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Solvent-Directed Hydrolysis and Morphological Evolution of 3-(trimethoxy silyl) propyl Methacrylate (TPM) Silica Colloids

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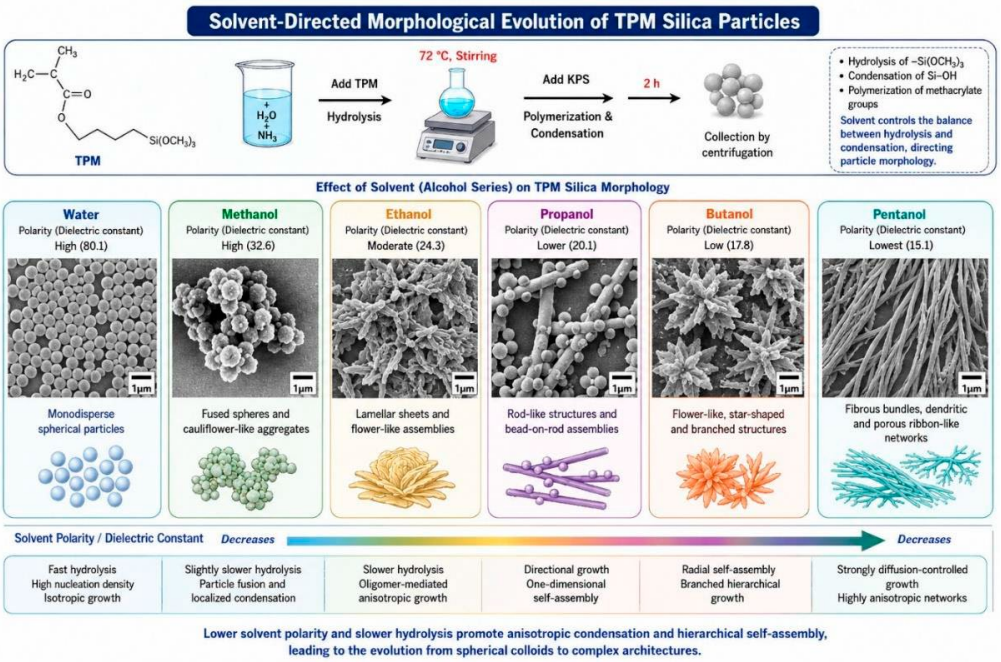
Abstract

The morphology of colloidal particles is fundamentally governed by the kinetics of precursor hydrolysis, condensation, and particle growth. Among organosilane precursors, 3-(trimethoxysilyl)propyl methacrylate (TPM) has attracted considerable interest due to its ability to form deformable organosilica colloids possessing both inorganic siloxane and polymerizable methacrylate functionalities. Conventionally, TPM particles are synthesized in aqueous media at elevated temperatures (~72 °C), where the high polarity of water facilitates rapid hydrolysis of methoxy groups and subsequent condensation into nearly spherical particles. However, the influence of alternative alcohol solvents on the hydrolysis pathway and resulting particle morphology remains poorly understood. In this work, the hydrolysis behavior of TPM was systematically investigated in a homologous series of alcohols ranging from methanol to pentanol. Significant variations in particle morphology, including anisotropic and non-spherical structures, were observed as the solvent polarity decreased. The effects of ammonia catalyst concentration, potassium persulfate (KPS) initiator, and reaction temperature were further examined to establish their roles in regulating hydrolysis, siloxane condensation, methacrylate polymerization, and particle growth. A mechanistic framework is proposed linking solvent physicochemical properties with reaction kinetics and colloidal morphology. This study provides new insights into solvent-directed synthesis of deformable organosilica colloids and establishes a versatile strategy for morphology control without employing templates or surfactants.



Keywords: TPM, Alcohol Solvent

1. Introduction

Morphology-controlled colloidal particles have become indispensable in advanced materials because their shape, size, and surface characteristics directly influence optical behavior, mechanical properties, self-assembly, wettability, catalysis, and biomedical performance [1]. While spherical particles remain the most extensively studied owing to their synthetic simplicity, anisotropic colloids often exhibit superior packing behaviour, directional interactions, and enhanced functional performance [2]. Consequently, understanding the fundamental mechanisms governing particle shape evolution has emerged as an important objective in colloid science. Organosilica colloids derived from organosilane precursors offer unique opportunities for designing multifunctional materials by combining the chemical stability of silica with the flexibility of organic polymers [3]. Among these precursors, 3-(trimethoxysilyl)propyl methacrylate (TPM) is particularly attractive because it contains two chemically distinct functional groups. The trimethoxysilane moiety undergoes hydrolysis followed by siloxane condensation to generate an inorganic silica network, whereas the methacrylate functionality remains available for free-radical polymerization, enabling the formation of deformable hybrid particles with tunable mechanical properties [4,5]. These characteristics have made TPM-based colloids promising candidates for photonic materials, soft robotics, coatings, encapsulation systems, and responsive materials.

