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Experimental implementation and characterization of two-dimensional material optomechanical cavities with strain engineering based on spin-crossover nanomaterials.

End of Degree Project

Bachelor's degree in Engineering Physics

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Abstract

This Bachelor's Thesis aims at the experimental implementation and characterization of tunable optomechanical and photonic platforms based on two-dimensional materials and integrated photonic devices using strain engineering strategies enabled by spin-crossover (SCO) nanomaterials. These materials exhibit stimulus-induced changes in volume and optical properties, providing a mechanism for the dynamic tuning of photonic and optomechanical systems.

The work is structured around two complementary experimental platforms. First, the actuation capabilities of SCO materials are validated in silicon-based photonic devices. Silicon Micro-Ring Resonators (MRRs) are functionalized with an active PMMA/SCO nanocomposite layer, enabling the transduction of the SCO phase transition into measurable optical resonance shifts. This demonstrates the feasibility of exploiting SCO-induced strain to tune integrated photonic devices under ambient conditions.

The second part focuses on optomechanical platforms based on suspended graphene membranes, commonly known as nanodrums. A deterministic dry-transfer methodology is implemented and optimized to fabricate suspended graphene membranes on both rigid silicon cavities and flexible elastomeric PDMS microcavities. The resulting devices are characterized by optical microscopy, atomic force microscopy, and Raman spectroscopy to evaluate their morphology, structural integrity, crystalline quality, and strain state.

This work establishes the experimental foundations for the integration of SCO nanomaterials into advanced tunable photonic and optomechanical devices operating under ambient conditions.

Keywords: Optomechanical cavities; two-dimensional materials; strain engineering; spin crossover; functional nanomaterials; experimental characterization

Resumen

Este Trabajo Fin de Grado tiene como objetivo la implementación y caracterización experimental de plataformas fotónicas y optomecánicas sintonizables basadas en materiales bidimensionales y dispositivos fotónicos integrados, utilizando estrategias de ingeniería de deformación habilitadas por nanomateriales de cambio de espín (spin-crossover, SCO). Estos materiales presentan cambios de volumen y de propiedades ópticas inducidos por estímulos externos, proporcionando un mecanismo para la sintonización dinámica de sistemas fotónicos y optomecánicos.

El trabajo se estructura en torno a dos plataformas experimentales complementarias. En primer lugar, se validan las capacidades de actuación de los materiales SCO en dispositivos fotónicos basados en silicio. Para ello, resonadores de anillo de silicio (Micro-Ring Resonators, MRRs) se funcionalizan con una capa híbrida de PMMA/SCO, permitiendo la transducción de la transición de fase SCO en desplazamientos medibles de la resonancia óptica. Esto demuestra la viabilidad de explotar la deformación inducida por SCO para la sintonización de dispositivos fotónicos integrados en condiciones ambientales.

La segunda parte se centra en plataformas optomecánicas basadas en membranas suspendidas de grafeno, comúnmente denominadas nanodrums. Se implementa y optimiza una metodología determinista de transferencia en seco para fabricar membranas suspendidas de grafeno tanto sobre cavidades rígidas de silicio como sobre microcavidades elastoméricas flexibles de PDMS. Los dispositivos obtenidos se caracterizan mediante microscopía óptica, microscopía de fuerza atómica y espectroscopía Raman para evaluar su morfología, integridad estructural, calidad cristalina y estado de deformación.

Este trabajo establece las bases experimentales para la integración de nanomateriales SCO en dispositivos fotónicos y optomecánicos avanzados y sintonizables que operen en condiciones ambientales.

Palabras clave: Cavidades optomecánicas; materiales bidimensionales; ingeniería de deformación; *spin crossover*; nanomateriales funcionales; caracterización experimental

Resum

Aquest Treball de Fi de Grau té com a objectiu la implementació i caracterització experimental de plataformes fotòniques i optomecàniques sintonitzables basades en materials bidimensionals i dispositius fotònics integrats, utilitzant estratègies d'enginyeria de deformació habilitades per nanomaterials de canvi d'espín (spin-crossover, SCO). Aquests materials presenten canvis de volum i de propietats òptiques induïts per estímuls externs, proporcionant un mecanisme per a la sintonia dinàmica de sistemes fotònics i optomecànics.

El treball s'estructura al voltant de dues plataformes experimentals complementàries. En primer lloc, es validen les capacitats d'actuació dels materials SCO en dispositius fotònics basats en silici. Per a això, ressonadors d'anell de silici (Micro-Ring Resonators, MRRs) es funcionalitzen amb una capa activa nanocomposta de PMMA/SCO, permetent la transducció de la transició de fase SCO en desplaçaments mesurables de la ressonància òptica. Açò demostra la viabilitat d'explotar la deformació induïda pels materials SCO per a la sintonia de dispositius fotònics integrats en condicions ambientals.

La segona part se centra en plataformes optomecàniques basades en membranes suspeses de grafé, comunament denominades nanodrums. S'implementa i optimitza una metodologia determinista de transferència en sec per a fabricar membranes suspeses de grafé tant sobre cavitats rígides de silici com sobre microcavitats elastomèriques flexibles de PDMS. Els dispositius obtinguts es caracteritzen mitjançant microscòpia òptica, microscòpia de força atòmica i espectroscòpia Raman per a avaluar-ne la morfologia, la integritat estructural, la qualitat cristal·lina i l'estat de deformació.

Aquest treball estableix les bases experimentals per a la integració de nanomaterials SCO en dispositius fotònics i optomecànics avançats i sintonitzables que operen en condicions ambientals.

Paraules clau: Cavitats optomecàniques; materials bidimensionals; enginyeria de deformació; *spin crossover*; nanomaterials funcionals; caracterització experimental.



RESUMEN EJECUTIVO

La memoria del TFG del GIFIS debe desarrollar en el texto los siguientes conceptos, debidamente justificados y discutidos, centrados en el ámbito de la IFIS

CONCEPT (ABET)	CONCEPTO (traducción)	¿Cumple? (S/N)	¿Dónde? (páginas)
1. IDENTIFY:	1. IDENTIFICAR:		
1.1. Problem statement and opportunity	1.1. Planteamiento del problema y oportunidad	S	7 – 10
1.2. Constraints (standards, codes, needs, requirements & specifications)	1.2. Toma en consideración de los condicionantes (normas técnicas y regulación, necesidades, requisitos y especificaciones)	S	11–12
1.3. Setting of goals	1.3. Establecimiento de objetivos	S	10–11
2. FORMULATE:	2. FORMULAR:		
2.1. Creative solution generation (analysis)	2.1. Generación de soluciones creativas (análisis)	S	24–67
2.2. Evaluation of multiple solutions and decision-making (synthesis)	2.2. Evaluación de múltiples soluciones y toma de decisiones (síntesis)	S	24–67
3. SOLVE:	3. RESOLVER:		
3.1. Fulfilment of goals	3.1. Evaluación del cumplimiento de objetivos	S	67–68
3.2. Overall impact and significance (contributions and practical recommendations)	3.2. Evaluación del impacto global y alcance (contribuciones y recomendaciones prácticas)	S	69–70

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List of Acronyms

NTC	Nanophotonics Technology Center
PIC	Photonic Integrated Circuit
SOI	Silicon on Insulator
OM	Optomechanical
FWHM	Full Width at Half Maximum
Q	Quality Factor
ER	Extinction Ratio
SNR	Signal-to-Noise Ratio
SCO	Spin-crossover
LS	Low Spin
HS	High Spin
IAM	Innovative Advanced Materials
RT	Room Temperature
MRR	Micro-Ring Resonator
MRRW	Windowed Micro-Ring Resonator
AFM	Atomic Force Microscopy
TEM	Transmission Electron Microscopy
DLS	Dynamic Light Scattering
PMMA	Poly(methyl methacrylate)
PDMS	Poly(dimethylsiloxane)
HOPG	Highly Oriented Pyrolytic Graphite
CCD	Charge-Coupled Device

1. Introduction

Integrated photonics combines fundamental physics and advanced nanofabrication to miniaturize complex optical systems onto a single semiconductor chip. Just as the invention of the first macroscopic transistor [1] paved the way for modern state-of-the-art microprocessors containing billions of components, integrated photonics is driving the next technological revolution in high-speed data communications, quantum computing, and ultra-sensitive biosensing [2, 3, 4]. By utilizing photons rather than electrons as the primary information carriers, these photonic platforms overcome several physical bottlenecks inherent to traditional electronics. Because photons possess zero rest mass and no electric charge, they propagate with minimal thermal dissipation and without electromagnetic crosstalk [5]. This fundamental behavior enables significantly higher transmission bandwidths alongside reduced energy consumption.

However, while standard silicon-based platforms excel at guiding and confining light, they are intrinsically passive. Consequently, expanding the capabilities of these architectures relies on developing **tunable integrated photonic devices** [6]. Achieving dynamic control over optical signals requires confining light to the nanoscale, transforming the optical field into a sensitive probe to explore enhanced light-matter interactions. By integrating low-dimensional materials into this optical near field, the refractive index and mechanical response of the underlying photonic circuits can be actively modulated, offering a versatile framework to study the coupled physics of emerging material systems.

Framed within this context, this bachelor’s thesis focuses on the experimental implementation and characterization of **tunable photonic and optomechanical platforms enabled by functional phase change nanomaterials**. The work is structured around two complementary architectures: Windowed Micro-Ring Resonators (MRRWs), used to study optical modulation induced by Spin-Crossover (SCO) phenomenon [7], and suspended graphene nanodrums [8], developed as optomechanical cavities for strain-dependent characterization.

This work details the fabrication and characterization protocols required to evaluate both technological domains, establishing a structural basis where these optical and mechanical research lines converge through a single active driving force: Spin crossover (Spin-crossover (SCO)) complexes [9]. First, the optical response of MRR devices is analyzed, exploiting the interaction of the local evanescent field with the surrounding medium as a sensitive platform for targeted functionalization. Concurrently, the project details the deterministic fabrication and nanoscale analysis of 2D material nanodrums, engineering these suspended graphene architectures over both passive silicon micro-cavities and compliant polymeric (Poly(dimethylsiloxane), PDMS) substrates. By acting as stimuli-responsive molecular actuators, the integrated SCO nanomaterials provide the physical mechanism to drive dynamic tuning across both host architectures. Whether by modulating the optical resonances of the photonic rings or by inducing mechanical strain within both nanodrums architectures, the integration of these complexes enables reconfigurable

device behaviors. The principles and structural characteristics of these two host platforms are detailed below.

1.1. Active Photonic Sensing: The MRRW Platform

The foundational architecture for guiding light in this thesis relies on Photonic Integrated Circuit (PIC) technology within the Silicon on Insulator (SOI) platform. Light is tightly confined within these micro-waveguides due to the high refractive index contrast between the silicon core and the surrounding silicon dioxide (SiO_2) cladding. An MRR consists of a closed-loop waveguide—typically circular or racetrack-shaped—positioned close to a straight bus waveguide. Its operational principle relies on the evanescent field of the propagating light; when phase-matching conditions are met, specific wavelengths couple into the ring, constructively interfering to generate sharp resonance dips in the transmission spectrum.

In standard applications, these waveguides are covered by a thick protective oxide layer to isolate the optical mode from environmental noise. However, to implement an active sensing platform, a localized etching process opens a sensing window directly over a section of the resonant loop, as illustrated in Figure 1.1. This structural modification defines the Windowed Micro-Ring Resonator (MRRW) configuration, deliberately exposing the evanescent tail of the resonant light. Consequently, the resonator becomes highly sensitive to perturbations in this specific cladding area. Any variation in the material deposited over the window alters the local refractive index, shifting the effective refractive index (n_{eff}) of the guided optical mode. This interaction induces a measurable shift in the resonance wavelength ($\Delta\lambda$), establishing the MRRW as a precise optical transducer.

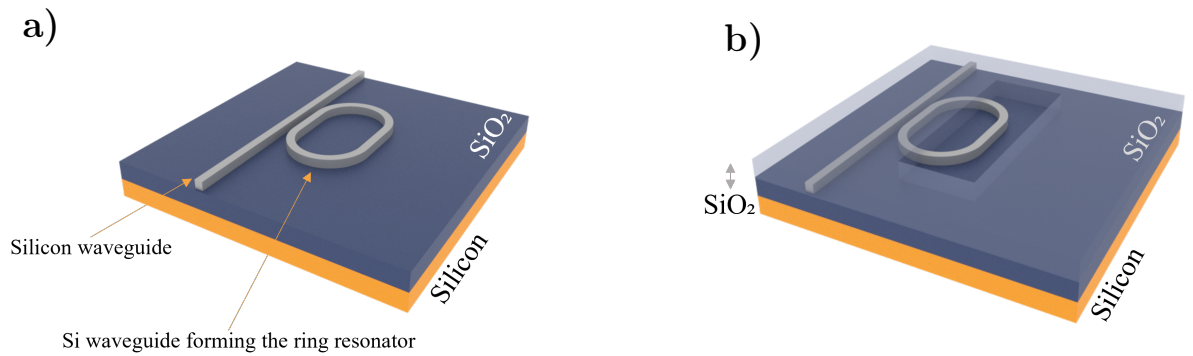


Figure 1.1: 3D schematic illustration of the optical resonators. (a) Standard Micro-Ring Resonator (MRR). (b) Windowed Micro-Ring Resonator (MRRW) showcasing the exposed sensing area.

1.2. Nanomechanical Oscillators: The Graphene Nanodrum Architecture

While integrated waveguides enable optical routing, the transduction of external physical stimuli requires responsive mechanical interfaces. Nanomechanical resonators formed by suspending thin two-dimensional (2D) membranes, such as graphene, over pre-patterned micro-cavities define the foundational Optomechanical (OM) nanodrum architecture, as illustrated in Figure 1.2. Similar to macroscopic membranes, the mechanical resonance frequency (f_0) and quality factor (Q) of the suspended structure are governed by its mass, geometry, and built-in tensile strain. Because few-layer graphene exhibits an extremely low mass-per-area density and high mechanical strength, these nanodrums operate as sensitive nanoscale oscillators. External perturbations—such as fluctuations in local pressure, applied strain, or mass deposition—alter the membrane’s vibrational dynamics, providing a versatile platform for OM sensing and actuation.

Traditionally, these suspended architectures are fabricated on rigid substrates. The baseline methodology developed in this thesis involves the deterministic transfer of mechanically exfoliated graphene flakes onto standard silicon micro-cavities using a high-precision micromanipulation setup to minimize interfacial defects. In this configuration, the static silicon substrate allows the analysis of the intrinsic vibrational properties of the isolated 2D membrane.

To expand upon these results, this project develops a complementary architecture based on polymeric nanodrums. Utilizing the high replication fidelity and conformal wetting properties of elastomeric molding [10, 11] to fabricate the pre-patterned viscoelastic PDMS substrates. The graphene flakes are then transferred onto them, setting the stage for their subsequent characterization. Ultimately, both the rigid silicon and the compliant polymeric platforms are engineered to serve as the framework for the subsequent integration of active, stimuli-responsive systems, realizing the concept of a tunable OM device.

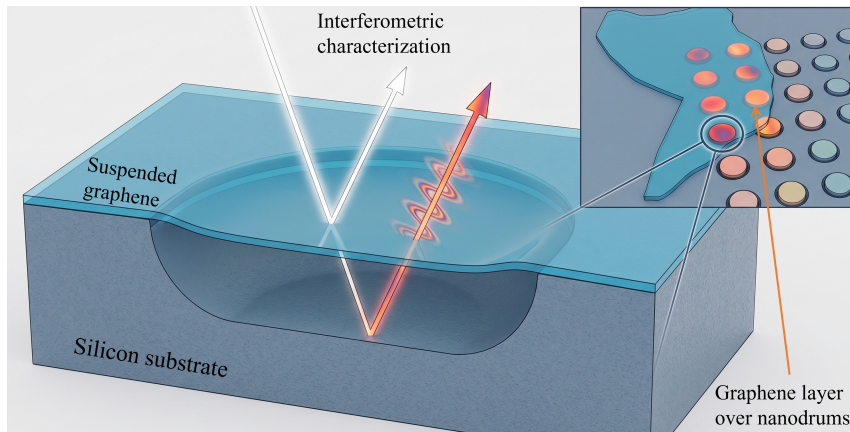


Figure 1.2: 3D schematic illustration of a suspended Graphene Nanodrum architecture.

2. Theoretical Background

2.1. Fundamentals of Spin Crossover (SCO) Nanomaterials

SCO behavior is a phenomenon present in specific molecular compounds, such as the coordination complexes of iron (II) transition-metal ions, in which the electronic configuration can be reversibly switched between two distinct spin states under certain external stimuli. The SCO process involves the rearrangement of $3d$ electrons between a configuration with a maximum number of paired electrons Low Spin (LS) and one with a maximum number of unpaired electrons High Spin (HS) [12].

To illustrate this phenomenon at the molecular scale, Figure 2.1a shows the electronic rearrangement of an octahedral Fe(II) complex during the spin transition. As depicted, the switch from a HS ($S = 2$) state to a LS, ($S = 0$) state involves a redistribution of the electrons between the t_{2g} and e_g orbitals. This splitting into two distinct energy levels, separated by an energy gap denoted as Δ (or $10Dq$), occurs because the ligands surrounding the central metal ion generate an electric field that lifts the degeneracy of the $3d$ orbitals. The core mechanism of SCO arises from a competition between this energy gap (Δ) and the electron pairing energy (P). When the local environment is modified such that $\Delta \approx P$, the system becomes thermodynamically unstable, and external stimuli can readily trigger the spin transition. This fundamental electronic redistribution is the direct cause of the metal-ligand bond length contraction, which ultimately translates into the macroscopic volume reduction of the SCO nanoparticle [13].

The most common physical perturbations that yield a spin state transition are variations in temperature and pressure, alongside applied magnetic fields, light irradiation, or electrical voltage [14]. The macroscopic manifestation of this spin crossover involves simultaneous alterations in the material's structural volume, magnetic susceptibility, and electrical properties. Optically, this fundamental change is often evidenced by a pronounced thermochromic shift, as illustrated in Figure 2.1b.

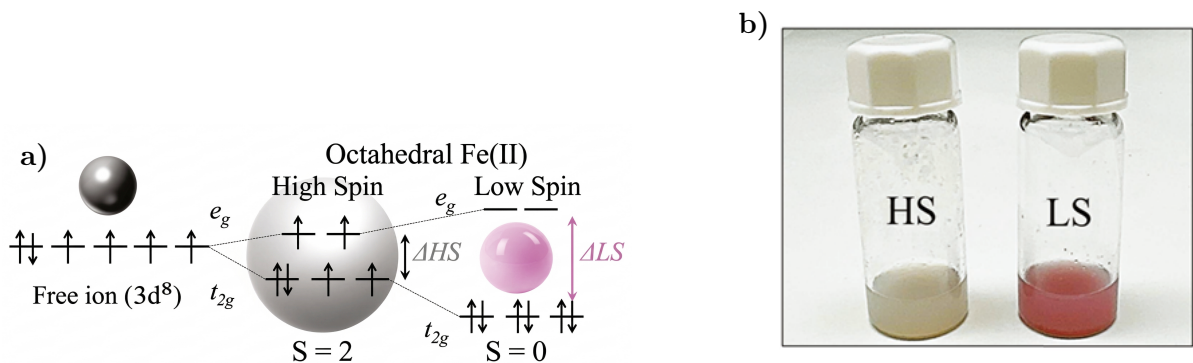


Figure 2.1: SCO phenomenon. (a) Electronic configuration diagram. (b) Thermal transition profile. Reproduced from [13].

A particularly promising class of SCO materials exhibits strong intermolecular cooperativity, resulting in a distinctly hysteretic response. This hysteresis confers thermal bistability to the system, effectively establishing a molecular memory effect [15]. This cooperative behavior is fundamentally driven by the significant volumetric expansion, often of the order of several percent in volume ($\Delta V \approx 1 - 10\%$ in typical Fe(II) complexes), arising from the structural rearrangement between the HS and LS configurations. Crucially for active nanophotonics, this unit cell volume change upon the SCO can be directly linked to a measurable refractive index change (Δn) through the empirical Gladstone-Dale relationship:

$$\frac{\Delta V}{V} = \frac{\Delta n}{1 - n} \quad (1)$$

This correlation predicts a substantial $\Delta n \approx 0.01 - 0.1$ across the whole vis-NIR range when transitioning from the HS to the LS [6].

To be suitable for practical implementation in integrated photonic circuits and optoelectronic systems, phase-change materials must meet key requirements such as high optical contrast, fast and reversible switching, low energy consumption, and scalability [16]. The ability to externally modulate the aforementioned mechanical and optical properties via temperature (T), pressure (P), or optical stimuli establishes SCO materials as excellent candidates for ultra-low power optomechanical dynamic actuators that fulfill these strict technological demands. This hysteretic behavior is depicted in Figure 2.2.

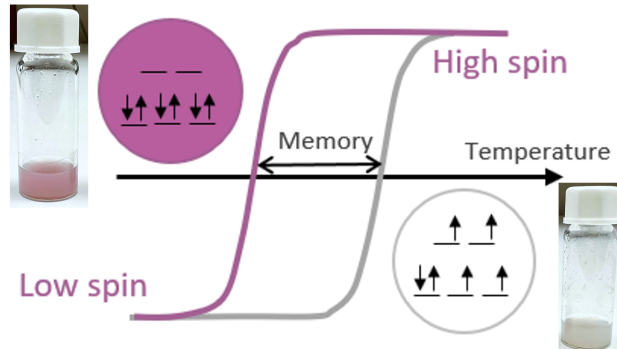


Figure 2.2: SCO thermal transition showing the bistability window and the corresponding electronic configurations of the LS and HS states.

This thermal bistability enables the system to retain either the HS or LS state at the exact same ambient temperature, strictly dictated by its thermal history [17]. The transition to the HS state is thermally induced upon heating, whereas the reversion to the LS state occurs upon cooling. The magnitude of this thermal hysteresis loop defines the operational robustness of the memory effect: a wider hysteretic window provides a highly stable bistable regime, effectively shielding the structural state from unwanted volatility caused by minor environmental thermal fluctuations.

From a materials engineering perspective, while isolated SCO nanoparticles undergo microscopic volumetric changes during the spin transition, these individual expansions are inherently insufficient to deform a macroscopic solid structure. Achieving robust opto-elastomeric actuation requires embedding these active nanoparticles within compliant polymeric matrices, such as Poly(methyl methacrylate) (PMMA) or PDMS. This generates a synergistic composite where the viscoelastic host homogeneously collects the localized molecular expansions, effectively translating isolated atomic switching into usable macroscopic mechanical work for the dynamic tuning of resonant devices.

2.2. Principles of Optical Resonance and Resonator Characterization

The fundamental operational principle of MRR is governed by the constructive interference of light propagating within the closed-loop waveguide. When a straight bus waveguide is positioned in close proximity to the resonator, the evanescent field of the guided mode overlaps spatially with the modal profile of the ring. This overlap facilitates the directional coupling of optical power into the cavity, provided that the phase-matching condition is satisfied:

$$\lambda_{\text{res}} = \frac{2\pi R n_{\text{eff}}}{m} \quad (2)$$

where m is an integer representing the azimuthal mode order, λ_{res} is the resonance wavelength, R is the physical radius of the ring, and n_{eff} is the effective refractive index of the guided optical mode. In the specific architecture utilized in this thesis (MRRW) the targeted removal of the top oxide cladding allows the evanescent field to interact directly with the external environment. Consequently, any highly localized variation in the refractive index or structural geometry at this interface perturbs n_{eff} , inducing a precisely measurable shift in the resonance wavelength ($\Delta\lambda$). A comprehensive visual representation of these coupling dynamics and their corresponding spectral footprint is illustrated in Figure 2.3.

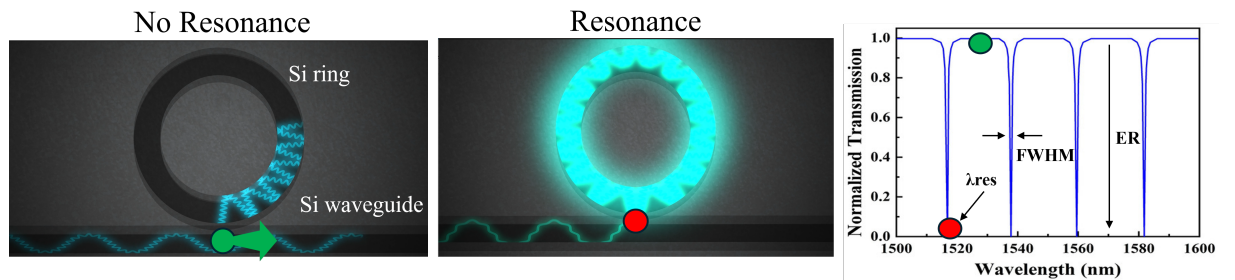


Figure 2.3: Operational principle of the MRR, illustrating the optical behavior during the off-resonance and on-resonance states, alongside its corresponding transmission spectrum.

To quantitatively evaluate the performance of these photonic devices and their viability as ultra-sensitive transducers, three critical spectral parameters must be defined:

-
- **Full Width at Half Maximum (FWHM):** The spectral width of the resonance dip measured at half of its maximum depth. It provides a direct metric of the resonator’s spectral selectivity.
 - **Quality Factor (Quality Factor (Q)):** Defined as the fractional bandwidth of the resonance ($Q = \lambda_{\text{res}}/\text{FWHM}$), the Q-factor quantifies the photon lifetime within the cavity. Physically, it represents the ratio of the time-averaged energy stored in the ring to the energy dissipated per optical cycle. A higher Q-factor denotes minimized internal propagation losses, translating into sharper, narrower resonance dips that are essential for resolving infinitesimal environmental perturbations.
 - **Extinction Ratio (Extinction Ratio (ER)):** This parameter determines the absolute contrast of the resonance, calculated as the logarithmic ratio between the baseline transmission power and the residual power at the resonance minimum ($ER = 10 \log_{10}(P_{\text{baseline}}/P_{\text{min}})$). A maximized ER indicates optimal critical coupling between the bus waveguide and the ring, which fundamentally enhances the Signal-to-Noise Ratio (SNR) in optical sensing readouts.

Within the scope of this project, these parameters serve as the primary quantitative metrics for evaluating the integrated sensing platform.. A characterized MRRW exhibiting a high Q-factor and a distinct ER provides the spectral resolution required to detect minute $\Delta\lambda$ shifts. Crucially, in our experimental realization, this optical precision enables the direct transduction of the physical phenomena occurring at the sensing window—specifically, the detection of the mechanical strain and localized refractive index modulation exerted by the integrated SCO nanomaterials. By fulfilling these optical criteria, the MRRW platform successfully provides a dynamic, real-time optical readout of the molecular spin-state transition.

This spectral shift can be mathematically described to a first-order approximation by the fundamental sensing equation of the resonator:

$$\Delta\lambda = \Delta n \frac{\lambda_{\text{res}}}{n_g} \quad (3)$$

where $\Delta\lambda$ is the induced resonance shift, Δn is the perturbation in the effective refractive index caused by the sensing window, and n_g is the group index of the guided mode, which accounts for the chromatic dispersion within the silicon waveguide.

3. State of the Art

3.1. SCO Nanomaterials in Modern Applied Physics

Traditionally, the study of SCO complexes was predominantly confined to fundamental coordination chemistry study, with a primary focus on characterizing their bulk magnetic susceptibility and optical absorption at cryogenic temperatures. However, the state of the

art in modern applied physics has experienced a profound paradigm shift. The contemporary research frontier is no longer solely concerned with synthesizing new SCO compounds, but rather with harnessing their stimulus-induced phase transitions at the nanoscale for practical integration into solid-state devices operating at Room Temperature (RT) [18].

This transition towards nanotechnology is fundamentally driven by the bistability of SCO materials, which enables them to act as non-volatile memory elements and ultra-low power molecular actuators. Recent applied research has successfully branched into main technological avenues to exploit the dramatic structural expansion and dielectric variation associated with the transition from the LS to the HS state [19].

