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Research Article

Anisotropic Growth of Doublet and Triplet Silica Colloids in a Butanol–PVP System

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ABSTRACT

The controlled fabrication of anisotropic silica colloids such as doublets and triplets remains a significant challenge in colloidal materials chemistry due to the tendency of silica to form isotropic spherical particles under classical conditions. Herein, we report a solvent-modulated and polymer-assisted strategy for synthesizing discrete doublet and triplet silica particles using a modified Wilhelm Stöber-type reaction conducted in n-butanol in the presence of PVP. Replacement of ethanol with n-butanol reduces hydrolysis kinetics of TEOS, lowers dielectric screening and increases particle-particle interaction time. Concurrently, partial surface adsorption of PVP generates anisotropic shielding, enabling controlled neck formation upon collision. By tuning TEOS feed rate, ammonia concentration, PVP molecular weight and particle density, discrete doublet and triplet colloids were achieved with minimal higher-order aggregation. Further anisotropic morphology of organosilica from TPM was observed and studied briefly. Electron microscopy confirms silica neck growth at contact interfaces, supporting a condensation-driven fusion mechanism. The presented method offers a scalable, solution-based route toward colloidal molecules suitable for directional self-assembly, photonic structures and hierarchical material design.

Introduction

Monodisperse silica nanoparticles synthesized via the classical Wilhelm Stöber process[1] have been extensively employed in catalysis, photonics, sensing and surface science. In its conventional form, base-catalyzed hydrolysis and condensation of Tetraethyl orthosilicate (TEOS) in ethanol-ammonia media yields highly uniform spherical particles. The isotropic nature of nucleation and growth, combined with strong electrostatic stabilization in polar solvents, typically prevents controlled anisotropic assembly.

However, colloidal clusters such as doublets (two fused spheres) and triplets (three fused spheres) are of increasing interest because they function as "colloidal molecules[2]" with directional bonding and tunable valency. Such structures are valuable in photonic bandgap materials, programmable self-assembly and anisotropic coating technologies. Achieving discrete fused clusters rather than uncontrolled aggregation requires precise control over of hydrolysis and condensation kinetics, interparticle electrostatic repulsion, collision frequency and surface stabilization Solvent polarity plays a fundamental role in modulating reaction kinetics and particle stabilization. Ethanol promotes rapid TEOS hydrolysis and strong charge

stabilization, limiting particle fusion. In contrast, n-butanol possesses lower polarity and higher viscosity, which slows hydrolysis and reduces electrostatic repulsion.

Polymeric additives such as Polyvinylpyrrolidone (PVP) are known to adsorb onto silica surfaces via hydrogen bonding between its carbonyl groups and surface silanol (Si-OH) groups. Depending on coverage and molecular weight, PVP can act as steric stabilizer, bridging agent and as anisotropic surface modifier.

In this work, we demonstrate that combining solvent polarity reduction with controlled PVP adsorption enables directional fusion and formation of doublet and triplet silica colloids in a scalable batch process.

Experimental Section

Materials

Tetraethyl orthosilicate (TEOS),3-(Trimethoxysilyl) propyl methacrylate(TPM)Polyvinylpyrrolidone(Mw40,000), Sorbitan Monooleate (Span 80), Cetyltrimethylammonium bromide (CTAB), Potassium persulfate (KPS), n-Butanol, Ammonium hydroxide solution (25-28 wt%) from Sigma Aldrich and Deionized water (DI). All reagents were used as received.

Synthesis of silica seed particles

A typical reaction mixture contained with n-butanol (solvent phase) and ammonium hydroxide as catalyst. 0.1wt% TEOS was added dropwise under moderate stirring at room temperature. Once the solution turns turbid PVP was introduced at concentrations between 0.05 wt%. A secondary controlled feed of TEOS at same concentration of 0.1wt% was added slowly. Reaction goes on for overnight Particles were purified by centrifugation and redispersed in fresh n-butanol. SEM and TEM characterisation was conducted to analyse the morphology of particles.

