Study on de-agglomeration of the silica microsphere

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Abstract: Silica microspheres are easily agglomerated in anhydrous and aqueous media, which would seriously affect the properties and correlative studies of these particles. In order to effectively investigate and improve the characteristics of silica microspheres, the de-aggregation technology is indispensable. Through analysis of the mechanism of this aggregation phenomenon, a method was proposed to de-agglomerate the large-scale-agglomerated silica particles by ten steps. Experimental results observed by Nikon microscopy indicate that this method could greatly improve the dispersity and stability of the particles.

Key words: silica microsphere; anhydrous and aqueous media; agglomeration; de-agglomeration

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二氧化硅微球颗粒解团聚研究

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摘 要: 二氧化硅微球颗粒在无水和水相介质中都极易发生团聚现象，进而严重影响该颗粒的特性研究。为了更好地使用和研究二氧化硅微球颗粒,需要进行解团聚工艺研究。实验研究了不同尺度的颗粒的团聚特性和现象,提出了一种工艺,该工艺方法可以很好地实现大团聚的二氧化硅微球颗粒的解团聚。经过尼康显微镜观察,显示该工艺不仅很好地完成了二氧化硅微球的解团聚,而且提高了颗粒的分散性和稳定性。

关键词: 二氧化硅微球； 无水和水相介质； 团聚； 解团聚

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0 Introduction

Micro -particles have many unique properties, such as small size effect, surface and boundary effect, quantum size effect and special optical-electrical effect, high reluctance phenomenon and nonlinear resistance phenomenon, which is the reason they are widely used in the field of optical and electrical information[1-2]. Among these micro-particles, silica microsphere is a significant category which finds increasing applications in biomedical engineering, material engineering, and industrial engineering. Silica microspheres have consistent size and can be fabricated into a colloid crystal according to FCC mode[3-4]. There is about 26% interstitial space between every two particles, which allows silica microspheres to be mixed with various filling substrates to fabricate special materials such as photonic crystal[5-10]. However silica microspheres belong to the unstable thermodynamic system and they intend to be agglomerated into a large scale with several connection interphases. One cause of this phenomenon is that micron or nano -sized particles are easily agglomerated by the Van der Waals force and Coulomb force among them and difficult to be seperated[11-12]. The conventional dry preservation will exacerbate the agglomeration. Long term agglomeration will likely change the properties of the particles and forms secondary particles, which will reduce the advantages and applications of the particles. For example, because of their small size effect, surface and boundary effect, in microsphere nanoscope research, silica microspheres could be placed uniformly to form a self-assembly monolayer on the top of the object surface to generate magnified virtual images. But the agglomeration of silica microspheres would irreversibly squash and deform the particles, which makes them impossible to self-assemble in regular arrays[10-14]. Therefore, how to realize the de-agglomeration and maintain the stability of particles is the first essential issue for many frontier researches[15-19].

By studying existing de-agglomeration technologies of various particles, we proposed a novel concise and effective technology to disperse the large scale agglomeration. In this paper, we start with the discussion of the agglomeration and de-agglomeration mechanisms of various material particles. Micro-scale silica sphere is used as experimental material to study the dispersity and stability of microspheres in water and anhydrous alcohol by several methods such as sonic oscillation, centrifugation and spin. Then we report our new technology and provide the experimental result of de-agglomeration which shows improvement of the dispersity and stability of microsphere in anhydrous alcohol and air. This work would not only supply basic raw materials for optical imaging and photonic crystal, but also contribute to the future study of de-agglomeration of the nano-scale particles.

1 Mechanism of agglomeration and de-agglomeration

Since microspheres belong to the unstable thermodynamic system and they have special properties such as big relative proportion, numerous superficial atomicity, and insufficient atomic coordinate and high surface energy, they are extremely easy to reunite with each other and become some big reunion bodies with several connection interphases. These reunion bodies destroy the size distribution which may cause the massive agglomeration settling or phase separation[20-21]. These microspheres will lose their due physical properties and functions so that the aim of using them to improve the performance of material and the whole system could not be achieved.

