

Fabrication of Nanoporous Membrane-like
Thin Layers *via* Block Copolymer
Lithography of P2VP-*b*-PS “Inverse”
Systems and their Potential Applications



A thesis submitted to the School of Chemistry,
Trinity College Dublin,
For the degree of Doctor of Philosophy
By **Aislan Esmeraldo Paiva**
B.Sc., M.Sc. (Materials Engineering)

Supervisor: Prof. Michael A. Morris
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Declaration

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Aislan Esmeraldo Paiva
PhD Candidate



Michael A. Morris
Supervisor

Abstract

The large-scale fabrication of nanoporous materials and substrates has generated significant research interest on account of the wide range of possible applications, including nanophotonics, optoelectronics, biomedical systems, and environmental sciences. Block copolymer (BCP) self-assembly is one such potential fabrication strategy, owing to its low cost and large-area production of periodically ordered domains. In this work, an alternative method to produce these porous materials is developed and studied. A cylinder-forming P2VP-*b*-PS BCP was chosen as a model system to generate highly ordered, vertically aligned PS cylinders in a P2VP matrix using a static solvent vapour annealing (SVA) process. The choice of solvent was carefully tailored by considering the balance in surface energetics of the substrate and the free surface. Moreover, the SVA process was optimized based on the different BCP molecular weights (M_w) by fine-tuning the annealing time, temperature, and film thickness. The organized BCP films were obtained with cylinder diameters varying from ~ 35 to 400 nm, for the lowest and highest M_w , respectively. The BCP films were subsequently infiltrated with metal ions and exposed to UV/ozone treatment, hence removing the polymeric material, and leaving a thin, patterned metal oxide layer. The influence of the metal cations on the infiltration process was analysed. It was observed that by increasing the oxidation state of the cation, better infiltration occurred. Moreover, X-ray photoelectron and Raman spectroscopies elucidated differences in the binding between the pyridinic nitrogen and the metal cations. As potential applications, the metal oxide structures were then utilised as hard masks on silicon for dry etching *via* (deep) reactive ion etching/inductively couple plasma (RIE-ICP), which produced silicon nanoporous membranes showing interesting properties for light absorption and thermal management. Finally, iron oxide structures also obtained through liquid-phase infiltration were applied to wastewater treatment *via* a Photo-Fenton reaction, leading to the degradation of a commonly used antibiotic, levofloxacin.

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List of abbreviations

AFM	Atomic Force Microscopy
BCP	Block Copolymer
CV	Coefficient of Variation
di-BCP	Di-Block Copolymer
DRIE	Deep Reactive Ion Etching
EDX	Energy Dispersive X-ray Spectroscopy
<i>f</i>	Volume Fraction
FIB	Focused Ion Beam
HAADF	High-Angle Annular Dark Field
HCP	Hexagonally Close Packed
HRTEM	High-Resolution Transmission Electron Microscopy
ICP	Inductively Coupled Plasma
ISR	Intermediate Segregation Regime
L_0	Natural Period of a BCP
LPI	Liquid-Phase infiltration
LVF	Levofloxacin
MW	Molecular Weight
N	Degree of Polymerisation
NCM	Noncontact Mode
ODT	Order-Disorder Transition
P2VP-<i>b</i>-PS	Poly(2vinyl-pyridine- <i>b</i> -styrene)
PL	Perforated Lamellar
RIE	Reactive Ion Etching
SA	Self-Assembly
SAM	Self-Assembled Monolayer
SCMF	Self-Consistent Mean Field
SEM	Scanning Electron Microscopy
SSR	Strong Segregation Regime
STEM	Scanning Transmission Electron Microscopy
SVA	Solvent Vapour Annealing
<i>t</i>	Film Thickness
TA	Thermal Annealing
TEM	Transmission Electron Microscopy

T_g	Glass Transition Temperature
UVO	Ultraviolet/Ozone
VPI	Vapour-Phase Infiltration
WSR	Weak Segregation Regime
χ	Flory-Huggins Parameter
χ_{eff}	Effective Flory-Huggins Parameter
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

Chapter 1.

Introduction

1.1. Background and motivation

Block copolymers (BCPs) are a type of soft material that exhibits molecular-level disorder while simultaneously displaying ordered structures on a macroscopic scale.¹ They have attracted significant attention due to their ability to form a diverse variety of periodic arrangements with feature sizes ranging from 5 nm to 100 nm via self-assembly (SA). This unique group of polymers possesses appealing characteristics, in particular rapid processing, scalable synthesis, low cost, and nanoscale precision.² Therefore, BCPs have demonstrated potential applicability in energy, photonics, environmental and biological fields.^{2, 3} According to the Scopus database, the number of papers related to BCPs has exponentially increased (**Figure 1.1**) reaching a value of 2,360 in 2022.

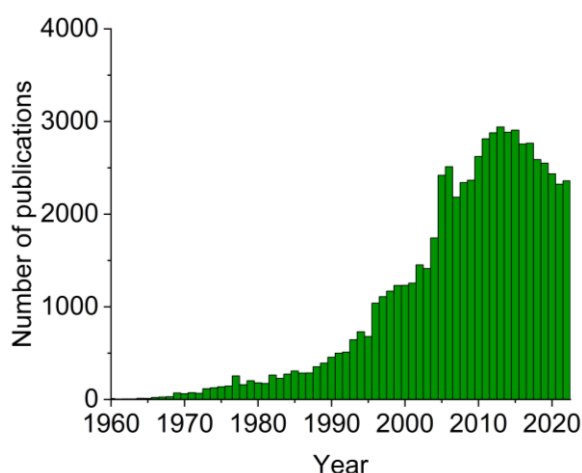


Figure 1.0. The number of publications related to block copolymers over the years (1952 - 2022) according to the Scopus database.

One of the possible applications of BCPs relates to the fabrication of nanoporous materials in substrate form, especially owing to their characteristics *e.g.*, tunability of pore size, narrow pore size distributions and possible functionalization.⁴ Porous materials are utilised in both industrial and research settings, with applications in diverse fields that include catalysis,⁵ filtration,⁶ ion exchange,⁷ drug delivery,⁸ medical diagnosis,⁹

adsorbents,¹⁰ and thermal management.^{11, 12} Among porous materials, nanoporous systems are of great interest for several applications (e.g., separation membranes, microchip devices and electrodes), and can be classified by pore diameter dimensions: macropores (1000 nm – 50 nm), mesopores (50 nm – 2 nm) and micropores (below 2 nm). For a specific application, the characteristics of the pores, namely volume, shape, and size, directly impact the performance.¹³ One common procedure to generate nanopores is based on BCP self-assembly. The BCP material is usually coated onto substrates to form thin films and assembled to produce vertically aligned cylinders. The minor block is then selectively removed, leading to pore formation with dimensions similar to the BCP template.¹⁴ Numerous reports in literature showcase the versatility of this method as well as the diverse range of applications, which include oil/water separation/filtration, energy harvesting and storage, catalysis, sensing, and drug delivery.¹⁵⁻¹⁹

1.2. Polymers: an overview

Polymers are defined as macromolecules composed of structural entities called monomers, which repeat throughout the chain. According to their molecular structure (**Figure 1.2**), the polymers can be classified as linear, in which the repeating units are bonded in only one chain; branched, which consists of lateral chains bonded to the main chain; cross-linked, in which the linear adjacent chains are bonded *via* covalent bonds; and network, in which functional repeating units have three or more covalent bonds forming a net.²⁰

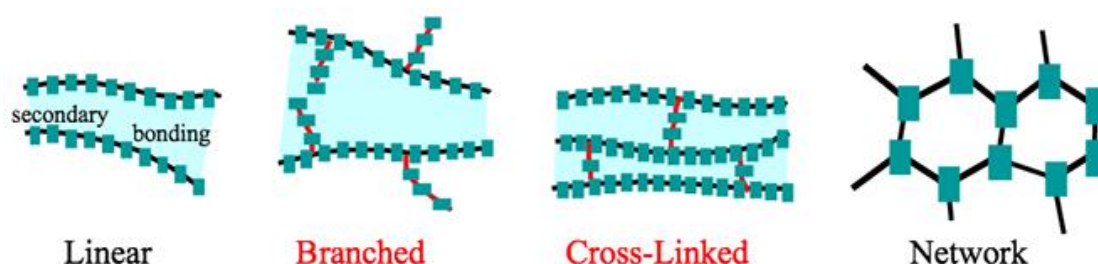


Figure 1.2. Classification of the polymers regarding the molecular structure.

Adapted from Redwig.²¹

It is also possible to further classify the polymers by the nature of the repeating units in the polymeric chain. If a single monomer composes the polymeric chain, it is referred to

as a homopolymer. On the other hand, if more than one monomer in a chain is present, it is known as a copolymer. Depending on how the monomers are arranged, there are four types of copolymers (for two repeating units) (**Figure 1.3**): random, where the two units are randomly dispersed in the chain; alternating, where the two repeating units alternate in the chain; block, where the identical units are agglomerated in blocks throughout the chain; and graft, where one homopolymer is grafted to the main chain of another homopolymer.²⁰

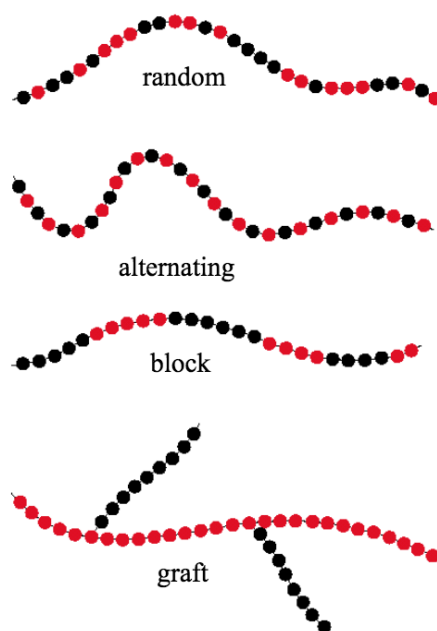


Figure 1.3. Classification of copolymers by the arrangement of monomers.
Adapted from Redwig.²¹

1.3. The theory of block copolymer self-assembly

The simplest and most common BCP architecture is that of a di-block copolymer (di-BCP) and comprises of two covalently bonded blocks, A-B. Adding other blocks to the chain enables the formation of triblocks (e.g., ABC or ABA) or multiblocks. However, many other arrangements can be created when considering nonlinear structures, including branched di-BCPs, di- and triblock-arm stars, miktoarm stars, among others.²² Increasing the complexity of the BCP architecture leads to an abundance of possibilities for self-assembled BCP phases, including cylinders, lamellae, micelles, gyroids, among others.^{23, 24} In this work, only di-BCPs are considered; thus, they will be the focus of this thesis.

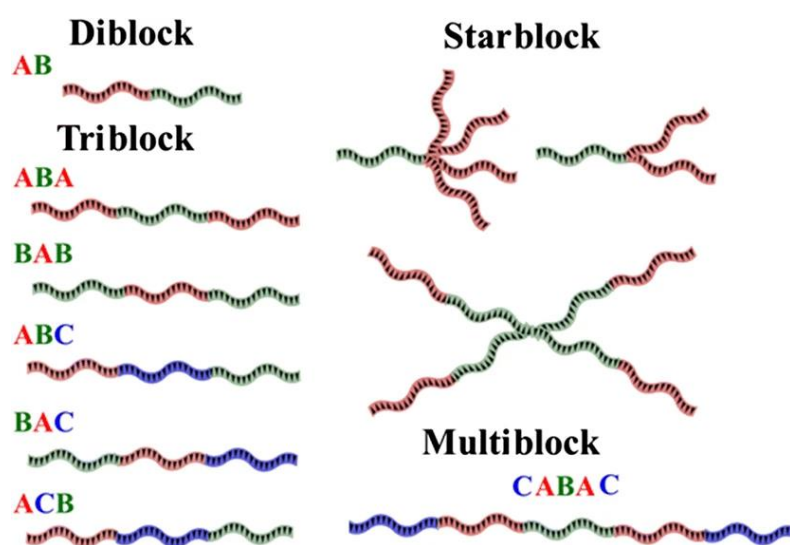


Figure 1.4. Different types of block copolymers based on the block arrangement.
Adapted from Khimani *et al.*²⁵

One of the most exciting features of BCPs is their capacity to self-assemble, creating ordered phases at the nanoscale. This process occurs because of a balance between the enthalpy of de-mixing (related to the chemical incompatibility between the blocks) and a small entropy of mixing related to the long chain (inversely proportional to the molecular weight). Nevertheless, as covalent bonds connect the blocks, macrophase separation is not observed.²⁶ Moreover, the resulting structures have a size range of a few times the radius of gyration (the root-mean-square distance of the polymeric segments in the chain from its centre of mass) of the BCP under consideration.²⁷

The observed morphology after the self-assembly process is dependent on three experimentally controllable factors: the degree of polymerisation, N ; the volume fraction, f ; and the Flory-Huggins interaction parameter χ . The degree of polymerisation represents the total number of segments/monomers of each block; in the case of di-BCPs, $N = N_A + N_B$, where subscripts A and B represent the two blocks; the chain size is directly related to the size of the phase-separated. The volume fraction is expressed by the ratio between the number of monomers of one block and the total number of monomers; hence the sum of the volume fractions is $f = f_A + f_B = 1$. This parameter influences the phase-separated morphology. It is important to note that f can be tuned via the degree of polymerisation N . Finally, the Flory-Huggins parameter is a number that quantifies the magnitude of dissimilarity between the blocks, and the choice of the monomers can alter it.²⁸

The theory related to the BCP self-assembly process has been well-elucidated. The Gibbs free energy of mixing relating to monomer-monomer and monomer-solvent interactions can be described by **(Equation 1.1)**.²⁷

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad \text{(Equation 1.1)}$$

Where ΔG_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing, T is the temperature, and ΔS_{mix} is the entropy of mixing.

Based on the **Equation 1.1** and considering a lattice model for polymer solutions/mixtures, the Flory-Huggins theory was developed and can be represented by **(Equation 1.2)** for a di-BCP:

$$\frac{\Delta G_{\text{mix}}}{k_B T} = \frac{1}{N_A} \ln f_A + \frac{1}{N_B} \ln f_B + f_A f_B \chi \quad \text{(Equation 1.2)}$$

Where k_B is the Boltzmann constant.

(Equation 1.2) defines the equilibrium thermodynamic properties, particularly phase behaviour and swelling, of both polymer-solvent and polymer-polymer systems. As discussed previously, it is possible to control a BCP system's characteristics through various parameters. The first two terms on the right-hand side of **(Equation 1.2)** are related to the configurational entropy, while the last one is associated with the enthalpy and the entropy of the dissimilarity between the two blocks.²⁷

The parameter χ is dependent on the temperature and can be represented as the sum of the entropic (χ_H) and enthalpic (χ_S) contributions to the covalent bonding **(Equation 1.3)**.²⁷

$$\chi = \chi_S + \frac{\chi_H}{T} \quad \text{(Equation 1.3)}$$

For polymer mixtures, the enthalpic term representing the interaction between the two distinct components dominates the entropic one, which is small due to the large polymer chain length. Therefore, we can observe an inverse relationship between temperature and χ .²⁹ For instance, at positive values of χ_H , reducing the temperature yields higher

overall values of χ , in other words, more substantial segregation is observed, and interfaces between the two blocks are reduced.¹ The Flory-Huggins parameter can also be employed as a qualitative parameter when analysing the polymer solubility in a specific solvent. In general, if $\chi < 0.5$, the polymer is considered miscible throughout the entire composition.²

1.4. Phase behaviour of block copolymers

According to the Self-Consistent Mean Field (SCMF) theory, the phase diagram of a BCP can be described by two parameters: χN and f , where the product χN accounts for the difference in the chemical affinity between the two blocks. Several morphologies can be obtained by tuning these two parameters. Initially, theories were based on two postulated regimes: the strong segregation regime (SSR) ($\chi N \gg 10$), developed by Helfand and Wasserman *apud* Matsen;³⁰ and the weak segregation regime (WSR) ($\chi N < 10$), developed by Leibler *apud* Matsen.³⁰ Later, Matsen and Bates³⁰ unified both theories and introduced new values for the regime limits and an intermediate segregation regime (ISR): WSR at $\chi N < 12$, $12 < \chi N < 50$ and $\chi N > 50$. Furthermore, one may estimate the value of the natural period (L_0), *i.e.* the domain spacing of BCPs, according to **(Equation 1.4)** and **(Equation 1.5)**, for the WSR and SSR, respectively:

$$L_0 \sim aN^{1/2} \quad \text{(Equation 1.4)}$$

$$L_0 \sim aN^{2/3} \chi^{1/6} \quad \text{(Equation 1.5)}$$

Where a is a characteristic segment length.³⁰

χN also influences the diffusion of BCP chains, which significantly reduces as the molecular weight (M_w) increases. Accordingly, the SA kinetics are slow for large χN values due to high chain entanglements.³¹ In practice, the SCMF theory proves invaluable for predicting di-BCP phases.

Figure 1.2 depicts the phase diagrams calculated for general di-BCP systems illustrating the classical phases:³²

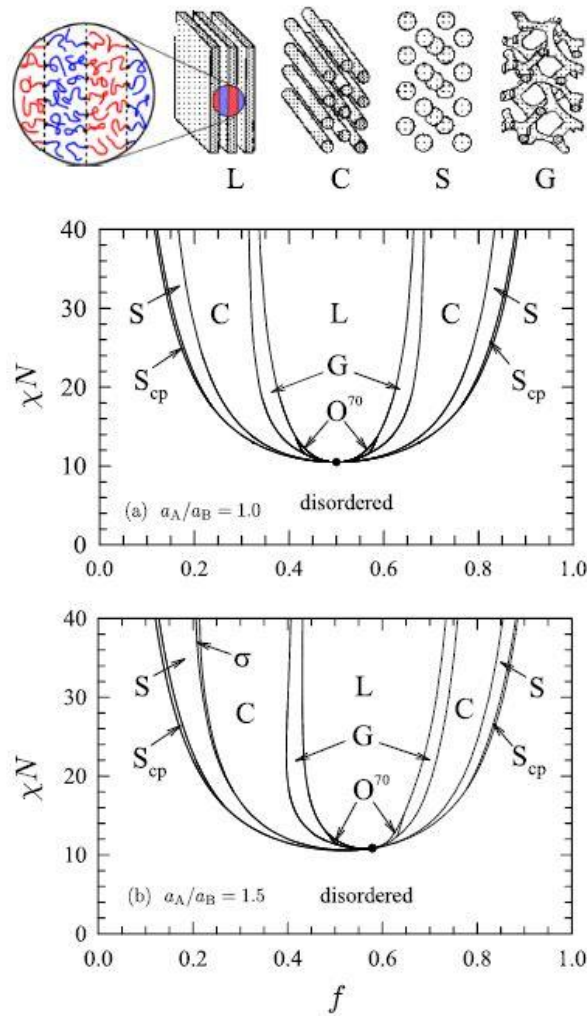


Figure 0.2. The phase diagrams for di-BCP systems: conformationally symmetric (a) and asymmetric (b). a_A and a_B stand for the segment length of blocks A and B, respectively. The phases depicted are S (bcc spherical), S_{cp} (hcp spherical), C (cylindrical), L (lamellar), G (gyroid), O^{70} (F_{ddd}) and σ (Frank-Kasper phase).

Adapted from Matsen.³²

The O^{70} structure is one of the more recently discovered phases that is stable in conformationally symmetric di-BCP systems and was first predicted by Tyler *et al.*³³ It consists of an orthorhombic lattice with a space group of 70, creating a network of threefold connected struts of a minority component. Similarly, Xie *et al.*³⁴ predicted the σ phase to be stable in conformationally asymmetric BCPs. It is formed by a tetragonal unit cell with 30 spherical domains. The existence of both the O^{70} and σ phases has been experimentally confirmed.³²

Besides the stable structures, a metastable phase has also been observed in di-BCP arrangements. The perforated lamellar (PL) structure is a phase that occurs between the lamellar and gyroid phases; it can be described as alternating lamellar and close-packed cylindrical layers. As the polymer temperature is increased, a lamellar structure transforms into the PL phase and, subsequently, into the gyroid one. Although this morphology is not thermodynamically stable, it has a durable transient structure, allowing experimental obtention.^{1, 35}

For symmetric di-BCPs ($f_A = f_B = 0.5$), there is a critical point at $\chi N \sim 10.5$ where the system undergoes an order-disorder transition (ODT), also called phase separation.³² Below this value, the BCP system stays in a disordered melt state, while above it, it becomes ordered. It should be emphasized that deviations from the χN_{ODT} value can occur due to changes in several important parameters *e.g.*, block asymmetry (where $f \neq 0.5$), the relative selectivity of film interfaces and the use of ultrathin films.^{36, 37}

In summary, by increasing the volume fraction of one component, it is possible to achieve different morphologies. If we consider that f might represent f_A , in the first half of the diagram ($f_A < 0.5$), the A block forms structures in a B matrix. Nonetheless, for $f_A > 0.5$, we can observe inverse structures.

1.5. Self-assembly in block copolymer thin films

BCP thin films can be used in several industrial applications. The confinement of a polymer in a nanometre-thick film (< 100 nm) changes its behaviour compared to the bulk counterpart. Thin films are subjected to interfacial interactions *e.g.*, with the substrate and air. Moreover, in thin films, the domains can be highly ordered over macroscopic distances, whereas, in bulk, ordered domains are organised in randomly distributed grains in mm and sub-mm.³⁸

The restriction within two interfaces creates a structure where the BCP natural period (L_0) is on the same scale as the film thickness. Considering that different blocks of a BCP chain have dissimilar surface energies, they interact differently with the interfaces. Two regimes can dictate the stability and ordering of the films. The first regime is related to non-preferential surfaces, or symmetric boundaries; in this situation, both surfaces interact similarly with the blocks (*i.e.*, the surfaces possess the same surface energies),

leading to the wetting of the interfaces by the two blocks.³⁸ Nonetheless, when there is a difference between the two interfaces, one block may preferentially migrate to one interface, creating a wetting layer of that block. This regime is known as preferential surfaces or asymmetric boundaries.^{38, 39}

It is possible to relate the film thickness (t) of a BCP and its natural period (L_0), therefore predicting the film stability. For a lamellar forming di-BCP, when there is preferential wetting (symmetric), if $t/L_0 = n$, and n is an integer (1, 2, 3 ...), the commensurability relationship is achieved. However, when both surfaces are similar, and the blocks can interact similarly with them (asymmetric), the commensurability happens when $t/L_0 = n + 0.5$. For t values different from the former equalities, the formation of terraces *i.e.*, islands or holes, can be observed.⁴⁰ This occurs due to exposure of the film to one or two free surfaces, leading to local thickness adjustments *i.e.*, the film displays thinner and thicker regions. Commonly, the microstructure of the islands differs from the rest of the film.⁴¹

Figure 1.3 illustrates the above-mentioned cases.³⁹

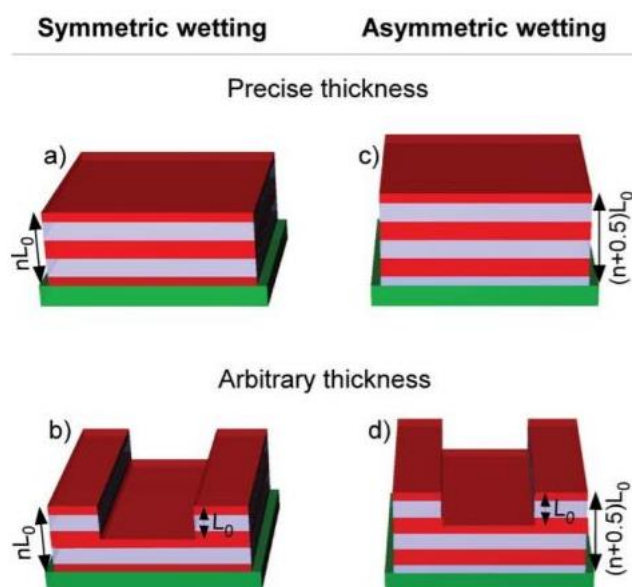


Figure 0.3. Commensurability criteria for lamellar forming di-block copolymers. Commensurate film thickness for symmetric and asymmetric wetting (a and c); formation of terraces when the criteria is not respected (b and d).

Adapted from Hu *et al.*³⁹

In many applications, the goal is to achieve a perpendicular orientation of the BCP domains. In the case of patterning purposes, for instance, the vertical alignment of the domains enables a high aspect ratio of the features.⁴² Nanoporous membranes can also be produced *via* pattern transfer of an out-of-plane cylinder BCP template.^{15, 43} Therefore, when no preferential wetting is observed for the different blocks, the phases align vertically to compensate the block stretching.⁴² Some approaches can produce neutral surfaces in order to yield out-of-plane features; nonetheless, it is necessary to mention that the quality of the patterns and the perpendicular orientability are also dependent on other parameters *e.g.*, BCP composition, annealing parameters, film thickness and the type of surface modification.⁴⁰ Among the surface engineering methods, modification of the substrates with random copolymers, self-assembled monolayers (SAMs), end-functional homopolymer blends, BCP brushes, thermal and solvent vapour annealing, and use of external forces (*e.g.*, electric fields) can be applied to generate vertical features.^{39, 40, 42}

The stability of thin films is essential to enable their applicability. When a film presents enough thickness, the gravitational pull preserves its structure. Nevertheless, below a critical value of the liquid capillary length, there is an imbalance between the higher values of molecular forces and gravity, resulting in the rupturing of the film and detachment from the substrate *i.e.*, dewetting.⁴⁴ The dewetting process is influenced by an ensemble of parameters, including interactions with the substrate, film thickness, molecular weight, temperature, and annealing time. Strategies to avoid this phenomenon are based on two main approaches: modification of the surface energy of the polymer/substrate interface and the reduction of chain mobility.⁴⁴

1.6. Production of block copolymer thin films

Among the various methods used to produce BCP thin films, two are especially popular among researchers due to the ease of implementation. Dip coating is a facile technique that involves submerging the substrate in the polymer solution and then subsequent withdrawal. The speed at which the substrate is removed from the solution dictates the film thickness. Moreover, the polymer deposition is influenced by gravity, surface tension and viscous force.^{45, 46} Spin coating is another method that produces highly uniform thin films and is preferred due to its simplicity in controlling the film thickness. Its principle is based on the rotation at elevated speeds, creating centripetal forces opposing the

viscous ones. The spinning spreads the polymer solution, covering the substrate and expelling the excess. Additionally, the film thickness is affected by the rotating disk's speed, the BCP solution's concentration, and rheology. In both methods, the use of volatile solvents is expected since its evaporation is rapid, allowing the formation of uniform surface films.⁴⁵

1.7. Annealing of block copolymer thin films

The dissimilarities between two or more blocks in BCP chains are responsible for their microphase separation. As discussed in the previous section, to create BCP thin films, one may use spin coating. However, when the solvent rapidly evaporates, leaving the polymeric film, the chains may be left in a nonequilibrium disordered state due to insufficient time for reorganisation. Therefore, post-film deposition treatments are often required to induce ordering of the domains.

Thermal annealing (TA) is one method that promotes the ordering of BCP films and can be easily conducted using a hot plate or a vacuum oven. Other heating methods, including zone annealing, laser pulses and radiation devices, have also been employed by researchers.⁴⁷ Typically, the BCP sample is heated to a temperature above the glass transition temperature (T_g) and below the ODT temperature (in some cases, even above the ODT) and kept at this state for some time, causing chain mobility and allowing the system to achieve the equilibrium phase, depending on the processing time and the cooling rate.^{48,49} Nevertheless, this technique has limitations for high χ_N BCPs *i.e.*, either the blocks are very chemically different or dissimilar, or the chains are incredibly long. Heating to temperatures above the T_g /ODT in those systems is detrimental since it can induce polymer degradation. Furthermore, in some cases, the necessary amount of time for the organisation of the BCP film is excessively long. This, coupled with the high energetic costs of running such equipment, hinders the further applicability of TA to industrial settings.⁴⁹

Solvent vapour annealing (SVA) is another technique commonly used to induce the ordering of the BCP domains. In SVA, the film is exposed to solvent vapours (generally, a neutral solvent), inducing swelling, which reduces the T_g and increases chain mobility. The system is kept in a solvent atmosphere for a certain amount of time to facilitate ordering. Once the appropriate exposure time has been reached, the solvent is

subsequently removed, trapping the formed phase. SVA is also effective in reducing defects and producing metastable phases. Additionally, one of the main advantages of SVA as compared to TA is the possibility of working with high χ polymers and long BCP chains since high temperatures are avoided.⁵⁰ The use of near-neutral solvents produces a screening of unfavourable interactions between the blocks due to the solvent molecules.⁵¹

The increase in chain mobility due to swelling by the solvent can be interpreted *via* an effective χ parameter (χ_{eff}), according to **(Equation 1.6)**:⁵¹

$$\chi_{\text{eff}} = \chi \phi_{\text{BCP}}^{\beta} \quad \text{(Equation 1.6)}$$

Where: χ is the Flory-Huggins parameter for the BCP in the dry state, ϕ_{BCP} is the volume fraction of the BCP in the swollen state, and β is a value dependent on the solvent concentration in the film, morphology of the polymer and solvent selectivity, varying between 1 and 2.

Therefore, by increasing the solvent concentration in the BCP film, the χ_{eff} is reduced, promoting an ODT and enabling improved chain mobility.

There is no specific setup to conduct SVA. However, three different approaches are commonly applied, as depicted in **Figure 0.44**:⁴⁷

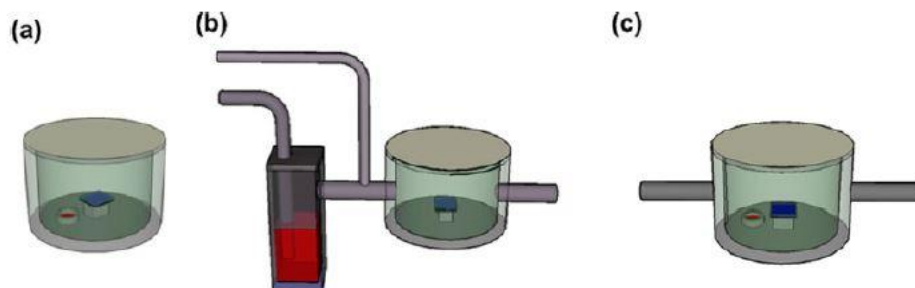


Figure 0.4. SVA approaches. (a) Static SVA (b) solvent conducted by inert gas flow and (c) solvent reservoir with a counterflow of inert gas.

Adapted from Gu *et al.*⁴⁷

Figure 0.44a illustrates the most straightforward procedure to conduct SVA. A solvent reservoir is placed inside a closed chamber and is left for a certain amount of time. In **Figure 0.44b**, the solvent reservoir is outside of the annealing chamber, and an inert gas is bubbled into it, carrying the solvent vapours to the chamber. Finally, in **Figure 0.44c**, a solvent reservoir is placed inside the chamber, and an inert gas flows through it.⁴⁷ The SVA process is influenced by several parameters, including temperature, humidity, chamber volume, solvent reservoir surface area, chamber seal, solvent inflow/outflow rate, and vapour pressure.^{47, 49, 51}

1.8. Solubility of polymeric systems

The interaction between a polymer *e.g.*, a BCP, and a solvent is crucial in many applications. For instance, it is necessary to conduct solvent selection to induce swelling of a polymer network, influencing microdomains' order and orientation. One possible approach to evaluating the miscibility in polymer/solvent and polymer/polymer systems is through the Hildebrand solubility parameter (δ). This value accounts for the strength of attraction between the molecules in a volume. However, the theory presents significant discrepancies when polar interactions are involved.²⁷ Empirically, if the difference between δ values of a solvent/polymer or a polymer/polymer system is greater than 2 MPa^{1/2}, the components are predicted to be non-miscible.⁵²

In response to the Hildebrand parameter's limitations, Hansen developed a set of parameters that include the polar and hydrogen bonding contributions.⁵³ The solubility criteria are based on polymers and solvents visualised as points in a 3D vector space. If we graphically represent a sphere with the centre as the polymer coordinates, a solvent point within the sphere would indicate solubility, in contrast to a point outside of this space.⁵³ For practical purposes, the radius of the sphere is considered to be 8 MPa^{1/2},⁵² and the distance between the solvent and the polymer points (R_a) is calculated via **(Equation 1.7)**:⁵³

$$(R_a)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad \text{(Equation 1.7)}$$

Where δ_{D2} and δ_{D1} are the dispersion solubility parameters; δ_{P2} and δ_{P1} are the polar solubility parameters; δ_{H2} and δ_{H1} are the hydrogen bonding solubility parameters and the indices 1 and 2 represent the solvent and the polymer, respectively.

Although the Hansen model emerged as a solution to the Hildebrand approach's limitations, there is still a lack of data for many existing polymers. Additionally, polymer solubility depends on several other parameters, including temperature, polymer structure and solvent concentration. Thus, both models offer a relatively constrained representation of the interactions that occur due to the inherent complexity of the solubility process. Moreover, a comparison between the two approaches demonstrated similar accuracies.⁵² Despite some over-simplification in the two theories, they can still be used as a qualitative prognostic tool for polymer solubility.

1.9. Polystyrene-*b*-poly(2-vinylpyridine) as a model system

As discussed previously, the morphology of di-BCPs can be described by the product χN and the volume fraction, f , of one of the blocks. Furthermore, it is well-known that the size of features formed after microphase separation is dictated by the total chain size (N). There is an increasing interest in the miniaturisation of devices, especially in microelectronics, where patterning is essential. Therefore, as BCPs appear as promising candidates to achieve sub-10 nm features, research on the synthesis of high χ systems has been growing. When the dissimilarity between two blocks in a chain increases, it is possible to achieve phase separation with shorter chains ($\chi N > 10.5$), enabling access to small features. Additionally, higher χ can improve long-range order and reduce line edge roughness.⁵⁴

Polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) is a classical BCP system in industry, especially in the semiconductor field, which uses both PS and PMMA as photoresists. Moreover, the chemistry and methods for controlling the orientation of the phases are well established.⁵⁵ Although widely employed, the dissimilarity between PS and PMMA is relatively small, which renders the usable size of MW to the range of $M_n \geq 28$ kg/mol and the size of the obtained domains are limited to $D \geq 24$ nm.⁵⁶

In this regard, high χ BCPs have been seen as an alternative for the traditional PS-*b*-PMMA. Among these different BCPs, some are based only on organic compounds (e.g., polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) and polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP)) and others with an inorganic moiety (e.g., polystyrene-block-poly(dimethylsiloxane) (PS-*b*-PDMS)). **Table 1.1** demonstrates how the Flory-Huggins

parameter χ varies for a range of BCPs at 25 °C and at 180 °C; the table acts as an aid for selecting a suitable BCP system.

Table 1.1. A range of BCPs and their correspondent Flory-Huggins parameters (χ). Adapted from *Gu et al.*⁵⁷

BCP	χ	χ at 25 °C	χ at 180 °C	χ normalised by reference volume 118 Å ³
PS- <i>b</i> -PMMA	$4.46T^{-1} + 0.028$	~ 0.043	~ 0.038	$3.5T^{-1} + 0.022$
PS- <i>b</i> -PEO	$29.8T^{-1} - 0.023$	~ 0.077	~ 0.043	$29.8T^{-1} - 0.023$
PS- <i>b</i> -PI	$33T^{-1} - 0.0228$	~ 0.088	~ 0.050	$59.1T^{-1} - 0.071$
PS- <i>b</i> -P2VP	$63T^{-1} - 0.0033$	~ 0.178	~ 0.106	n.a.
PS- <i>b</i> -PLA	$98.1T^{-1} - 0.0112$	~ 0.217	~ 0.105	$57.4T^{-1} - 0.061$
PS- <i>b</i> -PDMS	$68T^{-1} + 0.037$	~ 0.265	~ 0.187	$90.7T^{-1} - 0.095$
PTMSS- <i>b</i> -PLA	$51.3T^{-1} + 0.029$	~ 0.478	~ 0.403	n.a.

