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Synthesis and characterization of silica nanospheres using nonsurfactant template

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Abstract

In the present work monodispersed silica spheres were successfully synthesized using nonsurfactant approach of neutral palm oil derived fatty alcohols based microemulsions. The resulting silica spheres have diameter in two size clusters; ca. 560 nm and ca. 700 nm, respectively. The synthesis was acomplished by using straight chain fatty alcohols in a combined approach of sol–gel and Stöber method without extensive washing. Translucent nonsurfactant microemulsions containing straight chain fatty alcohols namely octyl alcohol (C8), decyl alcohol (C10) and dodecyl alcohol (C12) were successfully obtained. Short chain alcohols such as ethanol and methanol were used as co-solvent in the formation of silica spheres. Tetraethylorthosilicate were used as silica source as well as co-structure directing agent. The resulting silica spheres were successfully functionalized with octyl-4-methoxy cinnamate (OMC) as UV-absorbing compounds in a direct nonsurfactant co-condensation during the synthesis process. The technique employed was found to be most viable in producing silica spheres for applications as meta-atom in the fabrication of metamaterials.

Keywords: Silica spheres; Chemical synthesis; Nonsurfactant template; Metamaterial

1. Introduction

Monodisperse porous nano silica (SiO_2) spheres as well as hard spheres are useful for a host of applications such as reaction surfaces of complex enzymes, protein deliveries, drug deliveries, nanosensors, hard template for nanocasting, hazardous gases adsorbents, chromatographic packing materials and electron relay materials for photocatalysis [1–14]. Various applications of these materials are possible due to their spherical morphology and nanoscale size. Recently, the most interesting application of silica spheres is in the field of optical negative-index metamaterials (NIMs) or lefthanded materials (LHM) [15]. Metamaterials are engineered materials that obtained their properties from the 2-dimensional or 3-dimensional arrangements of nanostructured particles rather than from fundamental physical properties of their constituents [15–17]. By changing the design of unit cell or "meta-atom" the optical properties of the metamaterials can be tailored to reach negative values of effective dielectric permittivity and magnetic permeability thus giving overall negative refractive index in a given frequency range [15–17]. It was suggested that nanosize and sub-nano silica spheres with homogeneous shape and size could be arranged into 2-dimensional or 3-dimensional arrays (i.e. opal-based photonic crystals) by self-assembly method to fabricate NIMs in the optical range [15–17]. Although much work have been done on the synthesis of monodisperse silica spheres by controlled hydrolysis of alkoxide precursors based on Stöber et al. [18] approach, there is still new research being conducted on several possible synthesis approaches due to the versatility of the material. In general, the morphology and monodispersity of the resulting silica spheres are important key-enabling factors to be controlled in order for the materials to be useful as building block in new applications of metamaterials.

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Bogush et al. [19] reported that by increasing up to a certain threshold concentration of ammonia and water during synthesis, the size of silica spheres increased accordingly. However, increasing the concentration of ammonia and water beyond this threshold concentration will cause the particles size to decrease. The widely used method of synthesizing monodisperse nanoparticles materials involved the use of carbon-templating agents such as ionic (cationic and anionic) surfactant of alkyltrimethylammonium bromide or neutral surfactants such as block co-polymers [20–23]. Zhang and Zhu [24] have successfully produced square Bi_2WO_6 nanoplates at ca. 50–100 nm sized by controlling the synthesis in 2 directions under hydrothermal treatment. On the other hand, Zhu et al. [25] have synthesized hollow mesoporous silica spheres using the combination of cationic surfactant and nanosized polymer to create the hollow structure in the nanospheres by hydrothermal method. By using carbon-templating synthesis methods, various morphologies of the nanostructured inorganic oxides were obtained which are feasible as meta-atom. Such morphologies include nanotubes, nanospheres and nanoplates resulted from manipulating the reaction condition, concentration ratios, as well as the starting raw materials compositions [21–25]. The use of surfactants at high concentration (liquid crystal and micellar solution) as structure directing agents in carbon-templating method to synthesize porous silica spheres materials were extensively studied and had become general procedure since their first discovery [21–26]. On the other hand, the effects of surfactants at low concentration on the particle growth, morphology and size of silica spheres were also studied [27,28]. However, surfactants are expensive and less environmental-friendly and the extensive use will result in abundance of undesired scheduled liquid waste. Therefore, by substituting surfactants with simple hydrocarbons derived from biomass, greener and low-cost synthesis method can be achieved.

Fatty alcohols molecules were reported to self-assemble at the air/water interface forming monolayers with rich phase behavior [29]. These desirable properties of fatty alcohols molecules render them as suitable candidate to substitute ionic surfactant molecules for the nonsurfactant sol–gel method in producing porous materials [30]. The formation of mesoporous structure using nonsurfactant small molecules as template was attributable to the removal of template aggregates or assembly of aggregates that are already occluded inside the gel matrix during sol–gel synthesis process by calcination at high temperature [30].

In this paper, we report on the attempt to substitute surfactants with straight chain fatty alcohols to produce oil-in-water microemulsions. These micromulsions were further used to synthesize monodispersed silica spheres in a nonsurfactant templating approach. The surfactants were substituted with palm oil derived fatty alcohols bearing several carbon chain lengths from C8 to C12 (octyl, decyl, and dodecyl alcohols) to generate carbon template *in situ* for the formation of silica spheres. In addition, the functionalizations of silica spheres using UV-absorbing compound were also carried out using this nonsurfactant method. The synthesis approach introduced in this study was a simple, facile and cost-effective method of producing silica spheres as building block (meta-atom) for the applications in metamaterials.

