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Original Article

Synthesis of spherical silica nanoparticles through Sol-Gel method with controllable size for water repellent applications

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ABSTRACT

Functional materials propose various unique characteristics for industrial applications and human life. The popular functional surface can be seen as anti-reflective, anti-biofouling, anti-icing, water collection, etc., that can not be found on the initial materials. In this work, we propose a facile method to synthesize the SiO_2 particles with the desired size by controlling the temperature and concentration of elements including ethanol, Isopropyl Alcohol (IPA), and tetraethyl orthosilicate. After collecting, the SiO_2 nanoparticles exhibit the perfect spherical shape with uniform sizes ranging from 200 to 400 nm depending on the setting condition. In addition, functionalized SiO_2 can be incorporated with a water-repellent chemical compound to conveniently spray on a common surface and illustrate the ultra hydrophobicity. This can be explained by the low surface energy given by nanoparticles' roughness and a chemical coating layer, which is inspired by the rose leaf and lotus leaf structure. The measurement of wettability shows outstanding performance compared to the as-received substrates, demonstrating the potential for further investigations.

Keywords: Silica particles, coating, controllable size, water repellency

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INTRODUCTION

Silica-based materials have demonstrated numerous applications and have been widely used in catalysts, multimodal imaging, electronics, photonics, biosensors, medicine, agent delivery, and drug discovery.[1-7] The mesoporous silica particles-related products can be easily found in coatings manufacturing, chromatography, biotechnology, cultural heritage restoration, energy conservation, and environmental fields in innovative technology generation.[5-9] The nucleation, growth, and finalization are controlled through an appropriate combination of relevant factors such as chemical concentration, temperature, and time reaction… for synthesizing fine-tuned particle shapes and sizes.[10] Furthermore, the silica-based coating also has proposed great potential for application owing to its transparency.[11] The roughness of SiO_2 particles presenting on the surface might enhance the hydrophobicity for anti-icing applications,[12,13] water repellency, or slippery liquid-infused porous surfaces.[14]

Among the convenient chemical fabrication method, Sol-gel proposes a simple, homogeneous, facile, and economical approach for the collection of silica particles.[1,4,7-10,15] The "Sol-Gel" term has been first proposed by Graham in 1864 when he fabricated SiO_2 particles from the silica solution.[16] In 1915, Patrick *et al.* have developed an economic and rapid Sol-gel routine to collect silica gel from sodium silicate (Na_2SiO_3).[17] The preponderance of the Sol-gel method is given by the complex chemical compositions including organic ligands and networks, where silica precursors are dissolved to form the amorphous siloxane bonds networks. The advantages of the sol-gel methods in silica particle formation have been discussed in Zulfiqar's work when he synthesized silica nanoparticles from sodium silicate solution in alkaline conditions.[18] The results illustrated the inverse correlation between silica nanoparticles' size and pH variables. Other works also have been introduced by Isobe *et al.* when they tried to synthesize the porous silica particles from spray-dried sodium silicate solution and demonstrated the importance of pH for the morphology of SiO_2 particles. In the other work, Rao and Ismail reported that the growth of SiO_2 nuclei strongly depended on the pH and alcohol solvent owing to the effects of nuclei production during the reaction of silica particles and

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enhancing the solubility for better uniformity of SiO_2 nuclei. By modulation of the alcohol solvents, the smallest and most uniform silica nanoparticles were found when using a methanol solution and increased significantly when using the longer alcohol chain such as ethanol or propanol.

Here, we have emphasized a facile and homogeneous approach to fabricating the silica particle with controllable size. By approaching the precise process of particle formation by tuning the reaction kinetics and additional variables such as temperature and tetraethyl orthosilicate (TEOS) concentration. Our approach is also bio-friendly as the ultra-low concentration of sodium is present in the system with minimal hazardous waste.

