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Controllable Synthesis of Hollow Silica Nanospheres

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Abstract: Nano hollow SiO_2 refers to a unique form of nanoscale silica material that has an inner cavity structure. This hollow configuration offers several advantages over solid structures, including a larger specific surface area, lower density, and improved permeability. Additionally, hollow silica is chemically inert and thermally stable, making it an excellent candidate for drug delivery applications. Silica's transparency to both light and magnetism ensures that it does not absorb light or disrupt magnetic fields, preserving the inherent optical or magnetic properties of certain composites. In addition, its porosity, biocompatibility, and mechanical stability are adjustable and controllable, making it an ideal and cost-effective material for both industrial and biological uses. This study synthesised a range of hollow spherical silica samples via the sol-gel process. The aim was to investigate the impact of different factors on their sphericity and wall thickness.

Keywords: Hollow, Silicon Dioxide, Controlled Synthesis, Wall Thickness.

1. Introduction

Nanostructures and nanomaterials play a pivotal role in the advancement of contemporary science and technology. Unlike conventional materials, nanomaterials are distinct not only in terms of size but also exhibit unique physical properties, such as extensive specific surface areas and surface energy. [1]Nanomaterials have a wide range of applications in various fields such as the chemical industry, metallurgy, light industry, aerospace, ceramics, nuclear technology, catalysis, and pharmaceuticals. The synthesis of nanomaterials involves various approaches that allow for precise control over their size, shape, particle distribution, and chemical composition. The versatility of synthesis techniques ensures that nanomaterials can be tailored to meet the specific requirements of various material applications[2].

The synthesis of materials with specific functionalities and nanoscale hollow spherical structures has attracted significant attention from researchers. [3]Hollow sphere structures are particularly intriguing due to their potential properties, such as adjustable surface area, pore volume, thermal conductivity, and photorefractive index[2]. Silica is a unique material due to its low density, high mechanical strength, chemical stability, and exceptional thermal stability[4]. Research has shown that hollow nanoscale silica materials have potential applications in drug and biomolecule release, photocatalysis, energy storage, and sensing, providing precise control over release mechanisms.

Microsphere-type materials, occupying the size range between nanoscale and microscale, are characterized by their spherical or near-spherical microscopic morphology. This unique shape, combined with the effects of their small size, has led to their increasingly widespread application in both macroscopic and microscopic domains, where they play a pivotal role[5]. Key functions include serving as micro-reservoirs, such as encapsulating various drugs within hollow spheres to act as drug carriers, thereby optimizing drug utilization; acting as micro-reactors to confine reactions within the spheres, like photocatalytic reactions, with each hollow sphere functioning as a micro-reactor that extends the path of light incidence and significantly enhances reaction efficiency[6]; functioning as micro-separators for the adsorption of various toxic organic compounds, facilitating separation and purification; and serving as microstructural units that, when added to various materials, enhance material performance. Consequently, nano hollow silica materials are envisioned to have broad application prospects across multiple fields.

In a recent study, hollow silica microspheres were successfully synthesised using a templating method. In this approach, polymer microspheres were used as templates. Silica was deposited on their surfaces using a sol-gel process, after which the template was removed, leaving a hollow structure. It was found that by changing the pH of the sol and the reaction temperature, the wall thickness and pore size of the product could be effectively controlled. Another study achieved the synthesis of hollow silica nanoparticles using a template-free strategy. This technique relied on the self-assembly of silica precursors in a specific solvent system, followed by selective etching, thus avoiding the complexity and cost associated with traditional templating methods. The hollow silica nanoparticles produced by this approach demonstrated exceptional drug loading capacity and release properties. More recently, the use of microemulsion technology has enabled the synthesis of hollow silica nanoparticles with highly controllable shapes and sizes. By modifying the phase ratios and types of surfactants in the microemulsion, researchers were able to precisely tailor the inner and outer diameters of the nanoparticles, as well as the thickness of their walls. This paper describes the synthesis of hollow spherical nano-silica using ethyl silicate (TEOS) as the silicon source via a one-step sol-gel process. Furthermore, improvements in sphericity, wall thickness and microstructure were achieved by adjusting factors such as the amount of TEOS, the type of surfactant used and the stirring time.

