



# Surface modification of nanosilica with 3-mercaptopropyl trimethoxysilane: Experimental and theoretical study on the surface interaction



Jianbing Wu<sup>a,b</sup>, Lixia Ling<sup>c</sup>, Junbao Xie<sup>d</sup>, Guozhang Ma<sup>b</sup>, Baojun Wang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Ministry of Education and Shanxi Province, Taiyuan 030024, China

<sup>b</sup> Shanxi Research Institute of Applied Chemistry, Taiyuan, Shanxi 030027, China

<sup>c</sup> Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

<sup>d</sup> College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

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## ABSTRACT

Surface modification of nanosilica with 3-mercaptopropyl trimethoxysilane (MPTMS) has been investigated. FTIR, TGA, CA, <sup>29</sup>Si NMR and DFT method have been applied to study the interaction between nanosilica and MPTMS. The results show that the organic functional groups are successfully grafted onto the nanosilica surface and the grafting ratio firstly increases and then decreases with the increasing MPTMS. In addition, four different grafting modes between nanosilica surface and MPTMS have been studied by DFT method. It indicated that the favorable grafting structures are mono-, di-grafting mode when the MPTMS is lower and ladder-like grafting mode when the MPTMS is higher.

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## 1. Introduction

There have been increasing activities in the development of organic–inorganic hybrid material in recent years, especially the incorporation of inorganic nanoparticles into organic coatings and other polymers matrix [1–4]. Nanosilica has attracted enormous attention for its high abrasion resistance, hardness and scratching resistance in the photocurable coatings [5–7]. However, the nanosilica tends to strongly agglomerate due to the large surface-area/particle-size ratio, which reduces the resultant mechanical properties of the hybrid material [8]. Many physical and chemical efforts have been done to overcome this problem and to enhance organic–inorganic phase interaction.

Different silane coupling agents for surface modification of nanosilica is recommended to achieve proper dispersion of nanosilica in polymer matrix and to yield a better compatibility between nanosilica and host polymers [9–11]. Usually, the silane coupling agents undergo stepwise hydrolysis reactions in a mixture of water/ethanol leading to the formation of silanol units, which can react with hydroxyl of nanosilica surface not only to form Si–O–Si but also hydrogen bond O···H–O [12]. The influences of temperature [13], solvent [14], concentration [15] and pH [12] on the hydrolysis of different silane coupling agents have been investigated during the modified nanosilica preparation.

However, the grafting mechanism and the grafting situation (or mode) of silane coupling agent onto the nanosilica surface are still not clear.

Recently, the theoretical calculation method has been applied to confirm the interaction between small molecule or radical group and nanosilica [16]. The silica cluster with different structure from Si<sub>2</sub>O<sub>3</sub>H<sub>4</sub> to Si<sub>12</sub>O<sub>14</sub>H<sub>24</sub> have been comprehensively used to study the interaction between silica and different molecular structure, including CH<sub>3</sub> [17], HF [18], trihydroxysilane, trichlorosilanes [19], triethoxysilane and bis (3-triethoxysilylpropyl)-tetra-sulfane [20]. The hydroxyl groups of the hydrolyzed silane interacts to the cluster in one way with a strong covalent bond Si–O–Si, and in the other way to the cluster by moderated hydrogen bond O···H–O. It shows that the Si–O–Si bond length and strength are different with the different silane coupling agents onto the silica cluster [21]. However, the detail information of bonding pattern and situation, the priority between hydrolysis, self condensation of silane coupling agent and grafting is unclear. Recently, calculations were also carried out on the fully and partially hydrolyzed products of silane, and the good model for frequencies of the SiO/SiC symmetric stretching vibrations was provided [22].

Considering the complexity of silanol structure of hydrolyzed silane coupling agent and diversity of hydroxyl on the nanosilica surface, it is very essential and helpful to conduct a systematic and theoretical study on the interaction between silane coupling agent and nanosilica surface. In this study FTIR, TGA, <sup>29</sup>Si NMR and CA were used to characterize the grafting effect, and the DFT theoretical calculation was used to study the grafting mode of

\* Corresponding author. Address: No. 79 Yingze West Street, Taiyuan 030024, China. Fax: +86 351 6041237.

