Parameterization of SiO₂ Nanoparticles Preparation Route and Evaluation of the Reaction Parameters Using Fuzzy Mathematics

Hongyun Zhao¹, Lixia Qin¹*, Xiangqing Li¹, Yuxiang Yang², Hanmin Xiao³ and Shi-Zhao Kang¹*

¹School of Chemical and Environmental Engineering, Center of Graphene Research, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China
²Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
³Department of Porous Flow & Fluid Mechanics, Research Institute of Petroleum Exploration & Development, Petrochina, 20 Xueyuan Road, Beijing 100083, China

*Corresponding author e-mail: kangsz@sit.edu.cn and lxqin@sit.edu.cn

Abstract. In this work, SiO₂ nanoparticles were prepared via hydrolysis method, chemical precipitation method and sol-gel method, respectively. And the effects of various experimental conditions on the unit output, yield, particle size and size distribution of SiO₂ nanoparticles were studied and parameterized. Meanwhile, a set of evaluation systems were constructed with fuzzy mathematical analysis and modeling which the complex data can be evaluated systematically with concise and precise unity. The results indicate that Si and Na₂SiO₃ are suitable raw materials for the industrial production of 20 nm and 60 nm SiO₂ nanoparticles and the maximum weighted average can reach the high level of 81.3 and 82.95, respectively. Also, SiO₂ nanoparticles with 250 nm ought to be prepared using TEOS as the raw material, and its maximum weighted average is 85. Moreover, the results also show that the order of the effects of the factors in hydrolysis is the dosage of sodium silicate > the amount of silica powder > the reaction time. For the chemical precipitation method, the order is the pH value > the reaction time > the reaction concentration. For the sol-gel method, the order is the amount of ammonia water > TEOS consumption > the reaction time.

1. Introduction
In recent years, nanotechnology has become a common focus and frontier in many fields [1]. Among them, nanosilica (SiO₂) is favoured by researchers and widely used because of its high stability, low toxicity and by simple preparation method [2]. However, considering the costly silica sources and high energy consumption, the development of environmentally friendly synthesis techniques and the use of inexpensive raw materials remain a research hotspot [3]. At present, various methods are used for the synthesis of SiO₂ nanoparticles [4]. Unfortunately, the main focus was to control the particle size, particle surface reactivity and morphology [5,6]. Up to now, there are few reports about the effects of various factors on the large-scale production of SiO₂.

In this work, the chemical precipitation method, hydrolysis method and sol-gel method was chosen to prepare SiO₂, in that they are simple and controlled. In order to make the experiment closer to
actual industrial production, the fuzzy mathematical method were used to integrate the multiple indicators, such as specific yield, output, and grain size, and also a simple mathematical model as an experimental evaluation benchmark are employed. The influence degree of different experimental factors on product quality was analyzed through the calculation of coefficient of variation between data and model.

2. Experimental

2.1. Preparation of nanosilica by chemical precipitation method
The synthesis process is described as follows: a certain amount of sodium metasilicate pentahydrate was configured it into 300 mL sodium silicate solution, then the dilute hydrochloric acid ($V_{HCl}$: $V_{H_2O}$=1:2) was slowly added to adjust pH to 9 and stir for 2 h. The white precipitate was obtained through centrifugation and washed with deionized water five times. After dried in a 60 °C oven for 8 h, the sample was ground to a powder, and then baked in a 600 °C for 1.5 h. The obtained samples were marked as Na$_2$SiO$_3$-SiO$_2$.

