

## Surface Modification of Colloidal Silica Nanoparticles: Controlling the size and Grafting Process

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Surface modification of colloidal silica nanoparticles without disrupting the electric double layer of nanoparticles is a major challenge. In the work, silane was employed to modify colloidal silica nanoparticles without inducing bridge flocculation obviously. The effect of pH value of the silica sol, the amount of silane in feed, and reaction temperature on the graft amount and the final size of modified particles was investigated. The increased weight loss by TG and the appearance of T<sup>2</sup> and T<sup>3</sup> except for Q<sup>2</sup> and Q<sup>3</sup> signals by CP/MAS <sup>29</sup>Si NMR of the modified samples verified the successful grafting of silane. The graft amount reached 0.57 mmol/g, which was slightly lower than theory value, and the particle size remained nearly the same as unmodified particles for acidic silica sol at the optimum condition. For alkaline silica sol after modification, aggregates composed of several nanoparticles connected together with silane moleculars as the bridge appeared.

**Key Words** : Silica sol, Modification, Silane, Graft amount, Particle size

### Introduction

Inorganic fillers, specially silica nanoparticles, have been widely used in polymers to improve the mechanical properties, conductivity and so on.<sup>1-4</sup> However, the weak compatibility between organic matrix and inorganic nanoparticles, which usually results in unevenly dispersion of inorganic nanoparticles in the matrix, is the main problems in practical applications. The covalent grafting of silane molecular on inorganic surfaces has been attempted to improve the dispersion and received some effect.<sup>5,6</sup> Also Liu *et al.* proposed a new method to organically functionalize nano-scaled silica particles through the reaction between the silanol group of silica and the oxirane ring of epoxy compounds.<sup>7</sup> However, in most studies the grafting of silane was performed in organic solvent, which is undesired due to environmental concerns.<sup>5-8</sup>

Now, the treatment with modified inorganic sols could be an advantageous alternative, but there has been relatively little work on colloidal polymer nanocomposites.<sup>9,10</sup> Recently, some groups reported the synthesis of polymer/silica nanocomposites by polymerization of unsaturated monomers in the presence of silica sol.<sup>11-13</sup> Wu *et al.*<sup>12</sup> prepared poly(L-lactic acid)/SiO<sub>2</sub> nanocomposites *via in situ* melt polycondensation of L-lactic acid in the presence of acidic silica sol. The results demonstrated some OLLA chains were grafted onto the surface of silica nanoparticles and provided extra steric stabilization for the nanoparticles, which ensured satisfactory nano-scale dispersion in the final nanocomposites. Therefore surface modification of colloidal silica nanoparticles instead of powder silica nanoparticles will have the greater applications.

Colloidal silica nanoparticles, namely silica sols, are aque-

ous suspension of silica particles with particle size ranging from 1 nm to 1 μm. The stability of silica sol is related to electrolyte, silica concentration, pH value and so on. Silica sol is usually considered as stable due to the lack of significant rate of sedimentation or agglomeration. However, surface modification of silica sol with silane moleculars without disrupting the electric double layer of nanoparticles is difficult because the silica nanoparticles are in the intermediate stable state and minimal change of surface environment will lead to aggregation. Most of previous research employed γ-aminopropyltrimethoxysilane (KH550) to modify the surface of silica nanoparticles, however, amino groups is hydrophilic and alkaline, which will very likely disrupt the electric double layer of nanoparticle in silica sol. Recently some effort<sup>14-17</sup> has been made to modify the surface of silica sol with different silanes to suit different needs. Still, systematic investigations about the influencing factors of the graft amount and the final size of modified silica sol are not reported.

One objective of this study was to modify colloidal silica nanoparticles with γ-glycidoxypolytrimethoxysilane (KH560) without obviously disturbing the colloidal stability. In order to achieve this purpose, silica sol with different pH value and silane moleculars with different end functional groups were employed. Another objective was to study the effect of reaction conditions, including silane concentration, reaction temperature and dialysis time on the graft amount of silane moleculars and physicochemical properties of final products.

