Porous Silicon Polymer Composites

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Abstract

The emerging class of nanocomposites that integrate polymers with nanostructured porous silicon displays unparalleled properties that spring up from characteristics of each building block and their interactions. Recent research reveals their enormous potential as extremely promising materials for chemical sensors, optoelectronic devices, photovoltaics, energy storage, and numerous biomedical applications such as smart drug delivery systems, lab-on-chip devices, and tissue engineering scaffolds. In this updated chapter, these nanomaterials and their applications are discussed with emphasis on basic design guidelines and fabrication strategies.

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Introduction

The combination of polymers with nanostructured silicon scaffolds, in particular porous silicon (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, actuators, optical devices, drug delivery systems, and tissue-engineered 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 polymer, polymer-coated PSi, polymer-capped PSi, released PSi film supported by polymer, PSi particles encapsulated by 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 2007; Massad-Ivanir 2010, 2012a; Perelman 2010; Krepker 2013). The polymer is confined within the nanoscale pores, and its interaction with the pore wall can be enhanced by covalent attachment (Bonanno 2010, 2011; Sciacca 2011; Massad-Ivanir 2012a). 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 (McInnes 2009; Segal 2009). Polymer-capped PSi is a more sophisticated design (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 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 either selective chemical removal of the Si scaffold or by physical detachment (Li 2003; Park 2007; Brodoceanu 2015; Hakshur 2016). The previously described designs make use of intact PSi substrates. However, the following PSi-polymer composite configurations require mechanical processing of the PSi. A

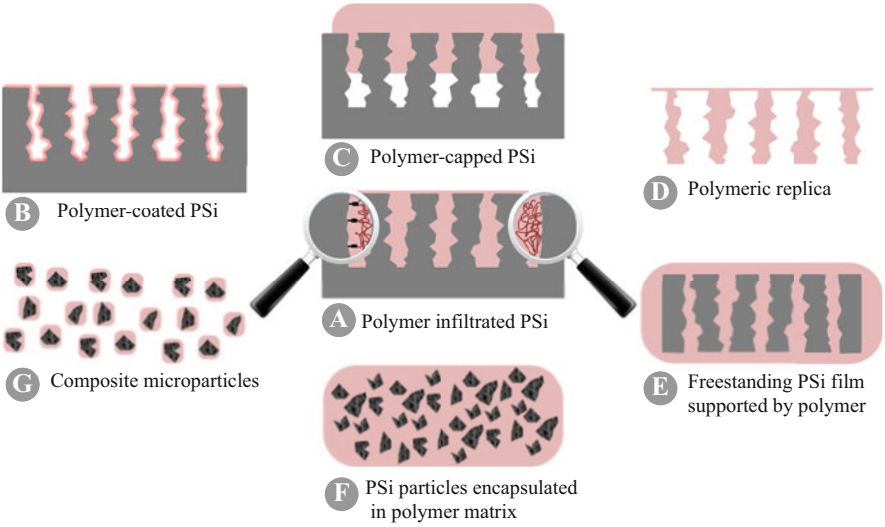

Fig. 1 Common structures of PSi-polymer composites. Insets in *A* illustrate interfacial chemistry where polymer is not attached to PSi (*right*) and is covalently attached to the PSi surface through different linkers. Schematics are not drawn to scale

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 at a high current density or at low HF concentrations (DeLouise 2005; McInnes 2016a). A freestanding PSi film can be subjected to mechanical fragmentation by sonication or ball milling, and the resulting PSi micro-/nanoparticles can be embedded within a polymer matrix (Fig. 1f) or encapsulated individually by a polymer layer (Fig. 1g).

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 components, PSi substrate nanostructure, and fabrication strategy is 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.

