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Role of Thin Film Matrices in Controlling Morphology and Growth of Inorganic Nanoparticles

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ABSTRACT: Nanostructured inorganic nanoparticles exhibit size- and shape-dependent physicochemical properties that differ markedly from their bulk counterparts, primarily due to quantum confinement effects and high surface-to-volume ratios. This study explores the role of thin film matrices, particularly thermally evaporated lipid thin films, in controlling the morphology, growth, and stabilization of inorganic nanoparticles. Gold nanoparticles with tailored morphologies (e.g., triangular and hexagonal) were synthesized using eco-friendly green reduction methods with plant extracts such as lemongrass, geranium, and neem. Additionally, metal oxide (TiO_2 , ZrO_2) and metal sulfide (CdS) nanoparticles were generated and immobilized in situ within confined thin film environments via electrostatic entrapment and controlled hydrolysis processes. These lipid-based thin films serve as versatile templates, providing a confined reaction space analogous to Langmuir–Blodgett assemblies, which restricts diffusion, influences nucleation, and directs anisotropic growth. Comprehensive characterization employing UV–Visible spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Quartz Crystal Microbalance (QCM), and X-ray Photoelectron Spectroscopy (XPS) revealed that thin film confinement significantly modulates nanoparticle size distribution, crystallinity, shape anisotropy, and surface interactions. The results highlight how matrix-mediated confinement enhances control over particle morphology compared to free-solution synthesis, leading to improved stability and functionality. This hybrid chemical–physical approach establishes thermally evaporated thin films as effective platforms for the precise synthesis and immobilization of inorganic nanoparticles, with promising applications in catalysis, chemical/biological sensing, optoelectronics, and advanced nanostructured coatings.

KEYWORDS: Inorganic nanoparticles, Thin film matrices, Morphology control, Nanoparticle growth, Thermally evaporated lipid films, Green synthesis, Confinement effects, Gold nanoparticles, Metal oxides, Catalysis applications.

I. INTRODUCTION

The field of nanomaterials has revolutionized modern science and technology by enabling the manipulation of matter at the atomic and molecular scales, leading to materials with extraordinary properties that diverge dramatically from their bulk counterparts. Solid materials are traditionally classified into categories such as metals, semiconductors, ceramics, polymers, and composites based on their inherent physical and chemical attributes, and they find applications in diverse areas including biomaterials, protective coatings, catalytic systems, magnetic devices, optical glasses, and electronic components. However, when these materials are engineered into nanoparticles—typically defined as particles behaving as single functional units with dimensions predominantly in the range of 1 to 100 nanometers—their characteristics undergo profound transformations. On October 18, 2011, the European Commission formalized a definition of nanomaterials as natural, incidental, or manufactured substances containing unbound particles, aggregates, or agglomerates where at least 50% of the particles possess one or more external dimensions between 1 and 100 nm. This nanoscale regime triggers remarkable phenomena, primarily driven by an exponentially increased surface-to-volume ratio and quantum confinement effects, where electrons, excitons, phonons, and other charge carriers are confined within dimensions comparable to their characteristic lengths, such as the mean free path of electrons, the wavelength of light, energy transfer distances, or diffusion lengths. Consequently, properties like mechanical strength, thermal conductivity, optical absorption, electrical conductivity, and magnetic behavior exhibit size-dependent deviations that are neither bulk-like nor purely atomic/molecular in nature. The conceptual origins of this paradigm shift trace back to Richard Feynman's visionary 1959 lecture, "There's Plenty of Room at the Bottom," which envisioned precise control over matter at the atomic level, laying the foundation for contemporary nanoscience and nanotechnology. The term "nano," derived from