This transition towards practical solid-state integration has progressed through distinct avenues of applied nanotechnology. In the field of micro-electromechanical systems (MEMS), Manrique-Juárez *et al.* [20] integrated SCO films onto rigid silicon micro-cantilevers, proving that the interfacial stress generated during the phase transition is sufficient to drive macroscopically visible, reversible bending. Concurrently, within active nanophotonics, Molnár *et al.* [6] employed the pronounced refractive index modulation inherent to SCO phase transition, to dynamically tune optical resonances without requiring structural geometric reconfigurations. To overcome the recurring issues of crystalline fatigue and brittle delamination on these rigid platforms, Salmon *et al.* [21] pioneered the synthesis of SCO-polymer nanocomposites, demonstrating that integrating the active nanoparticles within elastomeric matrices preserves their switching cooperativity while utilizing the polymer network as a continuous strain-transfer medium. Nevertheless, isolating and quantifying the pure mechanical work generated by these individual building blocks remained heavily constrained by substrate clamping and thermal drift. To resolve this limitation, Pinilla-Cienfuegos *et al.* [13] deployed an optical levitation setup within a Paul trap to isolate single SCO nanoparticles, definitively verifying a substrate-free, reversible opto-volumetric expansion that confirms their capability to act as autonomous nanoscale actuators.

The empirical confirmation of this localized, material-intrinsic mechanical actuation provides a promising framework for addressing open bottlenecks in nanophotonics. Specifically, the capability of SCO complexes to generate controlled structural deformation at the nanoscale can be strategically exploited to drive the next generation of OM architectures, where the precise management of internal mechanical stress has recently emerged as a fundamental tool to overcome ambient thermal limitations.

3.2. OM and the Strain Engineering Frontier

The field of cavity optomechanics has traditionally faced a fundamental physical barrier: thermal decoherence. To observe quantum phenomena or to achieve ultra-high sensitivity in mechanical sensing platforms, the thermal noise inherent to the environment must be rigorously suppressed. Historically, this required operating OM cavities within cryogenic dilution refrigerators at temperatures approaching absolute zero [22, 23]. However, transitioning these technologies from fundamental laboratory physics to scalable, real-world applications demands stable operation at RT, representing one of the most pressing

challenges in modern nanophotonics.

Recent advancements have demonstrated that the mechanical quality factor (Q) of nanoscale resonators can be drastically enhanced without cryogenic cooling through the implementation of elastic strain engineering. As pioneered by Ghadimi *et al.* [24], concentrating high intrinsic tensile stress within suspended structures allows the resonator to leverage the phenomenon of dissipation dilution. This mechanism significantly increases the mechanical resonance frequency—thereby boosting the stored energy (E_{stored})—while geometrically diluting the internal bulk acoustic losses ($E_{\text{dissipated}}$). When applied to two-dimensional materials and graphene, as detailed by Peng *et al.* [25], these localized strain fields modify the atomic bond lengths and directly alter the low-energy electronic Hamiltonian of the crystal lattice, offering a reliable path to tune both the electronic band structure and the resulting photonic properties. This strain-driven paradigm recently culminated in the milestone achieved by Huang *et al.* [26], who engineered an ultralow-noise cavity platform to demonstrate quantum optomechanics at RT, proving that high mechanical Q -factors can definitively outpace the thermal decoherence rate under ambient conditions.

Despite its theoretical and empirical success, the practical implementation of dynamic strain engineering within photonic integrated circuits (PIC) presents significant integration challenges. Currently, inducing and modulating tensile strain on-chip relies heavily on external, bulky mechanisms, such as piezoelectric actuators, mechanical bending of the underlying substrate, or high-voltage electrostatic gates. These conventional approaches severely limit device miniaturization, increase overall power consumption, and hinder scalable on-chip integration.

Consequently, a critical technological void exists in the current state of the art: the field requires an intrinsic, self-contained mechanism to dynamically induce localized, high-magnitude strain at the nanoscale, entirely bypassing the need for external macroscopic hardware.

3.3. Motivation - SCO as Tunable Strain Actuators

To overcome the scaling bottlenecks, high operational voltages, and structural footprint inherent to conventional macroscopic actuation hardware, the frontier of nanophotonics must transition toward intrinsic, self-contained tuning mechanisms. Given that room-temperature (RT) optomechanical (OM) devices urgently demand localized strain fields to mitigate thermal noise, and that molecular spin crossover (SCO) complexes undergo a profound volumetric expansion upon their electronic transition, a compelling solution lies in the hybrid co-integration of these two independent domains. Utilizing stimulus-responsive molecular materials as chip-intrinsic actuators offers a scalable paradigm to dynamically manipulate mechanical and optical fields directly within the device near-field, completely bypassing the need for external positioning elements.

However, establishing a reliable mechanical link between molecular-level electronic transitions and the active region of solid-state devices requires an efficient nanomechanical interface. Because isolated SCO nanoparticles cannot deform rigid semiconductor struc-

tures on their own, this research leverages thin-film polymeric nanocomposites to bridge this structural mismatch. Acting as a continuous viscoelastic transducer, the compliant polymer matrix absorbs the localized volumetric expansion of the embedded nanoparticles and transfers this collective strain directly to the underlying device. Ultimately, this multi-material synergy converts molecular energy into macroscopic structural actuation, providing the fundamental mechanism required to realize self-contained, tunable nanophotonic platforms.

4. Objectives of the Bachelor’s Thesis

The main objective of this thesis is to demonstrate the experimental viability of room-temperature (RT) tunable optomechanical (OM) and photonic platforms by utilizing spin crossover (SCO) nanocomposites as solid-state, material-intrinsic strain actuators. To achieve this, the project explores the practical co-integration of molecular magnetism, polymer mechanics, and nanoscale architectures, aiming to entirely bypass the need for external macroscopic hardware.

To systematically realize this fundamental goal, the experimental investigation is structured into three specific, interconnected objectives:

4.1. O1. Characterization of Hybrid SCO/PMMA Photonic Resonators (MRR)

To quantify the mechano-optical transduction efficiency of a hybrid SCO/PMMA thin-film composite integrated onto rigid silicon PICs. This involves the localized deposition of the active matrix onto windowed MRR architectures to evaluate the optical modulation—specifically, tracking resonance wavelength shifts ($\Delta\lambda$), thermal hysteresis profiles, and variations in cavity coupling dynamics, including the quality factor (Q) and extinction ratio (ER)—induced by the molecular phase transition.

4.2. O2. Fabrication and Characterization of Graphene Optomechanical Nanodrums on Silicon

To fabricate and characterize suspended graphene nanodrums over rigid silicon microcavities using a high-precision micromanipulation protocol. Addressing the physical handling constraints of 2D materials, this objective focuses on optimizing the deterministic transfer of exfoliated flakes, mapping their structural morphology via optical and Atomic Force Microscopy (AFM), and probing their vibrational mechanics and intrinsic strain profiles through Raman spectroscopy, establishing a reference state prior to the subsequent integration of the SCO material.

4.3. O3. Design, Fabrication and Characterization of Graphene Optomechanical Nanodrums on PDMS

To engineer and evaluate an unprecedented class of optomechanical devices by translating the cavity architecture from rigid silicon to a viscoelastic PDMS. This novel approach aims to establish the viability of incorporating molecular actuators directly within the structural matrix of the cavity itself, turning the passive substrate into an active platform capable of directly straining the 2D membrane.

4.4. Chronogram: Gantt Chart

The project timeline is organized on a weekly basis from its inception. The following Gantt chart breaks down the planned activities according to their corresponding specific objectives, mapping out the start and end dates for each task to trace the progression toward the main goal:

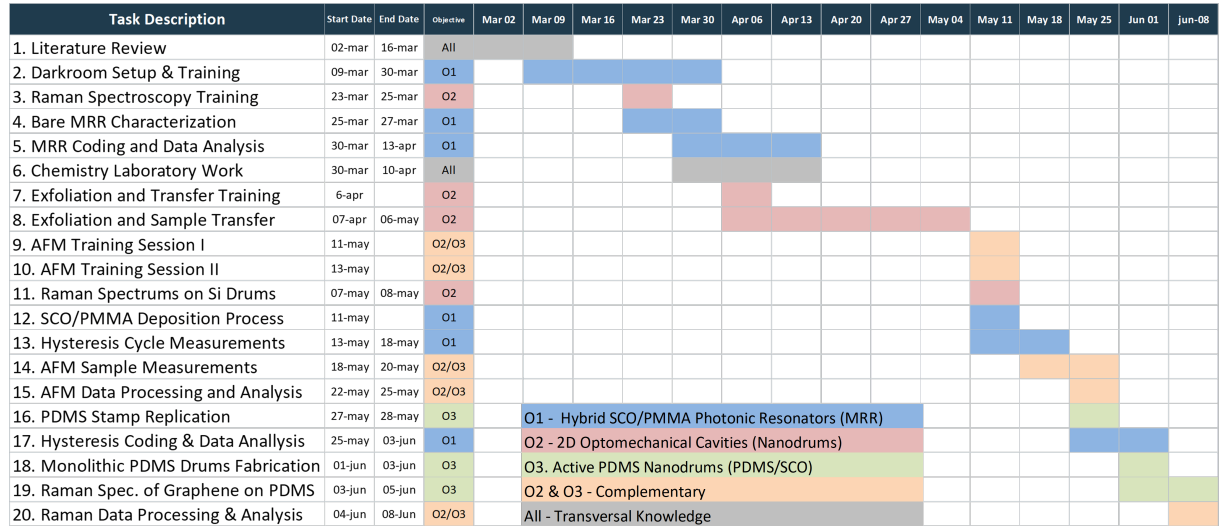


Figure 4.1: Project chronogram detailing the task scheduling and specific objectives.

5. Experimental Methodology

The experimental work was carried out at the Nanophotonics Technology Center (NTC) within *Universitat Politècnica de València*, using certified research facilities and equipment that comply with the applicable laboratory safety regulations and institutional protocols. All experimental procedures were conducted under the supervision of experienced researchers, ensuring adherence to technical, operational, and safety requirements throughout the project. The experimental methodology detailed herein relies on both fundamental baseline platforms detailed previously. These were provided as pre-fabricated substrates to serve as the structural samples for the experimental work. Both semiconductor structures were previously designed and fabricated at the NTC, employing high-

resolution Electron-Beam (E-beam) nanolithography [27]. The first platform utilizes a pre-fabricated photonic integrated circuit (PIC), specifically the MOSAIC J67 chip, which comprises an array of alternating standard and windowed MRR structures designed to host the active SCO composite matrix. The second, consists of a pre-patterned SiO₂ substrate featuring specialized nanoscale cavities, establishing the rigid foundation required for the subsequent micro-assembly of the suspended nanodrums.

Consequently, the core of the experimental procedure does not involve the initial lithographic fabrication of these base architectures, but rather focuses on their specific functionalization, the deterministic transfer of 2D nanomaterials, and the custom synthesis of complementary elastomeric substrates built upon these initial foundations.

5.1. Materials

5.1.1. Phase-change Nanomaterial: BF₄ Nanoparticles (SCO)

The active spin crossover (SCO) material utilized in this study consists of silica-coated iron(II)-triazole coordination polymer nanoparticles, which were specifically synthesized and provided through a research collaboration with the *Instituto de Ciencia Molecular* (ICMol). According to the chemical formulation, the precise composition of the employed nanostructures is Fe(Htrz)_{2.9}(NH₂Trz)_{0.1}(BF₄)₂@SiO₂ [28]. In this supramolecular architecture, the iron(II) centers are bridged by triazole (Htrz) and amino-triazole (NH₂Trz) ligands to form one-dimensional polymeric chains, while the tetrafluoroborate (BF₄⁻) groups act as the counterions to balance the overall structural charge. The complex is encapsulated within a silica shell (SiO₂), a critical synthetic step designed to constrain the particle growth, prevent severe agglomeration, and enhance colloidal stability in organic solvents.

The morphological and dimensional properties of these functional nanoparticles were systematically characterized. Transmission Electron Microscopy (TEM) analysis reveals that the nanoparticles exhibit a distinct anisotropic, needle-like structural morphology (Figure 5.1a). To further quantify the size distribution of the colloidal suspension, Dynamic Light Scattering (DLS) measurements were conducted. DLS is an advanced optical technique used to determine the hydrodynamic diameter of particles in suspension by analyzing the time-dependent fluctuations of scattered laser light induced by Brownian motion. The profile confirms a uniform size distribution with a characteristic peak centered at 80 ± 20 nm, successfully verifying that the predominant nanoparticle population is tightly confined within the 60 to 100 nm size range (Figure 5.1b).

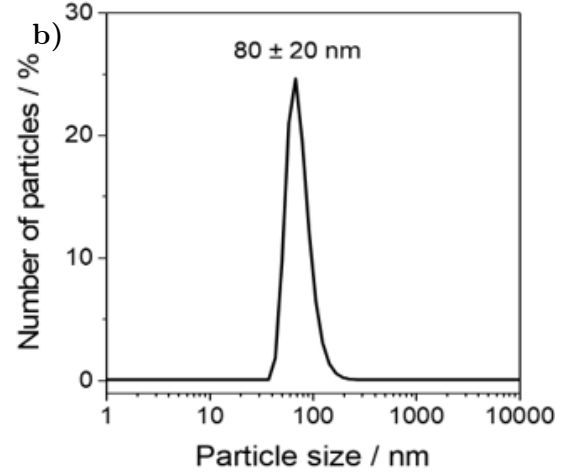
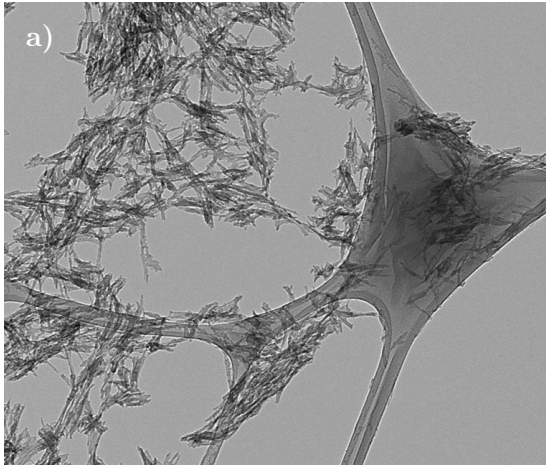


Figure 5.1: Morphological and dimensional characterization of the BF_4 nanoparticles. (a) TEM micrograph detailing the needle-like nanostructure. (b) DLS profile confirming a hydrodynamic size distribution centered at 80 ± 20 nm.

Beyond its morphological properties, the defining feature of the BF_4 nanoparticles is their thermally induced spin-state transition. To precisely identify the critical temperatures governing this phenomenon, the magnetic susceptibility ($\chi_M T$) of the bulk powder was characterized as a function of temperature (Figure 5.2a). The magnetic profile exhibits a well-defined thermal hysteresis loop, a signature of cooperative SCO materials. During the heating phase, the transition from the diamagnetic Low-Spin (LS) state to the paramagnetic High-Spin (HS) state occurs predominantly within the 335–345 K range (highlighted in red). Conversely, upon cooling, the HS to LS relaxation is delayed, centering around the 320–330 K window (highlighted in blue). This ≈ 15 K wide memory effect is the fundamental mechanism that dictates the operational temperature window of the final integrated devices.

Furthermore, when these nanoparticles are embedded within a polymeric matrix (PMMA), the molecular spin-state switching translates into macroscopic, measurable variations in the composite's physical properties. As complementary characterization, the thermomechanical and thermo-optical responses of the SCO/PMMA blend were evaluated at the targeted telecom wavelength of 1550 nm. As shown in Figures 5.2b-d, the composite film demonstrates a clear hysteretic behavior in its thickness (Δh), refractive index (Δn), and extinction coefficient (Δk), perfectly mirroring the magnetic transition profile. These highly localized physical perturbations explicitly confirm the material's viability as an active transducer for optical sensing, bridging the molecular transition with a measurable macroscopic optical shift.

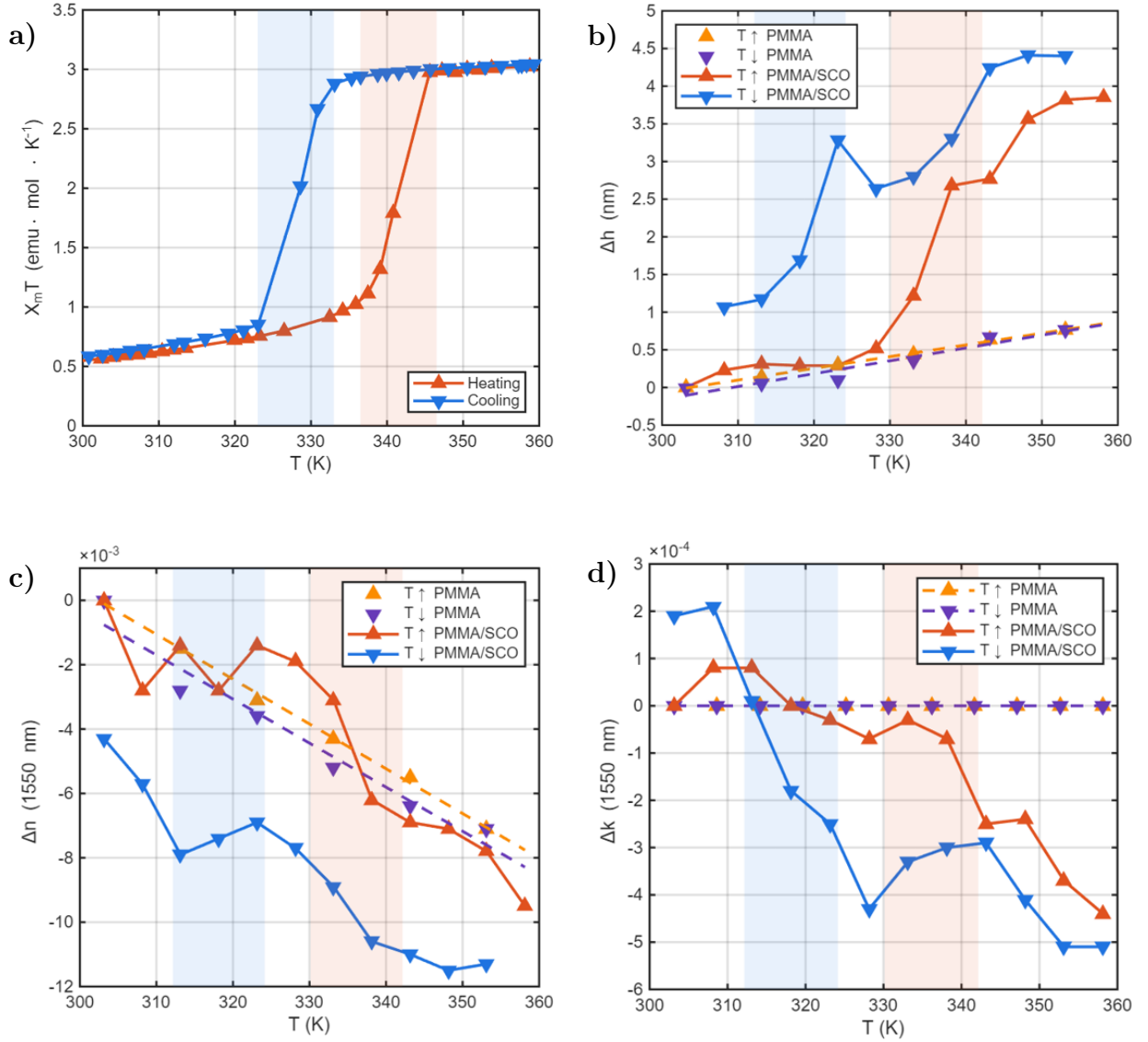


Figure 5.2: Thermophysical characterization of the SCO material. (a) Magnetic susceptibility ($\chi_M T$) of the bare nanoparticles. Macroscopic variations of the SCO/PMMA composite at 1550 nm: (b) thickness (Δh), (c) refractive index (Δn), and (d) extinction coefficient (Δk).

5.1.2. PMMA Polymeric Host Matrix

To mechanically interface the active SCO nanoparticles with the photonic structures, PMMA was selected as the passive elastomeric host matrix. The material was commercially sourced from Sigma-Aldrich in the form of a dry powder, specifically characterized by a relatively low average molecular weight ($M_w \approx 15,000$ by GPC).

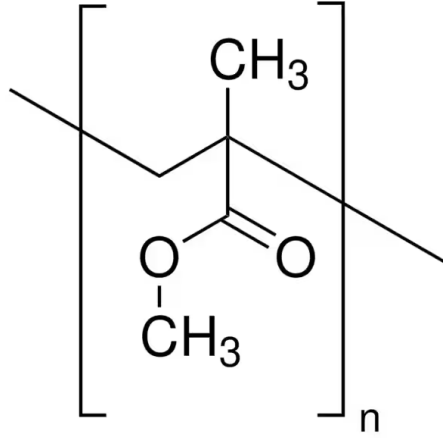


Figure 5.3: Chemical structure of the PMMA polymer network.

As illustrated by its backbone (Figure 5.3), the amorphous nature of the PMMA network provides optical transparency in the near-infrared regime, which is strictly required to minimize parasitic scattering and absorption losses over the photonic cavity [29]. Furthermore, its intrinsic chemical stability and mechanical elasticity make it an ideal host medium, capable of efficiently transferring the mechanical strain generated by the SCO phase transition directly to the underlying structures without degrading the optical mode.

Beyond its optical and mechanical suitability, the selection of a low molecular weight variant constitutes a critical design parameter governed by the fluid-dynamic requirements of the functionalization protocol. When dissolved in the organic solvent, low- M_w PMMA yields a precursor composite solution with significantly reduced viscosity compared to its heavier polymeric counterparts. This low-viscosity characteristic is essential during the drop-casting deposition to ensure optimal fluid dynamics and wettability. It allows the SCO/PMMA composite to effectively infiltrate the micro-scale sensing windows of the MRRW, completely filling the spatial gaps without bridging or trapping interfacial air voids [30]. Consequently, this guarantees an intimate, conformal contact between the active matrix and the exposed silicon waveguides, which is strictly necessary to maximize the evanescent field coupling required for an efficient mechano-optical transduction [31].

5.1.3. Highly Oriented Pyrolytic Graphite (HOPG)

The primary precursor material selected for the mechanical exfoliation of the graphene membranes was Highly Oriented Pyrolytic Graphite (HOPG), specifically the commercial grade, ZYA (TipsNano). The employed bulk crystals possessed macroscopic dimensions of $10 \times 10 \times 2$ mm and a certified mosaic spread of $0.4^\circ \pm 0.1^\circ$.

The selection of the high-quality ZYA grade over lower-tier alternatives (such as ZYB or ZYC) is a critical parameter in the deterministic transfer protocol. The mosaic spread is a crystallographic metric that quantifies the angular deviation of the c-axes of the individual microscopic graphite crystallites relative to the macroscopic basal plane. A

low mosaic spread ($\leq 0.4^\circ$) indicates a highly ordered internal structure, translating into exceptionally large, defect-free single-crystal domains that extend laterally across the cleavage plane.

As extensively documented in the literature regarding micromechanical cleavage [32], the spatial yield and structural integrity of large-area, pristine few-layer graphene flakes are fundamentally limited by the grain size of the parent bulk material. Exfoliating from ZYA-grade HOPG drastically minimizes the presence of step edges, grain boundaries, and intrinsic lattice defects during the viscoelastic peeling process. In the context of this research, obtaining structurally continuous and mechanically robust membranes with sufficient lateral dimensions (tens of micrometers) to successfully span the suspended PDMS micro-cavities absolutely necessitated the use of this highly ordered precursor material.

5.1.4. *Elastomeric PDMS: Viscoelastic Stamp and Monolithic Substrate*

Poly(dimethylsiloxane) (PDMS) possesses physicochemical and elastomeric properties that are highly advantageous for nanofabrication. In this methodology, commercial Sylgard 184 PDMS is implemented with a dual critical purpose: it acts as the viscoelastic stamping medium required for the deterministic transfer of graphene flakes onto rigid silicon micro-cavities, and it simultaneously serves as the primary structural substrate for the monolithic elastomeric nanodrum platforms. Chemically, PDMS is an organosilicon elastomer; its molecular structure features a highly flexible inorganic silicon-oxygen (Si-O) backbone with organic methyl ($-\text{CH}_3$) pendant groups, successfully combining inert chemical stability with deep physical compliance (Figure 5.4).

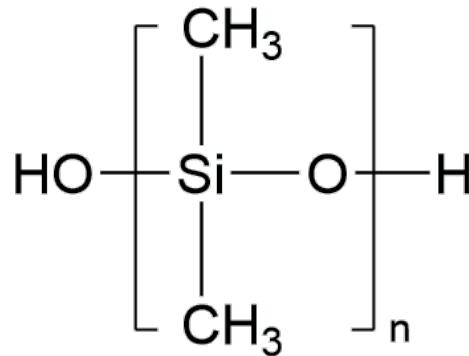


Figure 5.4: Chemical structure of the PDMS polymer network.

The PDMS surface exhibits intrinsically low surface energy due to the outward orientation of its methyl groups. Consequently, it does not form strong covalent bonds with the graphene layer; rather, the interface is governed purely by weak Van der Waals forces. These non-covalent interactions are critical for the transfer process, as they provide sufficient initial adhesion to lift the exfoliated graphene, yet remain gentle enough to permit

a clean physical release onto the final target substrate. Furthermore, its chemical inertness guarantees that the electronic and mechanical properties of the graphene remain intact, while its broad optical transparency in the visible spectrum is critical for achieving high-precision alignment under the microscope [33], necessary properties for a successful transfer [34]. Additionally, its Young’s modulus can be precisely tuned via the base-to-curing-agent ratio [35]—a feature vital both for optimizing the stamp’s tackiness during transfer and for defining the mechanical compliance of the monolithic elastomeric cavities. Finally, the exceptional structural flexibility of the siloxane backbone allows the elastomer to achieve conformal contact with diverse topographies at a nanoscale level, vital to perform the PDMS micro-cavities. This ensures an intimate, void-free interface, maximizing the effective area for Van der Waals interactions without trapping macroscopic air pockets [36].

5.2. Methods

5.2.1. Optical and Thermal Characterization Setup

The optoelectronic characterization of the MRR devices was performed using a vertical coupling station. This setup is specifically designed to precisely align optical fibers to the chip’s grating couplers while simultaneously controlling the thermodynamic environment of the sample, a critical requirement for evaluating the thermally induced phase transitions of the SCO active layer.

The optical signal pathway is driven by a tunable continuous-wave laser and collected by an optical power meter. Both instruments are synchronized and managed via centralized software, which dictates the measurement parameters such as the wavelength sweep range, the scanning step resolution ($\Delta\lambda$), and the integration time per data point. Before reaching the integrated circuit, the polarization state of the incident light is adjusted via an inline polarization controller to exclusively match the Transverse Electric (TE) mode supported by the silicon waveguides. Whole optical path is captured and schematized in Figure 5.5a

To inject and extract this optical signal, single-mode optical fibers are mounted on multi-axis micro-positioners, enabling sub-micrometer translational accuracy. The fiber probes are positioned above the PIC with a strict 10° vertical inclination. This specific angle is engineered to match the acceptance cone and maximize the coupling efficiency of the standard grating couplers fabricated on the substrate [37]. This delicate physical alignment process is visually monitored in real-time using a top-view digital camera integrated into the microscope body.

Crucially for the scope of this project, the central sample stage is equipped with a closed-loop thermal control system to perform the temperature sweeps. The chip rests directly on a Peltier thermoelectric cooler, which acts as the active heating and cooling element, while an embedded thermistor operates in a feedback loop with a dedicated temperature controller to ensure precise thermal stabilization during the optical scans (Figure 5.5b).

