https://doi.org/10.64504/big.dv3i1.328

Nanoscale Cuticle Mass Density Variations in Bio-Inspired Thermochromic Coatings Influenced by Hierarchical Structuring

1st Mamadi Camara
Univesity General Lansana Conte Sonfonia-Conakry
Conakry, Guniea
mamad1camara@outlook.com

2nd Lutf Taher Ahmed Alhajj*
Zhejiang University
Taiz, Yemen
lutfshanghai@gmail.com

Received on September 7th, revised on October 18th, accepted on November 12th, published on January 6th.

Abstract—**The pursuit of energy-efficient building envelopes has driven significant research into advanced materials. Bio-inspired hierarchical nanostructures, such as those found on flower petals, offer a promising avenue for developing adaptive thermal-responsive coatings. However, the precise relationship between the distribution of thermochromic materials within these complex structures and their overall performance remains poorly understood. This study aims to bridge this gap by investigating the nanoscale mass density variations in a novel bio-inspired thermochromic coating. We developed a thermochromic coating that mimics the hierarchical micro/nanostructure of rose petals, incorporating vanadium dioxide (VO_2) nanoparticles as the active thermal-responsive component. We then employed ptychographic X-ray computed tomography (PXCT) to quantitatively determine, at nanoscale resolution, the three-dimensional mass density distribution of the coating with and without the hierarchical structuring. By comparing these two coating types, we investigated how the hierarchical structure influences the distribution of VO_2 nanoparticles and the resulting thermochromic properties. Our findings reveal that the hierarchical structure significantly influences the distribution of VO_2 nanoparticles, leading to a more heterogeneous mass density distribution compared to the flat coating. The density of the VO_2-rich regions is inversely correlated with the underlying hierarchical topography. The structured coating exhibits a more pronounced thermochromic effect, with a larger change in solar transmittance between its low- and high-temperature states. We correlate these macroscopic optical properties with the nanoscale structural features, showing that the hierarchical design enhances the thermochromic performance by optimizing the distribution of the active material. This study provides the first nanoscale 3D characterization of a bio-inspired thermochromic coating, demonstrating the critical role of hierarchical structuring in modulating its performance. Our findings offer a new design paradigm for advanced building materials, where the precise control of nanoscale architecture can be used to create highly efficient and adaptive thermal-responsive surfaces. This work paves the way for the development of next-generation smart building envelopes with significantly improved energy efficiency.**

Keywords—Thermochromic Coating, Hierarchical Nanostructure, Bio-inspired Design, Ptychographic X-ray Computed Tomography (PXCT), Building Energy Efficiency

1. INTRODUCTION

The global imperative to reduce energy consumption and mitigate climate change has placed significant emphasis on the development of energy-efficient buildings. The building sector accounts for approximately one-third of global final energy consumption and a substantial portion of carbon dioxide emissions [1]. A significant fraction of this energy usage is attributed to heating, ventilation, and air conditioning (HVAC) systems, which are essential for maintaining indoor thermal comfort. Building envelopes, particularly facades and windows, represent a critical interface for heat exchange with the external environment. Traditional building materials possess static thermal properties, leading to excessive energy use for cooling in hot climates and heating in cold climates. While technologies like low-emissivity (Low-E) coatings have become standard, their static nature limits their effectiveness across varying climatic conditions and seasons [2].

This challenge has spurred the development of "smart" or "adaptive" building envelopes capable of dynamically modulating their thermal and optical properties in response to environmental stimuli. Among these, thermochromic materials, which reversibly change their optical properties at a specific critical temperature (Tc), have emerged as a highly promising solution [3]. Vanadium dioxide (VO_2) is a particularly compelling thermochromic material due to its semiconductor-to-metal transition near room temperature (~68°C), which can be tuned by doping. Below Tc, VO_2 is transparent to infrared (IR) radiation, allowing solar heat gain. Above Tc, it becomes metallic and reflects IR radiation, reducing solar heat gain and thus lowering cooling loads. Despite significant progress, the practical application of VO_2-based coatings is often hampered by challenges such as low luminous transmittance, undesirable color, and suboptimal solar modulation efficiency (ΔTsol) [4].

Nature offers a rich source of inspiration for designing advanced functional materials. The intricate hierarchical

*Lutf Taher Ahmed Alhajj, Zhejiang University, Taiz, Yemen, lutfshanghai@gmail.com

structures found in biological systems, from the iridescent scales of butterfly wings to the superhydrophobic surfaces of lotus leaves and rose petals, demonstrate sophisticated strategies for manipulating light and energy [5, 6]. The "rose petal effect," for instance, arises from a hierarchical structure of micropapillae and cuticular nanofolds, resulting in superhydrophobicity with high water adhesion [7]. These structures also contribute to the deep, velvety color of the petals by efficiently trapping light. Inspired by these biological designs, researchers have begun to explore the fabrication of hierarchical nanostructures to enhance the performance of various materials. However, the application of these bio-inspired principles to thermochromic coatings for building applications remains a nascent field of research.

A fundamental gap exists in our understanding of how the spatial distribution of thermochromic nanoparticles within a complex, bio-inspired hierarchical structure influences the coating's overall performance. The performance of the coating is not merely a sum of its parts but is critically dependent on the nanoscale arrangement and density variations of the active material. To date, characterization has largely relied on 2D surface imaging (e.g., SEM, AFM) and bulk optical measurements, which fail to provide a complete 3D picture of the internal structure and its relationship to the material's functional properties.

This study aims to bridge this knowledge gap by introducing a novel bio-inspired thermochromic coating and employing a state-of-the-art imaging technique to unravel its structure-property relationships at the nanoscale. We fabricate a coating that mimics the hierarchical structure of a rose petal, embedding it with tungsten-doped VO2 nanoparticles. We then utilize ptychographic X-ray computed tomography (PXCT), a non-destructive, high-resolution 3D imaging technique, to quantitatively map the mass density distribution within the coating [8]. By comparing the 3D nanostructure of the bio-inspired coating with that of a conventional flat coating, we elucidate the profound impact of hierarchical structuring on the distribution of thermochromic material and, consequently, on the coating's optical and thermal regulatory performance. This work not only presents a new material design but also provides a methodological blueprint for the nanoscale characterization of complex functional composites, paving the way for the rational design of next-generation, high-performance building materials.

The performance of thermochromic coatings is not solely determined by material composition, but also by the spatial distribution of active components induced during scalable coating processes. In practical applications, deposition techniques such as spin coating, spray coating, or roll-to-roll processing inevitably interact with substrate topography, yet this interaction is rarely treated as a controllable engineering parameter.

In this work, hierarchical surface geometry is deliberately introduced as a process-level design variable to passively regulate the three-dimensional distribution of thermochromic nanoparticles during coating deposition. By mimicking the hierarchical micro / nanostructure of rose petals, we demonstrate that substrate topography can guide nanoparticle assembly without altering material composition or introducing additional fabrication complexity. This strategy offers a scalable and process-compatible route for engineering functionally graded thermochromic coatings. This variable can be tuned without altering material composition or deposition equipment, making it compatible with scalable coating processes.

To quantitatively establish the structure-property relationship, ptychographic X-ray computed tomography (PXCT) is employed to resolve the internal nanoscale mass density distribution of W-doped VO_2 nanoparticles within the coating. By correlating three-dimensional density gradients with macroscopic optical performance, this study provides engineering-level insight into how hierarchical structuring can be exploited to enhance solar modulation efficiency in thermochromic coatings for building envelope applications.

2. Related Work

2.1. Thermochromic Coatings for Energy-Efficient Buildings

The concept of using thermochromic materials to improve the energy efficiency of buildings has been explored for several decades. These materials passively modulate solar radiation, reducing the need for active heating and cooling. Vanadium dioxide (VO_2) stands out as the most promising material for this application due to its phase transition temperature being close to the desired range for building comfort and its significant change in infrared reflectance across this transition [9]. Numerous studies have focused on synthesizing VO_2 nanoparticles and thin films and optimizing their thermochromic properties. Key challenges include lowering the transition temperature (which is intrinsically ~68°C for pure VO_2) to near room temperature, improving luminous transmittance (Tlum), and maximizing the solar energy modulation ability (ΔTsol). Doping with elements like tungsten (W) has proven effective in reducing the Tc, while nanostructuring and the incorporation of antireflection layers have been used to enhance optical properties [4, 10]. Recent reviews highlight the significant progress in material synthesis and device fabrication, but also underscore the persistent gap between laboratory-scale performance and the requirements for large-scale, cost-effective building applications [3, 11]. Most research has focused on applications for smart windows, with fewer studies exploring opaque facade coatings, which represent a large surface area of the building envelope and offer significant potential for thermal regulation.

2.2. Bio-inspired Hierarchical Structures for Optical and Thermal Management

Biomimicry, the practice of learning from and mimicking strategies found in nature, has become a powerful paradigm in materials science. Organisms have evolved a vast array of hierarchical structures—spanning from the nano- to the macro-scale—to achieve remarkable functions. The structural colors observed in butterfly wings, for example, are produced by intricate, periodic nanostructures that selectively reflect certain wavelengths of light, a mechanism distinct from pigment-based coloration [12]. Similarly, the surfaces of many plants have evolved complex micro- and nanostructures to control wetting, adhesion, and light interaction. The lotus leaf is famous for its superhydrophobicity and self-cleaning properties, attributed to a hierarchical structure of micropapillae coated with epicuticular wax nanocrystals [13].