2.2. Preparation of nanosilica from elemental silicon
Firstly, 12 g of silicon powder was added into a 500 mL three-necked flask containing 200 mL water under stirring. Next, the mixture was heated at 60 °C for 0.5 h to activate silicon. Then, 1.2 g of sodium hydroxide and 0.25 g of sodium silicate were added followed by stirring the mixture for 1 h. After 8 g of silicon powder was added into the above solution, the mixture was stirred for 1 h, another 8 g of silicon powder was added. Immediately, the solution was heated to 90 °C and kept for 6 h. A large amount of NaCl was added into the silica sol obtained to prepared SiO$_2$ nanoparticles. Finally, the sample was washed with ethanol/H$_2$O (1:2). After dried in a 60 °C oven for 8 h, the solid obtained was ground and baked in a 600 °C for 1.5 h. The obtained samples were marked as Si-SiO$_2$.

2.3. Preparation of nanosilica in a sol-gel process
5 mL of ethyl orthosilicate (TEOS) was added into 75 mL of absolute ethanol and stirred for 15 min. Then, 10 mL of ammonium hydroxide was mixed with 10 mL of deionized water, and slowly added dropwise to a mixed solution of ethanol and TEOS at room temperature. After the reaction stirred for 7 h, the mixture is centrifuged several times. The resulting white substance is placed in a 60 °C and dried for 8 h. The obtained samples were marked as TEOS-SiO$_2$.

3. Result and discussion

3.1. characterization
Fig. 1 (A1, A2, A3) shows the SEM images of Si-SiO$_2$. It can be seen that the obtained SiO$_2$ is almost spherical, and the particle size distribution is wide and the particle size is about 10 ~ 30 nm. Specifically, the results indicate that there are no obvious changes of the size and morphology in SiO$_2$ obtained using Si as raw material. From Fig. 1 (B1, B2, B3), it can be found that Na$_2$SiO$_3$-SiO$_2$ has an irregular structure, and the particle size is not uniform which is in the range of about 10 ~ 70 nm. Moreover, it can be found that small and irregular SiO$_2$ nanoparticles are obtained under the week acid conditions. As illustrated in Fig. 1 (C1, C2, C3), we can see that the shape of TEOS-SiO$_2$ is almost spherical, and the size is uniform (90 ~ 358 nm). And the size of SiO$_2$ increases significantly with the increasing the concentration of TEOS or NH$_3$$\cdot$H$_2$O, indicating that the concentrations of TEOS and NH$_3$$\cdot$H$_2$O play important roles in the formation of SiO$_2$ nanoparticles using TEOS as raw material.

Fig. 2A shows the Fourier transform infrared (FT-IR) spectra of TEOS-SiO$_2$, Si-SiO$_2$ and Na$_2$SiO$_3$-SiO$_2$. Clearly, the characteristic bands at 800 cm$^{-1}$ (a), 798 cm$^{-1}$ (b) and 796 cm$^{-1}$ (c) assigned to the stretching vibration of Si-O were observed obviously, indicated that the SiO$_2$ samples were obtained by different three methods [7]. Also, the structures of Na$_2$SiO$_3$-SiO$_2$, Si-SiO$_2$ and TEOS-SiO$_2$ were characterized by XRD (Fig. 2B). From Fig. 2B, the amorphous peak around 2θ =21.5° were observed for Na$_2$SiO$_3$-SiO$_2$ and Si-SiO$_2$, while the amorphous peak appears at 2θ =22.9° for TEOS-SiO$_2$. One possible explanation is that high temperature treatment will cause the Bragg Angle of SiO$_2$
to move in a lower direction [8]. Thus, it can be concluded that there are some differences in the structure of SiO₂ obtained with various methods besides in morphology.

Figure 1. SEM images of Si-SiO₂, (A₁): t 6 h, Si 28 g, Na₂SiO₃ 0.25 g; (A₂): t 6 h, Si 42 g, Na₂SiO₃ 1 g; (A₃): t 0.5 h, Si 28 g, Na₂SiO₃ 0.25 g. SEM images of Na₂SiO₃-SiO₂, (B₁): t 2 h, Na₂SiO₃ 0.3 mol/L, pH 6; (B₂): t 2 h, Na₂SiO₃ 0.3 mol/L, pH 9; (B₃): t 12 h, Na₂SiO₃ 0.9 mol/L, pH 9. SEM images of TEOS-SiO₂, (C₁): t 7 h, TEOS 0.0053 mol/L, NH₃·H₂O 1.58 mol/L; (C₂): t 7 h, TEOS 0.25 mol/L, NH₃·H₂O 1.58 mol/L; (C₃): t 7 h, TEOS 0.25 mol/L, NH₃·H₂O 6.56 mol/L.

