Preparation of Nanometer Silica by Freeze-Drying Chemical Precipitation Method

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Abstract

Nanometer SiO_2 with different sizes and shapes is synthesized by coprecipitation technique using sodium silicane as Si source, ammonium chloride as precipitant, ethanol as dispersant, CTAB as regulator. Nanometer SiO_2 \is obtained from the titration precipitation method and reverse titration precipitation method, respectively. Morphology size distribution and structure of SiO_2 particles is characterized by laser particle size analyzer microscope and FTIR. The results show that the optimum condition of synthesizing nanometer SiO_2 were as follows, the concentration of sodium silicane was 0.4 mol/L, volume ratio of ethanol to water was1:8, pH value was 8.5, concentration of CTAB was 6mmol/spherical silica particles ranging from 3 to 6nm are prepared by the method of reverse titration precipitation and freeze-drying.

Keyword：Nanoscale, Reverse Titration，Freeze-Drying

1 Introduction

opttical, and electronic properties are remarkably different from that of bull materials and from their atomic counterparts. Several new effects have been observed in mesoscopic nanoscaled systems. For example, quantum size, small size effect, surface effect and macroscopic quantum tunnel effect. These novel properties may enable new or improved solutions to problems that have been challenging to solve with conventional technology [2]. Therefore, the high dispersion of nanometer SiO_2 is widely used in rubber, plastic, paint, catalyst, durable building materials, and other fields [3~4].

During the past decades, scientists have developed techniques for synthesizing and characterizing of nanometer SiO_2 [5]. The design and fabrication of nanoscale materials with controlled properties are still a significant and ongoing challenge with nanoscience. The most applicable fabrication procedures include physical methods and chemical methods. [6] Physical methods mainly include crushing up method, Dyno-mill, low temperature crushing up method and ultrasound-assisted synthesis. Chemical methods mainly include chemical precipitation method, sol-gel method, vapor phase method, microemulsion method etc. [7~8]. Among these methods, chemical precipitation method [9] is the most prevalent method because of its simple process and low energy consumption [10~11]. However, nanometer SiO_2 obtained by chemical precipitation method is agglomerated easily and distribute unevenly, therefore in order to overcome above-mentioned problems, the effect of the concentration of surfactant, the drying and the titration style on the chemical precipitation method were studied.

In this paper, nanometer SiO_2 in the range of 3~6 nm particle size is synthesized by using sodium silicane as Si source, ammonium chloride as precipitant, ethanol as dispersant under reverse titration precipitation and freeze-drying method.

2 Experimental

2.1 Materials

Sodium silicane（$Na_2SiO_3·9H_2O$, Ammonium chloride（NH_4Cl）, AR, Anhydrous ethanol, Tianjin wind boat chemical reagents Technology Co., Ltd; cationic surfactant cetyl trimethyl ammonium bromide (CTAB)， AR, Tianjin Guangfu Fine Chemical Research Institute;

TG16-WS desktop high-speed centrifuge, Hunan Xiangyi Group; WQF-510 FTIR infrared spectrometer, Beijing North sub-Rayleigh Analytical Instruments Group; Motic-BA310MET-type metallographic microscope, Beijing Khan Zunxiao Star Instrument Co., Ltd.

2.2.1 Preparation of nanometer SiO_2

The sodium silicate is dissolved in ethanol solution, and a small amount of cationic surfactant cetyl trimethyl ammonium bromide was added into it. The ammonium chloride solution was then placed in a constant temperature magnetic stirrer, the temperature was controlled at 40 ℃, and then the sodium silicate solution was slowly dropped into the ammonium chloride solution until the certain pH value is reached. The reaction was continued for 1 h, and the precipitate was centrifuged with the aqueous ethanol solution of CTAB, and finally the white powder was dried and calcined.

2.2.2 Determination of bulk density

Calculated by the following formula:

$$\text{Bulk density} = (m_1 - m_2)/V$$

First weigh the quality of the cylinder, write down the data(m_1), and then slowly pour the sample into the funnel, falling freely into the cylinder, weigh the mass(m_2,) and read the product volume in the cylinder (V) [12].

