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Current Status and Future Perspectives of Functional and Smart Materials in Daily Life

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1.1 Introduction

Smart materials in general, are defined as materials with adaptive properties that undergo change upon exposure to an external stimulus. These changing properties can be very diverse including, but not limited to, reversible changes in volume, shape, opacity, or color, which may be triggered by changes in pH, temperature, magnetic/electric fields, or light. Because of their adaptive nature, these properties play a key role in the manufacture of many technical devices used in daily life, and the ability to switch them is the basis for the surging interest in smart materials for emerging technologies and applications. Besides the responsive features outlined above, materials with optoelectronic and thermoelectric properties that allow conversion of light or heat to electricity at different temperature levels are also sometimes termed as smart materials, but will not be covered in this chapter. Self-healing materials that have the intrinsic ability to repair damage have also not been included. On the other hand, shape memory materials are included. In this chapter, a brief outline on the current status and future perspectives of smart materials in daily life will be given, with a special focus on polymeric materials and inorganic polymeric materials in particular.

1.2 Properties and Applications

The properties and applications outlined in this section rely mainly on the features of smart materials related to their mechanical and rheological properties, electronic excitation, optical features, supramolecular recognition, and chemical reactivity, and further aspects such as switchable polarity.

1.2.1 Applications Based on Mechanical and Rheological Properties

Shape memory polymers (SMPs) are capable of changing shape and dimensions upon stimuli such as heat or upon exposure to light of suitable wavelength.

The behavior is comparable with that of shape memory metals and alloys that are already in use for medical purposes but may sometimes entail biological side effects owing to their metallic constituents. Besides their superior biocompatibility, SMPs show a faster switching time owing to their lower heat conductivity and capacity that make them attractive candidates for medical implants in minimal invasive surgery [1]. Recently, hybrid inorganic–organic SMPs have been developed that show improved cycling behavior for a series of switching events with response times (<0.5 seconds) and a transformation temperature near body temperature (40°C) [2].

Polyhedral silsesquioxane (POSS) cages are nanostructures with diameters in the range of 1–3 nm and, hence, may be considered as the smallest existing silica particles. POSS cages are compatible with many polymer matrices and improve their viscosity, strength, modulus, rigidity, and flammability [3–6]. Moreover, they may affect gas permeation through membranes, which is the basis for application of POSS cages in food packaging. Similar applications may be envisaged for polymers and polymer blends involving carboranes based on the intriguing properties of the latter (cf. Chapter 2) [7–9].

Aiming at further improvements in medical implant and handling technology, antimicrobial properties have been endowed to cellulosic fibers, by coating with hydrophilic TiO_2 , and subsequently equipped with a fluorinated silanol coating. The resulting amphiphobic material featured excellent water- and hexane-repellent properties, originating from both surface chemistry and morphology. It was further demonstrated that *Escherichia coli* cells did not adhere to such surfaces owing to the rather low surface energies (Figure 1.1) [10].

The sizing of natural fibers is an important step in paper or textile manufacturing by which the surface properties can be modified to control the wear and sorption characteristics. While reactive organic components (e.g. alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA)) are used for the sizing of bulk cellulosic fibers, surface sizing uses mainly modified starch to form a water-repellent film on the paper surface. Owing to cost restrictions, improved processes are limited to advanced purposes such as nanopapers and applications in electronics where highly hydrophobic surfaces with well-defined surface properties can be obtained using vapor phase processing of cellulosic fibers with alkoxysilanes [11]. Similarly, modification of wool fibers via coating with a siloxane-based polymer film equipped the fibers with anti-felting properties and significantly improved the shrinkage behavior of the wool upon heat treatment [12]. Silicon-based precursors and their polymeric condensation products have found application in hair care as well. A variety of patents and products reported silanetriols as important binder materials for improved hair dyeing, or to incorporate permanent fragrances [13, 14]. Moreover, it has been reported that conditioning agents containing silanetriols may reduce the stress on hair during dyeing processes as was demonstrated for Caucasian and Afroethnic hair [15, 16].