Most reported TPM syntheses employ water as the primary reaction medium together with ammonia as a base catalyst at temperatures around 70–75 °C. Under these conditions, the high polarity and extensive hydrogen-bonding network of water promote rapid hydrolysis of the methoxy groups, producing silanol intermediates that readily condense into siloxane networks. The fast and relatively homogeneous reaction kinetics generally result in isotropic nucleation and growth, leading predominantly to spherical particles. Although this synthetic approach has been widely adopted, it provides limited opportunities for controlling particle morphology beyond conventional spherical structures. The solvent plays a critical role in sol-gel chemistry by influencing precursor solubility, hydrolysis kinetics, diffusion, dielectric environment, hydrogen-bonding interactions, and condensation pathways. Alcohols with different carbon chain lengths possess distinct physicochemical properties, including polarity, dielectric constant, viscosity, and miscibility with water, all of which can alter the local reaction environment surrounding hydrolyzing TPM molecules.

Despite these considerations, a systematic understanding of how different alcohols direct the hydrolysis and morphological evolution of TPM-derived colloids remains largely unexplored. Besides solvent effects, reaction parameters such as ammonia concentration, radical initiator concentration, and reaction temperature are expected to exert significant influence on particle formation. Ammonia catalyzes the nucleophilic hydrolysis of the methoxy groups, thereby controlling the balance between hydrolysis and condensation. Potassium persulfate (KPS) generates sulfate radicals that initiate polymerization of the methacrylate functionality, affecting the internal organic network and deformability of the resulting particles. Temperature simultaneously governs hydrolysis kinetics, diffusion rates, condensation reactions, and polymerization, thereby influencing both nucleation and final particle morphology.

In this work, a comprehensive mechanistic investigation of TPM hydrolysis was conducted using methanol, ethanol, propanol, butanol, and pentanol as reaction solvents under otherwise identical experimental conditions. By systematically varying solvent identity, ammonia concentration, KPS concentration, and reaction temperature, the relationships between reaction kinetics and particle morphology were established. The observed transition from spherical particles in highly polar media to anisotropic and deformable structures in less polar alcohols is interpreted through a solvent-dependent hydrolysis and condensation mechanism. The proposed framework provides a fundamental understanding of solvent-directed organosilica colloid formation and offers practical guidelines for tailoring particle morphology through simple modifications of the reaction environment rather than template-assisted approaches.

2.Methods

2.1. Synthesis of TPM Silica Colloidal Particles

TPM silica colloidal particles were synthesized through a base-catalyzed hydrolysis–condensation process followed by free-radical polymerization. Initially, batchwise deionized water, methanol, ethanol, propanol, butanol and pentanol was added with aqueous ammonia were mixed in a round-bottom flask under continuous magnetic stirring at room temperature to obtain a homogeneous alkaline reaction medium. The required amount of 3-(trimethoxysilyl)propyl methacrylate (TPM) precursor was then added dropwise into the solution while maintaining constant stirring. The alkaline environment initiated the hydrolysis of the trimethoxysilyl groups, leading to the formation of silanol intermediates. The reaction mixture was subsequently heated to 72 °C under continuous stirring to promote hydrolysis and siloxane condensation. Once the reaction temperature reached 72 °C, a predetermined amount of potassium persulfate (KPS) was added to the reaction mixture as a free-radical initiator. The decomposition of KPS at elevated temperature initiated the polymerization of the methacrylate groups present in TPM, while simultaneous condensation of the silanol groups resulted in the formation of hybrid organosilica colloidal particles. The reaction was maintained at 72 °C for 2 h under continuous stirring to ensure complete particle formation. After completion of the reaction, the suspension was allowed to cool naturally to room temperature. The synthesized TPM silica colloidal particles were collected by centrifugation, washed several times with deionized water to remove residual reactants and by-products, and finally redispersed in deionized water for subsequent characterization.

3.Results and Discussions

3.1. Effect of TPM Concentration on the Morphology of Silica Colloidal Particles

The influence of TPM precursor concentration on the morphology of organosilica colloidal particles was investigated using field emission scanning electron microscopy (FESEM), as shown in Figure 1(a–c). The synthesis was performed under identical reaction conditions while varying only the TPM concentration in the aqueous reaction medium. Distinct differences in particle number density, surface coverage, and size distribution were observed, highlighting the critical role of precursor concentration in controlling particle nucleation and growth. At the lowest TPM concentration (Figure 1a), well-dispersed spherical particles with relatively low surface coverage were obtained. The particles were uniformly distributed with minimal aggregation, indicating that the available precursor concentration was sufficient for homogeneous nucleation but limited subsequent particle growth. The lower supersaturation of hydrolyzed silanol species resulted in fewer nucleation events, producing isolated particles with comparatively larger interparticle distances.

Increasing the TPM concentration to an intermediate level (Figure 1c) increased the number of particles formed within the reaction medium. The higher availability of hydrolyzed silanol species promoted additional nucleation events while maintaining isotropic growth, leading to a greater particle population without significant morphological distortion. The particles remained predominantly spherical, confirming that hydrolysis and condensation occurred uniformly in the highly polar aqueous environment. At the highest TPM concentration (Figure 1b), the FESEM image revealed a densely packed assembly of highly monodisperse spherical particles covering almost the entire substrate surface. The substantial increase in particle population indicates that higher precursor concentrations generated greater supersaturation of hydrolyzed TPM species, thereby increasing the nucleation rate. Although nucleation became more extensive, the particles retained excellent sphericity and relatively narrow size distribution, suggesting that the hydrolysis and condensation reactions remained well balanced under the selected reaction conditions. The close packing observed after drying is attributed to solvent evaporation during sample preparation rather than irreversible aggregation, reflecting the high monodispersity of the synthesized colloids. Importantly the size of the particles have reduced with some bigger particles. The observed morphological evolution can be explained by classical nucleation and growth theory.

