Preparation of Nano-SiO$_2$ by Silica Sol In-Situ Complexation Protective Precipitation Method

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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, SEM and TEM analyses. The results show that the nano-silica particles prepared by complexation precipitation method employing silica sol as silicon source has good dispersion with average particle size controlled about 19.44 nm. The method has numerous advantages over the conventional inverse extraction method under colloid protection, and is expected to achieve industrial production.

Keywords Citric acid · Complexation precipitation method · Ethyl acetate · Nanosilica particles · Silica sol

1 Introduction

Nano-SiO$_2$ 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 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-SiO$_2$, with the unique four effects of nanomaterials, has a small particle size, a large specific surface area, 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-SiO$_2$ can be widely used in various fields [1–6], e.g., SiO$_2$ 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 [7]. Optically, the surface effect and small size effect shown by the particle size of several nanometers to more than ten nanometers make Nano-SiO$_2$ resist UV rays [8]. At the same time, the quantum tunneling effect and volume effect of nano-SiO$_2$ 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 [9]. Dispersion of nano-SiO$_2$ 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 [10, 11].

Owing to the great application potential of nano-SiO$_2$ powder materials, it is particularly important to study and develop methods for preparing ultrafine SiO$_2$ materials. The methods for preparing nano-SiO$_2$ mainly include
production [12], gas-phase method, sol–gel method, microemulsion method, and micelle method [13].

At present, the raw materials for preparing nano-SiO₂ are mainly tetraethyl orthosilicate (TEOS) [14], 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 [15]. 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 [16].

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 [17]. 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 [18].

It is also reported preparation of nano-SiO₂ in the conventional inverse extraction method using silica sol as the silicon source [19, 20], an amphoteric polymer surfactant as colloidal protective agent, named: Dimethyl ethylene-propyl ammonium chloride carboxymethyl fiber (NCMC) is directly added into the silica sol under stirring. After that, the copolymer of NCMC has excellent protective effect on colloidal silica particles. The dimethylallyl chloride cationic groups of the NCMC can bond well with the silicon hydroxyl groups, and the electrostatic repulsion between the carboxyl negative charges of the anionic end plays a good process, a large surface area was obtained, and uniformly dispersed nano-SiO₂ was prepared.

2 Experimental

2.1 Experimental Reagent

Citric acid(C₆H₈O₇), ethyl acetate(C₄H₈O₂), urea(CH₄N₂O), sodium hydroxide(NaOH), ammonia(NH₃·H₂O) (all AR grade, 99.9%) 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 preparation of Nano-SiO$_2$ particles with silica sol by complexation precipitation method can be seen from Figs. 1 and 2. Due to isoelectric point of silica about 2, colloidal silica particles “mSiO$_2$·nH$_2$O” is about 10–20 nm in size and carries a very large amount of negative charge, which can result in better coagulation efficiency. The chemical name of citric acid is 3-hydroxy-1,3,5-glutaric acid. It has three carboxylic acid groups and one hydroxyl group. Citric acid and a silicon anion form a core–shell structure by hydrogen bonding, with mSiO$_2$ as the core and citric acid and hydrogen bonding as the shell, as if a silicon anion is used as the guest molecule, the space surround by citric acid and hydrogen bonds can be considered as hosts. When latent acid reagent acetate release certain amount of H$^+$, the H$^+$ can catalyze multiple hydrated SiO$_2$ monomers polymerize into crosslinked highly dispersed SiO$_2$ nanoparticles, while citric acid as a hosts, takes role of colloidal protective agent, makes the formed nano-SiO$_2$ gel more uniform and dispersed.

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-SiO$_2$ with a small acid gradient and uniform polymerization, and

Fig. 1 Process flow chart for the synthesis of nano-SiO$_2$ by complexation precipitation method

Fig. 2 Formation mechanism of nano-SiO$_2$ synthesized by complexation precipitation method

$$\text{XCH}_2\text{COOC}_n\text{H}_{2n+1} + \text{H}_2\text{O} \rightleftharpoons \text{XCH}_2\text{COO}^+ + \text{H}^+ + \text{C}_n\text{H}_{2n+1}\text{OH}$$

$$\text{SiO}_2^{2-} + 2\text{H}^+ \rightleftharpoons (\text{SiO}_2)\cdot \text{H}_2\text{O}$$

X: Cl, Br
n=1-4

SiO$_3^{2-}$
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-$\text{SiO}_2$ with excellent dispersion and uniform particle size distribution.