2.2.3 Sedimentation test

Nanometer SiO_2 powders were dispersed in water under sonication. After 24 h, observe the sedimentation of particles. According to the Stoke rule [13]：the sedimentation velocity V is proportional to the square of the diameter r of the particles. Therefore, the relative size of the particle can be determined based on the sedimentation of particles.

3 Results and discussion

3.1 Effect of the concentration of CTAB

In this experient, the concentration of sodium silicane was 0.4 mol/L, volume ratio of ethanol to water was1:8, pH value was 8.5. The change of bulk density of SiO_2 at different concentration of CTAB is shown in Table I and Fig. 1, average size of SiO_2 is listed in Table I and Fig. 2.

It can be indicated from Table I and Fig. 1, when the concentration of CTAB is less than 4mmol/l, the bulk density of samples decrease obviously with the increase of concentration of CTAB. When the concentration of CTAB is more than 4mmol/l, the bulk density of samples increase with the increase of concentration of CTAB

It can be indicated from Table Ⅰ and Fig. 2, When the concentration of CTAB is less than 6mmol/l, the particle size decreases with the increase of the concentration of CTAB. When the concentration of CTAB is more than 6mmol/l, the particle size increases with the increase of the concentration of CTAB. When the concentration of CTAB is 6mmol/l, the average particle size of the sample is the smallest.

It is known that too high or too low concentration of CTAB will lead to the particle size of sample is too large. This is because the ammonium chloride solution is weak acid, the polycondensation reaction rate of silicic acid is very slow, but with the continuous addition of sodium silicate solution, the pH of solution gradually close to the weak alkaline, the polycondensation reaction rate of silicic acid is the fastest at this point, the surface of nanoparticle is negatively charged. When the concentration of CTAB is higher, the negative charge on the surface of the nanoparticle is neutralized and the repulsive force between the particles decreases due to the cationic surfactant. With the increase of the concentration of CTAB, micelles will be formed on the surface of particles, so that nanometer SiO_2 is better dispersed. when the concentration of CTAB continues to increase, the electric double layer of particles was destroyed, in addition, the particles is agglomerated because of the strands of macromolecules twine around each other, which leads to the increase of particle size.

Therefore, when the concentration of CTAB in the solution is within 4~6 mmol/L range, the particle size of the sample is small.

3.2 Effect of the drying methods

Samples were prepared at the CTAB concentration of 6 mmol /L by using hot air drying and freeze-dried method respectively, the other conditions were the same as before.

The products of hot air drying are compact and block, need to be lapped before calcine. But the products of freeze-drying are fluffier, can be directly calcined Samples under different drying methods are seen in Fig. 3.

The bulk density and particle size of the calcined sample are shown in Table Ⅱ and the microscopic photograph is listed in Fig. 4(a) and Fig. 4(b).

It can be indicated from Table Ⅱ, Fig. 4(a) and Fig. 4(b) that the sample prepared by freeze drying has a smaller bulk density, a smaller average particle size and better dispersibility. In the hot air drying process [14], the sample is seriously agglomerated because of the capillary effect of the large gas-liquid interfacial tension produced by solvent evaporation. But the freeze-drying technique is based on the direct transformation of solid ice into vapor, there is no liquid, the capillary effect is avoided [15~17], so that the silica particles cannot be close to each other and agglomerate.

3.2 Effect of the titration methods

Under the above experimental conditions, effect of the titration methods on the particle size was studied, one group is the reversetitration method using sodium silicate titration of ammonium chloride, another group was titration method using ammonium chloride titration of sodium silicate. the bulk density of the samples by different titration methods were shown in Table, Sedimentation test results were listed in Fig.5.

It can be indicated from TableⅢand Fig.5 that the sample obtained by the reverse titration method has a smaller bulk density, the dispersity of the sample at the same time is better and the sedimentation rate is slower than the other sample.