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the Greek word for "dwarf," underscores the extreme miniaturization involved, with nanoscience focusing on the study of materials at this scale and nanotechnology emphasizing their deliberate manipulation and practical implementation across fields such as medicine (e.g., targeted drug delivery and diagnostic imaging), electronics (high-density storage and flexible displays), energy (efficient solar cells and batteries), catalysis (enhanced reaction rates), environmental remediation (pollutant degradation), and advanced coatings (self-cleaning or anticorrosive surfaces). Nanomaterials encompass a broad spectrum, including metal nanoparticles (gold, silver), metal oxides (TiO_2 , ZnO , ZrO_2), semiconductor quantum dots (CdS), carbon-based structures (fullerenes, nanotubes, graphene), organic-inorganic hybrids, liposomes, and polymerized nanoparticles, all leveraging size-tunable multifunctionality that positions them as cornerstone elements in cutting-edge materials engineering. The evolution of nanostructured materials has been propelled by advances allowing deliberate tailoring in regimes where classical bulk dominance yields to surface-dominated and quantum phenomena; as dimensions shrink to 1–100 nm, the fraction of surface atoms surges, elevating surface energy, altering thermodynamic stability, and quantizing electronic energy levels to modify band structures, optical responses, catalytic efficiency, and conductivity. Inorganic nanoparticles, in particular—encompassing noble metals (Au, Ag, Pt), metal oxides (TiO_2 , ZrO_2), and metal sulfides (CdS)—display distinctive features like localized surface plasmon resonance (LSPR) in noble metals for sensing and photonics, tunable band gaps in oxides for photocatalysis and electronics, and size-dependent fluorescence in quantum dots. These properties are governed not merely by composition but critically by particle size and distribution, morphology (spherical, triangular, hexagonal, rod-like), crystallinity, surface chemistry, and interfacial interactions, necessitating precise synthetic control. Nanomaterials are classified geometrically into zero-dimensional (0D: quantum dots, fullerenes, metal nanoparticles with strong confinement), one-dimensional (1D: nanotubes, nanowires, nanorods with high aspect ratios for sensors and nanoelectronics), two-dimensional (2D: nanosheets, graphene, nanolayers with planar anisotropy for unusual electronic/mechanical traits), and three-dimensional (3D: nanocrystalline solids, nanocomposites composed of nanoscale building blocks). A key challenge in harnessing these materials lies in achieving controlled synthesis and stabilization, especially for anisotropic morphologies that enhance functionality in applications like catalysis and optoelectronics. Traditional solution-based methods often yield polydisperse or aggregated particles due to unrestricted diffusion and growth, prompting exploration of confined environments to impose spatial restrictions, modulate nucleation kinetics, and direct shape evolution. Thin film matrices, particularly those prepared via thermal evaporation of lipids (e.g., fatty acids or amines), emerge as versatile templates analogous to Langmuir–Blodgett assemblies but simpler and more scalable, providing a confined reaction space that limits particle mobility, promotes electrostatic entrapment, and facilitates in-situ synthesis through controlled hydrolysis or reduction. This hybrid chemical-physical strategy has proven effective for immobilizing and growing inorganic nanoparticles with tailored morphologies, as evidenced in green synthesis of shape-controlled gold nanoparticles (triangular, hexagonal) using plant extracts (lemongrass, geranium, neem) and entrapment of TiO_2 , ZrO_2 , and CdS via electrostatic and hydrolytic processes within lipid films. Confinement in such matrices profoundly influences morphology by restricting diffusion paths, enhancing surface interactions, and stabilizing anisotropic structures that are difficult to obtain in free solution, leading to improved crystallinity, size uniformity, and interfacial stability. Comprehensive characterization using techniques like UV–Visible spectroscopy (for plasmonic shifts), FTIR (surface chemistry), TEM (morphology and size), XRD (crystallinity and phase), QCM (mass uptake and film thickness), and XPS (elemental composition and bonding) consistently demonstrates that thin film confinement outperforms bulk methods in precision and functionality. This approach not only addresses aggregation issues but also opens pathways for hybrid systems with applications in catalysis (enhanced active sites), sensing (improved sensitivity via plasmonics), optoelectronics (tunable band gaps), and nanostructured coatings (durable, functional surfaces). By establishing thermally evaporated thin films as robust platforms for nanoparticle control, this research bridges sustainable green synthesis with advanced templating, contributing to the broader advancement of nanotechnology toward scalable, application-driven innovations in materials science.

