Surface modification to produce hydrophobic nano-silica particles using sodium dodecyl sulfate as a modifier

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ABSTRACT

Hydrophobic silica particles were prepared using the surfactant sodium dodecyl sulfate (SDS) as a modifier by a new route comprising three processes, namely, aqueous mixing, spray drying and thermal treatment. Since SDS dissolves in water, this route is free of an organic solvent and gave a perfect dispersion of SDS, that is, there was excellent contact between SDS and silica particles in the modification reaction. The hydrophobicity of the modified surface was verified by the contact angle of the nano-sized silica particles, which was $107°$. The SDS grafting density reached $1.82\,nm^{-2}$, which is near the highest value in the literature. The optimal parameters of the SDS/SiO$_2$ ratio in the aqueous phase, process temperature and time of thermal treatment were determined to be 20%, 200 °C and 30 min, respectively. The grafting mechanism was studied by comparing the modification with that on same sized TiO$_2$ particles, which indicated that the protons of the Brønsted acid sites on the surface of SiO$_2$ reacted with SDS to give a carbocation which then formed a Si–O–C structure. This work showed that the hydrophilic surface of silica can be modified to be a hydrophobic surface by using a water soluble modifier SDS in a new modification route.

1. Introduction

Nano-silica particles are widely used in many products such as rubbers, resins, pigments and paints [1–4]. However, due to the high surface energy and abundant hydroxyl groups on the silica surface, these nano-particles tend to agglomerate, which result in a weak affinity with the polymer matrix and poor performance of the composite material in applications. Therefore, a modification to produce a hydrophobic surface is necessary to improve the dispersion and compatibility of nano-silica particles in an organic matrix.

The most commonly used organic modifier is the silane coupling agent [5–8]. Silane reacts with OH groups on the silica surface by a condensation reaction, sometimes with the help of a catalyst [9,10]. The modification with silane is often done in a non-aqueous solvent such as toluene or hexane [11–13] to avoid the hydroxylation and self-condensation of silane in aqueous solution. Other organic modifiers such as alkanoic acids [14–16] and long chain alcohols like octanol and dodecanol [17,18] also have to be used in an organic solvent because they are water insoluble. The solvent has to be removed and recycled, and this can easily cause pollution.

Also, hydrophilic particles agglomerate in a hydrophobic solvent, resulting in the diffusion limitation of the modification process. Gas phase modification [19,20] avoids the use of an organic solvent but it also suffers from diffusion limitation in the modification process as the hydrophilic nano-particles exist as agglomerates in the gas phase.

Sodium dodecyl sulfate is a common surfactant. It has been used to prepare surfactant-coated adsorbents for solid phase extraction because it can adsorb on an oppositely charged metal oxide surface such alumina [21,22], Fe$_3$O$_4$ [23,24] and ferrihydrite [25] to form hemimicelles and admicelles. This causes hydrophobic organic compounds to concentrate in the hydrophobic phase to effect the extraction. However, it has not yet been used as a chemical modifier to produce a hydrophobic surface for particles.

In this paper, a new route for preparing hydrophobic silica without any organic solvent was developed using sodium dodecyl sulfate (SDS) as the modifier. Since SDS dissolves in water, it can be well mixed with the SiO$_2$ particles in an aqueous solution. The hydrophobic modification of the silica particles was completed by a subsequent spray drying and thermal treatment. The grafting density and contact angle were determined, and the optimal parameters for the SDS/SiO$_2$ ratio, reaction temperature and time were determined. The mechanism of the surface modification is discussed.

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2. Experimental

2.1. Reagents

Commercial nano-silica particles (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 $m^2 g^{-1}$, which was measured by a surface area analyzer (Autosorb-iQ, Quantachrome Instruments USA). The average diameter of the primary particles was 20 nm. The TiO_2 particles (AEROXIDE P25, Degussa, Germany) have 80% anatase and 20% rutile crystal structure with an average primary diameter of 21 nm. The TEM images of the SiO_2 and TiO_2 nanoparticles used are shown in Fig. 1. All the chemicals, namely, sodium dodecyl sulfate (SDS) (Sinopharm Chemical Reagent Co. Ltd., China), anhydrous ethanol (Modern Oriental Technology Development Co. Ltd., Beijing, China), methyl orange (Modern Oriental Technology Development Co. Ltd., Beijing, China), Na_2SiO_3 (Beijing Chemical Works, China), H_2SO_4 (Beijing Chemical Works, China), and NaOH (Beijing Chemical Works, China), were analytical reagent (AR) grade.

