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Effects of the Cool Beginnings: Modulation of SiO_2 Nanoparticles

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As one of the most famous anticake agents, SiO2 nanoparticle synthesis was investigated via a modified method and results were reported. For this reason, tetraethoxysilane presursor was subjected to varying synthesis procedures such as concentration change and surface modification ligants. pH value and all the other reactant concentrations were kept the same and by implying sol-gel reaction mechanism, basic catalysis and temperature allowed us to obtain spherical and monodispersed nanoparticles. Additionally it was shown that surface composition which provides hydrophobic character could also be controlled by spontaneous reaction of the long alkyl chain containing alkyltrialkoxysilanes with tetraalkoxysilane. Statistical analysis of the nanoparticle sizes with atomic composition unveiled that SiO_2 nanoparticle size can be modulated sensitively. Octyl modified SiO_2 nanoparticles can be produced. Monodispersed, spherical and surface controlled nanoparticles seem promising candidates for the applications in sensors, controlled surface coatings and chemical delivery applications.

1. Introduction

SiO_2 studies were intensified in the recent years due to its wide applications in food technology, sensors and adsorption technology. SiO_2 can be utilized as nanofiller or it can be an actor in nanoparticle embedded nanocomposites for scratch or abrasion resistant coatings (Advani, 2006; Hannon, Kerry, Cruz-Romero, Morris, & Cummins, 2015; Pokropivny, 2007; Stelzner vd., 2008). Nanoapplications of SiO_2 nanoparticles can be widened and extensified due to the surface and size characteristics. Advantageous mechanical and thermal properties of nanocomposite materials with SiO_2 is reported such as antimicrobial activity, superhydrophobic applications together with anti-corrosion, self-cleaning, anti-icing, anticontamination and non-stick surfaces are prominent examples (Arslan, Aytac, & Uyar, 2017; Çamurlu, Akarsu, Arslan, & Mathur, 2016). In a sample study, we see that self-cleaning, water-resistant hybrid nanofiber mats are obtained with modified cellulose acetate nanofibers that separate oil-water structures from each other (Arslan, Aytac, & Uyar, 2016).

It is known that chemical and optical properties of SiO_2 nanoparticles depend on their size, surface features and monodispersity. Therefore effective methods of preparing particles of different sizes and surface character with controlled chemical composition requires deep attention (LaMer & Dinegar, 1950; Murray, Born, Weber, & Kraus, 2010). It is necessary to control the chemical structure with desired surface modification for special applications (Bracho, Dougnac, Palza, & Quijada, 2012; Grosso, 2011; Guglielmi, 1997; Qi, Liu, Chen, Dong, & Cao, 2015). For the comprehensive control on the morphology and desired chemical characteristics, surface modification was also applied in different studies but since SiO_2 nanoparticles have a strong tendency to agglomerate, surface modification process should be also sensitively observed (Vidal, Gómez, Goitandia, Angulo-Ibáñez, & Aranzabe, 2019). In solge nanoparticle synthesis, by hydrolysis and condensation reactions of the silane precursor, SiO_2 is bound to the resulting silanol due to the hydrolysis but this provides a hydrophilic character (Kessler, 2018; X. Zhang vd., 2014). It is known that these silanol groups are modified with carboxylic acids, other silane compounds, phosphonic acids etc. Mostly hydrophilic to hydrophobic transformation is utilized for the surface of the SiO_2 nanoparticles (H. Wang, Chen, Jia, Liang, & Wang, 2015).

Stoeber et.al. basically utilized hydrolysis-condensation reactions for the fabrication of the SiO_2 nanoparticles with a chemical route in alkali medium. This method was extremely sensitive to modulate the monodispersity, size and surface character since basic medium allows the formation of perfect spherical nanoparticles due to the thermodynamic reasons (Yong, Zhang, Cristobal, & Chin, 2014). This technique is considered to be a simple and effective way to fabricate uniform silica spheres since the reaction conditions can be controlled with delicate parameters (X.-D. Wang vd., 2010). Generally, silicon alkoxide (usually tetraethyl orthosilicate -TEOS)

