Polymer - Porous Silicon Composites

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Contents

Abstract

A variety of PSi-polymer composites have been developed, from the perspectives of different polymers, different composite morphologies, and different targeted applications.

The field is comprehensively reviewed, focusing on the different design and synthesis strategies, together with a brief discussion of the emerging fields of application.

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Introduction

The combination of polymers with nanostructured silicon scaffolds, in particular porous Si (PSi), into a single composite system opens vast opportunities for developing advanced functional materials. These composites display unique properties that are culminated by the characteristics of each building block, to allow the design of highly tunable nanomaterials. Over the past decade, various PSi-polymer composites were introduced and their application as sensors (chapter "▶ Porous Silicon Optical Biosensors"), actuators, optical devices (e.g., chapter "▶ Porous Silicon Optical Waveguides"), drug delivery systems (chapter "▶ Drug Delivery with Porous Silicon"), and tissue-engineered scaffolds (chapter "▶ Porous Silicon and Tissue Engineering Scaffolds") was demonstrated.

In this chapter, we will describe the basic considerations in designing functional PSi-polymer composites, synthesis strategies, and emerging applications of these nanomaterials. Future prospects and challenges in both fabrication and implementation of PSi-polymer-based devices will be discussed.

Design of PSi-Polymer Composites

Porous Si-polymer composites may be designed in diverse configurations. Figure 1 schematically illustrates the most common structures: PSi infiltrated with a polymer, polymer-coated PSi, polymer-capped PSi, released PSi film supported by a polymer, PSi particles encapsulated by a polymer, and composite microparticles. Each of these structures possesses different properties, which can be further refined by a proper choice of the polymer constituent and the PSi nanostructure.

The simplest composite structure is that of a polymer-infiltrated PSi substrate (Fig. 1a), wherein the polymer fills the entire porous volume (Segal et al. 2007; Massad-Ivanir et al. 2010; Perelman et al. 2010; Massad-Ivanir et al. 2012a; Krepker and Segal 2013). The polymer is confined within the nanoscale pores, and its interaction with the pore wall can be enhanced by covalent attachment (Massad-Ivanir et al. 2012a; Bonanno and Delouise 2010; Bonanno and Segal 2011; Sciacca et al. 2011). To some extent, polymer-coated PSi (Fig. 1b) has a similar design, where the polymer only forms a uniform layer onto the pore walls, resulting in an open porous structure (Segal et al. 2009; McInnes et al. 2009). Polymer-capped PSi is a more sophisticated architecture (Fig. 1c), in which the polymer only forms a blocking layer on top of the PSi, leaving the greater fraction of the porous volume unoccupied (Wu and Sailor 2009). The fabrication of these composites is more challenging, as the degree of polymer penetration into the pores needs to be precisely controlled. Figure 1d presents a polymeric replica from PSi. These replicas are usually prepared from polymer-infiltrated PSi by selective removal of the Si scaffold (Li et al. 2003; Park et al. 2007). The previously described designs make use of intact PSi substrates. However, the following PSi-polymer composite configurations require mechanical processing of the PSi.

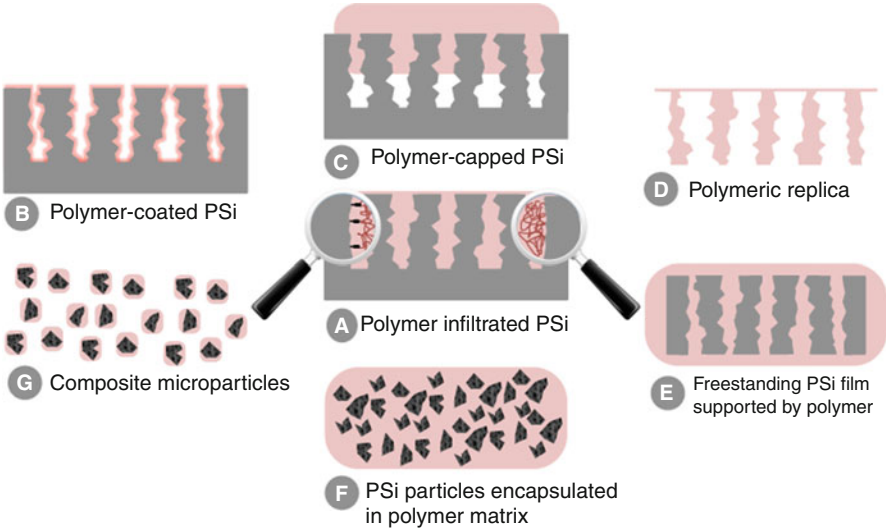

Fig. 1 Common structures of PSi-polymer composites. *Insets* in *A* illustrate interfacial chemistry where the polymer is not attached to PSi (*right*) and is covalently attached to the PSi surface through different linkers. Schematics are not drawn to scale

