

Thermally Carbonized Porous Silicon and Its Recent Applications

Jarno Salonen* and Ermei Mäkilä

Recent progress in research on thermally carbonized porous silicon (TCPSi) and its applications is reported. Despite a slow start, thermal carbonization has now started to gain interest mainly due to new emerging areas for applications. These new areas, such as optical sensing, drug delivery, and energy storage, require stable surface chemistry and physical properties. TCPSi is known to have all of these desired properties. Herein, the above-listed properties of TCPSi are summarized, and the carbonization processes, functionalization, and characterization of TCPSi are reviewed. Moreover, some of the emerging fields of TCPSi applications are discussed and recent advances in the fields are introduced.

1. Introduction

The formation of porous silicon (PSi) has already been known since 1956,^[1] but the phenomenon remained a peculiarity of the electrochemical polishing of silicon wafers until the 1970s. The porous nature of the silicon structure was first suggested soon after the initial discovery by Turner,^[2] but it was presumably named as porous silicon for the first time in a paper by Watanabe and Sakai in 1971, although they used the phrase “anode film” in the title of the paper.^[3]

Despite intense studies on the electrochemistry of silicon in the 1960s, PSi did not receive much more than cursory attention until 1973 when Watanabe et al. introduced a process to selectively etch and then convert the formed PSi into electrically isolating SiO₂.^[4] This approach eventually matured into an industrial silicon-on-insulator wafer fabrication technique^[5] called the epitaxial layer transfer process.^[6] With the applications focusing on electronic insulation, the chemical stability of PSi was not an acute concern, as its role was either to provide a

facile route for selective and fast oxidation or to be a sacrificial layer, enabling wafer splitting.

After Canham reported a strong visible photoluminescence at room temperature in 1990,^[7] the chemical stability of PSi started to raise some interests and concerns among PSi researchers for the first time. Quite quickly, after the initial articles on the photoluminescence of PSi, the lack of chemical stability of the anodized PSi was recognized as a serious problem considering the applications of photoluminescence. This was seen as even more drastic issue for electrolumi-


nescence applications, also including electrical issues at PSi/electrode interfaces.^[8] This then led to numerous reports on different methods to stabilize PSi,^[9] but none of them seemed to be fully applicable considering electrooptical applications. Despite intense research on the topic, the quantum efficiency of electroluminescence devices based on PSi remained low, and the interest in luminescence-related applications started to wane. Fortunately, after the initial spark of interest, new areas of applications began to rapidly emerge and PSi became an increasingly popular material to study, with over 1200 articles published still in 2016 alone. Also, new methods and approaches for producing novel PSi structures are published continuously.^[10,11]

Figure 1 shows the results of a bibliographic survey of PSi and of how the various fields of PSi research have changed during the last decades. While some areas of research have decreasing numbers of publications, like luminescence, there are new emerging fields, such as drug delivery and battery technology which, together with steadily increasing optical and sensor applications, account for the annual increase in publications.

This interest is quite understandable as PSi is a very versatile material. A large surface area is common to mesoporous materials, such as silica and metal-organic framework, but an easily adjustable pore size, even during the etching, and many different routes for surface functionalization distinguish PSi from many other mesoporous materials. Other differentiating properties are good mechanical and reasonable hydrolytic stabilities. The pore structure does not collapse, even in the case of high porosity, during a solution phase drug loading and drying cycles. PSi may become oxidized, but the pore structure still remains intact.

Some of the properties can be seen as both drawbacks and advantages. One of the most commonly obtained pore structure is shown in **Figure 2a**. Instead of a smooth, regularly arranged pore structure, like in the bottom-up materials, the pores in PSi are usually branching (fir-tree type structure) and form a naturally hierarchical porosity. The pore structure depends on the

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fabrication parameters and properties of the initial Si, and can be varied from moderately smooth and columnar pores to a sponge-like, almost randomly orientated interconnecting pore network.^[12] In addition, a top-down approach enables many other interesting possibilities, such as porosification of already fabricated nanoscale structures like nanoneedles is shown in Figure 2b.

An adjustable pore morphology together with a surface chemistry that can be easily modified offer an excellent platform for many different applications including different kinds of sensing applications.^[14,15] For instance, the refractive index of PSi is strictly dependent on the porosity and can be controlled by the current density of electrochemical etching. This enables the simple, yet precise control of the refractive index, allowing the fabrication of highly complex optical structures for many interesting applications.^[15,16]

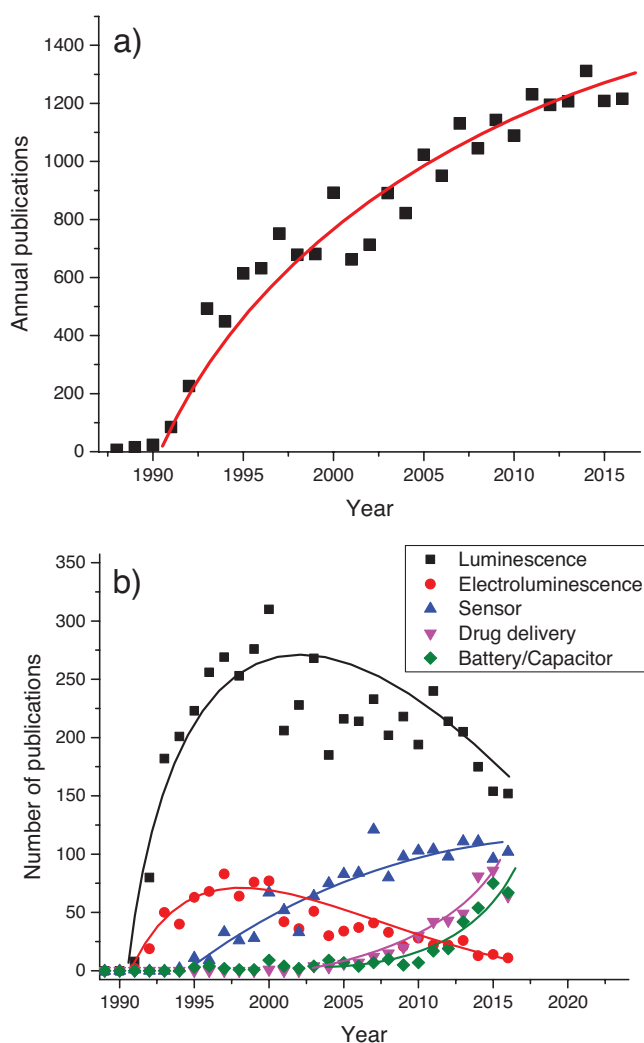


Figure 1. Bibliographic survey of PSi research in 1987–2016. The survey was conducted using Web of Science and certain keyword combinations with PSi (presented in the Figure). a) shows the total number of papers published annually related to PSi and b) a survey of publications under the additional keywords (PSi + keyword). “Luminescence” includes results of “electroluminescence” and “optical” may also contain some luminescence-related articles.



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Nevertheless, one of the most fascinating properties of PSi is its variable biocompatibility already discovered in 1995.^[17] This is also a quite unique property compared to many other mesoporous materials. Depending on its porosity, PSi can be bioinert (low porosity), bioactive (medium), or bioresorbable (medium to high).^[18–20] This enables interesting bioactive, but also bioresorbable biomaterial applications, in which, for instance, the PSi skeleton slowly dissolves while promoting the formation of hydroxyapatite on it.^[20] The variable biocompatibility also enables the controlled dissolution of PSi in biological environments. The dissolution rate of PSi in biologically relevant media can be tuned from mere hours to months by simply changing the morphology of the porosity or by changing the surface chemistry.^[21] In addition, the dissolution product of PSi in a biological medium, orthosilicic acid, is essentially a dietary form of silicon for higher animals and important, e.g., for normal bone growth.^[22]

All of these new applications need some sort of additional stability. For example, even though in certain drug delivery application stability of a few hours would be enough, the carrier material should not react or cause any degradation to the drug payload loaded in the pores. In the sustained drug release applications, extended stability was desired. Example applications, where the outermost stability is needed, are different kinds of sensor applications, where a stability expanding over several years is needed. It is also worth noting that the majority of these new applications do not rely on the luminescent properties of PSi.

Besides the different oxidation methods for stabilizing PSi, which were the first to be used, it took almost a decade before methods, which would not drastically change the chemical

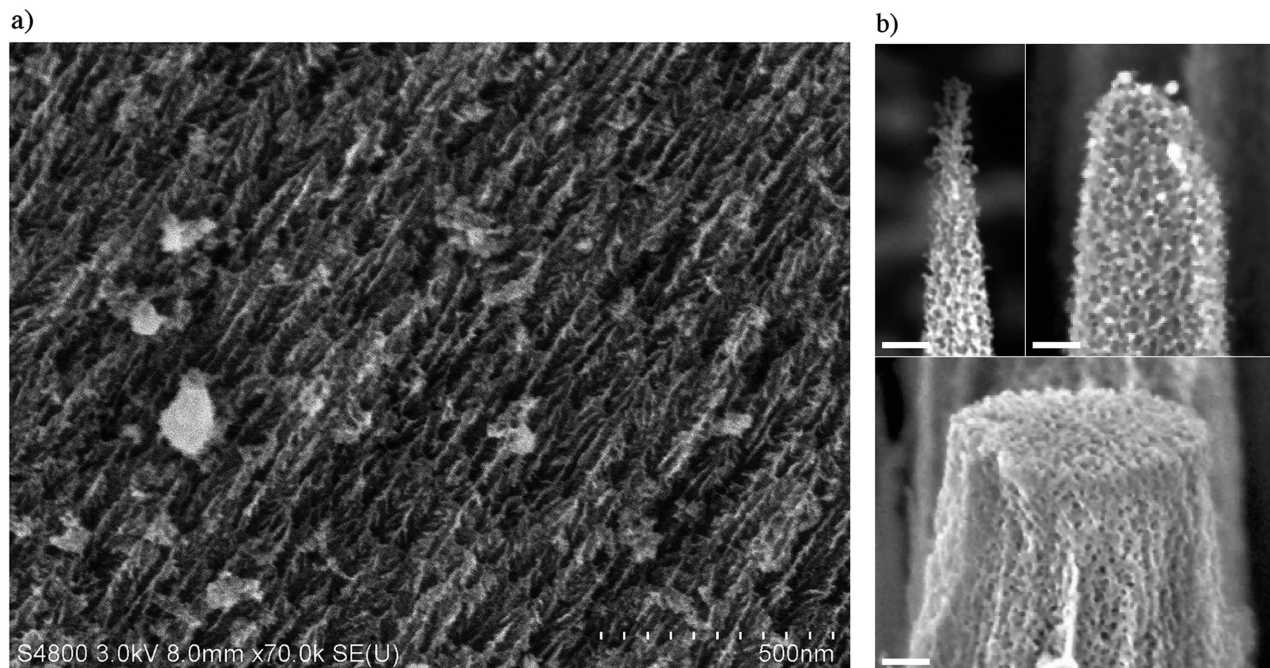


Figure 2. a) Semi-cross-sectional SEM image of PSi with clearly branching, fir-tree type structures and b) postfabrication porosified mesoporous silicon nanoneedles (scale bars = 2 μm). a) Reproduced with permission.^[13] Copyright 2014, American Chemical Society. b) Reproduced with permission.^[11] Copyright 2015, Nature Publishing Group.

composition of PSi, were reported.^[23] Most of these methods were related to the creation of Si–C bonds on the surface of PSi.^[24] These bonds are much more stable against chemical degradation than oxides or other surface chemistries proposed so far.^[25]

One of the most convenient methods for creating Si–C bonds is hydrosilylation using liquid aliphatic organic compounds.^[25] In hydrosilylation, unsaturated bonds of alkenes or alkynes react with hydrides on the as-anodized PSi surface leading to the formation of covalent Si–C bonds. The reaction can be conducted catalytically, but there are also other ways to initiate the reactions, such as light,^[26] heat,^[27] electrografting,^[28] etc.^[29] In **Figure 3** some examples of surface functionalizations

produced by thermal hydrosilylation are shown. At the end of the 1990s, a number of different approaches for hydrosilylation were published and significant improvements were achieved in the stability of PSi.^[18,30] Most importantly, the electrical, optical, and even luminescent properties remained almost intact when compared to the as-anodized PSi. However, the stability achieved with liquid alkenes or alkynes was not enough for certain applications. With long hydrocarbon chains, the extent of the hydrosilylation reaction is, however, limited. On flat Si(111), the maximum obtained surface coverage reaches 50–70% and is limited by steric hindrance of the adjacent chains.^[31] With PSi, the lack of well-defined surfaces, and the presence of morphological features that prevent the entry of

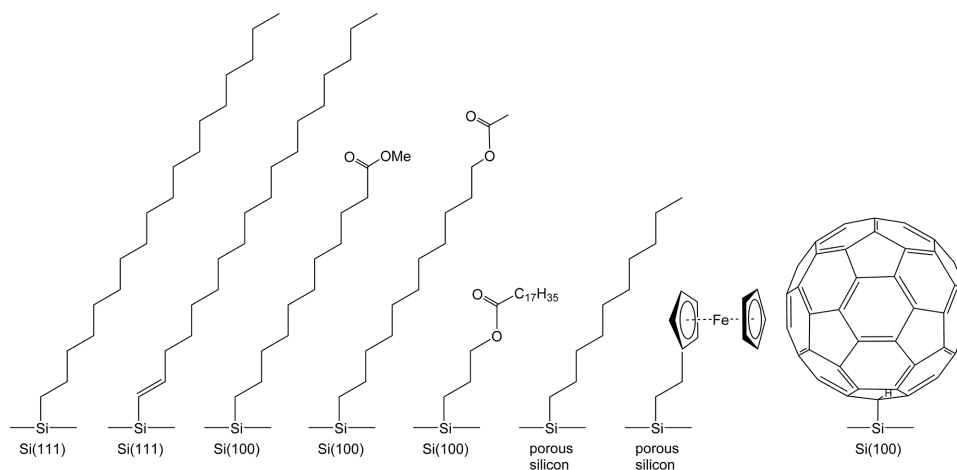


Figure 3. Examples of surface functionalizations produced by thermal hydrosilylation. Redrawn with permission.^[25] Copyright 2002, American Chemical Society.

long molecules, the highest obtainable coverages are by necessity smaller than under ideal circumstances.^[32] Utilization of mixed layers of two types of guest molecules has, however, been shown to enable greater coverage with hydrosilylated PSi. Lees et al.^[33] demonstrated that methyl endcapping with iodomethane enhanced the stability of PSi against oxidation and hydrolysis as the small molecule was able to reach much of the remaining hydrides on the surface of the PSi. While hydrosilylated PSi is partially prone to hydrolysis, the achieved stability is often more than enough for various applications. For this reason, hydrosilylation is one of the most common stabilization methods applied on PSi.

At the same time with hydrosilylation studies, the first reports on the thermal carbonization of PSi were published.^[34,35] At the beginning they did not gain much attention in the PSi community. This was most probably because these treatments required far higher treatment temperatures combined with gaseous carbon source, such as acetylene or ethylene. Nevertheless, using a small gaseous molecule as the carbon source for the treatment overcame the problems of using liquid hydrocarbons as the source. Fast diffusion even in the smallest pores and negligible steric hindrance solved most of the problems related to the hydrosilylation of liquid organic compounds. With this approach, a superb stability compared to other treatments was achieved and, as will be explained later in the paper, this approach also still allowed further chemical modifications of the surface making the surface not only stable, but also functionalizable, which is a very desired property considering, e.g., sophisticated applications for targeted drug delivery.

