

Surface modification of porous silicon microparticles by sonochemistry†

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Ultrasound is employed to functionalize the surface of porous silicon microparticles at room temperature with unsaturated organic compounds, with no need for heating or for UV treatment.

Sonochemistry is the application of ultrasound to activate or modify the rate of chemical reactions in liquid media. It has proven effective to speed up chemical reactions.¹ Acoustic cavitation at the solid–liquid interface induces bubble collapse,² which is the mechanism responsible for sonochemical effects in liquids.¹ The cavitation collapse of bubbles causes intense localized heating, producing hot spots where the temperature could increase up to 5000 °C, and pressure up to about 500 atmospheres, with a lifetime of few microseconds.² As reported by Suslick, the shock waves from cavitation in liquid–solid slurries produce high-velocity interparticle collisions, the impact of which is sufficient to melt most metals.^{1,2} In the literature, different effects of ultrasound on chemical reactions have been demonstrated, such as decreasing reaction times and enhancement of the reactivity of reagents.^{1,3–5} Sonochemistry has also been recently employed for the synthesis and functionalization of nanomaterials,^{3,5–9} in particular to deposit nanosized materials (metals, metal oxides, semiconductors) into the pores of mesoporous materials,¹⁰ or onto the surfaces of ceramics and polymers,^{11,12} or to form spherical proteins.¹³

In the past decade, ultrasound has also been used to prepare colloidal suspensions in a variety of solvents (methanol, ethanol, toluene...), and to obtain porous silicon (pSi) particles.^{14,15} In fact, Heinrich *et al.* demonstrated that electrochemically etched Si wafers were dispersed by ultrasound, forming Si particles,¹⁴ by their disruptive mechanical action. The authors stated that such a technique for producing Si particles avoided the formation of contaminants, compared to other conventional grinding techniques. Moreover, the size of the particles can be tuned according to the ultrasound exposure time: the longer the pSi membrane is

exposed to ultrasound, the smaller the size of the particles formed. In this manner it's possible to create nanoparticles of pSi.¹⁶ However, membrane sonication it is not the only method to fabricate pSi particles: even if not widely used, ball milling is an alternative approach.^{17–19}

In this paper, sonochemistry is employed to fabricate and functionalize porous silicon (pSi) microparticles with olefins. pSi particles formed by electrochemical anodization are usually used as a vector for drug delivery,^{20–24} because their porosity, pore size and surface areas can be accurately tuned by adjusting the electrochemical conditions.²⁵ Freshly etched pSi is unstable in aqueous media due to oxidation of the reactive surface hydrides,²⁶ and therefore, surface modification is necessary in order to improve stability and to introduce functional groups useful for further conjugations.²⁷ Various approaches have been proposed to functionalize the internal and external surfaces of the porous matrices in a controllable way,^{28,29} and to improve their stability under physiological conditions.^{27,30} There is a real need to improve the stability of pSi and avoid its oxidation during functionalization. The sonochemical reaction can combine formation and functionalization of pSi microparticles with a reduced processing time and oxidation rate.

Porous Si microparticles were prepared by electrochemical etching of highly doped, (100)-oriented, p-type Si wafers in a solution of 20% aqueous hydrofluoric acid diluted in absolute ethanol. A Si wafer with an exposed area of 7.065 cm² was etched at a constant current density of 192 mA cm⁻² for 15 cycles comprising 1 s of etching and 1 s of stopping to avoid the formation of a depletion layer. The resulting porous layer was then lifted off by electropolishing with a current pulse of density of 353.8 mA cm⁻² for 15 s. The etching and electropolishing procedure was repeated 20 times per wafer. The free-standing Si film formed after the electrochemical reaction was rinsed in ethanol, and immersed either in pure 10-undecenoic acid, or in pure 1-dodecene, or in pure octane or absolute ethanol, the latter two being the control conditions, and fractured into millimeter to micron-sized pieces in an ultrasonic bath for 2 h.¹⁴ The pSi membrane is converted into microparticles under sonication.³¹ In order to compare the quality of the surface functionalization, the

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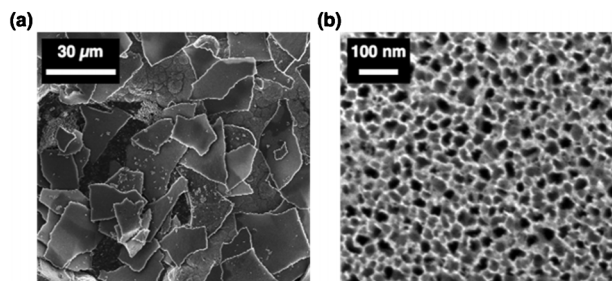


Fig. 1 FESEM images of the pSi microparticles: (a) pSi particles obtained after 2 h of sonication in ethanol, the scale bar corresponds to 30 μm ; (b) magnification of the surface of the particle, the scale bar correspond to 100 nm.

particles formed in ethanol were afterwards thermally hydrosilylated with neat undecenoic acid at 120 $^{\circ}\text{C}$ for 120 min under argon. The particles were collected by centrifugation at 4000 rpm for 5 min, the excess solvent was removed and the particles were rinsed with acetone and then with ethanol.