Poly(vinylpyridine) (PVP) is such an exciting material due to its capability to form sub-10 nm features and the pyridine group's presence. Two isomeric forms are commonly reported in the literature: P2VP (the nitrogen is in an *ortho* position) and P4VP (the nitrogen is in a *para* position) (**Figure 1.5**).⁵⁷

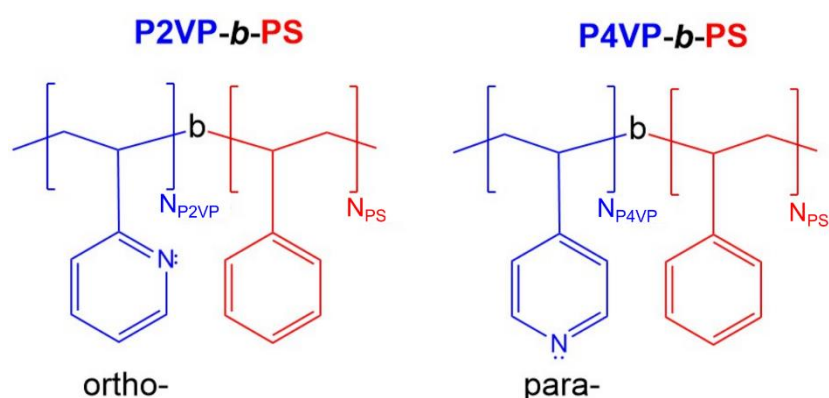


Figure 0.5. The chemical structures of poly(2-vinylpyridine) and poly(4-vinylpyridine).

The nitrogen in the pyridine group provides the opportunity for chemical modifications. Moreover, this group is an excellent chelating agent for several inorganic species, enabling interaction with nanoparticles and metal ions. Additionally, small organic

species can be adsorbed into the PVP phase due to hydrogen bonding and basicity.^{58, 59} The nitrogen's position in the pyridine group leads to differences in material and chemical properties. For instance, the T_g for P2VP is 104 °C and for P4VP is 142 °C. P2VP can also present some binding difficulties to larger species due to the nitrogen's proximity to the alkyl backbone (*i.e.*, steric repulsion).⁶⁰ Despite such differences, both polymers have been successfully applied to various systems, including magnetic storage media,⁶¹ lithography and fabrication of semiconductor features,^{51, 58, 62} electrochemical sensors,⁶³ ionic conductivity membranes,⁶⁴ photonics⁶⁵ and drug delivery.⁶⁶

In literature, the vast majority of reports of cylinder-forming PS-*b*-P2VP/P4VP relies on systems of PS-majority phase, which refers to P2VP/P4VP cylinders in a PS matrix.^{58, 67, 68} However, in the present work, P2VP-*b*-PS with P2VP-majority phase will be originally employed to produce a nanoporous membrane template, with PS forming the cylinders inside a P2VP matrix, also called an "inverse" structure. As previously stated, the P2VP domain readily accommodates various moieties, which can then function as an effective hard mask for pattern transfer.

1.10. Metal infiltration and fabrication of inorganic structures

In some applications *e.g.*, electronics, the self-assembled BCP patterns must be transferred onto the substrate. However, most BCP systems present a low etch contrast, which creates poor fidelity of the features. To increase the contrast, researchers developed BCPs with inorganic moieties. Moreover, it is also possible to incorporate these inorganic species into an ordered BCP film. Several techniques can be applied to this end, such as evaporation and sputtering, atomic layer deposition, aqueous metal reduction and spin coating of metal precursor solutions.⁶⁹ Therefore, a variety of applications can be achieved by using the BCP-templated inorganic structures.

As previously mentioned, a diverse array of techniques exists for infiltrating a BCP film, which can be broadly categorized into two main groups: vapour-phase infiltration (VPI) and liquid-phase infiltration (LPI). Within the VPI methods, atomic layer deposition (ALD) and sequential infiltration synthesis (SIS) have gained significant popularity. ALD, a form of chemical vapour deposition (CVD), involves controlled introduction of the material precursor in a gaseous state within a chamber, allowing surface reactions on the substrate and the fabrication of the aimed material layer.⁷⁰ SIS is similar to ALD, and

allows the infiltration of polymers with inorganic precursors by subjecting the polymer to alternating and self-regulating exposures of precursor vapours. The SIS is based on the nucleation of inorganic species on the substrate functional groups, followed by their growth.⁷¹

A significant drawback of VPI processes is their reliance on precursors with high vapor pressure. These precursors typically require high-temperature conditions for processing, which poses a challenge when working with polymers that have a low glass transition temperature. Concerning LPI, this category of techniques present some advantages when compared to VPI, including absence of volatile compounds, lower temperatures requirements, reduced cost and a wider range of accessible precursor compounds (*e.g.*, nitrates, chlorides, and cyanates).⁷² In summary, the LPI is based on the coordination of inorganic species to one of the blocks. The inorganic precursor can be dissolved in water or other solvents and the infiltration can be conducted either via dip coating or spin coating of the BCP film.⁷³ The spin coating infiltration method is a facile and rapid method that enables the creation of high-quality features. Our group has successfully worked with this technique followed by UV/Ozone treatment to create metal oxide arrays when fabricating hard masks derived from different BCP morphologies.^{43, 51, 74, 75} The fabrication of inorganic arrays on BCP templates is based on the dissimilarity between the constituent blocks. The metal precursor should be soluble in a solvent capable of interacting with one of the blocks. Additionally, the chosen block must bind with the metal *e.g.*, via complexation; hence the precursor is confined to just the desired block.

1.11. Characterisation techniques

Each of the techniques used to characterise the obtained materials is briefly outlined in this section.

Reflectometry⁷⁶

One common metrology method for determining a thin film thickness is reflectometry. This non-destructive technique, which uses interferometry, is especially well-suited for evaluating thin-film coatings in lab environments. Using a spectrometer, the approach compares the reflected intensity of coated and uncoated materials. A reflectance curve

is produced by subtracting the dark noise measured by the instrument. The coating thickness can be estimated using this curve as a guide.

Atomic force microscopy (AFM)⁷⁷

This method uses a sharp probe supported by a flexible cantilever. Hooke's law governs the force that the tip applies to the sample at a distance of 0.1 - 100 nm. As a result, the sample topography can be recorded in two or three dimensions by tracking the deflection of the probe due to various forces acting on the sample at different points. These forces can be broadly divided into repulsive forces, such as electrostatic Coulombic interactions, capillary forces, and covalent forces, and attractive forces like van der Waals, chemical, and electrostatic forces.

Scanning electron microscopy (SEM)⁷⁷

SEM is a versatile tool that is widely used to analyse the surface of materials. High-energy electrons are directed to the material, and the resultant electrons and X-rays are examined. The material topography, morphology, composition, grain orientation, crystallographic information, and other features are revealed by these emitted electrons and X-rays.

X-ray photoelectron spectroscopy (XPS)⁷⁷

X-ray energy spans from a few hundred to a few thousand electron volts. This energy range specifically pertains to the core electrons of an atom. When X-rays of a specific energy illuminate a sample, electrons may be expelled from various electronic states. By examining the kinetic energy of these ejected electrons, one can deduce the binding energy. Consequently, XPS serves as a tool for investigating the deeply situated core states of atoms in solids. Analysing such aspects of XPS data allows for insights into the constituent elements, their respective percentages, the nature of bonding, and additional interactions, including spin-orbit splitting. Moreover, XPS is a surface-sensitive technique that exclusively enables characterisation within a depth of 10 nm.

Transmission electron microscopy (TEM)⁷⁸

TEM imaging and associated spectroscopic methods depend on the interplay between a high-energy electron beam and a solid sample. An illumination system generates the electron beam, which is then concentrated on the specimen by electromagnetic lenses. The transmitted and/or diffracted electrons exiting the sample create an image of the specimen. This enables the study of sample morphology and structure at the nanoscale. Furthermore, secondary signals produced by the specimen interaction with the electron beam can provide insights into its composition.

Energy dispersive X-ray spectroscopy (EDX)⁷⁷

EDX is known as a straightforward method for compositional analysis when used in conjunction with SEM and TEM. In inelastic interactions, electrons can be ejected from inner shells, causing a shift from higher levels to the core levels with the emission of X-rays. The energy of these characteristic X-rays provides information about the chemical composition of the material.

Raman spectroscopy⁷⁷

Raman spectroscopy is a non-destructive technique that can be used to identify the chemical bonding in molecules or solids and doping in semiconducting materials. The vibrational transitions can be observed in either Raman spectra or infrared (IR) spectra. However, the Raman spectra is generated through an entirely different mechanism as compared to IR spectra. In IR spectra, one measures the absorption of infrared light by the sample as a function of frequency. On the other hand, in Raman spectroscopy, a sample is irradiated by an intense light (laser) of frequency ν_0 , and then the scattered light is observed in perpendicular direction to the incident light. Thus, in Raman spectroscopy, one measures the molecular vibration frequency (ν_R) as a shift from the incident frequency (ν_0).

Ultraviolet-visible spectroscopy (UV-Vis)⁷⁹

UV-Vis spectroscopy is applied as a characterisation technique for assessing the absorbance of samples at specific wavelengths. This method relies on the concept of

electronic transition in molecules or atoms, triggered by the absorption of light within the ultraviolet (100 - 400 nm) and visible (400 - 800 nm) range of the electromagnetic spectrum, leading to the excitation of an electron from the ground state to a higher energy orbital. In UV-Vis, there exists a direct correlation between the absorbance and the concentration of the absorbing compound (Beer-Lambert law), making this particularly interesting for accurate quantitative measurements.

X-ray diffraction (XRD)⁸⁰

XRD, a non-destructive technique, provides comprehensive information about a material crystallographic structure, chemical composition, and physical properties. The generated X-rays are directed towards a sample and their interaction produces a diffracted ray that is then detected. Plotting the intensity of these diffracted rays, scattered at different angles by the material, generates a diffraction pattern, which is unique for each material phase and attributed to its specific chemistry and atomic arrangement.

Reflectance⁷⁷

Reflectance measurements are valuable for studying bulk samples, as it represents the ratio between reflected and incident radiation, and they can be classified in internal and external. Internal reflectance is exemplified by attenuated total reflectance (ATR), where an infrared radiation beam passes through a crystal in contact with the sample. External reflectance can be categorised as specular and diffuse. In specular reflectance, incident radiation focused onto the sample is directly reflected by its smooth surface, similar to a mirror. This method is particularly useful for working with thin films. Conversely, diffuse reflectance is the more commonly used technique for rough surfaces. Measurements of diffuse reflectance are conducted in UV-vis spectrophotometers coupled to an integrating sphere. This sphere can collect the reflected light, allowing all radiation to reach the detector through repeated reflections.

Contact angle (CA)⁸¹

The wettability of a solid surface by a liquid is defined by the contact angle due to the liquid-solid interactions, which is influenced by the surface roughness and chemical properties. A liquid with a small contact angle exhibits high wettability, leading to

spreading on the solid surface. Physical and chemical heterogeneities cause deformation of the three-phase contact line *i.e.*, solid/liquid/vapour. The surface contact angle, denoted as θ , is a general term encompassing various angles formed by a droplet on a surface (Young CA, advancing and receding CAs).

1.12. Thesis overview

The overall objective of this work was to investigate/develop a reliable, reproducible and facile process of obtaining hexagonally closed packed structures by utilising P2VP-*b*-PS in different molecular weights and inducing their self-assembly. In sequence, those block copolymer templates were selectively infiltrated to create porous inorganic structures with potential applications. It is important to note that this is an unusual system in which the PS is the minority block, a so called “inverse” structure. By using this arrangement, the insertion of metal precursors into the P2VP structure can be processed to form a mask where the etch resistant component allows the formation of pores.

In Chapter 2, the phase separation of an “inverse” P2VP-*b*-PS system, in which P2VP is the majority block, was extensively studied. In this work, process parameters such as temperature, time and film thickness were investigated. Hexagonally closed packed nanopatterns were observed, in which PS cylinders with a diameter of ~ 35 nm in a matrix of P2VP. The BCP was infiltrated with different metal ions and converted to metal oxide hard masks. Finally, the masks were used in a dry etching process, in which porous silicon substrates were fabricated. Aislan Paiva designed the project and conducted the characterisation of the material. Nadezda Prochukhan executed the etching. FIB/STEM analyses were performed in the Advanced Microscopy Laboratory (AML - <https://www.tcd.ie/crann/aml/>), Trinity College Dublin, with the help of Megan Canavan and Raman Bekaravich.

In Chapter 3, the investigation of the metal infiltration process in P2VP-containing BCP was conducted. Differences in the liquid-phase infiltration were observed for the evaluated ions and could be related to different interactions between the metal and the pyridine group. Aislan Paiva conceived the study and prepared the samples. Jhonattan Baez helped with the XPS analyses. Tatiana Perova performed the Raman measurements.

In Chapter 4, an application of iron oxide porous structures on pharmaceutical wastewater treatment was studied. By varying the molecular weight of the BCP, pore sizes with different diameters were obtained. The BCP templates were then infiltrated with iron ions with subsequent polymer oxidation, and porous structures on glass substrates were fabricated. The nanopatterns were capable of degrading a commonly used antibiotic, levofloxacin, *via* a Photo-Fenton reaction. Aislan Paiva and Jhonattan Baez prepared the samples and characterised them. Jhimli Guin performed the degradation experiments. FIB/STEM analyses were performed in the Advanced Microscopy Laboratory (AML - <https://www.tcd.ie/crann/aml/>), Trinity College Dublin, with the help of Clive Downing.

In Chapter 5, the etch selectivity of BCP-templated chromium oxide porous masks was studied towards advanced deep reactive ion etching of silicon substrates. Two BCPs with different molecular weights were used to produce chromium masks *via* selective infiltration. Then, the porous masks were applied in the optimisation of a newly developed etch recipe to obtain high aspect ratio features. The porous structures achieved an unprecedented aspect ratio of 50 for the lower molecular weight BCP template. As potential applications, the obtained porous silicon materials were evaluated for light absorption and thermal management. Aislan Paiva prepared/characterised the samples and conducted the contact angle measurements. Michael Gerlt and Nino Laubli conducted the advanced etching experiments. Nadezda Prochukhan performed the light absorption measurements. Jhonattan Baez helped with the setup for the contact angle evaluation. FIB/STEM analyses were performed in the Advanced Microscopy Laboratory (AML - <https://www.tcd.ie/crann/aml/>), Trinity College Dublin.

In Chapter 6, a summary of the work developed in this thesis is shown and potential future developments based on the current results.

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Chapter 2.

Highly Ordered Porous Inorganic Structures *via* Block Copolymer Lithography: an Application of the Versatile and Selective Infiltration of a “Inverse” P2VP-*b*-PS System

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2.1. Abstract

A facile and versatile strategy was developed to produce highly ordered porous metal oxide structures *via* block copolymer (BCP) lithography. Phase separation of a poly(2-vinylpyridine)-*b*-polystyrene (P2VP-*b*-PS) was induced by solvent vapour annealing (SVA) in a nonselective solvent environment to fabricate cylindrical arrays. In this work, we thoroughly analyse the effects of film thickness and solvent annealing time on the ordering of a majority P2VP system for the first time, resulting in “inverse” structures. Reflectometry, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and Transmission Electron Microscopy (TEM) were used to characterize the formation of the highly ordered BCP morphology and the subsequently produced metal oxide film. At 40 min solvent annealing time, hexagonally close packed structures were produced with cylinder diameters ~ 40 nm. Subsequently, the BCP films were infiltrated with different metal cations. Metal ions (Cr, Fe, Ni and Ga) selectively infiltrated the P2VP domain, while the PS did not retain any detectable amount of metal precursor. This gave rise to a metal oxide porous structure after a UV/Ozone (UVO) treatment. The results showed that the metal oxide structures demonstrated high fidelity compared to the BCP template and cylindrical domains presented comparable size to the previous PS structure. Moreover, XPS analyses revealed the complete elimination of the BCP template and the presence of the metal oxides. These metal oxides were used as hard masks for pattern transfer via dry etching as a further application. Silicon nanopores were fabricated which mimicked the BCP template and demonstrated a pore depth of ~ 50 nm. Ultimately, this strategy can be applied to create different inorganic nanostructures for a diverse range of applications *e.g.*, solar cells, diodes, and integrated circuits.

Furthermore, by optimizing the etching parameters, deeper structures can be obtained via ICP/RIE processes, leading to many potential applications.

2.2. Introduction

The fabrication of dense inorganic structures plays a significant role in many fields, including optoelectronics,¹ photonics,² catalysis,³ sensors,⁴ microelectromechanical systems (MEMS),⁵ field emission,⁶ and nanomedicine.⁷ Moreover, laterally ordered nanostructures are important in the field of electronics, in which it is essential that the structures are homogeneously distributed, size-tailored and monodisperse.⁸ A diverse range of methods can be applied to fabricate these features, such as electron beam lithography, ultraviolet and imprint lithography. Nevertheless, those technologies generally entail high machinery costs and complex processes.⁹⁻¹¹

Block copolymer lithography is an exciting patterning technology due to the possibility of creating highly ordered nanostructures alongside rapid processing, scalable synthesis, low cost, and nanoscale precision.¹² The self-assembly of the BCPs arises from the chemical dissimilarities between the constituent polymer blocks, leading to microphase separation and ordered morphologies of a multitude of patterns. Control over the microphase separation/self-assembly can be achieved through fine tuning the process parameters, which include molecular weight, volume fraction of the blocks, chemistry of the blocks, and surface energy.¹³

In surface technology, the application of BCP thin films is notably compelling. By decreasing BCP film thickness to scale consistently with the natural period of the polymer (LO), it is possible to generate a range of structures. These morphologies can be utilised in several industrial applications, such as lithographic masks,¹⁴ membranes,¹⁵ and photonics.¹⁶ Moreover, the BCP can act as an engineered template for inclusion of inorganic species.^{17, 18} The confinement of a polymer in a thin film (typically < 100 nm) changes its behaviour compared to the bulk counterpart: thin films are subjected to interactions with the interfaces *e.g.*, the substrate and the air, for example. Moreover, in thin films, the domains are highly ordered throughout the film, whereas, in bulk, ordered domains are organised in randomly distributed grains.¹⁹

A number of methods have been developed to induce the self-assembly of the BCP films. One of the most commonly used techniques is thermal annealing, which consists of

exposing the BCP film to temperatures above the glass transition temperature (T_g) and hence improving the chain mobility. However, this method has limitations for BCPs with high Flory-Huggins or the interaction parameter (χ) between the blocks and high molecular weight (MW) BCPs.²⁰ Another regularly applied method is solvent vapour annealing (SVA), where the BCP film is exposed to a carefully chosen solvent vapour system. The solvent vapour can selectively swell the blocks and thus reduce the effective T_g , leading to enhanced chain mobility and ordering. Other annealing methods include the modification of surface energy via polymer brush layers, application of external forces, graphoepitaxy, and chemoepitaxy.²¹⁻²⁵

There exists a diverse range of BCPs, many of which have been utilised for applications such as drug delivery, lithography, catalysis, and for the design of separation membranes^{26, 27}. As electronics become more miniature, the required feature sizes also become progressively smaller. Therefore, self-assembling systems such as BCPs can be used to achieve this goal.²⁸ Polystyrene-*b*-polymethacrylate (PS-*b*-PMMA) is still one of the most researched BCP systems due to the ease of controlling the orientation of domains (similar surface energies between the two blocks), established processing routes and availability. Nevertheless, it has a low Flory-Huggins parameter between the blocks ($\chi = 0.04$), which directly affects the minimum period achievable.²⁹ For that reason, researchers have focused on the development of higher χ BCPs, increasing the thermodynamic incompatibility between the two blocks, allowing a facile microphase separation and a reduction of feature sizes.^{30, 31} P2VP-*b*-PS is another system with high χ (0.178 at 25 °C³²) and with an interesting characteristic related to the P2VP block. Pyridine is an excellent chelating agent for several inorganic species, enabling the interaction with nanoparticles and metal ions. Additionally, small organic species can also be adsorbed into the vinylpyridine (VP) domain due to the hydrogen bonding and basicity of the nitrogen lone pair.^{33, 34} Two isomeric forms with different binding capabilities are reported in the literature (P2VP and P4VP), and both materials have been successfully applied for magnetic storage media,^{35, 36} lithography and fabrication of semiconductor features,^{33, 37, 38} electrochemical sensors,³⁹ ionic conductivity membranes,⁴⁰ photonics⁴¹ and drug delivery.⁴²

Thus, this research focused on the study of the phase separation of a cylinder-forming P2VP-*b*-PS block copolymer system, in which P2VP is the majority phase; hence allowing the fabrication of porous nanopatterns. In literature, the use of PVP block copolymers is mainly based on polystyrene being the majority block or equally volume fraction.^{33, 43-47} Nevertheless, in this work, a P2VP-majority phase (~70 %) BCP was

used, and produced “inverse” structures, in which PS cylinders are embedded in a P2VP matrix. We note an important paper on a similar system where tin oxide was introduced via an atomic layer deposition method.⁴⁸ The nanostructures were produced via a thorough study of the phase separation of a thin film exposed to a non-selective solvent (chloroform). The solvent induced the formation of perpendicular structures to the substrate with a hexagonally close-packed (HCP) pattern. Moreover, as previously mentioned, P2VP is capable of binding to different species *e.g.*, nanoparticles and ions, via the nitrogen lone pair. Therefore, based on liquid-phase metal infiltration, it was possible to fabricate thin metal oxide layers on silicon substrates using Cr, Ni, Fe and Ga ions. Those layers presented highly ordered porous structures which can be used for nanofabrication, optoelectronics and catalysis. Finally, as an application, the oxide structures were used to produce nanopores on silicon substrates by RIE/ICP etching.

2.3. Materials and methods

All materials and reagents were used as received without further purification. Single crystal, B-doped p-type silicon (100) wafers with a native oxide layer ($\cong 2$ nm) (University Wafer) were used as substrates. P2VP-*b*-PS block copolymer with molecular weight $MW = 86 \text{ kg.mol}^{-1}$ ($M_{n\text{P2VP}} = 60 \text{ kg.mol}^{-1}$, $M_{n\text{PS}} = 26 \text{ kg.mol}^{-1}$) and polydispersity index $PDI (M_w/M_n) = 1.15$ (where M_n and M_w are number average and weight average molecular weights) was purchased from Polymer Source™, Inc. Toluene (TOL, C_7H_8 , 99.8 %, anhydrous), tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$, 99.8 %, anhydrous), acetone (ACT, $\text{C}_3\text{H}_6\text{O}$, 99.0 %), chloroform (CHL, CHCl_3 , 99.9% , anhydrous), ethanol (EtOH, $\text{C}_2\text{H}_5\text{OH}$, $\geq 99.5\%$, anhydrous), 2-propanol (IPA, $\text{C}_3\text{H}_8\text{O}$, 99.5%, anhydrous), 1-butanol (ButOH, $\text{C}_4\text{H}_{10}\text{O}$, 99.8 %, anhydrous), chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ≥ 99.99 %), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999%), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.99 %) and gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9 % trace metal basis) were obtained from Sigma-Aldrich.

A schematic of the nanoporous membrane fabrication process is shown in **Figure 2.1**.

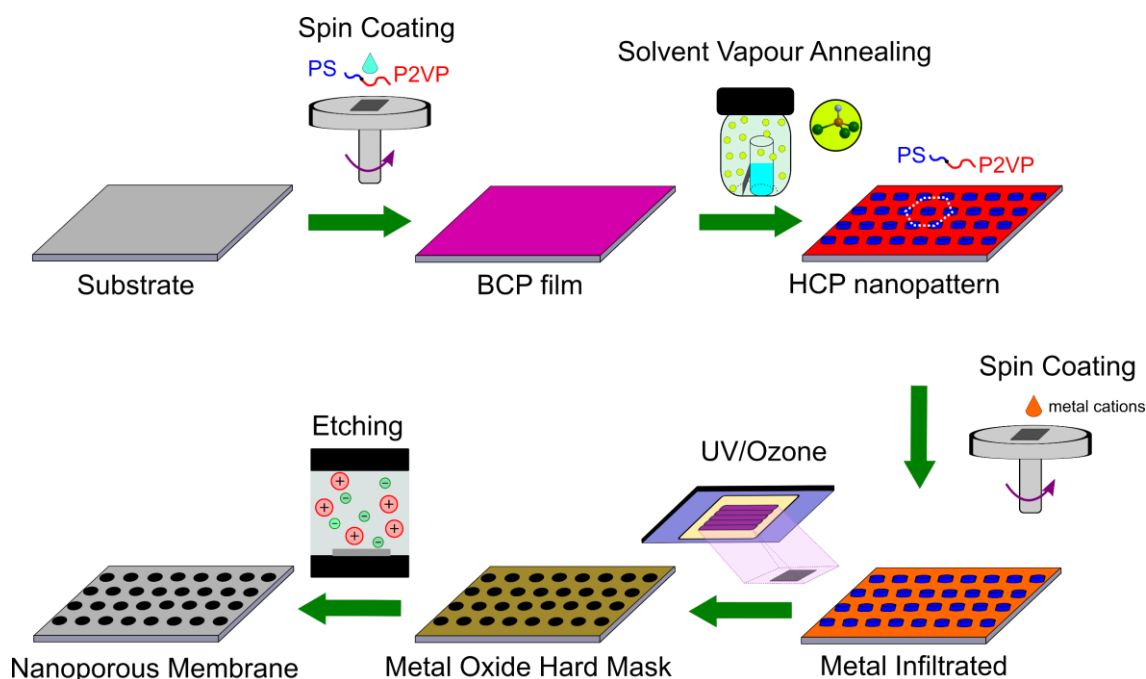


Figure 2.1. General procedure for fabricating nanoporous membranes based on a P2VP-*b*-PS BCP capable of forming hexagonally close-packed (HCP) features. The hard mask is created through metal infiltration and subsequent UV/Ozone treatment, allowing the reproduction of the BCP pattern. Finally, plasma etching is conducted to generate pores on the substrate.

2.3.1. Highly ordered BCP thin film preparation

The silicon wafers were cut into 4.0 cm² squares and cleaned by ultrasonication in acetone for 20 min, followed by drying in a N₂ stream. The BCP was dissolved in a mixture of TOL:THF (1:4) to yield concentrations of 0.5, 1.0, 1.5 and 2.0 % wt. The BCP thin films were obtained by spin coating the polymer solution onto the silicon substrates at 5s ramp, 3000 rpm for 25 s. The SVA process was then conducted as follows: the as-spun films on the substrates were placed in a 150 mL glass jar completely closed containing a vial (50 mm × 12 mm × 4 mm) with 2 mL of chloroform for different periods of time (20 min to 3 h) and at three temperatures (5 ± 2 °C, room temperature (20 ± 2 °C) or 60 ± 2 °C) through the use of temperature-controlled fridge and oven. Samples were removed from the jars at specific times and allowed to dry at room temperature.

2.3.2. Ordered metal oxide structure development

Solutions of the metal nitrates (Cr, Ni, Fe and Ga) were prepared in butanol with concentration of 2.0 % wt. and spin-coated on the BCP films after SVA at 5 s ramp,

3000 rpm for 25 s (SCS G3P-8 spin coater, PI-KEM). Subsequently, the samples were placed in a UV/Ozone (UVO) system with two low pressure mercury lamps (output current of 0.8-0.95 A, power of 65-100 W, emissions at 184.9 nm and 253.7 nm) (PSD Pro Series Digital UV Ozone System, Novascan Technologies, Inc.) in order to promote the polymer elimination and metal precursor oxidation. The UVO process was performed for 3 h and samples were at 4 cm distance from the UV source.

2.3.3. Dry etching and pattern transfer

Due to its high etch selectivity,⁴⁹ the chromium oxide layer was used as a hard mask in a pattern transfer process conducted on a Plasmalab System100 ICP180 etcher (Oxford Instruments Plasma Technology). Substrates were etched with an ICP power of 1200 W, RIE power of 20 W, etch time of 30 to 120 s, CHF₃ (80 sccm) and SF₆ (15 sccm) gases at 20 mTorr.

2.3.4. Characterisation

The as-spun BCP film thicknesses were measured by a Filmetrics® reflectometer system at a fixed angle of incidence of 90°; a two-layer model (SiO₂ + BCP) was used to simulate experimental data. Five measurements were performed in different regions of the sample and the results were presented as mean ± standard deviation.

AFM images were acquired in a Park XE-100 (Park Systems) in non-contact mode (NCM) with an AC160TS cantilever type (force constant = 26 N.m⁻¹, resonance frequency = 300 kHz). Cylinder diameter and cylinder-cylinder spacing were estimated via the measurement of 100 features and results were expressed as mean ± standard deviation.

SEM images were recorded on a Zeiss Ultra Plus system with the accelerating voltages in the range of 2-6 kV, at a working distance between 4 to 5 mm using an in-lens detector. EDX spectra (point scans) were acquired at 15 kV on an Oxford Inca EDX detector.

XPS analysis was performed using an Al K α X-ray source (1486.6 eV, CTX400, PSP Vacuum Technology); the spectra were corrected setting the C 1s peak at 284.8 eV. A Shirley background and Gaussian-Lorentzian functions were used for peak fitting. The pass energies for the survey and for the core level scans are CPE100 and CPE50, respectively. Dwell times were set to 0.1 s for the survey and 0.05 s for the core level scans. 3 scans were performed for the survey spectra and 4 for the core level spectra.

TEM coupled with EDX analyses were performed on a FEI Titan G2 80-300FEG S/TEM with a Schottky-type electron gun operated at 300 kV and a Bruker XFlash 6T-30 detector (resolution 129 eV). Lamellae for TEM cross section images were prepared on a Zeiss AURIGA Focused Ion Beam (FIB), accelerating voltages of 30 kV and ion beam currents of 50 pA - 2 nA.

2.4. Results and discussion

2.4.1. Solvent vapour annealing and ordering of P2VP-*b*-PS

Initially, the self-assembly of P2VP-*b*-PS 60-*b*-26 kg.mol⁻¹ was studied. Therefore, films with different thicknesses were prepared by spin-coating different concentration solutions onto the substrates. The following film thickness values were obtained: 31 ± 1 nm (0.5 % wt.), 47 ± 2 nm (1.0 % wt.), 77 ± 1 nm (1.5 % wt.) and 100 ± 1 nm (2.0 % wt.). Additionally, the as-spun films were imaged via AFM (**Figure 2.2**). It was noted that all four samples exhibited a disordered state, although some microphase separation was observed due to rapid solvent evaporation during spin-coating. It is important to mention that the solutions of BCPs were prepared with a mixture of TOL and THF, which are selective to PS and P2VP, respectively.⁵⁰⁻⁵² Therefore, it is expected that chains would stay elongated in solution instead of forming micelles and thus, phase separation post spin-coating can occur.⁵¹ Moreover, no apparent preferential wetting occurred at the free interface (air) due to the lack of a wetting layer in the samples.

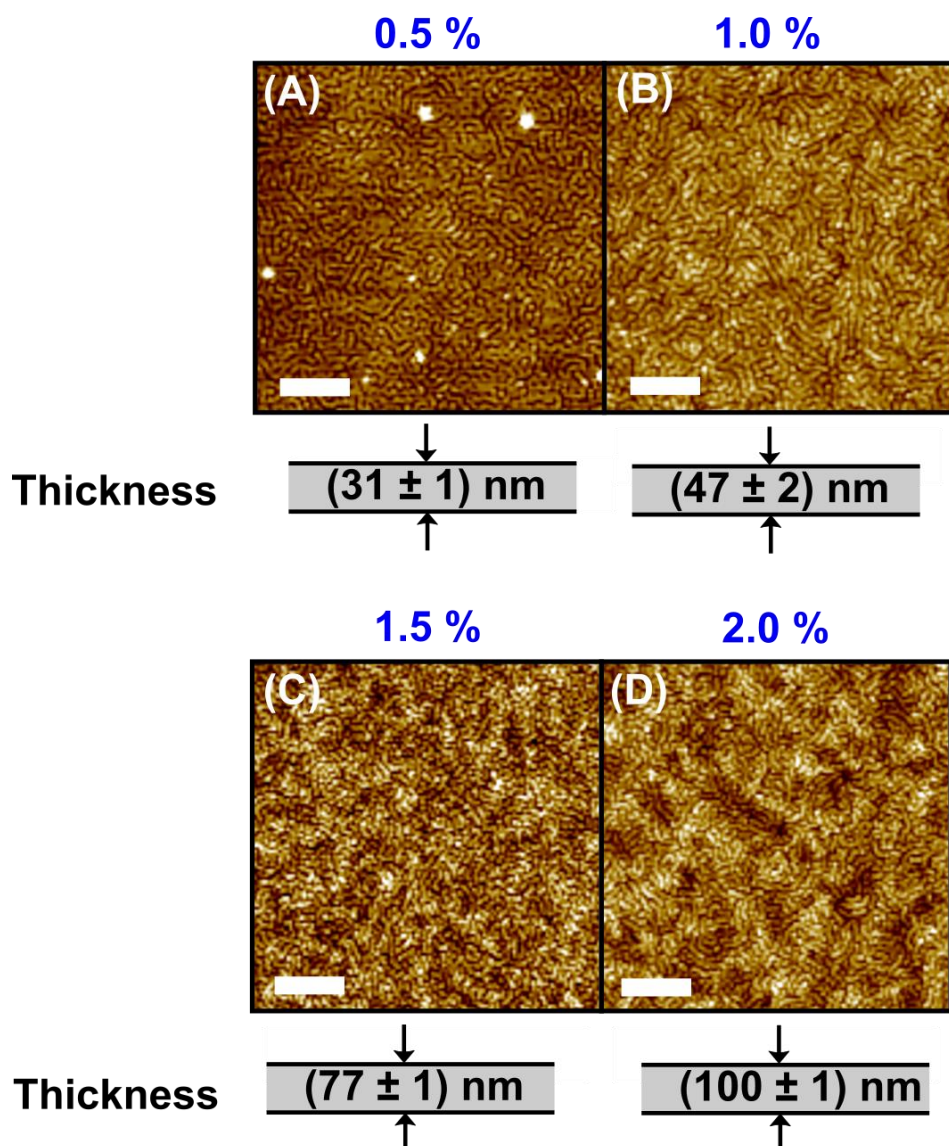


Figure 2.2. AFM images of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ films after spin-coating from different polymer concentrations with respective film thicknesses as measured from reflectometry: (A) 0.5 %, (B) 1.0 %, (C) 1.5 % and (D) 2.0 % wt. All scale bars are 500 nm.

The samples were placed in jars to conduct a static SVA process in the presence of a chloroform atmosphere. Chloroform was chosen as a neutral solvent *i.e.*, the solvent can interact with both blocks; thus, screening unfavourable interactions and balancing the surface energetics differences (air and the substrate), which leads to the perpendicular orientation of the blocks with respect to the substrate.⁵³ The solubility/swelling behaviour of BCP in chloroform can be analysed using the Hansen solubility parameters (**Table A.2.7.1**).

The first SVA experiments were conducted at room temperature (20 ± 2 °C) for different annealing times to analyse the BCP phase behaviour in the presence of a nonselective solvent, and the samples were characterised via AFM (**Figure 2.3**). For all the film thickness analysed, except for the 0.5 % wt. sample (~ 30 nm thickness), there were changes in the observed morphology; for higher concentrations and longer times, vertically aligned cylinders were predominantly observed. It is suggested that the 0.5 % wt. sample (~ 30 nm thickness) exhibits high polymer chain confinement, hence hindering both the chain mobility and the vertical alignment. The dry film thickness of ~ 30 nm is lower than the cylinder-cylinder spacing in this system (~ 60 nm). Therefore, the confinement is deduced to affect the domain orientation, creating frustrated morphologies.¹² By increasing the polymer solution concentration and thus the film thickness, more space for chains to move and rearrange is available. Regarding the annealing time, extended time periods enabled higher solvent uptake by the film, leading to improved chain mobility. Moreover, no dewetting was observed, demonstrating the process robustness and macroscale coverage of the substrate.

