

PREPARATION OF AMORPHOUS SILICA FROM OIL SHALE RESIDUE AND SURFACE MODIFICATION BY SILANE COUPLING AGENT

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Two kinds of modified amorphous silica, grafted vinyl trimethoxysilane (AH-171) and N-(n-butyl)-3-aminopropyl trimethoxysilane (DYNASYLAN 1189), were obtained from oil shale residue by the technical process of calcination and activation, alkaline dissolution, homogeneous sedimentation with ethylacetate and modification with silane coupling agents. The number of surface hydroxyl groups, modification degree, the structure and other properties of amorphous silica were investigated by chemical method, infrared analysis, nuclear magnetic resonance analysis, X-ray diffraction and scanning electron microscopy. The results show that amorphous silica treated with coupling agents AH-171 and DYNASYLAN 1189 is characterized by modification degrees of surface hydroxyl groups 93.7% and 71.2% and hydrophobic degrees 98% and 94%, respectively, as well as also by improved dispersion in organic solutions. This work gives a valid method to prepare surface modified amorphous silica from the oil shale residue.

Introduction

SiO₂ is a main component of the oil shale residue (more than 50%) that contains also Al₂O₃ (about 20%) and Fe₂O₃ (about 10%), etc. Researches in applying oil shale residue have been made extensively [1–9]. Coarse SiO₂ product can be prepared by removing impurities from the oil shale residue by the sulfuric acid leaching method, and it is a mixture of crystal and amorphous silica. Homogenous amorphous silica can be prepared by the alkaline dissolution method, and it has many potential fields of application –

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as a reinforcing agent, a thickening agent in silicone rubber, paint and other polymers. However, the surface of amorphous silica is rich in hydroxyl groups that make it hydrophilic. Amorphous silica is easy to agglomerate and poor to compatible with organic compounds, so it hardly infiltrates and disperses in organic solutions. These properties limit the application of amorphous silica in organic materials. Modifiers are used to modify the surface of amorphous silica to be hydrophobic-lipophilic and to improve the compatibility between amorphous silica particles and polymer molecules, the interaction between the filler and polymer, the processing technology, and the performance of reinforcing filler [10-16]. In order to investigate the methods of preparing amorphous silica from oil shale residue and modifying its surface, in this paper an alkaline dissolution – homogeneous chemical sedimentation method is applied. Silane coupling agents are used as modifiers, and the product obtained is the modified amorphous silica with better performance.

Experimental

Experimental equipment and raw materials

The following analytical instruments were used: XRD-6000 X-ray diffractometer; HP8453 UV spectrophotometer; JW-K specific surface area detector; Nicolet AVATAR 370 IR spectrometer; Varian MercuryPlus 400 NMR; HITACHI scanning electron microscope (S-4800); DCA-322 Dynamic Contact Angle Analyzer contact angle analyzer; SX2 box-type resistance furnace (muffle furnace).

The oil shale residue was from Huadian (China); vinyl trimethoxysilane (AH-171, Peking Chemical Factory), N-(*n*-butyl)-3-aminopropyl trimethoxysilane (DYNAS YLAN 1189, Degussa Co. Ltd.), and ethylacetate (analytical reagent).

Extraction of amorphous silica from oil shale residue

The sample of oil shale residue (2–4 g) was ground into particles (grain size of 0.1 mm) and loaded into a porcelain crucible. The crucible was put into a muffle furnace and hold there at a temperature between 700 °C and 800 °C for 1.5 hours. Thereafter the sample was cooled down in ambient air, and the calcined and activated oil shale residue was obtained. The calcined oil shale residue was mixed with 25% NaOH solution (liquid-solid ratio 4:1) in a circular flask, the flask was kept at a constant temperature in a water bath, magnetic stirring was applied for 3 h, and the mixture was filtrated before cooled down. pH value of the filtrate was adjusted to 12 with 0.2 M HCl solution, ethylacetate was added to the filtrate in a flask (molar ratio of ethylacetate to SiO₂ in H₂SiO₃ 9:10) at a constant temperature using magnetic stirring, thereafter H₂SiO₃ sediment was separated from the solution in a centrifuge, washed with deionized water and dried under

105 °C for 2 h. The white powder obtained was put into a porcelain crucible and calcined under 500 °C for 2 h to get the end product amorphous silica.

