



High density silanization of nano-silica particles using γ -aminopropyltriethoxysilane (APTES)



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ABSTRACT

A novel and efficient process was developed for high density silanization of nano-silica particles using APTES, in which $13.48 \text{ APTES nm}^{-2}$ was achieved. This process comprises three stages, namely, aqueous mixing, spray drying and thermal treatment. After the successive stages, the APTES conversions were 25.3%, 50.7% and 80.6%. In the aqueous mixing stage, the chemical reaction was fast and quite limited. In the spray drying stage, APTES was distributed on the surface of nano-silica particles uniformly by both physical and chemical adsorption. In the thermal treatment stage, the processing temperature (T) and time in the thermal treatment had large effects on the grafting density, and the reaction was reversible. When $T < 300^\circ\text{C}$, the reverse reaction dominated, causing a decrease of APTES grafting density. When $T > 300^\circ\text{C}$, the forward reaction dominated, leading to increased grafting density. The optimum processing temperature and time for high grafting density were 360°C and 30 min, respectively.

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1. Introduction

Nano-silica particles are widely used in many fields as filler, catalyst carrier, and biological and medicinal materials. In order to improve the application performance, their surfaces usually need to be modified by functional chemical groups. γ -aminopropyltriethoxysilane (APTES) is a commonly used coupling agent because of its amino group. Amino-terminated silica particles can be used as filler in rubber and plastic to increase tensile strength, abrasion resistance, and improve rheological behavior [1]. Mesoporous molecular sieves can immobilize amine catalysts, which makes them easier to be separated and reused [2]. Amino-terminated silica particles also has a large adsorption capacity and good selectivity for metal ions, such as Cu^{2+} , Pb^{2+} , Hg^{2+} , thus it can be used as a chromatography stationary phase or adsorbent [3–9]. Since amino groups can react with proteins and DNA, these silica materials have important uses in the separation of biomaterials, enzyme immobilization and targeted medicine [10–14]. In many applications, high surface coverage of amino groups is desired in order to have a large number of active sites on the surface for improving the performance of the nanoparticles.

The modification process can be basically divided into two types, i.e., in liquid phase and in gas phase. Modification in the liquid phase includes those in an aqueous phase and in a non-aqueous

phase. In the aqueous phase, such as ethanol/water [15,16], acetone/water [10,17] or pure water [18–20], the ethoxy group of APTES hydrolyzes first, and then forms Si–O–Si bonds with surface silanol groups [21]. However, the grafting density in aqueous media is usually low due to the limitation of the reaction temperature, and the hydrolyzed APTES is easily condensed if the reaction time is too long. The reaction performed in a non-aqueous phase such as toluene [11,21–25] or hexane [17] can avoid the hydrolysis of APTES in the modification, which is helpful to form a monolayer grafting. But the solvent needs to be removed and recycled, which can easily cause solvent pollution. Also, this operation is a lengthy procedure and has low efficiency. For the case of the hydrophilic particles mixing in hydrophobic solvents, diffusion controlled process exists in the modification due to the serious particle agglomeration. An improved impregnation process was also used for the silanization of the silica surface, in which the silica particles were immersed in methyl [(dimethylamino)dimethylsilyl]undecanoate/pentane solution, and then followed by pentane evaporation under reduced pressure and thermally treatment at 140°C for 16 h [26]. A modification process in the gas phase can eliminate the hydrolysis and condensation of silane molecules. The equipment used in the gas phase modification includes fluidized beds [27] for glycidoxypropyltrimethoxysilane and APTES and ALD reactors [28–33] for γ -aminopropylalkoxysilanes, γ -aminopropyltrialkoxysilanes and APTES. However, because the nano-silica particles are easily agglomerated, the agglomerates in a fluidized bed are usually in size of tens μm , which is the agglomeration of about billions of primary particles ($\sim 20 \text{ nm}$), also causing a diffusion controlled process.

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The formation of the APTES layer on the silica surface is a complicated multistep process which is very sensitive to reaction conditions [34]. Typical structures in an APTES-modified layer include physically adsorbed, hydrogen-bonded, protonated, and covalently attached silanes. The first three structures would further react on the silica surface or desorb under certain conditions. Covalently attached silanes include those that have reacted only with surface silanol groups and those that have bonded with neighboring silane molecules [35]. Some studies [21,34] have used a post-curing step to strengthen and densify the modified APTES layers on the assumption that horizontal polymerization is enhanced by heating. The temperature ranges from 70 °C to 250 °C and reaction times from 10 min to 24 h were used in the post-treatment process [21,34,36,37]. However, there was also a report [23] that the post-processing at 70 °C had little or no effect on the film. So far the effect of the post curing treatment is still not clear.

The grafting density of amino groups varies for different processes and conditions. Earlier studies showed that in a non-aqueous solvent, the grafting density was from 1.69 nm⁻² to 2.5 nm⁻² [5,38–40]. Cuoq et al. [20] compared APTES grafting density on a non-preheated silica surface in both water and toluene. In water, the grafting density was 1.26 nm⁻², which was slightly less than the reported value in a non-aqueous phase [5,38,39]. In toluene, the grafting density was 4.16 nm⁻², but after a simple rinsing in water, it decreased to be the same as the water phase result. Many studies showed that there was a loss of covalently attached silane layers upon exposure to water, which was attributed to siloxane hydrolysis catalyzed by the amine group [5,35,36]. For the process performed in the gas phase, the grafting density was 1.6–1.8 nm⁻² [25,27,29]. Ek et al. [31] developed a gas phase procedure for a high density APTES network that gave a grafting density up to 3.0 nm⁻² through several consecutive reactions of vaporized aminosilane and water on the silica surface in an ALD reactor.

The aim of this study is to develop a novel and efficient process for the modification of commercial nano-silica particles and to give a high grafting density of APTES on nano-silica particle surfaces for improving the application performance. The process includes three stages, i.e., first, silica particles were mixed with APTES in an aqueous phase to form a well dispersed suspension. Then, the slurry was spray dried for achieving an excellent contact between APTES and silica particle surface. Finally, the dried particles were thermally treated under optimal conditions to further enhance the silanization. The conversion after each stage was studied and the effects of reaction temperature and time in the thermal treatment were analyzed. The interactions of APTES and the silica surface, grafting density and structure of the grafted APTES were studied.