Under alkaline conditions, TPM undergoes rapid hydrolysis to form silanol intermediates, which subsequently condense into siloxane oligomers. At lower TPM concentrations, the concentration of hydrolyzed monomers remains below the critical supersaturation required for extensive nucleation, resulting in fewer nuclei and lower particle density. As the TPM concentration increases, the concentration of reactive silanol species rises, accelerating nucleation and producing a larger number of stable nuclei. Since water possesses a high dielectric constant and strong hydrogen-bonding capability, hydrolysis proceeds uniformly throughout the reaction medium, enabling isotropic condensation around each nucleus. Consequently, spherical particle morphology is preserved across all precursor concentrations despite significant variations in particle number density. Overall, the FESEM observations demonstrate that TPM concentration primarily governs the nucleation density and particle population rather than inducing morphological transitions. Increasing precursor concentration enhances the availability of hydrolyzed silanol species, resulting in increased particle yield and more densely packed monodisperse colloids while maintaining excellent spherical morphology. These results establish aqueous synthesis as a highly reproducible route for producing uniform TPM-derived silica colloids and provide a reference system for evaluating morphology evolution in alternative solvent systems.

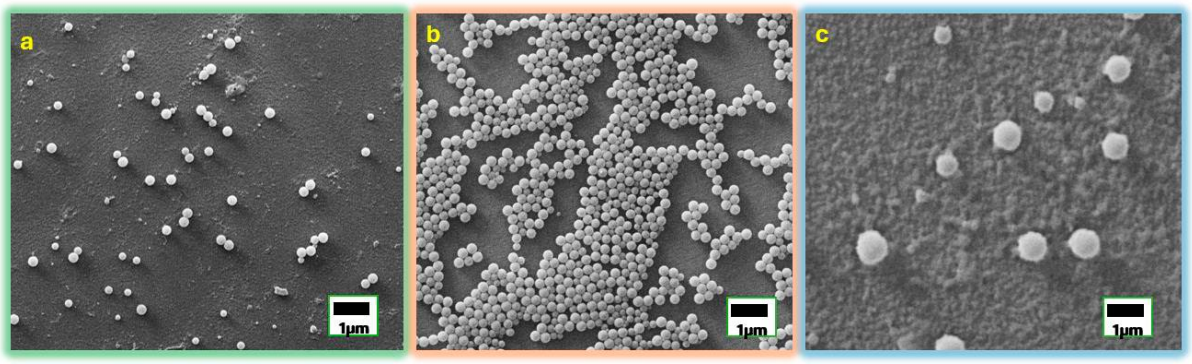


Figure 1: TPM Silica Particles Synthesised using Water as Solvent

3.2. Effect of Methanol on the Morphology of TPM Silica Colloids

The influence of methanol as the reaction solvent on the synthesis of TPM-derived organosilica colloids was investigated by FESEM, as presented in Figure 2(a–c). In contrast to the highly monodisperse spherical particles obtained in water, methanol resulted in pronounced variations in particle morphology, revealing that the solvent strongly influences the hydrolysis, condensation, and growth behavior of TPM. At lower TPM concentrations (Figure 2a), the particles exhibited irregular cauliflower-like aggregates composed of numerous fused primary nanoparticles. Instead of discrete spherical colloids, extensive particle

coalescence was observed, indicating that nucleation and growth occurred simultaneously without complete stabilization of the primary nuclei. The rough surface morphology suggests localized condensation of silanol oligomers followed by continuous particle attachment during growth.

At intermediate TPM concentration (Figure 2b), larger fused microspheres consisting of partially coalesced spherical domains were formed. The particles appeared interconnected through neck-like junctions, indicating incomplete separation of neighboring nuclei during growth. This morphology suggests that hydrolyzed TPM oligomers continued to condense between adjacent particles, promoting particle fusion rather than independent isotropic growth. Further increasing the TPM concentration (Figure 2c) produced highly heterogeneous structures comprising large spherical particles together with irregular fragmented aggregates and numerous fine particulates. The broad size distribution and coexistence of multiple morphologies indicate that excessive precursor concentration accelerated hydrolysis and condensation beyond the stabilization capacity of the colloidal system. Consequently, uncontrolled secondary nucleation and aggregation became dominant, resulting in the formation of irregular organosilica clusters.

The observed morphological evolution can be attributed to the physicochemical properties of methanol. Although methanol is a polar protic solvent and is completely miscible with water, its polarity, dielectric constant, and hydrogen-bonding characteristics differ from those of water. The partial replacement of water by methanol reduces the effective hydrolysis environment surrounding TPM molecules, thereby modifying the balance between hydrolysis and siloxane condensation. Under alkaline conditions, hydrolysis of the trimethoxysilyl groups proceeds to generate silanol intermediates; however, the subsequent condensation occurs more rapidly around localized oligomeric species, producing uneven particle growth. Instead of uniform isotropic nucleation observed in pure aqueous media, methanol favors localized condensation and particle–particle attachment, leading to fused microspheres and cauliflower-like aggregates.

