An Optimum Condition of Surface Modification Improving the Dispersity of Nano-Silica in Organic Solvents Using 2-Propenoic-2-methyl-3-trimethoxysilyl-propyl Ester Water Solution

YULIN LI[1,2], ZHENGXING CHEN[1,2,*], XIAOXUAN LI[1,2] and HUAWEI ZENG[3]

[1]The State Key Laboratory of Food Science and Technology, Jiangnan University, 1800 Lihu Rood, Wuxi 214122, P.R. China
[2]The School of Food Science and Technology, Jiangnan University, 1800 Lihu Rood, Wuxi 214122, P.R. China
[3]The Key Laboratory of Industrial Biotechnology Minister of Education, School of Biotechnology, Jiangnan University, 1800 Lihu Rood, Wuxi 214122, P.R. China

*Corresponding author: Fax: +86 510 85888301; Tel: +86 510 85917025; E-mail: zxchen2007@126.com

Surface modification improving the dispersity of the prepared nano-silica in organic solvents using different concentrations and amounts of 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester in aqueous solution were investigated. The result suggested that the optimum modification condition was that the concentration of 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester in aqueous solution was 0.4 mol/L and the amount of 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester water solution was 30 mL/10 g nano-silica. The dibutyl phthalate absorption number of the optimum modified nano-silica was 3.5 cm^3/g. The result from Fourier transform infrared suggested that the surface of the prepared nano-silica was modified by 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester water solution (0.4 mol/L, 30 mL/10 g nano-silica). X-Ray diffraction further indicated that the prepared nano-silica was modified by surface modification using 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester water solution (0.4 mol/L, 30 mL/10 g nano-silica). Transmission electron microscopy images revealed that the dispersity of the prepared nano-silica in organic solvents was obviously improved. The data of the dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents further demonstrated that the dispersity of the prepared nano-silica in organic solvents was improved by surface modification using 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester water solution (0.4 mol/L, 30 mL/10 g nano-silica).

Key Words: Surface modification, Dispersity, Nano-silica, Organic solvents, Dibutyl phthalate absorption number.

INTRODUCTION

Nano-silica well-dispersed in organic solvents can increase the strength of rubber and plastics, the whiteness of paper and the fluidity and resisting-electron ability of drugs[1-3]. It can improve the painting effect of coatings[4,5]. It can also keep fruits and vegetables fresh[6,7]. Improving the dispersity of nano-silica in organic solvents caused intensively interesting. In previous works, Voelkel[8] investigated surface modification improving the dispersity of nano-silica in organic solvents using titanate. Li and Zhu[9] investigated surface modification improving the dispersity of nano-silica in organic solvents using oleic acid. Su[10] investigated surface modification improving the dispersity of nano-silica in N,N'-*bis*maleimide-4,4'-diphenylmethane using vinyltriethoxysilane. Takai[11] investigated surface modification improving the dispersity of silica in polyimide using aminopropyl triethoxysilane. These modification agents had two disadvantages: (1) the organic groups in these modification agents could not react with the surface -OH groups of nano-silica completely[8-11]; (2) these modification agents were easy to be separated from the surface of nano-silica if they encoun-

tered polar mediums[8-11]. Moreover, the modification effects were not ideal. Therefore silane coupling agent as a new modification agent was considered and investigated[12]. Li *et al.*[12] investigated surface modification improving the dispersity of nano-silica in organic solvents using 0.05 mol/L 2-propenoic-2-methyl-3-trimethoxysilyl-propyl ester (KH-570) anhydrous alcohol solution. They did not demonstrate if the concentration and amount of KH-570 were optimum. Moreover the modification effect was not ideal.

The concentration and amount of KH-570 were the most two important factors affecting the modification effect. There were no reports on the effect of the concentration and amount of KH-570 water solution on improving the dispersity of nano-silica in organic solvents. The objective in this study is to gain an optimum concentration and amount of KH-570 water solution of improving the dispersity of nano-silica in organic solvents. The dibutyl phthalate (DBP) absorption number was used as the index of evaluating the modification effect. The prepared nano-silica and optimum modified nano-silica were characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM)

images. The dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents such as anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin were compared.