A freestanding PSi film supported by polymer is presented in Fig. 1e. In this case, separation of the porous layer from the bulk Si is typically achieved by electropolishing (DeLouise et al. 2005). Further fracturing of these porous films allows us to fabricate particulate composites (McInnes et al. 2012). The resulting PSi micro-/nanoparticles can be embedded in a polymer matrix (Fig. 1f) or encapsulated individually by a polymer layer (Fig. 1g). The latter case is more synthetically challenging.

The diversity in the design of these composites highlights the possibility to select a suitable configuration for tailoring specific mechanical, chemical, and optical properties for a desired function. Rational selection of the polymer component, PSi substrate nanostructure, and fabrication strategy are of utmost importance in tuning the behavior of the resulting composite.

Fabrication Methods of PSi-Polymer Composites

There are many synthetic approaches for integrating polymers with PSi. Figure 2 summarizes the main methods that are practiced for the fabrication of PSi-polymer composites. In general, these techniques can be divided into two main categories. The first is incorporating a preformed polymer with the Si scaffold. The second involves in situ polymerization of monomers within/on the PSi. Herein, we will focus only on the main techniques for the fabrication of PSi-polymer composites.

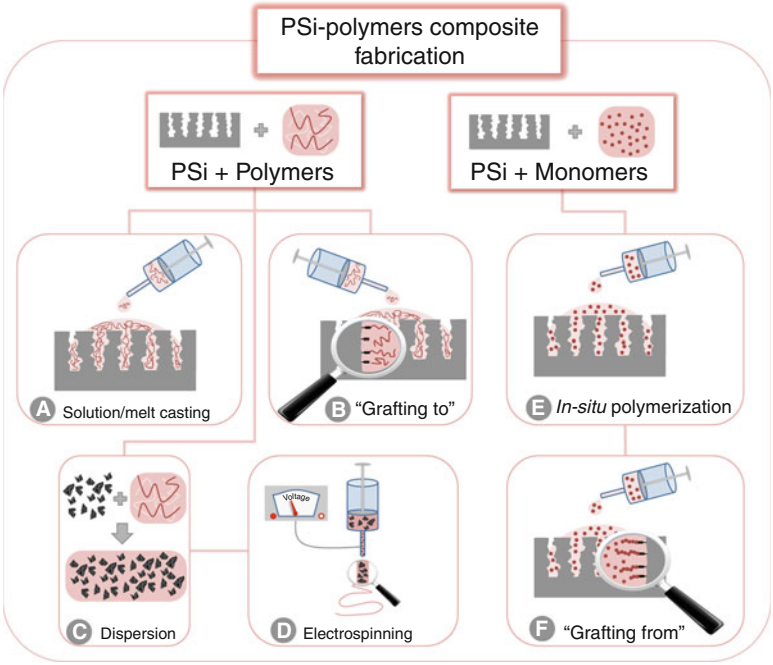

Fig. 2 Common practiced methods for the fabrication of PSi-polymer composites

Incorporation of a Preformed Polymer with PSi

Solution casting (Fig. 2a) is probably the simplest route for fabricating PSi-polymer composites, and thus, it is widely implemented (Wu and Sailor 2009; Park et al. 2007; McInnes et al. 2012; Gao et al. 2008; Orosco et al. 2006; Shang et al. 2011; De Stefano et al. 2009; Schwartz et al. 2006; Kim et al. 2008; Koh et al. 2008; Sychev et al. 2009; Whitehead et al. 2008; Li et al. 2005). In this case, a polymeric solution is prepared and cast onto the PSi. This procedure is usually followed by a subsequent spin-coating step to remove excess solution and to distribute the polymer evenly on the surface of PSi (Gao et al. 2008; Shang et al. 2011; Schwartz et al. 2006). The extent of polymer solution penetration into pores plays a vital role in determining the final structure of the composite. Generally, polymer infiltration into the porous scaffold depends on several key parameters: the molecular weight (MW) of the polymer, the solution viscosity and its surface tension, pore dimensions and morphology, and the pore wall surface chemistry. In addition, the small size of pores can trap air or other gases, inhibiting the penetration of the polymer solution into the pores. In this case, degassing under vacuum and PSi conditioning with the solvent is recommended. Overall, this technique is relatively straightforward, as it does not involve complex synthetic steps and specialized experimental setups. Moreover, the use of a preformed