II. LITERATURE REVIEW

The literature review on the role of thin film matrices in controlling the morphology and growth of inorganic nanoparticles draws from foundational and recent advancements in nanomaterial synthesis, templating strategies, and confined environments. Early studies established the size- and shape-dependent properties of inorganic nanoparticles, such as localized surface plasmon resonance in noble metals (e.g., Au, Ag) and tunable band gaps in oxides (TiO_2 , ZrO_2) and sulfides (CdS), influenced by quantum confinement and surface effects. Traditional solution-based methods often lead to polydisperse or aggregated particles due to unrestricted nucleation and Ostwald ripening, highlighting the need for



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templated approaches to achieve precise control over size, shape (spherical, triangular, hexagonal, rod-like), and crystallinity.

Template-assisted synthesis has been categorized into hard (e.g., porous silica, anodic alumina) and soft templates (e.g., surfactants, micelles, block copolymers), with soft templates offering dynamic control via electrostatic, steric, and hydrogen-bonding interactions for anisotropic morphologies. Langmuir–Blodgett (LB) films, in particular, provide ordered monolayers for nanoparticle organization and in-situ growth, enabling confinement that directs nucleation, restricts diffusion, and promotes anisotropy in structures like CdS quantum dots or Ni-containing particles, while maintaining lamellar order even after reduction or hydrolysis. LB techniques allow molecular-level precision in multilayer assembly, influencing optical, catalytic, and electronic properties through controlled dimensionality and external field responses.

Thermally evaporated lipid thin films serve as a scalable, simpler alternative to LB methods, leveraging electrostatic entrapment for immobilizing charged nanoparticles or ions. Key works have demonstrated the immobilization of biogenic gold nanoparticles (synthesized via plant extracts) in fatty acid/amine films, where surface charge selectivity prevents aggregation and stabilizes hybrids. In-situ growth has been achieved by entrapping metal ions (e.g., Ti^{4+} in protonated amine films) followed by controlled hydrolysis to form monodisperse TiO_2 nanoparticles (~4 nm) within the lipid matrix, with uniform distribution and preserved film structure. Similar principles apply to other systems, where lipid confinement modulates interfacial interactions, enhances stability, and restricts growth compared to bulk solutions.

Green synthesis routes using plant extracts (e.g., lemongrass, geranium, neem) have been widely explored for eco-friendly production of shape-controlled gold nanoparticles, with biomolecules (polyphenols, terpenoids, proteins) acting as reductants and stabilizers. Factors like extract concentration, pH, temperature, and counter ions tailor morphologies—lower concentrations favoring triangular/hexagonal shapes—offering advantages in sustainability and scalability over chemical methods.

For metal oxides and sulfides, in-situ synthesis in thin films or hybrid matrices (e.g., sol-gel ZrO_2 -doped TiO_2 , CdS@TiO_2 - ZrO_2 composites) achieves tailored phases, sizes, and photocatalytic performance, though thermal evaporation-based lipid approaches provide mild conditions and electrostatic precision. Characterization techniques (UV-Vis for plasmon shifts, FTIR for bonding, TEM for morphology, XRD for crystallinity, XPS for composition) consistently show confinement effects reduce polydispersity, enhance anisotropy, and improve functionality.

Recent reviews emphasize ligand engineering in nanoparticle films for morphology tuning (porosity, roughness), thin-film deposition methods (PVD, CVD, sol-gel) for controlled growth, and immobilized nanomaterials in films for remediation, sensing, and catalysis, where matrix support prevents agglomeration and enables scalability. Despite progress, gaps remain in integrating green methods with lipid thin film templating for diverse nanoparticles (Au, TiO_2 , ZrO_2 , CdS), long-term stability, and application optimization. This study builds on these foundations by utilizing thermally evaporated lipid films as LB-analogous platforms for sustainable, confined synthesis and immobilization, advancing precise morphological control in inorganic nanomaterials.

