Synthesis and characterization of SiO_2 nanospheres

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In the last few years, there is an increasing interest in fabrication of nanosphere structures from inorganic materials such as SiO_2, TiO_2, ZrO_2, ZnS, GaP, CdSe, ZrC, Bi_2Se_3 and Ni/SiO_2, owing to their important applications in optical, catalytic and sensing devices (such as drug-delivery carriers) in addition to the general core-shell and nanotubular structures. In this work monodispersed SiO_2 nanospheres were synthesized using a modified Stöber method. The obtained SiO_2 nanospheres were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

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Keywords: FTIR, SEM, SiO_2

1. Introduction

In the last few years, controlled growth of nanostructures with desired morphology is of great significance due to their novel properties and potential applications [1]. Especially, there is an increasing interest in fabrication of nanosphere structures from inorganic materials such as SiO_2, TiO_2, ZrO_2, ZnS, GaP, CdSe, ZrC, Bi_2Se_3 and Ni/SiO_2, owing to their important applications in optical, catalytic and sensing devices (such as drug-delivery carriers) in addition to the general core-shell and nanotubular structures [1, 2]. It has found that nano-scaled materials with sphere structure show a lower density, higher surface area and distinct optical property [1].

SiO_2 nanospheres have been extensively investigated for various biomedical and biotechnological applications such as controlled drug release and delivery, analytical tools, and imaging [3]. This is mainly due to their unique optical properties, low density, high specific surface area, low toxicity and high and selective adsorption capacity [2, 3, 4, 5].

The most common method used to prepare SiO_2 nanospheres is the Stöber method, which comprises the hydrolysis and condensation of TEOS under alkaline conditions in ethanol [6, 7, 8]. Stöber silica particles are generally described as nonporous and monodisperse spheres with diameters in the colloidal range [9]. This method is remarkable in its simplicity and does not require surface modification or addition of surfactants to achieve excellent control of size, size distribution and smooth spherical morphology of silica particles [10].

The aim of this work is the synthesis and characterization of SiO_2 nanospheres using a modified Stöber method varying the proportion of TEOS in the initial mixture and the temperature [11].

2. Experimental

Monodispersed SiO_2 nanospheres were synthesized by hydrolysis and condensation of tetraethoxysilane (TEOS) (99%, Fluka) in a water–ethanol mixed solution containing dodecylamine (DDA) (98%, Aldrich) as a template and hydrolysis basic catalyst. The precipitate was received by filtration and then it was thermally treated from 80 ^{0}C up to 700 ^{0}C with a heating rate of 10 ^{0}C/min and it remained at 700 ^{0}C for 4 h (Table 1).

The obtained SiO_2 nanospheres were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

The SEM studies were carried out in a FEI Quanta 200 Scanning Electron Microscope (SEM).

FTIR spectra were recorded using a Perkin Elmer Spectrum 2000, on discs prepared by mixing of the sample powder and KBr.

XRD measurements were performed with a Siemens D5000 X-Ray Diffractometer by using sample of the material as powder.

Table 1. Raw materials and processing conditions of the modified Stöber method used for the preparation of SiO_2 nanospheres.

Materials (SiO_2 nano-spheres)	**Raw materials**			
CODE	**TEOS (ml)**	**Ethanol (ml)**	**H_2O (ml)**	**DDA (g)**
M1/from ref. [11]	10	160	100	1
M2	8	160	100	1
M3	2	160	100	1
Processing conditions				
Stirring of mixture during hydrolysis	**Drying of precipitate after washing and filtration**		**Calcination**	
15 ^{0}C/4h	80 ^{0}C/4h		600 ^{0}C/4h	
23 ^{0}C/4h	80 ^{0}C/4h		700 ^{0}C/4h	
23 ^{0}C/4h	80 ^{0}C/4h		700 ^{0}C/4h	

Material M1: raw materials and processing conditions according to bibliography [11].

Materials M2 and M3: raw materials and processing conditions of the modified Stöber method used for the preparation of SiO_2 nanospheres.

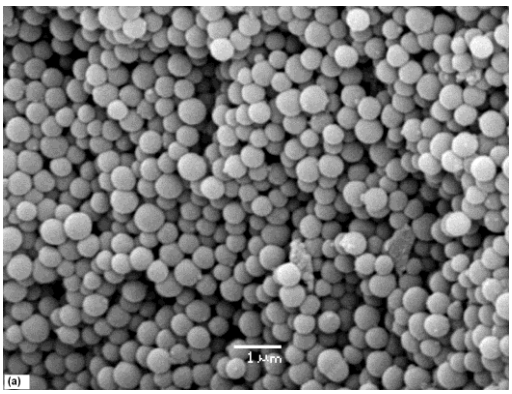
3. Results and discussion

SEM

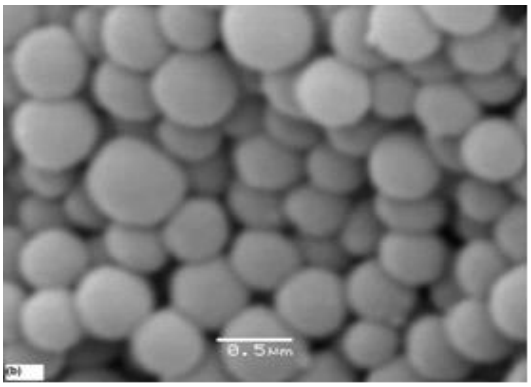
Fig. 1(a), (b), (c) shows SEM images revealing the general morphology of the SiO_2 nanospheres after thermal treatment up to 700 ^{0} C for 4h (M2).