2. Experimental procedure

2.1. Materials

Fatty alcohols derived from palm oil with various numbers of carbon chain backbone namely octyl alcohol (C8), decyl alcohol (C10) and dodecyl alcohol (C12) were obtained from Cognis Malaysia. The purity of the fatty alcohols was determined at ca. 99.7% purity by gas chromatography (GC). The silica source used in this study was tetraethylorthosilicate ($Si(OC_2H_5)_4$,TEOS, 99.5% Merck). Short-chain alcohols (methanol, ethanol, 2-propanol and *n*-butanol) from Aldrich and Merck, ammonia solution (27%, Merck) and octyl-4-methoxycinnamate (OMC, Acros Organic, 98% stabilized) were used in their as-received condition. UV-absorbing functional compound of OMC was stored in lightproof container at 273 K to prevent photoisomerization.

2.2. Preparation of monodispersed silica spheres

The synthesis of silica spheres was done using the oil–water–alcohol (o/w/alc) microemulsions containing palm oil derived fatty alcohols as the oil phase and short-chain alcohols as the alcohol phase. Unlike in the production of mesoporous silica using nonsurfactant method [30], the synthesis of silica spheres progressed in a Stöber-like procedure [18]. In a typical synthesis method, several compositions of translucent solution of fatty alcohol based microemulsions were prepared by optimizing the amounts of fatty alcohol, water and co-solvent. Then, TEOS were added drop-wise into the solution. The pH was adjusted immediately to be in basic range after the addition of TEOS to enable the hydrolysis and condensation–polymerization to occur. The solution mixtures were stirred for 1 h to allow hydrolysis and condensation–polymerization to complete. In order to study the effect of stirring speed on the formation of silica spheres, samples were stirred at 500 rpm and 700 rpm, respectively. The mixtures were filtered, washed and dried to obtain as-synthesized materials of white solid. The as-synthesized materials were calcined at 873 K to obtain silica spheres. Calcined samples were designated as MST-X, where X denotes the synthesis condition, i.e. the fatty alcohol and co-solvent used as listed in Table 1.

2.3. Functionalization of silica spheres via nonsurfactant route

Functionalization processes by UV-absorbing compound of octyl-4-methoxycinnamate (OMC) were carried out

Table 1
Synthesis conditions and properties of representative silica spheres.

Sample	Fatty alcohols carbon chain	Co-solvent (alcohol)	TEOS addition rate (mL/min)	Water/co-solvent ratio[a] (v/v)	Sphere formation[a]	Average diameter of silica spheres (nm)[b]
MST-1	C8	*ethanol*	1.67	1:2	O	560
MST-2	C10	*ethanol*	1.67	1:2	O	560
MST-3	C12	*ethanol*	1.67	1:2	O	560
MST-4	C8	*2-propanol*	1.67	1:2	X	N/A
MST-5	C10	*2-propanol*	1.67	1:2	O	560/100**
MST-6	C12	*2-propanol*	1.67	1:3	Δ	**
MST-7	C8	*n-butanol/methanol* (2:1)	1.67	1:3	Δ	**
MST-8	C10	*n-butanol/methanol* (2:1)	1.67	1:3	Δ	200**
MST-9	C12	*n-butanol/methanol* (2:1)	1.67	1:4.5	X	N/A
MST-11	C8	*methanol*	1.67	1:2	O	700
MST-12	C10	*methanol*	1.67	1:2.5	O	700
MST-13	C12	*methanol*	1.67	1:3	O	700

O: spheres formed, Δ: almost spherical, X: spheres not formed.

[a] Volume to achieve transparent solution, i.e. microemulsion.

[b] Determined from SEM images.

**Agglomerations with same size particles or agglomerations of spherical particles with various sizes.

using nonsurfactant microemulsions as described in Section 2.2 *via* one-pot co-condensation method. Fig. 1 shows the chemical structure of the UV-absorbing compound of OMC.

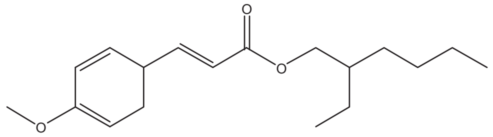

Fig. 1. Chemical structure of UV absorbing compound (octyl-4-methoxycinnamate).

The production of monodispersed silica spheres containing UV-absorbing functional materials within the silica shell were done by using fatty alcohols with C8, C10 and C12 carbon chains as the oil phase in which 10% by weight of UV absorbing compound of OMC was dispersed in. In a typical synthesis procedure, the oil phase containing UV absorbing compound were emulsified and dispersed into a solution having a polarity opposite to that of the solution containing TEOS followed by the addition of gelling catalysts to start the condensation–polymerization reaction so that the encapsulation of the UV absorbing materials with silica *via* sol–gel process could occur. Then, the emulsions were re-dispersed again into the solution having the opposite polarity from water phase. Throughout the encapsulation process, the pH of the solution mixture was adjusted to promote hydrolysis and condensation–polymerization of TEOS. The solution mixtures were stirred for several hours to obtain the as-synthesized silica spheres containing UV absorbing materials. The resulting solids were filtered, washed and dried at 313 K to obtain the final product denoted as MST-UV1 (using C8), MST-UV2 (using C10) and MST-UV3 (using C12).