Even though it is not always simple to assert the difference between thermal hydrosilylation and thermal carbonization, here we have chosen one clear criterium to separate these two treatments from each other. The criterion is the treatment temperature. In thermal hydrosilylation, treatment temperatures over 200 °C are rarely needed, while in thermal carbonization over 400 °C is almost obligatory. An additional criterion could be the physical state of the carbon source while the carbonization takes place. In thermal carbonization the physical state is almost always gaseous, but this is not an exclusive criterion. Also, we do not set any rules for chemical bonding, e.g., the obligatory formation of Si–C bonds. But, even with these loose criteria, it is not easy to distinguish between thermal hydrosilylation and thermal carbonization explicitly, which just goes to show how versatile and adaptable these two methods are.

This progress report is divided into several different sections, which cover different aspects of thermal carbonization and the properties of thermally carbonized PSi. Some of the sections are more detailed than others, but we hope that due to this division into sections, the reader can easily navigate the different topics related to the thermal carbonization of PSi.

2. History of Thermal Carbonization

The adsorption of acetylene and ethylene on different surfaces has been studied already for decades. Acetylene and ethylene are the two simplest hydrocarbon molecules with unsaturated bonds. This makes it easy to understand their role in

fundamental research of adsorption processes. Both were also discovered a long time ago, ethylene in 1669^[36] and acetylene in 1836,^[37] and they are produced industrially in vast quantities enabling cheap and easy experimental setups.

In the 1960s and 1970s, most of the adsorption studies of acetylene and ethylene were related to surfaces of platinum, silver oxide, tungsten, molybdenum, rhenium, etc. Semiconductor surfaces were mentioned in only a few papers. This changed in the late 1980s when papers on acetylene adsorption and thermal decomposition on different Si surfaces were published. The high reactivity of decomposed acetylene and ethylene with Si (100) and (111) surfaces raised hopes to find an inexpensive method to form an epitaxial silicon carbide (SiC) layer on the Si wafer. SiC has many advantageous properties compared with Si, but the price of SiC wafers has been a limiting factor for its wider use in microelectronics. Understandably, this kind of a potential method for overcoming the price issue of SiC gained interest in the research community. Since the pioneering works of Yoshinobu et al.^[38] there has been a continuous interest to study the thermal carbonization of Si with acetylene and ethylene.

Despite the challenges in producing an epitaxial SiC layer on cheaper Si substrates in a scale needed for the microelectronics industry, thermal diffusion of carbon in the Si crystal structure enabled at least the formation of a nonstoichiometric SiC layer on Si. Although nonstoichiometric SiC has different electrical and optical properties compared with stoichiometric SiC, it is still chemically and thermally a very resistant material.^[39] It also provides a protective layer to Si against different kinds of oxidations.^[40]

Adapted to PSi, the pioneering studies investigated how thermal carbonization of PSi could be used to stabilize the photoluminescence in PSi.^[34] These results did not lead to further studies on the topic. A few years later, the first paper was published, in which thermal carbonization was used as an attempt to improve the chemical stability of PSi.^[41] In the paper, thermally carbonized PSi (TCPSi) was found to be much more stable chemically and thermally than the initial as-anodized PSi. The following studies further explored the thermal carbonization process and led to a number of different applications for TCPSi in several very different fields from electrical and optical applications to gas sensors and drug delivery. These are discussed in detail later.

3. Thermal Carbonization Processes

There are three different routes to achieving sufficient thermal carbonization depending on the physical state of the carbon source. Usually, a gas phase carbon source is used,^[42] where small, rapidly diffusing and strongly physisorbing unsaturated hydrocarbon molecules, like acetylene, are preferred due to their strong physisorption strength on the Si surface.^[43]

A liquid carbon source can also be used.^[44] The liquid needs to be infiltrated into the pores prior to the thermal treatment and, in some cases, polymerized before using it as a carbon source.^[45] While using liquid carbon sources, the source should be selected carefully to obtain thorough infiltration and ensure sufficient surface coverage of the treatment.

The last possible route to introduce a carbon source in the pores is the use of solid source. Wang et al. used this method indirectly in their paper, in which polystyrene was first dissolved in toluene before it was infiltrated into the pores.^[46] Afterward, toluene was evaporated from the pores before the carbonization process. During the heat treatment the thermolysis of polystyrene creates radical fragments, which subsequently undergo hydrosilylation-type chemisorption with the pore walls. All the experimental results including Fourier transform infrared (FTIR) spectra, hydrophobicity, and good chemical stability in alkaline solutions indicated a successful thermolytic grafting of polystyrene to PSi.

Despite the physical state of the carbon source used, there are some guidelines for obtaining a good surface coverage with thermal carbonization. First, if an optimal Si–C bond formation during thermal carbonization is desired, a hydrogen-terminated PSi surface is an essential requirement. Even a thin oxide layer on the PSi surface may hinder the diffusion of carbon atoms into the Si skeleton leading to lower surface coverage of the treatment or to pyrolytic carbon formation. Nevertheless, in certain applications this carbon coating is more preferred and Si–C bond formation is not needed for the performance of the carbonized system.^[47] For the same reasons, an oxygen-free, inert atmosphere is usually required, although some additional reactive gases, like H₂, may be beneficial for the treatment and have been used, e.g., to grow graphene layers on the PSi surface.^[48]

A low treatment temperature and/or slow heating rate, especially without a continuous carbon source, leads to annealing of the PSi, i.e., pore coarsening through surface reconstruction of the pore walls. This lowers the treatment efficiency drastically. Also, the use of carbon sources that have low physisorption strengths or high decomposition temperatures leads to similar outcomes. The annealing effects,^[49] such as the aforementioned pore restructuring (coarsening)^[50] and surface reconstruction^[51] during the heat treatment, however, are one of the most important factors ensuring that thick silicon carbide layers can be obtained on the pore walls of PSi.

Because the structure and properties of carbonized PSi are strongly dependent on the treatment temperature, we need to divide the carbonization treatments into two different subcategories: thermally carbonized and thermally hydrocarbonized PSi (THCPSi). At treatment temperatures below 650 °C, not all of the hydrogen from the surface PSi or from carbon source molecules will desorb. This leads to the formation of a hydrocarbon-terminated surface (THCPSi). At higher temperatures, usually above 750 °C, all of the hydrogen atoms are desorbing and the surface forms a nonstoichiometric SiC layer (TCPSi), which upon exposure to ambient conditions becomes covered by a thin oxide layer.^[52]

While the latter obviously leads to a hydrophilic surface, the former retains the hydrophobic nature of the original hydride-terminated PSi due to the presence of nondissociated hydrocarbon groups (Figure 4). However, the clear categorization of these two outcomes is not as straightforward as the outcome is also dependent on the gas atmosphere of the treatment, e.g., whether additional H₂ is used,^[47] or on the timing of the applied carbon source.^[53] For example, the presence or the absence of a continuous acetylene flush during a treatment at 600–650 °C has a significant effect on the contact angle

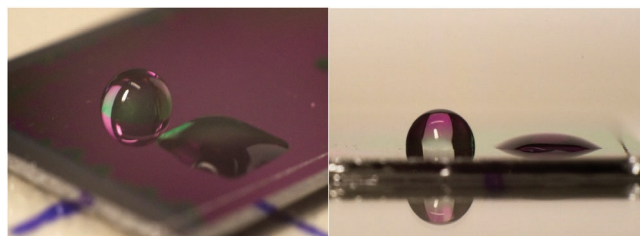


Figure 4. Water droplets on a hydrophobic THCPSi (left droplet) surface and on a hydrophilic TCPSi pad (right droplet).

(hygroscopicity) of the treated surface.^[54] There are also some other effects on the properties of TCPSi and THCPSi, and these are discussed later in the section related to properties.

4. Characterization of Thermally Carbonized Porous Silicon

Even though the large surface area of PSi enhances the usability of certain characterization methods, like FTIR spectroscopy, the intrinsic similarity of the Si–C bond to the Si–Si and C–C bonds makes the results of some characterization methods ambiguous and subject to interpretation.

Despite the limitations of FTIR, such as the weak IR activity of Si–C bonds and strong dependence of the absorbance band positions on the chemical neighborhood of the carbon atom,^[55] it is a good and convenient method to quickly assess the quality of your sample.^[56]

In well-ordered SiC, the characteristic Si–C peak disappears completely and usually a broad *Reststrahlen* band dominates over the spectral range from 750 to 1000 cm⁻¹.^[57] Unfortunately, almost all peaks related to different oxides are broad and very IR active. Those peaks overpower the spectral range of 1000–1200 cm⁻¹ masking several interesting peaks related to different Si–C and Si–O–C structures. Still, FTIR spectra are very practical for characterizing thermally carbonized PSi when the spectrum is assessed carefully. The possible presence of C–H_x stretching vibrations in the wavenumber range of 2700–3100 cm⁻¹ is usually a good indication of a successful thermal hydrocarbonization together with the attenuation or the absence of Si–H_x peaks above 2000 cm⁻¹. The presence of a strong and broad *Reststrahlen* band in the spectral range of 750–1000 cm⁻¹ together with the absence of C–H_x-related vibrations in the wavenumber range of 2700–3100 cm⁻¹ and all Si–H_x peaks above 2000 cm⁻¹ together are good indications for a proper TCPSi outcome. In Figure 5, the differences in the FTIR spectra of as-anodized PSi, THCPSi and TCPSi treated at different temperatures are shown. For the evaluation of further functionalizations of the carbonized surface, FTIR can also provide valuable information. However, the limitations of FTIR may become more prominent in these cases.

X-ray photoelectron spectroscopy (XPS) is another very good tool for surface characterization.^[52] However, it also suffers from some deficiencies related to carbon and oxygen, similar to FTIR. For example, adventitious carbon, which is always found on any surfaces after air expose, may mask the C(1s) peak making the interpretation of the XPS spectra complicated. It also complicates the correction of the binding energy in the

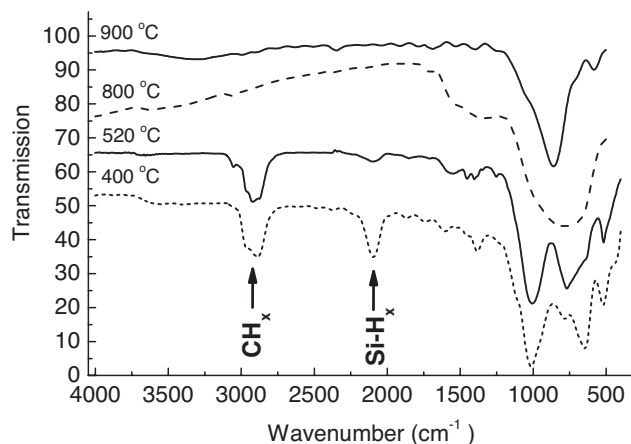


Figure 5. FTIR spectra of five at different temperatures carbonized PSI. At 400 °C treated sample peaks related to SiH_x above 2000 cm^{-1} are still visible whereas at 520 °C sample they have already almost completely disappeared. Adapted with permission.^[54] Copyright 2006, IEEE.

case of the sample charging effect if there are no other peaks suitable for the operation. It should be reminded here that cleaning the surface with sputtering does not solve this problem completely because new uncleaned surfaces of pore walls are exposed continuously during the sputtering process.

When analyzing the possible Si–C bonds from the Si(2p) core level spectra, problems may arise from the existing Si–O_x. The SiO₂ peak is located at 103.5 eV and it is only at a 4 eV higher energy than the peak of Si. Moreover, all of the suboxide structures ($x = 0.5, 1, 1.5$) of Si should appear in between these two peaks.^[58] That is, within exactly the same energy range where the SiC (100.3 eV) and Si–O–C (101–103 eV) peaks should also reside.^[59] However, despite the potential problems, it is possible to obtain clear evidence of the successful carbonization with XPS when good sample preparation is carefully considered^[60] (**Figure 6**).

There are a number of other methods that can be used indirectly to study TCPSi and THCPsi. In the simplest approach, dissolution of a sample in alkaline solution can be tested. Oxidized or hydrogen-terminated PSI does not withstand an alkaline environment and dissolves usually in minutes. Another way to test the samples is related to the oxidation of TCPSi and THCPsi. Both can be thermally oxidized, but the amount of oxides formed is much lower compared to as-anodized PSI and requires higher temperatures. For these reasons, thermoanalytical methods, such as differential scanning calorimetry (DSC) or thermogravimetry (TG), can be used to assess the oxidation rate.^[42] However, it should be noted that if the surface of PSI is already oxidized, these methods may give erroneous information when compared to carbonized PSI.

Also, Raman spectroscopy, CHNS elemental analysis (EA), and secondary ion mass spectroscopy (SIMS) can be used to map and study carbon content in a carbonized sample. Actually, Raman spectroscopy suffers slightly less from the limitations of FTIR, although both methods are based on the detection of a similar vibration mode.^[61] SIMS and EA, on the other hand, provide very little information about the bonding at the surface, but could be valuable tools in the mapping or determination of the carbon content in a sample.^[62,63]

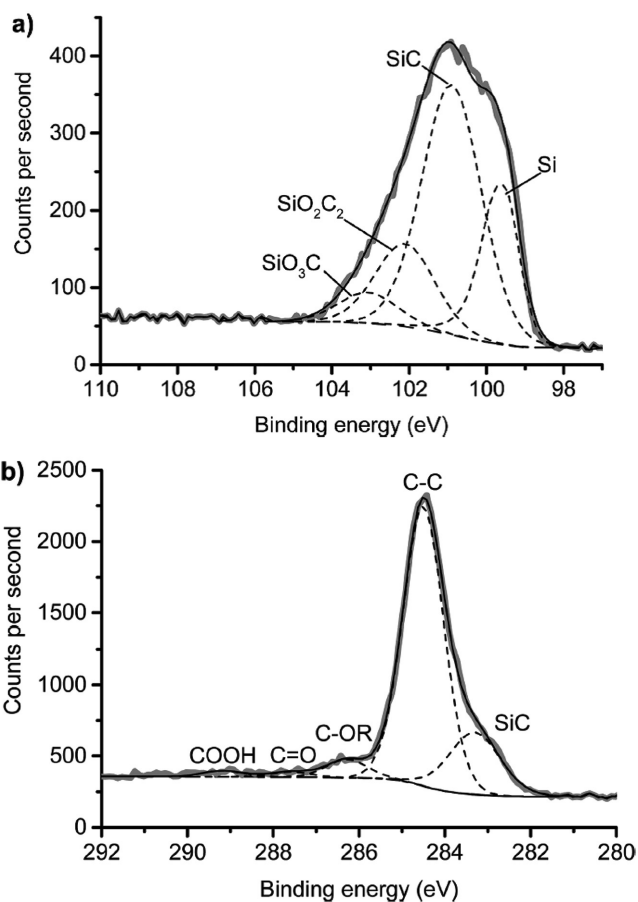


Figure 6. XPS core level spectra of a) Si(2p) and b) C(1s) regions of PSI two step thermally carbonized at 500 and 820 °C. Reproduced with permission.^[52] Copyright 2015, American Chemical Society.

