Review

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**Triggered and self-healing systems using nanostructured materials**

**Abstract:** Self-healing materials feature the outstanding ability of healing damage inflicted on them. This process leads to the (partial) restoration of the original properties of these materials, in particular of the mechanical properties. Several healing mechanisms involve processes on the nanoscopic level. These lead to the healing of the damage (e.g., crack or scratch) and, as a consequence, the macroscopic mechanical properties are reestablished. Moreover, self-healing of nanomaterials can also be achieved, which is of particular interest, because nanomaterials are particularly prone to damage due to their high surface volume ratio. This review summarizes the involvement of nanoscopic processes in the healing of macroscopic materials, and the healing of nanomaterials is discussed.

**Keywords:** nanomaterials; nanoparticles; nanoscopic processes; remendable polymers; self-healing materials.

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**1 Introduction**

**1.1 Self-healing materials in general**

Self-healing materials are currently in the focus of intensive research. Due to their remarkable ability to heal damage that was inflicted on them, they represent promising materials for a wide range of applications. The ability for self-healing offers the opportunity to increase the lifetime of the applied materials, which is also associated with less repair cycles required as well as less total exchanges of these materials. Hence, these materials are of particular interest for applications at places with poor accessibility (e.g., offshore windparks, tunnels) as well as for applications where a (partial) replacement will be required after a certain time of usage (e.g., bridge deck after ca. 20 years). Moreover, the ability to recover the material’s properties after damage can increase the safety. The occurrence of a damage event will not necessarily lead to a complete failure of the component. This ability qualifies these materials as interesting candidates in the field of aerospace.

Self-healing materials led to a paradigm shift in material design [1]. Up to now, materials were designed on the basis of “damage prevention”. A material had to withstand all external conditions without being damaged. These materials are not able to deal with damage. Hence, a “large” damage or, in particular, the accumulation of “smaller” damages will inevitably lead to the failure of the material. In contrast, self-healing materials are designed considering the concept of “damage management”. These materials can deal with the damage, i.e., “smaller” damage can be healed. Admittedly, large damage can still lead to failure of the material if they are beyond a certain limit.

Considering the great opportunities offered by these materials, different material classes have been investigated in the context of self-healing materials (for an overview on self-healing of different materials, see [2, 3]). Self-healing metals are rather difficult to achieve because the healing processes require high temperatures and are based on the transport of single, small atoms [1, 4]. For instance self-healing Al-Cu-Mg alloys could be fabricated [5–7]. Ceramics also require higher temperatures; the most prominent examples of self-healing ceramic coatings are the so-called MAX phases (ternary carbides) [8, 9]. In contrast, polymers and their composites represent the best-investigated material class in the context of self-healing materials [10–13]. In the following, the self-healing of materials on the nanoscopic level (i.e., the healing is achieved by the utilization of nanoscopic
materials as well as processes) and the self-healing of nanomaterials will be discussed.

1.2 Self-healing in nature: a source for bio-inspired materials

In contrast to most man-made materials, biological materials feature the ability for self-healing. This ability of natural materials promotes life on earth – it is even a prerequisite. Many of these processes are very familiar to us: healing of broken bones as well as the closure of cuts in the skin [14, 15]. Self-healing is not only limited to “living” materials (i.e., materials within living organisms); self-healing of materials produced by natural organisms could also be observed. The byssus threads of certain mussels revealed a self-healing ability (which is based on incorporated metal complexes) [16, 17]. These processes require healing mechanisms at the nanoscopic level, e.g., the remodeling of the broken bone, and result in the restoration of macroscopic properties. Moreover, nature also shows the self-healing of “natural nanomaterials”. For example, our genetic information – the DNA – can heal after damage [18]. The natural archetypes can be transferred to man-made materials if their intrinsic character is taken into account [19]. By doing this, some examples of self-healing polymers could be achieved by mimicking nature, e.g., vascular network mimicking bleeding [20].

2 Basic principles of self-healing materials

2.1 Mobility

All self-healing mechanisms are based on one prerequisite: generation of mobility. A damage, i.e., a crack or a scratch, can be healed only if a mobile phase is generated that can close the crack or scratch (Figure 1) [3]. This phase, generated either by the damage itself (i.e., autonomic self-healing) or by an external stimulus (e.g., heat, light, magnetic field), is required for the generation of the mobility. Subsequently, the mobile phase can close the damage. The healing process is finished when the mobile phase is immobilized again. It is noteworthy that the structure of the healed area has not necessarily been maintained; only the original function/property is (partially) restored. Nanoscopic processes can be involved in the generation of the mobile phase leading to the self-healing of the damage. Considering self-healing of nanomaterials, the generation of a mobile phase could be difficult due to their small size (i.e., mobility throughout the whole nanoparticle). Therefore, some self-healing processes concerning nanomaterials also involve the surrounding local environment of the nanomaterial, promoting the generation of a mobile phase.

