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One-Step Microemulsion Method Synthesis for Monodisperse organic Functionalized silica micro/nano spheres

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Abstract. Monodisperse organic functionalized silica micro/nano spheres have been extensive research due to their special structural features. In this study, the Monodisperse organic functionalized silica micro/nano spheres were prepared by one-step hydrolysis condensation reaction of organosilane including TCPTES、MPTES、CTES、CPTES、UPTES in microemulsion system. It was showed that it was no particles from UPTES in the presence of SDS, and organic silica spheres prepared with CTES and CPTES had uniform particle size and monodispersity. However, organic silica spheres with poor disperse can be obtained from UPTES in the presence of CTAB, due to the physical adsorption between charges. In the contrast with SDS system, other organic silica spheres had poor disperse and nonuniform particle size.

1. Introduction

There has been growing interest in the past decade in fabricating organic-inorganic hybrid materials, because they combine the versatility of the organic chemistry with the advantage of inorganic species among these hybrid materials, a typical and important class of hybrid materials is organic functionalzied silica materia[1-3]. More importantly, These organic functionalzied silica materials can be used to prepare core-shell structures[4], yolk-shell structures[5] and hollow mesoporous structures[6-8], and widely applied in in various fields, such as catalyst, adsorption, chromatography and so on.

Traditionally, organic functionalzied silica was always prepared by post-grafting method and co-condensation method[9-13].However, in the former method, organic groups were directly grafted onto the surface of pure silica materials. It may lead to a nonhomogeneous distribution of the organic groups within the silica and a lower degree of occupation. Compared with the post-grafting method, co-condensation synthesis involves the simultaneous condensation of corresponding silica and organosilica precursors. This case may result in decrease of order degree with increasing concentration of $(R'O)_3SiR$ in the reaction mixture [14-15].

For this reason, it is urgent to find an efficient and facile preparation for the organic functionalized silica materials. Therefore, this paper reported a facile and effective preparation for monodisperse different organic functionalized silica by one-step microemulsion method using organosilane as single silicon source, respectively.

2. Experiments

2.1 Materials

3-Thiocyanatopropyltriethoxysilane（TCPTES，99.9%）,γ-Mercaptopropyltriethoxysilane（MPTES，99.9%), 2-cyannethyltriethnxysilane（CTES，99.9%), 3-Cyanopropyltriethoxysilane（CPTES，99.9%）and [3-[Tri(ethoxy)silyl]propyl]urea（UPTES ，99.9%）were obtained from Sinopharm Chemical Reagent Co. Ammonia solution（$NH_3 \cdot H_2O$，25%-28%), Sodium dodecyl sulfonate（SDS）, Sodium dodecylbenzene sulfonate（SDBS) and cetyl trimethyl ammonium bromide（CTAB）were purchased from Damao Chemical Reagent Company in Tanjing.

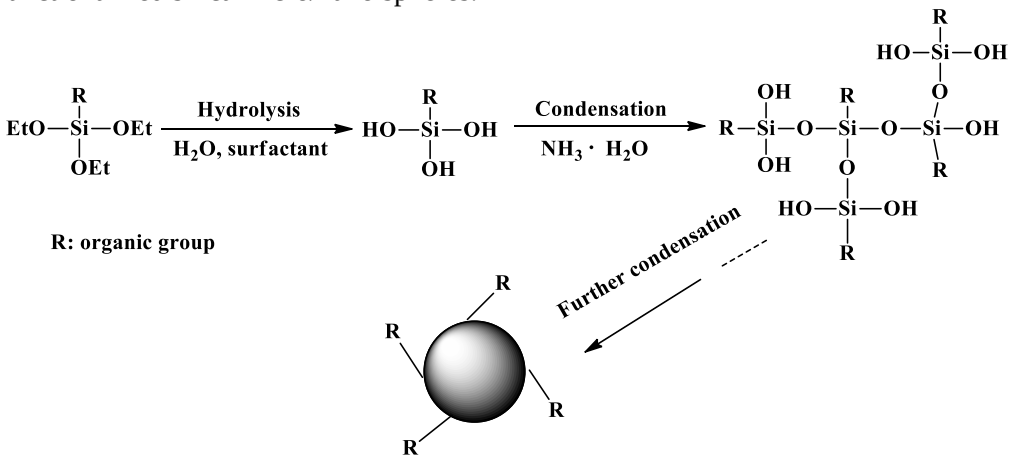
2.2 Organic functionalized silica micro/nano spheres

Monodisperse silica micro/nano spheres with various organic groups were prepared via one-step microemulsion method. The detailed synthetic procedure was as follows. An amount of SDS (or CTAB) was fully dissolved in 50 ml H_2O, and then 1ml of organosilane was added into the above aqueous solution to form homogeneous microemulsion system under stirring. After 30 min, 1 ml ammonia solution was dropwise added into the above microemulsion system to keep stirring for 6 hours. Finally, the mixture had cooled to room temperature, the mixture was centrifuged and washed three times with water and ethanol, separately.