Overall, the accurate characterization of THCPsi and TCPSi is challenging. Often results obtained only with a single method are vague and a combination of different direct and indirect methods (e.g., chemical stability in an alkaline solution, electrical conductivity, etc.) are needed for the assessment of a successful carbonization process. However, most of the studies so far have been conducted using conventional characterization methods. Due to the fast development of surface characterization techniques and instrumentation, there are now a number of new ways to characterize carbonized materials. Especially, the use of a combination of characterization methods, e.g., scanning transmission electron microscopy with electron energy loss spectroscopy, could be beneficial for the characterization. In addition, there are a number of different characterization methods which are never or very rarely used for THCPsi or TCPSi.

5. Properties of Thermally Carbonized Porous Silicon

The thermal carbonization of PSI has rather moderate effects on pore morphology and porosity.^[42] There are different plausible explanations for this. One is related to the lattice

expansion of carbonized Si, which is much lower than in oxidized Si. While the formation of SiO₂ leads to a volume expansion of about 30%, it is usually much less in the case of SiC. This is mainly due to 44% higher density of SiC compared with SiO₂, including, e.g., a higher surface state density compared with Si (Si: 6.8×10^{14} ; SiC: 10.5×10^{14}).^[64]

Another explanation is related to the annealing process in PSi at a higher temperature. After fabrication, PSi is hydrogen terminated, but the surface structure of the pore walls is not very stable and undergoes drastic changes during the annealing process. Partial annealing can also take place during the carbonization, which explains why the pore size remains almost the same or actually increases during the carbonization, not clearly decreasing as it is in the case of thermal oxidation. Nevertheless, this area of thermal carbonization needs more theoretical modeling and supporting experimental results.^[65]

In addition to only minor changes in the pore size, only slight changes in pore volume are usually observed.^[66,67] A clear difference in the properties of the initial starting PSi is a decrease in the surface area. However, most of the apparent reduction in surface area is actually due to the increase in weight, not a real loss in the surface area. The pore volume change is, however, a more complicated issue. If the weight increase due to the carbonization is taken into account,^[42] the pore volume usually increases.^[68] This could be another piece of indirect evidence for partial annealing.

Although the chemical stability, i.e., keeping the physical and chemical properties of PSi unchanged during a desired time period, is usually the main reason for the carbonization, it can

bring some additional and beneficial improvements to the properties important in certain electrical and optical applications. One of these properties is the remarkably improved electrical conductivity of TCPSi compared to PSi treated with other methods.

The resistance of TCPSi can be 10^{-5} times lower than in the as-anodized sample of the same thickness.^[47,69] When compared with oxidized PSi, the difference is even more drastic. The conductivity of TCPSi was also found to be well described by a thermistor equation and the temperature sensitivity was found to be very good ($5\% \text{ K}^{-1}$ at 25°C). This is a very beneficial property when accurate and easy electrical measurements are considered and has been exploited in several different sensor applications of TCPSi, including sub-ppm humidity detection^[70] and amine detection.^[70,71]

Although carbonization at higher temperatures ($>700^\circ \text{C}$) may have considerable impact on the optical properties of PSi, thermal hydrocarbonization at lower temperature has only small impacts on the optical properties of PSi as it has only mild effects on the refractive index and absorbance, and practically not much effect at all on, e.g., optical transmission.^[72] These changes can be predicted which allow considerations of the optical multilayer structures already before fabrication, which minimizes the potential drawbacks arising from the change in optical properties. This has encouraged the use of THCPSi, and even TCPSi carbonized at moderate temperatures, in optical structures and also in gas sensing applications.^[73–75]

Jalkanen et al. have shown visually how stable their TCPSi-stratified rugate filters are in an alkaline solution (**Figure 7**). While thermally oxidized and undecylenic acid hydrosilylated

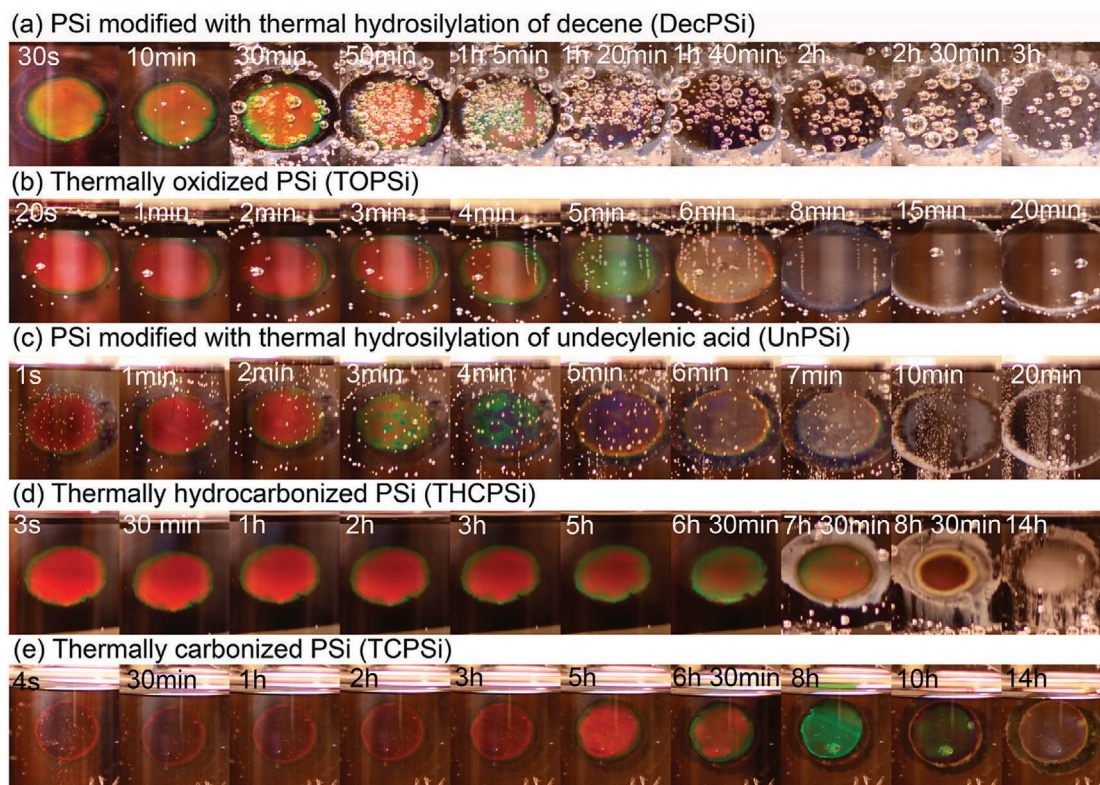


Figure 7. Temporal evaluation of differently modified PSi reflectors immersed in 1 M NaOH solution. Reproduced with permission.^[76] Copyright 2014, American Chemical Society.

Table 1. Measured Young's moduli and hardness of different thermally treated PSi compared to literature values of bulk (*). Measured data were reported by Salonen et al.^[72]

Material	Young's modulus E [GPa]	Hardness [GPa]
TCPSi	44.2	2.3
THCPSi	34.9	2.0
TOPSi (300 °C) ^{a)}	29.6	1.6
TOPSi (850 °C) ^{b)}	39.3	3.3
As-anodized PSi	19.5	0.9
Silicon	44.2	11.7
SiO ₂ *	66–75	4.5–9.5
SiC*	200–430	1–24.5

^{a)}Oxidation at 300 °C for 2 h; ^{b)}Oxidation at 850 °C for 4 h.

rugate structures were significantly dissolved and lost their characteristic reflectance spectra in minutes in a 1 M aqueous NaOH solution, thermally carbonized (and hydrocarbonized) structures stayed intact for hours, ≈ 78 times longer than other filter structures.^[76] There are many publications related to the chemical stability of TCPSi and THCPSi, but most of them are application orientated (like the long-term stability of TCPSi humidity sensor^[77]) or where the stability of carbonized samples has been compared to other stabilization treatments.^[78]

Some of the least studied properties of PSi are its mechanical properties.^[79] These properties, such as hardness and stiffness, may have remarkable effects in certain processes like milling^[80] or applications such as toothpaste.^[81] Still there are only a few experimental^[82] or theoretical modeling^[83] based papers published in this area of research, although these elastic properties should gain more attention due to the growing interests toward the use of PSi in lithium-ion battery applications.^[84]

If the hardness and stiffness of bulk SiC are compared with the values of Si, it is clear that even a thin SiC layer on Si nanostructures may have an observable effect on the mechanical properties of the material. The same applies to silicon oxide as well. In Table 1, the hardness and stiffness of bulk, crystalline Si, SiC, and SiO₂ are presented. Even though the values are surely not even close to those of their nanoscale and amorphous counterparts, they can still be seen as indicative information.

Rauhala et al. have measured the hardness and stiffness of TCPSi and THCPSi,^[85] and compared the results to as-anodized PSi (AAPSi) and to thermally oxidized PSi (TOPSi) using two different nanoindentation methods: a simple trapezoidal load function and a more complex load function introduced by Bellet et al. in 1996.^[82] As can be expected, the lowest Young's modulus (stiffness) and hardness of all the samples were observed in AAPSi. The obtained results of AAPSi are in good agreement with those reported previously (Table 1).^[79]

In the case of TCPSi, the Young's modulus and hardness with the trapezoid loading function were two times higher than in AAPSi and even higher than in the TOPSi sample oxidized at 850 °C for 4 h. However, the hardness of TOPSi is clearly higher than in TCPSi. Unexpectedly, also THCPSi has a relatively high Young's modulus and a hardness close to that of TCPSi, even though its surface chemistry is considerably different from

TCPSi. Based on the obtained experimental results, it can be concluded that thermal carbonization increases the stiffness of PSi but does not affect the hardness of PSi as much as thermal oxidation does.

Even though the first thermal carbonizations were performed in an attempt to stabilize the photoluminescence (PL) properties of PSi, an unfortunate disadvantage of thermal carbonization is the quenching of the intrinsic PL of PSi. This prevents all applications where photo- or electroluminescence could have been applicable. Fortunately, there are a number of other applications where these properties are not required.

Although there is a way to make TCPSi photoluminescing again, this has not received much attention. This is most probably because the treatment compromises many important properties of PSi considering the most common applications. In order to obtain a highly intense PL, TCPSi needs to be wet oxidized using water vapor and an inert carrier gas, such as argon or nitrogen.^[86] This has a significant effect on the structure of TCPSi, which turns into a fully oxidized carbon containing SiO₂ matrix during the wet oxidation treatment.^[87] The role of H₂O appears to be critical to the luminescence as dry oxidation does not generate luminescing material. But so far, it is unclear why the role of H₂O is so critical for obtaining PL. Apparently, the presence of hydrogen in the process leads to a completely different outcome than dry oxidation.

Interestingly, the intensity^[88] and the spectrum of PL^[89] in wet oxidized TCPSi is dependent on the treatment temperature (Figure 8). This enables tuning of the spectrum from yellowish white to bluish white, which is very appealing considering light-emitting device applications.

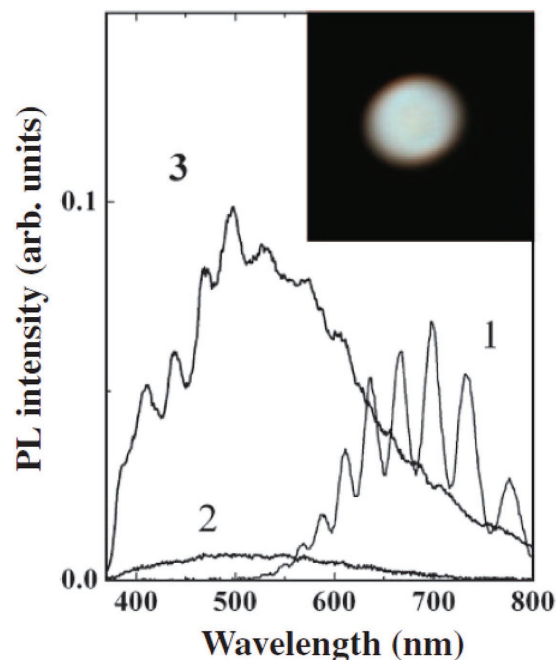


Figure 8. PL spectra of AAPSi (1), TCPSi wet oxidized at 650 °C (2) and at 800 °C (3). Reproduced with permission.^[88] Copyright 2008, American Institute of Physics.

6. Functionalization of Thermally Carbonized Porous Silicon

Even though TCPSi and THCPSi are chemically clearly more stable than as-anodized, hydrogen-terminated PSi, it is still possible to functionalize them further with different chemical routes. Some of these treatments are basically very similar to hydrosilylation chemistry, which have been presented for PSi during the past two decades.^[25] Other approaches share similarities with functionalization chemistries used for silica and SiC surfaces.

One chemical functionalization method for THCPSi was introduced in 2010 by Sciacca et al.^[90] Adapting the hydrosilylation-like process introduced by Linford and Chidsey,^[91] they utilized radical coupling of a dicarboxylic acid to a THCPSi surface with a benzoyl peroxide initiator, which resulted in a partially carboxylic acid terminated surface. The method enabled an easy route for further bioconjugation, which was demonstrated by coupling propylamine to the surface $-\text{COOH}$ groups through the intermediacy of pentafluorophenol and 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC). The chemical stability of the functionalized surface was tested in a phosphate buffered saline solution and was found to be superior to both thermally hydrosilylated (with undecylenic acid) and thermally oxidized porous Si surfaces.

Another possible route to functionalize the THCPSi surface is based on a scheme similar to that used in the thermal hydrosilylation of PSi with undecylenic acid.^[27] Although the reaction between the unsaturated carbons of the alkenoic acid and the hydrocarbon passivated surface is not clear and needs some additional studies, the thermal addition process leaves the distal carboxylic acid groups available for further functionalization. This modification, introduced in 2012 and later referred to as UnTHCPSi, has successfully been applied in drug delivery^[92] and also in optical applications.^[93]

The thermal addition of hydrocarbon molecules on the THCPSi is not limited to undecylenic acid. Wang et al. have showed that the THCPSi surface can also be modified with an α,ω -diyne, resulting in the partial alkyne termination of the

surface.^[94] The successful covalent attachment of the diyne was verified from the FTIR spectrum, which showed the disappearance of one of the alkyne groups and the appearance of an alkene bond (**Figure 9**). The alkyne modified surface provided an excellent template for further functionalization through copper-free azide-alkyne cycloaddition,^[95] enabling effective attachment of both peptide-targeting cellular components and coating the PSi nanoparticles with a polymer. Because of its great stability, various alkene-functionalized THCPSi have been used in complex multistep surface chemistry modifications including radiolabeling and targeted drug delivery applications.^[96,97]

One interesting difference between SiC and Si chemistry is related to the behavior of the silicon derivatives when they are immersed into an HF solution. HF removes all of the oxides of Si and leaves an almost perfectly hydrogen-terminated surface. But in the case of SiC, HF does not remove all the oxides. Instead, it leaves a thin oxide layer on the surface and leads to a $\text{CSi}-\text{OH}$ surface termination.^[60] The silanol groups on the surface enable the use of silane coupling chemistry that is very frequently used in the functionalization of silica or oxidized silicon surfaces.^[98] Silanization requires available hydroxyl groups, which can hydrolyze the alkoxy groups of a silane, forming a covalent $-\text{Si}-\text{O}-\text{Si}-$ bridge on the surface.

