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Internal Functionalization and Surface Modification of Vinylsilsesquioxane Nanoparticles

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Abstract

The interior of 237 nm spherical vinylsilsesquioxane nanoparticles has been covalently modified and their surface functionalized under mild conditions to yield a novel type of hybrid silsesquioxane nanoparticles. Data obtained from thermogravimetric and elemental analysis show that the vinyl groups inside the nanoparticles can be easily brominated or hydroborated, leading to the nanoparticles containing 59.9 wt% of bromine or 3.6 wt% of boron, respectively. Our results demonstrate that the vinyl groups inside the nanoparticles are highly accessible, which may lead to the preparation of a host of hybrid organosilica nanoparticles with complex structures. We also show that the surface of the brominated and boronated nanoparticles is unhindered for further amination.

Introduction

Inorganic nanoparticles are of great interest in many fields of science and technology.¹ They have already had an impact in areas ranging from surface coatings² to medicine where they can be used for drug delivery or act as protein detectors.³ The most common methods for the preparation of inorganic nanoparticles involve either the reduction of a metal salt to produce metal nanoparticles or polycondensation to afford inorganic oxide nanoparticles.¹ Specifically, well-defined spherical silica nanoparticles can be prepared by the hydrolysis of tetraethoxysilane (TEOS) in the presence of ethanol, water, and ammonia hydroxide.⁴

Silica nanoparticles have attracted much interest due to their low toxicity, ease of formation in a wide range of sizes and morphologies, high stability, and the surface that can be further functionalized.⁵ The structure of the silica nanoparticles is directly related to their applications. For example, monodisperse non-porous silica nanospheres can be used to prepare colloidal crystals with numerous applications.⁶ On the other hand, if a template is utilized to form mesoporous silica nanoparticles with well-defined pores they can be used in drug delivery by encapsulating a drug and capping the pores with a removable plug.⁷

There are several ways to modify silica nanoparticles to obtain a desired property. The most popular method is by a surface functionalization. The surface of a silica particle carries silanol groups that can readily react with a functionalized siloxane or chlorosilane.⁸ Thus, the silica surface can be modified with initiator moieties to grow polymers on the surface,^{10–12} or functionalized with small molecules, such as a fluorescent dye.^{13,14} However, the polymerization greatly alters the size and properties of the nanoparticles while the small molecule approach does not permit attachment of large amounts of material if one is interested in high particle loading with additional elements or functional groups.

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More rarely silica nanoparticles have been internally modified. This can be done during the particle formation where a functionalized trialkoxysilane is co-condensed with TEOS to form silica particles that are enriched with this functionality. For example, silica nanoparticles containing cancer-fighting drugs have been prepared by incorporating iodobenzyl-pyrosilane into the vinylsilsesquioxane nanoparticles using this method.¹⁵ Alternatively, a monolayer of organic molecules, such as fluorescent dyes^{15,16} or biological markers^{3,17} has been introduced onto the surface of silica nanoparticles, followed by growing another layer of pure silica.

Finally, organic moieties can be incorporated throughout the entire silica nanoparticle using the corresponding trialkoxysilane precursor instead of TEOS to provide organosilica nanoparticles. Due to their diverse structure, such nanoparticles may find a variety of applications, including fluorescent markers, chemical sensors, chemical sponges,¹⁸ and new polymer fillers.^{19,20} Organosilica particles have been used in chemical separations where the hybrid particles acted as a unique stationary phase for chromatography.²¹ However, pure organosilica particles have proven difficult to form and have had a limited number of functionalities incorporated, such as phenyl, methyl, ethyl, and vinyl groups.^{22–23}

We became interested in the preparation of hybrid silica nanoparticles as a method of incorporating a large load of an additional element inside the particle with an eye on biomedical applications. For example, if a boron-10 isotope is incorporated in or near a cancerous cell and is irradiated with thermal neutrons, a neutron capture event may occur followed by a fission reaction.²⁴ The fission releases high linear energy transfer particles in a confined space to destroy the cancerous cell while leaving surrounding cells unharmed. However, to be efficiently used to fight cancer, this method called Boron Neutron Capture Therapy (BNCT) requires a high number of boron atoms, approximately 10^9 atoms per cell.²⁴ Boron-rich nanoparticles could be useful in this respect as each particle would carry a large number of boron atoms, with a small number of particles being sufficient to reach the critical boron concentration.