Synthesis of multifunctional silica colloidal molecules

A precursor emulsion was first prepared by mixing 1 mL of TPM with 0.1 mL of DI in the presence of 0.03 wt% Span 80 under vigorous stirring to obtain a stable water-in-oil type emulsion. This emulsion was subsequently dispersed into 10 mL of n-butanol containing 0.05 wt% CTAB to enhance interfacial stabilization. The resulting precursor mixture was then introduced into an equi-volume solvent system (100 mL total) composed of n-butanol and DI, containing 1 wt% ammonium hydroxide solution (28% w/v in water), under continuous stirring at 72 °C. The basic environment facilitated the hydrolysis and condensation of TPM. After 15 minutes of reaction, 2 mL of an aqueous initiator solution of KPS (0.01% w/v) was added to initiate free-radical polymerization of the methacrylate groups. The reaction was allowed to proceed for 6 hours under constant stirring and temperature. Upon completion, the reaction mixture was cooled to room temperature and the resulting solid products were isolated by centrifugation, followed by repeated washing with ethanol and DI to remove residual surfactants and unreacted species. The purified solids were finally redispersed in DI for further analysis. The morphology and structural features of the synthesized particles were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Results

Solvent effect on particle interaction

Substituting ethanol with n-butanol fundamentally alters the reaction environment governing silica particle formation from TEOS. The lower polarity and dielectric constant of n-butanol reduce the rate of TEOS hydrolysis and subsequent condensation, thereby slowing nucleation kinetics and extending the growth window. In addition, diminished dielectric screening weakens electrostatic stabilization around silica particles, leading to a reduced magnitude of zeta potential[3]. As a result, particles experience less immediate electrostatic repulsion upon close approach. The higher viscosity of n-butanol further increases the residence time during particle-particle encounters, allowing sufficient interfacial contact for silanol groups (Si-OH) to undergo localized condensation[4]. Collectively, these solvent-mediated effects shift the system from a regime dominated by rapid charge-stabilized separation toward one favouring controlled interparticle fusion, thereby promoting the formation of stable doublet and triplet structures rather than isolated monodisperse spheres.

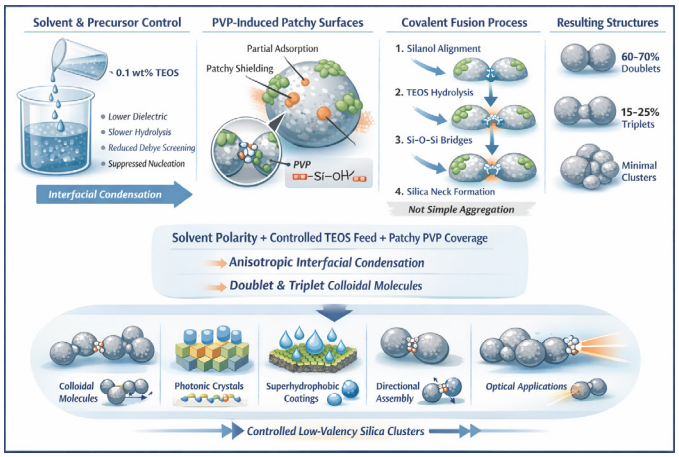

Figure 1: Schematic diagram of PVP controlled anisotropy work.

Influence of PVP concentration

The concentration and molecular weight of PVP played a decisive role in directing the morphology of the resulting silica assemblies. The observed structural evolution from isolated spheres to doublets, triplets and eventually irregular aggregates can be rationalized by considering polymer adsorption behavior, steric stabilization and interparticle bridging mechanisms[5].

At very low PVP concentrations, the silica surface remained largely exposed and polymer adsorption was insufficient to modify interparticle interaction anisotropically. Under these conditions, electrostatic stabilization dominated and particles either remained as isolated monodisperse spheres or underwent limited uncontrolled aggregation depending on collision frequency. The absence of selective surface masking prevented directional bonding[6].

At moderate concentration and molecular weight (≈40 kDa), discrete doublets became the dominant morphology. In this regime, PVP adsorbed partially and non-uniformly onto the silica surface through hydrogen bonding between carbonyl groups of the polymer and surface silanol (Si–OH) groups. Importantly, adsorption did not produce complete steric shielding. Instead, it generated patchy surface coverage, leaving localized reactive

domains exposed. During particle–particle collisions, these uncovered regions enabled silanol condensation and formation of permanent Si-O-Si bridges[7]. Because polymer coverage was incomplete yet sufficient to suppress random aggregation, directional fusion predominantly resulted in doublets rather than larger clusters.