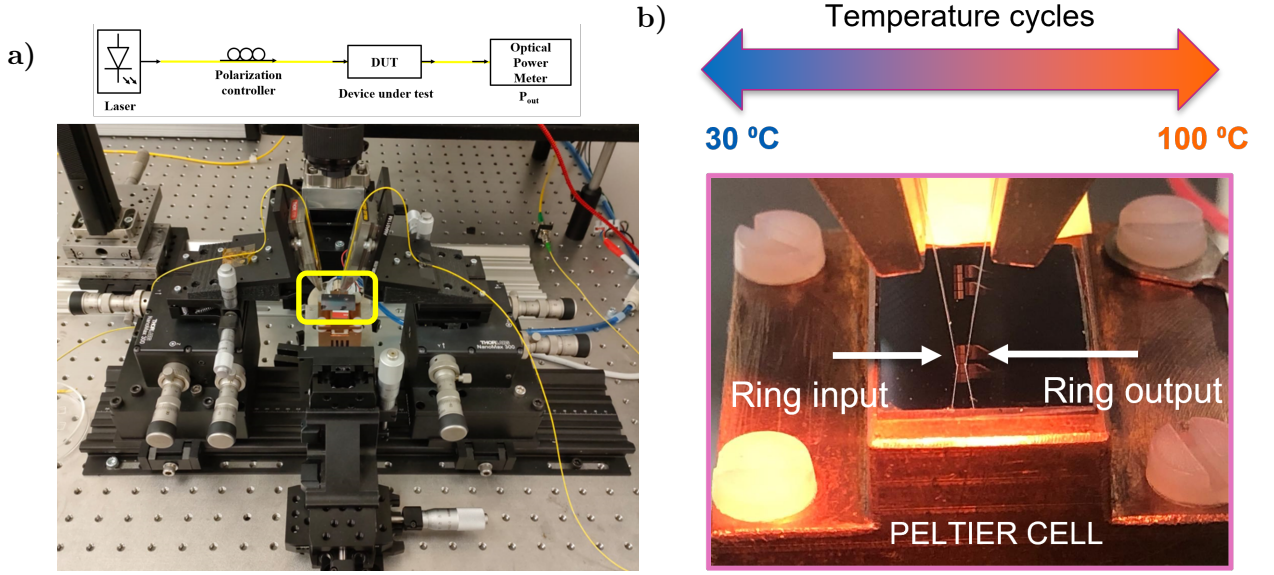


Figure 5.5: Optoelectronic vertical coupling setup for MRR characterization. (a) General view and optical signal pathway diagram. (b) Close-up of the sample stage showing fiber alignment and the Peltier cell for thermal sweeps.

5.2.2. Deterministic 2D Material Transfer Setup

The fabrication of the suspended graphene nanodrums was executed utilizing a custom-built deterministic transfer setup, based on the all-dry viscoelastic stamping technique. The apparatus is configured as a dual-stage kinematic system designed for sub-micrometer alignment precision.

The lower stage supports the pre-patterned silicon substrate and is integrated into a multi-axis micro-manipulator, providing high-resolution control over translational (X, Y, Z) and angular (θ) degrees of freedom. This multi-degree of freedom capability is critical for the precise registration of the target cavities with the suspended material. The upper stage consists of a mount securing the PDMS stamp, onto which the graphene flakes were previously transferred. The stamp is suspended in a cantilever configuration above the target substrate, ensuring vibration-isolated mechanical control. The transfer process is initiated by the fine vertical approach of the stages, allowing the viscoelastic PDMS to achieve uniform, conformal contact with the silicon surface (detailed in Figure 5.6).

The progression of the contact front and the spatial alignment of the flakes are monitored in real-time via a top-view digital camera interfaced through its own uEye software (IDS Imaging Development Systems). While this optical system provides the necessary feedback to guide the macroscopic kinematics of the viscoelastic transfer, its resolution is fundamentally constrained by the diffraction limit of the objective. Consequently, this optical feedback is intended for positional registration rather than morphological assessment. Therefore, a comprehensive evaluation of the transferred membrane's structural integrity,

surface cleanliness, and flake thickness requires post-transfer metrology via high-resolution optical microscopy and AFM, as detailed in the subsequent sections of this document.

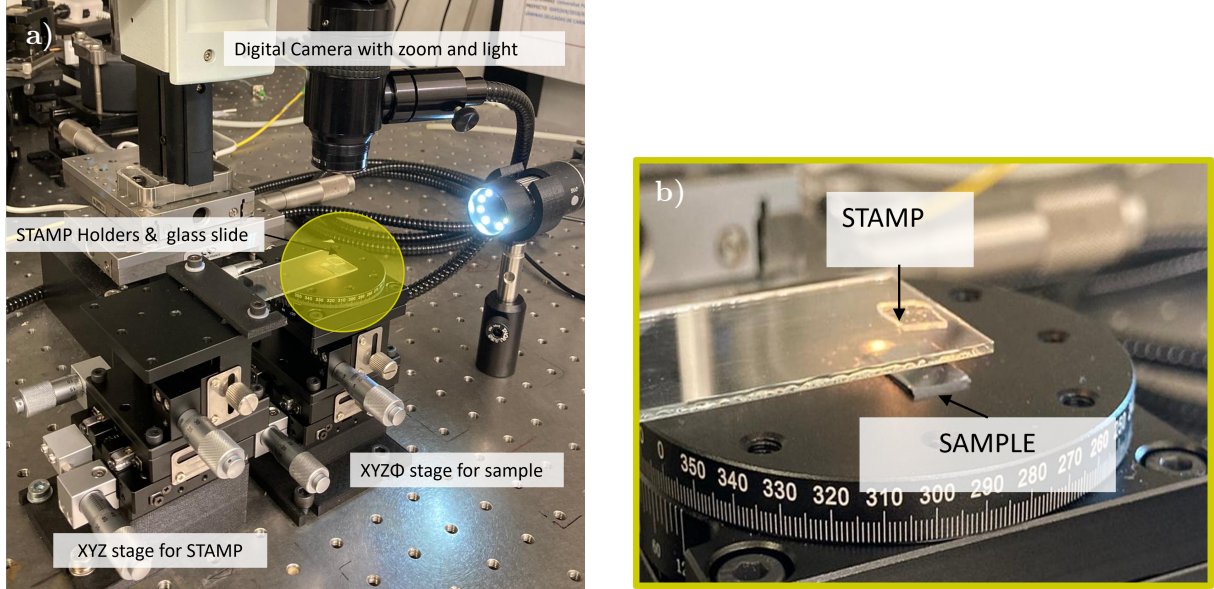


Figure 5.6: Deterministic 2D material transfer setup. (a) General view of the kinematic stages and digital camera. (b) Close-up of the PDMS stamp suspended over the target sample.

5.2.3. Optical Microscopy

High-resolution optical microscopy served as an intermediate and verification tool throughout the two-dimensional material transfer protocol. All optical characterizations and micrograph acquisitions were performed using a Zeiss Axiolab 5 MAT microscope (Figure 5.7), equipped with a digital camera and interfaced with the proprietary Zeiss software for image processing.

The utilization of this microscope was fundamentally divided into two operational phases. In the pre-transfer phase, it was employed to inspect the PDMS stamps immediately after the mechanical exfoliation of graphite. Due to the limited optical resolution of the in-situ camera on the transfer setup, scanning the transparent polymer directly in the transfer stage is highly inefficient. Instead, the Zeiss microscope was used to systematically scan the PDMS surface, identifying suitable graphene flakes based on their optical contrast—which provides a reliable preliminary estimation of their thickness. Once an optimal flake was identified, its precise location relative to macroscopic references on the stamp was mapped. This pre-localization step is crucial, as it drastically minimizes the search and alignment time required later in the deterministic transfer setup.

In the post-transfer phase, following the viscoelastic stamping process, the pre-patterned silicon substrates were re-examined under the optical microscope. This step provides an

immediate, macroscopic assessment of the transfer yield and structural integrity of the newly formed OM cavities. It allows for the rapid identification of successful nanodrums, as well as the detection of potential defects such as membrane ruptures, macroscopic wrinkles, or unwanted residues. Optical micrographs of the targeted devices were captured using the Zeiss software to provide an initial morphological screening, ensuring the viability of the graphene membranes before proceeding to high-resolution topographical characterization via AFM.



Figure 5.7: Zeiss Axiolab 5 MAT (NTC facilities)

5.2.4. Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) was selected for the high-resolution topographical characterization of the fabricated cavities and suspended membranes. All measurements were conducted utilizing a combined confocal micro-Raman and AFM system (WITec alpha300 RA) as shown in Figure 5.8. Unlike traditional optical techniques, AFM is not constrained by the diffraction limit, enabling accurate sub-nanometer spatial resolution. The system is equipped with a high-throughput piezo-driven scan stage ($200 \times 200 \times 20 \mu\text{m}^3$), providing exceptional position accuracy ($< 20 \text{ nm}$ laterally and $< 0.2 \text{ nm}$ vertically). To preserve the structural integrity of the delicate two-dimensional materials, measurements were strictly conducted in Tapping Mode (AC Mode). In contrast to Contact Mode, which applies a constant lateral drag that can easily rupture suspended graphene flakes, Tapping Mode drives the cantilever to oscillate near its mechanical resonance frequency (f_r). The tip intermittently interacts with the sample via Van der Waals forces, virtually eliminating destructive shear forces.

During the scanning process, an infrared laser reflected off the back of the cantilever is tracked by a four-quadrant photodiode, allowing the simultaneous extraction of three

critical data channels. The primary feedback loop adjusts the vertical piezoelectric extension (Z) to maintain a constant oscillation amplitude (setpoint), thereby generating the precise Topography map. Concurrently, the Amplitude signal captures abrupt topographical changes, making it exceptionally useful for delineating the sharp edges of the pre-patterned silicon cavities. Furthermore, the Phase contrast (ϕ) channel records the phase shift induced by energy dissipation processes. This is particularly valuable for distinguishing heterogeneous surfaces, as it provides a clear contrast between materials with differing viscoelasticity or hydrophobicity [38].

When interpreting the acquired micrographs, particularly those involving nanoscale features or nanoparticles, the tip convolution effect must be carefully considered [39]. Because the commercial AFM tip possesses a finite radius of curvature and aspect ratio, structures can appear laterally broadened. Nevertheless, the vertical Z -axis measurements remain highly accurate and unaffected by this geometric convolution. This reliability is crucial for precisely determining the depth of the cavities and evaluating whether the transferred graphene membranes are adequately tensioned or collapsed

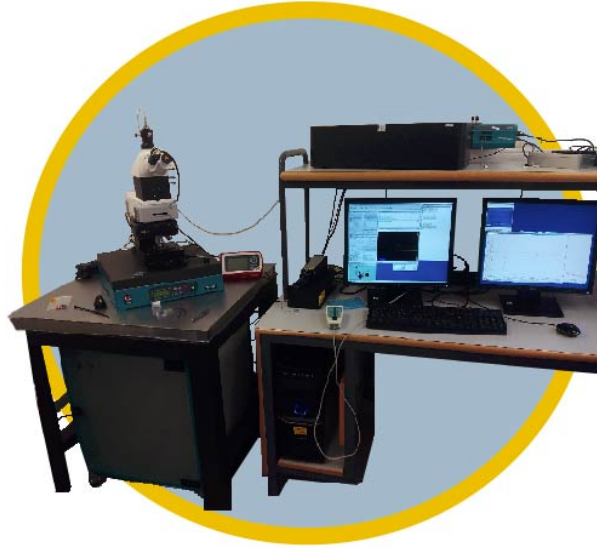


Figure 5.8: WITec combined confocal micro Raman imaging and AFM system alpha300 RA (NTC facilities)

5.2.5. *Raman Spectroscopy*

Raman spectroscopy is a non-destructive optical technique fundamentally based on the inelastic scattering of monochromatic light, typically from a laser source. When incident photons interact with the electron cloud and the chemical bonds of a material, the vast majority of the light is scattered elastically, maintaining its original energy and wavelength (Rayleigh scattering). However, a minute fraction of the incident photons ($\sim 1 : 10^6$) undergoes inelastic scattering, exchanging energy with the vibrational modes (phonons)

of the crystal lattice.

As illustrated in Figure 5.9, if an incident photon transfers a portion of its energy to the lattice to create a phonon, the scattered photon emerges with lower energy (longer wavelength). This process is denoted as Stokes Raman scattering and is typically the most intense signal measured at RT. Conversely, if the photon absorbs energy from a pre-existing phonon, it scatters with higher energy (shorter wavelength), resulting in Anti-Stokes Raman scattering. The energy difference between incident and scattered light, known as the Raman shift (conventionally expressed in cm^{-1}), provides a unique vibrational fingerprint of the molecular structure and the crystalline lattice [40].

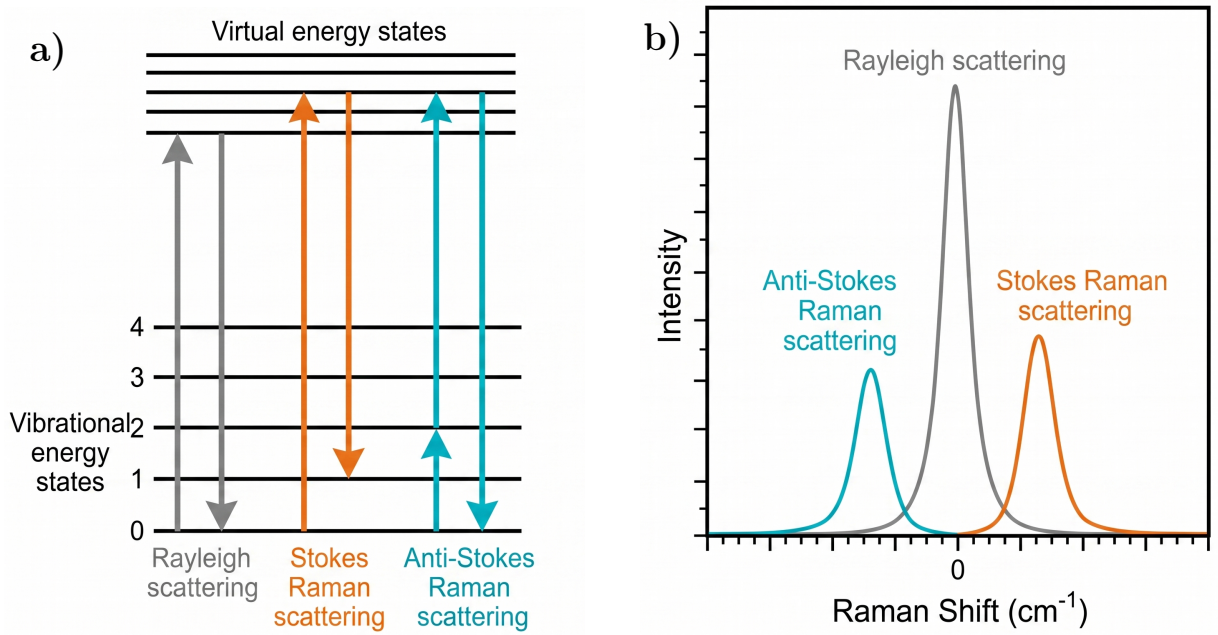


Figure 5.9: Fundamentals of Raman spectroscopy. (a) Scattering energy-level diagram. (b) Schematic Raman spectrum.

Experimentally, the structural characterization of the two-dimensional membranes was performed using the integrated WITec alpha300 RA spectrometer. The utilization of a combined Raman-AFM platform is highly advantageous, as it allows for spatial correlation between the topographical features of the nanodrums and their vibrational spectra without displacing the sample. The Raman scattering was excited using a frequency-doubled Nd:YAG laser at a wavelength of $\lambda = 532 \text{ nm}$. The scattered light was collected by a 100x objective (NA 0.9) and directed into an Ultra-High Throughput Spectrometer (UHTS) equipped with a high-quantum-efficiency Charge-Coupled Device (CCD) detector and a 600 lines/mm grating, ensuring optimal spectral resolution for the detection of subtle phonon shifts.

In the context of nanotechnology and two-dimensional materials, Raman spectroscopy stands as the gold standard for structural characterization [41]. For graphene, the Ra-

man spectrum is dominated by two prominent features: the G peak ($\sim 1580 \text{ cm}^{-1}$), arising from the in-plane stretching of the sp^2 carbon-carbon bonds, and the 2D peak ($\sim 2690 \text{ cm}^{-1}$), originating from a second-order two phonon resonant scattering process. Additionally, the presence of a D peak ($\sim 1350 \text{ cm}^{-1}$) serves as a direct indicator of lattice defects or symmetry breaking within the carbon lattice.

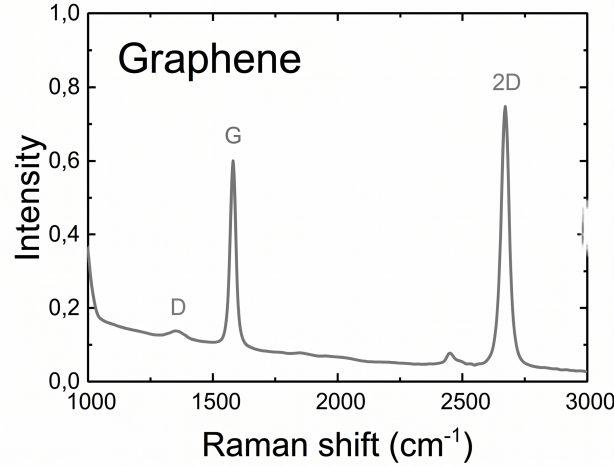


Figure 5.10: Graphene Raman Spectrum

Crucially for this project, the precise position of these Raman peaks is highly sensitive to external perturbations, particularly mechanical strain. When a suspended graphene nanodrum is subjected to tensile strain, the interatomic carbon-carbon bonds are physically elongated. This structural elongation softens the vibrational phonon modes, requiring less energy for excitation, which directly translates into a measurable red-shift (towards lower wavenumbers) of both the G and 2D peaks [42]. Consequently, Raman spectroscopy serves not only to verify the successful transfer and the structural quality of the graphene membranes but also acts as an ultra-sensitive, localized optical strain gauge to evaluate the mechanical tension applied to the OM cavities.

5.3. Project Context: The IGNATIUS Framework

The experimental work and the methodological protocols developed in this Bachelor's Thesis are formally framed within the research lines of the NTC at the *Universitat Politècnica de València*. Specifically, this research directly contributes to the ongoing IGNATIUS project (InteGrated aNd packaged elecTro-opto-mechanical systems towards quantum technologies), led by Dr. Elena Pinilla Cienfuegos.

The overarching ambition of the IGNATIUS project is to develop a new multifunctional capability to integrate and characterize high-Q OM cavities for quantum photonics applications, fundamentally eliminating the traditional reliance on cryogenic temperatures. To achieve quantum effects near RT, the project proposes the integration of Innovative Advanced Materials (IAM) to fabricate tunable, strain-engineered resonant cavities.

This thesis represents a step toward that goal. By empirically demonstrating the mechano-optical transduction capabilities of SCO nanoparticles embedded in a polymer matrix acting as tunable strain actuators, and by establishing the baseline deterministic transfer of 2D graphene nanodrums, this work provides a tangible proof of concept for the hybrid integration proposed by IGNATIUS.

Having established the theoretical background, defined the experimental methodology, and contextualized the project framework, the following chapter will present and rigorously analyze the optoelectronic and morphological results obtained from devices.



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IGNATIUS: InteGrated aNd pAckaged
elecTro-opto-mechanical systems
towards qUantum technologieS.
CNS2024-154922

6. Results

6.1. On-Chip Photonic Transduction: Hybrid SCO/PMMA Photonic Micro-Ring Resonators (MRR)

The MOSAIC J67 PIC is a highly integrated platform comprising 12 nominally identical devices. Each device incorporates a systematic arrangement of photonic structures, beginning with five reference waveguides: one standard fully clad waveguide, two featuring a short sensing window, and two featuring a long sensing window. Following these, the device integrates an array of 20 MRR waveguides, structured in an alternating sequence of fully clad resonators and windowed resonators (where the top cladding is removed to expose the evanescent field to the external environment).

To maintain a systematic and unambiguous nomenclature throughout the experimental characterization, each device is indexed as d_i for $i \in \{1, \dots, 12\}$. Within a specific device, the fully clad MRR are denoted as mrr_j , while the windowed MRR are designated as $mrrw_j$, where $j \in \{1, \dots, 10\}$.

To clearly illustrate the optical routing and coupling mechanism, Figure 6.1 presents a structural schematic of the sensing platform, specifically highlighting the grating couplers and the geometry of the targeted windowed resonator, $mrrw_{10}$. Furthermore, Figure 6.2 provides a high-resolution optical micrograph of this architectural layout, detailing the fabricated photonic structures.

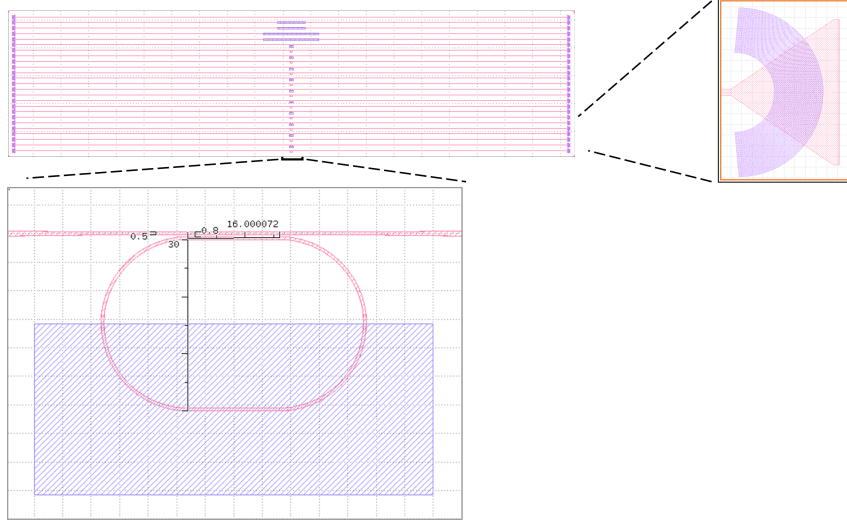


Figure 6.1: Schematic of the MOSAIC J67 MRR architecture and targeted $mrrw_{10}$ layout.

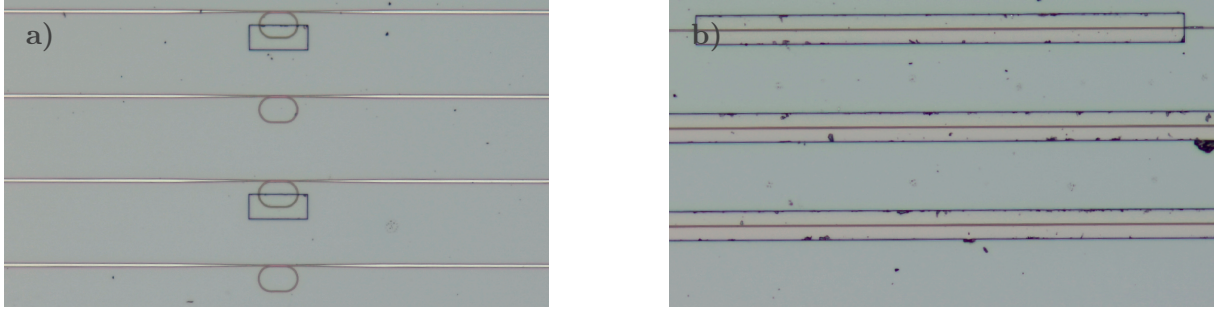


Figure 6.2: Device d_8 layout. (a) MRR array detailing resonators 9 and 10. (b) Reference waveguides.

6.1.1. Baseline Characterization of Bare Resonators

Establishing a robust baseline optical response for the windowed MRR is critical, as this exposed cladding region serves as the primary interaction volume for the subsequent deposition of the PMMA/SCO nanoparticle composites (BF_4).

Upon evaluating multiple devices with varying coupling parameters, the optimal spectral responses were consistently observed in waveguides $mrrw_{09}$ and $mrrw_{10}$, corresponding to coupling lengths of $15\ \mu m$ and $16\ \mu m$, respectively. These extended coupling dimensions yield deeper resonance profiles. Consequently, the systematic baseline characterization of the fabricated chips was explicitly focused on these two specific waveguide designs.

The optical characterization was performed using the custom probe station detailed in Figure 5.5. A tunable laser source was swept across the telecom C-band (from $1540\ nm$ to $1560\ nm$) with a constant input optical power of $P = 6\ dBm$. Measurements were deliberately conducted at ambient temperature without active thermal stabilization to

establish a passive baseline prior to the thermo-optical experiments. The transmitted optical power was continuously monitored by a power meter interfaced with a dedicated acquisition software. For post-processing, the raw spectral data was exported and analyzed using custom Python scripts to normalize the transmission profiles and accurately extract the key resonance metrics (wavelength, ER, and Q-factor).

The optical transmission spectra presented in Figure 6.3 identify device d_{08} as an optimal candidate for the active integration. The spectrum of waveguide $mrrw_{10}$ (Figure 6.3b) exhibits a highly stable baseline with well-defined, low-noise resonance peaks. Conversely, $mrrw_{09}$ (Figure 6.3a) displays elevated parasitic noise alongside a noticeably reduced ER. In the vicinity of the central wavelength ($\lambda \approx 1550$ nm), $mrrw_{10}$ demonstrates highly efficient coupling, approaching the critical coupling regime. Securing a high ER at this spectral region is a fundamental prerequisite to reliably resolve and track the optical wavelength shifts once the SCO nanoparticles are deposited over the sensing window.

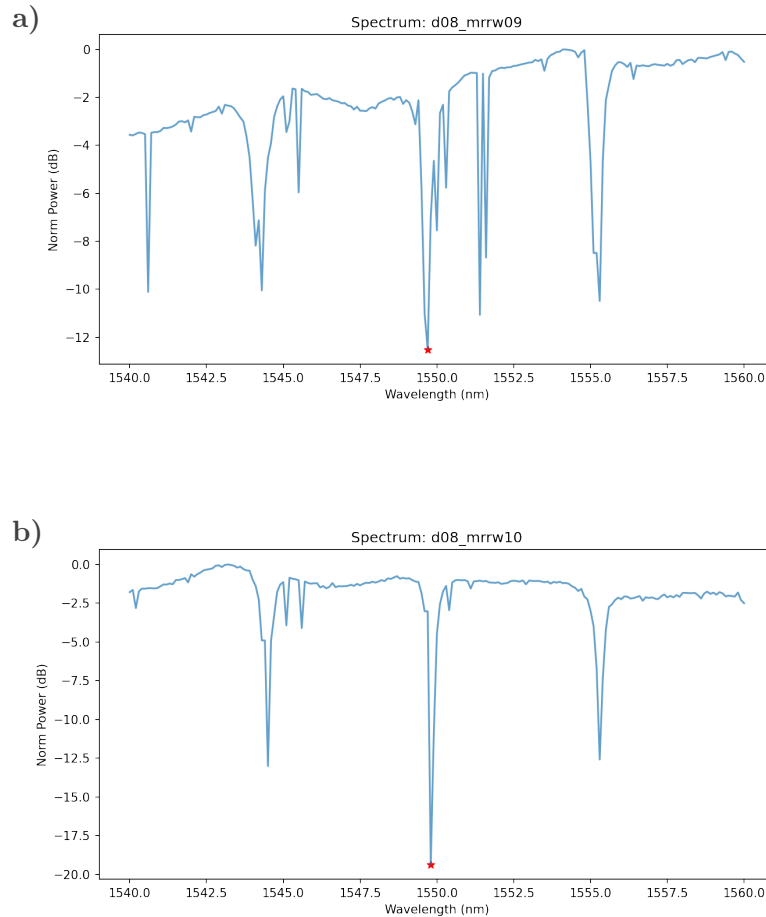


Figure 6.3: Baseline optical transmission spectra for device d_{08} . (a) Waveguide $mrrw_{09}$. (b) Waveguide $mrrw_{10}$.

As inherent to coupled micro-cavities, the spectral analysis reveals a fundamental optical trade-off between the loaded Q and the ER, as illustrated in Figure 6.4. Given the specific experimental requirements of this thesis, we strategically prioritize a maximized ER over an ultra-high Q-factor. While this selection yields a moderate Q, the deepened resonance dips provide a superior SNR. This high contrast ensures that the structural and refractive index variations induced by the SCO/PMMA phase transition will translate into highly resolvable and easily detectable optical shifts.

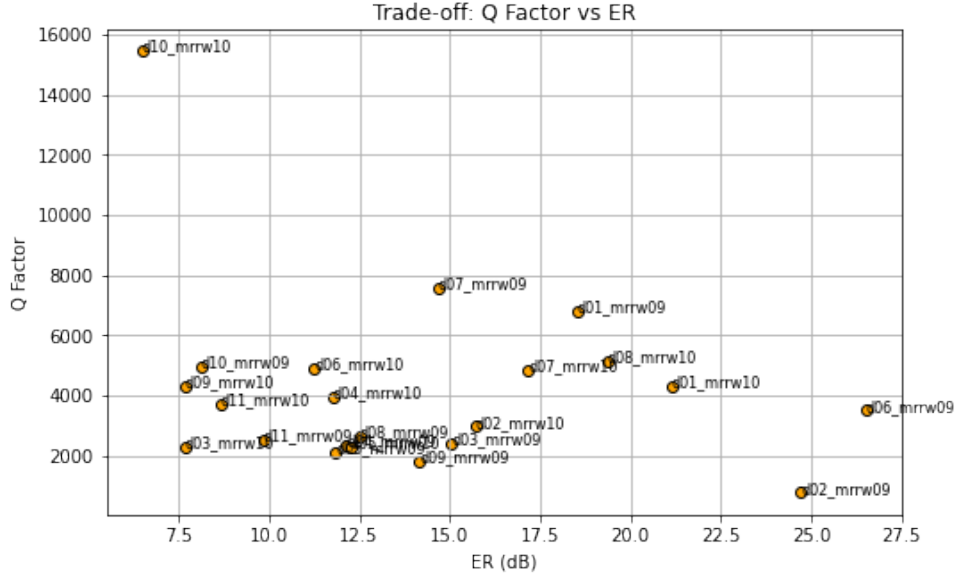


Figure 6.4: Experimental trade-off between the loaded Q-factor and the Extinction Ratio (ER) for the evaluated MRRW.