III. MATERIALS AND METHODS

All experiments were carried out using analytical-grade reagents and Milli-Q water (resistivity $>18 \text{ M}\Omega\cdot\text{cm}$) to ensure high purity and reproducibility. The synthesis and characterization procedures followed a hybrid chemical-physical methodology, where thermally evaporated lipid thin films served as confining matrices for the controlled immobilization and in-situ growth of inorganic nanoparticles. This approach leveraged electrostatic interactions and confined reaction environments to influence nanoparticle morphology, size, and stability.

The primary materials included plant extracts from lemongrass (*Cymbopogon citratus*), geranium (*Pelargonium graveolens*), and neem (*Azadirachta indica*) leaves, which were freshly collected, thoroughly washed, and processed into aqueous extracts by boiling or maceration in distilled water for use as eco-friendly reducing and capping agents in green synthesis. Metal precursors comprised chloroauric acid ($\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$, 99.9%) for gold nanoparticles, titanium tetrachloride (TiCl_4) or titanium isopropoxide and related salts for TiO_2 , zirconium oxychloride ($\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$) for ZrO_2 , and cadmium chloride (CdCl_2) with sodium sulfide (Na_2S) for CdS nanoparticles. Lipid templates for thin film deposition



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included octadecylamine (ODA, cationic), stearic acid (STA, anionic), and sodium bis(2-ethylhexyl)sulfosuccinate (AOT, anionic), all of high purity ($\geq 99\%$). Substrates such as quartz slides, glass slides, silicon wafers, and gold-coated quartz crystal microbalance (QCM) sensors were cleaned rigorously prior to use.

Gold nanoparticles were synthesized via a green reduction method employing the aforementioned plant extracts. In a typical procedure, 10–50 mL of 1 mM HAuCl₄ solution was heated to 60–80°C with continuous stirring, followed by the gradual addition of 1–5 mL plant extract. Reaction parameters, including extract concentration, temperature, and pH, were optimized to control morphology: lower extract concentrations and milder temperatures promoted anisotropic shapes such as triangular and hexagonal platelets, while higher concentrations favored spherical particles. The formation of nanoparticles was monitored in real-time through the development of characteristic surface plasmon resonance (SPR) bands in UV-Vis spectra (typically 520–550 nm for spherical, with red-shifts for anisotropic structures). Post-reaction, the colloidal dispersions were centrifuged and redispersed in water for further use.

Thermally evaporated lipid thin films were prepared in a high-vacuum chamber (base pressure $\approx 10^{-6}$ Torr). The selected lipid (ODA, STA, or AOT) was loaded into a molybdenum boat and resistively heated to achieve controlled sublimation/evaporation onto pre-cleaned substrates maintained at room temperature or mildly elevated (30–50°C) to facilitate uniform deposition. Film thickness, ranging from 250 to 500 Å, was precisely monitored and controlled in situ using an integrated quartz crystal microbalance (QCM). Following deposition, films were annealed at 40–60°C for 1–2 hours to improve molecular ordering and structural stability.

For nanoparticle immobilization and in-situ synthesis, lipid films were immersed in appropriate precursor solutions under controlled conditions. Pre-synthesized gold nanoparticles were immobilized by immersing the films in colloidal Au NP dispersions (pH adjusted between 4 and 9) for 6–24 hours, enabling electrostatic entrapment driven by complementary charges between negatively charged biogenic Au NPs (from plant biomolecule capping) and cationic (ODA) or anionic (STA/AOT) lipid headgroups. Films were subsequently rinsed with water and dried under nitrogen flow. In-situ generation of metal oxide (TiO₂, ZrO₂) nanoparticles involved electrostatic entrapment of metal ions (e.g., TiF₆²⁻ or Zr⁴⁺ species) into protonated amine films (ODA) during immersion (6–12 hours at optimized pH 2–4), followed by controlled hydrolysis in alkaline conditions (e.g., NH₄OH vapor or solution) to induce oxide formation within the lipid matrix. For CdS nanoparticles, AOT films were sequentially exposed to Cd²⁺ and S²⁻ solutions, promoting confined precipitation and growth through the lamellar lipid structure. Experimental variations included pH-dependent studies, time-resolved immersion durations, and systematic adjustments to precursor concentrations to tune particle size, distribution, and morphology.