When higher molecular weight PVP or higher concentrations were employed, the probability of triplet formation increased. Longer polymer chains extended further into solution and were capable of simultaneously interacting with multiple particles, introducing a mild bridging flocculation effect. This enhanced collision efficiency and increased the likelihood of a third particle attaching to an existing doublet. Additionally, higher surface coverage altered steric repulsion asymmetrically, further promoting anisotropic cluster growth. However, careful balance was required to avoid runaway aggregation[8].

Under excessive PVP conditions, two competing effects emerged. In some cases, dense polymer adsorption provided strong steric stabilization, preventing fusion and yielding predominantly isolated particles. In other instances, particularly at high molecular weight polymer chain entanglement induced non-specific bridging, resulting in random aggregates rather than well-defined doublets or triplets. Thus, excessive polymer disrupted the delicate kinetic balance required for controlled neck formation.

Overall, the results demonstrate that optimal PVP concentration creates a regime of partial surface coverage where steric stabilization and reactive exposure coexist. This intermediate state generates anisotropic reactive domains that enable directional condensation-driven bonding, thereby facilitating the formation of well-defined colloidal doublets and triplets instead of isotropic or randomly aggregated structures. Clearly the demonstrations in (Figures 2).

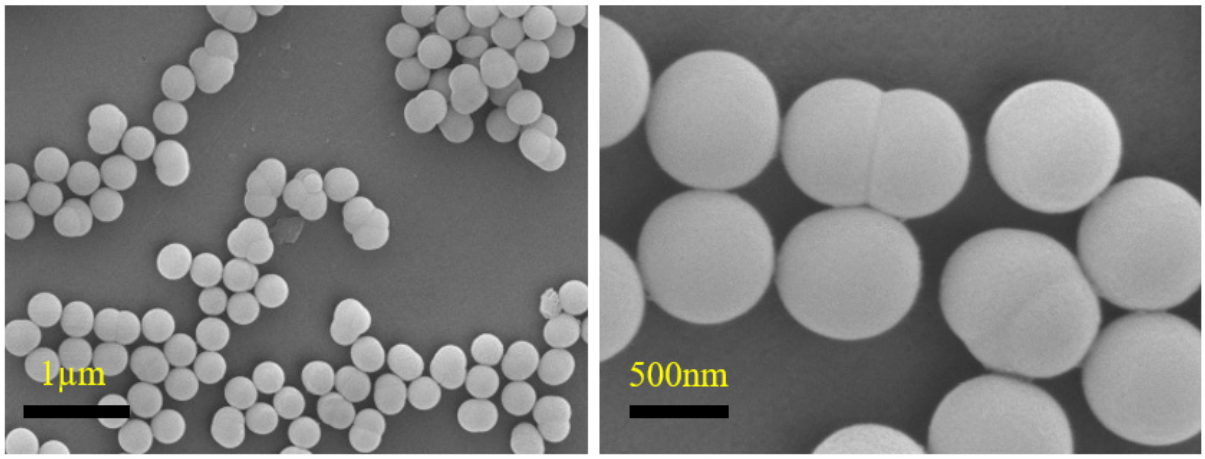

Figure 2: Images showcasing doublets and triplets colloidal molecules

Role of TEOS concentration in colloidal molecule formation

The controlled use of 0.1 wt% Tetraethyl orthosilicate (TEOS) in both the primary nucleation stage and the secondary feed played a central role in directing the formation of doublet and triplet silica structures. The relatively low precursor concentration ensured that silica growth proceeded under kinetically moderated conditions rather than rapid homogeneous nucleation.

During the initial addition of 0.1 wt% TEOS into the n-butanol–ammonium hydroxide medium, hydrolysis and condensation occurred gradually. The onset of turbidity indicated controlled nucleation of primary silica seeds. Because the TEOS concentration was limited, supersaturation levels remained modest, resulting in a reduced nucleation burst and favouring uniform particle growth rather than secondary particle formation.

Introduction of 0.05 wt% PVP after turbidity onset ensured that polymer adsorption occurred predominantly on pre-formed silica surfaces rather than interfering with nucleation kinetics. At this stage, particles possessed reactive silanol groups available for further condensation.

The secondary controlled feed of TEOS at the same low concentration (0.1 wt%) was particularly critical for colloidal molecule formation. Because the concentration was not high enough to trigger a new nucleation event, the freshly hydrolyzed silicate species preferentially condensed onto existing silica surfaces. When particles collided-facilitated by reduced electrostatic stabilization in n-butanol-the local concentration of silanol groups at contact interfaces became elevated. The slow supply of TEOS enabled localized interfacial condensation, resulting in neck formation rather than independent growth.