Modification of amorphous silica with silane coupling agents

Modification was carried out in a special flask equipped with a reflux apparatus and a magnetic stirring device. 60 ml of anhydrous ethanol and silane coupling agent (in the amount corresponding to surface hydroxyl number) were mixed in the flask evenly, adding a certain amount (10 g) of amorphous silica, and the mixture was let to react in the water bath at 70 °C for 2 h. Thereafter the mixture was let to reflux at 80 °C for 40 min. After cooling down the mixture was centrifuged. The separated powder was washed with anhydrous ethanol by 2 or 3 times to remove the unreacted silane coupling agents, after drying at 110 °C for 2 h the modified amorphous silica was obtained.

Measurement of the surface hydroxyl number

The amorphous silica (0.4–0.5 g) was put into a 100-ml beaker, 5 ml of anhydrous ethanol and 12 ml 20% solution of sodium chloride were added, mixed by stirring, adjusting pH value to 4.0 with HCl (0.1 mol/L) or NaOH (0.1 mol/L) solution. Thereafter NaOH (0.1 mol/L) solution was slowly added till pH value raised up to 9.0. The system was kept at pH 9.0 for 20 s, recording the volume of NaOH solution consumed to raise pH from 4.0 to 9.0. The surface hydroxyl number of amorphous silica is calculated using the equation (1).

$$N = \frac{CVN_A \times 10^{-3}}{Sm}, \quad (1)$$

where: N – surface hydroxyl number, number/nm²
 C – concentration of sodium hydroxide solution, 0.1 mol/L
 V – the volume of 0.1 mol/L NaOH solution (assumption in adjusting pH from 4.0 to 9.0), ml
 N_A – Avogadro constant
 m – the quality of amorphous silica, g
 S – specific surface area, m²/g (in this paper, S for amorphous silica is 150 m²/g and S for modified amorphous silica is 350 m²/g).

Analysis of the structure and properties

The amorphous silica prepared from the oil shale residue was characterized by X-ray diffraction analysis (XRD), infrared spectroscopy (IR), nuclear magnetic resonance spectral analysis of hydrogen (HNMR), scanning electron microscopy (SEM) and contact angle respectively.

The purity of amorphous silica was determined by the professional standard of People's Republic of China (HG/T3065-1999). The sample weighing 1.0 g (m_0) was put into a platinum crucible, the platinum crucible loaded with sample was kept in a furnace at 900 °C until reaching the constant weight, then the sample was weighed (m_2). 15 ml HF acid and 1 ml H₂SO₄ were added into the platinum crucible containing the sample residue m_2 , the mixture was evaporated to mash and cooled down. The materials on the wall of platinum crucible were washed down with water, 10 ml HF acid were added and evaporated to dry. The crucible with the residue was heated till no white gas rose, kept in the furnace at 900 °C for 15 min, and finally the sample was weighted (m_1). The purity of amorphous silica was calculated by the equation $(m_2 - m_1)/m_0$.

The degree of hydrophobic properties was measured by the transmittance method. The sample (1 g) was dispersed in 100 ml water in a container, shocking or stirring for 5 minutes, after standing for one minute, a small amount of liquid from the bottom of the container was drawn out for measurement. The transmittance (at $\lambda_{\max} = 550$ nm) was determined by an ultraviolet/visible spectrophotometer. The transmittance of the liquid drawn out was measured and compared with 100 of the pure water, and the liquid was defined to be hydrophobic.

Results and discussion

Structure and properties of amorphous silica from oil shale residue

Figures 1 and 2 are IR and XRD spectra of the amorphous silica extracted from oil shale residue. Absorption bands at 1105 cm⁻¹, 802 cm⁻¹ and 477 cm⁻¹ in Fig. 1 are absorption peaks characteristic of SiO₂, in which absorption peaks at 1105 cm⁻¹ and 802 cm⁻¹ correspond to the antisymmetric and symmetric stretching vibration of Si–O respectively. The absorption peak at 477 cm⁻¹ corresponds to bending vibration of the Si–O–Si bond, 3433 cm⁻¹ corresponds to the Si–OH and stretching vibration absorption of the O–H bond of physically adsorbed water, 1641 cm⁻¹ is bending vibration absorption of physically adsorbed water. In Fig. 2 only a diffusive peak emerges at about 20-30°, it shows that the sample extracted from oil shale residue has a typical structure of amorphous hydrated silica.

