

Preparation of Nano-SiO₂ by silica sol in-situ complexation protective precipitation method

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Research Article

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Abstract

In this study, nanosilica particles were prepared from self-made silica gel under the protection of citric acid *in situ* complexation and ethyl acetate as the latent acid reagent. The effects of ethyl acetate, citric acid, reaction temperature, and reaction time on the particle size of nanosilica were studied. The optimum process parameters were determined as follows: $V_{\text{ethyl acetate}}:V_{\text{silica sol}} = 9:50$, citric acid addition amount 3.64%, reaction time 8 h, and reaction temperature 70 °C. The products were characterized by IR, XRD, and TEM analyses. The results show that the silica prepared using this method has good dispersion, and the average controllable particle size is 19.44 nm. The method has the advantage of a simple preparation process and is expected to achieve industrial production.

1. Introduction

Nano-SiO₂ is a green and environment-friendly inorganic nonmetallic material, commonly known as ultrafine white carbon black, referred to as white carbon black for short. It has hydroxyl groups on the surface, and the diameter of particles ranges from 1 nm to 100 nm. It is an amorphous white powder. The microstructure is spherical and shows a reticular and flocculent quasi granular structure under transmission electron microscope. Nano-SiO₂, with the unique four effects of nanomaterials, has good optical, electrical, thermal, mechanical, magnetic, absorption, radiation, and other special properties, as well as high toughness, high strength, and good stability at a high temperature, so that nano-SiO₂ can be widely used in various fields [1,2]. Optically, the surface effect and small size effect shown by the particle size of several nanometers to more than ten nanometers make it resist UV rays [3]. At the same time, the quantum tunneling effect and volume effect of nano-SiO₂ make it produce osmosis, penetrate a polymer's pi bond, overlap with its electron cloud, form a spatial network structure, thus greatly enhancing the mechanical strength of polymer compounds, and increasing the antiaging properties and wear resistance of other materials [4]. Dispersion of nano-SiO₂ particles into other materials can improve the comprehensive properties of products. For example, when added to polymer materials, it can resist UV aging and thermal aging. When used to modify polymers, it can improve the optical, electrical, thermal, mechanical, and processing properties of materials, and improve the strength, toughness, flame retardancy, and heat resistance of polymers [5,6]. Nano-SiO₂ has a wide range of applications. As one of the most widely used nanomaterials at present, it is applied in many fields, including composites, electronic packaging materials, coatings, pigments, plastics, cosmetics, glass carriers, adhesives, and drug carriers [7].

At present, the raw materials for preparing nano-SiO₂ are mainly tetraethyl orthosilicate (TEOS) [8], 3-aminopropyl triethoxysilane (APTES), methyl orthosilicate (TMOS), and other organosilicon compounds as silicon sources, while there are few reports on the preparation of Nano-SiO₂ using silica sol [9]. Although nano-SiO₂ with good dispersion can be prepared using a silicone source, it is expensive and requires extreme conditions, which is not suitable for mass production [10]. It is also reported in the literature that silica sol is used as the silicon source [11], a colloidal protective agent NCMC is directly added under stirring, a back-extractant isopropanol is added dropwise, and then dried in an oven. The silica sol particles are dehydrated to gel and then removed by natural sedimentation or filtration. Most of the aqueous solutions containing isopropanol are removed. The transparent wet gel is dried at 200 °C in an oven for 6 h. The pure white nano-SiO₂ can be obtained by natural cooling in the rear dryer. Then, the dried nano-SiO₂ is calcined in an 800 °C muffle furnace for 1 h to remove the residual

surface hydroxyl water, colloidal protective agent, and other impurities to obtain high-purity white nano-SiO₂. However, 100 g of silica sol requires 3 g of a colloidal protective agent NCMC and 105 g of antiextractant isopropanol to form SiO₂ hydrogel, and a hydrogel is added to isopropanol for 6 h after drying in a 200 °C oven. After calcination in a 800 °C muffle furnace for 1 h, nano-SiO₂ powder can be obtained after natural cooling. However, this method consumes a large amount of back-extractant isopropanol, which evaporates into the air after being dried in a 200 °C oven for 6 h, resulting in high cost and air pollution. In addition, it requires high-temperature calcination at 800 °C to whiten the chromaticity and consumes a high amount of energy [12]. Domestic researchers also used an alkaline silica sol and inorganic acid as the raw materials, water and methanol as the reaction medium, and added an appropriate dispersant (sodium hexametaphosphate and polymer stable dispersant C). The reaction was carried out for a certain time under appropriate reaction temperature and pH conditions, and a stable nano-SiO₂ powder was obtained through vacuum dehydration drying and ultrafine screen screening. However, the particle size distribution is uneven, and due to the addition of inorganic acids such as hydrochloric acid and sulfuric acid, the local acidity in the silica sol is too high, making it easy to agglomerate and deteriorate. In contrast, it increases the viscosity, because it loses fluidity and becomes a gel, causing difficulties for mixing. Therefore, it is difficult to obtain nanoparticles with a uniform particle size and monodispersity [13]. At the same time, the particle size of the obtained nano-SiO₂ powder was determined using its production process and raw material ratio, and there is basically no repeatability.

Nano-SiO₂ also has many unique properties [14–16]. For example, nanoparticles have a small particle size, spherical appearance, hydroxyl group and adsorbed water exist on the surface, a large specific surface area, good dispersion performance, and strong surface adsorption. Nano-SiO₂ has superior stability, reinforcement, thixotropy, and excellent optical properties. Therefore, SiO₂ nanoparticles are widely used in the preparation of catalysts, ceramics, electronic materials, fillers, and cosmetics. Sol particles are used in chemical mechanical polishing, coating, and precision casting [17].

Owing to the great application potential of nano-SiO₂ powder materials, it is particularly important to study and develop methods for preparing ultrafine SiO₂ materials. At present, the methods for preparing nano-SiO₂ mainly include precipitation [18], gas-phase method, sol–gel method, microemulsion method, and micelle method [19].

There are few reports on the preparation of nano-SiO₂ using silica sol. Because the surface of silica sol contains a large number of hydroxyl groups, when concentrated and gelled, the hydroxyl groups shrink through hydrogen bonding, and the colloidal particles merge to form large particles of SiO₂ [20]. Shi Li [12] added a protective agent to combine with the surface hydroxyl groups of silica sol, so that the hydroxyl groups of the colloidal particles cannot be dehydrated and condensed when the silica sol gels, so as to obtain nano-SiO₂. However, there are certain defects, such as the use of flammable isopropanol, and the cost is higher due to a large amount of use. During the preparation, with the vacuum concentration of isopropanol, it is easy to agglomerate, and it is difficult to obtain well-dispersed nano-SiO₂.

In this study, silica sol was used as the silicon source. For the first time, the citric acid and silyl hydroxyl groups that complex with strong complexation were used as the protectant, and ethyl acetate was used as a latent acid reagent. By slowing down the rate of gelation reaction of SiO₂ colloidal particles directly with latent acid reagents in silica sol and controlling the gelation temperature, reaction time, complexing protectant, and precipitant

amount in the reaction process, a large surface area was obtained, and uniformly dispersed nano-SiO₂ was prepared.

2. Experimental

2.1 Experimental reagent

Citric acid, ethyl acetate, urea, sodium hydroxide, ammonia (all AR grade) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Silicon powder (semiconductor grade) was obtained from Jinan Yinfeng silicon products Co., Ltd.

