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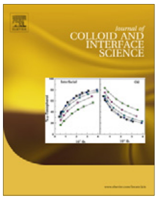

Highly monodisperse polysilsesquioxane spheres: Synthesis and application in cotton fabrics

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ABSTRACT

Highly monodisperse methyl-functionalized, vinyl-functionalized, and thiol-functionalized polysilsesquioxane spheres (MPSQ, VPSQ, and MPPSQ spheres) have been successfully prepared through a one-pot emulsion approach with one organosilane as sole precursor in aqueous medium. The morphology, size distribution, and chemical structure were characterized by SEM, DLS, FT-IR, solid NMR, XRD, etc. The thermodecomposition and hydrophobicity of these spheres were investigated with TGA and water contact angle measurement. Our research turns out that the organofunctional groups play a key role in thermostability and hydrophobicity of polysilsesquioxane spheres, MPSQ, and VPSQ spheres possess better thermostability than MPPSQ spheres, the order of hydrophobicity is as follows: MPSQ > VPSQ > MPPSQ. Cotton fabrics can become superhydrophobic when treated with methyl- or vinyl-functional silica spheres.

1. Introduction

The properties and applications of materials rely not only on the chemical composition but also on the structural morphology. On one hand, organic–inorganic hybrid materials possess many unique properties. On the other hand, microscopic and nanoscopic monodisperse spheres have attracted tremendous attention for their many scientific and industrial applications. Recently, considerable interest has been focused on the synthesis of polysilsesquioxane (PSQ) spheres in chemistry and physic fields due to their specific properties such as excellent thermostability, lubricity, weather resistance, solvent resistance, and good physiological inertia. The preparation of PSQ spheres has an equally wide range of applications, including photonic crystals [1,2], biosensors [3,4], pollution treatment [5–7], plastic [8,9], catalyst [10,11], and luminescence [12–17]. These characters and potential applications make PSQ spheres most attractive issue in colloidal science.

There are several methods, Stöber method, seeded regrowth process, emulsion approach, and sol–gel route, can be employed to prepare silica spheres. In 1968, Stöber et al. [18] reported the preparation of monodisperse silica spheres in water/ethanol solution with TEOS as the precursor and ammonia as the catalyst. The limitation of this way is that large amounts of ethanol are needed to generate the homogeneous phase. Hartlen et al. [19] utilized seeded regrowth process to synthesize highly monodisperse small silica spheres with diameters in the range of 15–200 nm. Sankaraiah et al. [20] prepared multifunctionalized polysilsesquioxane hard spheres in aqueous medium with disodium laurylphenol ether disulfonate as the surfactant and polyvinylpyrrolidone as the stabilizer. Lee et al. [21] developed a procedure for preparing silica spheres with sizes ranging from one to several micrometers using a sol–gel reaction, and neither the ethanol nor surfactant was added.

It is generally recognized that the wettability of a solid surface is affected by both chemical composition and geometrical microstructure on the surface [22–25]. To achieve superhydrophobicity, silica micro- or nano-sized particles have been widely used for surface roughness. Either co-condensation with alkylated silanes [26–29] or fluorination surface treatment [22,30–35] is often necessary for the hydrophilic nature of SiO_2. Xiu et al. [26] reported a method for the preparation of inorganic superhydrophobic silica coatings using sol–gel processing with tetramethoxysilane and isobutyltrimethoxysilane as precursors. Bae et al. [22] introduced superhydrophobicity to the hydrophilic cotton fabric by the combined treatment of silica nanoparticles and a fluorinated water-repellent agent, a water contact angle above 130° was obtained even at the very low concentration of water-repellent agent. However, the change of wettability on cotton fabrics obtained by combining polysilsesquioxane spheres with isocyanate cross-linking agent has been less investigated.

Here, we report a one-pot emulsion approach to synthesize series of highly monodisperse polysilsesquioxane spheres with different organofunctional groups. First, it is so convenient that only one process, one precursor, and one solvent are required. In addition, the influence of organofunctional groups on the thermostability

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and hydrophobicity was studied. Furthermore, we intend to mimic the lotus effect on the surface of cotton fabrics by compositing the synthetic polysilsesquioxane spheres with cross-linking agent. The precursors include Methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), and 3-mercaptopropyltrimethoxysilane (MPTMS). And their corresponding PSQ spheres are named MPSQ, VPSQ, and MPPSQ spheres. The structure and properties of PSQ spheres with different functional groups were characterized by SEM, DLS, FT-IR, solid NMR, XRD, TGA, etc.

2. Experimental section

2.1. Materials

Methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), 3-mercaptopropyltrimethoxysilane (MPTMS) were supplied by Liyang Mingtian Chemical (China). Triethylamine (TEA,99%), AR grade ethanol, sodium dodecyl benzene sulfonate (SDBS), and polyvinylpyrrolidone (PVP) were purchased from Tianjin Bodi Chemicals (China), Tianjin Fuyu Chemicals (China), Dongxing Chemicals (China) and Guangzhou Qintian Chemicals (China), respectively. Cross-linking agent, AF3600, which is an emulsion consisting of large amounts of blocked isocyanates, was obtained from Herst International Group. All chemicals used in these experiments were used as received without further purification. The cotton fabric used in this research was desized and bleached. Water was purified using a Millipore Milli-Q filtration system.