2. Experimental

2.1. Reagents

Commercial nano-silica particles (abbreviated as “Sp” in the marked samples hereinafter) (Luodiya Silica White Co. Ltd, Qingdao, China) from an aqueous precipitation process were used. The BET surface area of the nano-silica particles was 163 m² g⁻¹, which was measured by Surface Area Analyzers (Autosorb-iQ, Quantachrome Instruments U.S.) and the diameter of the primary particles was about 20 nm. γ -aminopropyltriethoxysilane (APTES) (Alfa-Aesar, Johnson Matthey Co. USA) used was analytical reagent (AR) grade, which has purity of 98% and density of 0.948 g cm⁻³. Other chemicals, i.e., salicylaldehyde (Sinopharm Chemical Reagent Co. Ltd, China), anhydrous ethanol (Modern Oriental Technology Development Co. Ltd, Beijing, China), CuSO₄·4.5H₂O (Beijing Modern Eastern Fine Chemical, China) were analytical reagent (AR) grade.

2.2. Modification and sampling

(1) The aqueous mixing of APTES with the nano-silica particles.

The hydrolysis of APTES in an aqueous phase is a fast process, and the hydrolyzed APTES is easily condensed, which is unfavorable for the modification process of nano-silica particles. In order to minimize the self-condensation, the aqueous mixing of APTES with the nano-silica particles was conducted in a conical flask in a short time. The hydrolysis of APTES in deionized water was set for a fixed time of 10 min under magnetic stirring at room temperature, through which the hydrolysis of APTES was finished [41]. The concentration of APTES in the solution was set at 1.3% (v/v). Subsequently, a weight of nano-silica particles was mixed into the prepared solution of APTES under stirring for a fixed time of 10 min to get a good dispersion. The ratio of silica to APTES in the slurry was 1 g/mL.

The slurry was sampled for examining the quantity of APTES grafted on the surface of the silica particles in the aqueous mixing process. The slurry sample was centrifuged, and the supernatant was decanted. The precipitates obtained were washed by ethanol to remove the physically adsorbed APTES. The operation of ethanol washing process was introduced in the followed paragraph (4). The powder sample obtained was marked as Sp-M-EW, in which the symbol M, EW stands for the aqueous mixing and the ethanol washing, respectively.

(2) The spray drying of the mixed slurry.

Once the aqueous mixing process finished, the slurry was dried immediately through a spray dryer. In the spray drying process, the inlet air temperature was set at 200 °C, and the outlet air temperature was controlled at 94 ± 2 °C by adjusting the feed rate of the slurry. After spray drying, the formed agglomerated particles with a diameter of 2–10 μ m were collected and conducted for thermal treatment process.

The agglomerated particles were sampled for examining the quantity of APTES grafted on the silica surface after the spray drying process. The sample was marked as Sp-S, in which the symbol S stands for the spray drying. For comparison, part of the sample Sp-S was washed through the ethanol washing process, which was marked as Sp-S-EW.

(3) The thermal treatment of the agglomerated particles.

1 g of the agglomerated particles was filled into a steel pipe. Then the pipe was sealed and put in a muffle furnace which had been pre-heated to a set temperature and kept for a fixed time to enhance the silanization reaction. The steel pipe was 150 mm in length and 10 mm in inner diameter and had a wall thickness of 1 mm. The process temperature was set at different values in the range of 100–450 °C, and the process time was in the range of 0–3 h.

After thermal treatment the nano-silica particles were sampled for examining the quantity of APTES grafted on the silica surface. The sample was marked as Sp-T, in which the symbol T stands for the thermal treatment. The sample Sp-T was then washed through the ethanol washing process, which was marked as Sp-T-EW. For a clear expression, some key parameters were used to mark the samples, e.g., the sample after thermal treatment at 360 for 30 min was marked as Sp-T-360-30.

(4) The ethanol washing of the sample.

In order to examine the chemical grafted APTES on the silica particle surface, a thorough washing with anhydrous ethanol was used to remove the unreacted APTES in the sample. 500 mg of the sample was washed using 100 mL anhydrous ethanol in a conical flask on a shaking table. After 1 h shaking, the suspension was then centrifuged, and the precipitate was dispersed in anhydrous ethanol again, which was one time washing. Because the reaction of salicylaldehyde with the amino groups

of APTES forms a bright yellow colored Schiff Base, a salicylaldehyde/ethanol solution with a concentration of 2% was used to detect the presence of APTES in the supernatant of the washing ethanol through ultraviolet detection [20,22]. After each washing, the concentration of APTES in the supernatant was reduced obviously. Five times' washing ensured that the unreacted APTES in the sample had been washed off. Then the obtained modified silica particles were dried at 80 °C for 12 h before further analysis.

2.3. Cu^{2+} adsorption of the modified particles

Cu^{2+} adsorption was employed to verify the grafting density of the available amine functionality. 100 mg $\text{CuSO}_4 \cdot 4.5\text{H}_2\text{O}$ was added in 1000 mL deionized water to form a CuSO_4 solution. The Cu^{2+} concentration of the CuSO_4 solution was measured by atomic adsorption spectroscopy. 25 mg sample of amino-modified silica particles was dispersed in the CuSO_4 solution of 50 mL. Adsorption was conducted in a conical flask which was shaken on a shaking table at 25 °C for 2 h. Then the solution was centrifuged, and the Cu^{2+} concentration in the supernatant was measured. For comparison, Cu^{2+} adsorption capacity of unmodified silica particles were also measured.

2.4. Characterization of the samples

The morphology of the silica particle samples was characterized by a high-resolution transmission electron microscope (HRTEM, JEM-2011, JEOL Co., Tokyo, Japan). The chemical state of the sample surface was analyzed by X-ray photoelectron spectra (XPS, PHI Quantera SXM, Ulvacphi, Japan). All binding energies were calibrated referring to the C 1s peak being 284.8 eV. The shifting delta of the measured binding energy of C 1s in the sample from the standard peak position of elementary carbon at 284.8 eV was calculated, and then the binding energy of other element was calibrated by shifting the delta. The grafting amount was determined by a thermogravimetry analyzer (TGA/DSC 1, Mettler toledo, Swiss). TGA scans at a heating rate of 20 K/min were recorded from 30 °C to 1000 °C under a flow of nitrogen gas. The TG analysis for weight loss has a precision of 0.01%. The nitrogen and carbon contents of the modified silica samples were analyzed by an elemental analyzer (EA, Vario EL III, Elementar, Germany), which has a precision of 0.01%. An ultraviolet spectrophotometer (TU-1901, PERSEE, Beijing, China) was used to detect the concentration of APTES in the washing supernatant. Polarized Zeeman atomic adsorption spectroscopy (Z-5000, Hitachi High-Technologies Corp., Japan) was used to determine the Cu^{2+} concentration.

3. Results and discussion

3.1. Modification and interaction between APTES and the silica surface

The morphology and particle size of the silica particles before and after APTES modification were examined through TEM. Fig. 1 gives the particle images of the unmodified silica and the sample Sp-T-360-30-EW. It is shown that the silica particles have a spherical shape. For sample Sp-T-360-30-EW, there was a film coated on the silica surface with a thickness about 3 nm, which basically corresponded to the magnitude of the APTES quantity fed (silica/APTES = 1 g/mL) through the quantity estimation. When the electron beam focused on the local area of the particles at higher magnification, gradually disappearance of the modified film was observed in 5–7 s. After backing to the previous magnification, the surface morphology of the particles was shown in Fig. 1(c).