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is hydrolyzed in the presence of an alcohol under the basic catalyst such as ammonia (Dixit, Bhakta, Kumar, Suib, & Rusling, 2016; Liu vd., 2011; J. H. Zhang, Zhan, Wang, Zhang, & Ming, 2003). Even though other precursors are also available, sol-gel process is mainly based on two reactions, hydrolysis and condensation of precursors of metal alkoxides or metal salts (Brinker & Scherer, 2014; Sajid & Płotka-Wasylka, 2020). Especially Si-O-Si bonds are formed necessarily by the hydrolysis and condensation of alkoxysilanes for fabricating SiO_2 nanostructures. As shown in Figure 1, the development of a three-dimensional cross-linked inorganic network structure with $Si(OR)_4$ precursor is easily detectable.

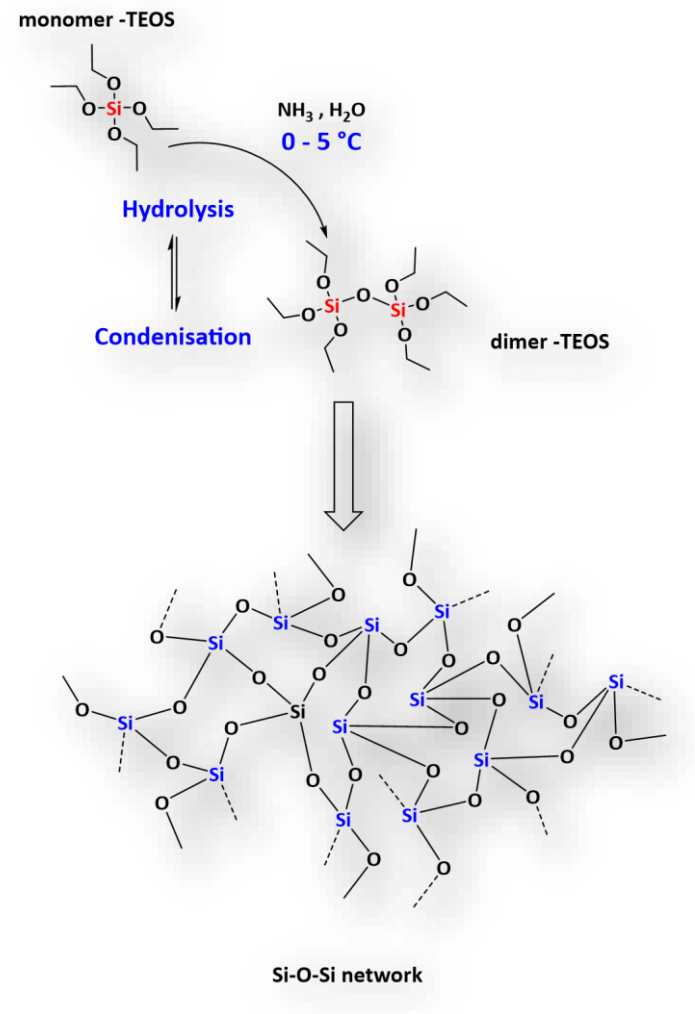

Figure 1: Formation of the 3D silicate network by sol-gel reactions

Since surface state of the SiO_2 nanoparticles is extremely important, modification procedures posed as vital for the SiO_2 for industrial applications (Bracho vd., 2012; Meier, Ungerer, Klinge, & Nirschl, 2018). It is known that fabrication of Si-O-Si bond depends on the catalysts and precursor nature when alkyl trialkoxysilanes are implied for the skeleton modification. Availability of different alkoxysilanes enables the development of a three-dimensional cross-linked inorganic network structure with different features (Figure 2).When observed, alkoxide chemistry governs the condensation reactions and when basic catalysis is applied thermodynamically stable and spherical nanoparticle shapes are formed (X.-D. Wang vd., 2010).