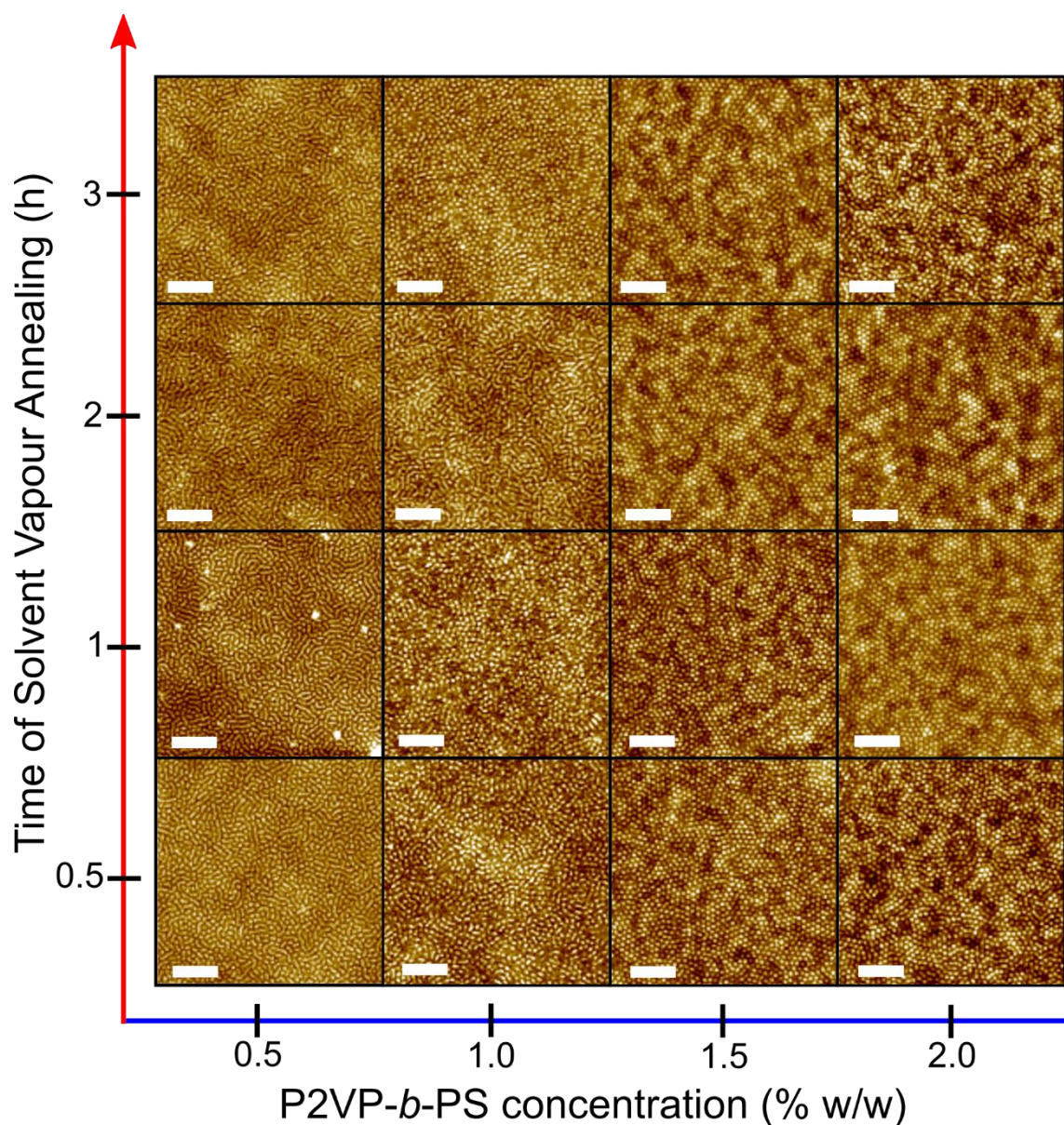


Figure 2.3. AFM images of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ films after solvent vapour annealing at room temperature from different polymer concentrations and at different annealing times. All scale bars are 500 nm.

Similarly, a second set of SVA experiments was conducted. For those tests, two different annealing temperatures were analysed: 5 °C and 60 °C. These temperatures were selected as examples of extreme scenarios: near 0 °C and near chloroform boiling point (61.2 °C).

The vapour pressure in the static SVA is subjected to the experimental temperature, given that all other parameters are fixed. Thus, in a sealed container, a saturated vapour pressure *i.e.*, when the number of molecules leaving the liquid surface equals the number

of molecules going back, is achieved at a particular temperature. The saturated vapour pressures for the three temperatures analysed were estimated via the Antoine equation (**Equation 2.1 and Table A2.7.2**):⁵⁴ 10.4 kPa (5 °C), 21.1 kPa (20 °C) and 97.4 kPa (60 °C).

$$\log_{10}(p) = A - \frac{B}{C+T} \quad (\text{Equation 2.1})$$

Where: p is vapour pressure, T is temperature, and A, B, C are coefficients for the specific solvent.

However, the swelling process is also affected by the solvent uptake by the film, which cannot be controlled in a static SVA setup. **Figure 2.4** shows the AFM images of samples after SVA at 60 °C. By increasing the annealing time, the samples lost their microstructure, and it is possible to observe a disordered melt state. This behaviour is likely due to a high vapour pressure in the system, leading to high solvent uptake. Consequently, a drastic reduction of the effective Flory-Huggins parameter χ_{eff} (**Equation 2.2**) occurs, resulting in an order-disorder transition (ODT) of the system³⁷ and therefore elucidating that 60 °C is not an ideal temperature to conduct the SVA process.

$$\chi_{\text{eff}} = \chi \phi_{\text{BCP}}^{\beta} \quad (\text{Equation 2.2})$$

Where: χ is the Flory-Huggins parameter for the dry film, ϕ_{BCP} is the polymer concentration in the swollen state, and β is an exponent factor with values between 1 and 2.

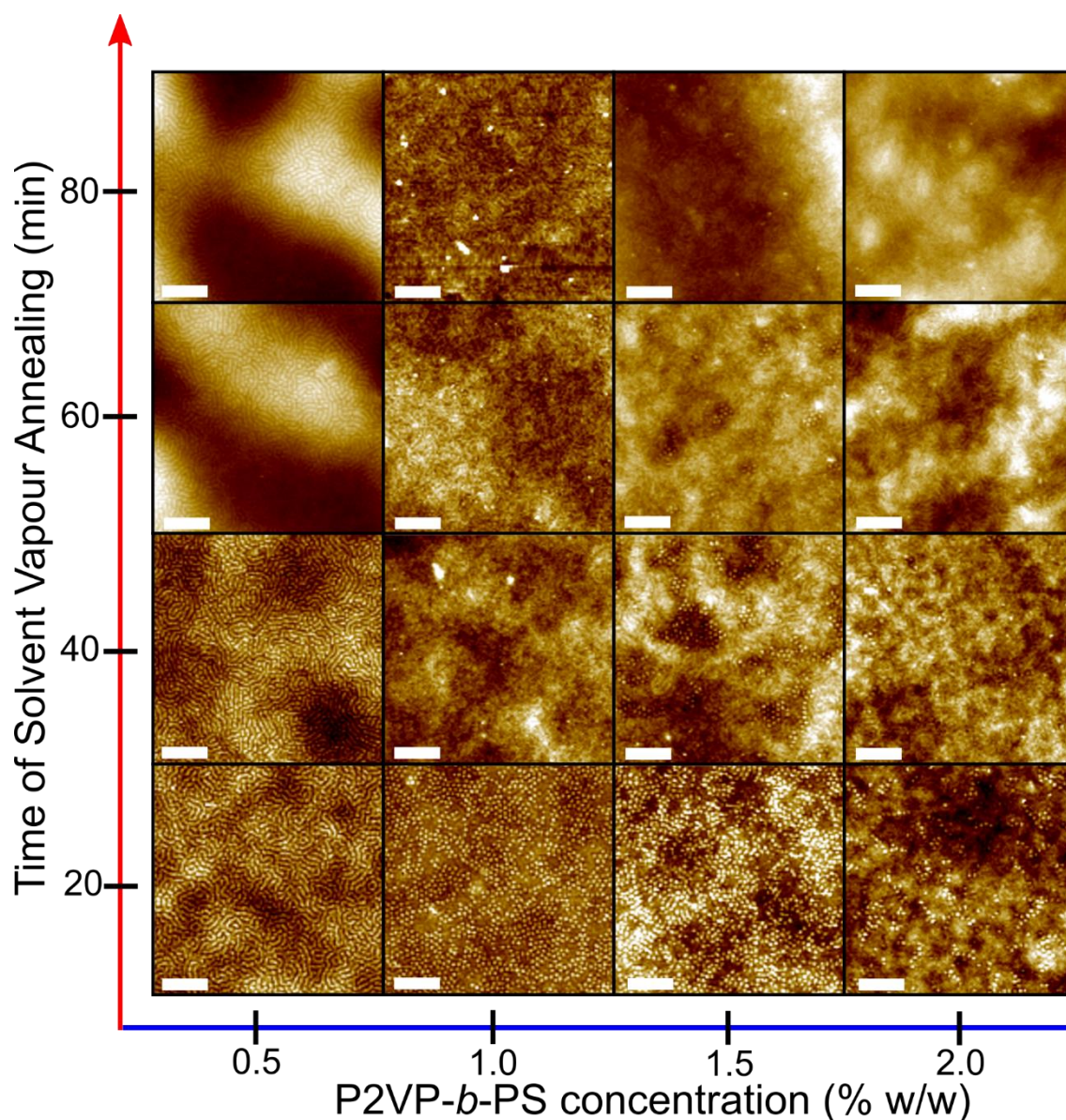


Figure 2.4. AFM images of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ films after solvent vapour annealing at 60 °C produced from different polymer concentrations and at different annealing times. All scale bars are 500 nm.

At 5 °C, slow microphase separation kinetics were expected due to lower vapour pressure and solvent uptake compared to RT and 60 °C; nevertheless, highly ordered vertically aligned cylinders were obtained. In **Figure 2.5A**, the AFM images show that all film thicknesses demonstrated microphase separation after SVA, including the 0.5 % wt. sample at a lower extent. After a 40 min SVA, some samples started to display the formation of terraces; it is possible to observe some differences in morphology compared to the rest of the film.⁵⁵ This may have occurred because of the high solvent uptake by the film at sufficient exposure time, leading to local deviations from commensurability.⁵⁶

The highly ordered phases could be explained by an optimal swelling ratio during annealing *i.e.*, allowing the film to efficiently microphase separate without undergoing an ODT or dewetting. For a film thickness of ~ 77 nm (1.5 % wt.) after 40 min annealing, high-quality hexagonally closed packed cylinders were obtained (**Figure 2.5B**) with cylinder diameter values of (34 ± 3) nm and cylinder-cylinder spacing values of (60 ± 4) nm (**Figure A2.7.1**).

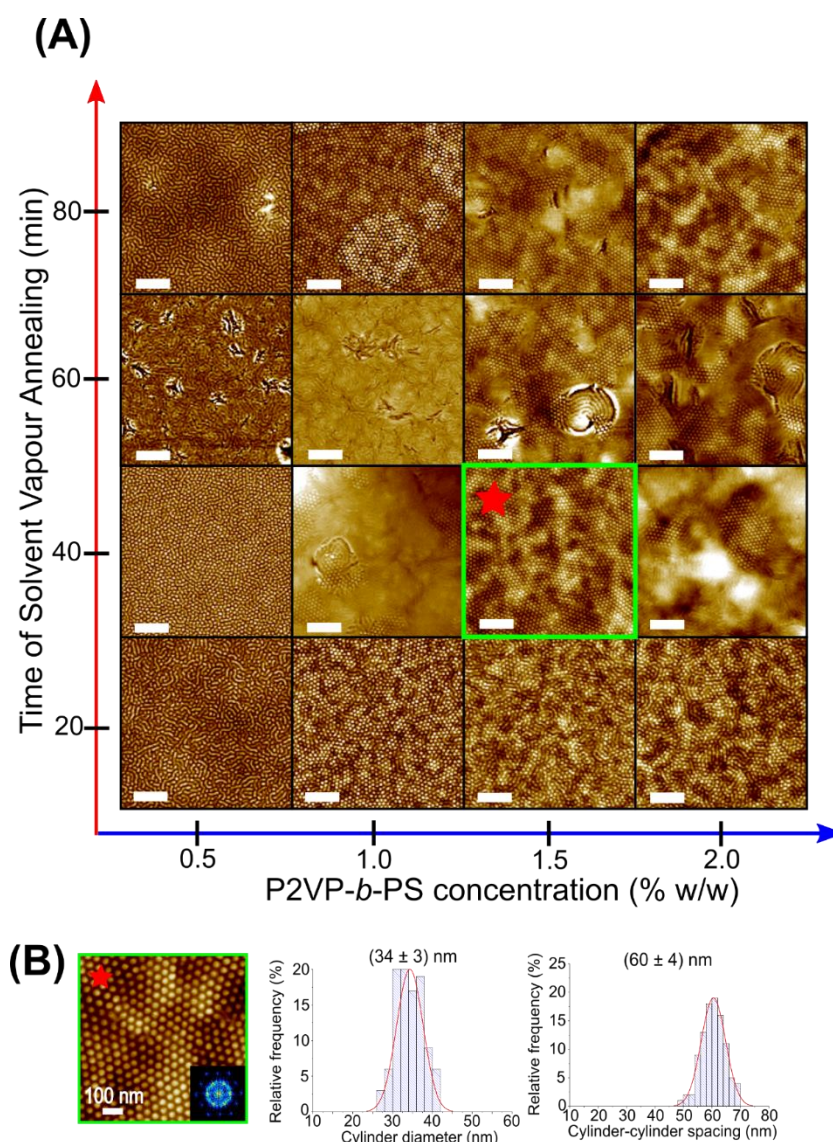


Figure 2.5. (A) AFM images of P2VP-*b*-PS ($60\text{-}b\text{-}26$) $\text{kg}\cdot\text{mol}^{-1}$ films after solvent vapour annealing at 5°C obtained from different polymer concentrations and after different annealing times (scale bars are 500 nm). (B) AFM image of 1.5 % wt. BCP film after SVA at 5°C for 40 min with a corresponding fast Fourier-Transform image inset, and the size distributions of the cylinder diameter and the cylinder-cylinder spacing.

2.4.2. Selective metal infiltration

To study the capability of P2VP in creating ordered domains, selective metal infiltration via spin-coating of the precursor solutions onto the highly ordered BCP thin films was investigated. UVO treatment was used to convert the metal ions to the corresponding metal oxides. Four different metal ions (chromium (Cr^{3+}), nickel (Ni^{2+}), iron (Fe^{3+}) and gallium (Ga^{3+})) were selected to be infiltrated into the ordered BCP thin films based on previous reports.^{37, 49, 57, 58} In metal infiltration studies, an ethanol swelling treatment is commonly applied to increase interaction between the metal and the desired block by creating a porous structure.^{39, 59, 60} However, for the BCP analysed in this research (P2VP-majority), it was not possible to apply this procedure. The EtOH swelling led to the film destruction and the loss of pattern, possibly due to ethanol's selectivity towards the P2VP block, thus resulting in a complete collapse of the matrix (**Figure A2.7.2**). Therefore, metal infiltration was evaluated directly on the as-prepared BCP film.

One of the requirements for effective infiltration is the solvent choice. According to previous studies,^{37, 57} ethanolic solutions of the metal precursors were prepared and spin-coated onto the BCP films. However, such treatment yielded negligible metal incorporation into the pattern (**Figure A2.7.3i**). In order to study other possible solvents, IPA and ButOH were selected to prepare the metal precursor solutions (2.0 % wt.). For the IPA solution, no considerable infiltration was observed. In contrast, the ButOH-based process produced dense metal masks with high pattern fidelity after UV/Ozone treatment (**Figures A2.7.3ii and A2.7.3iii**). This behaviour of the film in contact with the different alcoholic solutions may be explained by the Hansen solubility parameters (**Table A2.7.1**). R_a values for the polymer blocks and the respective solvents show a reduction for more substituted alcohols (in order of increasing degree of substitution: EtOH, IPA, ButOH). Hence, ButOH demonstrated higher interaction with the P2VP block compared to other studied alcohols; ButOH demonstrates no affinity for the PS block.

Butanolic solutions of the four metal precursors were prepared and spin-coated onto the silicon substrates. The samples were imaged via AFM after UVO treatment (**Figure 2.6**). It is evident that the metals were selectively infiltrated into the P2VP domain of the film maintaining the BCP self-assembled pattern and avoiding the step of ethanol swelling, required for other polymers. Although the number of defects on the metal oxide pattern is slightly higher than on the BCP pattern, it is possible to observe that the oxide pattern reproduces well the BCP template. This is confirmed by observing similar values of pore diameter and spacing related to the BCP template (34 ± 3 nm and 60 ± 4 nm). The NiO

(36.5 ± 5 nm and 66 ± 8 nm) patterns were of lower quality than those obtained from Cr_xO_y (32 ± 4 nm and 60 ± 5 nm), Fe_xO_y (32 ± 4 nm and 61 ± 6 nm) and Ga_2O_3 (30 ± 4 nm and 57 ± 5 nm). It is suggested that the metal penetration into the P2VP matrix directly influenced the pattern quality. The metal ions can interact with the P2VP block by coordination and by π - π^* interactions as underlined by previous studies.⁵⁸ Moreover, the presence of oxyanions may have possibly resulted in better infiltration.⁵⁸ However, the rate of diffusion into the pyridine group will also depend on the type of ion.³⁴ Therefore, it is likely that chromium, iron and gallium ions exhibited a higher interaction with the P2VP layer compared to nickel ions, leading to a more ordered pattern. These results highlight the capacity of this method to produce porous metal oxide thin layers and the versatility of the metal infiltration for different metals.

XPS analyses were conducted in order to evaluate the metal infiltration and polymer removal after UVO treatment. The BCP spectra display peaks related to carbon (C 1s ~ 284.8 eV), nitrogen (N 1s ~ 400 eV) and oxygen (O 1s ~ 531 eV) (**Figure A2.7.4**); the presence of oxygen is related to adventitious carbon species. After spin coating the metal nitrate solutions, peaks related to chromium (2p), iron (2p), nickel (2p) and gallium (2p) were observed along with carbon, nitrogen, and oxygen peaks (**Figure 2.7A, C, E and G**).⁶¹

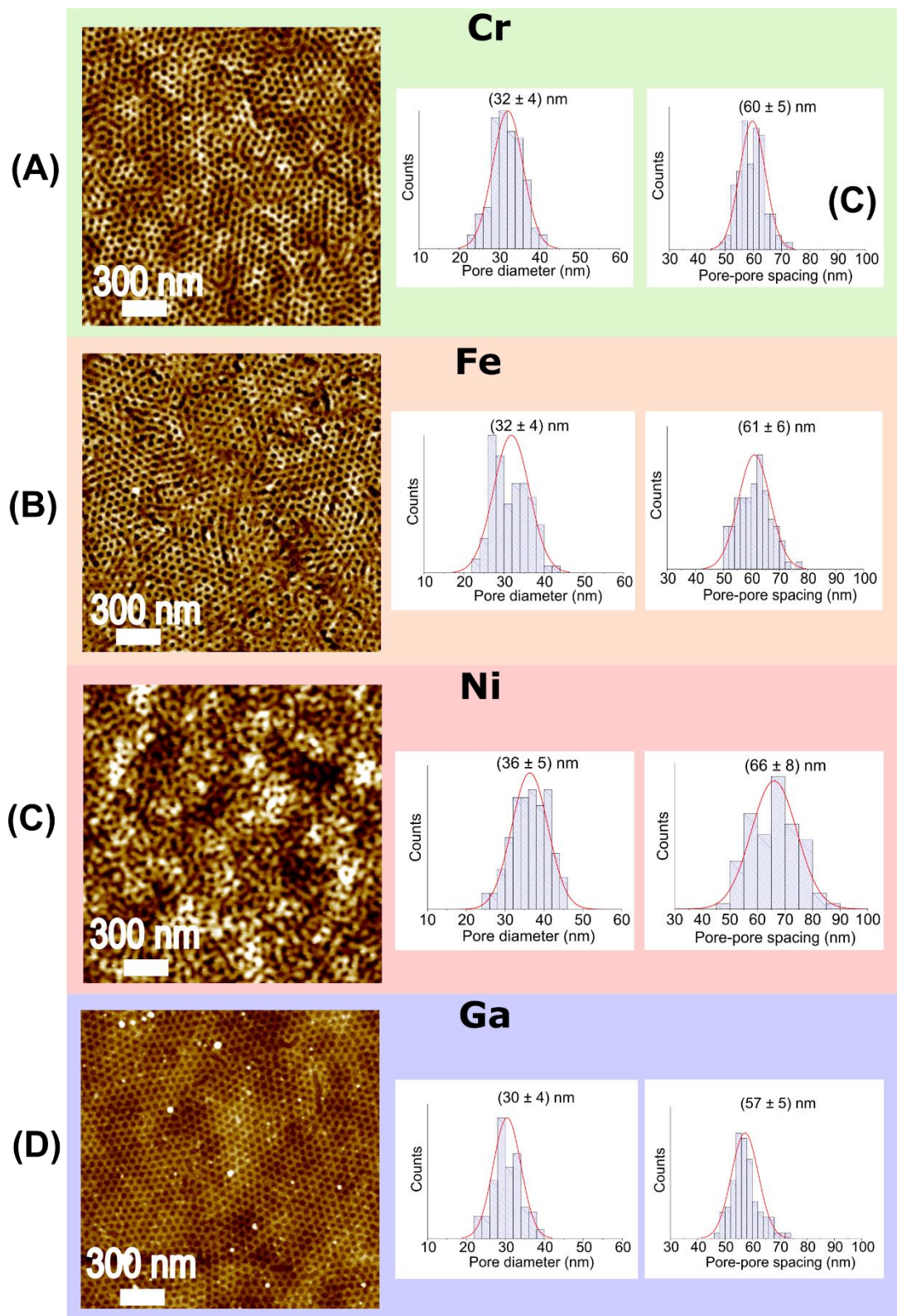


Figure 2.6. AFM images of metal oxide nanoporous membranes prepared from 2.0 % wt. metal precursor solutions after UVO treatment and pore diameter and pore-pore spacing distributions: (A) Cr_xO_y , (B) Fe_xO_y , (C) NiO , and (D) Ga_2O_3 .

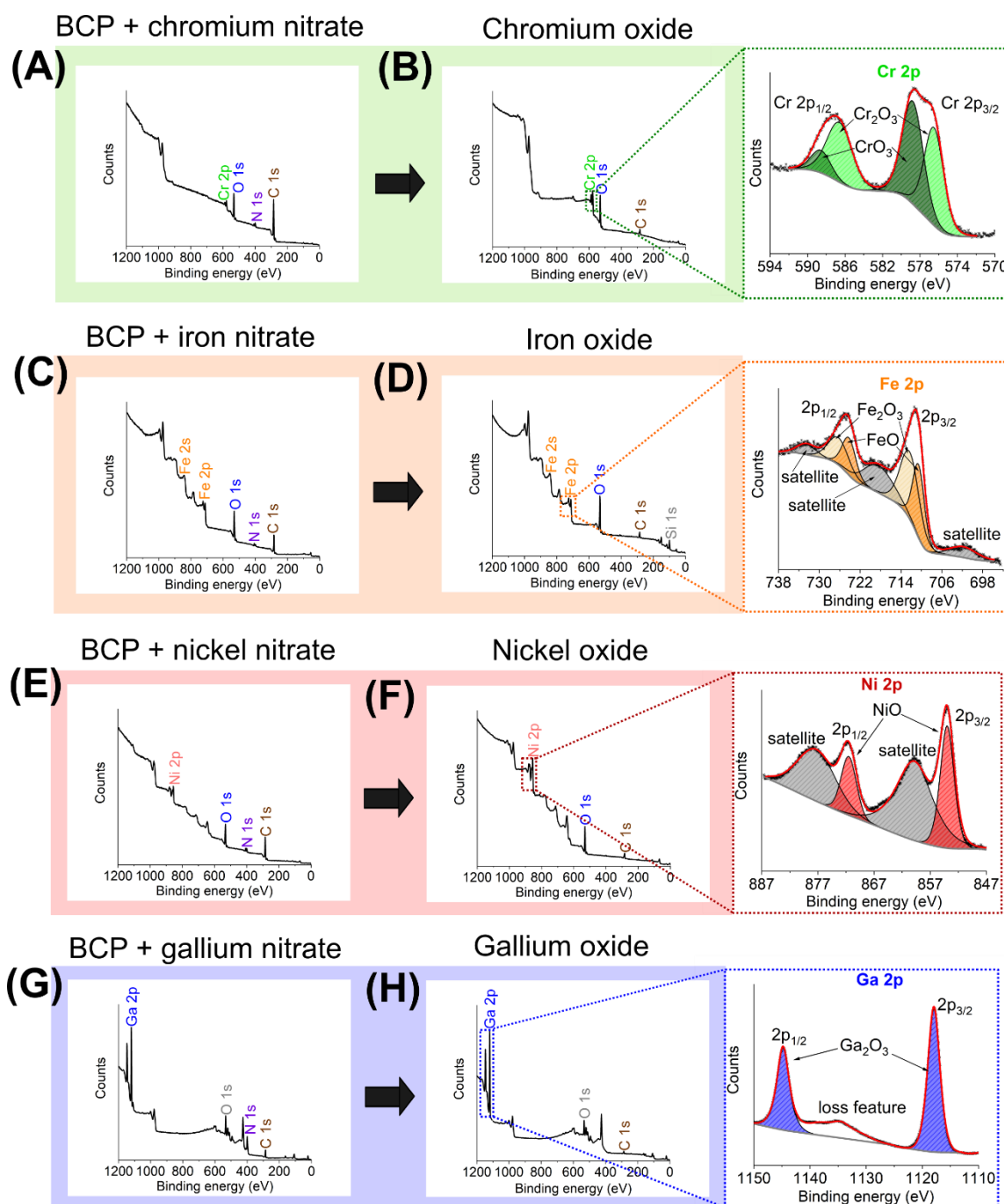


Figure 2.7. XPS spectra of metal infiltrated BCP films, metal oxide films after UVO and respective core level spectra: chromium (A, B), iron (C, D), nickel (E, F) and gallium (G, H).

The goal of the UVO step is to eliminate the BCP template and to convert the metal cations into metal oxide. The XPS spectra of the samples after UVO did not display any nitrogen peaks (**Figure 2.7B, D, F and H**), which corroborates the complete elimination of the polymer. Core level scans of the metal peaks revealed the presence of the oxides (2p_{3/2}): Ni oxide ~ 854 eV and Ga oxide ~ 1118 eV. For chromium and iron, two oxidation

states were observed ($2p_{3/2}$): Cr (III) oxide ~ 576 eV and Cr (VI) oxide ~ 579 eV; Fe (II) ~ 710 eV and Fe (III) ~ 712 eV.^{57, 61, 62}

SEM was conducted as a complementary analysis. **Figure 2.8** shows the micrographs of chromium, iron, nickel, and gallium oxide ordered layers obtained from 2.0 % wt. precursor solutions (**Figure A2.7.5**). The four samples present a good coverage of the substrate by the metal oxide, with no significant defects. Additionally, EDX confirmed the presence of the elements involved in the process (**Figure A2.7.6**).

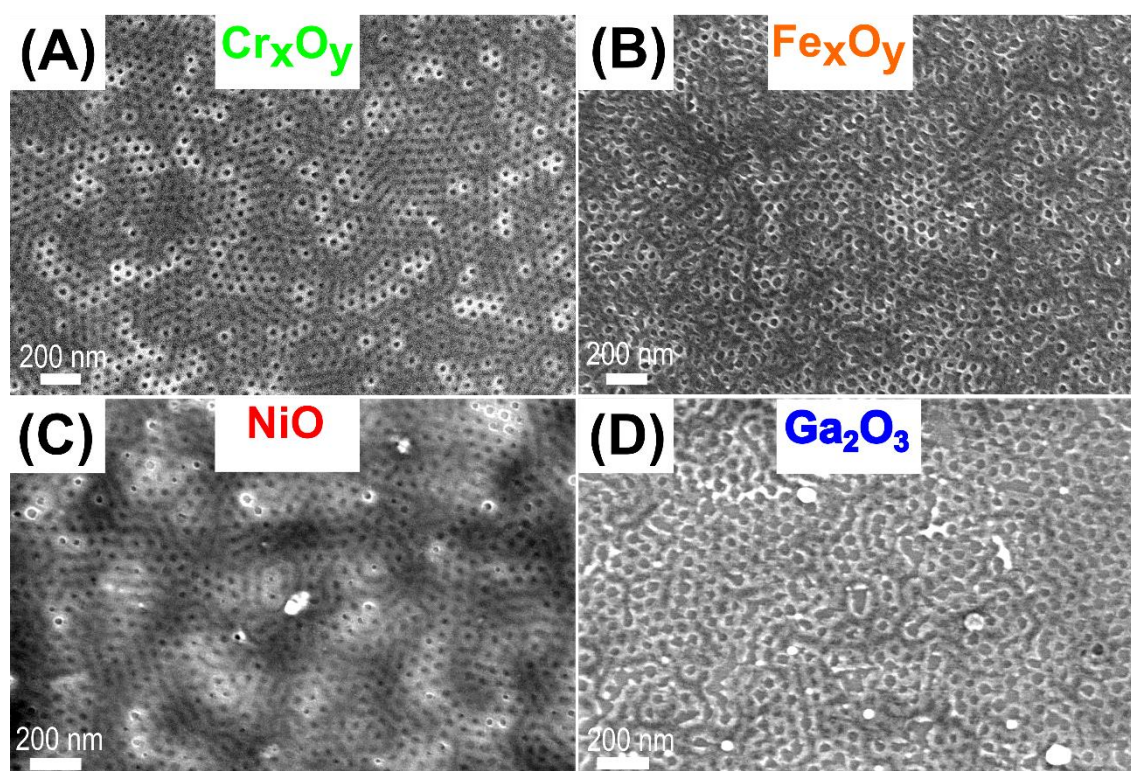


Figure 2.8. SEM micrographs of metal oxide masks obtained via UVO treatment: (A) chromium, (B) iron, (C) nickel and (D) gallium.

2.4.3. Dry etching and fabrication of silicon nanopores

Pattern transfer is an effective method for mimicking the BCP template pattern on a selected substrate by the means of etching. Hereby, plasma etching was employed to fabricate nanoporous silicon membranes from metal oxide hard masks and to demonstrate the potential applicability of the ordered metal oxide layers. To produce the nanopores, the plasma needs to create holes in the silicon throughout the substrate. Thus, the optimisation of the etch recipes and the etch time is fundamental to achieving the desired result.

Chromium oxide was selected as a hard mask due to its high selectivity towards silicon etching⁴⁹. Therefore, TEM cross section images were acquired in order to characterize the chromium oxide porous layer obtained from the BCP template. In **Figure 2.9A**, it is possible to observe the undulated shape of the chromium oxide layer sitting on the silicon oxide native layer. High-resolution TEM (HRTEM) highlights the details of the oxide pore. The cross-section through the pores shows a wave-like pattern with peaks or crests between the pores, and troughs or the lowest points in the middle of the pores. The chromium oxide layer presents a height of ~ 10 nm in its top part (the crest), while the chromium oxide thickness at the bottom of the pore is ~ 3 nm (the through). EDX mapping was applied to confirm the presence of the elements and it is shown in **Figure 2.9B**.

The silicon substrates were etched via ICP/RIE for 30 to 120 s. SEM top-down view images of the resultant nanoporous silicon substrates are displayed in **Figure 2.10**. It was observed that by increasing the etch time, an increase in both the number of created pores and the contrast occurred until mask destruction at 120 s. Size distributions of pore diameters and pore-pore spacings were obtained for the etching time of 75 s. By comparing those distributions with the previous BCP template, it is possible to observe that the average pore diameter increased by ~ 30 % and the pore-pore spacing increased by ~ 10 % occurred. Additionally, the sizes were significantly monodispersed, with coefficients of variation (CV) of 12 and 13 % for pore diameter and pore-pore spacing, respectively. Moreover, it is important to note that the resistance to etch is related to the specific etch recipe employed rather than to the quality of the masks. Therefore, the optimisation of the etch parameters is compulsory to achieve high-quality deep pattern transfer.

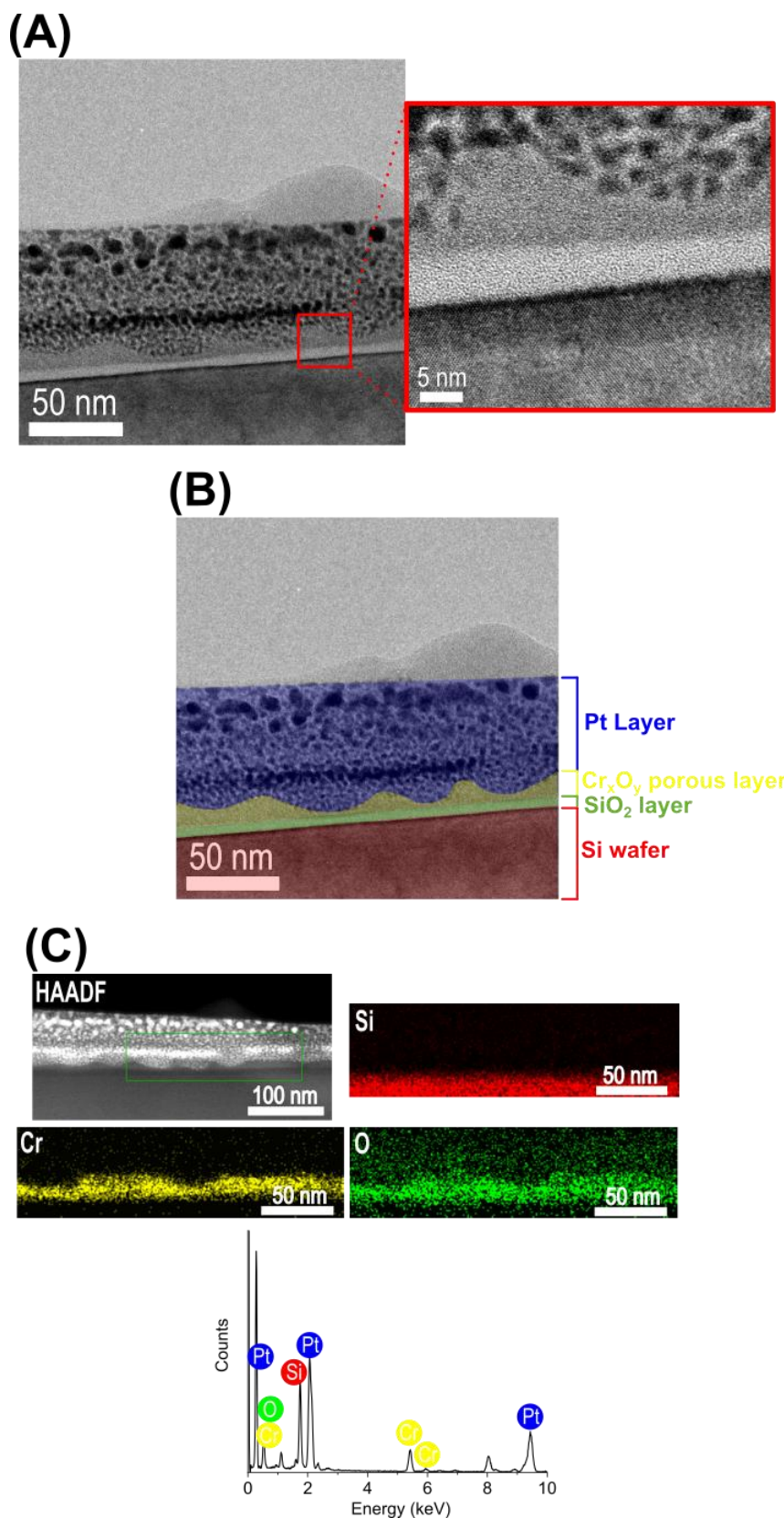


Figure 2.9. (A) TEM cross-section image displaying the chromium oxide layer and HRTEM evidencing details of the oxide pore. (B) Schematic detailing the different layers of the cross-section (C) EDX and elemental mapping of Si, Cr and O.