EXPERIMENTAL

KH-570 was purchased from Crompton Shuguang Organo-silicon Co. (Nanjing). Nano-silica was produced from rice hull ash. All other reagents were of analytical grade and used without further treatment.

Flowchart of this research: The procedures of this research were shown in Fig. 1.
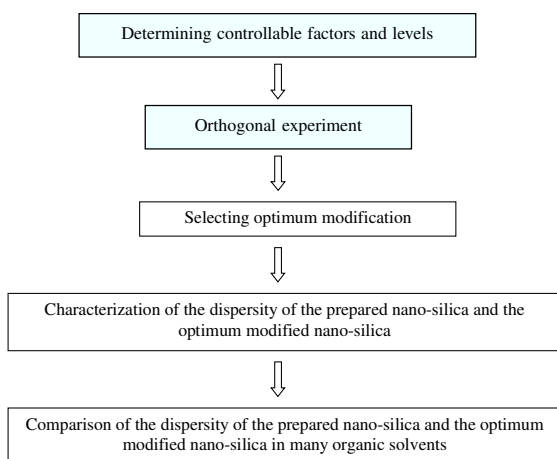

Fig. 1. Flowchart of the research

Determining the optimum modification condition

Orthogonal experiment design: The concentration and amount KH-570 water solution were used as the controllable factors. Their levels were listed in Table-1. An orthogonal array L_4 (2^3) was used to determine the optimum modification condition (Table-2).

TABLE-1
FACTORS AND LEVELS DESIGN OF
THE ORTHOGONAL EXPERIMENT

Level	Factors	
	Concentration of KH-570 water solution (mol/L) (A)	Amount of KH-570 water solution (mL) (B)
1	0.2	25
2	0.3	30
3	0.4	35

Preparation of the different modified nano-silica samples: Thirty g of the prepared nano-silica and 300 mL of water were added in a 500-mL flask. The mixture was heated at 80 °C in water bath with stirring at 250 rpm. KH-570 water solution (the concentration from 0.2-0.3 mol/L, the volume from 25-35 mL, respectively) were added to the flask at 3 mL/min by a constant flow pump[12]. The mixtures were treated by an Ultrasonic Cell Muller at 90 W for 15 min after they reacted for 90 min. Finally the mixtures were centrifuged at 3000 rpm for 10 min and filtered through Whatman ashless filter paper[12]. The filter cakes were repeatedly washed with deionized water[12]. The filter cakes were dried at 80 °C for 12 h to get different modified nano-silica samples.

TABLE-2
ORTHOGONAL ARRAY* (DIBUTYL PHTHALATE (DBP) ABSORPTION NUMBER OF NANO-SILICA: 2.0 cm³/g)

Sample	A	B	DBP absorption number (cm³/g)
L1	1	1	2.7 ± 0.1^a
L2	1	2	2.8 ± 0.1^a
L3	1	3	2.7 ± 0.1^a
L4	2	1	3.1 ± 0.1^b
L5	2	2	3.2 ± 0.1^b
L6	2	3	3.0 ± 0.1^b
L7	3	1	3.4 ± 0.1^c
L8	3	2	3.5 ± 0.1^c
L9	3	3	3.4 ± 0.1^c
K_1 (cm³/g)	8.2	9.2	
K_2 (cm³/g)	9.3	9.5	
K_3 (cm³/g)	10.3	9.1	
Variance (cm³/g)	2.1	0.4	

*Values are means ± SD (n = 3). Values followed by the different letter in the same column are significantly different (p ≤ 0.05).