### Experimental

**Materials.** Acidic silica sol (pH 2.6; particle size, 30-40 nm; the solid content, 25 wt %) was purchased from Qingdao

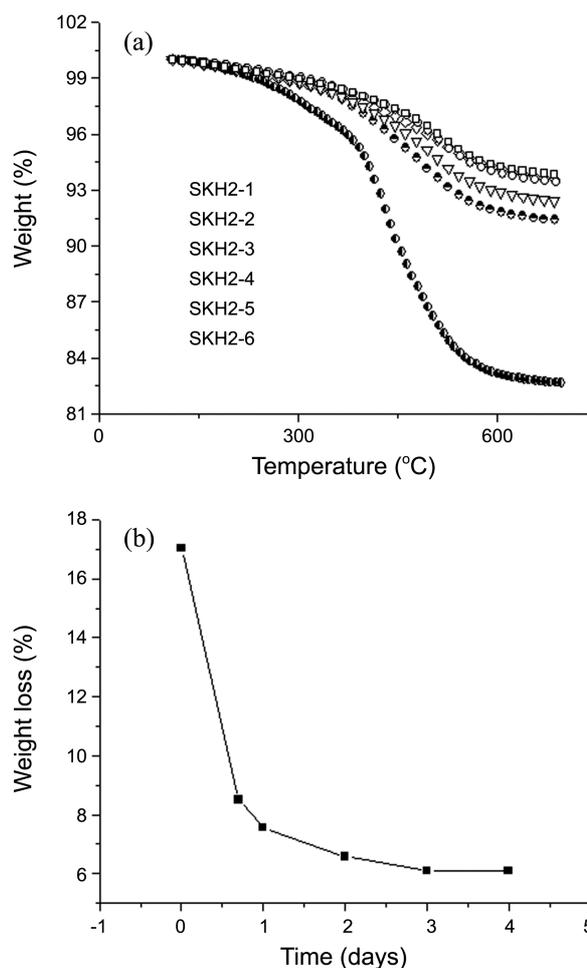
yumingyuan silica-gel reagent factory, China. Alkaline silica sol (pH 9.0; particle size, 22 nm; the solid content, 50 wt %) was purchased from Adrich, USA. KH550 and KH560 were provided by Hubei Debang Chemical Co. Ltd (China). All other reagents and solvents were used as received without further purification

**Preparation of the Surface-modified Silica Sol.** In a typical procedure, 10 g of silica sol was added to an appropriate amount of ethanol in a round flask equipped with an electric stirring rod and spherical condenser. After stirred for 30 min, the solution was heated to a predetermined temperature and a certain amount of KH560 was added. The reaction was maintained for 6 h at set temperature. The product was purified by dialysis against pure water for different times using a cellulose membrane Mw cutoff 3000 with water changed every 4 h. The grafted products are designated as SKHm/(-n), where m represents the amount of KH560 in feed (mmol/g SiO<sub>2</sub>) and n represents the dialysis time (day).

**Characterization.** Thermogravimetric analysis of the untreated and treated MMTs was performed on a TA instruments Q50 to quantitatively determine the grafting amount as well as the thermal stability. Samples were heated from 100 °C to 750 °C at the rate of 10 °C/min under a nitrogen flow (60 mL/min). An organic Elemental Analyser (Elementar, Germany) was used to determine the carbon content of the bare and the functionalized MMT. And the results are compared with that of TG analysis to survey the degree of measurement data reliability. The average size of unmodified and modified silica sol was measured by a dynamic light scattering instrument (DLS, Malvern). For TEM, a drop of diluted solution was dried on a grid with 300 mesh for 2 min and analyzed using a JEM 100 CX TEM with an accelerating voltage of 100 kV. The CP/MAS <sup>29</sup>Si spectrum were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 7 mm standard bore CP/MAS probehead whose X channel was tuned to 79.50 MHz, using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in the ZrO<sub>2</sub> rotor closed with Kel-F cap which were spun at 5 kHz rate. A total of 3000 scans were recorded with 3 s recycle delay for each sample. All CP/MAS <sup>29</sup>Si chemical shifts are referenced to the resonances of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) standard.

## Results and Discussion

For the purpose of surface modification of silica sol, a commonly used silane KH550 was first employed. After the silane was added to silica sol (pH 2.6 or 9.0) and remained for some period, the solution changed from light blue to milky and some aggregates appeared, indicating the irreversible agglomeration of nanoparticles. In contrast, addition of KH560 to the above silica sol did not induce the same phenomenon; instead, the solution remained light blue. The probable causes include: (1) the alkalinity of KH550 disturbs the intermediate stable state of silica sol; (2) the



**Figure 1.** The TG curve (a) and weight loss (b) of SKH2 with different dialysis time.

homocondensation is faster than the grafting process for the hydrolyzed KH550 and the silane molecules react with each other, forming aggregates instead of grafting to the surface of silica nanoparticles. So the surface modification was performed with KH560 in the following experiments.

