

Controlled synthesis of monodisperse spherical microsilica from rice husk via precipitation process

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Spherical microsilica was synthesized from rice husk-derived silica via a precipitation-based process. The effects of key synthesis parameters, including PEG characteristics, nitric acid concentration, aging temperature, and time, were systematically investigated to identify the dominant factor governing particle morphology. Aging time was found to be the most critical parameter, with effective spheronization occurring within a narrow time window around 35.5 h. Under optimized conditions, uniform spherical silica particles with an average diameter of approximately 5.8 μm , narrow size distribution, and high purity (99.7%) were obtained. Structural analyses confirmed that the synthesized silica was amorphous and porous. These results demonstrate that rice husk can be converted into high-quality spherical microsilica through a simple and controllable process without complex pretreatment, indicating its potential applicability in morphology- and purity-sensitive functional material applications.

Keywords: Rice husk, Silica, Sodium silicate, Microsphere, Monodisperse, Sustainable material.

Introduction

Silica is a key material widely used in modern industries, and silica particles with controllable morphologies are in high demand for diverse high-value applications, including cosmetics, catalysts, drug delivery systems, and rubber [1–7]. In this context, rice husk, which contains a high SiO_2 content, has recently attracted increasing attention as a sustainable alternative source of silica [1, 3, 8–16]. Three main approaches have been reported for obtaining silica from rice husk: combustion, acid leaching, and alkali extraction [8, 10, 15]. Combustion involves direct burning of rice husk to produce rice husk ash with a high silica content. In this approach, the particle size of the resulting silica can be controlled by adjusting the combustion temperature, typically yielding silica nanoparticles in the range of 10–80 nm [4–6]. The acid leaching method is commonly combined with combustion to enhance the Si purity of rice husk ash, and the particle sizes reported in the literature are generally comparable to those obtained by combustion alone [6, 17]. In contrast, alkali extraction enables the dissolution of silica from rice husk in the form of sodium silicate, which can subsequently be used as a versatile precursor for controlled silica synthesis [3, 11, 13, 14]. This approach offers greater flexibility in tuning particle

size, morphology, and pore structure through adjustment of synthesis parameters, making it a promising route for producing value-added silica materials from rice husk [3, 10, 13, 14].

To date, most silica particles synthesized from rice husk have been reported in the nanoscale range [18, 19], with relatively limited studies focusing on the controlled synthesis of micro-sized silica particles. Micro-sized silica particles exhibit low toxicity and high physicochemical stability, which enable their broad application in diverse industrial fields such as food, pharmaceuticals, cosmetics, chromatography, and construction materials [20–25]. The synthesis of microsilica is often accompanied by particle aggregation and Ostwald ripening, which result in broad size distributions and significant non-uniformity [26–28]. Such size irregularities not only affect particle morphology but also compromise the consistency of physicochemical properties in final applications, thereby directly influencing product quality and stability. For instance, in cosmetic applications, large variations in particle size can lead to poor uniformity in spreadability, texture, and optical appearance, ultimately reducing consumer satisfaction. Similarly, in polymer composites, particle size heterogeneity can cause uneven stress distribution and variability in mechanical performance. Therefore, establishing a reliable technique capable of stably controlling particle size and morphology is a key prerequisite for the industrial application of silica materials.

Consequently, advancing rice husk-derived silica

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beyond its conventional use as a raw material toward the controlled synthesis of uniform microsilica has emerged as an important research challenge for maximizing its industrial value. Such an approach directly addresses the safety, handling, and cost limitations associated with nanosilica-centered studies, while simultaneously enabling precise control over particle size and morphology. Moreover, the sustainable and low-cost conversion of rice husk—a renewable and abundant biomass—into functional microsilica offers both academic significance and practical advantages for a wide range of high-value-added applications. Accordingly, this study aims to develop a simple and controllable synthesis strategy for producing uniform, spherical microsilica from rice husk-derived sodium silicate and to systematically elucidate the key parameters governing particle formation.