Unfortunately, $\text{Si}-\text{O}-\text{Si}$ bonds are susceptible to hydrolysis and are not very stable in aqueous solutions, which limits the use of surfaces functionalized through this approach. However, silanization is a simple method and is commonly used to obtain an amine-terminated functionalization (e.g., using (3-aminopropyl)triethoxysilane) on the silica surface. When applied on the TCPSi surface, it can sustain the inevitable siloxane hydrolysis for slightly longer than silanized TOPSi.^[63] Despite the inherent hydrolytic instability, which causes limitations to the usability of the aminopropylsilane-modified TCPSi, it can be used as an effective drug carrier in, e.g., combination drug therapy, where the surface amine groups provide a linkage to the anticancer drug methotrexate and the remaining pore volume is loaded with the antiangiogenic drug sorafenib.^[99]

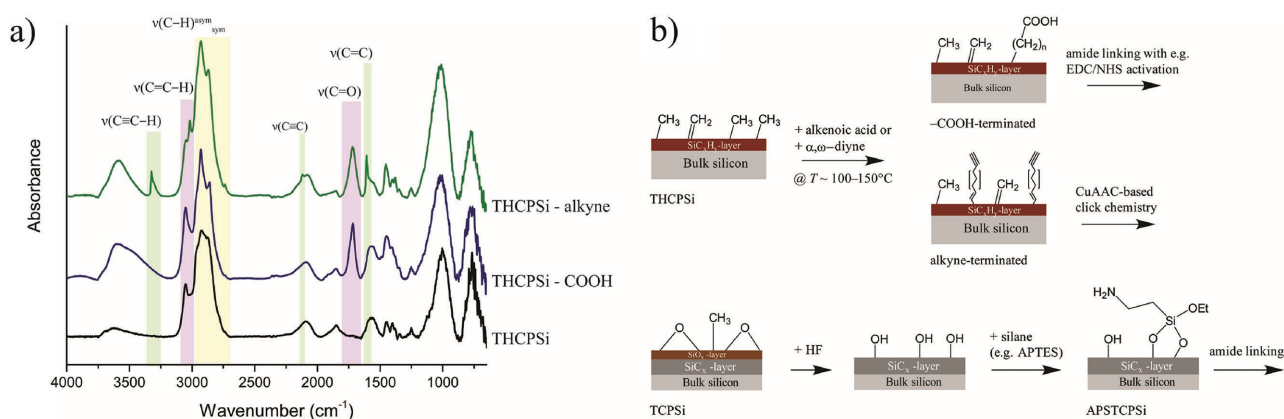


Figure 9. a) FTIR spectra of plain, COOH-terminated and alkyne-terminated THCPSi showing the successful attachments of functional groups. For example, a carboxylic acid is clearly visible due to the presence of a $\text{C}=\text{O}$ stretching band at 1710 cm^{-1} . The inclusion of a distal alkyne group is also verified due to the appearance of a $\equiv\text{C}-\text{H}$ stretch at 3300 cm^{-1} along with a $\text{C}=\text{C}$ stretch band at 1605 cm^{-1} . b) Typical functionalization routes with THCPSi and TCPSi. Reproduced with permission.^[72] Copyright 2015, The Electrochemical Society.

7. Recent Progress in Applications of Thermally Carbonized Porous Silicon

7.1. Drug Delivery

Compared to any other applications of PSi, biomedical, especially drug delivery sets strict and somewhat contradictory requirements to the chemical stability of the drug carrier material. The PSi may not react with the adsorbed drug payload or cause any degradation of it under any circumstances. On the other hand, the carrier material needs to be bioresorbable within a specified period of time, which depends on the application, and its dissolution products should be nontoxic and easily excreted from the body.

When considering the properties of an inorganic material, these requirements are quite contradictory and excluding. Most of the inorganic materials proposed for biomedical applications do not fulfill these requirements, but, fortunately, PSi does it in certain applications. However, the balance between the chemical stability considering the carrier–drug interactions and the in vivo dissolution rate of the carrier in the potential target tissue always requires reasonable and justifiable compromises.

The first paper, where TCPSi microparticles were used in drug delivery, was published in 2005. In the paper, we used TCPSi and TOPSi in the loading of five different model drugs: antipyrine, ibuprofen, ranitidine, griseofulvin, and furosemide.^[66] In this paper the importance of surface stabilization was already evident, when a strong reaction between antipyrine and AAPSi was observed. The authors also observed that the surface chemistry affected the drug loading through the complex interactions taking place during the adsorption between the carrier, drug, and the used solvent.^[100]

Different kinds of effects, depending on the type of the drug loaded to the pores of PSi, were observed. With quickly dissolving drugs, the effects were minimal or some sustained release behavior was observed (antipyrine, ibuprofen, and ranitidine), while in the case of a drug suffering from poor aqueous solubility, namely griseofulvin, the effect of PSi was significant. The dissolution rate of the drug improved at every studied pH value (5.5., 6.8, and 7.4). With furosemide, which suffers from significant pH-dependent solubility, the pH-dependent behavior was almost completely diminished. Later, when TCPSi loaded furosemide was studied further, it was found that the loading not only improved the solubility properties of furosemide, but it also improved permeation across Caco-2 monolayers, which are commonly used to mimic the condition of the small intestine.^[101] In the same year, 2007, Linnell et al. published a study on how surface chemistry affects the loading and release of ibuprofen.^[67] After these first studies, TCPSi and THCPSi microparticles have been used in several drug delivery studies.^[102] During the first years, the main focus of the studies was to improve the dissolution rate of poorly soluble drugs for oral administration. PSi is an excellent candidate for this purpose because the small size of its pores can confine the loaded drug usually in its amorphous form^[13] and hence may significantly increase the dissolution rate of the drug.^[103]

The possible toxicity of TCPSi and THCPSi has been studied for almost as long as that of drug delivery. However, cytotoxicity studies of nanostructured materials are not always so

straightforward as those of conventional drug molecules. In 2007, Laaksonen et al. reported that the most commonly used cytotoxicity assay, 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT), failed dramatically when applied to PSi microparticles.^[104]

Viability values of 200% and even 300% were obtained for TCPSi and TOPSi with Caco-2 cells. The failure of MTT was discredited when the microparticles were studied alone without any cells. An MTT assay gave viabilities of up to 200% even in this case. In the paper, the authors also tested a fluorogenic, cell-permeant peptide substrate (CellTiter-Fluor) assay, which is a fluorescent assay where a single reagent is added, and found it to give more realistic cytotoxicity values.

This observation was among those bringing forth the now well-known challenge in nanomedicine research, especially when nanostructured inorganic materials are involved. Nothing can guarantee that the conventional pharmaceutical methods are applicable with the new nanotechnology. This needs to be considered with extra caution when novel drug delivery systems are assessed.^[105]

Later, TCPSi and THCPSi micro- and nanoparticles have been studied with many different cytotoxicity assays and with various cultivated cell lines, such as RAW264.7, HT-29, HepG2,^[106] EA.hy926,^[107] monocyte derived DC,^[108] MCF-7,^[109] MDA-MB-231,^[110] U87 MG,^[111] PC3MM2,^[112] BDCM, KG1,^[113] etc. Most of the results have given indications of negligible or minor toxicity of carriers, but some exceptions have been reported. In 2010, Santos et al. found that the smallest microparticles of TCPSi and THCPSi (1–25 μm) were toxic compared to TOPSi at high concentrations ($>2 \text{ mg mL}^{-1}$) and strongly size dependent.^[114] They measured the metabolic activity of the viable cells by means of their ATP production using a luminescence-based assay. When they used flow cytometry, the difference between TCPSi and THCPSi compared to TOPSi was no longer that strong. But it can be concluded that high concentrations of microparticles may induce toxic effects. Another interesting observation was that even though TCPSi is chemically more stable than THCPSi, it may have some negative effects considering toxicity, like the generation of intracellular ROS.

The first in vivo studies of THCPSi microparticles were published in 2009.^[115] In the study, D-lys-GHRP_6 , a ghrelin antagonist, was used as a model peptide and the effects of peptide-loaded THCPSi microparticles on food intake and blood pressure were examined in mice and rats, respectively, after a single subcutaneous injection. In addition, the effects of THCPSi microparticles on cytokine secretion in mice after a single injection were examined by determining the concentration of several plasma cytokines. The peptide-loaded microparticles showed a prolonged effect on cytokine secretion compared with the peptide solution. These results suggest that the peptide was released from the particles in a controlled manner. In addition, a single injection of the THCPSi microparticles did not acutely change plasma cytokine concentrations with one exception: IL-1 α at 6 h after administration was increased in the plasma. Otherwise, the results suggested the THCPSi could represent a suitable material for drug delivery.

After the paper, differently functionalized PSi surfaces have been studied for the delivery of multiple kinds of peptides, such as melanotan II,^[116] peptide YY,^[92] glucagon-like peptide 1,^[117]

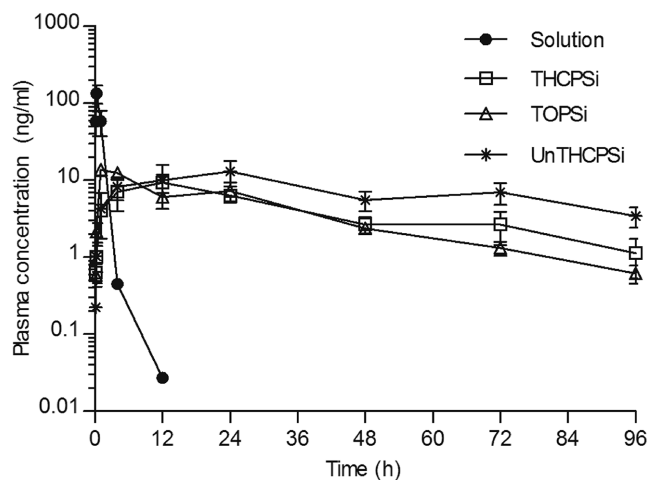


Figure 10. In vivo plasma concentration of peptide YY release from subcutaneously administered PSi nanoparticles in mice.^[119] UnTHCPsi denotes THCPsi in which undecylenic acid is thermally attached covalently. Reproduced with permission.^[119] Copyright 2013, American Chemical Society.

and insulin^[118] using micro and nanoparticles, in several papers.^[119] Some of the results are very encouraging, such as those presented in **Figure 10**. Although some recent in vivo studies suggest that the intravenous administration of nanoparticles, even in the absence of any drug, may induce cardiovascular effects and interfere or prevent the action of the drug,^[120] the advantageous properties related to PSi, such as the very mild loading process needed for the drug adsorption and high loading efficacy,^[119,121] make PSi a very interesting carrier material especially for fragile components like peptides.^[122]

Novel, targeted cancer therapies have always been the primary interest when attempts have been made to apply nanotechnology for drug delivery purposes, although this task has not been as easy as was expected in the early days, due to the sophisticated human immune system including the mononuclear phagocytic system^[123] and several different biological barriers.^[124] The same applies to PSi too. For example, THCPsi nanoparticles, with^[125] or without^[126] additional surface functionalization, are usually rapidly captured by the mononuclear phagocyte system and removed from the circulation mainly to the spleen and liver. Despite the problems, this field has been most active in studying PSi as a carrier material.^[127]

Due to the appropriate stability and possibility for further functionalization, TCPSi and THCPsi have been used in several studies aiming at novel chemotherapeutic applications including the delivery of sorafenib,^[128] methotrexate,^[111,129] paclitaxel,^[130] doxorubicin,^[131] erlotinib, and afatinib.^[132] Several different approaches have been used to improve the homing efficiency of the delivery system and to improve the precisely controlled delivery or to avoid rapid clearance from the circulation.^[94,130,133]

Even though some promising results have been obtained in targeted cancer therapy, more in vivo results and systematic information about the biocompatibility of the nanoparticles are needed before any clinical tests can be considered.^[134]

There are several other interesting drug delivery areas where TCPSi and THCPsi may be a potentially good carrier material.

Intraocular delivery is one of these areas. There is some additional functionality which PSi-based delivery systems may offer like a self-reporting delivering system,^[135] and PSi^[136] and TCPSi^[137] could serve as safe carriers for delivering therapeutic compounds into the eye.

The use of PSi in wound healing applications has also gained interest lately. This is also one of the applications where additional functionality,^[138] such as the possibility for glucose^[139] or pH sensing, would be beneficial.^[140] However, so far, the main focus of the studies has been delivering essential components for wound healing to the site, such as antibacterial nitric oxide,^[141] Flightless I siRNA,^[142] vancomycin, resveratrol,^[143] or using plain platelet lysate-modified particles to deliver growth factors into the wound.^[144] Also, heart homing particles have been used recently, and interesting in vitro^[145] and in vivo^[146] results have been published.

7.2. Sensor Applications

Both TCPSi and THCPsi have been used for different gas^[71] and humidity sensing^[53,54,70] applications for years. The improved chemical stability and electrical properties are necessary for obtaining stable gas sensing systems that are calibrated infrequently.^[77] Despite good results obtained with resistive and capacitive humidity and gas sensors, the biggest advantage lies in the possibility to tune the optical properties of PSi during the electrochemical etching over a wide range. This enables a simple production of very complicated, but stable optical multilayer structures, such as Bragg^[147,148] or rugate filters.^[149] Since optical PSi structures are sensitive to changes in ambient gas content, these structures are very interesting for remote gas sensing applications.^[148,149] Even though the selectivity or even sensitivity is not yet as good as in electrical sensors,^[74,150] the completely passive sensing element, without any need for external power (i.e., wiring), is a very tempting alternative to certain, demanding sensing applications. It is also possible to combine electrical and optical sensing to improve the selectivity of the sensing system.^[151]

For example, Ruminski et al. used a THCPsi rugate filter attached to a glass fiber with epoxy to study the sensing of volatile organic compounds such as isopropyl alcohol and heptane in the air.^[75] This approach enabled a simple setup for an efficient probe-type gas sensing instrument (**Figure 11**). The two different surface chemistries showed divergent responses to the different analytes, isopropanol and heptane. The TOPsi surface showed a greater response to isopropanol than to heptane vapors, while the THCPsi surface responded more strongly to heptane than to isopropanol vapors. The results suggest that these surface chemistries can be used to classify selectively different analytes and can be used in a microsensor system.