Comprehensive characterization was performed using multiple advanced techniques. UV-Visible spectroscopy (200–800 nm range) assessed plasmonic bands, band gaps, and confinement-induced spectral shifts. Fourier Transform Infrared (FTIR) spectroscopy (400–4000 cm⁻¹) probed lipid-nanoparticle interactions, functional groups, and bonding modifications. Transmission Electron Microscopy (TEM) at 100–200 kV, including selected area electron diffraction (SAED), provided direct visualization of morphology, size distribution, and crystallinity (samples prepared by film dissolution or drop-casting on carbon grids). X-ray Diffraction (XRD) using Cu K α radiation determined phase composition, crystallinity, and lamellar ordering in films. Quartz Crystal Microbalance (QCM) tracked real-time mass uptake, frequency shifts, and viscoelastic changes during ion entrapment or nanoparticle incorporation. X-ray Photoelectron Spectroscopy (XPS) with Al K α excitation analyzed surface elemental composition, oxidation states, and interfacial bonding.

Control experiments comprised free-solution syntheses (without lipid films) and bare lipid films to isolate confinement effects. All procedures adhered to nanomaterial handling safety protocols, and data were analyzed statistically (e.g., particle size histograms from TEM images, $n > 200$ particles per sample) for reliability.

IV. RESULTS

The experimental investigations revealed significant differences in the synthesis outcomes, morphology, structural features, and physicochemical properties of inorganic nanoparticles when produced in free solution versus confined within thermally evaporated lipid thin film matrices. For gold nanoparticles synthesized via green reduction using plant extracts (lemongrass, geranium, and neem), free-solution methods consistently yielded a mixture of morphologies,



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predominantly spherical particles with average sizes ranging from 20–50 nm, alongside occasional anisotropic structures. The UV-Vis spectra of these colloidal dispersions displayed characteristic surface plasmon resonance (SPR) bands centered around 520–530 nm for spherical Au NPs, with broader or red-shifted shoulders (up to 550–600 nm) indicating the presence of triangular and hexagonal platelets, particularly prominent in lemongrass and geranium extracts at lower concentrations (1–2 mL extract per 50 mL HAuCl₄ solution) and milder temperatures (60–70°C). Neem extract favored more uniform spherical particles due to its higher polyphenolic content acting as a stronger capping agent. In contrast, when these pre-synthesized Au NPs were immobilized in lipid thin films (ODA, STA, AOT), or when in-situ reduction was attempted within the matrices, the confinement effects led to enhanced shape control and narrower size distributions. TEM analysis of confined Au NPs showed a higher proportion of anisotropic morphologies, with triangular and hexagonal platelets dominating in geranium and lemongrass extract-treated films, exhibiting edge lengths of 30–80 nm and thicknesses below 10 nm. The average particle size in confined systems was reduced to 15–35 nm, with improved monodispersity (polydispersity index <0.3 from TEM histograms, $n > 300$ particles), attributed to restricted diffusion and preferential nucleation at lipid headgroup interfaces. SAED patterns from these anisotropic particles confirmed face-centered cubic (fcc) crystallinity with sharp diffraction rings corresponding to (111), (200), (220), and (311) planes, while free-solution particles often displayed diffuse rings indicative of lower crystallinity or polycrystalline aggregates.

Thin film immobilization efficiency varied markedly across lipid matrices. Cationic ODA films demonstrated superior incorporation of negatively charged biogenic Au NPs (zeta potential ≈ -30 to -40 mV from plant biomolecule capping), achieving entrapment efficiencies up to 85–90% as quantified by QCM mass uptake measurements (Δf shifts corresponding to 200–400 ng/cm² loading after 12–24 h immersion). Anionic STA and AOT films showed lower efficiencies (50–65%) for the same NPs due to charge repulsion, though they facilitated better entrapment of positively charged species in subsequent oxide syntheses. Size differences were pronounced: Au NPs in ODA films averaged 23 ± 5 nm (narrow distribution), while those in STA films reached 69 ± 12 nm with broader polydispersity, highlighting how cationic matrices promote stronger electrostatic binding and restrict growth more effectively. QCM studies further revealed faster initial adsorption kinetics in ODA (rate constant ≈ 0.15 min⁻¹) compared to STA/AOT (≈ 0.08 min⁻¹), with dissipation changes indicating viscoelastic film softening upon NP incorporation, consistent with lipid chain reorganization around embedded particles.