It is conclusively determined that device d_{08} (specifically via $mrrw_{10}$) maintains an optimal operational balance, exhibiting superior coupling efficiency and signal contrast. Consequently, this specific device architecture was selected as the definitive platform for the subsequent integration and thermal testing of the SCO hybrid composite.

6.1.2. SCO/PMMA Composite Matrix Formulation and Device Functionalization

Stable colloidal suspensions of SCO nanoparticles, pre-dispersed in chloroform (CHCl_3), were provided through a research collaboration with the *Instituto de Ciencia Molecular* (ICMol). However, due to the time elapsed prior to device functionalization, the exact nanoparticle concentration became uncertain as a result of potential solvent evaporation and particle settling. To restore the dispersion quality, additional chloroform was introduced, which necessitated a precise recalibration of the active concentration on the day of deposition prior to polymer integration.

To determine the effective concentration, a $200\ \mu\text{L}$ aliquot of the homogenized suspension was extracted into a pre-weighed Eppendorf tube ($m_{\text{empty}} = 0.8589\ \text{g}$). To accelerate

the solvent evaporation process without risking nanoparticle loss, the aliquot was centrifuged to precipitate the solid phase, allowing for the careful extraction of the clear supernatant. Once the remaining solvent completely evaporated, the tube containing the dry SCO powder was re-weighed ($m_{\text{full}} = 0.8641 \text{ g}$). The mass of the solid residue was determined to be 5.2 mg, confirming a working nanoparticle concentration of 26 mg/mL (or 0.026 mg/ μL).

The objective for the active sensing layer was to synthesize a composite matrix of PMMA and SCO nanoparticles with a 1:1 mass ratio, while maintaining a PMMA concentration close to 2.5% wt (0.025 mg/ μL) to ensure optimal drop-casting viscosity. To achieve this, 120 μL of the recalibrated suspension—containing exactly 3.12 mg of SCO nanoparticles—were directly added to 3.4 mg of dry PMMA. This formulation successfully achieved a PMMA:SCO mass ratio of approximately 1.09, correctly aligning with the mechanical transduction requirements.

The resulting mixture was then utilized for the functionalization of the targeted MRR device (d_{08}). The deposition was performed via drop-casting directly onto the sensing window inside a chemical fume hood to control the solvent evaporation rate. A total of three successive 5 μL droplets were deposited. The initial droplet served to pin the contact line and define the spatial boundaries over the photonic structures, while the subsequent droplets systematically increased the layer thickness and stabilized the polymer matrix. This sequential process yielded a robust, visually identifiable macroscopic composite layer (Figure 6.5).

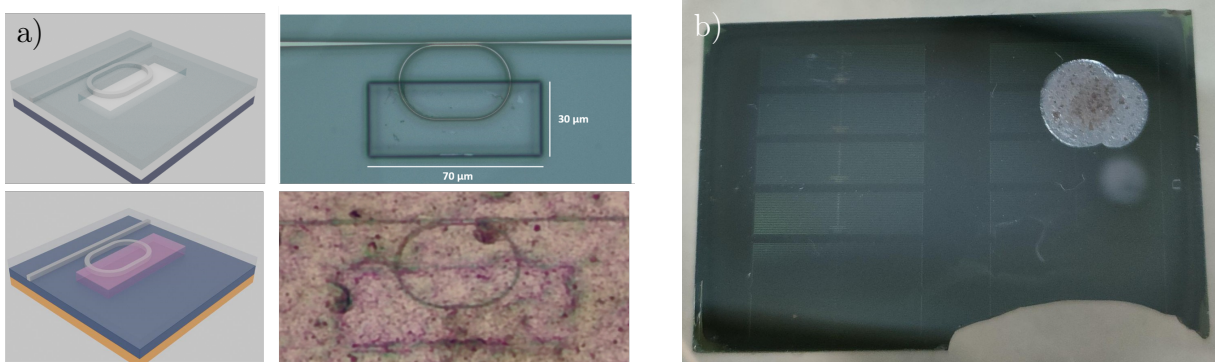


Figure 6.5: (a) 3D schematics and optical micrographs of the MRR before and after active material deposition. (b) Macroscopic photograph of the SCO/PMMA nanocomposite drop-casted onto the resonators region.

6.1.3. *Thermo-Optical Response and Hybrid Matrix Performance*

The experimental procedure focused on characterizing the thermal hysteresis response of the selected device (d_{08} , $mrrw_{10}$) after the deposition of the PMMA/SCO active layer. To perform this characterization, the sample was placed on a temperature-controlled stage and initially brought to 368 K progressively. The measurement cycle began with

the cooling phase, progressively lowering the temperature down to ambient conditions (293 K), followed by a subsequent heating phase back up to 368 K to close the hysteresis loop.

This measurement was conducted using an optical input power of $P = 6$ dBm, with a wavelength scanning step of $\Delta\lambda = 0.1$ nm and an integration time of 0.5 ms. To optimize the data acquisition process while accurately capturing the phase transitions, the temperature increments were dynamically adjusted: 10 K steps were applied in regions outside the expected transition bounds, whereas finer 5 K steps were utilized within the critical transition zones.

As observed in the extracted data (Figure 6.6, the resolution of this first hysteresis loop was suboptimal. This is primarily attributed to the selected wavelength step ($\Delta\lambda = 0.1$ nm). While this resolution is adequate for resolving distinct spectra at RT, it becomes insufficient when thermal noise and thermo-optic fluctuations degrade the SNR at elevated temperatures, making peak tracking significantly harder. Nevertheless, despite the noisy spectra, the resonance peaks could still be identified and tracked across the thermal cycle. As depicted in Figure 6.6a, while the extracted wavelength shifts ($\Delta\lambda$) do not yet exhibit a fully resolved hysteretic loop, clear phase-transition dynamics are observable approximately within the characteristic temperature ranges anticipated for the BF_4 nanoparticles. These localized optical variations confirm that the molecular spin-state switching successfully induces a measurable perturbation in the effective refractive index of the cavity.

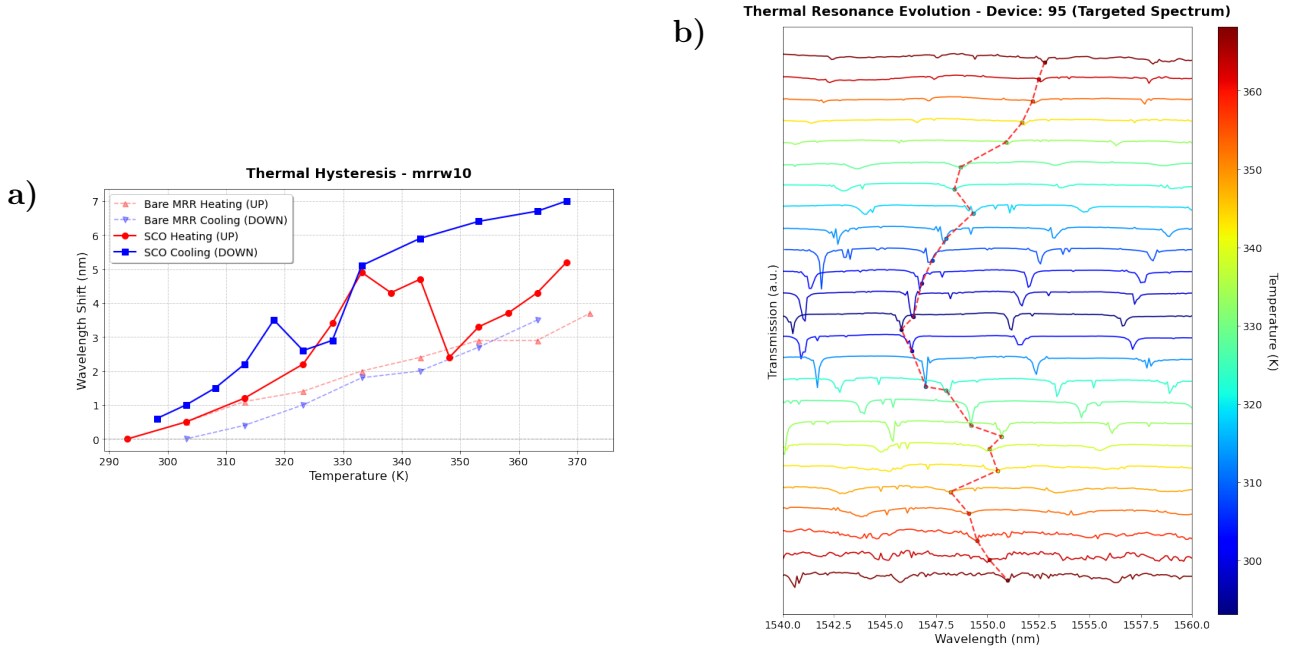


Figure 6.6: Initial thermal hysteresis of d_{08} (mrrw₁₀). (a) Thermally induced hysteresis loop. (b) Cavity resonance wavelength shift during the thermal cycle.

Figure 6.7 illustrates the complete experimental thermal cycle designed for the characterization process. The system successfully maintained a highly stable temperature profile at each programmed setpoint, guaranteeing optimal thermal equilibrium across both the cooling and heating phases before initiating the optical wavelength sweeps.

However, following the analysis of the initial data acquired during these thermal plateaus, it was concluded that the spectral resolution was insufficient to reliably track the resonance peaks under high-temperature noise conditions. Consequently, the experiment was repeated with an optimized optical configuration. The sole modification to the setup was the reduction of the wavelength scanning step from $\Delta\lambda = 0.1$ nm to $\Delta\lambda = 0.05$ nm, thereby doubling the spectral resolution, while all other parameters (including the thermal cycle) remained constant. This enhancement allowed for much more robust peak detection, significantly mitigating the impact of thermal noise at elevated temperatures. As a result, the extracted data yielded an optimal and well-defined hysteresis loop, in agreement with the theoretical expectations for the SCO phase transition. Figure 6.8 presents the hysteresis cycles and their corresponding spectral evolution pathways for the three distinct resonance peaks tracked during these optimized sweeps.

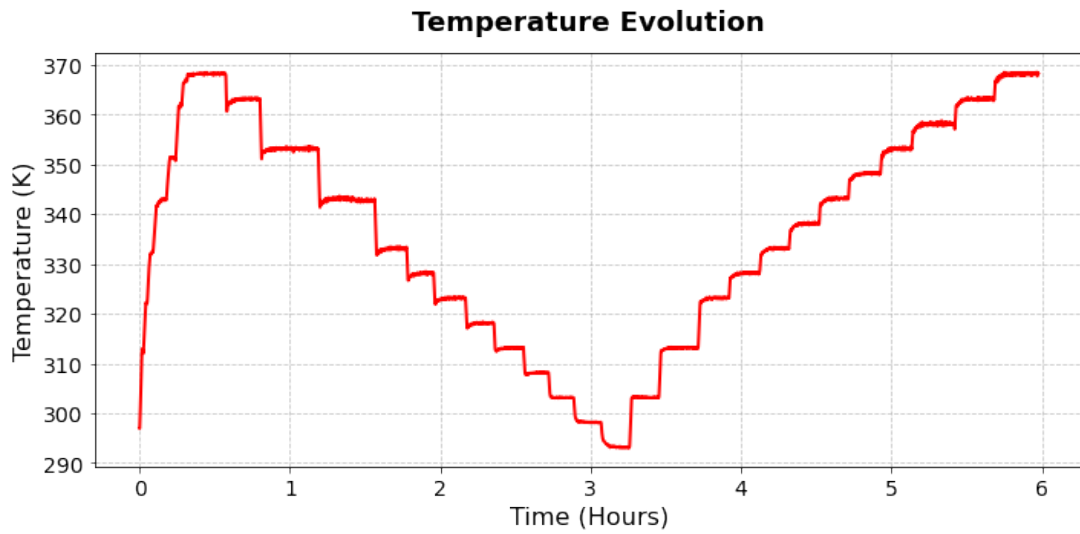


Figure 6.7: Step-wise temperature evolution during the experimental thermal cycle.

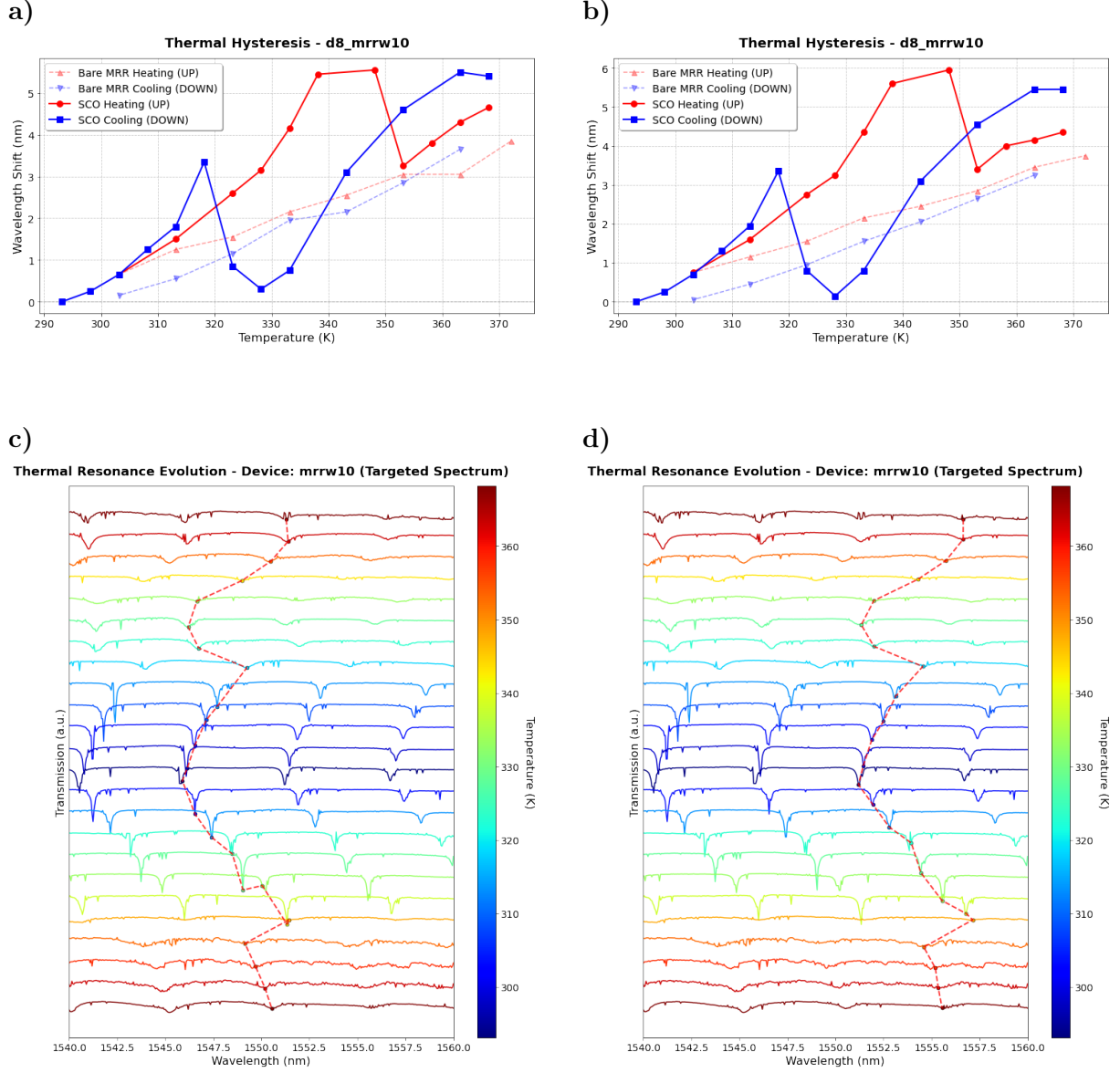


Figure 6.8: Thermal hysteresis of device d₀₈ (mrrw₁₀). (a, b) Hysteresis loops for two adjacent resonance peaks. (c, d) Corresponding spectral evolution (waterfall plots) for each respective peak during the thermal cycle.

The thermal response of the MRRW is governed by the interplay of two distinct physical mechanisms: the thermo-optic effect of the silicon waveguide and the thermo-mechanical transduction of the SCO/PMMA matrix.

Fundamentally, silicon exhibits a strong positive thermo-optic coefficient ($dn/dT > 0$). In the absence of an active cladding, this intrinsic property dictates a linear and reversible wavelength shift: as the device is heated, the effective refractive index (n_{eff}) increases, leading to a red-shift of the resonance peak (λ_{res}) as seen in Figures 6.8a and 6.8b. Con-

versely, cooling the device induces a proportional blue-shift. This thermo-optic baseline is experimentally corroborated by the control measurements of the uncoated device (denoted as Bare MRR). As depicted by the dashed trajectories in the corresponding plots, the bare silicon resonator exhibits a linear and reversible thermal response. However, the deposition of the SCO nanoparticles introduces a highly non-linear, strain-induced optical modulation. SCO materials are characterized by a dramatic structural volume change associated with their spin-state transition. At higher temperatures, the nanoparticles transition into the HS state is accompanied by an elongation of the metal-ligand bonds and a consequent lattice expansion. When the temperature is lowered, the material transitions back to the LS state, resulting in a volumetric contraction.

Crucially, the optical readout of the SCO phenomenon is fundamentally governed by the interplay between the thermodynamic phase transition and the localized refractive index modulation. As previously evidenced by the magnetic susceptibility ($\chi_M T$) characterization (Figure 5.2a), reaching the critical heating temperature ($T_{c\uparrow}$) triggers the electronic transition of the iron(II) centers from the LS to the HS state [7, 15]. This thermal excitation populates anti-bonding e_g orbitals, inducing an elongation of the metal-ligand bonds and a subsequent macroscopic volumetric expansion of the BF_4 nanoparticles within the PMMA matrix. According to the Lorentz-Lorenz relation [43], the refractive index of a dielectric medium is intrinsically tied to its molecular density. Therefore, the volumetric expansion during the LS-to-HS transition causes a sharp decrease in the local density of the cladding, leading to an abrupt drop in its refractive index (n_{clad}).

Because the evanescent field of the guided optical mode penetrates this active cladding, the sudden reduction in n_{clad} directly translates into a pronounced decrease of the mode's effective refractive index (n_{eff}). In terms of the resonance condition, a lower n_{eff} dictates a spectral blue-shift ($\Delta\lambda < 0$) [44]. This strain-induced blue-shift strongly competes with the intrinsic thermo-optic red-shift of the underlying silicon waveguide. Consequently, during the heating phase, the resonance trajectory visibly deviates from the linear baseline as the SCO expansion counteracts the silicon's thermal response. Upon cooling, the delayed HS-to-LS relaxation at $T_{c\downarrow}$ causes the material to abruptly contract, restoring its higher molecular density and refractive index, which in turn generates a corrective red-shift. This thermodynamic irreversibility between the heating and cooling pathways breaks the linear symmetry of the device's thermal behavior. As shown in the hysteresis plots (Figure 6.8), the spectral deviation between the heating (red) and cooling (blue) pathways mirrors the structural memory and transition temperatures of the BF_4 nanoparticles, confirming the successful transduction of the spin-state transition.

Figure 6.9 presents the averaged thermal hysteresis profile of the functionalized d_{08} (mrrw_{10}) device, plotting the mean wavelength shift ($\Delta\lambda$) alongside its standard deviation. This global representation also includes the thermal response of the bare MRR as a linear reference.

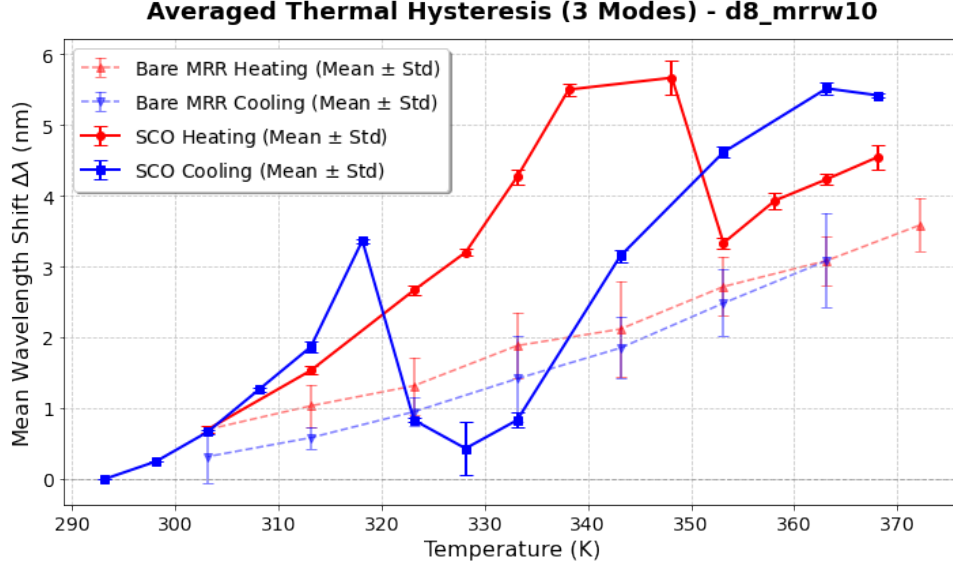


Figure 6.9: Averaged thermal hysteresis profile of the windowed MRR (d_{08} , $mrrw_{10}$).

As expected, the bare silicon device exhibits a linear and strictly reversible wavelength shift, driven solely by the intrinsic thermo-optic effect. In stark contrast, the functionalized device exhibits a broad, well-defined hysteresis loop. Furthermore, the relatively small standard deviation (error bars) across the three independent modes confirms that the macroscopic strain exerted by the SCO/PMMA matrix is transferred homogeneously across the entire sensing window. It should be noted that the control measurements for the bare MRR exhibit a noticeably larger standard deviation, as evidenced by the wider error bars. This increased variance does not imply physical instability within the silicon resonator, but rather stems directly from the experimental acquisition parameters. Specifically, the baseline control cycle was recorded using a lower spectral resolution with a wavelength scanning step of $\Delta\lambda = 0.1$ nm. In contrast, the SCO-functionalized hysteresis loop was acquired using the optimized resolution of $\Delta\lambda = 0.05$ nm. This higher resolution significantly reduced peak-tracking uncertainties, yielding the tighter confidence intervals observed for the active device despite the added complexity of the polymer cladding.

To facilitate a more in-depth physical analysis and avoid redundant descriptions, a data quality assessment was performed to select the most optimal dataset. A comparative evaluation of the acquired spectra reveals that Peak 2 (Figure 6.8a) presents the most robust thermal response, featuring the highest SNR and the most clearly defined phase transition boundaries. Given that the underlying thermo-mechanical transduction mechanism is identical across all resonances within the same device, the subsequent detailed interpretation will focus exclusively on the thermal evolution of Peak 2 (Figure 6.10).

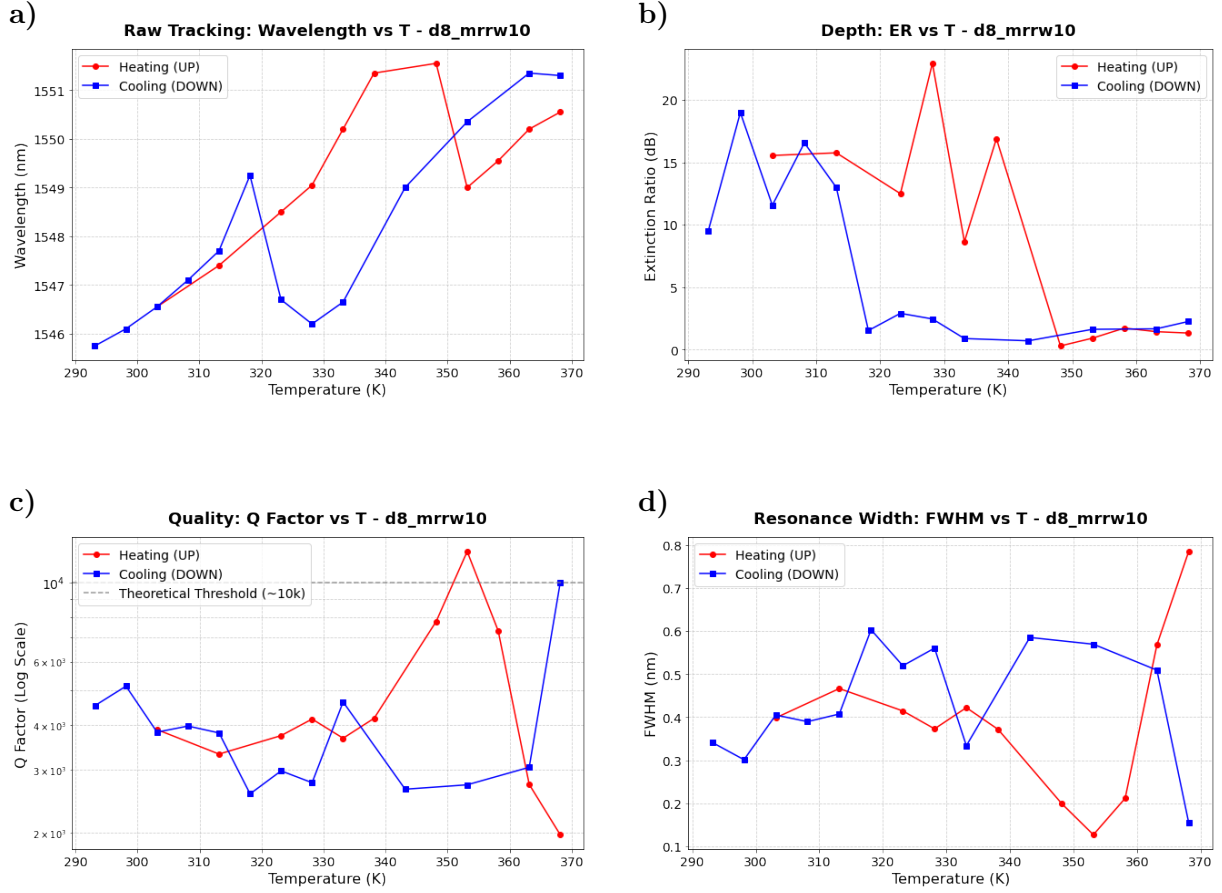


Figure 6.10: Thermally induced evolution of the optical parameters for resonance peak 2. (a) Wavelength shift. (b) Extinction ratio (ER). (c) Loaded Q-factor. (d) FWHM variation.

A comparison between the raw resonance wavelength tracking (Figure 6.10a) and the previously presented normalized wavelength shift ($\Delta\lambda$) in Figure 6.8a confirms the structural identity of the hysteresis loops. This consistency validates the accuracy of the spectral data extraction and ensures that the thermo-optic baseline subtraction does not distort the intrinsic hysteresis signature of the SCO material.

Regarding the cavity's optical confinement, prior characterizations indicated that the unclad platform exhibits a baseline quality factor near $Q \approx 5000$. Following the PMMA/SCO functionalization, the additional scattering and absorption losses introduced by the active composite cladding establish a new operational baseline of approximately $Q \approx 4000$ at RT. As the thermal cycle progresses, the loaded Q (Figure 6.10c), the FWHM (Figure 6.10d), and the ER (Figure 6.10b) exhibit a clear, interconnected temperature-dependent evolution. The Q-factor undergoes a progressive degradation down to $Q \approx 1500$ at elevated temperatures, perfectly mirrored by the broadening of the FWHM and a pronounced degradation of the ER. Crucially, as the device cools back to RT, all these

parameters recover toward their baseline values. This reversibility confirms the structural integrity of the composite cladding throughout the thermal cycle and ensures that the observed spectral evolution is a genuine physical response linked to the temperature sweep, rather than permanent material degradation or optical damage.