E-mail addresses: [wangbaojunwork@hotmail.com](mailto:wangbaojunwork@hotmail.com), [wujianbin\\_1982@126.com](mailto:wujianbin_1982@126.com) (B. Wang).

silane coupling agent 3-mercaptopropyl trimethoxysilane (MPTMS) onto nanosilica surface.

## 2. Experimental

### 2.1. Materials

Nanosilica powder with an average particle size of 20–50 nm, a specific surface area of 640 m<sup>2</sup>/g and silanol group content of 1.9 mmol/g was obtained from Zhejiang Hongsheng Materials Co., China. 3-mercaptopropyl trimethoxysilane (MPTMS) was purchased from Sigma Chemical Co. and was used as coupling agent. All other chemicals were analytical pure reagents (AR) and were used as received without further treatment.

### 2.2. Surface modification of nanosilica with MPTMS

10 g of nanosilica were kept in a vacuum chamber for 24 h at 100 °C, and then dispersed in 150 mL anhydrous toluene under mechanical stirring and ultrasonic dispersing for 30 min. The mixture was stirred at 300 rpm for a further 1 h, and then dropped into another prepared mixture consisting of 10 mL water, 10 mL anhydrous ethanol, 2 mL formic acid (as pH adjuster) and different levels (25, 50, 75, 100 and 125 mL) of MPTMS under vigorously stirring. After continuously stirring for 4 h at 50 °C, the obtained suspension was separated by centrifugation. After drying at 90 °C under vacuum, the mixture was extracted using Soxhlet extractor for 12 h using toluene. Finally, the modified nanosilica was dried at 90 °C under vacuum condition for 12 h.

### 2.3. Characterizations

The mercapto group on the nanosilica surface was determined with the DTNB according to the method of Ellman [23]. FTIR analysis was performed in potassium bromide on a Nicolet 360 FTIR spectrometer collecting 16 scans in the 400–4000 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution. The thermo gravimetric analysis (TGA) was performed on a HCT-1 thermal gravimetric analyzer (Henven Scientific Instrument Co., China) under a nitrogen atmosphere from room temperature to 700 °C with the heating rate of 20 °C/min. The grafting ratio ( $R_g$ ) was calculated according to the following equation [24]:

$$R_g = \left( \frac{W_1}{W'_1} - \frac{W_0}{W'_0} \right) \times 100\%$$

where,  $W_1$  is the starting weight of the modified nanosilica particles,  $W'_1$  is the residual weight of the modified nanosilica particles at 700 °C,  $W_0$  is the starting weight of unmodified nanosilica particles,  $W'_0$  is the residual weight of unmodified nanosilica particles at 700 °C.

The particle (or particle agglomeration) size and the distribution of nanosilica before and after modification were characterized by a laser particle analyzer Bettersize 2000 (Dandong Bettersize Instruments Corporation, Dandong, China). Ethanol was used as the following liquid.

The water contact angles (CA) was measured with deionized water drops on the nanosilica surface pellet, which was obtained by compacting nanosilica powder with 100 kN force. The measurement was carried out within 10 s by a Krüss contact angle instrument (Easydrop DSA 20) at room temperature using the sessile drop fitting method for the static CA.

Solid-state <sup>29</sup>Si MAS NMR measurements were performed on a Bruker DMX 600 spectrometer. A pulse repetition time of 2.0 s, an acquisition time of 20.0 ms, a contact time of 10.0 ms, and a frequency of 59.582 MHz were used.

### 2.4. Quantum chemistry calculations

The density functional theory (DFT) calculations are performed within the Materials Studio software developed by Accelrys Inc. [25]. The structure is fully optimized without any structural restrictions within the functional of generalized gradient approximation (GGA) proposed by Perdew and Wang (PW91) [26,27], which is generally used to study the structures and energies of SiO<sub>2</sub> with different clusters [28,29]. The DNP basis set, which is equivalent in accuracy to the 6-31G\*\* GAUSSIAN orbital basis set, is also used [30]. The solvent effect is investigated using the conductor-like screening model (COSMO) according to the experimental reaction condition. The calculated O–H distance in 8T (tetrahedral) silica cluster is about 0.97 Å, which is in good agreement with the literature [17]. The Si–O bond lengths are about 1.64 Å and Si–O–Si angles are in the range of 143–150°. The hydrolyzed MPTMS is chose as reactant with four different grafting modes onto the silica cluster surface.