2.2 Preparation flow chart and mechanism

The chemical name of citric acid is 3-hydroxy-1,3,5-glutaric acid. It has three carboxylic acid groups and one hydroxyl group. In the space surrounded by the hydrogen bonds formed by two citric acid carboxylic acids, a silicon anion is used as the guest molecule. In this study, citric acid with a strong complexation performance was used for *in-situ* complexation protection, and H⁺ was released by latent acid reagent acetate. Thus, multiple SiO₂ monomers were polymerized into crosslinked highly dispersed SiO₂ nanoparticles in the space surrounded by the three carboxyl groups of citric acid. In this manner, too high local acidity and a fast decrease in alkalinity when an acid is directly added were avoided. Direct addition of a strong inorganic acid to a system will lead to a higher acid gradient, causing excessive local acidity and forming an uneven gel. Compared with the direct addition of strong inorganic acids to a system, the three carboxyl groups of citric acid can provide a microenvironment for the formation of nano-SiO₂ with a small acid gradient and uniform polymerization, and latent acid acetate can provide more mild reaction conditions as a slow-release agent of acid H⁺. Only a combination of the two can produce nano-SiO₂ with excellent dispersion and uniform particle size distribution.

2.3 Preparation of nano-SiO₂

The silica sol used in this study was prepared under the optimum conditions, i.e., at 95 °C, without using a reflux device, the silica sol was prepared by maintaining the addition time of silica powder for 2.5 h, the amount of catalyst sodium hydroxide is 2.5% of the amount of silica powder. The amount of ammonia is 38% of that of silica powder. The total reaction time is 9 h, and the reaction was aged for 10 h.

2.3.1 Preparation of different dosages of ethyl acetate

(1) Typical preparation process: After adding 50 mL of silica sol into a three-neck flask, 5 mL of ethyl acetate and 0.5 g of citric acid were added, the reaction mixture was refluxed at 76 °C under magnetic stirring. The reaction mixture became milky white. After 3 h of reaction, the reaction mixture was centrifuged using a high-speed centrifuge and washed with 95% ethanol. After vacuum drying, nano-SiO₂ was obtained by grinding.

(2) Under the condition that the steps and dosage described in Section 2.3.1 (1) remain unchanged, the volume ratio of ethyl acetate to silica sol is 0, 1:100, 1:50, 1:20, 2:25, 1:10, 7:50, and 9:50. Nano-SiO₂ was obtained by centrifugation, washing, drying, and grinding.

2.3.2 Preparation without citric acid dosage

According to the steps described in Section 2.3.1 (1) and dosage unchanged, only the amount of citric acid was changed, and the quality of silica sol was 0, 0.23%, 0.45%, 0.68%, 0.91%, 1.14%, 1.36%, 3.64%, and 7.27%, and the obtained SiO₂ gel was centrifugally washed, dried, and ground to obtain nano-SiO₂.

2.3.3 Reaction time

In accordance with the procedure described in Section 2.3.1 (1) and dosage unchanged, the reaction time was 1.5 h, 2 h, 2.5 h, 3 h, 3.5 h, 4 h, 8 h, and 15 h, and the obtained SiO₂ gel was centrifugally washed, dried, and ground to obtain nano-SiO₂.

2.3.4 Reaction temperature

In accordance with the procedure described in Section 2.3.1 (1) and dosage unchanged, only 25 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, and 90 °C were changed, and the obtained SiO₂ gel was centrifugally washed, dried, and ground to obtain nano-SiO₂.

2.4 Material characterization

Powder X-ray diffraction (XRD) and phase analysis were carried out using a D/max 2550 VB/PC X-ray diffractometer (Cu target K α line, $\lambda = 0.15406$ nm) at room temperature. A Tecnai-12 type (120 kV) transmission electron was used. The morphology and size of the particles were observed using a microscope (TEM). The FTIR spectra of the samples were recorded using a Nicolet Impact 410 FTIR spectrometer. The surface morphology of nano-SiO₂ was observed using a JEOL JSM-6360LV scanning electron microscope.

3. Results And Discussion

3.1 Characterization of self-made silica sol

The concentration of silica sol was determined using the constant weight method. A certain amount of silica sol was taken in a crucible, dried it in an oven at 70 °C for 6 h, calcined in a muffle furnace at 500 °C for 250 min, weighed, data recorded, dried in a vacuum drying oven overnight, weighed, data recorded using an electronic balance, dried in a vacuum drying oven for a period of time, weighed, data recorded, and the above steps were repeated until the error is less than 0.01 g. By dividing the final recorded weight and the initial weight, the concentration of the prepared silica sol was found to be 14.55%.

3.1.1 FTIR spectrum

Figure 3 shows the FTIR spectrum of self-made silica sol. The absorption peak at 3433.81 cm⁻¹ can be attributed to the antisymmetric stretching vibration peak of OH group of structural water in silica. The corresponding absorption peak at 1632.43 cm⁻¹ can be attributed to the bending vibration peak of H-O-H of water in silica. The absorption peak at 1096.27 cm⁻¹ can be attributed to the antisymmetric stretching vibration peak of Si-O-Si bond, and the Si-O-Si bending vibration peak also appeared at 795.22 cm⁻¹. The symmetric stretching vibration peak of Si-O bond appeared at 469.72 cm⁻¹.

3.1.2 SEM Characterization

Figure 4 shows a scanning electron microscope map of silica sol. From this diagram, we can clearly observe that silica sol is arranged in sequence, regular and nonagglomerated Nano-SiO₂ gel appears, and the size of silica sol is about 24.66 nm as determined using an electronic ruler.

3.2 Characterization of Nano-SiO₂

3.2.1 TGA / DTA

Figure 5 shows the TGA / DTA diagram of nanosilica. The DTG curve shows that the weight loss rate of the material reached the maximum when the temperature reached 119.8 °C, indicating that a large amount of physically adsorbed water was lost at this time. The TG curve also shows that the slope of the curve is the largest, and the weight loss rate is the largest. When the temperature reached 220 °C, the DTG curve became flat. When the temperature continued to increase to about 360 °C, the weight loss rate reached the maximum again. The TGA shows an endothermic peak at 373.2 °C, probably because the water molecules strongly bonded to the surface hydroxyl groups started to desorb gradually. When the temperature increased 373.2 °C, the surface hydroxyl groups started to desorb a lot. After 600 °C, the sample was no longer weightless. This shows that water and other organic components were completely volatilized, and the rest is pure nanosilica powder.

3.2.2 TEM and particle size analysis of nano-SiO₂

Figure 6 shows the TEM image of nano-SiO₂. Figure 6A shows that the dispersion of nanoparticles is relatively uniform, and the particle size is relatively good. Figure 6b shows the local enlarged version of Fig. 6A. The particle size was roughly measured at 13.07–29.82 nm, and the average particle size was about 19.44 nm.

Figure 6c shows the particle size analysis and test results of nano-SiO₂. The nano-SiO₂ not only has a small particle size and relatively uniform distribution, but also the average particle size of the secondary particle size is about 27.56 nm.

3.2.3 FTIR spectrum and XRD analysis

Figure 7a shows the FTIR spectrum of the prepared nano-SiO₂ sample. The peak at 3435.60 cm⁻¹ can be attributed to the antisymmetric stretching vibration peak of structural water OH group in silica, and the weak absorption peak of 1627.31 cm⁻¹ can be attributed to the bending vibration of H–OH, which may be caused by the adsorption of a small amount of water on the surface after nano-SiO₂ is placed in air. The maximum absorption peak appears at 1102.00 cm⁻¹, which is the antisymmetric stretching vibration of Si–O–Si bond. The symmetric stretching vibration of Si–O–Si bond appears at 798.94 cm⁻¹, and the bending vibration of Si–O–Si bond appears at 475.66 cm⁻¹.