EXPERIMENTAL SECTION

The initial mixture consists of 40 mL Butanol-2 (C_4H_9OH), 40 mL Ethanol (CH_3CH_2OH), 3 mL Tetraethoxysilane ($Si(C_2H_5O)_4$) (abbreviated as TEOS), and 9 mL ammonia NH_4OH (40 wt.–%NH_3) (Merck KGaA, USA). The above mixture was stirred for 120 min (to ensure that TEOS in the mixture will be completely reacted), then 3ml of TEOS will be injected and continued stirring for another 120 min. Finally, the mentioned routine will be repeated one more time before cleaning and centrifugation. The fabrication process is described in Figure 1.

The wettability of spray-coated surfaces is investigated using a contact angle measurement system (Kyowa Co, Ltd, Japan).

RESULTS AND DISCUSSION

Quantitatively, the initial mixed solution after stirring for about 15 min gradually changed from clear to blue color and finally to opalescent. This can be explained by the Rayleigh scattering law of Tindal scattering: when particles are formed, the light passing through the solution is scattered strongly, so the solution gradually turns blue. Initially, the particle size is small, and the scattered light intensity is inversely proportional to the 4th power of the light wavelength. On the opposite side, the scattered light intensity irradiance is inversely proportional to the second power of the wavelength of light when the particles have a large size, which might be comparable to the light wavelength. Through scanning electron microscope (SEM) imaging results of SiO_2 spheres, we found the importance of the initial concentration of TEOS, NH_3, and H_2O in the mixture, which is 0.12 M, 0.94, and 2.65 M, respectively.

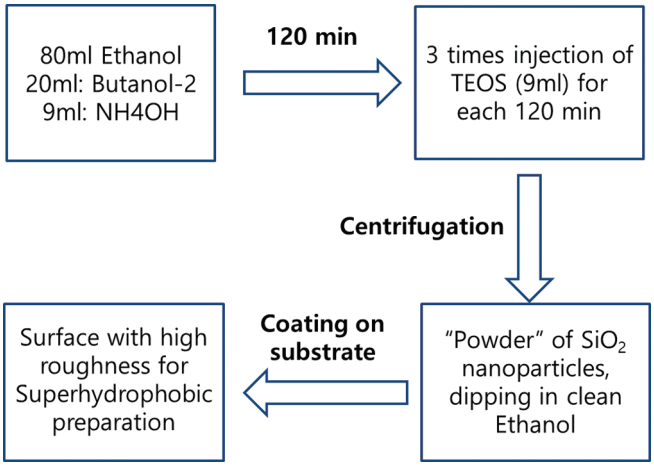

Figure 1: The schematic of the fabrication process

The particle size showed a strong dependence on the stirring time. After 120 min, the particles are ~270 nm in diameter, demonstrating that TEOS has fully reacted and achieved the maximum (the size did not increase after stirring for another 60 min). Hence, 3 mL of TEOS was added and continued stirring for 120 min. The particle diameter reaches ~360 nm after the second time injection. The TEOS residual also was tested by continuing stirring for additional 60 min and checking the STEM images. The third time injection was assigned after 120 min and continued for the last 120 min. The particle diameter reaches ~400 nm with an absolute spherical shape [Figure 2a-c]. The additional stirring overnight (about 16 h) illustrated the same particle size owing to the completed reaction of TEOS. For the investigation of Butano l-2, Ethanol, and NH_3OH, we added another 3 mL of TEOS and continued stirring for 120 min. The SEM revealed the maintenance of particle size, indicating that the amount of water contained in the solution had completely participated in the reaction.

To investigate the further growth of the particles, we repeated the above procedure, but 18 mL of TEOS and 2.3 mL of NH_4OH were added and followed by stirring for 120 min. The particle size was found of ~405 nm in diameter. The additional injection of TEOS (3 mL) and NH_4OH (2.3 mL) increase trivially to around 415 nm in diameter. This procedure is repeated a few times, and the obtained results were maintained, indicating the hypothesis. The qualitative investigation can be expressed through uniformity and concentration. The estimated particle size standard deviation is <~5%, demonstrating the amount of water participating in the reaction is the proportion to water contained in NH_4OH (25 wt.- %NH3) in comparison.