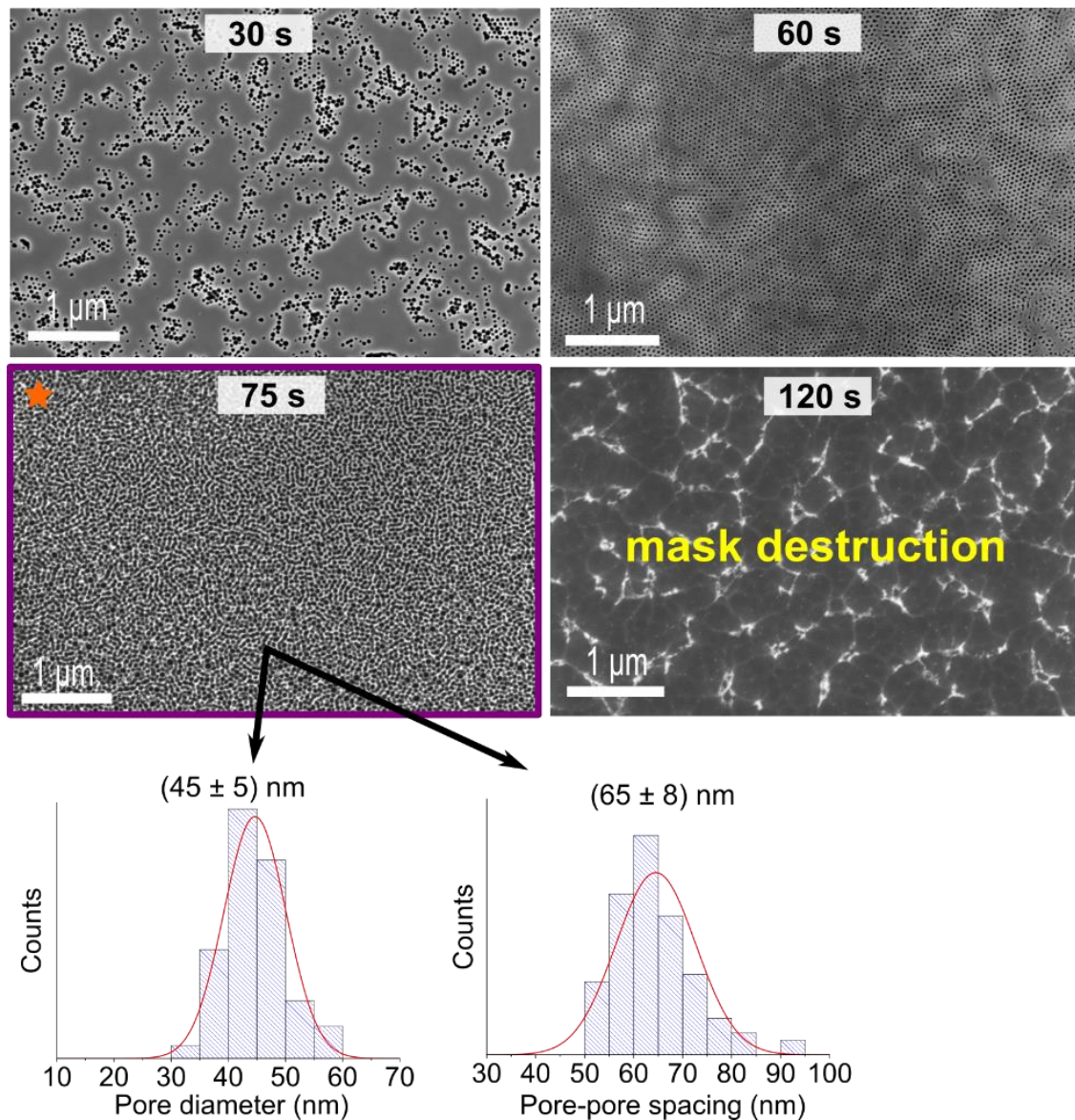


Figure 2.10. SEM top-down micrographs of different etch times and pore diameter and pore-pore spacing distributions for 75 s etching processing time.

Figure 2.11A depicts the cross section of the porous silicon substrate, underlying the depth and significant formation of pores throughout the substrate surface. In **Figure 2.11B**, TEM elucidated the pore characteristics with depth ~ 50 nm and HRTEM showed lattice fringes along the pore wall with planar distance of 3.1 angstrom, which can be correlated with (111) plan on the Si FCC structure.⁶³ It verifies that the etching process did not produce any new structures. EDX mapping was also conducted, and it showed the elemental distribution within the pore (**Figure 2.11C**).

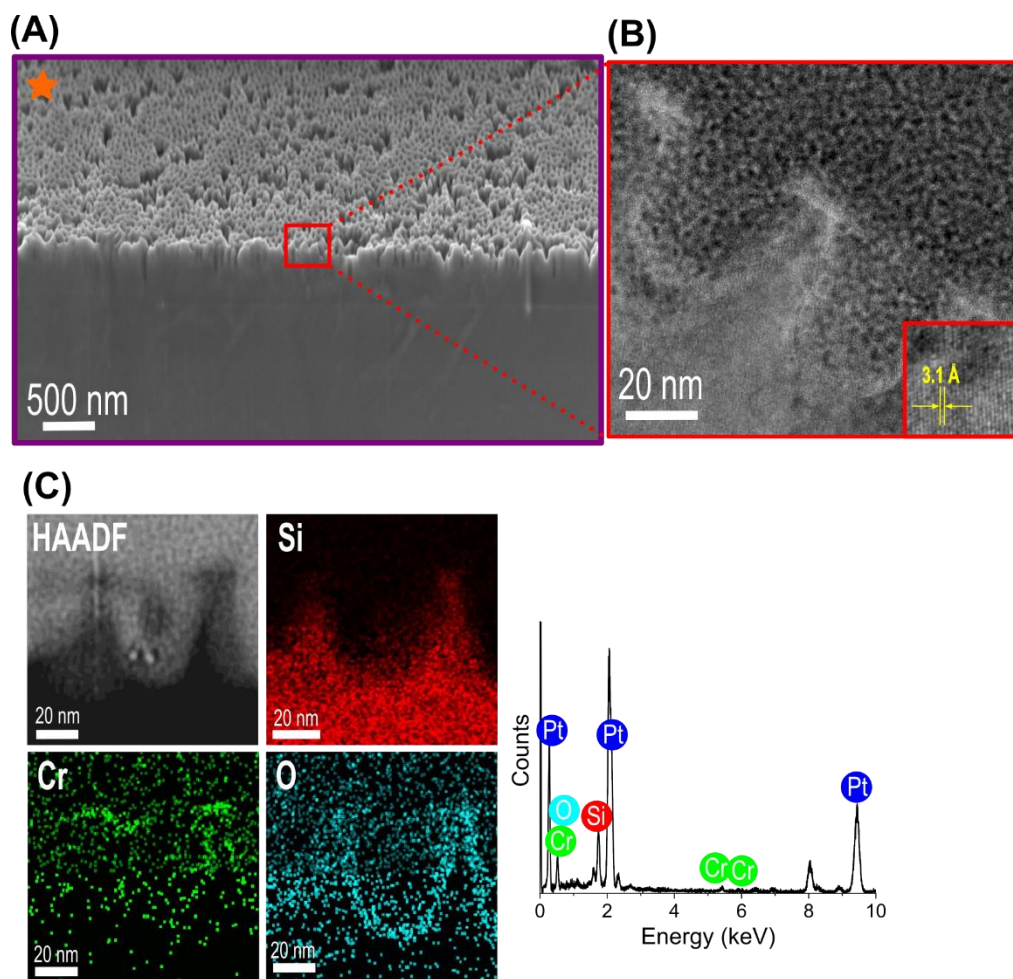


Figure 2.11. (A) SEM cross-section image displaying the formation of pores after 75 s etching processing time. (B) TEM image detailing pore structure and HRTEM evidencing lattice fringes of silicon. (C) EDX of one pore and elemental mapping of Si, Cr and O.

Si follows the same contour of the pore, and it is present on the substrate. Although chromium was not well-resolved, it is possible to observe a higher concentration (colour coded green) near the top surface, indicating where the hard mask was. For oxygen, we can notice its presence following the border of the pore, and it is related to both the chromium oxide and the native silica oxide. Some pattern degradation of the etched pores is seen due to the nature of the etching process; RIE/ICP is often not completely uniform, as different areas of the substrate are etched at varying rates. However, this variation is negligible.⁶⁴ The etch recipe can be improved and tailored for the mask in question in the future. Nevertheless, those promising results demonstrate the potential of the metal oxide porous masks for the fabrication of porous silicon materials. Moreover, it is possible to tune the size of the pores by changing parameters of the SVA process, making this a versatile strategy.

2.5. Conclusion

A facile and direct method to produce highly ordered metal oxide nanostructures based on the selective liquid-phase infiltration of P2VP-*b*-PS thin films is demonstrated. An innovative strategy of using a P2VP-majority BCP was applied to produce “inverse” structures, in which perpendicular PS cylinders were present inside a P2VP matrix and needed no pre-treatment or coating of the substrate. To create the hexagonally close packed pattern, SVA with a nonselective solvent was applied, followed by fine tuning of process parameters. Thin films in the order of 77 nm presented highly ordered structures with cylinder diameter and cylinder-cylinder spacing in the order of 34 and 65 nm, respectively. The P2VP binding characteristics were also studied. Four different metals (Cr, Fe, Ni and Ga) were selectively infiltrated in the P2VP block, and the BCP functioned as a template, fabricating ordered metal oxide layers, confirmed by XPS. Image analysis elucidated the fidelity of the metal oxide layer when compared to the previous BCP template. Furthermore, as one of the potential applications of such materials, pattern transfer was conducted via ICP/RIE etch of the silicon substrate. The obtained silicon nanoporous membranes displayed similar pattern to the metal oxide mask and pore depth of ~ 50 nm. Overall, this strategy displays great potential for applications in the fabrication of different sizes of pores in various substrates.

2.6. References

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2.7. Appendix – Chapter 2

Table A2.7.1. Hansen solubility parameters (left) and distance R_a (right) between solvent and polymer.

Material	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}						
TOL ¹	18.0	1.4	2.0						
THF ¹	16.8	5.7	8.0						
CHL ¹	17.8	3.1	5.7						
PS ¹	21.3	5.8	4.3						
P2VP ²	16.3	7.1	11.6						
EtOH ¹	15.8	8.8	19.4						
IPA ¹	15.8	6.1	16.4						
ButOH ¹	16	5.7	15.8						

Ra	TOL	THF	CHL	EtOH	IPA	ButOH
PS	8.2	9.7	7.6	18.9	16.4	15.6
P2VP	11.7	4.0	7.7	8.0	5.0	4.5

According to **Equation A2.7.1**,¹ the distance between the solvent and polymer points in the Hansen sphere (R_a) was calculated for different BCP/solvent pairs, and it is presented in Table A2.7.1: toluene (TOL), tetrahydrofuran (THF), CHL (chloroform), EtOH (ethanol), IPA (2-propanol) and ButOH (butanol). For practical purposes, solubility occurs for R_a values ≤ 8 MPa^{1/2}.³ Thus, we confirmed the non-selectivity of chloroform towards PS ($R_a \approx 7.6$) and P2VP ($R_a \approx 7.7$) blocks due to similar R_a values.

$$(R_a)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad \text{(Equation A2.7.1)}$$

Where δ_{D2} and δ_{D1} are the dispersion solubility parameters; δ_{P2} and δ_{P1} are the polar solubility parameters; δ_{H2} and δ_{H1} are the hydrogen bonding solubility parameters and the indices 1 and 2 represent the solvent and the polymer, respectively.

Table A2.7.2. Antoine coefficients for 1-butanol.⁴

Temperature range (°C)	A (mmHg)	B (mmHg)	C (mmHg)
0 - 118	7.92484	1617.52	203.296

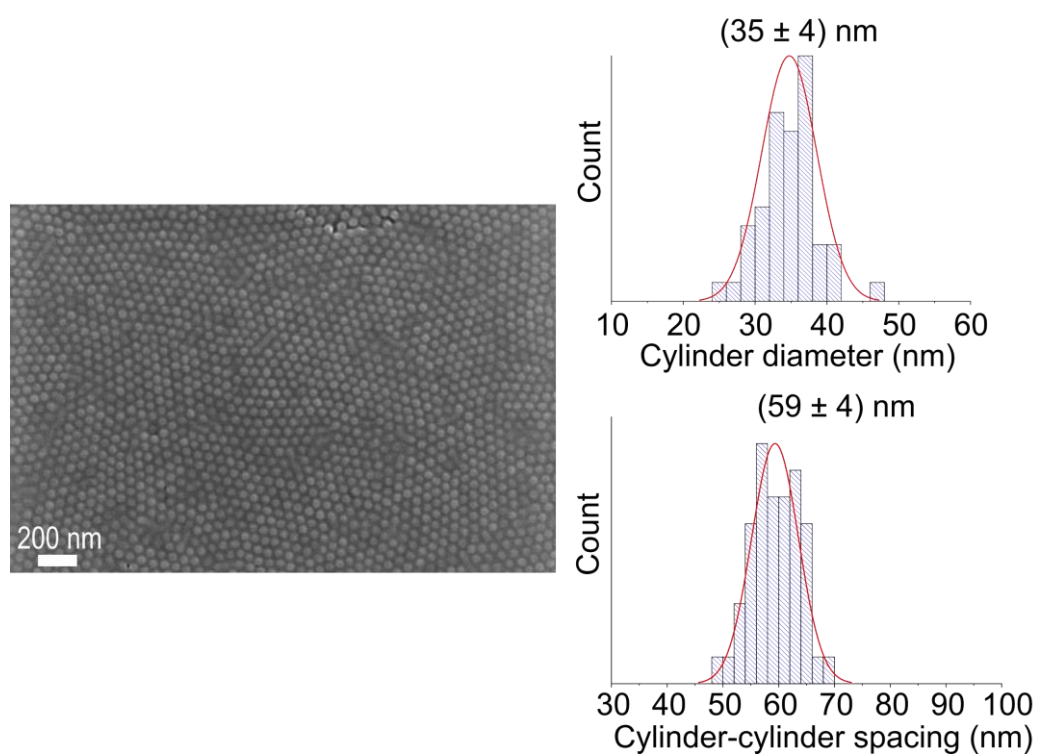


Figure A2.7.1. SEM micrograph of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ thin film after solvent vapour annealing and the size distributions of the cylinder diameter and the cylinder-cylinder spacing obtained from the SEM analysis.

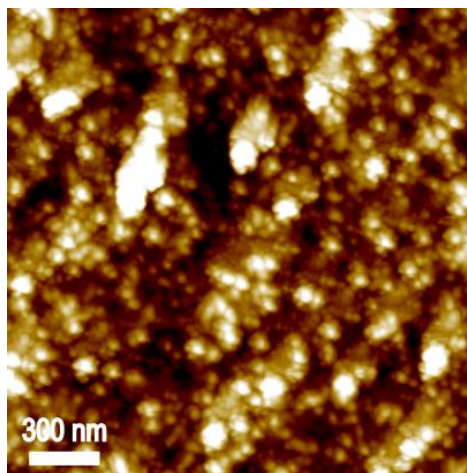


Figure A2.7.2. AFM image of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ film after ethanol immersion.

The ethanol swelling is a commonly applied method to increase interaction of the metal cation with one specific block. However, for a P2VP-majority BCP, this procedure led to destruction of the film structure.

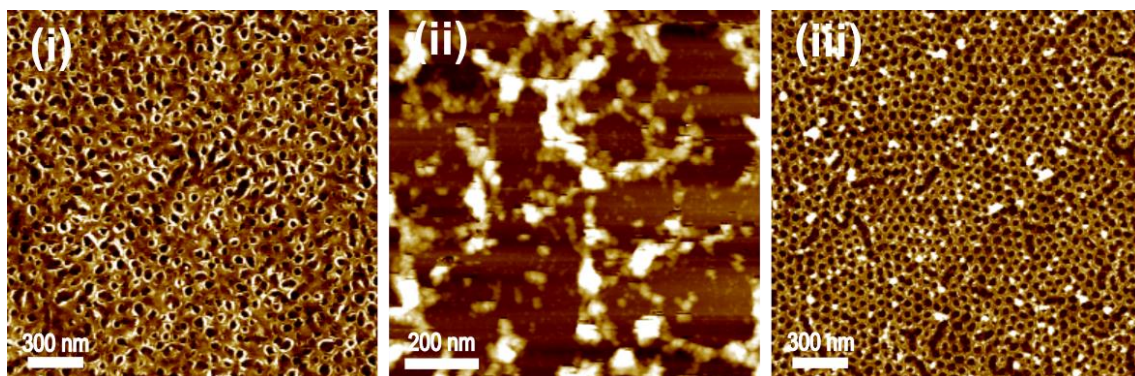


Figure A2.7.3. AFM images of metal oxide layers after UV/Ozone treatment prepared from 2.0 % wt. metal precursor solutions in: (i) ethanol (EtOH), (ii) propanol (IPA) and (iii) butanol (ButOH).

Different alcoholic solutions were studied in order to fabricate the best infiltration processes. Ethanol and propanol did not lead to high fidelity metal oxide layer. However, butanol presented high quality porous metal oxide. This behaviour is suggested to be related to the interaction between P2VP and the solvent, which can be explained by the Hansen solubility parameters.

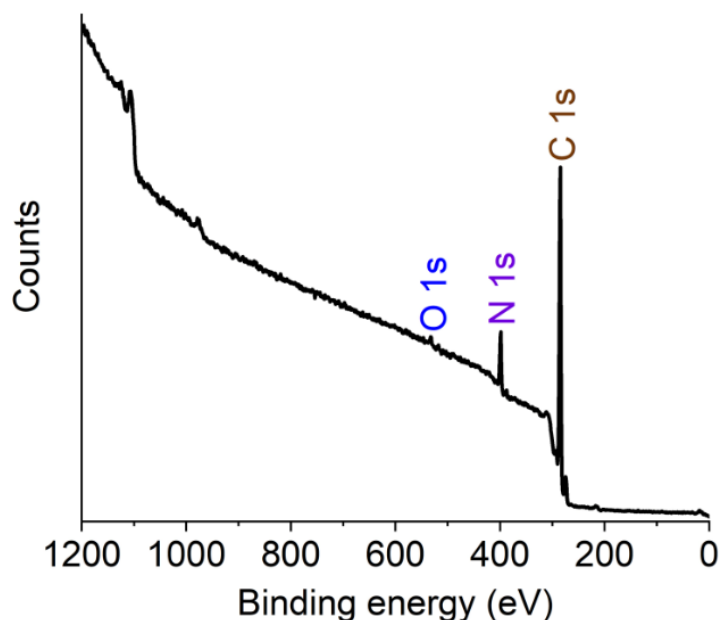


Figure A2.7.4. XPS spectrum of P2VP-*b*-PS (60-*b*-26) kg.mol⁻¹ thin film before metal infiltration depicting oxygen, nitrogen, and carbon peaks.

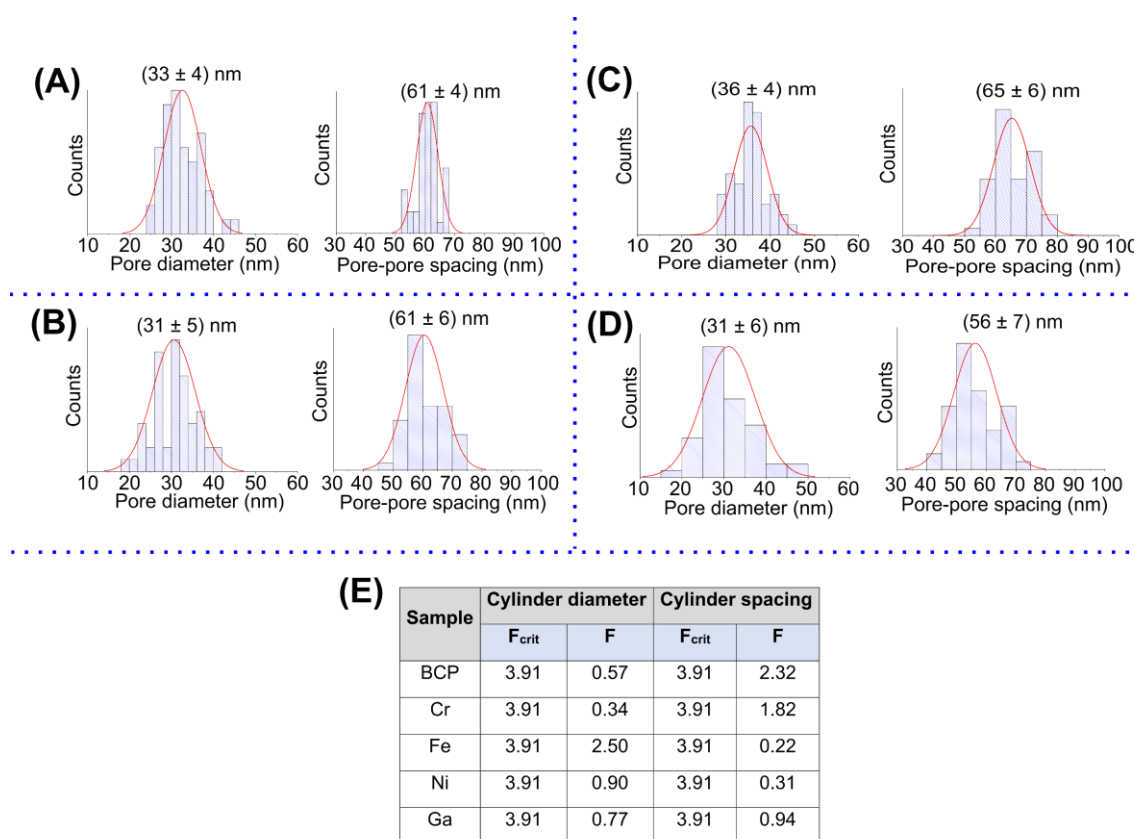


Figure A2.7.5. Size distributions of the pore diameter and the pore-pore spacing of metal oxide masks obtained from the SEM analysis: (A) chromium, (B) iron, (C) nickel and (D) gallium. (E) Analysis of variance (ANOVA) of sizes measured by AFM compared to the values obtained by SEM ($\alpha = 0.05$).

The results of the ANOVA analysis demonstrate that the size distributions obtained by AFM and SEM are statistically similar for all samples ($F < F_{crit}$).

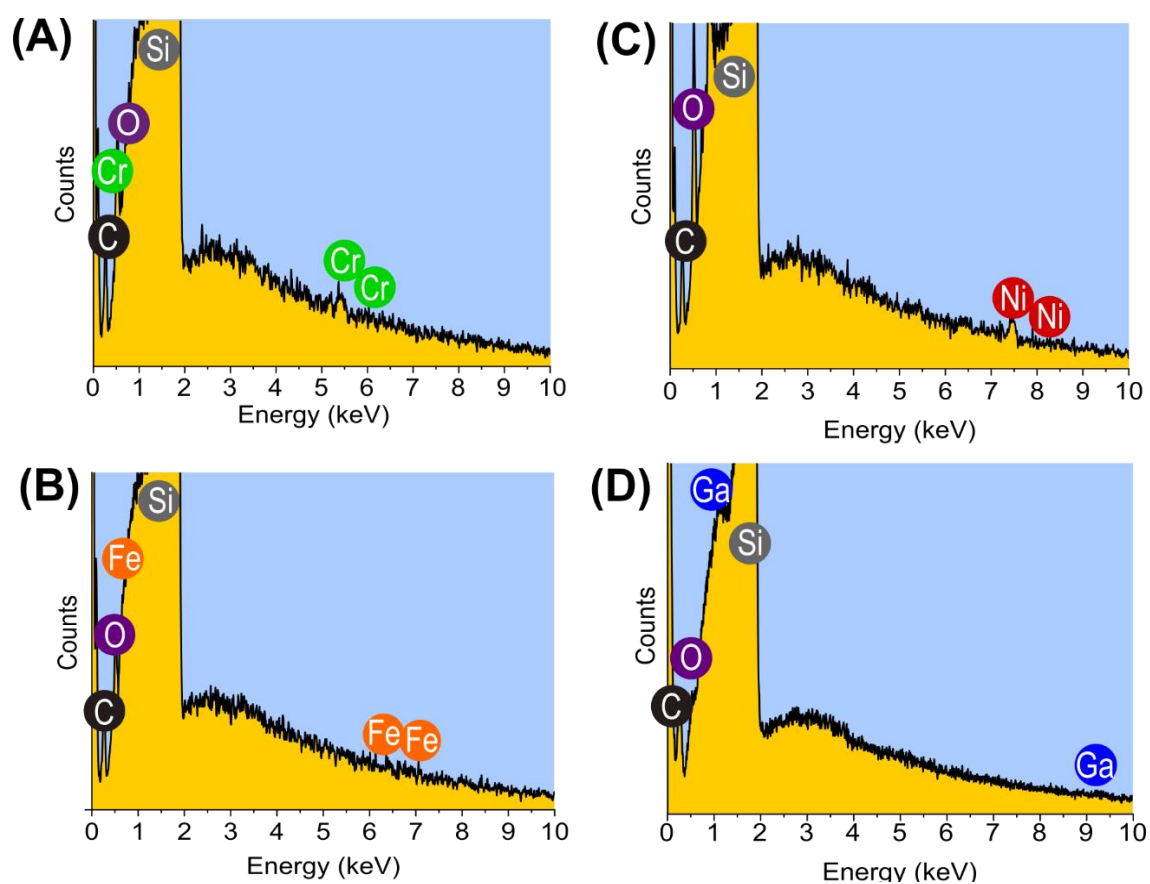


Figure A2.7.6. EDX spectra of metal oxide masks obtained *via* UVO treatment: (A) chromium, (B) iron, (C) nickel and gallium (D).

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Chapter 3.

Mechanism of Liquid-Phase Metal Infiltration into Pyridine-Containing Polymeric Thin Films

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3.1. Abstract

This research examined the liquid-phase selective metal infiltration of a pyridine-containing block copolymer (BCP). The results demonstrated that the metal cations interact differently with the poly(2-vinylpyridine) in polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP); the oxidation state and the type of cation play a key role in the infiltration process, which is also affected by the solvent. Silver (Ag^+) ions did not present effective infiltration, while nickel (Ni^{2+}) and chromium (Cr^{3+}) ions were able to reproduce the pattern of the BCP. These differences can be associated with the coordination of the pyridinic nitrogen and the metal, in parallel with the π -interactions. Furthermore, in the case of chromium, the presence of oxyanions led to an improved infiltration and high-fidelity formation of the ordered metal oxide layer.

3.2. Introduction

The fabrication of thin layers of metals, metal oxides and dielectric materials is significant to the semiconductor/electronics industry. The understanding and the change of properties by depositing a material layer on a semiconductor substrate has enormous implications on developing and optimizing applications¹ e.g., solar cells,² diodes,³ and integrated circuits.^{1, 4}

Polymer brushes and BCPs can be used as platforms to create patterns on the substrates as a cost-effective, rapid, and simple methodology.⁵⁻⁷ This can be achieved by selective infiltration; one polymer/block acts as an active moiety which interacts with the metal cation, while the other block does not. After infiltration, the polymeric template can be removed, and the metal/metal oxide will present the same structure as the BCP.⁸

Nevertheless, there is still a lack of understanding of the liquid-phase metal infiltration (LPMI) mechanism, which is important for the development of thin layers with different chemical species. In the literature, authors describe the infiltration process as adsorption,⁹ loading,¹⁰ or inclusion,¹¹ and the mechanism is either complexation or electrostatic.¹² The type of solvent and the cation directly affect the formation of a metal oxide layer or pattern on a substrate. The metal precursor should be soluble in a solvent capable of interacting with the polymer brush or one of the BCP blocks.¹² This interaction might be evaluated by the Hansen solubility parameters,¹³ in which the swelling of the polymer film is aimed to allow the effective penetration of the metal. Then, the metal cation can selectively complex with the polymer active group.^{10, 14} Pyridine-containing polymers are interesting materials for LPMI owing to the presence of the nitrogen in the pyridinic ring, which can interact with ions via its lone pair.¹⁵

In that respect, this research studied the differences in liquid-phase infiltration for three metal cations, Ag^+ , Ni^{2+} and Cr^{3+} elucidating a possible mechanism for this process. The fabrication of ordered metal oxide layers using a P2VP-majority P2VP-*b*-PS BCP was used as a parameter to assess the quality of the infiltration by AFM along with Raman spectroscopy and XPS.

3.3. Materials and methods

Poly(2-vinylpyridine)-*b*-polystyrene (P2VP-*b*-PS) block copolymer, molecular weight $\text{MW}_{\text{P2VP}} = 60 \text{ kg.mol}^{-1}$ and $\text{MW}_{\text{PS}} = 26 \text{ kg.mol}^{-1}$ was purchased from Polymer Source™. Toluene (99.8 %, anhydrous), tetrahydrofuran (99.8 %, anhydrous), butanol (99.8 %, anhydrous), silver nitrate (AgNO_3 , $\geq 99.0\%$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999%), and chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99.99\%$) were obtained from Sigma-Aldrich. B-doped type silicon (100) wafers with a native oxide layer ($\cong 2 \text{ nm}$) were acquired from University Wafer.

3.3.1. Metal infiltration

The BCP thin films were prepared by spin-coating 20 μL of a 1.5 % wt. PS-*b*-P2VP solution in tetrahydrofuran:toluene (1:4) on 4 cm^2 silicon substrates at 3000 rpm for 30 s. Then, 0.3 % wt. butanolic solutions of Ag^+ , Ni^{2+} and Cr^{3+} were prepared and spin-coated on the polymeric films at 3000 rpm for 30 s. Finally, the infiltrated BCP coated-

substrates were placed in a UV/Ozone chamber for polymer elimination and conversion to oxides.

3.3.2. Characterisation

The infiltrated films were characterized using Raman spectroscopy in a Renishaw 1000 micro-Raman system (He Ne laser, $\lambda_{\text{exc}} = 633 \text{ nm}$ at 3 mW power).

XPS analysis was performed using an Al K α X-ray source (1486.6 eV, CTX400, PSP Vacuum Technology); the spectra were corrected setting the C 1s peak at 284.8 eV. A Shirley background and Gaussian-Lorentzian functions were used for peak fitting. The pass energies for the survey and for the core level scans are CPE100 and CPE50, respectively. Dwell times were set to 0.1 s for the survey and 0.05 s for the core level scans. 3 scans were performed for the survey spectra and 4 for the core level spectra.

The metal oxide samples (produced in a UV/Ozone chamber, Novascan Technologies) were imaged *via* atomic force microscopy (AFM) using a Park XE7 (Park Systems) in non-contact mode (NCM) and scanning electron microscopy (SEM, Zeiss Ultra Plus, Zeiss) with accelerating voltage of 2 kV and working distance of 5 mm.

3.4. Results and discussion

Metal infiltration into polymeric templates and conversion to metal oxide via UV/Ozone can be used to create ordered thin oxide layers on substrates. Therefore, a highly ordered BCP thin film can function as a template for the metal oxides if metal ion infiltration is feasible. In this study, a hexagonal close-packed (HCP) PS-*b*-P2VP acted as template (**Figure 3.1A**); the P2VP matrix selectively interacts with the metal cations while the PS cylinders do not, leading to a porous matrix after BCP removal. Additionally, the solvent used to prepare the metal precursor solutions influences the infiltration efficacy. Therefore, butanol was chosen based on the selective swelling of the P2VP but not the PS domain. AFM and SEM images were acquired after polymer elimination and are displayed in **Figure 3.1B**. For the infiltration with Ag⁺, the BCP template lost its structure, confirming that Ag⁺ was not effectively infiltrated. For Ni²⁺ and Cr³⁺ samples, higher fidelity metal oxide masks were obtained compared to the silver oxide morphology. However, the NiO pattern presented slightly lower quality when compared

to the Cr_xO_y one. Root Mean Square (RMS) roughness was estimated to be 11.8, 2.8 and 1.7 nm for AgO, NiO and Cr_xO_y respectively, which also confirm a flatter surface for the Cr_xO_y layer.

For the BCP, bands were identified at 1306 cm^{-1} , related to C-C stretch between ring and backbone; at 1374 cm^{-1} , associated with methylene twist; at 1448 cm^{-1} , which can be correlated to methylene deformation; and at 1592 cm^{-1} , linked to pyridine ring stretch.¹⁶ In complex formation, the literature reports that the type of ligand will directly affect the ion coordination due to the presence of functional groups, and the connection between the ions and the chemical group is known as specific complexation.¹⁷ Differences in metal infiltration of silver (Ag^+), nickel (Ni^{2+}) and chromium (Cr^{3+}) were identified in the Raman spectra. For the Ag-infiltrated film, Raman bands were observed at 1311, 1380, 1447 and 1593 cm^{-1} , but there were no significant changes in their positions relative to the BCP. This behaviour might be associated with poor interactions between Ag^+ and chemical groups in the BCP chain. According to literature data, the presence of hydroxyl groups plays a significant role in complexation with silver ions.¹⁸ In addition, a significant difference in the affinity of the metal cation for solvent and BCP is required during the infiltration process. Since butanol was used as a solvent, and Ag^+ has a strong affinity for OH groups, it is possible that the cation interacts more with the solvent than with BCP.

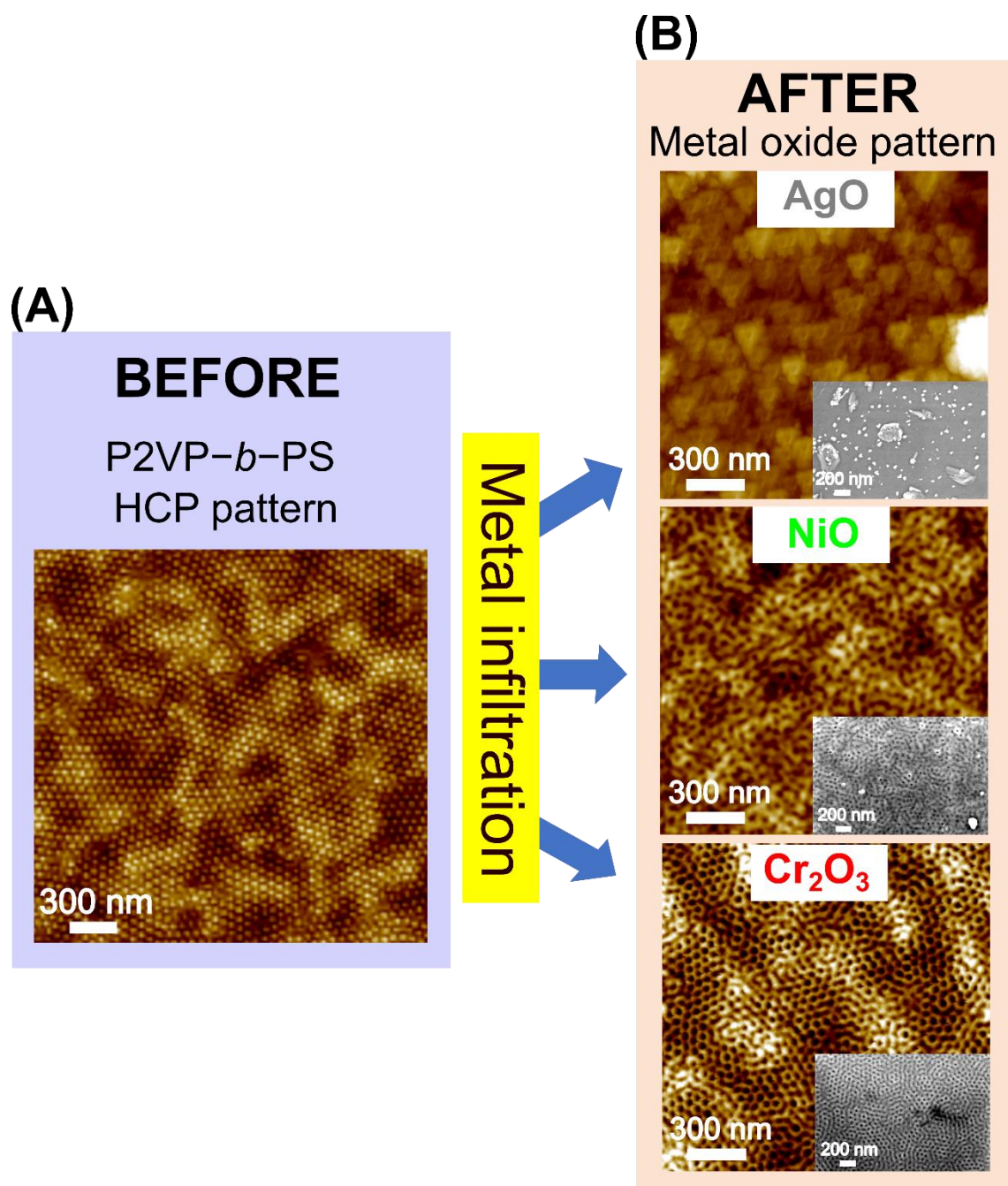


Figure 3.1. AFM images of the (A) BCP with HCP cylindrical structure and of (B) metal oxide layers post UVO treatment.