2.2. Modification process

The modification process was adopted from our previous work [26]. It comprised three processes, namely, aqueous mixing, spray drying and thermal treatment. In the aqueous mixing process, an amount of SDS was added to 150 mL deionized water in a conical flask under magnetic stirring until the SDS was dissolved completely. Then 4 g SiO_2 particles was added to the solution. The mass ratio of SDS/SiO_2 was chosen to be from 0 to 75 wt%. The slurry

was kept stirred for 1 h at room temperature to give a good dispersion. Then the slurry was dried in a spray dryer. The agglomerated particles formed were collected and given a thermal treatment in which the agglomerated particles were put in a sealed steel pipe and heated in a muffle furnace. The process temperature used was in the range of 150–250 °C, and the processing time used was in the range of 0–2 h. After the thermal treatment, the product (marked as sample SiO_2-T) was thoroughly washed with anhydrous ethanol to remove unreacted SDS. The ethanol washing process was adopted from our previous work [26]. Since SDS is slight soluble in anhydrous ethanol, the TG curves of the spray dried sample after ethanol washing and water washing were compared to confirm that the unreacted SDS was completely removed by the rigorous ethanol washing. The sample after ethanol washing was dried at 80 °C for 12 h, and marked as SiO_2-T-EW. For indicating the samples clearly, the key parameters were used to name the samples, e.g., the sample after thermal treatment at 200 °C for 30 min and with ethanol washing was marked as SiO_2-T-200-30-EW.

2.3. Preparation of silica coated TiO_2 particles

Modification of TiO_2 and silica coated TiO_2 particles were carried out for comparing how the nature of the particle surface affected the modification. The TiO_2 particles were about the same average size as the SiO_2 particles. The surface coating of the TiO_2 particles was conducted as described in our previous works [27,28]. It was conducted in a flask with the temperature and pH monitored online with a thermometer and pH meter. The TiO_2 particles were dispersed in deionized water at a concentration of 50 g/L (10 g TiO_2 particles + 200 mL water). The temperature was controlled at 60 °C by a constant temperature bath. Then 1 mol/L Na_2SiO_3 solution and H_2SO_4 solution were simultaneously titrated into the suspension of TiO_2 particles. The suspension was stirred vigorously and controlled at pH 9 by adjusting the titration rate of the H_2SO_4 solution using a peristaltic pump while the titration rate of the Na_2SiO_3 solution was kept constant. The thickness of the coated film was designed to be 2 nm, which corresponded to the silica coating amount of 30 wt% (SiO_2/TiO_2). After titration, the suspension was aged for 2 h while stirred. Then, the coated TiO_2 particles were filtrated and washed repeatedly, and dried at 105 °C for 24 h. The product obtained was marked as SiO_2@TiO_2.