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 $\text{SiO}_2$ monomers were polymerized into crosslinked highly dispersed $\text{SiO}_2$ 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-$\text{SiO}_2$ 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-$\text{SiO}_2$ with excellent dispersion and uniform particle size distribution.

2.3 Preparation of Nano-$\text{SiO}_2$

The preparation of silica sol can be referenced our previous work [23]. The silica sol used in this study was prepared 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.

We have characterized the particles of silica sol by TEM, as can be seen following Fig. 3. The initial particle size of silica sol is measured about 16.45 nm by e-rule.

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 at 8000–8500 rpm and washed with 95% ethanol. After vacuum drying, nano-$\text{SiO}_2$ was obtained by grinding.

(2) Under the condition that the steps and dosage described in Sect. 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-$\text{SiO}_2$ was obtained by centrifugation, washing, drying, and grinding.

2.3.2 Preparation Without Citric Acid Dosage

According to the steps described in Sect. 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 $\text{SiO}_2$ gel was centrifugally washed, dried, and ground to obtain nano-$\text{SiO}_2$.

2.3.3 Reaction Time

In accordance with the procedure described in Sect. 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 $\text{SiO}_2$ gel was centrifugally washed, dried, and ground to obtain nano-$\text{SiO}_2$.

2.3.4 Reaction Temperature

In accordance with the procedure described in Sect. 2.3.1 (1) and dosage was kept unchanged, only reaction temperature were changed, then the obtained $\text{SiO}_2$ gel was centrifugally washed, dried, and ground to obtain nano-$\text{SiO}_2$.

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 Kα line, $\lambda=0.15406$ nm) at room temperature. A Tecnai-12 type (120 kV) transmission electron was

Fig. 3 TEM of silica sol nanoparticles
used. The morphology 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-SiO$_2$ was observed using a JEOL JSM-6360LV scanning electron microscope. The laser scattering particle analyzer (WJL-612, made in Shanghai Xiren Scientific Instrument Co., LTD) was also used to determine the average particle size of obtained nano-SiO$_2$.

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 4a 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 [24], 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 469.7 cm$^{-1}$.

3.1.2 SEM Characterization

Figure 5a and b 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 non-agglomerated Nano-SiO$_2$ gel appears, and the size of silica sol is about 24.66 nm as determined using an electronic ruler.

3.2 Characterization of Nano-SiO$_2$

3.2.1 TGA/DTA and DTG

Figure 6 shows the TGA/DTA and DTG diagram of Nano-SiO$_2$. 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, indicating 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 DTA 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 nano-SiO$_2$ powder.

3.2.2 TEM and Particle Size Analysis of Nano-SiO$_2$

Figure 7 shows the TEM image of nano-SiO$_2$. Figure 7a shows that the dispersion of nanoparticles is relatively uniform, and the particle size is relatively good. Figure 7b shows the local enlarged version of Fig. 7a. The particle size was roughly measured at 13.07–29.82 nm, and the average particle size was about 19.44 nm.

Figure 7c shows the particle size analysis and test results of nano-SiO$_2$. The nano-SiO$_2$ 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 4b shows the FTIR spectrum of the prepared nano-SiO$_2$ 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-SiO$_2$ 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$^{-1}$. By comparing the infrared spectra of the nano-SiO$_2$ sample with silica sol, it is found that the peak at 1096.27 cm$^{-1}$ shifts to 1102.00 cm$^{-1}$, and its intensity increased sharply, indicating formation of amorphous silica.

Figure 8 shows a wide-angle diffraction pattern of nano-SiO$_2$, and there is a strong diffraction peak at 2$\theta$ 22.3$^\circ$, indicating that the synthesized sample is amorphous silica.