2.2 Basic mechanism of self-healing

An intrinsic property of nanomaterials is their high interface-to-volume ratio [21]. As a result, the creation of an interface has a high energy cost, which makes the nanostructures less stable compared to the corresponding bulk materials. This is particularly important under critical conditions, e.g., intensive laser irradiation, high temperatures, and oxidative surroundings [14, 22]. This problem can be circumvented with the ability of these materials/systems to self-heal due to the management of structural and functional damages. However, it is not possible to just transfer the known strategies for micro- or macro-sized materials because of the extreme size confinement [3].

The basic mechanisms concerning different material classes are summarized in Table 1. Some mechanisms that were utilized for macroscopic materials can also be transferred to nanomaterials. However, some of these mechanisms are not applicable for nanomaterials mainly due to the above-mentioned size limitations. The encapsulation and the channel transport of healing agents are applicable for macroscopic as well as some nanomaterials. Nevertheless, the small size of nanomaterials limits

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**Figure 1** Basic mechanism of self-healing process. (A) Crack induction by mechanical load, (b) crack in detailed view, (C) induction of a “mobile phase”, (D) closure of the crack by the B “mobile phase”, and (E) immobilization of the “mobile phase” after healing (reprinted with permission from [3]). Copyright 2010, John Wiley and Sons.
the opportunities for the encapsulation. The required mobility can also be received by a phase expansion. This process is suitable for many materials, also for nanomaterials. The same accounts for the generation of mobility by a temperature increase as well as the utilization of a phase separation as driving force. In contrast, reversible cross-links can be exclusively used for polymeric materials. The utilization of the reversibility of certain bonds is also applicable for nanomaterials. Biological processes are limited to polymeric as well as ceramic materials. Comparable to the biological archetypes, the self-healing of nanomaterials can also be achieved by biological processes. Electrochemical processes are mainly limited to ceramics as well as metals. The reorganization process is a typical mechanism for nanomaterials. These can reorganize by the transport of atoms or molecules through the surrounding environment. As a consequence, the self-healing of these nanomaterials can only be achieved in a suitable environment.

3 Self-healing at the nanoscale

The first part of this review is devoted to self-healing processes at the nanoscopic level. Moreover, the utilization of nanosized compounds within materials to achieve self-healing will be discussed.

3.1 Self-healing in two-dimensional supramolecular structures

In 1990, Lehn coined the term “supramolecular” by describing large molecular systems that are formed by self-assembly of single molecules and are stabilized by weak noncovalent intermolecular interactions [23, 24]. Self-assembly is a process that spontaneous leads to a high ordered arrangement of basic building blocks due to their specific interactions [25].

The stability of these systems is determined by the thermodynamic binding strength of their intermolecular interactions as well as the reversibility of their bonds. The rather low binding strength opens potentials for the self-healing ability of these materials. As a result, topological defects, which can hardly be avoided during the self-assembly of large structures, can be corrected afterward. This represents an important precondition for the emergence of highly ordered structures. Therefore, important candidates for these self-healing applications are supramolecular monolayers with weaker, reversible interactions, e.g., van der Waals interactions, electrostatic interactions, metal coordination bonds, and hydrogen bonds [26].

Furthermore, the liquid/solid interface represents a perfect environment to investigate self-assembly processes, and scanning tunneling microscopy (STM) is the favored methodology to characterize the structure and the properties of two-dimensional monolayers on the nanoscale [27].

In Figure 2 the experimental situation of the self-assembly process is depicted and the basic processes at the liquid-solid interface are demonstrated. The first step is the adsorption of dissolved molecules on the substrate. This process is driven by the fact that the enthalpy of adsorption is more favorable than the enthalpy of dissolution. Then the molecules can desorb back into the solution, diffuse over the surface, or interact with other molecules that are adsorbed at the surface. In addition, they can associate with other molecules to larger and

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The color code specifies the applicability of the mechanism for macroscopic materials (M) (partially involving nanoscopic processes) and nanomaterials (N) (dark gray, positive; light gray, potential; white, negative).
less mobile aggregates and then self-assemble to highly ordered monolayers. The growth process is complete when the surface is totally covered. The molecules in the monolayer are in dynamic equilibrium with the dissolved molecules. This represents a unique effect for interfacial monolayers and is also of critical importance for the self-healing ability of such systems [26].