2.4. *Characterization of silica spheres*

X-ray diffraction (Shimadzu 6000, Japan) patterns of calcined silica spheres were obtained under ambient conditions using Cu–Kα as the radiation source from 2θ 10° to 70°. The calcined silica spheres morphology were studied by bright field transmission electron microscope (TEM) using a Philip Tecnai at an acceleration voltage of 200 kV. Samples were prepared by dispersing in acetone by ultrasonification and placing on a carbon coated copper grid. Chemical structure of the materials were determined using solid state ^{29}Si NMR and ^{13}C NMR analyses measured using a Bruker AV400WB spectrometer equipped with a magic angle spinning probe. The 4 mm zirconia rotor was spun at 7 kHz and 1000 times scans. FT-IR measurements were done on as-synthesized samples using a Bruker IFS 66v/S in nitrogen environment using KBr pellet method. In order to investigate the fatty alcohols properties inside the as-synthesized samples, nitrogen gas environment was used to eliminate the environmental factors such as water vapor absorbed on the surface of the materials. The absorption spectra were taken from wavenumber $400\,\mathrm{cm}^{-1}$ to $4000\,\mathrm{cm}^{-1}$. The SEM images were taken using a LEO 1400VP at an acceleration voltage of 20 kV. Images were taken using a CCD camera. Specimens for imaging were prepared by dispersing sample powder in acetone and subjected to ultrasonification in a bath cleaner for several minutes. After that, sample solutions were placed drop-wise on the carbon tape mounted on the observation plate and dried in an oven for several minutes prior to sputter-coating with gold at ca. 50 nm. UV-absorbing properties for OMC as plain absorber and when anchored in silica spheres were investigated. In order to measure the UV absorption efficiency of the OMC functionalized silica spheres, freshly prepared samples were dispersed in distilled deionized water and were placed in 1 cm pathlength plastic cuvettes with Teflon® stopper. The distilled deionized water was used as the baseline reference. The spectra were measured using a Shimadzu UV-1659PC UV–vis spectrophotometer equipped with a double beam at 298 K. The wavelength was extended from 220 nm to 400 nm. For comparison purpose, UV absorbance spectra of pure silica sample and as-received liquid of UV absorbing compound were taken.

3. Results and discussion

3.1. Fatty alcohol based microemulsions

Translucent nonsurfactant microemulsions were successfully obtained without any surfactants by optimizing the amounts of fatty alcohols, TEOS, water and co-solvent palm oil derived fatty alcohols with various carbon chain length was the oil phase and water with short chain alcohol became the water phase [30]. This was due to the behavior of fatty alcohols molecules that were reported to form aggregates at the air–water interface similar to those obtained with surfactant molecules micelles [29]. Thus, it was possible to obtain nonsurfactant microemulsions as observed in the previous study [30].

White precipitates were observed shortly after the addition of silica precursor to the nonsurfactant microemulsions. It was suggested that immediately after the addition of silica precursor, the formation of silica spheres that occurred at room temperature as observed in this study could probably be due to the strong polar interactions of hydrogen bonding between the fatty alcohols molecules or their aggregates with the anionic silicate species.

The strong interactions were suggested to promote the formation of silica spheres obtained *via* sol–gel method in the absences of surfactant molecules [30]. The condensation–polymerization at basic condition in the sol–gel processing method occurs by the same nucleophilic mechanism. However, in basic condition all condensed silicate species are more likely to be ionized and mutually repulsive to each other. Thus, particle growth occurs primarily by the addition of silicate species to highly condensed particles rather than by aggregations of particles [31]. Therefore, it was suggested that the formation of silica spheres in the nonsurfactant microemulsions system went through the different mechanism as proposed in the two-step acid-base synthesis method reported before [30]. In basic condition, the solubility of silica and size-dependent solubility are greater [31]. As such, the particle grow rapidly to a size that depended mainly on the synthesis temperature as observed in this study.

Thus, fatty alcohol based microemulsions templating method was suggested to be an alternative of a facile and cost-effective method in producing silica spheres for possible use as meta-atom.

3.2. Structural characteristics of silica spheres

Optimizations of microemulsions constituents and silica precursors successfully resulted in the formation of silica spheres at various size clusters from diameter ca. 560 nm to 700 nm, respectively. In general, all samples prepared with microemulsions exhibited spherical morphology. It was suggested that these factors are highly dependent on the resulting silica spheres size and textures. Morphology and surface texture of calcined silica spheres prepared from octyl, decyl and dodecyl alcohol using ethanol as co-solvent are shown in Fig. 2. Calcined silica spheres prepared using fatty alcohols microemulsions exhibited spherical particles at ca. 560 nm for samples MST-1(C8), MST-2(C10) and MST-3(C12) with ethanol as the co-solvent. SEM images observed in Fig. 2 suggested that the monodispersed silica spheres were of uniform size with smooth surface texture. The corresponding mean size of the silica spheres is shown in Fig. 3. The XRD analysis indicated that the calcined silica spheres was of amorphous nature as typically shown in Fig. 4.