To ensure complete removal of ungrafted silane molecules and gain more insight into the size change after dialysis, the dialysis process was monitored by TG and DLS at intervals. The weight loss of samples gradually reduced as

**Table 1.** The weight loss and average size of modified silica sol SKH2 with different dialysis time

Samples	Dialysis time (day)	size (nm)	Weight loss (%)
SKH2 <sup>a</sup>	0	34.9	17.0
SKH2-0.7	0.7	29.2	8.5
SKH2-1	1	38.9	7.6
SKH2-2	2	37.2	6.6
SKH2-3	3	28.1	6.1
SKH2-4	4	40.8	6.1

<sup>a</sup>For SKH2, the reaction was performed at 50 °C for 6 h with acidic silica sol as pristine sol.

**Table 2.** The effect of pH on the grafting process

pH <sup>a</sup>	Size before modification (nm)	Size after modification (nm)	Weight loss (%)
2.6	34.9	40.8	6.1
9.9	22	199.7	8.7

<sup>a</sup>Both reaction was performed at 50 °C for 6 h, with the amount of KH560 fixed in 2 mmol/g for both silica sol.

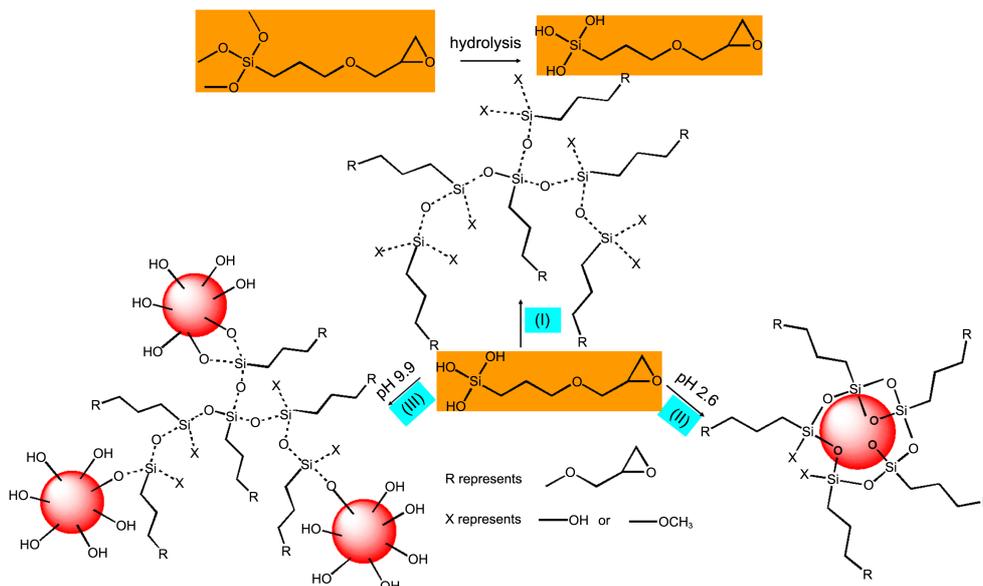
dialysis time increased, and eventually reached a constant value, indicating the dialysis process can effectively remove the unreacted silane coupling agent KH560 in the product. The increased weight loss compared to unmodified silica sol also verified the successful grafting of silane moleculars. For SKH2, the weight loss reached 6.1% and the particle size remained below 45 nm after 4 days dialysis (Table 1 and Figure 1). As the amount of KH560 in feed increased, the dialysis time increased. For SKH6-0 and SKH10-0, the dialysis time was 11 days and 13 days, respectively (supporting information).