polymer, which its characteristics are already defined (e.g., MW and chain configuration), offers significant advantages in terms of the properties and behavior of the final composite. Capping layer on PSi film (Wu and Sailor 2009; Gao et al. 2008; Orosco et al. 2006; Shang et al. 2011), PSi infiltrated with polymers (McInnes et al. 2012; De Stefano et al. 2009; Schwartz et al. 2006), polymer replicas of PSi templates (Li et al. 2003; Park et al. 2007; Kim et al. 2008), and a freestanding PSi film supported by a polymer (Koh et al. 2008; Sychev et al. 2009) are the most common designs of PSi-polymer composites prepared by solution or melt casting.

Another simple technique for preparation of PSi-polymer composites is by dispersing PSi particles within a molten polymer or a polymeric solution (Fig. 2c). Further processing of these **dispersions** is required in order to form coatings (Svrcek et al. 2009), monoliths (McInnes et al. 2012; Mukherjee et al. 2006), and fibers (Fan et al. 2011; Kashanian et al. 2010).

Fibrous PSi-polymer systems can be fabricated by **electrospinning** (Fig. 2d) which is an established method for the production of large area networks of thin flexible fibers. In this case, the PSi-polymer dispersion or melt is squeezed through a nozzle, to which a strong electrical field is applied. The applied voltage causes a cone-shaped deformation of the drop of polymer solution/melt and a jet is formed. As the spurt makes its way to the counter electrode, the melt solidifies or the solvent evaporates and a polymer fiber is formed (Greiner and Wendorff 2007). The resulting properties of electro-spun fibers are controlled by the process parameters, e.g., electrical conductivity, electrode separation and geometry, temperature, concentration, and the polymer characteristics. Coffer et al. (Fan et al. 2011; Kashanian et al. 2010; Fan et al. 2009) have applied this technique to produce electro-spun fibers of PSi particles encapsulated within a polycaprolactone matrix.

Grafting involves covalent attachment of the polymer to a surface. Grafting provides a versatile tool for surface modification and functionalization in a highly controllable manner. Two main grafting categories can be identified. The first is termed "grafting to," in which a preformed polymer is attached to the surface. In the second approach "grafting from," polymerization is initiated from the substrate surface by the attachment of initiating groups (Minko 2008). The latter method will be discussed in the following section, dealing with polymerization techniques.

In the "grafting to" method (Fig. 2b), end-functionalized polymer chains are reacted with complementary functional groups located on the PSi surface to form tethered polymer chains (Minko 2008). The versatile chemistry of Si/SiO_2 allows functionalization of the PSi surface with a wide repertoire of reactive groups (Buriak 2002; Ciampi et al. 2008; Kilian et al. 2009a; Alvarez et al. 2009; Jarvis et al. 2012). Some of the most common PSi functionalization routes are presented in Fig. 3.

The advantage of the "grafting to" method is that the end-functionalized polymers with a predetermined configuration (e.g., MW and functional groups) are employed for grafting, and, as a result, well-defined layers can be readily obtained. It should be mentioned that a disadvantage of this method is the limited grafting density that can be achieved (Zdyrko et al. 2006). Thus, this technique was implemented for grafting

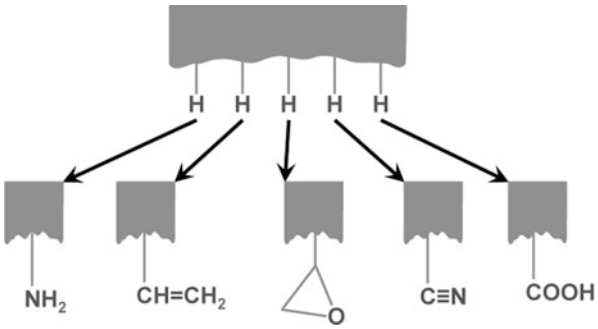

Fig. 3 Commonly practiced surface chemistries for the functionalization of PSi. These end groups can be reacted with a wide variety of polymers

poly(n-isopropylamide) (polyNIPAM) (Segal et al. 2009), chitosan (Sciacca et al. 2011), and gelatin (Kilian et al. 2009b). "Grafting to" is typically used for fabricating polymer-coated PSi surfaces and nanostructures (see Fig. 1b).

