic systems reach only 1 %, making them currently non-competitive with established PEC systems
- Photochemical and chemical stability – photocatalyst must exhibit resistance towards harsh oxidative and reductive conditions and should maintain structural integrity for at least 10 years
- Low toxicity – the material should be non-toxic and preferably biocompatible to avoid environmental hazards – a factor that has been overlooked so far
- Cost-effectiveness and abundance – efficient photocatalysts rely on expensive and scarce noble metals, which hinders their large-scale use
- Scalability – high-performance photocatalysts often require complex and costly synthesis methods, which again limits the large-scale use
- Fabrication versatility – modifications in synthesis routes allow tailoring of specific properties, such as surface area increase, improving the photon absorption and light harvesting properties, tuning of the charge transfer mechanism, etc.

Aside from constraints listed on the previous page, there are still many crucial aspects in play when integrating water, solar light and semiconductor-based photocatalysts that hinder the technology's full potential and limit higher efficiency gains. In general, the limitations stem from thermodynamics, kinetics and physical requirements [5].

2.4 Mechanisms of photocatalytic water splitting

As the semiconductor photocatalyst absorbs a photon with energy equal to or greater than its bandgap, the electron is excited into the conduction band (CB), leaving a positively charged hole in the valence band (VB). In the case of photon absorption with greater energy, the excited electrons drop to the conduction band minimum (CBM) and holes to the valence band maximum (VBM). In case the excitation is driven by a photon of greater energy than the bandgap, the relaxation process occurs in which excited electrons drop to the conduction band minimum (CBM) and holes to the valence band maximum (VBM). The electrons and holes are now in a position to transfer to the cocatalyst or surface reaction sites where reduction and oxidation of water into H_2 and O_2 occurs [24].

If the process of water splitting as direct as mentioned above, with no intermediate steps, the semiconductor then splits water by one-step excitation, which occurs when the potential of CBM is more negative than the water reduction potential and the potential of VBM is more positive than the water oxidation potential. If this condition is not met, i. e. the photocatalyst cannot perform both half reactions, then two-step excitation (Z-scheme) systems are employed, in which two photocatalysts are present, each handling one half of the water splitting reaction. The electrons and holes then recombine through an electron mediator [24].

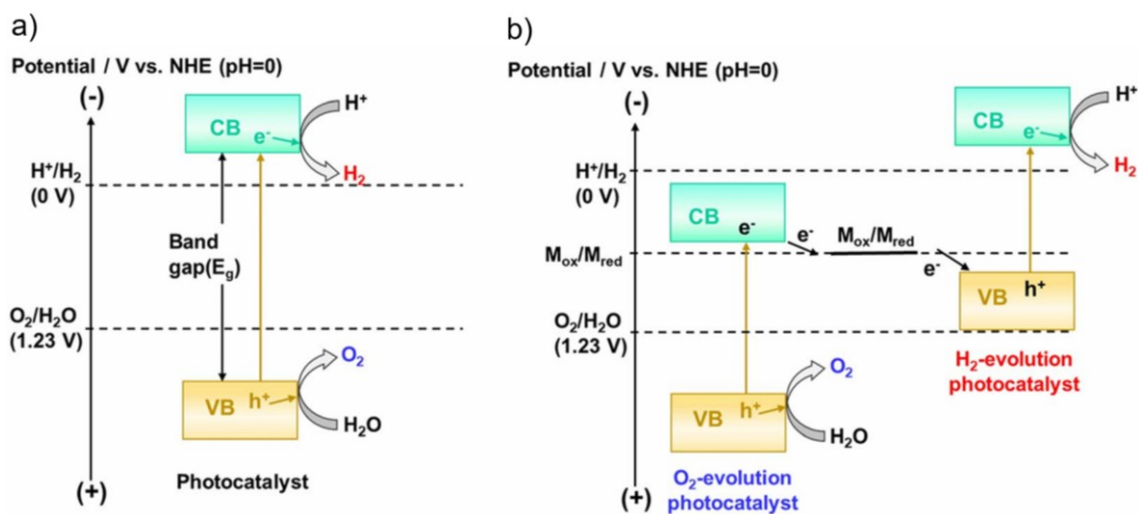


Figure 9 – Charge transfer mechanism; a) one-step excitation; b) two-step excitation.

Adapted from [24].

2.5 Performance enhancement strategies in PC systems

Various strategies aimed at improving charge carrier separation efficiency, increasing surface reaction rates or enhancing the photon absorption are employed [5], [4]. These often utilise a cocatalyst loaded on a photocatalyst, forming an interfacial junction that modifies the transport properties of electrons and holes [4], [25]. Other approaches introduce dopants into the photocatalyst's crystal lattice, intrinsically altering its band structure and bandgap, thus extending the light absorption into the visible spectrum. [5], [25], [26]. While many cocatalysts based on the noble metals (Pt, Pd, Ru) [4] form a interfacial junction (at a metal-semiconductor interface), some metals exhibiting strong plasmonic properties (Ag, Au) can also contribute to the enhancement mechanisms via localized surface plasmon resonance (LSPR) effect, generating a strong electrostatic field in the near-surface region, effectively promoting charge carriers separation [27], [28]. The electron-hole recombination can be further suppressed by employing sacrificial agents, such as methanol, ethanol, isopropanol, ethylene glycol or glycerol, which serve as electron donors or hole scavengers [29].

2.6 Examples of PC systems

Compounds that exhibit photocatalytic behaviour include metal oxides, metal sulphides, metal nitrides, metallo-organic compounds or 2D nanomaterials [30].

Aside from already mentioned TiO_2 , which can be integrated with reduced graphene oxide (rGO) to promote the VIS absorption, other compounds that found use in the photocatalytic processes include ZnO (zinc oxide) coupled with CuO (copper oxide) or doped with nitrogen, and CeO_2 (cerium oxide) incorporated with TiO_2 or ZnO [26]. Other inorganic binary photocatalytic compounds include ZnS (zinc sulphide), CdS (cadmium sulphide), MoS_2 (molybdenum sulphide), SiC (silicon carbide) and others [5]. An example of a 2D photocatalyst non-metallic nanomaterial is network g- C_3N_4 (graphitic carbon nitride) having C-N units tied into a polymeric network [5], [30].

Widely investigated compounds with complex and fine-tuned lattice structure include BiVO_4 (bismuth vanadate) or perovskite SrTaO_2N (strontium tantalum oxynitride), both suitable for photocatalytic water splitting under VIS [31], [32].

Ohno et. al., 2012 [33] investigated a suspension system of GaN:ZnO solid solution (gallium nitride-zinc oxide) photocatalyst modified with $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ (rhodium-chromium oxide) as a cocatalyst, which exhibited a 50 % loss of initial photocatalytic activity after 6 months of

operation due to degradation and possible decomposition of GaN:ZnO. The reloading of the $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ cocatalyst, however, enabled activity regeneration up to 80 % of the original activity, addressing the challenge of long-term photochemical stability.

In spite of general lack of large-scale demonstrations of PC systems, example of such experimental setup was reported by Nishiyama et. al., 2021 [34], who demonstrated that 100 m^2 array of panel reactors based on $\text{SrTiO}_3\cdot\text{Al}$ (aluminium-doped strontium titanate) photocatalytic sheets is capable of passive gas collection and hydrogen separation using polyimide-based membrane unit, although reaching only 0.76 % in STH efficiency.

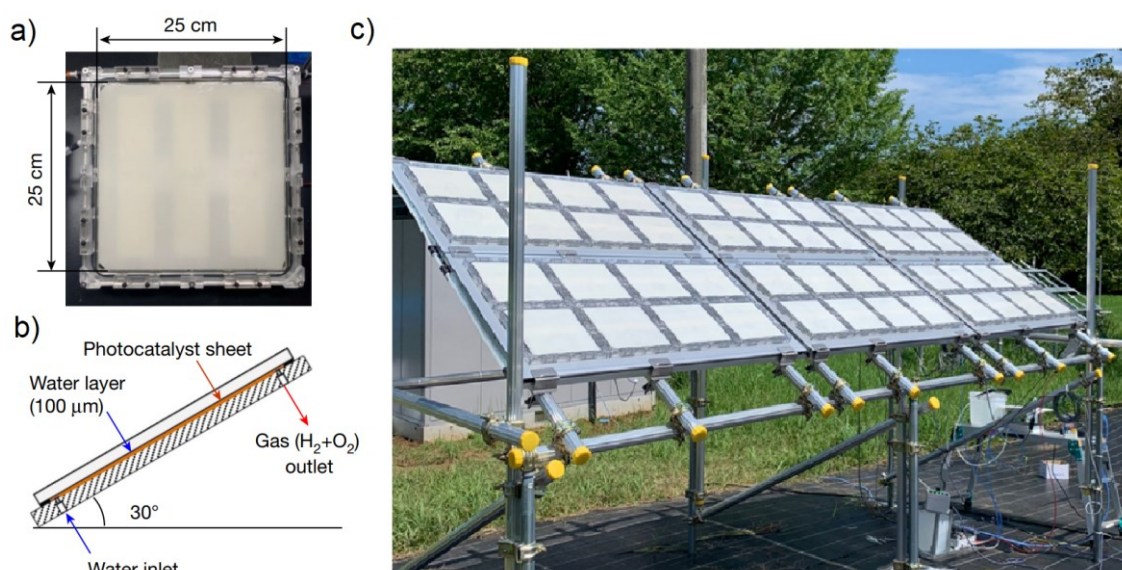


Figure 10 – Water splitting photocatalyst panel reactor; a) panel reactor unit; b) scheme of the panel reactor unit, c) panel reactor. Adapted from [34].

2.7 $\text{Ga}_2\text{O}_3/\text{Ga}$ on $\text{Gr}/\text{SiO}_2/\text{Si}$ photocatalytic system

Bartošík et. al., 2024 [28], described a novel system for photocatalytic water splitting reaction based on gallium oxide-modified gallium nanoislands ($\text{Ga}_2\text{O}_3/\text{Ga}$) deposited on a silicon/silicon dioxide wafer covered with a CVD-grown graphene ($\text{Gr}/\text{SiO}_2/\text{Si}$). In this one-step excitation system, electron-hole pair generation occurs in the 1-2 nm thick Ga_2O_3 semiconductor layer covering a Ga liquid metal core, which promotes the separation of charge carriers via a localised electromagnetic field induced by the LSPR (localised surface plasmon resonance) effect.

2.7.1 $\text{Ga}_2\text{O}_3/\text{Ga}$ nanoparticles

Gallium is a post-transition metal with a low melting point (relative to most other metals) of $29.76\text{ }^\circ\text{C}$ [35]. Gallium exhibits a stable orthorhombic phase, $\alpha\text{-Ga}$, at room temperature or

metastable monoclinic, β -Ga, which crystallises from deeply undercooled liquid gallium nanoparticles (GaNPs). Other less common polymorphs include δ -Ga, γ -Ga and Ga-II [36]. GaNPs have been investigated for their plasmonic properties, which can be tuned from UV to the IR region, offering notable versatility compared to conventional plasmonic metals, e. g. Ag or Au [37], [38]. The ability to form localised surface plasmons can be utilised in imaging techniques, such as surface-enhanced Raman spectroscopy (SERS) [38], antireflection structures on solar cells, or other plasmonic devices [37].

The GaNPs are essentially Ga₂O₃/Ga core-shell structures with a 1-2 nm thick stable layer of native oxide covering the metal core, which forms upon contact with air after the deposition process [37].

2.7.2 Preparation of Gr/SiO₂/Si substrate

The authors prepared a graphene layer in-house via chemical vapour deposition (CVD): the low-pressure deposition chamber was filled with hydrogen and the copper plate substrate was annealed at 1000 °C, after which the gas precursors (methane/hydrogen mixture) were introduced over the course of 30 minutes. The graphene was subsequently transferred onto a SiO₂/Si wafer via the wet transfer method [28].

2.7.3 Physical vapour deposition

Physical vapour deposition (PVD) is a process in which a material is vaporized and subsequently transported onto a substrate, forming a thin film, or in case of gallium, discrete nanoislands formed as a consequence of coalescence and merging of deposited gallium atoms (Ostwald ripening mechanism), which is promoted at higher substrate temperatures, due to the higher thermal energy, thus leading to larger GaNPs [37], [39]. The GaNPs relaxation induced by surface tension to take a quasi-hemispherical shape, rather than discrete spheres [37]. Bartošík et. al, 2024 [28] used physical vapour deposition (PVD) to

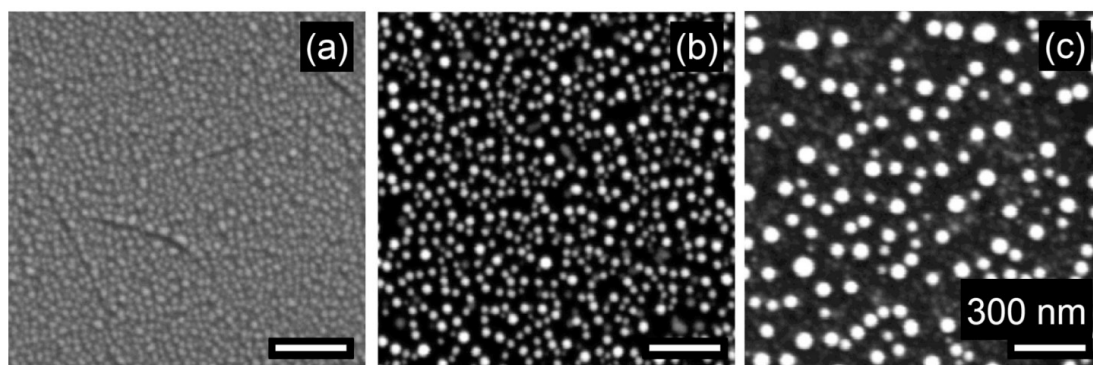


Figure 11 – UHV SEM images of Ga₂O₃/Ga nanosilands on a SiO₂ substrate deposited at: (a) room temperature, (b) 200 °C, (c) 300 °C [28].

grow GaNPs on a Gr/SiO₂/Si substrate under ultra-high vacuum (UHV) conditions. In their setup, the gallium metal undergoes thermal evaporation in an effusion cell, comprising pyrolytic boron nitride inside a molybdenum crucible, developed at the Brno University of Technology, Department of Physical Engineering. The 10⁻⁸ Pa with the deposition time of 180 min and 2 µg of deposited gallium. Three samples at different substrate temperatures: room temperature, 200 °C and 300 °C. The SEM analysis showed the notable difference in size and number of deposited Ga₂O₃/Ga nanoislands, as can be seen in Figure 11. The calculated surface-to-height ratio from 61 % to 90 % also confirms their quasi-hemispherical nature, which is also demonstrated in the height profile of a cross-section obtained from atomic force microscopy (AFM) imaging in Figure 12.

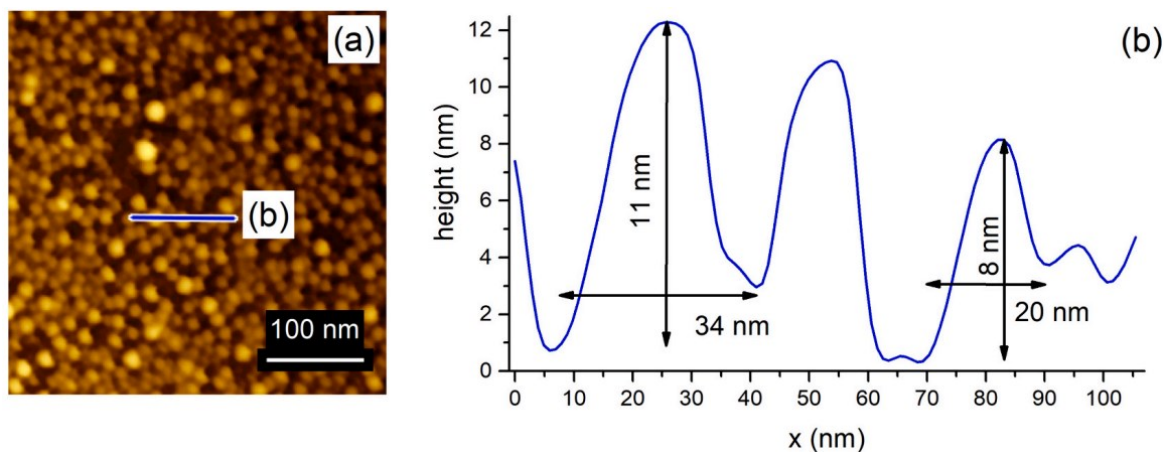
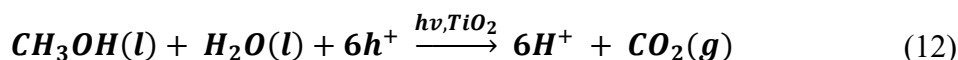


Figure 12 – AFM profile of Ga₂O₃/Ga nanoislands deposited on a SiO₂ surface at room temperature [28].

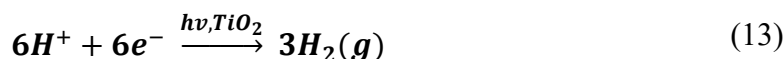
2.7.4 Photocatalytic experiment

The photocatalytic experiment, as described by the authors [28], was performed in a batch stainless steel photoreactor filled with 100 ml of a 50 % aqueous methanol solution, under the helium atmosphere at 120-130 kPa, with Ga₂O₃/Ga on Gr/SiO₂/Si placed on the bottom. The illumination of $\lambda_{\text{max}} = 254$ nm was provided by 8 W UV-C Hg lamp through the quartz glass window of the photoreactor. Collection of gaseous samples in defined time intervals with a gas-tight syringe, followed by their analysis on a gas chromatograph. In total, three Ga₂O₃/Ga on Gr/SiO₂/Si samples, together with a commercial TiO₂ – P25 posing as a standard, were subjected to 4 hours of irradiation with continuous measurement.

The hydrogen evolution in this experiment occurred as a result of two half-reactions, as proposed by the authors:



as per oxidation, and:



as per reduction. See the overall reaction in Figure 13.

2.7.5 Effect of LSPR on overall photocatalytic performance

While wavelengths of incident radiation corresponding to the Ga_2O_3 bandgap of 4.8 eV, i.e. 258 nm or shorter, are effectively absorbed by the Ga_2O_3 shell, longer wavelengths penetrate this semiconductor layer and are absorbed by metal Ga core, inducing plasmons (collective oscillation of free electrons) or even plasmon resonance if the incident light matches the plasmons resonance frequency, resulting in strong enhancement of electric intensity localised to the surface of Ga core, i. e. directly to the Ga_2O_3 semiconductor layer, which ultimately leads to efficient separation of charge carriers. For Ga metal, the incident wavelength that leads to the most prominent LSPR effect was calculated as 669 nm [28].

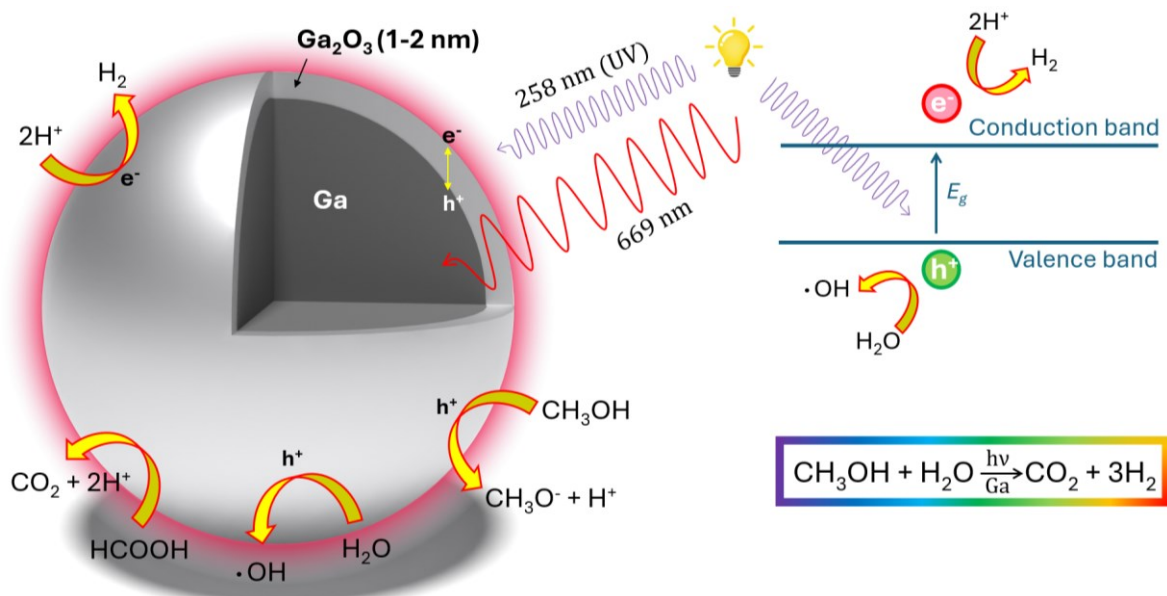


Figure 13 – Scheme of photocatalytic water splitting in $\text{Ga}_2\text{O}_3/\text{Ga}$ on $\text{Gr}/\text{SiO}_2/\text{Si}$ system in 50 % aqueous methanol solution, depicting the electron-hole pair generation, LSPR effect and overall water splitting reaction.

Although the UV-C radiation source in this experiment had a $\lambda_{\max} = 254$ nm, the authors note that the batch reactor was not shielded to completely prevent sunlight exposure, thereby allowing visible spectrum wavelengths to participate in the photocatalytic reaction through the LSPR effect [28].

It was further proposed that nanoparticles with the smallest radii (deposited at room temperature) exhibit the highest surface-to-volume ratio, promoting enhanced charge carrier generation, but contributing minimally to LSPR. Conversely, nanoparticles with the largest radii (deposited at 300 °C) display the strongest LSPR due to their increased metal core volume, but have the lowest surface area, resulting in less effective charge carrier generation. A synergy between these effects can therefore be achieved by optimising the particle dimension. This assumption strongly correlates with the photocatalytic performance of samples with different deposition temperatures, as can be seen below [28].

2.7.6 Photocatalytic performance of Ga₂O₃/Ga deposited on Gr/SiO₂/Si

It was demonstrated that after 4 hours of UV-C irradiation, the absolute hydrogen yields of Ga₂O₃/Ga on Gr/SiO₂/Si were comparable or slightly worse than that the yields produced by commercial TiO₂. However, when hydrogen yields are assessed per unit mass of active photocatalyst, all of the Ga₂O₃/Ga on Gr/SiO₂/Si exhibit yields more than four orders of magnitude higher than those of TiO₂, as shown in Figure 14. Out of all the Ga₂O₃/Ga on Gr/SiO₂/Si samples deposited at various temperatures, the sample deposited at 200 °C (medium-sized GaNPs) significantly outperformed all other samples (Ga-S for room temperature and smallest particles and Ga-L for 300 °C and largest particles). This is because both electron-hole pair generation and LSPR contribute optimally [28].

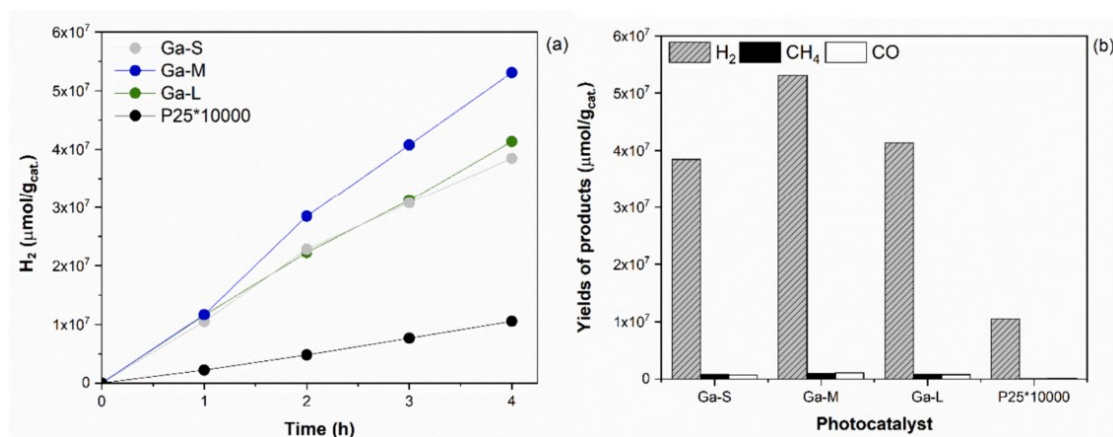


Figure 14 – Time dependence of yields of hydrogen in $\mu\text{mol/g}_{\text{cat}}$ in Ga₂O₃/Ga on Gr/SiO₂/Si system with 50% aqueous methanol solution after 4 hours of UV-C irradiation [28].

This thesis builds on the findings of Bartošík et. al. and aims to replace the SiO_2/Si substrate in the $\text{Ga}_2\text{O}_3/\text{Ga}$ on $\text{Gr}/\text{SiO}_2/\text{Si}$ system with a polymer material that is cheaper, flexible, and suitable for surface modifications.

3 POLYMERS

Polymer materials are increasingly utilised in composites or as substrates due to their flexibility, low cost, and tunable surface properties. However, despite their versatility, they present challenges, such as limited thermal stability [40]. The use of a polymer substrate for metal nanoparticles deposited via the PVD is not entirely novel. For instance, Waters et. al., 2016 [41] deposited gallium nanoparticles via the PVD method on a polyethene terephthalate (PET) substrate nanostructured by focused ion beam milling, but they did not investigate its catalytic properties.

3.1 Polymer solutions

From the thermodynamic perspective, polymer solutions differ significantly from those of low-molecular-weight compounds. When a polymer chain adopts a random coil conformation (a statistically probable conformation) in a solution, the dissolution occurs if permitted by the Gibbs free energy of mixing [42]:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (14)$$

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. During dissolution (when $\Delta G_{mix} < 0$), interactions between the polymer and solvent are favourable, leading to an expanded coil conformation that maximises the polymer-solvent contact area. When $\Delta G_{mix} > 0$, the dissolution is thermodynamically unfavourable, and the random coil adopts a compact conformation. If the $\Delta G_{mix} \approx 0$, then the overall interactions are balanced and the polymer adopts an ideal random coil conformation. These thermodynamic principles of polymer-solvent interactions then give rise to concepts of good, poor and theta solvents. As each pair of a polymer-solvent is thermodynamically unique, a solvent that is poor for one polymer can be a good solvent for another. The Gibbs free energy of mixing is not typically used as a criterion to determine whether, for a given polymer, a solvent is good or poor. Instead, derived parameters, such as the Hildebrand solubility parameter (δ) or the Flory-Huggins interaction parameter (χ), are employed [42].

3.2 Polymer surface modification techniques

The morphology of the polymer surface, and consequently its properties, can be modified and precisely tailored by variety of techniques, including photolithography, micro-printing, replica moulding, phase inversion [43], phase separation induced by time sequenced dosing of mixed solvents [44], treatment in plasma [45], breath figures patterning and others.

3.2.1 Breath figures patterning

Breath figures patterning, also known as “breath-figures self-assembly” [46], is a surface modification technique that allows the formation of micro- and nano-porous patterns at the polymer surface (or polymer interfaces in general) of highly ordered nature. Polymer films with pores packed into a hexagonal array are commonly referred to as honeycomb-patterned (HCP) films [47]. This cost-effective and experimentally straightforward patterning method relies on the simple phenomenon of water droplet condensation on a cooled surface – in this case, the surface of a polymer solution cooled by the rapid evaporation of a volatile solvent, which is an endothermic process. The condensed water droplets, organised into an ordered array, leave a porous pattern in the solidified polymer film after evaporation [48]. This process is illustrated in Figure 15:

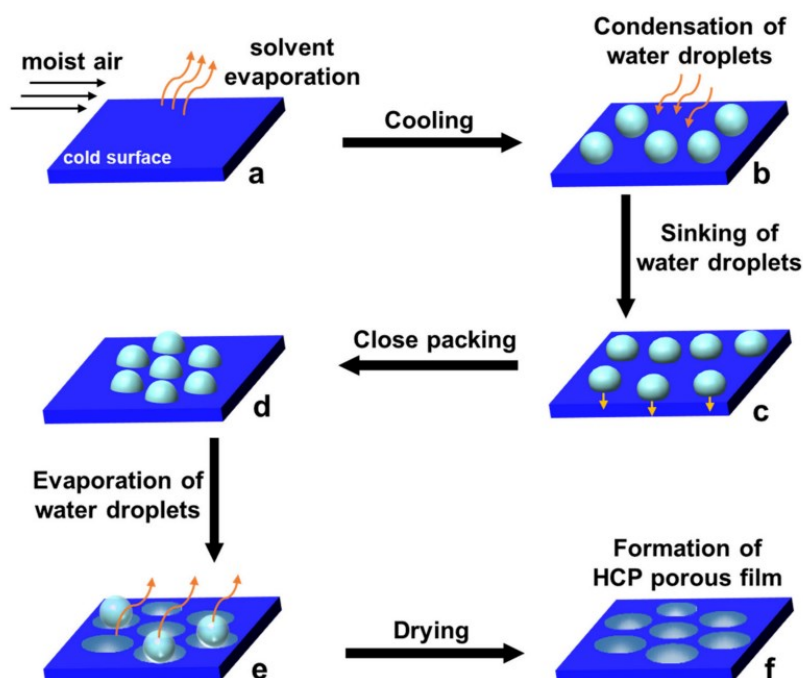


Figure 15 – A mechanism of BF patterning; (a) evaporation of volatile solvent from the polymer solution, (b) evaporation-induced cooling and water condensation, (c) growing of the water droplets and their sinking into the solution, (d) droplets packing into hexagonal array, (e) evaporation of the droplets, (f) formation of HCP film after drying [47].

The following table presents key factors influencing pore size and distribution, as identified by Rodríguez and Bormashenko, 2020 [46].

Table 2 – The effect of experimental conditions on the BF patterning process.

Factor	Consequences
Humidity	An increase in RH usually increases pore size
Airflow	Pore size decreases with higher airflow rates as the time required for total evaporation decreases
Interfacial tension	Higher interfacial tension provides stabilisation to the water droplets during solvent evaporation
Solution concentration	Higher pore size is achieved with a solution of lower polymer concentration
Substrate	Parameters like roughness or wettability of the substrate's surface affect the periodicity of the pores
Solvent	Higher volatility leads to smaller pores, and lower volatility leads to larger pores, as the condensation process is prolonged
Pressure	A decrease in pressure accelerates the evaporation of the solvent, similarly to the increase in airflow rate
Temperature	A decrease in temperature reduces the evaporation rate and prolongs the condensation, resulting in large pores. Higher temperatures also induce convective flows that can disturb pore formation

That BF patterning does not occur only in water-vapour-based environments, as it has been demonstrated that alcohol vapours (methanol, ethanol and propanol) can also be successfully employed in the droplet templating process [49], [50]. The BF patterning is commonly performed by drop-casting, spin-coating or dip-coating and finds its application in membrane manufacturing [51].

3.2.1.1 Convective flows and underlying mechanisms in breath figures patterning

The pore formation in the breath figures patterning is attributed to three main convection mechanisms. The rapid onset evaporation of the solvent and subsequent cooling drive large-scale pattern formation, followed by the migration of the pores to the borders of a cell-like network. One hypothesis suggests that these borders/knots represent zero-velocity points where pores accumulate due to the tangential velocity field of the polymer solution's flow. Although the origin of this flow is not fully understood, one proposed mechanism responsible for the formation of large-scale patterns is the Bénard-Marangoni instability,

a convective instability resulting from the coupling of Marangoni flows with Rayleigh-Bénard convection. The Marangoni flows arise because the surface tension of the polymer solution depends on both the temperature and the concentration. Evaporation of the solvent from the surface increases the concentration relative to the bulk, inducing the soluto-capillary flow. The rise in concentration also alters the surface tension of the solution. Additionally, subcooling of the surface during solvent evaporation generates a thermal gradient, triggering thermo-capillary flow [46].

In addition to the Marangoni flows, a temperature-induced density gradient, driven by the buoyancy, induces a Rayleigh-Bénard convection. The combined effects of Marangoni flows (driven by thermal and concentration gradients) and the Rayleigh-Bénard convection (driven by density gradient and buoyancy) result in the so-called Bénard-Marangoni instability, which is responsible for the formation of organised convective cells. This hypothesis is supported by the frequent co-occurrence of thermo- and soluto-capillary flows [46]. Other factors complicating the BF formation include the potential formation of a solidified crust in the solvent-depleted region near the solution's surface and also the thickness of the deposited layer of polymer solution [52]. Thermo- and soluto-capillary Marangoni flows drive the hexagonal droplet packing in a standard BF patterning of thin polymer films, as the hexagonal packing is the lowest-energy configuration for droplets in two dimensions, maximising packing density and minimising interfacial energy [46].