It can be shown from Table Ⅲand Fig.6 that the average particle size of the sample obtained by the reverse drop

method under the same conditions is small and the particle size distribution is also uniform. The size distribution of the sample obtained by the titration method is relatively irregular and the distribution range is wider.

During the precipitation reaction, the growth of the particles is divided into three stages, the nucleation stage, the nucleation growth stage, and the aggregation stage. [18] These three stages compete with each other. According to the characteristics of the precipitation reaction, it can be indicated that the speed V_1 and the growth rate V_2 of the nucleation decide the size of the particles obtained [19]. When $V_1 > V_2$, the particles are very small and have good dispersion. When $V_1 < V_2$, the growth rate of crystal nucleus is accelerated, which is conducive to the formation of precipitation. It can be indicated from Fig. 4(c) that the sample obtained by the reverse titration method is fluffier, and the samples from Fig. 4(d), have serious agglomeration phenomenon. This is because the sodium silicate is surrounded by a large number of ammonium ions when it dropped into the ammonium chloride solution and the reaction produces a large number of cations at the same time, they are mutually exclusive by Coulomb force and dispersed evenly. In addition, because of low viscosity of reaction system, a rise in temperature is beneficial for particles to collide with each other to form precipitation, and the growth rate of crystal nucleus V_2 is promoted, finally, $V_1 < V_{2,\text{resulting}}$ in precipitation, the formation of sol is inhibited, which the particle size of the product can be controlled [16].

3.4 FT-IR

The IR spectra of the nanometer SiO_2 powder before and after calcination is shown in Fig. 7. It can be indicated from Fig. 7 (2), the absorption peaks of calcined silica powders agree with the standard spectra of silica. In Fig. 7(1), the absorption peak at 440 cm^{-1} is corresponding to the bending vibration absorption peak of Si-O-Si bond. The peaks at 797and 1049cm-1 are corresponding to symmetric stretching and antisymmetric stretching vibration absorption peaks of Si-O-Si bonds, respectively. The peak at 956 cm-^{1} is corresponding to the bending vibration absorption peak of Si-OH. And the peaks at 1647 and 3445 $cm^{-1}$are corresponding to the absorption peak of the water molecule. The peak at 1647 cm^{-1} is the bending vibration absorption peak of the H-O-H bond which associated with the free water. The peak at 3445 $cm^{-1}$is caused by the antisymmetric O-H bond of the silanol group and the bound water stretching vibration absorption peak. The stretching vibrations of the carbon chain in the surfactant CTAB is at 2914 and 2843 cm^{-1}.Compared with the sample uncalcined, the peak at 3445, 1647 and 956 cm^{-1} is reduced and the peaks at 1049, 797 and 440 cm^{-1} are enhanced and moved in the direction of high wave number, indicating that during the high temperature calcination process, the silica formed Si-O-Si bonds through Si-OH condensation. The absorption peak associated with the carbon chain disappears.

4 Conclusion

In this research, 3-6 nm silica was synthesized by chemical precipitation method of reverse titration and freeze-drying with the CTAB concentration of 4~6 mmol/l, the concentration of sodium silicate of 0.4 mol/l, the volume ratio of ethanol to water of 1:8, pH of 8.5.

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TABLE Ⅰ. Effect of the concentration of CTAB on bulk density and average size

No	CTAB /(mmol·L^{-1})	V/cm^{-3}	(m_1-m_2) /g	Bulk density /(g·cm^{-3})	D50/(nm)	Average size/（nm）
1	0	1.02	0.1885	0.1848	16.695	20.353
2	2	1.72	0.1810	0.1052	10.672	12.331
3	4	1.60	0.1580	0.0988	10.087	12.697
4	6	1.22	0.1420	0.1164	5.797	7.223
5	8	1.24	0.1273	0.1027	14.023	15.969
6	10	1.05	0.1875	0.1785	15.146	17.856