Measurement the dibutyl phthalate absorption number of different modified nano-silica samples: According to the STANDARD (HG/T 3061-2008) of China, 1 g of the sample was dried at 105 °C for 1.5 h and placed on a glass board (170 mm × 140 mm). The dibutyl phthalate was rapidly added in the prepared sample. The mixture was stirred by a glass rod and constantly pressured until it was completely crushed. Then the dibutyl phthalate was slowly added in the crushed sample with stirring and pressuring until the sample was totally infiltrated by it. The volume of the dibutyl phthalate consumed was designated as the dibutyl phthalate absorption number of the sample.

Characterization of the prepared nano-silica and the optimum modified nano-silica: The prepared nano-silica and the optimum modified nano-silica were characterized using FT-IR, XRD and TEM image. Their test conditions were listed in Table-3[13,14].

TABLE-3
TEST CONDITIONS OF FT-IR, XRD AND TEM IMAGE

Characterization method	Test equipment	Test conditions
FT-IR	Nicolet Nexus 470 FT-IR spectrometer (Thermo Electron Company, America)	Scanning rate: 32 times/min; Resolution: 4 cm⁻¹
XRD	D8 Advance Bruker Rotaflex Diffractometer (Bruker Axs Company, German)	Acceleration voltage: 40 kV; Current: 45 mA; 2θ: from 10°-40°; Rate: 5°/min.
TEM image	JEM-2010 microscopy (JEOL, Japan)	Voltage: 200 kV; Current: 80 mA.

Comparison of the dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents: The sample (m_1, g) and an organic solvent (50 mL, such as anhydrous alcohol, CH_2Cl_2, CCl_4, liquid paraffin and cyclohexane) were added and stirred in a beaker. The supernatant was discarded. The sediment was dried and weighed (m_2, g). The dispersity of the sample in the organic solvent was calculated according to eqn. 1:

The dispersity of the sample

$$= \frac{(m_1 - m_2)}{50} \times 100 \ (g/100 \ mL) \tag{1}$$

Statistical analysis: Statistical analysis was carried out using ORIGIN 7.5 (OriginLab Inc., USA).

RESULTS AND DISCUSSION

Modification principle of nano-silica: Silicate was produced when sodium silicate and sulfuric acid were mixed up[12,15]. The elements Si and O in the silicate connected by a covalent bond form a defective three-dimensional structure[12,15]. A number of -OH groups are left on the surface of nano-silica. Therefore nano-silica is hydrophilic, easy to agglomerate and difficult to be dispersed in organic solvents[12,15]. KH-570 is a long chain organic molecule (Fig. 2) and can be hydrolyzed to produce R-Si-OH (R, CH$_2$=C(CH$_3$)-COO-(CH$_2$)$_3$-Si-). The -OH group of the R-Si-OH group reacts with the -OH group of nano-silica when nano-silica and KH-570 are mixed together[12,15]. The -Si-R group is connected with the surface of nano-silica. The combination produces steric hindrance, which prevents nano-silica from agglomeration[12,15]. The principle was shown in Fig. 3.
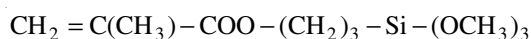
$$CH_2 = C(CH_3) - COO - (CH_2)_3 - Si - (OCH_3)_3$$

Fig. 2. Molecule structure of KH-570

$$SiO_3^{2-} + H_2O \longrightarrow Si - (OH)_4 \qquad (1)$$

$$R - Si - (OCH_3)_3 + H_2O \longrightarrow R - Si - OH + CH_3 - OH \quad (2)$$

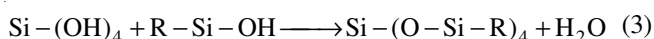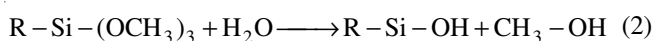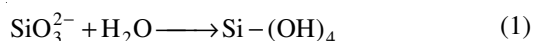$$Si - (OH)_4 + R - Si - OH \longrightarrow Si - (O - Si - R)_4 + H_2O \quad (3)$$

Fig. 3. Modification principle of nano-silica

Characteristics of the prepared nano-silica: Nano-silica used in this study was prepared from rice hull ash. Its characteristics and measuring method and equipment were listed in Table-4[14]. These characteristics suggested that the prepared nano-silica was qualified and could be used to modify.