2.4. Characterization

The morphologies of the TiO_2 and SiO_2@TiO_2 particles were characterized by high resolution transmission electron microscope (HRTEM, JEM-2011, JEOL Co., Tokyo, Japan). The amount of silicon in sample SiO_2@TiO_2 was determined by energy dispersive X-ray spectroscopy (EDS). The grafted amount on the samples after ethanol washing was determined by a thermogravimetric analyzer (TGA/DSC 1, Mettler toledo, Swiss). In the TG analysis, the heating rate was 20 K/min from 30 °C to 1000 °C under a flow of nitrogen. The contact angle of the samples was measured by a contact angle analyzer (HARKE-SPCA, Beijing Harke, China). The characteristic groups on the sample were determined by a FTIR spectrometer (Nexus 670, Nicolet, USA) using KBr as the matrix. The sulfur and carbon contents in the modified silica samples were determined by an elemental analyzer (EA, Vario EL III, Elementar, Germany) with a precision of 0.01%. The crystal structure of the samples was determined by a X-ray diffraction analyzer (XRD, D8-Advance, Brucker, Germany) over the range of 10–90° (2θ angle) at a scan speed of 5°/min. The chemical state of the sample surface was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Ulvacphi, Japan). All binding energies were calibrated by reference to the C 1s peak, which was fixed at 284.8 eV.
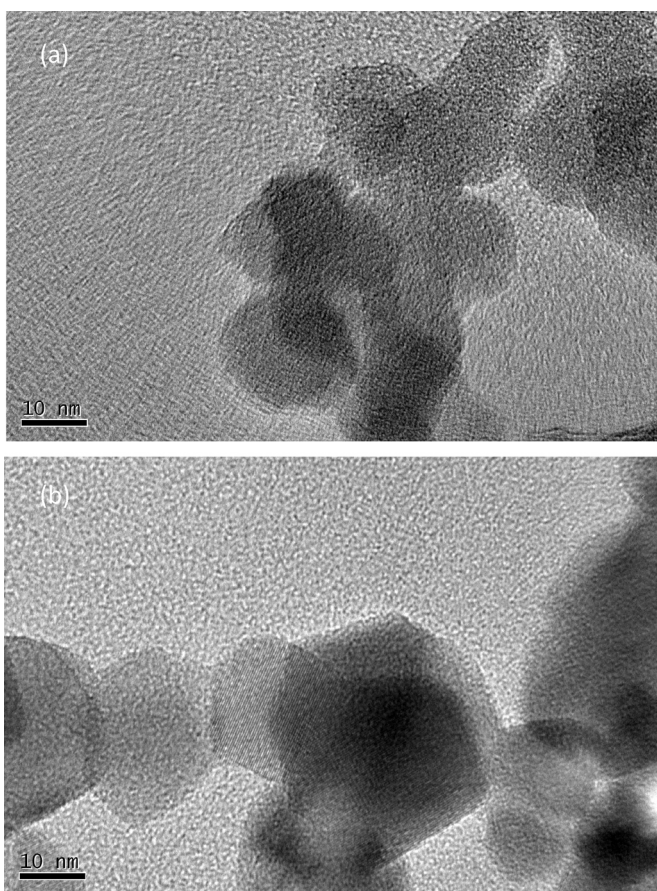
Fig. 1. Morphology of SiO_2 and TiO_2 particles (a) TEM image of SiO_2; (b) TEM image of TiO_2.
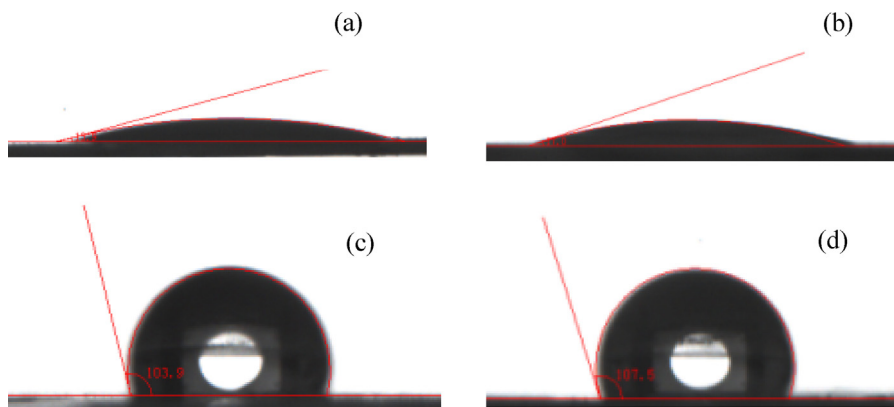
Fig. 2. Contact angle of (a) SiO$_2$ particles, (b) spray dried sample, (c) thermally treated sample SiO$_2$-T-200-30, (d) thermally treated sample SiO$_2$-T-200-30-EW.

3. Results and discussion

3.1. Hydrophobicity of the SDS modified silica particles

The water contact angles of the pure silica particles, spray dried sample and thermal treated samples before and after ethanol washing (SiO$_2$-T-200-30 and SiO$_2$-T-200-30-EW) are shown in Fig. 2. The pure silica particles were hydrophilic with a water contact angle of 14°. The spray dried sample with SDS presence had a water contact angle of 17°, which was still hydrophilic. However, the water contact angle of sample SiO$_2$-T-200-30 and sample SiO$_2$-T-200-30-EW were 104° and 107°, respectively. This showed that the silica surface was successfully modified from hydrophilic to hydrophobic. This also showed that a reaction occurred between SDS and the silica particles in the thermal treatment process.

Fig. 3 shows the FTIR spectra of SDS, pure silica particles and SiO$_2$-T-200-30-EW. In the spectrum of SiO$_2$-T-200-30-EW, the absorption peaks at 3400 and 1630 cm^{-1} were assigned to the stretching and bending vibration modes of the hydroxyl groups of physical adsorbed water molecules and silanol groups. The absorbance peak at 1106 cm^{-1} was assigned to Si–O–Si groups. The 2923 and 2852 cm^{-1} peaks were assigned to the stretching vibration of CH$_2$, and the 1463 and 1387 cm^{-1} peaks to the deforming vibration of C–H, which were not found in the spectrum of the pure silica particles but were in the spectrum of SDS, indicating that SDS was successfully grafted onto the silica surface.