The two primary methods used so far to form boron-rich nanoparticles involve a ball-milling method in which boron nitride is finely ground into nano-sized pieces,²⁵ and the reduction of a boron salt to form spherical particles that range in diameter from 1 to 45 nm.²⁶ However, the ball-milling method, while relatively simple, does not allow much control over the size and shape of the particles. The salt reduction method lacks the control over the size and size distribution of the particles and requires a stabilizing agent, but the shapes of the particles are better defined and preparing very small particles is possible.

We decided to utilize vinylsilsesquioxane nanoparticles as a precursor for hybrid organosilica nanoparticles due to the presence of highly reactive alkenyl groups throughout their interior and due to their high porosity ($77 \text{ cm}^3 \text{ g}^{-1}$ surface area²⁷ compared to $36 \text{ cm}^3 \text{ g}^{-1}$ for Stöber silica nanoparticles²⁸). We hypothesized that the porosity would allow access to the interior of the nanoparticles and thus allow a high degree of functionalization inside the nanoparticles. Additionally, a few examples of the post-modification of such organosilica nanoparticles have been reported. For instance, spherical amine-containing nanoparticles prepared using aminophenyltrimethoxysilane have been post-modified using acylation with moderate success.¹⁹ Gold nanoparticles have been incorporated into vinyl- and thiol-rich nanoparticles by the treatment with a metal salt solution. This process led to the gold particles immobilized on the surface and inside the silica particles.²⁹

In the present paper we describe the reactivity of alkenyl groups inside the vinylsilsesquioxane nanoparticles using typical alkene reactions, bromination and hydroboration.³⁰ We also show that after the vinylsilsesquioxane nanoparticles have been internally functionalized their surface can be further modified with a trialkoxylaminosilane.

Experimental Section

Materials

Sodium silicate solution (27% SiO₂, 10% NaOH, Aldrich), dansyl chloride (99%, Aldrich), 3-amino-propyltriethoxysilane (APTES 98%, Aldrich), ammonium hydroxide (NH₄OH 30%, Mallinckrodt), triethoxyvinylsilane (TEVS 97%, Aldrich), borane tetrahydrofuran complex (1M, stabilized, Acros organics), bromine (>99.5%, Mallinckrodt Chemicals) and 2,6-lutidine (99%, Aldrich) were all used as received. 18 M Ω -cm water used in all experiments was obtained from a Barnstead "E-pure" water purification system. All ethanol used was 200 proof. Acetonitrile (HPLC grade, Mallinckrodt), tetrahydrofuran (THF, GC grade, EMD) and dichloromethane were dried using standard procedures. IR spectra were recorded in the 400 to 4000 cm⁻¹ range using a Bruker Tensor 37 IR Spectrophotometer as KBr pellets. Scanning electron microscopy (SEM) images were obtained using a Hitachi S3000N instrument at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained using a Technai T-12 instrument. Diameters of at least 100 nanoparticles have been measured using their SEM images and averaged to calculate the corresponding particle size. Elemental analysis was conducted by Columbia Analytical Services using Inductively Coupled Plasma spectroscopy (ICP). Thermogravimetric Analysis (TGA) measurements were performed using a TA Instruments/Q500 series instrument using a type P Platinel II thermocouple in an open platinum pan. The isotropic ¹¹B NMR data were collected on a 600 MHz Varian Infinity spectrometer using a 4.0 mm probe and a sample spinning speed of 10.0 kHz. Analysis was performed using a single pulse excitation at a frequency of 192.437 MHz and no decoupling. A total of 256 scans were acquired using a 2.0 μ s 90 pulse and a 200 kHz spectral width with a 10 s delay between pulses. The spectrum was referenced to the ¹¹B resonance in sodium borate decahydrate at 2.1 ppm. A Branson 1510 sonicator was used for all sonications.

