

## Highly loaded COOH functionalized silica particles



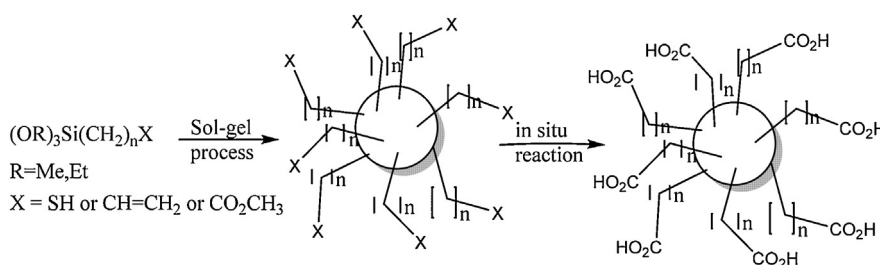
Reut Cohen, Chaim N. Sukenik\*

Department of Chemistry and the Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan, Israel

### HIGHLIGHTS

- Highly loaded silica particles bearing carboxylic acid groups have been prepared.
- The overall strategy was to make the particles using different kinds of protected acids and to deprotect them after particle fabrication.
- The loading of the acid groups on the various particles has been determined and their ability to immobilize a biomolecule has been demonstrated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Highly functionalized monodisperse silica particles are attractive as unique additives and fillers and as carriers for biomolecule immobilization. Uniform micron and nanometer scale silica particles are well known and coating methods have been developed for their surface modification. However, such coatings provide only limited loading capacity. Hybrid silica particles whose physical and chemical properties are controlled by a very high loading of non-hydrolyzable pendant group have been developed based on different functionalized silanes. The more polar and/or reactive the pendant functionality, the more difficult it is to achieve uniform, stable, particle formation. Nevertheless, making hybrid particles with masked carboxylic acids is a worthwhile goal since they should enable the production of highly acid-functionalized particles.

Various kinds of protected carboxylic acids have been considered and their respective advantages and disadvantages have been established. These included esters and thioesters wherein deprotection is by hydrolysis, and terminal olefins wherein the acid group is created by ozonolysis.

Systems were identified wherein particle synthesis and subsequent installation of carboxylic acids could be achieved in high yield and with excellent control over particle size and uniformity. The loading of acid groups in these particles has been established and the ability to use these acid groups for anchoring active biomolecules has been demonstrated.

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## 1. Introduction

Carboxylic acid functionalized surfaces (e.g. on silicon wafers or silica particles etc.) are of interest for a wide range of applications in

surface science [1–5], electrochemistry [6], biology [7], biomineralization [8], surface engineering [9], sensor development [24] and nanoparticles [10]. Such materials are also important due to the pH dependence of their charge and solubility in water. If heavily functionalized, carboxylic acid bearing particles can also provide a high density of anchoring sites for enzymes and other biomolecules. This would facilitate the examination of the bioactivity of bound biomolecules.

\* Corresponding author.

E-mail address: [chaim.sukenik@biu.ac.il](mailto:chaim.sukenik@biu.ac.il) (C.N. Sukenik).

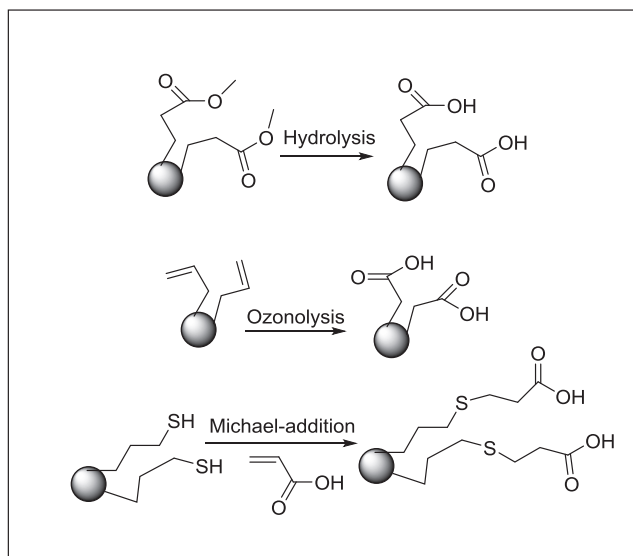


Fig. 1. Syntheses of carboxylic acid functionalized silica particles.

One approach to making silica particles bearing carboxylic acid groups is based on modifying particles that are coated with 3-aminopropyl triethoxysilane and reacted with glutaric anhydride [11,12]. Another approach modifies the silica with self-assembled monolayers of an appropriate trichlorosilane/trialkoxysilane. In such cases, the carboxylate must be masked to ensure compatibility with the hydrolyzable silane anchoring group. This masking has been achieved using monolayers terminated with vinyl groups, esters and thioesters and then liberating the acid functionality by ozonolysis, hydrolysis or oxidation [13–18]. A third approach is to use the surface polymerization of poly(acrylic acid) (PAA) or poly(methacrylic acid) [poly(MAA)] [19].