Beyond the spectral shifts governed by the real part of the refractive index, the coupled evolution of the cavity's figures of merit can be physically unified under the same intrinsic thermomechanical SCO phase transition. As previously established, the LS to HS transition induces a macroscopic volumetric expansion of the SCO nanoparticles (typically on the order of $\sim 1 - 10\%$ [6]). This drastic structural reorganization not only impacts the local optical density but also severely modifies the complex refractive index ($\tilde{n} = n + i\kappa$) of the active medium. Specifically, the dynamic variation in the imaginary part (κ) and the enhanced scattering cross-section—driven by the changing dielectric contrast between the expanding SCO domains and the PMMA host matrix—simultaneously alter the internal propagation losses and the evanescent modal overlap of the cavity.

Consequently, the SCO-induced optogeometric modulation governs two distinct phenomena in the cavity's response. First, the increase in internal optical losses degrades the Q-factor and broadens the FWHM. Although these parameters should theoretically display a hysteresis loop, this subtle signature is experimentally masked by the thermal fluctuations of the polymer matrix and the SNR limits of the Lorentzian fitting in highly lossy regimes. Second, these dynamic losses alter the cavity's coupling regime. As formalized by Chrostowski and Hochberg [44] (Figure 6.11), transmission depth depends on a delicate balance between internal losses and the coupling coefficient. The SCO phase transition breaks this balance, driving the resonator away from critical coupling. This physical shift naturally imprints a robust and clearly resolvable hysteresis signature onto the ER profile.

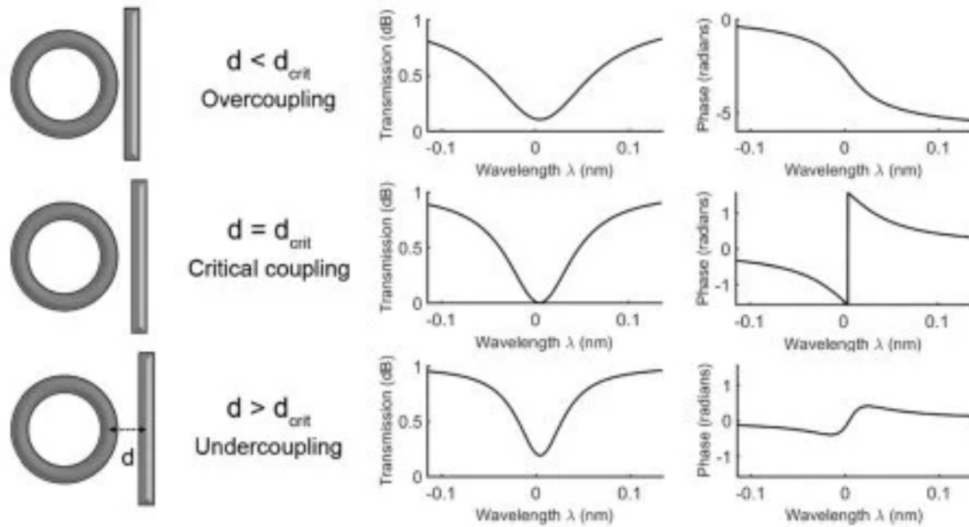


Figure 6.11: Fundamental optical coupling regimes in MRR. Reproduced from [44].

6.2. Fabrication and Characterization of Silicon-Based Graphene Nanodrums

6.2.1. Nanodrum Fabrication Protocol

The deterministic transfer methodology and two-dimensional material handling techniques implemented in this protocol were acquired through specialized training provided by Dr. Samuel Mañas at the *Instituto de Ciencia Molecular* (ICMol).

The mechanical exfoliation of the HOPG crystal was performed using a semiconductor-grade dicing tape (Nitto SPV-224) to minimize residual adhesive contamination [45]. To prevent cross-contamination, rectangular segments of the tape were prepared and manipulated exclusively using Teflon-coated tweezers.

The initial exfoliation step was executed directly from the bulk HOPG crystal—immobilized on a sample holder via double-sided adhesive—yielding a macroscopically flat graphite layer of uniform optical contrast. To obtain few-layer graphene, repeated tape-to-tape mechanical exfoliation was performed, typically requiring a minimum of four consecutive iterations. This process was visually monitored until the flakes exhibited a semi-transparent optical contrast, indicative of the target nanometric thickness regime. Subsequently, the tape containing the thinned material was brought into conformal contact with the PDMS viscoelastic stamp of approximated $1 \times 1 \text{ cm}^2$ section.

Following the transfer onto the elastomer, a rigorous optical inspection of the stamp was conducted. Suitable few-layer graphene flakes were identified based on their optical transmissivity, macroscopic morphological uniformity, and the absence of structural wrinkles or pre-existing strain. Selected candidates were documented and spatially mapped to facilitate rapid optical registration within the transfer setup.

The target silicon substrate comprised five periodic arrays of circular micro-cavities with varying diameters ($4 \mu\text{m}$, $6 \mu\text{m}$, $8 \mu\text{m}$, $10 \mu\text{m}$, and $12 \mu\text{m}$). The deterministic transfer was initiated by aligning the mapped flake directly over the selected cavity array. The vertical approach was then executed via the micro-manipulators until physical contact was established.

The progression of the conformal contact—visually identified by the propagation of a wave-like optical interference front—confirmed the intimate adhesion between the PDMS and the silicon surface. This front was advanced at a low velocity to prevent the entrapment of interfacial air pockets across the active regions. Finally, the detachment phase was performed at ultra-low velocity retraction at a recommendable velocity ($\sim v < 1 \mu\text{m/s}$). This kinetically restricted peeling allows the stronger Van der Waals affinity between the graphene and the target silicon to effectively overcome the viscoelastic adhesion to the PDMS, successfully yielding the suspended nanodrum architectures.

6.2.2. Fabrication and Dimensional Optimization of the PDMS Stamp

The elastomeric mixture was prepared utilizing the standard 10:1 mass ratio of prepolymer base to curing agent. To eliminate the dissolved gases and macroscopic air bubbles introduced during the mechanical mixing phase, the blend was covered with parafilm and subjected to ultrasonication inside a chemical fume hood for 20 minutes at ambient

temperature, until it was completely degassed.

The optimal thickness for the deterministic transfer of 2D materials via PDMS is empirically established in the literature as 1-3 mm [46]. This specific tolerance is dictated by the delicate mechanical equilibrium required between sufficient structural compliance to conform to the target topography, and adequate rigidity to prevent stamp rupture or flake deformation:

- **Too thin (< 1 mm):** The stamp becomes mechanically constrained by the "substrate effect". When attached to a rigid glass slide for micromanipulation, the stiffness of the glass dominates the mechanical response of the thin polymer layer. Consequently, the stamp lacks sufficient elastic volume to deform controllably, preventing a uniform and conformal contact with the silicon surface.
- **Too thick (> 3 mm):** The stamp becomes excessively compliant and prone to macroscopic lateral deformations or mechanical buckling. Under vertical applied pressure, a thick PDMS layer expands laterally, generating induced shear stresses that can stretch, wrinkle, or catastrophically tear the fragile graphene flakes. Furthermore, an over-thick optical medium compromises the focal precision during microscopic alignment.
- **Optimal range (1–3 mm):** This thickness operates as an ideal elastic cushion. It provides the precise viscoelastic damping required to uniformly distribute the applied hydrostatic pressure, allowing the stamp to seal the cavities seamlessly without inducing the structural collapse of the suspended graphene membranes.

To synthesize the stamp, a standard Petri dish with a diameter of 8.5 cm (radius $r = 4.25$ cm) was utilized. Given that the density of PDMS at a 10:1 ratio is $\rho \approx 0.975$ g/cm³, the theoretical mass required to achieve a target thickness of $h = 0.25$ cm (2.5 mm) was calculated. The required volume (V) is determined by the cylindrical geometry:

$$V = \pi r^2 h = \pi \times (4.25 \text{ cm})^2 \times 0.25 \text{ cm} \approx 14.18 \text{ cm}^3 \quad (4)$$

Applying the density relation, the target mass for the mixture is $m = \rho V \approx 13.83$ g. However, considering the unavoidable material retention on the walls of the mixing vessels when pouring highly viscous polymers, a slight mass excess was prepared to safeguard the target thickness. Specifically, 14.2007 g of the elastomer base and 1.4377 g of the curing agent were carefully weighed using a precision balance, accurately maintaining the 10:1 cross-linking ratio.

Subsequently, the degassed polymer was cured in a laboratory oven at 90 °C for 45 minutes. This specific thermal profile accelerates the cross-linking kinetics of the polymer network without inducing severe thermal degradation or residual stress, successfully preserving the dimensional stability and optimal viscoelasticity required for high-precision transfers [35]. As detailed in Figure 6.12, the final cured PDMS stamp yielded a central

thickness of 2.32 mm (measured via digital caliper), perfectly falling within the optimal range established by the literature.

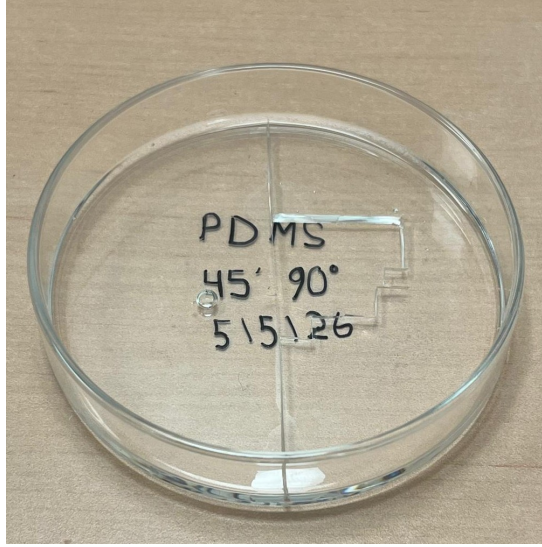


Figure 6.12: Macroscopic photograph of the PDMS elastomer prepared for the 2D material transfer.

6.2.3. *Initial Trials and Methodological Challenges*

The fabrication of suspended graphene nanodrums was an iterative process that required extensive optimization, driven by the systematic analysis of initial experimental failures. Preliminary trials were conducted to establish proficiency in the mechanical exfoliation of graphite and the deterministic transfer onto bare silicon substrates. Once the baseline technique was mastered, the functionalization of the pre-patterned micro-cavities commenced. We utilized four identical silicon substrates for this project. Initial attempts were performed on sample G1, which contained residual organic contaminants from a prior transfer of commercial large-area graphene provided by Graphenea.

The first major experimental challenge arose during the mechanical exfoliation process. Achieving sufficiently thin graphene flakes proved difficult; upon optical inspection of the PDMS stamp, the transferred flakes were frequently too thick, despite having performed up to seven consecutive tape-to-tape cleavages and observing a macroscopically transparent residue on the final tape prior to stamping (6.13).



Figure 6.13: Tape-to-tape mechanical exfoliation of bulk HOPG.

These initial exfoliation attempts involved applying high pressure between the adhesive tapes, followed by a slow peeling retraction. As observed under the optical microscope (Figure 6.14a), this specific mechanical approach yielded predominantly thick flakes exhibiting a high density of macroscopic wrinkles. Consequently, the majority of the 1×1 cm PDMS surface was populated with highly folded graphite structures. Occasionally, flat but multi-layered graphite flakes (Figure 6.14b) were identified and subsequently transferred onto the patterned substrate to test the alignment and stamping setup (Figures 6.14c and 6.14d). These preliminary iterations were fundamentally necessary to calibrate the deterministic viscoelastic stamping methodology and the micro-manipulator axes, even though the resulting transferred material was too thick for optimal optomechanical interaction.

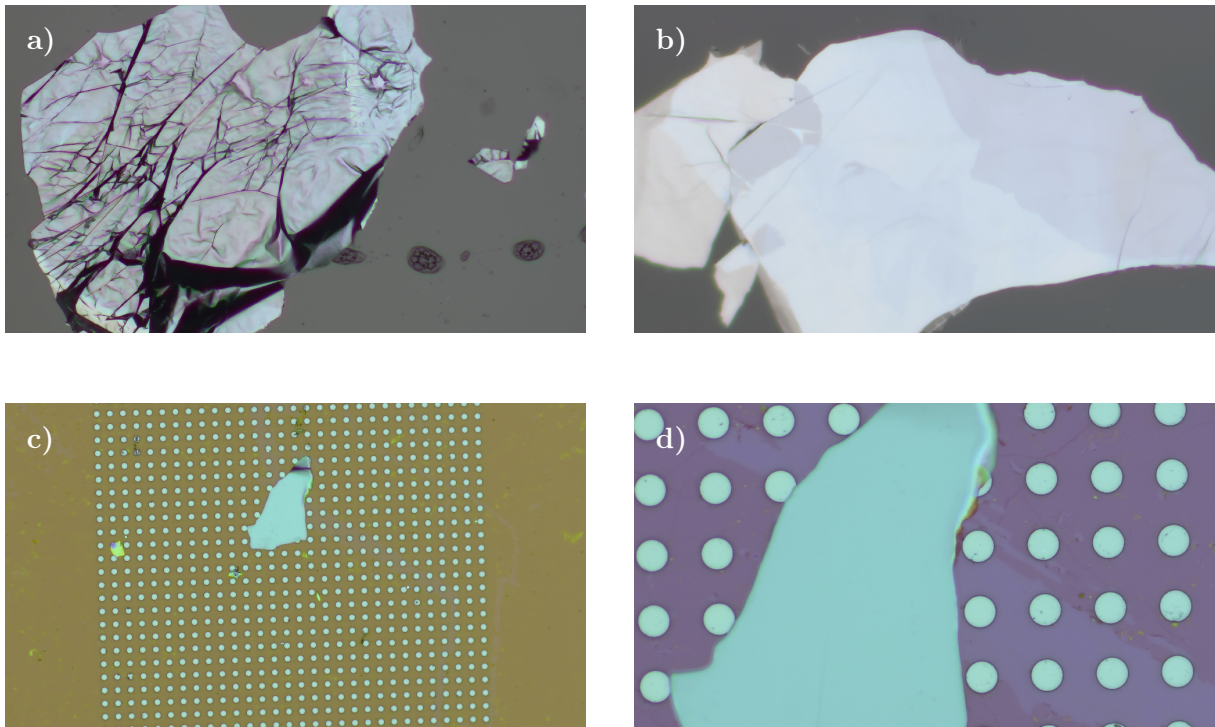


Figure 6.14: Deterministic transfer calibration. (a) Wrinkled and (b) flat multi-layer graphite flakes on PDMS. (c, d) Optical micrographs ($10\times$ and $50\times$) of the bulk transferred membrane.

Following numerous unsuccessful transfer attempts, the process was systematically refined, starting with a more rigorous optical selection criterion for the flakes (Figure 6.15). It was empirically determined that smaller and thinner flakes exhibit better conformal adhesion to the target substrate. Nevertheless, this presented a critical physical trade-off: as the flake thickness approached the few-layer regime, internal mechanical stress and intrinsic folding became significantly more pronounced.

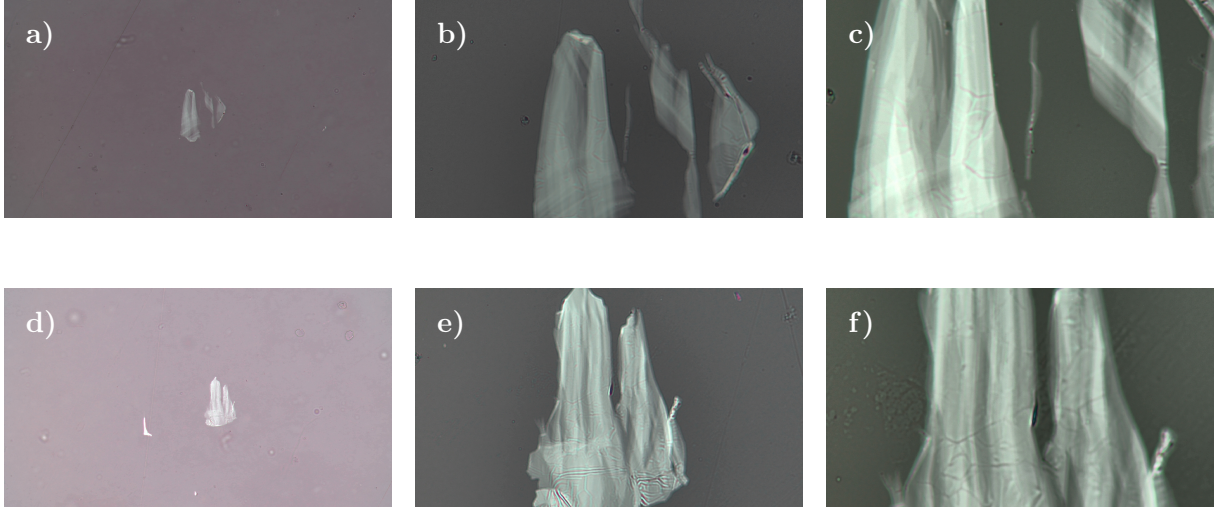


Figure 6.15: Optical micrographs of two mechanically exfoliated flakes on PDMS at increasing magnifications ($10\times$, $50\times$, $100\times$). (a–c) First flake morphology. (d–f) Second flake morphology.

To overcome the transfer bottleneck, three distinct stamping protocols were systematically evaluated using the same target array and selected flakes (Figure 6.15):

1. A slow vertical approach by elevating the silicon platform, followed by a 5-minute stabilization period and a slow retraction. This resulted in zero adhesion to the substrate.
2. A standard-velocity descent of the PDMS stamp (slowing down near the contact point), followed by 30 seconds of subtle in-plane (X-Y) platform movements to force conformal contact, and a slow peeling phase. This also yielded no transfer.
3. A standard-velocity descent followed by in-plane X-Y adjustments and a prolonged 15-minute resting period under contact. The subsequent peeling was performed at an extremely slow velocity. This attempt achieved only partial success, transferring a minimal flake fragment strictly at the outer edge of the cavity array (Figure 6.16).

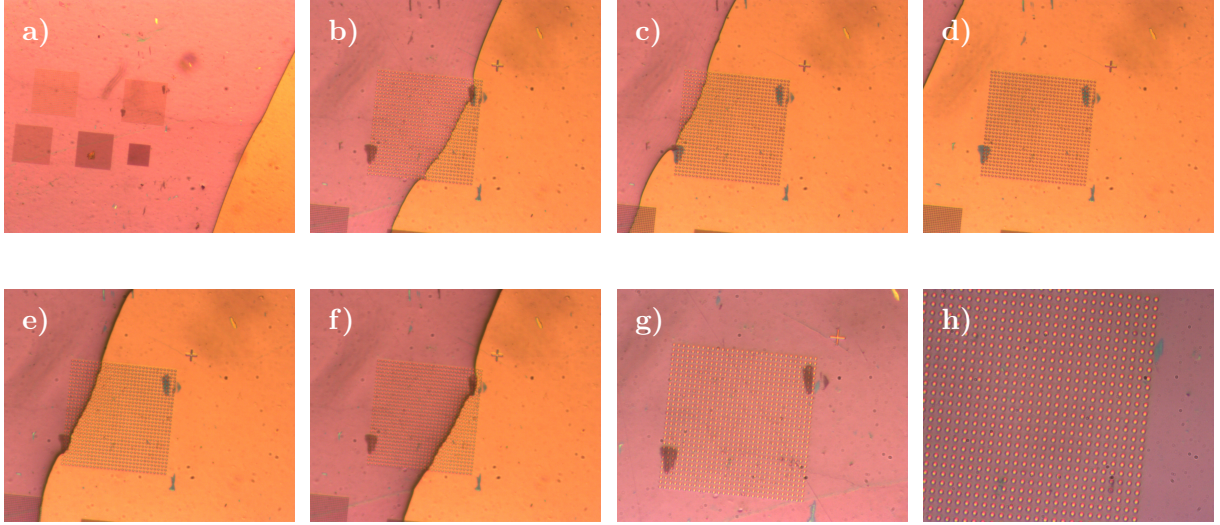


Figure 6.16: Sequential optical micrographs of a deterministic transfer. (a–d) Flake alignment and physical contact. (e–g) Vertical detachment phase. (h) Final transfer outcome.

These observations led to the hypothesis that transferring two-dimensional materials outside the pre-patterned regions was inherently easier due to two competing factors: the reduced effective contact area over the arrays and the upward pressure exerted by the air trapped within the micro-cavities during the PDMS compression.

6.2.4. Iterative Optimization: Refinement of the Anchoring and Detachment Strategy

To validate our methodology and mitigate these limitations, a collaborative visit to the *Instituto de Ciencia Molecular* (ICMol) at the *Universitat de València* (UV) was conducted under the guidance of Dr. Samuel Mañas. Comparing experimental setups confirmed that our mechanical transfer execution was fundamentally correct. The primary issue was traced back to the G1 sample itself; the substrate’s residual organic contamination severely hindered Van der Waals adhesion and promoted the formation of microscopic air bubbles at the graphene-silicon interface. These defects were undetectable in our transfer setup due to the limited optical resolution of the top-view camera compared to the high-resolution microscopy available at ICMol.

Having verified the integrity of our transfer protocol, subsequent experiments were exclusively performed on sample G4 (Figure 6.17). This pristine, highly clean silicon substrate had been intentionally reserved for this exact optimization phase, ensuring that future transfer outcomes would be governed solely by the physical parameters of the process rather than substrate contamination.

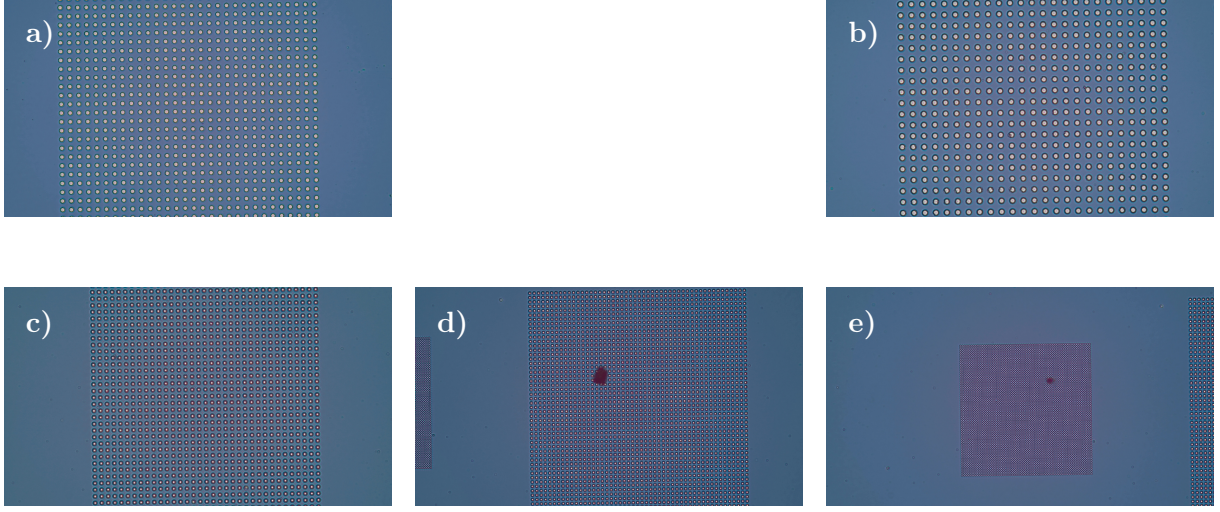


Figure 6.17: Optical micrographs detailing the five periodic micro-cavity arrays on the pristine G4 silicon substrate. (a) Array 4 and (b) Array 5. (c–e) Arrays 3, 2, and 1, respectively.

To further optimize the yield, the mechanical exfoliation technique was empirically modified. Instead of a slow separation between the adhesive tapes, a rapid contact followed by an immediate, swift retraction was employed. This dynamic approach required precise manual execution but significantly reduced the formation of wrinkles. Additionally, the thinned graphite was stamped onto PDMS substrates with a $\sim 0.5 \times 0.5$ cm reduced surface area. This strategy not only accelerated the optical screening process but also yielded thinner, larger-area flakes with minimized internal strain (Figure 6.18). Consequently, the number of necessary tape-to-tape iterations was successfully reduced to approximately four.

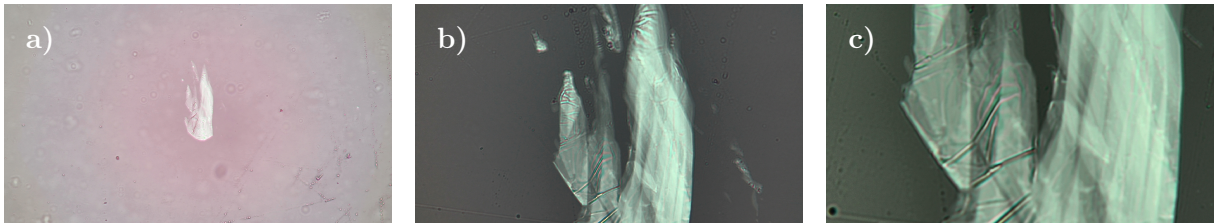


Figure 6.18: Optical micrographs of the flake on PDMS at (a) 10 $\times$, (b) 50 $\times$, and (c) 100 $\times$ magnification.

Subsequent transfer attempts were directed towards Array 4 (A4), characterized by a 10 μm pitch, to test a new mechanical anchoring hypothesis. We postulated that the transfer could be substantially enhanced if a portion of the flake was first firmly adhered to the unpatterned, bare silicon surrounding the array. Crucially, during the peeling phase,

the detachment wave (the contact line between the polymer and the substrate) must be strategically steered so that it initiates at this firmly anchored region and propagates towards the cavities. To validate this, controlled experiments were performed comparing two distinct peeling trajectories across the same graphene-PDMS interface:

1. **Detachment initiating over the patterned array:** In this standard scenario, the peeling wave was steered to first interact with the portion of the flake located directly over the micro-cavities. Because the effective contact area is significantly reduced by the patterned voids, the initial Van der Waals adhesion is inherently weak. Consequently, the shear forces from the retracting PDMS easily overcome this minimal substrate adhesion, typically causing the flake to delaminate or tear before the wave can establish a solid contact line (Figure 6.19).

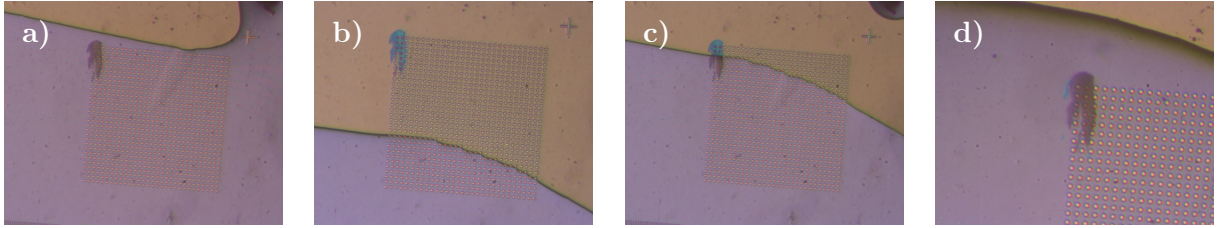


Figure 6.19: Deterministic transfer sequence detaching over the micro-cavity array. (a, b) Initial conformal contact phase. (c, d) Vertical detachment phase.

2. **Detachment initiating over the bare silicon (Anchoring strategy):** In this modified approach, the detachment wave was forced to originate at the solid, unpatterned silicon region, where the flake experiences maximum continuous contact area. This establishes a robust Van der Waals anchor. As the quasistatic peeling wave subsequently propagates towards the cavities, the firmly pinned section acts as a mechanical pivot. It effectively resists the upward traction of the elastomer, forcing the remainder of the flake to continuously strip away from the PDMS and suspend over the adjacent micro-cavities (Figure 6.20).

