One-Pot Synthesis of Hydrophobic Silica Nanoparticles with Long-chain Alcohol 1-Octadecanol

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1- Introduction

Nano silica particles, due to their special physical and chemical properties and high surface area, have been widely studied and used: as a stabilizer in emulsion systems; as a concentration enhancer in the paint industry; as filler in the rubber industry, etc. Nevertheless, hydroxyl groups (OH) absorb moisture on the surface of the nanosilica, causing them to coalesce together and weakly disperse in the environment which greatly limits their application. For the vast majority of this problem, the surface of the nanoparticles should be modified toward hydrophobic nature using various surface modification agents. Surface modification by sol-gel process has been extensively used due to simpler operating conditions and low laboratory cost.

Here, we show that silica nanoparticles can be produced directly from on-pot synthesis with tunable hydrophobicity by adding long-chain alcohol 1-Octadecanol. Particle characterization data from transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), and contact angle measurements are presented.

2- Experimental

In the current work, fractional factorial experimental design was used at two levels with two repetitions of each experiment. The main variables are shown in Table 1.

Table 1 Main variables

Level	High (+)	Low (-)	Center point
Concentration of modifier [wt%]	7	2	5
Time of reaction [min]	180	90	120

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2-1- Silica nanoparticle synthesis

Silica nanoparticles were prepared by hydrolysis of TEOS in water/ethanol mixtures, similar to the approach of Stöber, but with the addition of 1-Octadecanol as a surface modifier. All reactions were carried out a few degrees below the boiling temperature of the mixture (about 70 °C), with a TEOS and NH_4OH concentration of 0.25M and 0.5M, respectively and a water/TEOS molar ratio of 38. A range of 1-Octadecanol concentration and time of reaction were explored (Table 1).

In a typical preparation procedure, a mixture of water and ethanol is first mixed for 5 min. A solution of water and NH_4OH (0.5M) is then added to the alcohol mixture under vigorous stirring. The reaction mixture is heated to about 70 °C under N_2 atmosphere followed by dropwise addition of TEOS. For surface modification, the pH of the mixture after 15 min is adjusted at 8 by adding hydrochloric acid 1M followed by dropwise addition of 1-Octadecanol. After 60 – 90 min, the resulting silica nanoparticles were precipitated by centrifugation at 10,000 rpm for 10 min. The supernatant was discarded and the nanoparticles were dispersed in water and EtOH with brief sonication. This washing procedure was repeated twice before dispersing the nanoparticles in EtOH.

3- Results and Discussion

TEM images of the modified and unmodified silica nanoparticles synthesized at various reaction times (Fig. 1) shows this fact that during the first 90 minutes, surface modification has been completed and continuing the reaction only resulted in increasing the size of the nanoparticles. Considering 90 min time of reaction, with increasing 1-Octadecanol concentration from 2 wt.% to 7 wt.%, in addition to improving the dispersion of the nanoparticles, the contact angle increased from 22° to 63°. These changes are highlighted in Fig. 1 and Fig. 2.

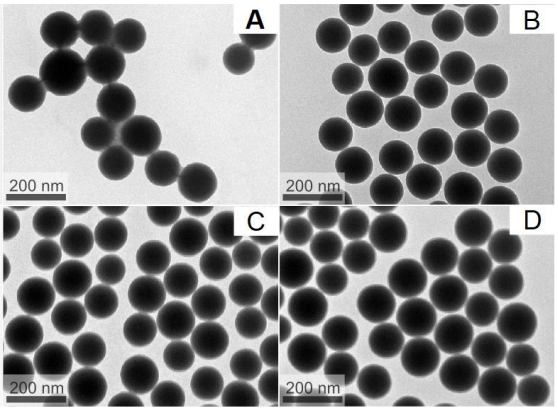

Fig. 1 TEM images of nanosilica, A) Unmodified; Modified for 90 min with, B) 2, C) 5 and D) 7 wt% of 1-Octadecanol