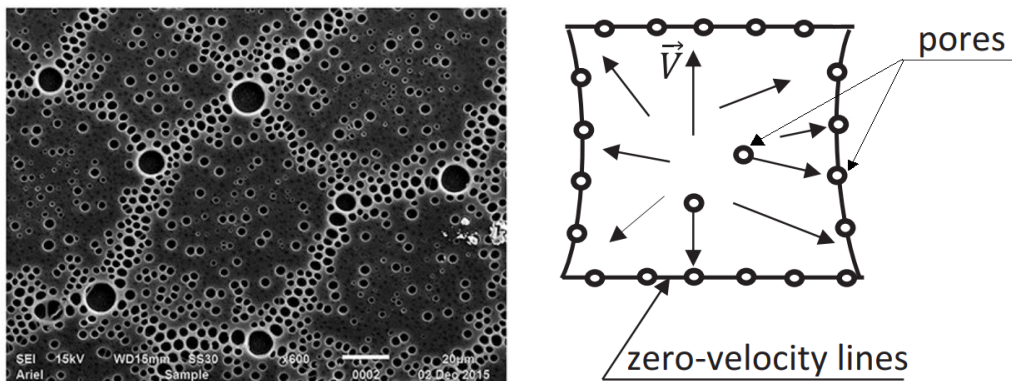


Figure 16 – (a) large-scale porous patterns in the polystyrene, (b) velocity field observed at the interface of the evaporating solution. Adapted from [46].

Despite a robust empirical comprehension of the process, there is currently no unifying theory that accounts for all the contributing mechanisms, and the exact mechanism behind BF patterning remains elusive due to its complexity. This is partly due to inconsistent results in the studies of underlying mechanisms, such as the condensation kinetics, convection

effects, and polymer stabilisation. The general consensus is that the formation of ordered porous patterns in polymer films results from self-assembly under non-equilibrium conditions [47], [51].

3.2.1.2 Polymer-solvents systems in breath figures patterning

Examples of polymers where breath figures patterning was observed include polycarbonate, polystyrene, polymethylmethacrylate or polylactide, with organic solvents such as acetone, dichloromethane, chloroform, carbon tetrachloride, tetrahydrofuran, toluene, xylenes, carbon disulfide, and N-N dimethylformamide [46], [51].

Preuksarattanawut et al., 2019 [48] prepared microporous polylactide (PLA) films from solutions of PLA in chloroform and dichloromethane at concentrations of 1.5 wt %, 3 wt %, 5 wt %, and 10 wt %, with film thicknesses ranging from 50 to 80 μm , under two relative humidity conditions: 58–65 % and 80–85 %. The authors investigated the effects of solvent type, polymer concentration, and relative humidity on the pore size distribution and concluded that their findings align with those presented in Table 2. Specific results indicated that the highest pore surface area was achieved with 3 wt % PLA and that higher relative humidity led to more highly ordered porous structures. However, the authors did not investigate the effect of airflow rate, as the films were prepared in a chamber without airflow, nor did they report whether convective flows had any effect on the pore formation.

The importance of this method lies in the increase of the surface area of the polymer's surface, which may enhance the photocatalytic performance via larger surface contact or enable a larger amount of catalyst to be deposited on the surface.

3.3 Selected polymers

Listed below are the polymers chosen for the experimental part of this work with key characteristics, physical properties and chemical structure shown in Figure 17.

3.3.1 Polycaprolactone

Polycaprolactone (PCL) is a biodegradable polyester synthesised via ring-opening polymerisation of ϵ -caprolactone. It is a semicrystalline (up to 69 %) thermoplastic polymer with a glass transition temperature of $-72\text{ }^{\circ}\text{C}$ and a melting point of $58\text{ }^{\circ}\text{C}$. PCL is soluble in common organic solvents [53].

3.3.2 Polylactide

Poly(lactide) (PLA) or polylactic acid is a biodegradable poly- α -hydroxy ester synthesised by a cationic ring-opening polymerisation of lactide. It is a thermoplastic polymer low in crystallinity, with a glass transition temperature of 53-64 °C and a melting temperature of 171 °C. PLA is soluble in fewer solvents than PCL [53].

3.3.3 Polyetheretherketone

Polyetheretherketone (PEEK) is an aromatic thermoplastic polymer suitable for high-performance applications, insoluble in most organic solvents. It is synthesised via nucleophilic aromatic substitution. It is a semicrystalline polymer with a glass transition temperature of 152 °C and a melting point of up to 343 °C [53].

3.3.4 Polystyrene

Polystyrene (PS) is a thermoplastic vinyl polymer, synthesised via radical polymerisation of styrene monomer units. PS is amorphous (absent of crystalline regions), thus a transparent polymer with a glass transition temperature of 100 °C. It is soluble in organic solvents [53].

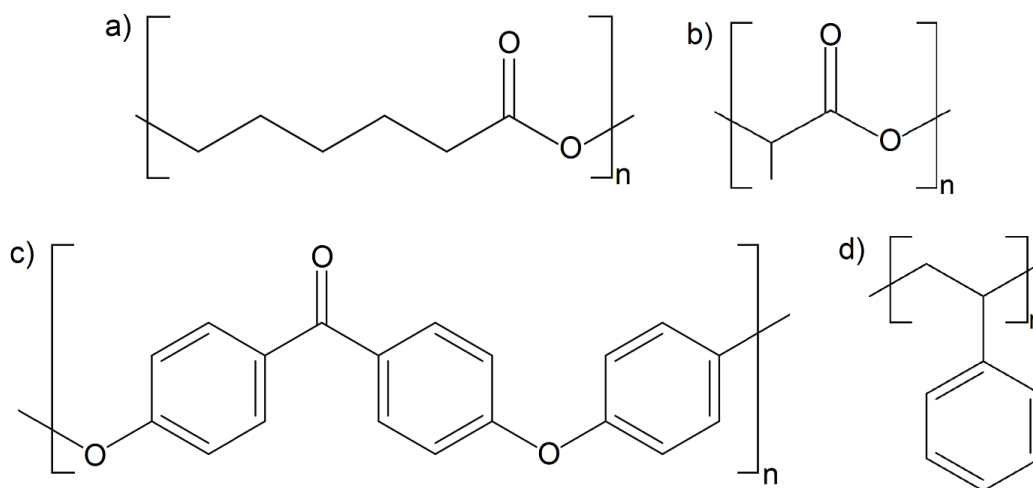


Figure 17 – Structure of selected polymers; (a) polycaprolactone (PCL); (b) polylactide (PLA), (c) polyetheretherketone (PEEK), (d) polystyrene (PS). Adapted from [53].

4 SURFACE CHARACTERISATION AND IMAGING TECHNIQUES

4.1 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a high-resolution imaging technique that employs an electron beam, focused by electromagnetic lenses, to examine a surface morphology or composition. As the resolution of both optical and electron microscopy is fundamentally limited by the diffraction limit, which depends linearly on the wavelength of a photon or an electron (considering the particle-wave dualism), an electron accelerated by a voltage of 20-30 kV can achieve a resolution on the order of nanometres, compared to the optical microscope's resolution limit of 0,2 μm [54]. The electron's wavelength λ (in nm) as a function of the accelerating voltage V (in kV) is described in the de Broglie equation:

$$\lambda = \frac{h}{\sqrt{2m_0eV}} = \frac{1,23}{\sqrt{V}} \quad (15)$$

where m_0 is the electron mass and e is the elementary charge [54]. Higher accelerating voltages or corrections for chromatic or diffraction aberrations can further enhance SEM resolution to the sub-nanometre scale. The resolution is nowadays limited to approximately 1 nm which is determined by an electron beam spot diameter [54].

Various interactions occur when the electron beam strikes the sample surface. Secondary electrons (SE) are low-energy electrons ejected from the near-surface region of the sample due to inelastic scattering of incident electrons, providing excellent topographical contrast. Backscattered electrons (BSE) are electrons with energy close to that of the primary beam, resulting from elastic scattering. The probability of backscattering increases with atomic number, enabling material contrast imaging as regions with heavier elements will appear brighter. Other interactions may produce Auger electrons or X-rays. It must be noted that non-conductive samples, such as polymer materials, cannot effectively dissipate electrons and suffer from charge accumulation, leading to image distortion or reduced resolution. For polymer materials, this issue can be mitigated by depositing a thin layer of conductive material, such as gold or palladium, via sputter coating [54].

4.2 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a high-resolution scanning probe microscopy (SPM) technique capable of imaging details at the atomic scale. Surface topography analysis and precise surface characterisation are achieved through raster scanning of the sample surface

using a mechanical probe mounted on a flexible cantilever. Imaging is based on measuring the interatomic forces between a sharp probe tip and the sample surface, detected via the deflection of the cantilever, which reflects a laser beam onto a photodetector. Scanning precision and accurate movements are facilitated by piezoelectric elements. The interaction between the probe tip and the sample surface arises from van der Waals attractive forces and Pauli repulsive forces, described by the Lennard-Jones potential [55], [56]:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (16)$$

where ε represents the depth of the potential well, σ is the distance at which $V(r) = 0$, and r is the distance between two atoms. The plotted Lennard-Jones potential is illustrated in Figure 18, which also includes both the repulsive and attractive terms:

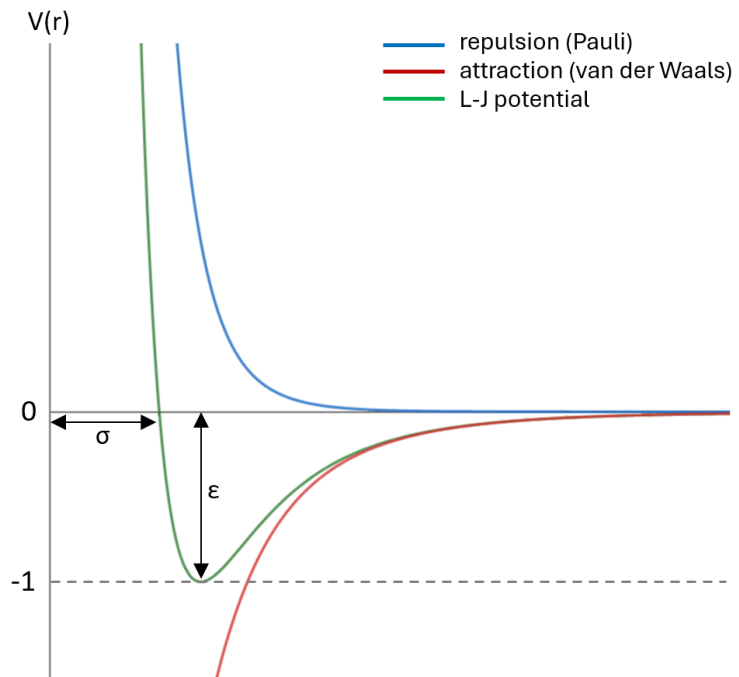


Figure 18 – Lennard-Jones potential plotted in GeoGebra Graphing Calculator.

Based on the probe tip-sample surface distance, three measuring modes are distinguished in the AFM topography imaging: contact mode, in which the tip is in direct contact with the surface; semi-contact mode, where the probe oscillates near its resonance frequency, intermittently contacting the surface, and non-contact mode with probe oscillating above the sample surface [57].

4.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique for chemical analysis, used to determine the elemental composition, chemical environment, or electronic states of a material's surface. XPS relies on the photoelectric effect: the sample surface is illuminated by soft X-rays with low penetration depth (on the order of nanometres), which eject core-level electrons from the atomic orbitals [58]. The kinetic energy E_k of emitted electrons is measured and used to calculate the binding energy E_B of the atomic orbital from which the photoelectron is ejected:

$$E_B = h\nu - E_k - \phi \quad (17)$$

Where $h\nu$ is the energy of the incident X-ray photon and ϕ is the spectrometer's work function [58].

As each element has unique binding energies, the XPS can identify elements, determine their concentration, and provide information about their chemical states and bonds. Techniques such as peak deconvolution and curve fitting resolve overlapping signals in high-resolution XPS spectra (number of electrons vs binding energy), enabling both quantitative and qualitative analysis. The surface-specific information obtained from photoelectrons is due to the short mean free path of electrons in solids [58].

4.4 Raman spectroscopy

Raman spectroscopy is a non-destructive vibrational spectroscopy technique that measures the vibrational and rotational modes of molecules, arising from the inelastic scattering of monochromatic light. This method enables both quantitative and qualitative chemical and structural analysis [59].

During the scattering process, incident light distorts the electron cloud of a molecule, inducing a short-lived virtual vibrational state, followed by immediate re-emission of the photon. If the electron cloud reinstates its original state after scattering, the frequency of the scattered photon remains unchanged (compared to the incident photon), resulting in elastic (or Rayleigh) scattering, a phenomenon which dominates photon-molecule interaction. If a vibrational or rotational state is present in a molecule or induced by scattering, energy transfer occurs between the molecule and the scattered leading to re-emission of a photon with energy from that of the incident photon. This process, known as inelastic (Raman) scattering, affects only one in every 10^6 - 10^8 photons [59].

The difference between the frequency (or wavelength) of incident and inelastically scattered photon is called Raman shift (Stokes shift when the $E_{\text{photon scattered}} < E_{\text{photon incident}}$ or anti-Stokes shift when the $E_{\text{photon scattered}} > E_{\text{photon incident}}$). This energy shift corresponds to the specific vibrational or rotational modes of a molecule, serving as a molecular fingerprint [59].

The weak Raman scattering signal can be enhanced through a phenomenon known as Surface-Enhanced Raman Scattering (SERS). This is typically achieved via electromagnetic enhancement by metallic nanoparticles, where collective oscillations of electrons (localised surface plasmon resonances) generate a strong local electric field that amplifies both incident and scattered light. This enhancement occurs when the analyte molecule is adsorbed on the surface of a metal nanoparticle or in its close proximity [59].

4.5 Contact angle measurement

The contact angle measurement is performed to assess the wettability of a surface, which determines its hydrophobic or hydrophilic nature, providing insight into its interfacial properties or enabling the assessment of the surface energy and adhesion behaviour. In a system where a liquid drop resides on a flat solid surface, the contact angle is defined as the angle between the tangent to the liquid surface and the solid-liquid interface at the three-phase contact line, as illustrated in Figure 19 [60]:

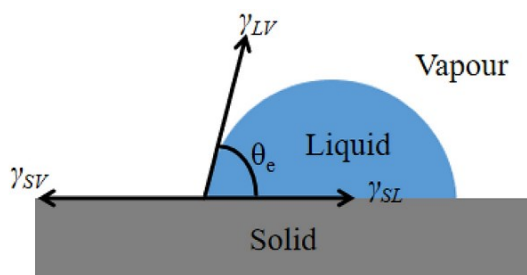


Figure 19 – Illustration of the contact angle [60].

The equilibrium condition at the three-phase contact line is described by the Young equation:

$$\cos \theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (18)$$

where γ_{SV} , γ_{SL} , γ_{LV} represent the surface energies of the solid-vapour, solid-liquid, and liquid-vapour interfaces, respectively. A surface is hydrophobic if $\theta_e > 90^\circ$ and hydrophilic if $\theta_e < 90^\circ$. By modifying the surface energy of the solid, the contact angle can be adjusted [60].

The Young equation describes the contact angle on an ideally flat surface. An extension of this equation, accounting for the roughness and assuming the liquid fully conforms to the surface texture, is the Wenzel model:

$$\cos \theta_w = r \cos \theta_e \quad (19)$$

where θ_w is the contact angle adjusted by a roughness factor r . However, it is usually the case that the liquid does not fully penetrate the irregularities of the surface morphology, and the droplet rests partially on air pockets trapped within the surface roughness. This wetting regime is described by the Cassie-Baxter equation:

$$\cos \theta_c = f_{SL} \cos \theta_e - f_{SW} \quad (20)$$

where f_{SL} represents the fraction of the liquid in contact with the solid and f_{SW} corresponds to the fraction of the liquid in contact with air. The Cassie-Baxter wetting regime is common in the polymer surfaces patterned via the breath figures approach [51], [60].

II PRACTICAL PART

5 MATERIALS AND METHODS

5.1 Materials and chemical reagents

Materials and chemical reagents used in this work include chloroform (Sigma-Aldrich), dichloromethane (Sigma-Aldrich), tetrahydrofuran (RCI Labscan), acetone (Thermo Fisher Scientific), ethyl-acetate (Sigma-Aldrich), polystyrene dishes (P-LAB), polycaprolactone (Sigma-Aldrich).

The following reagents, together with Arduino Nano V3.0 microcontroller and sensors, were obtained commercially: virgin granulate of polylactic acid (PLA Luminy LX17 by TotalEnergies Corbion), epoxy resin EpoxyPlast 3D B50 Deep Pour used for sealing and coating of the 3D printed atmospheric chamber, and 3Å molecular sieves.

Samples of PEEK sheets were prepared by extrusion moulding from granulate and supplied by the Centre of Polymer Systems, Tomas Bata University in Zlín, and cut into 1x2 cm pieces.

5.2 Large-scale breath figures

To fabricate polymer substrates suitable for carrying GaNPs with tailored porosity (and thus tunable surface area or wettability), custom atmospheric chambers were designed and built. One of these chambers was engineered to allow the BF patterning process to occur under defined humidity and airflow conditions. Given their dimensions, these chambers were utilised to prepare porous polymer surfaces with diameters of 35 mm or larger. The whole process will be abbreviated as LSBF (large-scale breath figures) in the following text.

The solutions employed were as follows: 10 wt% solution of PCL in tetrahydrofuran (THF) or CHCl_3 (chloroform), 10 wt% solution of PLA in CHCl_3 or CH_2Cl_2 (dichloromethane), all of which were prepared by dissolving corresponding amount of polymer pellets or a granulate in corresponding amount of solvent and stirred on a magnetic stirrer over the course of 4 hours. Additional sets of experiments included drop-casting 2.5 ml of the solvent (CHCl_3 , THF, ethyl-acetate, acetone, CH_2Cl_2) onto a polystyrene Petri dish.

5.2.1 Prototype BF chamber

A prototype atmospheric chamber (Figure 20) was used for preliminary experiments exploring various polymer-solvent-vapour combinations with undefined humidity and airflow conditions. The core idea is to actively introduce air enriched with water or ethanol

vapour into the chamber under a constant airflow rate. This promotes the droplet condensation on the surface of a polymer solution during solvent evaporation.

The chamber's frame was fabricated via 3D printing, with PMMA sheets inserted to serve as walls. Air enriched with water or ethanol vapour was generated in the glass bubbler and introduced into the chamber through an opening at its base. This air was distributed to the chamber's interior via a sieve, on which the Petri dish containing the polymer solution was placed, and subsequently escaped through a set of holes in the top of the 3d-printed frame along with the solvent vapours.

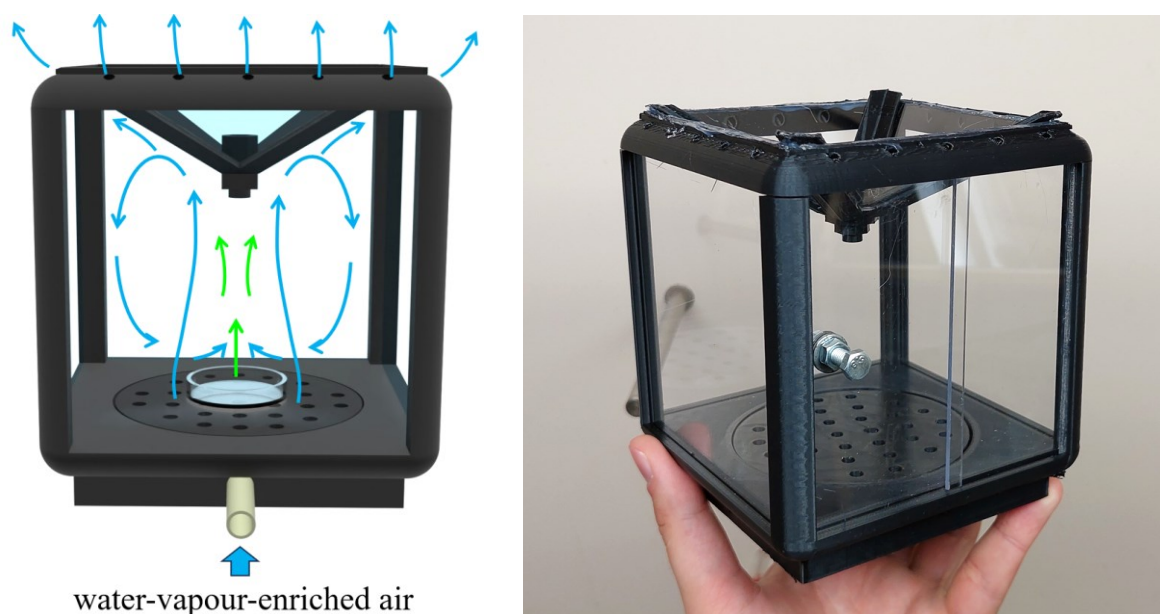


Figure 20 – Prototype BF atmospheric chamber.

While this chamber design the execution of preliminary experiments, it does not allow the measurement and thus control of the key experimental parameters, such as humidity or airflow. The process itself is also characterised by intense turbulent flows in this chamber.

5.2.2 Atmospheric chamber for LSBF with sensor unit

An atmospheric chamber was designed that would enable BF patterning across larger surface areas of polymer solutions while allowing for the precise control of the experimental conditions throughout the process. The chamber was designed using Blender and Fusion 360 software and constructed using 3D printing. The design layout, illustrating the flow paths of water-vapour-enriched air, as well as the solvent vapours, is shown in Figure 21.

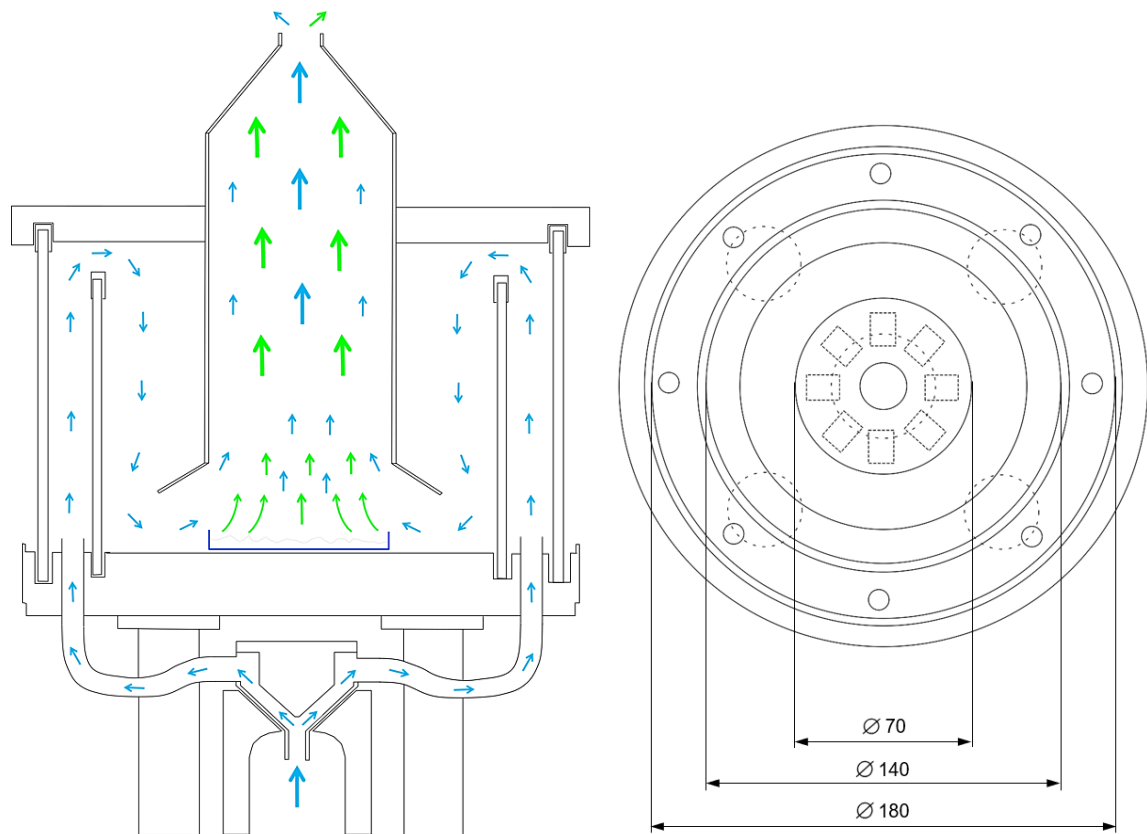


Figure 21 – Design layout of the atmospheric chamber for LSBF.

The presented atmospheric chamber design offers several advantages that collectively promote uniform, stable and predictable formation of a porous surface:

- The design ensures solvent vapours are continuously removed from the surface of a polymer solution, minimising possible variations of evaporation rate over time.
- Water-vapour-enriched air is introduced to the polymer solution with a flow direction aligned with that of the solvent vapours, reducing interference between these flows. This facilitates efficient solvent vapours removal while carefully bringing introducing water vapour at the same time.
- The prolonged path of the water-vapour-enriched air, as well as the division of the original flow into eight streams upon entry, ensures the uniform delivery of the water phase to the polymer solution from all directions, promoting consistent condensation and thus uniform pore formation.
- While the main frame is 3D-printed (from PLA), the inner and outer walls of the chamber are made of the polyethene terephthalate (PET) sheets, which provide excellent gas barrier properties and resistance to solvent vapours. The chamber's

base and lid are coated with a layer of epoxy resin to counter the porous nature of the PLA 3D prints and to enhance chemical and mechanical resistance, ultimately increasing both the performance and the lifespan of the chamber.

5.2.3 Sensor unit

For gathering experimental values, an Arduino-based sensor unit was implemented to establish the measurement of key parameters, such as air flow rate, relative humidity and temperature, all within an acceptable accuracy range. This unit employed an Arduino Nano V3.0 microcontroller mounted on a solderless prototyping board with a unipolar hall sensor for RPM measurement of the anemometer and a humidity and temperature sensor HTU21D placed inside the atmospheric chamber. Processed data were displayed in real-time on a 1,3" 128x64 OLED display and included RPM, RPS (revolutions per second), temperature and RH values, and updated once per second. Data could also be simultaneously sent to the serial monitor in Arduino IDE 2.3.4 software which was also utilised for programming the microcontroller or streamed into the CoolTerm software for further data processing. The wiring diagram is presented in Figure 22 and the complete code is in Appendix I.

For a chosen code logic that proved to deliver reliable data regarding the hall sensor, the RPM are calculated as follows:

$$RPM = \frac{pulseCount \cdot 60}{4} \quad (21)$$

where pulseCount represents the number of changes in the magnetic field per second and can only take integer values, thus providing measured RPM in increments of 15. To gather even more precise data, this smallest measurement step size could be further altered by increasing the number of magnets (4 in this case), counting pulses over a longer period, or opting for a different logic that measures the time between pulses.

Although the measured data displayed on the OLED display were updated every second, minor code adjustments were implemented to collect these data on a serial monitor in defined time intervals (such as 30 seconds or 5 minutes) so that the total data output during prolonged experiments was reduced.

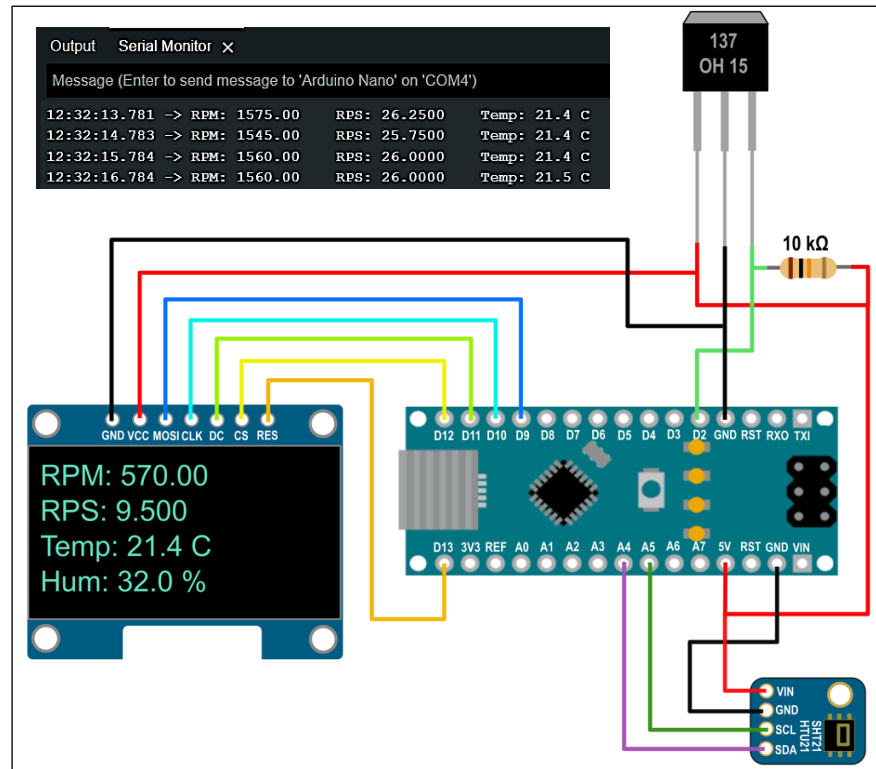


Figure 22 – Wiring diagram of an Arduino-based sensor unit.

5.2.4 Airflow control and measurement

The range of airflow values (expressed as RPM) used in this work is primarily constrained by the ability of a glass bubbler to maintain its structural integrity due to the excessive internal pressure at higher airflows (i. e. secure attachment of the lid to the body of the bubbler), as per the upper limit. The lower limit is determined by the minimum airflow required to overcome the hydrostatic pressure of the water column above the glass bubbler's outlet, thus ensuring continuous gas passage. To quantify this range, the geometry of the tubing was modified by introducing a constriction in the flow domain and therefore increasing the airflow velocity and allowing RPM readings to be obtained within the empirically determined range of airflow values.

For experiments performed in this work, the airflow was supplied by a centrally distributed compressed air system and delivered through a piping system extending to the fume hoods, further controlled by adjustment of installed valves and followed by flexible silicon tubing of inner diameters of 5, 6 and 7 millimetres, delivering the airflow to the atmospheric chamber. The airflow rate was measured indirectly using a 3D-printed paddle wheel flowmeter. This indirect measurement is based on the assumption that under ideal

conditions, the relationship between the speed of air particles v (airflow velocity) and RPMs is linear and defined as:

$$v \approx RPM \quad (22)$$

or with a correction factor of k as:

$$v \approx k \cdot RPM \quad (23)$$

One of the key process characteristics of presented system is a response time, which determines the time period after which the change in air composition coming to the chamber will manifest at various RPMs (change in humidity detected by a sensor). This parameter directly reflects the system's dynamic behaviour, efficiency of mass transport and mixing process of dried and humid air, all of which is determined by given by the system's geometry, length of tubing and airflow rate. The response time, described as a residence time by Bird et al., 2002 [61], is equal to:

$$t_{res} \approx \frac{V}{Q} \approx \frac{V}{A \cdot v} \approx \frac{V}{A \cdot k \cdot RPM} \quad (24)$$

where V is the system volume (constant value), Q is the volumetric flow rate and A is cross-sectional area. By inserting (2) into (4), we get:

$$t_{res} \approx RPM^{-1} \quad (25)$$

or more general equation:

$$t_{res} \approx RPM^{-k} \quad (26)$$

Where $k \neq 1$ for non-ideal systems.

5.2.5 Humidity control and measurement

The humidity was measured using a digital HTU21D sensor that measures temperature and relative humidity using capacitive sensing while providing accurate readings via I²C communication. The adjustment of the humidity conditions could be achieved real-time by small adjustments of the pinch-like valve with a screw mechanism, acting as a flow restrictor, installed after the first flow divider (see Figure 23) that either promotes or inhibits the flow of the drier air through the glass bubbler. This leads to notable differences in RH values of mixed air after these two branches meet at the flow merger.

The RH conditions at which experiments in the constructed atmospheric chamber were conducted were set to 55 %, 70 % and 85 %. This was later adjusted to 60 %, 70 % and 85 %

as the lowest RH values at which the pore generation is generally promoted start at approximately 60 % [48].