The form of agglomeration can be mainly divided into soft-agglomeration and hard-agglomeration. The soft-agglomeration is due to the Van der Waals force (which is inversely proportional to the particle size) and the Coulomb force among particles. Because of these attractions, particles are likely to be agglutinated

and formed into secondary particles when they collide with each other in the process of Brownian motion. Although secondary particles have slower velocity than original single particles, they still have opportunities to collide with other particles and form larger reunions until they have to deposit because of the sufficient scale and weight[22]. The hard agglomeration is caused by not only Van der Waals force and Coulomb force but also the chemical bond action. It is generally recognized that the condensed matter formed by the agglutination of the connecting surfaces of the particles is the hard agglomeration and the cluster due to the fusion of points/angles of small particles or the agglomerate due to the adsorption from large particles to smaller particles or the flocculating constituent could be categorized into soft agglomeration[23]. The silica microsphere is a rigid, solid and teeny particle of irregular shape. There are many hydroxyl ions on the surface of the silica molecule which could create hydrogen bonds by interaction with water molecule. Thus microspheres are easily agglomerated by the hydrogen bonds and Van der Waals force and are prone to re-agglomerate after dispersion by external force[22].

Currently, common de-agglomeration methods include physical dispersion and chemical dispersion. The physical dispersion method is to change the crystal structure of the particle surface by mechanical stress, such as mechanical dispersion method and ultrasonic dispersion method, to retain the dynamic stability. The chemical dispersion method is to change the surface property of particles to produce the stronger repel force between the particle and liquid medium and among the particles. There are two ways to achieve the chemical stable state. One is to make the particles to carry the same electric charge so that they can repel each other. The other is to attach some substances such as polymer on the surface of particles to prevent them from getting close to each other[24].

Water is a regular dispersant. However, it is inadequate to complete the de-agglomeration of silica microspheres by merely using water because silica particle is hydrophilic and they will create chemical bond with water molecule which will lead to larger scale agglomeration. Recently, many research groups has improved the dispersion of microspheres in water by changing the particles′ surface property and the PH value of water through some technological approaches or adding other dispersants[25-31]. Huang Suping et al[28-29] enhanced the electrostatic force and the steric force and decreased the Van der Waals force among the silica particles to improve the powders′ dispersion in aqueous solution by using the hyper-dispersant PSE. They also studied the effect of the PH value and dispersant concentration on the particle′s surface electric potential and dispersal stability by using non-ionic hyper-dispersant YRC. Ren Jun et al [30] investigated different dispersion actions of different dispersant to different particles (silica, calcium carbonate, talc and graphite) in aqueous media. Yuan Yan et al [31]. verified that using anhydrous alcohol as the dispersant could effectively achieve the dispersion of the silica particles.

2 Experiment research and technology design

2.1 Experiment material and its characteristics

In this experiment, we used the silica microspheres with certified mean diameter of 2.0 μm± 0.4 μm from DUKE Company. The experiment sample was preserved in a brown glass vessel with desiccant and kept in a refrigerator away from light. The parameters of the standard particle are shown in Tab.1.

Tab.1 Parameters of the standard particle

Name	Value
Certified mean diameter/μm	2.0±0.4
Standard deviations/μm	0.6
Coefficient of variation	30%
Microsphere composition	Borosilicate glass
Microsphere density/g·cm^{-3}	2.50
Index of refractive/@589 nm	1.56

The sample was in agglomerated powdered form when it was kept in the vessel. Figure 1 shows the condition of the experiment sample in the vessel.

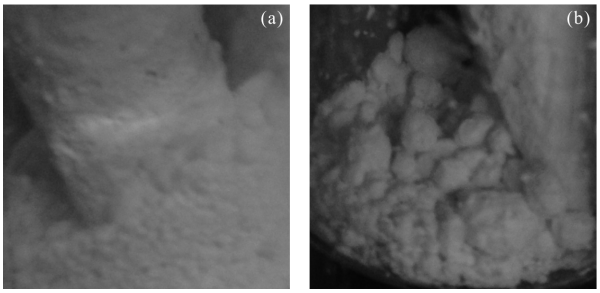

Fig.1 Hermetically preserved silica microspheres

We placed some of the silica particles into a sample bottle of ultrapure water. After mechanical stirring and longtime standing, a small amount of the mixture was placed on the glass slide by a micro-pipettor for observation. Under the microscopy the particles were found to become a major three dimensional agglomeration. Figure 2 shows the microscopic observation of the agglomeration.

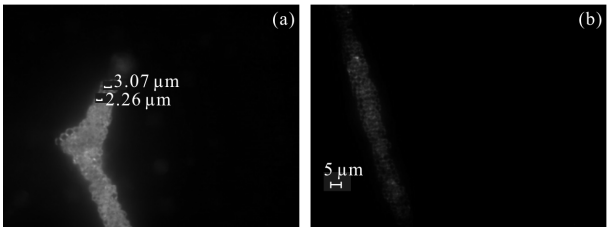

Fig.2 Condition of the silica microspheres in ultrapure water

Then we used the deionized water as dispersant and repeated the de-agglomeration operations for ten times. But the effect of de-agglomeration is not ideal. Figure 3 shows the effect of de-agglomeration after one operation. Figure 4 shows the effect of de-agglomeration after ten operations.