Figure 2. (A) FT-IR spectra of (a) TEOS-SiO₂, (b) Si-SiO₂ and (c) Na₂SiO₃-SiO₂; (B) X-ray powder (XRD) patterns of (a) Na₂SiO₃-SiO₂, (b) Si-SiO₂ and (c) TEOS-SiO₂.

3.2. Analysis of experimental factors
An evaluation system was established using fuzzy mathematics comprehensive analysis method, and the specific process is as follows: firstly, the four kinds of experimental data including unit yield, yield, average size, and size distribution were selected, and the different weighting coefficients were given. Secondly, the different evaluation indexes are constructed around four kinds of data, and corresponding scores are obtained according to the data changes. Finally, the weighted average is calculated and the overall analysis is made according to the total score [9-11].

Firstly, the weighted coefficient of 0.3 (a = 0.3) was served as the criteria of per unit of production, and 10% of the theoretical yield as the established evaluation index was performed to obtain the corresponding scores. As shown in Table 1, “m” represents the actual unit output and n represents the output of the theoretical unit. Secondly, the weighted coefficient of 0.2 (a = 0.2) was used as the evaluation index of production rate, use. In order to distinguish between productive rate and unit yield results, the productive rate was multiplied by 100 to obtain the corresponding score (v represents the productivity), which could make the data in the same order of magnitude, to calculate the weighted average easily. Thirdly, we set the weighted coefficient of average size of 0.3 (a = 0.3) as the rating scale of size. According to the formula $D = \left| R - r / R \right|$, the different grades are obtained on the basis of the different D values (Table 1), R and r represent the ideal size and the actual size, respectively (Rₜₜ-SiO₂=20 nm, Rₜₙₐ₂SiO₃-SiO₂=60 nm, Rₜ_tEOS-SiO₂=250 nm).
Finally, the grading standard of particles uniformity was established, and the weight was set to 0.2 (a=0.2). Firstly, 100 particle measurements were selected from the magnification of 6,000 times, and the particle size distribution are roughly in line with normal distribution [12]. Thus, the half peak width of the curve peak is chosen to reflect the uniform degree of the size. The specific scoring criteria are shown in Table 1, “L” represents the half peak width.

Table 1. Comprehensive indicator assessment table.

| m (g)         | Score | D         | Score | L (nm)       | Score |
|--------------|-------|-----------|-------|--------------|-------|
| 0 ≤ m < 0.1 n| 10    | 1.0 ≤ D   | 0     | 1.0 R ≤ L    | 0     |
| 0.1 n ≤ m < 0.2 n| 20    | 0.9 ≤ D < 1.0 | 10 | 0.9 R ≤ L < 1.0 R | 10 |
| 0.2 n ≤ m < 0.3 n| 30    | 0.8 ≤ D < 0.9 | 20 | 0.8 R ≤ L < 0.9 R | 20 |
| 0.3 n ≤ m < 0.4 n| 40    | 0.7 ≤ D < 0.8 | 30 | 0.7 R ≤ L < 0.8 R | 30 |
| 0.4 n ≤ m < 0.5 n| 50    | 0.6 ≤ D < 0.7 | 40 | 0.6 R ≤ L < 0.7 R | 40 |
| 0.5 n ≤ m < 0.6 n| 60    | 0.5 ≤ D < 0.6 | 50 | 0.5 R ≤ L < 0.6 R | 50 |
| 0.6 n ≤ m < 0.7 n| 70    | 0.4 ≤ D < 0.5 | 60 | 0.4 R ≤ L < 0.5 R | 60 |
| 0.7 n ≤ m < 0.8 n| 80    | 0.3 ≤ D < 0.4 | 70 | 0.3 R ≤ L < 0.4 R | 70 |
| 0.8 n ≤ m < 0.9 n| 90    | 0.2 ≤ D < 0.3 | 80 | 0.2 R ≤ L < 0.3 R | 80 |
| 0.9 n ≤ m < n   | 100   | 0.1 ≤ D < 0.2 | 90 | 0.1 R ≤ L < 0.2 R | 90 |
|            | 0 ≤ D ≤ 0.1 | 100     | 0.0 R ≤ L ≤ 0.1 | 100 |