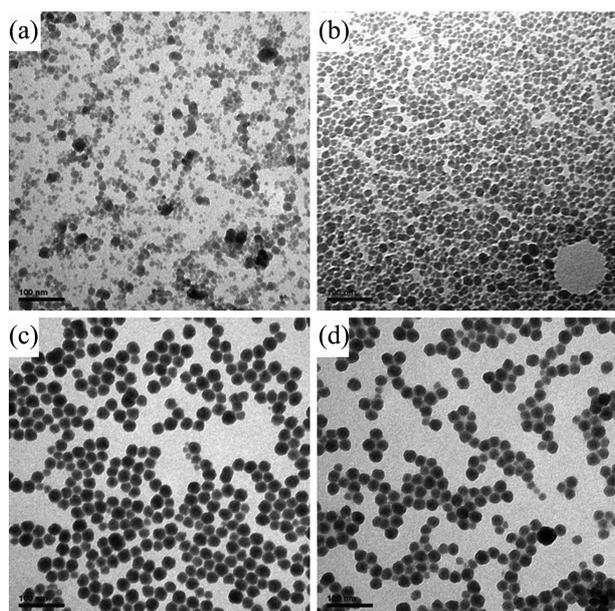
As mentioned above, after addition of KH560 to the silica sol, whether acidic or alkaline, the appearance of silica sol did not change obviously. The effect of pH on the grafting process was investigated and shown in Table 2. Though the weight loss of modified silica sol in the case of pH 9.9 reached 8.7%, higher than that at pH 2.6, the average size increased from 22 nm to 199.7 nm. After modification, the average size of acidic silica sol slightly increased from 30 nm to 40 nm and the weight loss was 6.1%. The difference in average size and weight loss was mainly due to the different grafting routes (Scheme 1). To condense an alkoxy silane to the silica surface the alkoxy groups of the silane first must be hydrolyzed to produce silanol groups. This is a fast reaction and the reaction rate is significantly increased when the pH is increased.<sup>18</sup> After hydrolysis, the condensation falls into three categories. (1) Small part of silane moleculars

react with each other and form oligomers. (2) Some silane moleculars are grafted to the surface of silica nanoparticles. (3) Some silane moleculars react with each other and are grafted to the surface of nanoparticles simultaneously, forming large aggregates, which are composed of several nanoparticles connected together with silane moleculars as the bridge. Similarly, the condensation reaction is, within the pH range 1-10, significantly faster at high pH than low pH and occurs before the silanes are completely hydrolyzed.<sup>19</sup> Therefore the hydrolysis and condensation of silane at high pH is more difficult to control. It is probable that in acidic sol reaction (II) is the main reaction whether reaction (III) dominates in alkaline sol.

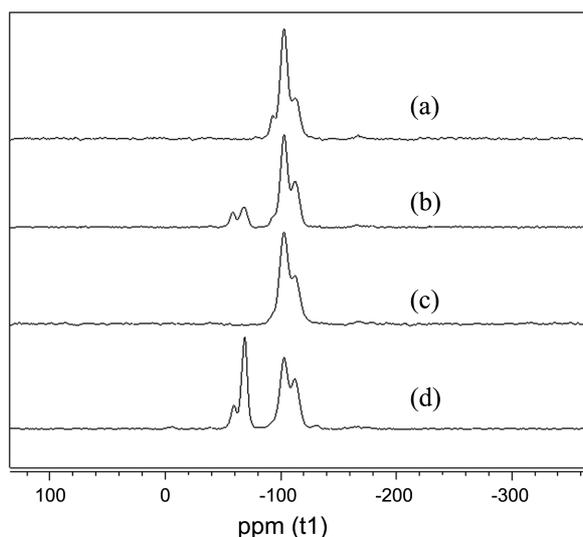
TEM results confirmed our speculation. From TEM, pristine acidic silica sol presented irregular spherical particles and small aggregates could be observed due to hydrogen bonds between the surface hydroxyl groups of silica nanoparticles. After silane grafting, the silica sol showed regular spherical structure. The modified silica sol was monodisperse and no large aggregate was observed, indicating that silane grafting can prevent aggregation of silica nanoparticles to some extent. For the alkaline sol, the nanoparticles stucked to each other and formed large aggregations after silane modification (Figure 2). This results support our proposal about the different grafting routes on silica surface based on the DLS analysis.

CP/MAS <sup>29</sup>Si NMR spectra of unmodified and modified silica sol are shown in Figure 3. The peaks at -93.3 ppm, -102.8 ppm, -112 ppm are ascribed to Q<sup>3</sup>[Si(OSi)<sub>3</sub>OM] (M stands for Al, Mg, etc.), Q<sup>3</sup>[(SiO)<sub>3</sub>SiOH], and Q<sup>4</sup>[(SiO)<sub>4</sub>Si] (Q represents the tetrafunctional) for unmodified acidic silica sol. The Q<sup>3</sup>[Si(OSi)<sub>3</sub>OM] is characteristic of Si atoms in acidic silica sol since Al<sup>3+</sup> is known as counterions. The Q<sup>3</sup>[Si(OSi)<sub>3</sub>OH] and Q<sup>4</sup>[(SiO)<sub>4</sub>Si] are attributed to isolated silanol groups present at the surface of silica nanoparticles and Si-O-Si bond in the bulk of particles respectively. After