If TEOS concentration had been higher, two competing phenomena would likely dominate:

- Secondary nucleation, producing new smaller particles rather than promoting fusion.
- Rapid isotropic shell growth, thickening individual particles and reducing probability of directional bonding.

Conversely, if TEOS concentration were significantly lower, insufficient silicate species would be available to reinforce particle contacts and collisions would remain reversible, preventing permanent doublet or triplet formation.

Thus, maintaining TEOS at 0.1 wt% in both stages created a kinetic regime in which:

- Nucleation was controlled and limited.
- Growth occurred preferentially on existing particles.
- Interparticle contacts were chemically stabilized via condensation.
- Cluster size remained restricted to doublets and triplets rather than higher aggregates.

The overnight aging period further allowed gradual condensation at contact points, strengthening Si-O-Si bridges and stabilizing the colloidal molecule architecture. Overall, the controlled low TEOS concentration functioned as a key parameter in shifting the system from homogeneous particle growth toward anisotropic, condensation-driven colloidal cluster formation.

Morphology distribution

Under optimized reaction conditions-specifically controlled TEOS feed (0.1 wt%), moderate 40 kDa Polyvinylpyrrolidone concentration (0.05 wt%) and regulated ammonia content-the system exhibited a highly selective formation of anisotropic silica clusters. Quantitative morphological analysis from SEM micrographs revealed that approximately 60-70% of the population consisted of doublets, while 15–25% formed triplets, with only a negligible fraction of higher-order aggregates.

The predominance of doublets indicates that the kinetic window favored single fusion events between two particles[9]. This suggests that collision frequency and surface reactivity were sufficiently balanced to promote one stable interfacial condensation event before steric stabilization and reduced mobility limited further aggregation. Once a doublet formed, partial PVP coverage and increasing steric hindrance around the fused structure likely decreased the probability of additional particle attachment, thereby limiting uncontrolled cluster growth. Triplet formation occurred at a lower but significant frequency. Importantly, most triplets exhibited linear configurations, rather than triangular or symmetric arrangements. SEM images of doublets and triplets are shown in (Figure 2). This structural preference strongly supports a sequential attachment mechanism rather than simultaneous three-body fusion. In this process, an initially formed doublet retains one reactive, partially unshielded domain. A third particle subsequently collides and condenses at this exposed interface, forming a chain-like structure (sphere-sphere-sphere). The likelihood of three particles simultaneously colliding and condensing symmetrically is statistically low in dilute colloidal systems, further reinforcing the sequential growth model. The minimal presence of higher-order aggregates indicates that steric stabilization from adsorbed PVP and the low TEOS concentration effectively suppressed runaway cluster formation. As clusters grow, their hydrodynamic size increases, diffusion slows and steric barriers become more pronounced, reducing additional attachment probability. Consequently, the system self-limits at low valency structures, primarily yielding doublets and some triplets.

In a moderately polar solvent such as n-butanol, PVP adsorbed non-uniformly on TPM-functionalized silica spheres can act as a nanoscale capillary bridge that locally concentrates hydrolyzed species derived from TEOS. Due to its carbonyl functionality and flexible chain architecture, PVP forms hydrogen-bonding interactions with surface silanols while simultaneously retaining polar silicate oligomers within polymer-rich microdomains, especially at particle–particle contact points or surface irregularities. In the lower dielectric environment of n-butanol, polymer chains partially collapse and increase local viscosity, reducing precursor diffusion and creating confined regions of enhanced supersaturation. This localized enrichment promotes preferential siloxane condensation (Si-O-Si) at specific interfacial sites rather than uniform radial shell growth, thereby directing anisotropic silica deposition and reinforcing neck formation between TPM spheres. Thus, beyond steric stabilization, PVP functions as a transient capillary microreactor that spatially biases TEOS condensation and enables controlled directional growth.

Mechanistic Discussion

Condensation-driven neck growth

When silica particles bearing partially adsorbed PVP collide in the butanol-based reaction medium, their interaction is governed not only by physical contact but by localized surface chemistry. Because PVP coverage is incomplete at optimized concentrations, certain regions of the silica surface remain exposed, particularly silanol (Si-OH) groups that are highly reactive under basic conditions.