## 3. Results and discussion

### 3.1. Surface modification of nanosilica and characterization

Figure 1 shows the FTIR spectrums of nanosilica, modified nanosilica and MPTMS. In Figure 1a, the peak at 2570 cm<sup>-1</sup> corresponds to the –SH groups of MPTMS, the vibration bands at 2926 and 2855 cm<sup>-1</sup> relate to the symmetric and asymmetric stretching of –CH<sub>2</sub>, which is observed in the vibration spectra of modified nanosilica (Figure 1c–g). It indicates that the long alkyl chain has been grafted onto nanosilica surface, and the peak strength firstly increases and then decreases with the increasing amount of MPTMS. From the FTIR spectra of nanosilica, the presence of adsorbed water and free surface silanol groups as well as siloxane linkages can easily be conceived. In the spectra, the broad band located in the range 3000–4000 cm<sup>-1</sup> corresponds to the fundamental stretching vibration of different hydroxyl groups, and the Si–OH group at 3750 cm<sup>-1</sup> is covered by the broad bands at 3451 cm<sup>-1</sup> corresponding to the associated water vapor on the nanosilica surface. While the asymmetric stretching vibration is near 810 cm<sup>-1</sup>, the symmetric stretching vibration and bending vibration is near 470 cm<sup>-1</sup> of Si–O–Si (Figure 1b). From Figure 1c–g, The strength of peak at 3430 and 1650 cm<sup>-1</sup> decrease and Si–O–Si at 1100 cm<sup>-1</sup> increases with the increasing amount of MPTMS. However, the appearance of peak at 950 cm<sup>-1</sup> of modified nanosilica

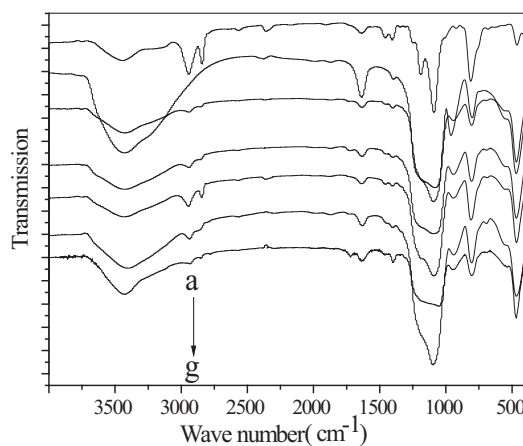


Figure 1. FTIR spectra of (a) MPTMS, (b) nanosilica, and modified nanosilica with different amounts of MPTMS, (c) 25 mL, (d) 50 mL, (e) 75 mL, (f) 100 mL and (g) 125 mL.

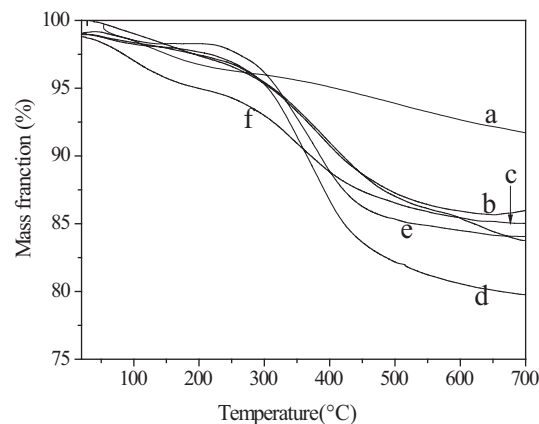
shows that –OH on the nanosilica surface has not reacted with MPTMS completely [31]. The –SH and other peaks corresponding to the grafting MPTMS molecules could not be clearly observed in the spectra of modified nanosilica owing to the strong vibration of nanosilica, which overlaps vibrations of MPTMS functional groups. It can be concluded that the optimum grafting ratio between nanosilica and MPTMS is existed, the more MPTMS does not lead to the higher grafting ratio owing to the steric hindrance, the different grafting modes or self condensation occur at the different MPTMS concentrations.