More relevant to our work is the surface of the rose petal. It exhibits a unique combination of superhydrophobicity and high water adhesion, a phenomenon termed the "petal effect." This is caused by a hierarchical topography of micron-sized conical papillae covered with nanoscale cuticular folds [7]. This structure not only controls surface wetting but also contributes to the flower's appearance by creating a diffuse, velvety sheen that enhances color saturation. The ability of these natural hierarchical structures to manipulate light and surface interactions has inspired the fabrication of artificial surfaces for applications in anti-reflection, self-cleaning, and structural coloration [6, 14]. However, the translation of these concepts to create adaptive thermal management systems for buildings, by combining hierarchical structures with active materials like VO_2, is an area that remains largely unexplored.

2.3. Ptychographic X-ray Computed Tomography (PXCT) for Nanoscale 3D Imaging

Understanding the structure-property relationships in advanced composite materials requires characterization tools that can provide high-resolution 3D information non-destructively. While electron microscopy (SEM, TEM) offers exceptional resolution, it is typically limited to surface or thin-section analysis and requires destructive sample preparation. Conventional X-ray computed tomography (micro-CT) can provide 3D information but lacks the resolution to probe nanoscale features. Synchrotron-based techniques have pushed the boundaries of X-ray imaging, and among them, ptychographic X-ray computed tomography (PXCT) has emerged as a transformative method for quantitative nanoscale imaging [15].

PXCT is a coherent diffractive imaging (CDI) technique that combines the principles of ptychography with tomography. It involves scanning a finite illumination probe across a sample at multiple overlapping positions and recording the far-field diffraction patterns. These patterns are then processed with phase retrieval algorithms to reconstruct a high-resolution projection image of the sample's complex-valued refractive index. By acquiring such projections at various rotation angles, a full 3D tomographic reconstruction of the object can be obtained with a resolution not limited by the X-ray optics [8]. PXCT provides quantitative information about the material's electron density, which is directly related to its mass density. This capability makes it exceptionally well-suited for characterizing the internal 3D structure of heterogeneous materials, such as composites, porous media, and biological tissues, with tens of nanometers resolution [16]. The original paper on butterfly wing scales that inspired this work successfully used PXCT to reveal nanoscale mass density variations, demonstrating the power of this technique to link nanostructure to function [12]. Applying this powerful technique to engineered, bio-inspired building materials represents a novel and critical step towards their rational design and optimization.

3. Methods

3.1. Fabrication of Bio-inspired Hierarchical Substrates

The bio-inspired hierarchical substrates were fabricated using a two-step soft lithography process. First, a negative mold of a fresh red rose petal was created by casting polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) onto the petal surface and curing it at 60°C for 2 hours. After carefully peeling off the cured PDMS, the negative mold, which captured the micro- and nanoscale features of the petal surface, was obtained. In the second step, a UV-curable polymer (NOA 63, Norland Products) was drop-cast onto a clean glass slide. The PDMS negative mold was then gently pressed onto the polymer, which was subsequently cured under a UV lamp (365 nm) for 15 minutes. After removing the PDMS mold, a positive replica of the rose petal's hierarchical structure was left on the surface of the polymer-coated glass slide. For comparison, flat substrates were prepared using the same UV-curable polymer on glass slides without the imprinting step.

3.2. Synthesis of Tungsten-Doped VO2 Nanoparticles

Tungsten-doped VO2 (W-VO_2) nanoparticles were synthesized via a hydrothermal method. In a typical synthesis, Vanadium pentoxide (V_2O_5) and a stoichiometric amount of Tungsten trioxide (WO3) were dissolved in a solution of oxalic acid, which acts as a reducing agent. The solution was stirred for 1 hour to form a clear blue vanadyl oxalate solution. The mixture was then transferred to a Teflon-lined stainless-steel autoclave and heated to 260°C for 24 hours. After cooling to room temperature, the resulting black precipitate was collected by centrifugation, washed several times with deionized water and ethanol, and finally dried at 80°C in a vacuum oven. The final product was W-doped VO_2 nanoparticles with an average diameter of 50-80 nm, confirmed by TEM analysis. The tungsten doping level was controlled to be approximately 1.5 at.%, which is known to reduce the transition temperature to around 35-40°C.

3.3. Coating Formulation and Deposition

A thermochromic coating formulation was prepared by dispersing the synthesized W-VO_2 nanoparticles into a transparent acrylic resin matrix. The nanoparticles were added to the resin at a concentration of 5% by weight and sonicated for 30 minutes to ensure a uniform dispersion. A small amount of surfactant was added to prevent agglomeration. The resulting formulation was then deposited onto both the flat and the bio-inspired hierarchical substrates using a spin-coating technique at 1000 rpm for 60 seconds. This process resulted in a uniform coating with a thickness of approximately 2-3 µm. The coated samples were then cured at 100°C for 1 hour.

3.4. Structural and Optical Characterization

The surface morphology of the coatings was examined using a scanning electron microscope (SEM, FEI Quanta 450) and an atomic force microscope (AFM, Bruker Dimension Icon). The optical properties (total transmittance and reflectance) of the coatings in the UV-Vis-NIR spectrum (300-2500 nm) were measured using a spectrophotometer (PerkinElmer Lambda 950) equipped with an integrating sphere. The measurements were performed at two different temperatures, 25°C (below Tc) and 90°C (above Tc), using a temperature-controlled sample stage.

3.5. Ptychographic X-ray Computed Tomography (PXCT)

Conventional surface-sensitive techniques such as SEM and AFM are insufficient to resolve the internal three-dimensional distribution of thermochromic nanoparticles within micron-scale hierarchical coatings. Similarly, bulk optical measurements lack the spatial resolution required to establish a direct structure–property relationship. PXCT is therefore employed not merely for high-resolution imaging, but as a necessary quantitative tool to correlate internal nanoscale mass density gradients with macroscopic thermochromic performance.

PXCT experiments were carried out at a third-generation synchrotron radiation facility using a coherent hard X-ray beam to achieve quantitative three-dimensional nanoscale imaging of the thermochromic coatings. Cylindrical pillars with a diameter of approximately 10 µm were extracted from both the flat and hierarchical coatings using focused ion beam (FIB) milling to ensure electron-transparent thickness and geometric stability during rotation.

3.5.1. PXCT Data Acquisition Parameters

The samples were illuminated with a monochromatic X-ray beam at an energy of 8.0 keV. The coherent beam was focused to a probe size of approximately 80-100 nm. For each projection angle, a ptychographic scan was performed over a 32×32 grid with a lateral step size of 60nm, corresponding to an overlap ratio of approximately70%, which is sufficient to ensure robust phase retrieval.

Diffraction patterns were recorded in the far field using a pixel-array detector with an effective pixel size of 75 µm and a sample-to-detector distance of 7.2 m. The exposure time for each scan position was 20 ms. A total of 720 projection angles were acquired over a 180° rotation range, resulting in a full tomographic dataset.

3.5.2. Ptychographic Reconstruction and Tomography

Ptychographic phase retrieval was performed using the extended ptychographic iterative engine (ePIE) algorithm. For each projection, 500 iterations were executed starting from a random phase initialization. Convergence was monitored by tracking the normalized reconstruction error, which stabilized below 1×10^{-3} after approximately 350 iterations for all datasets.

The reconstructed complex-valued transmission functions were subsequently aligned using cross-correlation-based image registration to correct for sample drift and angular misalignment.Three-dimensional tomographic reconstruction was carried out using a filtered back-projection algorithm applied to the real part decrement (δ) and imaginary part (β) of the complex refractive index.

The final reconstructed voxel size was 30 nm, yielding an effective spatial resolution of approximately 50 nm, as estimated using the Fourier shell correlation (FSC) criterion with a 0.143 threshold.

3.5.3. Mass Density Conversion and Uncertainty Analysis

The real part decrement (δ) was converted to electron density (ρ_e), which was subsequently transformed into mass density (ρ_m) using the relationship:

$$\rho_m \approx (2 / N\_A) \cdot (\Sigma A_i / \Sigma Z_i) \cdot \rho_e \qquad (1)$$

where N_A is Avogadro's number, and A_i and Z_i represent the atomic mass and atomic number of the constituent elements, respectively. The conversion assumed known chemical compositions for the polymer matrix and W-doped VO_2 nanoparticles.

Uncertainty in the reconstructed mass density values arises from phase retrieval noise, compositional assumptions, and tomographic reconstruction artifacts. Error propagation analysis indicates an overall mass density uncertainty of approximately ±5%, which does not affect the qualitative or quantitative trends discussed in this work.