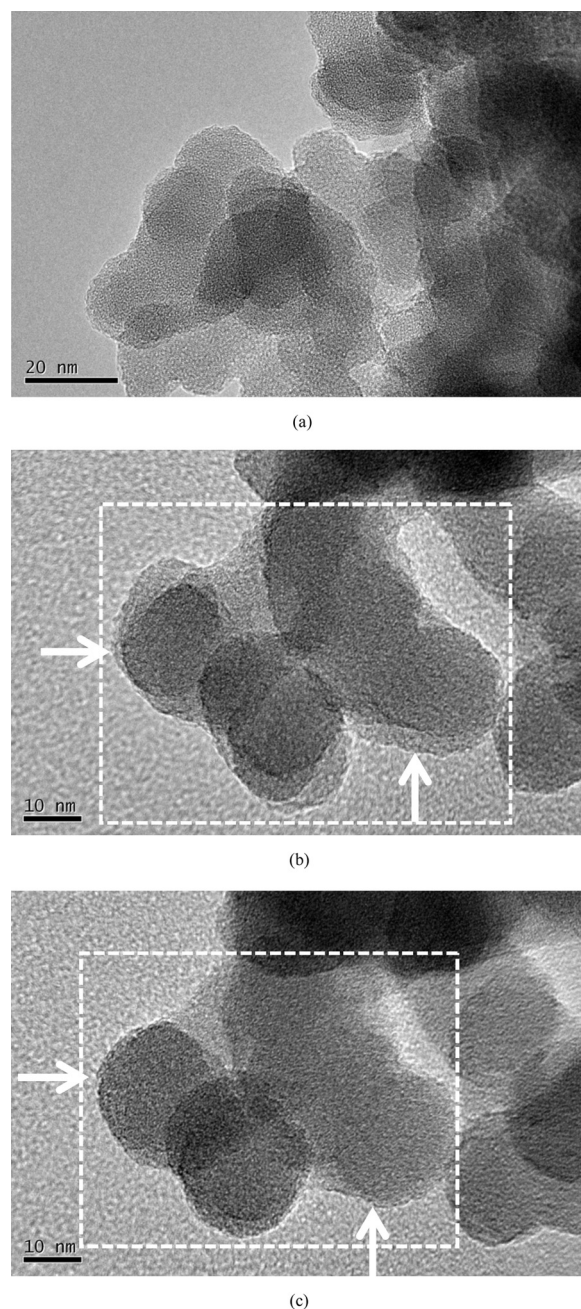


Fig. 1. TEM images of the samples. (a) Sp; (b) Sp-T-360-EW; (c) Sp-T-360-EW, after irradiation at higher magnification.

Comparing Fig. 1(b) and Fig. 1(c), it was observed that the structure of the coated layer in the two images were dissimilar, which indicates that this is not caused by the focal plane change. It is inferred that the irradiation of the high energy electron beam resulted in the decomposing or fusion of the APTES grafted on the particle surface and then volatilization.

The chemical states of the silica sample before and after APTES modification were analyzed by XPS. Fig. 2 gives the spectra of the Si 2p and O 1s binding energies of the unmodified silica particles and the APTES-modified silica sample Sp-T-360-30-EW. It is shown that the binding energies of Si 2p and O 1s in unmodified silica particles were 103.6 eV and 532.8 eV, respectively, while after modification, they were changed to 102.8 eV and 532.1 eV. The decrease of binding energy indicated that the chemical bond on the surface was changed from Si–O–H to Si–O–Si, as the electronegativity of Si is

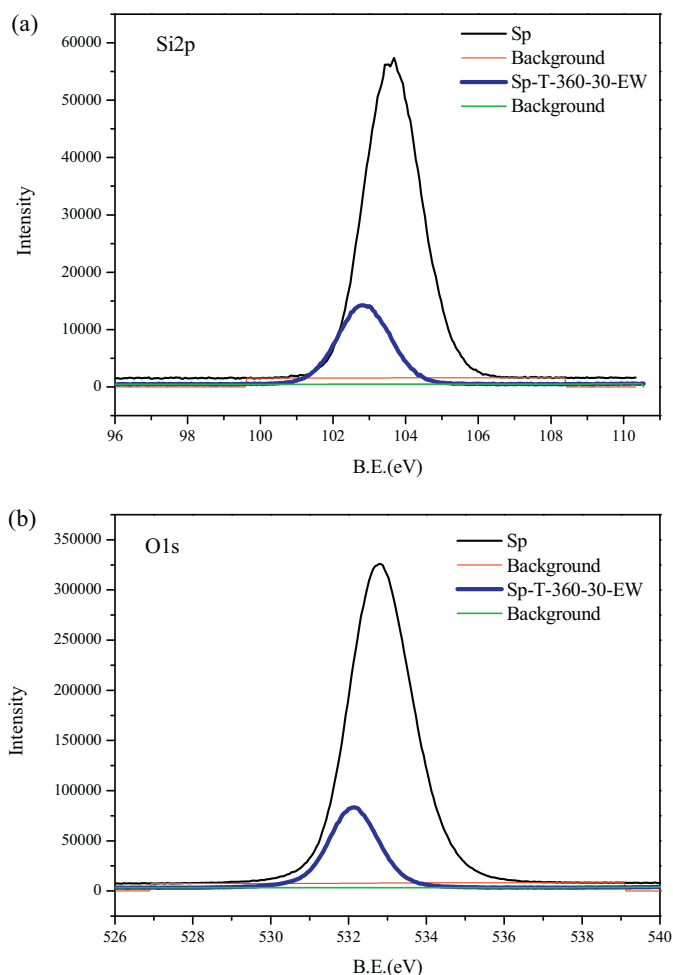


Fig. 2. Binding energies of Si 2p and O 1s of the sample Sp and Sp-T-360-30-EW. (a) Si 2p; (b) O 1s.

1.9, which is lower than the 2.2 of H. This indicated that APTES was chemically bonded on the silica surface.