Furthermore, methanol lowers the interfacial tension between the growing organosilica particles and the surrounding medium, facilitating collisions between partially condensed particles. Because the siloxane network remains incompletely condensed during the early stages of growth, these collisions promote irreversible coalescence, producing the fused morphologies observed in the FESEM images. Simultaneously, KPS-initiated polymerization of the methacrylate groups strengthens the interconnected hybrid network, preserving the aggregated structures after particle formation. Overall, the FESEM observations demonstrate that methanol significantly alters the nucleation and growth mechanism of TPM-derived silica colloids compared with water. Rather than producing highly monodisperse spherical particles, methanol promotes heterogeneous nucleation, localized condensation, particle coalescence, and secondary aggregation, resulting in irregular cauliflower-like assemblies and fused microspheres. These findings highlight the critical influence of solvent properties on the morphology evolution of organosilica colloids and establish methanol as a transition solvent between the highly isotropic growth observed in water and the increasingly anisotropic morphologies expected with higher-chain alcohols.

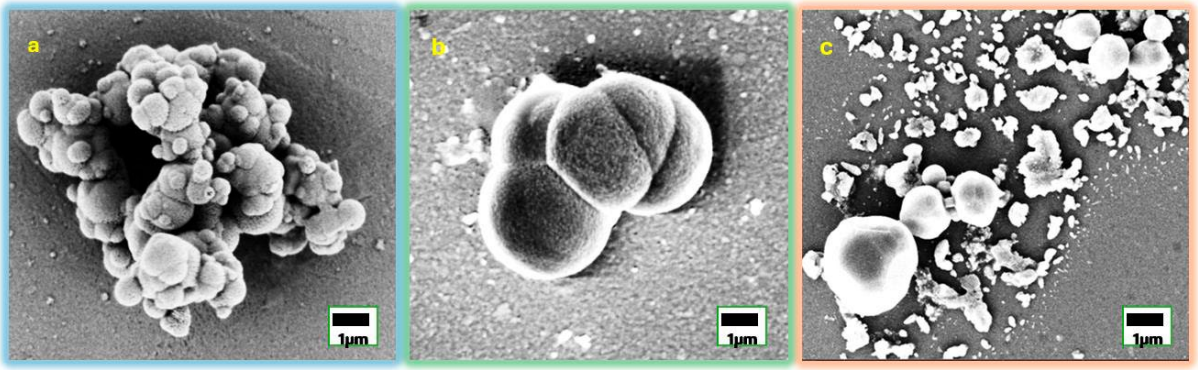


Figure 2: TPM Silica Particles Synthesised using Methanol as Solvent.

3.3. Effect of Ethanol on the Morphology of TPM Silica Colloids

The influence of ethanol as the reaction solvent on the morphology of TPM-derived organosilica particles was investigated by FESEM, as presented in Figure 3(a–d). Compared with the spherical colloids synthesized in water and the fused microspheres obtained in methanol, ethanol produced a remarkable transformation in particle morphology, leading to irregular porous aggregates, lamellar sheets, and hierarchical plate-like assemblies. These observations indicate that ethanol substantially modifies the hydrolysis–condensation kinetics of TPM, resulting in anisotropic growth rather than isotropic spherical particle formation. At lower TPM concentrations (Figure 3a), highly porous and sponge-like aggregates were observed. The structures consisted of interconnected nanoscale building blocks that formed irregular three-dimensional networks with numerous voids. The absence of well-defined spherical particles suggests that nucleation was relatively slow, while condensation between partially hydrolyzed oligomers dominated the growth process, resulting in continuous network formation instead of discrete colloids.

At intermediate TPM concentration (Figure 3b), the morphology evolved into interconnected lamellar structures composed of

thin, randomly oriented nanosheets. These sheet-like assemblies exhibited a highly porous architecture, indicating preferential growth along specific directions. The formation of such layered structures suggests that condensation proceeded anisotropically through localized oligomer association rather than by uniform deposition around spherical nuclei. Further increasing the TPM concentration (Figure c) resulted in the formation of well-developed plate-like crystalloid assemblies composed of stacked lamellae. The individual plates possessed smooth surfaces with sharp edges and appeared to radiate from common nucleation centers, producing hierarchical flower-like structures. Such morphology demonstrates that directional growth became increasingly dominant as the concentration of reactive silanol species increased, promoting preferential condensation along specific crystallographic or molecular orientations.

At the highest TPM concentration (Figure 3d), the particles developed into dense hierarchical superstructures with a compact core surrounded by numerous radially oriented plate-like subunits. The coexistence of a dense central region and an outer shell of nanoplates indicates a two-stage growth mechanism involving initial formation of condensed nuclei followed by secondary anisotropic growth through continuous deposition of hydrolyzed TPM oligomers. This hierarchical organization reflects the progressive assembly of primary nanosheets into larger micron-sized architectures. The dramatic morphological evolution observed in ethanol can be attributed to its physicochemical properties. Compared with water, ethanol possesses a lower dielectric constant, reduced polarity, and weaker hydrogen-bonding capability, which decrease the rate of TPM hydrolysis. Consequently, the generation of silanol species becomes slower and less homogeneous throughout the reaction medium. Under these conditions, condensation competes more effectively with hydrolysis, leading to the formation of oligomeric siloxane clusters before complete hydrolysis of the precursor.