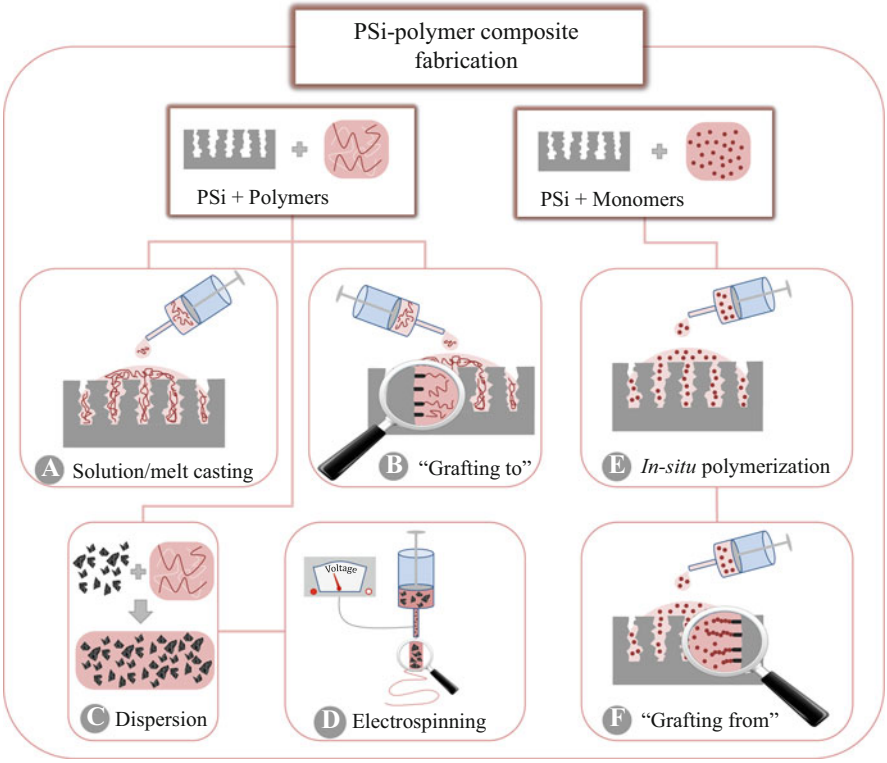

Fig. 2 Common practiced methods for the fabrication of PSi-polymer composites

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 (Li 2005; Orosco 2006; Schwartz 2006; Park 2007; Gao 2008; Kim 2008; Koh 2008; Whitehead 2008; De Stefano 2009; Sychev 2009; Wu 2009; Shang 2011; McInnes 2012a). 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 the excess solution and to distribute the polymer evenly on the surface of PSi (Schwartz 2006; Gao 2008; Shang 2011). 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 polymer, the solution viscosity and its surface tension, the pore dimensions and morphology, and the pore wall surface chemistry. In addition, 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, whose 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 (Orosco 2006; Gao 2008; Wu 2009; Shang 2011), PSi infiltrated with polymers (Schwartz 2006; De Stefano 2009; McInnes 2012a), polymer replicas of PSi template (Li 2003; Park 2007; Kim 2008), and a freestanding PSi film supported by a polymer (Koh 2008; Sychev 2009) is the most common designs of PSi-polymer composites prepared by the 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 (Gongalsky 2012; Araújo 2014; Henstock 2014), bilayer polymer-conjugated PSi (Shahbazi 2014), monoliths (Mukherjee 2006; McInnes 2012a), and fibers (Kashanian 2010; Fan 2011). Alternatively, aerosol flow reactor (AFR) method can be used to coat PSi particles with a polymer (Shrestha 2015).

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 electric 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 2007). The properties of resulting electro-spun fibers are controlled by the process parameters, e.g., electrical conductivity, electrode separation and geometry, temperature, concentration, and the polymer characteristics. This technique was applied for fabricating electro-spun fibers of PSi particles encapsulated within a polycaprolactone (PCL) matrix (Fan 2009, 2011; Kashanian 2010). Alternatively, premade electro-spun PCL fabrics can be pressed against PSi microparticles heated above the PCL melting temperature, embedding PSi in the outer surface of PCL microfibers (Irani 2015).

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 2008; Alvarez 2009; Kilian 2009a; Jarvis 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

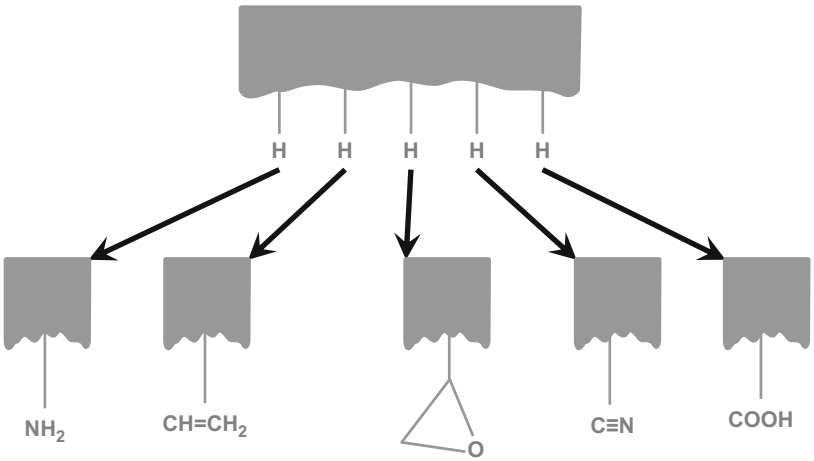

Fig. 3 Commonly practiced surface chemistries for the functionalization of PSi. These end groups can be reacted with a wide variety of polymers