Polymerization Within PSi

In many cases, when using high-MW polymers, these macromolecules are size excluded from the nanoscale pores, or their efficient infiltration into the PSi nanostructure is impaired. Thus, to circumvent these issues, in situ polymerization of low-MW monomers (or oligomers) within the PSi scaffold can be applied (Segal et al. 2007; Massad-Ivanir et al. 2010; Perelman et al. 2010; Krepker and Segal 2013; Massad-Ivanir et al. 2012b; El-Zohary et al. 2013). The PSi nanostructure is commonly filled with a prepolymer solution, which may contain a composition of a solvent, monomers, cross-linking agents, initiators, and catalysts. When the polymerization reaction is initiated, the polymer is formed inside the pores of PSi, resulting in a uniform and high pore filling. In certain cases, polymerization can be initiated from the PSi surface, generally termed as a "grafting from" technique, or the growing polymer chains can be tethered to the pore walls.

There are many different polymerization routes that have been employed for the fabrication of PSi-polymer composites, including free-radical polymerization (FRP), photopolymerization (Segal et al. 2007; Massad-Ivanir et al. 2010; Perelman et al. 2010; Krepker and Segal 2013; Massad-Ivanir et al. 2012b), atom transfer radical polymerization (ATRP) (Vasani et al. 2011; Yang and Choi 2010; Pace et al. 2013), ring-opening polymerization (McInnes et al. 2006, 2009, 2012; Yoon et al. 2003), and electro-polymerization (Belhousse et al. 2010; Jin et al. 2009; Chiboub et al. 2010; Fukami et al. 2009; Harraz et al. 2008; Betty 2009; Urbach et al. 2007a, b; Nahor et al. 2011; Badeva et al. 2012; Dian et al. 2013). Polymerization method has a profound effect on the resulting PSi-polymer composite structure and its properties. For example, FRP typically results in time invariant degrees of polymerization and a high polydispersity index (a wide MW distribution). ATRP, on the other hand, allows for achieving a controllable molecular weight and low polydispersity, as the polymer

chains preserve their ability to grow for a long time and their degree of termination or chain transfer is very low (Braunecker and Matyjaszewski 2007).

When "grafting from" approach is applied for polymer synthesis, an appropriate initiator is commonly immobilized onto the pore walls followed by polymer chains growth via different possible mechanisms (Jarvis et al. 2012; Vasani et al. 2011; Xu et al. 2004; Chen et al. 2009). The main advantage of the "grafting from" methods is the possibility to form polymer layers of high density in comparison to the "grafting to" approach.

It should be emphasized that in situ polymerization within nanostructures is a complex process in which nano-confinement conditions may affect the polymerization kinetics and the resulting properties of the polymer (Massad-Ivanir et al. 2012a; Alcoutlabi and Gregory 2005; Keten et al. 2010; Kruk et al. 2008; Liang et al. 2000; Uemura et al. 2010; Gorman et al. 2008). Recent studies have shown that the imprisonment of hydrogels in PSi nanoscale pores induces significant changes in the confined polymer properties, e.g., volume phase transition (VPT) kinetics, compared to those observed for the bulk "free" polymers (Segal et al. 2007; Massad-Ivanir et al. 2010; Perelman et al. 2010; Bonanno and Segal 2011). Moreover, significant differences between the thermal degradation behaviors of the confined polymers, poly(acrylamide), and polyNIPAM and neat polymer and thin polymer films deposited onto planar Si surfaces were observed. The confined polymers have inferior thermal stability than the neat polymers. These findings indicate that the in situ polymerization and the polymer confinement conditions have a profound effect on the nanostructure and resulting behavior of the polymeric phase (Massad-Ivanir et al. 2012a).

We expect that investigation and characterization of the properties of different polymeric systems confined within nanostructured porous Si hosts will allow to finely tune the polymer properties by controlling the confinement conditions and interfacial interactions between the polymer and the host material. This will expand the possibility for rational design of new PSi-polymer nanomaterials with tailored properties and functions.

Applications

As PSi-polymer composites exhibit unique properties that are culminated by the characteristics of each building block, they can be rationally designed to display highly tunable properties, e.g., mechanical, chemical, optical, and electrical. Over the past decade, these attractive nanocomposites have been studied as platforms for designing different devices. Applications of these composites range from drug delivery systems, sensors, and actuators to optoelectronics and photovoltaics.