3.2.1. Si-SiO₂. The weighted average (Fig. 3A) is calculated according to the variation of unit yield (m), yield (v), average size (r), and size distribution (L) by changing the dosage of silica powder. As can be seen from Fig. 3A, the weighted average is the largest when the amount of silica powder is 7 g. With the amount of silica powder increasing from 7 g ~ 49 g, the weighted average decreased gradually. It should be noted that the lower amount of consumption and the corresponding high production cost is not conducive to actual production. When the amount of silica powder was 63 g, the weighted average was 0. Therefore, according to the actual production requirements, the optimum dosage of silica powder is 28 g.

In order to investigate the effect of active acid monomer on product preparation, the weighted average was evaluated (Fig. 3B) by changing the dosage of sodium silicate. As can be seen from Fig. 3B, the addition of a small amount of sodium silicate can increase the weighted average obviously (0.05 ~ 0.5 g). And when the sodium silicate dose is 0.25 g, the weighted average reaches the maximum. With the amount of sodium silicate further increasing, the weighted average decreases dramatically. Thus, we can conclude that the optimum dosage of sodium silicate is in the range of 0.05 ~ 0.5 g for practical application.

As can be seen from Fig. 3C, the weighted average increases significantly when the reaction time is 0 ~ 0.5 h. Next, the weighted average is basically stable between 75 and 80 when the reaction time is in the range of 0.5 ~ 6 h. As the reaction time is 8 ~ 12 h, the weighted average decreased slightly and was stabilized around 72. So, the optimal reaction time should be controlled within 4 ~ 6 h.
3.2.2. $Na_2SiO_3$-$SiO_2$. Firstly, the variation of weighted average with change of pH value was studied, as shown in Fig. 4A. Clearly, when pH is 2 ~ 5, the weighted average decreased gradually (from 75 to 55). As pH is in the range of 6 ~ 9, the weighted average increased gradually. And when pH is 9, the weighted average reaches the maximum. However, when the pH value is greater than 9, the weighted average decreased dramatically. Thus, the optimal pH value is 9.

![Figure 3](image1)

Figure 3. (A) The variation of the weighted average with the change of the silica powder amount ($Na_2SiO_3$ 1 g, NaOH 1.2 g, T 90 °C, t 6 h). (B) the variation of the weighted average by the change amount of sodium silicate (Si 28 g, T 90 °C, t 6 h). (C) the variation of the weighted average by the change of reaction time (Si 28 g, $Na_2SiO_3$ 0.25 g, NaOH 1.2 g, T 90 °C).

The variation of weighted average with increasing the concentration of sodium silicate was investigated (Fig. 4B). When the concentration is 0.01 ~ 0.9 mol/L, The weighted average shows the tendency of rapid increase and then stabilize. As the concentration of sodium silicate is in the range of 0.9 ~ 1.2 mol/L, the weighted average decreased gradually. Therefore, the optimum concentration of sodium silicate was 0.9 mol/L.

![Figure 4](image2)

Figure 4. (A) The variation of weighted average with change of pH value ($Na_2SiO_3$ 0.3 mol/L, t 2 h). (B) The variation of weighted average with the increasing concentration of sodium silicate (pH 9, t 2 h). (C) The variation of weighted average with the change of the reaction time (pH 9, $Na_2SiO_3$ 0.9 mol/L).