These oligomers preferentially associate through localized siloxane condensation, promoting anisotropic assembly instead of uniform spherical growth. Furthermore, the reduced solvation capability of ethanol alters the stability of the growing organosilica nuclei. Rather than remaining as isolated colloidal particles, partially condensed oligomers undergo oriented attachment and continuous aggregation, producing layered and plate-like architectures. Simultaneously, KPS-initiated polymerization of the methacrylate groups reinforces these assemblies, preserving the hierarchical lamellar structures throughout the synthesis.Overall, the FESEM observations demonstrate that ethanol fundamentally changes the growth mechanism of TPM-derived organosilica colloids. The transition from spherical particles in water to lamellar and hierarchical structures in ethanol indicates that solvent-controlled hydrolysis and condensation govern the final particle morphology. The lower polarity of ethanol suppresses uniform isotropic growth and favors localized condensation, oriented attachment, and hierarchical self-assembly, resulting in complex anisotropic microstructures. These findings highlight the critical role of solvent selection in tailoring the morphology of TPM-based organosilica materials and provide further evidence that controlled modification of the solvent environment can direct colloidal growth without the need for templates or surfactants.

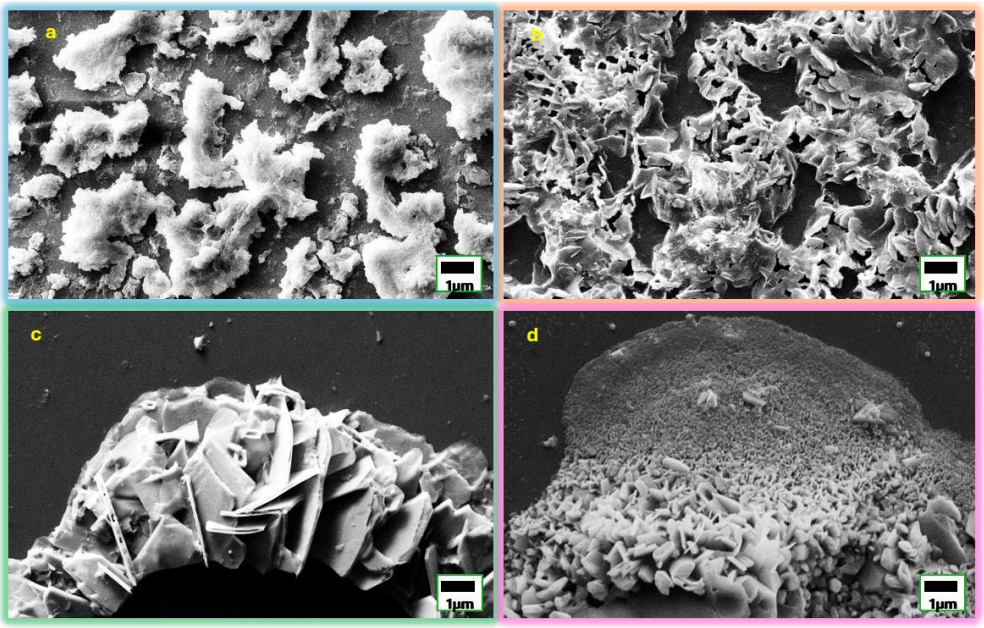


Figure 3: TPM silica particles synthesised using ethanol as solvent

3.4. Effect of Propanol on the Morphology of TPM Silica Colloids

The effect of propanol as the reaction solvent on the morphology of TPM-derived organosilica particles was investigated using FESEM, as shown in Figure 4(a–b). Compared with the spherical particles synthesized in water, the fused aggregates

obtained in methanol, and the lamellar architectures formed in ethanol, propanol produced highly anisotropic hierarchical structures consisting of elongated rod-like frameworks decorated with spherical particles. These observations demonstrate that increasing the alkyl chain length of the alcohol significantly alters the hydrolysis and condensation pathways of TPM, promoting directional growth over isotropic particle formation.

Figure 4a reveals a dense network of vertically aligned rod-like structures with numerous spherical and ellipsoidal particles attached along their length. The rods possess relatively uniform diameters and extend over several micrometres, forming a highly interconnected architecture. The spherical domains appear to nucleate directly on the road surfaces, suggesting a sequential growth mechanism in which one-dimensional structures are initially generated, followed by secondary nucleation and deposition of hydrolysed TPM oligomers. The coexistence of rods and spherical particles indicates that both anisotropic growth and localized isotropic nucleation occur simultaneously during particle formation.

A higher magnification image (Figure 4b) further confirms the hierarchical nature of the synthesized structures. The rod-like features are interconnected through irregular junctions and are surrounded by particles of varying sizes, producing a complex three-dimensional network. The broad particle size distribution and extensive interconnection indicate that condensation proceeds continuously throughout the reaction rather than terminating after primary particle formation. Unlike the well-defined plate-like structures observed in ethanol, propanol promotes the development of elongated frameworks that act as scaffolds for subsequent particle growth.

The formation of these anisotropic structures can be explained by the physicochemical characteristics of propanol. Compared with water and ethanol, propanol possesses a lower dielectric constant, reduced polarity, higher viscosity, and weaker hydrogen-bonding capability. These properties decrease the hydrolysis rate of the trimethoxysilyl groups, reducing the concentration of freely available silanol monomers during the early stages of the reaction.