It is difficult to quantitatively analyze the concentration of –SH on the nanosilica surface due to the weak characteristic peak of –SH in FTIR spectrums, and titrimetric analysis according the method of Ellman is necessary to carry out. The –SH concentration of modified nanosilica with the different amount of MPTMS are shown in the Table 1. With the increasing amount of MPTMS, the concentration of –SH on the nanosilica surface firstly increases and then decreases, and the maximum –SH concentration is about 0.9 mmol/g. If each MPTMS molecule reacts with mono-, di- and tri-hydroxyl groups on the nanosilica surface, respectively, and the maximum theoretical grafting percentage can be deduced. The theoretical amount of MPTMS for 1 g nanosilica would be 1.9 mmol = 0.3 g for mono-grafting mode, 0.15 g for di- and 0.10 g for tri- (the molecule weight of full hydrolyzed MPTMS is 154.34 g/mol, considering to Si–OCH<sub>3</sub> fully hydrolyzed as Si–OH and without considering dehydration effect). It means that the maximum theoretical grafting percentage of nanosilica is about 0.3 g/g = 30% for mono-grafting mode, 15% for di- and 10% for tri-.

### 3.2. The grafting ratio of MPTMS on the nanosilica surface

In order to identify the possible grafting mode, the grafting ratio of MPTMS onto the nanosilica surface has been determined by TGA, which is performed on a comprehensive thermal analyzer from room temperature to 700 °C with the heating speed of 20 °C/min. The result (Figure 2) shows that the untreated nanosilica had a weight loss (about 8 wt%) before 700 °C, which relates to the elimination of physically absorbed water on the surface. From this figure, there are two weight loss stages for the modified nanosilica, the first weight loss occurs before 250 °C, which can be ascribed to the physically and chemical absorbed organic compounds. The sharp weight loss beginning at 250 °C and continuing till 700 °C for modified nanosilica is probably attributed to large scale thermal decomposition of MPTMS chains. The grafting ratio for modified nanosilica with various amount of MPTMS are listed in Table 1.

The grafting ratio firstly increases from 7.2 to 16.7 wt% and then decreases to 10.6 wt% with the amount of MPTMS increase from 25 to 125 mL, and the maximum grafting ratio of 16.8 wt% is obtained when the feed ratio of 75 mL MPTMS to 10 g nanosilica. The results are in good agreement with the –SH concentration variation and the FTIR results. The existing of the maximum grafting ratio may be ascribed to the different grafting modes or self condensation. The maximum experimental grafting ratio of 16.8% is nearly to the theoretical di-grafting modes with the grafting ratio of 15%.



**Figure 2.** The TGA curves of nanosilica (a) and modified nanosilica with different amount of MPTMS (b) 25 mL, (c) 50 mL, (d) 75 mL, (e) 100 mL, (f) 125 mL.

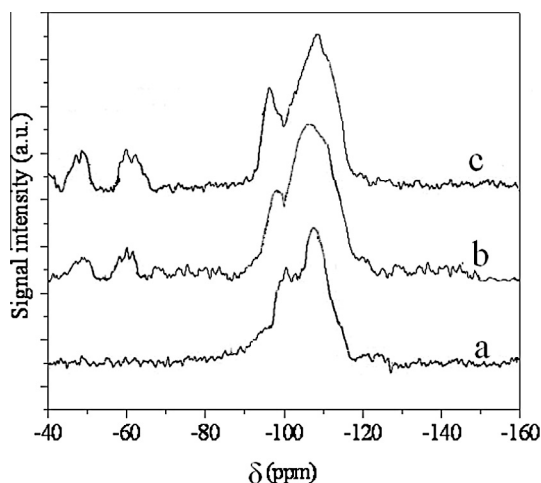
However, the theoretical grafting ratio is obtained on the basis of assumption that the MPTMS was fully hydrolyzed and the nanosilica surface was completely grafted, which is overturned by the hydroxyl groups of modified nanosilica observed in FTIR spectrum. The silane coupling agent is easily to hydrolyze completely under the condition of acid environment and abundant water [32], so it can be inferred that the nanosilica surface was not completely grafted and the grafting modes may be multiple with mono- and di-grafting modes. The results are also valid for the grafting ratio about 10% corresponding to 100 and 125 mL MPTMS, the grafting ratio of 10% is nearly identical to maximum theoretical grafting ratio for tri-grafting mode, but the still existed hydroxyl group in FTIR spectra overturned the tri-grafting mode, the lower grafting ratio may be owing to the self condensation of MPTMS with higher concentration.