As already mentioned above, the functionalized THCPsi is very stable even in alkaline aqueous solutions. Therefore, it is also an ideal material to be used in severe liquid sensing applications. Practically, all saline solutions with a neutral or an alkaline pH are severe for AAPS and TOPsi. Thus, an enhanced chemical stability is crucial for proper biosensing in a liquid, e.g., for the optical detection of biomolecules.^[152] **Figure 12**

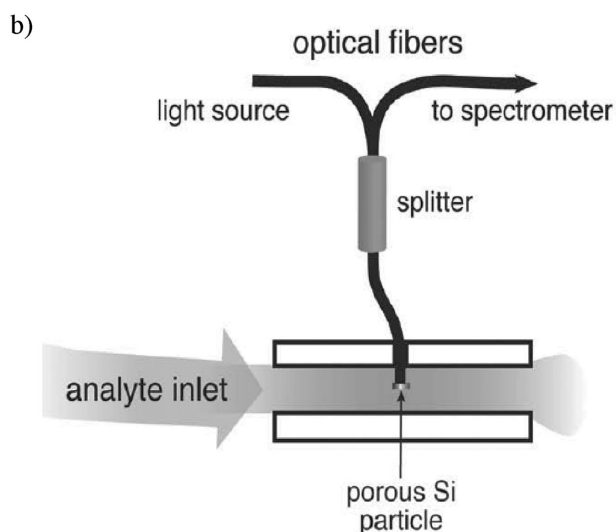
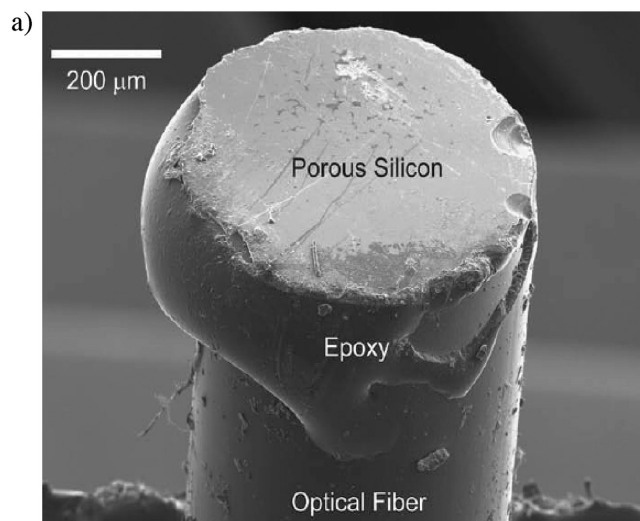


Figure 11. a) Image of an optical fiber capped with a PSi rugate filter. b) Schematic depicting the optical configuration used for remote gas sensing. Reproduced with permission.^[75] Copyright 2010, Wiley-VCH.

shows the experimental result where the EDC/NHS-activated UnTHCPSi microcavity was subjected for 10 min to an aqueous solution of urea at a concentration of 210 mg L⁻¹. The succinimide group is replaced by the smaller urea molecule, which is seen as a blueshift in the reflectance spectrum. The ATR-FTIR spectra before and after the sensing experiment show the appearance of two N-H stretching bands around 3300 cm⁻¹, confirming the formation of a carboxamide structure.

Another very demanding approach regarding the surface chemistry is the use of electricity during sensing. PSi is very vulnerable to all kinds of electrochemical reactions and is oxidized easily even in a simple aqueous electrolyte.^[153] Chen et al. used the improved conductivity of TCPSi in their application, in which electric-field-assisted protein transportation and capture were used to improve the selectivity of interferometric sensing of proteins.^[154] They showed that the bias dependence of the voltage-induced transport in mesoporous, conductive optical films can be used to identify molecules

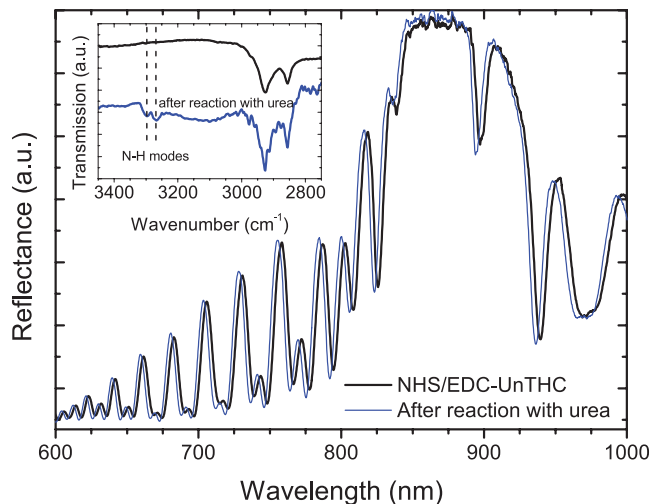


Figure 12. The EDC/NHS activated UnTHCPSi microcavity was used for detecting urea from water. The sensor was soaked for 10 min in water with a 210 mg L⁻¹ urea concentration. A blueshift in the order of 3.3 nm was observed in the reflectance spectrum. The shift is attributed to replacement of the larger succinimidyl ester moieties by the smaller urea molecules. The observation is further supported by the ATR-FTIR spectra, which is shown in the inset. Reproduced with permission.^[152] Copyright 2013, The Electrochemical Society.

based on their size, charge, and diffusional characteristics. A bulk lysozyme solution at a concentration of 25 μg mL⁻¹ was not detectable without an applied bias, but with an appropriate bias of ΔV = -2.75 V, a significant accumulation of protein was detected. The optical data indicated that lysozyme accumulated in the PSi film with a concentration factor of 9600 by electric-field-assisted transportation.

In 2016, Tong et al. proceeded even further in their sensing approach and used THCPSi *in vivo*.^[155] They used a THCPSi rugate filter as a subcutaneously implanted biosensor. The results demonstrated that THCPSi is a potential material to be used in *in vivo* biosensing applications. The reflectance band of a preincubated THCPSi rugate filter remained clearly detectable in the far-red range (**Figure 13**) and subcutaneous

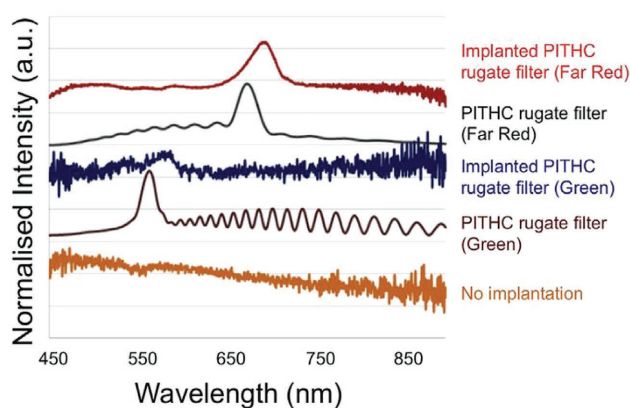


Figure 13. Reflectance of green and far-red preincubated THCPSi rugate filters being read through the skin along with the reflectance of these filters immersed in water and a blank skin section.^[155] Reproduced with permission.^[155] Copyright 2016, Elsevier.

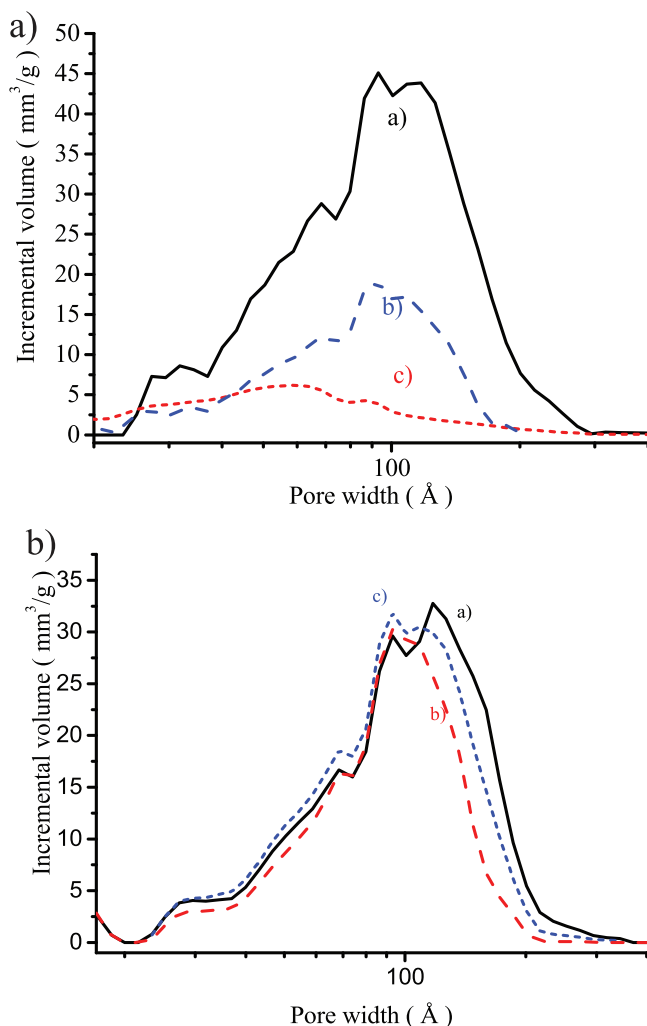


Figure 14. a) Incremental volume versus pore width of AAPSi (a), after electrochemical oxidation (b), and after pyridine-assisted liquid oxidation of AAPSi (c). b) Incremental volume versus pore width of TCPSi (a), after vapor (b), and after pyridine-assisted liquid oxidation (c). Reproduced with permission.^[156] Copyright 2008, Elsevier.

tissues in close proximity to the implanted sensor indicated normal healing processes in immunohistochemical and microtome studies.

Although this section has focused mostly on optical sensing applications, two particular demonstrations are worth mentioning because the extreme chemical stability of TCPSi is essential to them. In the first approach, an active TCPSi sensing layer is electrically isolated from the Si wafer by an additional oxide layer between them.^[156] The electrically isolated sensing layer was obtained by the electrochemical etching of a new layer beneath the TCPSi layer. Subsequently, the new layer was oxidized either by electrochemical, chemical (pyridine-assisted), or thermal oxidation. The first method was found to be the best in this application because it turned the layer into an electrically isolating oxide and almost completely closed the pores. **Figure 14** shows how the different oxidations affect AAPS and TCPSi. While the pore size and volume of AAPS decrease drastically during oxidation, hardly any changes can be seen in TCPSi.

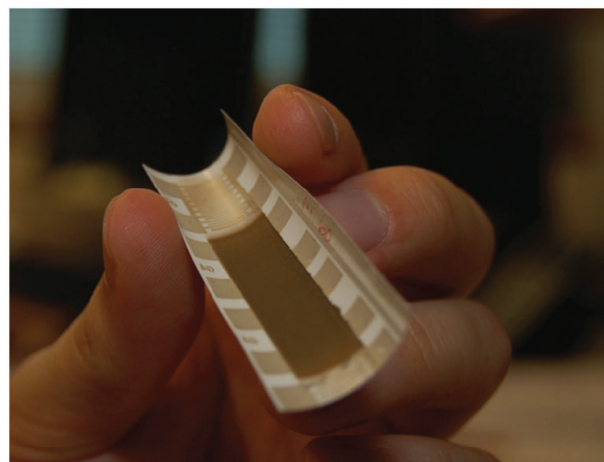


Figure 15. Flexible humidity sensing element on paper utilizing a spray-coated PSi layer on flexographically printed silver electrodes. Reproduced under the terms of the CC BY 3.0 licence.^[158] Copyright 2015, The Authors, published by Hindawi.

In the second application, PSi nanoparticles have been utilized for the potential cheap mass production of sensor systems. Jalkanen et al. produced undecylenic acid treated THCPSi micro- and nanoparticle ink, which was used to drop cast fully functional humidity sensors on a glass substrate on the top of inkjet-printed silver electrodes.^[157] Interestingly, a narrow distribution of nanoparticles was found to provide the best adhesion between the particles. However, the affinity of the drop-casted particle layers to the glass substrate was insufficient, and the layer exfoliated from the substrate surface. In contrast, a broader size distribution containing both nano- and microparticles provided much better adhesion between the particles and to the glass substrate. The sensors provide fast and reproducible results with very low hysteresis, which serves as a proof of concept that stabilized PSi particles are well suited for the production of printed sensors. Later, the same group applied a roll-to-roll compatible fabrication processes to produce real-time humidity sensing elements on a flexible paper substrate using spray-coating of TCPSi particles on flexographically printed interdigitated silver electrodes (**Figure 15**).^[158]

7.3. Battery and Supercapacitor Applications

Due to the recent interest in the potential use of Si in the electrodes of lithium-ion batteries and in supercapacitors,^[159] PSi has also gained some attention related to these application.^[84,160] One interesting applications is to use TCPSi in electrochemical supercapacitors.^[48] In a recent paper, Oakes et al. demonstrated that thermal carbonization in a hydrogen-containing atmosphere is a universal route for transforming PSi into stable electrodes for electrochemical devices through the growth of an ultrathin, conformal graphene coating on the surface. This graphene coating simultaneously passivates surface charge traps and provides an ideal electrode–electrolyte electrochemical interface. This leads up to a 40-fold improvement in energy density, and a two-time wider electrochemical window compared to an identically structured unpassivated PSi.

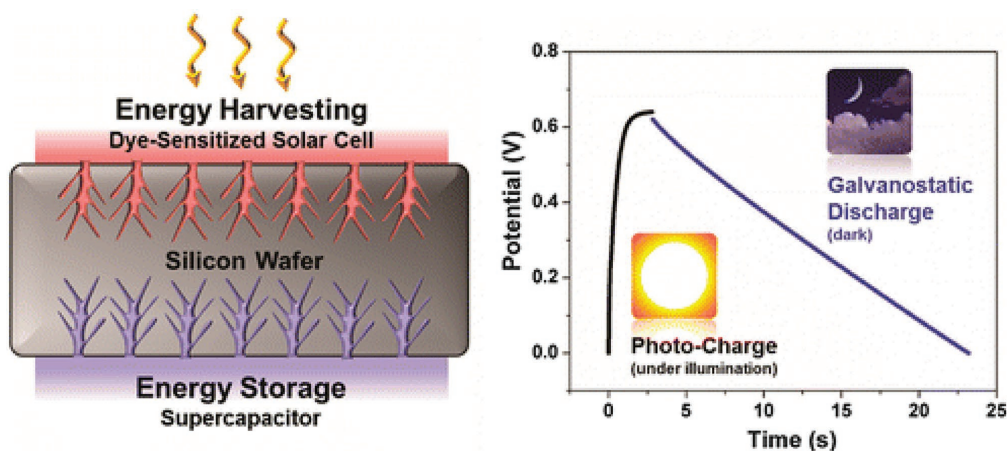


Figure 16. Schematic of an all silicon electrode photocapacitor for integrated energy storage and conversion. Reproduced with permission.^[163] Copyright 2015, American Chemical Society.

The authors also stated that TCPSi with a graphene coating is a promising new platform for grid scale and integrated electrochemical energy storage with excellent electrochemical and corrosion stability.^[47] This is an ideal example for combining two intensively studied electrode materials, Si and graphene,^[161] into the same application.

Gardner et al. have also studied an electrochemical supercapacitor based on TCPSi, considering integrated on-chip energy storage applications, and found that the TCPSi provided a stable capacitance over 1000 cycles. On the other hand, Westover et al. demonstrated the operation of a graphene-passivated on-chip PSi material as a high-rate lithium battery anode with over a 50× power density, and 100× energy density improvement compared to identically prepared on-chip supercapacitors.^[162] In addition, the graphene-passivated PSi showed a cycling performance of over 10 000 cycles with a capacity above 0.1 mA h cm⁻² without any notable fade in capacity.

The same group has also demonstrated many interesting applications of the graphene-coated PSi, such as an all-silicon electrode photocapacitor for integrated energy storage and conversion (Figure 16),^[163] and a load-bearing solid-state supercapacitor application.^[164] Other related innovations include the use of PSi as a sacrificial material for producing a new class of functional mesoporous carbons optimized for the dual chemical and physical confinement of soluble polysulfides in lithium–sulfur battery cathodes^[165] and the use PSi as a catalyst for graphene growth.^[166]

7.4. Other Applications

One of the simplest exploitations of TCPSi was introduced in 2010 by Fang et al.^[167] They used rapid thermal carbonization to precisely tune the pore size of ultrathin porous nanocrystalline silicon. Hydraulic permeability studies showed that carbonized membranes follow theoretical predictions for water transport and retain the nanoparticle separation capabilities of the untreated ultrathin membrane. They also showed that TCPSi membranes have the potential to be used in protein sieving and molecular separation applications.