Preparation of Vinylsilisesquioxane Nanoparticles

Vinylsilisesquioxane nanoparticles were prepared following a literature method²⁷ with SiO₂ used as a seed. The following is a typical procedure for the preparation of the nanoparticles. Absolute ethanol (6.30 mL) and ammonium hydroxide (8.40 mL) were placed into a 100 mL round bottom flask and vigorously stirred. To this solution, 0.84 mL (4 mmol) of triethoxyvinylsilane were carefully added in a single portion. In a scintillation vial, 0.25 mL of a 2.2% SiO₂ solution was added to (12.50 mL) of pure ethanol. The vial was swirled and briefly sonicated to disperse the solution evenly. This seed solution was added in single portion shortly after the addition of the vinylsiloxane. The reaction flask was then sealed. The solution was stirred overnight (~16 hours) during which time a white precipitate formed. Following sonication, the solution was centrifuged at approximately 1800 rpm. The precipitate was washed several times with ethanol and water to remove ammonia and any unreacted vinylsiloxane. The white solid was air-dried overnight and dried under vacuum for at least ten hours. An IR spectrum was recorded to verify the composition of the product. SEM images were obtained to determine the particle size, which was 237 $\pm$ 24 nm.

Preparation of Bromine-Enriched Nanoparticles

Note *Bromine is highly toxic and very volatile, and needs to be treated with caution.*

Dichloromethane (10 mL) was added to 0.25 g (3.13 mmol based on monomer unit) of vinylsilisesquioxane nanoparticles in a scintillation vial and sonicated to evenly disperse the solution. To this solution three equivalents of bromine (0.48 mL) were carefully added; the vial was then sealed. The contents were briefly sonicated and stirred overnight (~16 hours). The particles became much denser and precipitated out of solution more rapidly compared to the non-brominated particles while the color of the solution slightly lightened. The particles were centrifuged at ~1800 rpm and washed at least five times with dichloromethane to ensure

that all bromine was removed. Once washed the particles were air-dried and vacuum-dried for at least 18 hours. The particles were isolated as a fine white/off white powder. The powder was analyzed by IR spectroscopy, TGA, SEM, and elemental analysis (ICP). EA results: Si%: 13.05, C%: 9.125, H%: 1.315, Br%: 59.85.

Preparation of Boron-Enriched Nanoparticles

Vinylsilisesquioxane nanoparticles (0.25 g, 3.13 mmol based on monomer unit) were placed in a 25 mL round bottom flask. Dry THF (3 mL) was added under the nitrogen atmosphere to disperse the particles. Three equivalents of 1 M $\text{BH}_3 \cdot \text{THF}$ (9.5 mL) solution were then added. The contents were briefly sonicated to disperse the particles and then vigorously stirred. At first, the particles dispersed evenly in the THF/ BH_3 solution. After approximately twenty minutes, the particles began to precipitate out of the solution and appeared to cluster and could not be easily re-dispersed. The particles were sonicated again and stirred overnight. The solid was then collected via centrifugation at 1800 rpm and washed five times with THF to remove excess BH_3 . After the THF washings, the particles were washed with pure ethanol containing a small amount of water to remove any residual BH_3 while also converting the free borohydride groups to boric acids.^{31,32} The particles were then rinsed three times with water to further remove any impurities and assure the conversion of the free hydrides. The nanoparticles were isolated by centrifugation as a white solid that was air-dried and dried under vacuum for at least 18 hours. The boron-enriched particles disperse evenly into pure water while the vinyl-particles are too hydrophobic to do so offering an indication that a modification took place. The nanoparticles were analyzed by IR, TGA, SEM, ICP, and CP-MAS ^{10}B NMR. EA results: Si%: 23.45, C%: 16.44, H%: 3.785, B%: 3.585.

Amine Functionalization of Nanoparticle Surface

A literature method was used for the amine functionalization of the surfaces for the vinyl, brominated, and boronated nanoparticles.³³ An example of the procedure used is as follows. Dry acetonitrile (6 mL) was added to 26 mg of vinylsilisesquioxane nanoparticles in a scintillation vial and sonicated to evenly disperse the particles. APTES (90 μL , 0.336 mmol) was added to the vial and the reaction mixture was stirred for approximately 20 hours. The nanoparticles were collected by centrifugation and washed several times with acetonitrile to remove any excess APTES. The white/off white solid was air-dried and then dried under vacuum for at least 18 hours. The amine-modified particles were used without further characterization.