Figure 7b shows a wide-angle diffraction pattern of nano-SiO₂, and there is a strong diffraction peak at 2θ 22.3°, indicating that the synthesized sample is amorphous silica.

3.2.4 BET analysis

Figure 8 shows the N₂ adsorption desorption curve of nano-SiO₂ under this condition. It presents the type IV adsorption isotherm of IUPAC. This indicates that the silica material is mesoporous. The adsorption capacity in the second half of the relative pressure continues to increase, indicating that still certain macropores are present.

The average data of specific surface area obtained by a BET test are 393.64 m²/g, 389.67 m²/g, and 380.88 m²/g, which far exceeds the national standard of precipitation method (70–220 m²/g).

3.3 Discussion on variables in reaction conditions

3.3.1 Amount of ethyl acetate

Table 1
Effects of adding different amounts of ethyl acetate on silica particle size

$V_{\text{ethyl acetate}}:V_{\text{silica sol}}$	Citric acid (%)	Reaction time (h)	Temperature (°C)	Average particle size (nm)
0	0.45	3	75	59.14
1:100	0.45	3	75	86.40
1:50	0.45	3	75	51.63
1:20	0.45	3	75	55.29
2:25	0.45	3	75	56.49
1:10	0.45	3	75	53.29
7:50	0.45	3	75	52.85
9:50	0.45	3	75	48.54

Figure 9 shows a statistical analysis of the effect of different addition amounts of ethyl acetate on the particle size of nanosilica through HRSEM. Table 1 shows that when $V_{\text{ethyl acetate}}:V_{\text{silica sol}}$ changes from 0 → 1:100 → 1:50 → 1:20 → 2:25 → 1:10, the average particle size changes from 59.14 nm → 86.6 nm → 51.63 nm → 55.29 nm → 56.49 nm → 53.29 nm. As the amount of ethyl acetate increased, the particle size first increased and then decreased. It gradually remained unchanged (see Fig. 9 (i)), and the particle size is about 53.01 nm.

However, with the increase in the amount of ethyl acetate, the particle size changed slightly when the ratio of $V_{\text{ethyl acetate}}$ to $V_{\text{silica sol}}$ is 1:20, but the dispersion is different. In Figs. 9 (c) → 9 (H), the probability of particle size in the range of < 50 nm is 65.0% → 47.5% → 42.5% → 45.0% → 55.0% → 67.5%, showing first a downward trend and then an upward trend. The probability of a large particle size > 80 nm is 10.0% → 5.0% → 12.5% → 0 → 7.5% → 5.0%. When $V_{\text{ethyl acetate}}:V_{\text{silica sol}} = 1:10$, not only the content of small particles < 40 nm is lower (45%), but also the content of large particles > 80 nm is higher, which is 12.5%. When $V_{\text{ethyl acetate}}:V_{\text{silica sol}}$ is 1:20, the particle size of 30% is 40–45 nm. When $V_{\text{ethyl acetate}}:V_{\text{silica sol}}$ is 9:50, the particle size and dispersion are better than others.

3.3.2 Amount of citric acid

Table 2
Effects of adding different amounts of citrate on silica particle size

$V_{\text{ethyl acetate}}:V_{\text{silica sol}}$	Citric acid (%)	Reaction time (h)	Temperature (°C)	Average particle size (nm)
1:10	0	3	75	43.84
1:10	0.23	3	75	43.93
1:10	0.45	3	75	55.29
1:10	0.68	3	75	58.68
1:10	0.91	3	75	59.84
1:10	1.14	3	75	88.71
1:10	1.36	3	75	62.92
1:10	3.64	3	75	42.28
1:10	7.27	3	75	40.86

Figure 10 (a) shows that when citric acid is not added, the percentage content of particle size < 50 nm is 87.5%, and when citric acid with a silica sol content of 0.23% is added, the percentage content of particle size < 50 nm in Fig. 10 (b) is 85%. When the addition amount of citric acid increases, particles with particle size > 80 nm appeared. With the increase in the amount of citric acid, the proportion of small particle size decreased, and the proportion of large particle size gradually increased. When citric acid is added to 1.14% of the silica sol content, the proportion of large particle size > 80 nm reached the maximum, which is 50.0% (see Fig. 10 (f)). With the increase in the amount of citric acid, the proportion of large particle size > 80 nm started to decrease gradually, and the percentage of particle size < 45 nm is 82.5% and 85.0%, respectively (Figs. 10 (h) and (i)).

As shown in Fig. 10 (j), with the increase in citric acid content, when the addition amount of citric acid is 0, 0.23%, 0.45%, 0.68%, 0.91%, and 1.14% of the amount of silica sol, the average particle size increased from 43.84 nm → 43.93 nm → 60.14 nm → 58.68 nm → 59.84 nm → 88.71 nm. When the amount of citric acid was 1.14% of the amount of silica sol, the particle size of nano-SiO₂ reached the maximum, i.e., 88.71 nm. However, when the amount of citric acid increased from 1.14% → 1.36% → 3.64% → 7.27%, the particle size changed from 88.71 nm → 62.92 nm → 42.28 nm → 40.86 nm, showing a trend of decreasing and then changing slowly or even unchanged. Therefore, on the whole, with the increase in the amount of citric acid, the particle size first increases, then decreases, and then remains unchanged. This is probably because the H⁺ in the carboxylic acid group of citric acid reacts with the hydroxyl group in silica sol to protect SiO₂ particles, but when citric acid is added to a certain amount, the protective effect reaches saturation, and when the amount of citric acid is increased, the particle size is unchanged. The addition amount of citric acid with a smaller average particle size is 0, 0.23%, 3.64%, and 7.27% of the amount of silica sol, but the proportion of a large particle size with product > 80 nm at 0 and 0.23% (2.5% and 2.5%, respectively) is higher than that at 3.64% and 7.27% 27% of the products (all 0) with a large particle size. For 7.27% of the amount of silica sol, the proportion of particle size < 50 nm when citric acid is added is slightly larger than that when citric acid is added, but the amount of citric acid is doubled. Therefore, the most appropriate amount of citric acid is 3.64% of the amount of silica sol.