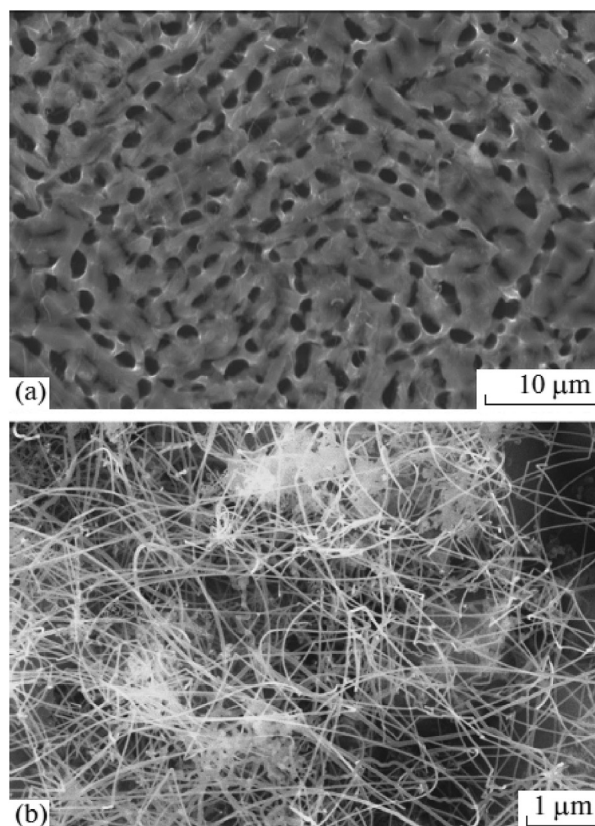


Figure 17. a,b) SEM images of the surfaces of macroporous silicon before (a) and after (b) high-temperature carbonization. Reproduced with permission.^[168] Copyright 2017, Springer.

Recently, Pavlikov et al. observed that SiC nanowire structures of 40–50 nm in diameter were produced by the high-temperature carbonization of macroporous silicon and Si nanowires using hydrogen as a carrier gas (Figure 17).^[168] The X-ray structural and Raman data suggest that the cubic 3C-SiC polytype is dominant in the nanowires. They also observed a broad Reststrahlen band in the region of 800–900 cm⁻¹ in an infrared reflectance spectrum, which is indicative for the

formation of SiC structures. This simple and straightforward method to produce 3C-SiC-type nanowires may be very interesting for different kinds of microelectronic, photonic, and gas sensing applications, especially considering very low turn-on and threshold fields for electron emission, which have been observed in SiC nanowires.^[169]

Stable PSi may have also some applications in the field of bioreactors,^[170] or for increasing biological metabolization processes and producing new, more active metabolites.^[171] Another potential field of applications is radioimaging,^[172] dual imaging,^[173] or a sophisticated pretargeting approach in which bioorthogonal chemical reactions take place in a living biological system without interfering with or being interfered by any of the system's native biochemical processes.^[96]

8. Conclusions and Future Aspects

The thermal carbonization of PSi has slowly gained attention in different fields of PSi research. Superb chemical stability, significantly enhanced electrical conductivity, and minor effects on the optical properties of the initial PSi are beneficial improvements for many applications. Even though most of the recent publications have involved applications, there have been some improvements in the initial thermal carbonization process too.

Due to their advantages, TCPSi and THCPSi have been increasingly used in many new emerging areas such as in drug delivery and energy storage applications. Unfortunately, the terminology related to thermal carbonization varies a lot depending on the research group, so any kind of literature survey on the topic would lead to a limited result on the subject. Nevertheless, as illustrated in Figure 1 b, it can be seen that new areas, where chemical stability is needed, are emerging in PSi research. Thus, it is easy to predict that the thermal carbonization of PSi will be used increasingly in the future. However, it is almost impossible to predict what would be the new emerging field in PSi research. But, if any kind of stability is desired in those fields, thermal carbonization will surely be one of the best candidates to obtain suitable and appropriate material for them.

Nevertheless, there are still challenges concerning TCPSi, e.g., the carbonization process and even the stability itself has to be improved. Also, the precise characterization of THCPSi and TCPSi, and their functionalization chemistries, is challenging and some novel characterization tools should be tested in order to find fast and accurate ways for providing unambiguous identification. For example, the precise chemistry of the thermal addition of alkenes on THCPSi is still unclear, although it has been used in dozens of articles already.

The thermal carbonization of nanoparticles is also rather problematic. The need for a relatively fast gas flow during the process in itself is challenging, but another problem is sintering of the nanoparticles. These problems may be solved by using a fluidized bed-reactor-type system. Even then, there would be some technical problems to solve, e.g., how to heat the reactor fast enough and how to achieve a uniform temperature profile throughout the process.

Finally, we can still improve the properties or stability of THCPSi and TCPSi somehow. The most obvious way to do

that is to deposit something stable on the surface, but again, the pore structure will be the critical issue. The atomic layer deposition (ALD) technique has improved considerably in recent years and it has been used previously to deposit different materials into PSi. However, PSi has only a limited aspect ratio, which restricts the depth of the effective thickness of deposition that can be obtained. Still, ALD could be the best method for introducing further improvements in TCPSi.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] A. Uhler, *Bell Syst. Tech. J.* **1956**, *35*, 333.
[2] D. R. Turner, *J. Electrochem. Soc.* **1958**, *105*, 402.
[3] Y. Watanabe, T. Sakai, *Rev. Electr. Commun. Lab.* **1971**, *19*, 899.
[4] Y. Watanabe, Y. Arita, T. Yokoyama, Y. Igarashi, *J. Electrochem. Soc.* **1973**, *120*, C235.
[5] K. Imai, H. Unno, *IEEE Trans. Electron Devices* **1984**, *31*, 297.
[6] T. Yonehara, T. Sakaguchi, *JSAP Int.* **2001**, *4*, 10.
[7] L. T. Canham, *Appl. Phys. Lett.* **1990**, *57*, 1046.
[8] A. J. Simons, T. I. Cox, A. Loni, L. T. Canham, R. Blacker, *New Developments in Porous Silicon, Relation with Other Nanostructured Porous Materials: Proceedings of Symposium L on New Developments in Porous Silicon—Relation with Other Nanostructured Porous Materials of the 1996 E-MRS Spring Conf.* June 4–7, 1996, (Ed.: L. T. Canham, D. Bellet), Elsevier, Strasbourg, France **1997**.
[9] a) L. Canham, *Properties of Porous Silicon*, Vol. 18, Short Run Press Ltd., London, UK **1997**; b) A. G. Cullis, L. T. Canham, P. D. J. Calcott, *J. Appl. Phys.* **1997**, *82*, 909; c) J. H. Song, M. J. Sailor, *Comments Inorg. Chem.* **1999**, *21*, 69.
[10] a) L. Batchelor, A. Loni, L. T. Canham, M. Hasan, J. L. Coffey, *Silicon* **2012**, *4*, 259; b) K. W. Kolasinski, J. Yalovskiy, *Phys. Status Solidi C* **2011**, *8*, 1749; c) K. W. Kolasinski, N. J. Gimbar, H. B. Yu, M. Aindow, E. Makila, J. Salonen, *Angew. Chem., Int. Ed.* **2017**, *56*, 624; d) A. T. Tesfaye, R. Gonzalez, J. L. Coffey, T. Djenizian, *ACS Appl. Mater. Interfaces* **2015**, *7*, 20495; e) N. Wareing, K. Szymanski, G. R. Akkaraju, A. Loni, L. T. Canham, R. Gonzalez-Rodriguez, J. L. Coffey, *Small* **2017**, *13*, 1602739; f) C. Chiappini, P. Campagnolo, C. S. Almeida, N. Abbassi-Ghadi, L. W. Chow, G. B. Hanna, M. M. Stevens, *Adv. Mater.* **2015**, *27*, 5147.
[11] C. Chiappini, E. De Rosa, J. O. Martinez, X. Liu, J. Steele, M. M. Stevens, E. Tasciotti, *Nat. Mater.* **2015**, *14*, 532.
[12] X. G. Zhang, *J. Electrochem. Soc.* **2004**, *151*, C69.

- [13] E. Makila, M. P. A. Ferreira, H. Kivela, S.-M. Niemi, A. Correia, M.-A. Shahbazi, J. Kauppila, J. Hirvonen, H. A. Santos, J. Salonen, *Langmuir* **2014**, *30*, 2196.
- [14] L. Canham, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 733.
- [15] G. Shtenberg, E. Segal, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 857.
- [16] a) A. Jane, R. Dronov, A. Hodges, N. H. Voelcker, *Trends Biotechnol.* **2009**, *27*, 230; b) R. J. Martin-Palma, V. Torres-Costa, M. Arroyo-Hernandez, M. Manso, J. Perez-Rigueiro, J. M. Martinez-Duart, *Microelectron. J.* **2004**, *35*, 45; c) V. Torres-Costa, R. J. Martin-Palma, *J. Mater. Sci.* **2010**, *45*, 2823; d) V. Torres-Costa, R. J. Martin-Palma, in *Porous Silicon for Biomedical Applications*, Vol. 68 (Ed: H. A. Santos), Woodhead Publishing Ltd, Cambridge, UK **2014**, p. 185; e) Y. Mirsky, A. Nahor, E. Edrei, N. Massad-Ivanir, L. M. Bonanno, E. Segal, A. Sa'ar, *Appl. Phys. Lett.* **2013**, *103*, 033702; f) N. Massad-Ivanir, Y. Mirsky, A. Nahor, E. Edrei, L. M. Bonanno-Young, N. Ben Dov, A. Sa'ar, E. Segal, *Analyst* **2014**, *139*, 3885; g) X. Wei, S. M. Weiss, *Opt. Express* **2011**, *19*, 11330; h) Y. L. Zhao, G. Gaur, S. T. Retterer, P. E. Laibinis, S. M. Weiss, *Anal. Chem.* **2016**, *88*, 10940.
- [17] L. T. Canham, *Adv. Mater.* **1995**, *7*, 1033.
- [18] L. T. Canham, *Adv. Mater.* **1999**, *11*, 1505.
- [19] A. Bowditch, K. Waters, H. Gale, P. Rice, E. Scott, L. Canham, C. Reeves, A. Loni, T. Cox, *Mat. Res. Soc. Symp. Proc.* **1998**, *536*, 149.
- [20] S. H. C. Anderson, H. Elliott, D. J. Wallis, L. T. Canham, J. J. Powell, *Phys. Status Solidi A* **2003**, *197*, 331.
- [21] Q. Shabir, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 395.
- [22] J. R. Henstock, L. T. Canham, S. I. Anderson, *Acta Biomater.* **2015**, *11*, 17.
- [23] a) J. M. Buriak, M. J. Allen, *J. Am. Chem. Soc.* **1998**, *120*, 1339; b) M. P. Stewart, J. M. Buriak, *Angew. Chem., Int. Ed.* **1998**, *37*, 3257.
- [24] M. P. Stewart, J. M. Buriak, *Comments Inorg. Chem.* **2002**, *23*, 179.
- [25] J. M. Buriak, *Chem. Rev.* **2002**, *102*, 1272.
- [26] M. P. Stewart, J. M. Buriak, *J. Am. Chem. Soc.* **2001**, *123*, 7821.
- [27] R. Boukherroub, J. T. C. Wojtyk, D. D. M. Wayner, D. J. Lockwood, *J. Electrochem. Soc.* **2002**, *149*, 59.
- [28] E. G. Robins, M. P. Stewart, J. M. Buriak, *Chem. Commun.* **1999**, 2479.
- [29] J. M. Buriak, *Chem. Mater.* **2014**, *26*, 763.
- [30] a) B. Gelloz, H. Sano, R. Boukherroub, D. D. M. Wayner, D. J. Lockwood, N. Koshida, *Appl. Phys. Lett.* **2003**, *83*, 2342; b) R. Boukherroub, D. D. M. Wayner, G. I. Sproule, D. J. Lockwood, L. T. Canham, *Nano Lett.* **2001**, *1*, 713; c) L. T. Canham, M. P. Stewart, J. M. Buriak, C. L. Reeves, M. Anderson, E. K. Squire, P. Allcock, P. A. Snow, *Phys. Status Solidi A* **2000**, *182*, 521; d) J. M. Buriak, M. J. Allen, *J. Lumin.* **1998**, *80*, 29.
- [31] a) X. Wallart, C. H. de Villeneuve, P. Allongue, *J. Am. Chem. Soc.* **2005**, *127*, 7871; b) L. Scheres, B. Rijkens, M. Giesbers, H. Zuilhof, *Langmuir* **2011**, *27*, 972.
- [32] L. A. Huck, J. M. Buriak, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 683.
- [33] I. N. Lees, H. Lin, C. A. Canaria, C. Gurtner, M. J. Sailor, G. M. Miskelly, *Langmuir* **2003**, *19*, 9812.
- [34] a) Y. J. Seo, H. J. Cheon, D. J. Choi, *J. Mater. Sci. Lett.* **1998**, *17*, 313; b) B. M. Kostishko, S. R. Atazhanov, S. N. Mikov, *Tech. Phys. Lett.* **1998**, *24*, 633.
- [35] J. Salonen, V. P. Lehto, M. Bjorkqvist, E. Laine, L. Niinisto, *Phys. Status Solidi A* **2000**, *182*, 123.
- [36] H. E. Roscoe, *A Treatise on Chemistry*, D. Appleton and Company, New York **1878**.
- [37] E. Davy, in *Reports of Sixth Meeting of the British Association for the Advancement of Science, held at Bristol in August 1836*, Vol. 5, John Murray, London, UK **1837**, p. 62.
- [38] a) J. Yoshinobu, H. Tsuda, M. Onchi, M. Nishijima, *Chem. Phys. Lett.* **1986**, *130*, 170; b) J. Yoshinobu, H. Tsuda, M. Onchi, M. Nishijima, *Solid State Commun.* **1986**, *60*, 801; c) M. Nishijima, J. Yoshinobu, H. Tsuda, M. Onchi, *Surface Sci.* **1987**, *192*, 383.
- [39] a) G. L. Harris, *Properties of Silicon Carbide*, INSPEC, London, UK **1995**; b) P. Melinon, B. Masenelli, F. Tournus, A. Perez, *Nat. Mater.* **2007**, *6*, 479.
- [40] J. Roy, S. Chandra, S. Das, S. Maitra, *Rev. Adv. Mater. Sci.* **2014**, *38*, 29.
- [41] J. Salonen, V.-P. Lehto, M. Bjorkqvist, E. Laine, L. Niinisto, *Phys. Status Solidi A* **2000**, *182*, 123.
- [42] J. Salonen, E. Laine, L. Niinisto, *J. Appl. Phys.* **2002**, *91*, 456.
- [43] C. C. Cheng, P. A. Taylor, R. M. Wallace, H. Gutleben, L. Clemens, M. L. Colaianni, P. J. Chen, W. H. Weinberg, W. J. Choyke, J. T. Yates, *Thin Solid Films* **1993**, *225*, 196.
- [44] C. K. Tsang, T. L. Kelly, M. J. Sailor, Y. Y. Li, *ACS Nano* **2012**, *6*, 10546.
- [45] D. Y. Chan, A. G. Sega, J. Y. Lee, T. Gao, F. Cunin, F. Di Renzo, M. J. Sailor, *Inorg. Chim. Acta* **2014**, *422*, 21.
- [46] J. Wang, J. Joo, R. M. Kennard, S.-W. Lee, M. J. Sailor, *Chem. Mater.* **2016**, *28*, 79.
- [47] S. Chatterjee, R. Carter, L. Oakes, W. R. Erwin, R. Bardhan, C. L. Pint, *J. Phys. Chem. C* **2014**, *118*, 10893.
- [48] L. Oakes, A. Westover, J. W. Mares, S. Chatterjee, W. R. Erwin, R. Bardhan, S. M. Weiss, C. L. Pint, *Sci. Rep.* **2013**, *3*, 3020.
- [49] J. Salonen, E. Makila, J. Riikonen, T. Heikkila, V. P. Lehto, *Phys. Status Solidi A* **2009**, *206*, 1313.
- [50] G. Muller, M. Nerding, N. Ott, H. P. Strunk, R. Brendel, *Phys. Status Solidi A* **2003**, *197*, 83.
- [51] Y. H. Ogata, N. Yoshimi, R. Yasuda, T. Tsuboi, T. Sakka, A. Otsuki, *J. Appl. Phys.* **2001**, *90*, 6487.
- [52] J. Riikonen, S. Rigolet, C. Marichal, F. Aussenac, J. Lalevee, F. Morlet-Savary, P. Fioux, C. Dietlin, M. Bonne, B. Lebeau, V. P. Lehto, *J. Phys. Chem. C* **2015**, *119*, 19272.
- [53] J. Paski, M. Bjorkqvist, J. Salonen, V.-P. Lehto, *Phys. Status Solidi C* **2005**, *9*, 3379.
- [54] M. Bjorkqvist, J. Paski, J. Salonen, V. P. Lehto, *IEEE Sens. J.* **2006**, *6*, 542.
- [55] J. H. Song, M. J. Sailor, *Inorg. Chem.* **1999**, *38*, 1498.
- [56] P. J. Launer, in *Silicone Compounds Register and Review*, Petrarch Systems Inc., Bristol, UK **1987**, p. 100.
- [57] J. E. Spanier, I. P. Herman, *J. Porous Mater.* **2000**, *7*, 139.
- [58] H. Munder, M. G. Berger, S. Frohnhoff, M. Thonissen, H. Luth, M. Jeske, J. W. Schultze, *J. Lumin.* **1993**, *57*, 223.
- [59] S. P. Pujari, L. Scheres, T. Weidner, J. E. Baio, M. A. C. Stuart, C. J. M. van Rijn, H. Zuilhof, *Langmuir* **2013**, *29*, 4019.
- [60] S. Dhar, O. Seitz, M. D. Halls, S. Choi, Y. J. Chabal, L. C. Feldman, *J. Am. Chem. Soc.* **2009**, *131*, 16808.
- [61] E. Lopez-Honorato, P. J. Meadows, J. Tan, P. Xiao, *J. Mater. Res.* **2008**, *23*, 1785.
- [62] A. Huotari, W. J. Xu, J. Monkare, M. Kovalainen, K. H. Herzog, V. P. Lehto, K. Jarvinen, *Int. J. Pharm.* **2013**, *454*, 67.
- [63] E. Mäkilä, L. M. Birbo, M. Kaasalainen, B. Herranz, A. J. Airaksinen, M. Heinonen, E. Kukkk, J. Hirvonen, H. A. Santos, J. Salonen, *Langmuir* **2012**, *28*, 14045.
- [64] G. Dufour, F. Rochet, F. C. Stedile, C. Poncey, M. DeCrescenzi, R. Gunnella, M. Froment, *Phys. Rev. B* **1997**, *56*, 4266.
- [65] a) Y. S. Nagornov, *J. Exp. Theor. Phys.* **2015**, *121*, 1042; b) Y. S. Nagornov, *Tech. Phys.* **2015**, *60*, 700; c) Y. S. Nagornov, *J. Nano-Electron. Phys.* **2016**, *8*, 03001.