From the literature [28,42], it is known that there are different kinds of interactions between the silica surface and the APTES modifier, namely, van der Waals force, hydrogen bonding and

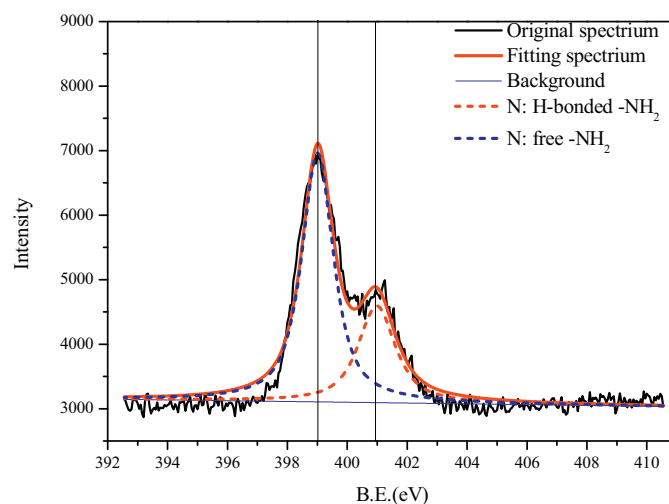
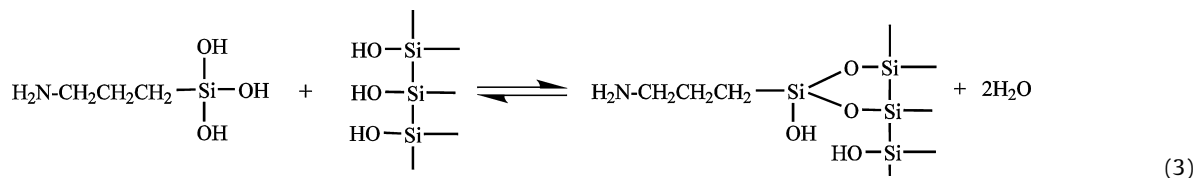
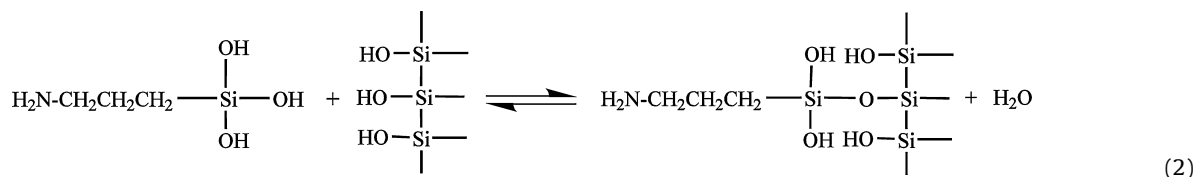
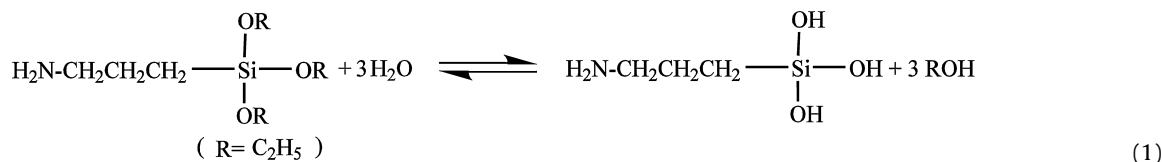


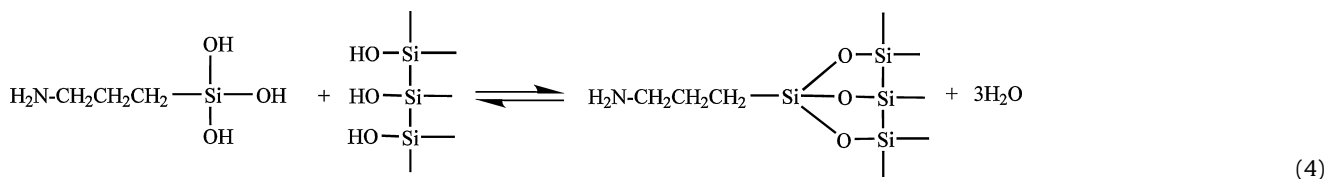
Fig. 3. N 1s binding energy of sample Sp-T-360-30-EW.

protonation of the amine, and chemical bond. The van der Waals force is relatively weak, and APTES on the silica surface held by van der Waals force offers a free $-NH_2$ and is easily removed by ethanol washing. Hydrogen bonding and protonation of the amine on the silica surface is a stronger interaction than that by van der Waals force, but they do not offer free $-NH_2$ because the amine group is linked on the silica surface. The chemical bonded APTES on the silica surface has four types: monodentate, bidentate, tridentate and crosslinking. They all contribute free $-NH_2$. In the XPS spectrum of N 1s shown in Fig. 3, the peak component at 399.1 ± 0.1 eV was assigned to free $-NH_2$ in the molecules of the chemical bonded and possible remains held by van der Waals force, and the shoulder at 400.8 ± 0.2 eV was assigned to hydrogen bonded and protonated molecules [19,37,42].

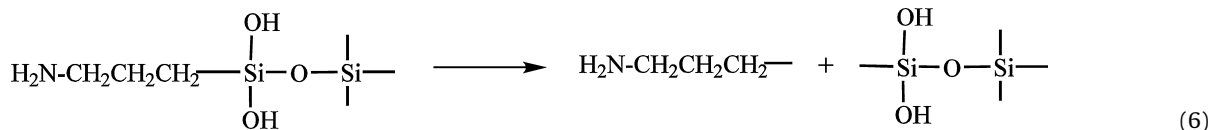
3.2. APTES grafted amount on the silica surface

In the aqueous mixing process, APTES hydrolysis occurs as Eq. (1). The hydrolyzed APTES then reacts onto the silica surface. As shown in Eqs. (2)–(4), there are three possible paths, leading to monodentate, bidentate, tridentate structure of grafted APTES.





The amount of APTES grafted on the silica surface was analyzed by TGA. The TGA curves of the unmodified silica particles (sample Sp) and the APTES-modified sample (sample Sp-T-360-30-EW) are shown in Fig. 4. It is analyzed that the weight loss of APTES-modified silica came from three contributions. The first contribution was the dehydration and dehydroxylation of the nano-silica particle itself,



which occurred during the heating in the TGA measurement. In the temperature range of 30–190 °C, the weight loss was mainly from the elimination of the molecular water adsorbed on the silica surface [26]. When the temperature was higher than 190 °C, all the molecular water was removed and the contribution of dehydroxylation became small compared to the weight loss resulting from the APTES molecules. The second contribution came from the physically adsorbed APTES, which can be removed by ethanol washing. However, thorough removal of physically adsorbed APTES is hardly achieved, and any possible remains still gave a contribution to the weight loss during the heating in TGA. As the boiling point of APTES is 217 °C, it is assumed that physically adsorbed APTES is completely desorbed till 300 °C. The third contribution came from the decomposition of chemically bonded APTES. From the differential curve, it can be seen that the main decomposition occurred around 500 °C. This temperature is in agreement with the results of Dugas et al. [43] that the thermal decomposition of grafted silane took place above 450 °C and the C–Si bond started breaking up at 450–510 °C when APTES was heated in a nitrogen gas atmosphere. Therefore, the weight loss $\Delta W(\%)$ calculated from 300 to 750 °C was used to characterize the amount of APTES grafted on the silica surface, then there is,

$$\Delta W(\%) = \frac{m_{300} - m_{750}}{m_{300}} \times 100\% \quad (5)$$

where m_{300} and m_{750} were the residual weight of the sample at 300 °C and 750 °C in the TGA analysis, respectively.