A recent review (Bonanno and Segal 2011) provides an updated overview on the biomedical applications of these materials, highlighting the construction of smart drug delivery systems (Wu and Sailor 2009; Vasani et al. 2011; Godin et al. 2011), improved label-free optical biosensors (Massad-Ivanir et al. 2010; Massad-Ivanir et al. 2012b; Holthausen et al. 2012), or sensors (Bonanno and Delouise 2010) for

"point-of-care" applications such as temperature sensors to monitor wound healing (Pace et al. 2012), lab-on-chip systems (Chen et al. 2009), and tissue engineering scaffolds (Coffer et al. 2005). In addition to the vast biological applications, PSi-polymer composites are being investigated as chemical sensors for different targets (Belhousse et al. 2010; Jin et al. 2009; Wang et al. 2012; Levitsky et al. 2007; Pang-Leen and Levitsky 2011), optoelectronics devices, photovoltaics (Svrcek et al. 2009; Badeva et al. 2012; Halliday et al. 1996; Mishra et al. 2008; Nguyen et al. 2003a, b; Gongalsky et al. 2012), and energy storage (Ge et al. 2012). Thus, the versatility of polymers in combination with the unique properties of PSi offers a wealth of opportunities for the design of new functional materials for a range of applications. We have yet to see the widespread translation of these composite-based devices into commercial application, and only the future will reveal the true impact of these materials.

References

Alcoutlabi M, Gregory BM (2005) Effects of confinement on material behaviour at the nanometre size scale. J Phys Condens Matter 17:R461

Alvarez SD, Derfus AM, Schwartz MP, Bhatia SN, Sailor M (2009) The compatibility of hepatocytes with chemically modified porous silicon with reference to in vitro biosensors. J Biomater 30:26

Badeva D, Tran-Van F, Beouch L, Chevrot C, Markova I, Racheva T, Froyer G (2012) Embedding and electropolymerization of terthiophene derivatives in porous n-type silicon. Mater Chem Phys 133:592

Belhousse S, Boukherroub R, Szunerits S, Gabouze N, Keffous A, Sam S, Benaboura A (2010) Electrochemical grafting of poly(3-hexylthiophene) on porous silicon for gas sensing. Surf Interface Anal 42:1041

Betty CA (2009) Highly sensitive capacitive immunosensor based on porous silicon-polyaniline structure: bias dependence on specificity. Biosens Bioelectron 25:338

Bonanno LM, Delouise LA (2010) Integration of a chemical-responsive hydrogel into a porous silicon photonic sensor for visual colorimetric readout. Adv Funct Mater 20:573

Bonanno LM, Segal E (2011) Nanostructured porous silicon/polymer-based hybrids: from biosensing to drug delivery. Nanomedicine 6:1755

Braunecker WA, Matyjaszewski K (2007) Controlled/living radical polymerization: features, developments, and perspectives. Prog Polym Sci 32:93

Buriak JM (2002) Organometallic chemistry on silicon and germanium surfaces. Chem Rev 102:1271

Chen L, Chen Z-T, Wang J, Xiao S-J, Lu Z-H, Gu Z-Z, Kang L, Chen J, Wu P-H, Tang Y-C, Liu J-N (2009) Gel-pad microarrays templated by patterned porous silicon for dual-mode detection of proteins. Lab Chip 9:756

Chiboub N, Boukherroub R, Szunerits S, Gabouze N, Moulay S, Sam S (2010) Chemical and electrochemical grafting of polyaniline on aniline-terminated porous silicon. Surf Interface Anal 42:1342

Ciampi S, Bocking T, Kilian KA, Harper JB, Gooding JJ (2008) Click chemistry in mesoporous materials: functionalization of porous silicon rugate filters. Langmuir 24:5888

Coffer JL, Whitehead MA, Nagesha DK, Mukherjee P, Akkaraju G, Totolici M, Saffie RS, Canham LT (2005) Porous silicon-based scaffolds for tissue engineering and other biomedical applications. Physica Status Solidi (A) Appl Mater Sci 202:1451

De Stefano L, Rotiroti L, De Tommasi E, Rea I, Rendina I, Canciello M, Maglio G, Palumbo R (2009) Hybrid polymer-porous silicon photonic crystals for optical sensing. J Appl Phys 106:023109

DeLouise LA, Fauchet PM, Miller BL, Pentland AA (2005) Hydrogel-supported optical-microcavity sensors. Adv Mater 17:2199

Dian J, Konečný M, Broncová G, Kronďák M, Matolínová I (2013) Electrochemical fabrication and characterization of porous silicon/polypyrrole composites and chemical sensing of organic vapors. Int J Electrochem Sci 8:1559

El-Zohary SE, Shenashen MA, Allam NK, Okamoto T, Haraguchi MJ (2013) Electrical characterization of nanopolyaniline/porous silicon heterojunction at high temperatures. Nanomater 2013:1–8

Fan D, Loni A, Canham LT, Coffer JL (2009) Location-dependent controlled release kinetics of model hydrophobic compounds from mesoporous silicon/biopolymer composite fibers. Physica Status Solidi (a) 206:1322