The TG and dTG curves of the pure silica particles, and SiO$_2$-T-200-30 and SiO$_2$-T-200-30-EW samples are shown in Fig. 4. For the pure silica particles, the weight loss in the temperature range of 30–190 °C was from the removal of molecular water adsorbed on the silica surface [29]. When the temperature was higher than 190 °C, the weight loss was from dehydroxylation, which was not
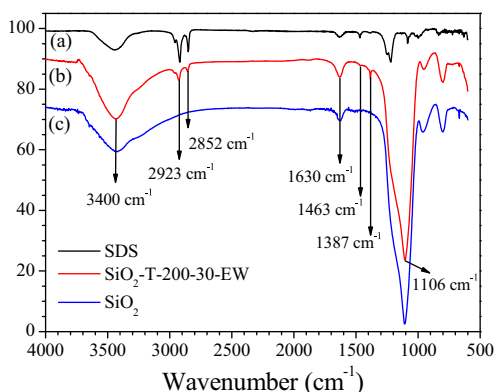

Fig. 4. TG curves of SiO$_2$, SiO$_2$-T-200-30 and SiO$_2$-T-200-30-EW.

significant. For the SiO$_2$-T-200-30 sample, two obvious weight loss peaks at 190–360 °C and 360–600 °C were observed. For SiO$_2$-T-200-30-EW, the weight loss at 190–360 °C was small while the weight loss at 360–600 °C was quite obvious. This indicated that the weight loss at 190–360 °C for SiO$_2$-T-200-30 was mainly from physical adsorbed SDS, which was removed by ethanol washing. The weight loss at 360–600 °C was from the decomposition of the grafted SDS on the silica surface [26,30], indicating that SDS was chemically bonded on the silica surface. The high decomposition temperature of 360–600 °C was much higher than the decomposition temperature of SDS (220 °C), indicating that the SDS was grafted onto the silica surface. The weak peak at around 300 °C of sample SiO$_2$-T-200-30-EW was inferred to be from the strong adsorption of SDS on the silica surface.

The grafting density of SDS on sample SiO$_2$-T-200-30-EW was calculated from the weight loss at 360–600 °C. It was defined as the number of SDS molecules grafted onto the silica surface per square nm. The calculation method was illustrated in our previous work [26]. This gave 1.82 nm^{-2} from the TG result. Earlier reports [19,31] suggested that a grafting density of 1.6–2 nm^{-2} is the maximum surface coverage for a monolayer of the silane coupling agent grafted onto porous silica particles. Our measured grafting density of 1.82 nm^{-2} for SDS was consistent with the value for the silane coupling agent, indicating that an effective chemical modification was achieved in this process.

3.2. Effects of the SDS/SiO$_2$ ratio on the modification

The effects of the SDS/SiO$_2$ ratio from 0 to 75 wt% on the modification were investigated. The process temperature and time were
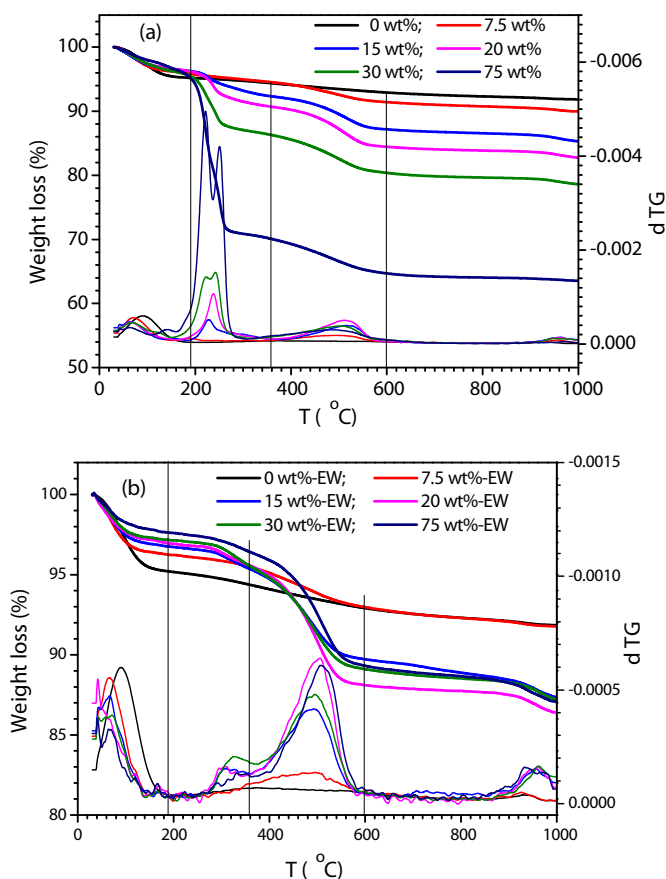