The purity of the amorphous silica determined according to the standard HG/T3065-1999 is 99%. The specific surface area of amorphous silica measured by JW-K specific surface area detector is 150–160 m²/g (reaches B grade of the national standard of China). According to the reference method, the number of surface hydroxyl groups of the amorphous silica is 4–6 /nm².

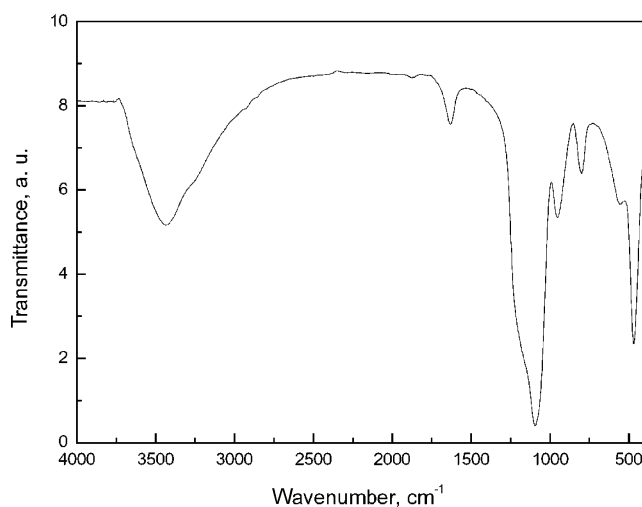


Fig. 1. IR spectra of amorphous silica.

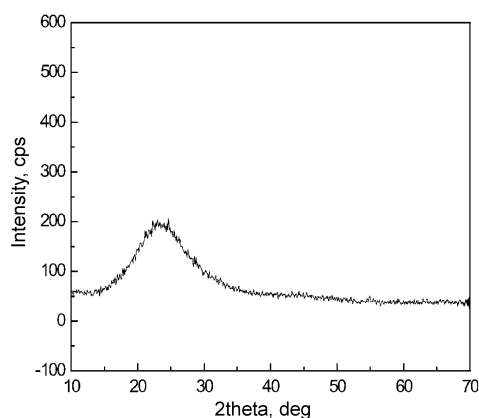
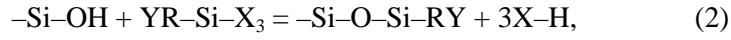


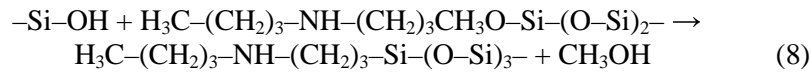
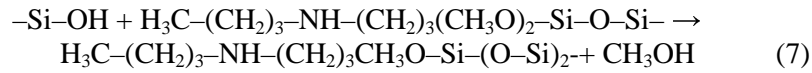
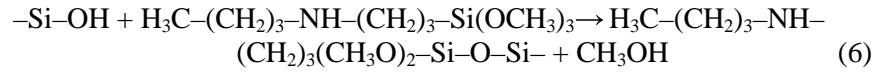
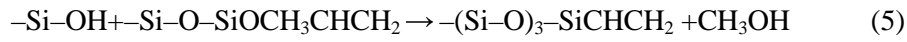
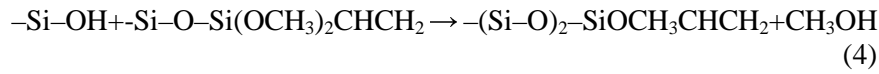
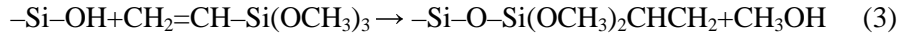
Fig. 2. XRD spectrogram of amorphous silica.