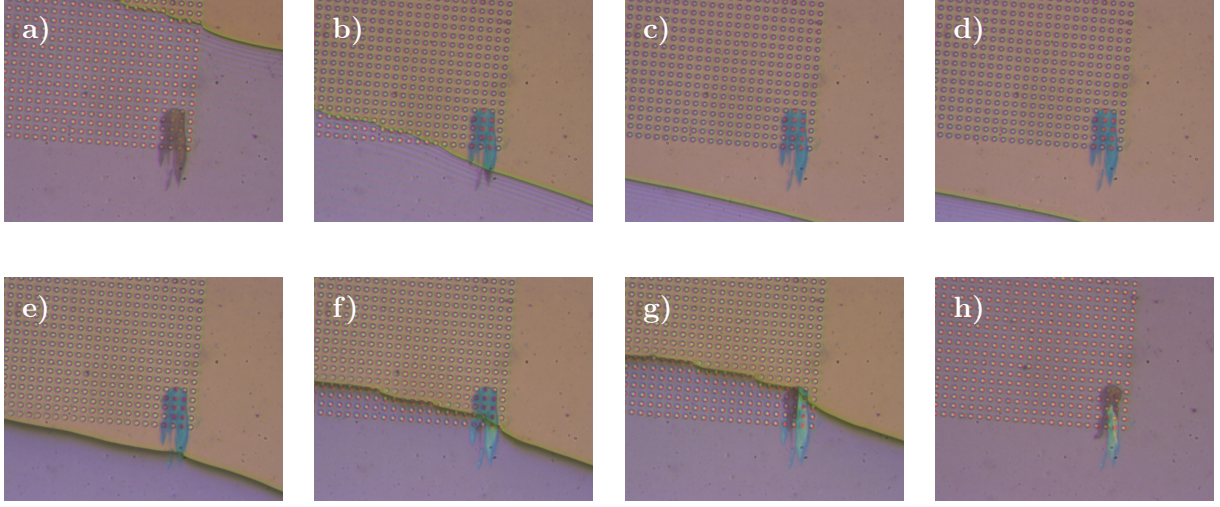


Figure 6.20: Transfer sequence using the optimized anchoring strategy. (a–c) Approach and conformal contact. (d) Static relaxation. (e–g) Vertical detachment phase. (h) Final transfer outcome.

The modified peeling strategy yielded our first successful controlled transfer of a few-layer graphene membrane over the micro-cavities (Figure 6.21). However, despite executing a meticulously slow retraction, a significant portion of the flake fractured and remained adhered to the PDMS. This mechanical rupture is attributed to inhomogeneous internal tensions and step edges between regions of varying layer thickness within the same flake. Furthermore, optical microscopy of the transferred nanodrums revealed a lack of topological flatness. Heterogeneous optical contrast across the suspended regions indicated non-uniform refraction, a direct consequence of the built-in strain and localized deformations induced during the non-uniform detachment process.

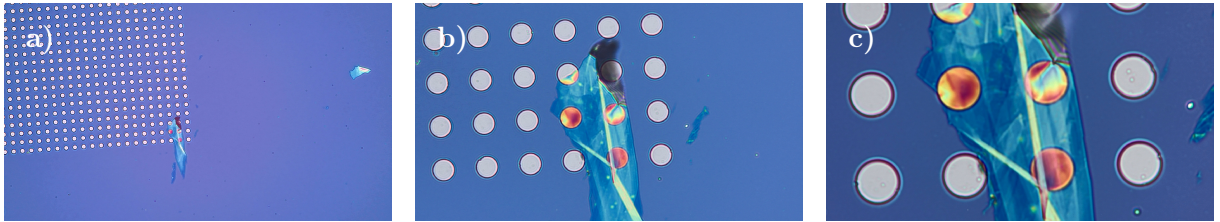


Figure 6.21: Optical micrographs of the transferred graphene flake over Array 4 at (a) 10 $\times$, (b) 50 $\times$, and (c) 100 $\times$ magnification.

6.2.5. *Successful Integration of Graphene Suspended Membranes*

For the definitive deterministic transfer, Array 3 (A3), characterized by an 8 μm periodicity, was selected as the optimal target architecture. Recognizing the inherent stochastic

nature of the exfoliation process, numerous iterations were performed until an exceptionally high-quality graphene flake was isolated. This optimal candidate was selected based on its large continuous area, uniform thickness contour (minimal layer-count variations), and the absence of macroscopic folds (Figure 6.22).

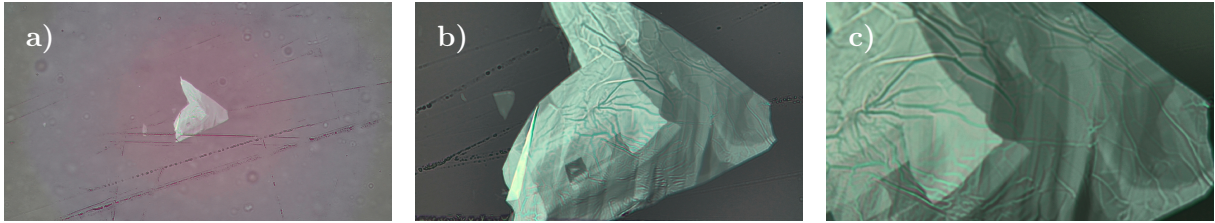


Figure 6.22: Pre-transfer optical micrographs of the few-layer graphene flake on PDMS at (a) 10 $\times$, (b) 50 $\times$, and (c) 100 $\times$ magnification.

The PDMS stamp was tactically oriented within the transfer setup to align the optimal peeling direction with the previously validated bare silicon anchoring strategy. Following a slow vertical approach and precise alignment, the system was left in conformal contact for a 5-minute stabilization period. The subsequent peeling phase was executed under a highly sophisticated, quasistatic regime. At critical junctions (specifically, as the detachment wave traversed the edges of the micro-cavities) the vertical retraction was dynamically modulated. By employing slight, controlled advances and retreats of the contact line, optimal adhesion was ensured while preventing sudden shear forces. This ultra-slow detachment process spanned exactly 19 minutes and was meticulously documented via the top-view optical system, whole process is shown in Figure 6.23.

Similar to previous attempts, the flake underwent a mechanical rupture during the final release, exactly in Figure 6.23i flake started to split, exactly when entering in contact with micro-cavities. However, in this instance, the separation occurred uniformly. This clean fracture prevented the membrane from folding back onto itself, resulting a structurally pristine transfer over the target cavities. High-resolution optical microscopy confirmed the success of the process, showing a uniform refractive contrast across the majority of the covered nanodrums, indicative of a flat, evenly tensioned membrane (Figure 6.24).

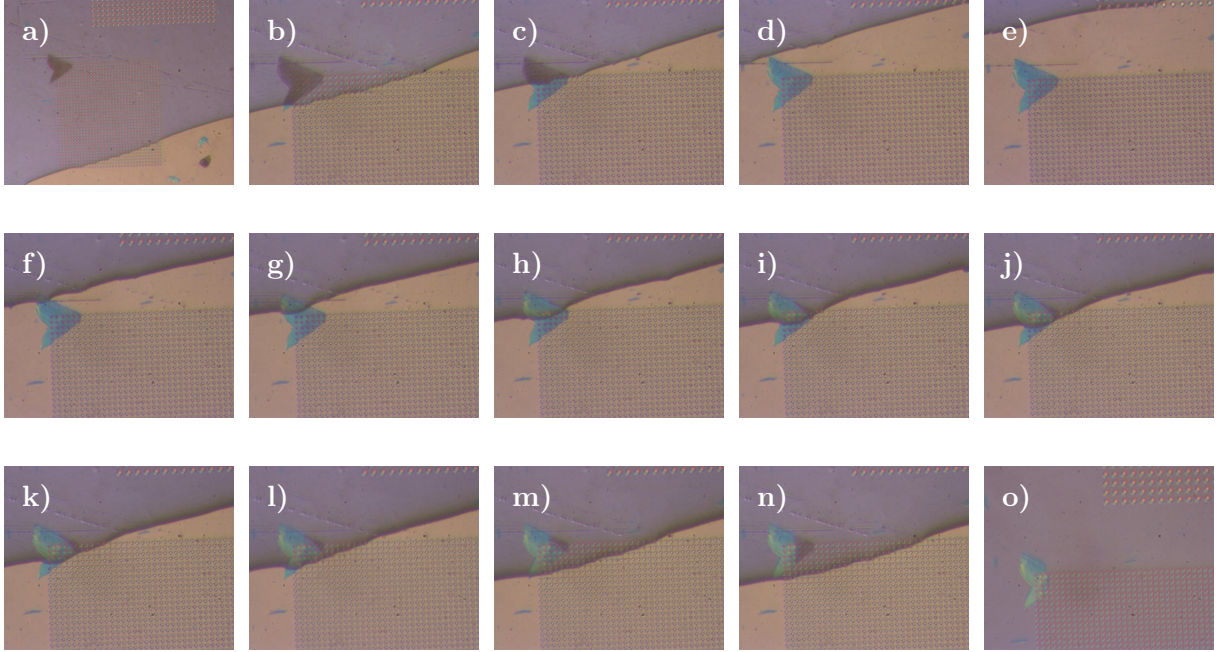


Figure 6.23: Quasistatic deterministic transfer sequence of the few-layer graphene flake. (a–d) Approach and conformal contact. (e) Static relaxation. (f–n) Vertical detachment phase. (o) Final transfer outcome.

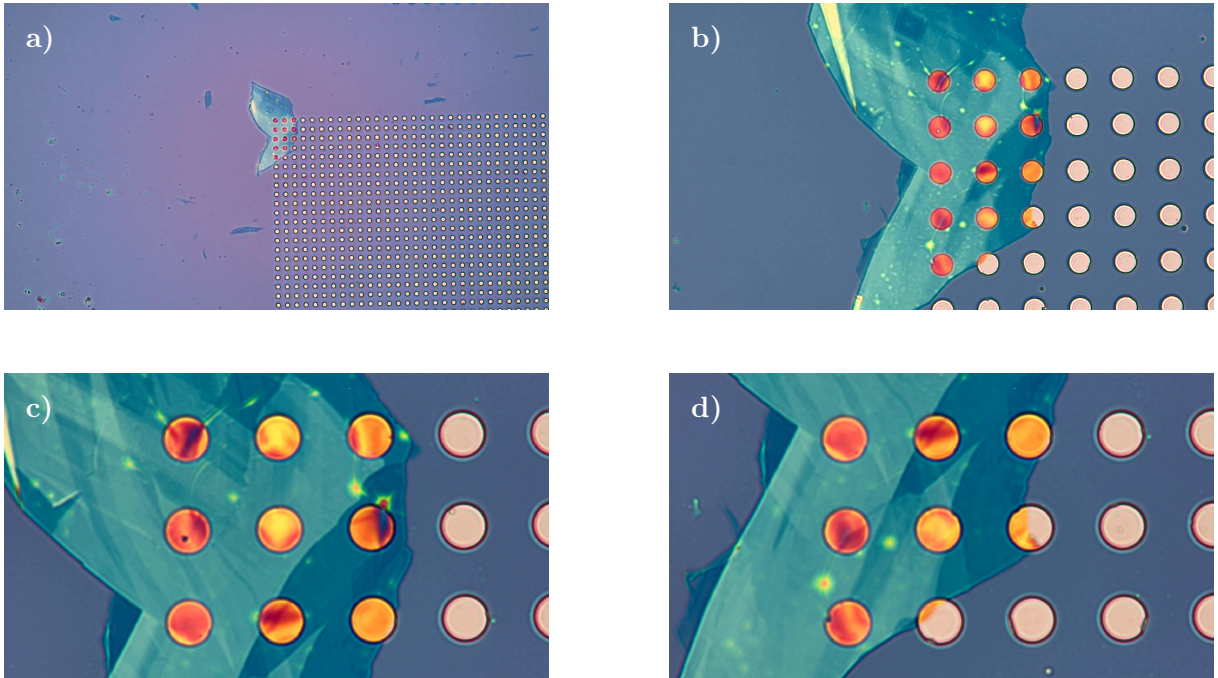


Figure 6.24: Post-transfer optical micrographs of the succesful few-layer graphene flake over the micro-cavity array at (a) 10 $\times$, (b) 50 $\times$, and (c, d) 100 $\times$ magnification.

Nevertheless, a comparative analysis between the optical micrographs of the initial PDMS stamp (Figure 6.22) and the final silicon substrate (Figure 6.24) revealed a fundamental physical constraint: the thinnest regions of the original flake, likely approaching the monolayer regime, failed to transfer. This observation confirms that ultra-thin graphene remains the most challenging structural domain to reliably detach from the viscoelastic polymer.

6.2.6. Graphene Raman Spectroscopy

As previously introduced, Raman spectroscopy provides a definitive, non-destructive optical fingerprint of the structural integrity of carbon allotropes. To evaluate the quality of the successfully transferred graphene nanodrums, we analyzed the three primary Raman features characteristic of this material. Drawing on the foundational work by Ferrari *et al.* [41], these peaks allow us to extract precise physical parameters regarding our suspended membranes:

- **The G peak ($\sim 1580 \text{ cm}^{-1}$):** Arising from the primary in-plane vibrational stretching of the sp^2 hybridized carbon atoms, corresponding to the doubly degenerate E_{2g} phonon mode at the Brillouin zone center. Its exact position and intensity serve as a baseline for the spectrum, and it is highly sensitive to external perturbations such as doping and applied mechanical strain.
- **The 2D peak ($\sim 2690 \text{ cm}^{-1}$):** An overtone of the D band resulting from a second-order, two-phonon resonance process. Crucially, unlike the D peak, it does not require defects to be active. Its line shape and FWHM, along with the intensity ratio relative to the G peak (I_{2D}/I_G), are the most reliable indicators to determine the exact number of graphene layers.
- **The D peak ($\sim 1350 \text{ cm}^{-1}$):** A defect-activated ring breathing mode (transverse optical phonons near the K point). Because its activation requires an intervalley scattering process driven by a break in the translational symmetry of the lattice, its intensity relative to the G peak (I_D/I_G) provides a direct, quantitative measure of structural disorder, or the physical proximity to the flake edges.

As mentioned, the relative intensity ratio between the 2D and G peaks (I_{2D}/I_G) serves as a standard empirical guideline to estimate the layer count of the membrane. Generally, a ratio significantly greater than 2 is indicative of pristine monolayer graphene. As the number of layers increases, the I_{2D}/I_G ratio progressively decreases due to the evolving electronic band structure. In experimental setups, ratios ranging between 1 and 2 typically correspond to bilayer or trilayer configurations. When the ratio drops below 0.7, the material is structurally transitioning toward bulk graphite, where the ratio eventually stabilizes between 0.3 and 0.5 [47]. Nevertheless, the membrane still retains distinct multi-layer features rather than bulk-like properties as long as the 2D line shape remains certainly symmetric and can be mathematically fitted by a single profile, confirming the preservation of its two-dimensional nanostructural behavior [47].

To make replicable measures, all Raman measurements were conducted using an excitation laser wavelength of $\lambda = 535$ nm and an incident optical power of $P = 2$ mW to prevent localized thermal damage to the matrix. To perform an initial assessment of the suspended membrane's quality, a preliminary single-point Raman acquisition was conducted at the center of a transferred nanodrum as shown in Figure 6.25. To achieve an optimal SNR without inducing thermal damage or local heating to the suspended graphene interface, the spectrum was collected using 20 accumulations of 1 second each, (left-bottom drum detailed in Figure 6.25b).

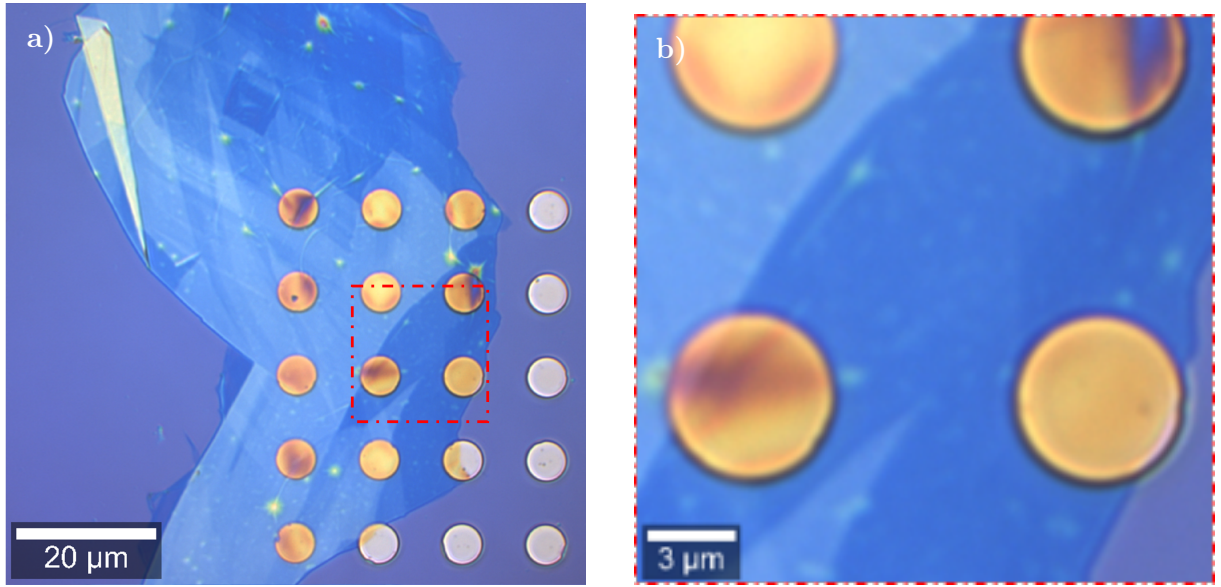


Figure 6.25: Optical micrographs of the transferred few-layer graphene flake prior to Raman spectroscopy. (a) Field of view at 100 $\times$ magnification. (b) Digitally zoomed region highlighting the specific micro-cavity targeted for subsequent characterization.

The resulting spectrum, presented in Figure 6.26, confirms the successful transfer of a high-quality few-layer graphene membrane. It should be noted that the spectral intensities are reported in arbitrary units (a.u.) rather than raw CCD counts. This is a standard convention in Raman spectroscopy, as absolute detector counts are heavily dependent on specific hardware configurations, integration times, and incident laser power. Instead, the fundamental physical characterization of the material relies entirely on the relative spectral features. In this regard, the well-resolved 2D peak alongside a prominent G peak yields an I_{2D}/I_G ratio characteristic of few-layer graphene, aligning perfectly with our prior optical microscopy observations. Additionally, while a minor D peak is discernible, its low intensity relative to the G peak confirms that the overall crystalline lattice remains structurally pristine and well-preserved following the deterministic transfer, as detailed in Table 6.1.

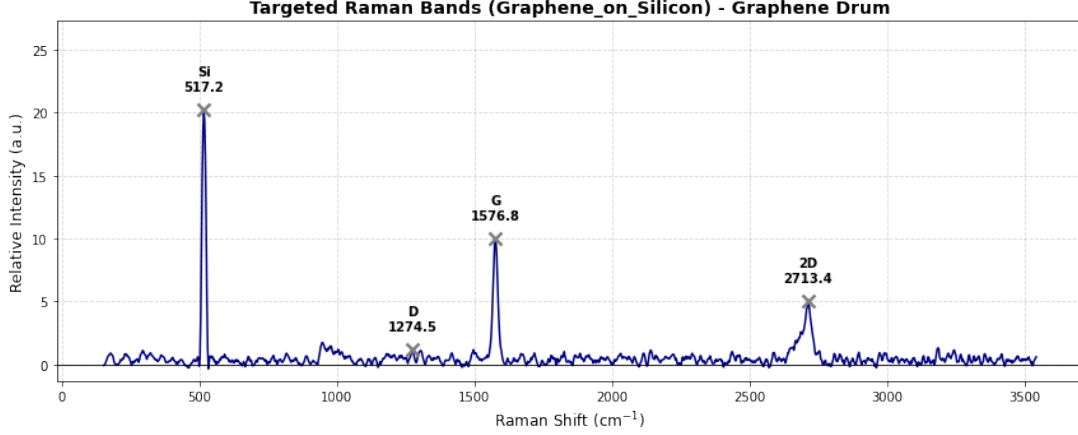


Figure 6.26: Representative Raman spectrum of the suspended few-layer graphene membrane over the targeted micro-cavity.

Table 6.1: Experimental Raman peak positions, and their corresponding intensities for the analyzed graphene nanodrum.

Band	Detected Pos. (cm ⁻¹)	Intensity (a.u.)
Si	517.17	20.20
D	1274.49	1.20
G	1576.82	10.03
2D	2713.39	5.03

A quantitative analysis of the extracted intensities provides a comprehensive validation of the membrane’s structural profile. The calculated 2D-to-G intensity ratio is $I_{2D}/I_G \approx 0.50$. Although this value falls within the regime of thicker few-layer graphene, in the context of suspended OM cavities, it confirms the successful integration of a robust membrane possessing the necessary mechanical rigidity for OM actuation. This multi-layer nature is further corroborated by the spectral broadening of the 2D band. Physically, as the layer count increases beyond a pristine monolayer, interlayer electronic coupling causes the π band structure to undergo splitting. Consequently, the second-order 2D peak deviates from the single narrow Lorentzian profile characteristic of single-layer graphene, transitioning into a broader convolution of multiple scattering pathways. Furthermore, the calculated defect intensity ratio remains remarkably low at $I_D/I_G \approx 0.12$. In micro-Raman spectroscopy, a value of this magnitude indicates a highly crystalline and well-preserved basal plane. The minor D band contribution is fundamentally attributed to momentum conservation requirements at the physical edges of the flake (edge scattering) or minor localized stress induced during the viscoelastic peeling phase, rather than intrinsic lattice damage. This rigorously confirms that the deterministic transfer process over the micro-cavity was essentially non-destructive.

From an OM engineering perspective, achieving a few-layer configuration rather than a strict monolayer is highly desirable. While monolayer graphene possesses extraordinary in-plane tensile strength, its extremely low out-of-plane flexural rigidity makes suspended monolayers highly susceptible to mechanical collapse (stiction) against the bottom of the cavities due to Van der Waals interactions. Therefore, this few-layer nanodrum represents an optimal structural compromise: it remains sufficiently thin to act similar to a highly responsive two-dimensional membrane, yet possesses the necessary flexural stiffness to maintain a stable, free-standing suspended architecture without collapsing.

To evaluate the spatial uniformity of these structural properties and verify the integrity of the membrane across the entire micro-cavity, a high-resolution Raman spatial scan was subsequently performed (Figure 6.27).

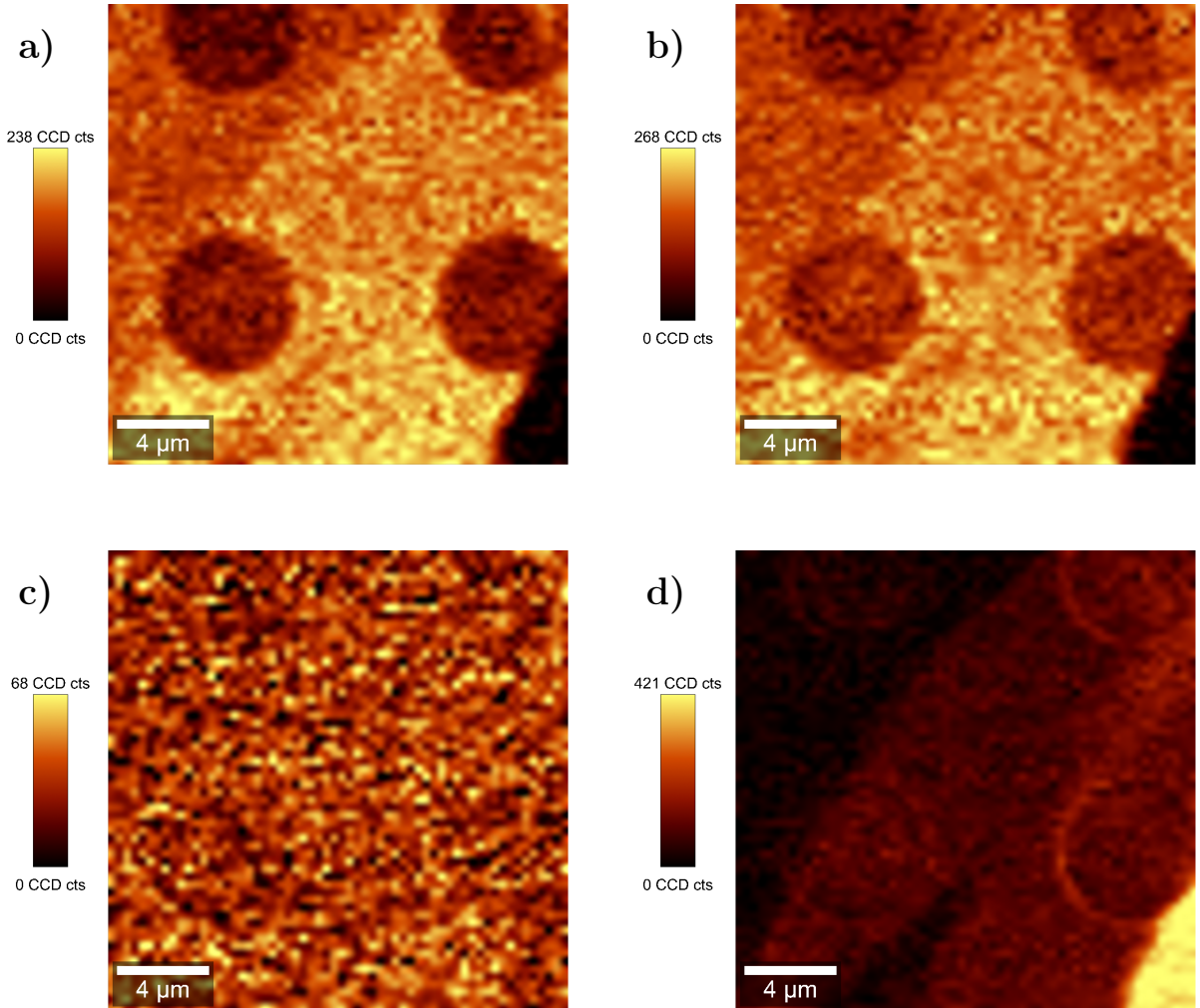


Figure 6.27: Confocal Raman spatial mapping of the transferred few-layer graphene flake. Intensity maps of the (a) G band, (b) 2D band, (c) D band, and (d) silicon substrate.

A detailed spatial analysis of the acquired confocal colormaps reveals critical opto-geometric features of the transferred nanodrum architecture. As observed in Figures 6.27a and 6.27b, the G and 2D band intensities exhibit both macroscopic gradients and highly localized discrete domains. The macroscopic variations, specifically, the expanded high-intensity domain that encompasses the central diagonal and extends across the lower-left portion of the flake (contrasting with the lower-intensity zone in the top-left) corresponds to discrete thickness differences, or terraces, within the few-layer flake, scaling with the scattering volume of sp^2 carbon atoms. However, the sharply defined circular regions of attenuated G and 2D intensity directly correspond to the suspended graphene over the micro-cavities. Rather than a localized reduction in layer count, this attenuation is a signature optical interference phenomenon. For the supported regions, the underlying highly reflective silicon substrate enhances the local optical field, amplifying the Raman scattering cross-section. Conversely, the absence of an immediate reflective interface beneath the suspended membranes alters the Fabry-Pérot interference conditions, resulting in the observed signal drop.

Crucially, the D band intensity map (Figure 6.27c) remains uniformly low across all structural domains. This observation is physically significant: it confirms that neither the internal terracing of the flake nor the mechanical stress induced at the physical boundaries of the micro-cavities introduced significant intralayer defects, amorphization, or tearing. The continuous crystalline lattice is highly preserved despite the transition from supported to suspended regimes.

Finally, the Silicon substrate map (Figure 6.27d) serves as an in-situ optical transmission and depth profile. The unclad substrate at the bottom-right yields a saturated maximum intensity. In the supported graphene regions, the Si signal is attenuated proportionally to the local layer count, perfectly corroborating the thickness gradient observed in the G band (where the thicker central and lower-left domains yield the highest Si attenuation). Notably, the Si signal drops precipitously within the circular boundaries of the nanodrums, rendering the underlying periodic holes clearly visible as sharply defined regions of attenuated intensity. Because the confocal pinhole is aligned to the focal plane of the top surface, the bottom of the etched cavities lies significantly out-of-focus, resulting in minimal back-scattered Si collection. This dual dependence on absorption and focal depth provides a valuable optical estimation of the underlying periodic topography. Nevertheless, due to the inherent diffraction limits of confocal microscopy, precise quantitative extraction of the topography requires AFM characterization

6.2.7. *AFM characterization*

To complement the spectroscopic data and provide a rigorous quantitative analysis of the membrane's topographical profile, high-resolution AFM characterization was performed. The raw AFM data, presented was processed and analyzed utilizing the WSxM 5.0 software [48]. Initial measurements targeted the thinnest suspended regions of the flake, spatially correlating with the previously discussed Raman maps. As depicted in Figure 6.28, the topographical scan allows for the direct extraction of the height profile across

the micro-cavity, confirming the structural suspension of the nanodrum and enabling the evaluation of its out-of-plane deformation.