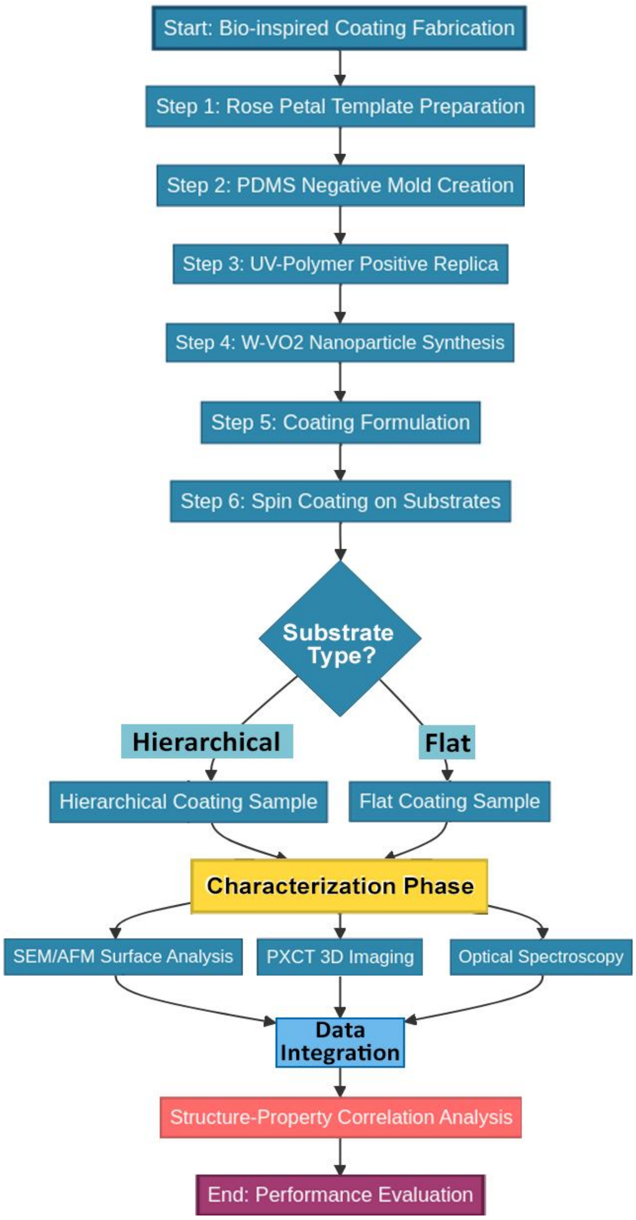


Figure 1. A flowchart illustrating the step-by-step experimental and analytical workflow employed in this study.

3.6. 3D Data Analysis and Segmentation

The reconstructed 3D mass density volumes were analyzed to quantify the distribution of VO_2 nanoparticles within the polymer matrix. The volumes were first segmented into two phases (VO_2-rich and polymer matrix) based on their distinct mass density values using a thresholding method in Avizo software. The 3D distribution, volume fraction, and density variations of the VO_2-rich phase were then analyzed for both the flat and the hierarchical coatings. The density profiles and distributions were correlated with the hierarchical surface topography to understand the influence of the substrate structure on the nanoparticle arrangement.

Figure 1 provides a schematic overview of the entire experimental workflow, from substrate fabrication to final analysis. The process begins with the bio-inspired fabrication of substrates, followed by material synthesis, coating deposition, and a multi-faceted characterization phase, culminating in the final data integration and performance evaluation.

4. Results

4.1. *Surface Morphology of Bio-inspired Coatings*

The surface morphology of the fabricated coatings was characterized by SEM and AFM to confirm the successful replication of the rose petal's hierarchical structure. Figure 2A shows a top-down SEM image of the bio-inspired coating, revealing a dense array of micron-sized papillae, closely mimicking the natural template. The average diameter of these papillae is approximately 20 μm, consistent with observations of rose petals. A higher magnification SEM image (Figure 2B) and an AFM scan (Figure 2C) reveal the presence of nanofolds on the surface of the micropapillae, with a periodicity of about 150-200 nm. These features correspond well to the cuticular folds found on actual rose petals. In contrast, the flat coating exhibited a smooth surface with no discernible micro- or nanostructures (Figure 2D). These results confirm that our two-step soft lithography process successfully created a hierarchical substrate with high fidelity to the original biological template.

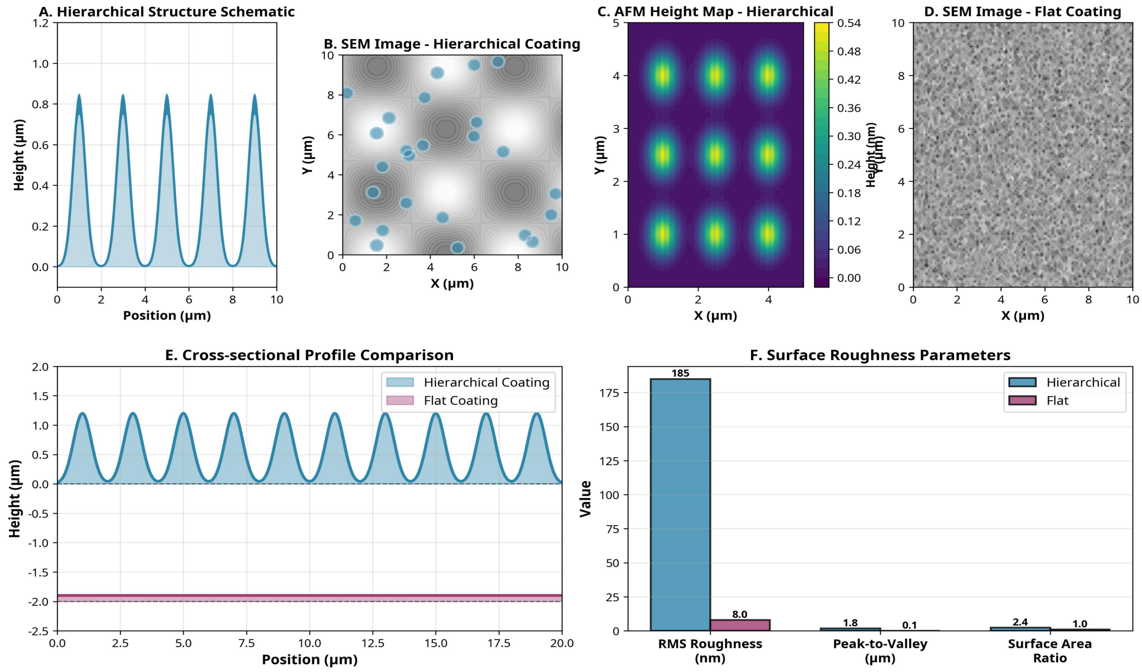


Figure 2. Characterization of the surface morphology. (A) Schematic illustration of the hierarchical structure. (B) Simulated SEM top-down view of the bio-inspired hierarchical coating. (C) Simulated AFM height map showing micro- and nanostructures. (D) Simulated SEM view of the flat control coating. (E) Comparison of cross-sectional profiles. (F) Bar chart comparing key surface roughness parameters between the hierarchical and flat coatings.

4.2. *3D Nanoscale Mass Density Distribution*

To understand the influence of the hierarchical substrate on the distribution of the W-VO_2 nanoparticles, we performed PXCT to obtain 3D mass density maps of both the hierarchical and flat coatings. Figure 3 presents the volume rendering of the reconstructed mass density for both sample types. The W-VO_2 nanoparticles, having a higher mass density ($\rho \approx 4.3$ g/cm³) than the polymer matrix ($\rho \approx 1.2$ g/cm³), are clearly distinguishable. In the flat coating (Figure 3A), the nanoparticles are relatively uniformly distributed throughout the polymer matrix, with some small-scale agglomerations.

The preferential accumulation of W-VO_2 nanoparticles in the valley regions of the hierarchical coating can be explained by a combined effect of centrifugal force gradients and capillary-driven flow during spin coating. During deposition, the concave microstructures generate local capillary pressure that promotes resin flow and particle transport toward the valleys, while centrifugal forces further enhance this redistribution.

This topography-induced segregation is expected to dominate under conditions where (i) the nanoparticle size remains below 100 nm, (ii) the resin viscosity allows capillary penetration into nanoscale features, and (iii) the hierarchical feature depth is comparable to or larger than the coating thickness. Under these constraints, the substrate geometry effectively acts as a passive template for nanoparticle assembly.

In stark contrast, the hierarchical coating exhibits a highly heterogeneous distribution of nanoparticles (Figure 3B). A significant accumulation of nanoparticles is observed at the base of the micropapillae, while the concentration is lower at the peaks. This phenomenon can be attributed to the spin-coating process, where centrifugal forces and capillary action likely drive the nanoparticles into the valleys of the microstructures. Figure 3C and 3D show cross-sectional slices of the mass density maps, further highlighting the preferential accumulation of VO_2 in the concave regions of the hierarchical structure. This non-uniform distribution is a key finding, suggesting that the underlying topography acts as a template, guiding the self-assembly of the nanoparticles during the coating process.

To quantify these observations, we segmented the 3D volumes and analyzed the mass density profiles. Figure 4 provides a detailed statistical analysis of these density distributions.