As a result, condensation becomes increasingly dominant over hydrolysis, promoting the formation of siloxane-rich oligomeric species that preferentially assemble along specific directions rather than condensing uniformly around individual nuclei. The slower diffusion of hydrolyzed intermediates in propanol further contributes to localized growth by restricting homogeneous distribution of reactive species throughout the reaction medium. Under these conditions, oligomeric clusters preferentially attach to existing structures, giving rise to one-dimensional rod-like assemblies through anisotropic condensation and oriented attachment. Simultaneously, potassium persulfate (KPS) initiates polymerization of the methacrylate groups, stabilizing the growing hybrid framework and preserving the hierarchical morphology. The appearance of spherical particles decorating the rod surfaces suggests that secondary nucleation remains active throughout the reaction. Newly generated silanol species continue to condense onto the pre-existing rod-like structures, producing bead-on-rod morphologies characteristic of diffusion-limited growth. Such hierarchical organization indicates that the synthesis proceeds through multiple growth stages involving initial anisotropic framework formation followed by continuous heterogeneous nucleation. Overall, the FESEM observations demonstrate that propanol induces a significant transition in the growth mechanism of TPM-derived organosilica particles. The reduction in solvent polarity and increased diffusion resistance suppress homogeneous isotropic growth while promoting localized condensation, oriented attachment, and one-dimensional self-assembly. Consequently, the synthesis evolves from spherical colloids in water, to fused aggregates in methanol, to lamellar sheets in ethanol, and finally to hierarchical rod-like architectures in propanol. These findings further confirm that solvent-controlled hydrolysis kinetics play a decisive role in directing the morphology evolution of TPM-based organosilica colloids without the need for external templates or structure-directing agents.

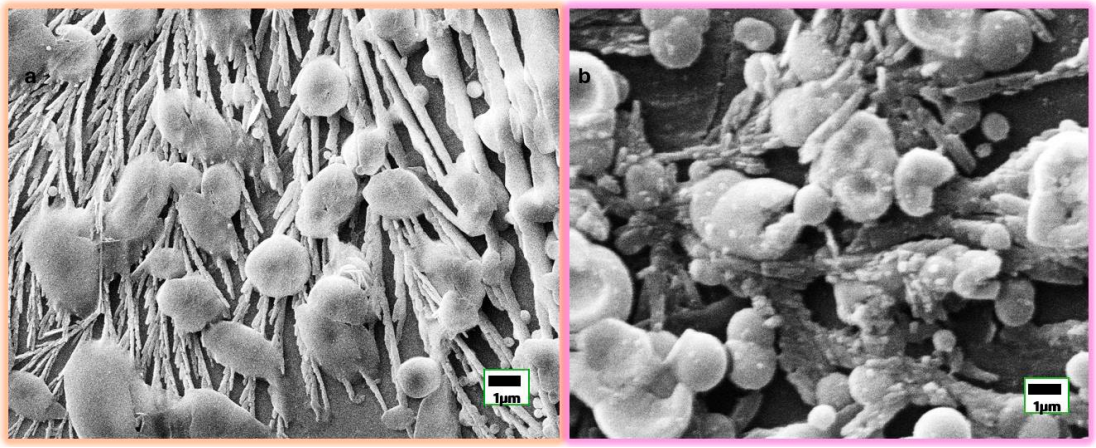


Figure 4: TPM silica particles synthesised using propanol as solvent

3.5 Effect of Butanol on the Morphology of TPM Silica Colloids

The morphology of TPM-derived organosilica particles synthesized in butanol was examined by FESEM, and the representative micrographs are presented in Figure 5(a–b). Compared with the rod-like architectures obtained in propanol, butanol produced highly anisotropic hierarchical structures consisting of flower-like assemblies, branched platelets, and star-shaped particles. These observations indicate that further increasing the alcohol chain length profoundly alters the nucleation and growth mechanism of TPM, favoring localized self-assembly and directional condensation over conventional isotropic colloidal growth.

Figure 5a shows numerous flower-like microstructures uniformly distributed throughout the sample. Each structure is composed of radially arranged nanosheets originating from a common nucleation center, producing rosette-like architectures with well-defined petal morphologies. Alongside these rosettes, elongated plate-like bundles and irregular lamellar aggregates are also observed, suggesting the coexistence of multiple anisotropic growth pathways. The highly branched morphology indicates that particle growth proceeded preferentially along specific directions rather than through uniform deposition around spherical nuclei. A higher magnification image (Figure 5b) reveals the formation of isolated star-shaped and multi-lobed particles surrounded by numerous nanoscale nuclei dispersed over the substrate surface. The star-like particles possess distinct protruding arms extending from a central core, while several small spherical particles remain attached to the surface of the larger structures. The coexistence of mature anisotropic particles with abundant nanoscale primary nuclei suggests continuous nucleation throughout the reaction, followed by preferential growth on energetically favorable surfaces. This hierarchical organization is consistent with a multistage growth process involving initial oligomer formation, localized condensation, and subsequent anisotropic assembly.

