

Vibrational study on styrene functionalized porous silicon: A method for determining the relative yield of different grafting routes

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Abstract

A new semi-quantitative method providing the relative efficiency of three different organic functionalization reactions onto porous silicon has been set up, based on infrared absorption data. Compared to previously reported techniques, it enables a direct titration of the grafted molecules. We demonstrated that grafting of Si-styrenyl moieties by ethylaluminum dichloride mediated hydrosilylation of phenylacetylene leads to higher yields than organometallic addition onto either hydrogenated or brominated silicon.
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1. Introduction

Porous silicon (por-Si) owes its initial consideration to its being a light emitting material at room temperature [1,2]. Later on, it was found to be usable also in completely different technological frames, ranging from bio-recognition [3,4] to prosthetic systems [5], from catalysis [6] to chemical sensing [7]. Whatever its application is, por-Si surface termination is of fundamental importance [8–11]: the grafting of chemical functionalities for specific applications is an example of how tailoring interfacial properties multiplies the opportunities of use for a single material. Obviously, these functionalities must be etch-resistant: organic molecules covalently bonded through silicon–carbon have to lead to stable modified por-Si surfaces [12].

Methods achieving molecular grafting onto por-Si make use of (1) metallorganic species such as Grignard [13] or lithiated [8,14–16] compounds onto hydrogen or halogen [17] terminated surface; (2) cathodic or anodic electrograft-

ing onto Si–H-terminated surface [18–20]; (3) either thermally induced [21,22,10], exciton-mediated [23], triphenylcarbenium cation [24] mediated, microwave assisted [25], or Lewis acid mediated [26] hydrosilylation reactions; or (4) photochemical reaction involving diazomethane or similar species [27].

In this paper we have carried out a vibrational study to compare three different grafting methods, all in principle leading to the formation of the same styrenyl-terminated porous silicon: (1) functionalization through styrenylmagnesium bromide on hydrides-terminated surface; (2) functionalization through styrenylmagnesium bromide on bromine-terminated surface; and (3) functionalization through EtAlCl₂ mediated hydrosilylation of phenylacetylene on hydrides-terminated surface. Their vibrational spectra were studied in depth, paying special attention to modifications occurring after each chemical step (grafting, water rinsing, re-hydrogenation) in order to give an extensive assignment of the absorption signals [28]. To the aim of evaluating the reaction yield, a method for semi-quantitative analysis of the relative surface coverage has been put forward based on the integral absorbance of the Si_{surf}CH=CHPh stretching mode.

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2. Experimental section

2.1. Porous p-silicon surface preparation

Porous silicon samples were prepared by galvanostatic photoetch of p-Si (B-doped, 6–8 Ω cm, (100) oriented). The etching solution was a 1:1 solution of ethanol (Fluka, 99.8%) and HF (Riedel de Haen, 48% wt.). A cell made of two polyethylene plates was used: the sample (2×2 cm²) was inserted in between. Back-contacts to Si were obtained by using a Cu strip protected from the solution by two Viton O-rings. Si back-surface was previously scratched with a diamond tip and a ohmic Si–Cu was made by applying an InGa film onto Si. A Pt strip was used as a counter-electrode. Samples were etched at an anodization current density of 7.1 mA/cm² for 30 min. The etching reaction was carried out under ambient conditions. After etching, the sample was rinsed in CH₂Cl₂ (Fluka, 99.8%) and dried under N₂ for 30 min. As-prepared porous silicon is hydrogen terminated. This process is expected to provide a thick porous layer that can be examined by infrared spectroscopy [26].

2.2. Brominated surface preparation

The bromination reaction was carried out in a flat-bottom flask under N₂ flux where hydrogenated porous silicon samples were let react for 30 min in a 1×10^{-1} M solution of bromine in dry and deoxygenated CH₂Cl₂ under illumination.

2.3. Functionalization with in-lab synthesized styrenemagnesium bromide [13]

The functionalization reaction was carried out in a flat-bottom flask under N₂ flux where hydrogenated or brominated porous samples were let react with 5 ml of PhCH=CHMgBr 1 M in THF, for 5, 13 and 24 h. The solution was added at 0 °C and then let warm back to room temperature. Afterwards, it was removed and 5 ml of HCl in diethyl ether, used as quenching reagent [16], was added preventing any contact with air. The sample was rinsed in CH₂Cl₂. A first IR spectrum was then measured. The sample was put under N₂ flux in a deoxygenated HCl 37% aqueous solution, removing crystallization salt without oxidising surface. The sample was finally re-hydrogenated in an HF:ethanol = 1:1 solution, so that Si–O formed during grafting is moved out. Dichloromethane was always used as rinsing solvent. In order to monitor the effect of the previous three steps, after each of them an IR spectrum was collected.

Styrenemagnesium bromide was synthesized as follows: 124 mmol of magnesium turnings, previously activated in dry ether for 5 h at 130 °C, were mechanically stirred at room temperature overnight under N₂, with a small quantity of I₂. Then 24 ml of THF were added to the flask, which was subsequently put in a bath of acetone/liquid

N₂ (–78 °C). Afterward, 25 mmol of ultra pure isomeric β -bromostyrene (Sigma Aldrich, 98%) was added drop by drop and the flask was warmed slowly to 0 °C. The solution was then left under stirring for 1 h at 0 °C for the reaction to reach completion.

2.4. Functionalization with EtAlCl₂ mediated hydrosilylation of phenylacetylene [26]

The functionalization reaction was carried out in a flat-bottom flask under N₂ flux where hydrogenated silicon samples were let react 30 min with 4 ml of ethylaluminium dichloride (1 M in hexane, Sigma Aldrich) at 0 °C. Afterward, 4 ml of hexane (anhydrous, 98%, Sigma Aldrich) and 8 ml of trichloroethylene (anhydrous, 99%, Sigma Aldrich) were added and 0.5 ml of phenylacetylene (99%, Sigma Aldrich) were slowly dropped in the mixture, always kept at 0 °C. The dilution of the catalyst solution was needed because otherwise a reaction in homogeneous phase occurs between phenylacetylene and EtAlCl₂, forming a by-product (possibly a trimerization compound [29]) whose consistency goes from compact solid to fine powder depending on the amount of diluents and on the use of an ultrasonic bath. The reaction lasted 3 h and was carried out at room temperature. Afterwards, the solution was removed and the sample rinsed in CH₂Cl₂, then rinsed in pure (GR for analysis, MERCK, conductance at 25 °C ≤ 1 μ S/cm) water, and finally re-hydrogenated. At the end of each of the three final steps an IR spectrum was collected.

2.5. Infrared spectroscopic measurements

Fourier Transform Infrared (FT-IR) spectra were measured in transmission configuration at room temperature. A BIORAD FTS 6000 spectrophotometer was used, with a resolution of 4 cm⁻¹. Prior to each measurement the sample chamber was purged with a flux of dry nitrogen; 256 interferograms were acquired for each spectrum. Integral absorbance values were normalized toward the initial integral absorbance of Si–H_x groups (supposedly proportional to the number of sites available for reaction): this is expected to correct to some extent geometrical factors responsible for fictitious intensity differences, allowing different samples to be compared.

Decomposition of FT-IR spectra was carried out by assuming Gaussian bandshapes. This finds a rationale considering the distribution of moiety bond lengths and angles on porous silicon surfaces.

3. Results and discussion

For the sake of brevity, the surface terminations achieved by the three different methods are labelled as Gr/H (styrenylmagnesium bromide onto hydrides terminated porous silicon), Gr/Br (styrenylmagnesium bromide species onto bromine-terminated porous silicon) and

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