TABLE-4
CHARACTERISTICS OF THE PREPARED NANO-SILICA*

Characteristics	Value	Measuring method	Measuring equipment
Size	30 ± 1 nm	Laser method	Nano-2s size/zeta potential apparatus
DBP absorption number	2.1 ± 0.1 cm^3/g	STANDARD (HG/T 3061-2008)	
Lipophilic value	0	Computing method	
Specific surface area	141 ± 1 m^2/g	BET analysis	JW-BK surface area and pore size analyzer

*Values are means ± SD (n = 3).

Determination of the optimum modification condition of nano-silica: According to the chemical balance theory, the concentration of the reactants could greatly affect the chemical balance. The concentration of nano-silica and KH-570 in the reaction system were the two most important factors affecting the modification. The concentration of nano-silica was fixed in present study because preparation of nano-silica was difficult and not easy to be changed. The concentration of KH-570 in the reaction system was mainly depend on the concentration and amount of KH-570 water solution. So the concentration and amount of KH-570 water solution were selected as the controllable factors.

The agglomeration degree of nano-silica can be signified by the gap volume of the agglomerated nano-silica. This gap volume can be measured through the DBP volume absorbed by the agglomerated nano-silica. The DBP absorption number can reflect the agglomeration degree and the dispersity of nano-silica directly. The higher the DBP absorption number of nano-silica is in a range, the better its dispersity is in organic solvents. So the DBP absorption number was used as the index for evaluating the modification effect in this study. The index was according with the STANDARD (HG/T 3061-2008) of China and had the authority and universality. According to the STANDARD (HG/T 3061-2008), nano-silica could be dispersed in organic solvents only if its DBP absorption number was between 2.0 and 3.5 cm^3/g. The optimum modification condition was determined according to the higher DBP absorption number. Li et al.[12] used the light transmittance as the index for evaluating the modification effect. The light transmittance only reflected the dispersity indirectly and was not accurate.

As shown in Table-2, among these modified samples, the DBP absorption number of the modified nano-silica was the highest (3.5 cm^3/g) when the concentration of KH-570 water solution was 0.4 mol/l and the amount of KH-570 water solution was 30 mL/10g nano-silica. So the optimum modified condition was that the concentration of KH-570 water solution was 0.4 mol/L and the amount of KH-570 water solution was 30 mL/10 g nano-silica. It was due to that the modification reaction could not carry out completely when the concentration of KH-570 in the reaction system was too low and there was steric hindrance on the surface of nano-silica when the concentration of KH-570 in the reaction system was too high. The effect of the concentration of KH-570 water solution on the modification effect was greater than that of the amount of KH-570 water solution because the concentration of KH-570 in the reaction system was mainly depend on the concentration of KH-570 water solution.

Characterization of the prepared nano-silica and the optimum modified nano-silica