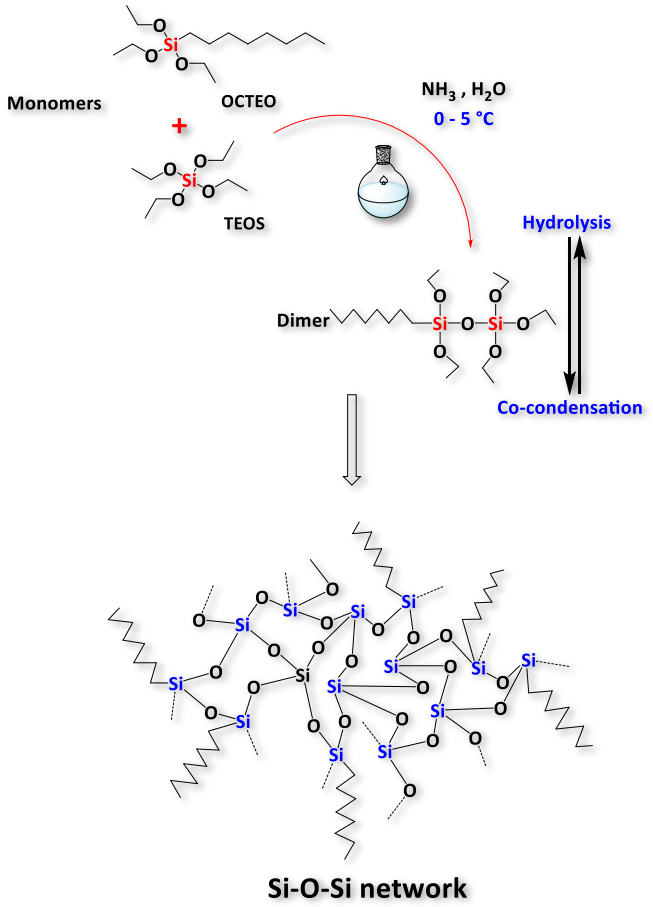

Figure 2: Formation of the alkyl modified 3D silicate network

In this study, varying reactant concentrations were applied to the modified Stoeber route with surface modification process. To observe the surface modification effects and behaviour of long alkyl chains, different synthesis parameters were applied and physical and chemical analysis were conducted. Investigations revealed that size, surface character together with monodispersity can be controlled with tailored Stoeber process. Additionally size of the SiO_2 nanoparticles can be controlled sensitively. Results revealed that surface modification of the nanoparticles can be realized with different properties since low temperature decelerates the rate of the particle size growth.

2. Material and Method

Chemicals For the synthesis, tetraethoxysilane (98%) (TEOS) was purchased from Acros Organics. Octyl triethoxysilane (OCTEO) was kindly provided by Degussa-Dynasilane. Distilled water was used for the hydrolysis-condensation reactions. Ethanol (technical), Isopropyl alcohol (99,95%), NH_3 (26%), HCl (37%) were purchased from Sigma-Aldrich. Obtained nanoparticles were washed with technical EtOH and acetone after the synthesis and dried under room conditions.

Methods and Characterization For the shape and monodispersity investigation Scanning Electron Microscopy (SEM), ZEISS GEMINI 500 device was used with EDX analysis. SEM Samples were placed on Cu tape and coated with 3-5 nm Au prior to the analysis. Shimadzu-IRTracer-100 with ATR module was employed to obtain the surface character of the obtained nanoparticles. Particle size analysis were investigated by counting the 50 particle and

plotting their frequencies versus particles sizes. Non linear analysis were applied to find the standart deviation.

Preparations of Silica nanoparticles Nanosized SiO_2 particles produced by modified Stoeber method. For the route, $IPA/H_2O/NH_3$ mixture was obtained between 0-5 °C (cold trap) for a certain period of time. For the octyl modified process same amounts were utilized with and without cold trap. In a flask, proportions of the $IPA/H_2O/NH_3$ were reacted with certain TEOS amounts. In surface modification process, octyl was also added together with TEOS. After the silane addition at 400 rpm reaction was continued for 15 minutes in cold trap. At the end of silane addition reaction were allowed to carry on at 400 rpm for another 6 hours at room temperature as applied to the octyl modified route. By completing the reaction, nanoparticles were centrifuged (HITACHI CR22N, Japan) (10000 rpm, 5 minutes) and washed with technical EtOH and acetone respectively and dried at room conditions.