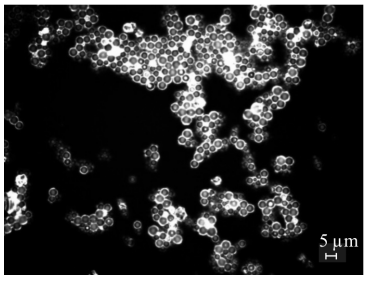

Fig.3 Effect of de-agglomeration after one operation using deionized water as dispersant

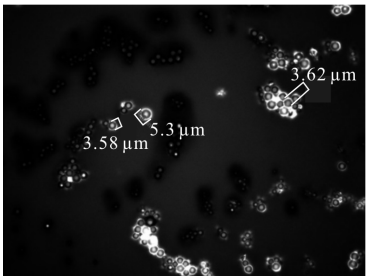

Fig.4 Effect of de-agglomeration after ten operations using deionized water as dispersant

These results show that the effect of de-agglomeration is barely satisfactory by merely using water as dispersant and mechanical stirring as operation. That is because silica particle is hydrophilic and they will create chemical bond with water molecule which will lead to larger scale agglomeration. In addition if water cannot be completely removed during the experiment, the O^{2-} of the silica molecule might be substituted by the OH^- of water molecule so that the physical property of the particles will change which might have significant influence on later application. To obtain perfect single silica particles, we need a new improved technology.

2.2 New de-agglomeration technology

During the transfer, dissolution, and preservation process, the micro-size particles are prone to be polluted by impurities or some large scale particles. Thus before the de-agglomeration experiment begins, it is important to clean the glass vessel, apparatus and other instruments by a brushless cleaning technology which is the ultrasonic vibration combined with chemical reaction.

Figure 5 shows the flowchart of the cleaningprocess. Figure 6 shows the flowchart of the secondary cleaning process. Neutral detergent is a surfactant which could help to mix the grease with water into a stable emulsion so that the grease would be dissolved.

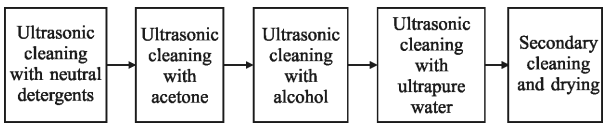

Fig.5 Flowchart of cleaning before de-agglomeration experiment

Acetone could further clean the residual grease. We used anhydrous alcohol to clean the acetone and used the ultrapure water to remove the anhydrous alcohol.

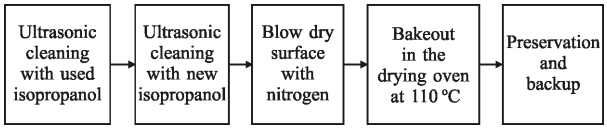

Fig.6 Flowchart of the secondary cleaning and drying technology

At the beginning of the de-agglomeration experiment, we used a glass drainage rod to extract the particles from the preservation vessel. When the spherical terminal of the glass drainage rod gently scraped the inner surface of the preservation vessel, some of the silica particle powder was adsorbed on the spherical terminal. This process must be carefully operated so as not to damage the shape or the property of the particles. Then we used deionized water to place these silica particles into a sample bottle. Around 1 to 2 mL extracted by a micropipette was dripped on the glass drainage rod and flowed into the sample bottle along the glass drainage rod. Thus the particle powder was dissolved in the deionized water and placed into the sample bottle without damage.

Then we added an appropriate amount of deionized water into the sample bottle and conducted the ultrasonic oscillation. Ultrasonic dispersion is an effective primary method to de-agglomerate the particles. The high pressure, high temperature, strong shock waves and micro-jets created by the ultrasonic cavitation could drastically weaken the interaction force among the particles. After that the sample bottle was put on the spin coater and centrifuged with medium spin velocity for about 3 minutes. This step aimed at using mechanical energy (i.e. centrifugal force) to fully disperse the particles in the medium. After 15 minutes standing, we carefully poured out about three quarters of the deionized water from the sample bottle. Then the bottle was put in the drying oven with low temperature to remove the remaining deionized water. Next we sequentially poured acetone, anhydrous alcohol, and isopropanol into the sample bottle. These additives mainly have two effects on the particles. One is that they could attach substances such as organic molecule on the surface of particles to prevent them from getting close to each other. The other is that these additives could hinder the hydrophilic particles′ absorption of water so that there would not be a complete water film on the particle surface to help them agglomerate with each other. Then we repeated the process of ultrasonic oscillation, centrifugal spin of medium speed, standing for 15 minutes, and low temperature drying. At last we added the anhydrous alcohol into the bottle, and repeated the same process of ultrasonic oscillation, centrifugal spin with low speed, and standing for 15 minutes again. Figure 7 shows the flowchart of the de-agglomeration method.