5.2.6 Experimental setup

The following Figure illustrates how all of the previously mentioned components (atmospheric chamber, sensors, etc.) are integrated to represent the full experimental setup used during experiments:

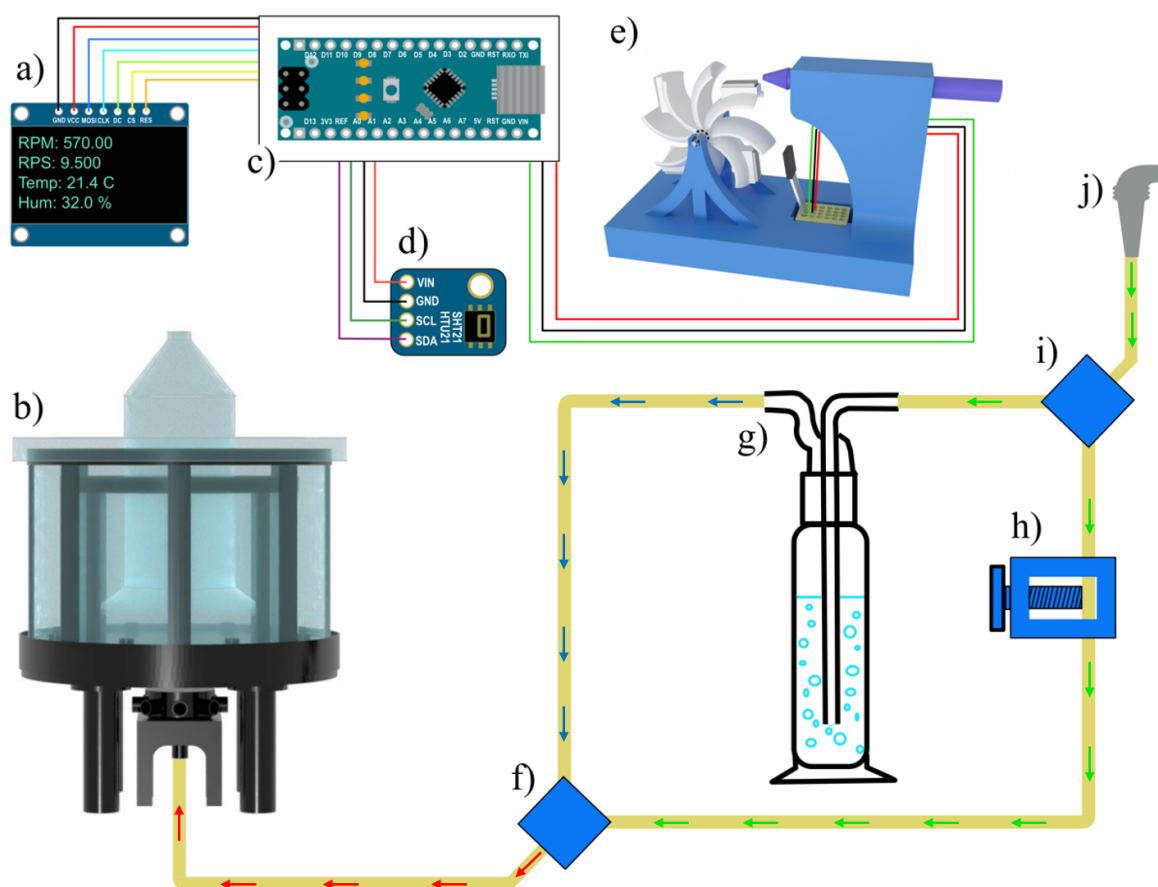


Figure 23 – Experimental setup; a) OLED display, b) atmospheric chamber, c) Arduino Nano microcontroller, d) HTU21D sensor placed inside the chamber, e) flowmeter with hall sensor, f) flow merger, g) glass bubbler, h) flow restrictor, i) flow divider, j) air valve.

5.2.7 Selection of a suitable polymer-solvent system

For this setup, a 10 wt% % solution of PLA in CHCl_3 was used. 2.5 ml of the solution was cast onto a glass Petri dish (35 mm in diameter) and placed inside the central part of the chamber. The BF patterning was performed under a series of combinations of the airflow settings and humidity conditions, as shown in the Results section of this thesis.

The choice of a given polymer-solvent pair is based on the assumption that BF patterning regarding the experimental part of this thesis should meet the following requirements:

- An amorphous or a low-crystallinity polymer is preferred over a semicrystalline one, as it may be difficult to distinguish which of the factors (the tendency of such polymer to form a spherulitic arrangement or a BF patterning) contributed more to the resulting surface structure. The opaque nature of dominantly crystalline polymers (such as PCL) caused by diffraction due to the difference in refractive index between the crystalline and amorphous region also makes it difficult to distinguish porous and non-porous regions on the sample surface – which is simple in case of the amorphous transparent polymers or polymers with low crystallinity (such as PLA)
- The ability of such a polymer to form a free-standing film is probably the most crucial, as one of this thesis's goals is to find a suitable polymer substrate that serves as a carrier of a photocatalytic system
- Apart from the solvent's volatility (given by its boiling point), another crucial aspect to consider is the solvent's miscibility with water, which could potentially interfere with the pore formation in the BF patterning. Water-immiscible solvent (such as CHCl_3) is therefore preferred.

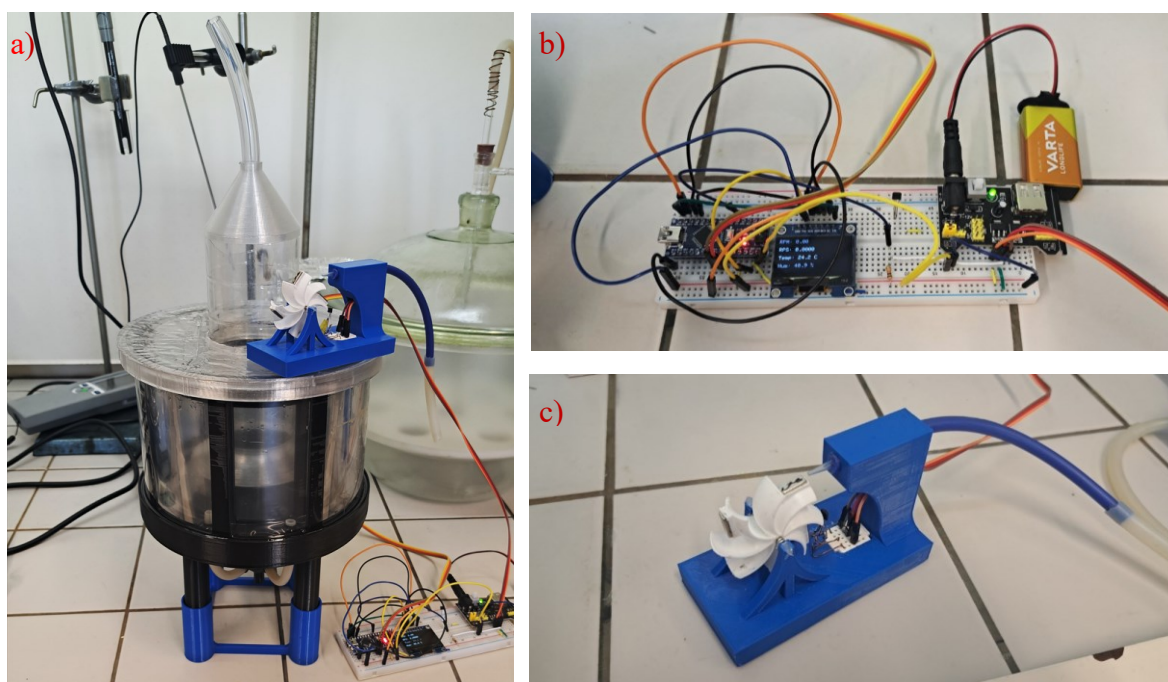


Figure 24 – Photographs of experimental setup for LSBF; (a) atmospheric chamber; (b) Arduino microcontroller and OLED display on a breadboard, (c) flowmeter.

5.3 Preparation of Ga/Ga₂O₃/polymer samples

The work of Bartošík et. al., 2024 [28], the experimental part of this thesis aimed to substitute the Si/SiO₂ substrate in Ga₂O₃/Ga on Gr/SiO₂/Si samples with a polymer material. Similarly to their work, this was achieved by a deposition of GaNPs under UHV conditions on a polymer substrate. The first experiment employed a PCL self-supporting film patterned by a BF method in a constructed atmospheric chamber. Despite its limited thermal stability at elevated temperatures, this polymer was initially selected as a substrate to enable a preliminary evaluation of the GaNPs deposition behaviour. Its selection also reflects ongoing research activities on the Department of Physics and Materials Engineering at the Thomas Bata University in Zlín, Faculty of Technology.

In addition to the Ga₂O₃/Ga on PCL sample, a total of seven samples of Ga₂O₃/Ga on a PEEK substrate were prepared, with four of these samples being covered with a CVD-grown graphene (via the wet transfer method) after the deposition of GaNPs. While the nature of the PCL allowed deposition of GaNPs only at room temperature, the PEEK's ability to withstand temperatures up to 324 °C (see) allowed elevated substrate deposition temperatures. For each of the following deposition temperatures: room temperature, 100 °C and 200 °C, two samples were prepared: Ga₂O₃/Ga on PEEK and Ga₂O₃/Ga on PEEK/Gr. One extra sample of Ga₂O₃/Ga on PEEK/Gr was prepared at the deposition temperature of 300 °C to promote the size of the Ga islands and increase the probability of detection during SEM imaging.

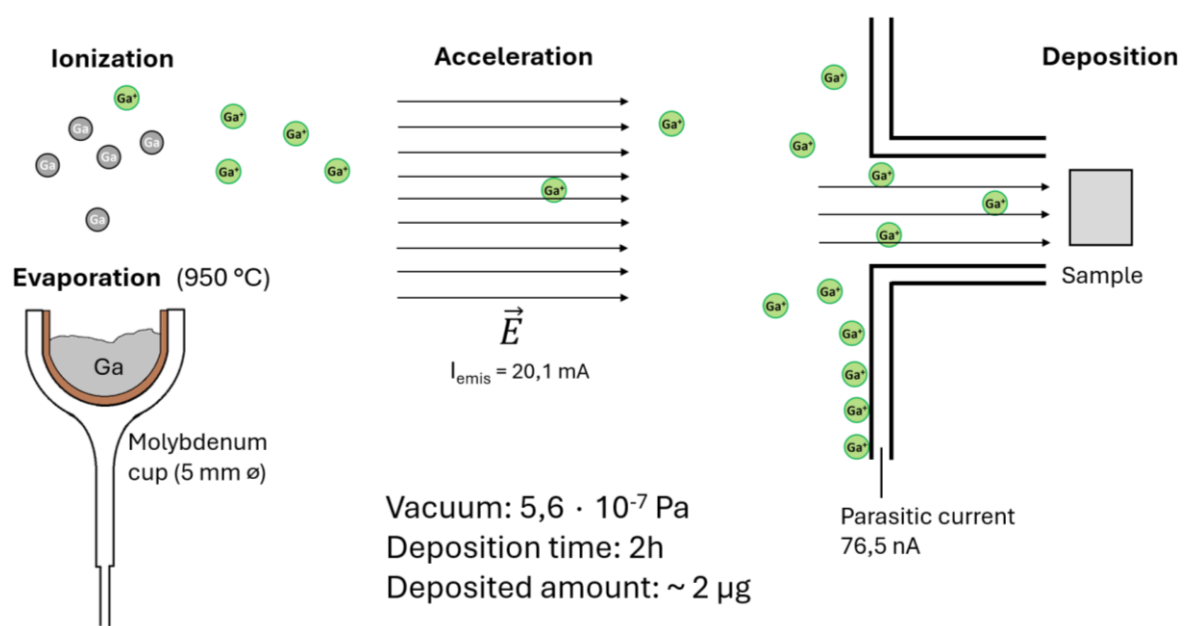


Figure 25 – Simplified scheme of the PVD process.

Experimental conditions, as well as the overall scheme of the process, are illustrated in Figure 25. The gallium metal was subjected to thermal evaporation in a molybdenum crucible positioned in the effusion cell, and it transitioned to the gas phase. Gallium atoms were then ionised and accelerated by the electric field towards the surface of the mounted sample. Atoms whose trajectory did not lead them to the sample were collected from the chamber's walls that was connected to the ground in a form of a parasitic current, whose experimentally determined value (76,5 nA) suggested an ideal flux of Ga ions, at which the two hours of deposition lead to approximately 2 µg of deposited gallium. The vacuum conditions were set to $5.6 \cdot 10^{-7}$ Pa – this increases the free mean path of gaseous Ga ions and also lowers the boiling point of the gallium metal.

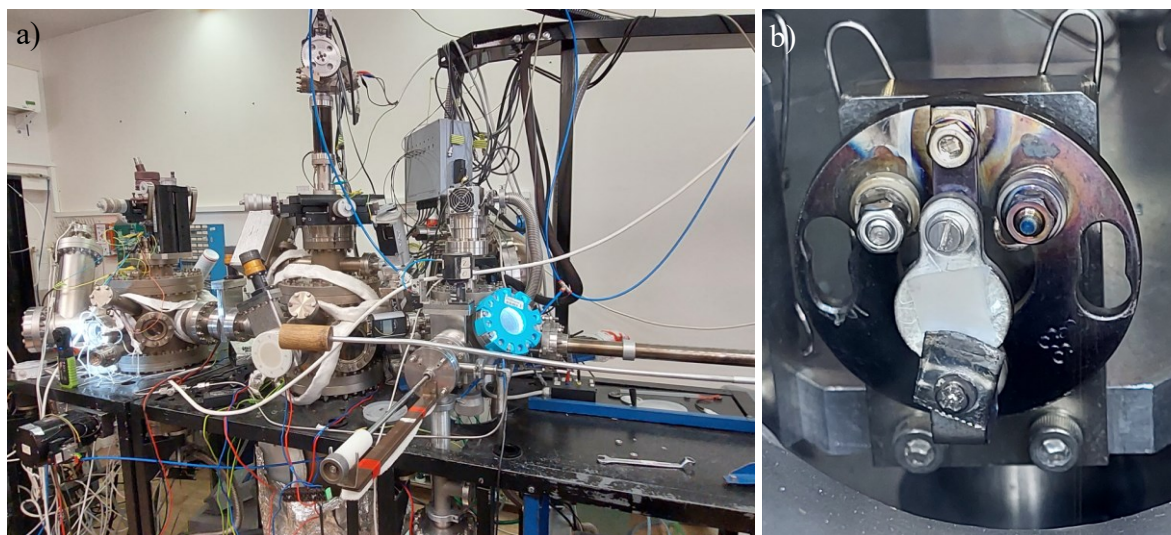


Figure 26 – (a) PVD chamber at the Brno University of Technology, Department of Physical Engineering, (b) PCL sample mounted on a holder prior to deposition.

The substrate deposition temperature of 300 °C was performed successfully only once – the combination of temperatures close to the PEEK's melting point, as well as the improper mounting of the sample in the holder lead to the bubbling and inflation of the polymer's surface – this is also probably due to the residual gas expansion allowed by the softening of the polymer. This is shown in the Figure 27 on the following page.

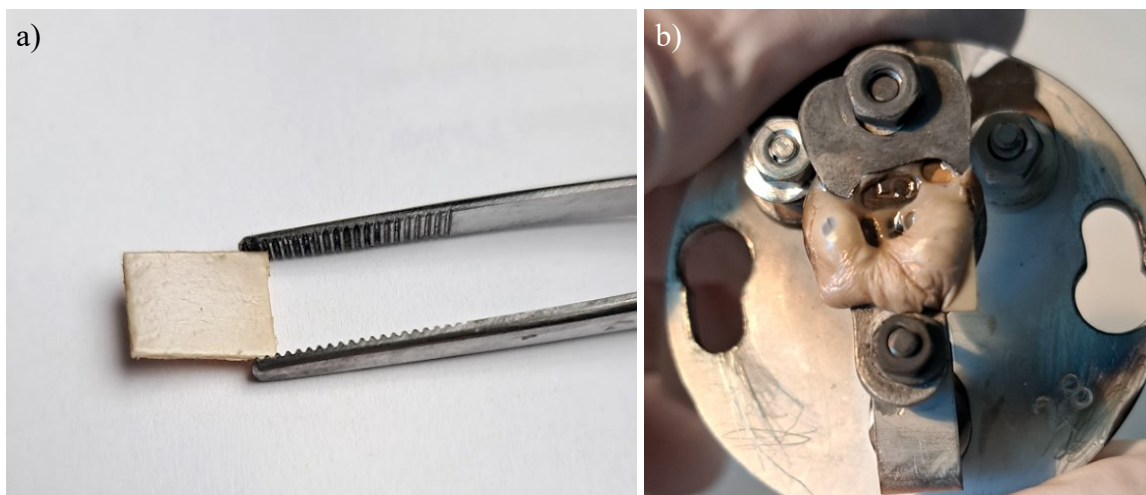


Figure 27 – (a) PEEK sheet prior to the deposition, (b) result of a PEEK's degassing at the substrate deposition temperature of 300 °C.

5.4 Photocatalytic experiment

The photocatalytic experiments were performed at the Institute of Environmental Technology, Technical University of Ostrava. The photocatalytic performance assessment of the samples was conducted in a batch stainless steel photoreactor of 348 ml in volume. The samples were loaded on the bottom of the reactor, which was then filled with 100 ml of a 50 % aqueous mixture of methanol. The reactor was sealed with a tight lid and saturated with helium at a pressure 125-130 kPa. An 8 W UV-C (254 nm) pen-ray lamp (or 365 nm LED lamp) was positioned on a quartz glass window in the photoreactor's lid and turned on to initiate the reaction. Via a septum in the reactor, gaseous samples were collected using a syringe in 1-hour intervals with a total irradiation exposure time of 4 hours. A gas chromatograph GC Shimadzu Nexis GC-2030 equipped with a barrier ionisation discharge detector was used to analyse the gaseous samples. The amount of hydrogen present in the chamber at a given time was given by a ppm value, expressing the number of present H_2 molecules per 1 million molecules of gas ($He + H_2 + \text{others}$). Aside from the hydrogen gas, other gases like methane and carbon monoxide were produced during the reaction, although only in a minuscule amount.

During experiments, the photocatalytic performance was compared either to the TiO_2 -P25 (nano powder) posing as a standard, or a clean sample of PCL or PEEK (with no photocatalyst). As can be seen in the section Results, even clean polymer surfaces seem to facilitate the hydrogen evolution out of the aqueous methanol solution. For this reason, a

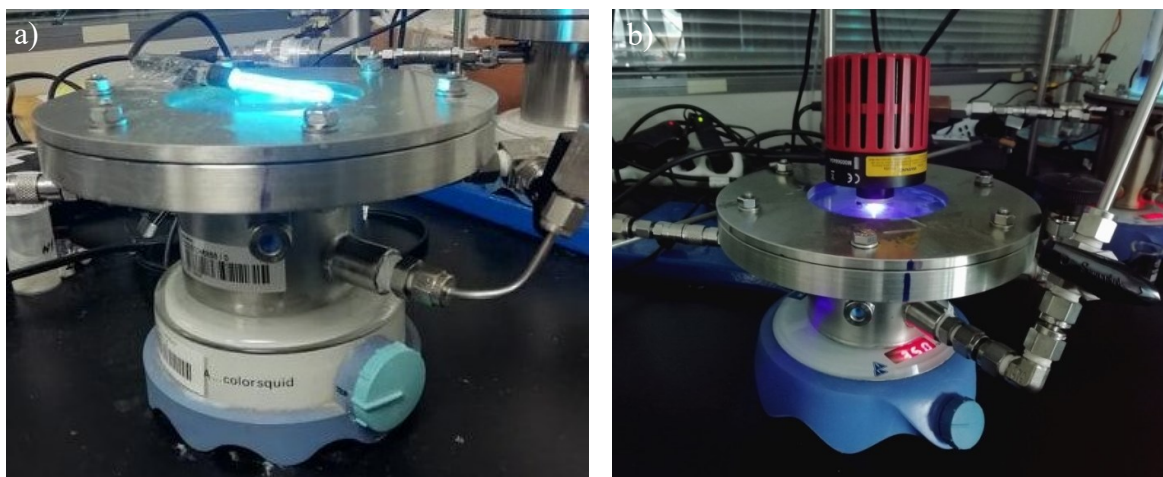


Figure 28 – Photocatalytic reactor irradiated by a 254 nm (a) or 365 nm (b) lamp.

thin layer of Au + Pd was deposited on the clean PEEK surface via the sputter coating process using sputter coater SC7620 Mini for 60 second from both sides under low pressure and Argon atmosphere. The layer was approx. 10 nm in thickness, as the deposition rate is approx. 10 nm /min as stated by the manufacturer.

5.5 Analytical and Imaging Techniques

The measurements performed using presented instruments were performed at the Department of Physics and Materials Engineering, Faculty of Technology, Tomas Bata University in Zlín, if not told otherwise.

5.5.1 SEM

The surface morphology of PLA and PS samples patterned by the BF method in the prototype chamber or the constructed atmospheric chamber was examined by the Phenom PRO under 10 kV with magnification varying based on the given surface topography. Samples were sputter-coated with Au + Ag for 30 seconds using SC7620 Mini sputter coater under an argon atmosphere, to dissipate surface charge during imaging. The porous nature of prepared surfaces was investigated via ImageJ and Python software.

SEM image of sputter-coated $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL sample (15 seconds, approximately 2.5 nm of sputtered layer) was taken using scanning electron microscope Nova NanoSEM 450, FEI (Centre of Polymer Systems, Tomas Bata University in Zlín) under 5 kV and 100 000x magnification.

Images of Ga₂O₃/Ga on PEEK/Gr (300 °C deposition temperature) were taken at the CEITEC Brno University of Technology using a high-resolution scanning electron microscope Verios 460L (FEI) under 5 kV and 350 000x and 250 00x magnification.

5.5.2 AFM

Atomic force microscopy was used in this work to obtain the surface morphology of PEEK samples (both clean PEEK surface and Ga₂O₃/Ga on PEEK samples) to surpass the SEM resolution limit and gain the z-information from the 3D profiles and cross-sectional cuts. For this, an atomic force microscope NTEGRA Prima was employed using a silicon probe (150 kHz resonant frequency, 5,5 N · m⁻¹ spring constant) with a scanning frequency of 0,50 Hz and 512x512 pixels resolution, both for the 100x100 µm and 100x100 nm profiles. All profiles were obtained by scanning in the semicontact regime and processed in the Gwyddion software.

5.5.3 XPS

The XPS spectrum for a clean PCL substrate was obtained using Omicron DAR400 X-ray source and EA125 electron spectrometer (Department of Physical Engineering, Brno University of Technology) prior to the PVD of GaNPs and also immediately after, when the Ga₂O₃/Ga on PCL sample did not come to the contact with the air yet. Rather than providing a detailed analysis of the chemical state via the deconvolution of high-resolution XPS spectra, this method was employed as the next detection method to confirm the presence of gallium on the polymer's surface.

5.5.4 Raman spectroscopy

Samples of clean PCL and Ga₂O₃/Ga on PCL were subjected to the measurement of Raman spectrum utilising lasers with excitation wavelengths of 325 (UV) and 532 (green) nm 15 mW lasers with a 30-second integration time. Fluorescence observed under 325 nm excitation was removed by baseline correction based on the Savitzky–Golay algorithm in the OriginPro software.

5.5.5 Contact angle measurement

The contact angle of water and water-methanol mixture on the PLA and PEEK surfaces was determined by the sessile drop method using an optical goniometer Krüss DSA30, with a total of ten 3 µl droplets analysed per sample.

6 RESULTS

6.1 LSBF – prototype chamber results

The results of BF patterning under undefined humidity and airflow conditions employing either the water or ethanol vapours are listed below. Experiments of BF patterning in the prototype chamber included either casting 2.5 ml of a polymer solution into a glass Petri dish, or casting 2.5 ml of solvent onto a polystyrene dish, in which case the solvent penetrated and swelled the PS, creating a polymer solution.

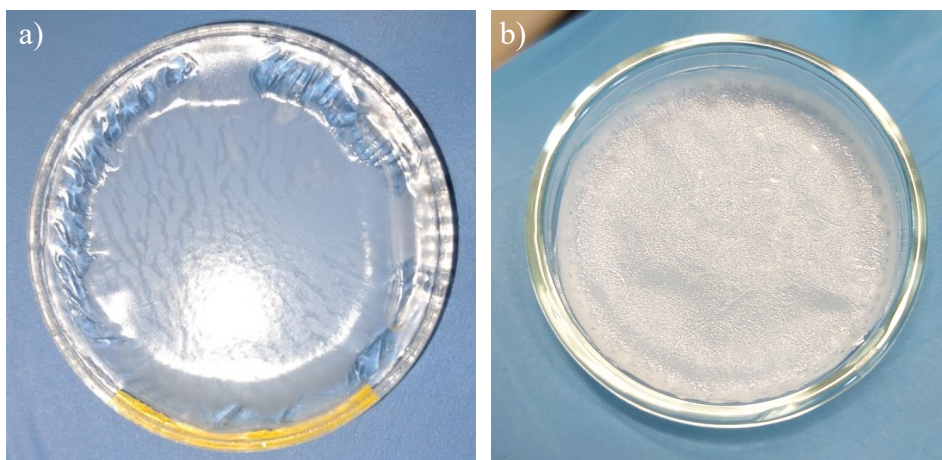


Figure 29 – Photographs of PS dish (a) and PCL film (b) patterned via BF method.

6.1.1 SEM

Figure 30 shows SEM results of a BF patterning of 10 wt% PCL in CHCl_3 and THF under unspecified humidity and airflow conditions.

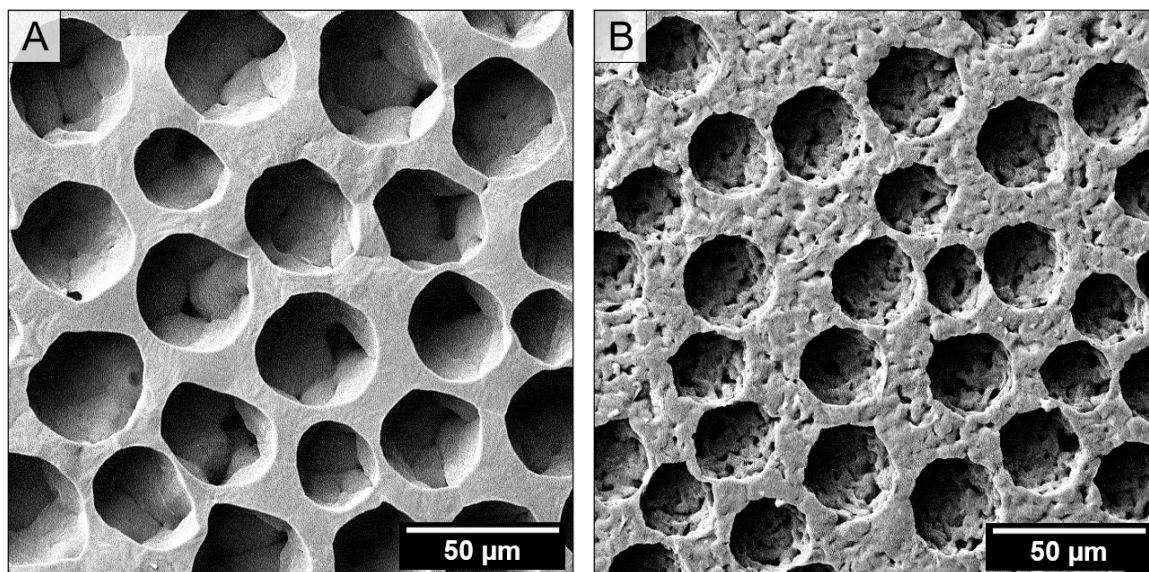


Figure 30 – SEM results of BF patterning of 10 wt% PCL in CHCl_3 (a) and 10 wt% PCL in THF (b), mag. 1200x.

It is apparent (in Figure 30) that during the solidification process, the crystallisation of the polymer distorted the spherical pore formation. This, however, led to the formation of a hierarchically structured surface characterised by multiple levels of patterning. The surface morphology shown in Figure 30 b) shows no distinct spherulitic arrangement, as is the case in Figure 30 a). This is due to the hygroscopic nature of THF, as the already present water interfered with the BF process and sample solidification. If the THF solvent is pre-dried using 3Å molecular sieves, the spherulitic nature of PCL is revealed as shown in Figure 31:

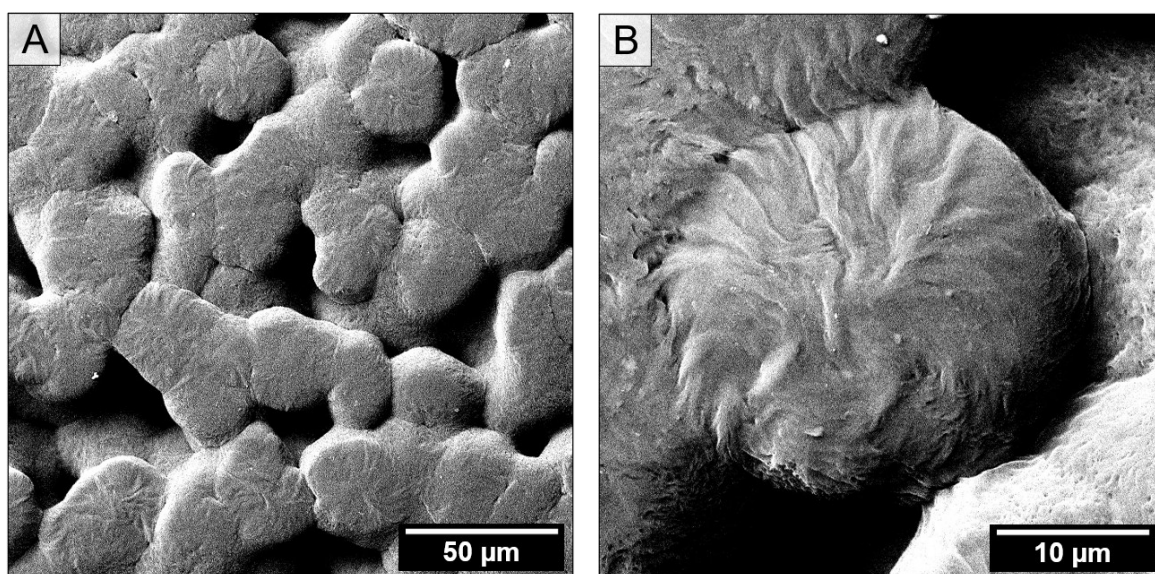
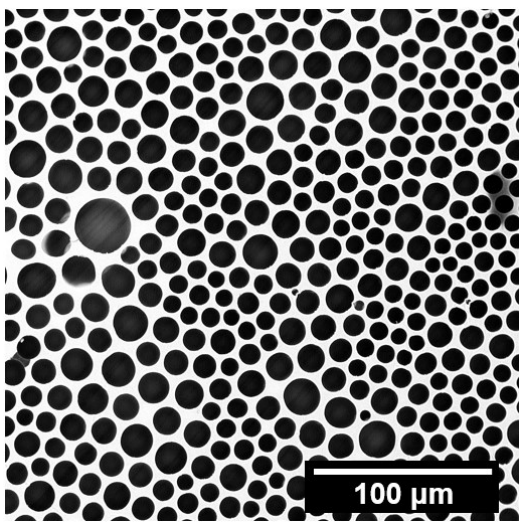
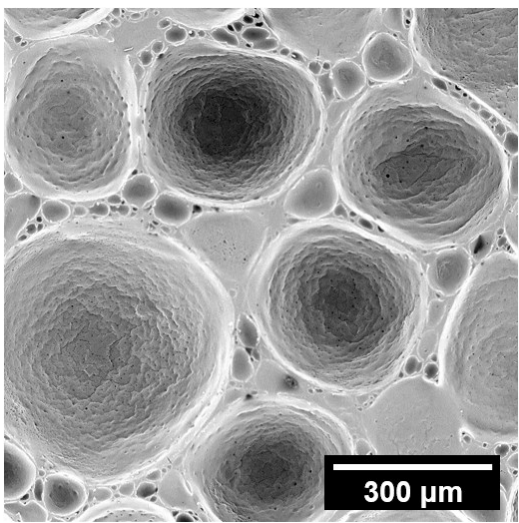
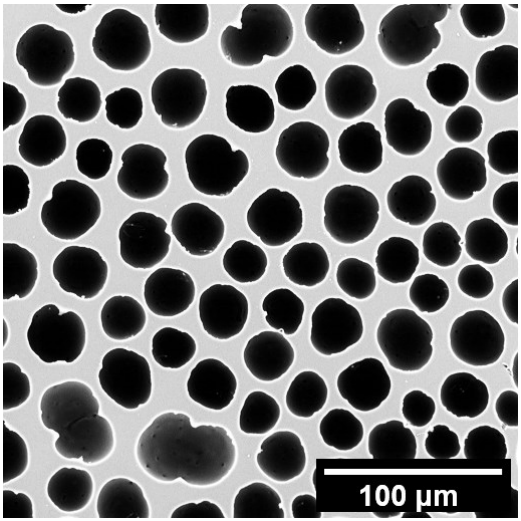
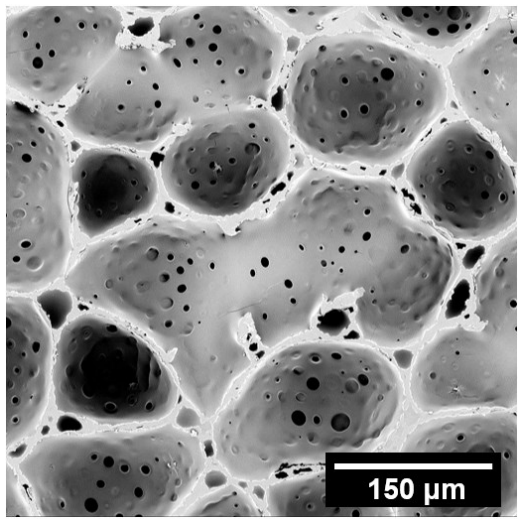
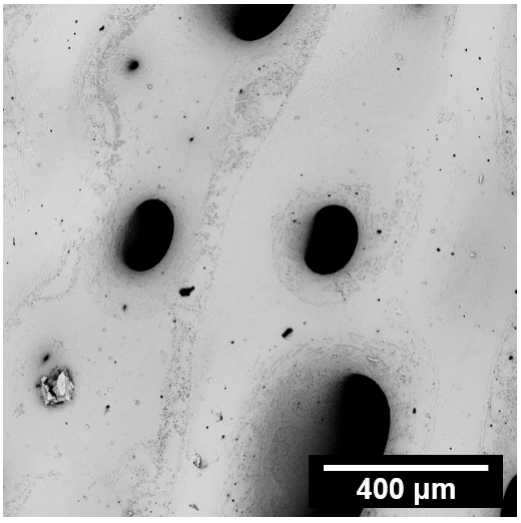
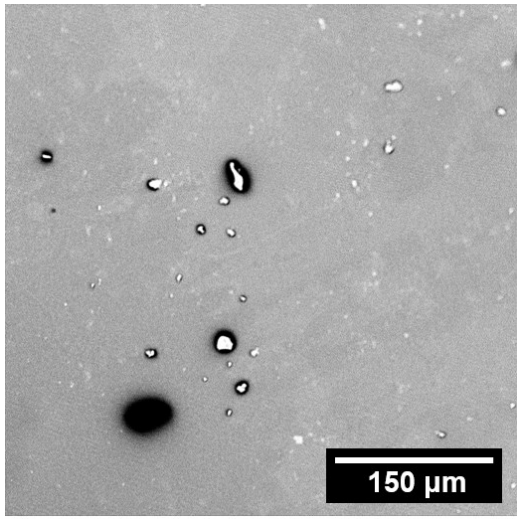


Figure 31 – SEM results of BF patterning of 10 wt% PCL in dried THF; (a) mag. 1200x., (b) mag. 5000 x.