The mole number of chemisorbed APTES and reaction conversion can then be calculated from $\Delta W(\%)$, assuming that the weight loss is resulted from the cleavage of C–Si bond, taking monodentate structure as an example as shown in Eq. (6), leading to $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ group release or further cleaving into smaller molecules of C, N, H compound.

Then there is a relationship between the mole number of chemisorbed APTES n_A (mol) and the residual weight at 300 °C m_{300} (g) of the APTES modified sample in the TGA analysis, as follows,

$$n_A = \frac{\Delta W(\%) \times m_{300}}{M_{\text{NH}}} \quad (7)$$

where M_{NH} (g/mol) is the molecular weight of $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ group, i.e., 58 g/mol.

The SiO_2 mass is determined by subtracting the mass brought by grafted APTES from m_{300} . The SiO_2 mass m_{SiO_2} in the APTES modified sample is given by,

$$m_{\text{SiO}_2} = m_{300} - n_A \times M_{A^*} \quad (8)$$

where M_{A^*} is the group weight of grafted APTES on the silica surface. For monodentate, bidentate, tridentate structure, M_{A^*} were calculated to be 119, 101, 83 g/mol, respectively.

In the measurement of the specific surface area, the SiO_2 sample is pre-dehydrated at 300 °C in order to eliminate the influence of the water in the sample, and the followed is the nitrogen adsorption. Then the corresponding surface area S (nm^2) is given by,

$$S = m_{\text{SiO}_2} \times S_{\text{BET-SiO}_2} \times 10^{18} \quad (9)$$

where $S_{\text{BET-SiO}_2}$ (m^2/g) is the specific surface area of silica particles which is $163 \text{ m}^2/\text{g}$ as mentioned above.

The number of APTES molecules grafted on the silica surface per square nanometers, n_A^s (nm^{-2}), is calculated as,

$$n_A^s = \frac{n_A \times N_A}{S} = \frac{(\Delta W(\%)/M_{\text{NH}}) \times N_A}{(1 - (\Delta W(\%)/M_{\text{NH}}) \times M_{A^*}) \times S_{\text{BET-SiO}_2} \times 10^{18}} \quad (10)$$

where N_A is Avogadro's constant.

The conversion of APTES is defined as the ratio of n_A^s (nm^{-2}) to the initial APTES fed $n_{A\text{-feed}}^s$ (nm^{-2}), that is,

$$C(\%) = \frac{n_A^s}{n_{A\text{-feed}}^s} \times 100\% \quad (11)$$

$n_{A\text{-feed}}^s$ can be calculated as,

$$n_{A\text{-feed}}^s = \frac{n_{A\text{-feed}} \times N_A}{(m_{\text{SiO}_2\text{-feed}} - m_{\text{water}}) \times S_{\text{BET-SiO}_2} \times 10^{18}} \quad (12)$$

where $m_{\text{SiO}_2\text{-feed}}$ is the initial mass of SiO_2 fed, m_{water} is the mass of water content of the SiO_2 from 30 to 300 °C. From the TGA curves of the unmodified silica particles (sample Sp) shown in Fig. 4, the weight loss of the water calculated from 30 to 300 °C was 5.26% based on the total mass of SiO_2 . Then m_{water} can be obtained.

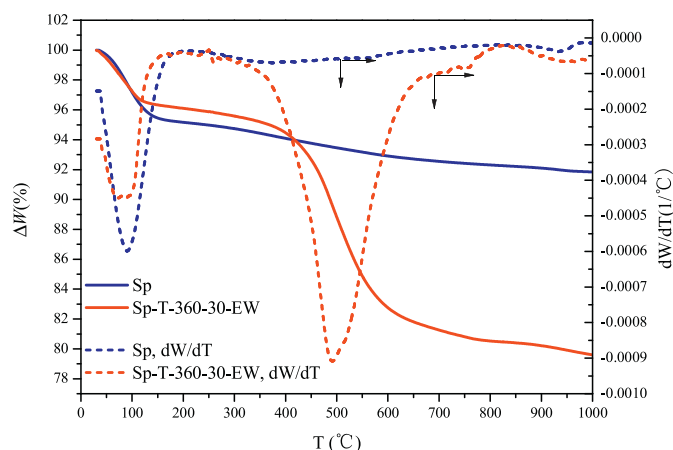


Fig. 4. TGA curves of sample Sp and Sp-T-360-30-EW.

Table 1
APTES grafting density and conversions for sample Sp-T-360-30-EW.

Structure	TGA		EA	
	n_{A}^s , nm ⁻²	C, %	n_{A-N}^s , nm ⁻²	C _N , %
Monodentate	14.42	86.2	15.15	90.6
Bidentate	13.48	80.6	14.11	84.4
Tridentate	12.65	75.6	13.20	78.9

To verify the TGA results, nitrogen content m_N (%) of the modified sample was also measured using elemental analyzer (EA). Because m_N (%) is based on the total weight of the sample, the water content should be subtracted in the calculation of the particle surface area. From the TGA curves of the APTES-modified sample (sample Sp-T-360-30-EW) shown in Fig. 4, the weight loss of water calculated from 30 to 300 °C was 4.42%. Similarly, mole number of chemisorbed APTES per square nanometers on the silica surface n_{A-N}^s (nm⁻²) and reaction conversion C_N (%) can also be calculated from m_N (%), as Eqs. (13) and (14),

$$n_{A-N}^s = \frac{(m_N(\%)/M_N) \times N_A}{(1 - (m_N(\%)/M_N) \times M_{A^*} - 0.0442) \times S_{BET-SiO_2} \times 10^{18}} \quad (13)$$

$$C_N(\%) = \frac{n_{A-N}^s}{n_{A-feed}^s} \times 100\% \quad (14)$$

where M_N (g/mol) is the atomic weight of nitrogen.

For sample Sp-T-360-30-EW (modified silica sample after thermal treatment at 360 °C for 30 min and ethanol washing), the weight loss ΔW (%) and m_N (%) are 15.46% and 3.69%, respectively. The mole number of chemisorbed APTES per square nanometers on the silica surface and reaction conversion calculated from Eq. (10)–(14) were listed in Table 1. The conversion calculated from EA is 4% higher than that from TGA, this is because the possible remains of physically adsorbed APTES is included in the measurement of elemental analyzer. In an actual reaction, monodentate, bidentate, tridentate structure of modified APTES can all exist, and it is difficult to determine the fraction of each structure. To simplify the calculation, bidentate structure was taken for the later calculation. The uncertainty for monodentate and tridentate of conversion is within 6%.