Surface Modification with Dansyl Chloride

A literature method was used for the dansylation of the amine functionalized vinyl, bromine-, and boron-enriched nanoparticles.³⁴ An example of the procedure used is as follows. Dry acetonitrile (10 mL) was added to 13 mg of amine-functionalized nanoparticles in a scintillation vial and sonicated to disperse the particles evenly. The vial was wrapped in aluminum foil and 10 mg (0.04 mmol) of dansyl chloride were added followed by three drops of dry 2,6-lutidine. The vial was sealed and the solution was stirred for about 17 hours. The resulting particles were collected via centrifugation and washed five times with acetonitrile to remove any excess dansyl chloride. The particles were air dried then dried under vacuum for approximately 18 hours to yield a white/off white powder. The powder was irradiated with short wave UV and showed blue/green fluorescence. A control experiment was performed for non-aminated particles under the same conditions and they did not exhibit fluorescence.

Results and Discussion

Brominated Nanoparticles

The bromination of 237 ± 24 nm vinylsilsesquioxane nanoparticles has been performed using the conditions typical for double bond halogenations.³⁰ The SEM images of vinylsilsesquioxane and of the corresponding brominated nanoparticles are shown in Figures 1 and 2, respectively. There seems to be little difference between the two particle sizes, as the diameter of the brominated nanoparticles was determined by SEM to be 232 ± 29 nm. There appears to be some agglomeration of the brominated particles, but this may be attributed to the sample preparation. Indeed, the unmodified particles were suspended in water, while the brominated particles were suspended in acetonitrile. The latter disperse very well in acetonitrile thus leading to a high particle concentration in solution and a thick layer of the particles on the silicon wafer.

The inner pores of the unmodified and brominated vinylsilsesquioxane nanoparticles were observed using TEM (Figure 3A–B). The numerous small nanopores can be seen within the unmodified particles. After the bromination, these pores become more difficult to observe which suggests the pores are closing due to the functionalization.

The IR spectra of the brominated particles (Figure 4) offered the initial insight into the chemical changes that took place inside the vinylsilsesquioxane particles. The stretch found at 960 cm^{-1} for the vinylsilsesquioxane particles³⁵ disappeared while the stretch at 1602 cm^{-1} was greatly reduced in intensity, suggesting that the double bonds have largely reacted. New bands at 874 and 650 cm^{-1} found for the brominated nanoparticles are within the range characteristic of the C-Br stretch. There is also a splitting of the 760 cm^{-1} band which could result from an overlap with a C-Br stretch.

The TGA data gathered for the brominated vinylsilsesquioxane nanoparticles show a significant change compared to the unmodified vinylsilsesquioxane nanoparticles (Figure 5). The brominated particles show a very significant weight loss around $400\text{ }^{\circ}\text{C}$ which can be attributed to the presence of the heavy bromine atoms. Indeed, the monomer unit of the vinylsilsesquioxane particle is $\text{SiO}_{3/2}\text{C}_2\text{H}_3$ with molecular weight of $79.1\text{ g}\cdot\text{mol}^{-1}$. Since each addition to the double bond introduces two bromine atoms at a molecular weight of $79.9\text{ g}\cdot\text{mol}^{-1}$ each, the molecular weight of each monomer triples. This weight change is clearly observed in the TGA data when comparing the vinylsilsesquioxane particles with weight loss of $\sim 9\%$ to the brominated particles with weight loss of $\sim 60\%$. Assuming the additional weight loss of the brominated particles originates only from the bromine the data suggests that nearly all of the vinyl groups in the particle have been reacted. This result is in good agreement with the elemental analysis which reveals that the particles contain 59.85% bromine by weight. Compared to the maximum of $66\text{ wt}\%$ this suggests that ca. 90% of the double bonds have been brominated. Examining the bromine/carbon ratio leads to a similar conclusions. The maximum theoretical bromine to carbon weight ratio for the nanoparticles is 6.6 assuming that every vinyl group has been brominated. The average Br:C ratio obtained by the elemental analysis is 6.83 , in good agreement with the theoretical calculation and TGA results. Silica and carbon contents are also within a few percent of the values calculated assuming full incorporation of bromine.