3. Results and Discussion

According to Stoeber technique, SiO_2 nanoparticle synthesis can be conducted by sol-gel method using basic catalysis. In this study two different important parameter was investigated. First one is the concentration parameter and the other one is surface modification application by changing the temperature values of the early stages of the reaction. Since it is known that particle formation can be controlled at the beginning period of the nucleation by hydrolysis-condensation reactions.

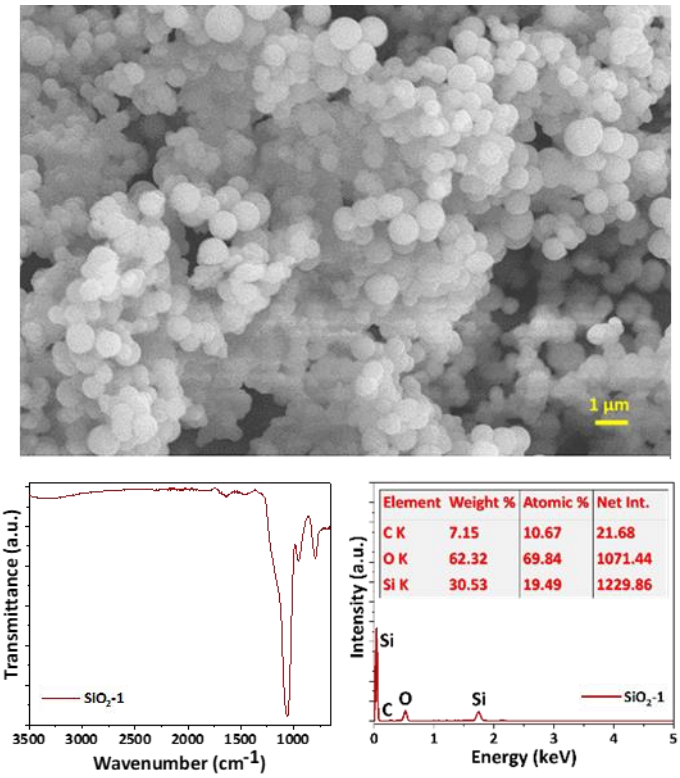

Figure 3. SEM, FT-IR and EDX investigation of SiO_2-1

For this aim, precursor solution was kept in ice bath at around 0-5 ˚C, and also in another synthesis, varying concentration values with surface modifier ligant was applied. When we applied mentioned ice bath, conditions allowed us to control the propagation of the sol-gel reactions and also modulate the particles sizes together with hydrophobic surface character.

For analyzing the effect of silane concentration, varied amounts of silane precursor was utilized. Concentration was increased in 3 applications and obtained nanoparticles were etiquetted as SiO_2-1, SiO_2-2 and SiO_2-3. Moreover, octyl modified nanoparticles were prepared with the same ice bath method (SiO_2-4) and room temperature conditions (SiO_2-5). Fabricated nanoparticles were investigated physically and compositionally together with nodified surface features.

In Figure 3, SEM image, FT-IR spectra and EDX measurement of SiO_2-1 nanoparticles were presented. SiO_2 nanoparticles show varying sizes but they represent highly spherical distribution. It was detected that sizes of the nanoparticles are slightly monodispersed but can be improved. Generally an average of the 500-600 nm range was obtained (Table 1). When SEM, FT-IR and EDX investigation of the SiO_2-2 is examined (Figure 4), small enhancement in the size is detected. Nanoparticle size for SiO2-2 is at 700-800 nm band.