Analysis of FT-IR patterns: FT-IR patterns of the prepared nano-silica and the optimum modified nano-silica were shown in Fig. 4. The peaks near 3420 cm^{-1} were the stretching vibration characteristic peak of the -OH group. The peaks near 1626 cm^{-1} were the bending vibration characteristic peak of the -OH group. These peaks were mainly caused by physically absorbed water and crystal water[12,16,17]. The peaks near 1103 cm^{-1} were the symmetric stretching vibration characteristic peak of the Si-O-Si group[12,16,17]. The peaks in 947 cm^{-1} region were the asymmetric stretching vibration characteristic peak of the Si-O-Si group[12,16,17]. The peaks near 472 cm^{-1} were the bending vibration characteristic peak of the Si-O-Si group[12,16,17]. The peaks 796 cm^{-1} were the stretching vibration
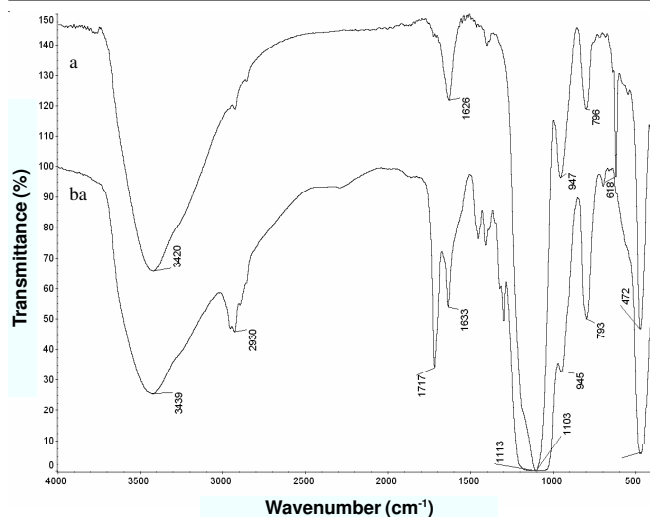
Fig. 4.   FT-IR patterns of (a) the prepared nano-silica and (b) the optimum modified nano-silica

Fig. 5.   XRD patterns of (a) the optimum modified nano-silica and (b) the prepared nano-silica

characteristic peak of the Si-OH group[12,16,17]. The peaks around 618 cm^{-1} were the bending vibration characteristic peak of the Si-OH group[12,16,17]. These peaks and groups would appear in all silica products. These results were according with previous researchers but only the intensity and the place of these peaks were slightly different.

Compared with Fig. 4a, there were some changes in Fig. 4b. There was a new peak near 2930 cm^{-1}, which is the stretching vibration characteristic peak of the -CH$_2$ group[12,16,17]. There was a new peak near 1717 cm^{-1}, which was the stretching vibration characteristic peak of the C=O group[12,16,17]. There was a new peak near 793 cm^{-1}, which was the characteristic peak of the Si-C group[12,16,17]. Three new peaks indicated that -Si-R of KH-570 was connected with the surface of the prepared nano-silica. The peaks near 796 and 618 cm^{-1} disappeared. It suggested that the -OH groups of the surface of the prepared nano-silic were replaced. The intensity of the peaks near 3439 and 1633 cm^{-1} were reduced. It also suggested that the -OH groups of the surface of the prepared nano-silic were replaced. These results demonstrated that the prepared nano-silic was modified by surface modification using KH-570 water solution. In previous study, Li *et al.*, only found the stretching vibration characteristic peak of the C=O group near 1717 cm^{-1} [12]. The stretching vibration characteristic peak of the -CH$_2$ group near 2930 cm^{-1} and the characteristic peak of the Si-C group near 793 cm^{-1} was not found and discussed.

Analysis of XRD patterns: XRD pattern was always used to characterize the crystalline structure of material. There were no data on the nano-silica and the modified nano-silica in powder diffraction file of international centre for diffraction data. XRD patterns of the prepared nano-silica and the optimum modified nano-silica were shown in Fig. 5. The peak at 22.5° in Fig. 5b was the characteristic peak of the amorphous structure of nano-silica[18]. The intensity of the peak of the prepared nano-silica was very low. It also indicated that the prepared nano-silica was steady. It was due to the reason that SiO$_2$ was arranged tetrahedron fashion and Si was located in the core of the tetrahedron and there are only -OH groups on the surface of the prepared nano-silica. This peak would appear in all silica products. The small peak at 32° in Fig. 5b
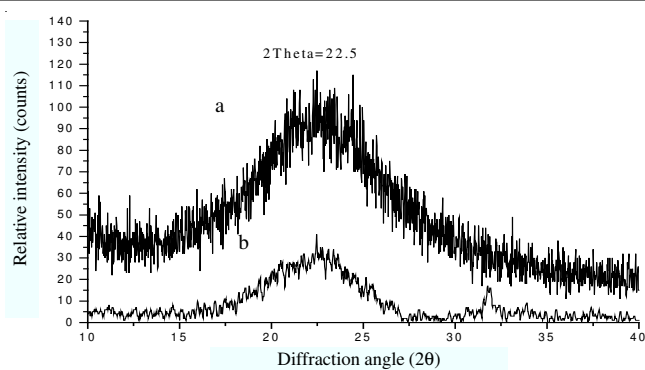
may be caused by the impurity. There was a peak at 22.5° in Fig. 5a. It also suggested the amorphous structure of the optimum modified nano-silica. The peak was heightened and widened. It was due to that R-Si- group was connected with the surface of the prepared nano-silica and the prepared nano-silica and the optimum modified nano-silica had different compositions. The result indicated that the prepared nano-silica was modified by surface modification using KH-570 water solution. The small peak at 32° in Fig. 5a disappeared because the optimum modified nano-silica did not contain the impurity.