It was observed that regardless of fatty alcohols with various carbon chain length used in the starting microemulsions, the final size of the silica spheres was observed to be at ca. 560 nm. Thus, there was no significant effect on the final size of resulting silica spheres when varying fatty alcohols carbon chain in the starting microemulsions without changing the co-solvents. The results indicated that the size of oil phase (i.e. fatty alcohol aggregates) in the microemulsion remain constant regardless of the change in number of carbon atoms in fatty alcohol chain from octyl to dodecyl alcohol and thus it is not a governing factor controlling the size of the spheres.

The effect of co-solvent on the size and morphology of final particles were investigated by substitution with methanol, 2-propanol and *n*-butanol. Silica spheres prepared from fatty alcohol based microemulsion with more polar co-solvents such as ethanol and methanol exhibited fairly homogeneous spherical morphology and monodispersity in comparison to materials prepared using less polar co-solvents with different diameters at ca. 560 nm and ca. 700 nm when using ethanol and methanol, respectively. The SEM images of silica spheres prepared using methanol as the co-solvent while changing the fatty alcohol carbon chain lengths are shown in Fig. 5 for samples MST-11 (octyl), MST-12 (decyl) and MST-13 (dodecyl).

The morphology of calcined samples prepared with less polar co-solvent such as 2-propanol and *n*-butanol exhibited less spherical morphology and had a broad size distributions due to the agglomerations of finer particles. Nevertheless, the spherical morphology was still retained in less polar co-solvents. On the other hand, the monodispersity was totally destroyed with less polar co-solvent. Thus, severe agglomerations consisting of many small spherical particles were observed in between of the primary larger particles for calcined samples MST-7 and MST-8 prepared with *n*-butanol/methanol as co-solvent as shown in Fig. 6.

The results suggested that in order to obtain monodispersed silica spheres, severe restricted synthesis condition were required. Monodispersed spherical particle could only

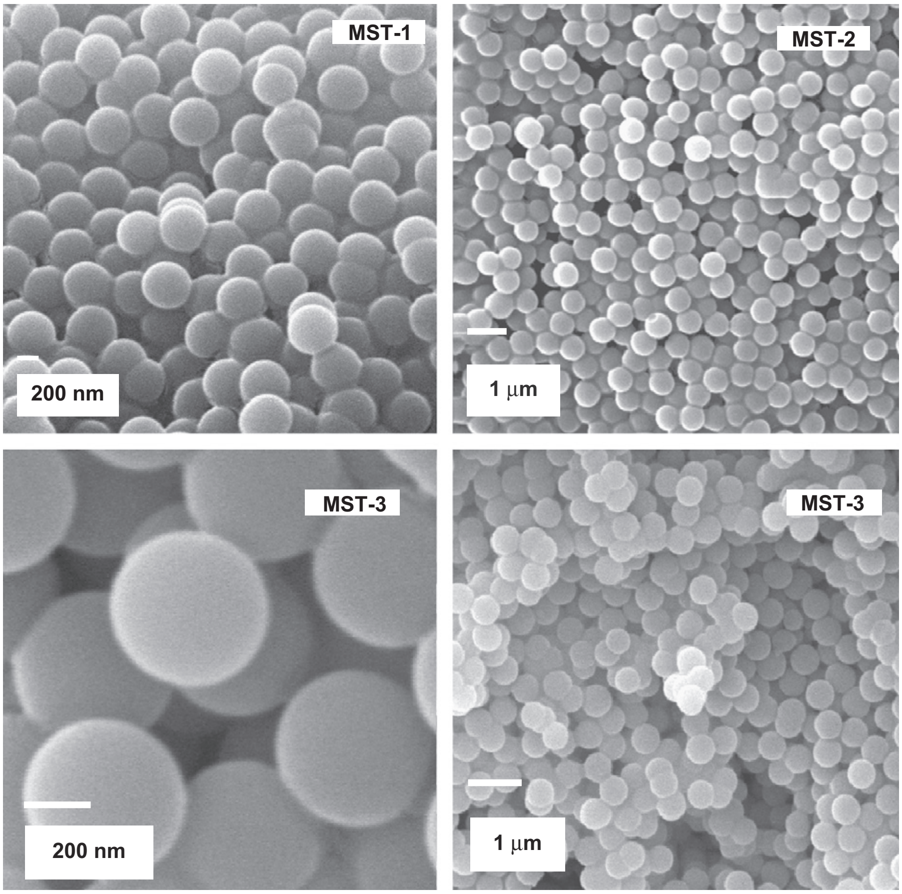

Fig. 2. SEM images of calcined silica spheres produced from the nonsurfactant method with ethanol as co-solvent, MST-1, MST-2 and MST-3.

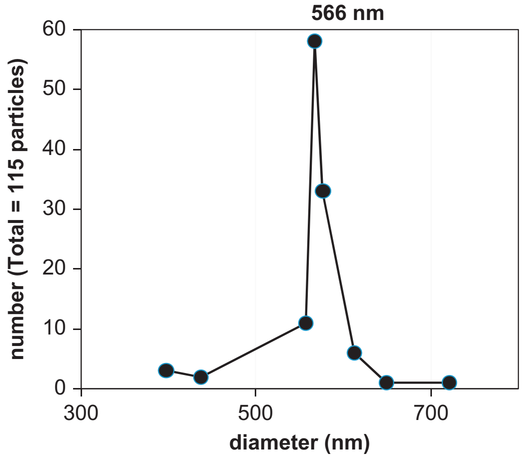

Fig. 3. Particle size distribution of silica spheres prepared with dodecyl alcohol (C12) MST-3 under vigorous stirring after counting 115 particles from SEM images.