1.2.2 Applications Based on Electronic Excitation

A salient feature of the compounds of heavier main group elements is the smaller energetic separation between bonding and anti-bonding states compared with

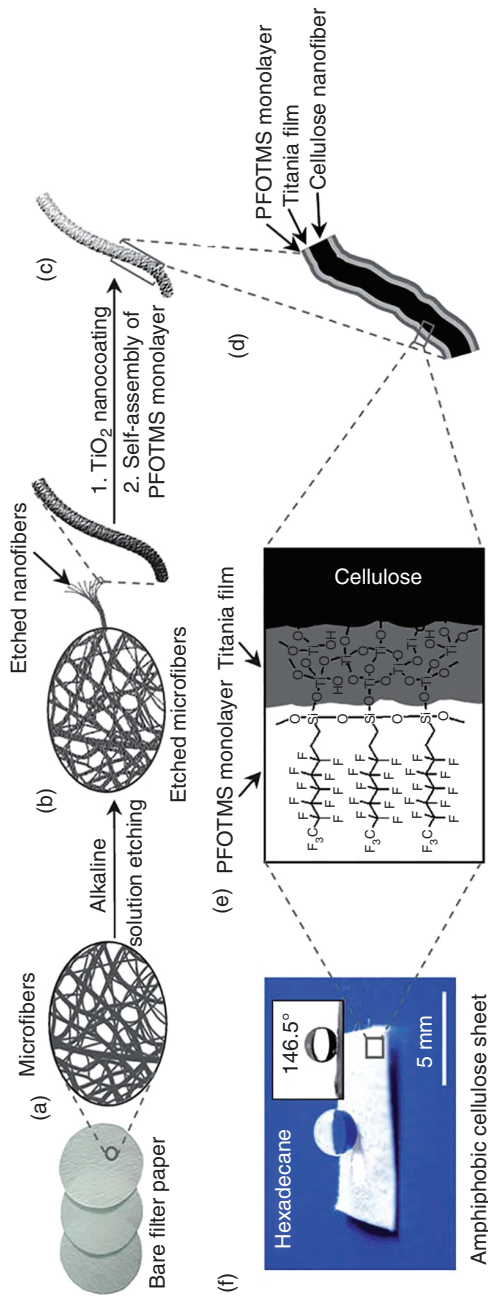


Figure 1.1 Sketch of the fabrication process of amphiphobic cellulose sheets: (a) Cellulose microfibers of commercial filter paper; (b) rougher cellulose fibers of filter paper resulting from alkaline solution etching; (c) cellulose nanofiber of etched filter paper deposited with titania–PFOTMS (perfluorooctyl trimethoxysilane) composite ultrathin films; (d, e) structure of titania–PFOTMS ultrathin film-modified cellulose nanofiber; (f) resulting amphiphobic cellulose sheet. Source: Jin et al. 2012 [10]. Reproduced with permission of Royal Society of Chemistry.

their organic counterparts. This aspect is not only relevant for π -bonding, but also for σ -bonding especially in the homonuclear bonding situations enabling σ -conjugation in polysilanes and polystannanes and conventional π -conjugation in multiple-bonded organopnictogen and especially organophosphorus compounds [17–21]. Based on these phenomena, electronic excitation is facilitated by incorporation of heavier main group elements into (in)organic hybrid materials giving rise to attractive properties (cf. Chapter 7). Owing to their desirable properties, such low band gap materials are the preferred choice for applications relevant for daily life such as light-emitting diodes, solar cells, and molecular electronics in general. The use of phospholes in organic light-emitting diodes (OLEDs) evolves from their emissive properties (fluorescence, phosphorescence), which makes them well suited as emissive layers in such devices (Figure 1.2) for which a brightness of $>44\,000\text{ cd/m}^2$ with a turn on voltage of $<3\text{ V}$ can be achieved [22]. By combining different components with complementary emissive colors it was possible to build white organic light-emitting diodes (WOLEDs) in which the phosphole oligomer contributes a more orange color tone. Besides the use of phosphole-based materials in the emissive layer, phospholes have been employed in electron-transporting layers as well. The principle of an OLED where charge recombination is used to generate photon emission can be reversed by using photon absorption to generate electron excitation followed by charge separation for instance in photovoltaic devices. In view of the close relationship between both types of devices phosphole-based materials have been implemented successfully in solar cells, e.g. in dye sensitized solar cells (DSSC) or bulk heterojunction solar cells (BHJ-SC).

By employing phospholes, a power conversion efficiency of 7.1% has been achieved in a BHJ-SC, whereas to date a power conversion efficiency of 5.6% is the highest η value reported for such materials in a DSSC [22]. With respect to organic electronics, silole-based materials are even more established than their phosphole analogs. The attractive properties of materials incorporating this group 14 heterocycle in part evolve around their large hole mobilities [23, 24]. Using silole-based materials a power conversion efficiency of 7.3% has been achieved in a BHJ-SC device [25]. Further details on the role and beneficial properties of organic inorganic hybrid structures for optoelectronic applications can be found in Chapter 7.