Fig. 3. FTIR spectra of (a) SDS, (b) SiO$_2$-T-200-30-EW and (c) pure SiO$_2$ particles.

Fig. 5. TG curves of SDS-modified samples SiO$_2$-T-200-30 (a) and SiO$_2$-T-200-30-EW (b) at different SDS/SiO$_2$ ratios.

Table 1
Weight loss of SDS-modified sample SiO$_2$-T-200-30-EW with different SDS/SiO$_2$ ratios.

SDS/SiO$_2$ ratio, wt%	0	7.5	15	20	30	75
Weight loss at 360–600 °C, %	1.45	2.50	5.63	7.45	6.42	7.10
Weight loss at 30–190 °C, %	4.79	3.75	3.25	3.04	2.83	2.37

set at 200 °C and 30 min, respectively. The weight losses of the thermally treated samples at different SDS/SiO$_2$ ratios before and after ethanol washing are shown in Fig. 5. Before ethanol washing, as shown in Fig. 5(a), as the SDS/SiO$_2$ ratio increased from 0 to 75 wt%, the weight loss at 190–600 °C increased from 2.29% to 30.5%, which indicated that a high SDS/SiO$_2$ ratio gave more SDS absorbed on the silica surface after the spray drying process, and resulting in the increased weight loss. However, most of the unreacted SDS were removed by ethanol washing as shown in Fig. 5(b), where the weight loss peaks at 190–360 °C had disappeared. Table 1 gives the weight loss of SDS modified SiO$_2$-T-EWs sample in the ranges of 360–600 °C and 30–190 °C at different SDS/SiO$_2$ ratios. As the SDS/SiO$_2$ ratio changed from 0 to 20 wt%, there was an obvious increase of weight loss at 360–600 °C from 1.45% to 7.45%, but as the ratio was further increased to 30 wt% and 75 wt%, there was a slight decrease of the weight loss. The maximum grafted amount was obtained when the SDS/SiO$_2$ ratio was 20 wt%. This was then kept constant in the following optimization. It was probable that at too high SDS/SiO$_2$ ratio, competition between the formation of SDS micelles in the solution and SDS adsorption on the surface of SiO$_2$ particles occurred, causing the decrease in the grafted amount. The weight loss at 30–190 °C showed an obvious decrease as the SDS/SiO$_2$ ratio increased. This was because adsorbed SDS occupied

Table 2
Weight loss of SDS-modified sample SiO$_2$-T-EWs using different process temperatures for 30 min with the SDS/SiO$_2$ ratio at 20 wt%.

Processing temperature, °C	Room temperature	150	170	200	220	250
Weight loss at 360–600 °C, %	1.96	1.96	2.02	4.54	4.87	4.48
Contact angle,°	17	15	67	107	107	*

* Cannot be tableted.

Table 3
Weight loss of SDS-modified sample SiO$_2$-T-EW at 200 °C for different process times with the SDS/SiO$_2$ ratio at 20 wt%.

Processing time, min	10	30	60	120
Wight loss at 360–600 °C, %	2.61	4.54	4.21	4.14

the hydroxyl sites and decreased the water molecules adsorbed on the SiO$_2$ particles.