TABLE Ⅱ. Effect of the drying methods on bulk density and average size

No	Drying methods	V/cm^{-3}	(m_1-m_2)/g	Bulk density /(g·cm^{-3})	D50/(nm)	Average size/ （nm）
1	Hot air drying	1.20	0.1143	0.0953	14.018	15.962
2	Freeze-drying	1.40	0.1222	0.8729	10.097	11.459

TABLE Ⅲ. Effect of the titration methods on bulk density and average size

No	Adding methods	V/cm^{-3}	(m_1-m_2)/g	Bulk density /(g·cm^{-3})	D50/(nm)	Average size/（nm）
1	Reverse titration	1.20	0.0942	0.0785	5.797	7.223
2	titration	1.60	0.1393	0.0871	5.713	8.046

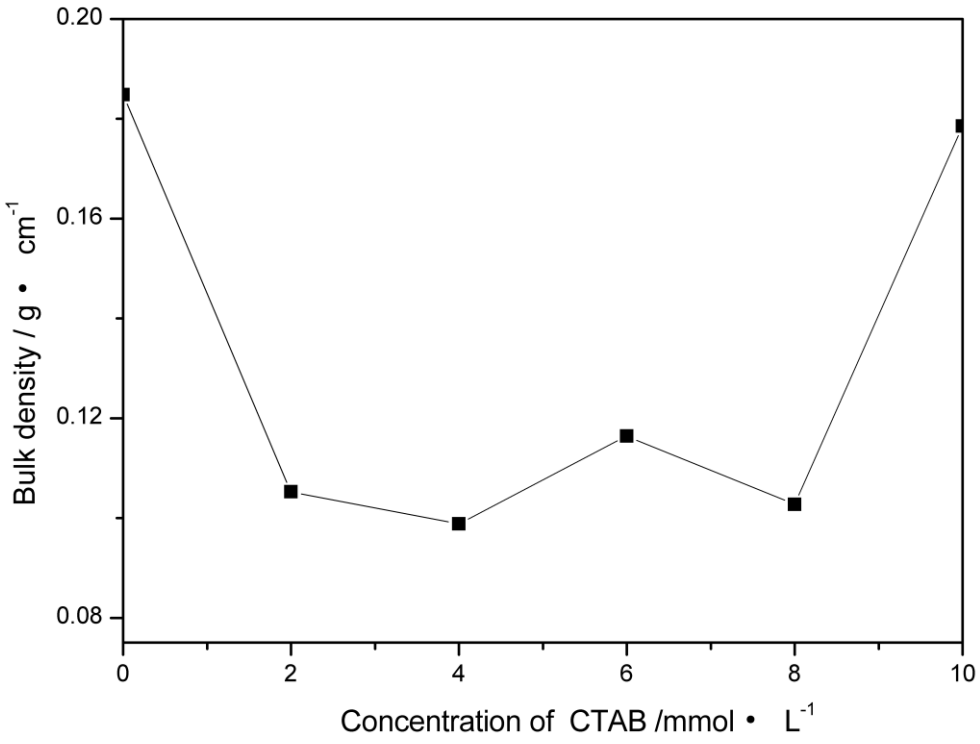

FIG. 1. Effect of the concentration of CTAB on bulk density

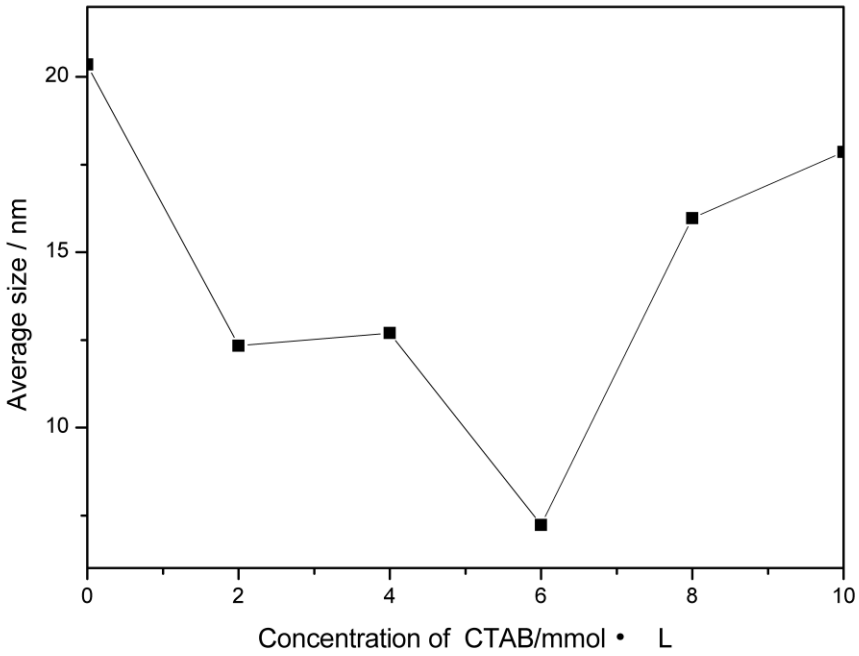

FIG. 2. Effect of the concentration of CTAB on average size

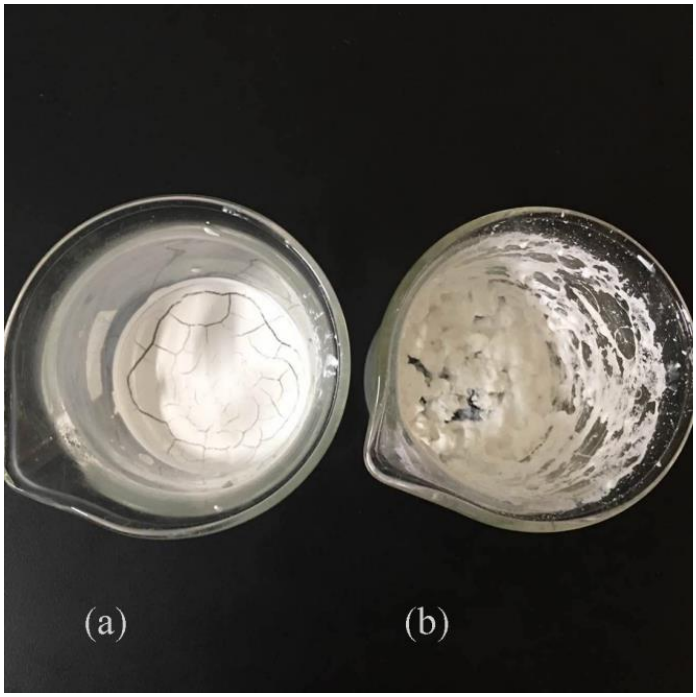

FIG.3. Sample under different drying methods. (a)using a hot air-drying method, (b) using a freeze-drying drying method.