Materials and Methods

Materials

Rice husk was obtained from Yeongju-si, Gyeongsangbuk-do, South Korea. The reagents used in the study were sodium silicate (57% (SiO_2), CAS No. 1344-09-8, Daejung Chemicals & Metals Co., Ltd., Rep. Korea), sodium hydroxide (98%, CAS No. 1310-73-2, Youngjin Chemical Co., Ltd., Rep. Korea), polyethylene glycol (PEG; CAS No. 25322-68-3, Daejung Chemicals & Metals Co., Ltd., Rep. Korea), nitric acid (65%, CAS No. 7697-37-2, Duksan Co., Rep. Korea), distilled water, and ethyl alcohol (99.9%, CAS No. 64-17-5, Duksan Co., Rep. Korea). Sodium hydroxide and nitric acid were diluted with distilled water.

Synthesis of silica microparticles

Rice husk was mixed with 0.5 M sodium hydroxide at a solid-to-liquid ratio of 1:5 (w/v) and reacted at 50 °C for 4 h to obtain a sodium silicate solution. Following

the reaction, the sodium silicate solution containing rice husk-derived Si was separated by vacuum filtration using a Whatman filter No. 41 (Cytiva, Marlborough, USA) and an aspirator (WJ-15, Taewon Shibata Co., Ltd., Japan). To induce silica precipitation, polyethylene glycol (PEG) was first added to 50 mL of the sodium silicate solution, followed by the dropwise addition of nitric acid solution. The resulting mixture was stirred at room temperature at 300 rpm for 10 min to ensure thorough mixing. Subsequently, the solution was aged under static conditions to promote particle formation. After aging, the solid phase was separated by filtration (Whatman filter No. 41, Cytiva, Marlborough, USA; aspirator WJ-15, Taewon Shibata Co., Ltd., Japan), thoroughly washed with distilled water and ethanol to remove residual impurities, and dried in an oven. Finally, the dried product was calcined at 500 °C for 2 h. A schematic illustration of the synthesis process for silica microparticles and the key parameters employed in this study to achieve uniform microsilica are presented in Fig. 1.

Analytical methods

The physicochemical properties of the synthesized microsilica particles were characterized using various analytical techniques. The chemical composition and purity of the silica were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 7600 Duo, Thermo Fisher Scientific, USA). The particle size distribution was measured using a particle size analyzer (PSA; LA-960, Horiba Ltd., Japan). The particle size distribution was evaluated using the Span value, which was calculated as $(D_{90} - D_{10})/D_{50}$, where D_{10} , D_{50} , and D_{90} represent the particle diameters at 10%, 50%, and 90% cumulative volume, respectively. The crystalline structure was analyzed by X-ray diffraction (XRD; MiniFlex, Rigaku Co., Japan). The surface