Surface hydroxyl number and modification degree of amorphous silica modified with silane coupling agent

Chemical modifiers react with hydroxyl groups of the amorphous silica surface reducing the number of surface Si–OH. Therefore the hydrophilic surface becomes hydrophobic, and its affinity with organics is improved. There is a variety of hydroxyl groups on the silica surface; in general, modification include drawing the hydrophobic link segments into the particle surface to form a certain targeted “surfactant” structure, to reduce the polarity of the particle surface and to improve its hydrophobic properties. In this work the silane coupling agents were applied to modify the amorphous silica extracted from oil shale residue, the following reactions occur (2):



where $\text{YR}-\text{Si}-\text{X}_3$ is a silane coupling agent, in our case Y is $-\text{NH}_2$, $-\text{SH}$ and other functional groups, X is $-\text{OMe}$ or $-\text{OEt}$, and R represents C-C bridge. When the silane coupling agent is the vinyl trimethoxysilane AH-171, $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$, specific reaction steps are (3) to (5); when the silane coupling agent is N-(*n*-butyl)-3-aminopropyl trimethoxysilane DYNASYLAN1189, $\text{H}_3\text{C}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$, specific reaction steps are (6) to (8).



The silane coupling agents vinyl trimethoxysilane (AH-171) and N-(*n*-butyl)-3-aminopropyl trimethoxysilane (DYNASYLAN 1189) work as modifiers, and the molar ratio of the reaction is 3:1 (amorphous silica surface hydroxyl : silane coupling agent). The number of surface hydroxyl groups before and after modification and the modification degree are given in Table 1. In Table 1 N_{OH} is the surface hydroxyl number of unmodified amorphous silica, N'_{OH} is the surface hydroxyl number of modified amorphous silica, ΔN_{OH} is the difference between hydroxyl numbers of unmodified and modified amorphous silica, $\Delta N_{\text{OH}}/N_{\text{OH}}$ is the modification degree. In Table 1 it is shown that the modification degree for modifier AH-171 is 93.7%, and the modification degree for modifier YNASYLAN 1189 is less than 71.2%. This may be a result of space obstacles due to molecular structure of DYNASYLAN1189.

Table 1. Number of surface hydroxyl groups and modification degree

Silane coupling agents	AH-171	DYNASYLAN 1189
N_{OH} (number/nm ²)	4.15	5.66
N'_{OH} (number/nm ²)	0.26	1.63
ΔN_{OH} (number/nm ²)	3.89	4.03
Modification degree (%)	93.7	71.2

Structure and property analysis

The infrared spectra of amorphous silica from oil shale residue are shown in Fig. 3. The absorption peak at 3422 cm^{-1} (Si–H and stretching vibration absorption peak of the HO–H bond in physically adsorbed water) obviously becomes weaker after modification. This is the result of Si–OH surface modification and reduced number of the surface hydroxyl. The remaining surface hydroxyl makes O–H peak still emerge in the IR spectrum providing a weaker one. In theory there are three types of hydroxyls on the surface of amorphous silica: the first is isolated, free of interference; the second is geminate one, that is, two hydroxyls are linked together at the same Si atom; the third is attached, the association hydroxyls form hydrogen bond between themselves. The isolated and geminate hydroxyls do not form hydrogen bonds, which are easier to be modified, while the attached hydroxyl is difficult to be modified. Figure 3 shows new absorption peaks at 2900 cm^{-1} and 2800 cm^{-1} , they are C–H stretching vibration peaks of alkane CH_3 and CH_2 , while they disappear in the spectrum of unmodified amorphous silica. It illustrates the fact that the organic chain segment of the modifier has been grafted to the amorphous silica surface.

Results of NMR analysis are shown in Table 2. For unmodified amorphous silica there exists a group of hydrogen peaks of Si–OH in the high field (chemical shift is 1.0–1.5 ppm), triple peak corresponds to three kinds of Si–OH hydrogen peak respectively (isolated hydroxyl, adjacent hydroxyl, double hydroxyl). For the modified amorphous silica a new hydrogen peak emerges in the lower field, the hydrogen peak belongs to hydrogen of silane chain or siloxane chain, which indicates that the silane coupling agents have modified the surface of amorphous silica successfully.