The remarkable morphological transformation observed in butanol is primarily attributed to its physicochemical properties. Butanol possesses a significantly lower dielectric constant and polarity than water, methanol, ethanol, and propanol, together with higher viscosity and reduced hydrogen-bonding capability. These characteristics substantially decrease the hydrolysis rate of the trimethoxysilyl groups, resulting in a relatively low concentration of silanol monomers during the early stages of the reaction. Consequently, condensation of partially hydrolyzed oligomers becomes the dominant process, promoting the formation of highly crosslinked siloxane clusters before complete precursor hydrolysis occurs. The slower diffusion of reactive intermediates in butanol further enhances localized supersaturation around growing nuclei. Under these conditions, newly generated oligomers preferentially condense onto existing structures instead of initiating homogeneous nucleation throughout the solution. This localized deposition promotes oriented attachment and anisotropic growth, giving rise to radially arranged nanosheets that eventually develop into flower-like and star-shaped superstructures. Simultaneously, KPS-initiated polymerization of the methacrylate groups stabilizes these hierarchical architectures, preserving their complex morphology during the later stages of synthesis.

The presence of numerous nanoscale particles surrounding the larger anisotropic structures further suggests that nucleation and growth remain active simultaneously throughout the reaction. While some nuclei continue to evolve into hierarchical flower-like assemblies, others remain as primary particles because of localized depletion of reactive silanol species. Such non-uniform growth behavior is characteristic of diffusion-limited aggregation under slow hydrolysis conditions and reflects the strong influence of solvent properties on the self-assembly of TPM-derived organosilica. Overall, the FESEM observations demonstrate that butanol promotes a substantial shift from one-dimensional rod growth to highly branched three-dimensional hierarchical architectures. The reduced polarity and slower hydrolysis kinetics suppress homogeneous isotropic particle formation while favoring localized condensation, oriented attachment, and radial self-assembly. Consequently, flower-like rosettes, star-shaped particles, and branched lamellar structures become the dominant morphologies. These findings further support the hypothesis that systematic variation of solvent properties provides an effective route for controlling the morphology of TPM-derived organosilica particles through solvent-directed hydrolysis and condensation mechanisms.

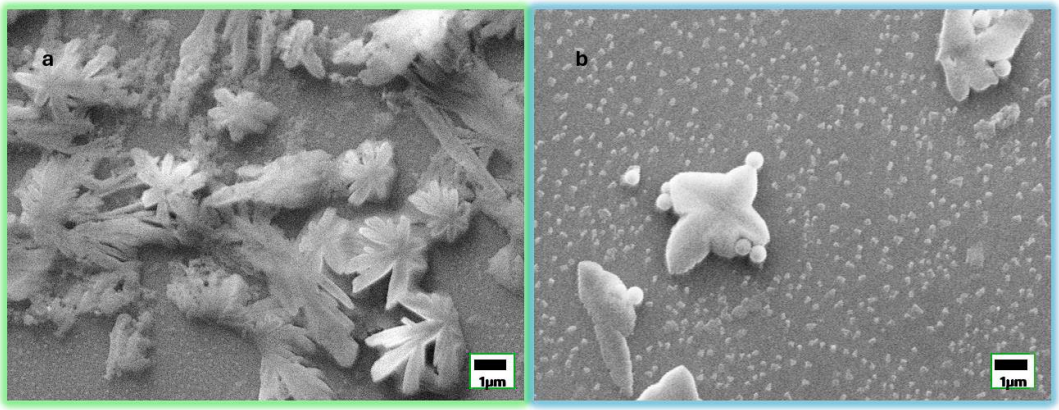


Figure 5: TPM Silica Particles Synthesised using Butanol as Solvent

3.6. Effect of Pentanol on the Morphology of TPM Silica Colloids

The morphology of TPM-derived organosilica particles synthesized in pentanol was investigated by FESEM, as shown in Figure 6(a–d). Among all the alcohol solvents examined, pentanol produced the most complex anisotropic structures, characterized by elongated fibrous bundles, dendritic assemblies, porous rod-like frameworks, and interconnected ribbon-like networks. These observations demonstrate that pentanol significantly alters the hydrolysis–condensation pathway of TPM, leading to highly directional growth and hierarchical self-organization instead of conventional colloidal particle formation. Figure 6a reveals densely packed bundles of long, high-aspect-ratio fibers extending from common nucleation sites. The fibers are aligned in nearly parallel orientations and exhibit smooth surfaces with relatively uniform diameters. The radial arrangement of these elongated structures suggests preferential growth along a single direction, indicating that condensation occurred predominantly through anisotropic extension rather than isotropic deposition around individual nuclei. A higher magnification image (Figure 6b) shows interconnected porous rod-like structures containing numerous surface cavities and channels. The porous morphology indicates that the growing siloxane framework was assembled through continuous aggregation of partially condensed oligomers rather than by direct growth of compact particles. The interconnected architecture further suggests that neighboring fibers fused during the later stages of condensation, producing an open three-dimensional network.

Figure 6c demonstrates the formation of highly branched dendritic assemblies composed of needle-like subunits radiating from central nucleation sites. These hierarchical structures exhibit secondary and tertiary branching, reflecting repeated localized growth events during synthesis. Such dendritic architectures are characteristic of diffusion-controlled growth, where reactive silanol species are incorporated preferentially at the tips of existing structures rather than uniformly across the particle surface. The surface morphology shown in Figure 6d further illustrates the hierarchical nature of the synthesized material. Broad ribbon-like structures are decorated with numerous nanoscale protrusions and primary particles distributed over their surfaces. The coexistence of elongated frameworks with residual nanoparticles suggests that nucleation and anisotropic growth proceed simultaneously throughout the reaction, with newly generated oligomers continuously depositing onto pre-existing structures. The rough surface texture also indicates progressive condensation and polymerization during the later stages of particle development.