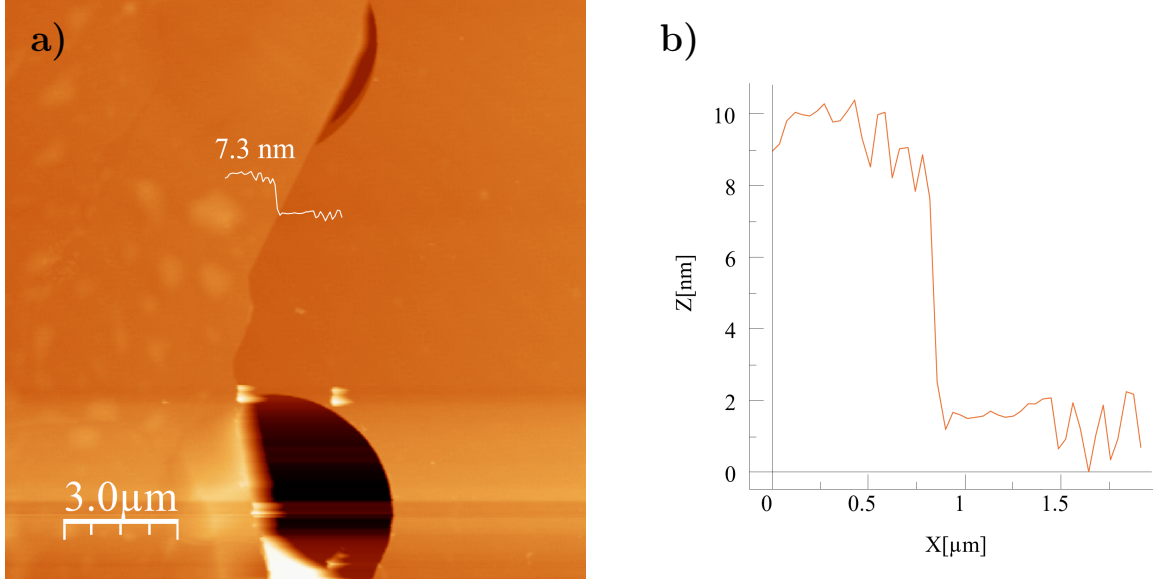


Figure 6.28: AFM topography of the suspended graphene nanodrum. (a) 2D height map of the targeted region. (b) Extracted height profile across the suspended membrane.

Following the extraction of the topographical profile, a quantitative estimation of the layer count was conducted. As extensively documented in the foundational work by Nemes-Incze *et al.* [49] regarding tapping-mode AFM characterization of carbon allotropes, the apparent thickness of graphene on a silicon-based substrate does not scale linearly from zero. Due to chemical contrast, tip-sample Van der Waals interactions, and the presence of adsorbed ambient molecules (such as a hydration layer) at the interface, the first graphene layer exhibits an anomalously large apparent thickness. Subsequent layers, however, strictly add the theoretical interlayer spacing of bulk graphite. This physical behavior is mathematically formalized by the following equation:

$$d_{AFM} = d_1 + (n - 1) \cdot \Delta z \quad (5)$$

where:

- d_{AFM} is the total apparent thickness measured experimentally across the step edge.
- n is the discrete number of graphene layers composing the flake.
- d_1 is the apparent instrumental thickness of the first graphene layer in contact with the substrate. Due to the aforementioned tip-sample interactions, this value typically ranges between 0.8 nm and 1.0 nm.

-
- Δz represents the constant interlayer Van der Waals spacing of bulk graphite, established at 0.335 nm.

Based on the acquired height profile (Figure 6.28b), the suspended membrane exhibits a relative thickness of approximately 7.3 nm. Applying the theoretical model and assuming an average initial offset of $d_1 \approx 0.9$ nm, this measurement directly correlates to a multi-layer graphene configuration consisting of $n \approx 20$ layers. This calculation is in excellent agreement with our previous Raman spectroscopic assessment ($I_{2D}/I_G \approx 0.50$).

From a nanomechanical perspective, as previously commented, implementing a few-layer graphene membrane rather than a strictly monolayer counterpart is highly strategic for our OM architecture. Since the ultimate objective is to utilize these nanodrums as dynamic platforms for strain engineering driven by the PMMA/SCO composite, the membrane must possess a high degree of mechanical durability. A few-layer configuration provides significantly enhanced flexural rigidity compared to a monolayer. This structural robustness is critical to withstand the continuous out-of-plane stress modulations induced by the volumetric expansion and contraction of the SCO nanoparticles, effectively preventing mechanical failure, tearing, or irreversible stiction against the cavity floor during the thermal transition cycles.

Further topographical investigation was extended to adjacent regions of the transferred flake to assess its large-scale structural uniformity. As illustrated in Figure 6.29, a region exhibiting a drastic morphological step-edge was identified. This abrupt terrace likely originates from a structural rupture induced by shear forces during the deterministic viscoelastic peel-off process.

The extracted height profile (Figure 6.29b) reveals a macroscopic transition from a thick, bulk-like region of approximately 16 nm down to an ultra-thin region of 2 nm. Contrary to a visual approximation, applying the established AFM apparent thickness model ($d_{AFM} = d_1 + (n - 1) \cdot \Delta z$) confirms that a 2 nm step does not correspond to a monolayer. Assuming the standard 0.9 nm initial offset, this region consists of approximately 4 layers. This quantitative assessment confirms that while isolating a pure, macroscopic monolayer via deterministic dry transfer remains statistically challenging under standard ambient conditions; achieving highly uniform, large-area few-layer regions is feasible.

In addition to the topographical data, phase-contrast imaging was simultaneously acquired. The phase map (Figure 6.29c) is highly sensitive to local variations in energy dissipation and adhesion, revealing the presence of nanoscale interfacial inclusions. These features are commonly attributed to trapped air pockets or ambient adsorbates between the graphene basal plane and the underlying substrate. From an OM perspective, identifying these interfacial bubbles is crucial. Such inclusions can locally modify the membrane's built-in tension and mass distribution, thereby acting as dissipation centers that could unpredictably alter the fundamental resonance frequency and the mechanical quality factor (Q) of the suspended drum.

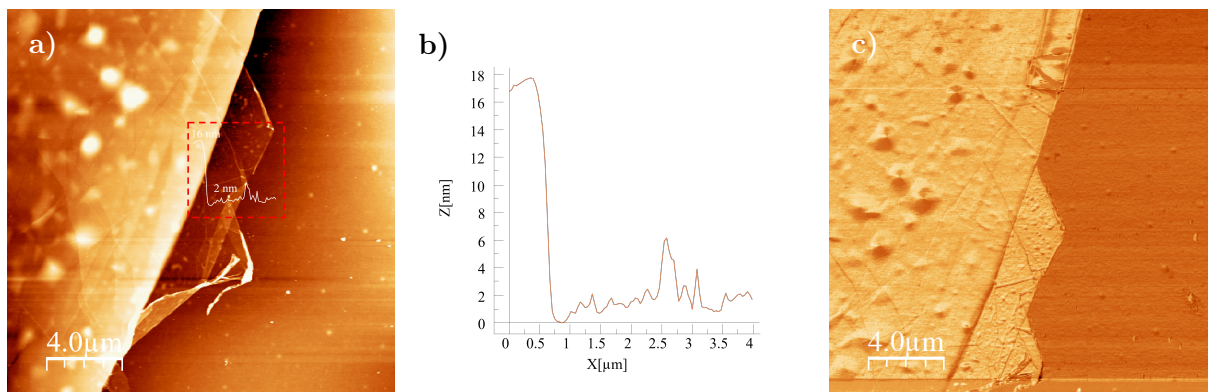


Figure 6.29: AFM characterization of a structural terrace within the transferred flake. (a) 2D topographic map. (b) Extracted height profile across the step. (c) Phase image.

6.3. Fabrication and Characterization of Polymeric PDMS Nanodrums

Moving beyond the established protocols for the deterministic transfer of two-dimensional materials onto silicon platforms, the specific development of a highly disruptive alternative approach was conceptualized during the course of this research. Conventional OM platforms rely on silicon arrays; however, silicon is a mechanically rigid material, which fundamentally limits the dynamic range of macroscopic strain that can be applied to the cavity. Furthermore, the most sophisticated step of the standard fabrication protocol, the viscoelastic peeling of the PDMS stamp from the silicon surface, frequently results in the rupture or collapsing of the suspended graphene flakes.

To avoid these fundamental limitations, we propose the fabrication of fully polymeric OM cavities, transitioning from silicon-based devices to monolithic PDMS nanodrums. By pre-patterning the micro-cavities directly into the PDMS elastomer, the polymer intrinsically serves as both the structural substrate and a highly compliant medium, making it exceptionally suited for advanced strain-engineering architectures.

Crucially, this methodology drastically simplifies the fabrication workflow by entirely bypassing the complex deterministic transfer setup. The mechanical exfoliation of the HOPG crystal, carried out using the semiconductor dicing tape, is stamped directly onto the pre-patterned PDMS. Because the graphene flake is never transferred to a secondary rigid substrate, the delicate quasistatic peeling phase is completely eliminated. The flake simply remains adhered to the PDMS surface via Van der Waals forces, naturally suspending over the polymeric cavities to form the nanodrum.

According to the current state-of-the-art, the conceptualization and direct experimental implementation of suspended graphene membranes over flexible PDMS micro-cavities represents an unprecedented approach, with no prior reports in the current cavity optomechanics literature. This novel paradigm not only circumvents the traditional transfer bottlenecks but also opens a completely new research frontier for extreme, ultra-flexible strain-engineering devices.

To achieve this, a pre-patterned master mold is required to cast the elastomer. The master mold utilized in our soft lithography process was fabricated via micro-imprint lithography, patterning an acrylate polymer resin deposited directly onto a standard glass microscope slide.

The mold was designed incorporating four distinct sections, each targeting a different theoretical pillar height: 300 nm, 400 nm, 500 nm, and 600 nm. Within each of these sections, the spatial layout replicates the five periodic arrays previously established for the silicon devices. For the scope of this morphological analysis, we specifically focus on Array 3 (A3), which is characterized by an $8\mu\text{m}$ periodic distance. As observed in the optical micrographs (Figure 6.30), the micro-imprint process successfully yielded highly periodic and well-defined acrylate pillar arrays across the glass substrate.

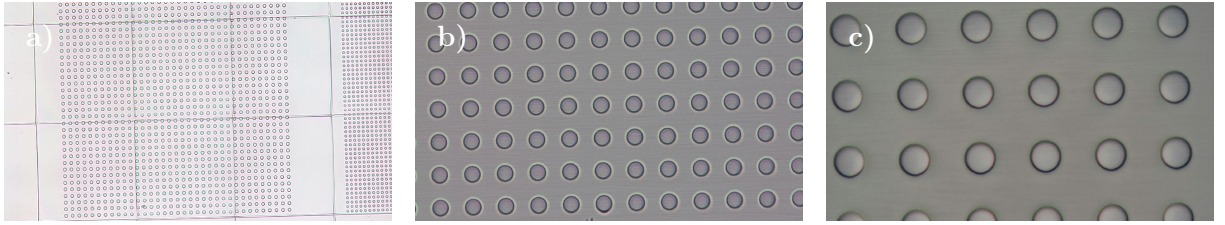


Figure 6.30: Optical micrographs of the acrylate master mold (Array 3) at (a) 10 $\times$, (b) 50 $\times$, and (c) 100 $\times$ magnification.

6.3.1. AFM Profiling of the Pillar Array Master

While optical microscopy confirmed the macroscopic uniformity of the acrylate mold, a rigorous quantitative assessment of its vertical dimensions was required. To evaluate the structural fidelity of the imprinted pillars, the four grating sections were characterized via AFM. The optimal morphological definition was observed in the section with the highest nominal depth. However, the quantitative topographical analysis revealed a discrepancy between the target and the fabricated dimensions. Despite a theoretical design specifying a 600 nm height, the experimental measurements demonstrated an actual average pillar height of approximately 350 nm.

The raw AFM topographical data, presented in Figure 6.31, was processed and analyzed utilizing the WSxM 5.0 software [48]. The image post-processing was strictly limited to a standard first-order plane tilt correction (flattening). This minimal adjustment is routinely applied to compensate for any macroscopic sample inclination during the scanning process, ensuring that the genuine topographical features and the ≈ 350 nm height profile of the pillars were accurately preserved. Ultimately, these pillars will dictate the geometry of the PDMS nanodrums, providing a theoretical 350 nm deep cavity for the suspended graphene membranes.

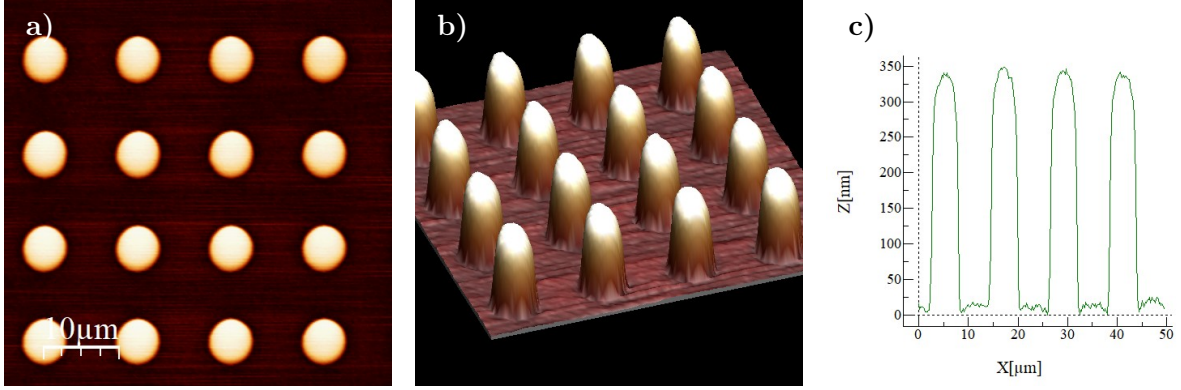


Figure 6.31: AFM characterization of the Array 3 (A3) acrylate master mold. (a) 2D topography map. (b) 3D representation. (c) Height profile.

6.3.2. Fabrication of the Monolithic PDMS Micro-cavity Array

The fabrication of the monolithic OM cavities required casting the PDMS elastomer over the glass slide containing the acrylate master mold. To ensure an optimal balance between mechanical flexibility (essential for strain engineering) and structural stability (to support the suspended graphene), a precise target thickness of $h_{target} = 0.5$ mm (0.05 cm) over the master mold was established.

Achieving this specific thickness demanded a rigorous volumetric calculation, accounting for the displaced volume of the glass slide ($7.6 \times 2.55 \times 0.106$ cm) placed within the circular Petri dish (diameter $d = 8.5$ cm). The total required volume (V_{total}) was determined by modeling the final elastomer layer as a continuous solid cylinder with a total height h_{total} , and subtracting the physical volume already occupied by the glass slide (V_{mold}).

$$\begin{aligned}
 h_{total} &= h_{mold} + h_{target} = 0.106 \text{ cm} + 0.05 \text{ cm} = 0.156 \text{ cm} \\
 V_{cylinder} &= A_{petri} \cdot h_{total} = 56.745 \text{ cm}^2 \cdot 0.156 \text{ cm} \approx 8.852 \text{ cm}^3 \\
 V_{mold} &= A_{mold} \cdot h_{mold} = 19.380 \text{ cm}^2 \cdot 0.106 \text{ cm} \approx 2.054 \text{ cm}^3 \\
 V_{total} &= V_{cylinder} - V_{mold} \approx 6.798 \text{ cm}^3
 \end{aligned} \tag{6}$$

Using the established PDMS density ($\rho \approx 0.975$ g/cm³), the theoretical mass required to achieve exactly 0.5 mm of top cladding was calculated as $m_{target} = V_{total} \cdot \rho \approx 6.628$ g.

Experimentally, the PDMS was prepared maintaining the standard 1:10 curing agent-to-base ratio. To compensate for the inevitable material retention on the walls of the mixing container, an excess total mass of 8.0402 g (7.177 g of elastomer base and 0.8625 g of curing agent) was formulated. The compound was manually stirred using a glass rod and subsequently sonicated for 20 minutes to completely degas the mixture and eliminate trapped air bubbles.

The polymer was then carefully poured over the master mold assembly. A precise

mass of $m_{poured} = 6.4597$ g was deposited into the Petri dish. Following the exact thermal profile established in previous sections, the sample was cured in an oven at 90 °C for 45 minutes.

To validate the accuracy of the deposition, the final thickness of the PDMS substrate over the mold was measured with a digital caliper, yielding a height of 0.48 mm. This experimental result exhibits an exceptional correlation with the mathematical model. By reverse-calculating the poured mass (6.4597 g corresponds to a total volume of 6.625 cm³), the expected theoretical top layer height dictates 0.47 mm. The minimal 0.01 mm discrepancy between the expected and measured height is acceptable within the experimental tolerance, easily attributed to the capillary meniscus effect at the edges of the Petri dish and microscopic variations in the internal diameter of the plastic container. This strict geometric control guarantees the mechanical reproducibility of the monolithic optomechanical cavities.

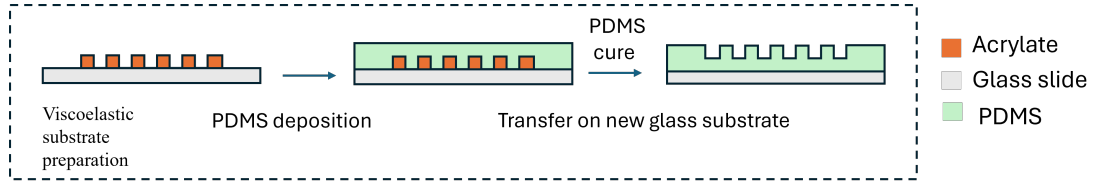


Figure 6.32: Schematic illustration detailing the soft lithography replica molding process for the PDMS viscoelastic stamps.

Following the successful curing and demolding process, the monolithic PDMS substrate was inspected via optical microscopy to evaluate the fidelity of the soft lithography replication. The resulting polymeric surface exhibited exceptional optical clarity and a complete absence of macroscopic residues or trapped micro-bubbles. As presented in Figure 6.33, the patterned micro-cavities (specifically demonstrating Array 3) display a highly uniform periodic structure, perfectly inheriting the exact inverse topography of the acrylate master mold. This pristine structural replication confirms the viability of the PDMS elastomer as an optimal, defect-free platform for the subsequent direct transfer of two-dimensional materials.

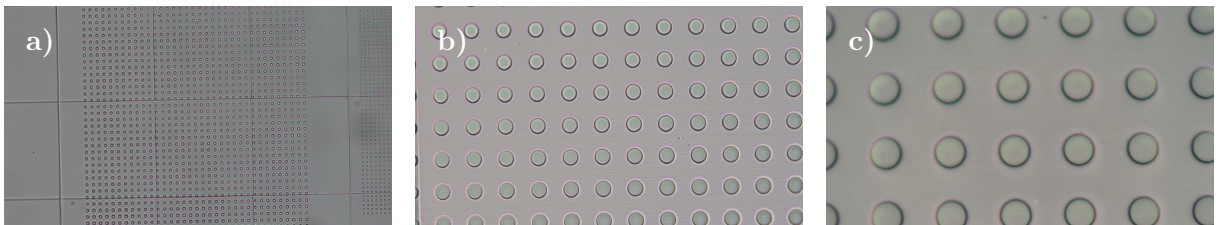


Figure 6.33: Optical micrographs of the demolded PDMS stamp A3 at (a) 10×, (b) 50×, and (c) 100× magnification.

6.3.3. *Direct Placement of Suspended Membranes over PDMS*

The deterministic transfer process presented a substantial technical challenge, primarily due to the absolute scarcity of established protocols or literature regarding the direct transfer of graphene onto polymer-based PDMS cavity arrays. Leveraging our prior expertise with standard, rigid silicon nanodrums, we hypothesized that the graphene flake could be directly transferred from the scotch tape to the elastomer substrate. However, this approach demanded the critical pre-selection of an optimal candidate directly on the adhesive tape.

This selection process is inherently hindered by the mechanical nature of mechanical exfoliation; the cleavage of two highly sticky surfaces frequently results in structural irregularities and multi-layer fragments due to uneven material splitting between the interfaces. We modified the exfoliation geometry by using significantly smaller adhesive tape segments, in order to reduce the contamination when transfer takes part. Only the initial tape strip utilized to cleave the bulk HOPG block maintained a standard size, ensuring the extraction of a continuous, large-area graphite layer from the parent crystal.

Numerous exfoliation iterations were executed until a suitable target flake was achieved. This specific candidate had to meet certain geometric criteria: it needed to be extremely flat, uniform, and possess a few-layer thickness characteristics to prevent structural tearing during final transfer. The morphology of the optimized target flake is presented in Figure 6.34. To isolate this flake and protect the surrounding PDMS matrix from excessive carbon residue, the specific region of the tape containing the candidate was meticulously excised using a cutter. This process successfully minimized the effective contact area during the subsequent stamp phase.



Figure 6.34: Optical micrographs ($10\times$, $50\times$, $100\times$) of the selected few-layer graphene candidate supported on adhesive tape.

To execute the final transfer, the pre-patterned PDMS substrate was positioned under the optical microscope. Alignment was performed via a manual, free-hand procedure. This critical alignment demanded a long working distance to accommodate the tape-elastomer clearance, which was successfully achieved by utilizing a $10\times$ long focal length objective (Figure 6.35a). Once the flake was spatially correlated with the target micro-cavity array (A3), a optical rod was employed to gently press the adhesive tape down (Figure 6.35). The applied mechanical force was intentionally kept at a minimum to avoid excessive conformal contact, ensuring that only the thinnest layers of the flake were

decoupled from the tape. Finally, the tape was peeled off at a constant manual velocity. This complete deterministic transfer sequence is illustrated in Figure 6.35, which yielded a promising, high-transparency membrane exhibiting a distinct few-layer optical contrast (Figure 6.35c).

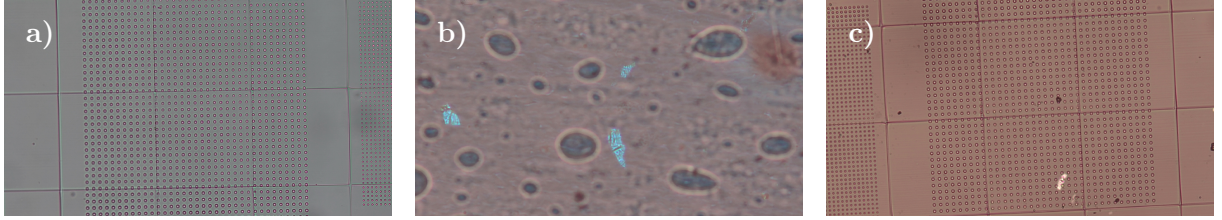


Figure 6.35: Optical micrographs (10 $\times$) of the deterministic transfer sequence onto the PDMS substrate. (a) Target micro-cavity array (A3). (b) Alignment of the tape-supported graphene flake. (c) Transferred suspended membrane.

As depicted in Figure 6.36, the transferred nanodrum exhibits distinct optical contrast and light transmission, which clearly differentiates it from an opaque bulk graphite flake. Furthermore, the suspended membrane displays a highly planar morphology with a remarkable absence of macroscopic wrinkles or folds, suggesting a uniform, thin structural profile. However, while these initial optical microscopy observations are highly indicative of a successful few-layer graphene transfer, a structural characterization requires Raman analysis.

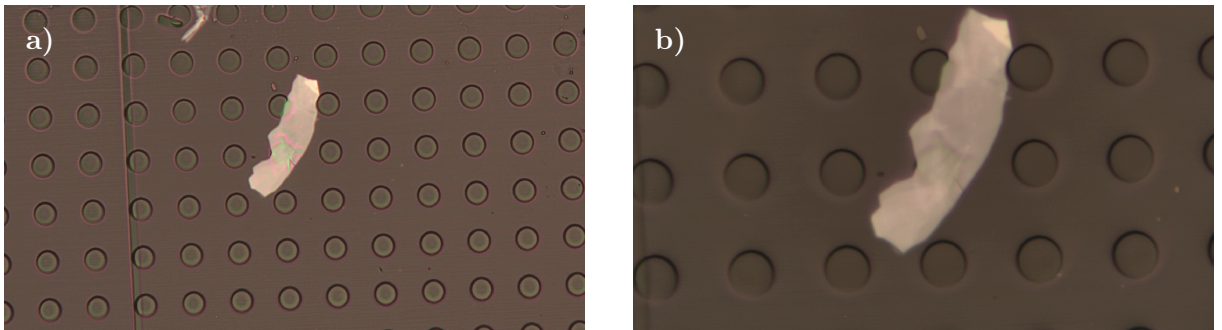


Figure 6.36: Post-transfer optical micrographs of the suspended graphene membrane over the PDMS micro-cavity array at (a) 50 $\times$ and (b) 100 $\times$ magnification.

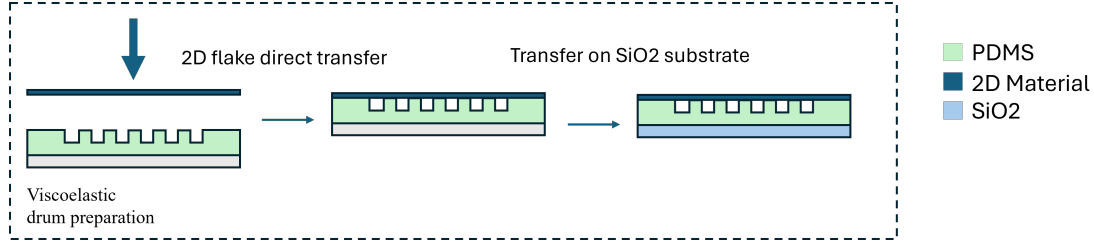


Figure 6.37: Schematic illustration detailing the graphene transfer process into the PDMS substrate.

Following the successful transfer of the graphene flake, the monolithic PDMS substrate was subsequently positioned onto a bare silicon wafer, as Figure 6.3.3 explains. This step was implemented to enhance the overall light-matter interaction; the highly reflective underlying silicon surface acts as a macroscopic mirror, maximizing the optical contrast and the back-scattered light collection required for the subsequent interferometry future characterization.

6.3.4. Graphene Raman Spectroscopy

As a result of technical issues compromising the internal laser tracking system of the AFM, direct topographical measurements could not be acquired at this stage. However, as demonstrated in conventional graphene-on-silicon architectures, Raman spectroscopy provides an alternative, yielding critical insights into both the crystalline quality of the graphene sheet and an accurate estimation of its layer count.

Since the supporting substrate in this monolithic architecture is PDMS, its intrinsic vibrational modes introduce specific spectral features that must be thoroughly decoupled from the graphene response. To establish a reliable baseline, Raman spectroscopy was initially performed directly on the pristine polymeric substrate. The Raman measurements were conducted using an excitation laser wavelength of $\lambda = 535 \text{ nm}$ and an incident optical power of $P = 2 \text{ mW}$. As documented in the literature regarding silicone elastomers for optical applications [50], PDMS is a polymer defined by a highly flexible siloxane backbone (Si-O-Si) enveloped by peripheral methyl groups (CH_3) as detailed in Figure 5.4. Consequently, its Raman spectrum exhibits several prominent and distinct scattering peaks associated with these specific atomic linkages (Figure 6.38):

- **Si-O-Si symmetric stretching ($480 - 500 \text{ cm}^{-1}$):** This intense peak corresponds to the symmetric stretching vibrations of the siloxane (Si-O-Si) backbone, which constitutes the main structural framework of the polymer. Its prominence is a direct indicator of the cross-linked elastomer's structural integrity.
- **Si-C symmetric stretching ($680 - 870 \text{ cm}^{-1}$):** This lower-intensity feature is attributed to the symmetric stretching mode of the silicon-carbon bonds. It fundamentally reflects the covalent attachment of the methyl side groups to the inorganic siloxane backbone.

- **CH₃ asymmetric bending (1250 – 1420 cm⁻¹):** This peak originates from the asymmetric bending (also known as scissoring) vibrations of the C-H bonds within the peripheral methyl groups.
- **(CH₃ symmetric stretching 2900 - 2970 cm⁻¹):** This highly dominant peak is unequivocally associated with the symmetric stretching vibrations of the C-H bonds in the methyl groups. As typical in organic polymers, it represents the absolute strongest optical scattering signature in the high-frequency region of the PDMS spectrum.