3.2.4 BET Analysis

Figure 9 shows the N$_2$ adsorption desorption curve of nano-SiO$_2$ 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 m$^2$/g, 389.67 m$^2$/g, and 380.88 m$^2$/g, which far exceeds the national standard of precipitation method (70–220 m$^2$/g).

### 3.3 Discussion on Variables in Reaction Conditions

#### 3.3.1 Amount of Ethyl Acetate

Figure 10 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. 10i], and the particle size is about 53.01 nm.
Fig. 9  \( \text{N}_2 \) adsorption desorption curve of nano-SiO\(_2\)

Fig. 10  Effects of adding different amounts of ethyl acetate on silica particle size. a \( V \) ethyl acetate: \( V \) silica sol = 0; b \( V \) ethyl acetate: \( V \) silica sol = 1:100; c \( V \) ethyl acetate: \( V \) silica sol = 1:50; d \( V \) ethyl acetate: \( V \) silica sol = 1:20; e \( V \) ethyl acetate: \( V \) silica sol = 1:10; f \( V \) ethyl acetate: \( V \) silica sol = 2:25; g \( V \) ethyl acetate: \( V \) silica sol = 7:50; h \( V \) ethyl acetate: \( V \) silica sol = 9:50
However, with the increase in the amount of ethyl acetate, the particle size changed slightly when the ratio of $V_{\text{ethyl acetate}}:V_{\text{silica sol}}$ is 1:20, but the dispersion is different. In Fig. 10c–h, the probability of particle size in the range of $<50$ nm is $65.0\% \rightarrow 47.5\% \rightarrow 42.5\% \rightarrow 45.0\% \rightarrow 55.0\% \rightarrow 67.5\%$, showing a first a downward trend and then an upward trend. The probability of a large particle size $>80$ nm increased from $10.0\% \rightarrow 5.0\% \rightarrow 12.5\% \rightarrow 0\% \rightarrow 7.5\% \rightarrow 5.0\%$. 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 $V_{\text{ethyl acetate}}:V_{\text{silica sol}}=1:20$, the particle size of 30% is $40–45$ nm. When $V_{\text{ethyl acetate}}:V_{\text{silica sol}}=9:50$, the particle size and dispersion are better than others (Table 2).

### 3.3.3 Reaction Time

Figure 12 shows the effect of different reaction times on nano-SiO$_2$ 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 are larger than 77.5%, 72.5%, 22.5%, and 62.5% of the total number of particles, respectively, and the larger particles with size more than 80 nm are 5.0% 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. 12i). 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

Fig. 11 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%
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.

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

| V ethanol / V 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                     |
3.3.4 Reaction Temperature

Figure 13 shows a statistical analysis of the effect of different temperatures on the size of nano-SiO$_2$. 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-SiO$_2$ particles cannot be formed. Only when the temperature is higher than

![Graphs showing particle size distribution at different temperatures](image)

**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 |
65 °C can the hydroxyl groups on the surface of silica sol condense to form nano-SiO$_2$.

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 and 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 SiO$_2$ 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 SiO$_2$ particle structure through diffusion. When the monomer concentration is very high, the polymerization speed is very fast, and SiO$_2$ 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 SiO$_2$ monomers. Owing to hydrogen bond association, the carboxyl group will attract H$_3$O$^+$ in the sol. The addition of a sol precipitant promotes the polymerization of multiple SiO$_2$ monomers to crosslinked SiO$_2$ 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-SiO$_2$ 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 paper, 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-SiO$_2$ 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-SiO$_2$ particles are the best.

Author Contributions YY: methodology, investigation. YY: conceptualization, supervision, writing—original draft, project administration, funding acquisition, writing—review and editing, data curation. CN: formal analysis, visualization, validation, resources, software.

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Data Availability Supplementary data to this article can in the following article. [1]T.M. Tian, Preparation of silica sol and nano silica and immobilization of horseradish peroxidase [D]; East China University of Science and Technology. 2014.

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