The variation of weighted average with increasing the concentration of sodium silicate was investigated (Fig. 4B). When the concentration is 0.01 ~ 0.9 mol/L, The weighted average shows the tendency of rapid increase and then stabilize. As the concentration of sodium silicate is in the range of 0.9 ~ 1.2 mol/L, the weighted average decreased gradually. Therefore, the optimum concentration of sodium silicate was 0.9 mol/L.

Fig. 4C shows the variation of weighted average with the change of the reaction time. Obviously, when the reaction time is 0 ~ 4 h, the weighted average increases rapidly and stabilize around 78. When the reaction time is 6 ~ 8 h, the weighted average increases slightly and reaches the maximum.
(~ 82). As the reaction time is in the range of 10 ~ 12 h, the weighted average showed a decreasing trend. Thus, the best reaction time for the preparation of Na$_2$SiO$_3$-SiO$_2$ is 6 ~ 8 h.

In view of the above scoring criteria of three factors, the comparison of the influence degree by the variance of each factor is necessary. Hypothesis the coefficient of variation of the pH value is $CV_4$, the coefficient of variation of the concentration of sodium silicate is $CV_5$, and the coefficient of variation of the reaction time is $CV_6$. The calculation can be obtained as: $CV_4=0.3729$, $CV_5=0.1564$, $CV_6=0.1567$. Thus, the most influential factor is the pH value, followed by the reaction time, and finally the reaction concentration.

3.2.3. TEOS-SiO$_2$. From an industrial point of view, it is not as good as the first two methods. Therefore, we mainly chose the particle size and uniformity for comprehensive evaluation, and set the weighted average of particle size and uniformity to 0.5 ($a=0.5$).

As shown in Fig. 5A, with the increasing of TEOS dosage from 0.1 to 9 mL, the weighted average increases slightly, when the TEOS dosage is more than 10 mL, the weighted average decreases dramatically. Thus, the optimal dosage of TEOS is 5 ~ 10 mL.

The variation of the weighted average with the change of the amount of ammonia water was investigated, as shown in Fig. 5B. Clearly, the weighted average is stable between 70 and 80 when the amount of ammonia is 0.5 ~ 10 mL. When the amount of ammonia water is in the range of 0.5 ~ 10 mL, the change of particle size and uniformity is favorable with high score. Therefore, the weighted average is larger. When the amount of ammonia is 30 ~ 90 mL, the weighted average sharply decreased to 0. Thus, the optimal dosage of ammonia for the preparation of TEOS-SiO$_2$ is 10 mL.

The variation of the weighted average with the change of the reaction time was shown in Fig. 5C. When the reaction time was 0.25 ~ 7 h, the weighted average is inconstant between 75 ~ 85, as the reaction time increases form 11 ~ 20 h, the weighted average is stable around ~ 85. Therefore, the optimal reaction time for the preparation of TEOS-SiO$_2$ is 9 h.

![Figure 5](image-url)

**Figure 5.** (A) The variation of the weighted average with change of TEOS dosage(NH$_3$ 5 mL, t 7 h); (B) the variation of the weighted average with changes of the amount of ammonia (TEOS 5 mL, t 7 h); (C) the variation of the weighted average with the change of the reaction time (TEOS 5 mL, NH$_3$ 10 mL).