Kalapathy used XRD pattern to characterizing the nano-silica structure. The amorphous characteristic peak occurred at $2\theta = 22°$ in nano-silica product[6]. Present result was according with his result.

TEM images: TEM image was used to characterize the agglomeration degree and morphology of the particle. TEM images of the prepared nano-silica and the optimum modified nano-silica were shown in Fig. 6. The background colours of two images were different because the prepared nano-silica and the optimum modified nano-silica were two different matters and the light intensities used were different. The number of particles with various sizes of the optimum modified nano-silica were listed in Table-5. The prepared nano-silica in this study was agglomerative and the size was big. The result was according with other researcher's silica products. Water molecules in wet silica gel interacted with the free hydroxyls on the surface of the gel particles through hydrogen bonds. When the gel particles got close, these molecules would draw neighbouring particles together. These bridging water molecules were removed when the gel began to dry and the hydrogen bonds between hydroxyls on the surface of two neighbouring particles would draw them closer. Further drying would cause the formation of strong chemical bonds between neighbouring particles. Then the hard agglomeration appeared. The agglomeration principle of the nano-silica was shown in Fig. 7.

However, the hydroxyl groups on the surface of the prepared nano-silica were replaced by -Si-R group of KH-570 after surface modification. Then the possibility for the formation of chemical bonds was greatly eliminated. So the agglomeration was prevented. The result could be explained by the following facts. (1) KH-570 could not draw particles together through the formation of hydrogen bonds. (2) No
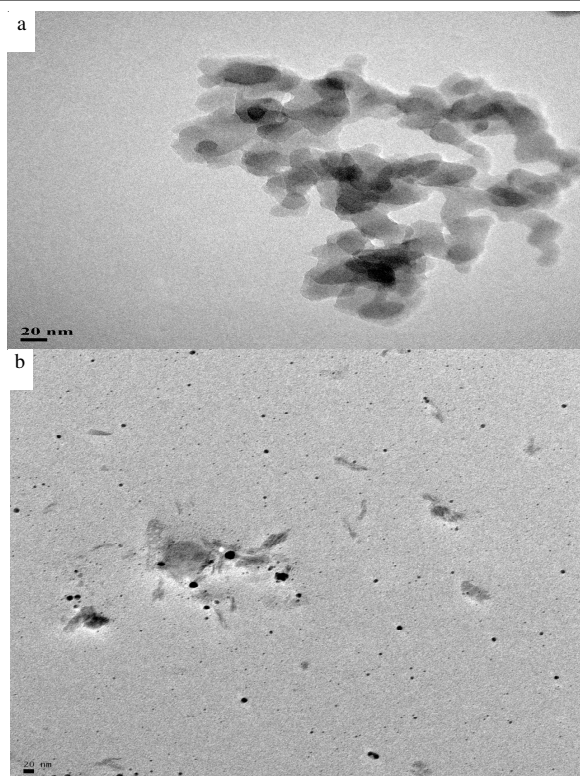
Fig. 6.　TEM images of (a) the prepared nano-silica (magnification: 50000 times) and (b) the optimum modified nano-silica (magnification: 20000 times)