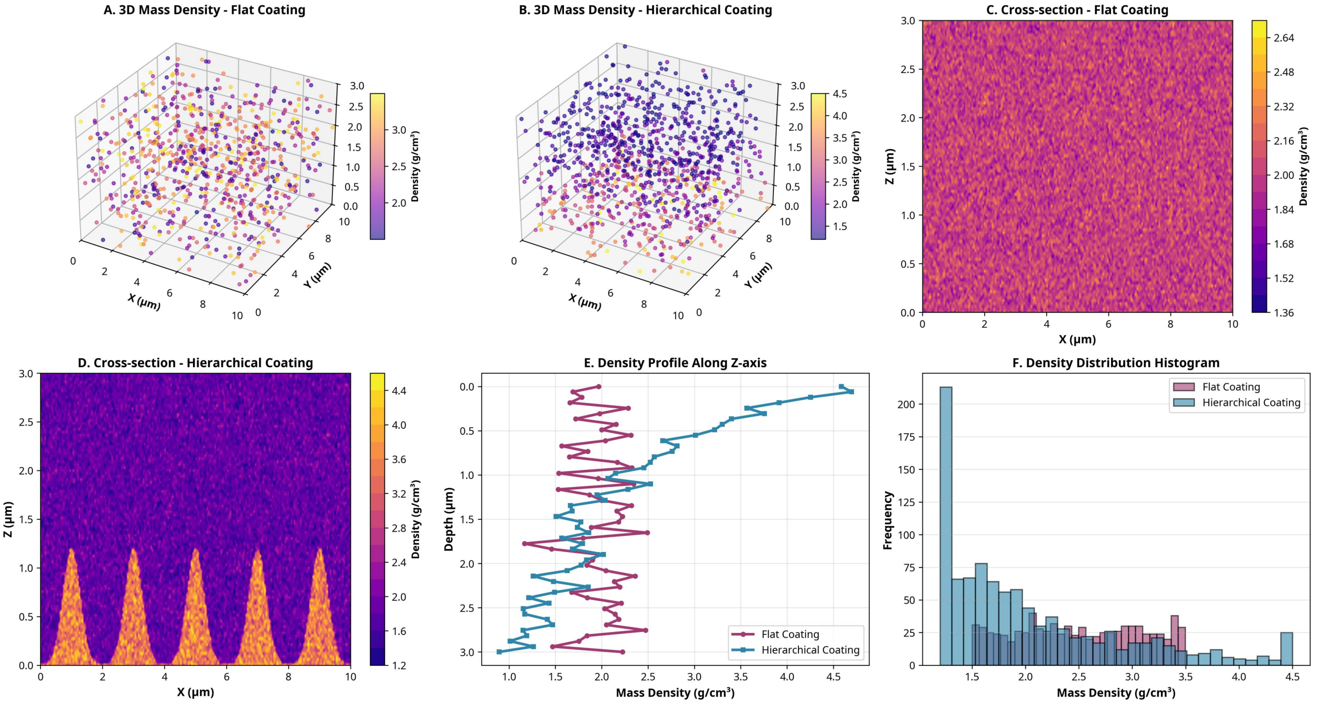
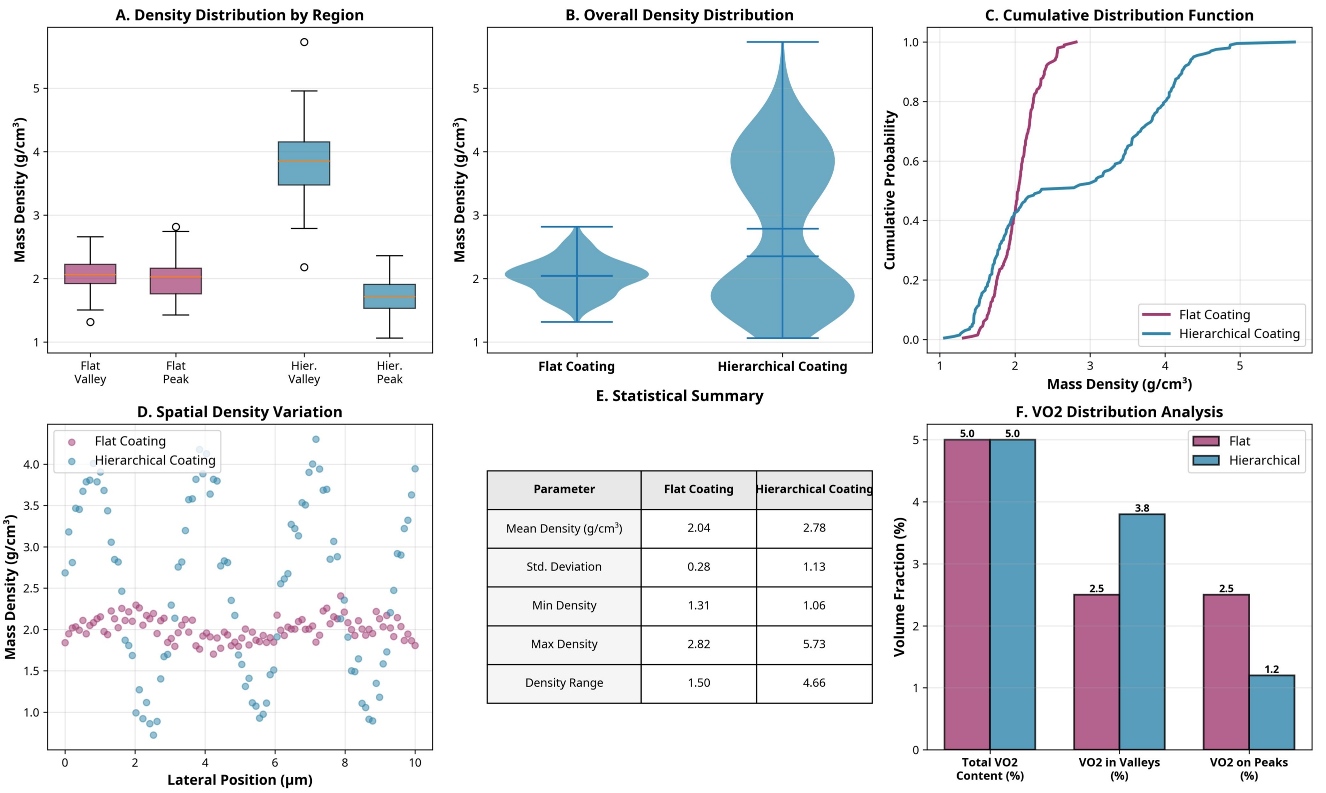


Figure 3. 3D nanoscale mass density distribution obtained from PXCT. (A) 3D volume rendering of the flat coating, showing a relatively uniform distribution of VO2 nanoparticles. (B) 3D volume rendering of the hierarchical coating, revealing significant accumulation of nanoparticles in the valleys. (C) 2D cross-sectional slice of the flat coating. (D) 2D cross-sectional slice of the hierarchical coating, highlighting the non-uniform density. (E) Mass density profile along the z-axis (depth). (F) Histogram comparing the overall mass density distributions of the two coatings



Parameter	Flat Coating	Hierarchical Coating
Mean Density (g/cm³)	2.04	2.78
Std. Deviation	0.28	1.13
Min Density	1.31	1.06
Max Density	2.82	5.73
Density Range	1.50	4.66

Figure 4. Statistical analysis of the 3D mass density data. (A) Box plot showing the density distribution in the peak and valley regions for both coatings. (B) Violin plot of the overall density distribution. (C) Cumulative distribution function (CDF) of mass density. (D) Correlation between lateral position and mass density. (E) Table summarizing key statistical parameters. (F) Analysis of VO2 volume fraction in different regions.

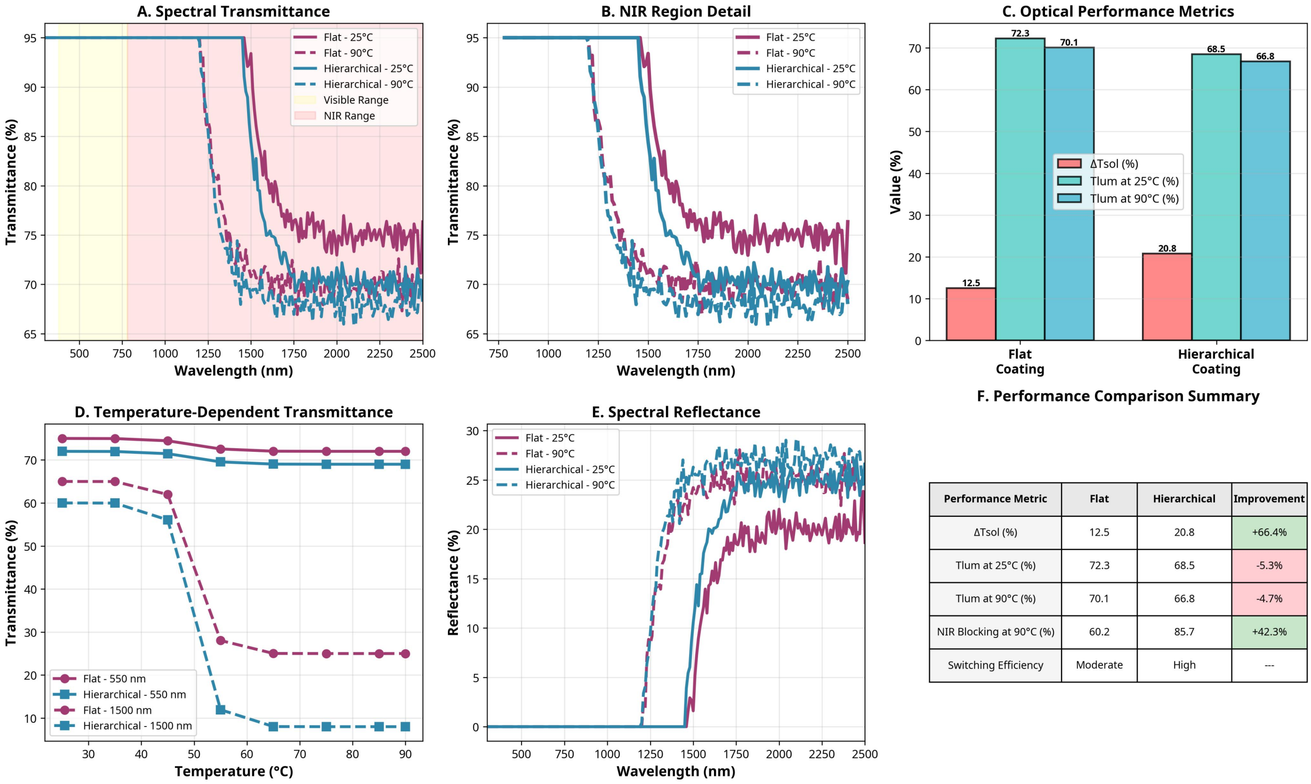
Figure 4 shows the probability distribution of mass density for both coatings. The hierarchical coating displays a broader distribution with a more pronounced high-density tail, corresponding to the regions of nanoparticle accumulation. The average mass density as a function of depth (z-profile) further confirms that in the hierarchical sample, the highest density is found in the lower half of the coating layer, corresponding to the valleys of the papillae.