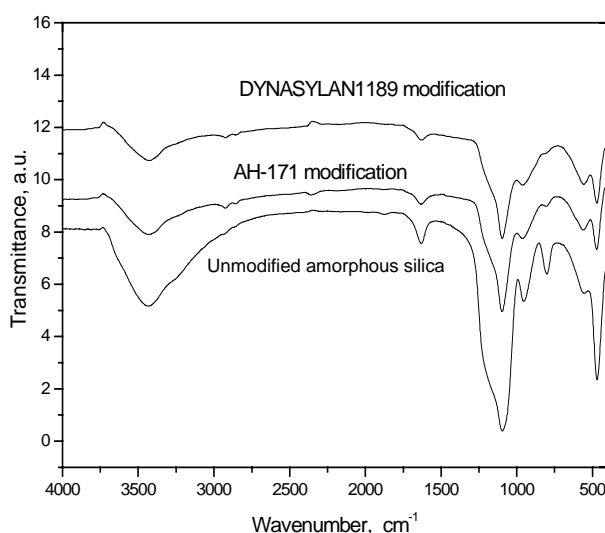


Fig. 3. IR spectra of unmodified and modified amorphous silica.

Table 2. Data from nuclear magnetic resonance of amorphous silica

Sample	H chemical shift δ	The number of split peaks	H assignment
Unmodified	1.0–1.5	Triple peak	–OH
AH-171 modification	3.2–3.5	Multiple peak	–CH ₃ , –CH ₂ and –NH
DYNASYLAN1189 modification	3.2–3.6	Multiple peak	–CH=CH ₂ , –CH ₃

Figures 4 and 5 are SEM pictures of unmodified and modified amorphous silica. In Fig. 5 the particle agglomeration for modified amorphous silica is weaker than that for unmodified one in Fig. 4. This is because the surface of unmodified amorphous silica contains a large number of hydroxyls which easily join together, while the surface hydroxyl number of modified

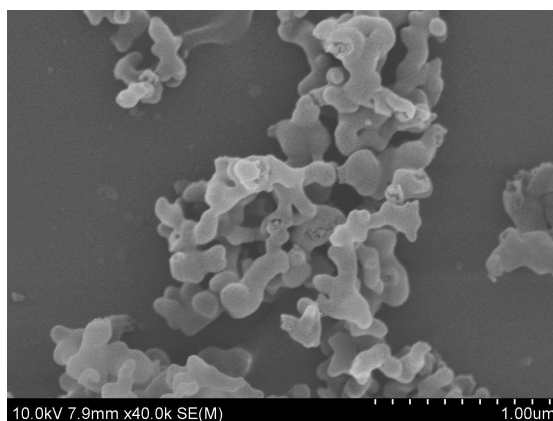


Fig. 4. SEM image of unmodified amorphous silica.

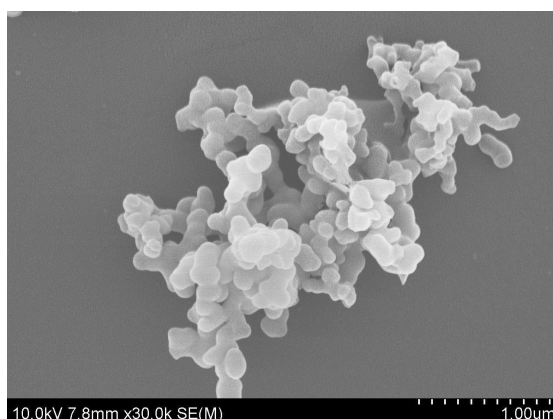


Fig. 5. SEM image of amorphous silica modified by AH-171.

amorphous silica is reduced by modification, so the agglomeration phenomenon is relatively weaker. By measuring the contact angle and hydrophobic rate of the modified amorphous silica, it is known that the hydrophobic properties of the modified amorphous silica are excellent. The determined data are shown in Table 3.

Table 3. Hydrophobic rate of amorphous silica

Sample	Unmodified amorphous silica	AH-171 modification	DYNASYLAN 1189 modification
Contact angle, °	0	120	108
Hydrophobic rate, %	23	98	94

Conclusions

1. Amorphous silica of the purity 99% has been successfully prepared from oil shale residue by a homogeneous chemical sedimentation method with alkaline dissolution. IR and XRD analysis proved amorphous structure of the product.
2. Silane coupling agents vinyl trimethoxysilane and N-(*n*-butyl)-3-amino-propyl trimethoxysilane used as modifiers yield modification degrees 93.7% and 71.2%, respectively. Both IR and NMR determinations show that modification has given good results.
3. SEM image, contact angle measurement and ultraviolet/visible spectra analysis illustrate less agglomeration, better dispersion ability, good hydrophobic properties (hydrophobicity degree higher than 94%) of the amorphous silica modified with silane coupling agent.