The tendency to return to the thermodynamically most stable state, if the equilibrium is disturbed, is the most important condition for the self-healing reorganization process. Different kinds of perturbations and defects are possible. If a local mechanical impact happens and only a single molecule is affected and the rest of the monolayer is unaffected, no change of the microstructure is visible after self-healing and the molecule is easily replaced. If a global damage occurs and the thermodynamic stability of the monolayer is affected, e.g., by a temperature increase or a decrease in the concentration, self-healing cannot take place as long as the non-ideal conditions exist. Afterward, if the favorable condition is restored the monolayer can reassemble back to its thermodynamically stable state. Two basic requirements have to be individually achieved for a self-healing ability of each monolayer: Temperature, concentration or solvent conditions have to be adjusted for the thermodynamically most stable state of the monolayer, and a kinetic trap should not be effective, either by elimination of the traps or by the availability of the thermal energy to overcome the traps. That means the molecular building blocks have to be available and mobile [26].

An example of the influence of global thermodynamic perturbations and the self-healing recovery of the favorable conditions are shown in Figure 3. At room temperature the monolayer of tricarboxylic acid 1,3,5-benzenetribenzoic acid (BTB) results in a highly ordered network with larger cavities. After the temperature is increased to 55°C, a reversible structural phase transition appears and yields a densely packed row order. The structural phase transition is completely reversible after the temperature is decreased to 25°C. As a result, the original highly ordered network is fully restored. This is demonstrated by a series of STM images and shows that the molecules do not desorb from the surface by increasing the temperature. Due to the thermoreversible transformation of the pore size, it is also possible to incorporate guest species, and an application for a temperature-controlled release of guest species is possible [29].

The ability of self-assembly and self-healing of these monolayers can also be used for rheological applications, surface functionalization or the replacement of...
damaged molecules with intact molecules. Another possible application is the preparation of electronic circuits based on interconnected molecular units. The problem for these applications is the presence of the liquid phase. As a consequence, in further steps a preparation technique has to be developed to remove the liquid phase without impairing the monolayer arrangement; the self-healing process must be carried out by adding a liquid surface with dissolved building block for healing the monolayer inside [26].

3.2 Self-healing nanocomposites

Nanocomposites are multiphase materials that consist of a bulk matrix and one or more nanodimensional phases [30]. They can be classified into three different classes based on their matrix, which can consist of metals, ceramics, or polymers. The most popular nanocomposites are the polymer-based systems due to their interesting structural and functional properties; the combination of polymers and nanoparticles can result in significant improvement of their chemical and physical properties [31].

3.2.1 Gold nanoparticles as reinforcing nanofillers

In their study, Park et al. used films consisting of 7.5 bilayers of anionic poly(NIPAm-co-AAc) microgels and cationic poly(diallyldimethylammonium chloride) on poly(dimethylsiloxane) substrates [32]. The authors investigated the absorption of citrate-stabilized Au nanoparticles (AuNPs) into these microgel/polyelectrolyte multilayer films. The resistance to strain-induced scratches is highly increased for those films in the dry state. These films also show effective self-healing properties after water exposure (Figure 4).

The AuNPs could be successfully embedded into the swollen hydrogel films by a simple immersion method achieved by the favorable Coulombic interactions between the anionic AuNP and the polycation. Unfilled hydrogel films show damages vertical to the stretching direction (10% strain). In addition, AuNP-doped films reveal drastically reduced damages under identical stretching conditions. After higher strains (20–30%), the AuNP-filled films also show damage (Figure 5). The film containing the lowest concentration of AuNPs (Au film-10) has a similar resistance to damage as the unfilled films. Whereas Au film-50 and Au film-100 do not show significant damage under the lowest strain conditions (ε=0.1), but at ε=0.2 Au film-50 and Au film-100 reveal small damage. This is
due to the fact that AuNPs may increase the elasticity of the film. Furthermore, in all cases the original structure is completely healed by exposure to water.

The improved mechanical properties can be explained by different effects. The first effect is the filling effect of the AuNPs because the elastic modulus of native films is much lower than the elastic modulus of AuNP-containing films [33]. The second effect is that AuNPs can inhibit crack generation and propagation because the coulombic interactions between AuNPs, polycations and microgel could absorb the energy that is generated during the stretching process [34]. At the moment, the whole self-healing mechanism is not really understood and more investigations have to be achieved to obtain detailed information.