Our goal was to make silica particles with particularly heavy loading of acid groups. Using modified Stöber syntheses, we used monomers with built-in masked acid groups to synthesize the silica particles. If the deprotection could be done efficiently, this would guarantee that each silicon atom within the entire particle would have an attached acid group.

The three kinds of particles used in this study are shown schematically in Fig. 1. We investigated two protected acids: methyl esters that are deprotected by hydrolysis and terminal olefins that are deprotected by ozonolysis. A third strategy was to make thiol functionalized particles and react them with acrylic acid to install acid groups by Michael addition chemistry.

In recent years there have been a number of significant advances in the methodologies available for making functionalized silica particles with good control over size and dispersity. Lee et al. [20] synthesized silica particles using a sol–gel reaction that included a functionalized organosilane precursor (no TEOS) without adding ethanol and with no surfactants. This one-pot route gave microparticles wherein size selectivity was controlled by the concentration of the organosilane and the reaction temperature. The main limitation of this process was that it made microparticles not nanoparticles.

Nanometric monodisperse silica spheres were reported by Meng [21] using a one-step procedure that resulted in 30–200 nm silica particles. These particles were prepared under conditions compatible with various organic functional groups. This one-step silica particle preparation can make colloidal hybrid particles with pendant thiols [20], vinyl groups [20,21], octyl chains [20], and phenyl groups [20] but fails for the more polar 3-aminopropyltriethoxysilane [21].

We have identified only one precedent for highly loaded silica particles bearing carboxylic acid groups. Shen et al. [22] reported the reaction between mercaptoacetic acid and a vinyl-functionalized particle (thiol-ene chemistry) as a route to such particles. Their reported loading of acid groups was 100  $\mu\text{mole/g}$ .

We report herein the preparation and modification of hybrid silica particles prepared by the one-pot approach of Lee et al. [20] and Meng et al. [21]. We explore the preparation of particles with a number of different kinds of acid precursors and define the kinds of functional groups that are compatible with such particle preparation. We focus on the preparation and hydrolysis of methyl ester bearing particles along with the preparation and ozonolysis of olefin decorated particles using both vinyl and allyl silanes. So too, thiol particles and their reaction to form acid decorated particles via Michael addition chemistry is described. These approaches allow us to control particle size in both the micron and nanometer domain and to achieve a loading of acid groups that are as much as 30 times higher than what had been previously reported. In one case, the accessibility and reactivity of the acid groups was tested by attaching an active biomolecule (kanamycin).

## 2. Experiment

### 2.1. Materials and methods

Vinyltriethoxysilane (VTES) and mercaptopropyltrimethoxysilane and sodium dodecylbenzene sulfonate (SDBS) were obtained from Acros, allyltriethoxysilane from Alfa Aesar, and 2-(carbomethoxy) ethyltrimethoxysilane (CMTMS) from Gelest. Ammonium hydroxide (28–30%) was supplied by Frutarom Ltd. All chemicals were used as received without further purification. Water was deionized and then distilled in an all-glass apparatus. Ozone was created using an Ozomax (Model: OZO 2VTT) ozone generator by flowing oxygen or air through an electrical discharge ozone generator.

Sonication was done using a Telsonic, TPC-15 ultrasonic cleaning bath containing two transducers with an operating frequency of 30 kHz and ultrasonic peak output maximum of 150 W per transducer.

### 2.2. Analyses

**IR**—spectra were measured as KBr pellets using a Bruker Vector 22 Infra Red spectrometer equipped with a liquid nitrogen-cooled MCT detector (500 scans, spectral resolution  $4\text{ cm}^{-1}$ ). The background was collected using a KBr pellet containing untreated  $\text{SiO}_2$  particles. Automatic baseline correction and water subtraction were applied to the resulting spectra.

**Solid NMR**—The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were acquired on a Bruker Advance III 500 MHz spectrometer using a 4 mm VTN CPMAS HX probe, covering the necessary frequency range, using MAS at (typically) 8 kHz. Cross polarization (CP) experiments were carried out using a typical ramped pulse on the protons and a square pulse of 43 kHz on  $^{13}\text{C}$  and  $^{29}\text{Si}$ . Decoupling power using the SPINAL64 scheme at a field of 88 kHz was used in all experiments. Typical CP contact times were 2 ms ( $^{13}\text{C}$ ) and 0.25 ms ( $^{29}\text{Si}$ ).

**Elemental analysis** of the particles was performed using a Model EA1110, CE Instrument (Thermoquast).

**TEM**—Transmission electron microscopy images were obtained with a FEI TECNAI C2 BIOTWIN electron microscope with 120 kV accelerating voltage. Samples for TEM were prepared by placing a drop of dispersed particles on a 400-mesh carbon-coated copper grid.

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