Upon collision, these exposed silanol groups from two approaching particles come into close proximity and align at the contact interface. The reduced electrostatic repulsion in n-butanol allows sufficient residence time for molecular reorganization at this junction clearly indiated in (Figure 3). Simultaneously, the secondary feed of hydrolyzed TEOS supplies reactive silicate species into the surrounding medium. Because particle surfaces provide energetically favourable condensation sites, hydrolysis and condensation reactions become locally concentrated at the interface between touching particles.

This localized reaction leads to the formation of siloxane (Si-O-Si) bridges, progressively converting reversible physical contact into irreversible chemical fusion. As condensation continues, a solid silica neck develops, structurally integrating the two particles into a stable doublet. If an additional collision occurs at an exposed reactive domain of a pre-formed doublet, the same mechanism enables triplet formation through sequential attachment.

This process is fundamentally distinct from simple aggregation. In physical aggregation, particles are held together by weak van der Waals or electrostatic interactions and can be redispersed under mild perturbation. In contrast, the present mechanism involves covalent siloxane bond formation, permanently fusing particles into a unified structure. The resulting neck region exhibits continuous silica framework growth, confirming that cluster formation arises from condensation-driven interfacial polymerization rather than reversible colloidal flocculation which is clearly demonstrated in **(Figure 3)**.

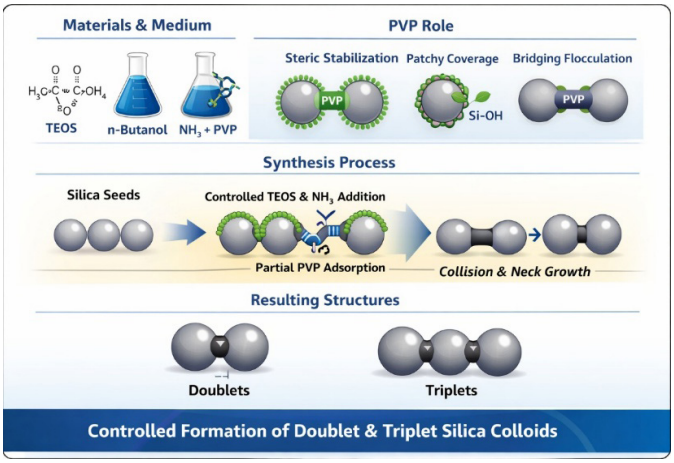

Figure 3: Intermediate transitions during PVP based controlled anisotropy.

Role of solvent polarity

The solvent environment plays a fundamental physicochemical role in dictating colloidal interaction forces and growth pathways. When the reaction medium is shifted from ethanol to n-butanol, the dielectric constant decreases significantly. In colloidal systems, the dielectric constant directly influences the thickness and effectiveness of the electrical double layer surrounding charged particles. Under basic conditions, silica particles possess negatively charged siloxide ($Si\text{-}O^-$) groups on their surfaces, which generate electrostatic repulsion between approaching particles.

In a higher dielectric solvent such as ethanol, charge stabilization is strong and the Debye screening length is effectively extended, meaning that electrostatic repulsion acts over a longer range. As a result, particles rarely approach closely enough for surface silanol groups to interact chemically. Collisions are brief and largely reversible, favoring monodisperse spherical growth.

In contrast, n-butanol has a lower dielectric constant, which compresses the electrical double layer and reduces Debye screening efficiency[10]. Consequently, the magnitude and effective range of electrostatic repulsion decrease. Particles can approach more closely before repulsive forces dominate, increasing the probability of intimate surface contact. This close approach is critical because condensation reactions between silanol groups require molecular-level proximity.

Simultaneously, hydrolysis of Tetraethyl orthosilicate (TEOS) proceeds more slowly in n-butanol due to reduced solvent polarity and altered solvation of reactants. Slower hydrolysis leads to lower supersaturation of silicate species in solution. This suppresses homogeneous nucleation of new particles, which would otherwise compete with cluster formation. Instead of forming independent nuclei, hydrolysed silicate species preferentially condense on energetically favourable sites-namely, existing silica surfaces and particularly particle–particle contact interfaces.

Thus, two synergistic effects occur:

- Reduced electrostatic repulsion enables particles to remain in contact long enough for chemical reactions to occur.
- Slower hydrolysis minimizes new particle formation and channels silica growth toward interfacial condensation.