2. Experimental Section

(1) Reagents and materials

All reagents were purchased from commercial sources. Ammonium citrate and ammonia were purchased from Aladdin.Ethanol, tetraethyl orthosilicate and cetyltrimethyl bromide were purchased from Longxi Chemical Co, Ltd. All reagents were of analytical grade and were used as received

without further purification.

(2) Preparation

Ammonium citrate was mixed with surfactant and the ammonia was stirred thoroughly. This mixture was then gradually added to ethanol, stirred for 2 minutes and then combined with TEOS. The solution was allowed to stand overnight at room temperature. The next day, the product was isolated by centrifugation, washed once with alcohol and twice with water, and then dried in an oven at 80°C. Finally, it was calcined at 900°C. The amounts of ammonium citrate, ammonia, ethanol and TEOS were varied to determine the optimum experimental conditions. In addition, different types and amounts of surfactant were tested to identify the most suitable surfactant for the process.

(3) Characterizations

Thermal field emission scanning electron microscopy (TFE-SEM) analyses were performed using a JSM-7610F instrument. The instrument was operated at an acceleration voltage varying from 5 to 10 kV. The biological transmission electron microscope (TEM) was sourced from JEOL Ltd., Japan. The instrument was operated at an acceleration voltage of 10 kV.

3. Results and Discussion

In 1968, Stöber et al. developed a base-catalysed method for synthesising amorphous silica particles from tetraethoxysilane (TEOS) with ammonia as the catalyst. This method, known as the Stöber method, has become a prevalent technique for fabricating spherical SiO_2 particles. It is acclaimed for its simplicity, size controllability, and the excellent monodispersity of the resulting SiO_2 particles.[7] During the Stöber process, TEOS undergoes hydrolysis and condensation to form small primary SiO_2 particles. These primary particles have a tendency to aggregate into stable entities due to their limited colloidal stability. Subsequently, the hydrolysis of tetraethyl orthosilicate (TEOS) on the surface of these particles generates soluble silicic acid molecules or oligomers, culminating in the formation of final spherical SiO_2 particles.In this study, we improved the Stöber method by incorporating citric acid and ammonium citrate as surfactants and templates, which facilitated the creation of a hollow structure. The high-purity, nano-hollow structured silica was obtained by eliminating the templates through washing and calcination.

Silicon dioxide nanotubes were synthesized using a sol-gel process. Citric acid was used as a structure-directing agent and CTAB was used as the seeding surfactant in an ethanol-ammonia solution mixture. The morphology and microstructure of the samples were analysed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In Scheme 1, 0.5625 g of ammonium citrate and 0.2 g of citric acid were mixed in 15.74 ml of ammonia water and stirred until fully dissolved. It is important to note that citric acid has limited solubility in ethanol and requires time to fully dissolve in ammonia water. The solution was added gradually to 225 ml of ethanol. After stirring for 2 minutes, 6 ml of Tetraethyl Orthosilicate (TEOS) was introduced. The mixture was left to stand at room temperature overnight. The product was isolated through centrifugation and washed once with alcohol and twice with water. Subsequent drying in an oven and calcination at 900°C were carried out. Scheme 2 was an expansion of the system described in Scheme 1, which was examined to provide a foundational basis for potential industrial scaling.

Ammonium citrate and citric acid are mixed and stirred in ammonia to facilitate dissolution, producing intermediates rich in reactive hydroxyl groups. Tetraethyl orthosilicate (TEOS) undergoes ammonia-catalysed hydrolysis, where ethoxy groups are nucleophilically substituted by hydroxyl groups, leading to the formation of numerous silicate molecules. These molecules undergo dehydration or dehydrogenation to form Si-O-Si condensates. When supersaturation is reached, the condensates quickly come together to form primary silica particles, which are usually between 5-10 nm in size.These particles are then stabilized through further growth, with soluble silicate molecules or condensates persistently reacting and controlling the surface growth. Eventually, this process leads to the formation of silica nanotubes and shells. The final product is purified through centrifugation and washed with alcohol and water to remove any unreacted precursors and by-products. The gel is then oven-dried to remove any remaining solvents and water, before being calcined at 900°C. This process eliminates all organic components, resulting in stable silica nanostructures. The internal microstructure of the material is reorganized during calcination, and crystal growth produces nanoscale spherical silica structures.