3.3. APTES grafting in the three stages

The mixing stage is the first step of the modification process. The effects of mixing time and temperature in the aqueous mixing stage were examined, as shown in Table 2. The mixing time had a little effect on the amount of weight loss, which increased slightly from 5.96% to 6.28% as the mixing time increased from 10 min to 2 h. When the mixing time lasted to 30 h, ΔW (%) gradually increased to 6.76%. The temperature also had a little effect on the amount of weight loss. When the temperature increased to 80 °C, the difference of ΔW (%) was not large comparing with that at room temperature, as shown in Table 2. It indicated that the quantity of APTES grafted on the silica surface was quite limited in the aqueous mixing stage. Then the conditions of the aqueous mixing were set at room temperature for 10 min before the stage of spray drying.

The quantities of APTES grafted on the silica surface of sample Sp-M-EW, Sp-S-EW and Sp-T-360-30-EW were measured, which

Table 2
The time and temperature effects on weight loss ΔW (%) in aqueous mixing.

Time	10 min	30 min	30 min (80 °C)	1 h	2 h	2 h (80 °C)	30 h
ΔW , %	5.96	5.87	6.06	6.08	6.28	6.43	6.76

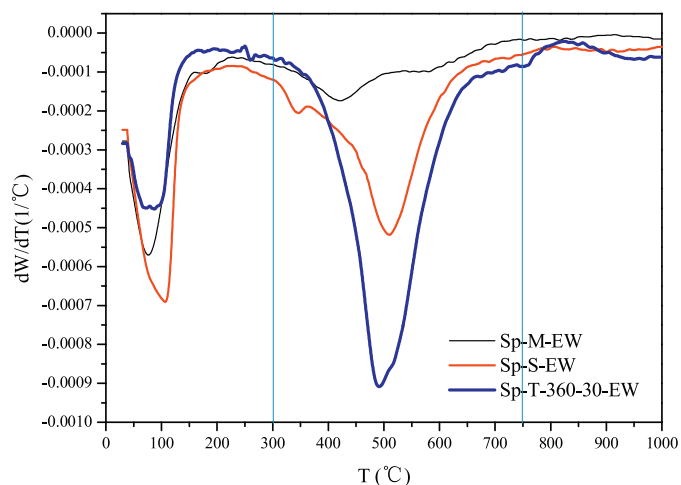


Fig. 5. Differential TGA curves of APTES-modified silica particles after each stage.

corresponds to the samples after the stage of aqueous mixing, spray drying, and thermal treatment, respectively. The differential curves of the weight loss for the three samples are shown in Fig. 5. The weight loss ΔW (%) of the APTES modified silica particles and APTES conversions C (%) after each stage are listed in Table 3. After aqueous mixing stage, the weight loss ΔW (%) of the sample Sp-M-EW was 5.96%, which corresponded to a conversion of APTES at 25.3%. After the spray drying stage, the weight loss of sample Sp-S-EW was 10.81%, which corresponded to a conversion of APTES of 50.7%. Compared with sample Sp-M-EW, the increase of grafted APTES molecules on the silica surface indicated that some APTES molecules physically adsorbed or mixed in the droplets/agglomerates continuously reacted on the silica surface in the spray drying process. After the thermal treatment stage, more APTES were chemically bonded onto the silica surface, and the conversion increased to 80.6%. This is because the reaction on the silica surface of the physically adsorbed APTES in the spray dried powder and the crosslinking between APTES molecules were enhanced in the thermal treatment, which increased the grafting density of APTES effectively. According to Eq. (10), after the stage of aqueous mixing, spray drying, and thermal treatment, the grafted APTES densities of sample Sp-M-EW, Sp-S-EW and Sp-T-360-30-EW were calculated to be 4.24, 8.48, 13.48 nm⁻², respectively. The grafted APTES density of sample Sp-T-360-30-EW was much higher than previously reported data [5,20,35,36,38,39]. Vrancken et al. [38] reported that an APTES molecule occupies $\sim 50 \text{ \AA}^2$ on the silica surface, and accordingly the maximum number of APTES molecules in a monolayer can be estimated to be about 2 nm⁻². Therefore, it was inferred that there was fast reaction in the aqueous mixing stage and then a multilayer was formed due to the condensation of APTES molecules in the spray drying stage and thermal treatment stage.

3.4. Effects of thermal treatment on the grafting density

The effects of reaction time and temperature on the grafting density in the thermal treatment were studied. For sample Sp-T-360-30-EW, the change of the weight loss from TGA with processing

Table 3
APTES grafting conversions in the stages of aqueous mixing, spray drying and thermal treatment.

Sample	ΔW , %	n_A^s , nm ⁻²	C, %
Sp-M-EW	5.96	4.24	25.3
Sp-S-EW	10.81	8.48	50.7
Sp-T-360-30-EW	15.46	13.48	80.6

Table 4The change of weight loss with processing time in the thermal treatment ($T=360^{\circ}\text{C}$).

Time/min	0	10	20	30	45	60	75	90	120	180
$\Delta W, \%$	10.81	13.71	14.11	15.46	15.04	15.68	16.50	15.78	15.49	12.70

time is shown in Table 4. It is shown that the APTES grafting density increased as processing time increased in the first 30 min, and then the grafting density reached a maximum at a processing time in the range of 30–75 min. As the processing time was further increased, the grafting density decreased. This result was also confirmed by the change of nitrogen content from the elemental analysis shown in Table 5. Moreover, for a processing time in the range of 0–60 min, the C/N ratio was about 3, corresponding to the group of $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ grafted on the silica surface. As the processing time was increased, the C/N ratio gradually increased to 4.2 at 180 min, indicating the loss of nitrogen containing group. Considering the average bond energy of C–N, C–C, C–Si bond are 305 kJ/mol, 346 kJ/mol, 318 kJ/mol, respectively [44–46], and the Si–C bond started breaking up at 450–510 $^{\circ}\text{C}$ [43], it is assumed that evolution of the C/N ratio is attributed to the release of $-\text{NH}_2$, as C–N bond cleavage is easier to happen. For a processing time of 30 min, the effects of reaction temperature were investigated. Fig. 6 shows the changes of the weight loss, nitrogen content and C/N ratios with the processing temperature increase. Compared with sample Sp-S-EW, when the processing temperature was lower than 300 $^{\circ}\text{C}$, the weight loss of the sample decreased, indicating the thermal treatment had a negative effect on the increase of grafted APTES. As the temperature increased, the negative effect became stronger till 280 $^{\circ}\text{C}$. When the temperature was higher than 300 $^{\circ}\text{C}$, the weight loss of the sample increased, indicating that the thermal treatment had a positive effect on enhancing the silanization process. The weight loss reached its maximum at 360 $^{\circ}\text{C}$. When the temperature was higher than 360 $^{\circ}\text{C}$, the weight loss and nitrogen content decreased, and the C/N ratio of the sample increased obviously, indicating $-\text{NH}_2$ release.