Boronated Nanoparticles

The incorporation of boron into the nanoparticles has been performed using the standard hydroboration conditions.³⁰ The SEM images of the boronated particles (Figure 6) show little difference compared to the vinylsilsesquioxane particles (Figure 1) as the diameter of the former was determined by SEM to be 234 ± 23 nm. The inner pores of the boronated

vinylsilsesquioxane nanoparticles were observed using TEM (Figure 3C). The numerous small nanopores found within the unmodified particles became more difficult to observe after the boronation, suggesting that the pores are closing due to the functionalization.

The first compelling evidence that the hydroboration took place came from the changes in the IR spectrum of the boronated particles (Figure 7). The once very sharp and well-defined band found for the vinylsilsesquioxane particles at 1410 cm^{-1} , which is characteristic of the Si-C bonds, has been considerably broadened and became more intense indicating the presence of the B-O vibration.³⁵ There is also a new band at 1712 cm^{-1} which is characteristic of the C-B-C stretch. The broad band centered around 3400 cm^{-1} suggests that the initially formed free hydrides of the borohydride have been converted to hydroxyl groups. There is also a considerable broadening around 770 cm^{-1} , which suggests the presence of O-B-O and/or B-C stretch.

The boronated nanoparticles also showed a significant change in TGA (Figure 8) compared to that of the vinylsilsesquioxane nanoparticles. However, it is important to note that the nature of the boron within the particles is somewhat ambiguous, which makes interpreting the TGA and elemental analysis data more complicated. It is unlikely that all of the boron atoms within the particles exist as a single boron atom covalently bound to a single carbon atom. It is more likely that some of the boron atoms form cross-linked divalent or trivalent species. Also, the borohydrides that are bound to less than three carbons are likely to be converted to boronic acid groups. This can add considerable weight to the particles complicating the interpretation of both TGA data and elemental analysis. To establish the degree of hydroboration the observed carbon and boron weight percent can be compared to that for $\text{SiC}_2\text{H}_6\text{BO}_{7/2}$, a monomer where every vinyl group has been hydroborated once. For this monomer unit the boron/carbon weight ratio is 0.45. The actual elemental analysis data gives an average boron/carbon ratio of 0.22. Thus, comparing the experimental and theoretical data suggests that ca. one boron atom is attached per two vinyl groups. This method of estimating the boron content does not provide the exact chemical structure of the boronated species (singly boronated vs. cross-linked) but shows that there is a high degree of boronation of the nanoparticles.

For the TGA data (Figure 8) a weight loss averaging 21.3% for the boronated samples compared to ca. 9% weight loss for the unmodified vinylsilsesquioxane nanoparticles is observed, giving 12.3 wt% loss corresponding to the boron species. If each of the boron atoms in the nanoparticle was bound to a single vinyl group and carried two hydroxyl groups, each monomer unit would increase in weight from 79 to $122\text{ g}\cdot\text{mol}^{-1}$. Using the estimated above boron to vinyl group ratio of 1:2, the average new monomer weight would be $100.5\text{ g}\cdot\text{mol}^{-1}$ and the corresponding boron species content would be 21.4 wt%. The difference between the predicted and the observed weight percent for the boron species is likely due to some of the boron atoms being bound to more than one vinyl group, thus carrying fewer hydroxyl groups. The weight loss of the boronated particles is less dramatic and more gradual than that of the brominated particles. This may stem from a more gradual breakdown of the diverse species inside the boronated nanoparticles. For example, singly bound boron species may decompose at a different rate than a di- or trisubstituted boron species. Overall, these observations offer yet another indication of how accessible the vinyl groups inside the nanoparticles are to functionalization.

We estimated the number of boron atoms in a single 237 nm organosilica nanoparticle using straightforward considerations. Assuming that the particle is comprised entirely of vinylsiloxane (which is a fair assumption given the molar ratio of the vinylsiloxane precursor to seed source of about 100:1), the volume of the sphere has been used to calculate the total number of vinyl groups available for the functionalization. Assuming that one half of the vinyl groups became boronated and estimating the density of the nanoparticle as $2\text{ g}\cdot\text{cm}^{-3}$, this number

of boron atoms per nanoparticle is ca. 5×10^7 , which is within the range suitable for BNCT,²⁴ as discussed above.