In general, homo-catenated polymers of group 14 are prominent examples that display the unique feature of σ -conjugation, which entails electronic excitation of the saturated backbone by light in the visible or long-wavelength UV region.

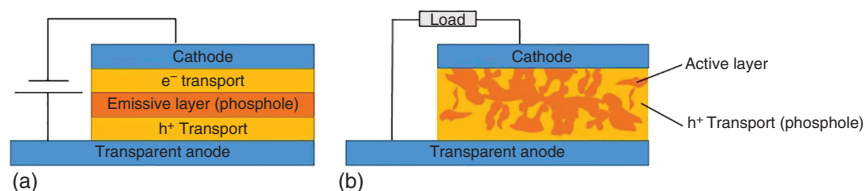


Figure 1.2 Simplified schematic sketch of phosphole-based optoelectronic devices: (a) OLED and (b) BHJ-SC.

Since anti-bonding states are populated during excitation, these polymers are then prone to fragmentation, yielding group 14-based radicals or tetrylenes among which silylenes are the most prominent ones [21]. In the case of polysilanes, applications have emerged where polysilanes serve as photoinitiators (PIs) for polymerizations behaving as a safe and stable polymeric radical precursor before initiation. Furthermore, the silylated by-products obtained from the PI's reactivity, which will be retained in the resulting polymer matrix, are nontoxic. Based on a similar principle, germanium-based photoinitiators have emerged as radical sources for advanced applications such as dental fillings. Such acylgermanes have a redshifted absorption characteristic, which is advantageous for use in restorative dental medicine as exposure of living tissue to harmful UV-radiation can be avoided. Moreover, photocuring at 500 nm is important for the development of bulk-curable restorative composites with increased curing depth and can be performed using an LED. Members of the COST action SIPs have developed acylgermanes that have improved radical efficiency and curing behavior [26]. Based on the excellent PI properties these materials have great potential as PIs for dental fillings and for additional applications such as photopolymerizable adhesives, coatings, or 3D-lithography techniques (Figure 1.3). Moreover, they extended this methodology to acylstannanes, which reveal a significant redshift of the longest wavelength absorption compared with that of the corresponding germanium compounds [27]. In contrast to the well-known toxicity of some trialkylstannanes, both the Ames-test, a biological assay to assess the mutagenic potential of chemical compounds, and cytotoxicity studies reveal intriguingly low toxicity for acylstannanes. The excellent performance of the latter as photoinitiators was demonstrated, which opened new avenues for polymer-based restorative dental medicine.

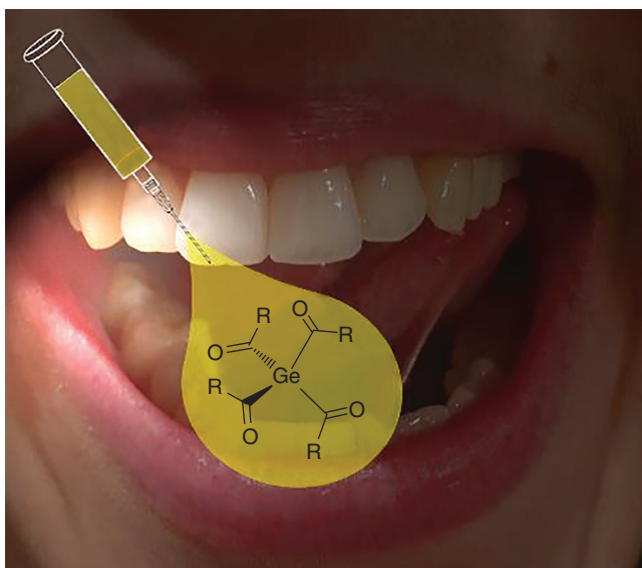


Figure 1.3 Sketch of a germanium-based PI developed as initiator for the curing of dental fillings. Source: Radebner et al. 2017 [26]. Reproduced with permission of John Wiley & Sons.