2.2. Preparation of PSQ spheres

In the typical preparation of MPSQ spheres, 10 g of MTMS was added into 40 ml of aqueous solution with 0.15 g of SDBS and 0.01 g of PVP under vigorous stirring for 40 min. 0.01 g of triethylamine was added into the mixed solution, and the reaction was allowed to proceed at 20–30 °C for approximately 10 h. Finally, residual precursors, catalysts, and surfactants were removed from aqueous solution containing silica particles by centrifugal sedimentation and ultrasonic dispersion (using ethanol and water) cycles, which processes were repeated at least three times. The silica particles were obtained after evaporating the liquid in a vacuum. The procedures for preparing VPSQ and MPPSQ spheres are based on the synthetic approach of MPSQ spheres.

2.3. Treatment of cotton fabrics with PSQ spheres

The cotton fabric (Area is 100 cm^2) was immersed in 50 g of ethanol solution with 5 g of MPSQ spheres and 0.2 g of cross-linking agent at 30 °C for 5 min while stirring. The wet fabric was squeezed using a laboratory mangle (EL-A, Ruibang, China) with a pressure 3.5 kgf cm^{-2} and a rate of 10 rpm, resulting in a wet-pick-up of ca. 70%. The fabric was then dried at 80 °C for 3 min and cured at 160 °C for 3 min. The fabric was then washed with 2 g of detergents in 400 ml of distilled water using a laboratory laundering machine (XPB20-2008, Little Duck, China) for 30 min to remove the residual spheres, which were not immobilized on the fabric. Finally, the treated cotton fabric was dried under vacuum. The procedures for treatment of VPSQ and MPPSQ spheres onto the cotton fabric are based on the same approach as that of MPSQ spheres.

2.4. Characterization

The morphology of the particles was observed with a FEI Quanta200 Scanning electron microscopy (SEM). Dynamic light scattering (DLS) which provided us with average particle size and size distribution was conducted by a Mircotrac NPA150 system. FT-IR spectra of KBr powder-pressed pellets were recorded on an Analect RFX-65 FT-IR spectrophotometer with a spectral resolution of 1 cm^{-1}. The scanned wavenumber range is 4000–400 cm^{-1}. The solid-state ^{29}Si CP-MAS (CP: cross polarization, MAS: magic angle spinning) NMR spectra were measured at room temperature on a Bruker Avance 400 MHz spectrometer. Powder XRD experiments were carried out using a Bruker D8 ADVANCE diffractometer by using a Cu Kα radiation source. The d-spacings were calculated according to Bragg's equation. Thermogravimetric analysis (TGA) was conducted with a NETZSCH TG 209 F1 thermogravimetric analyzer at a heat rate of 20 °C/min from room temperature to 700 °C under both a continuous nitrogen flow. The contact angles (CAs) were measured on a contact angle goniometer (Chengde Dingsheng JY-82) drop shape analysis system via the sessile drop method at ambient temperature. The probe fluid was deionized water, and the drop volume was 3.5 μL. The contact angle values and images were obtained 30 s after dropping the distilled water on the sample. The measurement was repeated nine times to acquire the averaged value for each sample.

3. Results and discussion

3.1. Structure and properties of PSQ spheres

3.1.1. SEM and DLS

SEM images and DLS results of PSQ microspheres are shown in Fig. 1. It is clear that three characteristics of PSQ spheres are spherical in shape, micrometer size, and mostly monodisperse. Additionally, the average particle size rises with increasing the number of carbon chains in the precursor under the same operation condition, which is confirmed by the order that 1.1 μm < 1.5 μm < 1.9 μm, as shown in Table 1. These results which are consistent with Lee's finding [21] show that the number of carbon chains plays a key role in silica particle size. It should be noted that the average particle sizes obtained from DLS are always larger than those obtained from the SEM images for the same samples. Particle swelling or chain expansion might be responsible for this phenomenon. So, SEM is the more effective method of measuring the true sizes of the PSQ spheres.

3.1.2. FT-IR

The FT-IR spectra in Fig. 2 shows the structural evidences of PSQ spheres. All PSQ samples show well-defined absorption at 1130 and 1030 cm^{-1} characteristic of Si—O—Si linkages, which are further confirmed by the distinct vibration at 440–470 cm^{-1}. Si—C and C—H stretching vibration bands appear at 767–802 and 2920–3070 cm^{-1}. The spectra in 3100–3700 cm^{-1} band corresponding to the broadening OH stretching vibration indicates that residual silanol groups exist in PSQ spheres. Furthermore, the FT-IR spectra exhibit the characteristic absorption peaks of —CH_3(1273 cm^{-1}), C=C(1603 cm^{-1}), —SH(2558 cm^{-1}) for MPSQ, VPSQ, MPPSQ spheres, respectively. These absorbing peaks confirm that the methyl group, vinyl group, and thiol group exist and connect to the silicon atom in PSQ spheres.

3.1.3. Solid NMR

^{29}Si NMR spectroscopy is a powerful approach to characterize the chemical structure of substances that can be prepared from organoalkoxysilanes [36]. The solid-state CP-MAS ^{29}Si NMR spectra of PSQ spheres are shown in Fig. 3. The ^{29}Si NMR spectra of all PSQ spheres exhibit two major peaks in the T region, indicating there were a great number of organic groups existing on the surface of the PSQ spheres. The peaks at −66.3 ppm for MPSQ, −79.7 ppm for VPSQ, and −64.2 ppm for MPPSQ reveal the presence of fully