Fan D, Akkaraju GR, Couch EF, Canham LT, Coffer JL (2011) The role of nanostructured mesoporous silicon in discriminating in vitro calcification for electrospun composite tissue engineering scaffolds. Nanoscale 3:354

Fukami K, Sakka T, Ogata YH, Yamauchi T, Tsubokawa N (2009) Multistep filling of porous silicon with conductive polymer by electropolymerization. Physica Status Solidi (a) 206:1259

Gao L, Mbonu N, Cao L, Gao D (2008) Label-free colorimetric detection of gelatinases on nanoporous silicon photonic films. Anal Chem 80:1468

Ge M, Rong J, Fang X, Zhou C (2012) Porous doped silicon nanowires for lithium ion battery anode with long cycle life. Nano Lett 12:2318

Godin B, Tasciotti E, Liu X, Serda RE, Ferrari M (2011) Multistage nanovectors: from concept to novel imaging contrast agents and therapeutics. Acc Chem Res 44:979

Gongalsky MB, Kharin AY, Osminkina LA, Timoshenko VY, Jeong J, Lee H, Chung BH (2012) Enhanced photoluminescence of porous silicon nanoparticles coated by bioresorbable polymers. Nanoscale Res Lett 7:446

Gorman CB, Petrie RJ, Genzer J (2008) Effect of substrate geometry on polymer molecular weight and polydispersity during surface-initiated polymerization. Macromolecules 41:4856

Greiner A, Wendorff JH (2007) Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angew Chem Int Ed 46:5670

Halliday DP, Holland ER, Eggleston JM, Adams PN, Cox SE, Monkman AP (1996) Electroluminescence from porous silicon using a conducting polyaniline contact. Thin Solid Films 276:299

Harraz FA, Salem MS, Sakka T, Ogata YH (2008) Hybrid nanostructure of polypyrrole and porous silicon prepared by galvanostatic technique. Electrochim Acta 53:3734

Holthausen D, Vasani RB, McInnes SJP, Ellis AV, Voelcker NH (2012) Polymerization-amplified optical DNA detection on porous silicon templates. ACS Macro Lett 1:919

Jarvis KL, Barnes TJ, Prestidge CA (2012) Surface chemistry of porous silicon and implications for drug encapsulation and delivery applications. Adv Colloid Interface Sci 175:25

Jin J-H, Hong SI, Min NK (2009) Integrated urea sensor module based on poly (3-methylthiophene)-modified p-type porous silicon substrate. J Porous Mater 16:379

Kashanian S, Harding F, Irani Y, Klebe S, Marshall K, Loni A, Canham L, Fan D, Williams KA, Voelcker NH, Coffer JL (2010) Evaluation of mesoporous silicon/polycaprolactone composites as ophthalmic implants. Acta Biomater 6:3566

Keten S, Xu Z, Ihle B, Buehler MJ (2010) Nanoconfinement controls stiffness, strength and mechanical toughness of [beta]-sheet crystals in silk. Nat Mater 9:359

Kilian KA, Bocking T, Gooding JJ (2009a) The importance of surface chemistry in mesoporous materials: lessons from porous silicon biosensors. Chem Commun (Camb) 2009:630

Kilian KA, Lai LMH, Magenau A, Cartland S, BoÃàcking T, Di Girolamo N, Gal M, Gaus K, Gooding JJ (2009b) Smart tissue culture: in situ monitoring of the activity of protease enzymes secreted from live cells using nanostructured photonic crystals. Nano Lett 9:2021

Kim J, Jang S, Koh Y, Ko YC, Sohn H (2008) Photonic polymer replicas from DBR PSi. Colloids Surf A Physicochem Eng Asp 484:313–314

Koh Y, Jang S, Kim J, Kim S, Ko YC, Cho S, Sohn H (2008) DBR PSi/PMMA composite materials for smart patch application. Colloids Surf A Physicochem Eng Asp 313–314:328

Krepker MA, Segal E (2013) Dual-functionalized porous Si/hydrogel hybrid for label-free biosensing of organophosphorus compounds. Anal Chem 85:7353

Kruk M, Dufour B, Celer EB, Kowalewski T, Jaroniec M, Matyjaszewski K (2008) Grafting monodisperse polymer chains from concave surfaces of ordered mesoporous silicas. Macromolecules 41:8584

Levitsky IA, Euler WB, Tokranova N, Rose A (2007) Fluorescent polymer-porous silicon microcavity devices for explosive detection. Appl Phys Lett 90:41904