The topology of the pSi microparticles, such as their porosity and thickness, were characterized by field emission scanning electron microscopy (FESEM) and by optical interferometry.

Fig. 1 shows the FESEM surface images of a pSi microparticle sonicated in ethanol for 2 h (Fig. 1a) and a magnification of the surface highlighting the porous structure (Fig. 1b), with pores size ranging from 17 nm to 27 nm. Table 1 presents the average particles size obtained by sonication in different organic solvents. A comparison between the sizes of the particles does not provide evidence of any particular effect of the different organic solvents. Therefore, the size of the particles is independent of the nature of the organic solvent used for formation during the sonication process.

The porosity of the microparticles was optically determined by measuring the reflectance spectrum of a pSi film not lifted from the silicon substrate, synthesized under the same conditions. The spectrum, collected over the range 200–3200 nm, displays fringes, which result from Fabry–Pérot interferences at the two boundaries of the pSi layer (data not shown).³² The porosity and the thickness were estimated by means of a commercial software SCOUT, based on the transfer matrix method, that calculates a best-fit of the experimental reflectance spectrum.³³ The resulting porosity was 77% and the thickness 0.94 μm for the freshly etched pSi film, confirming the value of the thickness obtained by FESEM.

Micro-Fourier transform infrared (FT-IR) spectroscopy was used to characterize the chemical groups present on the surface of the microparticles formed by sonicating a pSi membrane in an ultrasound bath for 2 h in the presence of different organic solvents (Fig. 2): ethanol (A), octane (B), 1-dodecene (C),

1-undecenoic acid (D) or ethanol followed by hydrosilylation with undecenoic acid (E). A 100 μl drop of the microparticles solution was deposited onto a p-doped silicon substrate (2–6 $\Omega\text{ cm}$) and let it dry prior to the measurement. For all the spectra, a 15 \times objective lens was used and the measurements were performed in the transmission mode. The commercial software OPUS was used for spectra acquisition, processing, and analysis. After the acquisition the baseline correction routine from OPUS was applied to linearize the spectra.

Spectrum A of Fig. 2 exhibits bands at 908 and 2103 cm^{-1} , which are assigned to the Si–H₂ bending mode and the SiH_x stretching mode, respectively. The presence of weak bands at 2926 and 2855 cm^{-1} could be assigned to a negligible contamination by aliphatic species. Spectrum B presents the specific bands of the SiH₂ and exhibits a band at 1068 cm^{-1} assigned to the Si–O stretching vibration mode, attesting to the presence of silicon oxide on the surface of pSi that forms during the ultrasonication process. Spectrum C displays bands at 1458, 2926 and 2855 cm^{-1} which are assigned to the deformation and stretching (symmetric and asymmetric) vibration modes of the aliphatic C–H₂ groups, respectively, confirming the success of the grafting of dodecene during the ultrasound formation of the particles in the presence of dodecene. The absence of the characteristic bands for C=C bonds (at 1637 cm^{-1}) and for =CH₂ stretching (at 3076 cm^{-1}) strongly suggests that dodecene is covalently attached to the porous silicon surface, presumably through the C1 carbon of dodecene, and the rinsing process removes unbound molecules. Sonication in the presence of undecenoic acid produced characteristic bands (spectrum D) at 1713 cm^{-1} , assigned to the $\nu_{\text{C=O}}$ stretching vibration mode of the carboxylic acid, and bands at 1458, 2926 and 2855 cm^{-1} assigned to the deformation and stretching (symmetric and asymmetric) vibration modes of the aliphatic C–H₂ groups, respectively. The presence of bands at 908 and 2103 cm^{-1} , respectively assigned to the Si–H₂ bending mode and to the Si–H_x stretching mode, indicates that part of the silicon hydride remains unreacted at the pSi surface.^{34,35} In spectrum D the band at 1068 cm^{-1} assigned to the Si–O stretching vibration mode attests to the presence of silicon oxide on the surface of pSi. The higher intensity of the band at 1068 cm^{-1} for spectrum C with respect to spectrum D, indicates a greater amount of oxidation for the samples modified with undecylenic acid compared to the samples modified with dodecene. Taking into account that the sonochemical reactions were conducted in air, a larger amount of atmospheric water is dissolved within undecylenic acid compared to dodecene, because of the higher hydrophilicity of the former with respect to the latter. In addition, the large broad band formed at 3465 cm^{-1} is associated to the O–H stretching vibration mode. Like in spectrum C, the absence of the characteristic bands of

Table 1 Size of the pSi particles obtained after sonication in different organic solvents, measured by SEM