3.3.3 Reaction time

Table 3
Effects of reaction time of citrate on silica particle size

$V_{\text{ethyl acetate}}:V_{\text{silica sol}}$	Citric acid (%)	Reaction time (h)	Temperature (°C)	Average particle size (nm)
1:10	0.45	1.5	75	42.01
1:10	0.45	2	75	43.59
1:10	0.45	2.5	75	45.77
1:10	0.45	3	75	55.29
1:10	0.45	3.5	75	60.14
1:10	0.45	4	75	44.48
1:10	0.45	8	75	38.48
1:10	0.45	15	75	45.86

Figure 11 shows the effect of different reaction times on nano-SiO₂ particles after statistical analysis by SEM. With the increase in time, when the reaction time is 1.5 h, 2 h, 2.5 h, 3 h, and 3.5 h, the particles with a small particle size less than 50 nm account for 77.5%, 72.5%, 82.5%, 22.5%, and 62.5% of the total number of particles, respectively, and the larger particles with size more than 80 nm account for 7.5%, 2.5%, 2.5%, 10%, and 7.5%, respectively. Table 3 shows that when the reaction time is 1.5 h, 2 h, 2.5 h, 3 h, and 3.5 h, the average particle size is 42.01 nm, 43.59 nm, 45.77 nm, 55.29 nm, and 60.14 nm, respectively, i.e., with the increase in reaction time, the particle size shows an upward trend (see Fig. 11 (i)). When the reaction time continues to increase, the proportion of small particle size changes from 62.5% at 3.5 h to 72.5%, and the average particle size also decreases, from 60.14 nm at 3.5 h to 44.48 nm at 4 h. However, when the reaction time increases to 15 h, the small particle size of < 50 nm occupied 80% at 8 h of reaction, while the small particle size slightly decreased to 75% at 15 h of reaction. This is because in a typical preparation, the ethyl acetate hydrolysate promotes the silicon hydroxyl polymerization of silica sol, and the amount of obtained nano-SiO₂ particles increase with time. On the other hand, citric acid, a complexation protection agent, plays a complexation protection function between the formed nano-SiO₂ and acts as a “bridge” between the nano-SiO₂ particles, improving the dispersion of nano-SiO₂ particles and maintaining the obtained nano-SiO₂ particles at a certain level. When the reaction time exceeded 3.5 h, the effect of complexing agent played a leading role, resulting in less change in the particle size of nanoparticles.

Considering the above factors and reaction cost, the dispersion and particle size of nanoparticles can be achieved the best when the reaction time is 8 h.

3.3.4 Reaction temperature

Table 4
Effects of reaction temperature of citrate on silica particle size

$V_{\text{ethyl acetate}}:V_{\text{silica sol}}$	Citric acid (%)	Reaction time (h)	Temperature (°C)	Average particle size (nm)
1:10	0.45	3	25	0
1:10	0.45	3	65	42.57
1:10	0.45	3	70	34.43
1:10	0.45	3	75	55.29
1:10	0.45	3	80	47.71
1:10	0.45	3	85	40.54
1:10	0.45	3	90	45.66

Figure 12 shows a statistical analysis of the effect of different temperatures on the size of nano-SiO₂. Table 4 shows that when the system does not react at room temperature, probably colloidal silica sol produces silica gel as a dynamic process. The acid hydrolyzed by citric acid or ethyl acetate promotes the condensation of hydroxyl groups on the surface of silica sol and is controlled by temperature. When the temperature is low (25 °C), the hydroxyl condensation rate on the surface of silica sol is very low, so nano-SiO₂ particles cannot be formed. Only when the temperature is higher than 65 °C can the hydroxyl groups on the surface of silica sol condense to form nano-SiO₂.

When the temperature is 75 °C, the particle size is the largest. At this temperature, not only the average particle size is relatively large, but also the distribution is uneven. The particle size is almost between 40–70 nm, accounting for 85% of the total particle size, while those at other temperatures are almost < 50 nm, accounting for a large proportion. The proportion of particle size < 50 nm at 65 °C, 70 °C, 80 °C, 85 °C, and 90 °C is 85%, 90%, 75%, 75%, and 82.5%, respectively. Particles with a large particle size of > 80 nm account for a small proportion in each temperature, i.e., 5.0%, 0, 7.5%, 2.5%, and 7.5%, respectively. At 75 °C, particles with a particle size of > 80 nm account for 12.5%. At 70 °C, not only the average particle size is small and the distribution is uniform, but also there are no particles with a large particle size. Therefore, the reaction temperature is more appropriate at 70 °C.

4. Conclusion

This study used the *in-situ* complexation protection uniform precipitation method, which is a new method to improve and develop the chemical precipitation method based on citric acid with multiple carboxyl and hydroxyl groups. Silica sol, also known as colloidal silica, is a stable dispersion system of amorphous SiO₂ colloidal particles in an aqueous solution. It is a charged molecular cluster polymerized by silicic acid molecules, and the monomers rapidly polymerize to a crosslinked SiO₂ particle structure through diffusion. When the monomer concentration is very high, the polymerization speed is very fast, and SiO₂ nanoparticles are formed. When the monomer concentration is low, the sol state can be maintained. Citric acid uses its three carboxyl groups to protect multiple SiO₂ monomers. Owing to hydrogen bond association, the carboxyl group will attract H₃O⁺ in the sol. The addition of a sol precipitant promoted the polymerization of multiple SiO₂ monomers to crosslinked SiO₂ nanoparticles at a certain speed. However, because of a limited space around the three carboxyl groups of citric

acid, the crystal nucleus cannot grow very large. Therefore, the particle size can be controlled within a certain range. On the other hand, citric acid containing hydroxyl groups will be adsorbed on the surface of nano-SiO₂ through hydrogen bonding. The nanoparticles are wrapped *in situ* by citric acid to form a protective layer, hindering the reaggregation between nanoparticles and making the particle size distribution uniform, thus affording fine and uniform nanoparticles. This method has the advantages of a simple process, convenient operation, easy availability of raw materials, and low cost, and it is suitable for industrial production.

(1) In this chapter, the silicon hydroxyl group is complexed and protected with inexpensive citric acid for the first time, and the silica sol is precipitated with hydrolyzed ethyl acetate. By controlling the gelation temperature of silica sol, the “soft agglomerated” nano-SiO₂ is prepared in advance, and then nanosized silica is obtained by ball milling. The process is simple, easy to control, and very suitable for industrial production.

(2) By evaluating the effects of addition amount of ethyl acetate and citric acid, reaction temperature, and reaction time on the particle size of nanosilica particles, the optimal values under various conditions were obtained, i.e., when $V_{\text{ethyl acetate}}:V_{\text{silica sol}}$ is 9:50, the mass of citric acid is 3.64% of the mass of silica sol, and the reaction temperature is 70 °C for 8 h, the particle size and dispersion of nano-SiO₂ particles are the best.

Declarations

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Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

Yubing Yang: Methodology, Investigation. **Yuxiang Yang:** Conceptualization, Supervision, Writing - original draft, Project administration, Funding acquisition, Writing - review & editing, Data curation. **Chaoying Ni:** Formal analysis, Visualization, Validation, Resources, Software.

Data Availability

Supplementary data to this article can in the following article.