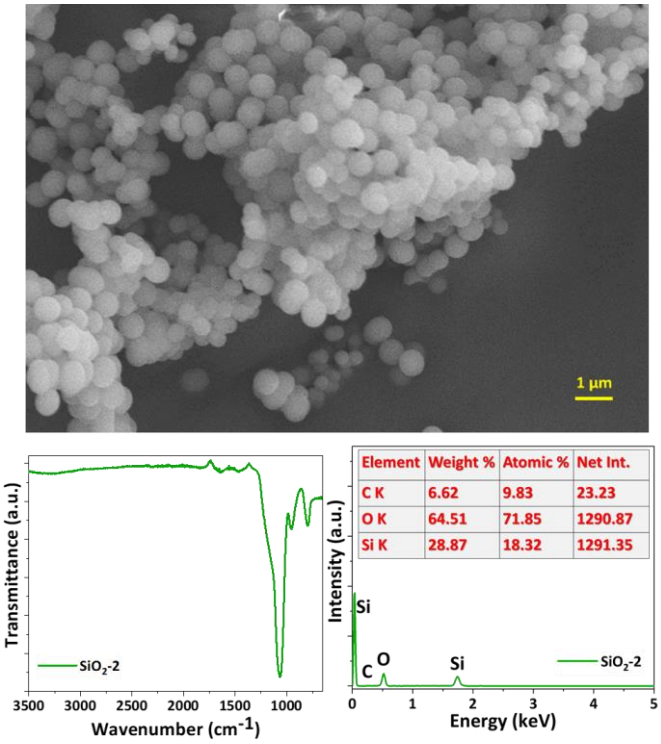

Figure 4. SEM, FT-IR and EDX investigation of SiO2-2

Similarly, SEM, FT-IR and EDX investigation of the SiO_2-3 can be observed in Figure 5. Interestingly two different size focus was detected. First is around 600 nm band and second is 900-1000 nm band. From this result we can conclude on two separate phenomena. Firstly with the increasing concentration of the silane precursor, under the ice bath conditions, every single addition of increased concentration provides size enhancement about 100 nm. Secondly we can conclude that this ice bath method which is a modified Stoeber technique, provides a straightforward route to obtain the monodispersed nanoparticles.

Therefore SEM investigations with size analysis showed that ice bath application at the early stages of sol-gel polymerization provides size control with monodispersed SiO_2 nanoparticles. Concentration increase in these reactions were resulted with detectable regular size enhancement as confirmed (Table 1). SEM images also reveal that there is no large agglomeration in the

obtained nanoparticles.

Table 1: Size values of the obtained nanoparticles

	SiO_2-1	SiO_2-2	SiO_2-3	SiO_2-4	SiO_2-5
Size(nm)	610	745	620-920	640	715

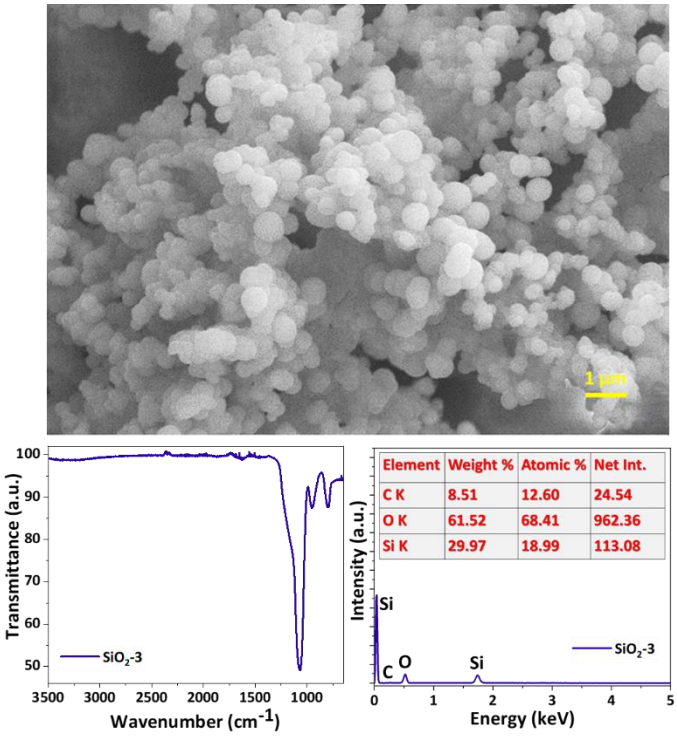

Figure 5. SEM, FT-IR and EDX investigation of SiO_2-3

Octyl modification of SiO_2 nanoparticles were conducted with two different method. Since programmable growth of the SiO_2 nanoparticles can be detected, surface modification behaviours should also be modulated. Therefore octyltriethoxysilane was reacted with tetraethoxysilane spontaneously at the early stages of the particle formation. In first method same ice bath was applied (SiO_2-4, Figure 6) but in the second attempt, reaction was conducted in room temperature conditions (22 ˚C) (SiO_2-5 Figure 7) without any prior setup.