Li YY, Cunin F, Link JR, Gao T, Betts RE, Reiver SH, Chin V, Bhatia SN, Sailor MJ (2003) Polymer replicas of photonic porous silicon for sensing and drug delivery applications. Science 299:2045

Li YY, Kollengode VS, Sailor MJ (2005) Porous-silicon/polymer nanocomposite photonic crystals formed by microdroplet patterning. Adv Mater 17:1249

Liang L, Liu J, Gong XY (2000) Thermosensitive poly(*N*-isopropylacrylamide)-clay nanocomposites with enhanced temperature response. Langmuir 16:9895

Massad-Ivanir N, Shtenberg G, Zeidman T, Segal E (2010) Construction and characterization of porous SiO_2/hydrogel hybrids as optical biosensors for rapid detection of bacteria. Adv Funct Mater 20:2269

Massad-Ivanir N, Friedman T, Nahor A, Eichler S, Bonanno LM, Sa'ar A, Segal E (2012a) Hydrogels synthesized in electrochemically machined porous Si hosts: effect of nano-scale confinement on polymer properties. Soft Matter 8:9166

Massad-Ivanir N, Shtenberg G, Segal E (2012b) Advancing nanostructured porous Si-based optical transducers for label free bacteria detection. In: Zahavy E, Ordentlich A, Yitzhaki S, Shafferman A (eds) Nano-biotechnology for biomedical and diagnostic research, vol 733. Springer, New York, p 37

McInnes S, Thissen H, Choudhury NR, Voelcker NH, Nicolau DV (2006) Characterisation of porous silicon/poly(L-lactide) composites prepared using surface initiated ring opening polymerisation. In: Nicolau DV (ed) SPIE proceedings, BioMEMS and nanotechnology II, vol 6036. Brisbane, Australia

McInnes SJ, Thissen H, Choudhury NR, Voelcker NHJ (2009) New biodegradable materials produced by ring opening polymerisation of poly(L-lactide) on porous silicon substrates. Colloid Interf Sci 332

McInnes SJ, Irani Y, Williams KA, Voelcker NH (2012) Controlled drug delivery from composites of nanostructured porous silicon and poly(L-lactide). Nanomedicine (Lond) 7:995

Minko S (2008) Grafting on solid surfaces: "grafting to" and "grafting from" methods. In: Stamm M (ed) Polymer surfaces and interfaces. Springer, Berlin/Heidelberg, p 215

Mishra JK, Bhunia S, Banerjee S, Banerji P (2008) Photoluminescence studies on porous silicon/polymer heterostructure. J Lumin 128:1169

Mukherjee P, Whitehead M, Senter R, Fan D, Coffer J, Canham L (2006) Biorelevant mesoporous silicon/polymer composites: directed assembly, disassembly, and controlled release. Biomed Microdevices 8:9

Nahor A, Berger O, Bardavid Y, Toker G, Tamar Y, Reiss L, Asscher M, Yitzchaik S, Sa'ar A (2011) Hybrid structures of porous silicon and conjugated polymers for photovoltaic applications. Physica Stat Solidi (C) Curr Top Solid State Phys 8:1908

Nguyen T-P, Rendu PL, Cheah KW (2003a) Optical properties of porous silicon/poly(p phenylene vinylene) devices. Physica E 17:664

Nguyen TP, Le Rendu P, Lakéhal M, de Kok M, Vanderzande D, Bulou A, Bardeau JP, Joubert P (2003b) Filling porous silicon pores with poly(p phenylene vinylene). Physica Stat Solidi (a) 197:232

Orosco MM, Pacholski C, Miskelly GM, Sailor MJ (2006) Protein-coated porous-silicon photonic crystals for amplified optical detection of protease activity. Adv Mater 18:1393

Pace S, Vasani RB, Farrugia B, Dargaville TR, Voelcker NH (2012) Temperature sensors to monitor wound healing. In: Canham LT, Koshida N, Sailor MJ, Cantarero A (eds) Porous semiconductors science and technology, vol 1. Institute for Materials Science, University of Valencia, Valencia/Malaga, p 98

Pace S, Vasani RB, Cunin F, Voelcker NH (2013) Study of the optical properties of a thermoresponsive polymer grafted onto porous silicon scaffolds. New J Chem 37:228

Pang-Leen O, Levitsky IA (2011) Fluorescent gas sensors based on nanoporous optical resonators (microcavities) infiltrated with sensory emissive polymers. Sens J IEEE 11:2947

Park JS, Meade SO, Segal E, Sailor MJ (2007) Porous silicon-based polymer replicas formed by bead patterning. Physica Stat Solidi a-Appl Mater Sci 204:1383