**Scheme 1.** The reaction mechanism of grafting process.



**Figure 2.** TEM of unmodified (a, c) and modified (b, d) acidic and alkaline silica sol.



**Figure 3.** CP/MAS  $^{29}\text{Si}$  NMR spectrum of unmodified (a, c) and modified (b, d) acidic and alkaline silica sol.

modification, the signal of  $\text{Q}^3[\text{Si}(\text{OSi})_3\text{OH}]$  became weak relative to  $\text{Q}^4$  as a portion of the surface  $(\text{SiO})_3\text{SiOH}$  groups had reacted with KH560 and was converted to  $(\text{SiO})_3\text{SiOSi}$  groups. Two new peaks at  $-58.5$  ppm,  $-68.3$  ppm appeared, ascribing to  $\text{T}^2$  [ $\text{Si}(\text{OSi})_2(\text{OH})\text{R}'$ ] ( $\text{R}' = \text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CHOCH}_2$ ) and  $\text{T}^3$  [ $\text{Si}(\text{OSi})_3\text{R}'$ ] ( $\text{T}$  represents the trifunctional) respectively.<sup>20,21</sup> This provides supporting evidence for the grafting of silane onto the silica nanoparticles. The spectrum of alkaline sol was similar to that of acidic sol except that the peak at  $-93.3$  ppm disappeared, which was due to the absence of metal ions in sol. A major difference between modified acidic and alkaline sol is that the signal of  $\text{T}^3$  is obviously stronger than  $\text{T}^2$  in alkaline sol. The higher signal intensities of the  $\text{T}^3$  [ $\text{Si}(\text{OSi})_3\text{R}'$ ] unit suggests that the graft-

ing or the condensation is faster than the hydrolysis.

TG and elemental analysis were both employed to calculate the grafted amount of silane on the surface of silica nanoparticles. Acidic silica sol is modeled for the next study. The following Eq. (1) is used to calculate the amount of grafted silane based on the weight loss between  $100$  °C and  $750$  °C,  $W_{100-750}$ , taking into account that the weight loss of dried silica sol in same temperature range is below 1 wt %.

$$\text{Grafted amount (mmol/g)} = \frac{10^3 W_{100-750}}{M(100 - W_{100-750})} \quad (1)$$

where  $M$  (g/mol) is the molecular weight of the grafted silane molecules.

The grafted amount (expressed in mmol of grafted silane per g of silica nanoparticles as mentioned above) is also calculated from the Eq. (2) based on the difference  $\Delta$  (wt %) of carbon content after and before grafting, where  $N_C$  and  $M$  (g/mol) designate the number of carbon atoms and the molecular weight of the grafted silane molecule:

$$\text{Grafted amount (mmol/g)} = \frac{10^3 \Delta C}{12 N_C - (\Delta C) M} \quad (2)$$

For SKH2, the content of carbon  $\Delta C$  is 3.77%. The grafted amount calculated from TG and elemental analysis is 0.57 mmol/g and 0.56 mmol/g, respectively. These results verify the successful grafting of silane molecules onto the nanoparticles and demonstrate that the calculation method of the grafted amount based on TG is reliable.

It can be anticipated, there is a restriction in the amount of silane for silica surface modification. In order to calculate maximum coverage of silica surface by silanes, an approximation depending on some known values can be made. The following Eq. (3) is used to calculate maximum coverage of silica surface by silane molecules, with some approximate values adopted.<sup>22</sup>  $S$  represents specific surface area of silica nanoparticles,  $\phi$  represents Si-OH groups/ $\text{m}^2$  on silica surface,  $A$  represents the surface area occupied by a silane molecular, and  $N_{\text{theory}}$  represents the maximum number of mol of grafted silane/g silica nanoparticles in theory:

$$N_{\text{theory}} = \frac{S}{(A \times 6.022 \times 10^{23})} = 0.675 \text{ mmol/g} \quad (3)$$

which corresponds to  $5.1 \mu\text{mol}/\text{m}^2$  based on the approximate value  $S$ . The percentage of consumed Si-OH group for maximum coverage can be calculated by Eq. (4):

$$P_{\text{consumed}} = N/(S \times \phi) = \frac{6.75 \times 10^4}{130 \times 8 \times 10^{-6}} = 65\% \quad (4)$$