The unique morphologies observed in pentanol can be attributed to its physicochemical properties. Pentanol possesses the lowest polarity and dielectric constant among the alcohols investigated, together with the highest viscosity and weakest hydrogen-bonding capability. These characteristics significantly reduce the hydrolysis rate of the trimethoxysilyl groups, resulting in slow and localized generation of silanol intermediates. Consequently, hydrolysis is no longer the dominant process governing particle formation; instead, condensation between partially hydrolyzed oligomers becomes the primary pathway for structural evolution.The reduced diffusion of reactive species in pentanol further enhances concentration gradients surrounding growing nuclei. Rather than promoting homogeneous nucleation throughout the solution, reactive oligomers preferentially migrate toward existing structures where siloxane condensation continues along energetically favorable directions. This diffusion-limited growth mechanism promotes one-dimensional extension, branching, and hierarchical self-assembly, ultimately producing fibrous bundles and dendritic architectures. Simultaneously, KPS-initiated polymerization of the methacrylate groups stabilizes the developing organic–inorganic framework, preserving the anisotropic morphology throughout the reaction.

The FESEM observations therefore indicate that pentanol suppresses the formation of conventional spherical colloids almost entirely and instead promotes the evolution of highly ordered hierarchical architectures through localized condensation and directional self-assembly. The transition from compact particles to elongated fibrous networks demonstrates that solvent properties exert a dominant influence over the balance between hydrolysis and condensation during TPM synthesis. As solvent polarity decreases and viscosity increases, the reaction progressively shifts from homogeneous nucleation toward diffusion-controlled anisotropic growth. Overall, pentanol produces the highest degree of structural anisotropy among the investigated solvents, yielding fibrous, dendritic, and porous hierarchical organosilica architectures. These findings complete the systematic solvent-dependent morphology evolution observed in this study and confirm that careful selection of the reaction solvent provides an effective strategy for directing the self-assembly of TPM-derived organosilica without the need for external templates or structure-directing agents.

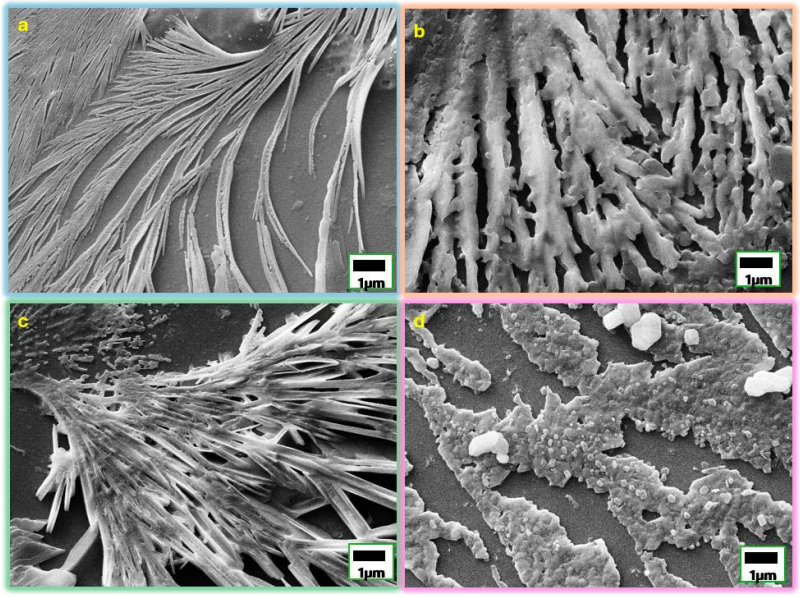


Figure 6: TPM Silica Particles Synthesised using Pentanol as Solvent

Solvent	Dominant morphology	Growth mechanism
Water	Monodisperse spheres	Rapid hydrolysis → homogeneous isotropic nucleation
Methanol	Fused spheres and cauliflower aggregates	Localized condensation and particle coalescence
Ethanol	Lamellar sheets and flower-like assemblies	Oligomer-mediated anisotropic condensation
Propanol	Rod-like and bead-on-rod architectures	One-dimensional directional growth
Butanol	Rosettes, star-shaped particles, branched platelets	Radial self-assembly and diffusion-limited condensation
Pentanol	Fibrous bundles, dendrites, porous ribbons	Strongly diffusion-controlled anisotropic growth with localized condensation

4. Conclusion

This study systematically demonstrates that the reaction solvent plays a decisive role in governing the hydrolysis, condensation, and morphological evolution of TPM-derived organosilica colloids. In water, rapid hydrolysis and homogeneous nucleation produced monodisperse spherical particles. Progressive replacement of water with alcohols of increasing alkyl chain length (methanol to pentanol) gradually reduced solvent polarity and hydrolysis kinetics, shifting the growth mechanism from isotropic nucleation to localized condensation and anisotropic self-assembly. Consequently, the particle morphology evolved from fused aggregates to lamellar sheets, rod-like structures, flower-like assemblies, and finally fibrous dendritic architectures. These findings establish solvent-controlled hydrolysis as an effective, template-free strategy for tailoring the morphology and hierarchical organization of TPM-based organosilica colloids for advanced materials applications.

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