Together, these solvent-induced changes redirect the reaction pathway from isotropic particle nucleation toward anisotropic, interface-driven fusion. The result is a system that favours the formation of chemically bonded doublets and triplets rather than isolated monodisperse spheres.

Polymer-mediated anisotropic shielding

The adsorption behavior of Polyvinylpyrrolidone (PVP) on silica surfaces is inherently dynamic and spatially non-uniform. PVP interacts with silica primarily through hydrogen bonding between its lactam carbonyl groups and surface silanol (Si-OH) functionalities. However, this interaction is not equivalent across the entire particle surface. Factors such as local curvature, silanol density, polymer chain conformation and solvent quality influence how and where the polymer adsorbs.

At moderate concentrations, PVP chains adopt loop-and-tail configurations rather than forming a dense, continuous layer. Some segments anchor to the surface, while other portions extend into the surrounding solvent. Because adsorption occurs through multiple weak, reversible interactions, surface coverage remains incomplete and heterogeneous. This results in “patchy” particles-regions of the surface are sterically shielded by polymer, while other domains remain exposed and chemically reactive.

These exposed silanol-rich domains act as localized reactive sites during particle–particle encounters. When two partially shielded particles collide, condensation is more likely to occur between unprotected regions, while polymer-covered regions resist further interaction. This spatial asymmetry effectively mimics directional bonding seen in molecular systems, where specific reactive sites dictate bonding geometry. As a result, fusion events become anisotropic rather than isotropic, favouring controlled doublet and triplet formation instead of random aggregation.

When higher molecular weight PVP is used, the polymer chains are longer and possess larger hydrodynamic radii. Such chains can extend far enough into solution to simultaneously interact with two neighbouring particles. This introduces a secondary mechanism known as mild bridging flocculation. In this scenario, a single polymer chain transiently binds multiple particles, increasing their probability of remaining in close proximity. While still moderated by steric stabilization, this effect enhances the likelihood that a third particle attaches to a pre-formed doublet, thereby increasing triplet formation.

Importantly, the bridging induced by high molecular weight PVP is subtle under optimized conditions. It promotes sequential attachment without causing uncontrolled clustering. Thus, polymer-mediated anisotropic shielding and controlled bridging together regulate particle valency, enabling selective formation of low-order colloidal molecules.

Anistopic Organosilica Colloidal Molecule

The formation of raspberry-like and buckle-hole colloidal molecules in this system shown in **(Figure 4)** can be understood as a consequence of the dynamic evolution of a double-emulsion template coupled with interfacial organosilica condensation and polymerization. Initially, the precursor mixture containing 3-(Trimethoxysilyl) propyl methacrylate and water, stabilized by Span 80 and further dispersed in a butanol phase with Cetyltrimethylammonium bromide, generates a water-in-oil-in-water (W/O/W) double emulsion, as evidenced by the optical micrograph showing multiple internal droplets confined within a larger parent droplet. These interfaces act as highly active reaction zones where, under basic conditions provided by ammonium hydroxide, TPM undergoes hydrolysis to form silanol groups followed by condensation into an organosilica network[11]. Due to the curvature and compositional heterogeneity of the emulsion, condensation does not occur uniformly; instead, it is localized at regions of high interfacial curvature and at contact points between internal droplets and the outer interface. As the reaction proceeds at elevated temperature, internal aqueous droplets undergo coalescence, shrinkage and migration driven by interfacial tension gradients and solvent exchange between butanol and water, generating Marangoni flows and transient concentration gradients of TPM oligomers[12]. These dynamic processes create anisotropic growth conditions, leading to the heterogeneous nucleation of secondary organosilica

domains on the surface of primary particles, which manifests as the characteristic raspberry-like morphology observed in SEM. Simultaneously, partial encapsulation followed by collapse or escape of internal droplets results in localized voids or indentations; because the surrounding organosilica network has already begun to solidify, these deformations cannot relax, giving rise to buckle-hole structures. The subsequent addition of KPS initiates free-radical polymerization of the methacrylate groups within TPM[13], forming a crosslinked hybrid network that kinetically arrests the evolving morphology and preserves these non-equilibrium features. Thus, the final structures arise from a complex interplay of double-emulsion templating, interfacial condensation, surfactant-mediated curvature stabilization and polymerization-driven fixation, resulting in anisotropic colloidal molecules with hierarchical surface and internal architectures.