3.3. Effects of process temperature and time

The effects of process temperature and time during the thermal treatment on the weight loss and contact angle of the modified particles were investigated. Table 2 shows the weight loss and contact angle of SDS-modified sample SiO$_2$-T-EWs at different process temperature for 30 min with the SDS/SiO$_2$ ratio at 20 wt%. The weight losses at 360–600 °C for the sample processed at 150 °C and 170 °C were nearly the same as the sample without a thermal treatment. Their contact angles were 15° and 67°, respectively, indicating the hydrophilicity of the surface. As the process temperature was increased to 200 °C and 220 °C, the weight loss of the samples increased to 4.54% and 4.87%, and their contact angles increased to 107°, indicating the hydrophobicity of the surface. After the processing at 220 °C, the sample color turned slightly yellow, which was assigned to SDS decomposition by referring to the TG curve. When the process temperature was further increased to 250 °C, the SDS decomposition became obvious and the weight loss of the sample decreased. Table 3 shows the weight loss of SDS-modified sample SiO$_2$-T-EWs at 200 °C for different processing time. The maximum weight loss was obtained at the processing time of 30 min, which gave the highest quantity of SDS that modified the silica surface. Therefore, the optimal process temperature and time in the thermal treatment were determined to be 200 °C and 30 min, respectively.

3.4. Effects of surface hydroxyl on the modification

As reported in the literature [32–34], the chemical modification of inorganic oxide particles occurs by the reaction between the hydroxyl group on the particle surface and the organic modifier. In order to compare the effect of different surfaces on the modification, TiO$_2$ nano-particles with an average diameter of 21 nm (nearly the same size as that of the silica particles) were modified with the same process. Silica coated TiO$_2$ particles, namely, SiO$_2$@TiO$_2$, were also modified for comparison. The surface morphology of the TiO$_2$ and SiO$_2$@TiO$_2$ particles, and the elemental composition on the surface of the SiO$_2$@TiO$_2$ particles are shown in Fig. 6. A continuous and dense silica film with a thickness of 2 nm was coated on the surface of the TiO$_2$ particles, indicating that the SiO$_2$@TiO$_2$ particles have the properties of a silica surface. The semi-quantitative EDS analysis indicated that the SiO$_2$@TiO$_2$ particles contained a Si component of 11 wt%. Fig. 7 shows the TG curves of the TiO$_2$, SiO$_2$@TiO$_2$ and SiO$_2$ particles. Their weight losses at 190–800 °C gave the hydroxyl group quantity on the surface as 0.77, 0.97, and 2.89%, respectively. After the coating of the silica, the hydroxyl amount on the surface
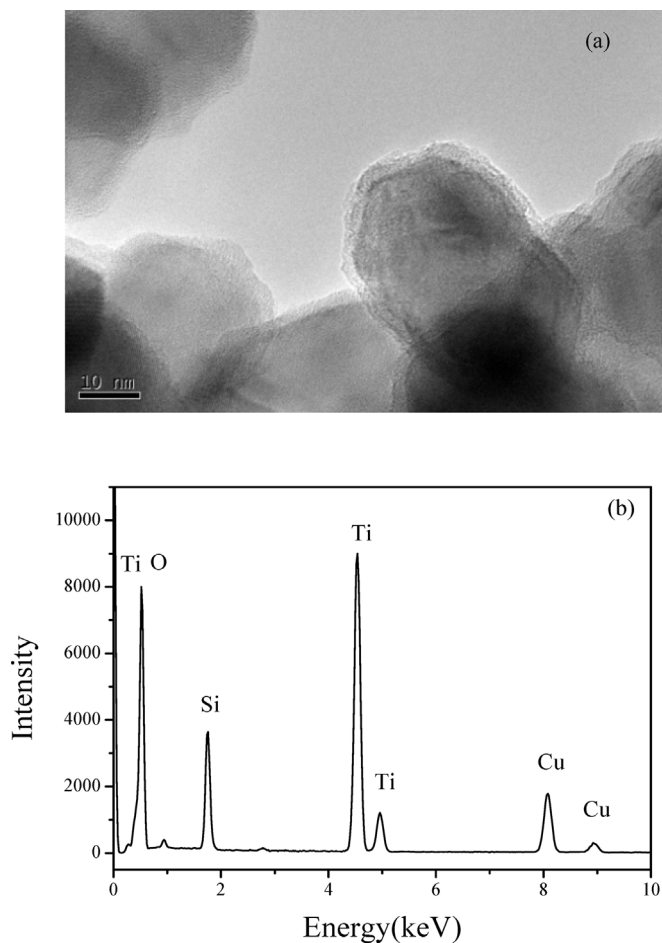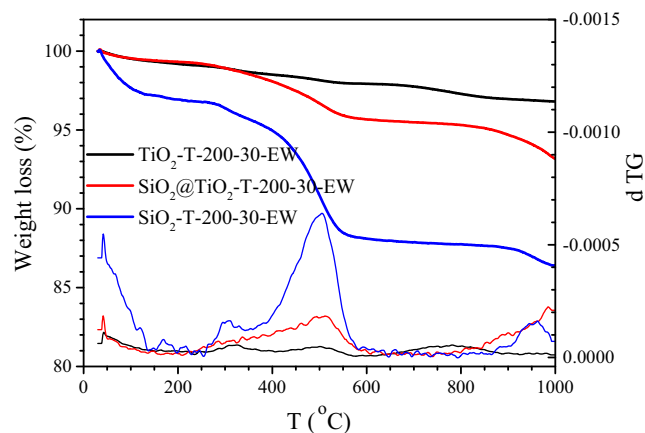
Fig. 8. TG curves of SDS-modified TiO₂, SiO₂@TiO₂ and TiO₂ particles after ethanol washing.