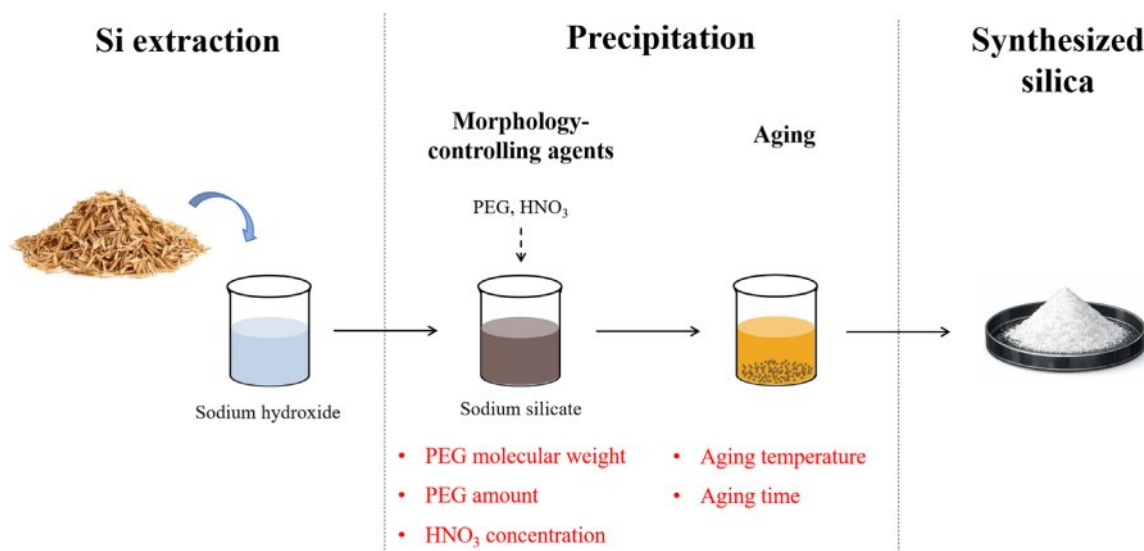


Fig. 1. Schematic illustration of the synthesis process and key parameters for uniform silica microparticle formation.

morphology of the silica particles was examined using field-emission scanning electron microscopy (FE-SEM; MIRA3, TESCAN, Czech Republic). The specific surface area, pore volume, and pore size distribution were evaluated by Brunauer–Emmett–Teller (BET; TriStar II, Micromeritics Instrument Co., USA) analysis.

Results and Discussion

The spheronization and size control of silica particles were governed by several parameters, including the molecular weight and concentration of polyethylene glycol (PEG), nitric acid concentration, aging temperature, and time. The influence of PEG molecular weight and concentration on particle size and morphology is summarized in Table S1. When PEG 1,000 was used, spherical particles were scarcely formed, while complete spheronization was not achieved with PEG 6,000. In contrast, PEG 4,000 produced the most uniform spherical particles. These results demonstrate that PEG is a key additive for silica spheronization and that the ethylene oxide (EO) chain length is the decisive factor governing particle formation [3, 13].

Specifically, the EO chain length of PEG significantly influences both the nucleation and growth stages of silica precipitation [29, 30]. During the nucleation stage, the EO units interact with silanol (Si–OH) groups via hydrogen bonding, where an optimal chain length helps modulate the nucleation rate by stabilizing embryonic silica species. During the growth stage, the PEG chains adsorbed on the silica surface provide steric stabilization, which is essential for preventing disordered aggregation and ensuring isotropic growth. In this study, the shorter EO chains of PEG 1,000 likely provided insufficient steric hindrance, leading to irregular growth, whereas the excessively long chains of PEG 6,000 may have caused unbalanced interactions or secondary bridging, preventing perfect spheronization. PEG 4,000, however, provided an ideal adsorbed layer thickness to maintain a stable and uniform growth environment. Nevertheless, varying the PEG concentration between 20 and 40 g/L had little effect on particle size or morphology, indicating that PEG concentration plays a minor role once an adequate amount is present. Given the negligible effect of PEG concentration, lower PEG dosages are preferable from an economic standpoint. The effect of nitric acid concentration on silica particle formation was investigated, and the formation of uniform particles was confirmed at a specific concentration (Fig. S1). Nitric acid plays a critical role in silica particle formation by promoting the condensation reaction in conjunction with PEG; accordingly, the results of this study demonstrate that uniform particles were not obtained when the nitric acid concentration was either below or above the optimal range. Similarly, aging temperature was identified as a critical parameter influencing silica particle formation, and the most uniform spherical particles were obtained

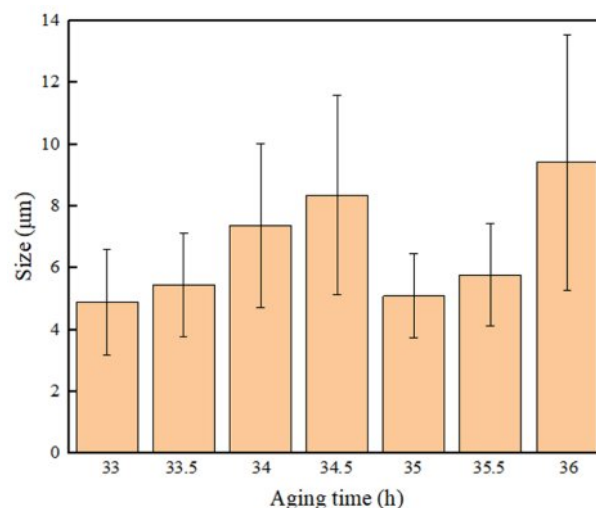


Fig. 2. Mean particle size of silica as a function of aging time.

at 80 °C (Fig. S2).