3.2.2 Functional nanophases with inorganic catalyses for self-healing reactions

Metal centers can nicely be used to catalyze self-healing reactions in composite materials. The most important example was investigated by White et al. in 2001 [35]. The authors achieved the storage of the healing agent in the material by using microcapsules. They were also the pioneers of developing self-healing polymeric materials based on ring-opening metathesis polymerization (ROMP) of microencapsulated monomer healing agents (Scheme 1).

Grubbs’ catalyst is embedded into the material; upon crack building in the bulk material the healing agent is released out of the microcapsules, and after reaction of the monomers on the catalyst the crack is healed (Figure 6).

Kamphaus et al. later used WCl₆ as catalyst precursor for the ROMP [36]. This catalyst is widely available and tolerates higher temperatures than the Grubbs’ catalyst. Rule et al. revealed that the amount of the healing agent integrated into a self-healing material is defined as the product of the microcapsule weight fraction and the microcapsule diameter [37]. Autonomic delivery of healing agents using microcapsules enables the same healing performance as when a similar amount of healing agent is delivered manually. The healing performance is maximized if sufficient healing agent is available to fill the crack volume. That means that if the crack volume exceeds the amount of stored healing agent, less successful healing is possible. The relationship between microcapsule size, microcapsules weight fraction, and crack volume represents the most important parameter for the design of self-healing systems that are tailored to repair specific types of scratches.

The hollow tubes and microcapsules containing extrinsic self-healing materials are limited to autonomic repair of a single damage event due to the fact that after usage of the healing agent of the damaged region no further repair is possible. To overcome this problem, Toohey et al. prepared a self-healing system with a three-dimensional microvascular network embedded in the substrate [38]. Their system worked similarly to human skin. When a cut damages the surface, the healing agent flows out of the surface and heals the crack after interaction with the catalyst that is also embedded in the material (Figure 7).
In the chosen examples, only the catalysts used are nanoscopic materials. The applied capsules or fibers are in the micrometer range to ensure that sufficient healing agent is available. Moreover, the fabrication of nanometer-sized capsules or fibers is highly challenging. Therefore, it is essential to use storage devices on the microscale, whereas the catalyst for the self-healing reaction can be used on the nanoscale; as a consequence, better dispersion in the whole bulk material is possible.

3.2.3 Functional nanophases with TiCl₄-filled polylactide fibers

Another self-healing nanocomposite was investigated by Liu et al. in 2008 [39]. In this case, a multilayer composite consisting of polymeric and brittle inorganic films, e.g., poly(methyl methacrylate) with a deposited alumina barrier layer, was used. The crack formation in the brittle inorganic layer of the nanocomposite allows the exposure of atmospheric water in the system due to damage and the flexibility of these multilayer composite materials. This combination of stress-induced cracks in the substrate and the self-healing ability upon the influx of environmental water could be applied for potential applications in multilayer composite materials. In the present study, the authors used TiCl₄ as reactive metal oxide precursor and encapsulated it within the pores of a degradable polymer, e.g., poly(lactic acid) (PLA). The PLA fibers are reactive to atmospheric water, which leads to the hydrolysis of the degradable polymer shell and, afterward, to a release of the reactive metal oxide precursor. In addition, the release of the reactive TiCl₄ leads to hydrolysis of the metal oxide precursor and the formation of solid titanium oxides at the surface of the fibers. The detailed self-healing mechanism is depicted in Figure 8. The undamaged nanocomposite fibers are embedded in the bulk material filled with a reactive metal oxide precursor. Damage to the polymer layers, e.g., pinholes or cracks, allow the exposure of water in the metal oxide layer. This influx of water is responsible for the hydrolysis of the water-degradable polymer; as a result, release of the metal oxide precursor into the crack

![Figure 7](Optical image of a self-healing system with a microvascular network after damage (scale bar, 5 mm). Reprinted with permission from [38]. Copyright 2007, Macmillan Publisher Ltd: Nature Materials.)

![Figure 8](Schematic diagram of the healing mechanism. (A) Undamaged polymer layer containing fibers with reactive metal oxide precursor, (B–D) healing occurs over four steps, and (E) healing nanocomposite (reprinted with permission from [39]). Copyright 2008, John Wiley and Sons.)
is possible. Afterward, the metal oxide precursor forms a solid metal oxide via hydrolysis for closure of the crack.