- [66] J. Salonen, L. Laitinen, A. M. Kaukonen, J. Tuura, M. Björkqvist, T. Heikkilä, K. Vaha-Heikkilä, J. Hirvonen, V. P. Lehto, *J. Controlled Release* **2005**, *108*, 362.
- [67] T. Linnell, J. Riikonen, J. Salonen, A. M. Kaukonen, L. Laitinen, J. Hirvonen, V. Lehto, *Int. J. Pharm.* **2007**, *343*, 141.
- [68] J. Riikonen, E. Makila, J. Salonen, V. P. Lehto, *Langmuir* **2009**, *25*, 6137.
- [69] J. Salonen, M. Björkqvist, J. Paski, *Sens. Actuators, A* **2004**, *116*, 438.
- [70] J. Salonen, J. Tuura, M. Björkqvist, V. P. Lehto, *Sens. Actuators, B* **2006**, *114*, 423.
- [71] M. Björkqvist, J. Salonen, J. Tuura, T. Jalkanen, V.-P. Lehto, *Phys. Status Solidi C* **2009**, *6*, 1769.
- [72] J. Salonen, M. Kaasalainen, O.-P. Rauhala, L. Lassila, M. Hakamies, T. Jalkanen, R. Hahn, P. Schmuki, E. Mäkilä, *ECS Trans.* **2015**, *69*, 167
- [73] V. Torres-Costa, J. Salonen, V. P. Lehto, R. J. Martin-Palma, J. M. Martinez-Duart, *Microporous Mesoporous Mater.* **2008**, *111*, 636.
- [74] T. Jalkanen, V. Torres-Costa, J. Salonen, M. Björkqvist, E. Makila, J. M. Martinez-Duart, V. P. Lehto, *Opt. Express* **2009**, *17*, 5446.
- [75] A. M. Ruminski, B. H. King, J. Salonen, J. L. Snyder, M. J. Sailor, *Adv. Funct. Mater.* **2010**, *20*, 2874.
- [76] T. Jalkanen, V. Torres-Costa, E. Makila, M. Kaasalainen, R. Koda, T. Sakka, Y. H. Ogata, J. Salonen, *ACS Appl. Mater. Interfaces* **2014**, *6*, 2884.
- [77] J. Tuura, M. Björkqvist, S. J., V.-P. Lehto, *Mater. Res. Soc. Symp. Proc.* **2005**, *876*, R8.8.1.
- [78] T. Jalkanen, E. Mäkilä, Y. I. Suzuki, T. Urata, K. Fukami, T. Sakka, J. Salonen, Y. H. Ogata, *Adv. Funct. Mater.* **2012**, *22*, 3890.
- [79] L. Canham, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Berlin, Germany **2014**.
- [80] L. Russo, F. Colangelo, R. Cioffi, I. Rea, L. D. Stefano, *Materials* **2011**, *4*, 1023.
- [81] a) Q. Shabir, C. Skaria, H. O. Brien, A. Loni, C. Barnett, L. Canham, *Nanoscale Res. Lett.* **2012**, *7*, 407; b) L. Canham, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 1.
- [82] D. Bellet, P. Lamagnere, A. Vincent, Y. Brechet, *J. Appl. Phys.* **1996**, *80*, 3772.
- [83] H. Magoaric, A. Danescu, *Physica Status Solidi C* **2009**, *6*, 1680.
- [84] N.-L. Wu, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 965.
- [85] O.-P. Rauhala, M. Kaasalainen, L. Lassila, E. Mäkilä, J. Salonen, presented at *Porous Semiconductor Science and Technology*, Tarragona, Spain, March **2016**.
- [86] A. V. Vasin, Y. Ishikawa, N. Shibata, J. Salonen, V. P. Lehto, *Jpn. J. Appl. Phys., Part 2* **2007**, *46*, L465.
- [87] S. Muto, A. V. Vasin, Y. Ishikawa, N. Shibata, J. Salonen, V. P. Lehto, in *Prism 6: Sixth Pacific Rim International Conference on Advanced Materials and Processing*, Parts 1–3, Vols. 561–565 (Eds: Y. W. Chang, N. J. Kim, C. S. Lee), Trans Tech Publications Ltd, Stafa-Zurich, Switzerland **2007**, p. 1127.
- [88] Y. Ishikawa, A. V. Vasin, J. Salonen, S. Muto, V. S. Lysenko, A. N. Nazarov, N. Shibata, V. P. Lehto, *J. Appl. Phys.* **2008**, *104*, 6.
- [89] A. Vasin, A. Rusavsky, A. Nazarov, V. Lysenko, G. Rudko, Y. Piryatinski, I. Blonsky, J. Salonen, E. Makila, S. Starik, *Phys. Status Solidi A* **2012**, *209*, 1015.
- [90] B. Sciacca, S. D. Alvarez, F. Geobaldo, M. J. Sailor, *Dalton Trans.* **2010**, *39*, 10847.
- [91] M. R. Linfood, C. E. D. Chidsey, *J. Am. Chem. Soc.* **1993**, *115*, 12631.
- [92] M. Kovalainen, J. Monkare, E. Makila, J. Salonen, V. P. Lehto, K. H. Herzig, K. Jarvinen, *Pharma. Res.* **2012**, *29*, 837.
- [93] T. Jalkanen, E. Makila, T. Sakka, J. Salonen, Y. H. Ogata, *Nanoscale Res. Lett.* **2012**, *7*, 311.
- [94] C. F. Wang, E. M. Makila, C. Bonduelle, J. Ryttonen, J. Raula, S. Almeida, A. Narvanen, J. J. Salonen, S. Lecommandoux, J. T. Hirvonen, H. A. Santos, *ACS Appl. Mater. Interfaces* **2015**, *7*, 2006.
- [95] C.-F. Wang, E. M. Makila, M. H. Kaasalainen, D. Liu, M. P. Sarparanta, A. J. Airaksinen, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2014**, *35*, 1257.
- [96] O. Keinanen, E. M. Makila, R. Lindgren, H. Virtanen, H. Liljenback, V. Oikonen, M. Sarparanta, C. Molthoff, A. D. Windhorst, A. Roivainen, J. J. Salonen, A. J. Airaksinen, *ACS Omega* **2017**, *2*, 62.
- [97] N. Shrestha, M.-A. Shahbazi, F. Araújo, E. Mäkilä, J. Raula, E. I. Kauppinen, J. Salonen, B. Sarmento, J. Hirvonen, H. A. Santos, *Biomaterials* **2015**, *68*, 9.
- [98] C. Chiappini, E. Tasciotti, J. R. Fakhoury, D. Fine, L. Pullan, Y. C. Wang, L. F. Fu, X. W. Liu, M. Ferrari, *ChemPhysChem* **2010**, *11*, 1029.
- [99] C. F. Wang, E. M. Makila, M. H. Kaasalainen, M. V. Hagstrom, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Acta Biomater.* **2015**, *16*, 206.
- [100] a) E. Makila, H. Kivela, N. Shrestha, A. Correia, M. Kaasalainen, E. Kukkk, J. Hirvonen, H. A. Santos, J. Salonen, *Langmuir* **2016**, *32*, 13020; b) V.-P. Lehto, J. Salonen, H. Santos, J. Riikonen, in *Drug Delivery Strategies for Poorly Water-Soluble Drugs* (Eds: D. Douroumis, A. Fahr), John Wiley & Sons Ltd, Chichester, UK **2013**, p. 477.
- [101] A. M. Kaukonen, L. Laitinen, J. Salonen, J. Tuura, T. Heikkilä, T. Linnell, J. Hirvonen, V.-P. Lehto, *Eur. J. Pharm. Biopharm.* **2007**, *66*, 348.
- [102] J. Salonen, A. M. Kaukonen, J. Hirvonen, V. P. Lehto, *J. Pharm. Sci.* **2008**, *97*, 632.
- [103] J. Salonen, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 909.
- [104] T. Laaksonen, H. Santos, H. Vihola, J. Salonen, J. Riikonen, T. Heikkilä, L. Peltonen, N. Kurnar, D. Y. Murzin, V. P. Lehto, J. Hirvonen, *Chem. Res. Toxicol.* **2007**, *20*, 1913.
- [105] L. M. Bimbo, L. Peltonen, J. Hirvonen, H. A. Santos, *Curr. Drug Metab.* **2012**, *13*, 1068.
- [106] D. F. Liu, E. Makila, H. B. Zhang, B. Herranz, M. Kaasalainen, P. Kinnari, J. Salonen, J. Hirvonen, H. A. Santos, *Adv. Funct. Mater.* **2013**, *23*, 1893.
- [107] C. F. Wang, E. M. Makila, M. H. Kaasalainen, D. F. Liu, M. P. Sarparanta, A. J. Airaksinen, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2014**, *35*, 1257.
- [108] M.-A. Shahbazi, T. D. Fernandez, E. M. Makila, X. Le Guevel, C. Mayorga, M. H. Kaasalainen, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2014**, *35*, 9224.
- [109] M.-A. Shahbazi, P. V. Almeida, E. M. Makila, M. H. Kaasalainen, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2014**, *35*, 7488.
- [110] P. V. Almeida, M.-A. Shahbazi, E. Makila, M. Kaasalainen, J. Salonen, J. Hirvonen, H. A. Santos, *Nanoscale* **2014**, *6*, 10377.
- [111] C.-F. Wang, E. M. Makila, M. H. Kaasalainen, M. V. Hagstrom, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Acta Biomater.* **2015**, *16*, 206.
- [112] B. Herranz-Blanco, D. F. Liu, E. Makila, M. A. Shahbazi, E. Ginestar, H. B. Zhang, V. Aseyev, V. Balasubramanian, J. Salonen, J. Hirvonen, H. A. Santos, *Adv. Funct. Mater.* **2015**, *25*, 1488.
- [113] F. Fontana, M. A. Shahbazi, D. F. Liu, H. B. Zhang, E. Makila, J. Salonen, J. T. Hirvonen, H. A. Santos, *Adv. Mater.* **2017**, *29*.
- [114] H. A. Santos, J. Riikonen, J. Salonen, E. Makila, T. Heikkilä, T. Laaksonen, L. Peltonen, V. P. Lehto, J. Hirvonen, *Acta Biomater.* **2010**, *6*, 2721.
- [115] M. Kilpelainen, J. Riikonen, M. A. Vlasova, A. Huotari, V. P. Lehto, J. Salonen, K. H. Herzig, K. Jarvinen, *J. Controlled Release* **2009**, *137*, 166.