Table 4
Weight loss and contact angle of SDS-modified SiO₂, SiO₂@TiO₂ and TiO₂ particles at the process temperature of 200 °C for 30 min with the SDS/particle ratio at 20 wt%.

	SiO₂-T-200-30-EW	SiO₂@TiO₂-T-200-30-EW	TiO₂-T-200-30-EW
Weight loss at 360–600 °C, %	7.45	2.78	0.71
Contact angle, °	107	96	16

Fig. 6. Morphology and composition of TiO₂ and SiO₂@TiO₂ particles. (a) TEM image of SiO₂@TiO₂; (b) composition of SiO₂@TiO₂ from EDS

Fig. 7. TG curves of TiO₂, SiO₂@TiO₂ and SiO₂ particles.

of the SiO₂@TiO₂ particles was slightly increased to be a little more than that on the TiO₂ particles.

Using the same modification procedure as the SiO₂ particles, the TiO₂ and SiO₂@TiO₂ particles were modified at 200 °C for 30 min with a SDS/particle ratio at 20 wt%. The TG curves are shown in Fig. 8. The weight loss at 360–600 °C and contact angle are listed in Table 4. The data showed that the SDS modified SiO₂@TiO₂ particles had obvious hydrophobicity, while the SDS modified TiO₂ particles was still hydrophilic. The weight loss of SiO₂-T-200-30-EW and SiO₂@TiO₂-T-200-30-EW were 7.45% and 2.78%,

respectively. Their contact angles were 107° and 96°, respectively. However, the weight loss of TiO₂-T-200-30-EW was only 0.71% and the contact angle was only 16°, indicating that there was less reaction between SDS and the hydroxyl on the surface of the TiO₂ particles.

3.5. Reaction mechanism of SDS on the silica surface

The hydroxyl quantities on the surface of the TiO₂ and SiO₂@TiO₂ particles, which were 0.77% and 0.97%, were not obviously different, but their SDS modified samples were quite different, being hydrophilic and hydrophobic, respectively, as shown in Table 4. This observation was used to infer that the difference was due to the difference in the hydroxyl acidity on the SiO₂ and TiO₂ particle surfaces, which has a key role in the modification. Earlier researchers [33–35] have reported that the SiO₂ particle surface has both Brønsted and Lewis acid sites, while the TiO₂ particle surface only has Lewis acid sites. Only the Brønsted acid sites can provide protons for the reaction between the surface silanol groups and modifier.