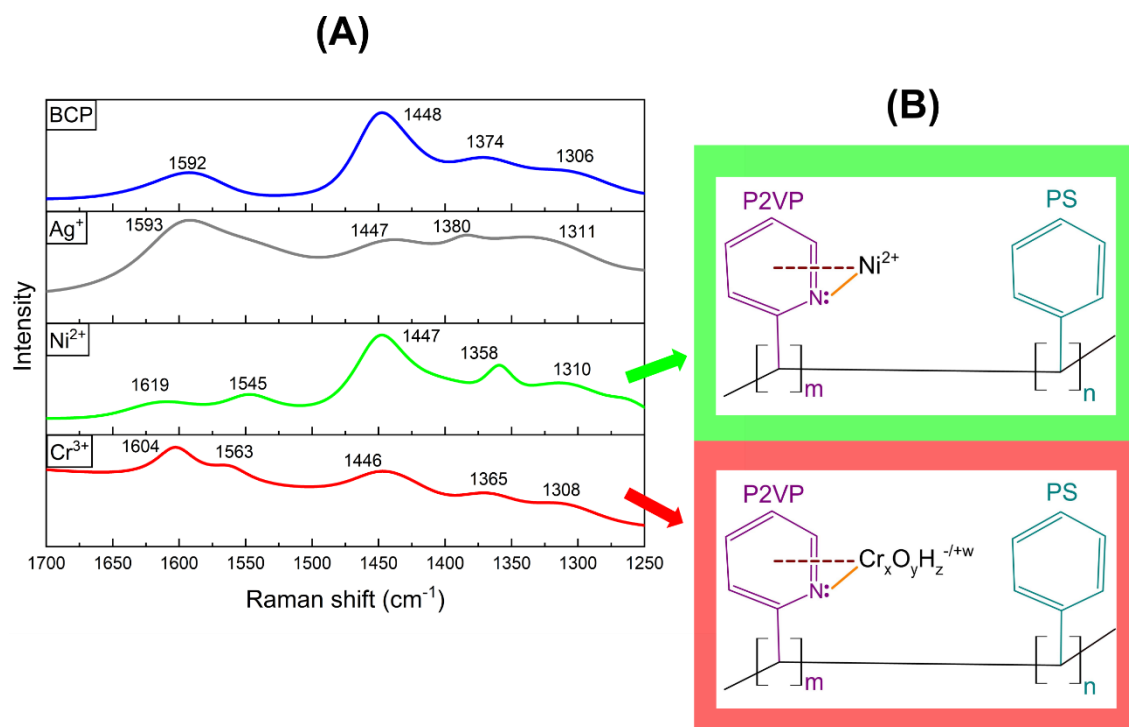


Figure 3.2. (A) Raman spectra of BCP and metal-infiltrated films and (B) proposed interactions between the metal cations and the BCP.

Unlike silver, nickel displayed a more prominent interaction with the P2VP domain. Raman spectra demonstrated bands at 1310, 1358, 1447, 1545 and 1619 cm^{-1} . Interestingly, the bands at 1619 and 1545 cm^{-1} , related to ring and pyridine ring stretch, respectively, can be clearly identified when compared with Ag and BCP samples. This indicates the coordination of Ni with nitrogen. Furthermore, the band at 1358 cm^{-1} , corresponding to the methylene twist, was shifted to the low-frequency side compared to Ag and pure BCP, which also indicates the interaction between Ni and the methylene group via π -interaction.¹⁹ As in the case of nickel, for the Cr-infiltrated film Raman bands at 1604 and 1563 cm^{-1} , associated with the ring (C-C) and the pyridine ring (N-C) stretch, were observed as well, which also indicates the interaction between Cr and the pyridinic nitrogen.¹⁶ **Table 3.1** summarizes the band assignments and the difference between a mode from a metal-infiltrated sample and the respective mode from the BCP.

Table 3.1. Raman band assignments for P2VP-*b*-PS BCP and metal-infiltrated BCP thin films with respective differences in modes (Δ)

BCP, cm^{-1}	Ag (Δ), cm^{-1}	Ni (Δ), cm^{-1}	Cr (Δ), cm^{-1}	Assignment
1306	1311 (5)	1310 (4)	1308 (2)	C-C stretch (ring and backbone)
1374	1380 (6)	1358 (16)	1365 (9)	Methylene twist
1448	1447 (1)	1447 (1)	1446 (2)	Methylene deformation
1592	1593 (1)	1545 (47)	1563 (29)	Pyridine ring stretch
-	-	1619	1604	Ring stretch

By comparing the relative intensity of the pyridine ring stretch to the reference band at $\sim 1447 \text{ cm}^{-1}$ (methylene deformation) which does not suffer any shifts,^{20, 21} for Cr ($I_{1563}/I_{1446} = 1.0$) and Ni ($I_{1545}/I_{1447} = 0.8$), Cr presented a greater value, which could imply higher degree of interaction between Cr and P2VP. The distinct levels of interaction observed between Cr^{3+} , Ni^{2+} , Ag^+ , and the nitrogen in P2VP domains of PS-*b*-P2VP can be potentially explained by the Hard and Soft Acids and Bases (HSAB) principle. The nitrogen in the pyridine group is considered a borderline base, capable of coordinating various types of metallic ions. However, it is more likely to form adducts with hard and borderline acids rather than soft acids. In this context, based on their electronic configuration and electric charge, Cr^{3+} and Ni^{2+} are classified as hard and borderline acids respectively, whereas Ag^+ is considered a soft acid. Moreover, the band at 1365 cm^{-1} was shifted compared to the BCP, suggesting changes in the methylene twist mode possibly due to metal- π interaction. These results suggest that the selective infiltration of nickel and chromium is related to the different modes of interaction between the cations and the BCP.

XPS analyses of the infiltrated samples in comparison with the BCP were conducted and are displayed in **Figure 3.3**. **Figure 3.3A** shows the BCP survey spectra containing peaks such as carbon belonging to the hydrocarbon chain and the nitrogen peak of the P2VP domain. When metal nitrate solutions were spun onto the BCP films, a peak corresponding to oxygen 1s was observed, which may be associated with the presence of NO_3^- . In addition, peaks related to the metal cations (Ag^+ , Ni^{2+} and Cr^{3+}) were also visible.

The core level scan in **Figure 3.3B** displays different contributions for the nitrogen spectrum. For all three infiltrated samples, a peak at $\sim 407 \text{ eV}$ (I) is observed, and it can

be related to nitrogen bonded with oxygen *i.e.*, NO^{3-} . According to the literature, pyridinic N has a peak ~ 399.3 eV.¹ It was observed the presence of that signal in all four samples (IV). After infiltrating the films with the metal nitrate solutions, two peaks appeared in higher binding energies for the Ni and Cr samples. Peak III occurring ~ 400.4 eV could be explained by protonation of the pyridinic nitrogen ($\text{C-N}^+\text{H}=\text{C}$), while peak II ~ 401.5 eV may be associated with quaternisation of the pyridine group via CH interaction ($\text{C}=\text{N}^+\text{CH}_x-\text{C}$).⁸ Only the protonation peak was noticeable in the Ag sample spectrum, suggesting that the metal cation may influence the protonation and quaternization equilibria. One may also notice that the Cr^{3+} seems to promote a higher quaternization rate of the pyridine when compared to the Ni^{2+} .

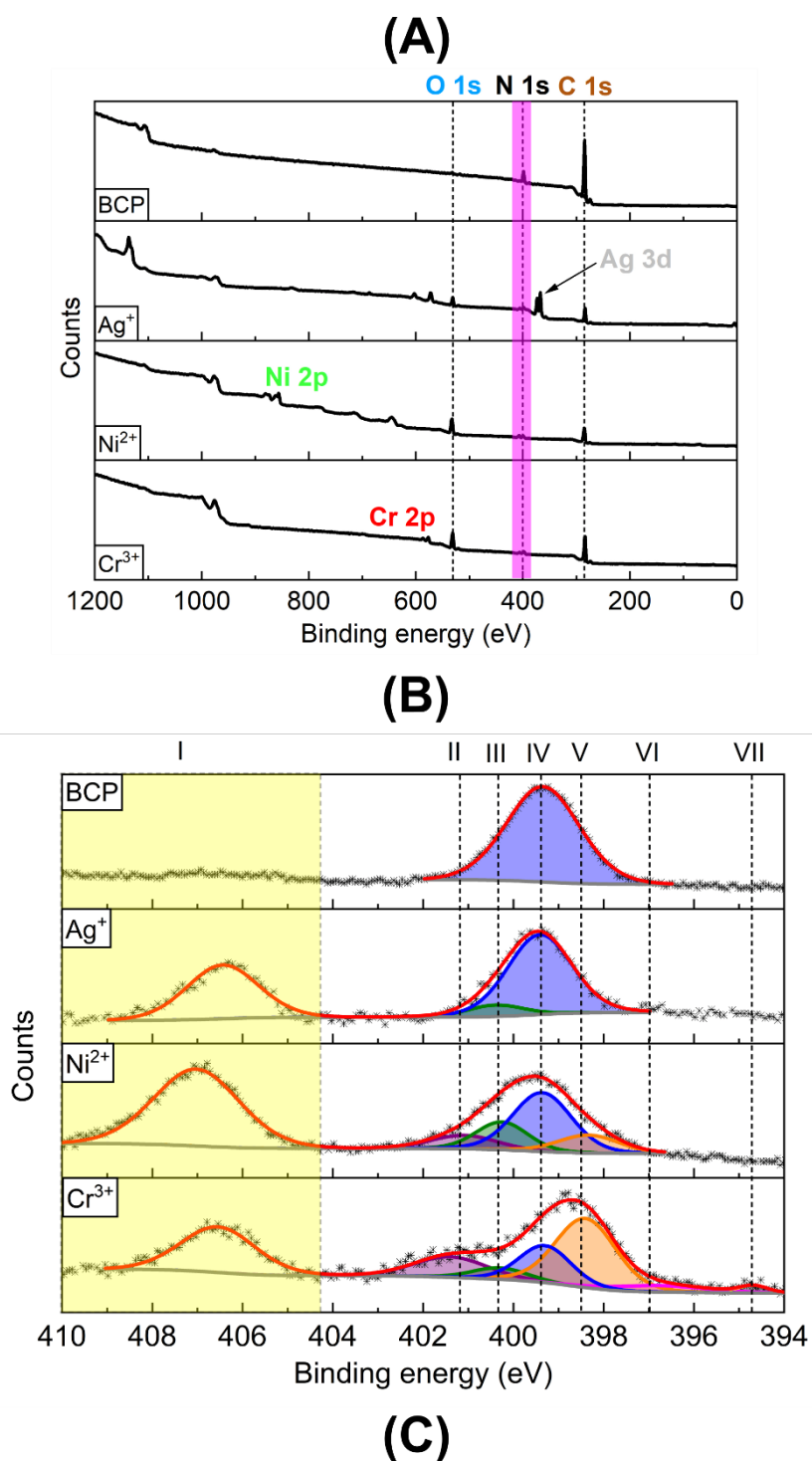


Figure 3.3. (A) XPS survey spectra, (B) N core level scan and (C) area ratio of metal-N and N-pyridine peaks for the BCP, Ag-, Ni- and Cr-infiltrated films.

Further analysis revealed the presence of a peak at ~ 398.4 eV for the Ni and Cr samples. Previous studies related this peak to the formation of a coordination bond between the metal cations and the nitrogen lone pair.^{1, 8} This peak was not observed in the Ag-infiltrated sample, which implies the lack of infiltration by this metal cation into the BCP structure corroborating with the Raman and AFM analyses. The ratio between the areas of the peaks related to the metal coordination and the pyridine were calculated and are shown in Figure 3.3C. There was no observable inclusion of Ag^+ into the BCP, while Ni^{2+} and Cr^{3+} were confirmed to successfully infiltrate the BCP. Cr^{3+} demonstrates a higher degree of infiltration than Ni^{2+} . Furthermore, in the Cr sample spectrum, two small peaks around 396.8 (VI) and 394.7 (VII) eV were observed. These peaks can be explained by the coordination between Cr oxyanions and the nitrogen *e.g.*, O-Cr-N, as already described by the Raman data, which may contribute to better infiltration of this ion when compared to the other metal ions.

3.5. Conclusion

This work demonstrates the effect of metal cations used to selectively infiltrate pyridine-containing polymers. A P2VP-majority P2VP-*b*-PS BCP was chosen as a template for the metal infiltration. It has been shown that distinct types of cations uniquely interact with the polymer. Silver demonstrates no infiltration, while nickel and chromium create BCP-templated metal oxide layers. Raman analysis showed changes in the pyridine ring stretch and methylene twist modes which suggest coordination between the metal cation and the nitrogen in the pyridine group along with π -interactions. XPS elucidated the presence of peaks related to the coordination between nitrogen lone pair and the metal cation for nickel and chromium. Moreover, chromium exhibited two other peaks in lower binding energy suggesting different types of interaction due to the presence of oxyanions, which led to better infiltration when compared to nickel. This methodology establishes a protocol to study the interaction between metal precursors and polymeric thin films allowing the expansion to other polymers and cations. Ultimately, it is expected that the understanding of the liquid-phase infiltration mechanism can help the development of applications in which dense and organized inorganic structures are essential *e.g.*, in electronics.

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Chapter 4.

Degradation of an Antibiotic *via* a Photo-Fenton Process on Block Copolymer-Nanopatterned Iron Oxide Coated Substrates

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4.1. Abstract

A facile strategy was developed to produce porous iron oxide structures on glass substrates based on block copolymer (BCP) templating. Porous iron oxides with pore sizes of 35 nm, 45 nm and 400 nm were formed based on the solvent vapour annealing of poly(2-vinylpyridine-*b*-polystyrene (P2VP-*b*-PS) systems followed by selective infiltration of metal precursor into BCP template and subsequent conversion to (Fe^{III}/Fe^{II}) oxides on the glass substrate. The XRD and XPS studies revealed the coexistence of Fe^{III}/Fe^{II}. Parameters such as film thickness, polymer concentration and annealing time were varied in order to obtain the best polymer nanopatterns on the substrates, which refers to vertically aligned PS cylinders in a P2VP matrix. An annealing time of 40 min was required to produce vertically aligned PS cylinders of 35 and 45 nm pore sizes, whereas a ~ 140-fold increase in the annealing time resulted in the formation of the same with 400 nm pore size as measured via AFM and SEM imaging techniques. The iron oxide-covered glass substrates were used in the degradation of a model antibiotic, levofloxacin, via a photo-Fenton process. ~ 90 % relative degradation of 20 µM aqueous solution of levofloxacin in the presence of 10 mM H₂O₂ has been achieved by irradiating the solution containing a 1 % wt. iron oxide (Fe^{III}/Fe^{II}) loaded glass slide having 400 nm pore diameter for 90 min. No iron leaching from the substrates was observed after 90 min of photo-Fenton process. Therefore, this strategy presents a potential use in the treatment of pharmaceutical wastewater through a heterogenous advanced oxidation process which could be scaled for application.

4.2. Introduction

Water is essential in the equilibrium of any ecosystem. The quality of the water directly affects its use e.g., irrigation, industry, drinking, and sanitation.¹ Water is becoming an

ever more valuable resource and of increasing scarcity due to factors such as population growth, industrialization and climate change.² Therefore, concern about sustainability in the use of water and its treatment has been steeply increasing over the years. One of the main sources of pollution in water bodies is related to the pharmaceutical industry, which produces a variety of effluents containing pharmaceutically active compounds³ such as residues of drugs, antibiotics, hormones, surfactants and volatile organic compounds. Several of these compounds are biologically active and, can lead to mutagenic, ecotoxicological and genotoxic effects.⁴ Further, the prolonged exposure of the antibiotics in the effluent drives bacteria to develop antibiotic-resistance genes and creates more antibiotic-resistant bacteria by spreading these genes into the ecosystem.^{5, 6} Levofloxacin (LVF), for instance, is part of the fluoroquinolone group (chiral fluorinated carboxyquinolone) and belongs to the quinolone family of antibiotics. It has a broad spectrum of action for gram-negative (*Klebsiella pneumoniae*, *Haemophilus Influenzae*, *Escherichia coli*) and gram-positive bacteria (*Staphylococcus epidermidis*, *Staphylococcus aureus*, *Streptococcus pneumoniae*)⁷ and therefore, is most widely used for treating urinary tract infection, pneumonia, acute pyelonephritis and skin infections.⁸ However, conventional water treatment plants have limited impact on its degradation due to the chemical stability (presence of strong C-F bond) and antimicrobial activity.^{7, 9, 10} Thus, development of an efficient degradation method of LVF and similar substances is highly needed.

Among the diverse range of technologies available to treat pharmaceutical effluents, Advanced Oxidation Processes (AOP), including photocatalysis,¹¹ wet air oxidation,¹² gamma irradiation,¹³ ozonation,¹⁴ Fenton and photo-Fenton are emerging as promising methods.^{15, 16} These methods involve the generation of highly reactive species such as the hydroxyl radical ($\bullet\text{OH}$) which is capable of degrading various kinds of organic pollutants.¹⁷

Metal oxides, especially in the form of nanomaterials, have attracted significant attention in water treatment processes due to their unique catalytic, magnetic, photoelectronic, electrical, and optical properties.¹⁸⁻²⁰ However, one of the drawbacks in the use of these relates to the incomplete recovery of the colloidal catalysts.²¹ A preferential strategy to overcome this issue is by immobilisation of the nanomaterial.²² Therefore, metal oxide thin layers can be fabricated via different methodologies e.g., physical vapour deposition (sputtering,²³ pulsed laser deposition²⁴), chemical vapour deposition (atomic layer deposition,²⁵ metal-organic chemical vapour deposition²⁶), electrochemical deposition,²⁷ and hydrothermal synthesis.²⁸

Considering the different methods for producing metal oxide thin layers, block copolymer lithography appears as a compelling strategy due to several advantages such as elevated feature density, feature size uniformity, cost reduction, reduced roughness, morphology and size tunability, scalability and rapid fabrication methodologies.^{29, 30} Block copolymers (BCP) are capable of forming a diverse range of morphologies in the nanometre range based on the self-assembly of the dissimilar polymer chains composing the BCP.³¹ They can act as templates for different inorganic ions and nanoparticles, allowing the formation of ordered structures on a substrate, which enables different applications *e.g.*, electronics, biomaterials, photonics, and photocatalysis.³¹⁻³³ The poly(2-vinylpyridine)-*b*-polystyrene (P2VP-*b*-PS) systems are interesting due to the presence of the nitrogen in the pyridine structure, which is capable of interacting with ions and nanoparticles.³⁴⁻³⁶ Moreover, due to the high Flory-Huggins parameter ($\chi = 0.178$ at 25 °C)³⁶, small structures can be achieved, and the variation of the MW enables the fabrication of different morphologies. In order to promote the phase separation, two methods are commonly applied: thermal annealing, consisting of exposing the BCP to temperatures above the glass transition temperature; and solvent vapour annealing (SVA), in which the BCP is exposed to a saturated solvent vapour atmosphere.³⁷ One significant advantage of the SVA compared to thermal annealing relates to the possibility of conducting the process in low temperatures, which prevent thermal degradation. Moreover, the solvent-based approach can induce the self-assembly of high χ BCPs.^{38, 39} A few studies related to the metal infiltration of P2VP-majority BCPs leading to the formation of “inverse” structures (pores) are reported in the literature.^{32, 40} The use of an “inverse” BCP as a template for metal oxides allows the tunability of pore sizes, which can increase the catalytic activity regarding surface area. Moreover, by fixation of the iron oxide thin layer, the reusability of the photocatalyst can be conducted.

The fabrication and immobilisation of iron oxide catalysts on substrates are mainly based on electrostatic links,⁴¹ pulsed laser deposition,⁴² complexation,⁴³ ion exchange,⁴⁴ radio frequency sputtering followed by annealing,⁴⁵ photocatalytic surface functionalisation deposition⁴⁶ and spin coating,⁴⁷ and they have been used for the photo-catalytic/Fenton degradation of various pollutants. Thus, to the best of the authors' knowledge, the fabrication of iron oxide nanostructures on the glass substrate using a BCP templating approach is not yet reported in the literature for the photo-Fenton degradation of LVF in water.

This work reports the use of P2VP-majority phase P2VP-*b*-PS block copolymers with different molecular weights (MW) to fabricate porous iron oxide layers on glass substrates. The phase separation of the BCP films was studied based on a SVA approach to obtain vertically aligned PS cylinders in a matrix of P2VP. Parameters such as film thickness, polymer concentration and annealing time were varied in order to produce the best nanopatterns on the glass substrates. The formation of the porous iron oxide structures with pore sizes varying according to the MW of the BCP was investigated using selective infiltration of the BCP template with iron ions, and subsequent oxidation/removal of the polymer layer. The iron oxide-covered glass substrate was applied in the photo-Fenton degradation of LVF in water. The optimisation of various parameters of the heterogenous photo-Fenton process including pore size of the iron oxide (Fe^{III}/Fe^{II}) thin layer, pH of the solution, time of irradiation and concentrations of iron precursor solution, LVF and hydrogen peroxide were optimised in order to achieve the highest relative degradation efficiency of LVF. The mechanism of the photo-Fenton degradation process of LVF was also proposed.

4.3. Materials and methods

All materials and chemicals were used as purchased with no further treatment. Microscope slides (soda lime glass, class 3, Marienfeld) and single-crystal, B-doped-type silicon (100) wafers with a native oxide layer ($\cong 2$ nm) (University Wafer) were used as substrates. P2VP-*b*-PS block copolymer systems were obtained through Polymer Source, Inc. in three different molecular weights (MW) (**Table 4.1**):

Table 4.1. Number average molecular weight and polydispersity index (PDI) for the different P2VP-*b*-PS systems.

Code	MW _{P2VP} *	MW _{PS} *	Total MW*	PDI
BCP1	60	26	86	1.15
BCP2	101	45	146	1.03
BCP3	598	189	787	1.22

* 10³ g.mol⁻¹

Acetone (ACT, 99.0 %), toluene (TOL, 99.8 %, anhydrous), tetrahydrofuran (THF, 99.8 %, anhydrous), chloroform (CHL, 99.9% , anhydrous), isopropanol (IPA, 99.5%, anhydrous), 1-butanol (ButOH, 99.8 %, anhydrous), iron (III) nitrate nonahydrate

(99.99 %), levofloxacin (> 98%) were sourced from Sigma-Aldrich. Hydrogen peroxide (H₂O₂) (> 30% wt.) was purchased from Fluka. The procedures were conducted at room temperature, unless specified.

4.3.1. SVA optimisation for P2VP-*b*-PS thin films

The microscope slides were cut into 1 cm x 5 cm rectangles and ultrasonicated in acetone for 20 min, followed by drying under a N₂ stream. For the SVA of the BCP1, we applied a recipe published on our previous work.³² A solution of 1.5 % wt. BCP1 in a 1:4 TOL:THF mix was prepared. The BCP1 thin films were obtained through spin coating (vacuum-free Ossila spin coater) the polymer solution at 3000 RPM for 30 s. Then, the covered glass slides were placed in 150 mL glass jars, each containing a glass vial with 2 mL chloroform. The jars were placed in a fridge for 40 min at 5 ± 2 °C. Afterwards, samples were removed from the jars and left it to dry at room temperature.

For BCP2 and BCP3, the SVA process was optimized regarding polymer concentration and time. For only optimization purposes, silicon wafers were used as substrates (4 cm²). Solutions of 0.5, 1.0, 1.5 and 2.0 % wt. BCP2 or BCP3 were prepared using a mix of 1:4 TOL:THF as solvent. Then, the films were again fabricated using the method described above followed by annealing for 20 min, 40 min, 1 h and 1 h 20 min for the BCP2 and 20 min, 1 h, 3 h, 24 h, 96 h and 1 week for BCP3 samples. At the end of the process, samples were removed from the jars and left to dry at room temperature.

After the complete optimisation, the times and concentrations which led to the best nanopatterns were chosen to be applied on the glass substrates.

4.3.2. Fabrication of metal oxide porous structures

A solution of iron nitrate 1.0 % wt. in butanol was prepared and spin coated on the BCP-nanopatterned covered glass slides at 3000 RPM for 30 s. Then, the substrates were placed in a UV/Ozone (UVO) chamber with two low pressure mercury lamps (output current of 0.8-0.95 A, power of 65-100 W, emissions at 184.9 nm and 253.7 nm) (PSD Pro Series Digital UV Ozone System, Novascan Technologies, Inc.). The samples were at 11 mm distance from the UV source and the process was conducted for 2 h. In sequence, the glass slides underwent a thermal treatment (TT) at 400 °C for 1 h (Thermo Scientific FB1415M). The combination of UVO and TT aimed at the completely elimination of the polymer and conversion of the iron nitrate to iron oxide, producing a nanoporous surface layer of iron oxide.

4.3.3. Characterisation

Reflectometry (Filmetrics®) was used to assess the BCP film thickness. A fixed incidence angle of 90° and a two-layer model (SiO₂ + BCP) was used to simulate experimental data. Five measurements were randomly performed in different regions of the sample and the results were presented as mean ± standard deviation.

A Park XE-100 (Park Systems) AFM microscope was used to acquire topographical images of the samples. Non-contact mode (NCM) was chosen with an AC160TS cantilever type (force constant = 26 N.m⁻¹, resonance frequency = 300 kHz). Cylinder diameter and cylinder-cylinder spacing were calculated through the measurement of 100 features and results were expressed as mean ± standard deviation.

SEM images were recorded on a Zeiss Ultra Plus system with an accelerating voltage of 2 kV, at a working distance between 4 to 5 mm and a secondary electrons (SE2) detector. To avoid charging, the iron oxide layer on the glass slides was Au-Pd covered (99.99 % Au: Pd 60/40 ratio, Ted Pella) using a 108A Sputter Coater (Cressington).

XPS analysis was performed using an Al K α X-ray source (1486.6 eV, CTX400, PSP Vacuum Technology); the spectra were corrected setting the C 1s peak at 284.8 eV. A Shirley background and Gaussian-Lorentzian functions were used for peak fitting. The pass energies for the survey and for the core level scans are CPE100 and CPE50, respectively. Dwell times were set to 0.1 s for the survey and 0.05 s for the core level scans. 3 scans were performed for the survey spectra and 4 for the core level spectra.

XRD patterns were acquired in a D8 Advance instrument (Cu-K α radiation λ = 1.5406 Å, Bruker). Measurements were performed in the 2 θ range from 2 to 59.849° with step size of 0.0204°. Due to the thickness of the iron oxide layer, no signal was observed initially. Therefore, XRD characterisation was performed on a bulk material obtained through drop casting the iron nitrate solution followed by UVO and TT in a repeated sequence.

A cross-sectional lamella of the substrate was prepared using focused ion beam (FIB, Zeiss AURIGA) with accelerating voltages of 30 and 15 kV and ion beam currents of 4 nA – 50 pA. Then, scanning transmission electron microscopy (STEM) images coupled with energy dispersive X-ray spectroscopy (EDX) were acquired on a FEI Titan G2 80-

300FEG S/TEM with a Schottky-type electron gun operated at 300 kV and a Bruker XFlash 6 T-30 detector (resolution 129 eV).

4.3.4. Photo-Fenton degradation of LVF and its analysis

The LVF degradation experiments were performed with 30 mL aqueous solution of LVF in 50 mL glass vials containing an iron oxide thin layer immobilised onto a glass slide and H₂O₂. The specific reaction conditions are mentioned in the results and discussion section. All the glass slides of similar dimensions were used for the experiment. The vials were placed inside a solar simulator reactor (Atlas SuntestTM CPS+) to initiate the photo-Fenton reaction. The irradiation of the vials using a 700 W Xenon lamp was performed under continuous stirring and for different time intervals. The samples were withdrawn at various time intervals and the absorbance values were measured using an Agilent Cary 60 UV Visible spectrophotometer. Radical scavenging experiments were performed following a similar procedure with 20 µM LVF solutions by adding 2 mM isopropanol scavenger to the vial. Control experiments were performed without irradiation. The actual and relative percentage degradations of LVF were monitored by investigating the change in the absorbance values at 290 nm as shown in **Equations 4.1** and **4.2**, respectively:

$$\text{Actual degradation of LVF} = \Delta OD = OD_0 - OD_t \quad \text{(Equation 4.1)}$$

OD₀ and OD_t are the initial and final absorbance values before and after (at time t) photo-Fenton degradation of LVF, respectively.

$$\text{Relative percentage degradation of LVF} = \frac{OD_0 - OD_t}{OD_0} \times 100 \quad \text{(Equation 4.2)}$$

The pseudo first order degradation kinetics of LVF were calculated using Equation 3

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \quad \text{(Equation 4.3)}$$

k is the pseudo first order degradation rate constant, and t is the time of irradiation. The OD₀ and OD_t values are proportional to the initial (C₀) and final (C_t) concentrations of LVF before and after irradiation, respectively

In order to investigate possible leaching of iron ions, atomic absorption spectroscopy (AAS) was performed (VARIAN AA System, model AA55B).

4.4. Results and discussion

4.4.1. Obtention of the vertically aligned cylinder patterns

Based on our previous work³², we selected chloroform as non-selective solvent for P2VP and PS, hence screening unfavourable interactions and enabling vertical alignment of the phases. Four different concentrations were studied (0.5, 1.0, 1.5 and 2.0 % wt.) for BCP2 and BCP3. **Figures 4.1** and **4.2** display AFM images of the as-spun thin films with varying concentrations. Both types of BCPs demonstrated a disordered state, which is consistent with a rapid solvent evaporation during the spin coating process. It is possible to observe that the polymer chains in BCP2 stayed elongated and are horizontally aligned. However, for BCP3, spheres were formed. Film thicknesses for BCP3 were higher when compared to BCP2, which can be related to the size of the chains.

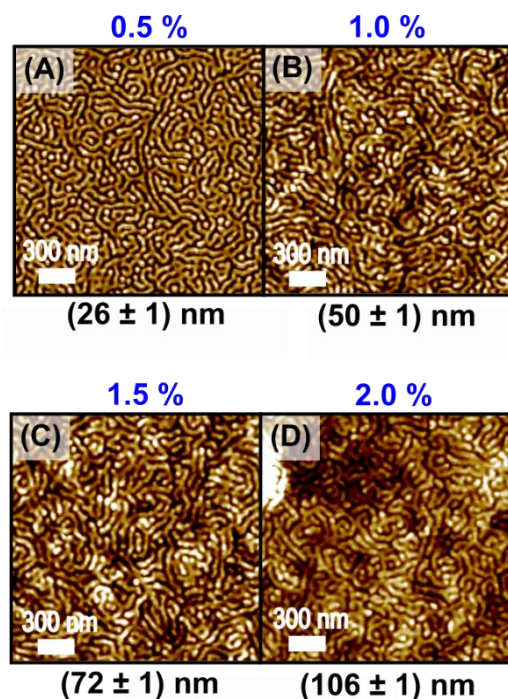


Figure 4.1. AFM images of P2VP-*b*-PS (101-*b*-45) kg.mol⁻¹ (BCP2) films after spin-coating from different polymer concentrations with respective film thicknesses as measured from reflectometry: (A) 0.5 %, (B) 1.0 %, (C) 1.5 % and (D) 2.0 % wt. All scale bars are 300 nm.

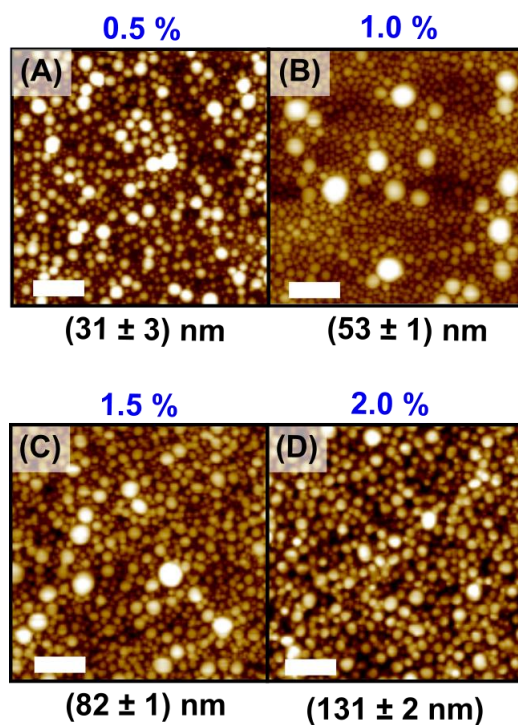


Figure 4.2. AFM images of P2VP-*b*-PS (598-*b*-189) kg.mol⁻¹ (BCP3) films after spin-coating from different polymer concentrations with respective film thicknesses as measured from reflectometry: (A) 0.5 %, (B) 1.0 %, (C) 1.5 % and (D) 2.0 % wt. All scale bars are 1 μ m.

Subsequently, the SVA process was conducted at temperatures of 5 ± 2 °C. For BCP2, similar behaviour to BCP1³² was noticed (**Figure 4.3**), which can be explained by the similar MWs. The 0.5 % wt. sample exhibited no significant changes in the structure post SVA. After 40 min of SVA, changes were observed in the morphology for the other three film thicknesses. Moreover, longer times favoured the parallel orientation of cylinders, especially for 1.0 and 2.0 % wt. samples. This shows that there exists a relationship between the film thickness and the natural period of the BCP. The film thickness and also the local thickness affect the morphology and orientation of BCP phases. Optimal conditions for obtaining ordered perpendicular cylindrical domains were achieved for 1.5 % wt. BCP2 after an annealing time of 40 min, leading to cylinder diameter of ~ 41 nm and cylinder-cylinder spacing of ~ 60 nm (**Figure 4.3B**).