Table 3 on the following page shows SEM results of the BF patterning of a PS dish on which 2.5 ml of a solvent (CHCl_3 , THF, ethyl-acetate, acetone, CH_2Cl_2) was cast. For the same polymer-solvent system, different vapour environment leads to pores of various morphologies or sub-structures, which arise from the uniqueness of the given polymer-solvent-vapour interaction (or polymer-good solvent-poor solvent interaction). It is evident that not every combination leads to the porous structure – the surfaces are either non-porous (such as for the PS-acetone-ethanol) or lead to the ball-like structures scattered across the PS surface, likely caused by the precipitation of the polystyrene on the interface of condensed ethanol droplet and the surrounding polystyrene solution – detailed SEM image of these is illustrated in Figure 32 below the table.

The SEM results of BF patterning by casting 2.5 ml of 10 wt% PLA solution onto a glass Petri dish in water vapours are not presented in this section, as they align with the SEM results presented in section 6.2.2 BF patterning of PLA films.

Table 3 – SEM results of BF patterning of a PS dish using water and ethanol vapours.

	Water vapours	Ethanol vapours
Chloroform		
Tetrahydrofuran		
Acetone		

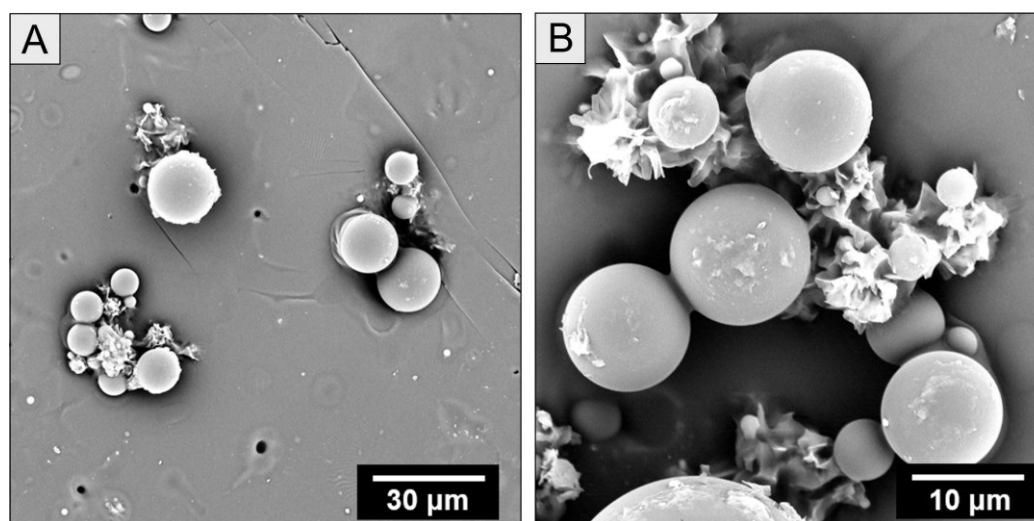
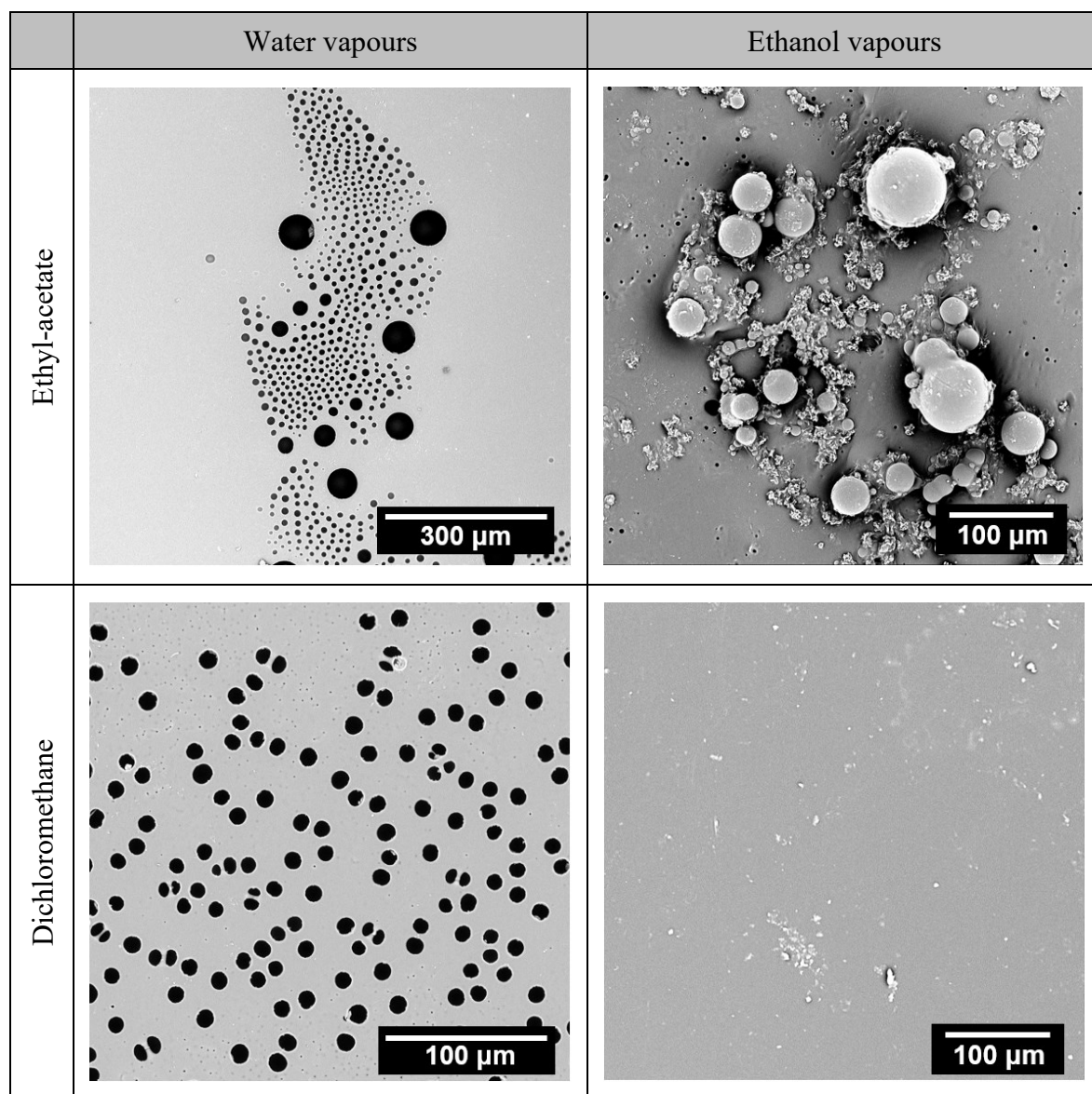


Figure 32 – Detail of SEM results of BF patterning in ethanol vapours via casting 2.5 ml of ethyl-acetate on a PS dish; (a) mag. 1500x, (b) mag. 5500x.

6.2 LSBF – constructed atmospheric chamber results

Experiments in the chamber were carried out under defined humidity conditions (60 %, 70 % and 85 % RH) and controlled airflow settings (indirectly expressed as 400, 800, 1200 and 1600 RPM). A BF patterning process was performed using a 10 wt% PLA solution in CHCl_3 with each sample being exposed to water vapours for a duration of 90 minutes.

6.2.1 Sensor output analysis – RPM and RH charts

The Figure below presents results from preliminary measurements demonstrating the behaviour and stability of the airflow supplied by the central compressed air system.

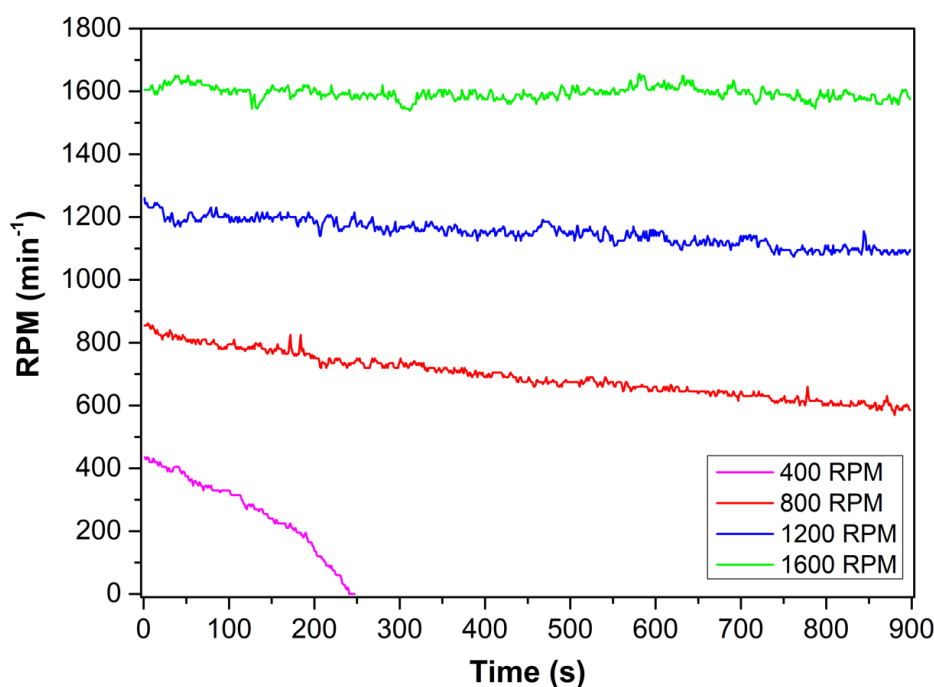


Figure 33 – RPM measurement at various initial airflow settings.

The RPM data shown in Figure 33, gathered over a 15 minute-period, indicate that the system can maintain stable airflow settings or exhibit a gradual decline (within a reasonable range of values) for initial valve positions corresponding to 1200 and 1600 RPM. The experiments performed at lower airflow settings (800 and 400 RPM) revealed either a slow decline in the initially set RPM value or a sharp drop to zero. Consequently, continuous RPM measurements and valve re-adjustments were necessary for the experiments carried at lower airflow settings. It should be noted that the act of RPM measurement involved redirecting the airflow stream into the flowmeter, during which the supply of the water vapour-enriched air was briefly interrupted. However, this interruption lasted no longer than 10 seconds and caused only minor disruption.

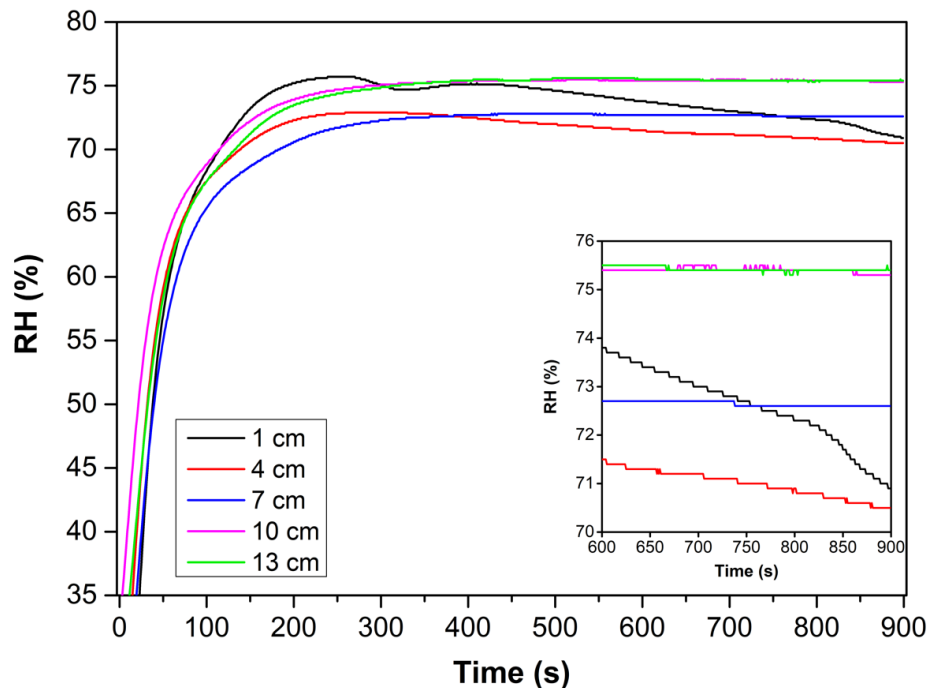


Figure 34 – Humidity evolution over time in the chamber for different water column heights in a glass bubbler.

The data illustrated in Figure 34 shows the evolution of humidity values, as measured by a sensor placed inside the chamber, for various water column heights in a glass bubbler under a constant airflow of 600 RPM. The results indicate that taller water columns are preferred, as they allow prolonged contact between the air passing through the bubbler and the water phase, thus promoting greater humidity enrichment. Water column heights above 10 cm are therefore preferred in this setup, as they enable maximal humidity to be reached and kept constant.

Results of a similar experiment, where the humidity was monitored over time at various airflow settings while keeping the water column height constant at 10 cm, are shown in Figure 35. The data show that higher airflow settings establish stable humidity conditions faster (see the intersections of the dotted line with individual RH curves). However, it is also observed that lower airflow settings lead to higher humidity values at $t = 900$ s. This occurs because, at lower flow rates, humid air accumulates in the chamber faster than it is removed due to the flow division and reduced flow velocity. Once the equilibrium is reached, the efficient humid air removal is supported by diffusion.

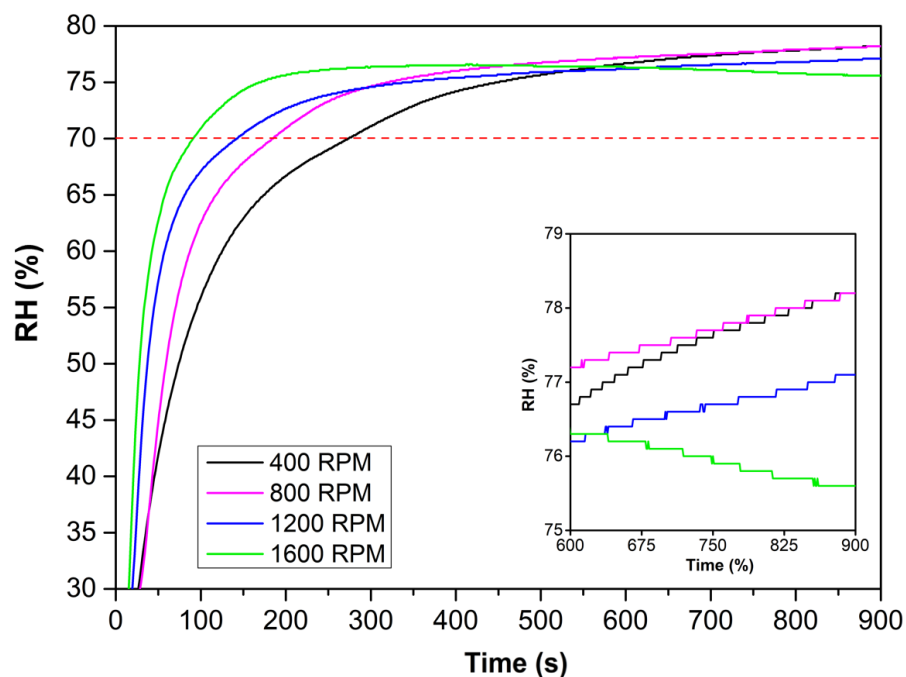


Figure 35 – Humidity evolution over time in the chamber for airflow settings.

To assess how long does it take for the sensor to detect the changes in humidity conditions under different airflow settings, an additional experiment in which the screw valve was fully open to promote the flow of the dried air through the branch that excluded the bubbler directly to the chamber was conducted, results of which are illustrated in Figure 36. Results show that the highest airflow leads to the fastest replacement of the humid environment.

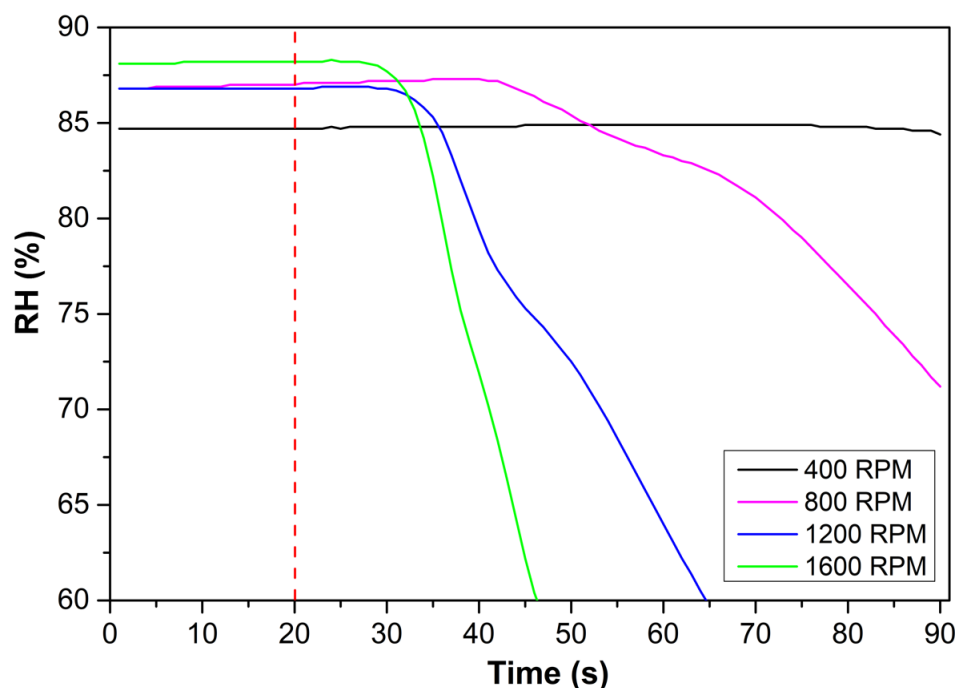


Figure 36 – Humidity evolution over time in the chamber after the passage of the dried air through the glass bubbler is shut at $t = 20$ s.

If the time between the passage opening for the dried air and the first decrease of the humidity value is determined, then this parameter, expressing a response time, can be plotted for individual RPM settings, and the relationship between the response time and RPM can be established:

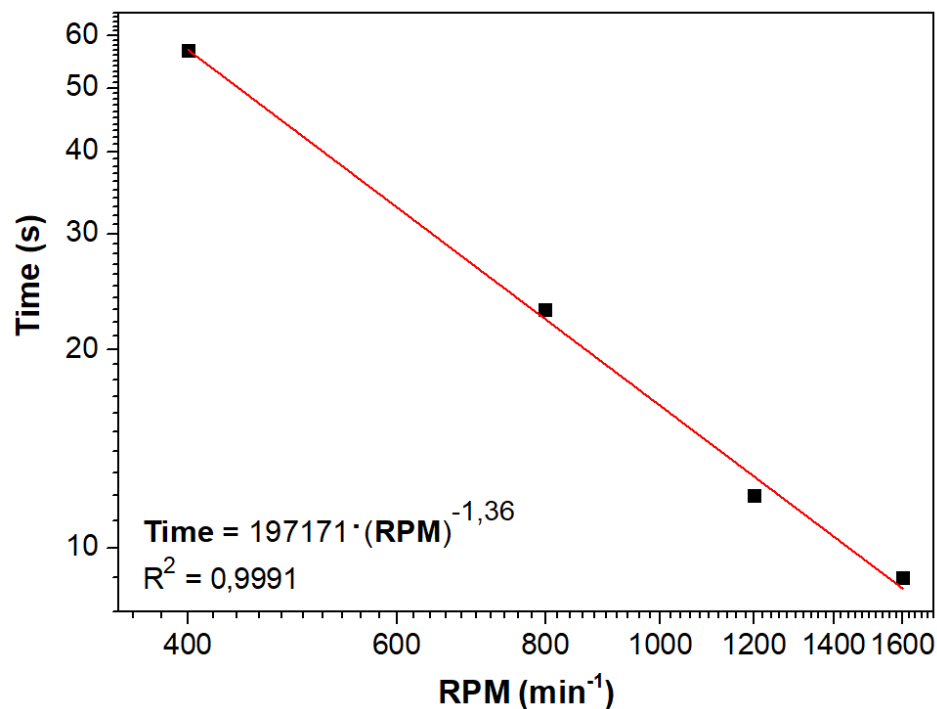


Figure 37 – Response time of control intervention as a function of revolutions per minute (RPM).

The graph depicted in Figure 37 shows the dependence of time (in this case, response time) on RPM, plotted in logarithmic coordinates to demonstrate the power-law relationship between the variables. It takes 9 seconds at 1600 RPM, but almost 60 seconds at 400 RPM for air to travel from the first flow divider to the sensor and thus for the system to detect the change in air composition, which also represents the minimum time required for the new humidity level in the chamber to be reached. In a presented flow geometry, this time is equal to:

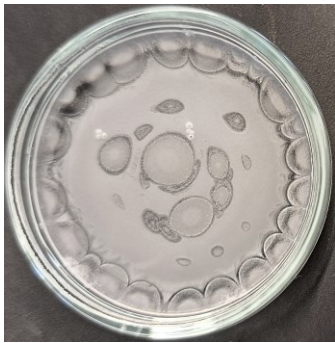
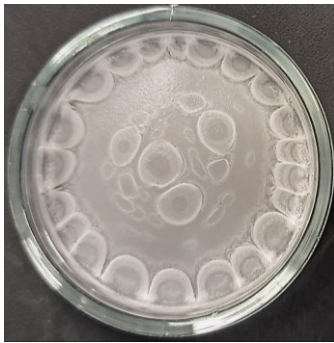
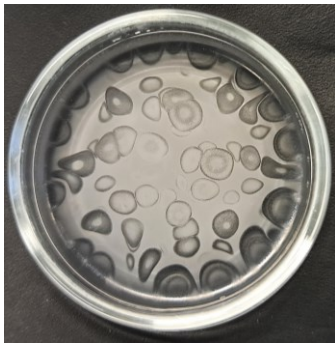
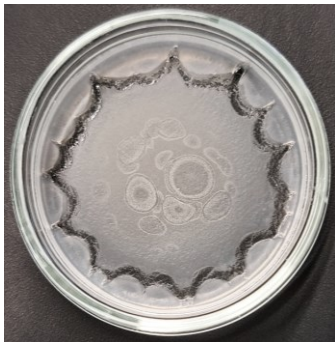
$$\text{Response time} \sim \text{RPM}^{-1.36} \quad (27)$$

which describes the inverse power-law relationship between response time of presented atmospheric chamber and airflow expressed as RPM, which is considered a linear function of airflow rate. The value $k = -1.36$ implies that an increase in RPM leads to disproportionally faster response time reduction, indicating the prevalence of turbulent flow, improved mixing and faster transport within the system at higher RPMs.

6.2.2 BF patterning of PLA films

The photographs of PLA films patterned via BF in water vapour environment by casting 2.5 ml of a 10 wt% PLA in CHCl_3 at defined airflow and humidity conditions are shown in Table 4.

Table 4 – Photographs of porous PLA films prepared under defined RH and RPM conditions.

	60 % RH	70 % RH	85 % RH
400 RPM			
800 RPM			
1200 RPM			
1600 RPM			

Photographs of the PLA surfaces reveal that substantial porosity was achieved for all the samples at RH = 70 % and 85 %, with very little to no porosity observed at RH = 60 %. The low-crystalline nature of the PLA enables the clear manifestation of convective flows, commonly referred to as Marangoni cells. These circular patterns, observed across all samples, mark areas with reduced or distorted porosity due to the excessive convective flows that establish in the polymer during the solvent evaporation (Figure 38). The formation of these circular zones, particularly along the edges where the polymer film meets the glass Petri dish, is attributed to humid air flowing along the dish walls as well as to boundary effects of the polymer solution. It is evident that higher humidity and airflow values promote the formation of more convective cells. The most uniform sample in terms of the cell spacing and size was observed at RH = 70 % with 1200 RPM, suggesting these conditions were optimal for the presented range of experimental parameters.

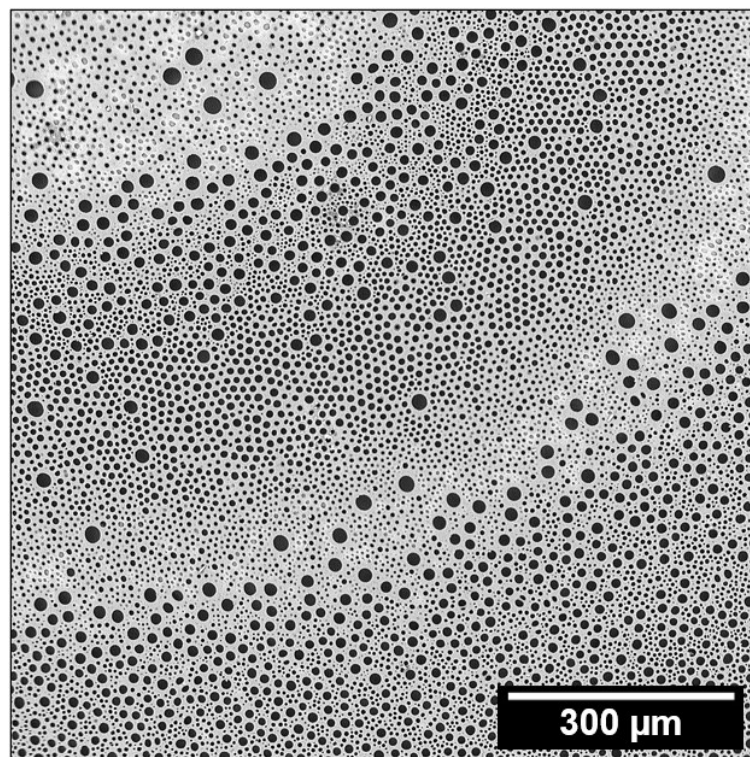


Figure 38 – SEM image of distorted porosity on the border of the convective cell, mag. 300x.

During the preparation of each sample (defined by specific RH and RPM values), RH data were recorded over a one-minute period. These RH charts are presented in Appendix II. SEM results shown on the following pages demonstrate how the various combinations of experimental parameters influenced pore formations.

6.2.3 SEM

Following Figures show SEM analysis results of BF patterned PLA films at 60 %, 70 % and 85 % RH for various RPM (400, 800, 1200, 1600 RPM) conditions.

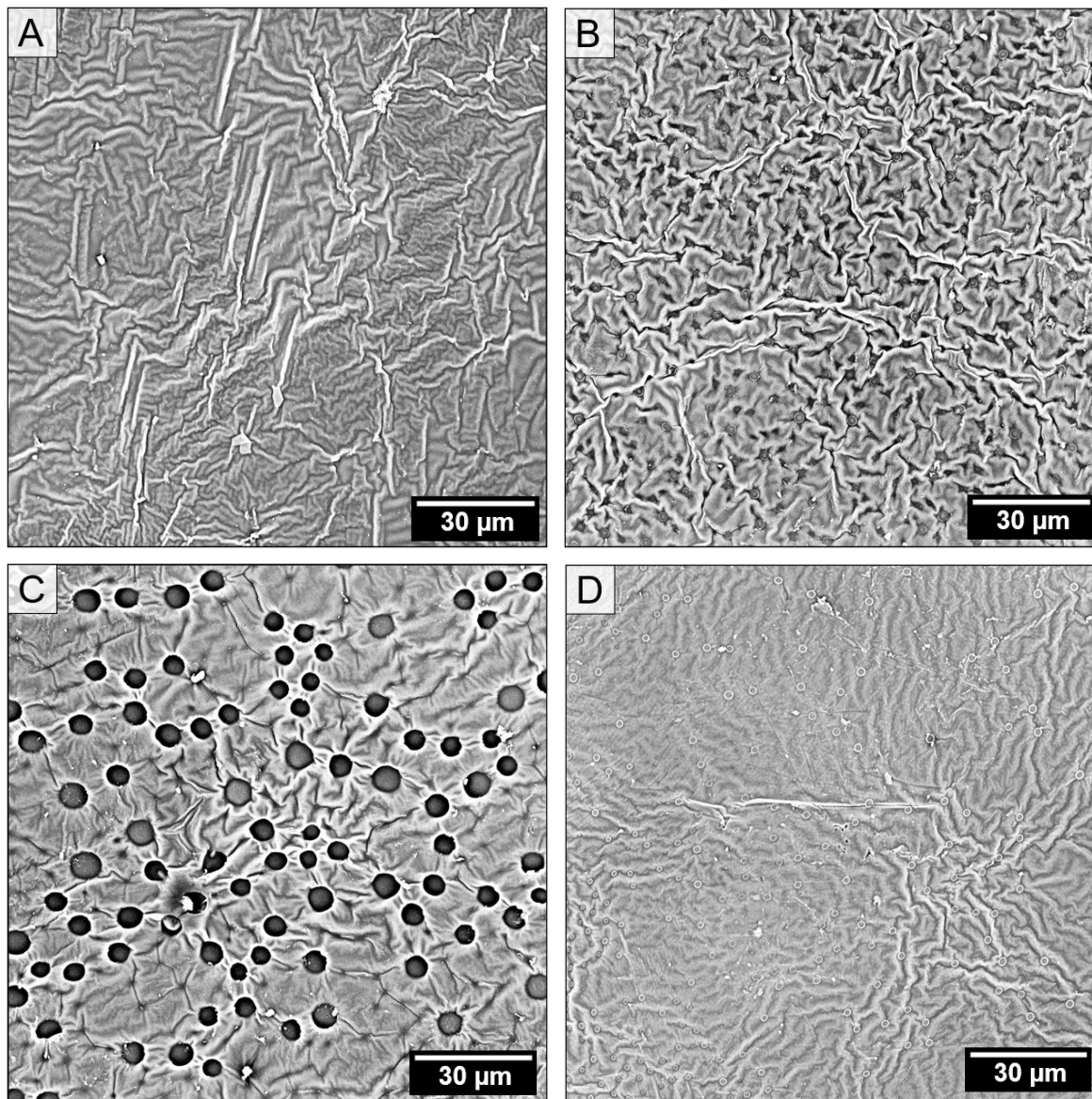


Figure 39 – SEM results of PLA films prepared under RH = 60 % at airflows expressed as (a) 400 RPM, (b) 800 RPM, (c) 1200 RPM, (d) 1600 RPM, mag. 2000x.

The SEM results in Figure 39, together with the results in Table 4, indicate that no or very limited patterning occurred under 60 % RH, with signs of sparse pore formation observed in samples prepared at 800 and 1200 RPM. Surface patterns observed in samples prepared at 400 and 1600 RPM suggest shrinkage likely caused by the mechanical stress induced by uneven solidification.

