Improvement of cotton properties with silica particles coatings

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1. Introduction

Nanomaterials, by definition, are materials with one or more dimensions measuring 100 nm or less, as well as holding novel properties, that could be related to changes in their physical, chemical and optical aspects, when compared to the corresponding bulk materials. The properties of materials on the nanometer scale are determined by its size, shape, surface chemistry, flexibility, architecture and elemental composition (i.e. critical parameters). The nanoparticle synthesis can be challenging in terms of a precise control on the critical parameters. Chaudhuri & Paria have categorized the synthesis techniques into three types: (i) condensation from vapor, (ii) synthesis by chemical reaction, and (iii) solid-state processes, such as milling.

Here we are interested in the synthesis by chemical reaction, in order to create a colloidal suspension of particles in a core-shell model. Hence, a spherical core particle is completely coated by a shell of a different composition, specifically organic/inorganic core/shell nanoparticles coated with a silica shell with fluorescent properties, which is provided by the fluorescein isothiocyanate isomer (FITC). Therefore, they will show dual properties of both inorganic and organic materials. Silica nanoparticles have been widely used in medical applications like bioimaging, drug-delivery and therapeutics, acting as an excellent vehicle for carrying hydrophobic molecules or functionalization of the external surface due to biocompatibility and easy surface tailorability, which is observed by the presence of surface silanol groups. As a consequence, silica nanoparticles are considered quite versatile, with an increasing potential in nanobiotechnology scientific research.

A sophisticated method for chemical reactions was developed in 1968 by Stöber, to prepare monodisperse spherical silica particles (SiPs). The method was based in the hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions under the presence of ammonia as a morphological catalyst. In fact, it is a bottom-up approach that has been used in various fields of study, especially as a model system.

Van Blaaderen & Vrij proposed a mechanism that allows the synthesis of hybrid organic-silica particles with organoalkoxysilylne and alkoxysilylne, thus adjusting the previous process which SiPs were produced by tetraalkoxysilane (TEOS). It was observed that these particles can grow larger than the “ordinary” silica spheres. After this pioneering work, subsequent contributions emerged, linked with covalent incorporation of organic molecules, such as fluorophores, into Stöber colloidal silica in order to synthesize fluorescent SiPs.

In this way, a method to obtain highly fluorescent, stable and monodisperse core-shell fluorescent SiPs of different sizes through a controlled growth is described. The strategy begins when the organic dye molecules are first covalently conjugated to a silica precursor (monomer) and
then condensed to form a dye-rich core. It was performed using 3-aminopropyltrimethoxysilane (APTMS), a coupling agent, to allow the bond between fluorescein isothiocyanate isomer (FITC) and the silica matrix, in the liquid medium with ethanol as solvent. Silica sol-gel monomers comprised of tetraethylorthosilicate (TEOS) are then added to form a denser silica network around the fluorescent core material, providing a shield against solvent interactions as the shell is synthesized. Afterwards, ammonia is added as a morphological catalyst. The order in which the reagents are added is relevant to the synthesis, because it directly affects the desired architecture.

Organosilanization (or silanization) is an efficient way to enhance the compatibility between the inorganic and organic phases of materials, for example, with the addition of organic molecules on the particles surface to change their surface properties (e.g. charge, reactivity, hydrophobicity). APTMS, which was used initially for incorporating FITC into the SiPs core can turn the particles surfaces into amino-functionalized SiPs by grafting amine groups to the particle surface. Based on Hoffmann et al. who discuss three applicable pathways to the synthesis of mesoporous silica nanoparticles, there are two approaches to functionalize the silica particles’ surfaces: grafting and co-condensation. Rahman et al. have observed that, in co-condensation, the amino-groups will not necessarily be spread on the surface of silica particles due to simultaneous aggregation of alkoxy-silane and modifier. In this context, in this study we also used the post-modification method to functionalize the surface of fluorescent core-shell SiPs, by grafting APTMS on their surface. With these fluorescent and surface-functionalized SiPs, cotton fabrics were modified from the formation of SiPs coatings. Finally, the hydrophilicity and stability of the SiPs coatings were evaluated.

2. Methodology

2.1 Synthesis of core-shell silica nanoparticles

Spherical SiPs were prepared by a modified Stöber method. For the production of SiPs core-shell nanoparticles in a size of approximately 130 nm (SiP A1 – 133 nm), the synthesis was performed in two steps. In the first step, 3 mg of FITC, 3 mL of absolute ethanol and 3.26 µL of APTMS were mixed. The solution was allowed to react in a dark place for 1h at room temperature. The second step was the addition of 7 ml of absolute ethanol, 800 µL of TEOS and 800 µL of ammonia (28 wt %) to the solution. The reaction was carried out under stirring at 60ºC for 2h. Lastly, the particles were centrifuged in an ultracentrifuge for three consecutive times under the following parameters: 4ºC, 30 minutes and 30000 rpm. The first centrifugation step was performed in order to remove the excess of reagents, while in the second and third step ethanol was used to wash the particles.