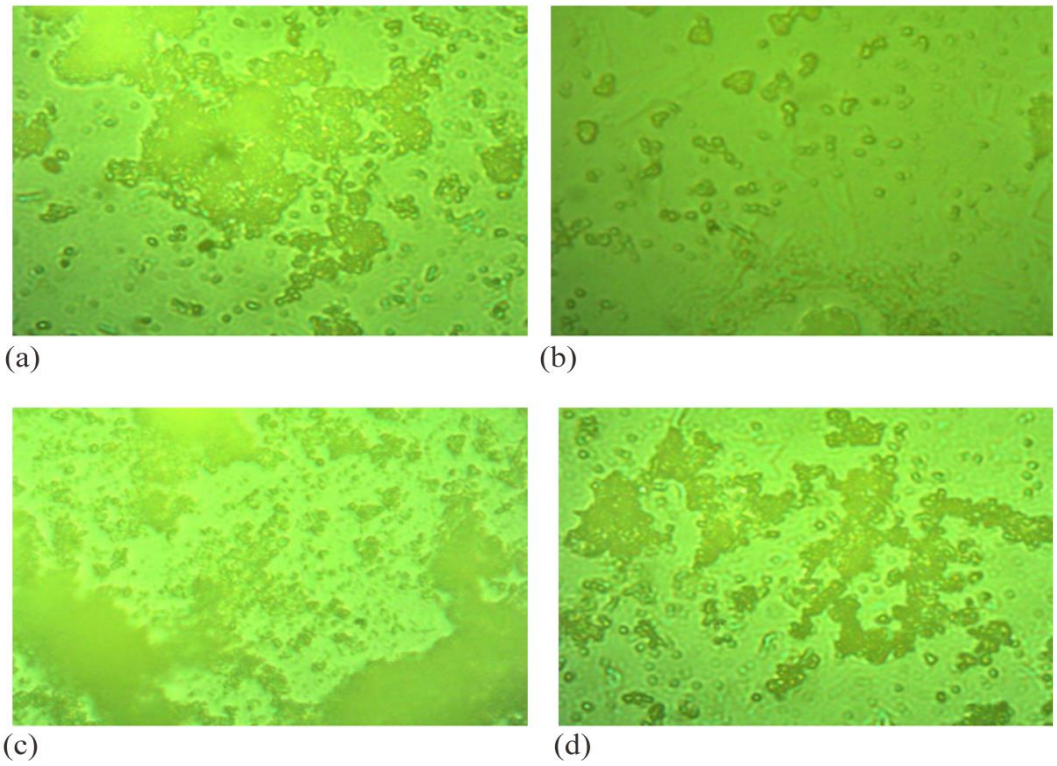

FIG. 4. Micrographs (a） hot air-drying method (b) freeze-drying method (c)titration (d)reverse titration

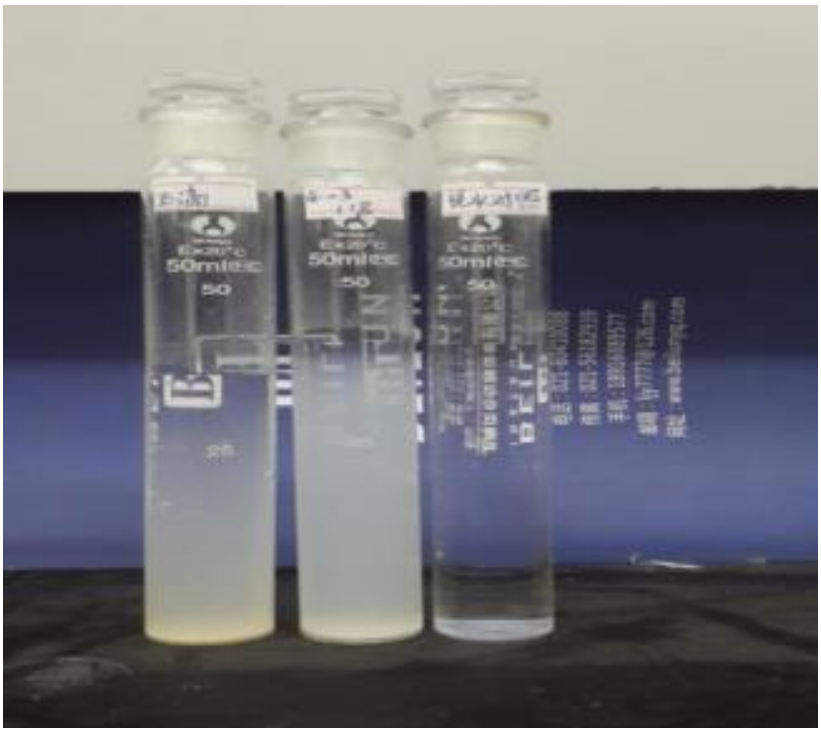

FIG. 5. Effect of sample suspension by different titration methods after sedimentation for 24 h. the samples

from the left to the right are the titration method, the reverse titration method, and the water.