- [116] M. Kilpelainen, J. Monkare, M. A. Vlasova, J. Riikonen, V. P. Lehto, J. Salonen, K. Jarvinen, K. H. Herzig, *Eur. J. Pharm. Biopharm.* **2011**, *77*, 20.
- [117] a) F. Araujo, N. Shrestha, M.-A. Shahbazi, P. Fonte, E. M. Makila, J. J. Salonen, J. T. Hirvonen, P. L. Granja, H. A. Santos, B. Sarmiento, *Biomaterials* **2014**, *35*, 9199; b) N. Shrestha, F. Araujo, M. A. Shahbazi, E. Makila, M. J. Gomes, M. Airavaara, E. I. Kauppinen, J. Raula, J. Salonen, J. Hirvonen, B. Sarmiento, H. A. Santos, *J. Controlled Release* **2016**, *232*, 113; c) F. Araujo, N. Shrestha, M. J. Gomes, B. Herranz-Blanco, D. Liu, J. J. Hirvonen, P. L. Granja, H. A. Santos, B. Sarmiento, *Nanoscale* **2016**, *8*, 10706.
- [118] a) N. Shrestha, F. Araujo, M.-A. Shahbazi, E. Mäkilä, M. J. Gomes, B. Herranz-Blanco, R. Lindgren, S. Granroth, E. Kukku, J. Salonen, J. Hirvonen, B. Sarmiento, H. A. Santos, *Adv. Funct. Mater.* **2016**, *26*, 3405; b) N. Shrestha, M.-A. Shahbazi, F. Araujo, H. Zhang, E. M. Makila, J. Kauppila, B. Sarmiento, J. J. Salonen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2014**, *35*, 7172.
- [119] M. Kovalainen, J. Mönkäre, M. Kaasalainen, J. Riikonen, V.-P. Lehto, J. Salonen, K.-H. Herzig, K. Järvinen, *Mol. Pharmaceutics* **2013**, *10*, 353.
- [120] M. A. Vlasova, J. Ryttonen, J. Riikonen, O. S. Tarasova, J. Monkare, M. Kovalainen, A. Narvanen, J. Salonen, K.-H. Herzig, V.-P. Lehto, K. Jarvinen, *Eur. J. Pharm. Sci.* **2014**, *63*, 96.
- [121] M. Kaasalainen, J. Ryttonen, E. Makila, A. Narvanen, J. Salonen, *Langmuir* **2015**, *31*, 1722.
- [122] M. Kovalainen, J. Monkare, J. Riikonen, U. Pesonen, M. Vlasova, J. Salonen, V.-P. Lehto, K. Jarvinen, K.-H. Herzig, *Pharmacol. Rev.* **2015**, *67*, 541.
- [123] M. Yu, J. Zheng, *ACS Nano* **2015**, *9*, 6655.
- [124] E. Blanco, H. Shen, M. Ferrari, *Nat. Biotechnol.* **2015**, *33*, 941.
- [125] a) M. Sarparanta, L. M. Bimbo, J. Ryttonen, E. Makila, T. J. Laaksonen, P. Laaksonen, M. Nyman, J. Salonen, M. B. Linder, J. Hirvonen, H. A. Santos, A. J. Airaksinen, *Mol. Pharmaceutics* **2012**, *9*, 654; b) A. M. Kallinen, M. P. Sarparanta, D. Liu, E. M. Makila, J. J. Salonen, J. T. Hirvonen, H. A. Santos, A. J. Airaksinen, *Mol. Pharmaceutics* **2014**, *11*, 2876.
- [126] L. M. Bimbo, M. Sarparanta, H. A. Santos, A. J. Airaksinen, E. Makila, T. Laaksonen, L. Peltonen, V. P. Lehto, J. Hirvonen, J. Salonen, *ACS Nano* **2010**, *4*, 3023.
- [127] H. A. Santos, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2016**, p. 1.
- [128] C.-F. Wang, M. P. Sarparanta, E. M. Makila, M. L. K. Hyvonen, P. M. Laakkonen, J. J. Salonen, J. T. Hirvonen, A. J. Airaksinen, H. A. Santos, *Biomaterials* **2015**, *48*, 108.
- [129] F. Zhang, A. Correia, E. Makila, W. Li, J. Salonen, J. J. Hirvonen, H. B. Zhang, H. A. Santos, *ACS Appl. Mater. Interfaces* **2017**, *9*, 10034.
- [130] D. Liu, H. Zhang, E. Makila, J. Fan, B. Herranz-Blanco, C.-F. Wang, R. Rosa, A. J. Ribeiro, J. Salonen, J. Hirvonen, H. A. Santos, *Biomaterials* **2015**, *39*, 249.
- [131] F. Kong, X. Zhang, H. Zhang, X. Qu, D. Chen, M. Servos, E. Makila, J. Salonen, H. A. Santos, M. Hai, D. A. Weitz, *Adv. Funct. Mater.* **2015**, *25*, 3330.
- [132] F. Kong, H. B. Zhang, X. M. Qu, X. Zhang, D. Chen, R. H. Ding, E. Makila, J. Salonen, H. A. Santos, M. T. Hai, *Adv. Mater.* **2016**, *28*, 10195.
- [133] a) D. F. Liu, H. B. Zhang, F. Fontana, J. T. Hirvonen, H. A. Santos, *Lab Chip* **2017**, *17*, 1856; b) D. F. Liu, H. B. Zhang, B. Herranz-Blanco, E. Makila, V. P. Lehto, J. Salonen, J. Hirvonen, H. A. Santos, *Small* **2014**, *10*, 2029; c) Z. H. Liu, V. Balasubramanian, C. Bhat, M. Vahermo, E. Makila, M. Kemell, F. Fontana, A. Janoniene, V. Petrikaite, J. Salonen, J. Yli-Kauhaluoma, J. Hirvonen, H. B. Zhang, H. A. Santos, *Adv. Healthcare Mater.* **2017**, *6*, 1601009.
- [134] F. Fontana, D. Liu, J. Hirvonen, H. A. Santos, *Wiley Interdiscip. Rev.: Nanomed. Nanobiotechnol.* **2017**, *9*, e1421.
- [135] a) E. C. Wu, J. S. Andrew, L. Y. Cheng, W. R. Freeman, L. Pearson, M. J. Sailor, *Biomaterials* **2011**, *32*, 1957; b) L. Cheng, E. Anglin, F. Cunin, D. Kim, M. J. Sailor, I. Falkenstein, A. Tammewar, W. R. Freeman, *Br. J. Ophthalmol.* **2008**, *92*, 705; c) L. Y. Cheng, M. J. Sailor, O. Kayikcioglu, D. Kim, I. Kozak, G. Bergeron-Lynn, W. R. Freeman, *Invest. Ophthalmol. Visual Sci.* **2005**, *46*.
- [136] a) S. Kashanian, F. Harding, Y. Irani, S. Klebe, K. Marshall, A. Loni, L. Canham, D. M. Fan, K. A. Williams, N. H. Voelcker, J. L. Coffer, *Acta Biomater.* **2010**, *6*, 3566; b) S. P. Low, N. H. Voelcker, L. T. Canham, K. A. Williams, *Biomaterials* **2009**, *30*, 2873.
- [137] E. Korhonen, S. Ronkko, S. Hillebrand, J. Riikonen, W. J. Xu, K. Jarvinen, V. P. Lehto, A. Kauppinen, *Eur. J. Pharm. Biopharm.* **2016**, *100*, 1.
- [138] T. R. Dargaville, B. L. Farrugia, J. A. Broadbent, S. Pace, Z. Upton, N. H. Voelcker, *Biosens. Bioelectron.* **2013**, *41*, 30.
- [139] F. S. H. Krismastuti, W. L. A. Brooks, M. J. Sweetman, B. S. Sumerlin, N. H. Voelcker, *J. Mat. Chem. B* **2014**, *2*, 3972.
- [140] S. Pace, R. B. Vasani, W. Zhao, S. Perrier, N. H. Voelcker, *Nanoscale Res. Lett.* **2014**, *9*, 420.
- [141] M. H. Kafshgari, A. Cavallaro, B. Delalat, F. J. Harding, S. J. P. McInnes, E. Makila, J. Salonen, K. Vasilev, N. H. Voelcker, *Nanoscale Res. Lett.* **2014**, *9*, 333.
- [142] C. T. Turner, M. H. Kafshgari, E. Melville, B. Delalat, F. Harding, E. Makila, J. J. Salonen, A. J. Cowin, N. H. Voelcker, *ACS Biomater. Sci. Eng.* **2016**, *2*, 2339.
- [143] M. Mori, P. V. Almeida, M. Cola, G. Anselmi, E. Makila, A. Correia, J. Salonen, J. Hirvonen, C. Caramella, H. A. Santos, *Eur. J. Pharm. Biopharm.* **2014**, *88*, 635.
- [144] F. Fontana, M. Mori, F. Riva, E. Makila, D. F. Liu, J. Salonen, G. Nicoletti, J. Hirvonen, C. Caramella, H. A. Santos, *ACS Appl. Mater. Interfaces* **2016**, *8*, 988.
- [145] M. P. A. Ferreira, S. Ranjan, A. M. R. Correia, E. M. Makila, S. M. Kinnunen, H. B. Zhang, M. A. Shahbazi, P. V. Almeida, J. J. Salonen, H. J. Ruskoaho, A. J. Airaksinen, J. T. Hirvonen, H. A. Santos, *Biomaterials* **2016**, *94*, 93.
- [146] M. A. Tolli, M. P. A. Ferreira, S. M. Kinnunen, J. Rysa, E. M. Makila, Z. Szabo, R. E. Serpi, P. J. Ohukainen, M. J. Valimaki, A. M. R. Correia, J. J. Salonen, J. T. Hirvonen, H. J. Ruskoaho, H. A. Santos, *Biomaterials* **2014**, *35*, 8394.
- [147] N. Naderi, M. R. Hashim, J. Rouhi, H. Mahmodi, *Mater. Sci. Semicond. Process.* **2013**, *16*, 542.
- [148] V. Torres-Costa, R. J. Martin-Palma, J. M. Martinez-Duart, J. Salonen, V. P. Lehto, *J. Appl. Phys.* **2008**, *103*, 4.
- [149] T. Jalkanen, J. Salonen, V. Torres-Costa, K. Fukami, T. Sakka, Y. H. Ogata, *Opt. Express* **2011**, *19*, 13291.
- [150] V. Torres-Costa, J. Salonen, T. M. Jalkanen, V. P. Lehto, R. J. Martin-Palma, J. M. Martinez-Duart, *Physica Status Solidi A* **2009**, *206*, 1306.
- [151] T. Jalkanen, J. Tuura, E. Makila, J. Salonen, *Sens. Actuators, B* **2010**, *147*, 100.
- [152] J. Salonen, E. Makila, T. Urata, V. Torres-Costa, T. Jalkanen, in *State-of-the-Art Program on Compound Semiconductors*, Vol. 58 (Eds: C. Odwyer, E. Douglas, S. Jang, M. T. Carter, Y. L. Chueh, M. H. Jo, M. Suzuki, J. H. He, S. Albin, L. J. Chou, S. Jin, R. J. MartinPalma), Electrochemical Soc. Inc., Pennington, NJ **2013**, p. 63.
- [153] a) R. Herino, in *Porous Silicon Science and Technology* (Eds: J.-C. Vial, J. Derrien), Springer-Verlag, Berlin, Germany **1995**, p. 54; b) M. J. Sailor, in *Handbook of Porous Silicon*, (Ed: L. Canham), Springer International Publishing, Cham, Switzerland **2014**, p. 355.

- [154] M. Y. Chen, M. D. Klunk, V. M. Diep, M. J. Sailor, *Adv. Mater.* **2011**, *23*, 4537.
- [155] W. Y. Tong, M. J. Sweetman, E. R. Marzouk, C. Fraser, T. Kuchel, N. H. Voelcker, *Biomaterials* **2016**, *74*, 217.
- [156] J. Tuura, M. Bjorkqvist, J. Salonen, V. P. Lehto, *Sens. Actuators, B* **2008**, *131*, 627.
- [157] T. Jalkanen, E. Makila, A. Maattanen, J. Tuura, M. Kaasalainen, V. P. Lehto, P. Ihalainen, J. Peltonen, J. Salonen, *Appl. Phys. Lett.* **2012**, *101*, 263110.
- [158] T. Jalkanen, A. Maattanen, E. Makila, J. Tuura, M. Kaasalainen, V.-P. Lehto, P. Ihalainen, J. Peltonen, J. Salonen, *J. Sens.* **2015**, *2015*, 927396.
- [159] X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B. W. Sheldon, J. Wu, *Adv. Energy Mater.* **2014**, *4*, 1300882.
- [160] S. E. Rowlands, R. J. Latham, W. S. Schlindwein, *Ionics* **1999**, *5*, 144.
- [161] Y. Ma, H. Chang, M. Zhang, Y. Chen, *Adv. Mater.* **2015**, *27*, 5296.
- [162] a) D. S. Gardner, C. W. Holzwarth, Y. Liu, S. B. Clendenning, W. Jin, B.-K. Moon, C. Pint, Z. Chen, E. C. Hannah, C. Chen, C. Wang, E. Mäkilä, R. Chen, T. Aldridge, J. L. Gustafson, *Nano Energy* **2016**, *25*, 68; b) A. S. Westover, D. Freudiger, Z. S. Gani, K. Share, L. Oakes, R. E. Carter, C. L. Pint, *Nanoscale* **2015**, *7*, 98.
- [163] A. P. Cohn, W. R. Erwin, K. Share, L. Oakes, A. S. Westover, R. E. Carter, R. Bardhan, C. L. Pint, *Nano Lett.* **2015**, *15*, 2727.
- [164] A. S. Westover, J. W. Tian, S. Bernath, L. Oakes, R. Edwards, F. N. Shabab, S. Chatterjee, A. V. Anilkumar, C. L. Pint, *Nano Lett.* **2014**, *14*, 3197.
- [165] R. Carter, D. EJORH, K. Share, A. P. Cohn, A. Douglas, N. Muralidharan, T. M. Tovar, C. L. Pint, *J. Power Sources* **2016**, *330*, 70.
- [166] K. Share, R. E. Carter, P. Nikolaev, D. Hooper, L. Oakes, A. P. Cohn, R. Rao, A. A. Puretzky, D. B. Geohegan, B. Maruyama, C. L. Pint, *J. Phys. Chem. C* **2016**, *120*, 14180.
- [167] D. Z. Fang, C. C. Striemer, T. R. Gaborski, J. L. McGrath, P. M. Fauchet, *Nano Lett.* **2010**, *10*, 3904.
- [168] A. V. Pavlikov, N. V. Latukhina, V. I. Chepurinov, V. Y. Timoshenko, *Semiconductors* **2017**, *51*, 402.
- [169] S. Z. Deng, Z. B. Li, W. L. Wang, N. S. Xu, J. Zhou, X. G. Zheng, H. T. Xu, J. Chen, J. C. She, *Appl. Phys. Lett.* **2006**, *89*, 023118.
- [170] V. Balasubramanian, A. Correia, H. B. Zhang, F. Fontana, E. Makila, J. Salonen, J. Hirvonen, H. A. Santos, *Adv. Mater.* **2017**, *29*, 1605375.
- [171] a) N. Vale, A. Correia, S. Silva, P. Figueiredo, E. Makila, J. Salonen, J. Hirvonen, J. Pedrosa, H. A. Santos, A. Fraga, *Bioorg. Med. Chem. Lett.* **2017**, *27*, 403; b) N. Vale, E. Makila, J. Salonen, P. Gomes, J. Hirvonen, H. A. Santos, *Eur. J. Pharm. Biopharm.* **2012**, *81*, 314.
- [172] A. Kallinen, D. F. Liu, E. Makila, M. Sarparanta, J. Salonen, J. Hirvonen, H. A. Santos, A. J. Airaksinen, *J. Labelled Compd. Radiopharm.* **2013**, *56*, S252.
- [173] M. Sarparanta, C. F. Wang, E. Makila, M. Hyvonen, P. Laakkonen, J. Salonen, J. Hirvonen, H. Santos, A. J. Airaksinen, *J. Labelled Compd. Radiopharm.* **2015**, *58*, S116.