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Figures

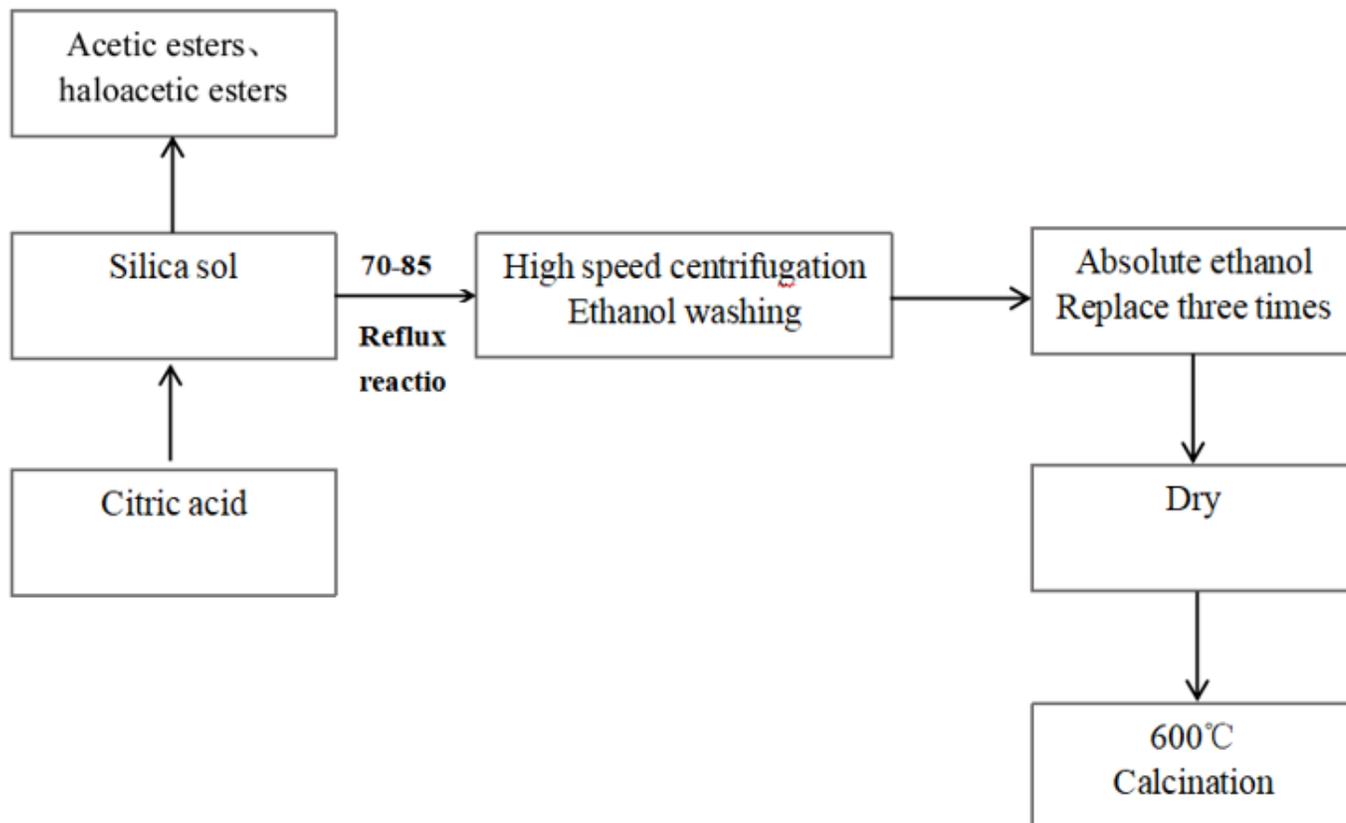


Figure 1

Process flow chart for the synthesis of nano-SiO₂ by *in-situ* complexation protection precipitation

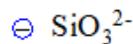
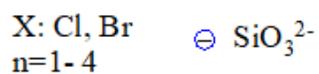
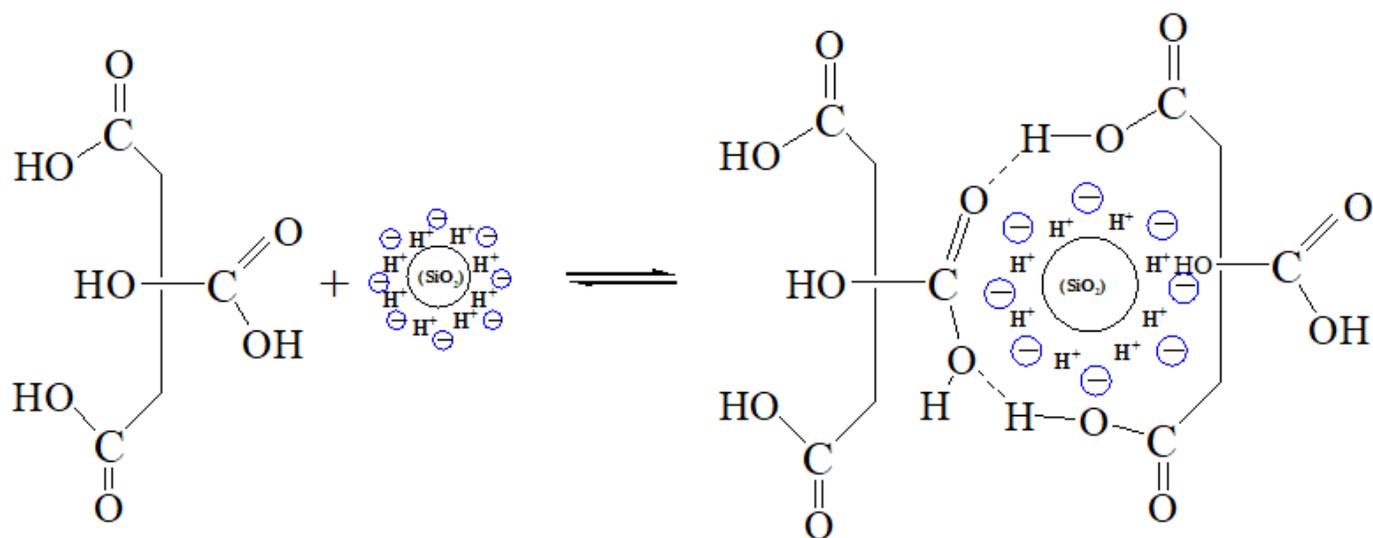


Figure 2

Formation mechanism of nano-SiO₂ synthesized by *in-situ* complexation protection precipitation method