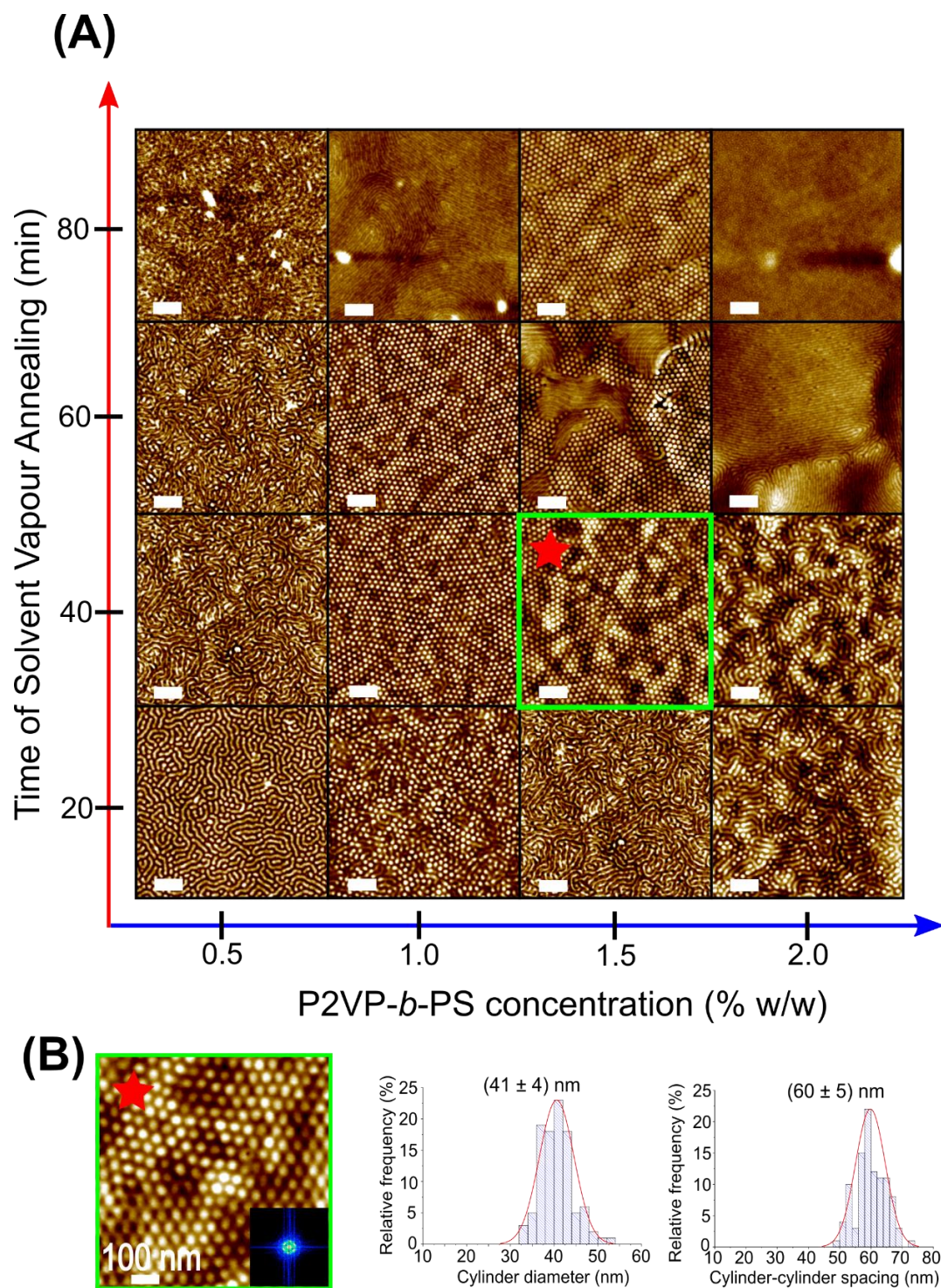


Figure 4.3. (A) AFM images of the BCP2 (146 kg.mol⁻¹) solvent vapour annealing optimisation at 5 ± 2 °C, in which polymer concentration and time were studied. All scale bars are 300 nm. (B) Details of the SVA with 1.5 % wt. solution/40 min annealing time with corresponding Fourier-Transform image inset, and cylinder diameter and cylinder-cylinder spacing distribution. All scale bar in (A) are 300 nm.

BCP3 has a high MW which implies slow ordering kinetics.⁴⁸ 0.5, 1.0 and 1.5 % wt. did not present vertical aligned cylinders over a time of 96 hours (**Figure 4.4A**). It is suggested that the film thicknesses for these concentrations hindered the chain movement and therefore created non-regular structures *i.e.*, frustrated morphologies.⁴⁹ Nevertheless, for the 2.0 % wt. sample, after 3 h, vertical aligned cylinders started to be observed. And then, after 96 h, a higher concentration of the cylinders was present. A long-time test was conducted in order to study possible improvement of the morphology. However, not significant changes occurred; this could be related to a limited solvent pressure achieved in the SVA jar.³² Therefore, the hexagonally closed packed cylinders might be fabricated by using higher vapour pressures, as in the case of dynamic SVA processes.⁴⁸ The optimal conditions for the BCP3 were found to be 2.0 % wt. and 96 h annealing time, creating cylinders with ~ 400 nm diameter and ~ 541 nm cylinder-cylinder spacing due to the chain size (**Figure 4.4B**).

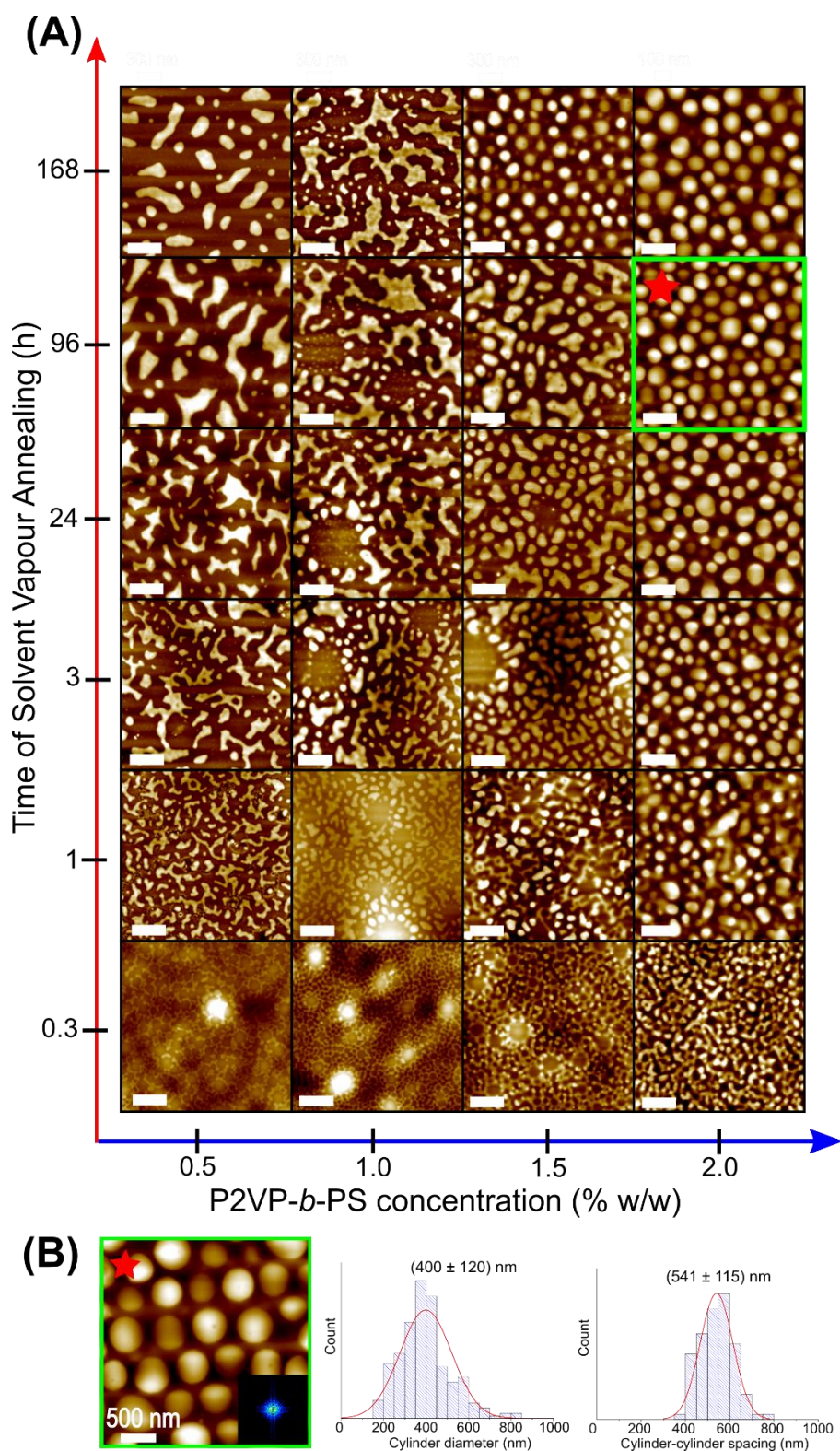


Figure 4.4. (A) AFM images of the BCP3 (787 kg.mol^{-1}) solvent vapour annealing optimisation at $5 \pm 2 \text{ }^{\circ}\text{C}$, in which polymer concentration and time were studied. All scale bars are $1 \text{ }\mu\text{m}$. (B) Details of the SVA with 2.0 % wt. solution/96 h annealing time with corresponding Fourier-Transform image inset, and cylinder diameter and cylinder-cylinder spacing distribution. All scale bars in (A) are $1 \text{ }\mu\text{m}$.

4.4.2. Fabrication of iron oxide patterns on glass substrates

Figure 4.5 shows the different polymer templates and the respective iron oxide patterns obtained on glass substrates. The BCP can function as a template to the metal oxide owing to the presence of the nitrogen in the pyridine ring (P2VP). The nitrogen lone pair can coordinate with the Fe ions, enabling its infiltration into the polymer matrix.³⁴ Nevertheless, the PS cylinders remain neutral and do not interact with the Fe ions. Based on the AFM images, it is possible to state that the BCP templating and infiltration is a versatile process, and it can be applied to different substrates. Additional SEM micrographs are available in the supporting information (**Figure A4.7.1**), demonstrating high coverage of the porous layers. Moreover, STEM/EDX analyses confirmed the presence and morphology of the iron oxide layer (**Figure A4.7.2**).

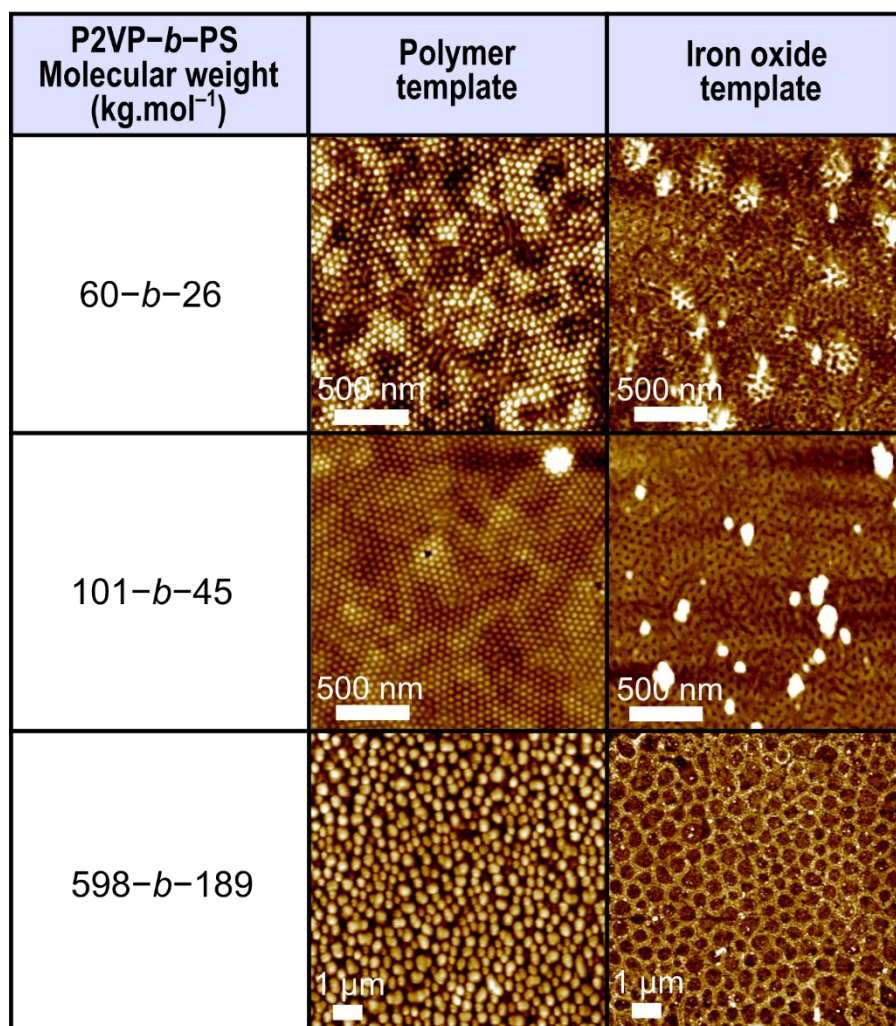


Figure 4.5. AFM images of the P2VP-*b*-PS templates with different molecular weights and corresponding iron oxide porous structures fabricated on glass substrates.

To further characterise the iron oxide structures, XPS analysis was conducted to determine the chemical state of the iron, and it is shown in **Figure 4.6**. The survey spectrum elucidates the presence of the C 1s peak (~ 284.5 eV), which relates to adventitious carbon. The presence of the Fe 2p peak confirms the presence of iron oxide. It is also important to underline the absence of the nitrogen peak, which indicates the complete elimination of the BCP layer after UVO + TT³² treatments. Moreover, the Na 1s (~ 1071.6 eV) and Si 1s (~ 103.2 eV) peaks are present, which are commonly part of the glass composition.⁵⁰ The Fe 2p core level scan (**Figure 4.6** inset) displayed two oxidation states of iron, Fe^{III} (~ 712 eV) and Fe^{II} (~ 710 eV),⁵¹ and consequently the presence of two iron oxides, similarly to previous results.³² This again shows the versatility of the infiltration process regardless the substrate.

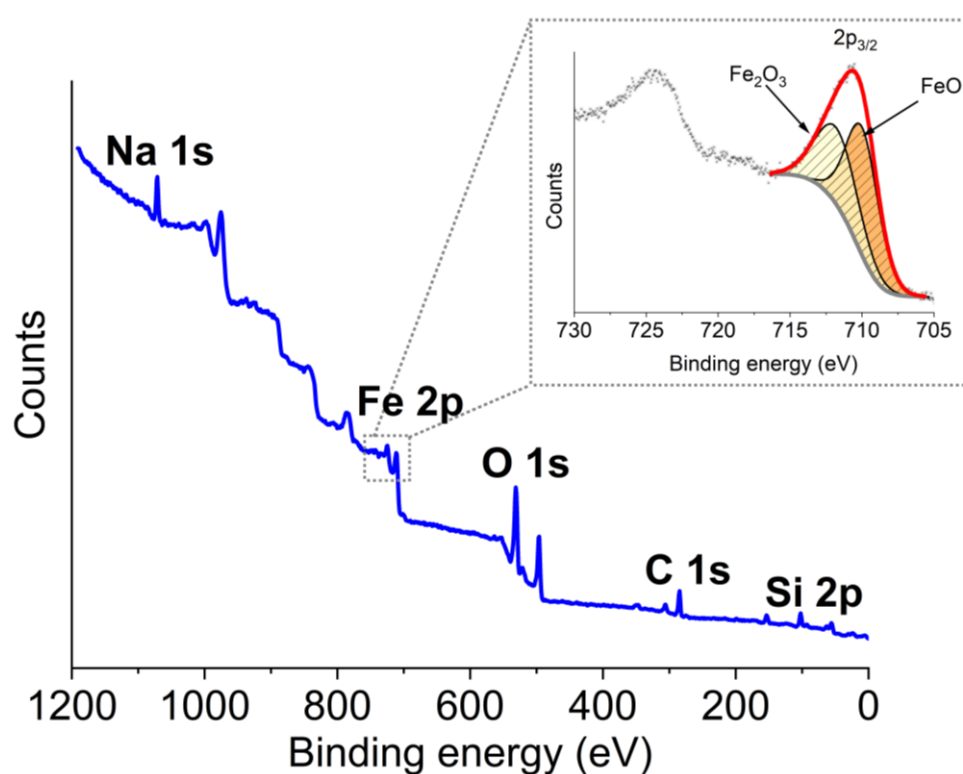


Figure 4.6. XPS survey spectrum of Fe oxide thin layer with 400 nm pore size and inset showing the core level scan for Fe. The inset shows the Fe core level scan spectrum with fitted components.

To determine the crystalline structure of the oxides, XRD was conducted (**Figure 4.7**). Peaks at 2θ values of 24.5, 33.5, 36.1, 41.2, 49.8, 54.4 and 57.8° were observed. These peaks can be assigned to the rhombohedral crystalline structure of the iron III oxide (hematite, α -Fe₂O₃) (ICDD 00-033-0664).⁵² The peaks related to FeO were not clear in

the diffractogram, this could be related to overlapping of peaks at $\sim 36^\circ$ and $\sim 42^\circ$ and with a possible rhombohedral structure (ICDD 01-089-0690).⁵³ Nevertheless, the XPS analysis corroborated the presence of the oxides related to Fe^{III} and Fe^{II} .

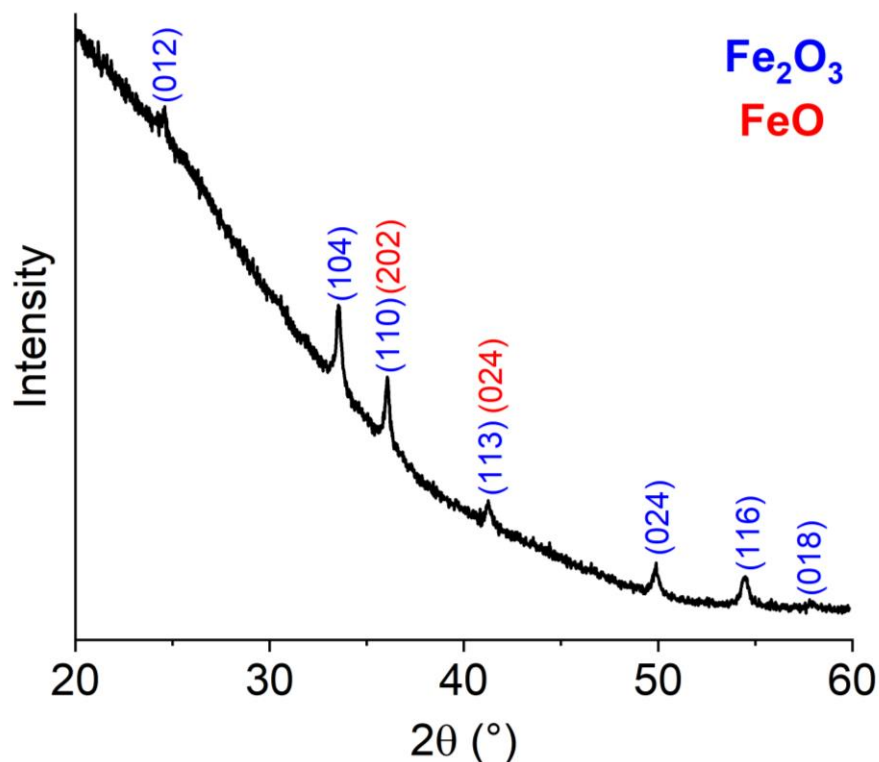


Figure 4.7. Diffractogram of iron oxide thin layer with 400 nm pore size.

4.4.3. Levofloxacin degradation

The iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer (400 nm pore size) immobilised onto glass slide was employed for the degradation of aqueous solution of 85 μM levofloxacin (LVF) by heterogenous photo Fenton reaction in the presence of H_2O_2 and on the exposure of simulated solar light (300 - 800 nm) irradiation. The relative % degradation of LVF was calculated by **Equation 2** from the change in the absorbance value of highest intensity peak at ~ 290 nm.⁵⁴ About 58% degradation of LVF was observed at 170 min of irradiation in the presence of 0.1 mM H_2O_2 (curve a in inset of **Figure 4.8A**) and it increased to 84% under similar condition in the presence of 10 mM H_2O_2 (curve c in inset of **Figure 4.8A**). Further high concentrations of H_2O_2 resulted into an interference in the spectroscopic absorbance measurements and thus avoided for this study. Therefore, H_2O_2 was appeared to be an important reactant for the degradation of LVF as the pseudo first order rate constant value of the degradation of LVF increased from 0.005 min^{-1} for 0.1 mM H_2O_2 to 0.01 min^{-1} for 10 mM H_2O_2 (**Figure 8A**).

On the other hand, the actual degradation (**Equation 4.1**) extent of LVF was increased from 0.43 (4.88 μM ; as calculated from corresponding calibration curve, **Figure A4.7.3**) for 20 μM LVF (curve d) to 1.33 (15.1 μM ; as calculated from corresponding calibration curve, **Figure A4.7.3**) for 85 μM LVF (curve f) during 90 min of solar irradiation in the presence of 10 mM H_2O_2 indicating an effective increase in the degradation of LVF with an increase in its initial concentration (**Figure 4.8B**). Whereas the relative % degradation of LVF decreased from 90% (curve d') to 71% (curve f') on increasing the concentration of LVF in analogous manner under similar conditions (**Figure 4.8B**). This reverse trend of degradation of LVF in these two representations was attributed to the fact of mathematical operation where an increase in the actual degradation became insignificant to the increase in the initial LVF concentration in **Equation 4.2**. The pH of the solution also effected the relative % degradation of 20 μM of LVF irradiated for 90 min in the presence 10 mM H_2O_2 . The relative % degradation of LVF was found to be high in acidic to neutral pH of the solution showing highest (90%) at pH ~ 4 , but it significantly decreased in alkaline pH due to the formation of iron hydroxides, reducing the efficiency of the process (**Figure 4.8C**).⁵⁵ Similarly, the homogenous and heterogenous photo Fenton degradation efficiencies of a varieties of pollutants have also been observed to be increased in the acidic pH (2.0 - 4.0) and decreased with increase in the pH from neutral to alkaline.⁵⁶⁻⁵⁹ In Fenton process, hydroxyl radical generation is favoured in the acidic pH range 2.0 - 4.0.⁵⁸ Also, the inorganic carbons present in the wastewater, which are known as the scavengers of hydroxyl radicals can be easily removed by controlling the pH to the acidic condition.⁵⁸

Although the % weight of iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide in the range of 1 - 5% showed no variation, within the experimental errors, in the relative % degradation of LVF (figure not shown); the average pore diameter of the oxide thin layer influenced the relative % degradation of LVF, which was decreased from 74 to 64 % on decreasing the average pore diameter from 400 to 35 nm in a time interval of 40 min. The authors suggest that this difference might be related to the wettability of the surfaces according to the Wenzel and Cassie-Baxter states.^{60, 61} For the smaller pore sizes (35 and 45 nm), the liquid penetration into the pores might be hindered by the size of the pores (Cassie-Baxter). However, for the bigger pore sizes, the liquid might be able to penetrate and wet the pore walls, increasing the surface area and the degradation (Wenzel). Therefore, 20 μM of LVF, 10 mM of H_2O_2 , pH 4, 1 % wt. iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide and 400 nm average pore diameter were chosen as optimum parameters for the heterogenous photo Fenton degradation studies of LVF.

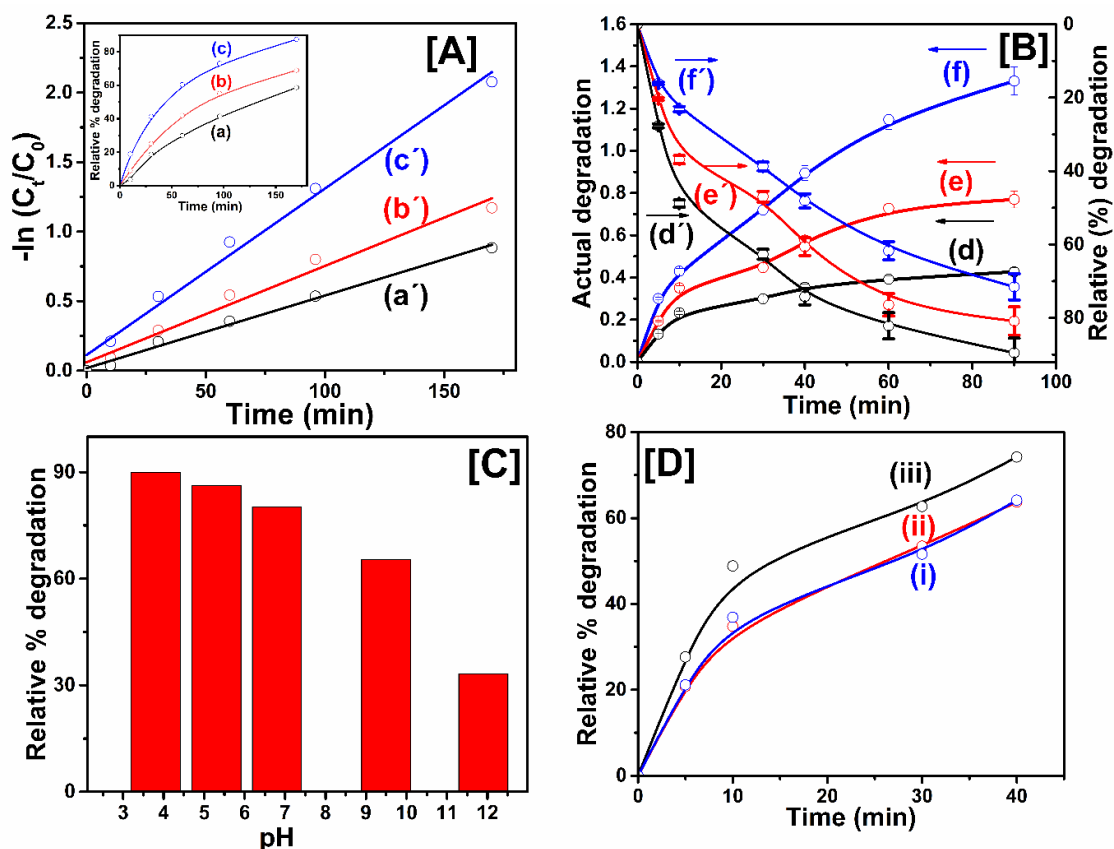


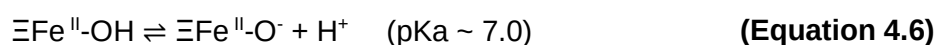
Figure 4.8. (A) Photo-Fenton degradation kinetics of 85 μM of LVF in the presence of (a') 0.1 mM (b') 1 mM and (c') 10 mM H_2O_2 and iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer (400 nm pore size); Inset shows the relative % degradation of LVF under similar conditions. (B) Actual degradation and relative degradation percentages of (d, d') 20 μM (e, e') 40 μM and (f, f') 85 μM of LVF in the presence of 10 mM H_2O_2 and iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer (400 nm pore size). (C) Relative degradation percentages of 85 μM of LVF in the presence of 10 mM H_2O_2 and iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer (400 nm pore size) at different solution pHs. (D) Relative degradation percentages of LVF in the presence of iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer of (i) 35 nm (ii) 45 nm and (iii) 400 nm pore size and 10 mM H_2O_2 at pH 4.0.

The above discussed results along with the results shown in **Figure 4.9** can reveal the overall mechanism of photo-Fenton degradation process of LVF. 1 % wt. iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide loaded glass slide having 400 nm average pore diameter immersed in 20 μM aqueous solution of LVF at pH 4 did not show any degradation up to 90 min in dark (**Figure 4.9(a)**). Nevertheless, the same on the exposure of solar light showed 31.3 % relative degradation of LVF (**Figure 4.9(b)**). Therefore, photons of wavelengths in the range 300 - 800 nm play a role in this degradation process. The UV-Visible spectra of iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide loaded glass slide has been shown in **Figure A4.7.4**. When the iron

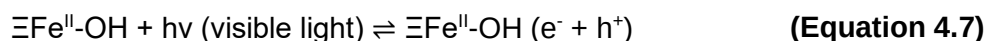
(Fe^{III}/Fe^{II}) oxide loaded glass slide was immersed in water at pH 4, the hydrolysis process at the solid-solution interface could introduce several hydroxyl groups (-OH) anchored to iron sites ($\equiv\text{Fe}^{\text{III/II}}$) (**Equation 4.4**)



This hydroxo interface in the aqueous solution established an independent Brønsted equilibrium (**Equations 4.5 and 4.6**) having the pH of zero charge in the range 5.8 - 6.3 at ~ 25 °C.⁶²



It is known that the surface hydroxyl groups of iron oxide thin layer can produce hydroxyl radical ($\bullet\text{OH}$) by the photogenerated hole (h^+) on the exposure of visible light (**Equations 4.7 and 4.8**).⁶³



The catalyst surface is again regenerated by **Equation 4.4**. Furthermore, the photogenerated electron (e^-) can produce a superoxide radical ($\text{O}_2^{\bullet-}$) by the reaction with dissolved O_2 and in acidic solution. The $\text{O}_2^{\bullet-}$ ultimately produces $\bullet\text{OH}$ and H_2O_2 (**Equations 4.9 - 4.11**).

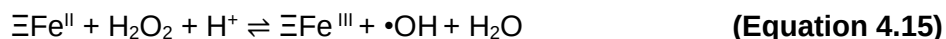


Therefore, the photocatalytic production of $\bullet\text{OH}$ and H_2O_2 at or near the oxide-solution interface on the exposure of visible light was appeared to be responsible for the degradation of LVF.^{64, 65} The production of $\bullet\text{OH}$ at pH higher than the pH of zero charge should be significantly decreased and it was evident in the pH studies as discussed above. H_2O_2 is an oxidising molecule, which possibly can oxidise LVF. Although insignificant relative % degradation of 20 μM aqueous solution of LVF in the presence of 10 mM H_2O_2 at pH 4 was observed in dark (**Figure 4.9(c)**), 44.5% of LVF degraded under

similar condition on the exposure of solar light (**Figure 4.9(d)**). The light of wavelength < 408 nm was sufficient to produce $\bullet\text{OH}$ by splitting H_2O_2 in water (**Equation 4.12**).^{66, 67}



Thus, it could be understood that the oxidative degradation of LVF could be achieved by the reaction with $\bullet\text{OH}$ radicals. The heterogeneous photo-Fenton process was utilised to improve the degradation efficiency of this process. The general Fenton process for the iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide loaded glass slide in the presence of acidic aqueous solution of H_2O_2 produces $\bullet\text{OH}$ radicals by the **Equations 4.13 – 4.15**.



Therefore, ~ 90% relative degradation of LVF was observed when 1 % wt. iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide loaded glass slide having 400 nm average pore diameter was immersed in 20 μM aqueous solution of LVF at pH 4 and exposed to solar irradiation for 90 min (**Figure 4.9(f)**) by the reactions with $\bullet\text{OH}$ radicals produced parallelly by the **Equations 4.7, 4.8, 4.12, 4.15**. The heterogenous photo-Fenton catalytic degradation of LVF have been investigated using dispersed catalysts in solution, and some of them have also used an additional oxidant peroxymonosulfate/persulfate as represented in **Table 4.2**.⁶⁸⁻⁷³ However, the aim of the present work was to fabricate the catalyst on solid support to develop a technologically viable solution for the treatment of polluted water in the absence of any external oxidant to eliminate the limitations associated with the post separation of dispersed catalysts from the solution as well as avoiding the generation of secondary waste.

Table 4.2. Comparison of reported photo-Fenton catalysts towards Levofloxacin degradation.

Catalyst	Operational condition of the catalyst	Time of irradiation (min)	Degradation efficiency (%) and initial LVF concentration [LVF] μM	Ref.
$\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$	Dispersed in solution	180	93.4 [550]	68
Mesoporous $\text{MnO}@\text{MnOx}$ microspheres + PMS	Dispersed in solution	30	98.1 [30]	69
2D/2D FeNi-layered double hydroxide/bimetal-MOFs nanosheets	Dispersed in solution	60	73.6 [55]	70
Fe-doped BiOCl Nanosheets + Persulfate (PS)	Dispersed in solution	60	95.0 [41.5]	71
BCP templated porous ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxides	Immobilised on glass support	90	90.0 [20]	This work

The isopropanol can scavenge the $\bullet\text{OH}$ radicals only in the bulk of the solution, and thus the presence of 2 mM isopropanol in similar reaction conditions, as mentioned above, decreased the relative degradation of LVF by 55.5 % (**Figure 4.9(g)**). Therefore, the $\bullet\text{OH}$ radicals both in the bulk of the solution and at the oxide-solution interface were responsible for the oxidative degradation of LVF. The AAS studies revealed that no Fe leaching more than 0.1 ppm (limit of detection of the AAS) was observed after 90 min confirming heterogenous photo-Fenton processes and potential reuse of the substrate.

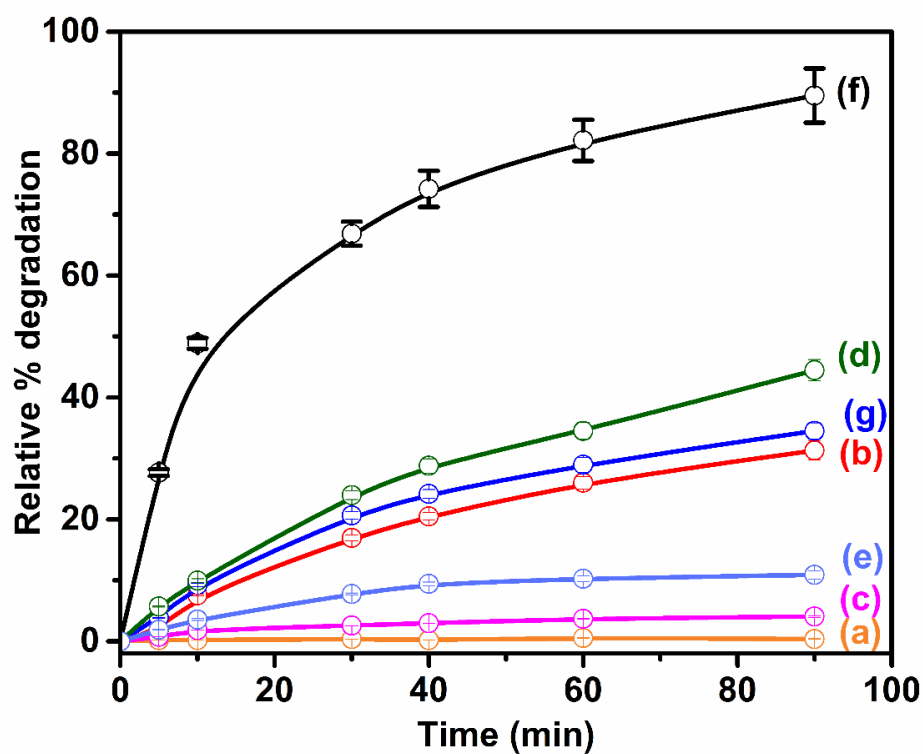


Figure 4.9. Relative % Degradation of 20 μM of LVF in the presence of: 1 % wt. iron oxide ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) loaded glass slide (400 nm pore diameter) at pH 4 (a) in dark and (b) on solar light exposure; 10 mM H_2O_2 at pH 4 (c) in dark and (d) on solar light exposure; 10 mM H_2O_2 and 1 % wt. iron oxide ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) loaded glass slide (400 nm pore diameter) at pH 4 (e) in dark (f) upon exposure of solar light and (g) in the presence of 2 mM isopropanol.

4.5. Conclusion

P2VP-*b*-PS thin films on glass substrates were prepared and underwent a solvent vapour annealing process leading to ordered cylindrical structures. Different molecular weights of the block copolymer were used, which enabled the fabrication of structures with varied sizes. These nanopatterns were used as templates for porous iron oxide structures. The pore sizes varied from 35 to 400 nm demonstrating the versatility of the process. The porous surface were characterised showing high coverage and homogeneity. Moreover, XPS analysis elucidated the presence of two oxidation states, Fe^{III} and Fe^{II}. As a potential application of the produced material, the iron oxide covered glass substrates were used in photo-Fenton processes for the degradation of levofloxacin. Results demonstrated 90 % degradation of 20 µM of LVF after 90 min of photo-Fenton process. The [•]OH radicals generated through photocatalysis from iron (Fe^{III}/Fe^{II}) oxide thin layer on the exposure of visible light, photo splitting H₂O₂ and general Fenton process played the leading role in degrading LVF as evidenced from scavenging experiment. Ultimately, the catalyst immobilised on solid glass support overcomes the limitations associated with the separation of dispersed catalyst from solution and has a great potential for the treatment of wastewater in large scale.