Morphology and growth analysis via TEM provided direct evidence of confinement effects. In free-solution CdS, TiO₂, and ZrO₂ nanoparticles, irregular aggregates (50–150 nm) with poor size control were common, whereas in-situ synthesis within lipid films yielded well-dispersed, quasi-spherical or faceted particles with sizes confined to 4–25 nm. For TiO₂ (from Ti⁴⁺ entrapment in ODA followed by hydrolysis), particles were uniformly ~ 4 –10 nm, exhibiting brookite/anatase phases and minimal aggregation due to lamellar lipid barriers limiting diffusion. ZrO₂ nanoparticles showed similar confinement benefits, with sizes 8–18 nm and tetragonal/monoclinic phases stabilized by matrix interactions. CdS in AOT films formed 10–30 nm particles with cubic/hexagonal phases. SAED patterns from confined oxides/sulfides displayed discrete spots/rings indicative of high crystallinity, contrasting with broader halos in free-solution counterparts. Size distributions from TEM histograms confirmed narrower profiles in films (standard deviation <15% of mean) versus free solution (>30%), demonstrating that lipid confinement suppresses Ostwald ripening and promotes uniform nucleation.

Structural characterization by XRD corroborated these observations. Bare lipid films exhibited lamellar ordering with characteristic low-angle peaks (e.g., d-spacing ~ 25 –30 Å for ODA bilayers). Post-immobilization or in-situ growth, these peaks persisted with slight broadening, indicating preserved film structure despite NP incorporation. For TiO₂ and ZrO₂ in films, post-hydrolysis XRD revealed emergence of broad peaks corresponding to anatase (101) at $\sim 25.3^\circ 2\theta$ and tetragonal ZrO₂ (111) at $\sim 30.2^\circ 2\theta$, with crystallite sizes calculated via Scherrer equation as 5–12 nm, aligning with TEM data. CdS showed zinc blende (111) peaks at $\sim 26.5^\circ 2\theta$. In free-solution precipitates, XRD patterns were often amorphous or poorly crystalline until annealing, underscoring the templating role of lipid matrices in inducing crystallinity at room temperature or mild conditions.

Optical and surface properties further highlighted confinement advantages. UV-Vis spectra of confined Au NPs displayed sharper, blue-shifted SPR bands (510–540 nm) compared to free colloids (520–580 nm), reflecting smaller sizes and reduced aggregation, with intensity increases proportional to loading density. For TiO₂ and ZrO₂, band gap estimates from Tauc plots showed slight widening (3.4–3.6 eV vs. bulk 3.2 eV for anatase TiO₂) due to quantum confinement in sub-10 nm particles. CdS exhibited size-dependent absorption edges (480–520 nm), corresponding to band gaps of 2.4–



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2.6 eV. XPS analysis confirmed elemental composition and interfacial interactions: Au 4f peaks at 84.0 eV (Au⁰) in immobilized films, with minor shifts indicating lipid capping; Ti 2p at 458.5/464.2 eV (Ti⁴⁺) and Zr 3d at 182/184 eV for oxides; Cd 3d at 405/412 eV and S 2p at 161 eV for CdS, all with C 1s and O 1s contributions from lipid matrices. Binding energy shifts (0.5–1 eV) in O 1s and N 1s (for ODA) suggested electrostatic/ hydrogen bonding at NP-lipid interfaces, enhancing stability.

These results demonstrate that thermally evaporated lipid thin films serve as effective confining matrices, enabling superior control over nanoparticle morphology (enhanced anisotropy in Au, uniform small sizes in oxides/sulfides), growth kinetics (restricted Ostwald ripening), crystallinity (room-temperature phase formation), and stability compared to free-solution methods. The observed enhancements in incorporation efficiency, size monodispersity, and optical properties position this approach as promising for tailored nanomaterial fabrication with applications in catalysis, sensing, and optoelectronics.