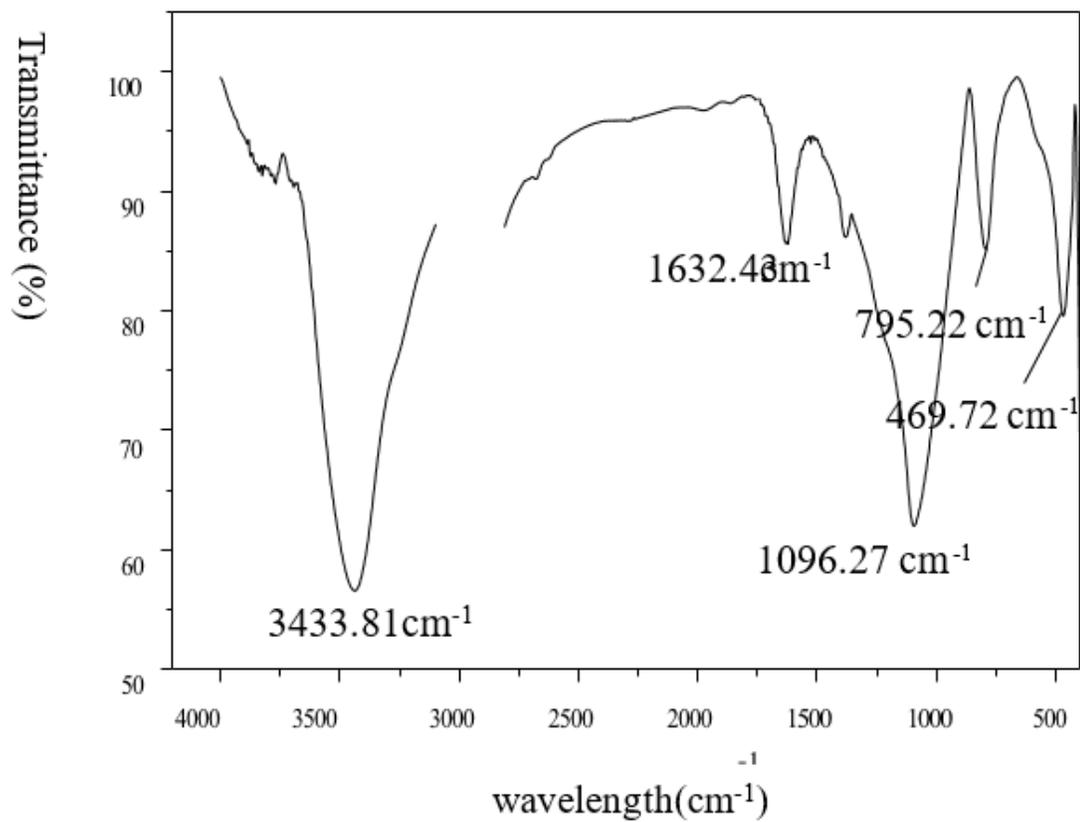


Figure 3

FTIR spectrum of silica sol

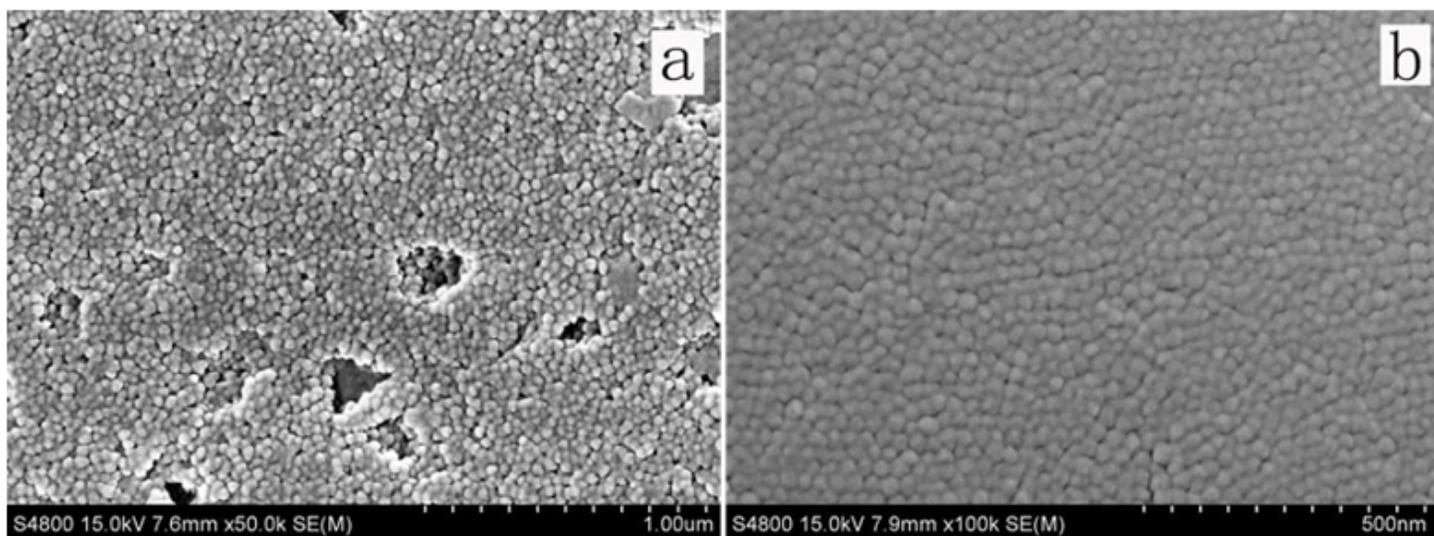


Figure 4

SEM images of Nano-SiO₂

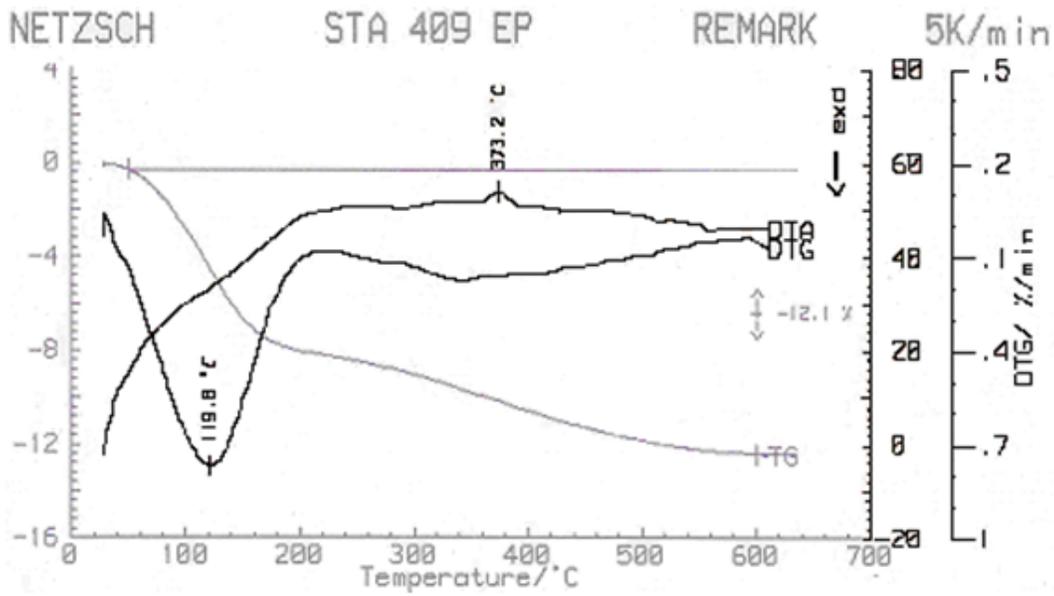


Figure 5

TG/DTA image of Nano-SiO₂

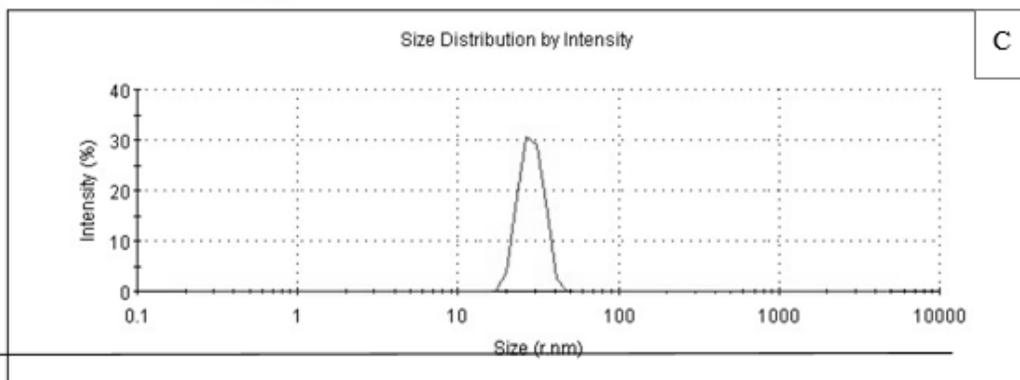
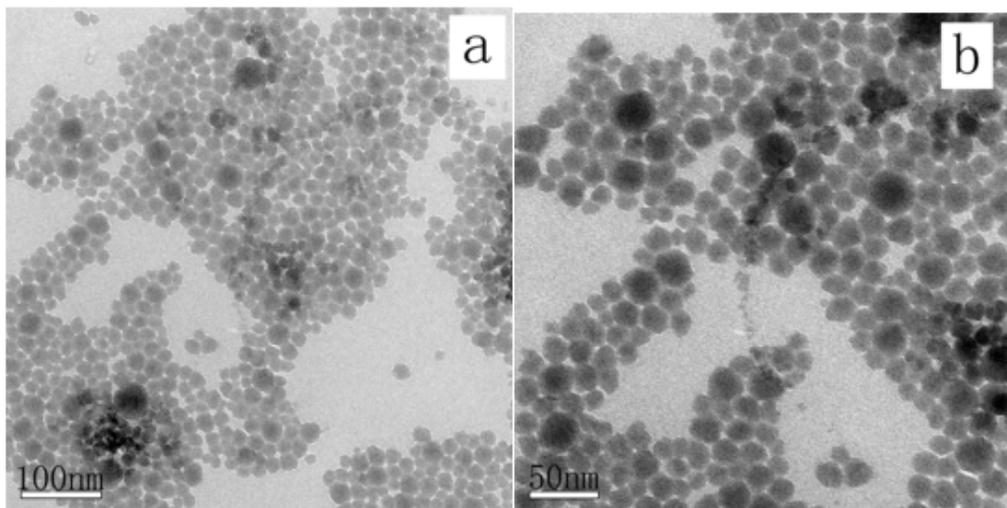