1.2.3 Applications Based on Optical Features

Smart materials changing optical features such as opacity and color upon exposure to an external stimulus are very attractive for applications in display technology and energy management in smart buildings. Such materials show thermochromic or electrochromic behavior changing color with temperature or the voltage applied. While smart materials show reversible color changes, there are other applications where a temperature seal indicates if a maximum temperature was maintained by inducing an irreversible change to ensure a cooling chain during storage and transport of temperature sensitive products (e.g. food, biological samples or tissue, medication). Materials undergoing reversible color change do not necessarily have a complex composition. For instance, simple inorganic compounds such as HgI_2 may show such thermochromic behavior. In the 1970s, thermochromic flat thermometers became quite popular using materials that are less problematic in terms of toxicity during the product lifecycle including production and disposal. Similarly, tea or coffee mugs changing color or motifs depending on the temperature of the liquid inside taking advantage of thermochromism are well-known examples from daily life as well. Heat flow in daily life applications is usually a rather slow diffusion-based process and given the limited temperature differences involved switching times are usually rather long.

Fast switching is usually required for electrochromic materials where the color change is usually effected by the voltage applied. There are smart materials that can be switched between two states such as colorless and dark for use as shades or blinds in smart windows in buildings (Figure 1.4) or in vehicles that cover a full range of colors relevant for display technology. Generally, switching properties via a voltage difference is favorable for integration into IT-based control systems, which is the reason for the high interest in electrochromic materials. Again, materials with simple chemical constitution such as WO_3 are capable of electrochromic behavior. In such thin films a cathodic current leads to injection of electrons into the pale yellow WO_3 lattice leading to partially reduced tungsten ions, which entails a color change [29, 30]. The ability to switch off vision through a window is essential for applications related to privacy and security. Thus, electrochromic windows are installed in the driver cabin of ICE 3 trains and in cockpits on airplanes. Alternatively, simple on/off switching of smart windows can be achieved by an array of micro-mirrors as well, which require very sophisticated production processes as compared with redox-active thin films outlined above [31].

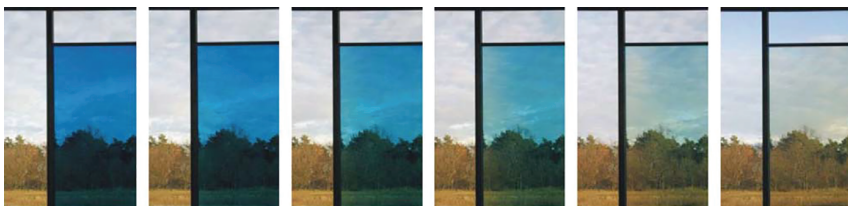


Figure 1.4 Switching sequence of an electrochromic laminated glass. Source: Baetens et al. 2010 [28]. Reproduced with permission of Elsevier.

To overcome the limitations of switching between only two states in mechanically inflexible solid state materials, ferrocene has been used to induce electrochromic behavior to smart polymeric materials [32]. By adjusting an appropriate voltage difference the redox-active ferrocene unit can be switched reversibly from the neutral ferrocene to the cationic ferrocenium form. These changes are accompanied by characteristic color changes between the reduced and oxidized forms and more than two colored states may be accessible by overlaying the color effects of the whole ensemble of ferrocene/ferrocenium units at the polymer chains with those of the conjugated polymer showing redox activity (doping) as well. EDOT-Fc based polymers with pendant ferrocenyl groups can be switched between purple and blue, for example [33]. Different numbers of achievable colored states can be achieved by substitution of the ferrocenyl unit with other units leading the way to multicolored electrochromic materials. It is worth mentioning that, for practical considerations, incorporation of the ferrocenyl substituent enhances the optical contrast in the visible region resulting in better transparency for the oxidized state [34]. Besides the composition of such materials, the method of preparation also impacts the properties and durability. For instance, ferrocene-based conjugated polymers prepared by electrochemical polymerization on transparent indium tin oxide (ITO) electrodes using potential cycling are superior to those produced potentiostatically [35]. For polymer films obtained using the potentiodynamic technique the electroactivity is retained even after hundreds of cycles between their redox states associated with distinctive color changes between neutral and reduced/oxidized forms involving metal-to-ligand charge transfer (MLCT) and/or intraligand charge transfer (ILCT) from Fc moieties to the polymer skeleton.