According to the results, for example SEM images for modified structures reveal that, obtained SiO_2 nanoparticles are embedded in organic clusters separately (Figure 6). Deeper investigation reveals that nanoparticles are veiled with these gel like pool and solid particles are only visible since their atomic mass is higher when compared with organic species. Theoretically extreme surface modification may be the reason for the structural, geometrical and distributional variation of the nanoparticles. It is detected that in ice bath synthesis procedure, particle size analysis shows an average of around 640 nm. Interestingly without ice bath procedure, particle formation and growth shows faster evolution. Results revealed that 715 nm nanoparticles were obtained. Possibly due to the extreme organic pool, growth of the SiO_2 nanoparticles were decelerated.

SEM images emphasize that, gel like matrix composed of organic long alkyl groups where SiO_2 nanoparticles are embedded is formed. This is possibly due to the slow hydrolysis-condensation reactions of the TEOS and OCTEO precursors. When ice bath is applied, slow and and competitive basic environment allows the continous sol-gel condensation reactions but decreased solubility and decreased removal of alcoholic side products enhances the formation of organic pool. Therefore we can conclude that octyl groups are providing an organic environment and leads deceleration for SiO_2 nanoparticle growth (Figure 6, Table 1). Resulted particles size distribution is relatively broad and not perfectly monodispersed. For the surface modification silane precursors show slow hydrolysis/condensation reactions without acid/base catalysis. If two different silane is coherently hydrolized, due to the side groups hydrolysis and condensation reaction rates may differ and final spherical nanoparticle may have different features due to the thermodynamical reasons.

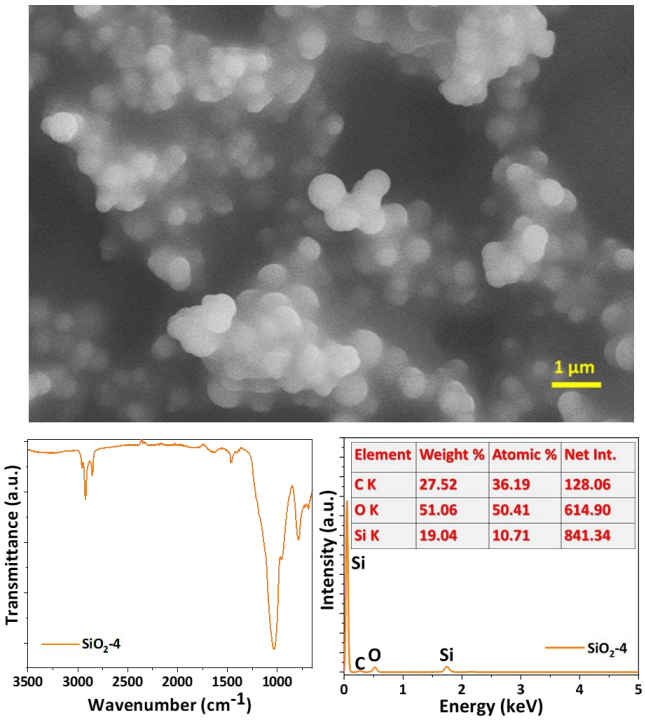

Figure 6. SEM, FT-IR and EDX investigation of SiO_2-4

FT-IR investigation of the SiO_2-1, SiO_2-2 ve SiO_2-3 clearly showed that there is no any carbon containing side group on the surface. Almost identical FT-IR spectrums are observed for all three nanoparticles. Si-O-Si stretching bands appear at around 1090 cm^{-1} together with Si-OH stretching at 939 cm^{-1} and Si-O bending at 800 cm^{-1}. Si-OH peak at 939 cm^{-1} for SiO_2-3 seems slightly higher in intensity when compared to other two corresponding similar peaks. Interestingly –OH stretching at around 3300 cm^{-1} is small and broad in all three nanoparticles. As shown, we obtained –OH side groups for unmodified SiO_2 nanoparticles but octyl condensation provides long alkyl chain modification. FT-IR investigation of the SiO_2-4 and SiO_2-5 (Figure 6 and Figure 7) proves the long alkyl chains on the SiO_2 nanoparticles. Basically surface features of SiO_2 nanoparticles show that, peaks at 2900-300