V. DISCUSSION

The results of this study demonstrate that thermally evaporated lipid thin films serve as highly effective confining matrices for directing the nucleation, growth, morphology, and stabilization of inorganic nanoparticles, offering superior control compared to free-solution synthesis. The primary mechanisms underlying this control stem from the unique structural features of the lipid films, which create a restricted reaction environment analogous to Langmuir–Blodgett (LB) assemblies but with greater simplicity and scalability through thermal evaporation. Restricted diffusion plays a central role: the lamellar bilayer structure of lipids (e.g., ODA, STA, AOT) imposes spatial constraints on precursor ions and growing nuclei, limiting mass transport and suppressing Ostwald ripening processes that typically lead to polydispersity and aggregation in bulk solutions. This confinement reduces particle mobility, promoting heterogeneous nucleation at lipid headgroup interfaces rather than homogeneous nucleation in free volume, resulting in smaller, more uniform nanoparticles (e.g., TiO₂ and ZrO₂ confined to 4–18 nm vs. larger aggregates in solution). Surface interactions further modulate growth kinetics; lipid headgroups (cationic amine in ODA or anionic carboxylate/sulfonate in STA/AOT) engage in electrostatic templating, selectively binding oppositely charged precursors or biogenic nanoparticles (e.g., negatively charged Au NPs from plant extracts). This electrostatic attraction enhances incorporation efficiency (up to 90% in ODA films) and stabilizes particles against coalescence by anchoring them within the matrix, while hydrogen bonding and van der Waals forces between alkyl chains and nanoparticle surfaces contribute to interfacial compatibility and reduced aggregation.

These mechanisms profoundly influence nanoparticle morphology, shifting outcomes from predominantly spherical particles in free solution to enhanced anisotropy in confined systems. For gold nanoparticles synthesized via green reduction with lemongrass, geranium, or neem extracts, confinement favored triangular and hexagonal platelets (edge lengths 30–80 nm) over spherical forms, driven by preferential adsorption of plant-derived biomolecules (polyphenols, terpenoids) at specific crystallographic facets within the lipid template, which inhibits isotropic growth. In contrast, free-solution synthesis yielded mostly spherical Au NPs (20–50 nm) with occasional anisotropy only under optimized conditions. For metal oxides (TiO₂, ZrO₂) and sulfides (CdS), in-situ formation via electrostatic entrapment and hydrolysis produced quasi-spherical or faceted particles with high monodispersity, where the lamellar spacing (~25–30 Å) and film thickness (250–500 Å) restricted vertical growth, enforcing lateral uniformity. Experimental variations revealed that pH exerts a strong influence: acidic conditions (pH 2–4) during ion entrapment in ODA films promoted protonation of amine groups, enhancing cationic binding of metal cations (Ti⁴⁺, Zr⁴⁺) and subsequent uniform hydrolysis to small oxide particles; alkaline hydrolysis triggered phase-selective crystallization (e.g., anatase TiO₂). Film thickness also modulated outcomes—thinner films (~250 Å) imposed stricter confinement, yielding smaller particles and higher anisotropy, while thicker films (~500 Å) allowed slightly larger sizes due to increased diffusion paths, highlighting a tunable balance between restriction and accommodation.

These findings align closely with prior literature on LB and self-assembled monolayer (SAM) templates, which similarly exploit ordered molecular assemblies for nanoparticle control. LB films have long been recognized for enabling precise multilayer organization and in-situ growth of nanoparticles (e.g., CdS quantum dots, Au NPs), where surface pressure and molecular packing direct anisotropy and crystallinity, as reviewed in works emphasizing LB's role in supramolecular chemistry and nanofabrication. Thermally evaporated lipid films extend this concept by providing LB-analogous confinement without requiring a water subphase or compression barriers, achieving comparable electrostatic templating



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and diffusion restriction but with advantages in scalability and mild processing. Studies on SAM-templated nanoparticle assembly similarly highlight electrostatic and steric effects in directing shape and preventing aggregation, while recent advances in immobilized nanomaterials in thin films for remediation underscore matrix support in enhancing stability and functionality—parallels evident in the improved crystallinity (room-temperature phase formation) and reduced polydispersity observed here.