A challenge in the field of electrochromic materials has been the realization of displays providing a full range of colors for applications in electronic books, billboards, shelf-edge labels, and charge gauges for batteries, to name just a few. A class of materials, which meets these requirements, is based on the inorganic polymer polyferrocenylsilane (PFS) as a cross-linked matrix in which silica spheres are embedded in an opal-like arrangement acting as a photonic structure [36]. Reversible expansion and contraction of the photonic lattice is achieved by expansion or contraction of the polymeric PFS matrix, which can be tuned by either chemical or electrochemical means. Thus, a solvent leads to the swelling of the matrix and ultimately a change in reflected color [37]. Similarly, the degree of swelling of the metallopolymer is dependent on the oxidation state of the metals in its backbone, providing a material whose structural color can be electrically tuned through (Figure 1.5). This material, for which the name “photonic ink” (P-ink) has been coined, enables a variety of optical functions that are attractive for display technology [36]. While the first demonstration of full-color tuning, based on the electroactive PFS polymer–gel/silica opal composite outlined above, was still limited by slow switching times and high drive voltage requirements, improved varieties have been developed [38]. Electrolyte permeation through the contiguous space-filling opal lattice embedded within the polymer–gel matrix was identified as a key parameter that impeded electron and charge transport via ion migration thus limiting the overall performance of the device. In variation of the same working principle, a high-performance

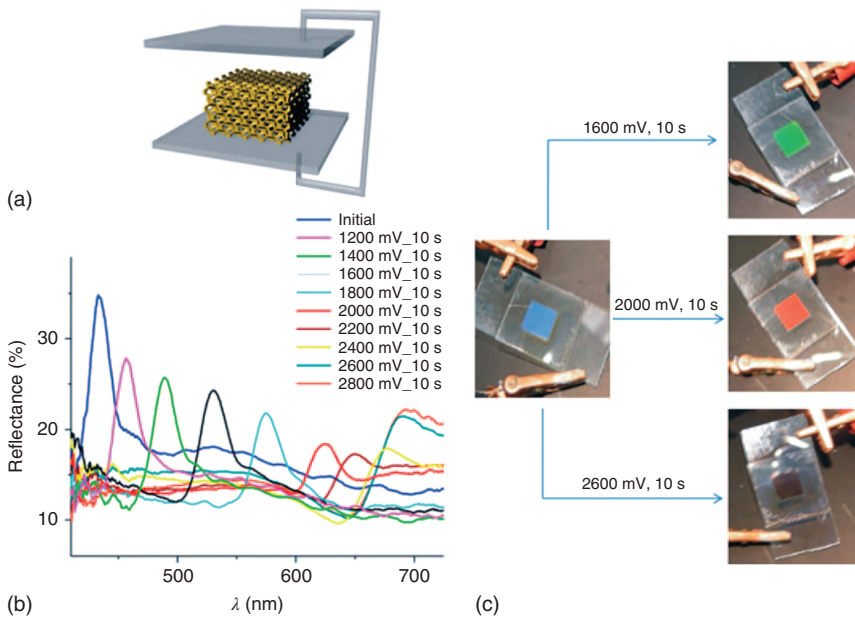


Figure 1.5 PFS-based P-ink at different charging levels. Source: Puzzo et al. 2009 [38]. Reproduced with permission of John Wiley & Sons.

electroactive photonic material has been obtained using an inverse polymer–gel opal in which the silica spheres are replaced by spherical voids through which the electrolyte freely infuses the nanoporous lattice.

The polymers chosen for the inverse polymer–gel opal are a blend of inorganic polymers derived from PFS, namely polyferrocenylmethylvinylsilane (PFMVS) and polyferrocenyldivinylsilane (PFDVS). A narrow molecular weight distribution (polydispersity, $PDI < 1.1$) is achieved through anionic ring-opening polymerization from the appropriate silaferrocenophanes where ring opening is favored over addition to the $C=C$ double bonds present in each monomer unit leaving the latter intact for subsequent cross-linking. Based on this inverse opal approach full color tuning at very low drive voltages (~ 2 V) with unprecedented wavelength shifts traversing the ultraviolet, visible, and near infrared spectral ranges has been accomplished. Future technological hurdles that need to be overcome include enhanced reflectivity, reverse scan speed, and cycle lifetime. The PFS-based approach relies on changing the lattice dimension by an electrical stimulus. One might speculate that future developments could take advantage of changing the lattice dimension by an optical or magnetic stimulus or by contrast, continuous, reversible, and rapid altering of the refractive index by electrical, optical, or magnetic stimuli. Regardless of the physical concept, the potential for practical application will depend on the ability to prepare any such material with high structural and optical quality, and on a large scale and at low cost.

A metal-free electrochromic material is the phosphol-based phosphaviologen, which is the primary example of a phosphaviologen that can switch between colors for all three electrochemically accessible states [39]. Although this principle

has been successfully implemented in a device, demonstrating the potential of these π -conjugated phosphorus species for applications such as dimming devices and multicolored displays, this technology is still in an experimental stage.