4.6. References

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4.7. Appendix – Chapter 4

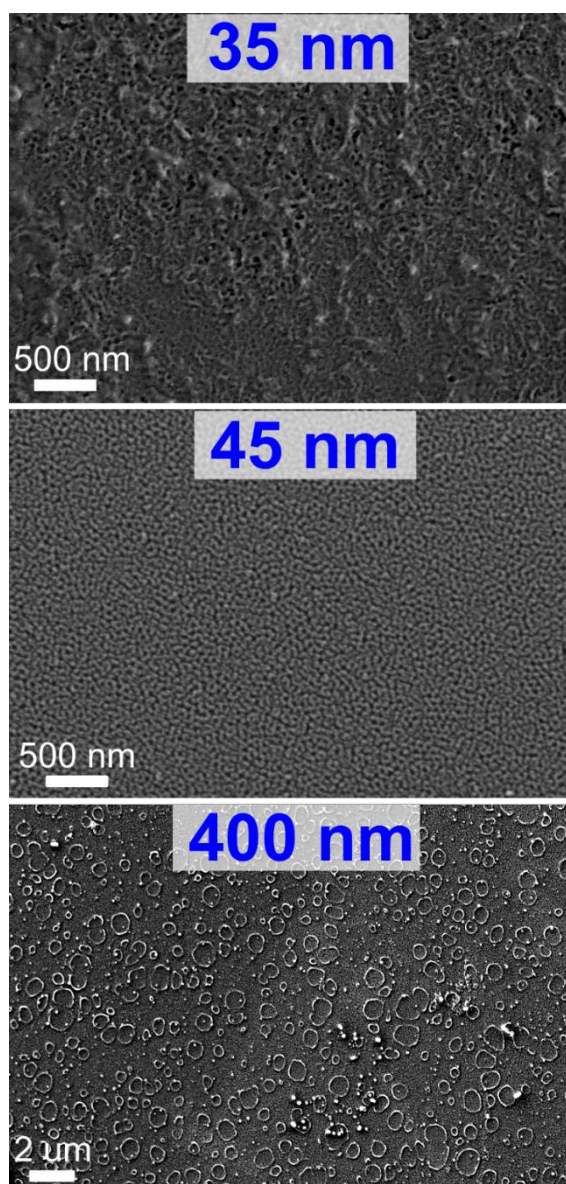


Figure A4.7.1. SEM micrographs of the iron oxide nanostructures with different pore sizes on glass substrates.

The SEM images demonstrate the high coverage of the porous iron oxide and the difference in pore sizes. Some defects are observed and are believed to be related to the Au-Pd coverage in order to avoid charging during imaging.

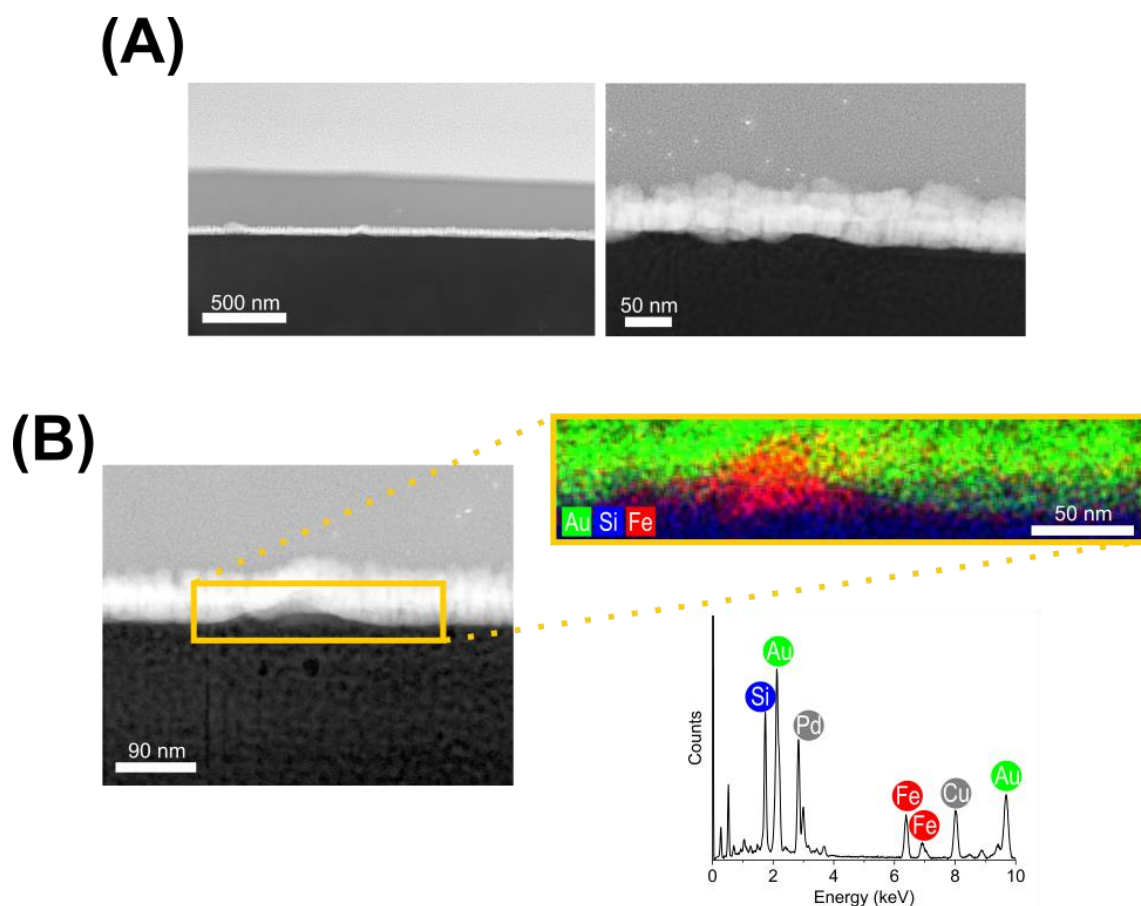


Figure A4.7.2. (A) STEM-HAADF cross-sectional images displaying the 400 nm-pore size iron oxide layer (small bumps) over a glass substrate. (B) EDX and elemental mapping of Au, Si and Fe.

The STEM micrographs display the iron oxide porous layer over the glass substrate. The sample was covered with Au-Pd in order to avoid charging. Based on the images, one may estimate an oxide layer with thickness of ~ 25 nm on the top of the pore.

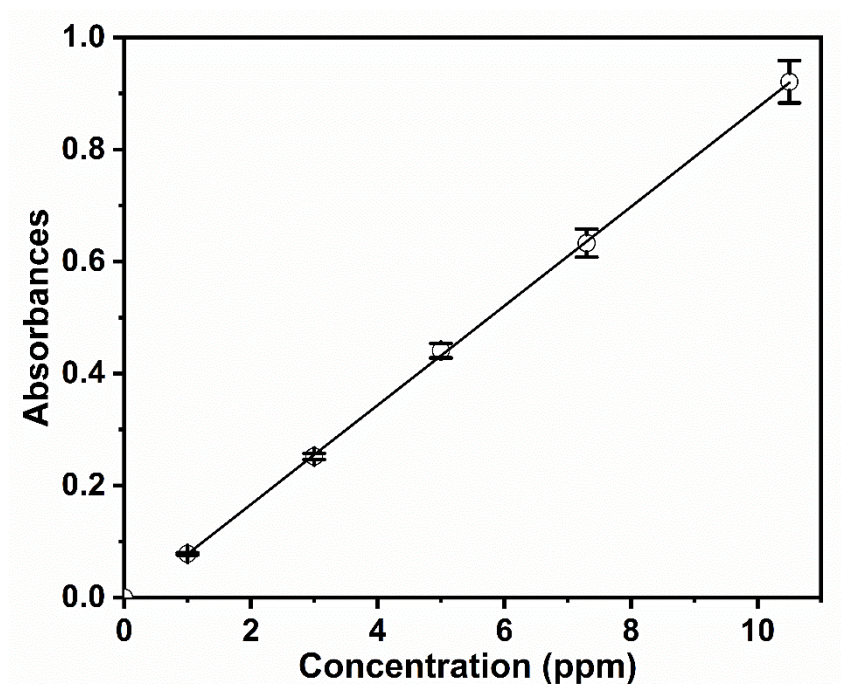


Figure A4.7.3. Calibration plot of aqueous solution of LVF.

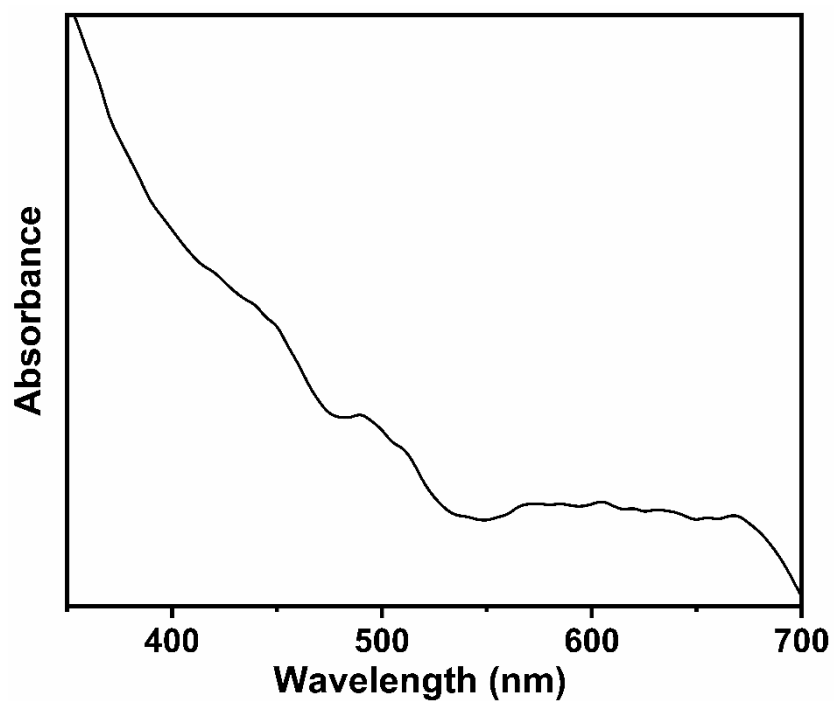


Fig. A4.7.4. UV-Visible absorption spectrum of iron ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) oxide thin layer (400 nm pore size) immobilised onto glass slide.

Chapter 5.

High Aspect Ratio Nanoscale Pores through BCP-Based Metal Oxide Masks and Advanced Dry Etching

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5.1. Abstract

The reliable and regular modification of the surface properties of substrates plays a crucial role in material research and the development of functional surfaces. A key aspect of this is the development of the surface pores and topographies. These can confer specific advantages such as high surface area as well as specific functions such as hydrophobic properties. Here, we introduce a combination of nanoscale self-assembled block-copolymer-based metal oxide masks with optimized deep reactive ion etching (DRIE) of silicon to permit the fabrication of porous topographies with aspect ratios of up to 50. Following the evaluation of our procedure and involved parameters using various techniques, such as AFM or SEM, the suitability of our features for applications relying on high light absorption as well as efficient thermal management is explored and discussed in further detail.

5.2. Introduction

The ability to control relevant surface properties, such as cooling and light absorption, at the nanoscale level is essential for a wide variety of applications and fields, including thermodynamics,^{1, 2} energy development,^{3,4} and materials science.⁵⁻⁷ Evaporative cooling, also known as evaporative heat transfer, describes the natural process where a liquid changes its state to vapor, resulting in a local decrease in temperature. Hence, it plays a fundamental role in refrigeration and air conditioning systems,⁸ cooling towers for power plants,⁹ and thermal management of electronics.¹⁰ On the other hand, light absorption is the process by which a material absorbs light and converts it into other forms of energy, such as heat or electricity. It is, therefore, an essential mechanism in solar energy conversion devices,¹¹ photovoltaic cells,¹² and optical coatings.¹³

One effective approach to enhance the performance of evaporative cooling and light absorption lies in the development of strictly controlled porous structures. Porous materials, in contrast to planar geometries, offer a higher surface to volume ratio, which enables efficient heat and mass transfer¹⁴ as well as enhanced light absorption.¹⁵ To achieve high spatial resolution patterns with low and periodic arrangements, block copolymer (BCP) lithography is a promising technique as it produces porous substrates at the nanoscale with well-defined and tuneable morphologies. However, block copolymer lithography has, so far, been limited to small topographical heights with low aspect ratios because of the poor etch selectivity of the BCP derived etch mask, made of a polymer block, over the substrate.¹⁶ This laboratory has been central in developing infiltration methods to yield hard masks that allow for larger aspect ratios,¹⁷⁻¹⁹ while other potential methods to create hard masks have been reported and involve sol-gel²⁰⁻²² and sputtering approaches.^{23,24} Nevertheless, the generation of hydrophobicity, which enables effective evaporative cooling, or effective light scattering, at very high (>25) aspect ratios remained challenging. In addition, such very deep features have not been achieved to date and require advanced etching to prevent damage to the nm size arrangements during the etch process.

At the core of the BCP-based lithography is the controlled self-assembly of the engineered polymer, which is composed of two or more chemically distinct polymer blocks, into periodic nanostructures,²⁵ which can act as templates.^{26,27} These nanostructures can then further be transferred into the underlying substrate using etching techniques once the BCP is converted into a mask,²⁸⁻³⁰ e.g., using advanced processing methods such as deep reactive ion etching (DRIE) suitable for the generation of high aspect ratio features with precisely controlled geometries.³¹ However, thus far, the number of successful attempts combining well-defined BCP masks with sufficiently high structural stability and reliable anisotropic etching at the nanoscale is limited, and, so far, none have been able to create very high aspect ratio pores at a substrate surface.

In this study, we present DRIE processing suitable for the fabrication of deep pore nanostructures with a high aspect ratio when combined with optimized BCP-templated etch masks. Two poly(2-vinylpyridine-*b*-styrene) (P2VP-*b*-PS) systems were employed for the mask production, with their phase separation induced by a solvent vapor annealing (SVA) method, leading to vertically aligned polystyrene (PS) cylinders with diameters of 32 and 343 nm. A wide range of feature sizes was selected to demonstrate the capability of hard mask preparation. Then, the porous masks were fabricated by selectively infiltrating a chromium precursor and subsequently oxidizing/removing the

BCP template, resulting in uniform porous metal oxide patterns. The different chromium oxide masks were finally used to transfer the features into a bulk silicon substrate via a newly developed three-step DRIE process. While previous work³² demonstrated the use of BCP-based porous structures to be applied as a hard mask in simple dry etching processes, the current process goes significantly further via the optimization and adaptation of the mask *e.g.*, by fabricating different pore sizes, which is crucial to demonstrate enhanced versatility of the fabrication procedure. Furthermore, we substantially extend the processing and application capabilities through the combination of our BCP masks with a custom and advanced dry etching technique to enable the creation of trenches with unprecedented aspect ratios and evaluate the resulting features and related process parameters in further detail. Moreover, the development of very high aspect ratio features is unique, as it opens possibilities for through-substrate structures to enable molecular transport across well-defined membranes. The resulting pores and devices were evaluated for potential applications through reflectance and thermal contact angle (CA) measurements, with the results highlighting low reflectance values as well as low CA hysteresis, both of which are properties that are highly desirable for various fields, including thermal management and solar energy conversion.

5.3. Materials and methods

Chemicals and materials were used as received. B-doped-type silicon (111) dummy wafers with a native oxide layer ($\cong 2$ nm; University Wafer) were used as substrates. Two poly(2-vinylpyridine-*b*-styrene) (P2VP-*b*-PS) BCP systems with their respective number-average molecular weight (MW) and polydispersity index (PDI) were obtained from Polymer Source Inc.: BCP1 ($MW_{P2VP} = 60$ kg.mol⁻¹, $MW_{PS} = 26$ kg.mol⁻¹, PDI = 1.15) and BCP2 ($MW_{P2VP} = 598$ kg.mol⁻¹, $MW_{PS} = 189$ kg.mol⁻¹, PDI = 1.22). Acetone (99.0%), toluene (99.8%, anhydrous), tetrahydrofuran (99.8%, anhydrous), chloroform (99.9%, anhydrous), isopropanol (99.5%, anhydrous), 1-butanol (99.8%, anhydrous), and chromium(III) nitrate nonahydrate ($\geq 99.99\%$) were sourced from Sigma-Aldrich. All of the procedures were conducted at room temperature, unless otherwise specified.

5.3.1. Phase Separation of the P2VP-*b*-PS Films and Fabrication of the Hard Masks

Phase separated P2VP-*b*-PS films were prepared according to previous studies.^{32, 33} Silicon wafers were cut into 4 cm² squares and subjected to ultrasonic cleaning in acetone for 20 min, followed by drying with a stream of N₂. Solutions of BCP1 (1.5 wt. %)

and BCP2 (2.0 wt. %) were prepared in a 1:4 mixture of toluene and tetrahydrofuran. Each solution was spin-coated onto the Si substrates at 3000 rpm for 30 s using a vacuum-free Ossila spin coater. Subsequently, the coated substrates were placed in 150 mL jars, each containing a glass vial with 2 mL of chloroform. The jars were stored in a refrigerator at 5 ± 2 °C for 40 min (BCP1) or 96 h (BCP2). Finally, the samples were removed from the jars and allowed to dry at room temperature.

A solution of 2.0 wt. % chromium nitrate in butanol was prepared and applied to the phase-separated BCP thin films using spin coating at 3000 rpm for 30 s. The coated films were then exposed to a UV/ozone (UVO) treatment in a chamber with two low-pressure mercury lamps (with an output current ranging from 0.8 to 0.95 A, power between 65 and 100 W, and emissions at 184.9 and 253.7 nm) using a PSD Pro Series Digital UV Ozone System (Novascan Technologies, Inc.). The samples were placed 4 cm away from the UV source, and the process was conducted for 2 h. Following this, the substrates were heated in a furnace (Thermo Scientific FB1415M) to 400 °C for 1 h.

5.3.2. Deep Reactive Ion Etching

Deep reactive ion etching (DRIE) was conducted on the hard-mask-covered substrates in a PlasmaPro Estrelas100 (Oxford Instruments) using C_4F_8 and SF_6 gases. During the etching procedures, the wafers were maintained at a temperature of 0 °C by utilizing liquid nitrogen backside cooling. The used process parameters are listed in **Table 5.1**. For simplicity, the process was summarized in three steps. However, the actual recipe contained intermediate phases between the main steps that are applied to reduce the pressure of the chamber, leading to an increased mean free path length, or to an exchange of the gas environment, as well as to a split of the first step into two components and, by that, to a reduction in the duration of the pre-etching passivation (**Figure A5.7.2**).

Table 5.1. DRIE Etching Process Parameters*

Steps	Duration [ms]	Pressure [mTorr]	ICP power [W]	HF power [W]	C ₄ F ₈ flow [sscm]	SF ₆ flow [sscm]
Passivation (I)	1350	120	2500	0	280	10
Break through (II)	400	20	2000	75	10	200
Chemical and physical etching (III)	500	120	2500	50	10	800

*Each etch cycle consists of three steps. The main process parameters are the duration time of the individual steps, the pressure inside chamber, the inductively coupled plasma (ICP) power affecting plasma density, the HF power inducing the acceleration of the ions toward the target, and the gas flow.

5.3.3. Characterisation

Atomic force microscopy (AFM) topographical images of the samples were captured by using a Park XE-100 microscope (Park Systems). Noncontact mode was selected for the imaging process, utilizing a AC160TS cantilever (with a force constant of 26 N.m⁻¹ and resonance frequency of 300 kHz). The measurement of 100 features was used to calculate the pore diameter and pore–pore spacing, with the results being expressed as the mean ± standard deviation.

SEM micrographs were captured using a Zeiss Ultra Plus microscope with an accelerating voltage of 2 kV, a working distance of 4–5 mm, and a secondary electron (SE2) detector. The pore surface area was evaluated via ImageJ software. The measurement of 50 features was used to calculate the pore depth, with the results being expressed as mean ± standard deviation.

To evaluate the metal oxide layer thickness, composition, and structure, the substrate was sectioned using a Zeiss AURIGA focused ion beam (FIB), utilizing an ion beam current ranging from 4 nA to 50 pA and accelerating voltages of 30 and 15 kV. Subsequently, images obtained through scanning transmission electron microscopy (STEM) were combined with energy dispersive X-ray spectroscopy (EDX) data. This was

done using a FEI Titan G2 80-300FEG S/TEM with a Schottky-type electron gun operated at 300 kV and a Bruker XFlash 6T-30 detector with a resolution of 129 eV.

Reflectance measurements were acquired on a LAMBDA 365 UV/vis Spectrophotometer (PerkinElmer) coupled with a 50 mm transmission-reflectance integration sphere (5 nm slit) in the range of 200–1100 nm.

A custom-designed system was utilized to measure the dynamic contact angle (CA) on 10 random regions of the samples. The room temperature and relative humidity on the day of the experiment were 20 ± 2 °C and $50 \pm 10\%$, respectively. Experiments were conducted at atmospheric pressure and with a duration of 3–5 s.

A high-speed camera was employed to capture the advancing and receding CAs of water at a sampling rate of 60 Hz. The liquids were dispensed using a 35-gauge needle (with an outer diameter of 135 μm) at a flow rate of $5 \text{ nL} \cdot \text{s}^{-1}$, resulting in droplet volumes of 100 nL. Before measuring the CAs, a diluted oxalic acid solution (1% wt.)³⁴ was used to remove any remaining Cr oxide mask. A heating PID-controlled stage was used to change the temperature of the experiment. The experimental results are displayed with error bars based on standard error or 95% confidence intervals (where stated).

5.4. Results and discussion

5.4.1. BCPs enable porous hard masks with precisely controlled dimensions

Despite increasing need in miniaturization, the fabrication of stable masks with nanoscale features suitable for etching processes remains challenging.³⁵ BCPs possess the remarkable ability to phase separate *e.g.*, via solvent vapor annealing (SVA), to create vertically aligned structures which, through subsequent selective metal infiltration,³⁶ permit the formation of metal oxide layers. **Figure 5.1A,B** display the general procedure for the fabrication and application of such porous hard masks on silicon (Si) substrates for subsequent bulk etching. Through the contact of the BCP thin film with chloroform vapours *i.e.*, a nonselective solvent, unfavourable interactions between the P2VP (poly 2-vinylpyridine) and the PS blocks can be reduced, which leads to the vertical alignment along the surface plane of the domains.³² Therefore, based on the two molecular weights studied in this work, different morphologies were obtained. **Figure 5.1C** presents topographical atomic force microscopy (AFM) images of the self-

assembled polymeric thin films with the PS cylinders of varying dimensions *i.e.*, diameters of about 32 and 343 nm, being embedded within the P2VP matrix. The significant difference in the annealing time between the two BCPs (see Materials and Methods) is related to the chain entanglement, as longer chains require more energy or time to self-order.^{37, 38}

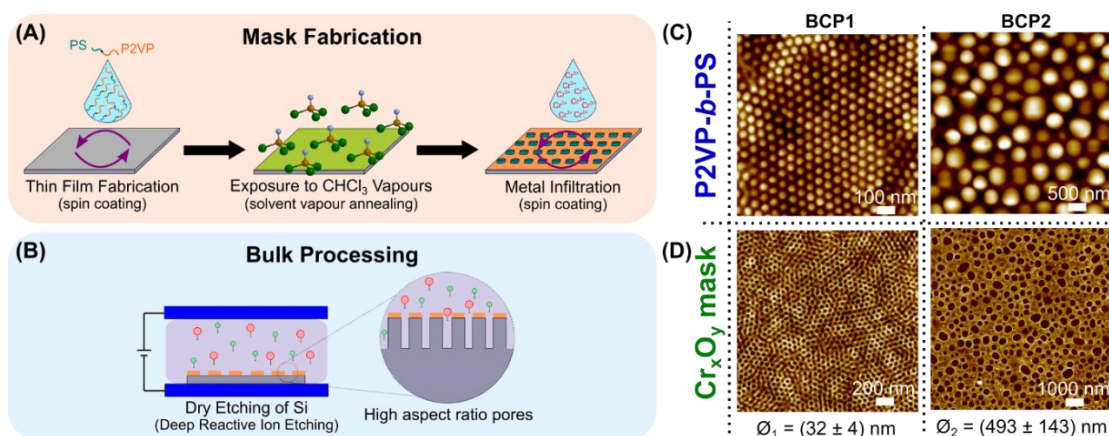


Figure 5.1. Fabrication procedure can be separated in two main components. (A) Schematic of the metal oxide porous layer mask fabrication and (B) subsequent bulk etching of Si. AFM images of (C) P2VP-*b*-PS ordered thin films: BCP1 (86 kg.mol⁻¹) and BCP2 (787 kg.mol⁻¹); and (D) chromium oxide hard masks with pore diameters ($\varnothing$) of 32 ± 4 and 343 ± 143 nm, respectively.

Following the formation of the polymeric thin film, the infiltration of the Cr ions and the subsequent oxidation of the BCP led to porous chromium oxide (Cr_xO_y) thin layers, previously confirmed by XPS and EDX,³² with a thickness of ~ 10 – 25 nm, as shown in **Figure 5.1D**. To establish the optimum concentration of the chromium precursor, BCP1 thin films were infiltrated with different concentrations of chromium nitrate solutions, while 2.0% wt. was determined as the highest possible concentration without overfilling of the pores (**Figure A5.7.1**). The optimized metal oxide masks did not present any significant changes in the pore diameter when compared to the initial polymer and resulted in average pore diameters for BCP1 and BCP2 of 32 ± 4 and 343 ± 130 nm, respectively. The successful transfer of the BCP template layout and structure to the Cr oxide masks strongly suggests that the PS cylinders were vertically aligned throughout the P2VP matrix. Nevertheless, further investigations are needed to confirm their verticality.

5.4.2. Combination with dry etching permits fabrication of very deep porous structures with high aspect ratios in silicon substrates

The pattern of the chromium oxide hard masks was transferred into the Si substrate via inductively coupled plasma deep reactive ion etching (ICP-DRIE). **Figure 5.1B** shows a sketch of the fabrication procedure, while **Figure A5.7.2** introduces the process cycle in further detail. A standard two step Bosch process³⁹ was expanded by an intermittent step to allow for higher controllability during the etching procedure and to permit the reliable fabrication of high aspect ratio structures with minimal variations in etch angles as necessary during the application of nanoscale masks.⁴⁰ Accordingly, the custom-designed etch cycle consisted of the following three steps: (I) deposition of a C_4F_8 protective layer covering the bottom and the sidewalls of the pores, (II) removal of the protective layer on the bottom of the pores through primarily physical etching (anisotropic) based on accelerated ions using SF_6 , and (III) combined chemical (isotropic) and physical etching of the protective layer on the sidewalls and the exposed silicon substrate at the bottom of the pores with SF_6 . During the additional second step, in contrast to the standard Bosch procedure, the ions were accelerated toward the wafer through the application of a strong high-frequency (HF) electric field, leading to a highly anisotropic etching with low selectivity. Finally, while traditional processes use low HF power paired with high gas flows during the last step to improve selectivity and promote isotropic chemical etching of Si, thanks to the high stability of the chromium oxide mask and in contrast to previous work,⁴⁰ our procedure permitted the use of continuously high HF powers in combination with a reduction in the duration of the third etch step. This, in turn, led to an increase in the proportion of the ongoing anisotropic silicon etching and, as such, minimized challenges associated with chemical etching and diffusion limitations within the long yet narrow pores.

Based on the above process, increasing numbers of etch cycles were applied to extend the depth of the pores and to evaluate device performance and process reliability (**Figure 5.2**). Accordingly, for 32 nm pores, 30 cycles led to a depth of $1.32 \pm 0.26 \mu m$ (**Figure 5.2B**) *i.e.*, an aspect ratio of more than 40, while 35 cycles produced pores with a depth of $1.56 \pm 0.21 \mu m$ and a high aspect ratio of about 50 (**Figure 5.2D**). The variation in depth is likely associated with minor variations in the diameter of each pore, which, due to limitations in gas exchange, result in faster or slower etching rates and, subsequently, lead to variations in pore depth also known as etch lag.^{40, 41} Nevertheless, these exceptional results demonstrate that the stability of the chromium oxide mask was sufficient to, in combination with the optimized etching recipe, allow for the production of

high aspect ratio features while preventing complete mask removal during the procedure. Further and to the best of the authors' knowledge, the production of features with similarly high aspect ratios and comparable feature sizes using standard DRIE equipment has not yet been demonstrated, as highlighted in **Table 5.2**, which summarizes previous aspect ratios of nano to microscale structures.

Table 5.2. Etch Depths Reported as Achieved through Silicon Etching Processes at Similar Length Scales Achieved Only Lower Aspect Ratios.

Etch type	Aspect ratio	Feature size (nm)	Depth	Reference
Cryo-ICP (SF ₆ /O ₂)	4.2	12	50 nm	⁴⁴
ICP (HBr/O ₂)	5	8 - 9	45 nm	⁴⁵
ICP (Cl ₂ /SF ₆)	10	50	500 nm	⁴⁶
ICP/RIE (SF ₆ /C ₄ F ₈)	17	75	1.3 μm	⁴⁷
Cryo-RIE (SF ₆ /O ₂)	26.5	400	10.6 μm	⁴⁸
ICP/RIE (SF ₆ /C ₄ F ₈)	50	32	1.6 μm	This work

$\varnothing = 32 \text{ nm}$

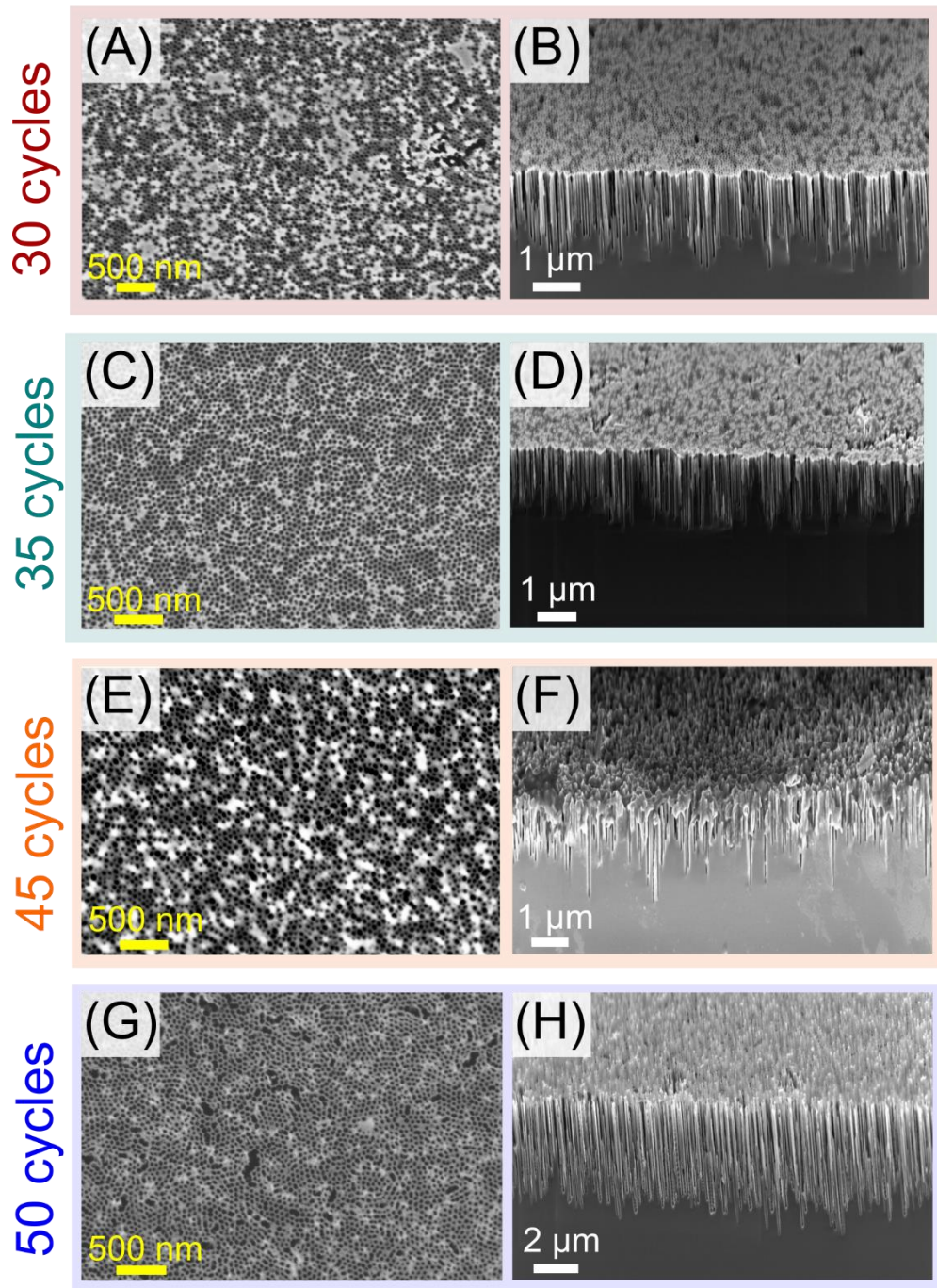


Figure 5.2. Above 35 etch cycles, the 32 nm mask and pores become unstable. The figures show top down and cross section scanning electron microscopy (SEM) micrographs of the etched silicon substrates with masks containing 32 nm pores and varying numbers of etch cycles: (A,B) 30 cycles, (C,D) 35 cycles, (E,F) 45 cycles, and (G,H) 50 cycles.

To study the morphology of the pores after etching, scanning transmission electron microscopy and energy dispersive X-ray spectroscopy (STEM-EDX) analyses were conducted (**Figure A5.7.3**). The results showed that our procedure was successful in preserving the crystalline structure of the silicon substrate, as demonstrated by the noticeable lattice spacing corresponding to the (111) plane of the Si FCC structure.⁴² As no amorphization was detected in the TEM observable area and due to the low processing temperature and short duration of the etching, it can also be assumed that no changes in the Si lattice structure are present in areas further away from the contact with the etching gases. Additionally, elemental mapping displayed the presence of the remaining Cr oxide mask as well as the other expected elements. However, from 35 etch cycles and onward, the pores started to lose their structure and stability, as presented in **Figure 5.2F**. Finally, for 50 cycles, while the hard mask was still partially present although showing clear signs of degradation (**Figure 5.2G**), the cross section demonstrated the uncontrolled formation of pillars, possibly resulting from the localized collapse of the pore walls required to separate the pores, as well as the creation of nanograin structures (**Figure 5.2H**) commonly occurring in processes involving highly directional plasma etching of silicon.⁴³ The observed limitations concerning the process reliability at increasing nanopore depths are expected to be associated with the increasing reduction in gas exchange, which leads to a lack of fluorocarbon needed for the deposition of the passivation layer as well as insufficient removal and subsequent redeposition of by-products.

To assess the effect of pore sizes on the etching performance and device quality, samples with different pore diameters *i.e.*, 32 and 343 nm (**Figure 5.3**), were etched using the same protocol and equal number of cycles (30). For 343 nm pores, a depth of $6.25 \pm 0.61 \mu\text{m}$ was obtained, which is a 5-fold increase in etch depth compared to the 32 nm pores, however, simultaneously a drop in aspect ratio to 18. This decrease in the aspect ratio can be attributed to the highly modified proportion of chemical etching in our newly developed etching process cycle, which, while ideal for narrow features, is not optimized for wider structures, as can also be seen by the formation of scallops along the walls of the pores (**Figure 5.3D**). Nevertheless, as etch performance is directly linked to constraints provided by the penetration of the ions during the etching and the transport of the reactants, products, and by-products, the simultaneous optimization for multiple features with strongly varying dimensions is commonly acknowledged as especially challenging, as often prominently highlighted through the presence of RIE lag or etch lag also mentioned above.⁴⁹ Additionally, only minor changes in pore sizes and pore–pore

distances throughout the patterning process, from the BCP thin film to the final etched surface, were detected (Table A5.7.1 and Figure A5.7.4).