### 3.3. The <sup>29</sup>Si NMR analysis of nanosilica and modified nanosilica

<sup>29</sup>Si NMR experiments were powerful tool to characterize the surface modification on nanosilica [33,34]. Here, we used the <sup>29</sup>Si NMR to test for the unmodified nanosilica, the modified nanosilica with the maximum grafting ratio and modified nanosilica with the most MPTMS usage, respectively. The results are shown in Figure 3. <sup>29</sup>Si NMR spectrum of nanosilica displays two signals at –98.5 and –110.3 ppm, corresponding to the Q<sub>3</sub> [Si(OSi)<sub>3</sub>OH] and Q<sub>4</sub> [Si(OSi)<sub>4</sub>], respectively. It was obvious that the major signal came from Q<sub>4</sub> [35]. After grafting, two additional <sup>29</sup>Si signals at –58.7 and –48.3 ppm correspond to the units of T<sub>2</sub> [Si(OSi)<sub>2</sub>(OH)R] (R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH) and T<sub>1</sub> [Si(OSi)(OH)<sub>2</sub>R], respectively [36]. This demonstrates the successfully grafting MPTMS onto the nanosilica surface. The stronger signal intensities of the T<sub>2</sub>, T<sub>1</sub> and almost no T<sub>3</sub> [Si(OSi)<sub>3</sub>R] at –70 to –60 ppm suggests that the possible grafting modes are multiple mono- and di-grafting modes. Even with the increasing MPTMS, their almost no difference reflect that the

**Table 1**  
The experimental data for nanosilica and modified nanosilica.

The amount of MPTMS (mL)	SH concentration (mmol/g)	Contact angle (°)	Grafting ratio (%)	Average particle size (μm)
0	–	0	–	6.1
25	0.37	15.3	7.164	5.1
50	0.43	30.1	8.915	4.8
75	0.90	54.5	16.774	3.6
100	0.59	42.2	10.125	2.5
125	0.62	30.4	10.631	2.5



**Figure 3.**  $^{29}\text{Si}$  NMR spectra of (a) unmodified nanosilica, nanosilica modified by (b) 75 mL MPTMS and (c) 125 mL MPTMS.

amount of MPTMS have small effect on the mono- and di-grafting modes [37].

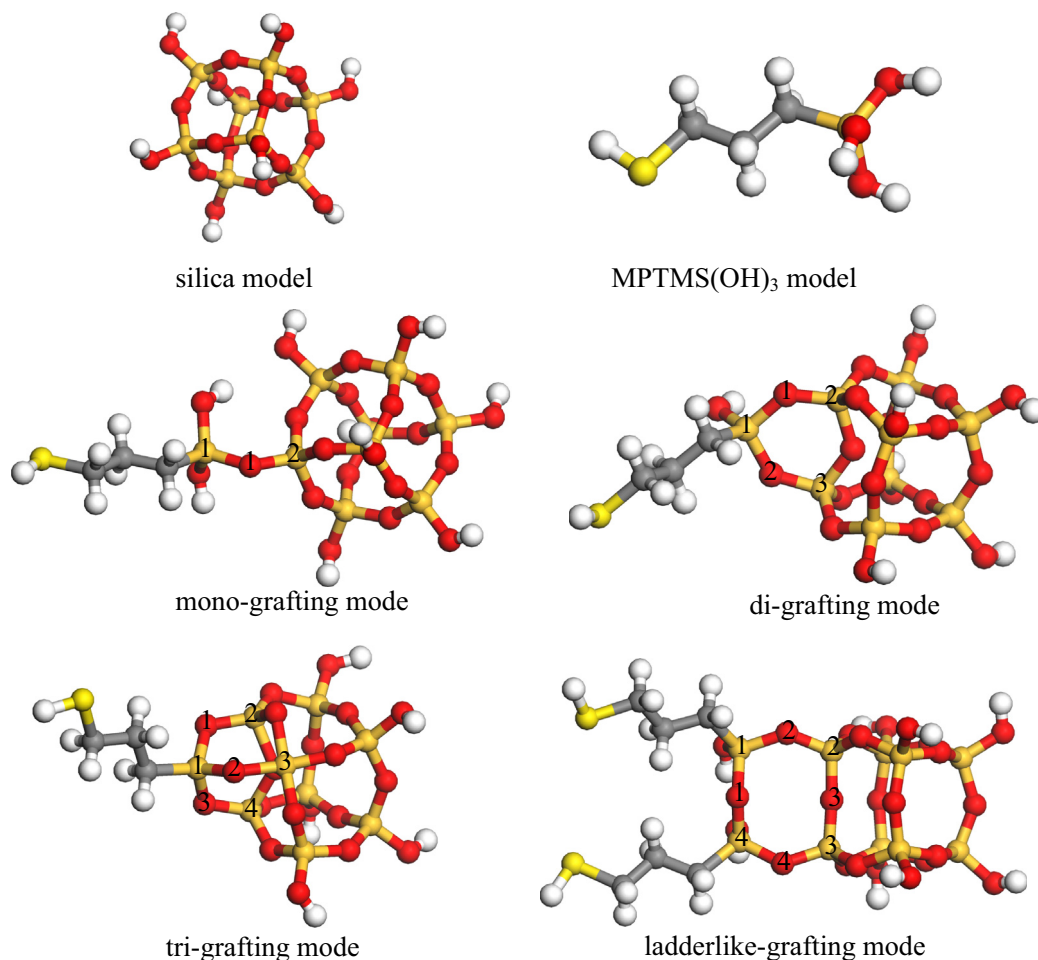
#### 3.4. The surface properties of modified nanosilica