	Sonication in ethanol	Sonication in dodecene	Sonication in undecenoic acid
Length	20.4 \pm 7.0 μm	14.7 \pm 7.8 μm	21.3 \pm 3.9 μm
Width	14.8 \pm 6.3 μm	10.4 \pm 4.1 μm	11.3 \pm 1.9 μm
Thickness	1.9 \pm 0.1 μm	0.7 \pm 0.3 μm	1.5 \pm 0.2 μm

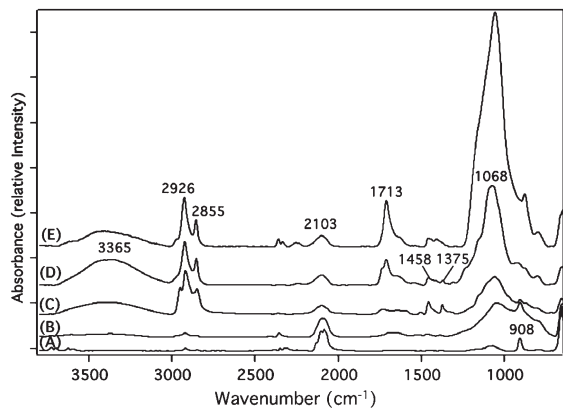
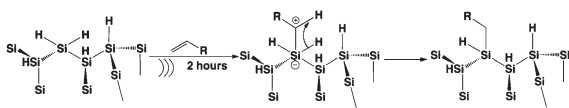


Fig. 2 FT-IR spectra for the pSi microparticles modified by ultrasonication in organic solvents: (A) after 2 h of sonication in ethanol, (B) after 2 h of sonication in octane, (C) after 2 h of sonication in dodecene, (D) after 2 h of sonication in undecenoic acid, (E) hydrosilylation of (A) for 2 h with undecenoic acid. The spectra are base line corrected.

unsaturated groups suggests that undecenoic acid is covalently bonded to the porous silicon surface. Spectrum E (sonication in ethanol and hydrosilylation with undecenoic acid) presents the same specific bands as spectrum D, but the band at 1068 cm^{-1} assigned to the Si–O stretching vibration mode is more intense. Oxidation of the particles most likely occurred during thermal hydrosilylation despite the fact that the reaction was performed under an inert atmosphere, as proven by the weak intensity of the Si–O band (1068 cm^{-1}) before thermal hydrosilylation (spectrum A).

The FT-IR data confirm the covalent attachment of unsaturated compounds (1-dodecene or 1-undecenoic acid) to the pSi surface. The absence of the carbon-carbon (C=C) double bond stretching at 1640 cm^{-1} allows us to suppose that the bond is formed through the C=C double bond. According to the FT-IR result we can reasonably confirm the chemical reaction pathway presented in Scheme 1. We have noted that the sonochemical functionalisation limits the oxidation of the pSi surface, despite the fact that the reaction didn't occur under an inert atmosphere.

At high temperatures, the surface of the silicon hydride, in the presence of the alkene, is either oxidized or hydrosilylated. Fig. 2 (Spectrum E) bears out the concomitant process of hydrosilylation (by the alkene) and oxidation. Hydrosilylation generated by sonochemistry performed at room temperature (Spectrum D), presents a low level of oxidation. The oxidation observed for the sample sonicated in ethanol and modified by hydrosilylation can be associated with the heating that occurs during the reaction. The



Scheme 1 The reaction pathway for the modification of the pSi surface by ultrasound irradiation. Hot spots, generated at the surface of pSi by bubble collapse, allow the direct nucleophilic attack by the π electron rich double bond.

oxidation of the surface can be influenced by the temperature at which the thermal hydrosilylation is performed ($120\text{ }^\circ\text{C}$).^{34,36} On the other hand, the bulk temperature of the pSi particles sonicated in ethanol or with alkenes does not significantly increase, thus reducing the oxidation rate. Suslick and Casadonte reported that high-intensity ultrasound generates some bubbles that can collapse and generate a high-speed jet of liquid directed at the surface.² This difference in temperature between sonochemical hydrosilylation and thermal hydrosilylation can explain the different amounts of Si–O groups formed at the surface (Fig. 2).

The high speed jets of liquid formed during the sonochemical process can also affect the stability of the material, thus causing mechanical stress, shown as fractures or cracks in the weaker parts of the porous structure. These generated defects are very reactive and could take part to the reaction pathway.

We have proposed a different way to graft alkenes (1-undecenoic acid or 1-dodecene) to the surface of pSi microparticles using a sonochemical reaction in an ultrasonic bath. Such a method guarantees minimum oxidation of the pSi surface and performs as well as hydrosilylation of alkenes in terms of the amount of species grafted on the surface. The FT-IR analyses performed demonstrate the successful modification, and supports the thesis of direct nucleophilic attack by the double bond; in fact, no grafting was observed with a saturated compound (octane).

To conclude, sonochemical hydrosilylation is a one step procedure, providing a fast method of surface modification and reducing oxidation at the surface of the pSi samples compared to classically used thermal hydrosilylation. Sonochemistry using pSi opens new avenues to process and modify nanostructured materials, and could be employed for many applications.

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