As reported in the literature [36–38], SDS undergoes hydrolysis to yield dodecanol and sodium hydrogen sulfate when heated. It was inferred that in this reaction, the dodecanol produced in the thermal treatment process is attacked by the protons of the Brønsted acid sites on the surface of the SiO₂ particles to generate a carbocation. The carbocation then reacts with the negatively charged Si–O moiety to form a Si–O–C structure and give the hydrophobic modification. The formation of the Si–O–C structure was characterized by the Si 2p spectra in the XPS analysis as shown in Fig. 9. The binding energies of the Si 2p in SiO₂ particles was 103.8 eV, while for the sample SiO₂-T-200-30-EW, it was shifted to 103.5 eV, which was assigned to the formation of the Si–O–C structure [39–41]. The sodium hydrogen sulfate was further converted to Na₂SO₄ and H₂SO₄ during the ethanol washing. H₂SO₄ dissolves in ethanol while Na₂SO₄ is insoluble in ethanol and cannot be removed by ethanol washing. Fig. 10 shows the XRD spectra of the SiO₂-T-200-30-EW and SiO₂ particles. The spectrum of
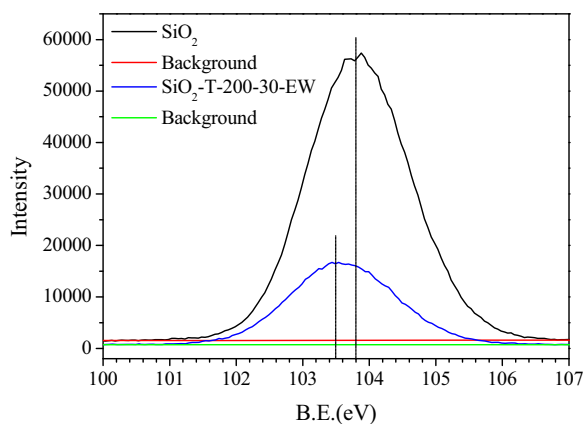
Fig. 9. Binding energies of Si 2p of the samples SiO_2 and SiO_2-T-200-30-EW.
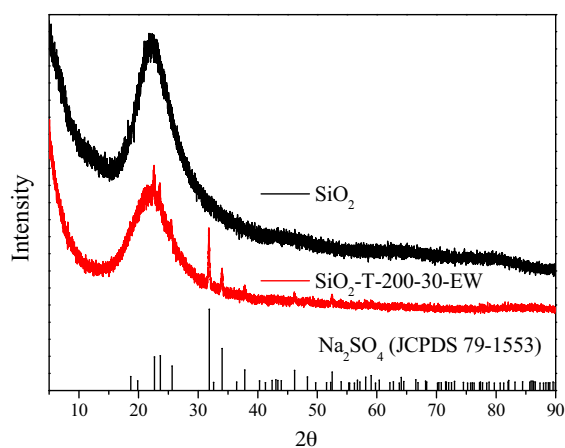

Fig. 10. XRD spectra of modified SiO_2-T-200-EW, SiO_2 particles and Na_2SO_4.

SiO_2-T-200-30-EW contains the XRD characteristic peaks of Na_2SO_4 that corresponded well with those of the standard spectrum. The weight loss at $900\,°C$ for sample SiO_2-T-200-30-EW in the TG curves in Fig. 8 also indicated the existence of Na_2SO_4 as its melting point is $884\,°C$. The presence of H_2SO_4 in the supernatant of the washing ethanol was detected by a 0.1% methyl orange solution. The color of the methyl orange solution changed from orange to red after the addition of the supernatant, while the color of the methyl orange solution with the addition of same volume of pure ethanol was still orange.

For further confirmation, the SDS-modified sample SiO_2-T-200-30-EW was washed by a mixed solution of water and ethanol (V/V = 3/2) to remove Na_2SO_4. This sample was marked as SiO_2-T-200-30-EW-W. After the thorough washing, sample SiO_2-T-200-30-EW-W was still hydrophobic. The carbon and sulfur content of SiO_2-T-200-30-EW and SiO_2-T-200-30-EW-W samples were determined by an elemental analyzer. The carbon content had changed from 6.06% to 5.54% after the washing. The slight decrease was caused by the hydrolysis of the grafted Si–O–C bond as this is easy to break [31,33]. As for the sulfur content, since Na_2SO_4 is soluble in water, a trace of sulfur with a content of 0.765% existing on sample SiO_2-T-200-30-EW was totally removed by the washing with a mixed solution of water and ethanol since the sulfur peak of SiO_2-T-200-EW-W was below the detection limit of the analyzer.

4. Conclusions

Hydrophobic modification of nano-silica particles was achieved using the common surfactant sodium dodecyl sulfate (SDS) as a modifier by a new route comprising three processes, namely, aqueous mixing, spray drying and thermal treatment. This route does not use an organic solvent and gives a perfect dispersion, which indicated an excellent contact between SDS and the SiO_2 nano particles for the modification reaction. The optimal SDS/SiO_2 ratio, and process temperature and time in the thermal treatment to give a high density of grafted SDS on the silica particle surface were determined to be 20 wt%, $200\,°C$ and 30 min, respectively. Under this condition, the hydrophobic nano-silica particles had a contact angle of 107°. The grafted density reached $1.82\,nm^{-2}$, which is near the highest value in the literature [19,31]. Brønsted acid sites on the surface of the SiO_2 particles supplied protons to react with SDS, which generated a carbocation that formed a Si–O–C structure. Thus the hydrophilic surface of silica can be modified into a hydrophobic surface by using the water soluble modifier SDS in a new modification route.

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