The dispersion of nanosilica in organic coatings is determined by the surface functional groups of nanosilica. One purpose of surface modification of nanosilica with silane coupling agent is to re-

place the surface silanol groups with silane functional groups and to change the silica surface from a hydrophilic nature to hydrophobic nature. The surface properties of modified nanosilica are investigated using the contact angle measurement. Table 1 shows the static contact angle on the surfaces of samples. The contact angle of water on the nanosilica is nearly  $0^\circ$ , which proves that the surface is hydrophilic. The contact angle increases to  $15.3^\circ$  corresponding to the feed ratio of 25 mL MPTMS to 10 g nanosilica, while the angles are  $30.1^\circ$ ,  $54.5^\circ$ ,  $42.2^\circ$ , and  $30.4^\circ$ , for the 50, 75, 100, and 125 mL of MPTMS, respectively. In the grafting course, the long alkyl chain of MPTMS increases the hydrophobicity of the nanosilica surface. The contact angle firstly increases and then decreases with the increasing amount of MPTMS, which is related to the grafting amount of MPTMS.

#### 3.5. DFT study on the interaction between MPTMS and nanosilica

In this section, a systematic theoretical investigation on the possible grafting modes of the MPTMS on the nanosilica surface is performed to determine the surface interaction. There are three different silanol groups can be obtained: isolated, geminal with two hydroxyl groups on the same silica surface, or vicinal with two hydroxyl groups in two neighbor silica surface, whereas the observed isolated silanol groups are higher than the others. So the 8T silica cluster model with isolated hydroxyl group is used as model of nanosilica according to the previous experimental and theoretical results [38]. The MPTMS is assumed fully hydrolysis and modeled by  $\text{MPTMS}(\text{OH})_3$ . The 8T silica cluster model and

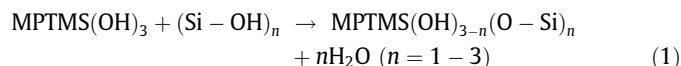


**Figure 4.** The model for 8T silica,  $\text{MPTMS}(\text{OH})_3$  and different grafting modes for MPTMS on the nanosilica surface.



MPTMS(OH)<sub>3</sub> are optimized by DFT method and the final structure models are given in Figure 4.

The MPTMS(OH)<sub>3</sub> entity is grafted onto the silica surface with different grafting modes, including mono-, di-, and tri-, respectively, in Eq. (1).



In addition, the self condensation of neighboring Si-OH of grafted MPTMS on the nanosilica surface can easily lead to ladder-like grafting mode [39], which is also considered in this section.

To understand the surface properties of modified nanosilica and validate the grafting modes, we first discuss the geometric properties of each final product. Figure 4 shows the optimized structure of four different grafting modes, namely, mono-, di-, tri- and ladder-like grafting modes. The related bond length and angle results are summarized in Table 2.