### 3.2.4 Nanoparticles for magnetic field-triggered self-healing

Another interesting example of self-healing in nanocomposites was published by Corten et al. in 2009 [40]. The authors showed the stimulated self-healing mechanism of physically separated thermoplastic polymers containing γ-Fe₂O₃ nanoparticles (Figure 9). This could be achieved without sacrificing the mechanical properties of the nanocomposites by applying an oscillating magnetic field (OMF). The γ-Fe₂O₃ nanoparticles could oscillate at the frequency of the magnetic field; therefore, localized amorphous flow occurs in the matrix. Due to Néel and Brownian relaxation this was converted to heat and self-healing of physically separated polymeric films could be achieved afterward. The authors used as bulk material p-methyl methacrylate/n-butyl-acrylate/heptadecafluorodecyl methacrylate and the mechanical properties of the films remained the same before and after the self-healing process.

Other interesting examples were published in combination with thermally activated self-healing strategies, e.g., the Diels-Alder reaction. In 2010 Adzima and coworkers achieved magnetic-field-induced self-healing in the presence of Diels-Alder cross-linked networks containing chromium dioxide (CrO₂) [41]. For this purpose, the authors used the Diels-Alder polymers investigated by Chen et al. in 2002 [42]. The thermally reversible polymeric network containing these ferromagnetic particles was synthesized via the Diels-Alder reaction. After applying an alternating magnetic field, the material is heated in situ by the vibrating ferromagnetic particles, and after heating over the temperature of the retro-Diels-Alder reaction the polymer becomes liquid and damage could be healed. After cooling to room temperature and again cross-linking via Diels-Alder reaction the material properties are unchanged even after 10 cycles of fracture and repair.

### 3.2.5 Nanophases for electrically triggered self-healing

Williams et al. investigated in 2007 a novel class of organometallic polymers containing N-heterocyclic carbenes and transition metals that have potential as electrically conductive, self-healing materials [43]. These polymers revealed structurally dynamic properties in the solid state. For this purpose, thin films were cast onto silicon wafers and imaged using scanning electron microscopy (SEM). Then the films were damaged and subsequently healed via thermal treatment. This allows the material to flow into the scratch due to a depolymerization process estimated by SEM and surface profilometry. The self-healing mechanism is shown in Figure 10. A dynamic equilibrium between a monomer species and an organometallic polymer is responsible for the self-healing mechanism that can be controlled via an external stimulus, such as heat.

### 3.2.6 Nanophases for light-triggered self-healing

Another auspicious way to produce self-healing materials is the introduction of light-triggered systems to a
bulk material. As a consequence, these systems insert self-healing features in the obtained nanophases. Nevertheless, not many examples of nanostructured phases or metal complexes have been described up to now as photo-stimulated self-healing systems. One example was published by Weder and coworkers in 2011 by using Zn-based metallosupramolecular polymers [44]. The most important publications in this field were made in combination with Diels-Alder cycloaddition reactions. A large number of olefins can be linked to each other via formation of new covalent bonds after irradiation and they can be reversibly cleaved into their single molecules after irradiation at shorter wavelength [45]. Moreover, coumarin, anthracene, maleimide, butadiene, and cinnamic acid derivates show photo-induced cyclization; by incorporation of these systems into polymer matrices, self-healing nanocomposites can be produced by cross-linking via ultraviolet (UV) irradiation [31, 46–48].

An especially interesting example was published by Chung et al. [49]. The authors used cinnamic acid derivates that were incorporated into a polymer matrix. The cross-linking of this cinnamate monomer, 1,1,1-tris(cinnamoyloxymethyl)ethane, via [2+2] photocycloaddition was successfully investigated and also degeneration of cyclobutane cross-links to normal cinnamoyl groups, and the rephotocycloadditions were studied via Fourier transform infrared (FT-IR) measurements. In addition, the crack healing was effectively investigated by the measurement of the flexural strength of cracked and healed samples. The photochemical self-healing mechanism (Scheme 2) is very fast and no additional catalyst, additive, or heat treatment was required to observe a healing efficiency of 14%. In combination with a thermal treatment, a healing efficiency up to 26% was reported.

Another interesting possibility to generate light-triggered self-healing nanocomposites is the use of metal
nanoparticles. Klaijn et al. described the fabrication of hybrid materials based on flexible organogels [50]. Photoresponsive metal nanoparticles, like gold or silver, were embedded within the material. The authors used 5-nm gold nanoparticles and coated them with mixed self-assembled monolayers (mSAMs) of dodecylamine and photoswitchable azobenzene-terminated thiol [4-(11-mercaptoundecanoyl)azobenzene (MUA)]. The system has three advantages: full reversibility of the aggregation, no self-assembly into well-ordered crystals of the nanoparticles, and stability of the surfactant-free nanoparticles in gel matrices. The nanoparticles were introduced in thin films of syndiotactic poly(methyl methacrylate) organogels and then the created films were colored red for AuNPs and yellow for Ag nanoparticles. Furthermore, the authors observed that in the absence of UV irradiation, the NPs in the gel exhibit UV/visible (Vis) spectra comparable to that of free NPs in toluene and, therefore, no aggregation of the particles should have occurred in the matrix. After irradiation of the films by UV light, they changed their color in the irradiated regions depending on the extent of UV irradiation. After the absence of irradiation, the images that have been written show a self-erase, with erasure times depending on the composition of the mSAMs. The mechanism is due to the rapid trans-to-cis isomerization of the azobenzene groups of MUA. Due to the reversibility of the nanoparticle aggregation all images gradually self-heal after reaggregation to free nanoparticles. After healing, the films can be rewritten multiple times.