The additional experiment with the same procedure but without using butanol-2 and replacing it with the corresponding amount of ethanol. Results revealed a relatively wide distribution of synthesized SiO_2 sphere sizes ranging from 250 nm to 300 nm, including the slightly distorted particles. This illustrated the important role of butanol-2 when in determining the uniformity of the particles and making them more spherical and smooth.

For oriented applications such as windshields, car shields, or self-cleaning devices, the fabricated SiO_2 particles were spray

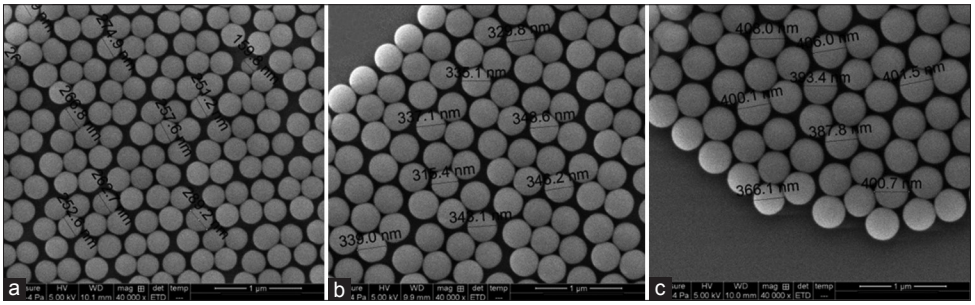

Figure 2: Size dependence of SiO_2 nanoparticles on tetraethyl orthosilicate concentration. Scanning electron microscope images measurement after one-time injection (a), two times (b), and three times (c)

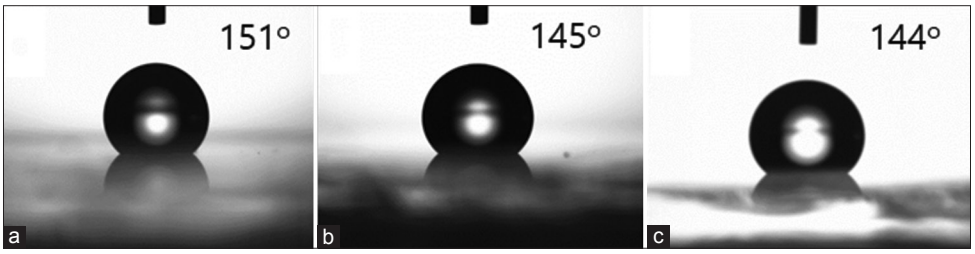

Figure 3: Surface wettability after coating with SiO_2 nanoparticles with 270 nm (a), 330 nm (b), and 400 nm (c)

Table 1: Wettability measurement on SiO_2-coated surface

Sample	Contact angle	Sliding angle
M-270	151±1	2±0.5
M-330	145±2	5±2
M-400	144±2	6±1.5

coated on aluminum plates to enhance the surface roughness. After coating, the surface was functionalized by dipping in perfluoropolyether solution for 60 min and followed by drying in the ambient air for another 60 min. The wettability of surfaces after coating was investigated by measuring the contact angle [Figure 3 and Table 1].

Figure 3 describes the wettability on the surface with different sizes of nanoparticles coating and shows the dependence of wettability on surface morphology. It is worth noting that the amount of SiO_2 particles was maintained for three sizes. The contact angle reaches the superhydrophobic state at 270 nm coating surface and can be explained by the fine surface roughness constructed by smaller particles. In addition, the sliding measurement conducted on surfaces illustrates the high mobility of superhydrophobic surfaces and demonstrates the high potential for outdoor applications.

CONCLUSION

In this work, we have obtained the process of synthesizing fine SiO_2 spheres with a wide diameter ranging from 280 nm to 400 nm in a short routine. The results exhibited the important role of TEOS concentration in determining the size of SiO_2 particles, dominating the other factors. In addition, Butanol-2 describes a great effect on ensuring a spherical shape for nanoparticles. To be able to apply for outdoor applications, the SiO_2 particles were sprayed coated on the surface and illustrated the high water-repellent property, demonstrating the potential for commercial products.

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