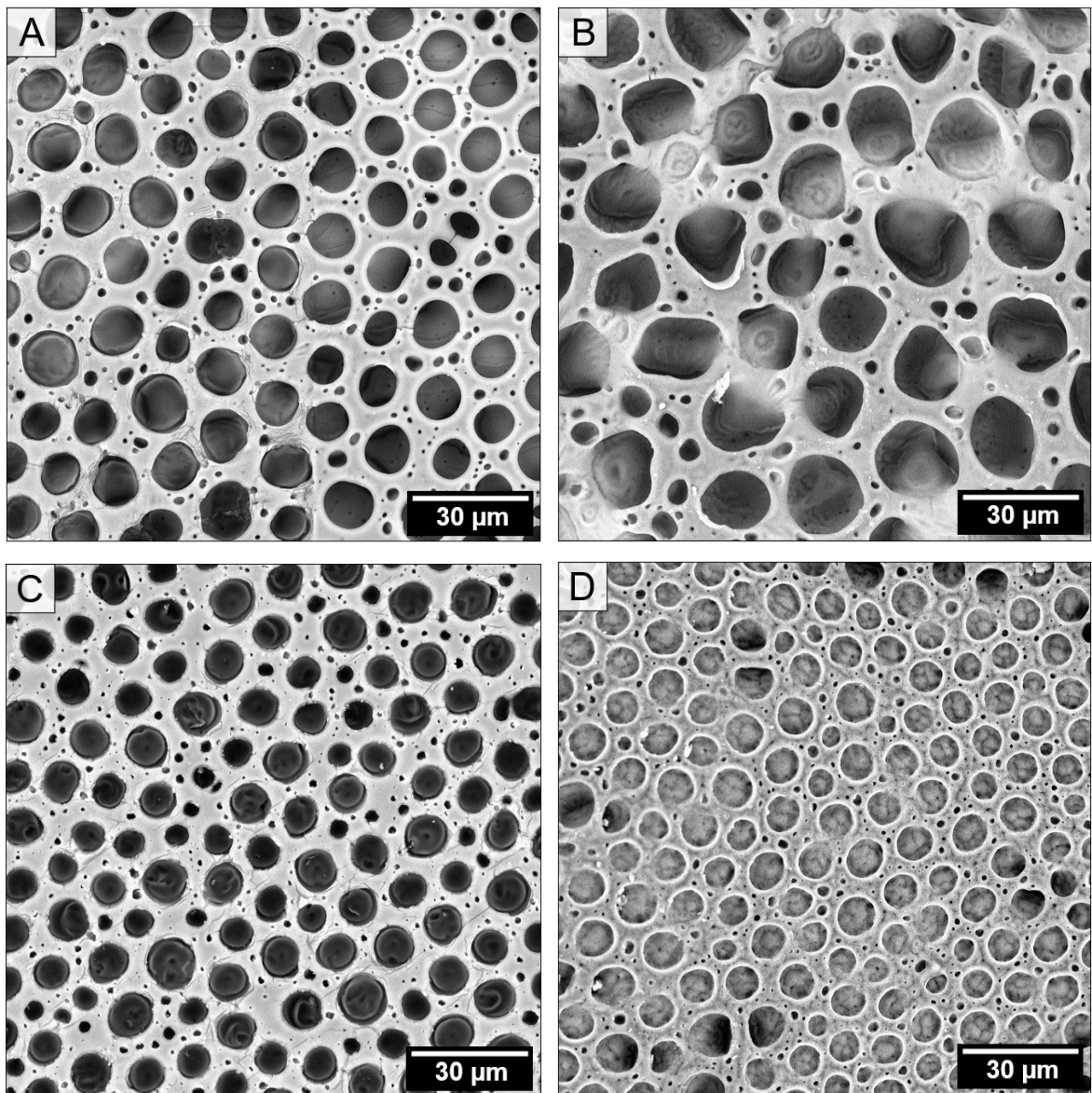


Figure 40 – SEM results of PLA films prepared under RH = 70 % at airflows expressed as (a) 400 RPM, (b) 800 RPM, (c) 1200 RPM, (d) 1600 RPM, mag. 2000x.

SEM results shown in Figure 40 indicate that substantial porosity occurs at RH = 70 % for all airflow settings, with the largest pores being observable at 800 RPM. The pore formation process at 1600 RPM is disturbed by the excessive airflow, causing the premature solidification of the surface, resulting in shallow pores.

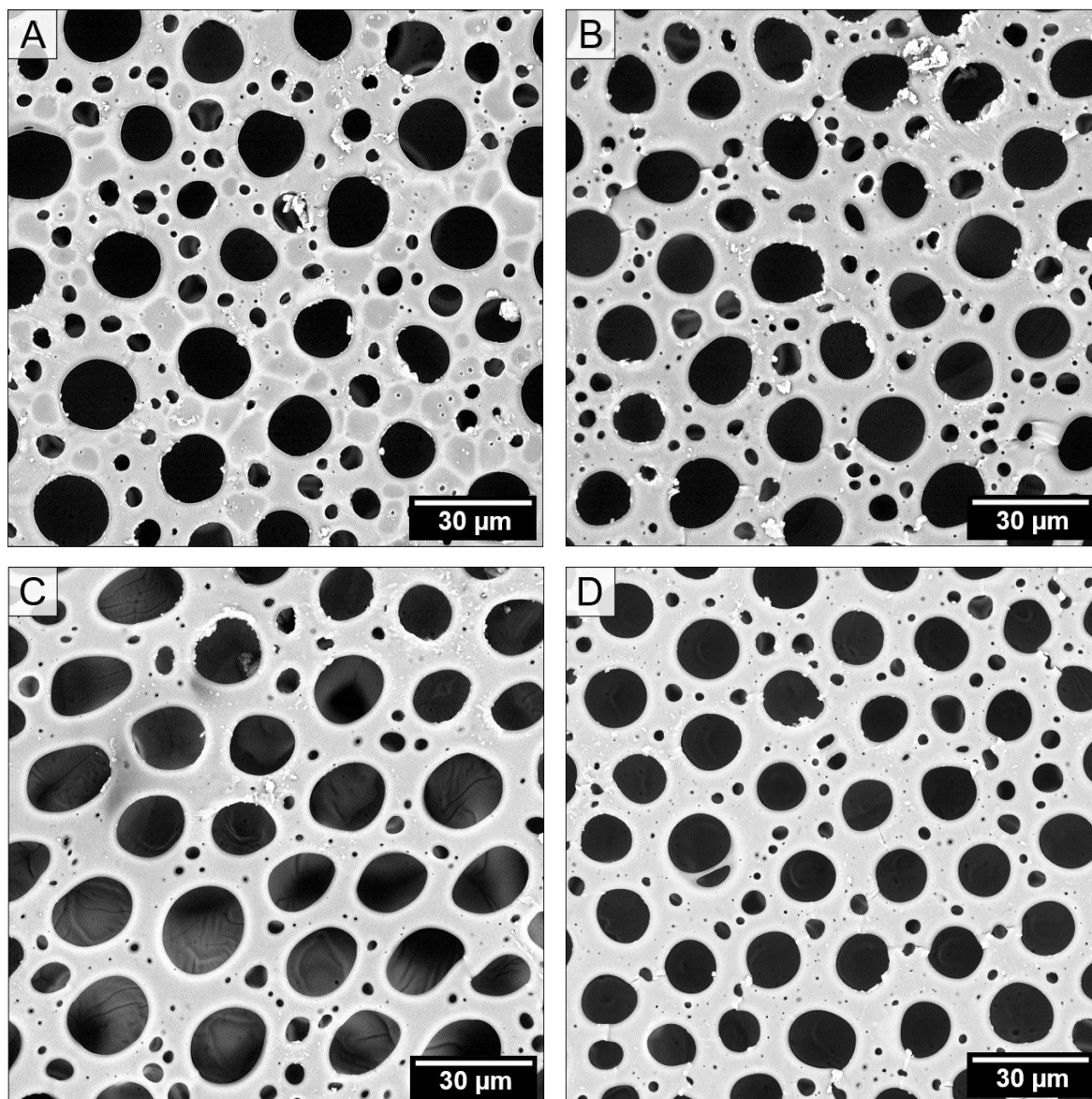


Figure 41 – SEM results of PLA films prepared under RH = 85 % at airflows expressed as (a) 400 RPM, (b) 800 RPM, (c) 1200 RPM, (d) 1600 RPM, mag. 2000x.

SEM results illustrated in Figure 41 demonstrate that higher humidity settings not only promote greater pore formation but also result in larger spacing between pores compared to the samples prepared at 70 % RH. In sample prepared at 1600 RPM, a small region was observed that deviated morphologically from both the rest of the sample area and the other samples (Figure 42). This surface morphology is characterised by pores arranged in distinct hexagonal-like cells, with surrounding free space exhibiting radial symmetry centred on the pores. This morphology likely resulted from the combination of excessive airflow and high humidity, which accelerated the solvent evaporation from the surface, forming a thin solidified crust while the water droplets were still present. The water droplets may have initiated a crystallisation from their centres, utilising free polymer chains from the solution

under the solidified crust. The presence of hole-like structures at the boundaries of the hexagonal areas, where these three cells competed for the free polymer chain, supports that the crystallisation most likely occurred.

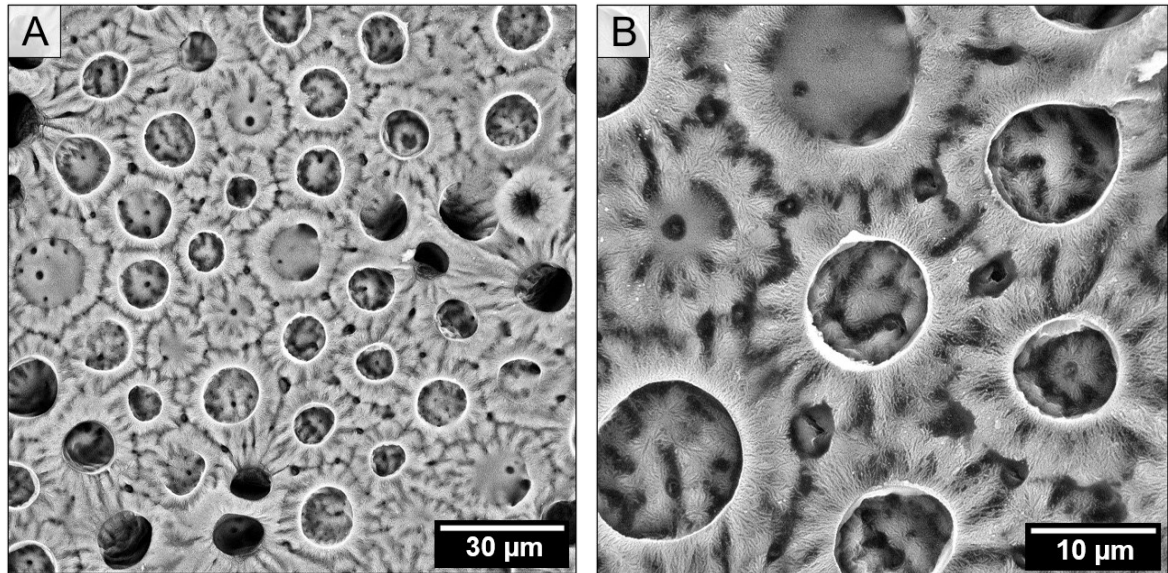


Figure 42 – SEM results of a unique porous region observed at PLA film prepared under RH = 85 % at 1600 RPM; (a) mag. 2000x, (b) mag. 5000x.

SEM results of PLA surfaces prepared at RH = 70 % and 85 % were analysed using ImageJ and Python software to determine both the pore size distribution and porosity. In this thesis, the porosity is a parameter defined as a ratio of the area covered by pores to the total area of the SEM image. The choice of porosity as a key parameter will be discussed later. Detailed results of the image analysis are presented in Appendix III and the Python code used to determine the porosity is included in Appendix IV. Summary plots of the image analysis results are shown in Figure 43 and Figure 44.

Figure 43 on the following page presents the mean pore size for samples prepared under 70 and 85 % RH at airflow conditions of 400, 800, 1200 and 1600 RPM. In three of the four cases, the mean pore size of samples prepared under 85 % RH is greater than that of samples prepared under 70 % RH at the same RPMs. Figure 44 demonstrates that the porosity is lower for all the samples prepared at RH = 85 %, which is attributed to the spacing between the pores. The data in this Figure further demonstrates that the porosity parameter more accurately reflects the influence of humidity conditions, as a clear trend across all RPM settings is evident and is not hindered by standard errors.

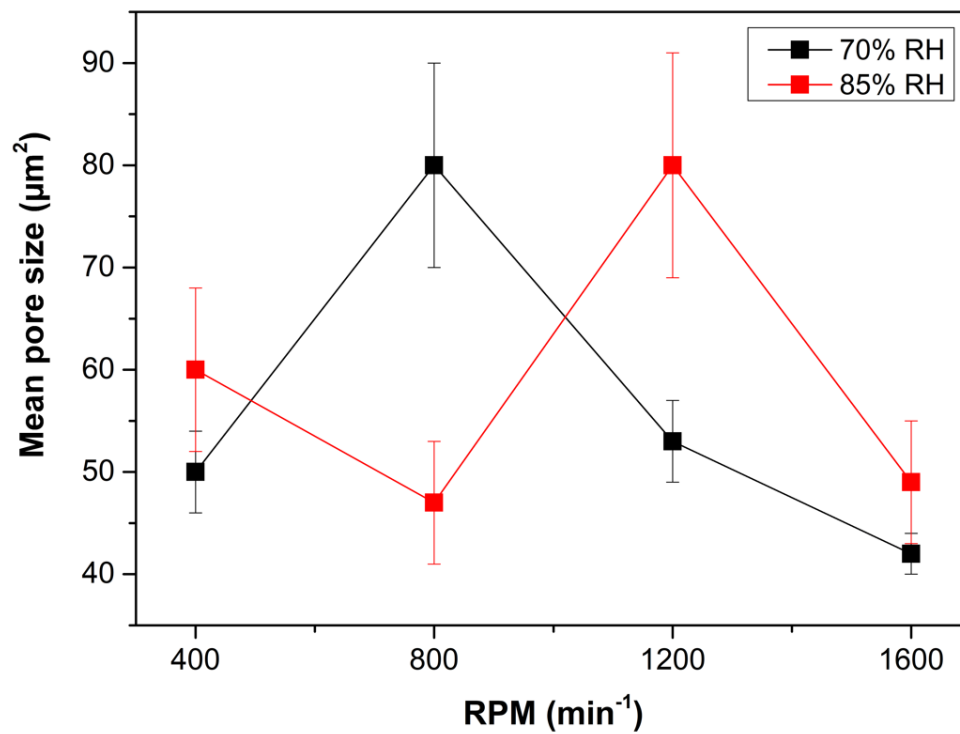


Figure 43 – Mean pore size of PLA samples prepared under 70 % and 80 % RH and various RPMs – summary.

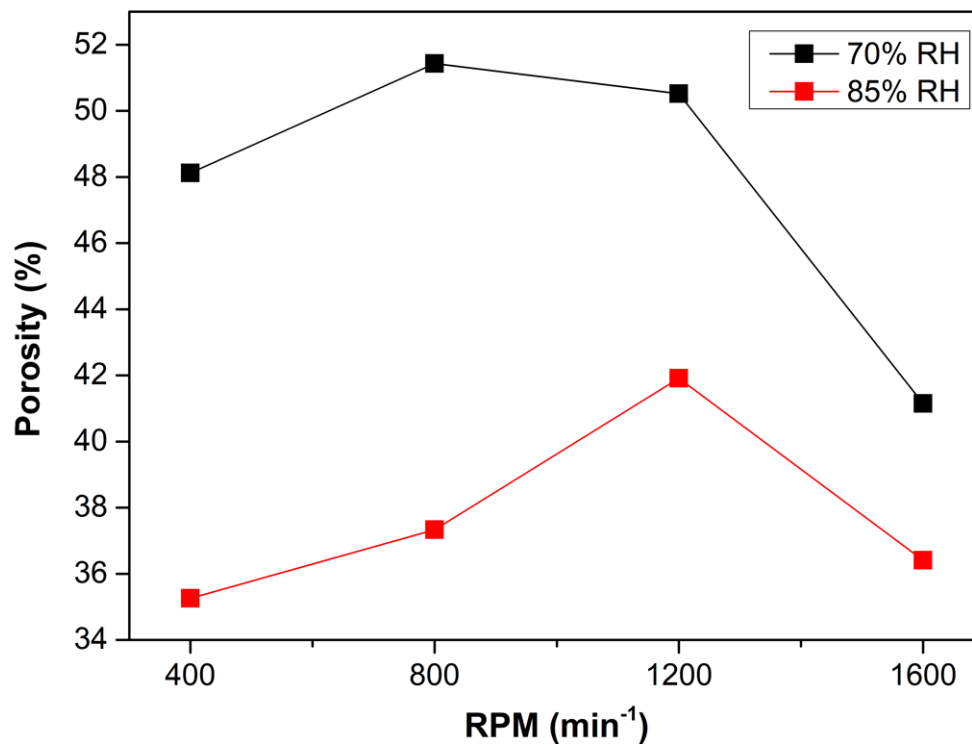


Figure 44 – Porosity values of PLA samples prepared under 70 % and 80 % RH and various RPMs – summary.

To assess whether the BF patterning can be successfully extended to a larger sample area, 10 ml of a PLA solution in CHCl_3 was cast into a 90 mm diameter Petri dish and subjected to patterning in the atmospheric chamber under 70 % RH and 1200 RPM. The outcome of this patterning is pictured in photographs in Figure 45. To evaluate pore formation across the entire surface, SEM images were taken from representative regions and analysed for porosity using ImageJ software and Python. In total, 25 SEM images were analysed for the porosity, defined as the ratio of the pore-covered area to the overall area (i. e. number of pixels representing pores divided by the total pixel count of 2048×2048). The choice of this parameter (instead of mean pore size) can be justified from the image analysis of a representative porous surface shown in Appendix 5, where it is demonstrated that the humidity conditions are not directly reflected in the mean pore size (which would be close to the mean pore sizes of other samples), but rather in the pore coverage of the area. The SEM images were collected from sample regions located along three diameters of 25, 50 and 75 mm, with eight images taken per diameter at 45° intervals, and one additional image taken from the centre. Appendix VI contains the code used for this analysis, together with determined porosity values. The results of the porosity analysis are shown in Figure 46.

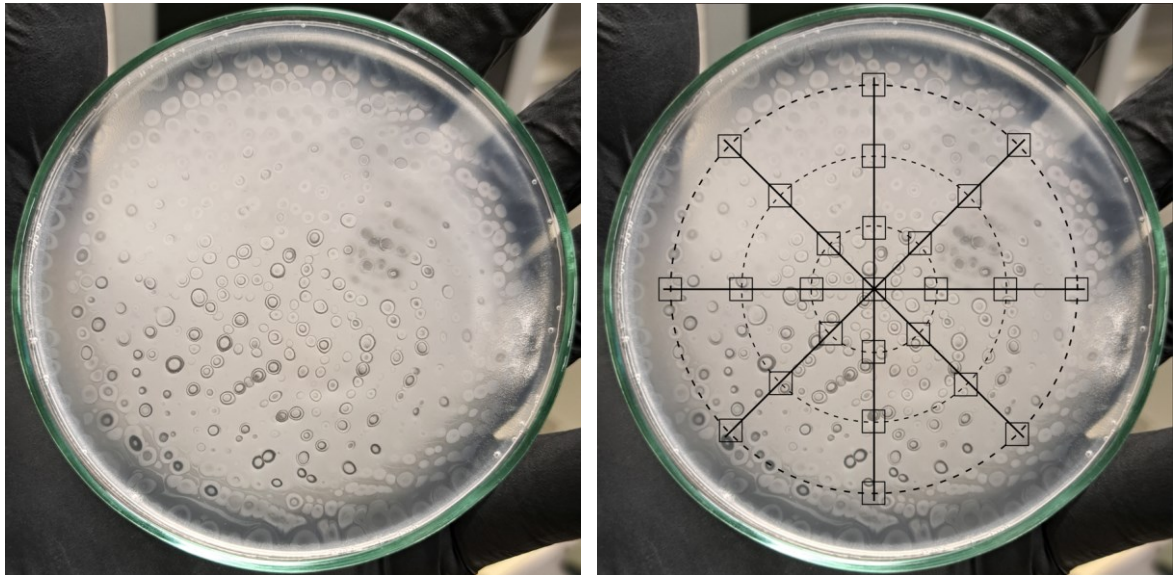


Figure 45 – Porous PLA film 90 mm in diameter with areas showing where the representative SEM images were taken.

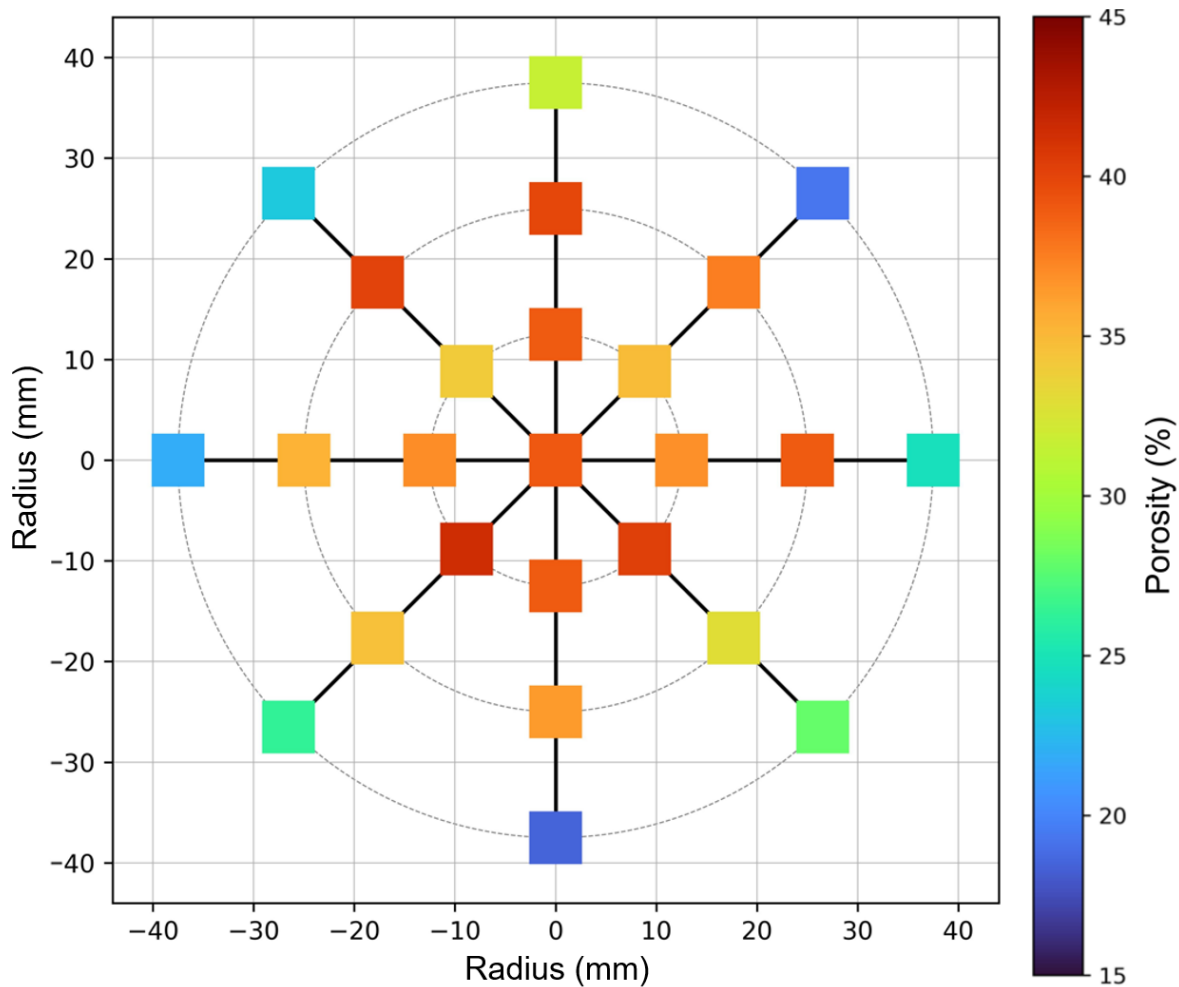


Figure 46 – Porosity of the representative areas on the PLA film.

The results in Figure 46 show that the porosity at diameters of 25 and 50 mm (as demonstrated by the colour gradient) reaches values equal to or exceeding 40 %. In contrast, the outermost circle with 75 mm diameter shows substantially lower porosity compared to the smaller diameter regions. This difference may be attributed to the effects at the polymer film-Petri dish boundary, air flowing over the edge of the Petri dish, or possibly due to the humidity gradient exhibiting central symmetry where humidity is higher near the centre, where airflow originally divided into eight separate flows meet and ideally combine at the near-centre region.

6.2.4 Contact angle measurement

The results of the water contact angle measurements are shown in Figure 47. The sessile drop measurements reveal that the non-porous surfaces (prepared at RH = 60 % at 400 and 1600 RPM) exhibit slightly hydrophilic behaviour, with contact angles below 90° (as indicated by the black dotted line). The introduction of porosity leads to an increase in contact angles – PLA surfaces prepared at RH = 70 % and 85 % show contact angles between 90° and 120°. The reason behind this increase (and also why the introduction of porosity did not improve the wettability of PLA surfaces) stems from the water droplet resting on the porous surface with air trapped in the cavities, as described by the Cassie-Baxter wetting regime. See the results table in Appendix VII.

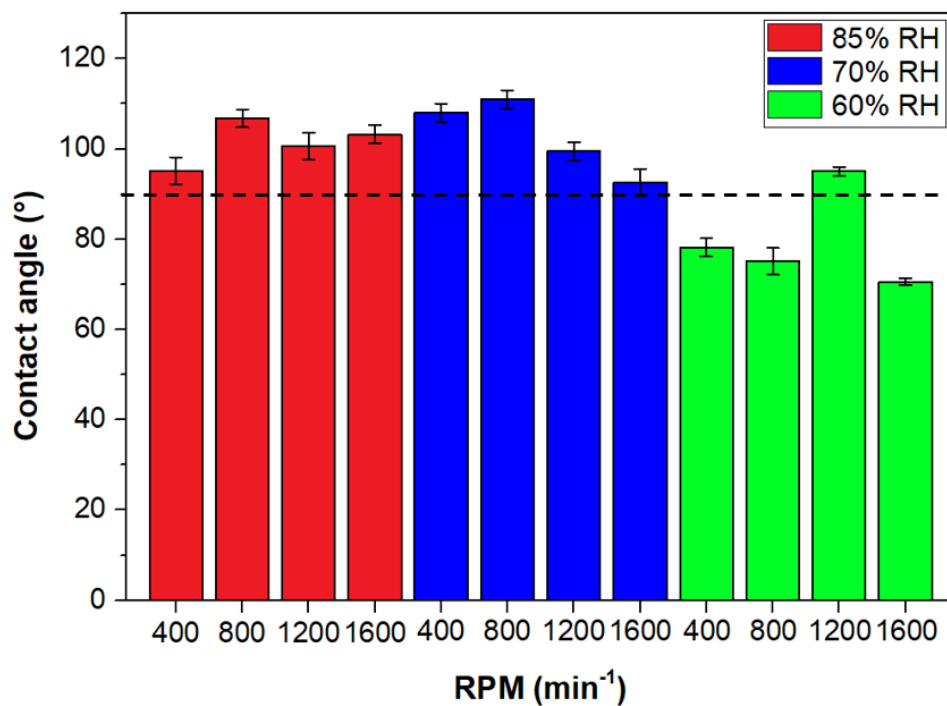


Figure 47 – Results of the contact angle measurement of PLA porous films.

6.3 Ga₂O₃/Ga on PCL samples

6.3.1 SEM

Image of the sputter-coated Ga₂O₃/Ga on PCL sample was obtained using Nova NanoSEM 450 under 5 kV acceleration voltage and 100 000x. magnification. The result in Figure 48 shows a surface topography of porous PCL film prepared by BF patterning, which was used as a substrate in the PVD of GaNPs. Result of the SEM imaging is shown in Figure 48, depicting the detailed view of the pore and a partially the pore boundary.

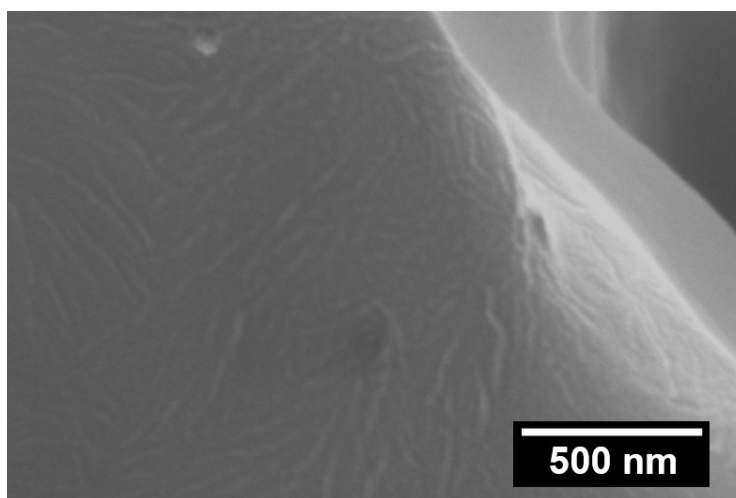


Figure 48 – SEM result of Ga/Ga₂O₃ on PCL sample, mag. 100 000x.

It is clear that, even at the highest achieved maximum magnification of 100 000x, where sufficient image clarity is still obtained, no structures resembling the gallium nanoislands, as shown in Figure 48, are observable. However, a subtle surface morphology is visible, resulting from the arrangement of polymer chains during solidification. The absence of observable gallium nanoislands may be due to the insufficient resolution of the SEM used or due to the size of deposited GaNPs being of the size in the order of units of nanometres. The sputter-coated layer, necessary for imaging of a non-conductive polymer surface, might have also effectively covered possible clusters of deposited GaNPs, as its thickness can be estimated to be 2.5 nm (15 seconds of sputter-coating with 10nm/min deposition rate).

6.3.2 XPS

Figure 49 shows XPS spectra of clean PCL collected prior to the deposition of GaNPs and of Ga on PCL sample collected immediately after the deposition, without exposure to the air, preventing the formation of the native oxide layer.

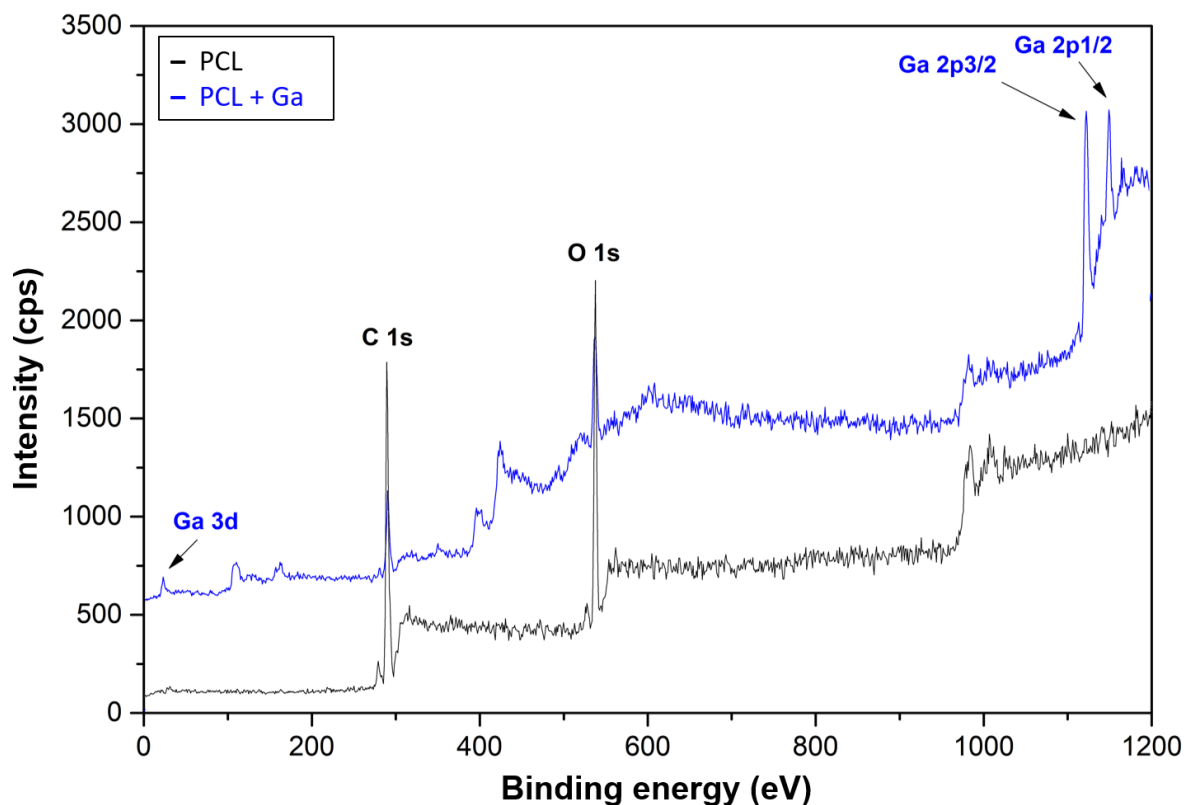


Figure 49 – XPS spectra of clean PCL surface and Ga on PCL sample.