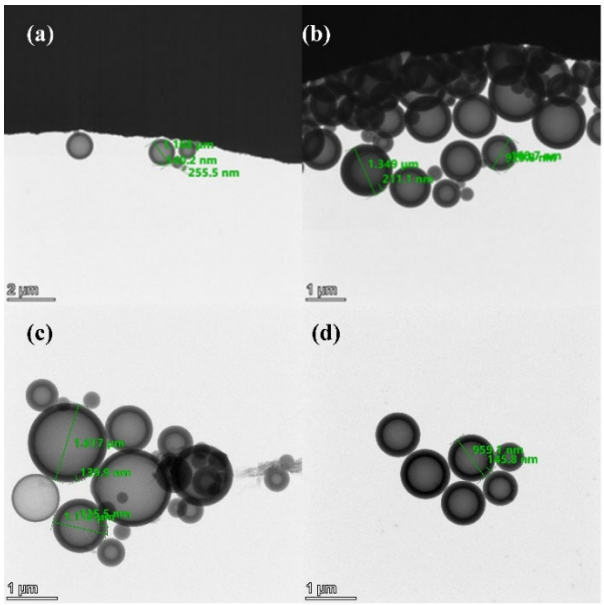

Figure 1. TEM images, Scheme 1 (a) (b); Scheme 2 (c) (d)

Transmission electron micrographs of the synthesized product are shown in Figure 1(a-b), revealing hollow spherical structures with somewhat non-uniform sizes. The diameters of these spheres were predominantly around 1 μm, with outer wall thicknesses consistently exceeding 100 nm. Fragmentation was infrequently noted, though a number of smaller particles or hollow spheres were detected. Micrographs of the product from Scheme II are presented in Figure 1(c-d), showing hollow spheres with non-uniform sizes. The diameter variation remained around 1 μm, with wall thickness uniformly over 100 nm, and minimal fragmentation. The occurrence of agglomeration is attributed to inadequate ultrasonic dispersion of the precursors.The stability and viability of the experimental approach are confirmed by the presence of hollow nanorods in both the original and scaled-up systems. However, the varying size,

which ranges from 1 to 2 μm, suggests a need for optimization. On the other hand, the wall thickness seems to be consistently controlled.

To investigate the effect of TEOS concentration on the citric acid and ammonium citrate system, two schemes were employed. Scheme 3 involved mixing 0.375 g of ammonium citrate with 0.13 g of citric acid monohydrate in 10.5 ml of ammonia. The resulting mixture was quickly transferred into 150 ml of ethanol and stirred for 2 minutes. Then, 4 ml of TEOS was added and the mixture was left to react overnight, approximately 12 hours. After the reaction, the product was sonicated in ethanol and then applied to a copper mesh for transmission electron microscopy (TEM) analysis. Scheme 4 shows that 0.5625 g of ammonium citrate was combined with 0.2 g of citric acid in 15.74 ml of ammonia. This mixture was gradually introduced into 225 ml of ethanol and stirred for 2 minutes. Finally, 6 ml of TEOS was added. The mixture was left to stand at room temperature overnight. The product was then isolated by centrifugation, washed with alcohol once and water twice, and subsequently dried in an oven. Next, the dried product was dispersed using ethanol sonication and placed on a copper mesh for TEM. Varying the TEOS dosage in these schemes could potentially affect the formation of nanocavity silica spheres, which in turn could affect the hollow structure and wall thickness of the spheres.

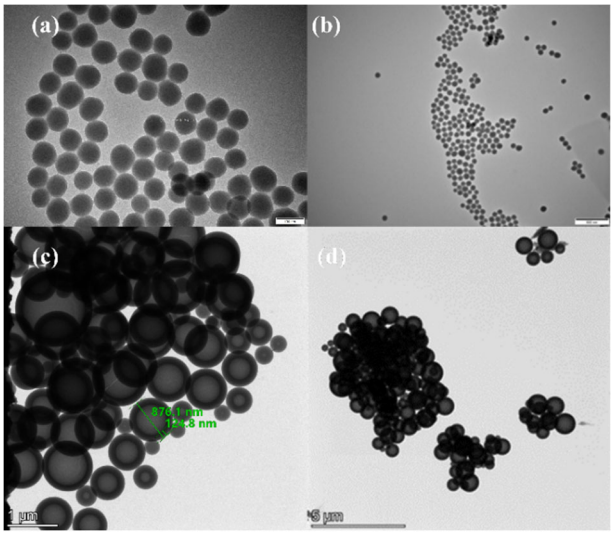

Figure 2. TEM images, Scheme 3 (a) (b);4 (c) (d)