TABLE-5
NUMBER OF PARTICLES WITH VARIOUS SIZES OF THE OPTIMUM MODIFIED NANO-SILICA

Size (nm)	Percentage (%)
1-5	81
6-10	10
11-15	5
16-20	3
Above 21	1

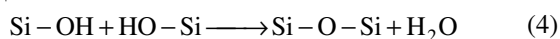$$Si-OH + HO-Si \longrightarrow Si-O-Si + H_2O \quad (4)$$

Fig. 7. Agglomeration principle of nano-silica

hydrogen bond could be formed among neighbouring particles because the hydroxyl groups on the surface of the prepared nano-silica were replaced by -Si-R group. (3) -Si-R group had steric hindrance that could prevent the approach of particles. As a result, surface modification by KH-570 water solution dramatically reduced the possibility of the formation of chemical bonds and prevented the formation of the agglomeration. The optimum modified nano-silica was well dispersed and the size was reduced in this study. It suggested that surface modification could reduce the size of the nano-silica. It was due to that KH-570 eliminated the chemical bonds of neighbouring particles and then the particles became small. In previous studies, there was agglomeration appearing in modified nano-silica[12]. The hard agglomeration still appeared in Li and Zhu[19]. OA-modified nano-silica and Takai's[11] modified nano-silica. These results suggested that surface modification by KH-570 water solution was successful in this study.

Comparison of the dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents: The data of the dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents (such as anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin) were listed in Table-6. The dispersity of the prepared nano-silica in these organic solvents was poor. The optimum modified nano-silica was well dispersed in these organic solvents. The result suggested that the dispersity of the prepared nano-silica in organic solvents was improved through surface modification using KH-570 water solution. The fact may be explained using the polarity theory. There are a lot of -OH groups on the surface of the prepared nano-silica. It can form hydrogen bond with water. So the prepared nano-silica is polar and hydrophilic and can be well dispersed in water. Organic solvents were apolar and hydrophobic. The prepared nano-silica can not form the steady combination with organic solvents. Nano-silica was not well dispersed in organic solvents. -Si-R group of KH-570 was apolar and hydrophobic. The optimum modified nano-silica became apolar and hydrophobic when -Si-R groups were connected with the surface of nano-silica. The optimum modified nano-silica can form the steady combination with organic solvents. According to the principle of "the similar, the soluble", the apolar and hydrophobic optimum modified nano-silica can be well dispersed when it was mixed up with the apolar and hydrophobic organic solvents.

TABLE-6
DISPERSITY OF THE PREPARED NANO-SILICA AND THE OPTIMUM MODIFIED NANO-SILICA IN MANY ORGANIC SOLVENTS*

Organic solvent	Dispersity (g/100 mL)	
	Prepared nano-silica	Optimum modified nano-silica
Anhydrous alcohol	0.0 ± 0.0^a	11.1 ± 0.1^a
CH_2Cl_2	0.0 ± 0.0^a	11.2 ± 0.1^a
CCl_4	0.0 ± 0.0^a	11.3 ± 0.1^b
Cyclohexane	0.0 ± 0.0^a	11.3 ± 0.1^b
Liquid paraffin	0.1 ± 0.0^a	11.5 ± 0.1^c

*Values are means $\pm$ SD (n = 3). Values followed by the different letter in the same column are significantly different ($p \leq 0.05$)

The fact that the dispersity of the prepared nano-silica in organic solvents was improved by KH-570 water solution may be explained using the rough surface theory. According to this theory, the rougher a surface is, the better its hydrophobicity is. There is only -OH group on the surface of the prepared nano-silica. These -OH groups are the same. The surface of the prepared nano-silica is smooth. So the prepared nano-silica is hydrophilic and easy to agglomerate. For a smooth surface, there are two ways to obtain the rough surface. One is to produce a rough structure on the smooth surface and the other is to change the smooth surface using some materials. When -Si-R group of KH-570 is connected with the surface of the prepared nano-silica, there are two quite different groups on the surface of the optimum modified nano-silica. The smooth surface turns into a rough surface. The new rough surface is hydrophobic and not easy to agglomerate. So the optimum modified nano-silica can be well dispersed in organic solvents.