Finally, we studied CP-MAS ^{11}B NMR of the boronated particles. There is no signal for boric acid (19.8 ppm) or borohydride (−1.1 ppm) in the spectrum, which confirms that all excess borohydride and the oxidized borohydride has been fully removed from the particles. The two peaks found for the boronated particles (Figure 9) are both within the range of the R-B(OH)₂ and R-BH-R region. Unfortunately, a more precise peak assignment is not possible since boron can exist in several different forms inside the particles as discussed above.

Surface Amination of the Nanoparticles

The ability to modify the surface of internally functionalized vinylsilsesquioxane nanoparticles is important for several reasons. Such ability would allow controlling the wettability of the particles, and would allow attaching a variety of moieties to the nanoparticle surface, ranging from fluorescent dyes to polymers to biological ligands.

A commonly used method for silica surface modification is amination.⁸ We demonstrated the feasibility of the amination using a UV-active species. Dansyl chloride by itself does not fluoresce but when coupled to produce a sulfonamide moiety it fluoresces with a bright blue/green color. Thus, brominated and boronated nanoparticles have been aminated using APTES. Next, both modified and unmodified nanoparticles have been treated with dansyl chloride. We found that only the amine-modified nanoparticles became fluorescent. This result indicates that the surface of the brominated and boronated vinylsilsesquioxane nanoparticles can indeed be aminated allowing further surface modifications as discussed above.

Conclusions

Vinylsilsesquioxane nanoparticles, prepared using a modified Stöber method, have been successfully enriched with boron and bromine and surface aminated following the enrichment. Our results demonstrate that the vinyl groups inside the nanoparticles are highly accessible for functionalization. The described internal functionalization method provides a new way for catalyst incorporation into silica nanoparticles, for their use as molecular sponges or in molecular recognition experiments, and for the preparation of nanoparticles that could exhibit unique internal and surface properties. Presently we are examining how accessible the alkenyl groups are when attached with different tethers, and exploring the ability to functionalize the nanoparticles that contain other groups such as amine or thiol. We are also exploring other reactions of the alkenyl groups, such as Diels-Alder addition, dihydroxylation and Grubbs metathesis, which could lead to even more interesting hybrid silica nanoparticles with increasingly complex structures.

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References

1. Feldheim, DL.; Foss, CA, Jr. Metal Nanoparticles: Synthesis, Characterization and Applications. Marcel Dekker Inc; Basel, New York: 2002.
2. Hayashi C, Kashu S, Oda M, Naruse F. Mater Sci Eng A 1993;A163:157–161.
3. Salata OV. J Nanobiotechnol 2004;2:3.
4. Stöber W, Fink A, Bohn E. Colloidal Interface Sci 1968;26:62.