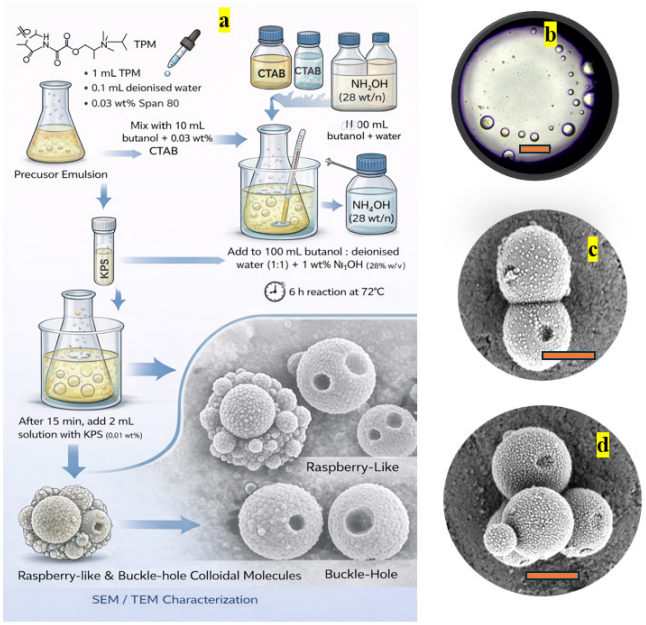

Figure 4: (a) Overall procedure of Anisotropic functionality of organosilica. (b) Microscopic image of W/O/W emulsion of precursor solution. (c) Raspberry buckled colloidal doublet. (d) Raspberry buckled colloidal quadruplet. Scale bar is 500nm

Applications

The synthesized doublet and triplet silica colloids possess intrinsic anisotropy that significantly expands their functional utility compared to conventional spherical particles. Because these structures consist of chemically fused lobes connected by a rigid silica neck, they behave as low-valency "colloidal molecules," where each lobe acts as a structural unit analogous to atoms in molecular systems. This directional geometry enables predictable bonding orientations during assembly, making them highly suitable for colloidal molecule assembly. Unlike isotropic spheres that pack randomly, doublets and triplets can organize into ordered architectures with defined angles and connectivity, enabling programmable mesoscale structures.

As photonic crystal precursors, these anisotropic colloids offer additional advantages. Photonic materials rely on periodic variations in refractive index to manipulate light propagation. The fused multi-lobed geometry introduces symmetry breaking and directional periodicity into assembled lattices. This can result in modified photonic band structures, anisotropic scattering behavior and polarization-dependent optical responses. Because silica has good optical transparency and chemical stability, such colloidal molecules can serve as building blocks for advanced photonic metamaterials.

For directional self-assembly platforms, these structures provide controlled valency. A doublet has two principal interaction domains, while a triplet can present three directional interaction points. Such geometry-dependent bonding promotes the formation of chains, branched networks or specific lattice arrangements under external fields or surface confinement. This makes them attractive for studying controlled assembly kinetics and emergent structural order.

Finally, in optical scattering studies, anisotropic silica clusters exhibit different light-scattering behavior compared to spheres of equivalent volume. The presence of multiple lobes alters scattering cross-sections, angular distribution and interference effects. This enables investigation of anisotropic Mie scattering, multiple scattering pathways and enhanced light–matter interaction phenomena.

Overall, the anisotropic geometry of doublet and triplet silica colloids enables controlled packing behavior, tunable interaction valency and enhanced optical functionality. These features position them as versatile building blocks for advanced materials engineering and fundamental colloidal science research.

Conclusion

A modified Wilhelm Stöber-type synthesis conducted in n-butanol with controlled Polyvinylpyrrolidone adsorption enables selective formation of doublet and triplet silica colloids from Tetraethyl orthosilicate. Solvent polarity modulation slows hydrolysis and reduces electrostatic stabilization, while partial polymer coverage generates anisotropic bonding sites. Controlled secondary TEOS feed promotes condensation-driven neck formation, yielding discrete colloidal clusters.

This scalable solution-based approach provides a versatile route toward colloidal molecules with tunable valency and structural precision, expanding the synthetic toolbox for advanced materials design.

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