Conclusion

This work demonstrated that the concentration and amount of KH-570 water solution could greatly affect the modification effect of nano-silica. The optimum modification condition was as follows. The concentration of KH-570 water solution was 0.4 mol/L and the amount of KH-570 water solution was 30 mL/10 g nano-silica. The DBP absorption number of the optimum modified nano-silica was 3.5 cm^3/g. FT-IR spectra phthalate indicated that there were three new characteristic peaks in the optimum modified spectra. They were caused by surface modification using KH-570 water solution. XRD patterns suggested that the amorphous characteristic peak of the optimum modified nano-silica was higher and wider than that of the prepared nano-silica. It was due to that -Si-R group of KH-570 was connected with the surface of the prepared nano-silica. TEM images revealed that the prepared nano-silica was agglomerative and the optimum modified nano-silica was well dispersed. This improvement was caused by surface modification using KH-570 water solution. The data of the dispersity of the prepared nano-silica and the optimum modified nano-silica in many organic solvents further demonstrated that the dispersity of the prepared nano-silica in organic solvents was greatly improved by surface modification using KH-570 water solution. These results suggested that the concentration of KH-570 water solution (0.4 mol/L) and the amount of KH-570 water solution (30 mL/10 g nano-silica) were applicable.

REFERENCES

1. S. Affandi, H. Setyawan and S. Winardi, *Adv. Powder Tech.*, **20**, 468 (2009).
2. G.-M. Gao, D.-R. Liu and H.-F. Zou, *Powder Tech.*, **197**, 283 (2010).
3. Y.M.Z. Ahmed, E.M. Ewais and Z.I. Zaki, *J. Univ. Sci. Tech. Beijing*, **15**, 307 (2008).
4. Q. Tang and T. Wang, *J. Supercrit. Fluids*, **35**, 91 (2005).
5. T. Li and T. Wang, *Mater. Chem. Phys.*, **5**, 252 (2008).
6. U. Kalapathy, A. Proctor and J. Shultz, *Bioresour. Tech.*, **73**, 257 (2000).
7. U. Kalapathy, A. Proctor and J. Shultz, *Bioresour. Tech.*, **85**, 285 (2002).
8. A. Voelkel, *Chromatographia*, **51**, 608 (2000).
9. Z. Li and Y. Zhu, *Appl. Surf. Sci.*, **211**, 315 (2003).
10. H. Su, *J. Appl. Polym. Sci.*, **103**, 3600 (2007).
11. C. Takai, *Colloids Surface. A: Physicochem. Eng. Asp.*, **292**, 79 (2007).
12. X.-H.g Li, Z. Cao and Z.-J. Zhang, *Appl. Surface. Sci.*, **252**, 7856 (2006).
13. G.-M. Gao, H.-F. Zou, D.-R. Liu, L.-N. Miao, S.-C. Gan, B.-C. An, J.-J. Xu and G.-H. Li, *Fuel*, **88**, 1223 (2009).
14. H. Zhang, X. Zhao and X. Ding, *Bioresour. Tech.*, **101**, 1263 (2010).
15. S.D. Bhagat and A.V. Rao, *Appl. Surface Sci.*, **252**, 4289 (2006).
16. F. Shi, L.-J. Wang and J.-X. Liu, *Mater. Lett.*, **60**, 3718 (2006).
17. D. Coutinho, Z. Yang and J.P. Ferraris, *Micropor. Mesopor. Mater.*, **81**, 321 (2005).
18. L.-J. Wang, A.-H. Lu and Z.-Y. Xiao, *Appl. Surface Sci.*, **255**, 7542 (2009).
19. Z. Li and Y. Zhu, *Appl. Surface Sci.*, **211**, 315 (2003).