Other examples of light-triggered self-healing systems were achieved by the use of thermoplasmonics. A self-healing nanocomposite based on plasmonic heating was published by Alessandri et al. [51]; the authors utilized pressure-sensitive adhesives (PSAs). In this case, commercial carbon-filled PSAs were used, which were prepared by mixing butyl acrylate, 2-ethylhexyl acrylate, acrylic acid, and carbon black. The self-healing process can be obtained in the same material at different stages and is due to the viscoelastic properties of the PSAs and the improved thermal conductivity achieved by a thin gold overlayer. The writing process is based on surface damage via laser irradiation; afterward, the material is able to restore its structural integrity or functionality. After focusing of a continuous wave He-Ne laser onto the surface of the gold overlayer, spherical rings were formed. These rings consist of gold aggregates. Even more complex figures can be obtained in good reproducibility via point-by-point irradiation. The AuNP-PSA films also revealed a strong plasmon resonance at ~500 nm. The damaged regions undergo spontaneous self-healing in air, and only weak markers of the original rings could be detected after 24 h, resulting from polymer degradation. It is also possible to make the self-erase process more efficient by dipping the freshly written material into water. After removal of the water the whole gold aggregates were washed away together with the organic slurry; as a consequence, the surface was fully restored. The obtained systems also demonstrate another self-healing process after generation of small holes produced by laser focusing on the surface. These holes are completely self-healed spontaneously after a few minutes. This self-healing mechanism can also be repeated multiple times and is caused by the viscoelastic response of the composite to the heat generation after interaction between the laser and the AuNPs. These observed investigations can also be extended to other viscoelastic systems and create new perspectives for light-triggered self-healing applications [31].

### 3.3 Thermoreversibility in polymeric systems

Thermoreversible polymeric systems belong to the non-autonomic self-healing polymers. They can be monomeric, oligomeric, or non-cross-linked materials. These systems can be separated by the nature of their reversible bonds: covalent or noncovalent [13]. Systems in which the polymerization or the cross-linking takes place by intermolecular interactions between the monomer units or the side chains are named noncovalently bound systems. The self-healing ability in supramolecular polymers can be varied by changing the length, the content of the cross-linker, constitution, and structure. Supramolecular polymers belong to the intrinsic self-healing systems that can heal the damage without any additional healing agent. Only the chain mobility and direct contradiction with a fixation is necessary to achieve the self-healing process by forming new noncovalent bonds in the system [52]. Examples of noncovalently bound systems are hydrogen-bonded polymers, metal-ligand coordination polymers, host-guest polymers, ionomers, and biologically inspired polymers. Examples of covalent bond systems are Diels-Alder-based polymers as well as thiol-based, N-O-based polymers and photodimerization-based polymers [13, 53].

#### 3.3.1 Diels-Alder reaction

The first example of the incorporation of furan/maleimide systems into polymers for thermal reversibility was published by Craven in 1969 [54]. Since this first report many systems have been developed that contain the furan/
maleimide unit to introduce self-healing properties via Diels-Alder reactions into materials.

The most important example was described by Chen et al. in 2002 with the synthesis of monomer 4F, which contains four furan moieties, and monomer 3M, which includes three maleimide moieties [42]. The authors investigated subsequently the synthesis of polymer 3M4F using bulk polymerization and characterized the resulting polymer using UV/Vis spectroscopy, differential scanning calorimetry (DSC) measurements, and solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. The self-healing can be achieved in these systems by heating the polymer over the temperature of the retro-Diels-Alder reaction. As a consequence, the cross-linked Diels-Alder units open, and due to the increased flow of the material the scratch can be healed. Furthermore, the fracture-mending efficiency of the original and the healed material could be determined with a compact tension test specimen, and the self-healing properties of the material were demonstrated using SEM (Figure 11).