mentioned that a disadvantage of this method is the limited grafting density that can be achieved (Zdyrko 2006). Overall, "grafting to" is typically used for fabricating polymer-coated PSi surfaces and nanostructures (see Fig. 1b). This technique was implemented for grafting poly(*n*-isopropylamide) (polyNIPAM) (Segal 2009), chitosan (Sciacca 2011; Shrestha 2015), gelatin (Kilian 2009b), polyethylene glycol (PEG) (Näkki 2015), etc. (Shahbazi 2014). While relatively simple and well-established one-step "grafting to" methods still dominate the field; multistep procedures are currently being developed, allowing for construction of novel and more advanced composites. For example, it was demonstrated that polystyrene within polystyrene-infiltrated PSi can be thermally depolymerized, grafting the polystyrene remains to PSi surface, forming a polystyrene coating on PSi for stabilization of the nanostructure at alkaline solutions (pH $>$ 12) (Wang 2016). In other studies, several polymers, with different functionalities, were grafted to the PSi surface to design complex architectures for controlled release of multiple drugs (Xu 2015) and potential therapeutic applications (Zhang 2014).

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 2007; Massad-Ivanir 2010, 2012b; Perelman 2010; El-Zohary 2013; Krepker 2013; Hernandez-Montelongo 2014). The PSi nanostructure is commonly filled with pre-polymer 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 2007; Massad-Ivanir 2010, 2012b; Perelman 2010; Krepker 2013), atom transfer radical polymerization (ATRP) (Yang 2010; Vasani 2011; Pace 2013), ring-opening polymerization (Yoon 2003; McInnes 2006, 2009, 2012a), and electro-polymerization (Urbach 2007a, b; Harraz 2008; Betty 2009; Fukami 2009; Jin 2009; Belhousse 2010; Chiboub 2010; Nahor 2011; Badeva 2012; Dian 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 2007). McInnes et al. (McInnes 2012b, 2016b) have demonstrated the application of initiated chemical vapor deposition (iCVD) for forming uniform polymer coatings onto PSi for responsive drug delivery applications. The iCVD technique offers several advantages, being low temperature and solvent-free; yet, it is more complex than conventional in situ polymerization methods, and it requires sophisticated equipment.

When "grafting from" approach is applied for polymer synthesis, an appropriate initiator is commonly immobilized onto the pore walls followed by polymer chain growth via different possible mechanisms (Xu 2004; Chen 2009; Vasani 2011; Jarvis 2012). 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. Moreover, "grafting" allows for sequential grafting of multifunctional polymers to the PSi surface (Soeriyadi 2014).

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 (Liang 2000; Alcoutlabi 2005; Gorman 2008; Kruk 2008; Keten 2010; Uemura 2010; Massad-Ivanir 2012a). 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 2007; Massad-Ivanir 2010; Perelman 2010; Bonanno 2011). Moreover, there are significant differences between the thermal degradation behavior of the confined polymers, poly(acrylamide) and poly(NIPAM), compared with neat polymer and thin polymer films deposited onto planar Si surfaces. 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 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.

An excellent review (Bonanno 2011) provides an overview on the biomedical applications of these materials, highlighting the construction of smart drug delivery systems (Wu 2009; Godin 2011; Vasani 2011; Beavers 2016; Muller 2016) and improved label-free optical biosensors (Massad-Ivanir 2010, 2012a; Holthausen 2012) or sensors (Bonanno 2010) for "point-of-care" applications, such as temperature sensors to monitor wound healing (Pace 2012), lab-on-chip systems (Chen 2009), and tissue engineering/interfacing scaffolds (Coffer 2005; Sun 2016). In addition to the vast biological applications, PSi-polymer composites are being investigated as chemical sensors for different targets (Levitsky 2007; Jin 2009; Belhousse 2010; Pang-Leen 2011; Wang 2012), optoelectronic devices, photovoltaics (Halliday 1996; Nguyen 2003a, b; Mishra 2008; Svrcek 2009; Badeva 2012; Gongalsky 2012), and energy storage (Ge 2012; Zheng 2016). 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.

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