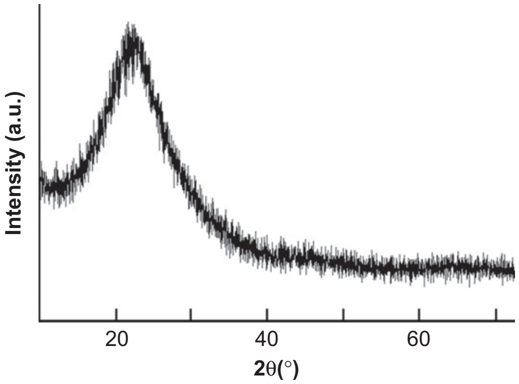

Fig. 4. Representative X-ray diffraction pattern of calcined silica spheres.

be obtained when more polar co-solvent such as methanol and ethanol were used as suggested by the SEM images in Figs. 2 and 5. This was probably due to the nature of fatty alcohol molecules to aggregates in air–water interface to form micelle-like aggregations. These resulted in the formation of a colloidal solution composed of nanosize spherical micelle-like fatty alcohols oil phase. Kosuge et al. [32] had observed the disappearance of smaller particles which drastically improved the spherical morphology and monodispersity of mesoporous silica hard spheres upon addition of ethanol. In addition, Schmid et al. [33] suggested that the polystyrene–silica nanocomposite spheres were larger when the synthesis were conducted in less polar solvent of 2-propanol than the size of particles obtained in more polar solvent of methanol. However, in this study, when using microemulsions made of fatty alcohol and less polar solvents (i.e. propanol and butanol)

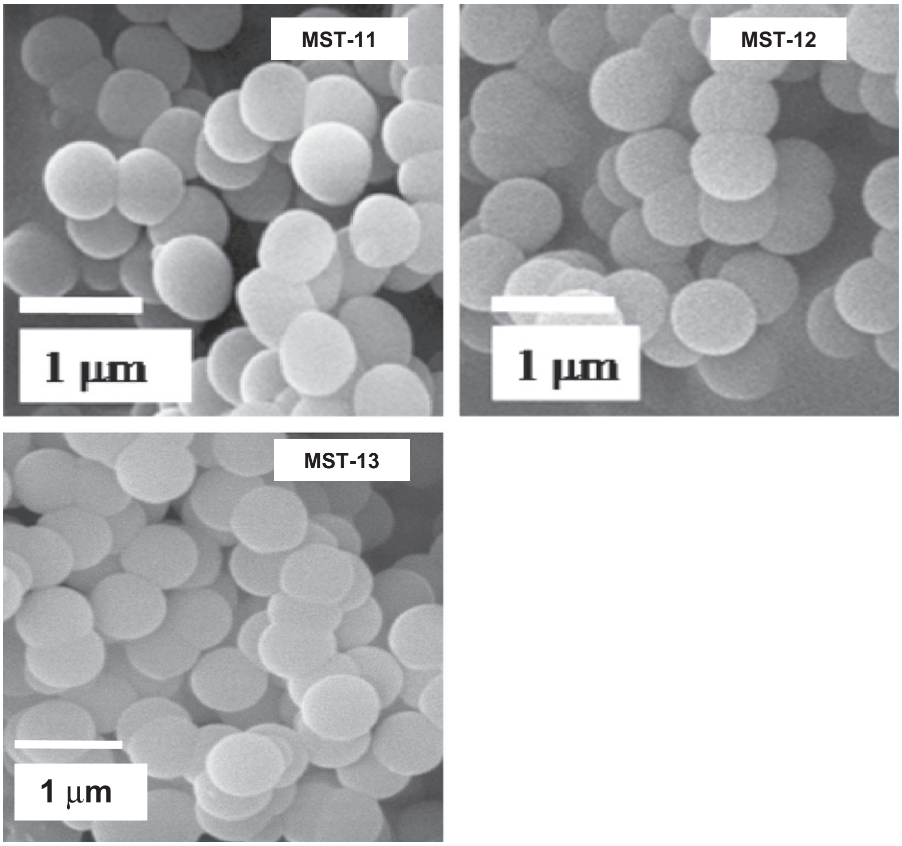

Fig.5. SEM images of calcined silica spheres produced from the nonsurfactant method with methanol as co-solvent.