In their further work in 2003, the synthesis of 1,8-bis(maleimido)-1-ethylpropane (2MEP) and the polymers 2ME4F and 2MEP4F was described [55]. Furthermore, the mechanical properties of polymers 2MEP4F and 3M4F were investigated; the self-healing behavior was studied by solid-state NMR spectroscopy and DSC measurements. In addition, the healing efficiency was tested using load vs. displacement diagrams of fracture toughness testing of compact tension test specimens of polymer 2MEP4F.

In 2008, Murphy et al. achieved the synthesis of a monomer containing a dicyclopentadiene that was subsequently used in melt polymerizations [56]. The resulting polymers revealed self-healing behavior. In 2008, the so-called mendomer 401 was used and the melting and polymerization of the monomer was studied using DSC measurements [57].

Moreover, Kavitha and Singha described the synthesis of furan-containing polymers [58–61]. In their first work in 2007, the synthesis of poly(furfuryl methacrylate) (PFMA) via atom transfer radical polymerization (ATRP), free radical polymerization, and the synthesis of PFMA-b-PFMA via ATRP were described [58]. In addition, these polymers were cross-linked with a bismaleimide (Figure 12) and characterized by FT-IR and DSC measurements.

In 2009 a kinetic study of the Diels-Alder and the retro-Diels-Alder reactions using FT-IR and swelling

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investigations was published and the solution properties of the cross-linked polymers were analyzed [61]. In addition, the mechanical properties of the thermoreversible cross-linked polymer at high as well as at low temperatures were investigated. The self-healing characteristics of the cross-linked polymer were studied via SEM, and the thermal properties of the cross-linked polymer were investigated using thermogravimetric analysis.

### 3.3.2 Hydrogen bonding

An important example of polymers containing hydrogen bonds was described by Berl et al. in 2002: A cyanuric wedge and a corresponding diaminopyridine-substituted isophthalamide are self-organized into a well-defined linear system with self-healing properties at room temperature (Scheme 3) [62].

Furthermore, Cordier et al. prepared a reversible cross-linked rubber whose tensile properties can be completely restored by simply bringing together the fractured surfaces (Figure 13) [64]. The oligomers used were cross-linked via multiple hydrogen bonds. As a result, mechanical damage leads to the rupture of many reversible interactions, which can reconnect after being brought back together.

### 3.3.3 Ionomers

Ionomers are a class of organic copolymers that have both electrical neutral and ionized repeating units, up to 20 mol% of ionic species, integrated into their structure (Figure 14). These ionic species generate interactions or induce aggregation that has an effect on the mechanical and physical properties of the polymer [65, 66]. The combination of the unique properties of the ionomers, e.g., elastic flexibility, high melt strength, and spontaneous formation of physical cross-links, enables a self-healing behavior upon ballistic impact. A relatively small mark is left on the impact side after passage of the bullet, but the hole produced by the bullet is completely closed (Figure 15).

### 3.4 Self-healing in ceramics, concretes and metals

Self-healing hydraulic concretes are a very old topic. Such materials have been known since Roman times [68].
However, the currently applied autogenous self-healing of hydraulic concrete materials represents an intensive scientific and application-oriented research field. The penetration of water into the damaged concrete through the cracks induces the local formation of hydrates. This leads, depending on water pressure, pH value, crack morphology, and crack width, to an autogenous crack healing process. The self-healing process involves the formation of a new, stronger material at the crack site, which restores the integrity of the concrete structure.

Figure 13  Sequential images of the self-healing test of a supramolecular rubber (A–D, cut, join, mend, and stretch, reprinted with permission from [63]). Copyright 2008, Ludwik Leibler, CNRS.

Figure 14  Schematic image of the structure of an ionomer (reprinted with permission from [65]). Copyright 2008, Elsevier.

Figure 15  Self-healing mechanism in an ionomer after ballistic impact (reprinted with permission from [67]). Copyright 2008, Elsevier.
In addition, the crack width plays an important role in the self-healing process and, therefore, engineered cementitious composites have been developed to control the crack width to values below 60 μm [70].

The detailed regeneration processes in ceramic materials are so far not understood in detail. There are still open questions, like the maximum crack length, the width of the mendable cracks, and the optimal conditions as well as the local heat transport properties. Such factors change with crack growth as well as shrinkage and are still uninvestigated. Mostly very high local temperatures are required for the healing of ceramics due to the high activation energies of the diffusive mass transport in the covalent or ionic structures of the ceramics [71]. Also, lower reaction temperatures can be expected after wetting of the gain boundary by an intergranular glass phase. Stress relaxation processes, viscoelastic flow processes, and diffusion can occur at lower temperatures depending on the glass transition temperature of the material. Healing reactions start at the contact points in the region of crack faces by grain boundary and surface diffusion [72]. Spherical and cylindrical pores are formed after energy supply. They can collapse at high temperatures and the driving force, therefore, is the reduction in surface energy (Rayleigh instability) [73]. Additionally, another self-healing mechanism that appears in ceramics is the oxidation of non-oxidic phases in oxidizing atmosphere (air) [74, 75].