1.2.4 Applications Based on Supramolecular Recognition

Larger supramolecular entities consisting of distinguishable subunits are capable of forming molecular patterns that offer the potential to serve as information storage and release carriers similar to genetic encoding in biological systems. The complexity of current systems imposes limitations on the synthetic reproduction of sets of identical patterns. This complexity is, however, the key to applications such as anti-counterfeiting protection for product safety and consumer protection. For SMPs the use as switchable QR-code carriers has been successfully demonstrated [40]. The underlying principle is to encode an information (e.g. a QR-code), which may be stored and erased for single use validation or allows decoding only with special equipment for instance as safety certificate or tag. This switching process can further be used as a means for tracking the exposure to temperature or radiation. Current research is aiming at improving the contrast of the encoded features for instance via implementation of thermochromic pigments and the extension to data matrix codes, other codes and alphanumeric characters [41]. While the pioneering examples of SMP-based codes used organic polymers where the encoding process can be realized via locally constricted guest diffusion of surface layers of two structurally different SMPs, inorganic components offer an even larger structural variety, resulting, in turn, in improved storage capacity.

A breakthrough to the third dimension is the supramolecular assembly of multi-block copolymers containing a metallopolymer sequence such as PFS in addition to other block sequences as pioneered by Manners and coworkers [42]. These block-copolymers phase-separate on the nanoscale due to the immiscibility of the PFS block with a wide range of organic or inorganic co-blocks, allowing the formation of a variety of interesting nanostructured materials with crystalline iron-rich domains and various shapes and morphologies. Such polymers are accessible via sequential living anionic polymerization of several block units in a controlled fashion. Following this methodology, cylindrical micelles can be prepared that can act as nanoscale pixels with fully tunable color emissions when equipped with fluorescent tags [43]. Seeded growth of different ratios of block-copolymer unimers enabled the preparation of monodisperse co-assembled cylindrical micelles that emitted different colors depending on the amount of each fluorescent unimer added, for which the luminescence was uniform throughout the micelle (Figure 1.6).

Such systems provide new possibilities for the preparation of encoded nanomaterials, bearing a defined pattern that is invisible to standard methods but may be identified or decoded with other techniques. Ultimately, these materials may serve as tools for invisibly identifying valuable objects or conveying sensitive information. As yet, micelles with 18 distinct colors as well as non-centrosymmetric structures with up to seven blocks have been achieved. Based on these colors, this platform allows in principle to fabricate micelles

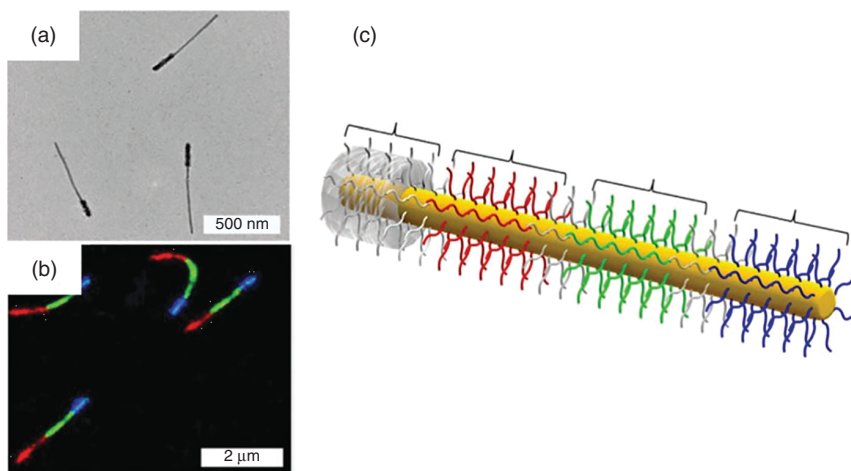
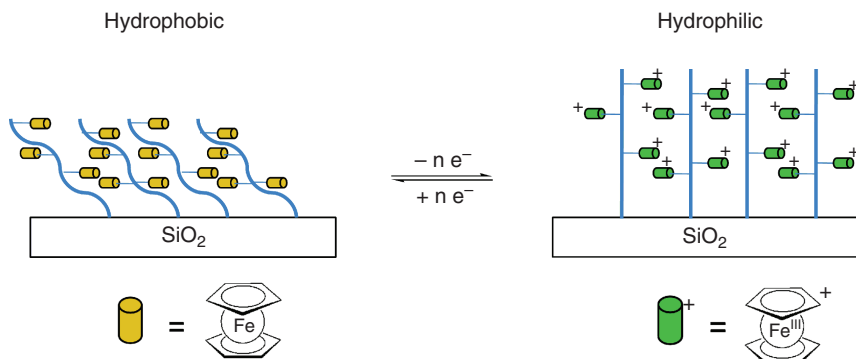