Perelman LA, Moore T, Singelyn J, Sailor MJ, Segal E (2010) Preparation and characterization of a pH- and thermally responsive poly(*N*-isopropylacrylamide-co-acrylic acid)/porous SiO_2 hybrid. Adv Funct Mater 20:826

Schwartz MP, Derfus AM, Alvarez SD, Bhatia SN, Sailor MJ (2006) The smart petri dish: a nanostructured photonic crystal for real-time monitoring of living cells. Langmuir 22:7084

Sciacca B, Secret E, Pace S, Gonzalez P, Geobaldo F, Quignard F, Cunin F (2011) Chitosan-functionalized porous silicon optical transducer for the detection of carboxylic acid-containing drugs in water. J Mater Chem 21:2294

Segal E, Perelman LA, Cunin F, Di Renzo F, Devoisselle JM, Li YY, Sailor MJ (2007) Confinement of thermoresponsive hydrogels in nanostructured porous silicon dioxide templates. Adv Funct Mater 17:1153

Segal E, Perelman LA, Moore T, Kesselman E, Sailor MJ (2009) Grafting stimuli-responsive polymer brushes to freshly-etched porous silicon. Physica Stat Solidi (c) 6:1717

Shang Y, Wang X, Xu E, Tong C, Wu J (2011) Optical ammonia gas sensor based on a porous silicon rugate filter coated with polymer-supported dye. Anal Chim Acta 685:58

Svrcek V, Fujiwara H, Kondo M (2009) Top-down prepared silicon nanocrystals and a conjugated polymer-based bulk heterojunction: Optoelectronic and photovoltaic applications. Acta Mater 57:5986

Sychev FY, Razdolski IE, Murzina TV, Aktsipetrov OA, Trifonov T, Cheylan S (2009) Vertical hybrid microcavity based on a polymer layer sandwiched between porous silicon photonic crystals. Appl Phys Lett 95:163301

Uemura T, Yanai N, Watanabe S, Tanaka H, Numaguchi R, Miyahara MT, Ohta Y, Nagaoka M, Kitagawa S (2010) Unveiling thermal transitions of polymers in subnanometre pores. Nat Commun 1:8

Urbach B, Korbakov N, Bar-david Y, Yitzchaik S, Sa'ar A (2007a) Composite structures of porous silicon and polyaniline for optoelectronic applications. Physica Stat Solidi (c) 4:1951

Urbach B, Korbakov N, Bar-David Y, Yitzchaik S, Sa'ar A (2007b) Composite structures of polyaniline and mesoporous silicon: electrochemistry, optical and transport properties. J Phys Chem C 111:16586

Vasani RB, McInnes SJP, Cole MA, Jani AMM, Ellis AV, Voelcker NH (2011) Stimulus-responsiveness and drug release from porous silicon films ATRP-grafted with poly(*N*-isopropylacrylamide). Langmuir 27:7843

Wang C, Jia X-M, Jiang C, Zhuang G-N, Yan Q, Xiao S-J (2012) DNA microarray fabricated on poly(acrylic acid) brushes-coated porous silicon by in situ rolling circle amplification. Analyst 137:4539

Whitehead MA, Fan D, Mukherjee P, Akkaraju GR, Canham LT, Coffer JL (2008) High-porosity poly(epsilon-caprolactone)/mesoporous silicon scaffolds: calcium phosphate deposition and biological response to bone precursor cells. Tissue Eng Part A 14:195

Wu J, Sailor MJ (2009) Chitosan hydrogel-capped porous SiO_2 as a pH responsive nano-valve for triggered release of insulin. Adv Funct Mater 19:733

Xu D, Yu WH, Kang ET, Neoh KG (2004) Functionalization of hydrogen-terminated silicon via surface-initiated atom-transfer radical polymerization and derivatization of the polymer brushes. J Colloid Interface Sci 279:78

Yang SH, Choi IS (2010) Thickness control of biomimetic silica thin films: grafting density of poly(2-(dimethylamino)ethyl methacrylate) templates. Anglais 31:753

Yoon MS, Ahn KH, Cheung RW, Sohn H, Link JR, Cunin F, Sailor MJ (2003) Covalent crosslinking of 1-D photonic crystals of microporous Si by hydrosilylation and ring-opening metathesis polymerization. Chem Commun (Camb) 2003:680

Zdyrko B, Swaminatha Iyer K, Luzinov I (2006) Macromolecular anchoring layers for polymer grafting: comparative study. Polymer 47:272–279