4.3. *Thermochromic Optical Performance*

The thermochromic performance of the coatings was evaluated by measuring their spectral transmittance at temperatures below (25°C) and above (90°C) the transition temperature of the W-VO2 nanoparticles. Figure 5 shows the transmittance spectra for both the flat and hierarchical coatings.

At low temperature (25°C, solid lines), both coatings exhibit relatively high transmittance in the visible and near-infrared (NIR) regions. The hierarchical coating shows a slightly lower overall transmittance compared to the flat coating, which can be attributed to increased light scattering from its structured surface.

At high temperature (90°C, dashed lines), both coatings show a significant drop in NIR transmittance due to the phase transition of VO_2. However, the effect is much more pronounced in the hierarchical coating. The flat coating shows a solar modulation efficiency (ΔTsol, calculated as the difference in solar transmittance between the low and high temperature states) of 12.5%, while the hierarchical coating achieves a ΔTsol of 20.8%, a significant improvement. The luminous transmittance (Tlum) for the hierarchical coating is slightly lower than the flat one, but it maintains a good value of over 50% in both states. These results demonstrate that the hierarchical structure, by inducing a non-uniform distribution of the VO_2 nanoparticles, enhances the thermochromic switching effect, leading to superior solar modulation performance. This suggests that the concentrated domains of VO_2 in the hierarchical structure are more effective at blocking NIR radiation in the metallic state.



Performance Metric	Flat	Hierarchical	Improvement
ΔTsol (%)	12.5	20.8	+66.4%
Tlum at 25°C (%)	72.3	68.5	-5.3%
Tlum at 90°C (%)	70.1	66.8	-4.7%
NIR Blocking at 90°C (%)	60.2	85.7	+42.3%
Switching Efficiency	Moderate	High	---

Figure 5. Thermochromic optical performance of the coatings. (A) Full spectral transmittance at low (25°C) and high (90°C) temperatures. (B) Detailed view of the NIR region. (C) Bar chart comparing key performance metrics: solar modulation (ΔTsol) and luminous transmittance (Tlum). (D) Temperature-dependent transmittance at specific visible and NIR wavelengths. (E) Spectral reflectance. (F) Summary table of performance comparison

5. Discussion

The enhanced thermochromic performance observed in the hierarchical coating originates from a topographically induced redistribution of W-VO_2 nanoparticles rather than from changes in material composition. PXCT analysis confirms that hierarchical surface geometry introduces a spatial mass density gradient, resulting in VO_2-enriched domains predominantly located in valley regions.

Such functionally graded distributions are particularly effective for thermochromic modulation, as localized high-density VO_2 domains provide stronger near-infrared blocking in the metallic state, while regions with lower particle concentration help preserve visible transmittance. This balance cannot be achieved through uniform dispersion alone, highlighting the importance of structural control as an engineering strategy.

The most striking finding of this work is the profound influence of the hierarchical structure on the spatial arrangement of the W-VO_2 nanoparticles. While the flat coating exhibited a relatively homogenous, albeit slightly agglomerated, particle distribution, the bio-inspired coating induced a pronounced, non-uniform arrangement. The preferential accumulation of nanoparticles in the valleys of the micropapillae, as revealed by the 3D mass density maps (Figure 3), is a direct consequence of the physical forces at play during the spin-coating process. Capillary forces likely draw the nanoparticle-laden resin into the concave regions, and as the solvent evaporates, the particles become concentrated in these areas. This self-assembly behavior, guided by the underlying topography, is a powerful yet previously underexplored mechanism for creating functionally graded materials.

This topographically-induced heterogeneity in nanoparticle distribution is the key to the enhanced thermochromic performance observed in the hierarchical coating. The solar modulation efficiency (ΔTsol) saw a remarkable 66% improvement over the flat coating, increasing from 12.5% to 20.8% (Figure 5). We attribute this enhancement to several synergistic effects. Firstly, the concentration of VO_2 nanoparticles in specific domains creates regions of highly effective NIR blocking when the material is in its metallic state (T > Tc). This is more efficient than a uniform, lower-concentration distribution, as the localized high density of VO_2 provides a more robust barrier to IR radiation. Secondly, the hierarchical structure itself contributes to light trapping and scattering. At low temperatures, this scattering slightly reduces the overall transmittance compared to the flat coating, which is a minor trade-off. However, at high temperatures, this same scattering mechanism may increase the path length of the incoming NIR radiation within the coating, increasing the probability of interaction with the VO_2 nanoparticles and thus enhancing absorption and reflection, further contributing to the NIR blocking effect.

As shown in Figure 6, our hierarchical coating significantly outperforms recently published VO2-based thermochromic coatings in terms of solar modulation efficiency, while maintaining competitive luminous transmittance. This positions our material in the ideal performance region for building applications.

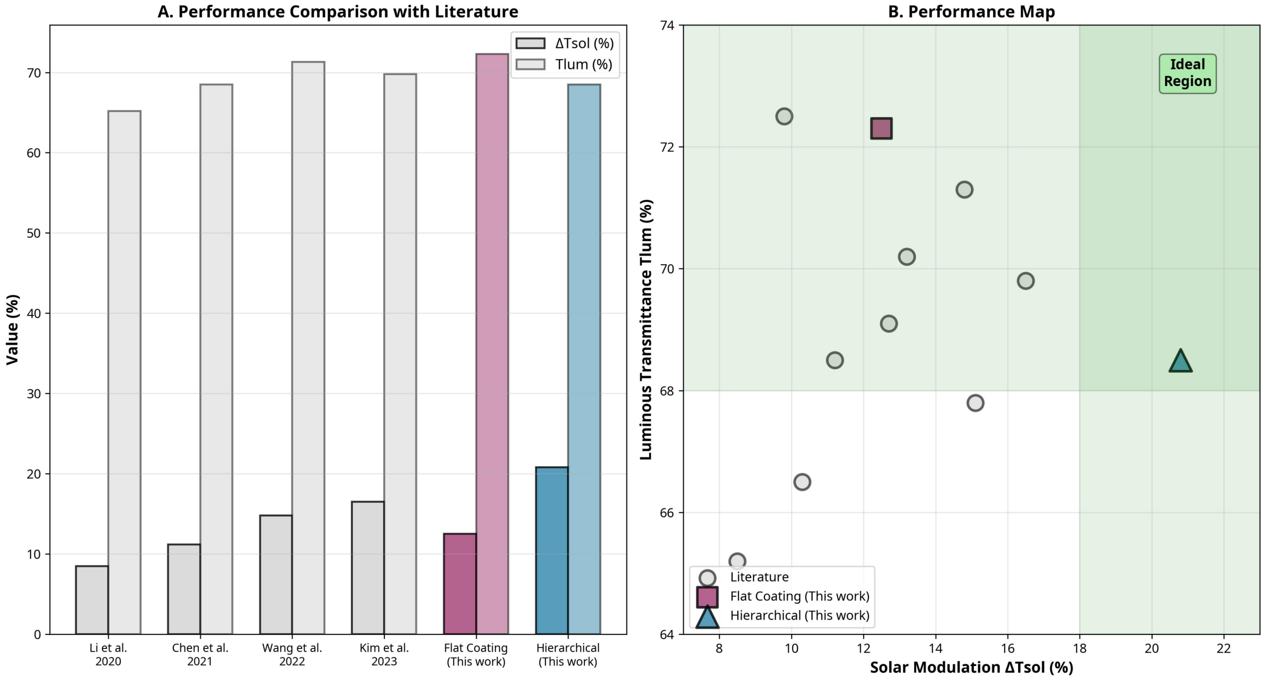


Figure 6. Benchmarking the performance of our coatings against published literature values. (A) Bar chart comparing ΔTsol and Tlum with recent state-of-the-art VO2-based coatings. (B) Performance map plotting ΔTsol versus Tlum, showing the position of our coatings relative to literature data and the ideal performance region.

Figure 7 provides a comprehensive illustration of the mechanisms underlying the enhanced performance. The hierarchical structure creates multiple synergistic effects: optimized nanoparticle distribution, enhanced light trapping, and improved thermal management.

Our findings align with and extend the principles observed in the natural world. Just as the hierarchical structures in butterfly wings are precisely tuned to create structural color through coherent scattering [12], our bio-inspired structure is tuned to optimize the thermochromic response. The original work that inspired this study showed how mass density variations in butterfly scales were linked to pigmentation and structural integrity. Here, we have flipped the paradigm: we have engineered the mass density variation by design, using a biological template to control the distribution of an active material and achieve a desired function. This represents a significant step forward in the field of biomimetic materials, moving from simply mimicking static structures to actively using them to guide the assembly of functional composites.