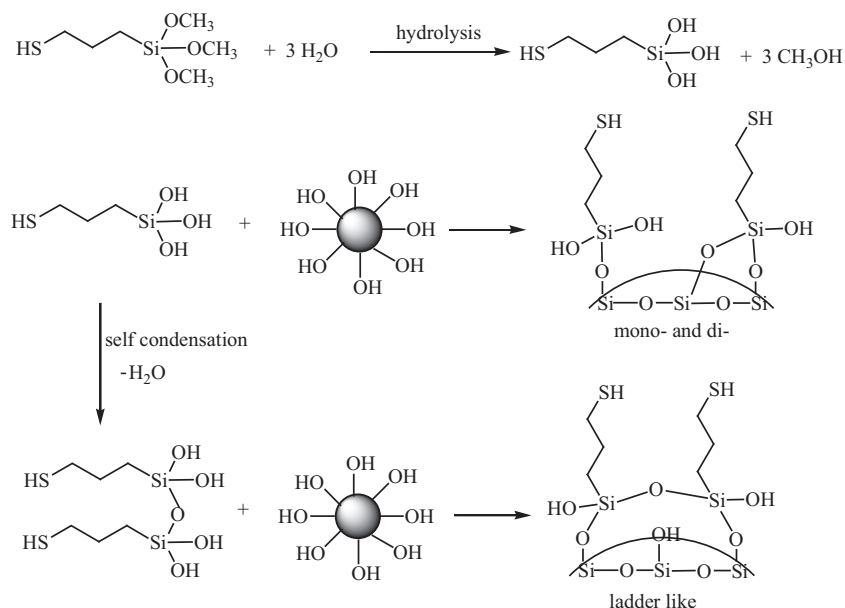
The interaction of MPTMS and 8T silica molecular cluster influences the silica cluster structure, which is important to maintain

the silica structure stability and grafting modes. Table 2 indicated that the average bond length and angle of MPTMS and silica had different change with the different grafting modes. The average calculated bond length of Si-O close to MPTMS is 1.676 Å for mono-, 1.681 Å for di-, 1.691 Å for tri- and 1.665 Å for ladder-like, while the average calculated bond length of Si-O close to silica is 1.623 Å for mono-, 1.627 Å for di-, 1.670 Å for tri- and 1.626 Å for ladder-like. The bond length of different grafting modes shows deviation with primary bond length of Si-O in MPTMS(OH)<sub>3</sub> and 8T cluster, which are 1.667 and 1.640 Å respectively. The difference suggests that the stability of different grafting modes is mono- > ladder-like > di- > tri-. The intermolecular angle of ∠Si-O-Si for different grafting modes was in good agreement with the bond length results. Especially, the tri-grafting mode leads to sharp bond elongations and structural distortion in the 8T silica cluster and MPTMS, which make the tri-grafting mode impossible.

Therefore, the thermodynamic data is necessary to determine the grafting mode and then we examine the reaction energy. Considering the reaction energy (ΔE<sub>react</sub>) as calculated according to reaction (1) for the best grafting modes, we obtained -477.97,

**Table 2**  
The bond length (Å) and angle data (°) of different grafting modes.

Mono-grafting mode		Di-grafting mode		Tri-grafting mode		Ladder-like grafting mode	
Si <sub>1</sub> -O <sub>1</sub>	1.676	Si <sub>1</sub> -O <sub>1</sub>	1.680	Si <sub>1</sub> -O <sub>1</sub>	1.716	Si <sub>1</sub> -O <sub>1</sub>	1.665
Si <sub>2</sub> -O <sub>1</sub>	1.623	Si <sub>2</sub> -O <sub>1</sub>	1.627	Si <sub>2</sub> -O <sub>1</sub>	1.626	Si <sub>4</sub> -O <sub>1</sub>	1.651
Si <sub>1</sub> -Si <sub>2</sub>	3.031	Si <sub>1</sub> -O <sub>2</sub>	1.681	Si <sub>1</sub> -O <sub>2</sub>	1.657	Si <sub>1</sub> -O <sub>2</sub>	1.671
∠(Si <sub>1</sub> -O <sub>1</sub> -Si <sub>2</sub> )	133.512	Si <sub>3</sub> -O <sub>2</sub>	1.627	Si <sub>3</sub> -O <sub>2</sub>	1.755	Si <sub>2</sub> -O <sub>2</sub>	1.622
		Si <sub>1</sub> -Si <sub>2</sub>	3.025	Si <sub>1</sub> -O <sub>3</sub>	1.706	Si <sub>2</sub> -O <sub>3</sub>	1.626
		Si <sub>1</sub> -Si <sub>3</sub>	3.027	Si <sub>4</sub> -O <sub>3</sub>	1.630	Si <sub>3</sub> -O <sub>3</sub>	1.625
		∠(Si <sub>1</sub> -O <sub>1</sub> -Si <sub>2</sub> )	132.325	Si <sub>1</sub> -Si <sub>2</sub>	2.739	Si <sub>3</sub> -O <sub>4</sub>	1.632
		∠(Si <sub>1</sub> -O <sub>2</sub> -Si <sub>3</sub> )	132.406	Si <sub>1</sub> -Si <sub>3</sub>	3.003	Si <sub>4</sub> -O <sub>4</sub>	1.671
				Si <sub>1</sub> -Si <sub>4</sub>	2.854	Si <sub>1</sub> -Si <sub>4</sub>	3.086
				∠(Si <sub>1</sub> -O <sub>1</sub> -Si <sub>2</sub> )	110.055	Si <sub>1</sub> -Si <sub>2</sub>	3.071
				∠(Si <sub>1</sub> -O <sub>2</sub> -Si <sub>3</sub> )	123.294	Si <sub>2</sub> -Si <sub>3</sub>	3.250
				∠(Si <sub>1</sub> -O <sub>3</sub> -Si <sub>4</sub> )	117.589	Si <sub>3</sub> -Si <sub>4</sub>	3.004
						∠(Si <sub>1</sub> -O <sub>1</sub> -Si <sub>4</sub> )	137.102
						∠(Si <sub>1</sub> -O <sub>2</sub> -Si <sub>2</sub> )	137.689
						∠(Si <sub>2</sub> -O <sub>3</sub> -Si <sub>3</sub> )	176.388
						∠(Si <sub>3</sub> -O <sub>4</sub> -Si <sub>4</sub> )	130.872