According to Fig. 1 (a), (b) and (c) based on SEM images, the SiO_2 particles (M2) produced after thermal treatment up to 700 ^{0}C, show uniform size and spherical morphology.

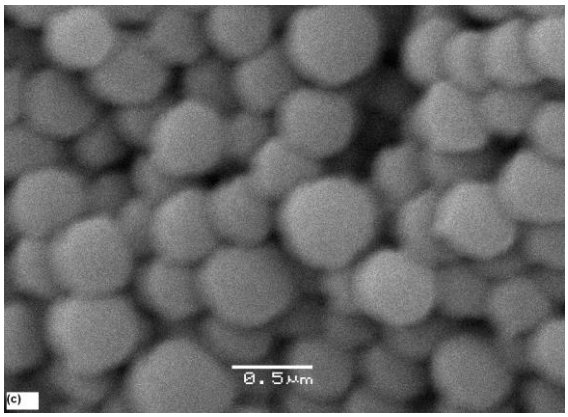
By decreasing the proportion of TEOS in the initial mixture from 10 to 8 ml and by increasing the temperature of hydrolysis from 15 to 23 ^{0}C the diameter of SiO_2 nanospheres were reduced from 700±50 nm [11], material M1, to 350 ± 50 nm, material M2.



a



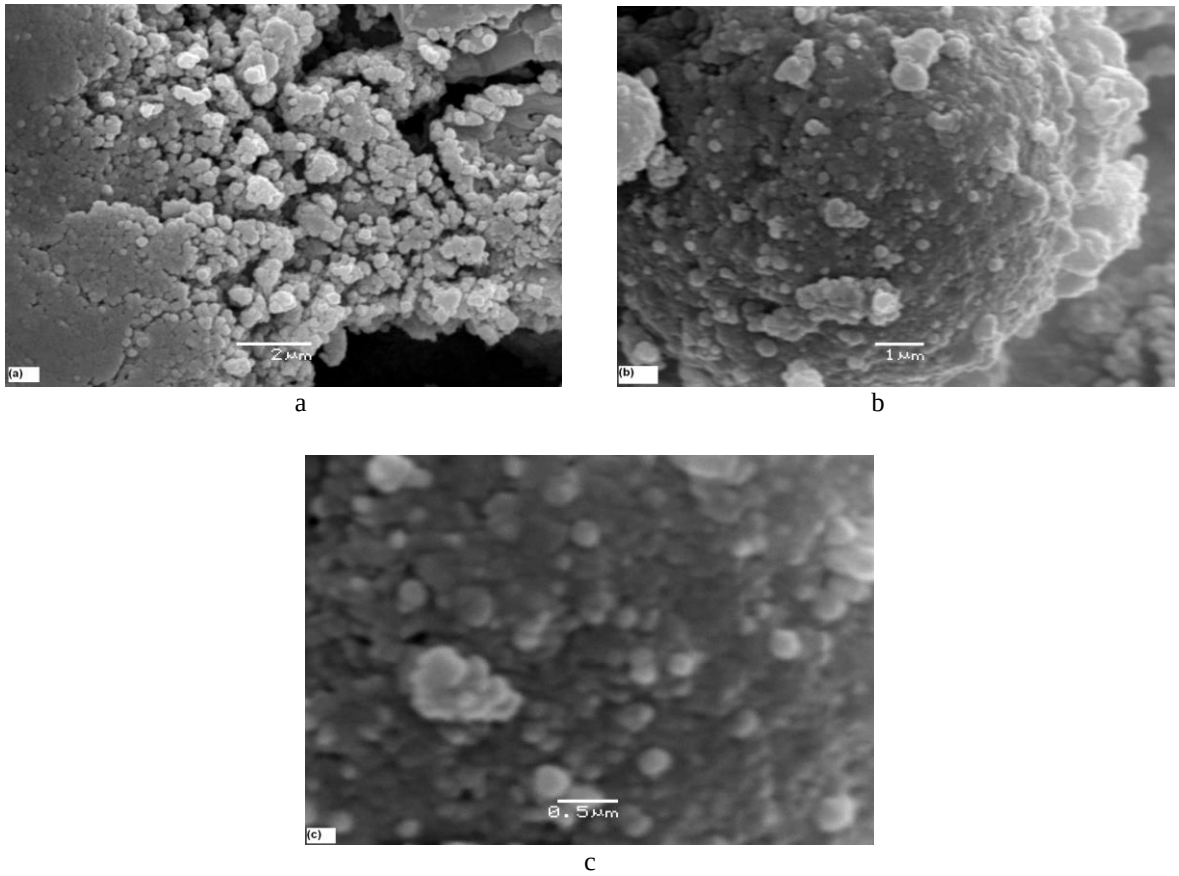
b



c

Fig. 1. (a), (b) and (c) SEM images of the SiO_2 produced particles (M2) at different magnifications.