To investigate the effect of aging time, a broad range of aging times from 15 to 48 h was initially applied (Fig. 2). A significant change in particle size and size distribution was observed between 33 and 36 h, indicating the presence of a time window in which Ostwald ripening can be effectively regulated [26–28]. This transition is attributed to the structural reorganization of silica species, where disordered silica oligomers and primary clusters, initially formed from sodium silicate, undergo a coalescence phase to minimize surface free energy [31]. Accordingly, additional aging experiments were conducted at 30 min intervals. Combined analysis of SEM images (Fig. S3) and PSA results (Table 1) indicated that particles with a fully spherical morphology and a relatively narrow size distribution were obtained at an aging time of 35.5 h. The Span value, which reflects the uniformity of particle size distribution, decreases with narrower distributions and smaller deviations. Although the lowest Span value was observed at 35 h (Table 1), SEM observations revealed incomplete spheronization under this condition, indicating that it was not optimal. In contrast, complete sphericity was achieved at 35.5 h (Fig. S3f), which was therefore identified as the most suitable aging time for

Table 1. Particle size distribution and corresponding span values of silica particles synthesized at different aging times.

Aging time (hr)	Particle size (µm)	Span
33	4.90 ± 1.71	0.90
33.5	5.46 ± 1.68	0.79
34	7.37 ± 2.64	0.92
34.5	8.36 ± 3.21	1.01
35	5.10 ± 1.37	0.70
35.5	5.78 ± 1.65	0.74
36	9.43 ± 4.13	1.16

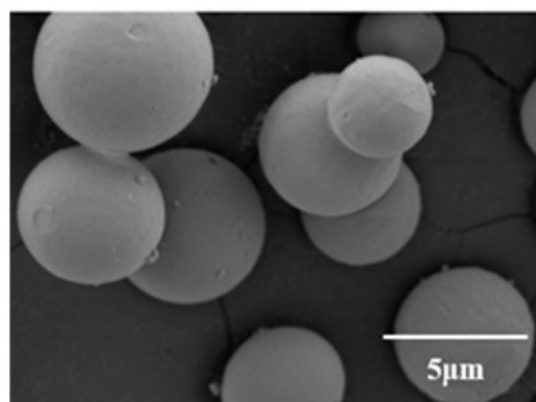
Table 2. Elemental composition of raw rice husk and synthesized silica determined by ICP-OES.

	Si	K	Ca	P	Mg	Fe	Al
Raw RH	75.7	17.8	3.3	1.7	1.1	0.2	0.1
Synthesized silica	99.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

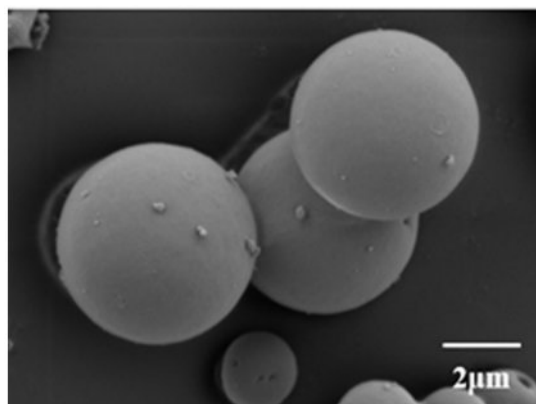
producing uniform microsized spherical silica particles. This indicates that a brief induction period following the achievement of maximum monodispersity is essential for the final structural refinement of the particles. These were further supported by ANOVA analysis, yielding a p -value of 0.00476 (< 0.05), which confirms that the observed differences were statistically significant. Taken together, the molecular weight and amount of PEG, nitric acid concentration, and aging temperature were identified as key factors influencing the spheronization of silica particles. However, even under optimized conditions for these parameters, aging time emerged as the most critical variable governing the formation of spherical silica particles. Notably, spheronization occurred decisively within a narrow time window around 35.5 h, a phenomenon consistent with previous reports on related silica precipitation systems where an