**Figure 5.** Idealized grafting modes of MPTMS on the nanosilica surface.

–62.78, 1330.19 and –860.88 kJ/mol for  $n = 1–3$  and ladder-like grafting mode, respectively. These values suggest that the grafting of MPTMS is favored for the mono-, di-grafting and ladder-like grafting specie, while it is endothermic for the tri-grafting species. Under an experimental temperature  $T = 323$  K, we can observe, that the free Gibbs energies ( $\Delta G_{\text{react}}$ ) for different grafting modes were –446.19, –220.82, 1015.04 and –949.50 kJ mol<sup>-1</sup> respectively. These results show an ability to easily graft MPTMS onto silica surface with mono- and di-grafting mode. When the grafting position is occupied fully by MPTMS, the self condensation can occur not only between isolated MPTMS molecules but also the nanosilica surface. The increasing MPTMS can not graft onto the nanosilica surface further because of the steric hindrance, however the self condensation between MPTMS grafted onto nanosilica surface lead to dehydration and decrease of grafting ratio. That is why the grafting ratio firstly increases and then decreases with the increasing amount of MPTMS.

On the basis of experimental and theoretical analysis, the ideal grafting mode is show in Figure 5. MPTMS is hydrolyzed as MTMMS(OH)<sub>3</sub>, then the mono-grafting mode between hydrolytic MPTMS and nanosilica surface is favorable when the concentration of MPTMS is lower, while the ladder-like grafting mode may occur by self condensation of MPTMS when the MPTMS concentration is higher.

#### 4. Conclusion

The interaction and grafting modes between nanosilica surface and MPTMS are investigated with FTIR and TGA. It is found that the grafting ratio and –SH concentration of nanosilica surface firstly increases and then decreases with the increasing amount of MPTMS. The maximum grafting ratio of 16.8% and the –SH concentration of 0.9 mmol/g were obtained with the feed ratio of 75 mL MPTMS to 10 g nanosilica. The results of contact angle and particle size distribution of modified nanosilica are in good agreement with the grafting ratio, the contact angle change indicates that the hydrophilic nature has been transferred to hydrophobic, the particle size distribution analysis indicates that the self agglomeration and dispersion of nanosilica has been improved. The <sup>29</sup>Si NMR results show that the possible grafting modes are mono- and di- but not tri-grafting mode.

With 8T silica cluster as the model of nanosilica, the DFT calculations indicate that the mono-, di- grafting mode and ladder like grafting mode are feasible in thermodynamic over the tri-grafting mode under the above experimental condition. The mono-grafting mode is favorable with the lower concentration of MPTMS, while the grafting mode may be transferred into ladder like grafting mode when more MPTMS introducing the system. The theoretical results can commendably illustrate why the grafting ratio firstly increases and then decreases with the increasing amount of MPTMS.

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