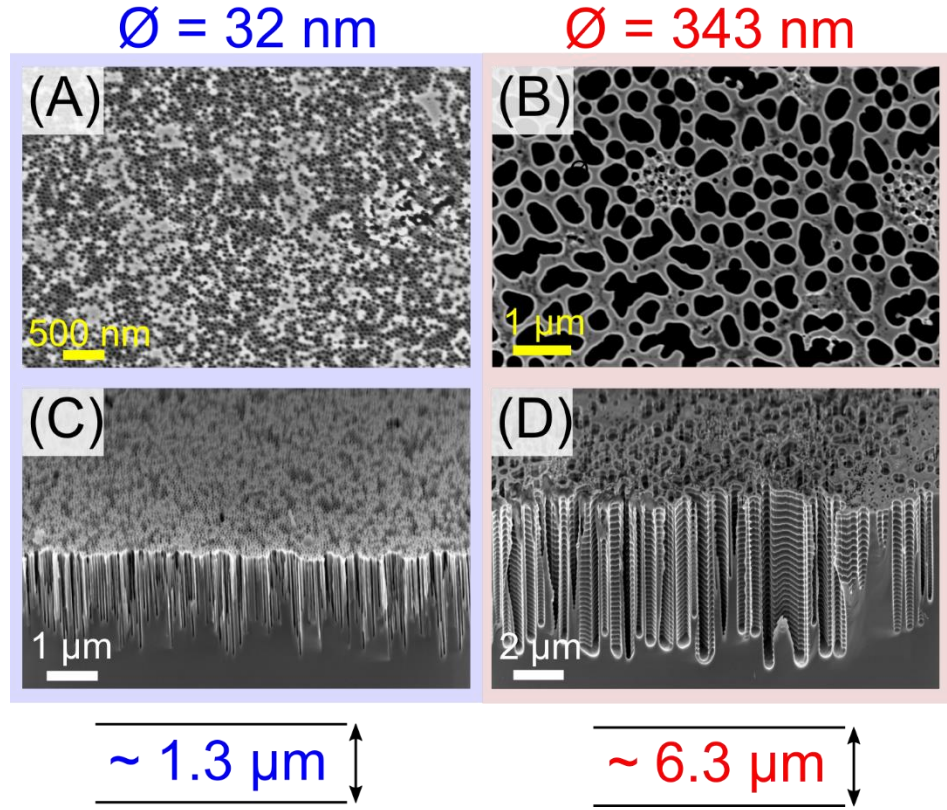


Figure 5.3. For 343 nm masks, the etch depth increases, but the etch quality is reduced. The figures show top down and cross section SEM micrographs of the etched silicon substrates with varying diameters ($\varnothing$): (A,C) 32 nm and (B,D) 343 nm.

5.4.3. Nanoscale porous silicon substrates demonstrate suitability for potential applications in light absorption and thermal management

As a part of the device's primary interaction with the environment, surface reflectance and absorption play crucial roles in the optical performance of microdevices and their subsequent application. Hence, standard reflectance measurements at a normal incidence angle were performed to quantify the optical properties and evaluate the suitability of the porous substrates for antireflection coatings. Overall, the spectra of the devices with varying depths demonstrated similar qualitative behaviours with a decrease in reflectance for increasing numbers of etch cycles. Further, increasing depths led to an attenuation of the interband transition peaks,⁵⁰ as observable at 272 and 364 nm (**Figure 5.4A**). For reference, the flat surface of a polished silicon substrate *i.e.*, without mask fabrication or subsequent etching, presented an average reflection value across the

visible range (380–700 nm) of 26%. Additionally, to analyse the effect of any Cr oxide remaining after the etching process, the reflectance of a Si substrate covered with a Cr oxide mask with 32 nm pores was measured, and an average reflectance value of 25%, similar to the one obtained for a planar silicon substrate, was detected, which confirmed that the mask itself did not contribute significantly to the change in optical properties. Then, the variation of etch cycles and their effect on the reflectance were assessed in further detail. Both, the samples with 30 and 35 cycles, had an average reflectance value of approximately 7% in the visible range. However, in the UV range, the intensity of the interband transition peaks for the 35-cycle sample were significantly reduced when compared to the 30-cycle one. Overall, both numbers of cycles presented similar spectra, which can likely be accounted for by both processes leading to a nanostructure depth at which their intensity along the spectrum reached a stable minimum.⁵¹ Additionally, for the 45-cycle sample, although an early collapse of the walls separating the pores was observed in the SEM analysis, the reflection value was found to be very similar to 35, further suggesting a plateau in reflectance for samples with diameters of 32 nm around this depth. Finally, the 50-cycle sample demonstrated an exceptionally low average reflectance value in the visible range of only 2.7%. However, this extra reduction can likely be assigned to the formation of the nanograss-like black silicon (BSi) features described above, which can create graded refractive index profiles at the interface between the air and the silicon and, by that, improve the material's light-absorbing characteristics.⁵² Nevertheless, given the reduced reliability in the formation of BSi structures during the use of our protocol, the fabrication and application of stable devices, such as those achieved with 35 etch cycles, would be suggested. To summarize, it is worth highlighting that our samples demonstrate a high absorption of light in the ultraviolet, visible, and infrared A ranges and do not rely on antireflection coatings, which makes them useful for various applications in need of light-absorbing surfaces.

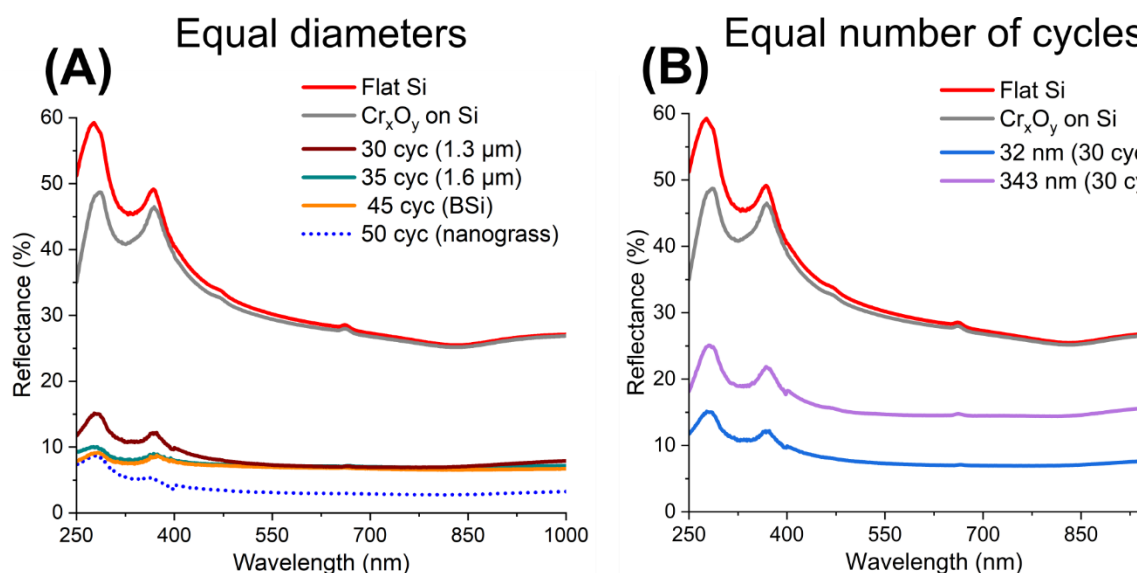


Figure 5.4. Performed etching significantly improves absorption for both pore diameters. The figures report reflectance measurements in the range of 250 to 1000 nm for (A) different etch cycles with 32 diameter pores and (B) different pore sizes.

In a next step, we analysed the effect of the pore width onto the derived reflectance. **Figure 5.4B** shows a reflectance comparison for the two different pore diameters. The 343 nm sample demonstrated an average reflectance value of 14% in the visible range, which is substantially greater than the 7% detected for the 32 nm sample. This difference in performance suggests that the optical behaviour of our samples is related to the moth-eye effect, in which subwavelength features form a continuous refractive index between the air and the surface that reduces light reflections.^{53, 54} Accordingly, it could be assumed that the 32 nm sample allows for a higher capacity in absorbing light when compared to the 343 nm sample due to its smaller dimension as well as its higher feature density. Alternatively or simultaneously, the increase in reflectance could also be caused by an increase in diffuse light scattering related to the increasing pore size.⁵⁵

To study the potential application of our structures in thermal management, water contact angles (WCAs) were measured at different temperatures for flat silicon and processed (35 cycles) silicon substrates based on 32 nm pores. For the flat silicon substrate, the WCA showed a hydrophilic character (**Figure 5.5A**) with an average advancing value of $\sim 55^\circ$ and a receding angle of $\sim 38^\circ$. A slight increase in the advancing contact angle was observed by increasing the temperature to approximately 60°C . After the fabrication of the porous patterns, the WCA displayed an increase in the hydrophobic character of the surface (**Figure 5.5B**), reaching values of $\sim 95^\circ$ for the advancing and $\sim 87^\circ$ for the receding angles. This behaviour can be explained by the Cassie–Baxter wettability

regime, in which nanostructured surfaces are able to trap air, leading to a reduction in the surface wetted by the liquid.^{56, 57} Accordingly, the Cassie–Baxter equation can be simplified as follows when air pockets are present on a rough single-component surface:⁵⁸

$$\cos\theta_{CB} = f_s (1 + \cos\theta_{\text{flat}}) - 1 \quad (\text{Equation 5.1})$$

where θ_{CB} is the contact angle for the porous surface, f_s is the fraction of the water/solid contact surface area, and θ_{flat} is the contact angle of the flat/smooth surface.

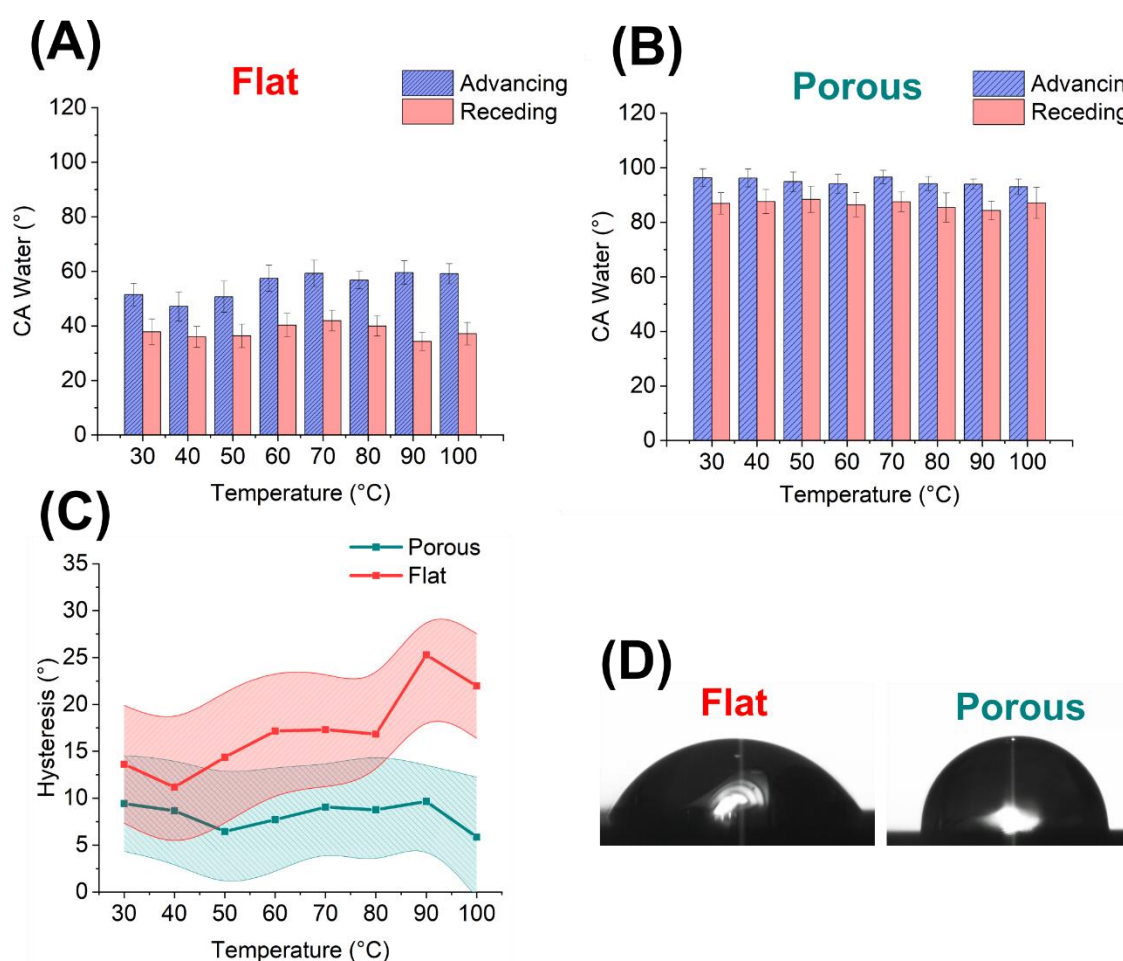


Figure 5.5. Surface modification improves device cooling performance and hydrophobicity. The figures present the advancing and receding water contact angles for (A) flat and (B) porous silicon substrates with 32 nm pore diameter and 35 etch cycles ($n = 10$). (C) Contact angle hysteresis (shaded areas = 95% confidence interval). (D) Droplet images at 30 °C.

Considering that the average static contact angle of the flat surface is 55° and f_s is $\sim 65\%$ (pore surface area: $\sim 35\%$ (for 32 nm/35 cycles) - based on SEM micrographs), the contact angle θ_{CB} is about 89° , which agrees well with the experimental data.

Subsequently, the hystereses of the advancing and receding contact angles were calculated ($|\theta_{advancing} - \theta_{receding}|$) (**Figure 5.5C**). The hysteresis arises from the dissimilarity in the interaction between the liquid and solid surfaces at the contact line during the advancement and recession of the liquid.⁵⁹ Compared to the flat surface, the etched sample, on average, demonstrated lower values, meaning that the advancing and receding WCA were more alike, which led to improved balancing of tensions at the liquid–solid interfaces. It has previously been shown that a lower hysteresis also permits improved heat transfer,⁶⁰ with further reports highlighting that the critical heat flux is reduced when the contact angle hysteresis increases.⁶¹ Moreover, lower CA values have been found to decrease the boiling heat efficiency in thermal systems.⁶² Finally, the presence of the pores in the substrate can enhance the heat transfer via the increased surface area in parallel with capillary wicking, while pore uniformity, as demonstrated for 32 nm masks and 35 etching cycles, has also been highlighted to play a key role in liquid evaporation.^{63, 64} Hence, while further testing is required, compared to flat substrates, our processed material is expected to display a significantly improved performance when applied for thermal management and heating/cooling systems. Nevertheless, prior to final applications or implementations, it is generally suggested that the relationship between the precise surface chemistry and the device performance should be studied in further detail to ensure long-term stability and reliability.

5.5. Conclusion

To conclude, the optimized DRIE process in combination with the advanced BCP-templated mask fabrication on silicon substrates presents a promising method to produce deep porous structures at the nanoscale, which is further amplified by the low-cost strategy and versatility applied during its production. Additionally, the developed procedures and corresponding devices have proven valuable for different applications, including tasks relying on low reflectance values, such as required in light sensing or absorption, as well as for thermal management via nanostructured substrates, as relevant in electronics, and are expected to further support advancements in miniaturization and membrane manufacturing.

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5.7. Appendix – Chapter 5

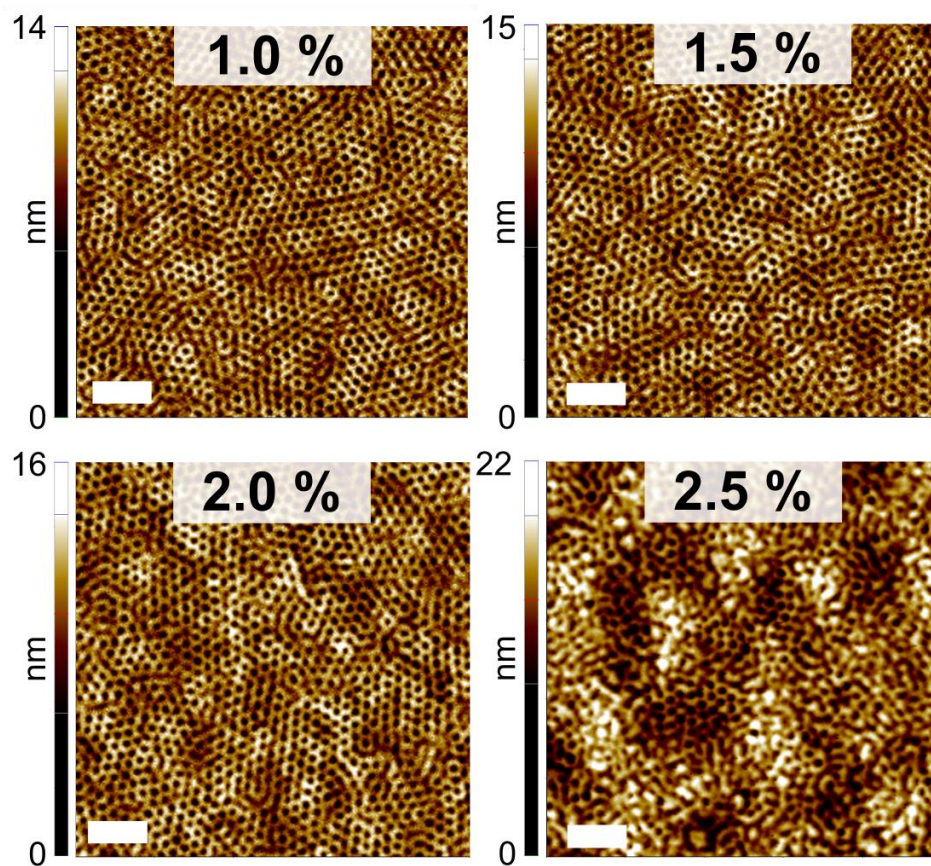


Figure A5.7.1. Variation in chromium precursor concentration (% wt.) and its effect on morphology for BCP1. All scale bars are 300 nm.

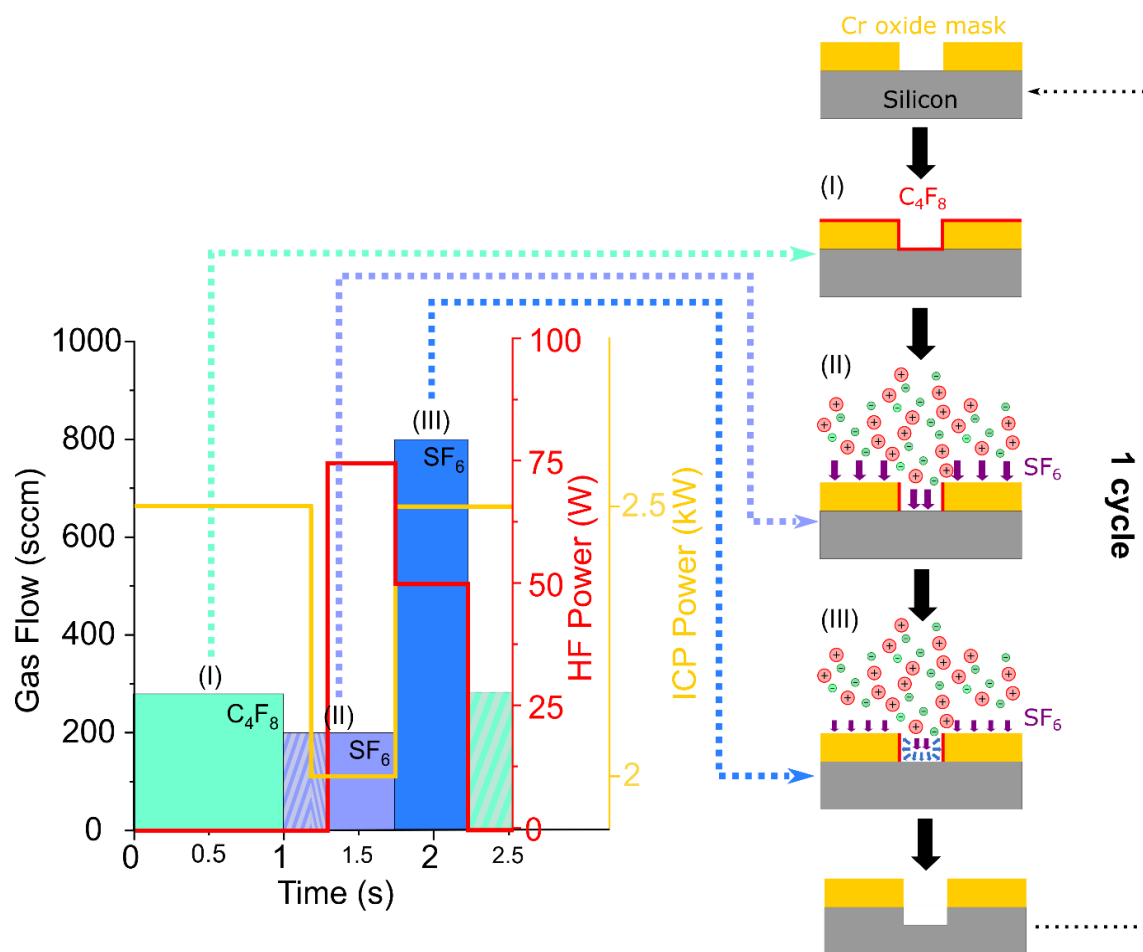


Figure A5.7.2. Schematic of the etching cycle with the three main steps for passivation (I), anisotropic break through etching (II), and isotropic Si etching (III), as well as the intermediate steps (grey boxes) used to prepare the chamber and sample for the subsequent procedure *i.e.*, through the exchange of the gas environment, the adjustment of the ICP power, or the phasing out of the passivation.

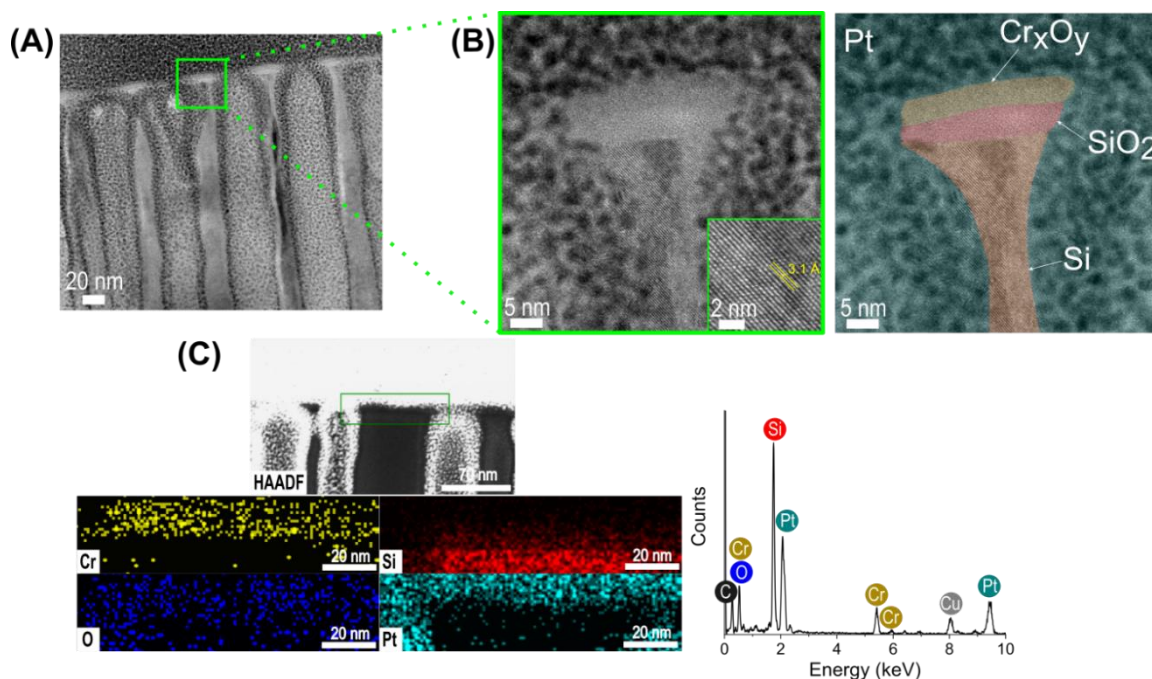


Figure A5.7.3. (A) TEM image of the porous silicon substrate (35 nm diameter pores). (B) High-resolution TEM of a pore wall and corresponding colour-coded image highlighting the different materials (Pt from capping protective layer, Cr_xO_y hard mask, SiO_2 native oxide layer and Si). The inset shows the lattice fringes of the Si structure ((111) plane - FCC). (C) STEM/EDX elemental mapping.

Table A5.7.1. Pore sizes and pore-pore distances quantified *via* AFM and SEM. The etched samples correspond to 30 cycles.

Pore size (nm)	BCP 1	Cr oxide 1	Etched Si 1
	34 ± 3	32 ± 4	37 ± 9
	BCP 2	Cr oxide 2	Etched Si 2
	400 ± 120	343 ± 85	366 ± 74
Pore- pore distance	BCP 1	Cr oxide 1	Etched Si 1
	60 ± 4	60 ± 5	67 ± 11
	BCP 2	Cr oxide 2	Etched Si 2
	541 ± 115	460 ± 86	480 ± 60

For pore sizes, a change in size of $\sim 8\%$ was detected from the BCP templates to the final material. Regarding the pore-pore distance, $\sim 11\%$ variation in value was observed. An additional analysis was conducted for the pore-pore distances based on power spectral density (PSD). The PSD spectra were obtained via the AFM and SEM images

(Figure A5.7.4). For BCP 1, pore-pore distances were found to be 50 nm, while for the respective Cr oxide mask (Cr oxide 1), 56 nm. For BCP 2, a pore-pore distance of 588 nm was detected, while it was 500 nm for the Cr oxide 2. Both results show minor changes in the sizes. For the etched surfaces, the PSD analysis did not show any clear peak which could be assigned to the pore-pore distance.

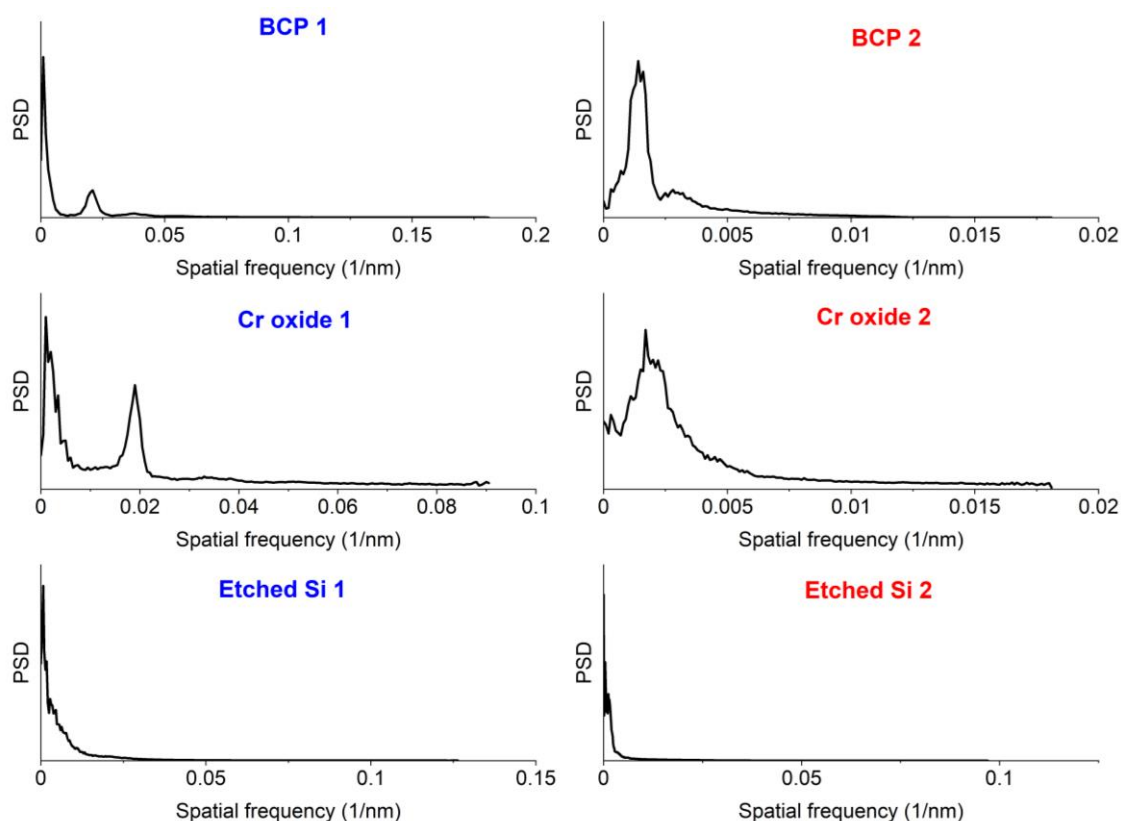


Figure A5.7.4: PSD spectra for the different BCP templates, Cr oxide masks, and etched silicon substrates. The spectra were calculated *via* the FFT of the AFM and SEM images.

Chapter 6

Conclusions and future work

The ability of self-assembly in block copolymer systems enables a wide range of morphologies with varied sizes. Moreover, their scalability and lateral order displays a significant potential to be applied in several applications *e.g.*, photonics, electronics, catalysis, biomaterials. A myriad of block copolymers have been designed throughout the years, many of them targeting a high χ , which improves phase separation and allows for the reduction of feature sizes. Among these, P2VP-*b*-PS systems demonstrate appealing characteristics; besides the high χ , the pyridinic nitrogen can bind to different ions, which allows the use of a patterned BCP as a template for inorganic structures. Nevertheless, the literature regarding “inverse” BCPs, in which the binding block is the majority phase, is still scarce. Hence, the aim of this thesis was to study such P2VP-majority P2VP-*b*-PS BCP systems and the subsequent fabrication of porous, thin layers.

In chapter 2, a thorough study of the phase separation of a P2VP-*b*-PS system was conducted in order to produce a vertical cylindrical phase. A static solvent vapour annealing method was applied by using a neutral solvent environment. Chloroform was chosen based on the solubility parameters related to the BCP, hence screening unfavourable interactions between the two BCP blocks and allowing vertical alignment. Time, temperature, and polymer concentration (film thickness) were varied and the influence on the morphology was observed. It was noticed that a temperature of 5 °C, a concentration of 1.5 % wt. BCP and a time interval of 40 min enabled the fabrication of highly ordered PS cylinders on a P2VP matrix. Subsequently, the cylindrical pattern was used as a template for metal cation infiltration. Fe, Ga, Ni and Cr oxide porous structures were obtained *via* selective infiltration followed by oxidation in an ultraviolet/ozone system. The metal oxide structures mimicked the BCP pattern with fidelity of the pattern period. Finally, the Cr oxide porous layer was employed as a hard mask for plasma etching of the silicon substrates. Porous silicon membranes were produced, which also mimicked the mask features. The pore depth observed was ~ 50 nm. Future experiments could include the infiltration with other inorganic species, such as nanoparticles. Moreover, improvement of the etch selectivity could be studied *via* the use of other metal oxide porous structures as hard masks.

In chapter 3, an investigation of the mechanism of liquid metal phase infiltration was performed. Our group has an extensive experience on metal infiltration into BCP templates and it was observed that different cations interact differently with a specific BCP. Therefore, three cations were selected, Ag^+ , Ni^{2+} and Cr^{3+} , to be infiltrated into a P2VP-majority BCP. The metal infiltrated-BCP films were then subjected to oxidation *via* ultraviolet/ozone. Differences on the metal oxide patterns were noticed; Ag^+ presented a complete loss of structure, Ni^{2+} and Cr^{3+} displayed a reproduction of the BCP pattern, while Ni^{2+} having lower quality compared to Cr^{3+} . Then, based on the differences observed, Raman spectroscopy was performed on the infiltrated BCP films before removal compared to the BCP. For Ag^+ , no shifts on the polymer bands were observed. For Ni^{2+} and Cr^{3+} , shifts on the pyridine modes indicated coordination of both metals to the pyridinic nitrogen. Moreover, shifts on the methylene twist also suggest interaction of Ni^{2+} and Cr^{3+} *via* π -interactions. XPS analyses elucidated the differences in infiltration regarding the three cations. Besides the peaks related to the quaternization and protonation of the pyridinic group, which was influenced by the type of cation, Ni^{2+} and Cr^{3+} displayed more peaks when compared to Ag^+ which are related to the binding between the nitrogen and the metal cation. Moreover, Cr^{3+} presented two more binding peaks, and it was suggested that the better infiltration might be related to the presence of Cr oxyanions. In future works, more metal cation interactions could be studied in BCP infiltration. For instance, one may choose other cations with the same oxidation states to compare with these results. Furthermore, similar studies could be conducted with another BCP.

Chapter 4 highlighted the use of porous iron oxide thin layers on glass substrates for the degradation of an antibiotic. Three P2VP-majority P2VP-*b*-PS systems with different molecular weights were employed to produce vertically aligned cylindrical morphologies. The BCP previously optimized in Chapter 2 was used along with two additional BCP systems. The phase separation of the two new systems was studied by varying time and polymer concentration in a SVA process. It was observed that an increase in the MW led to longer annealing times. Once the processes were optimised, the BCPs were used as templates for the infiltration of the iron ions. The polymers were then removed again by ultraviolet/ozone and characterised. In sequence, the porous iron oxide layer-covered glass substrates were applied in a photo-Fenton reaction enabling the degradation of levofloxacin. Parameters such as pore size, hydrogen peroxide concentration, and process time were varied to find the best set. The degradation experiments demonstrated the potential of the BCP templated iron oxide porous structures to be applied to pharmaceutical wastewater treatment. In terms of future work, additional

experiments could be performed with different antibiotics and also with solutions more similar to an actual effluent from industry.

In chapter 5, the high etch selectivity of BCP-templated chromium oxide porous masks towards silicon substrates was demonstrated. Two different molecular weight P2VP-*b*-PS BCPs were used to create polymer templates. Previous SVA optimisation was applied, generating vertical aligned cylinders, which were subsequently infiltrated with a chromium precursor. The infiltrated BCP template was oxidized, and the chromium precursor was converted into porous chromium oxide patterns. Those thin oxide layers were used as hard masks in a deep reactive ion etching procedure. A new recipe was developed, which consisted of three steps: passivation, break through and chemical/physical etching. The optimisation of the recipe allowed for the creation of pores with an aspect ratio of up to 50. Moreover, the use of the same recipe for a different pore size was also demonstrated. Finally, the porous silicon substrates were assessed for light absorption and thermal management as potential applications. The material showed low reflectance values which is ideal for solar energy harvesting, for instance, and low contact angle hysteresis, which is an interesting property for increasing thermal efficiency in evaporative cooling setups. One potential avenue for further expanding the research would be the optimisation of the etch recipe for different pores sizes to reduce defects. Furthermore, in thermal management, other liquids and temperatures could be applied to evaluate the porous silicon properties.

While this thesis documented new insights into the phase separation of “inverse” BCP systems and metal cation infiltration into BCP templates, there are still many challenges to be overcome in this technology; in particular, the currently unavoidable presence of some degree of pattern defects. In addition, other apparatus could be developed to enable a faster and controlled solvent vapour annealing, which would reduce costs and increase efficiency, hence further enabling possible translation into an industrial use. Regarding the metal oxide structures, they can find applications in diverse sectors *e.g.*, photovoltaics, catalysis and biomedical devices. The ability of the nitrogen to bind to different species can also lead to the production of different compounds following a nanostructured patterned, for example, metals or carbides. Then, by addressing the roadblocks of the BCP technology, more industries can potentially benefit from the myriad of BCP possibilities.

It is worthwhile exploring the major advances of this thesis. There is a clear need to develop patterning methods that can be used to create deep or through features at a

substrate surface. This work has extended the state-of-the-art and has defined the core methodology that allows these membrane-like structures rather than simple topographical patterning. The advantage of high aspect ratio features is the increase in the surface area of the substrate. This promotes additional surface activity for catalysis and other chemistries. Through pore systems, which is now demonstrated as possible for thin substrates, would bring tremendous advantages in terms of size selective filtration. We also believe this would allow membranes for advanced cooling systems where pore transport across the membrane and evaporation at the surface could develop highly efficient evaporative cooling setups. Finally, we assert this work has much enhanced our knowledge and understanding of “inverse” BCP systems and their potential applications.