For SKH2, the grafted amount is 0.57 mmol/g ( $4.4 \mu\text{mol}/\text{m}^2$ ) and the percentage of consumed Si-OH group is 54.8%, slightly smaller than theoretical calculation, but is believable according to similar researches. In previous study, the experimentally determined maximum values for the surface coverage of oxides by 3-methacryloxypropyltrimethoxysilane ranged from 2.8 to  $7.5 \mu\text{mol}/\text{m}^2$ , depending on the

**Table 3.** Effect of the amount of silane in feed on grafting process

Samples <sup>a</sup>	The amount of silane in feed (mmol/g)	Size (nm)	The grafted amount of silane <sup>b</sup> (mmol/g)
SKH0.25	0.25	36.9	0.18
SKH0.5	0.5	41.4	0.28
SKH1	1	39.5	0.43
SKH2	2	40.8	0.57
SKH6	6	42.4	0.58
SKH10	10	46.7	0.59

<sup>a</sup>The reaction was performed at 50 °C for 6 h for all samples. <sup>b</sup>The grafted amount was calculated by Eq. (1) based on TG.

type of oxide.<sup>23-25</sup> The slight inconsistency between calculated and theoretical values can be ascribed to the following reasons. On one hand, the calculation is an approximate prediction and not so accurate. Specially the A value is quoted from that of isobutyl(trimethoxy)silane and the orientation of the KH560 molecules (parallel or perpendicular to the surface) which will influence the grafted amount is uncertain.<sup>21</sup> On the other hand, the grafting condition may not be the optimum and the grafting process is not complete. So in the following experiments, the amount of KH560 in feed and reaction temperature was changed to optimize the grafting process for acidic silica sol.

Firstly the reaction was performed at 50 °C for 6 h with the amount of silane in feed increasing from 0.25 to 10 mmol/g. From Table 3, the grafted amount of silane increased obviously from 0.18 to 0.57 mmol/g when the amount of KH560 in feed increased from 0.25 to 2 mmol/g.

It is noteworthy that there is not obvious increase in particle size of modified silica sol, only from 36.9 nm to 40.8 nm. Further increasing the amount of KH560 in feed, the grafted amount remained nearly unchanged, from 0.57 to 0.59 mmol/g. The particle size slightly increased from 40.8 nm to 46.7 nm. Although the dialysis time increased with the increase of the amount of KH560 in feed, the particle size remained nearly unchanged even when the dialysis time reached 13 days (Table S1 and Table S2). The size distribution of modified silica sol SKH6 before and after dialysis for 11 days was shown in Figure S1. After dialysis, the size distribution of SKH6 became slightly wider but it seems no large aggregates existed. This phenomenon demonstrates that the modified silica sol is stable in water to some extent. In a second set of experiments, the reaction temperature was varied and the amount of KH560 in feed remained

**Table 4.** The effect of reaction temperature on the grafting process

Samples <sup>a</sup>	Temperature (°C)	Size (nm)	The grafted amount of silane <sup>b</sup> (mmol/g)
SKH2	25	39.2	0.46
SKH2	50	40.8	0.57
SKH2	80	67.7	0.59

<sup>a</sup>The reaction was performed for 6 h, with the amount of KH560 fixed in 2 mmol/g for acidic silica sol.

2 mmol/g (Table 4). As the reaction temperature increased, the reaction activity increased, resulting in increased grafted amount. But at 80 °C, slight agglomeration happened and the grafted amount was only 0.02 mmol/g higher than that at 50 °C. In a word, when the reaction was performed at 50 °C for 6 h with 2 mmol silane/g nanoparticles in feed, the grafting process for acidic silica sol was optimum and nearly complete.

## Conclusion

In summary, KH-560 can be successfully grafted to the surface of acidic silica sol with the size of silica nanoparticles nearly unchanged. The grafted amount of KH560 increased firstly with increasing the amount of KH560 in feed and then remained nearly unchanged. Instead, after modification, aggregates composed of several nanoparticles with silane moleculars as the bridge appeared in alkaline silica sol. When the reaction was performed at 50 °C for 6 h, with the amount of KH560 fixed in 2 mmol/g for acidic silica sol, the grafted amount reached about 0.57 mmol/g, which was slightly lower than the theoretical values. Further rising the temperature induced slight aggregation.

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