REFERENCES

1. Li Yong, Xue Xiang-xin, Feng Zong-yu. Preparation of precipitated silica from oil shale residue // The Chinese Journal of Process Engineering. 2007. Vol. 7, No. 4. P. 751–754 [in Chinese].
2. Trikkel, A., Kuusik, R., Maljukova, N. Distribution of organic and inorganic ingredients in Estonian oil shale semicoke // Oil Shale. 2004. Vol. 21, No. 3. P. 227–236.
3. Arro, H., Prikk, A., Pihu, T., Öpik, I. Utilization of semi-coke of Estonian shale oil industry // Oil Shale. 2002. Vol. 19, No. 2. P. 117–125.
4. Chen Jie-yu, Yan Chun-jie, Li Zi-chong, Jiang Lei. Comprehensive utilization of oil shale residue // Conservation and Utilization of Mineral Resources. 2006. No. 6. P. 41–45 [in Chinese].
5. You Jun-jun, Ye Song-qing, Liu Zhao-jun, Wang Yun-zhe. Comprehensive development and utilization of oil shale // Global Geology. 2004. Vol. 23, No. 3. P. 261–265 [in Chinese].

6. *Tan Xin, Wang Fu-liang, Wang Rong-sheng*. Study on preparation of white carbon black from deoiled residue of oil shale // *Mining & Metallurgy*. 2004. Vol. 13, No. 1. P. 59–63 [in Chinese].
7. *Feng Zong-yu, Li Yong, Xue Xiang-xin, He Yan, Liu Ping-xian*. Preparation of alumina and silica white from oil shale residue // *Mining and Metallurgical Engineering*. 2008. Vol. 28, No. 4. P. 53–57 [in Chinese].
8. *Xu Ying-mei, He De-min, Wang Dong-mei, Lian Yu-huan, Guan Jun, Zhang Qiu-min*. Influence of calcination temperature on leaching rate of aluminum and iron impurities in oil shale ash // *Oil Shale*. 2009. Vol. 26, No. 2. P. 163–168.
9. *Gao Gui-mei, Zou Hai-feng, Gan Shu-cai, Liu Zhao-jun, An Bai-chao, Xu Ji-jing, Li Guang-huan*. Preparation and properties of silica nanoparticles from oil shale ash // *Powder Technol.* 2009. Vol. 191, No. 1–2. P. 47–51.
10. *Jesionowski, T., Bula, K., Janiszewski, J., Jurga, J.* The influence of filler modification on its aggregation and dispersion behaviour in silica/PBT composite // *Compos. Interface*. 2003. Vol. 10, No. 2–3. P. 225–242.
11. *Zurawska, J., Krysztofkiwicz, A., Jesionowski, T.* Effect of ammonium salts on dispersive and adsorptive parameter of silicas precipitated from sodium metasilicate solution // *Colloid. Surface. A*. 2003. Vol. 223, No. 1–3. P. 201–214.
12. *Yu Xin-wei, Chen Yao*. Surface modification technology of silica // *Journal of Guangzhou University*. 2002. Vol. 1, No. 6. P. 12–16 [in Chinese].
13. *Wang Hui-ling, Ning Yan-sheng*. Preparation of new hydrophobic silica // *Inorganic Chemicals Industry*. 2002. Vol. 34, No. 2. P. 33–34 [in Chinese].
14. *Jesionowski, T., Krysztofkiwicz, A.* Influence of silane coupling agents on surface properties of precipitated silicas // *Appl. Surf. Sci.* 2001. Vol. 172, No. 1–2. P. 18–32.
15. *Tang Hong-bo, Zhang Xin-meng, Ma Bing-jie, Zhong Yu-hua*. Modification technology of nano-silica using hexamethyldisilazane // *Journal of Shenyang University of Technology*. 2007. Vol. 29, No. 6. P. 663–666 [in Chinese].
16. *Ouyang Zhao-hui, Wu Lin, Li Kong-biao, Cao Shuchao, Wang Yan*. Surface modification of nano-SiO₂ in gas phase // *Chemical Industry and Engineering Progress*. 2005. Vol. 24, No. 11. P. 1265–1268 [in Chinese].

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