cm^{-1} region belongs to the hydrogens of the carbon bonded skeleton. Also peaks at 1035, 950 and 785 cm^{-1} represents (Si – O – Si), (Si – OH) and another (Si– O – Si) bending for the both nanoparticles. CH_2 and CH_3 linkages are easily seen at 1400 cm^{-1} region both in SiO_2-4 and SiO_2-5. All of these findings are consistent with the literature values.

EDX investigation of the nanoparticles showed different atomic composition characteristics due to the preparation methods (Figure 3-7). When we compared the atomic compositions of the SiO_2-1, SiO_2-2 ve SiO_2-3 it is clearly seen that Si atomic amount is 18-19 % for all three nanoparticles.

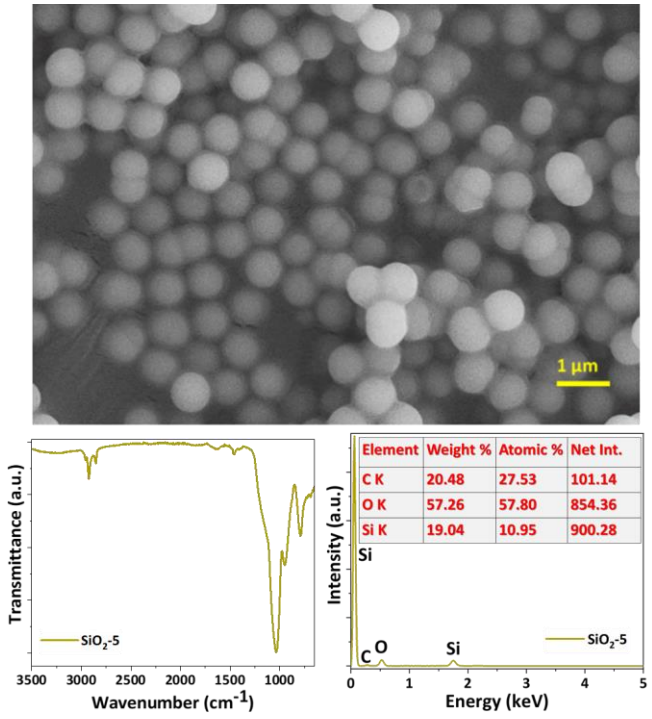

Figure 7. SEM, FT-IR and EDX investigation of SiO_2-5

Additionally O atomic amount seem 69-71 % range which is quite consistent when compared to each other. For SiO_2-3 carbon amount seems the highest which is an artifact of the measurement. Since lowest oxygen amount is in SiO_2-3 we can conclude that enhanced concentration increases the condensation rate and decreases the amount of oxygen in the composition. For octyl modified nanoparticles, it was observed that carbon amount is higher in SiO_2-4 which is a clear result of the organic pool. This also confirms the reduced condensation of the alkoxysilanes.

According to the investigations conducted in this study we can reveal that, concentration is main actor for the particle growth in our modified Stoeber method. By increasing the concentration we can increase the nanoparticle sizes sensitively. Additionally octyl modified nanoparticles can be prepared spontaneously for hydrophobic purposes as FT-IR and EDX results implied.

4. Conclusions

By analyzing the all reactions and morphologies with surface features we can conclude that, concentration enhancement in ice bath conditions is a very sensitive size distribution control method for SiO_2 nanoparticles. Additionally spontaneous reaction of TEOS with octyltrialkoxysilane in ice bath conditions reveal that surface modification can be achieved under these conditions but extreme organic environment decelerates the increase of nanoparticle size. Monodispersity is better without ice bath conditions as SEM investigation is revealed but surface attachment is always detectable which was confirmed by FT-IR and EDX analysis.

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