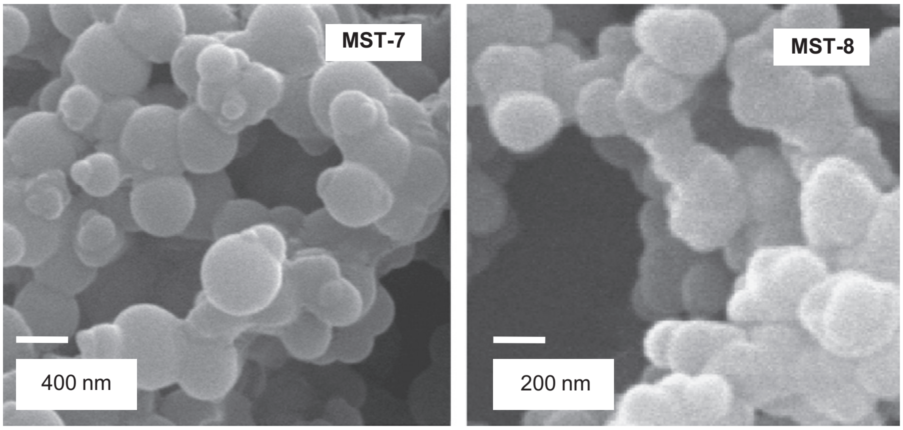

Fig. 6. SEM images of calcined silica spheres of sample MST-7 (octyl, *n*-butanol/methanol) and MST-8 (decyl, *n*-butanol/methanol).

the final silica spheres exhibited larger agglomerations made up of small spherical particles. In order to produce homogeneous particles, the agglomerations of particles in sols must be prevented. Steric and electrostatic barriers (i.e. electrosteric) stabilized the particles in sols and prevent them from agglomerations [34]. In general, surfactant molecules are used as the steric barriers in many sol–gel approaches but in the study the barriers were made of co-solvents.

Furthermore, in this study it was suggested that in the absence of surfactant as steric stabilizer, fatty alcohols micelle-like aggregations was stabilized by the presence of co-solvents of short-chain alcohols. The resulting agglomerations of silica spheres when using less polar solvents was suggested to be related to less higher rate of Ostwald ripening processes of fatty alcohol aggregations in colloidal solutions using less polar solvent [34]. Thus accounting for the non-uniform size of fatty alcohols micelles-like aggregations size in the colloidal solutions. Therefore, the hydrolysis and condensation of TEOS which occurred on the surface of oil nanodroplets with various sizes resulted in the formation of spherical particles with broader size distributions. These smaller particles sizes tend to form agglomeration upon further condensation of TEOS with other smaller particles resulting in larger particles and agglomerations of various sizes of particles.

Research conducted by Zhang et al. [35] showed that the difference in particle morphology was due to the differences in (1) hydrolysis rate of the anion (silicate anion) and (2) nucleation and growth rates in the ethanol-rich system. They also suggested that the larger the differences, more monodispersed particles will be obtained. Thus, in this study, the large differences in hydrolysis rate and nucleation and growth rates were observed in systems containing methanol and ethanol as co-solvents which resulted in monodispersed spherical particles. This was probably associated to the high polarity of the co-solvents of methanol and ethanol due to their short carbon chain.

The observations made by Zhang et al. correlated well with the present results. The evidence of hollow spherical spheres formation was somewhat difficult to be obtained by SEM images. However, in TEM images of calcined silica spheres of MST-2 as shown in Fig. 7 showed two distinct features of core-shell structure as indicated by the lighter core area in the center of the silica spheres and the surrounding darker (denser) area of the shell. It is believed that the lighter area comprised of a hollow structure and the surrounding darker area made up of a dense silica shell. Several attempts were made to rupture the thick shell of the spheres for closer imaging but were proved to be difficult to be carried out.

The FT-IR analyses of as-synthesized samples prepared from octyl, decyl and dodecyl alcohol with ethanol as co-solvent are shown in Fig. 8. A broad peak from wavenumber 3200 cm^{-1}–3745 cm^{-1} was attributed to the OH stretching vibration (υ_{stret}OH) of hydrogen-bonded network of adsorbed alcohol molecules on the silica surface (including those with bridged species) [36–38]. This peak is overlapping a broad peak observed from 3000 cm^{-1} to 3600 cm^{-1} which was assigned to the doubly hydrogen-bonded OH group [39,40]. A very small peak at 3745 cm^{-1} was attributed to the isolated silanols stretching vibrations (υ_{stret}OH) in vacuum [36–40]. These results suggested that the as-synthesized materials contained very small number of silanols. Hydrogen bonded silanols ($\text{Si–OH}\cdots\text{H}$) stretching vibration peaks were observed at 3550 cm^{-1} [37,38]. Furthermore, the absorption peaks attributed to the hydroxyl groups originating from absorbed alcohols on the silica surface were observed at 810 cm^{-1}, 1923 cm^{-1} and 3664 cm^{-1} [39].

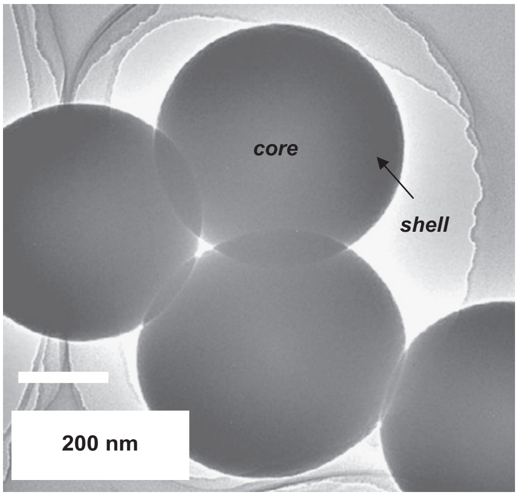

Fig. 7. TEM images of calcined MST-2 silica spheres.