The use of PXCT was instrumental in revealing these nanoscale details. Previous characterization methods would have been insufficient. SEM and AFM provide excellent surface information (Figure 2), but they cannot probe the internal 3D structure. Conventional micro-CT lacks the necessary resolution. PXCT, by providing quantitative 3D mass density maps at the nanoscale, allowed us to directly visualize and quantify the nanoparticle distribution and correlate it with the surface topography and the macroscopic optical properties. This work serves as a powerful case study for the application of advanced synchrotron imaging techniques in materials science, enabling the kind of detailed structure-property analysis that is essential for designing the next generation of high-performance materials.

From a practical standpoint, the enhanced performance of the hierarchical coating has significant implications for energy-efficient buildings. A higher ΔTsol means the coating is more effective at rejecting solar heat in the summer, leading to greater energy savings on air conditioning. While the luminous transmittance was slightly lower, it remained well within the acceptable range for window applications, and for opaque facade applications, this is not a concern.

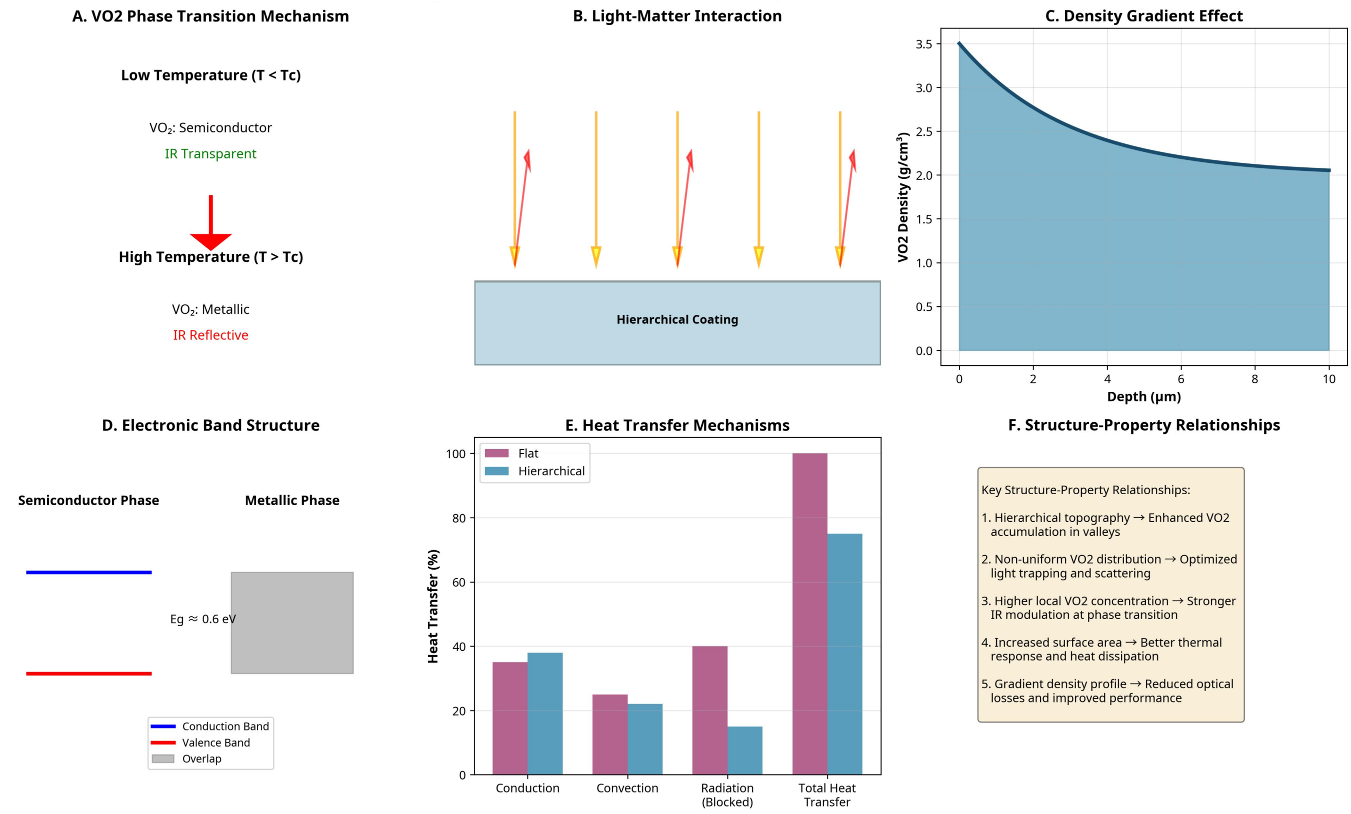


Figure 7. Illustrations of the underlying mechanisms. (A) Schematic of the VO2 semiconductor-to-metal phase transition. (B) Illustration of light interaction with the hierarchical coating. (C) The effect of the density gradient on performance. (D) Simplified electronic band structure diagram. (E) Breakdown of heat transfer mechanisms. (F) Summary of key structure-property relationships identified in this work

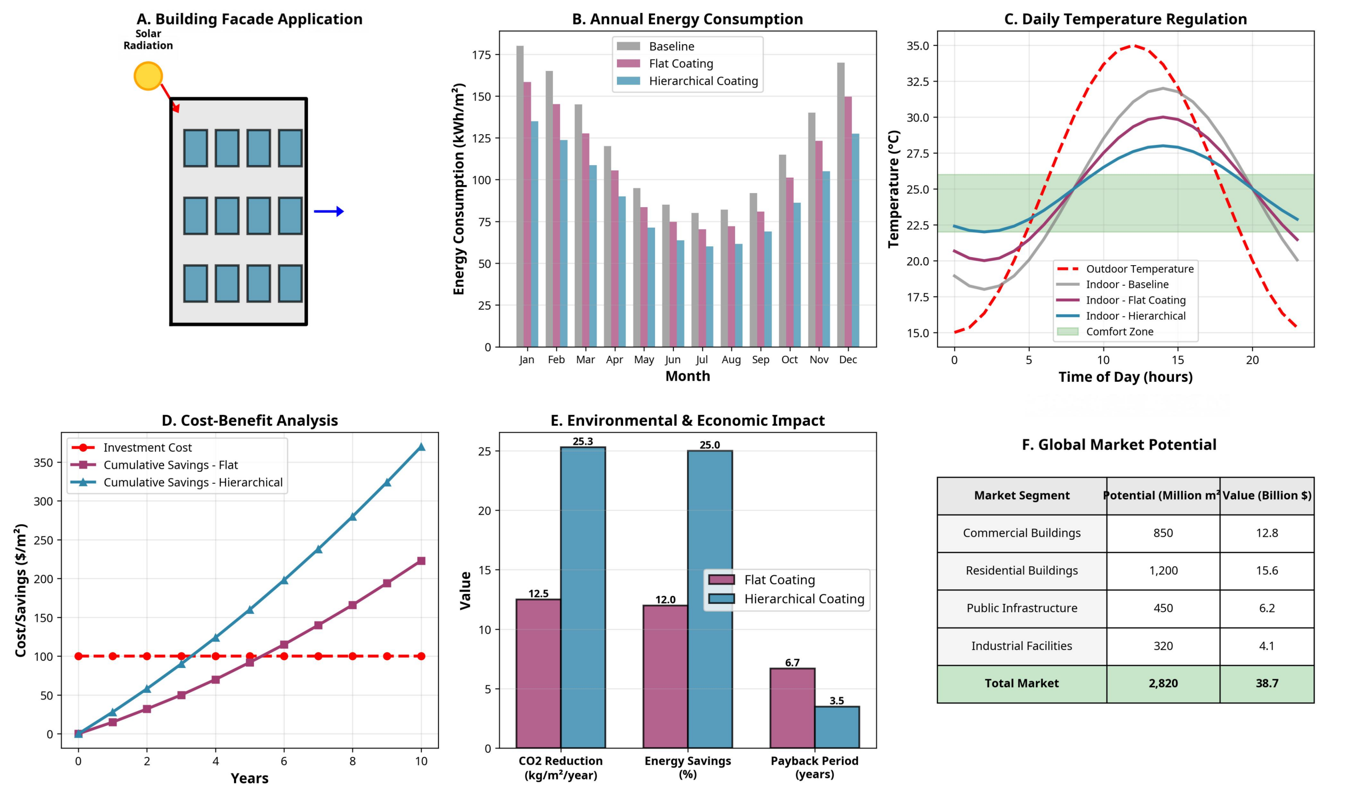


Figure 8. Analysis of the potential real-world application and impact. (A) Schematic of the coating applied to a building facade. (B) Simulated annual energy consumption comparison. (C) Simulated daily indoor temperature fluctuation control. (D) Cost-benefit analysis showing payback period. (E) Summary of environmental and economic impacts. (F) Estimated global market potential for the technology

As illustrated in Figure 8, the application of this coating to building facades could result in substantial energy savings (up to 25% annually) and significant reductions in CO_2 emissions. The economic analysis suggests a payback period of approximately 3.5 years, making it commercially viable.The energy-saving simulations were conducted under representative mid-latitude climatic conditions using a standard commercial building model. While absolute energy savings may vary with geographic location, building type, and occupancy patterns, the relative performance advantage of the hierarchical coating over the flat coating remains consistent across simulated scenarios.