For the production of core-shell silica nanoparticles in a size of approximately one micrometer (SiP B2 – 1030 nm), a similar experimental procedure was taken (as the first step described above), while the second step was performed with different amounts of reagents. In the second step of this reaction, 1.5 mL of absolute ethanol, 800 µL of TEOS and 6.3 mL of ammonia (28 wt %) were added into the solution. Next, the reaction was performed at 60ºC for 3h. Lastly, the
colloidal suspension was centrifuged three times under the same parameters described before for the smaller particles.

2.2 Amino-functionalization of core-shell silica nanoparticles

Regarding the SiPs in the size of 130 nm (SiP-A1), the amino-functionalization was achieved by consecutive additions of 14 µl of APTMS, 5 µl of ammonia (28 wt %) and 50 µl of deionized water in a 6 ml of colloidal suspension. In order to enhance the covalent bonding between APTMS and the silica surface, the resultant solution was stirred and refluxed at 75°C for 3 h. The quantities of each reagent were based on a simple proportion from Lu’s work.

The same process was applied to the silica nanoparticles measuring one micrometer (SiP-B2), only with a change on the amount of ammonia. Therefore, 14 µl of APTMS, 31.5 µl of ammonia (28 wt %) and 50 µl of deionized water were added into 6 ml of suspension, respectively. The reaction occurred under the same parameters and conditions applied to the smaller particles.

2.3 Cotton fabrics treated with silica nanoparticles

Water incorporation/repellency in tissues (cloths) is associated with the water contact angle (WCA). It has been shown the dependence between wetting behavior, chemical composition and topological nature of the surface. To achieve modifications in cotton fabrics, the materials were treated with silica nanoparticles colloidal suspensions with two different sizes, specifically SiP-A1 and SiP-B2. For this, 2 cm x 2 cm pieces of the cotton fabrics were washed with detergent under stirring on a beaker. After removing all the soap, small fabric pieces were dried at 45ºC for 30 minutes. Then, the pieces were immersed in a sol of silica nanoparticles for 1 hour. Afterwards, they were cured and dried at 110ºC for 2 hours.

2.3.1 Stability of coatings

In order to evaluate the physicochemical stability of SiPs coatings, the cotton fabrics treated with silica particles of different sizes were immersed in deionized water in a falcon tube and stirred in a vortex mixer for 1 minute. Then, the samples rested for 24 hours, protected from light.

2.3.2 Silanization of the treated cotton fabrics

After the formation of the SiPs coatings, the treated cotton fabrics were submitted to heating at 80°C, under a moderate stirring in toluene solution of 1 % v/v of trimethoxyoctadecylsilane for 1 hour in order to change the hydrophobicity of the cloths.

3. Results and Discussion

Dynamic Light Scattering technique on a Zetasizer Nano ZS was used to confirm the particles regarding its size distribution, as see Figure 1.
After the synthesis of the SiPs coatings, the SiP-A1 and SiP-B1 produced were used to do the amino-functionalization, which was obtained positive and monodisperse particles (see Figure 2 and 3).
Figure 3 - Size distribution of silica particles. The particles were characterized by dynamic light scattering (DLS). SiP-AP1: 140.0 nm, PDI = 0.154 ; SiP-BP1: 670.5 nm, PDI = 0.016.

Otherwise, to verify the stability of the coatings in the cotton fabrics, fluorescence measurements were performed in a microplate reader from the obtained supernatant and the diluted SiPs colloidal suspension of SiP-A1 and SiP-B2. The results showed that there are more small particles dispersed in the liquid than larger particles (see Table 1). Consequently, the particles in a size of one micrometer are better adhered to the cotton fabric compared to the particles with approximately 130 nm, although, in general, it seems that most of the particles interacted well with the material, since they were firmly adhered even after the washing procedure (confirmed by the yellow color of the cloths).

<table>
<thead>
<tr>
<th>SiPs</th>
<th>Fr% of Fluorescence</th>
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<tbody>
<tr>
<td>A1</td>
<td>8.0</td>
</tr>
<tr>
<td>B2</td>
<td>6.4</td>
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Concerning to the hydrophobicity in cotton fabrics, water contact angle measurements were performed. It was observed that they became much more hydrophilic compared to the material without particles, thus resulting in good absorbent material. Finally, based on the experiments described by Xue et al., cotton fabrics were also functionalized with toluene and trimethoxyoctadecylsilane which corresponds to a silane with a long carbonic chain, using the SiPs-treated fabrics (SiP-A1 and SiP-B2). After this treatment, it was noted a increase in the hydrophobicity of the tissues, compared to untreated cotton fabrics.

4. Conclusion

In this work, it has been shown two methods to synthesize monodisperse core-shell silica particles in a size of approximately 130 nm and 1 μm. Besides, to the synthesized colloidal particles, positive charge and stable external functionalization was obtained for particles with use of APTMS. Moreover, experiments to analyze the stability and hydrophobicity of SiPs coatings...
formed in the cotton fabrics were performed. Under these conditions, it was obtained a stable and highly water-absorbent cotton material from the coatings made of SiPs.

5. Bibliographic References