3. Results and Discussion

3.1 Synthesis of organic functionalized silica micro/nano spheres

The synthesis of monodisperse silica micro/nano spheres with different functional groups is schematically illustrated in Scheme 1. In a typical process, organosilane was firstly hydrolysed in microemulsion system to form hydrolysates with hydroxy groups, these hydrolysates with hydroxy groups were further condensed under the alkaline conditions using ammonia as the catalyst by a one-step method, forming spherical structure with organic groups on the surface of silica spheres, denoted organic functionalized silica micro/nano spheres.



Scheme 1 Schematic illustration for the synthesis and structure evolution of monodisperse organic functionalized silica micro/nano spheres

3.2 Effect of different organosilanes on the formation of products

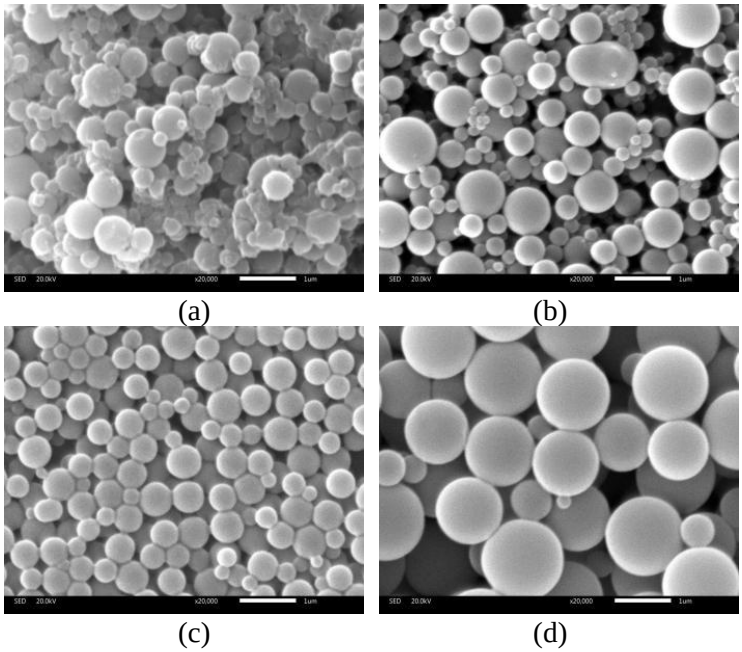
In this study, organic functionalized silica micro/nano spheres were obtained via one-step method in water emulsion, using organosilane as only precursor and ammonia as catalyst. Table1 showed the experimental results prepared by different organosilanes in the presence of SDS under the same

conditions. It could be found from the results that there was no particles by using UPTES as silane precursor in the same conditions.

Table 1. Experimental results of organic functionalized silica micro/nanospheres prepared with different organosilane under the same SDS concentration

Samples	products	H_2O (ml)	ammonia solution (ml)	SDS (g)	reaction time (h)	SEM [a]	
						size (nm)	RSD (%)
TCPTES	TC-SiO_2	30	1	0.01	6	508	0.059
MPTES	SH-SiO_2	30	1	0.01	6	488	0.067
CTES	CN-E-SiO_2	30	1	0.01	6	496	0.027
CPTES	CN-P-SiO_2	30	1	0.01	6	1350	0.003
UPTES	UD-SiO_2	30	1	0.01	6	no particles	no particles

[a] The average spheres size ($\bar{x}$ (nm)) and relative standard deviation (RSD(%)) of organic functionalized silica micro/nanospheres measured by SEM are defined as follows: $\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}, RSD = \frac{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 / (n-1)}}{\bar{x}} \times 100\%$, where x_i is the spheres size obtained by measuring n spheres (at least one hundred) for each samples using SEM.



(a) (b) (c) (d)

Figure 1. SEM images of (a) SCN-SiO_2, (b) SH-SiO_2, (c) CN-E-SiO_2 and (d) CN-P-SiO_2 prepared under SDS

Figure 1. showed the corresponding SEM images of organic functionalized silica micro/nano spheres obtained in the presence of SDS. In comparation with SCN-SiO_2 prepared with TCPTES and SH-SiO_2 prepared with MPTES in the same synthesized condition (Fig.1 (a) and (b)), CN-E-SiO_2 prepared with CTES and CN-P-SiO_2 prepared with CPTES revealed highly monodispersed spheres (Fig.1 (c) and (d)). In addition, CN-P-SiO_2 were larger and much more uniform than that of CN-E-SiO_2, the average spheres size were about 1350 nm due to its longer carbon chains (3C atoms) than that of CTES (2C atoms).