The amine quantity on the silica surface was measured by using Cu^{2+} adsorption to verify the APTES grafting density. Fig. 7 gives the change of Cu^{2+} adsorption capacity of the sample Sp-T-EW with the processing temperature for 30 min in the thermal treatment. It was shown that the APTES modification changed the Cu^{2+} adsorption capacity of the silica particles significantly, while the unmodified silica particles with the same post-treatment had little adsorption capacity. The change of Cu^{2+} adsorption capacity with temperature is similar to the weight loss curves and nitrogen content curves versus temperature shown in Fig. 6. Fig. 8 shows that Cu^{2+} adsorption capacity Q of the modified silica particles had a linear relationship with the grafting density n_A^s , i.e., $Q(\text{Cu}^{2+}) = 3.44 + 3.38 n_A^s$, with the linear correlation coefficient $R^2 = 0.92$, confirming that a high grafting density on the modified silica surface brings a high functionality. The sample Sp-M-EW with lower grafting density gave a lower Cu^{2+} adsorption capacity.

3.5. Temperature effects on the APTES grafting process in the thermal treatment

The temperature effects on the APTES grafting process in the thermal treatment were investigated by comparing the weight

Table 5The change of nitrogen content and C/N ratio with processing time in the thermal treatment ($T=360^{\circ}\text{C}$).

Time/min	0	10	30	60	120	180
N, %	2.31	3.28	3.57	3.59	3.27	2.51
C/N, –	3.12	2.98	3.07	3.10	3.41	4.20

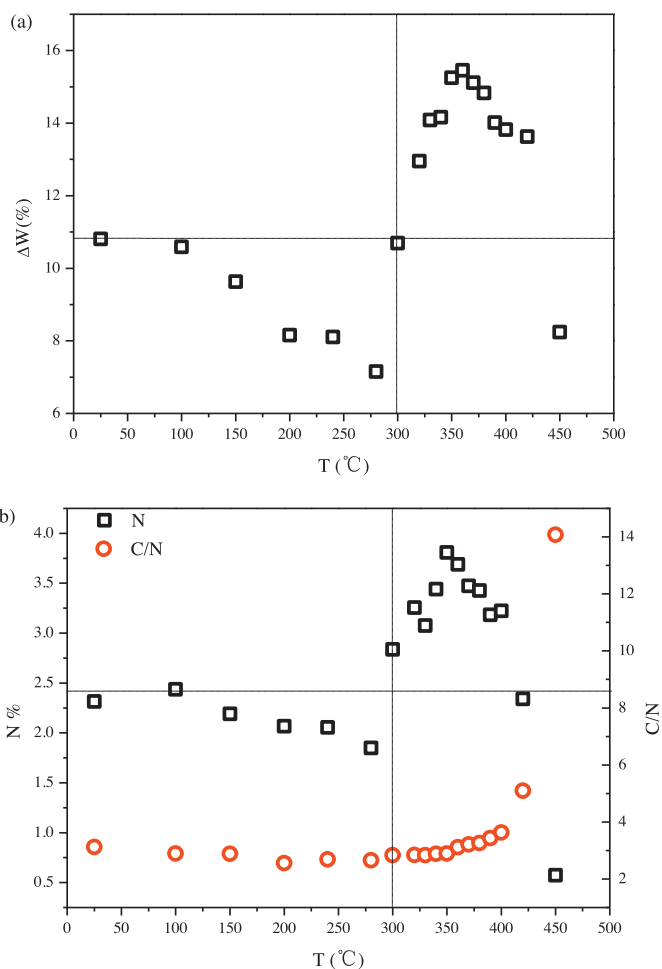


Fig. 6. The change of weight loss, nitrogen content and C/N ratios with processing temperature below and above 300 $^{\circ}\text{C}$ in the thermal treatment ($t=30$ min). (a) Weight loss; (b) nitrogen content and C/N ratios.

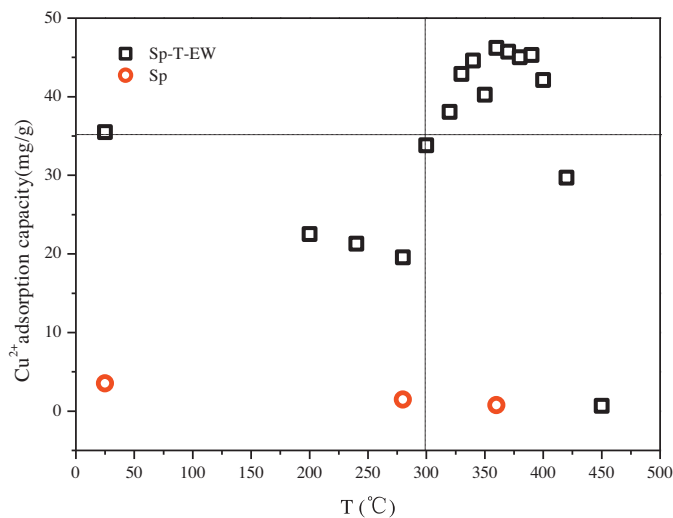


Fig. 7. Cu^{2+} adsorption capacity of Sp-T-EW samples and unmodified silica particles under identical conditions.

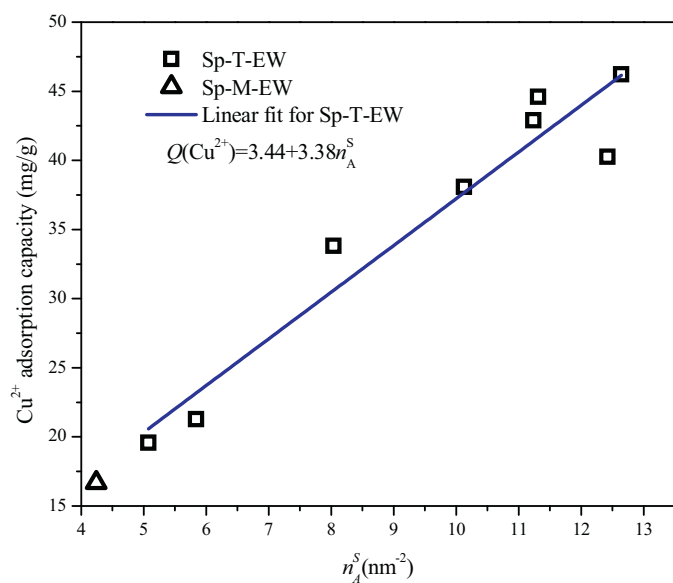


Fig. 8. Relationship between Cu^{2+} adsorption capacity and the grafting density of APTES.

loss and the nitrogen contents of the three samples before and after ethanol washing, i.e., Sp-S, Sp-T-280-30, Sp-T-360-30. Table 6 shows the TGA and EA results for the three samples. For sample Sp-S and Sp-S-EW, the weight loss ΔW (%) changed from 16.62% to 10.81%, i.e., there was a decrease of 35% in the weight loss. And the nitrogen content m_N (%) changed from 4.21% to 2.32%, with a decrease of 45% from the elemental analysis. The decrease indicated that the physically adsorbed APTES molecules in the spray dried sample were washed off by ethanol.