5. Radin S, El-Bassouini G, Vresilovic EJ, Schepers E, Ducheyne P. *Biomaterials* 2005;26:1043–1052. [PubMed: 15369693]
6. Iler, RK. *The Chemistry of Silica*. John Wiley & Sons Inc.; New York: 1979. p. 312
7. Trewyn BG, Giri S, Slowing II, Lin VSY. *Chem Commun* 2007;31:3236–3245.
8. Onclin S, Ravoo BJ, Reinhoudt DN. *Angew Chemie Int Ed* 2005;44:6282–6304.
9. Werne T, Patten TE. *J Am Chem Soc* 1999;121:7409–7410.
10. Radhakrishnan B, Ranjan R, Brittain WJ. *Soft Matter* 2006;2:386–396.
11. Tsubokawa N. *Polym J* 2007;39:983–1000.
12. Buchmeiser MR. *Adv Polym Sci* 2006;197:137–171.
13. Blaaderen AV, Vrij A. *J Colloid Interface Sci* 1993;156:1–18.
14. Burns A, Hooisweng O, Wiesner U. *Chem Soc Rev* 2006;35:1028–1042. [PubMed: 17057833]
15. Ohulchanskyy TY, Roy I, Goswami LN, Chen Y, Bergey EJ, Pandey RK, Oseroff AR, Prasad PN. *Nano Lett* 2007;7:2835–2842. [PubMed: 17718587]
16. Parida SK, Dash S, Patel S, Mishra BK. *Adv Colloid Interface Sci* 2006;121:77–110. [PubMed: 16879799]
17. Smith JE, Wang L, Tan W. *Trends Anal Chem* 2006;25:848–855.
18. Frenkel-Mullerad H, Avnir D. *Chem Mater* 2000;12:3754–3759. and references therein.
19. Jesson DA, Abel ML, Hay JN, Smith PA, Watts JF. *Langmuir* 2006;22:5144–5151. [PubMed: 16700606]
20. Jesson DA, Smith PA, Hay JN, Watts JF. *J Mater Sci* 2007;42:3230–3237.
21. Haberecht J, Krummland A, Breher F, Gebhardt B, Rüegger H, Nesper R, Grützmacher H. *Dalton Trans* 2003;11:2126–2132.
22. Arkhireeva A, Hay JN, Lane JM, Manzano M, Masters H, Oware W, Shaw SJ. *J Sol-Gel Sci Technol* 2004;31:31–36.
23. Takahashi K, Tadanaga K, Hayashi A, Tatsumisago M. *Chem Lett* 2007;2:324–325.
24. Soloway AH, Tjarks W, Barnum BA, Rong F-G, Barth RF, Codogni IM, JWilson JG. *Chem Rev* 1998;98:1515–1562. [PubMed: 11848941]
25. Mortensen MW, Sørensen PG, Björkdahl O, Jensen MR, Gundersen HJG, Bjørnholm T. *Appl Radiat Isot* 2006;64:315–324. [PubMed: 16290943]
26. Pickering AL, Mitterbauer C, Browning ND, Kauzlarich SM, Power PP. *Chem Commun* 2007;6:580–582.
27. Arkhireeva A, Hay JN. *J Mater Chem* 2003;13:3122–3127.
28. Lecloux AJ, Bronckart J, Noville F, Dodet C, Marchot P, Pirard JP. *Colloids Surf* 1986;19:359–374.
29. Kim YB, Kim YA, Yoon K. *Macromol Rapid Commun* 2006;27:1247–1253.
30. Smith, MB.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*. Vol. 5. Wiley-Interscience; 2007. p. 970
31. Stockmayer WH, Miller RR, Zeto RJ. *J Phys Chem* 1961;65:1076–1077.
32. Pecsok RL. *J Am Chem Soc* 1953;75:2962–2964.
33. Newton MR, Bohaty AK, Zhang Y, White HS, Zharov I. *Langmuir* 2006;22:4429–4432. [PubMed: 16618198]
34. White HS, Murray RW. *Anal Chem* 1979;51:236–239.
35. Villegas MA, Navarro JMF. *J Mater Sci* 1988;23:2464–2478.

Figure 1.
SEM image of vinylsilsesquioxane nanoparticles. Scale bar is 5 μm .

Figure 2.
SEM image of brominated vinylsilsesquioxane nanoparticles. Scale bar is 10 μm .

Figure 3. HR-TEM images of (A) unmodified, (B) brominated and (C) boronated vinylsilsesquioxane nanoparticles. Scale bar is 10 nm.

Figure 4. IR spectra of vinylsilsesquioxane (green) and brominated (red) vinylsilsesquioxane nanoparticles.

Figure 5.
TGA of vinylsilsesquioxane (green) and brominated (red) vinylsilsesquioxane nanoparticles.

Figure 6.
SEM image of boronated vinylsilsesquioxane nanoparticles. Scale bar is 5 μm .

Figure 7.
IR spectra of vinylsilsesquioxane (green) and boronated (magenta) vinylsilsesquioxane nanoparticles.

Figure 8. TGA of vinylsilsesquioxane (green) and boronated (red) vinylsilsesquioxane nanoparticles.

Figure 9. CP-MAS ^{10}B NMR spectrum of the boronated vinylsilsesquioxane nanoparticles. Spinning artifacts are marked with asterisks.