Table 2. Experimental results of organic functionalized silica micro/nanospheres prepared with different organosilane under the same CTAB concentration

Samples	products	H_2O (ml)	ammonia solution (ml)	CTAB (g)	reaction time (h)	SEM [a]	
						size (nm)	RSD (%)
TCPTES	TC-SiO_2	30	1	0.01	6	801	0.097
MPTES	SH-SiO_2	30	1	0.01	6	467	0.082
CTES	CN-E-SiO_2	30	1	0.01	6	833	0.076
CPTES	CN-P-SiO_2	30	1	0.01	6	1200	0.045
UPTES	UD-SiO_2	30	1	0.01	6	2167	agglomeration

Table 2 showed the experimental results prepared by different organosilanes in the presence of CTAB under the same conditions. In contrast, UD-SiO_2 can be obtained by using UPTES as silane precursor under 0.01 g of CTAB. However, UD-SiO_2 had poor dispersion and agglomeration. The corresponding SEM images showed in Figure 2 (e) and (f). At the same time, for TC-SiO_2 and SH-SiO_2 preparede by using TCPTES and MPTES as silane precursor, respectively, there were a little spheres in the samples, and had inhomogenous spheres and inferior disperse (see Figure 2(a) and (b)). CN-E-SiO_2 and CN-P-SiO_2 obtained under CTAB were relatively monodispersed and uniform.

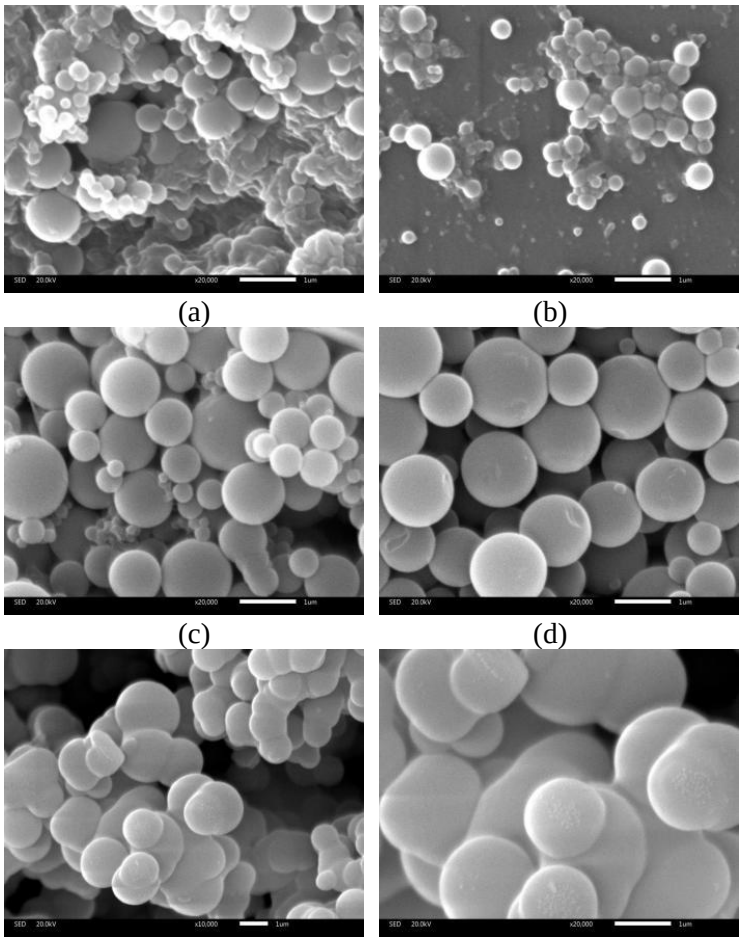


Figure 2. SEM images of (a) SCN-SiO_2, (b) SH-SiO_2, (c) CN-E-SiO_2, (d) CN-P-SiO_2, (e) and (f) UD-SiO_2 prepared under CTAB

4. Conclusion

In summary, monodisperse organic functionalized silica micro/nano spheres have been prepared by one-step microemulsion reaction of organosilane including TCPTES、MPTES、CTES、CPTES、UPTES. The research showed that no particles were obtained from UPTES in the presence of SDS, however, ureido silica spheres with poor disperse could be prepared from UPTES in the presence of CTAB. At the same time, organic silica spheres prepared from CTES and CPTES had uniform particle size and monodispersity, while other organic silica spheres had poor disperse and nonuniform particle size under the presence of SDS or CTAB system.

Acknowledgments

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