Figure 2(a-b) presents the TEM images from Scheme 3, revealing predominantly solid spheres with relatively uniform sizing, each under 100 nm in diameter. Conversely, Figure 2(c-d) displays hollow spherical silica with improved sphericity, where particle sizes are around the 1 μm mark, and wall thicknesses approximate 100 nm. Notably, an increase in solid spheres was observed, alongside agglomeration between solid and hollow spherical structures. Reducing the TEOS quantity resulted in insufficient coating, leading to agglomeration, which is detrimental to the synthesis of hollow spheres. An excessive increase in TEOS beyond the optimal level generated a multitude of free SiO_2 particles. This is attributed to the hydrolyzed TEOS monomer concentration exceeding the homogenous nucleation threshold, causing excess TEOS monomers to spontaneously nucleate, forming free nanoscale SiO_2 particles. Overabundant TEOS contributed to increased wall thickness and the coexistence of hollow and solid aggregates, illustrating the spontaneous agglomeration effect in the absence of proper TEOS encapsulation.

Citric acid was selected as the sole template for the experiment after assessing the experimental costs and the templating role. Experimental protocol 4 was designed as follows: 0.375 g of citric acid was stirred thoroughly in 10.5 ml of ammonia, then quickly mixed into 150 ml of ethanol, stirred for 2 minutes, and finally combined with 4 ml of TEOS. After drying, the product was dispersed in ethanol via ultrasonication and applied to a copper mesh for TEM analysis. The experiment demonstrated that the colloidal solution remained homogeneous, and reducing the amount of ammonium citrate did not affect the mixture's stability. This observation indicates that decreasing the concentration of ammonium citrate may not have a negative impact on the experimental system.

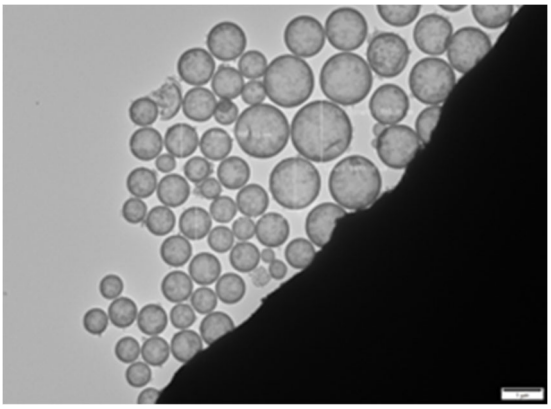

Figure 3. TEM images, Scheme 5

Nanohollow spheres were successfully synthesized even without the addition of ammonium citrate. Figure 3 displays the transmission electron micrograph from Scheme 5, showcasing hollow nanospheres around 1 μm in diameter with wall thicknesses in the vicinity of 100 nm. The results suggest that while ammonium citrate contributes to the stability of the experimental system, acting as a surfactant and partially directing nucleation, it is not essential for the formation of nanohollow spheres. Citric acid initiates the nucleophilic substitution of ethoxy groups in tetraethyl orthosilicate (TEOS) by hydroxyl groups, catalysed by ammonia, leading to the production of numerous silicate molecules. Subsequent intermolecular dehydration or dehydroxylation of these silicate molecules forms Si-O-Si condensates. Upon reaching supersaturation, these condensates rapidly aggregate, resulting in the nucleation and formation of primary silica particles.

4. Conclusion

This research examines the impact of expanding the experimental setup, varying TEOS dosage, and the presence or absence of ammonium citrate on the fabrication of silica nanostructures across three experimental phases. The expanded experimental framework validated the synthesis process's stability and viability, demonstrating consistent control over wall thickness, although with size fluctuations from 1 to 2 μm. The addition of TEOS had a significant impact on the development of nanoporous silica spheres, affecting their hollow nature and wall thickness. Inadequate

coating and agglomeration occurred when insufficient TEOS was added, while an excess resulted in spontaneous, non-encapsulated agglomeration and an abundance of free SiO_2 particles. The findings suggest that although ammonium citrate can enhance system stability and aid in nucleation, it is not essential for creating nanoporous spheres. Nanoporous silica spheres with precise size and wall thickness control were crafted by fine-tuning the TEOS concentration and modulating ammonium citrate usage. This lays a solid groundwork for future industrial scaling and application exploration.

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