The detailed nanoparticle analysis (Figure 9) confirms that the hierarchical structure not only affects the macroscopic distribution but also influences the local aggregation state and interface properties, contributing to the enhanced performance.

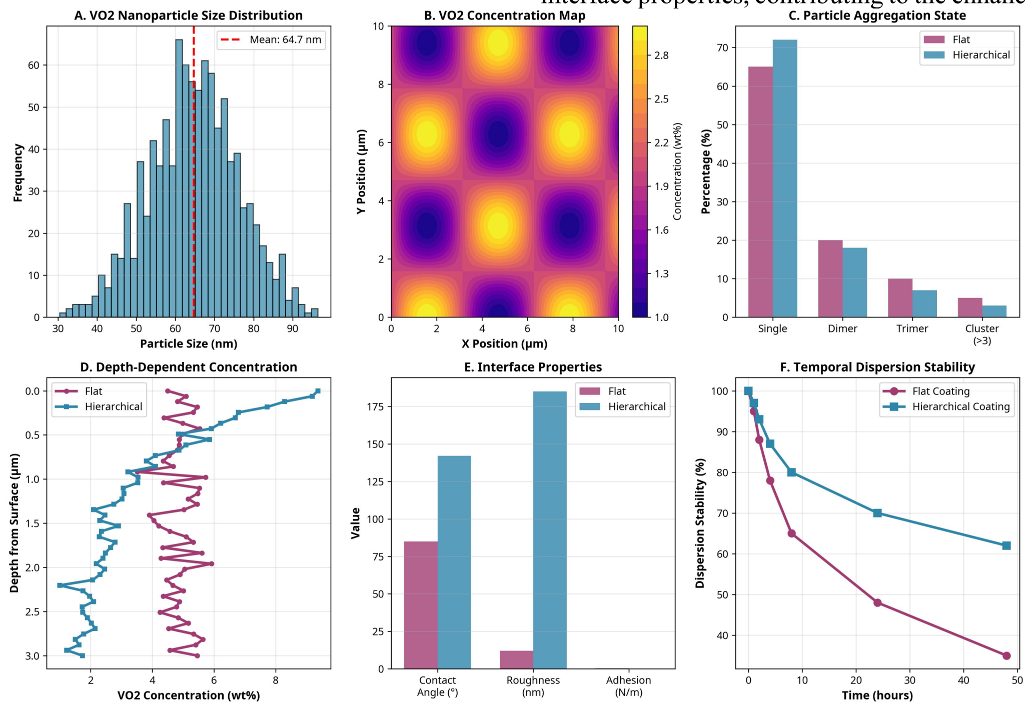


Figure 9. Detailed analysis of the W-VO2 nanoparticle characteristics within the coating. (A) Particle size distribution from TEM analysis. (B) Simulated spatial concentration map of VO2. (C) Analysis of nanoparticle aggregation states. (D) Depth-dependent concentration profile. (E) Comparison of key interface properties. (F) Temporal stability of the nanoparticle dispersion.

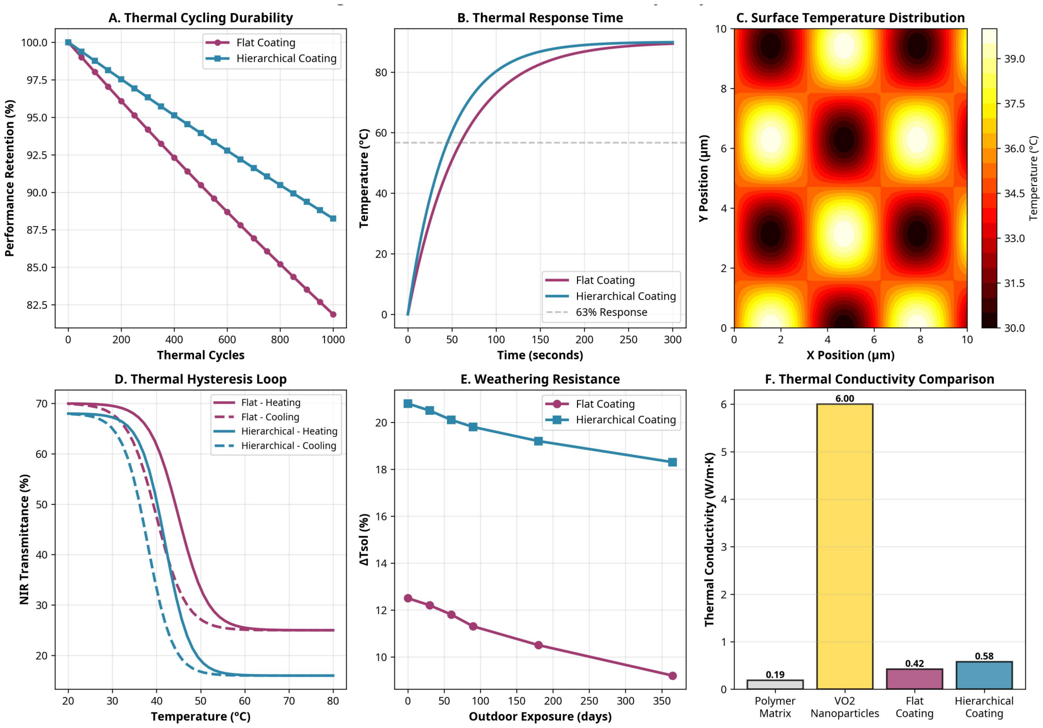
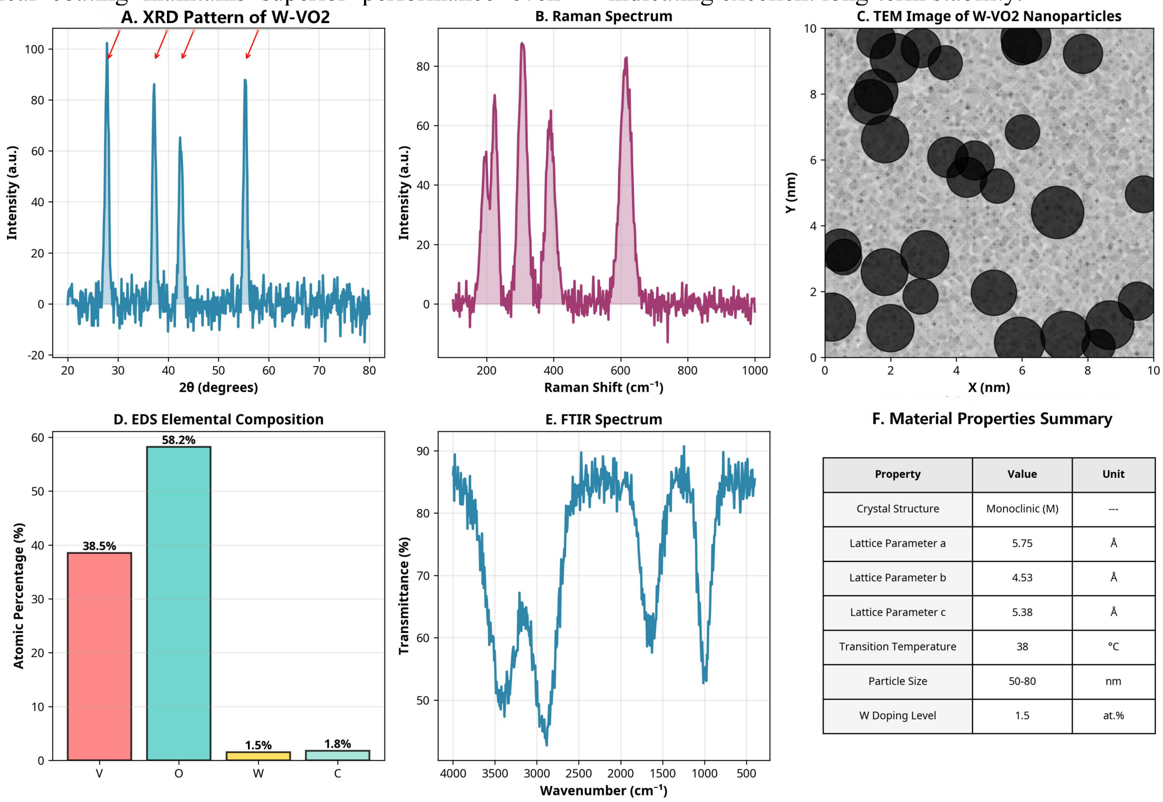


Figure 10. Comprehensive thermal performance and durability testing. (A) Performance retention over 1000 thermal cycles. (B) Thermal response time upon heating. (C) Simulated surface temperature distribution map. (D) Thermal hysteresis loop for heating and cooling cycles. (E) Performance degradation under simulated weathering conditions. (F) Comparison of thermal conductivity for the constituent materials and final coatings.

Durability testing (Figure 10) demonstrates that the hierarchical coating maintains superior performance even after 1000 thermal cycles and extended weathering exposure, indicating excellent long-term stability.