Figure 6

TEM image and Particle size analysis of nano-SiO₂

a, bnano-SiO₂, 6c Particle size analysis

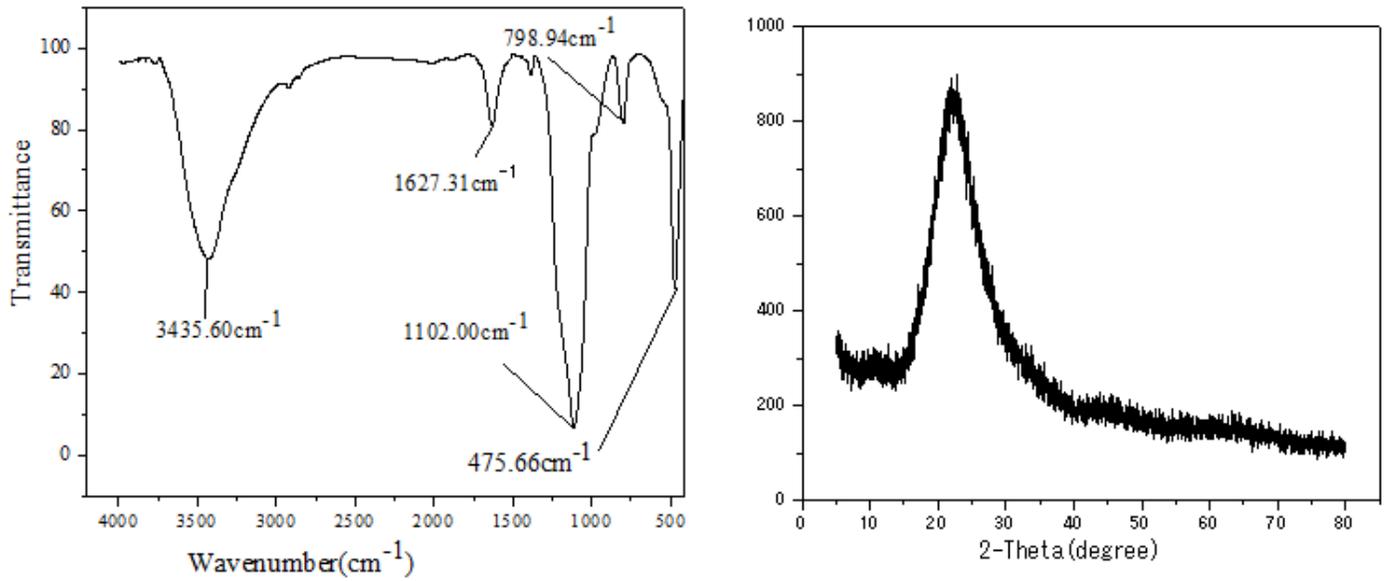


Figure 7

FTIR spectrum and XRD of nano-SiO₂

7a FTIR spectrum, 7b XRD

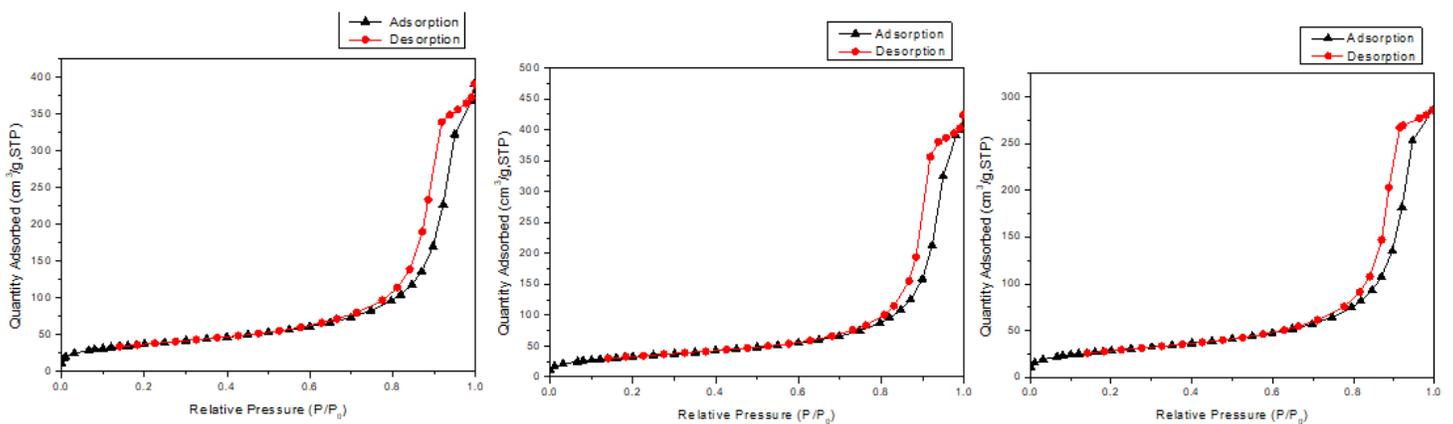


Figure 8

N₂ adsorption desorption curve of nano-SiO₂

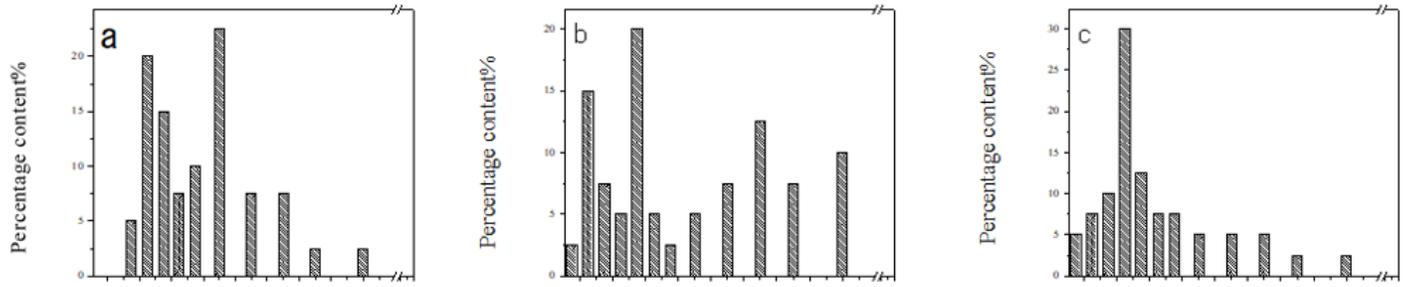


Figure 9

Effects of adding different amounts of ethyl acetate on silica particle size

a. $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 0$; b, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 1:100$; c, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 1:50$; d, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 1:20$,

e. $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 2:25$; f, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 1:10$; g, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 7:50$; h, $V_{\text{ethyl acetate}} : V_{\text{silica sol}} = 9:50$