optimal aging window is required for the coalescence of primary particles into stable spheres [29]. This highlights that precise control of reaction time is of paramount importance for the synthesis of uniform spherical silica particles.

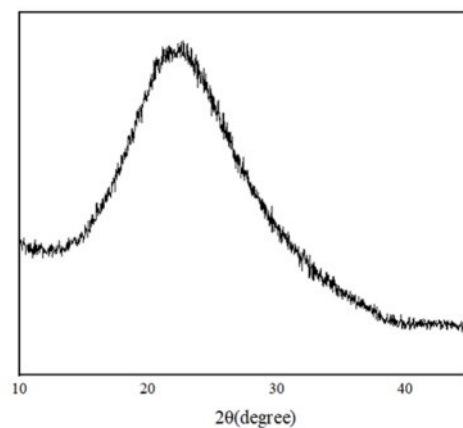
The physicochemical characteristics of silica particles synthesized under the optimized conditions (20 g/L PEG with a molecular weight of 4,000, 1.1 M nitric acid, and aging at 80 °C for 35.5 h) were analyzed. The synthesized silica exhibited a high purity of 99.7% (Table 2). Given that the Si content of the raw rice husk was approximately 75.7%, this result clearly demonstrates that the proposed synthesis process effectively enriched the SiO₂ content by removing other inorganic constituents. As shown in Fig. 3, the particles displayed a completely spherical morphology, indicating uniform nucleation and



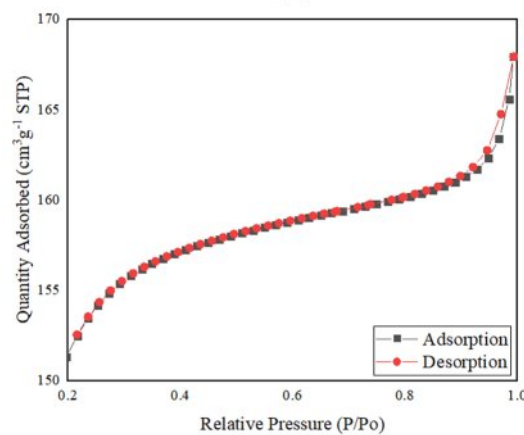
(a)



(b)

Fig. 3. FE-SEM micrographs of silica particles at different magnifications.

(a)



(b)

Fig. 4. (a) XRD pattern and (b) N₂ adsorption-desorption isotherm plot of the synthesized silica used to evaluate its structural and textural properties.

Table 3. Textural properties of synthesized silica determined by BET analysis.

S_{BET} (m^2g^{-1})	V_t (cm^3g^{-1})	V_{mic} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{meso}/V_t (%)	dp (nm)
474.6	0.3	0.2	0.1	41.9	2.8

(S_{BET} : specific surface area, V_t : total pore volume, V_{mic} : micropore volume (< 2 nm), V_{meso} : mesopore volume (2~50 nm), dp : pore diameter)