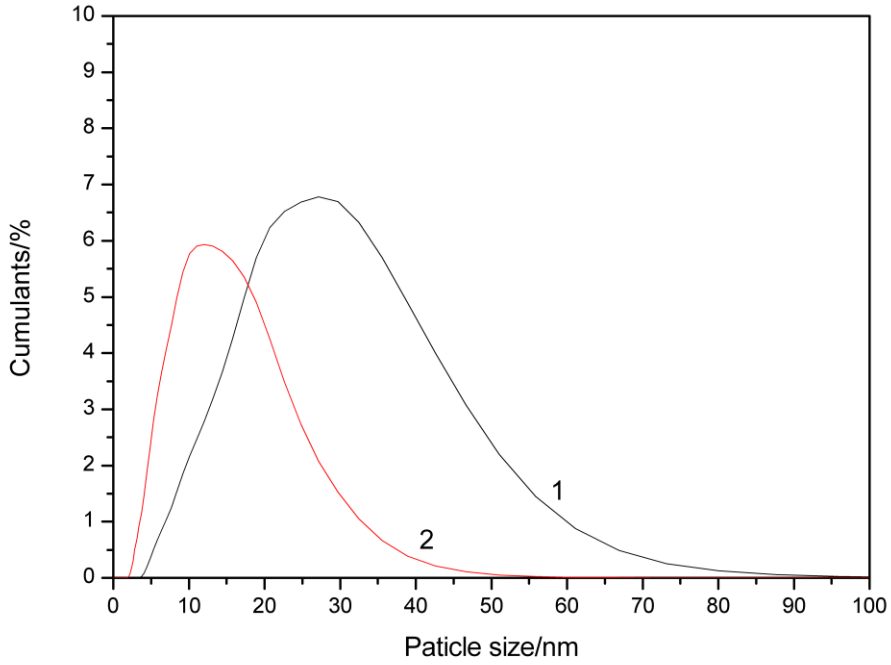

FIG. 6. The particle size distribution of SiO_2 are obtained by different titration methods.

1 titration 2 reverse titrations

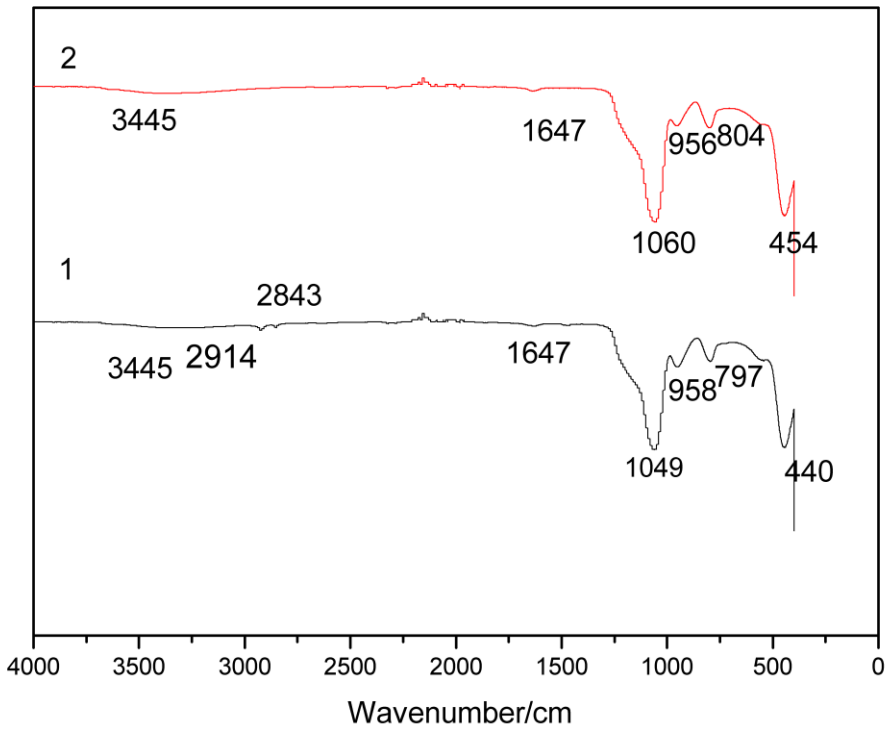

FIG. 7. Infrared spectra of silica before and after calcination 1 uncalcined 2 calcined