Figure 10

Effects of adding different amounts of citrate on silica particle size

a, 0; b, 0.23%; c, 0.45%; d, 0.68%; e, 0.91%; f, 1.14%; g, 1.36%; h, 3.64%; i, 7.27%

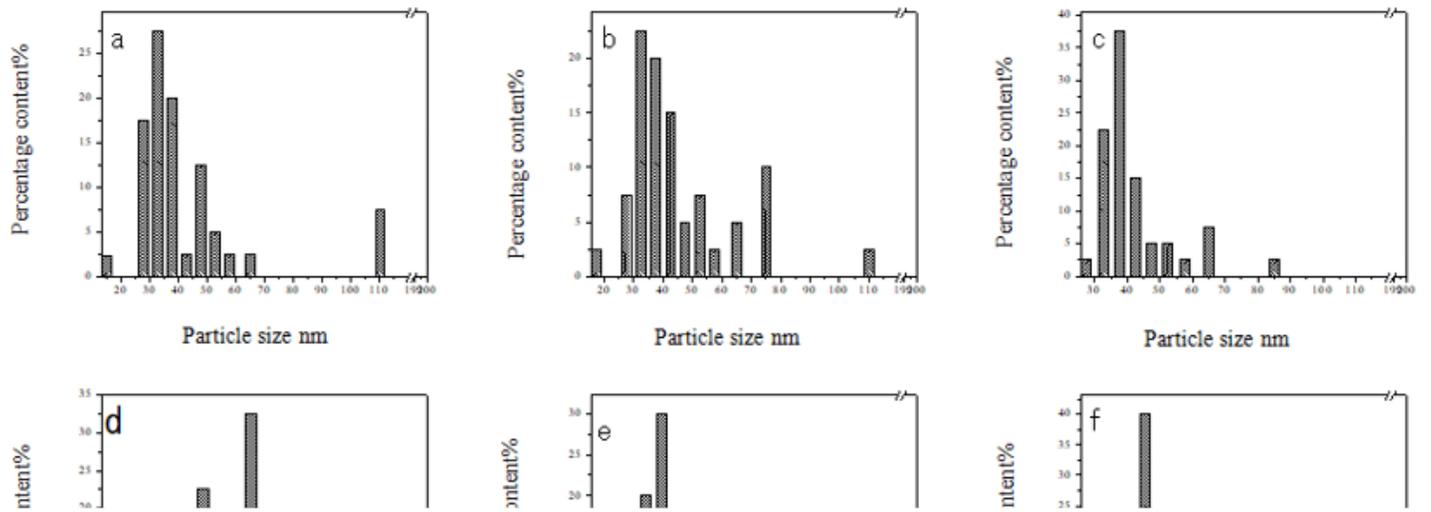


Figure 11

Effects of reaction time of citrate on silica particle size

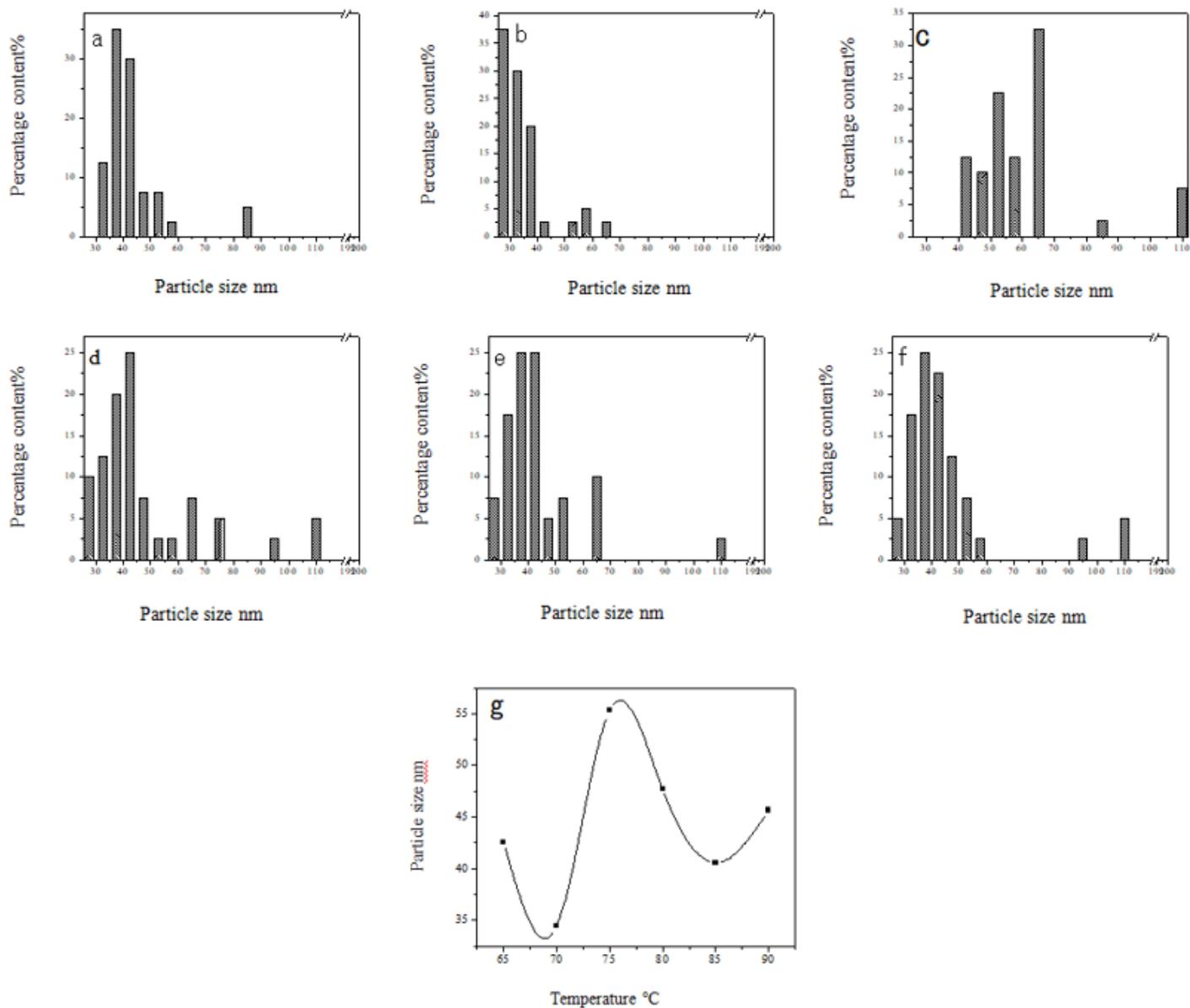


Figure 12

Effects of reaction temperature of citrate on silica particle size

a, 65 °C; b, 70 °C; c, 75 °C; d, 80 °C; e, 85 °C; f, 90 °C

Supplementary Files

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