While the C 1s and O 1s peaks are present in both spectra, the XPS measurement after the deposition leads to the additional Ga peaks: the Ga 3d peak at 24 eV (19 eV according to [58], Ga 2p_{3/2} peak at 1123 eV (1117 eV according to [58]) and Ga 2p_{1/2} peak at 1150 eV (1144 eV according to [58]).

Compared to the values presented in [58], it is evident that the binding energies in the presented spectrum are slightly shifted, likely due to the accumulation of the charge on the non-conductive polymer surface. The difference of binding energies between the values listed in [58] and in this work set the charge correction value at 6 eV.

6.3.3 Raman spectroscopy

The PCL surface with deposited GaNPs was measured using Raman spectroscopy under two excitation wavelengths: 532 nm (green laser) and 325 nm (UV laser). Maximum band intensity was achieved by optimal focusing of the laser on the sample. Raman spectra of PCL depicted in Figure 50 show some distinct bands present under both excitation wavelengths: 2800–3000 cm^{-1} in a) and 3000–3200 cm^{-1} b), attributed to CH_2 stretching and 1450–1500 in a) and 1470–1520 in b) attributed to CH_2 bending.

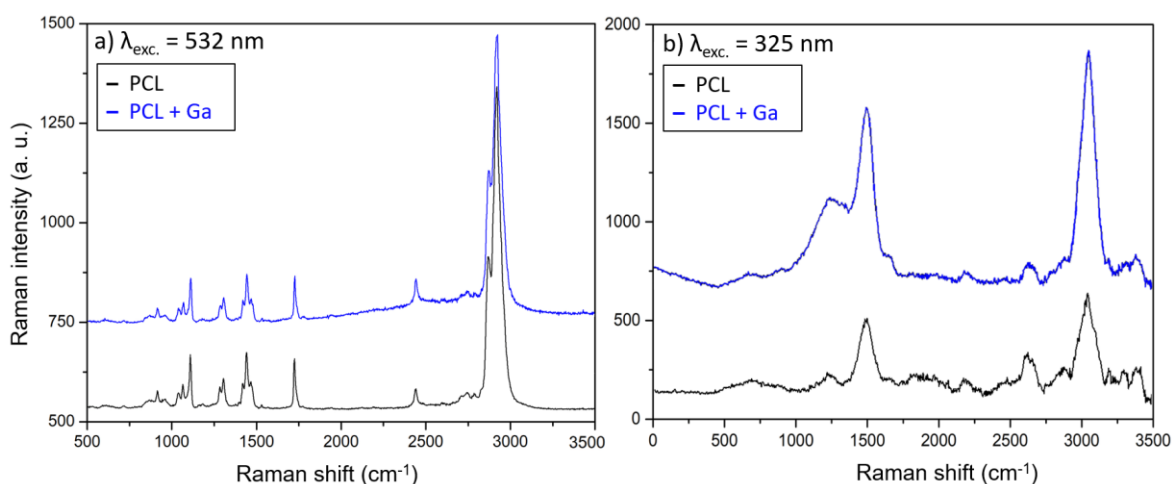


Figure 50 – Raman spectra of clean PCL surface and $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL sample obtained under 532 nm excitation wavelength (a) and 325 nm excitation wavelength (b).

There is no observable difference in the Raman intensity or band position at the clean PCL surface and the PCL sample covered with $\text{Ga}_2\text{O}_3/\text{Ga}$. The case for the excitation under 325 nm, however, is different: the bands in the presented spectra (b) are broadened and distorted by the excessive fluorescence, which was corrected through baseline subtraction using a Savitsky-Golay filter. After this correction, it is evident that the intensity of the bands is slightly higher at the PCL surface with $\text{Ga}_2\text{O}_3/\text{Ga}$, compared to the clean PCL. Although the comparison based on the intensities of bands is generally not revealing, higher bands intensity at the PCL with gallium suggest that there the gallium did organize in the spherical or semi-spherical islands few nanometers in diameter, rather than a continuous gallium cover layer, and these increase the band intensity of PCL via SERS induced by a LSPR in metallic cores – as the Ga_2O_3 outer shell has a bandgap corresponding to the 258 nm, the laser's wavelength of 325 nm is not absorbed by the oxide layer and enters the metallic core – although the LSPR resonance peak occurs at waveleghts around 669 nm, as was stated in the theoretical part of this work.

6.4 Ga₂O₃/Ga on PEEK and PEEK/Gr samples

6.4.1 SEM

High-resolution SEM images in Figure 51 of Ga₂O₃/Ga NPs on a PEEK/Gr (deposited at 300 °C) were taken using a scanning electron microscope Verios 460L (FEI) under an accelerating voltage of 5 kV.

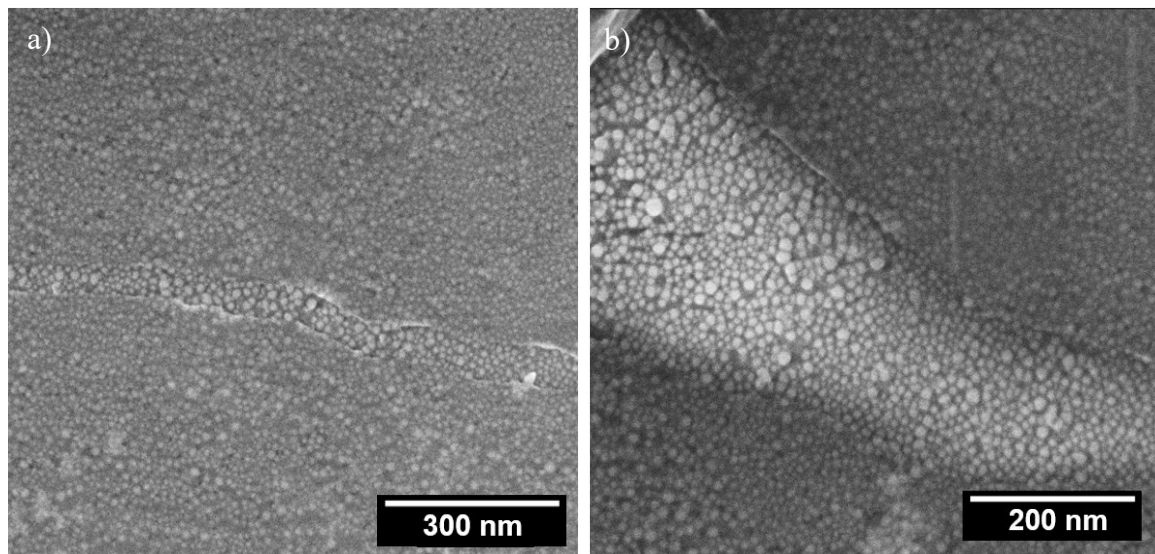


Figure 51 – SEM results of Ga₂O₃/Ga NPs on a PEEK/Gr with deposition temperature of 300 °C, (a) mag. 250 000x, (b) mag. 350 000x.

This demonstrated that the graphene can effectively disperse the charge and enable the imaging of nanostructures deposited on a non-conductive polymer surface. However, advanced instruments, such as high-resolution SEM, is necessary for successful imaging of

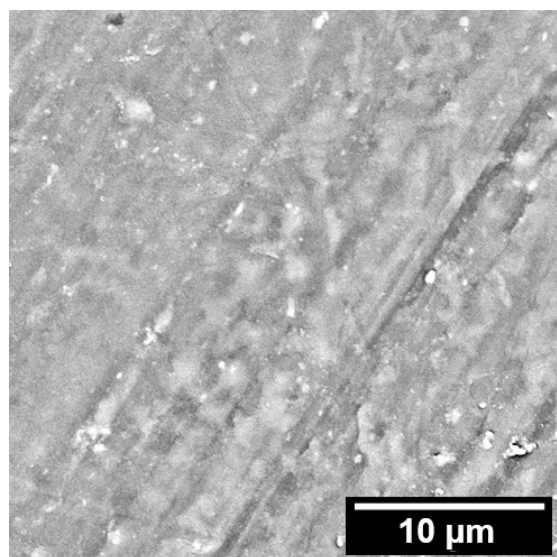


Figure 52 – SEM results of clean (native) PEEK surface morphology.

such surfaces, as the table SEMs at the Department of Physics and Materials Engineering, Faculty of Technology, Tomas Bata University in Zlín, were not able to display a non-distorted image of the sample surface even at lower magnification values and the same acceleration voltage. Observations conclude that the electron beam was causing warping and bending of the graphene monolayer, destabilising the image. Figure 52 shows the surface morphology of a clean (native) PEEK sheet, which was sputter-coated prior to the SEM imaging using the Phenom PRO.

6.4.2 AFM

Surface morphology of the native PEEK sample, presented in Figure 53, is demonstrated by a scanned area of $20 \times 20 \mu\text{m}$ in (a) and corresponding 3D view in (b). In the obtained topography (a), two representative profile cuts were taken; cut (c) corresponds to the horizontally oriented triangular marks and cut d) to the vertically oriented triangular marks.

The colour contrast presented in (a) highlights subtle height variation in surface topography, which generally does not exceed more than 250 nm or 550 nm due to randomly present artefacts. It is further evident in (a) that z-value variation follows a direction perpendicular to the lining pattern, most likely caused by imprints of the metal mould used during pressing.

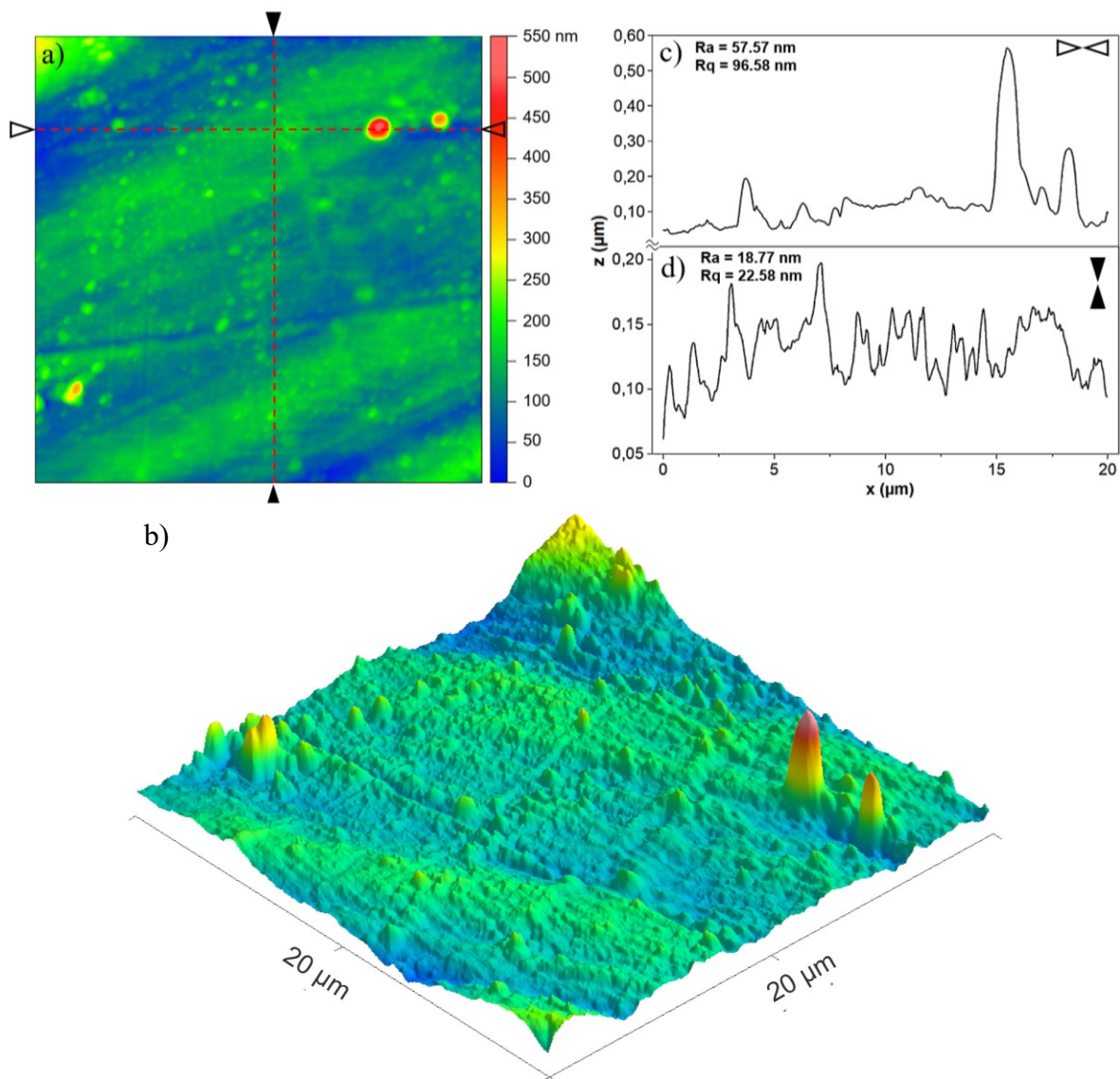


Figure 53: AFM measurement results; (a) topography of $20 \times 20 \mu\text{m}$ area, (b) corresponding 3D view; (c), (d) profile cuts

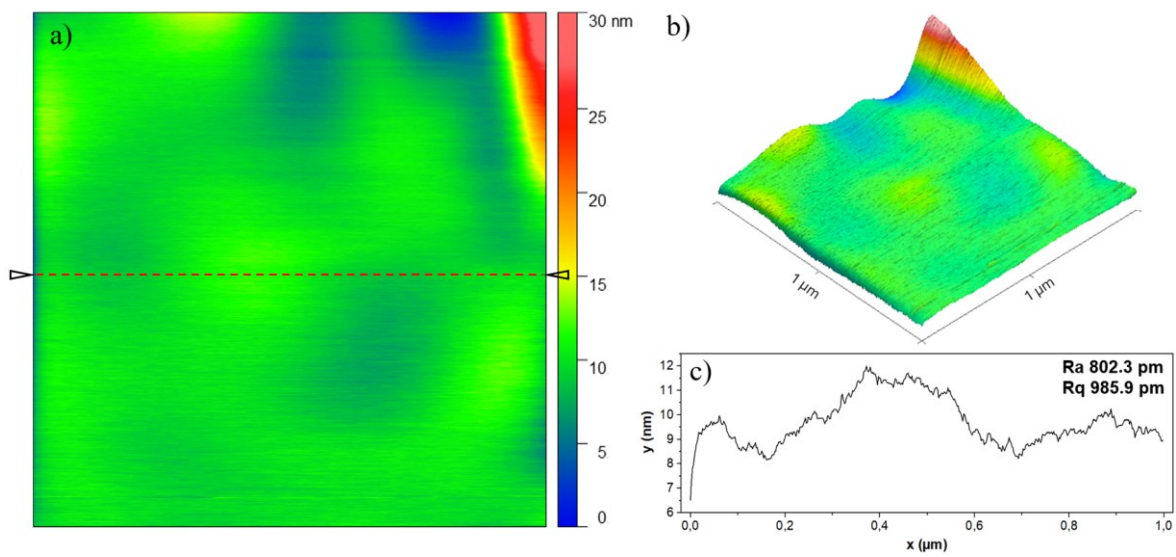


Figure 54 – AFM measurement results of $\text{Ga}_2\text{O}_3/\text{Ga}$ on PEEK (room temperature).

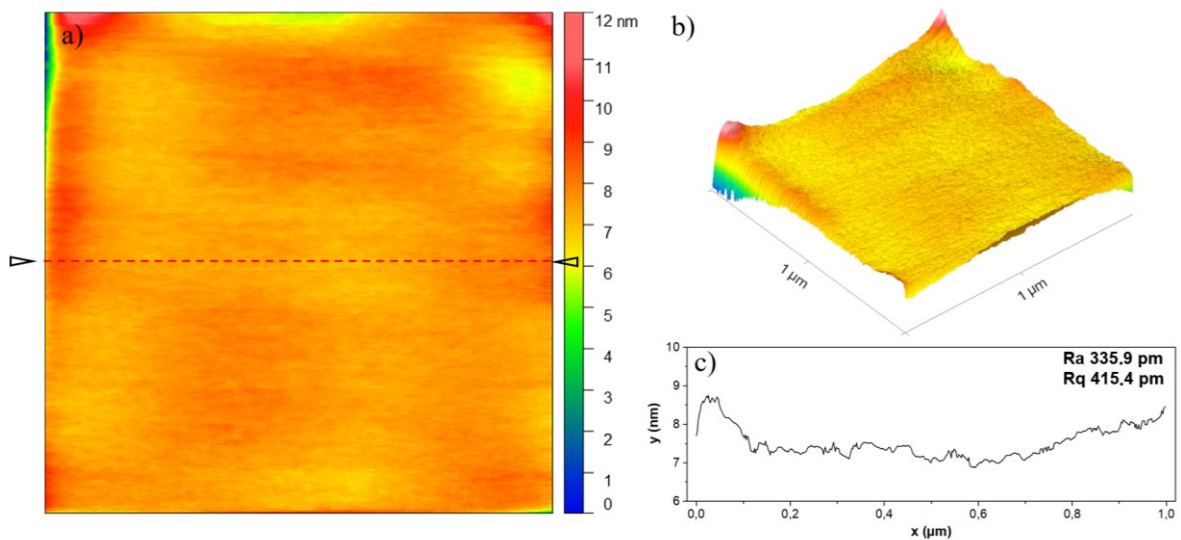


Figure 55 – AFM measurement results of $\text{Ga}_2\text{O}_3/\text{Ga}$ on PEEK (100 °C).

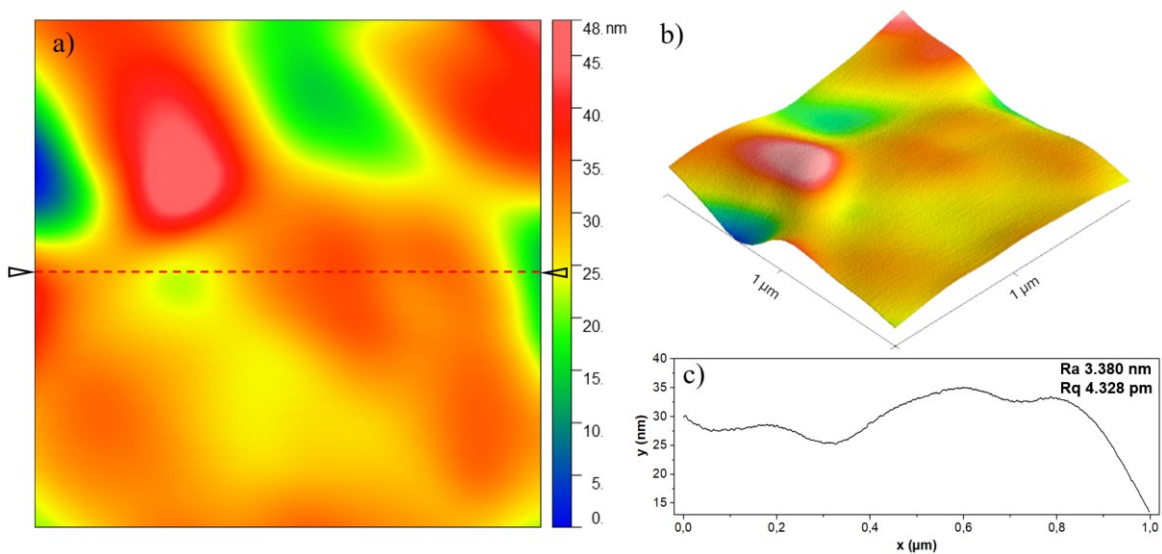


Figure 56 – AFM measurement results of $\text{Ga}_2\text{O}_3/\text{Ga}$ on PEEK (200 °C).

The surface morphologies of Ga₂O₃/Ga samples on PEEK of three deposition temperatures (room temperature, 100 °C, 200 °C) are shown in Figures 54–56, with a) representing the topography of a 1x1 µm area, b) representing a 3D view and c) corresponding profile cut. These measurements were taken from the central parts of the samples that were exposed to the gallium ion flux during PVD, after the photocatalytic experiment was conducted with these samples. This measurement aimed to bypass the issues regarding SEM imaging of these samples and to detect the present GaNPs and determine their dimension using AFM, as was performed by Bartošík et. al., 2024 [28]. The AFM results in Figures 54–56, however, indicate that no GaNPs or any structures resembling the nanoislands or semi-spherical formations in the order of tens of nanometres are present on these samples. This is clear mainly from the z-variations in the profile crosssections that are in the orders of nanometres (after the filtration of signal noise) and do not even remotely resemble profile cuts that were taken from Ga₂O₃/Ga on SiO₂/Si/Gr samples by Bartošík et. al., 2024 [28]. This indicates that the GaNPs desorbed from the PEEK surface during the photocatalytic experiment.

6.5 Photocatalytic experiments

The samples subjected to the assessment of photocatalytic performance in the Figures below are labelled as follows: $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL are labelled as PCL+Ga; $\text{Ga}_2\text{O}_3/\text{Ga}$ on PEEK or PEEK/Gr as PEEK+Ga or PEEK+Gr+Ga; reference photocatalyst TiO_2 as $\text{TiO}_2\text{-P25}$; polymer surfaces with no deposited catalyst are labelled as “clean” or without the “+Ga” attribute. The temperature value refers to the substrate deposition temperature; not explicitly stated, the PVD occurred at room temperature. The hydrogen concentration in the photoreactor, at any given time, is expressed in ppm, with the overall hydrogen yield reported in ppm after 4 hours of the experiment. See the data summary in Appendix VII.

The following Figure shows the results of the first photocatalytic experiment, in which the performance of $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL and clean PCL samples was assessed. The data shows that all tested samples, including reference TiO_2 , performed similarly in terms of the rate at which the hydrogen was produced, leading to similar values of hydrogen yields in ppm at $t = 4$ h. Interestingly, the data reveal that not only that the $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL sample achieved slightly better hydrogen yields than reference TiO_2 , but also that the clean PCL surface promotes the hydrogen evolution, yielding results similar or slightly better than those of the samples with active photocatalyst.

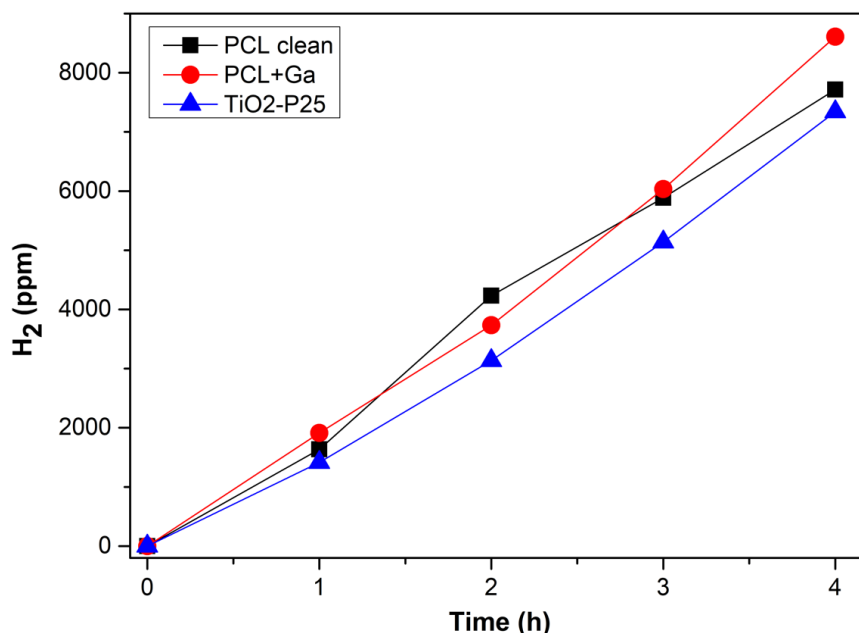


Figure 57 – Results of photocatalytic experiment: hydrogen evolution from PCL samples under 254 nm irradiation.

The results in Figure 58 partially replicate the previous experiment, utilising clean PCL surfaces without an active photocatalyst, under 254 and 365 nm irradiation, with TiO₂ serving as a reference standard.

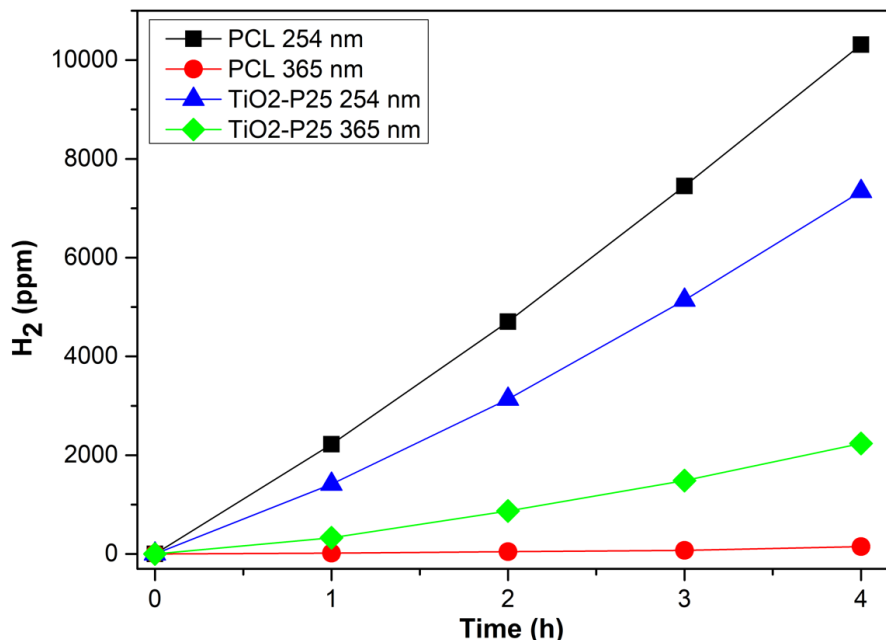


Figure 58 – Results of photocatalytic experiment: hydrogen evolution from PCL samples under 254 and 365 nm irradiation.

The data in Figure 58 clearly show that, similar to the previous experiment, the hydrogen evolution occurs not only at the clean PCL sample but also outperforms the TiO₂ under the same 254 nm irradiation wavelength. In contrast, irradiation with 365 nm results in limited hydrogen evolution facilitated by TiO₂, with virtually no hydrogen evolution observed from the PCL clean sample.

The experiment in which the clean PCL sample was irradiated by 254 nm in the environment consisting either of the aqueous methanol solution or pure water was conducted. Results shown in Figure 59 indicate that the presence of methanol (a sacrificial donor) in the reaction mixture is crucial for the hydrogen evolution, as no hydrogen evolution occurs in the methanol-free reaction environment for the same irradiation wavelength and the same clean sample surface.

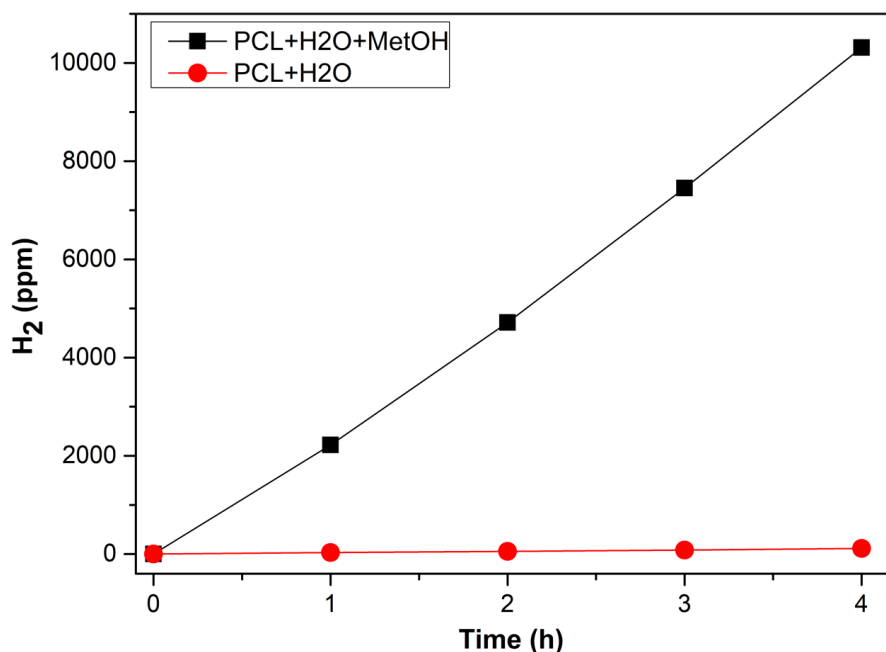


Figure 59 – Results of photocatalytic experiment: hydrogen evolution from PCL samples under 254 nm irradiation in the aqueous methanol solution and methanol-free environment.

Results of the side-by-side comparison of the photocatalytic performance of a clean PEEK sample and Ga₂O₃/Ga on PEEK with a 300 °C deposition temperature (therefore larger GaNPs) are depicted in Figure 60. Both PEEK surfaces exhibit comparable hydrogen yields, although slightly higher hydrogen evolution is apparent for the Ga₂O₃/Ga on PEEK sample. This strongly suggests (also considering the results shown in Figure 57) that in these

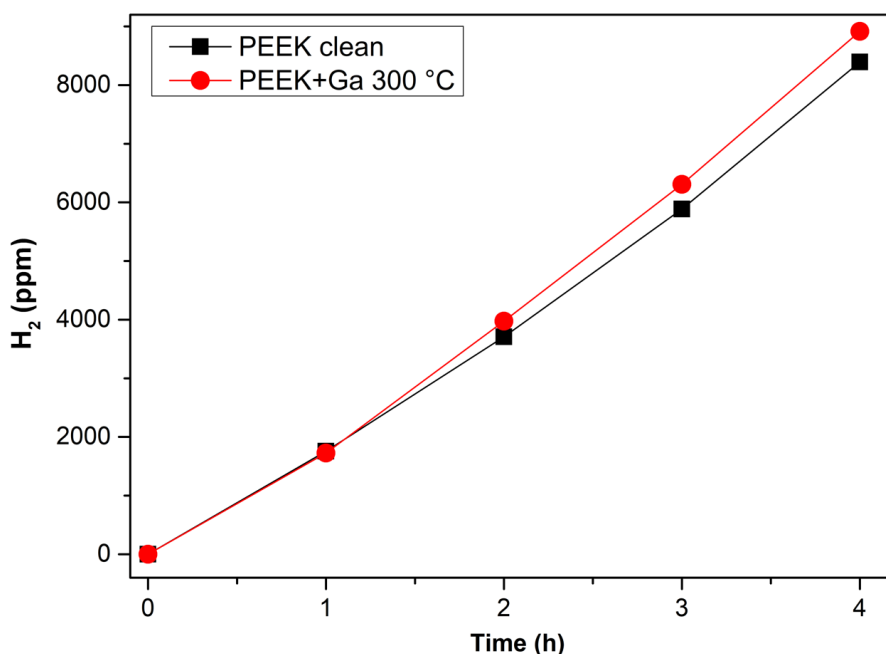


Figure 60 – Results of photocatalytic experiment: hydrogen evolution from two PEEK samples under 254 nm irradiation.

experiments, hydrogen evolution is not primarily driven by the photocatalyst, but rather by an alternative, yet unidentified mechanism.

The following Figure shows the photocatalytic performance of $\text{Ga}_2\text{O}_3/\text{Ga}$ on PEEK or PEEK/Gr samples under 254 nm irradiation. For clarity, the hydrogen yields in ppm after 4 hours of irradiation per sample are shown in Figure 64, where subtle differences in the performance of the samples are presented in the bar chart.

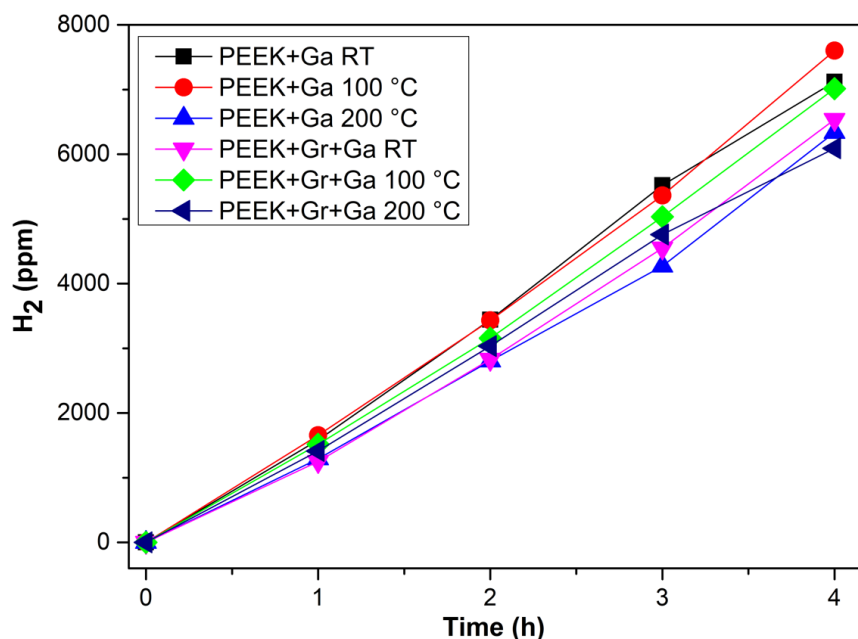


Figure 61 – Results of photocatalytic experiment: hydrogen evolution from PEEK samples under 254 nm irradiation.