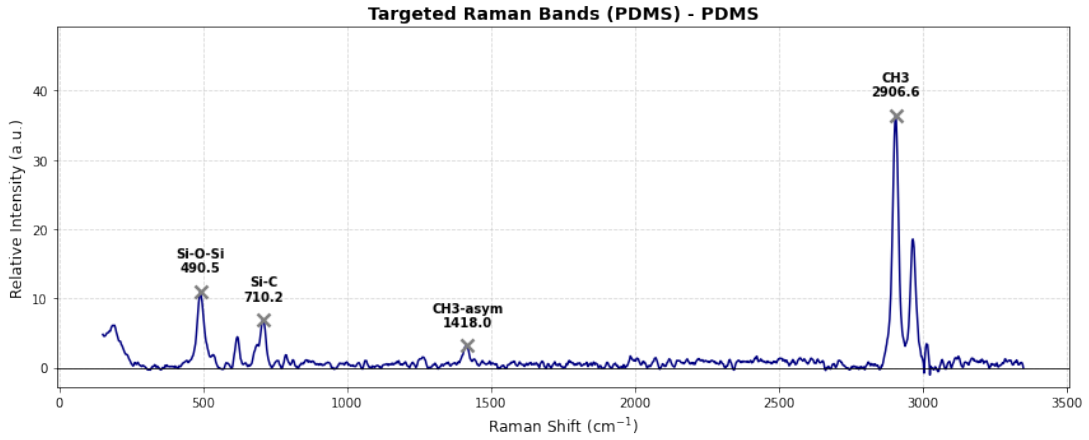


Figure 6.38: Representative Raman spectrum of the bulk PDMS stamp.

Table 6.2: Characteristic Raman scattering peaks detected for the PDMS substrate, including their vibrational mode assignments and relative intensities.

Band	Detected Pos. (cm ⁻¹)	Intensity (a.u.)
Si-O-Si	490.53	11.34
Si-C	710.24	6.78
CH ₃ -asym	1417.96	3.18
CH ₃	2906.62	36.45

Following the baseline characterization of the polymeric substrate, the vibrational response of the transferred monolithic graphene nanodrum was evaluated. To assess the spectral quality and structural integrity of the suspended membrane, an initial Raman acquisition was performed utilizing 20 accumulations with a 1-second integration time per scan. The resulting spectrum, illustrated in Figure 6.39, prominently displays the characteristic carbon phonon modes alongside a residual polymer signature. The precise peak positions and their corresponding absolute intensities are detailed in Table 6.3.

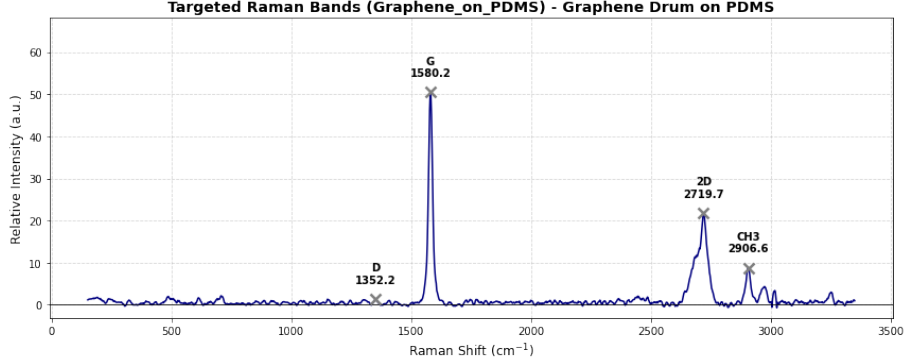


Figure 6.39: Representative Raman spectrum of the suspended few-layer graphene membrane successfully transferred onto the monolithic PDMS micro-cavity.

Table 6.3: Detected Raman scattering peaks and their experimental intensities for the graphene nanodrum transferred onto PDMS.

Band	Detected Pos. (cm ⁻¹)	Intensity (a.u.)
D	1352.15	1.37
G	1580.16	50.48
2D	2719.72	21.80
CH ₃ (PDMS)	2906.62	8.77

A quantitative analysis of the extracted intensity ratios yields critical insights into the membrane’s physical state. Notably, the defect-activated D band is virtually suppressed, resulting in an exceptionally low intensity ratio of $I_D/I_G \approx 0.03$. This negligible defect density confirms the rigorous pre-selection of the target flake and serves as direct spectroscopic evidence of a highly preserved crystalline lattice. It demonstrates a remarkable absence of macroscopic wrinkles, structural folds, or induced tearing, which is a particularly significant achievement given the free-hand nature of the mechanical transfer process over the patterned elastomer.

Furthermore, the spectrum yields a 2D-to-G peak intensity ratio of $I_{2D}/I_G \approx 0.43$. As previously discussed in the context of the silicon micro-cavities, this value and the associated spectral broadening of the 2D peak are indicative of a thick few-layer or multi-layer graphene profile. Rather than a limitation, this structural characteristic is highly advantageous—and arguably necessary—in the present experimental context. Given that the transfer was executed manually onto a highly compliant polymeric substrate (PDMS), bypassing high-precision micromanipulators, the increased mechanical rigidity and higher bending stiffness of a multi-layer membrane are critical to prevent stiction and structural collapse into the micro-cavities. Nevertheless, the distinct optical transparency observed under the microscope confirms that the suspended membrane retains essential two-dimensional characteristics. Consequently, achieving this robust, suspended architec-

ture via a direct tape transfer stands as a highly successful empirical validation of the PDMS nanodrum platform.

It is worth noting that the characteristic Raman scattering peak of the underlying silicon substrate (typically located at $\sim 520\text{ cm}^{-1}$) was entirely absent from the acquired spectra (or mimetized with the Si-O-Si peak). This complete attenuation indicates that the macroscopic thickness of the 0.48 mm PDMS layer substantially exceeds the effective optical penetration depth and the focal volume of the excitation laser. Consequently, while the current elastomeric thickness provides robust structural support and permits a clear Raman characterization of the superficial graphene, we conclude that future optical interferometry studies—which rely heavily on the back-reflection from the bottom silicon interface to form a resonant cavity—probably will require the fabrication of significantly thinner PDMS substrates to ensure an efficient optical coupling.

To ensure reliability beyond single-point acquisition and to confirm the morphological uniformity of the monolithic architecture, a high-resolution confocal Raman scan map was acquired over a $10\times 10\text{ }\mu\text{m}$ area. The map was collected with a spatial density of 100 points per line and an integration time of 0.15 seconds per point, ensuring an optimal trade-off between SNR and mapping resolution taking into account that the FWHM of our laser spot is $\sim 350\text{ nm}$. The resulting spatial distribution of the primary Raman modes, presented in Figure 6.40, provides definitive evidence regarding the crystalline quality and nanometric thickness of the transferred few-layer membrane.

The confocal Raman colormaps presented in Figure 6.40 provide a comprehensive spatial evaluation of the transferred graphene membrane on the compliant PDMS substrate. The G and 2D band intensity maps (Figures 6.40a and 6.40b) clearly delineate the continuous macroscopic contour of the transferred flake, where the uniform signal across the covered area confirms a homogeneous mechanical adhesion over the elastomer. Crucially, the D band intensity map (Figure 6.40c) exhibits negligible signal across the entire flake domain. Examining the intensity scale, which fluctuates symmetrically around zero (from approximately -77 to 76 CCD counts), it becomes evident that the recorded data constitutes pure background instrumental noise from the detector rather than physical defect scattering. This mathematical and visual baseline provides robust confirmation that the mechanical exfoliation and subsequent manual transfer left the crystalline basal plane structurally pristine, successfully avoiding localized tearing, structural folds, or amorphous disorder.

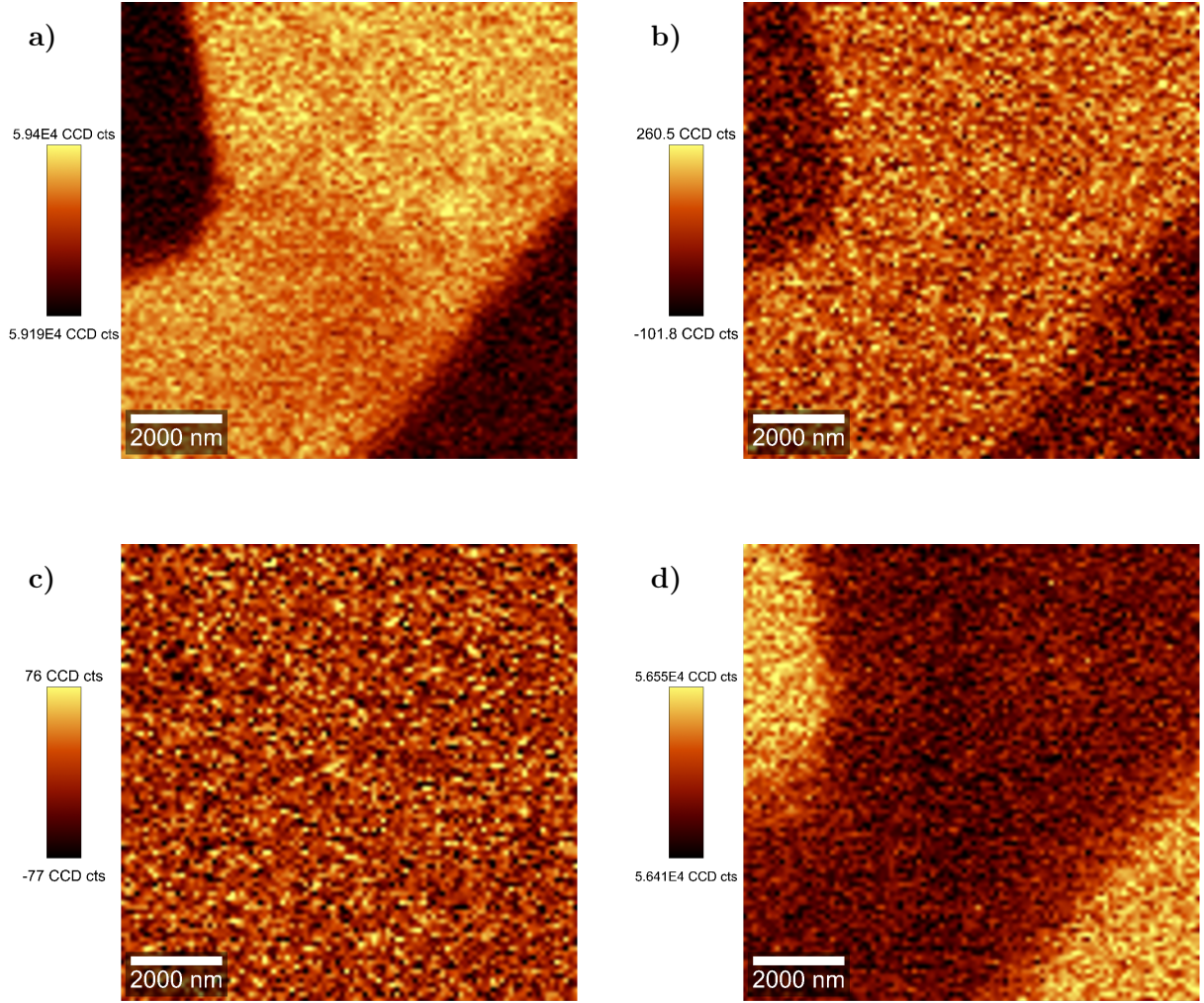


Figure 6.40: Confocal Raman spatial mapping of the transferred few-layer graphene flake over the PDMS substrate. Intensity maps of the (a) G band, (b) 2D band, (c) D band, and (d) CH_3 stretching band.

A remarkable feature of these colormaps, particularly when contrasted with the graphene-on-silicon architecture analyzed in previous sections, is the absence of clearly defined circular boundaries marking the underlying micro-cavities. In the silicon substrate, the precipitous drop in the G and 2D signals over the holes was strongly driven by the loss of the highly reflective Si interface, which drastically modulates the local Fabry-Pérot optical interference conditions. Conversely, PDMS is an optically transparent elastomer with a low refractive index ($n \approx 1.4$). Due to the lack of a highly reflective underlying interface capable of establishing a strong field-enhancement contrast, the Raman scattering cross-section of the graphene layer remains practically uniform when transitioning from the supported to the suspended regime. Furthermore, the optical transparency allows the incident laser to penetrate deep into the bulk polymeric matrix, causing the

extended confocal collection volume to volumetrically average out subtle surface topography variations. Consequently, while the geometric boundaries of the nanodrums remain structurally masked under Raman inspection due to these intrinsic photophysical properties, the physical continuity and structural integrity of the active few-layer membrane are definitively validated across the elastomeric platform.

Finally, the CH₃ symmetric stretching map (Figure 6.40d) provides critical physical insight into the optical transparency of the active membrane. As noted in the single-point spectrum (Figure 6.39), the polymeric Raman signature remains prominent. The spatial map demonstrates that while the back-scattered CH₃ intensity is maximized on the bare PDMS regions, a distinct and robust signal persists across the entirety of the graphene-covered domain. Rather than a difference in chemical interaction, this relative intensity drop is a direct measure of double-pass optical attenuation. It physically confirms that the few-layer graphene flake, despite the increased thickness required for mechanical stability during transfer, remains highly transmissive to the visible excitation laser. This optical transmissivity allows the incident field to effectively penetrate the suspended membrane and probe the underlying polymeric matrix. Maintaining this high optical transmission is a critical material property for the integration of these nanodrums into future OM architectures, as it ensures the viability of non-destructive optical interrogation and dynamic interferometric readout of the suspended cavities.

6.3.5. Optical and Spectroscopic Validation of Monolayer Domains

During the optical inspection of the transferred sample, a secondary, highly transparent microscopic flake was identified within the same array, although situated on the unpatterned PDMS surface rather than suspended over the micro-cavities (it can be seen also barely in Figure 6.36a). To ascertain its structural thickness and perform a comparative analysis against the suspended nanodrums, an identical Raman spectroscopic characterization was conducted.

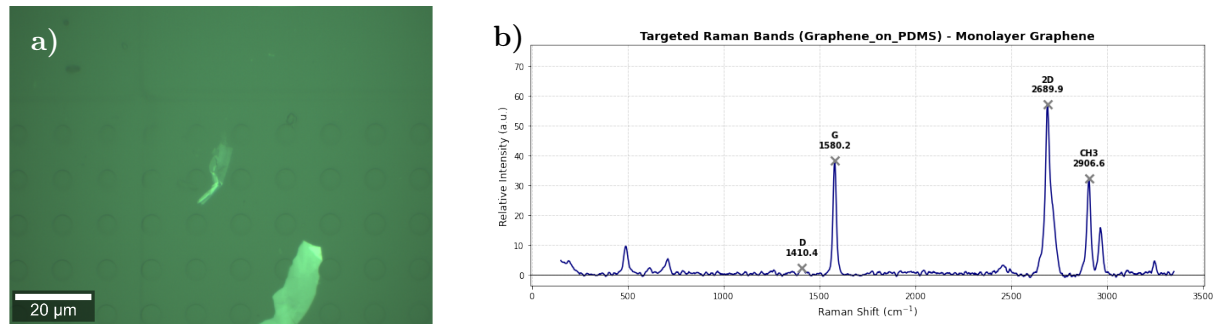


Figure 6.41: Characterization of a supported monolayer graphene flake on PDMS. (a) Optical micrograph at 100 $\times$ magnification. (b) Representative Raman spectrum.

As illustrated in Figure 6.41, the resulting spectrum exhibits a fundamental inversion in peak dominance: the 2D peak intensity strictly exceeds the G peak intensity, yielding a

ratio of $I_{2D}/I_G \approx 1.48$. In accordance with established carbon allotrope characterization, this specific intensity ratio constitutes the definitive optical signature of pristine monolayer (or bilayer) graphene. The precise peak positions and intensities are detailed in Table 6.4.

Table 6.4: Detected Raman scattering peaks and experimental intensities for the supported monolayer graphene.

Band	Detected Pos. (cm^{-1})	Intensity (a.u.)
D	1410.39	2.47
G	1580.16	38.32
2D	2689.87	57.01
CH ₃ (PDMS)	2906.62	32.36

To further corroborate the single-layer assessment and evaluate the spatial uniformity of the transferred material, a high-resolution confocal Raman scan was performed over an $8 \times 8 \mu\text{m}$ area mapping the supported monolayer region (Figure 6.42).

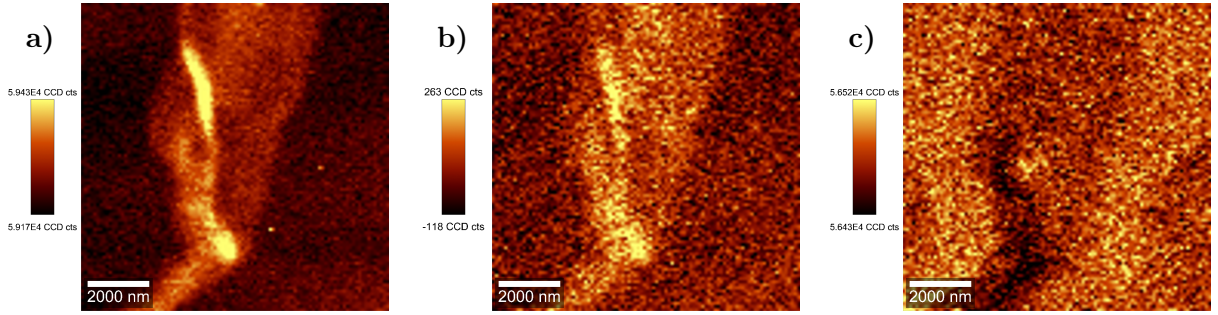


Figure 6.42: Confocal Raman spatial mapping of the supported monolayer graphene flake on the PDMS substrate. Intensity maps of the (a) G band, (b) 2D band, and (c) CH₃ stretching band.

The spatial distribution of the G and 2D bands (Figures 6.42a and 6.42b) clearly delineates the macroscopic boundaries of the monolayer domain. Notably, the maps reveal distinct, highly localized linear features exhibiting elevated Raman scattering intensity. These geometric variations correspond to structural wrinkles or macroscopic folds induced by the mechanical strain of the free-hand dry transfer process. This localized intensity increment is physically sound: the physical folding or overlapping of the monolayer effectively creates a localized multi-layer cross-section. This geometrically enhances the sp^2 carbon scattering volume at those specific coordinates, yielding the bright linear contrast observed in the maps.

Furthermore, the CH₃ symmetric stretching map (Figure 6.42c) provides compelling evidence regarding the optical transmissivity and focal depth of the system. The intense polymeric signature directly beneath the flake is governed by two concurrent physical

factors. First, the extreme optical transparency inherent to a single atomic layer of carbon (which theoretically absorbs only $\approx 2.3\%$ of incident visible light) results in minimal, yet detectable, laser attenuation. Second, unlike the suspended multi-layer membranes discussed previously, which are separated from the cavity floor by a structural depth of ≈ 350 nm (as established by the master mold profilometry), this specific flake rests conformally on the unpatterned PDMS surface. Consequently, the focal plane of the excitation laser remains coincident with the elastomer interface, maximizing the back-scattered collection volume from the PDMS matrix. This yields robust CH_3 signal that accurately traces the slight optical attenuation of the monolayer terrace, accompanied by a pronounced signal drop at the exact spatial coordinates of the structural fold, where the locally increased thickness noticeably attenuates the underlying polymer signal.

7. Conclusions

Achieving dynamic control in integrated photonics and nanomechanics requires moving away from purely passive substrates to develop stimuli-responsive architectures. This thesis has successfully demonstrated this concept by validating Spin Crossover (SCO) complexes as reliable phase-change materials actuators. By exploiting their intrinsic volume expansion at room temperature (RT), this work has proven that molecular-scale phase transitions can directly drive macroscopic changes in tunable photonic and optomechanical (OM) platforms.

To consolidate these results, the experimental work focused on two complementary lines of action. First, the actuation capability of SCO materials was proven by measuring direct mechano-optical transduction on functionalized micro-photonic waveguides. Second, the fabrication methodology for tunable 2D OM systems was optimized through the deterministic transfer and mechanical characterization of suspended graphene nanodrums. While the MRR served as a clear proof of concept for the nanocomposite's actuation power, both the rigid silicon and the flexible elastomeric (PDMS) nanodrums were successfully built and physically validated as target cavities for future molecular integration.

The specific experimental outcomes and final conclusions drawn from these parallel platforms are detailed below:

7.1. O1. Mechano-Optical Actuation in Photonic Ring Resonators

The capability of SCO nanomaterials to act as active tuning agents was proven through their integration into MRRW. By encapsulating the active nanoparticles within a compliant PMMA/SCO matrix, the resulting nanocomposite was deposited over the exposed window of the silicon waveguides. Thermal characterization confirmed the expected linear thermo-optic drift in the passive, bare resonators, establishing the baseline reference for the system. In contrast, measurements on the functionalized devices showed a distinct thermal hysteresis loop during the full temperature cycle. By tracking the resonance wavelength shift ($\Delta\lambda$), a bistability window of approximately 30 K was extracted within

the $\sim 320 - 350$ K transition regime. This result demonstrates that the polymeric matrix transduces the molecular volume changes into a measurable optical modulation, completing the first specific objective by validating the hybrid MRR architecture as a platform for solid-state transduction.

7.2. O2. Deterministic Fabrication of 2D Optomechanical Cavities

The second specific objective was fulfilled by establishing a methodological baseline for the fabrication and nanoscale analysis of suspended two-dimensional architectures. Utilizing a custom all-dry viscoelastic stamping technique, graphene flakes were deterministically transferred over pre-patterned rigid silicon micro-cavities. The structural integrity, physical dimensions, and crystalline quality of the resulting nanodrums were characterized through a combination of AFM and Raman spectroscopy.

Topographic AFM characterization and Raman analysis ($I_{2D}/I_G \approx 0.5$) confirmed that the suspended membranes have a thickness of approximately 7 nm, corresponding to few-layer graphene. This thickness provides the necessary structural robustness to remain securely suspended over the micro-cavities while preserving the flexible mechanical behavior required for optomechanical actuation. Crucially, this thickness ensures the membrane can sustain the subsequent deposition of the active nanocomposite without collapsing, establishing a reliable baseline on the passive silicon substrate before transitioning to elastomeric cavities.

7.3. O3. Development of Polymeric Nanodrums

The third objective focused on evolving the optomechanical platform from a rigid substrate to a fully compliant, stimuli-responsive architecture. This fundamental milestone was achieved through the fabrication of PDMS micro-cavities and the subsequent integration of suspended two-dimensional membranes.

Crucially, this work demonstrated the experimental viability of deterministically transferring few-layer graphene directly onto these highly viscoelastic substrates. Despite the fundamental interfacial challenges associated with performing all-dry stamping onto a soft elastomer—a pioneering approach with virtually no established precedent for this specific cavity configuration—the transfer was executed with a considerable degree of spatial control, successfully yielding the first functional prototypes of suspended PDMS nanodrums.

Furthermore, the transfer protocol demonstrated enough versatility to deposit monolayer graphene onto unpatterned PDMS regions. Although the few-layer configuration is expected to better sustain mechanical stress, the monolayer might withstand the actuation since the strain is generated uniformly by the underlying substrate itself. Evaluating the mechanical limits of both regimes under active actuation constitutes a direct path for future work.

7.4. Future Work

The results established in this thesis outline several direct avenues for the development of tunable optomechanical and photonic platforms. The initial step requires refining the deterministic transfer methodology by transitioning the current ambient-condition protocol into a controlled inert environment using a glovebox system. This modification aims to minimize interfacial contaminants and bubble formation beneath the 2D membranes. Additionally, integrating a dynamically controlled Peltier thermoelectric stage into the micromanipulation setup will optimize the release mechanics. By heating the target substrate, the viscoelastic adhesion of the PDMS stamping polymer can be temporarily reduced, facilitating a cleaner and more reproducible transfer of the graphene flakes.

With the transfer protocol optimized, the research will expand the active materials library to develop multi-responsive systems. Building upon the characterization of the PMMA nanocomposite doped with BF_4 -based SCO nanoparticles, upcoming experimental phases will incorporate NO_3 -based SCO complexes to exploit their distinct thermal bistability window. Furthermore, co-doping the polymeric matrix with vanadium dioxide (VO_2) nanoparticles will be explored. While VO_2 undergoes a different physical phase transition, it exhibits a hysteretic behavior at a shifted temperature regime relative to the SCO material. Combining both materials within a single waveguide could yield a dual-hysteresis thermal profile, enabling multi-resonant tuning landscapes for non-volatile memory applications.

Concurrently, the development of the OM platforms is being carried out within the IGNATIUS project framework. The structural baselines of the rigid silicon nanodrums are currently undergoing interferometric characterization in collaboration with Delft University of Technology. Following the mapping of the mechanical resonance of these pristine membranes, the subsequent step consists of depositing the characterized PMMA/SCO composite onto these architectures, as illustrated in Figure 7.1. This configuration will quantify how the volumetric expansion of the nanoparticles induces strain upon the graphene and shifts its resonance frequency.

To contextualize this expected behavior, Figure 7.1 displays a representative interferometric measurement of a bare graphene nanodrum, performed at a pressure of 300 mbar with a quality factor of $Q = 150$. As observed, the mechanical resonance frequency (f_0) of the pristine membrane shifts continuously as a function of the incident laser power due to standard thermomechanical coupling. However, upon the structural integration of the spin-crossover composite (Figure 7.1b), a different dynamic is expected. Since adjusting the incident laser power varies the local temperature of the cavity, sweeping the optical power will heat the system across the SCO transition threshold. This photothermal trigger is expected to induce an abrupt shift in the resonance frequency, driven by the volumetric expansion of the nanocomposite exerting mechanical strain directly onto the graphene. The viability of this specific photothermal actuation mechanism has been demonstrated at the single-particle level using optical levitation within a Paul trap [13], and its capability to drive macroscopic modulation is supported by the MRR wavelength

shifts ($\Delta\lambda$) validated in this thesis.

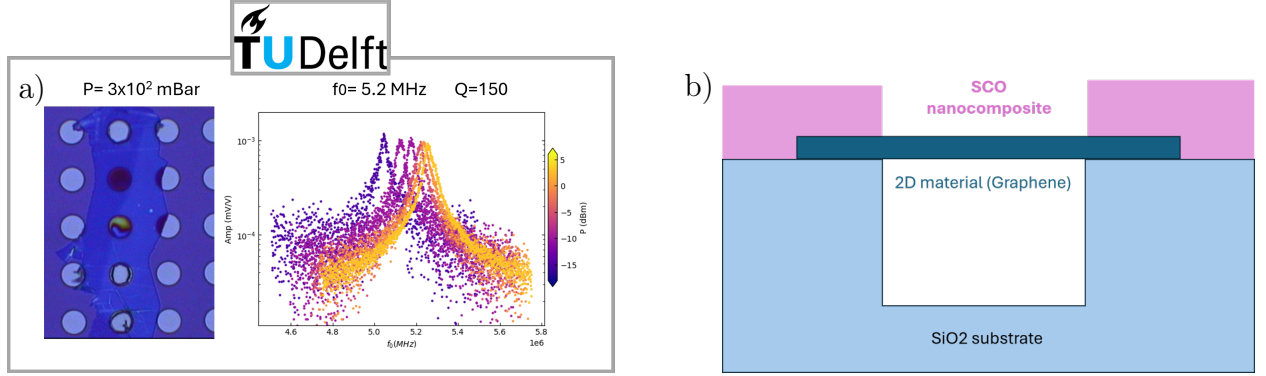


Figure 7.1: (a) Optomechanical response of the suspended graphene membrane showing resonance shift as a function of incident laser power. (b) Proposed active architecture featuring the PMMA/SCO nanocomposite deposited over the 2D cavity.

Ultimately, the long-term goal of this research line is the fabrication of a PDMS/SCO nanodrum. Having demonstrated the viability of the all-dry transfer onto a passive elastomeric substrate, the next step involves using the active, nanoparticle-loaded PDMS as the bulk cavity material. Since the macroscopic strain would be generated intrinsically and homogeneously by the supporting elastomeric substrate rather than by external mechanical probes, the stress distribution applied to the membrane is expected to be uniform. This homogeneous actuation could potentially allow the suspended graphene to withstand dynamic modulation without fracturing, demonstrating the advantage of substrate-integrated strain generation over localized mechanical loading.

The execution of these experimental phases follows as a direct continuation of the fabrication and characterization protocols validated in this thesis.

8. References

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