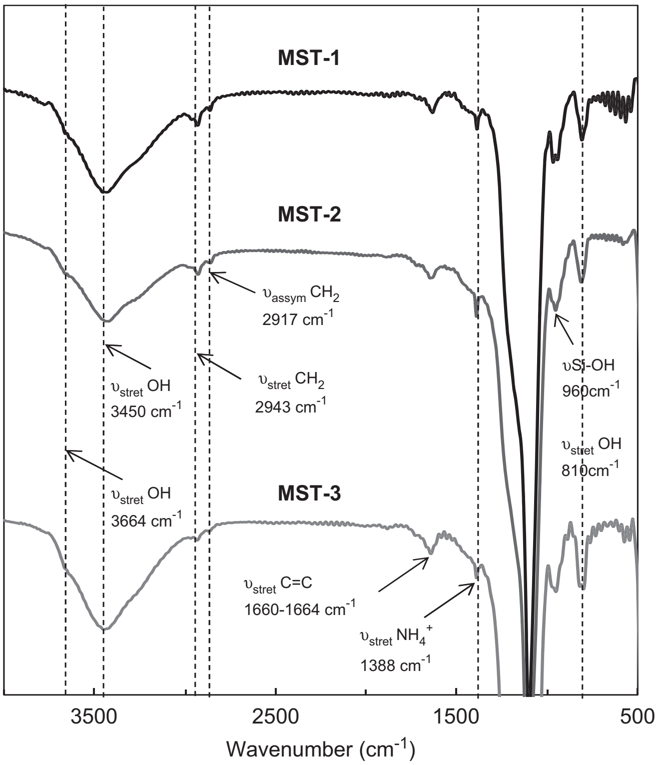

Fig. 8. FT-IR spectra of calcined silica spheres of MST-1, MST-2 and MST-3.

On the other hand, the stretching vibration peaks attributed to isolated silanols at 3740–3750 cm^{-1} were observed as shoulders. These results suggested that the fatty alcohols that act as the template core and the co-solvent of short-chain alcohols had interacted with the condensed siloxane bond during the synthesis. The appearance of two absorption peaks attributed to the stretching vibrations of CH_2 ($\upsilon_{stret}CH_2$) groups at 2943 cm^{-1} and asymmetric vibration of CH_2 ($\upsilon_{assym}CH_2$) at 2917 cm^{-1} were suggested to be originating from the backbone carbon chain of fatty alcohols as well as from co-solvents [39,41]. Other than these peaks, the stretching vibration of C–H (υ_{stret}C–H) at 999 cm^{-1}, the CH_2 wagging at 890 cm^{-1} and C–C stretching vibration (υ_{stret}C–C) in the presence of CH_2 rocking at 880 cm^{-1} were attributed to the carbon chain backbone in the fatty alcohols and co-solvents [39,41]. The stretching vibration of $C–H_x$, the aliphatic CH_2 and CH_3 groups with sp^3 hybridization observed between ca. 2800 cm^{-1} to 3000 cm^{-1} are also shown in Fig. 7. An asymmetric stretching absorption peak attributed to siloxane bridges (υ_{assym}Si–O–Si) was observed at 1007 cm^{-1} to 1009 cm^{-1} [42]. These results supported the suggestions that the fatty alcohols formed the template and were absorbed on the surface of the silica that surrounded them after hydrolysis and condensation to form siloxane bridges.

In addition, a peak was observed at ca. 1660–1664 cm^{-1}. This peak indicates the presence of C=C stretching vibration (υ_{stret}C=C) [39]. The existence of this peak together with the absorption peak observed at around 810 cm^{-1} suggested the presence of ethanol-like species that were absorbed on the silica surface. This finding was especially interesting and most probably due to the fact that some of the ethanol molecules originating from the co-solvents and from the TEOS condensation by-product were chemically adsorbed (chemisorbed) on some of the active sites on the silica surface during the drying process of the as-synthesized samples. The ethanol molecules underwent dissociation of one or two of the hydrogen atoms which enabled them to be chemisorbed on the silica surface [39]. A relatively sharp, isolated peak was observed near 1410 cm^{-1} attributable to the scissoring vibration of Si–CH$_2$ (υ_{sciss}Si–CH$_2$) [41]. This peak was observed due to the interaction between fatty alcohol carbon chain and silicon atom from the condensed silica. These results indicated that the silicate anion was directly condensed on the fatty alcohol template surface during the synthesis. On the other hand, stretching vibration peak associated with ammonium ion (υ_{stret}NH$_4^+$) peak originated from ammonia water residues used during the synthesis was observed at 1388 cm^{-1} [43]. The result suggested that thorough washing had successfully removed NH$_4^+$ ions that could become a hindrance when using the materials in any applications.