However, for sample Sp-T-280-30 and sample Sp-T-280-30-EW, the weight loss ΔW (%) changed from 16.87% to 7.18%, which was a larger decrease of 57% in the weight loss. And the nitrogen content m_N (%) changed from 3.99% to 1.85%, which was also a larger decrease of 54% from the elemental analysis. Compared with the decrease for the sample Sp-S, it was inferred that the reverse reaction dominated in the thermal treatment at 280 °C, which caused that more APTES molecules were washed off by ethanol. It shows that the thermal treatment at 280 °C has a negative effect on the APTES grafting increase. For the sample Sp-T-360-30 and Sp-T-360-30-EW, the weight loss ΔW (%) changed from 17.75% to 15.46%, which was only a small decrease of 13% in the weight loss. This showed that most of APTES molecules were chemically bonded onto the silica particle surface after the thermal treatment at 360 °C. And the nitrogen content m_N (%) from 3.51% to 3.69% gave a very little change in the elemental analysis. The slightly increase of m_N (%) also occurred in the repeated experiments, which needs to be further studied. It was inferred that the thermal treatment at 360 °C increased the grafting on the silica surface and crosslinking between APTES molecules, thus gave less molecules to be washed off. It shows that the thermal treatment at 360 °C has a positive effect on the silanization reaction.

Table 6
Weight loss ΔW (%) and nitrogen content m_N (%) of the sample Sp-S, Sp-T-280-30, Sp-T-360-30 before and after ethanol washing.

Sample	Before EW ΔW , %(TGA)	After EW ΔW , %(TGA)	Before EW m_N , %(EA)	After EW m_N , %(EA)
Sp-S	16.62	10.81	4.21	2.32
Sp-T-280-30	16.87	7.18	3.99	1.85
Sp-T-360-30	17.75	15.46	3.51	3.69

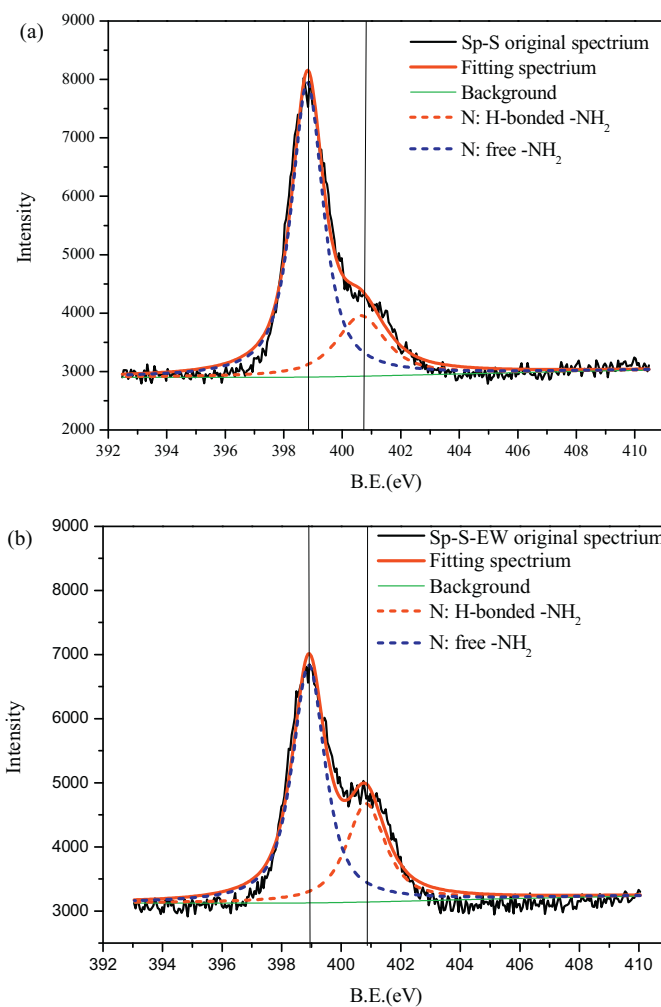


Fig. 9. N 1s energy of sample Sp-S and Sp-S-EW. (a) Sp-S; (b) Sp-S-EW.

The effects of temperature in the thermal treatment on the interaction between APTES molecules and silica surface were also analyzed by XPS. Fig. 9 shows the XPS spectra of the binding energies of the N 1s of the sample Sp-S and the sample Sp-S-EW. It is shown that after ethanol washing, the nitrogen fraction of free $-\text{NH}_2$ decreased from 75.7% to 67.0%. The decrease indicated that the free $-\text{NH}_2$ due to the van der Waals force adsorption was washed off. Similarly, for the sample Sp-T-280-30, the XPS spectra indicated that the nitrogen fraction of free $-\text{NH}_2$ had a larger decrease from 79.5% to 55.2% after ethanol washing. It was inferred that the reverse reaction occurred, which made the chemically bonded APTES partly convert to the held by van der Waals force, causing a decrease of APTES grafting density. However, for the sample Sp-T-360-30, the XPS spectra indicated that there was little change of N fraction from the free $-\text{NH}_2$ before and after ethanol washing, i.e., from 66.9% to 68.7%. It was inferred that at 360 °C, the forward reaction of APTES molecules on silica surface dominated, which made the APTES held by van der Waals force convert to the chemically bonded, leading to the increase of weight loss.

4. Conclusions

A novel and efficient process for APTES modification of nano-silica particle surface was developed and it gave a high grafting density. This comprised three stages, namely, aqueous mixing, spray drying and thermal treatment. The conversions after the successive stages were 25.3%, 50.7%, and 80.6%. In the thermal

treatment, the processing temperature and time affected the grafting density significantly, and the reaction was reversible. When $T < 300^\circ\text{C}$, the reverse reaction dominated, causing a decrease of APTES grafting density. When $T > 300^\circ\text{C}$, the forward reaction dominated, leading to increased grafting density. The optimal temperature and time in the thermal treatment process were 360°C and 30 min, respectively, under these conditions a high density of 13.48 nm^{-2} of APTES molecules chemically bonded on the silica surface was achieved.

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