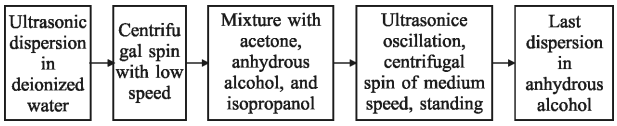

Fig.7 Flowchart of the de-agglomeration method

To observe the de-agglomeration result, we extracted about 100 μl from the sample bottle and dripped it on a clean glass slide by a micropipette. We placed the glass slide in a clean petri dish and dried it. By changing the magnification of microscopic objective lens, we could observe the dispersed particles. Figure 8 shows the effect of de-agglomeration.

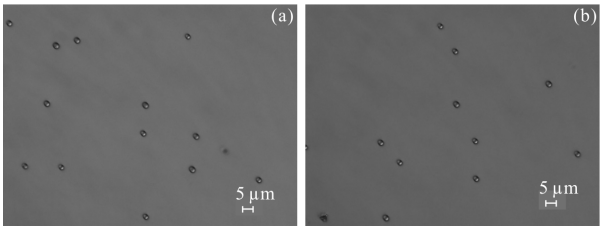

Fig.8 Effect of de-agglomeration

By this improved technology, we obtained dispersed silica microspheres. The preservation of these microspheres could simply conducted by placing them in acetone hermetically away from light. The

dispersion as well as other physical and chemical properties of the particles would be well preserved. Even if agglomeration happens again during long period preservation, we can repeat the ultrasonic oscillation, medium speed centrifugal spin, and the drying operation, then conduct the oscillation and low speed spin with anhydrous alcohol, and dry the sample for later use.

2.3 Experiment result analysis

According to experimental demonstration, we found using deionized water as the only dispersant cannot complete the de-agglomeration of the silica microspheres. In comparison, our new technology could not only obtain dried and uncontaminated silica microspheres, but also allow long time preservation of them by putting them into the acetone solution. Even if agglomeration occurs again, we can use this de-agglomeration technology to solve the problem.

3 Conclusion

In summary, we proposed a novel approach to de-agglomerate the large scale agglomeration of silica microspheres. We studied the agglomeration and de-agglomeration mechanism of various particles, and used the micron size silica microsphere as the experimental material to investigate the dispersion of microspheres in water. By the technology of ultrasonic oscillation and centrifugal spin, we achieved the satisfactory result of de-agglomeration and improved the stability of the microspheres. The stable dispersed silica particles can be preserved for long term. In contrast to other de-agglomeration research, our method is more concise and operable for every laboratory or factory. This work not only provides raw material for correlation experiment, but also contributes to the future study of de-agglomeration of other material particles of various sizes.

References:

[1] Liu Jingchun, Han Jiancheng. Application of the cross century high-tech materials of nano SiO_2[J]. ***The New Type Material of Chemistry Engineering***, 1998, 7: 3-6.

[2] Novotny V. Application of nonaqueous colloids [J]. ***Colloids and Surfaces***, 1987, 24: 361-364.

[3] Blanco A, Chomski E, Grabtchak S, et al. Large-scale synthesis of a silicon photonic crystal with a complete three-dimensional band gap near 1.5 micrometers[J]. ***Nature***, 2000, 405(6785): 437-440.

[4] Schroden R C, A1-Daous M, Blanford C F, et al. Optical properties of inverse opal photonic crystals [J]. ***Chemistry of Materialsl***, 2002, 14(8): 3305-3315.

[5] Jiang P, Bertone J F, Colvin V L. A lost-wax approach to monodisperse colloids and their crystals [J]. ***Science***, 2001, 291(5503): 453-457.

[6] Velev O D, Jede T A, Lobo R F, et al. Porous silica via colloidal crystallization[J]. ***Nature***, 1997, 389(6650): 447-448.

[7] Brain T Holland, Christopher F BLanford, Andreas Stein. synthesis of macroporous minerals with highly ordered three-dimensional arrays of spheroidal voids[J]. ***Science***, 1998, 281 (5376): 538-540.

[8] Velev O D, Tessier P M, Lenhoff A M, et al. Materials: A class of porous metallic nanostructures[J]. ***Nature***, 1999, 401 (6753): 548.