Based on the assumption made during previous experiments that the reaction leading to the hydrogen evolution might be facilitated by the polymer surface alone, an experiment was conducted in which the clean PEEK sample surface was sputter-coated (60 seconds) with approximately 10 nm thick layer of Au + Pd from both sides. This achieved that the aqueous reaction environment was not in direct contact with the polymer surface, as it was shielded by the metal coating, and ultimately led to the notable decrease in the photocatalytic performance with the hydrogen yields being approximately half of the non-sputtered PEEK sample, as is demonstrated in Figure 62. This yet again indicates that the chemistry and properties of the polymer surface play an essential role in the hydrogen evolution reaction.

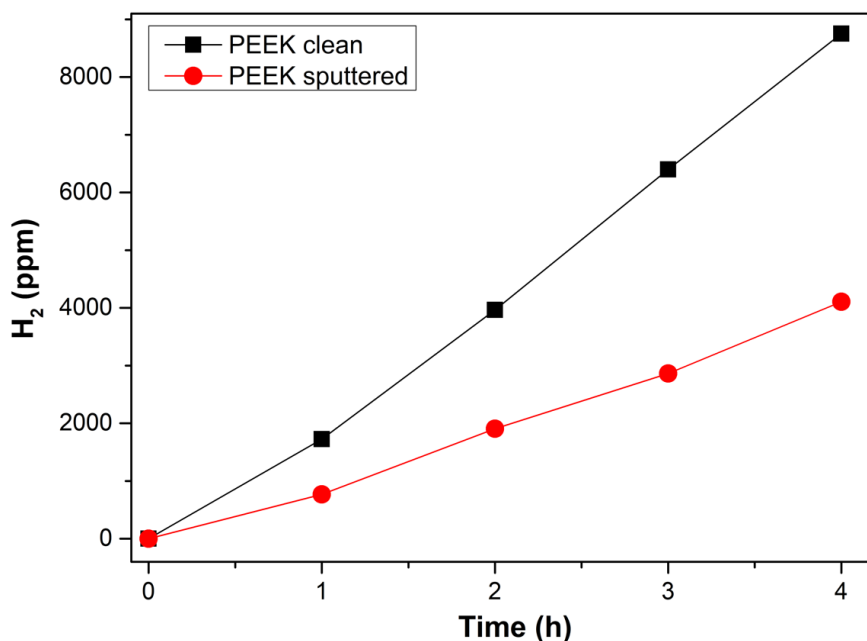


Figure 62 – Results of photocatalytic experiment: hydrogen evolution from clean and sputtered PEEK samples under 254 nm irradiation.

Bar chart in Figure 63 shows the comparison of hydrogen yields after 4 hours of irradiation of PCL samples. The first three bars show yields under 254 nm irradiation and demonstrate that GaNPs deposited at room temperature on a PCL surface contribute to the hydrogen yields only slightly higher compared to the clean PCL surface. Both PCL samples, however, outperform the yields from TiO₂ photocatalyst. The photocatalytic experiments of clean

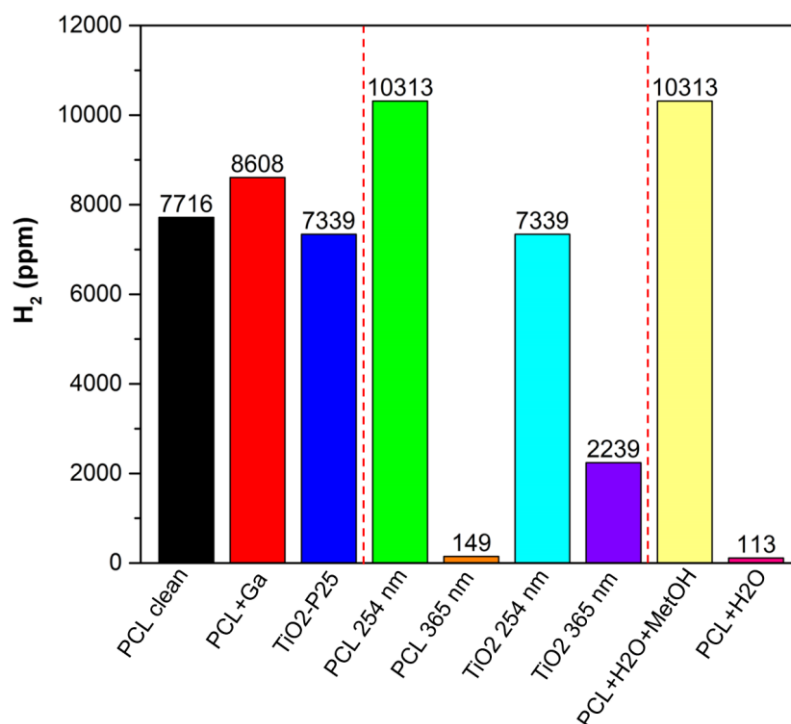


Figure 63 – Overview of overall hydrogen yields at $t = 4$ h from PCL samples.

PCL samples under the 254 and 356 nm irradiation demonstrate that virtually no hydrogen is produced at 356 nm from the PCL and only a small yield from TiO₂, with notably higher yields under 254 nm irradiation. The last two bars demonstrate that the presence of methanol in the aqueous reaction environment is essential for the hydrogen evolution to occur in these experiments. The bars showing hydrogen yields of 10,313 ppm correspond to a single experiment, but are displayed twice for clarity of comparison, as the results apply to both evaluation criteria.

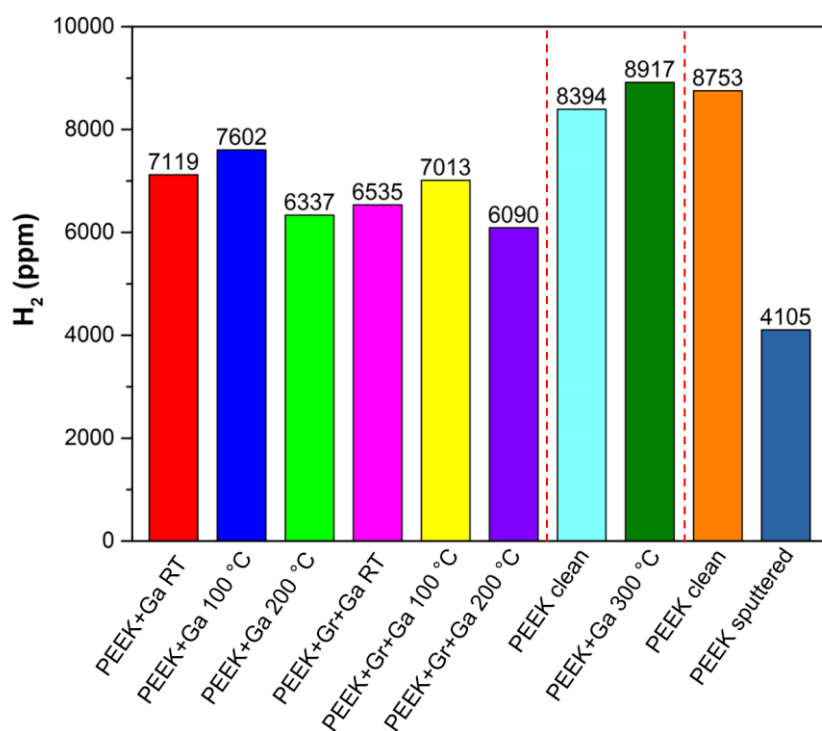


Figure 64 – Overview of overall hydrogen yields at $t = 4$ h from PEEK samples.

Figure 64 shows a bar chart with hydrogen yields after 4 hours of irradiation of PEEK samples. Results show that all the Ga₂O₃/Ga on PEEK or PEEK/Gr samples are outperformed by their graphene-free counterparts at the same deposition temperature. This may be because the graphene layer partially shields the PEEK surface covered with GaNPs from the reaction environment. It is also evident that the samples deposited at 100 °C exhibited the highest performance among the other Ga₂O₃/Ga on PEEK or PEEK/Gr samples. This suggests that, similar to the findings presented by Bartošík et. al, a synergy between the electron-hole generation facilitated by the oxide layer and the LSPR enhancement facilitated by the metallic core is achieved, linked to the dimensions of GaNPs deposited at various substrate temperatures. However, little is currently known about the dimensions of the Ga₂O₃/Ga nanoislands on polymer samples, as only the Ga₂O₃/Ga on PEEK/Gr sample had successful SEM imaging. The remaining bars show that Ga₂O₃/Ga on

PEEK perform slightly better than a clean PEEK surface; however, this marginal difference (similar to that observed for the $\text{Ga}_2\text{O}_3/\text{Ga}$ on PCL samples) indicates that the contribution of the $\text{Ga}_2\text{O}_3/\text{Ga}$ photocatalyst to the hydrogen yields is minuscule. Last two bars show a notable difference in the hydrogen yields between the sputter-coated and clean PEEK surface.

Compared to the work of Bartošík et. al., 2024 [28], the hydrogen yields in the presented graphs are not expressed in μmol of H_2 per gram of photocatalyst ($\mu\text{mol/g}$). While the amount of deposited gallium is approximately $2 \mu\text{g}$, the “catalyst” facilitating the hydrogen evolution at the clean PEEK or PCL samples is not defined as the mechanism behind the hydrogen evolution is not fully understood, and therefore, its amount cannot be defined. In addition, given that the polymer sample sheets (both clean and with deposited GaNPs) have a maximum surface area of 2 cm^2 , it is reasonable to compare the photocatalytic performance of polymer samples with deposited GaNPs to that of the corresponding clean polymer samples, rather than to the yields of the TiO_2 photocatalyst.

The raw data and the bar chart with samples ordered by hydrogen yield from lowest to the highest, are provided in Appendix VII and VIII.

DISCUSSION

Porous surfaces, such as those prepared by casting a solvent onto a polystyrene dish (shown in Table 3), demonstrated that casting a polymer solution is not required to achieve patterning via breath figures approach, as the polymer solution is created in the moment the good solvent penetrates and swells the surface of the polystyrene dish. This method accelerates the BF patterning; initially, the polymer concentration is zero and increases in time as the solvent evaporates and further swells and dissolves the polystyrene. The solvent's evaporation rate is higher due to the low initial viscosity (determined by the solvent alone), which rises gradually with increasing polymer concentration, thus slowing the diffusion of the solvent molecules towards the free surface. In contrast, casting of a polymer solution introduces a higher initial viscosity given by the already present polymer, which slows down solvent diffusion and overall evaporation. As a result, convective flows, inherently responsible for pore formation but also capable of the porosity distortion, have less time to develop in the solvent-casting approach, but can distort the established porosity in a solution-casting approach, as was in the case of casting a 10 wt% solution of polylactide in chloroform with results shown in Table 4. As each polymer-solvent system is unique, the effectiveness of casting a pure solvent onto a polymer surface varies. For instance, casting of 2.5 ml of chloroform onto a solidified polylactide film did not result in a porous surface, as the chloroform evaporated faster than the effective dissolution of the polymer and therefore formation of a polymer solution with viscosity enabling the breath figures patterning could occur. The experiments carried out in the prototype chamber, despite uncontrolled humidity and airflow conditions, provided insights into how polymer-solvent-vapour (or polymer-good solvent-poor solvent) combinations influence the pore morphologies. Many of these surfaces displayed hierarchical structuring with distinctive patterning within the pores. As such morphologies are often unreported in the literature, they may hold potential for applications not only as photocatalyst carriers, but also in tissue engineering.

The constructed atmospheric chamber, equipped with an Arduino-based sensor unit demonstrated effective control and long-term stability of airflow parameters and humidity conditions, despite its relatively simple design. The integration of sensors into the experimental setup demonstrated that the airflow parameters and humidity conditions can be effectively controlled and maintained stable over a long period, which was reflected in the results of BF patterning of polylactide solution in chloroform shown in Table 4. The Python analysis of BF patterning using the same solution cast over a 90 mm diameter Petri dish

suggested that the humidity gradient with central symmetry (given the chamber's circular geometry) might occur – although the results were inconclusive. Additionally, the porosity parameter, defined as the ratio of pore-covered area to the total image area, was used to more accurately reflect the humidity conditions in the chamber, rather than the mean pore size as employed in [48].

Achieving desired airflow settings (indirectly expressed as RPM) and humidity conditions is a key milestone in the pursuit of preparing a polymer surface with enhanced surface area due to the porosity. Moreover, the precise control over the experimental conditions allows further investigation into the kinetics of breath figures patterning, potentially yielding deeper insight into this process. It is, however, necessary to define the airflow values not as an expression of RPM (which allows for linearly spaced airflow settings), but rather to measure the absolute value of the volumetric airflow entering the chamber, for instance, by installing a hot-wire flowmeter across the diameter of the tube, effectively intersecting the airflow. The wire heated by an electric current would be cooled by the passing air, resulting in a change of its resistance, from which the airflow rate would be calculated. Furthermore, humidity control could be automated – as the RH value in the chamber is given by the position of the pinch-like valve with a screw mechanism (see Figure 23), which regulates the flow of dried air bypassing the glass bubbler into the chamber by compressing a silicone tube, the required rotational movement provided by the stepper motor (such as 5V stepper motor 28BYJ-48, which aligns with the operational voltage and the current supply limits of the Arduino-based setup), while Hall sensors could be employed to detect the positions for which the tube is fully open or closed. To further control convective flows or solvent evaporation rates, temperature regulation could be introduced by incorporating a Peltier cell beneath the Petri dish containing the polymer solution.

While the deposition of gallium onto a polymer surface was successfully performed in this work, as confirmed by the SEM imaging, the AFM measurements conducted on polymer/gallium samples after the photocatalytic experiment revealed that no gallium nanoparticles were present on these surfaces. This suggests that the desorption of these particles occurred during the irradiation at 254 nm in aqueous reaction medium due to the degradation of the polymer surface caused by the UV radiation. However, this is unlikely, as the PEEK is inherently resistant towards UV-induced degradation irradiation, and the SEM investigation showed no apparent structural changes on the surface. Furthermore, the 4-hour irradiation period is generally too short for substantial physical changes to occur, as

accelerated UV ageing tests often last for tens or hundreds of hours [62]. It is therefore necessary to investigate the adhesion behaviour of gallium nanoparticles on the polymer substrate. Additionally, confirming the presence of desorbed gallium nanoparticles in the aqueous reaction medium of the photoreactor would verify whether desorption is indeed occurring.

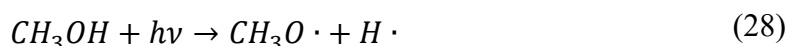
The covering of the samples with a graphene monolayer enabled SEM imaging without sputter coating, which typically involves deposition of a few-nanometres-thick metallic layer to enhance resolution by dissipating the surface charge. This novel method of SEM imaging can be extended to various non-conductive samples to obtain even higher topographical details without the distortion of the topographical information from a sputtered layer. Although the dimensions of GaNPs deposited on most samples could not be determined, with the exception of one sample, Raman spectroscopy results shown in Figure 50 indicate a weak signal enhancement due to the localised surface plasmon resonance induced by the gallium nanoparticles, suggesting the presence of gallium clusters with dimensions of at least a few nanometres. However, this enhancement is not on the order of magnitude typical for surface-enhanced Raman scattering. In the photocatalytic experiments, the graphene layer itself did not contribute to the photocatalytic performance, but rather reduced it, as is obvious from the results shown in Figure 64, where all of the samples covered with graphene consistently underperformed than their graphene-free counterparts, most probably due to the graphene shielding the polymer surface with deposited photocatalyst from the reaction environment.

The PVD process might therefore be the most ideal if the goal is to prepare a polymer substrate with an active photocatalyst on it. In the case of gallium, a synthesis approach that delivers colloidal gallium nanoparticles may be more direct, as the reaction conditions can be altered to obtain nanoparticles of the desired size distribution [63].

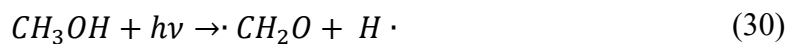
Based on the overall results of the photocatalytic experiments, it can be determined that the hydrogen evolution is not predominantly influenced by the presence of the active photocatalyst, but rather by the surface chemistry of the polymer in conjunction with the methanol present in the aqueous environment. This is supported by the data in Figure 64 demonstrating that hydrogen evolution from polymer samples (with or without the active photocatalyst) occurs under 254 nm only when methanol is present in the aqueous reaction environment. The presence of the active gallium photocatalyst improves the photocatalytic performance of polymer samples only briefly – comparable hydrogen yields are obtained

from clean polymer samples. The act of covering the native polymer sample with a sputter-coated metal layer leads to a 50% decrease in hydrogen yields, which again suggests that the surface chemistry of the polymer is essential. Hydrogen evolution on the metallic surface (Au + Pd) is likely driven by the excitations of hot carriers in metal that facilitate the reaction.

It can be argued that methanol, being less polar than water, may preferentially adsorb on the non-polar polymer surface, potentially increasing its local concentration and thus the likelihood of a reaction, such as photolysis, that could lead to hydrogen evolution under 254 nm irradiation:



or more probably:



while following recombination would have to occur:



whether or not this reaction could happen, it must be stated that the O–H bond dissociation energy is approximately 150 kcal/mol (4.55 eV, equivalent to 272 nm [64]). A 254 nm photon (approximately 4.8 eV) exceeds this threshold, potentially enabling O–H bond dissociation or a similar reaction, such as C–H bond cleavage, which has a lower dissociation energy. However, the literature does not indicate that such reactions occur without a catalyst to lower the activation energy and enhance the photon absorption. Furthermore, hydrogen evolution was observed in an aqueous methanol solution with a clean polymer sample (lacking a gallium photocatalyst), rendering direct hydrogen evolution from methanol photolysis or similar reaction pathways highly unlikely [64].

The polymer itself may directly participate in a process involving methanol that leads to the hydrogen gas evolution. UV photons with wavelengths corresponding to the carbon-carbon bond dissociation energies of polymers (typically 318–413 nm, depending on the polymer structure [65]), can trigger chain scission of C–C forming reactive alkyl radicals as demonstrated on the scission of the polycaprolactone chain illustrated on the following page.

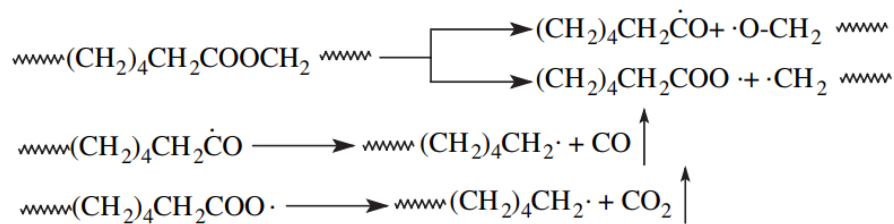


Figure 65 – PCL photodegradation [66].

However, even if the photolysis of methanol occurred (which is highly unlikely), the recombination process would not lead to the hydrogen gas due to the high reactivity of H· radicals, as their recombination with alkyl radical would occur predominantly, suggesting no clear reaction pathway for methanol photodissociation and polymer alkyl radicals to yield gaseous hydrogen. Although the experimental results indicate that the methanol and the polymer surface are critical to hydrogen evolution, the literature does not explain how this process may occur, as such mechanism has not yet been documented. Further experiments are needed to clarify the roles of the polymer surface or its chemistry in this process – for instance, by testing the photocatalytic performance of larger polymer samples (beyond 1x2 cm polymer sheets) to fully utilise the dimensions of the photoreactor. This substantial increase in the surface area, which could be further amplified by introducing porosity through breath figures patterning, could enhance the hydrogen yields if the polymer surface indeed plays a key role, as suggested by the experimental results. Alternatively, investigating whether the deliberate modification of the polymer surface's wettability by methanol, such as through plasma treatment, would affect the photocatalytic performance.

Perhaps the electron excitation within molecular orbitals can contribute to the photocatalytic performance of polymer surfaces, as these excitations can occur in various range of the UV-VIS spectrum. As each monomer unit in a polymer chain contributes atomic orbitals (AOs), they combine and form molecular orbitals (MOs). For example, in polymers with a conjugated system (alternating system of single and double bonds with overlapping p_z-orbitals and delocalised electrons), such as in polyaniline [67], polypyrrole, polyacetylene, polythiophene, poly(3-hexyl)thiophene (P3HT) [68], the π-MOs give rise to a highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), separated by a HOMO-LUMO gap, being analogous to the VB, CB and the band gap in crystalline semiconductors. Although the closely spaced π-MOs along the polymer backbone form a quasi-continuous distribution of energy levels (or bands), they are not equivalent to the fully continuous energy bands in crystalline solids. Although π → π* transitions are the primary and most utilised electronic transitions in conjugated polymers, enabling their

participation in various photocatalytic systems, the polymers employed in this thesis lack conjugated systems of π -MOs, nor is it likely for the isolated benzene rings (phenylene units) in the PEEK structure to participate in the photocatalytic reaction in any way, as these are confined local excitations with short lifetime [69].

The mechanism behind the photocatalytic water splitting in the presence of methanol at the clean polymer samples therefore remains unclear, and further experiments are necessary to provide insight into the driving mechanism behind the process of hydrogen evolution in these experiments, as no study has yet dealt with a similar experimental setup and observed similar results. It can, however, be concluded that the mechanism is likely linked to the UV-induced photodegradation of a polymer surface in the presence of methanol, both of which are an essential part in the reaction leading towards the evolution of hydrogen gas.

The employment of metal cocatalysts, such as colloiddally synthesised gold or silver nanoparticles, to enhance photocatalytic performance was not explored in this work, as it was unnecessary – the hydrogen evolution reaction occurs not only on samples with present gallium photocatalyst but also on the native polymer surfaces.

CONCLUSION

This study evaluated the feasibility of employing a polymer substrate as a carrier for photocatalytic gallium oxide/gallium nanoparticles deposited via physical vapour deposition, to facilitate photocatalytic water splitting.

To enhance control over the polymer substrate's surface properties and potentially increase surface area for future photocatalytic applications, porous polymer substrates were prepared using the breath figures approach. For this purpose, two custom atmospheric chambers were constructed via 3D printing. The first chamber allowed for exploratory patterning of drop-cast polycaprolactone and polylactide solutions in various solvents (chloroform, tetrahydrofuran, dichloromethane) under undefined humidity and airflow conditions or patterning of a polystyrene surface by drop-casting a good solvent in water or ethanol vapours. These experiments provided insight into the nature of the nature of resulting porous formations, many of which were observed for the first time. To achieve precise control over experimental conditions, a second chamber with an optimised airflow path and an Arduino-based sensor unit was developed. The ability to work under defined experimental conditions was demonstrated by the breath figures patterning of polylactide solution in chloroform. Results showed that no effective patterning occurs at RH = 60 % and the increasing RH from 70 % to 85 % generally led to larger pore size but reduced overall porosity. It was also determined that the response time parameter, crucial for assessing the scalability of the process within the given chamber and geometry, is directly proportional to the RPM^{-1.36}.

The porous polycaprolactone film served as an initial substrate for gallium oxide/gallium nanoparticles deposition. XPS measurement confirmed the presence of gallium, and Raman spectroscopy detected weak signal enhancement of polymer bands, suggesting localised surface plasmon resonances leading to the surface-enhanced Raman scattering from nanoscale gallium clusters. However, SEM analysis of such a surface treated with sputter coating revealed that gallium clusters are present. To promote larger nanoparticle formation, polyetheretherketone sheets were used at elevated deposition temperatures. On a substrate with the highest deposition temperature, i.e. 300 °C, gallium oxide/gallium nanoparticles were successfully visualised via high-resolution SEM employing a graphene monolayer for charge dissipation. The AFM imaging of polyetheretherketone surfaces post-photocatalysis indicated that desorption of nanoparticles occurred during the photocatalytic experiment.

The photocatalytic performance of polymer substrates with deposited gallium oxide/gallium photocatalysts was assessed by measuring hydrogen evolution under UV-C irradiation in a steel photoreactor. Among substrates with deposited nanoparticles, those prepared at a deposition temperature of 100 °C outperformed those prepared at 200 °C or a room temperature. However, differences in hydrogen yields among these were minor, as it was shown that a substantial hydrogen evolution was observed from clean, i. e. photocatalyst-free polycaprolactone and polyetheretherketone samples, with hydrogen yields comparable to that of the TiO₂ reference. Further experiments confirmed that both the presence of methanol and UV-C irradiation were essential for hydrogen generation, regardless of the presence of an active photocatalyst. The underlying mechanism remains unclear, as such results are not well documented in the literature but likely stems from the UV-C induced photodegradation of a polymer together with the tendency of a non-polar polymer to gather methanol molecules (being less polar than water) on its surface. This hypothesis was supported by the experiment in which a 10 nm thick metal layer was sputter-coated on a clean polymer surface, leading to a partial shielding and a roughly 50% reduction in hydrogen evolution.

Overall, the experiments in this thesis demonstrated that the polymer substrates can be feasibly employed as a carrier for photocatalytically active gallium oxide/gallium nanoparticles. However, further experiments and studies are needed to clarify not only the underlying reaction mechanism responsible for the hydrogen generation in this experimental setup, but also to closely examine the adhesion and long-term stability of deposited nanoparticles to support stable, long-term functionality of such a photocatalytic system.

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LIST OF ABBREVIATIONS

$\vec{k}$	K-vector
$\vec{p}$	Crystal momentum
ΔG	Gibbs free energy change
ΔH	Enthalpy change
ΔS	Entropy change
Å	Ångströms
AO	Atomic orbital
a	Lattice vector
AFM	Atomic force microscopy
b	Reciprocal lattice vector
BF	Breath figures
BSE	Back-scattered electrons
CB	Conduction band
CBM	Conduction band maximum
CCUS	Carbon Capture, Utilisation, and Storage
CVD	Chemical vapour deposition
E	Energy
E_B	Binding energy
E_F	Fermi energy
E_g	Bandgap energy
E_k	Kinetic energy
Ga	Gallium
GaNPs	Gallium nanoparticles
Gr	Graphene
h	Planck constant

$\hbar$	Reduced Planck constant
HCP	Honeycomb-patterned
k	Correction factor
k_B	Boltzmann constant
LSBF	Large-scale breath figures
LSPR	Localised surface plasmon resonance
MO	Molecular orbitals
OLED	Organic light-emitting diode
PC	Photocatalytic
PCL	Polycaprolactone
PEC	Photoelectrochemical
PEEK	Polyetheretherketone
PET	Polyethylene terephthalate
PLA	Poly lactide
PVD	Physical vapour deposition
r	Roughness factor
RH	Relative humidity
RPM	Revolutions per minute
RPS	Revolutions per second
SE	Secondary electrons
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman scattering
SPI	Serial Peripheral Interface
SPM	Scanning probe microscopy
STH	Solar-to-hydrogen
T	Temperature; Time

THF	Tetrahydrofuran
t_{res}	Residence time, Response time
UHV	Ultra-high vacuum
UV	Ultra-violet
v	Airflow velocity
V	Potential
VB	Valence band
VBM	Valence band minimum
VIS	Visible spectrum
XPS	X-ray photoelectron spectroscopy
γ	Surface energy
δ	Nearest-neighbouring vector
ε	Potential well depth
θ	Contact angle
ν	Frequency
Φ	Work function
Ω	Frequency of the phonon

APPENDICES

Appendix I: Source code for Arduino nano

```
#include <SPI.h>
#include <Wire.h>
#include <Adafruit_GFX.h>
#include <Adafruit_SH1106.h>
#include <Adafruit_HTU21DF.h>

#define OLED_MOSI    11
#define OLED_CLK     13
#define OLED_DC      10
#define OLED_CS      12
#define OLED_RESET   9

#define HALL_SENSOR_PIN 2

Adafruit_SH1106 display(OLED_MOSI, OLED_CLK, OLED_DC, OLED_RESET,
    OLED_CS);
Adafruit_HTU21DF htu = Adafruit_HTU21DF();

volatile int pulseCount = 0;
unsigned long lastTime = 0;
unsigned long lastSerialTime = 0;
float rpm = 0.0, rps = 0.0;
float temperature = 0.0, humidity = 0.0;

#define RPM_INTERVAL 1000
#define SERIAL_INTERVAL 1000 // or 60000 for 60 seconds

void count() {
    pulseCount++;
}

void setup() {
    Serial.begin(9600);

    display.begin(SH1106_I2C_ADDRESS, OLED_RESET);
```

```
display.display();
delay(2000);
display.clearDisplay();

pinMode(HALL_SENSOR_PIN, INPUT_PULLUP);
attachInterrupt(digitalPinToInterrupt(HALL_SENSOR_PIN), count,
FALLING);

if (!htu.begin()) {
    Serial.println("Couldn't find HTU21D sensor!");
    while (1);
}

display.setTextSize(1);
display.setTextColor(WHITE);
display.setCursor(0, 0);
display.print("RPM Counter");
display.display();
}

void loop() {
    unsigned long currentTime = millis();

    // Update OLED every 1 second
    if (currentTime - lastTime >= RPM_INTERVAL) {
        rpm = (pulseCount * 60.0) / 4.0;
        rps = rpm / 60.0;

        // Read sensor values
        temperature = htu.readTemperature();
        humidity = htu.readHumidity();

        display.clearDisplay();
        display.setCursor(0, 0);
        display.print("RPM: ");
        display.print(rpm, 2);

        display.setCursor(0, 16);
```

```
display.print("RPS: ");
display.print(rps, 4);

display.setCursor(0, 32);
display.print("Temp: ");
display.print(temperature, 1);
display.print(" C");

display.setCursor(0, 48);
display.print("Hum: ");
display.print(humidity, 1);
display.print(" %");

display.display();

pulseCount = 0;
lastTime = currentTime;
}

if (currentTime - lastSerialTime >= SERIAL_INTERVAL) {
    Serial.print(millis() / 1000);
    Serial.print("\t");
    Serial.print(rpm, 2);
    Serial.print("\t");
    Serial.print(rps, 4);
    Serial.print("\t");
    Serial.print(humidity, 1);
    Serial.println();

    lastSerialTime = currentTime;
}
}
```

Appendix II: RH charts

The following Figures illustrate the evolution of humidity conditions throughout the entire duration of the porous PCL samples preparation in the custom-built atmospheric chamber.

The green dotted line represents the midpoint of the RH range, spanning 10 % RH units. Its position on the charts may be slightly adjusted to ensure the entire captured RH curve is displayed. Significant drops in RH are either due to sudden pressure changes in the compressed air system, which reduced airflow, or are the result of briefly opening the chamber lid for the quick inspection of the sample (performed usually at the end of the time interval).

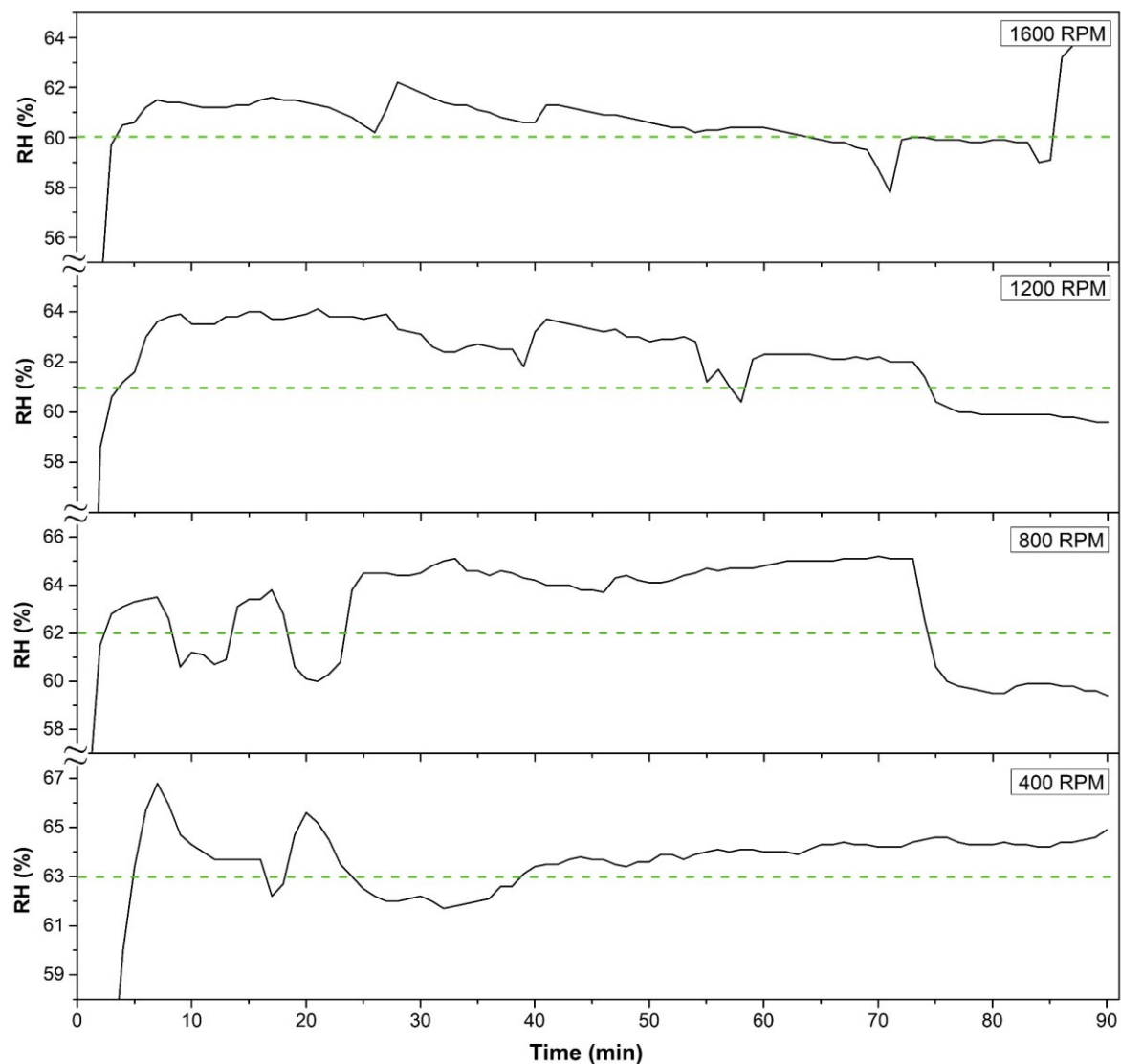


Figure 65 – Charts of RH conditions during the BF patterning of PLA solution in CHCl_3 at 60 % RH under varying airflow settings.