growth under well-controlled synthesis conditions. Such uniform spherical particles are advantageous in terms of dispersibility and processability and can further enhance the physical and optical properties of final products. XRD and BET analyses confirmed that the synthesized silica was amorphous and possessed a porous structure (Fig. 4 and Table 3). Overall, these results demonstrate that the proposed process enables the production of high-purity spherical silica while simultaneously allowing control over its structural and functional properties. The optimized synthesis conditions for microsilica identified in this study were applied to commercial sodium silicate, and the characteristics of the resulting silica were compared with those of silica synthesized from rice husk-derived sodium silicate. Both samples exhibited comparable particle size and morphology, as observed by SEM (Fig. 3 and Fig. S4), as well as similar pore characteristics determined by BET analysis (Table 3 and Table S2). However, BET analysis revealed that the silica synthesized from commercial sodium silicate possessed a higher specific surface area, approximately $130 \text{ m}^2 \text{ g}^{-1}$ greater than that of silica derived from rice husk-based sodium silicate. This discrepancy is primarily attributed to the influence of trace impurities and the inherent composition of the precursors. Trace metallic elements or residual organic components present in the rice husk-derived silicate can interfere with the self-assembly of silica oligomers, potentially promoting a more condensed framework or causing partial pore blockage during the aging stage [3]. Furthermore, the standardized molecular distribution in commercial sodium silicate facilitates the formation of a more intricate and open porous network, leading to a significantly higher surface area. These results suggest that while rice husk is a viable sustainable source, the presence of minor impurities is a critical factor that can modulate the internal pore structure and surface characteristics of the resulting silica. Despite this difference, the overall similarity in structural and textural properties indicates that rice husk-derived sodium silicate has strong potential as a viable alternative to commercial sodium silicate for microsilica synthesis.

The silica extraction process in this study, conducted under mild alkaline conditions (0.5 M NaOH at 50 °C), was strategically optimized for morphology control rather than maximum recovery. Although harsh extraction conditions can achieve near-theoretical yields, our previous research demonstrated that such severe

treatments lead to the co-dissolution of impurities, which subsequently causes the formation of irregularly shaped particles [3]. By employing milder conditions, we achieved an extraction yield of 47.7%. While lower in quantity, this selective extraction was essential to obtain a high-purity sodium silicate precursor free from interfering species. Consequently, the silica synthesized in this study achieved three key advantages simultaneously: high purity (99.7%), uniform spherical morphology, and controlled particle size in the micrometer range. These characteristics provide competitiveness in application fields such as cosmetic additives and functional fillers, where particle size, morphology, and purity directly influence product performance. Nevertheless, several limitations remain in the present study. First, the quantitative analysis of the pore structure of the synthesized silica was limited, and further investigation is required to evaluate the stability and durability of the porous framework under practical application conditions. In addition, although the proposed synthesis process showed good reproducibility at the laboratory scale, its scalability to large-scale production has not yet been assessed. Specifically, transitioning the 35.5 h aging period to larger scales may present challenges, as maintaining thermal uniformity across the entire volume under static conditions is difficult. Spatial thermal gradients or particle sedimentation in large reactors could compromise the Ostwald ripening kinetics and particle monodispersity. Furthermore, a systematic investigation of the interactions among key reaction parameters (e.g., temperature, pH, and additive concentration) is necessary to achieve more precise control over particle size and pore structure. Therefore, future studies should focus on (1) evaluating the structural stability of mesopores, (2) optimizing the synthesis process for scale-up through enhanced reactor designs that ensure consistent thermal and chemical environments, and (3) validating the functional performance of the material under relevant application conditions. These efforts will further support the industrial applicability of the high-purity, uniform, spherical, and porous silica developed in this study.

Conclusion

This study developed a simple synthesis route to produce uniform spherical microsilica from rice husk-derived silica. Systematic investigation of key parameters revealed that aging time is the most critical factor governing spheronization, with effective spherical particle formation occurring within a narrow time window around 35.5 h. Under optimized conditions, the synthesized silica exhibited high purity (99.7%), uniform spherical morphology, microscale particle size, and an amorphous porous structure. In addition, comparison with silica synthesized from commercial sodium silicate showed comparable particle morphology and structural characteristics, supporting the feasibility of using rice

husk-derived sodium silicate as an alternative precursor for microsilica synthesis. These results demonstrate the potential of rice husk as a sustainable resource for producing high-quality microsilica suitable for morphology- and purity-sensitive applications.

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