Figure 1.6 (a) TEM image, (b) laser scanning confocal microscopy (LSCM) image, and (c) schematic representation of non-centrosymmetric RGB “nanopixel” block comicelles. Scale bars are (a) 500 nm and (b) 2 μm . Source: Reproduced with permission of Hudson et al. 2014 [43]. Copyright 2014, Springer Nature.

with 18^7 or 6.1×10^8 combinations of fluorescent color. The number of combinations not only exceeds the data density of binary encoding, but facilitates the encoding of nanostructures with more complex patterns as well. A further advantage is the fact that such block comicelles are stable over long periods with no detected rearrangement of the fluorescent unimers along the length of the cylinders, which indicated that they exist as static, kinetically trapped structures.

1.2.5 Applications Based on Chemical Reactivity

The redox activity of metal-containing hybrid polymers has been employed to prepare responsive coatings that are able to switch between hydrophobic and hydrophilic behavior upon exposure to an external redox stimulus. Such switchable polarity can be achieved elegantly using ferrocene-based polymers. The application of this concept to surfaces dates back to Whitesides et al. who, two decades ago, reported the change of surface wettability of self-assembled monolayers of a ferrocene compound on a gold surface upon oxidation [44]. An instructive example is a study in which ferrocene polymers have been attached to a silicon-based surface allowing for switchable surface wettability (Scheme 1.1) [45]. In the case of PFcMA (poly(2-(methacryloyloxy)ethyl ferrocenecarboxylate) attached to a silicon substrate via surface-initiated atom transfer radical polymerization, a remarkable drop of the contact angle (CA) for water of approximately 70° could be observed upon oxidation. The reversible nature of switching the surface wettability has been demonstrated and different oxidants have been used to trigger the redox stimuli. Moreover, polymers with longer chain length show a more significant CA drop than those with shorter ones [45]. From an industrial point of view, the hydrophobization, either of fillers or other hydrophilic materials, is an important feature used in the building and



Scheme 1.1 Sketch of a surface with tunable wettability. Source: Pietschnig 2016 [32]. <http://pubs.rsc.org/ru/content/articlehtml/2016/cs/c6cs00196c>. Licensed under CC by 3.0.

construction industry for providing a water barrier for the construction of roads or buildings [46–49]. A switchable version of such behavior would be of great interest with respect to humidity management in smart buildings or in transport systems.

The redox activity of cross-linkable alkoxy silane PFS derivatives can be used to endow electrospun microfibers with properties that allow for electroactuation [50]. These materials display interesting strain-induced buckling behavior on electroactuation at low voltages (1.5–2.0 V). In contrast to fibers from organic polymers such as polyaniline (PANI) and polypyrrole (PPy), which require a polymer blend for electrospinning, inorganic hybrid polymers such as PFS do not have such limitations and may be spun as neat compounds. Compared with organic polyacrylonitrile (PAN) fibers that are not inherently redox active requiring large potentials to actuate electronically, PFS-based polymer fibers show electroactuation at low voltages (1.5–2.0 V). Future developments will aim at improving the mechanical strength of PFS yarns by combining hundreds of electrospun fibers in a rope-like manner while maintaining their rapid response times in order to be competitive with the existing bilayer actuators.

In general, highly charged polymer chains are prone to interact with biomolecules. Polyanionic heparin is a particularly important coating agent in the fabrication of medical materials in contact with blood due to its rather high charge density and specific inhibition of blood coagulation. In a similar vein, a polyanionic inorganic polymer with a polyphosphazene backbone has been demonstrated to act as adjuvant for intradermal immunization [51]. Current vaccine administration approaches rely strongly on immune enhancing additives (i.e. immunoadjuvants) to induce the desirable protective immune responses. Unfortunately, many of the currently used vaccine adjuvants such as the most commonly used alum are not compatible with intradermal delivery approaches owing to adverse side effects. By contrast poly[di(carboxylatophenoxy) phosphazene] (PCPP) is a potent adjuvant for intradermal immunization and its excellent immunomodulating potential has been demonstrated in multiple animal models with both viral and bacterial antigens. In addition, use of PCPP has progressed into clinical trials and PCPP formulated vaccines were found to be safe and immunogenic in humans.