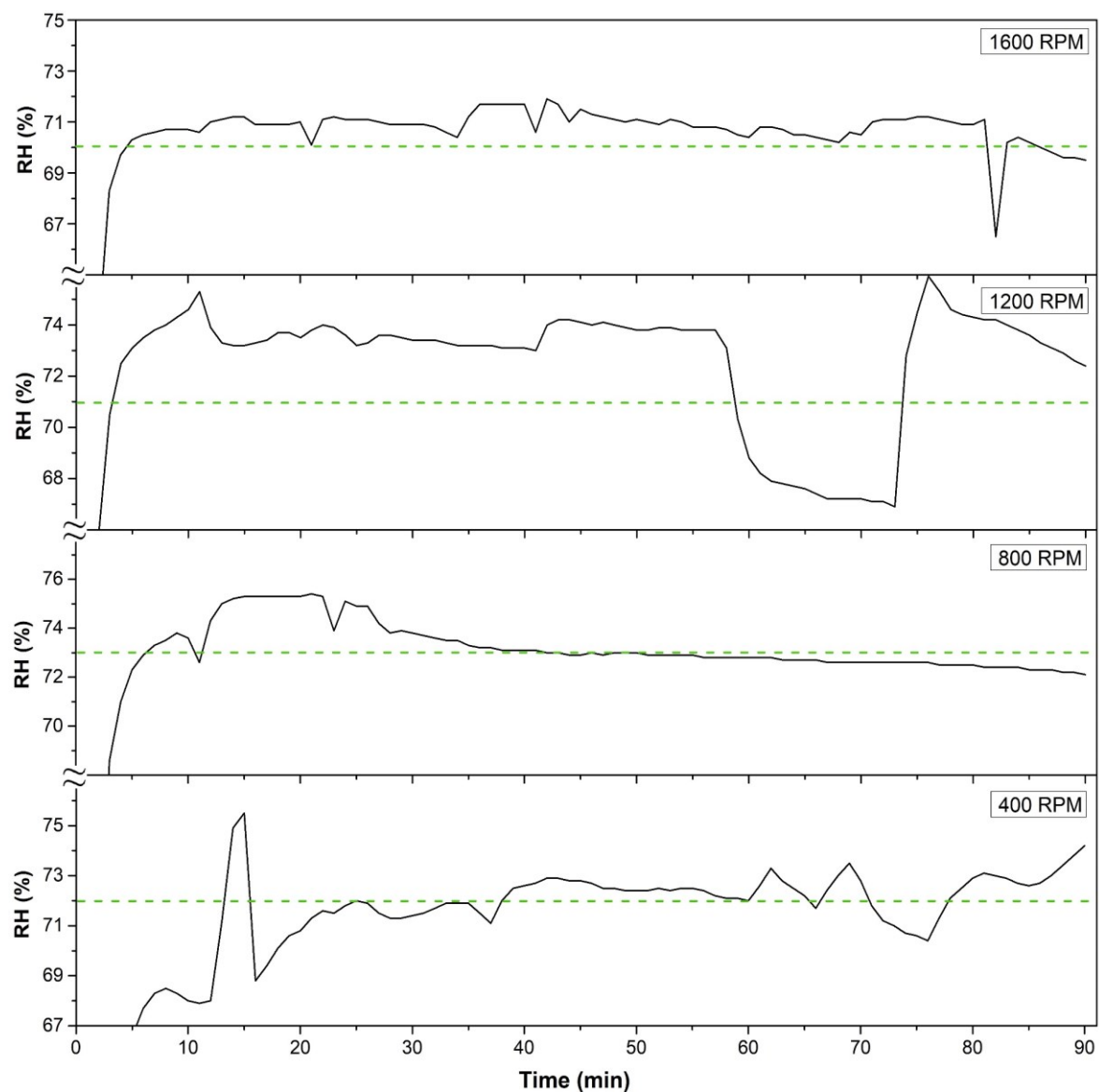


Figure 66 – Charts of RH conditions during the BF patterning of PLA solution in CHCl_3 at 60 % RH under varying airflow settings.

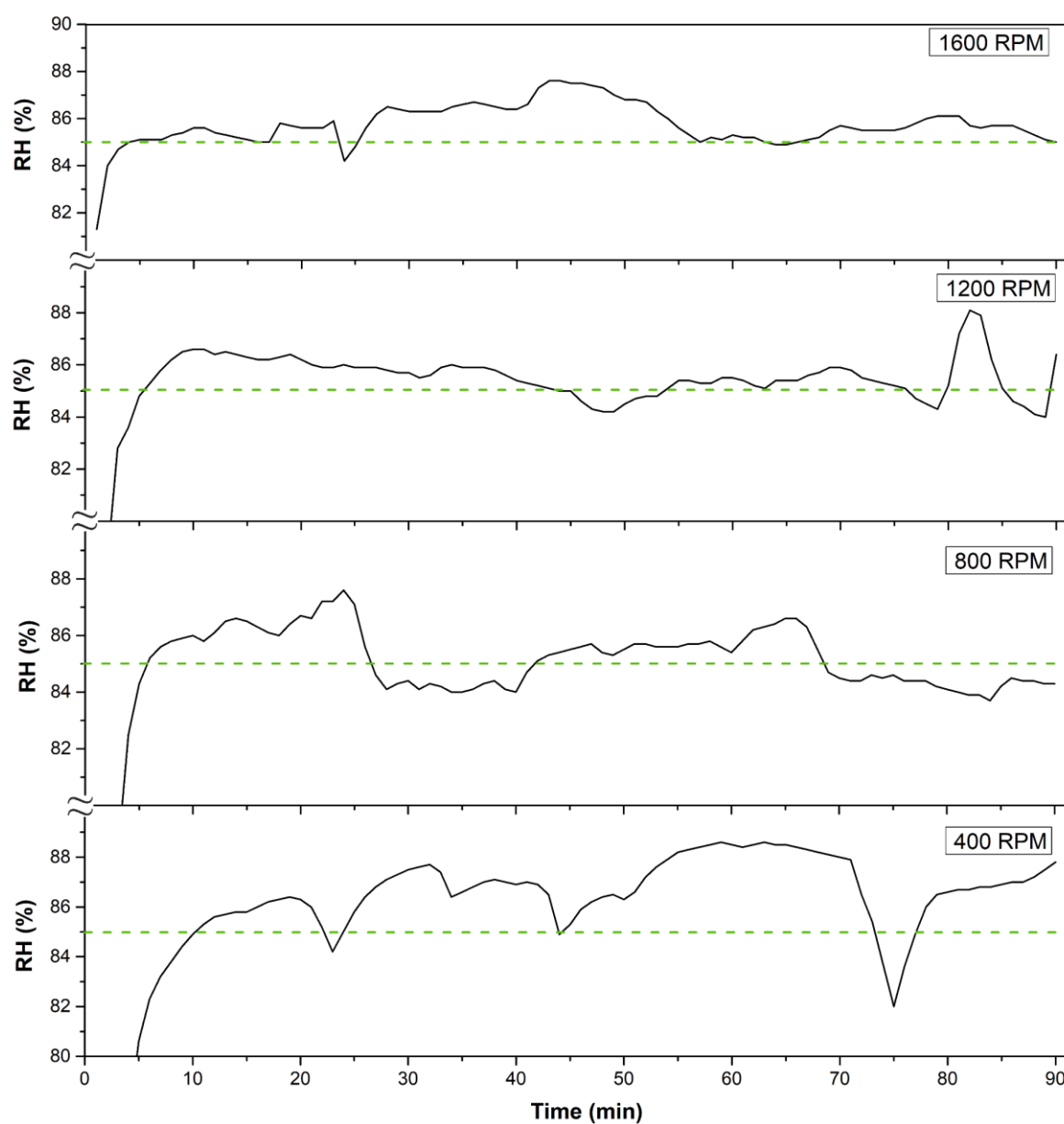


Figure 67 – Charts of RH conditions during the BF patterning of PLA solution in CHCl_3 at 60 % RH under varying airflow settings.

Appendix III: SEM results of the porous PLA films – image analysis.

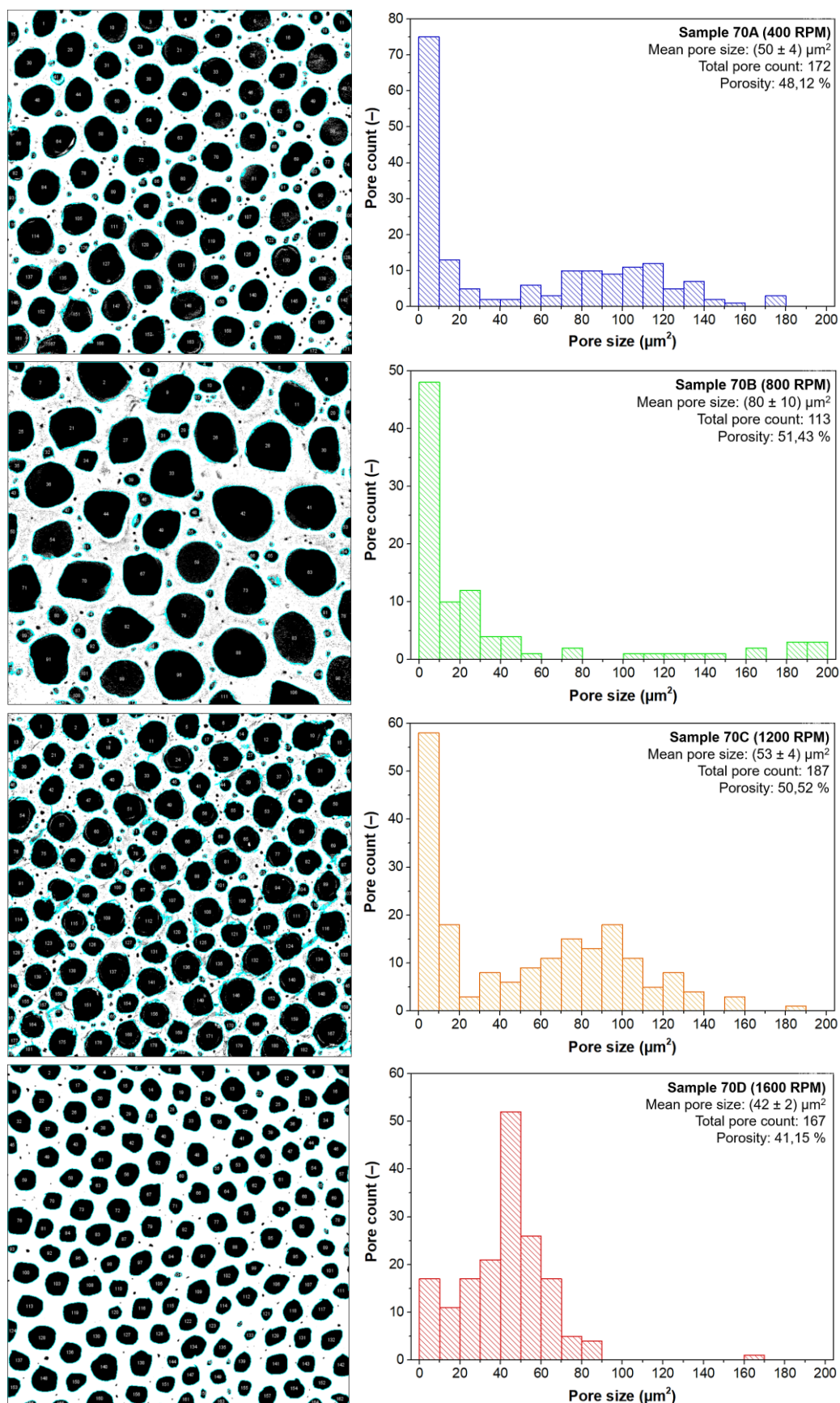


Figure 68 – SEM analysis of porous PLA films prepared at 70 % RH.

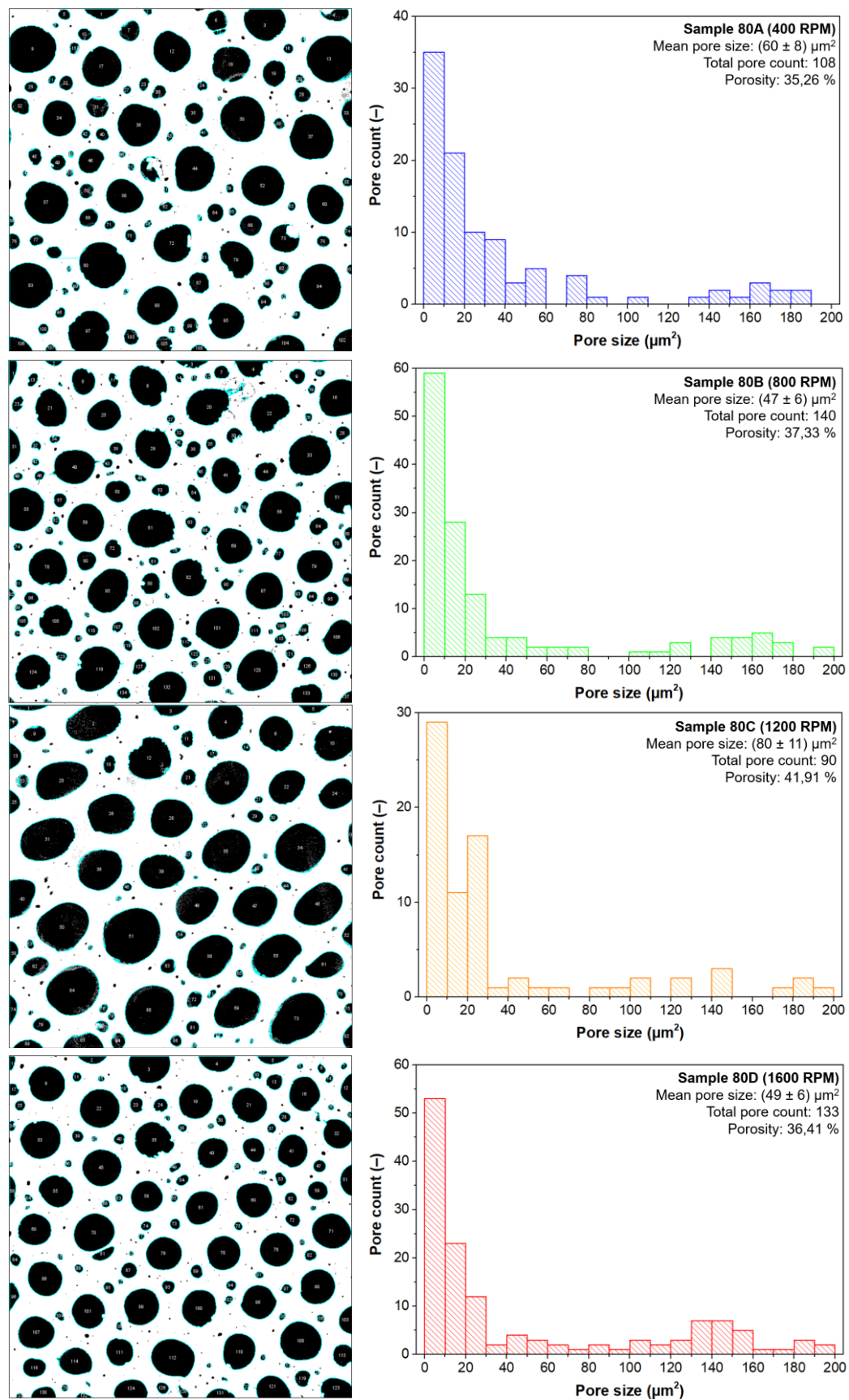


Figure 69 – SEM analysis of porous PLA films prepared at 85 % RH.

Appendix IV: Python code for the porosity determination

```
import cv2
import numpy as np
import matplotlib.pyplot as plt

image = cv2.imread('center.jpg', cv2.IMREAD_GRAYSCALE)

plt.imshow(image, cmap='gray')
plt.title('Original SEM Image')
plt.axis('off')
plt.show()

threshold_value = 175
_, binary_image = cv2.threshold(image, threshold_value,
                                255, cv2.THRESH_BINARY_INV)

plt.imshow(binary_image, cmap='gray')
plt.title('Binary Image (Pores in White)')
plt.axis('off')
plt.show()

pore_pixels = np.sum(binary_image == 255)
total_pixels = binary_image.size
porosity = pore_pixels / total_pixels

print(f'Porosity: {porosity:.4f} ({porosity*100:.2f}%)')
```

Appendix V: SEM results of the large-diameter porous PLA films – image analysis

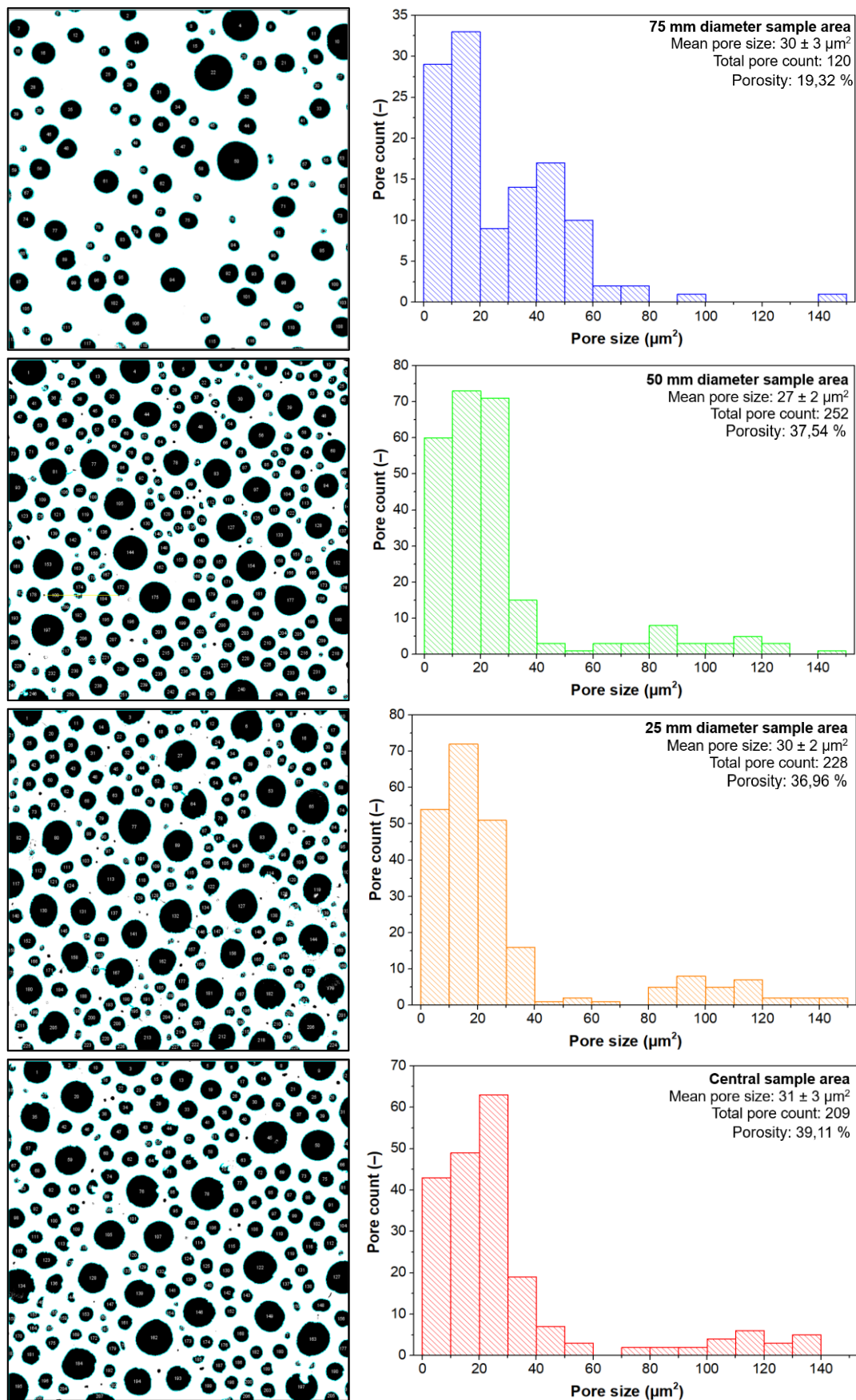


Figure 70 – examples of SEM analysis of a large-diameter porous PLA film.

Appendix VI: Python code for LSBF of a PLA film.

```

import numpy as np
import matplotlib.pyplot as plt
from matplotlib import cm
import matplotlib.colors as mcolors

num_circles = 3
points_per_circle = 8

diameters = [75, 50, 25]
radii = np.array([d / 2 for d in diameters])

porosity_values_per_circle = np.array([
    [24.64, 19.32, 31.54, 23.29, 21.84, 26.26, 18.47, 27.92],
    [38.95, 37.54, 39.96, 40.15, 35.30, 34.59, 36.38, 33.02],
    [36.84, 34.85, 39.02, 34.03, 36.96, 41.40, 38.98, 40.39],
])
center_porosity = 39.11
square_size = 5
cross_line_width = 1.5
show_circle_lines = True

vmin = 15
vmax = 45
cmap = cm.get_cmap('turbo')
norm = plt.Normalize(vmin=vmin, vmax=vmax)

X, Y = [], []
Colors = []

for i, r in enumerate(radii):
    angles = np.linspace(0, 2 * np.pi, points_per_circle, endpoint=False)
    x = r * np.cos(angles)
    y = r * np.sin(angles)

    X.append(x)
    Y.append(y)

    porosity_circle = porosity_values_per_circle[i]

    colors_this_circle = [cmap(norm(p)) for p in porosity_circle]
    Colors.append(colors_this_circle)

X.append([0])
Y.append([0])

```

```

Colors.append([cmap(norm(center_porosity))])

fig, ax = plt.subplots(figsize=(8, 8))

for i in range(len(X)):
    for j in range(len(X[i])):
        rect = plt.Rectangle(
            (X[i][j] - square_size / 2, Y[i][j] - square_size / 2),
            square_size, square_size,
            color=Colors[i][j],
            edgecolor='k',
            zorder=3
        )
        ax.add_patch(rect)

cross_length = radii[0] + 0.5
ax.plot([-cross_length, cross_length], [0, 0], color='black',
        linewidth=cross_line_width)
ax.plot([0, 0], [-cross_length, cross_length], color='black',
        linewidth=cross_line_width)

if show_circle_lines:
    for r in radii:
        circle = plt.Circle((0, 0), r, color='gray', fill=False,
                             linestyle='--', linewidth=0.5)
        ax.add_patch(circle)

ax.set_xlabel('X (mm)')
ax.set_ylabel('Y (mm)')
ax.set_title('Porosity')
ax.set_aspect('equal')
ax.grid(True, linestyle='-', linewidth=0.5, alpha=0.8)

diag_length = radii[0] * 0.70
ax.plot([-diag_length, diag_length], [-diag_length, diag_length],
        color='black', linewidth=cross_line_width, linestyle='-')
ax.plot([-diag_length, diag_length], [diag_length, -diag_length],
        color='black', linewidth=cross_line_width, linestyle='-')

sm = plt.cm.ScalarMappable(cmap=cmap, norm=norm)
sm.set_array([]) # Required for newer matplotlib versions
cbar = plt.colorbar(sm, ax=ax, label='Porosity (%)')

plt.savefig('porosity_plot_600dpi.jpg', dpi=600, bbox_inches='tight')

plt.show()

```

Appendix VII – Results of the contact angle measurement on porous PLA films.

Table 5 – Contact angle measurement – data.

RH (%)	85				70	
RPM (min ⁻¹)	400	800	1200	1600	400	800
θ (°)	94.42	96.04	94.59	106.21	105.43	116.37
	91.60	107.54	98.45	107.09	110.97	116.12
	94.34	111.01	90.20	101.04	111.63	101.79
	100.64	108.75	94.63	103.14	114.64	101.53
	89.27	107.80	109.16	100.71	99.06	110.50
	95.72	116.10	105.83	111.25	117.31	113.45
	106.61	104.88	110.11	99.51	111.38	116.95
	84.82	110.51	99.44	94.38	100.34	113.73
	89.34	97.53	96.26	107.65	106.24	116.66
	104.89	107.63	107.28	100.92	103.39	102.65
μ	95.17	106.78	100.60	103.19	108.04	110.98
σ	7.04	6.05	7.00	4.90	6.09	6.50
σ_μ	2.22	1.91	2.21	1.55	1.93	2.06
RH (%)	70		60			
RPM (min ⁻¹)	1200	1600	400	800	1200	1600
θ (°)	98.99	99.28	72.71	71.89	93.50	71.07
	97.11	111.92	73.94	75.22	90.51	68.52
	95.48	114.11	80.45	76.43	94.27	72.41
	99.53	99.39	74.71	73.70	93.92	72.68
	110.47	89.00	75.79	73.38	96.96	70.97
	94.28	100.90	87.34	76.75	97.81	66.15
	97.30	101.53	87.38	80.15	97.27	72.63
	97.83	108.15	72.96	72.90	98.52	72.21
	103.62	97.08	79.34	74.64	90.46	69.94
	100.17	94.34	77.41	76.48	97.01	69.24
μ	99.48	101.57	78.20	75.15	95.02	70.58
σ	4.65	7.81	5.46	2.41	2.94	2.14
σ_μ	1.47	2.47	1.73	0.76	0.93	0.68

Appendix VII – Results of the photocatalytic experiments.

Table 6 – Hydrogen yields of tested samples.

Time (h)	H ₂ (ppm)				
	PCL clean	PCL+Ga	TiO ₂ -P25	PCL 254 nm	PCL 365 nm
0	0	0	0	0	0
1	1633.734	1911.312	1413.594	2221.434	18.833
2	4232.225	3732.578	3135.031	4704.403	48.363
3	5886.258	6032.999	5139.999	7450.689	74.024
4	7716.076	8608.605	7339.443	10313.214	149.578
Time (h)	H ₂ (ppm)				
	TiO ₂ -P25 254 nm	TiO ₂ -P25 365 nm	PCL+H ₂ O+ MetOH	PCL+H ₂ O	PEEK+Ga RT
0	0	0	0	0	0
1	1413.549	328.3295	2221.434	30.473	1583.1435
2	3135.031	869.766	4714.403	55.562	3441.1435
3	5139.999	1485.964	7450.689	82.321	5520.128
4	7339.443	2239.055	10313.21	113.202	7119.317
Time (h)	H ₂ (ppm)				
	PEEK+Ga 100 °C	PEEK+Ga 200 °C	PEEK+Gr+ Ga RT	PEEK+Gr+ Ga 100 °C	PEEK+Gr+ Ga 200 °C
0	0	0	0	0	0
1	1656.203	1291.99	1249.414	1516.6415	1413.118
2	3432.694	2805.185	2829.366	3155.844	3032.777
3	5363.194	4270.466	4549.716	5032.428	4758.8765
4	7602.023	6337.203	6535.342	7013.369	6090.944
Time (h)	H ₂ (ppm)				
	PEEK clean	PEEK+Ga 300 °C	PEEK clean	PEEK sputtered	
0	0	0	0	0	
1	1757.467	1724.547	1726.071	767.425	
2	3707.456	3973.941	3964.117	1907.3855	
3	5885.462	6306.593	6399.83	2864.0735	
4	8394.35	8917.276	8753.475	4105.7725	

Appendix VIII – Photographs of the custom atmospheric chamber.

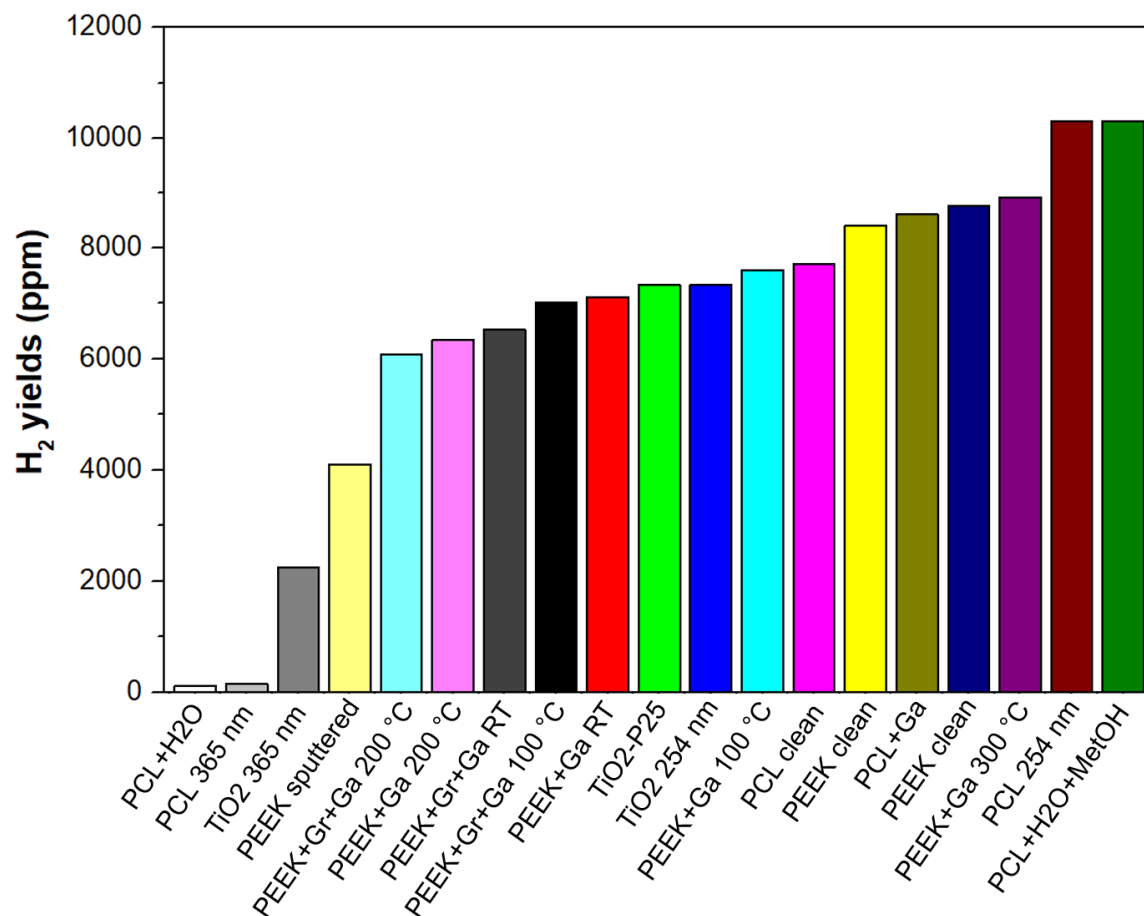


Figure 71 – Overall comparison of photocatalytic performance of samples presented in this work.

Table 7 – Summary of hydrogen yields at $t = 4$ h.

Sample	PCL+H ₂ O	PCL 365 nm	TiO ₂ 365 nm	PEEK sputtered	PEEK+Gr+Ga 200 °C	PEEK+Ga 200 °C	PEEK+Gr+Ga RT
H ₂ (ppm)	113	149	2239	4105	6090	6337	6535
Sample	PEEK+Gr+Ga 100 °C	PEEK+Ga RT	TiO ₂ -P25	TiO ₂ 254 nm	PEEK+Ga 100 °C	PCL clean	PEEK clean
H ₂ (ppm)	7013	7119	7339	7339	7602	7716	8394
Sample	PCL+Ga	PEEK clean	PEEK+Ga 300 °C	PCL 254 nm	PCL+H ₂ O+MetOH		
H ₂ (ppm)	8608	8753	8917	10313	10313		

Appendix IX – Photographs of the custom atmospheric chamber.

Figure 72 – Photographs of the custom atmospheric chamber during construction.