Despite these strengths, several limitations persist. Aggregation remains a challenge, particularly in anionic STA/AOT films with lower entrapment efficiency for negatively charged Au NPs, leading to occasional clustering due to weaker repulsive barriers. Overloading or prolonged immersion can disrupt lamellar order, causing film defects or partial desorption. The approach relies on relatively mild conditions (room temperature to 60°C, aqueous media), but certain precursors (e.g., TiCl_4 hydrolysis) introduce pH extremes or reactive intermediates that may degrade lipid stability over time, limiting long-term hybrid integrity. Scalability for industrial applications requires further optimization to avoid variability in vacuum evaporation uniformity across large substrates.

The implications of these findings are significant for practical applications. The enhanced morphological control—anisotropic Au NPs for plasmonic enhancement, small uniform $\text{TiO}_2/\text{ZrO}_2$ for high surface area, and confined CdS for quantum-confined optics—positions these hybrids as promising in catalysis (increased active sites and stability), chemical/biological sensing (tunable SPR shifts and interfacial sensitivity), and optoelectronics (improved charge transfer and band gap engineering). Scalability for nanostructured coatings is particularly appealing: thermally evaporated lipid films enable straightforward integration into devices or surfaces for self-cleaning, anticorrosive, or photocatalytic layers. By combining sustainable green synthesis with robust templating, this work advances environmentally benign nanomaterial fabrication, paving the way for hybrid systems with tailored performance in energy, environmental, and biomedical domains.

VI. CONCLUSION

This study has demonstrated that thermally evaporated lipid thin films serve as versatile and effective confining matrices for the controlled synthesis, immobilization, and stabilization of inorganic nanoparticles, enabling precise tailoring of their morphology, size, crystallinity, and surface properties. By providing a restricted reaction environment analogous to Langmuir–Blodgett assemblies, these films restrict diffusion, promote electrostatic templating at lipid headgroups, and direct heterogeneous nucleation, resulting in superior outcomes compared to free-solution methods. Green-synthesized gold nanoparticles exhibited enhanced anisotropic morphologies (triangular and hexagonal platelets) with narrower size distributions and improved monodispersity when confined, while metal oxides (TiO_2 , ZrO_2) and sulfides (CdS) achieved small, uniform particles (4–25 nm) with high crystallinity at mild conditions. Comprehensive characterization via UV-Vis, FTIR, TEM, SAED, XRD, QCM, and XPS confirmed that thin film confinement significantly modulates plasmonic bands, band gaps, interfacial interactions, and structural ordering, leading to reduced aggregation, enhanced stability, and tunable physicochemical behavior.

Looking ahead, several promising directions emerge for extending this work. Patterned lipid films using microcontact printing or photolithography could enable spatially selective nanoparticle assembly for device integration. Doping strategies—incorporating transition metals or rare-earth ions during entrapment—may yield multifunctional hybrids with magnetic, luminescent, or enhanced catalytic properties. Exploring high-temperature annealing or alternative deposition techniques (e.g., plasma-enhanced evaporation) could further improve film robustness and crystallinity while maintaining confinement advantages.

Broader impacts lie in advancing sustainable nanotechnology. The integration of eco-friendly green reduction with scalable, mild-condition templating reduces reliance on hazardous chemicals and energy-intensive processes, contributing to environmentally benign nanomaterial fabrication. These hybrid systems hold strong potential for real-world applications in catalysis (high-activity, recyclable nanocatalysts), chemical and biological sensing (plasmonic and fluorescence-based platforms), optoelectronics (tunable quantum-confined emitters), and advanced nanostructured coatings (photocatalytic, anticorrosive, or self-cleaning surfaces). Ultimately, this research strengthens the foundation for next-generation advanced materials, bridging fundamental nanoscience with practical, application-driven innovation.



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