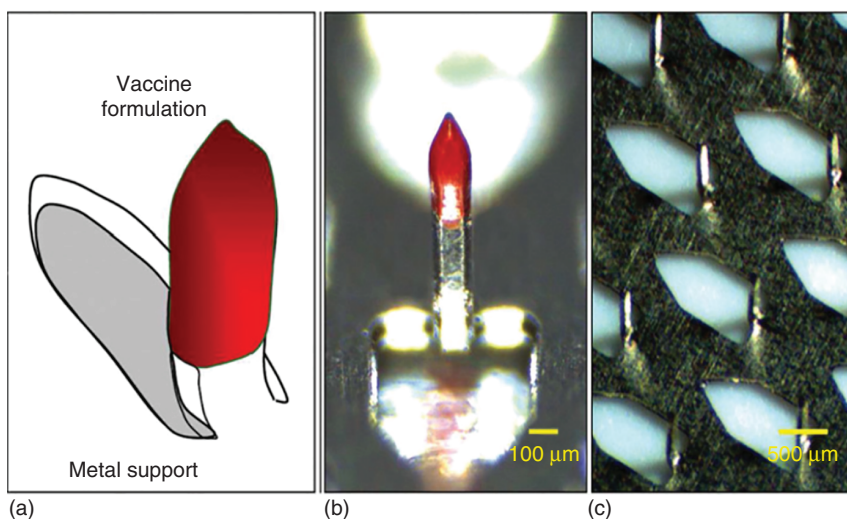


Figure 1.7 Microneedles and microneedle array with PCPP-coated tip (schematic representation (a), optical microscopy images of a coated microneedle (b), and an array of microneedles (c)). Source: Reproduced with permission of Andrianov et al. 2009 [51].

Its dual function as an immunoadjuvant and as a film forming/microfabrication material makes further macromolecular excipients obsolete. These smart properties have paved the way to PCPP-coated microneedles and microneedle arrays (Figure 1.7). Microneedles and microinjection devices can provide a convenient alternative potentially offering ease of application and distribution, with the possibility of self-administration and pain-free delivery of a vaccine. Further achievements in the field of biomedical applications that have evolved from closely related dendritic polymers are discussed in detail in Chapters 9 and 10 [52, 53].

1.2.6 Further Applications

Flame retardants are compounds that are present in consumer products, as for instance in clothing, toys, furniture, and seats in public transportation and also in construction materials. Flame retardants are in fact necessary additives if products are to meet legal fire-safety requirements. In recent years growing body of evidence has indicated that brominated flame-retardant chemicals used in upholstered furniture may, in some cases, be endocrine disruptors or have neurological and other health effects that make them unacceptable for use in daily life [54]. In line with these findings, since 2016, the *European Union* has prohibited the manufacture, placing on the market, and use of hexabromocyclododecane (HBCDD), an organic flame retardant used in a variety of consumer products. Therefore, finding replacements for these established brominated flame retardants is a surging field of investigation. Certain inorganic components and polymers were demonstrated to have great potential as replacements for the halogenated organic retardants and the detailed achievements in this area will be outlined in Chapter 8.

1.3 Perspective

Smart inorganic polymers are an emerging field of molecular materials with a bright perspective owing to their multifaceted properties. Other than for petrol-based organic polymers, the variety of fundamental building blocks is much larger for inorganic polymers, which helps avoiding limited resources in the production cycle. The nature of the elements involved is key to the versatile properties of this compound class. Based on their unique bonding situation, the energy barriers for torsional and rotational mobility of the backbone and the adjacent substituents are low, allowing increased flexibility with lower glass transition temperatures, higher gas permeation, and adaptive rheological properties as compared with their organic counterparts. The electronic features of heavier atoms endow such materials with optoelectronic properties relevant to LEDs, photovoltaic devices, applications such as flat-panel displays, and solid-state lighting. Charging and discharging of inorganic polymers can be used to switch polarity and wettability from hydrophobic to hydrophilic and vice versa. Such dynamic surface modification has potential for future applications in window screens, for transportation, and in the building sector. In a similar vein, dynamic switching of windows for privacy, security, or heat management is a strategy that has already entered the commercial market. For consumer safety and anti-counterfeiting purposes, molecular bar codes and encoded supramolecular entities have started to emerge on a high level of sophistication, and are almost ready for specialized applications. To summarize, smart inorganic polymers show high potential for numerous applications ranging from convenience and health care products to optoelectronic and information storage devices including security and safety purposes. Although the field has just started to emerge, a variety of applications has already passed the proof-of-principle state and future developments will help produce fascinating new materials based on smart inorganic polymers.

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