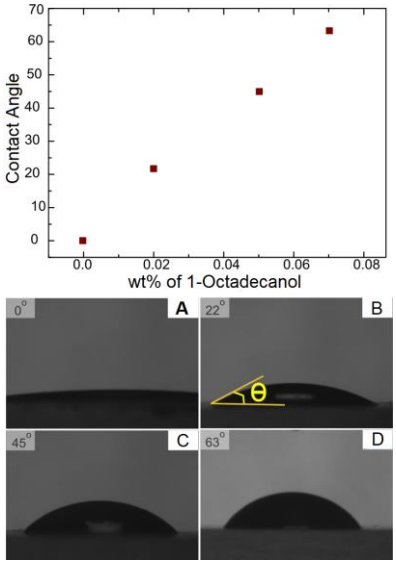

Fig. 2 (Top) Variation of contact angles; (Bottom) Images of nanosilica, A) Unmodified; Modified for 90 min with, B) 2, C) 5 and D) 7 wt% of 1-Octadecanol

Fig. 3 shows FT-IR spectra for nanosilica produced with and without the addition of 1-Octadecanol. The observed peaks and related functional groups are presented in Table 2.

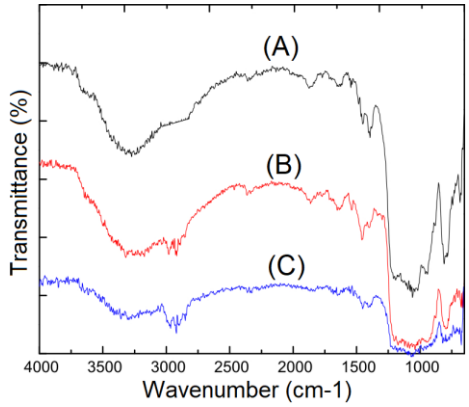

Fig. 3 FTIR spectra of nanosilica, A) Unmodified; Modified for 90 min with, B) 5 and C) 7 wt% of 1-Octadecanol

Table 2 Functional groups of FTIR spectra of silica nanoparticles

Wavenumber	Functional groups
700	Si-OEt
980	Si-OH
1150-1100	Si-O-Si
1700-1600	physical adsorbed water
2980-2915	C-H
3500-3150	Si-OH & physical ads. water

Table 2 indicates that the adsorbed water peaks and silanol groups have been reduced significantly by modifying the surface of the nanosilica, especially with 7 wt.% 1-Octadecanol. It also appears to have corrected peak levels of hydrocarbon bonds in the spectrum, which confirms the correction of the surface.

The results of TGA in Fig. 4 show two main weight loss events corresponding to the evaporation of absorbed moisture and trapped solvent below 200 °C and then silanol dehydration and pyrolysis of the organic surface modifier above 400 °C. The first part is related to the evaporation of moisture and solvent, which is lower for the hydrophobic modified silica; the second part is due to dehumidification of the silanol groups and decomposition of 1-Octadecanol indicating that higher 1-octadecanol concentration led to more adsorbed organic surface species.

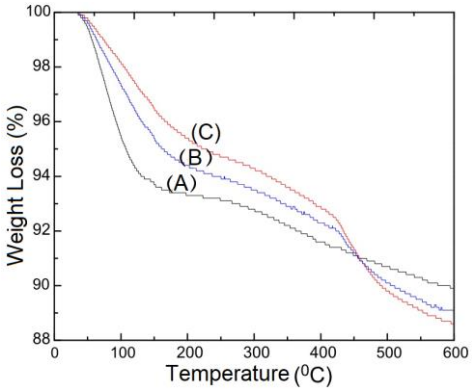

Fig. 4 TGA data for nanosilica, A) Unmodified; Modified with, B) 5 and C) 7 wt% of 1-Octadecanol

4- Conclusions

We have reported a straightforward single-step synthetic route to produce hydrophobic silica nanoparticles using 1-Octadecanol. TGA and contact angle measurements show that for 90 min time of reaction, the hydrophobicity of the nanoparticles is increased systematically with increasing 1-Octadecanol concentration used in the reaction.