The representative of solid state ^{29}Si spectra of calcined samples MST-3 and MST-11 are shown in Fig. 9. Three resonance peak were observed at ca. −110 ppm, −100 ppm and −90 ppm attributable to the resonance from Si atom in three different environments denoted as Q^2, Q^3 and Q^4, respectively [7,44]. The peak signals at −100 ppm and −110 ppm were assigned to Si atom of isolated silanols [Q^3, SiO$_3$(OH)] and siloxane bridges [Q^4, SiO$_4$]. In addition, a small peak at ca. −90 ppm attributable to the silicon atoms in geminal and vicinal silanols [Q^2, SiO$_2$(OH)$_2$] was also observed. These results indicated that the surface of the silica spheres consists of Si atom in three different environments with the silanols groups existed less than siloxane bridges. The peaks of silanols either isolated or vicinal or geminal were lower and less distinct indicating that the surface was relatively hydrophobic compared to the conventional mesoporous silica such as MCM-41. In addition, solid state ^{13}C of silica spheres exhibited no peaks from any C atoms suggesting that the fatty alcohols were removed completely during calcinations.

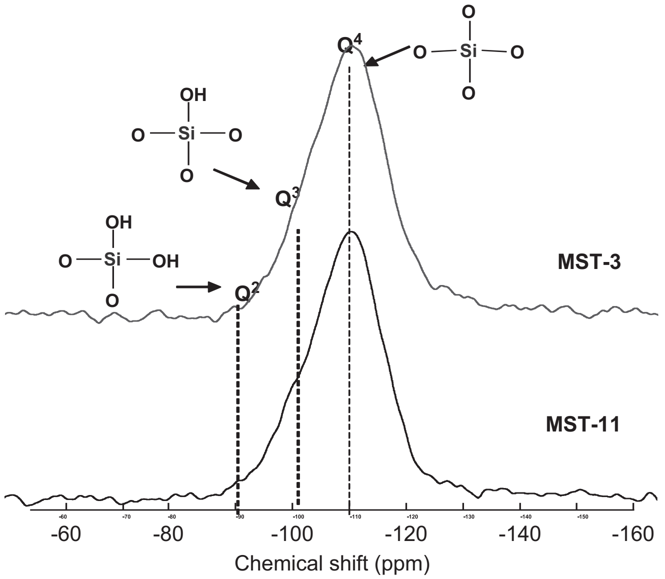

Fig. 9. Solid state ^{29}Si NMR spectra of calcined MST silica spheres.

3.3. UV absorbing properties

Fig. 10 shows the UV–vis spectra of pure silica microspheres containing OMC as plain UV absorber and when functionalized in silica spheres in water as solvent. Standard UV absorbance peak for OMC exhibited a broad peak over a range of wavelength from 280 nm to 350 nm with the highest absorption peak observed at 300 nm as reported by Huong et al. [45]. In this study, the UV–vis spectra exhibited high absorbance peaks at ca. 290 nm. In addition, the absorbance peak for plain OMC and functionalized OMC exhibited similar pattern. However, the UV absorbance peaks by plain OMC were observed as shoulders starting from ca. 300 nm to 350 nm. On the other hand, when the OMC was functionalized in silica spheres, the absorbance peak shifted to smaller wavelength where the absorbance peak ended at ca. 340 nm.

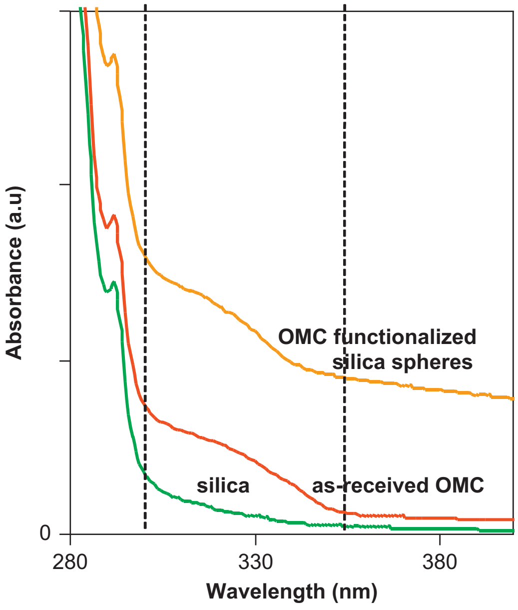

Fig. 10. UV–vis spectra of OMC functionalized silica spheres, pure silica spheres and as-received OMC.

This absorption peak was not observed in UV–vis spectrum of pure silica microspheres as shown in Fig. 9 because pure silica spheres have no UV absorption capabilities. These results showed that the silica spheres functionalized with OMC exhibited absorbing properties at UV wavelength. The absorbance for OMC functionalized silica spheres was higher than the absorbance of plain OMC. This was due to the partial degradation of plain OMC due to photoisomerization from E-OMC structure to Z-OMC isomer in the presence of UV irradiation [45]. In addition to the photoisomerization, plain OMC may have formed molecular dimers structures in the presence of UV irradiation which in turn affected the UV absorption capability.

4. Conclusions

A new facile, low-cost and environmental-friendly non-surfactant templating route to produce porous silica spheres at room temperature without undergoing any hydrothermal treatment was successfully introduced in this study. In addition, the starting microemulsions were also obtained using palm oil originated fatty alcohol without the aid of surfactants. The two step base-acid catalyzed hydrolysis and condensation–polymerization process of anionic silicate species at room temperature was achieved under controlled pH condition. Calcined materials exhibited relatively monodispersed spherical morphology with ca. 560 nm and ca. 700 nm when changing the co-solvent used during the synthesis. Furthermore, the functionalized materials exhibited good properties as low-cost support materials for UV absorbing materials thus it is also suitable candidate for hosting of other applications.

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