Fig. 2 (a), (b), (c) shows SEM images revealing the general morphology of the SiO_2 nanospheres after thermal treatment up to 700 ^{0}C for 4 h (M3).



a b c

Fig. 2. (a), (b) and (c) SEM images of the SiO_2 produced particles (M3) at different magnifications.

According to Fig. 2 (a), (b) and (c) based on SEM images, the SiO_2 produced particles (M3) after thermal treatment up to 700 ^{0}C, show poor spherical morphology and large aggregation. By decreasing the proportion of TEOS in the initial mixture from 10 to 2 ml and by increasing the temperature of hydrolysis from 15 to 23 ^{0}C the diameter of SiO_2 nanospheres were reduced from 700 nm [11], material M1, to 150 ± 50 nm, material M3.

FTIR

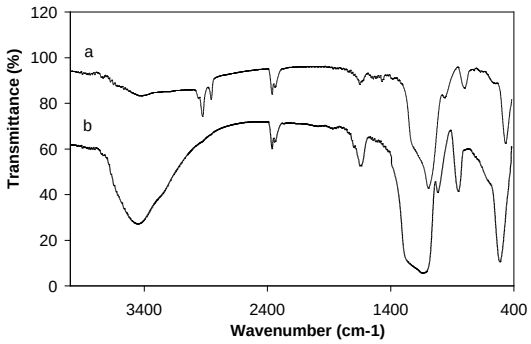


Fig. 3. FTIR spectra of material (M2) after different thermal treatments: (a) 80 ^{0}C/4h and (b) 700 ^{0}C/4h.

Table 2. Groups and wavenumbers of the FTIR spectra of the material (M2) produced.

Group	Wavenumber * (cm^{-1})	Wavenumber ** (cm^{-1})	
		Thermal treatment (80 ^{0}C/ 4h)	Thermal treatment (700 ^{0}C/4h)
Stretching of OH (water pore and surface water)	3000-3800	3443	3430
C-H stretching mode of hydrocarbon chain of dodecylamine	2925 2850	2918 2850	- -
Deformation vibration of –CH2, -CH3 of the incorporated dodecylamine	1543 1460	1540 1460	- -
Si-OH (surface silanol group)	960 1640	948 1633	944 1632
Assymetric stretching vibration band of Si-O-Si	1000-1300	1084	1088
Symmetric stretching vibration band of Si-O-Si	800 465	821 460	798 460

*: wavenumber (cm^{-1}) for the absorption peak according to the literature [12].
**: wavenumber (cm^{-1}) determined from the FTIR spectra of the material (M2) produced.

According to FTIR measurements dodecylamine was completely removed after thermal treatment up to 700 ^{0}C.

XRD

According to the Fig. 3, the XRD diffractogram of the SiO_2 particles thermally treated up to 700 ^{0}C for 4 h confirms the amorphous state of this material (M2)[13].

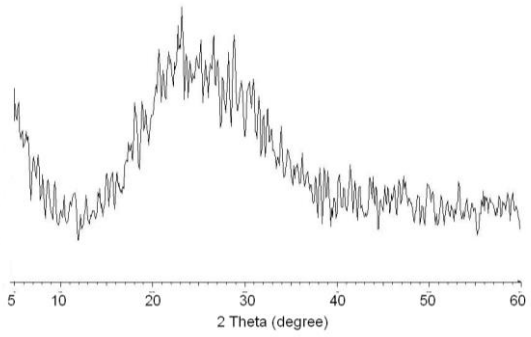


Fig. 3. XRD diffractogram of the SiO_2 produced particles (M2).

3. Conclusions

The final temperature of calcination was increased for the materials produced (M2, M3) compared to that of material M1 produced in ref. [11] in order to ensure that all the amount of the dodecylamine has been removed.

Comparison of the conditions used for materials M1 and M2:

By decreasing the amount of TEOS or its proportion in the raw materials mixture and by increasing the temperature of the hydrolysis, the SiO_2 nanospheres of final material after calcination were reduced from 700 ± 50 nm (M1) to 350 ± 50 nm (M2).

Comparison of the conditions used for materials M2 and M3:

By decreasing the amount of TEOS or its proportion in the raw materials mixture, the SiO_2 nanospheres of final material after calcinations were reduced from 350 ± 50 nm (M2) to 150 ± 50 nm (M3).

Consequently, the amount or the proportion of TEOS in the mixture has more important meaning compared to the hydrolysis temperature in order to reduce the diameter of nanospheres.

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