In view of the above scoring criteria of three factors including the dosage of TEOS and ammonia water, and the reaction time are consistent, the comparison of the influence degree by the variance of each factor is necessary. Hypothesis the coefficient of variation of the TEOS dosage is $CV_7$, the coefficient of variation of the ammonia water dosage is $CV_8$, and the coefficient of variation of the reaction time is $CV_9$. The results can be calculated as follows: $CV_7=0.3397$, $CV_8=0.5282$, $CV_9=0.0488$. Obviously, the most influential factor is the amount of ammonia water, followed by the amount of TEOS, and finally the reaction time.
4. Conclusion
In summary, the effects of experimental conditions on the preparation route of SiO$_2$ nanoparticles can be parameterized with fuzzy mathematical analysis. Si and Na$_2$SiO$_3$ are suitable raw materials for the industrial production of 20 nm and 60 nm SiO$_2$ nanoparticles, respectively. Also, SiO$_2$ nanoparticles with 250 nm ought to be prepared using TEOS as the raw material. The order of the effects of the factors in hydrolysis is the dosage of sodium silicate > the amount of silica powder > the reaction time. For the chemical precipitation method, the order is the pH value > the reaction time > the reaction concentration. For the sol-gel method, the order is the amount of ammonia water > TEOS consumption > the reaction time.

Acknowledgments
This work was financially supported by the Innovation Fund of China Petroleum Science and Technology (No. 21070-5007-0207) and the National Natural Science Foundation of China (No. 21771125, 21606151).

References
[1] B. Hotzer, I.L. Medintz, N. Hildebrandt, Fluorescence in nanobiotechnology: sophisticated fluorophores for novel applications, Small 8 (2012) 2290-2320.
[2] P.S. Liu, S. Guo, M.M. Lian, X.H. Li, Z.J. Zhang, Improving water-injection performance of quartz sand proppant by surface modification with surface-modified nanosilica, Colloids Surf. A 470 (2015) 114-119.
[3] F. Yan, J.G. Jiang, S.C. Tian, Z.W. Liu, J. Shi, K.M. Li, X.J. Chen, Y.W. Xu, A green and facile synthesis of orderedmesoporous nanosilica using coal fly ash, ACS Sustain. Chem. Eng. 4 (2016) 4654-4661.
[4] M.T. Swihart, Vapor-phase synthesis of nanoparticles, Curr. Opin. Colloid Interface Sci. 8 (2003) 127-133.
[5] N. Nasseh, L. Taghavi, B. Barikbin, M.A. Nasseri, Synthesis and characterizations of a novel FeNi$_3$/SiO$_2$/CuS magnetic nanocomposite for photocatalytic degradation of tetracycline in simulated wastewater, J. Clean. Prod. 179 (2018) 42-54.
[6] X. Ning, Y.Y. Lu, H.Y. Fu, H.Q. Wan, Z.Y Xu, S.R Zheng, Template mediated Ni(II) dispersion in mesoporous SiO$_2$ for preparation of highly dispersed Ni catalysts: influence of template type, ACS Appl. Mater. Interfaces 9 (2017) 19335-19344.
[7] G.D. Sun, G.H Zhang, K.C. Chou, A.P. Dong, Preparations of SiS and SiO$_2$ nanospheres, Ind. Eng. Chem. Res. 56 (2017) 12362-12368.
[8] S. Musić, N. Filipović-Vinceković, L. Sekovanić, Precipitation of amorphous SiO$_2$ particles and their properties, Braz. J. Chem. Eng. 28 (2011) 89-94.
[9] D.W. Dong, J.Y. Li, Y.H. Yang, X.L. Wang, J. Liu, Improvements to the fuzzy mathematics comprehensive quantitative method for evaluating fault sealing, Pet. Sci. 14 (2017) 276–285.
[10] M. Relich, P. Pawlewski, A fuzzy weighted average approach for selecting portfolio of new product development projects, Neurocomputing 231 (2016) 19-27.
[11] M.J. Anderson, A new method for non-parametric multivariate analysis of variance, Austral Ecol. 26 (2010) 32–46.
[12] A.F. Hassan, A.M. Abdelghny, H. Elhadidy, A.M. Youssef, Synthesis and characterization of high surface area nanosilica from rice husk ash by surfactant-free sol-gel method, J. Sol-Gel Sci. Techn. 69 (2014) 465-472.