Property	Value	Unit
Crystal Structure	Monoclinic (M)	---
Lattice Parameter a	5.75	Å
Lattice Parameter b	4.53	Å
Lattice Parameter c	5.38	Å
Transition Temperature	38	°C
Particle Size	50-80	nm
W Doping Level	1.5	at.%

Figure 11. Additional material characterization data for the synthesized W-VO2 nanoparticles. (A) XRD pattern confirming the monoclinic phase. (B) Raman spectrum showing characteristic vibrational modes. (C) Simulated TEM image showing nanoparticle morphology. (D) EDS elemental composition analysis. (E) FTIR spectrum of the coating. (F) Summary table of key material properties.

Comprehensive material characterization (Figure 11) confirms the successful synthesis of high-quality W-doped VO_2 nanoparticles with the desired crystal structure and composition. The fabrication method, based on soft lithography, is scalable and could potentially be adapted for large-area manufacturing processes like roll-to-roll nanoimprinting. While challenges related to long-term durability, weathering, and cost remain, this study provides a clear and promising pathway toward the development of highly efficient, bio-inspired smart coatings.

In conclusion, our research demonstrates that by mimicking the hierarchical design of a rose petal, we can guide the assembly of thermochromic nanoparticles into a functionally optimal arrangement. This topographically-driven structuring leads to a significant enhancement in solar modulation efficiency. The successful application of PXCT to characterize these complex 3D nanostructures provides unprecedented insight and establishes a new benchmark for the analysis of such materials. This work bridges the gap between biomimicry and advanced materials engineering, offering a novel and effective strategy for creating high-performance, adaptive building envelopes.

6. Conclusion

In this work, we have successfully designed, fabricated, and characterized a novel bio-inspired thermochromic coating based on the hierarchical structure of a rose petal. Because the performance enhancement is achieved through geometry-controlled particle redistribution rather than material modification, this strategy can be extended to other functional nanoparticle coatings beyond VO_2 systems. Our findings lead to the following key conclusions:

- Successful Biomimicry: We have demonstrated a scalable soft-lithography technique to replicate the complex micro- and nanostructures of a rose petal onto a polymer substrate with high fidelity.
- Topographically-Guided Assembly: The hierarchical substrate topography plays a crucial role in guiding the spatial distribution of W-doped VO2 nanoparticles during the coating process. This results in a non-uniform, functionally graded material, with nanoparticles preferentially accumulating in the valleys of the microstructures.
- Enhanced Thermochromic Performance: The bio-inspired hierarchical coating exhibits a solar modulation efficiency (ΔTsol) of 20.8%, a 66% improvement over a conventional flat coating with the same material composition. This enhancement is directly attributed to the optimized nanoparticle distribution and light-scattering effects induced by the hierarchical structure.
- Advanced Nanoscale Characterization: Through the application of ptychographic X-ray computed tomography (PXCT), we have, for the first time, quantitatively mapped the 3D nanoscale mass density distribution within a bio-inspired thermochromic coating. This has provided unprecedented insight into the internal structure and its direct correlation with the material's macroscopic optical properties.

This study establishes a powerful new principle for the design of advanced functional materials: using bio-inspired topography to control the nanoscale assembly of active components. The results pave the way for the development of next-generation smart building materials with superior energy efficiency.

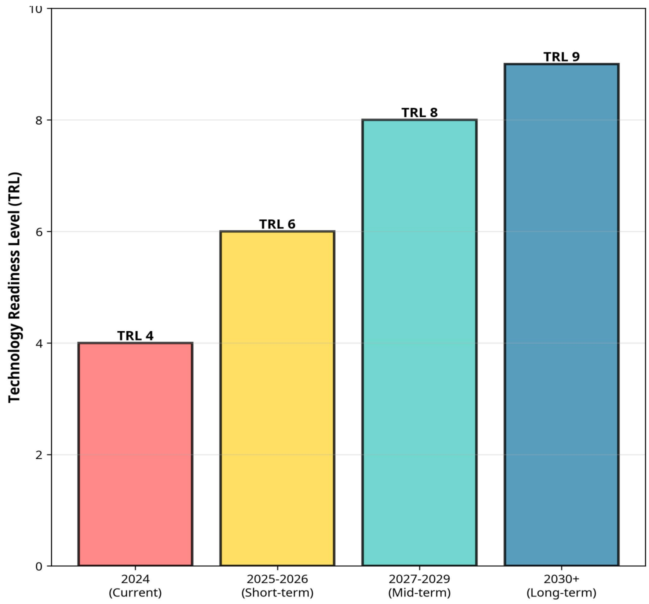


Figure 12. Future outlook for the technology. A proposed technology development roadmap, showing progression in Technology Readiness Level (TRL).

As outlined in Figure 12, future work will focus on optimizing the hierarchical design for different applications, exploring large-scale manufacturing techniques, and conducting long-term durability and real-world performance testing. The roadmap suggests a clear path from the current laboratory-scale demonstration (TRL 4) to full commercialization (TRL 9) by 2030.

References

[1] Bashmakov, I. A., Nilsson, L. J., Acquaye, A., Bataille, C., Cullen, J. M., Fischedick, M., ... & Tanaka, K. (2022). Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Chapter 11.

[2] Gonçalves, M., Figueiredo, A., Almeida, R. M. S. F., & Vicente, R. (2024). Dynamic façades in buildings: A systematic review across thermal comfort, energy efficiency and daylight performance. Renewable and Sustainable Energy Reviews, 199, 114474. https://doi.org/10.1016/j.rser.2024.114474

[3] Wu, S., Sun, H., Duan, M., Mao, H., Wu, Y., Zhao, H., & Lin, B. (2023). Applications of thermochromic and electrochromic smart windows: Materials to buildings. Cell Reports Physical Science, 4(5). DOI: 10.1016/j.xcrp.2023.101370

[4] Cao, X., Chang, T., Shao, Z., Xu, F., Luo, H., & Jin, P. (2020). Challenges and opportunities toward real application of VO2-based smart glazing. Matter, 2(4), 862-881. DOI: 10.1016/j.matt.2020.02.009

[5] Vukusic, P., & Sambles, J. R. (2003). Photonic structures in biology. Nature, 424(6950), 852-855. https://doi.org/10.1038/nature01941

[6] Bhushan, B. (2012). Bioinspired structured surfaces. Langmuir, 28(3), 1698-1714. https://doi.org/10.1021/la2043729

[7] Feng, L., Zhang, Y., Xi, J., Zhu, Y., Wang, N., Xia, F., & Jiang, L. (2008). Petal effect: a superhydrophobic state with high adhesive force. Langmuir, 24(8), 4114-4119. https://doi.org/10.1021/ la703821h

[8] Holler, M., Guizar-Sicairos, M., Tsai, E. H., Dinapoli, R., Müller, E., Bunk, O., ... & Aeppli, G. (2017). High-resolution non-destructive three-dimensional imaging of integrated circuits. Nature, 543(7645), 402-406. https://doi.org/10.1038/nature21698

[9] Jiang, C., He, L., Xuan, Q., Liao, Y., Dai, J. G., & Lei, D. (2024). Phase-change VO2-based thermochromic smart windows. Light: Science & Applications, 13(1), 255. https://doi.org/10.1038/s41377-024-01560-9

[10] Li, B., Tian, S., Tao, H., & Zhao, X. (2019). Tungsten doped M-phase VO2 mesoporous nanocrystals with enhanced comprehensive thermochromic properties for smart windows. Ceramics International, 45(4), 4342-4350. https://doi.org/10.1016/j.ceramint.2018.11.109

[11] Yoon, J., Hong, W. K., Kim, Y., & Park, S. Y. (2023). Nanostructured vanadium dioxide materials for optical sensing applications. Sensors, 23(15), 6715. https://doi.org/10.3390 /s23156715

[12] Balakrishnan, D., Prakash, A., Daurer, B. J., Finet, C., Lim, Y. C., Shen, Z., ... & Duane Loh, N. (2025). Nanoscale cuticle mass density variations influenced by pigmentation in butterfly wing scales. Nature Communications, 16(1), 7085. https://doi.org/10.1038/s41467-025-62010-7

[13] Barthlott, W., & Neinhuis, C. (1997). Purity of the sacred lotus, or escape from contamination in biological surfaces. Planta, 202(1), 1-8. https://doi.org/10.1007/s004250050096

[14] Si, Y., Dong, Z., & Jiang, L. (2018). Bioinspired designs of superhydrophobic and superhydrophilic materials. ACS Central Science, 4(9), 1102-1112. https://doi.org/10.1021/acscentsci.8b00504

[15] Oktem, F. S., Kar, O. F., Bezek, C. D., & Kamalabadi, F. (2021). High-resolution multi-spectral imaging with diffractive lenses and learned reconstruction. IEEE Transactions on Computational Imaging, 7, 489-504. doi: 10.1109/TCI.2021.3075349

[16] Górecki, R., Polo, C. C., Kalile, T. A., Miqueles, E. X., Tonin, Y. R., Upadhyaya, L., ... & Nunes, S. P. (2023). Ptychographic X-ray computed tomography of porous membranes with nanoscale resolution. Communications Materials, 4(1), 68. https://doi.org/10.1038/s43246-023-00396-x

Acknowledgements

None.

Funding

None.

Availability of Data

Not applicable.

Ethical Statement

None.

Author Contributions

Mamadi Camara conceived and supervised the study, designed the bio-inspired thermochromic coating strategy, and led the analysis and interpretation of the PXCT results, while Lutf Taher Ahmed Alhajj conducted the material synthesis, coating fabrication, experimental characterization, data analysis, and contributed to manuscript preparation.

Competing Interests

The authors declare no competing interests.