[9] Li Zhiyuan, Zhang Zhaoqing. Fragility of photonic band gaps in inverse-opal photonic crystals[J]. ***Phys Rev: B***, 2000, 62: 1516-1519.

[10] Wang Zengbo, Guo Wei, Li Lin, et al. Optical virtual imaging at 50 nm lateral resolution with a white-light nanoscope[J]. ***Nat Comm***, 2011, 2: 218-223.

[11] George M Whitesides, Bartosz Grzybowski. Self-assembly at all scales[J]. ***Science***, 2002, 295: 2418-2421.

[12] Mackay Michael E, Tuteja Anish, Duxbury Phillip M, et al. General strategies for nanoparticle dispersion [J]. ***Science***, 2006, 311: 1740-1743.

[13] Lee B I, Rives J P. Dispersion of alumina powders in nonaqueous media [J]. ***Colloids and Surfaces***, 1991, 56: 25-27.

[14] Lange F F. Powders processing science and technology for increased reliability [J]. ***J Am Geram Soc***, 1989, 72 (1): 3-15.

[15] Norris D J, Arlinghaus E G. Opaline photonic crystals: how does self-Assembly work [J]. ***Advance Materials***, 2004, 16: 1393-1399.

[16] Chen L, Dong P. Diffusion coefficient of petroleum residue fractions in a SiO_2 model catalyst [J]. ***Ind Eng Chem Res***,

2009, 23(6): 2862-2866.

[17] Hao Xiang, Kuang Cuifang, Li Yanghui. Hydrophilic microsphere based microscopic-lens microscope [J]. ***Opt Commun***, 2012, 285: 4130-4133.

[18] Kuang Cuifang, Liu Yong, Hao Xiang, et al. Creating attoliter detection volume by microsphere photonic nanojet and fluorescence depletion [J]. ***Opt Commun***, 2012 285: 402-406.

[19] Ku Yulong, Kuang Cuifang, Hao Xiang, et al. Superenhanced three-dimensional confinement of light by compound metal-dielectric microspheres [J]. ***Opt Express***, 2012, 20 (15): 16981-16991.

[20] Yokoyma T, Huang C C. Nanoparticle technology for the production of functional materials [J]. ***KONA, Powder and Particle***, 2005, 23: 7-17.

[21] Michael E Mackay, Anish Tuteja, Phillip M Duxbury, et al. General strategies for nanoparticle dispersion [J]. ***Science***, 2006, 311(5768): 1740-1743.

[22] Zhu Y P, Xu L L, Li C F. Research progress of nanoparticle agglomeration [J]. ***Journal of Tianjin Medical University***, 2006, 11(2): 338-341.

[23] Pampuch R, Haberko K. Agglomerate in Ceramic Micropowders and their Behaviour on Cold Pressing and Sintering [M]. Amsterdam: Elsevier Scientific Publishing Company, 1983, 16: 623-634.

[24] Kim J U, O′Shaughnessy B. Morphology selection of nanoparticle dispersions by polymer media[J]. ***Phys Rev Lett***, 2002, 89(23): 238301-1-238301-4.

[25] Cui H M, Liu H, Wang J Y, et al. Agglomeration and disperasion of nano-scale powders [J]. ***Materials for Mechanical Engineering***, 2004, 28(8): 38-41.

[26] Li Z H, Li F Q, Ma P H. Elimination methods and mechanism of agglomeration of ultrafine powders[J]. ***Journal of Salt Lake Research***, 2005, 13(1): 31-36.

[27] Lei L, Lu N N, Wu M H, et al. De-aggregation of nano-TiO_2 soft agglomeration in aqueous medium [J]. ***CIESC Journal***, 2009, 60(12): 3159-3163.

[28] Huang Suping, Zhang Qingcen. Dispersion mechanism of ultrafine silica [J]. ***The Chinese Journal of Nonferrous Metals***, 2001, 11(3): 522-526.

[29] Zhang Qingcen, Huang Suping. Effect of non-ionic dispersants on the stability of colloidal silica [J]. ***Multipurpose Utilization of Mineral Resources***, 2001, 4: 15-18.

[30] Ren J, Lu S C. Effect of dispersion of dispersant on particles in water media [J]. ***Journal of University of Science and Technology Beijing***, 1998, 20(1): 7-10.

[31] Yuan Yan, Zhang Rui, Qi Dongming, et al. Deaggregation behavior in the dispersion process of silica soft aggregation into ethanol media [J]. ***Journal of Zhejiang Sci-Tech University***, 2011, 28(4): 485-489.