Moreover, the self-healing behavior of metals was also the subject of intense research. In this context, complete understanding of the function and the surface of the metallic material during the exposure of physical as well as chemical effects are the critical targets. This aim is far from being achieved because self-healing in metals is much more difficult than in other materials like polymers, ceramics, or concretes [1]. The problem here is the small size of the metal atoms and the absence of directionality in the chemical bonds, and, therefore, only healing of small defects is possible on metals with the currently known mechanisms. One example of a self-healing mechanism in metals is

Figure 16 Graphical image of the simulation that shows the movement of a capsule to a microcrack from its initial position (A) to the crack (B), its motion further away from the crack (C), and the release of the nanoparticles (reprinted with permission from [84]). Copyright 2010, American Chemical Society.
the reaction of metallic surfaces with the surrounding material. For this purpose, a surface layer can protect the metal and save it from harmful effects of the atmosphere. Creep and diffusion processes can also lead to closing of microcracks and pores at higher temperatures, e.g., in Al-Cu-Mg materials [5–7]. Therefore, the deformed underaged aluminum alloy was aged at room temperature and the influence on the mechanical properties was investigated. In addition, creep steels also have the potential for self-healing creep cavities usually caused by nucleation, growth, and coalescence [76–78]. Material failure could be restored, e.g., in high-temperature applications of steel. Furthermore, the precipitation of copper, boron, and nitrogen could significantly improve the long-term stability of steel. In addition, a self-healing mechanism was also investigated by incorporation of capsules filled with liquid into an electroplated coating [79–81]. The polymer capsules are a few hundred nanometers in diameter and the coating was 15 μm thick. The largest problem was the introduction of the liquid-filled capsules into an electroplated coating because the electroplating process usually leads to the collapse of the capsules. Also, the introduction of an intermetallic phase is possible with this method, which delivers stress anomalies into metallic or intermetallic matrices. Therefore, a complete understanding of the interaction of phase composition, size distribution and topology, matrix, fabrication method, microstructure, and mechanical properties is required [3, 82].

3.5 Design of a “repair-and-go” system for site-specific healing at the nanoscale

The inspiration for the studies of repair-and-go systems was the functionality of biological leucocytes that are localized at wounds and make the healing process in natural systems possible. In an artificial system, the leucocytes are replaced by a polymeric microcapsule in which the healing agent is encapsulated as solid nanoparticles and the synthetic wound is a crack at the surface [83]. Therefore, simulations were performed about the motion of the microcapsule over the damaged surface, the capture into the crack, and the release of the nanoparticles as well as the re-movement of the capsule on the undamaged surface (Figure 16) [84].

For their experiments, the authors assumed that the surface of the microcapsules is amphiphilic in nature, and therefore they could have similar interactions with hydrophilic and hydrophobic domains. Furthermore, it was assumed that the microcapsules include an oil phase with dispersed hydrophobic nanoparticles inside [84]. Also a practical preparation of all the aspects of this model is possible [85–87].

In the first publication of Alexeev et al. in 2005, mesoscale models for hydrodynamics and micromechanics were integrated and investigated regarding the fluid-driven motion of microcapsules on different surfaces, like flat, mechanically uniform surfaces and mechanically patterned surfaces containing alternating regions of hard and soft domains [88]. Furthermore, isolation of conditions where the mechanically and topographically patterned surfaces can transmit “stop” and “go” instructions for the capsules was obtained. They can halt at specific locations at the substrate, and afterward, with an increase in the flow velocity, the moving of the capsule is resumed. It could also be shown that the substrates can affect the capsules to “crawl”, “walk”, or “jump” over the surface by containing regular arrays of compliant posts. The control over the capsule dynamics can enable the fabrication of mobile microreactors. A second publication of Alexeev et al. in 2007 contains the optimization of the efficient operation of microfluidic devices [89]. The authors pointed out that it is necessary to conduct the microcarriers to specific locations within microchannels and that they can release their contents in a prescribed manner. By using computational modeling, the authors obtained chemically patterned substrates that exploit these distinctive features and, furthermore, drive these capsules to burst and deliver their load in a “programmable” manner. In this way, the “instruction set” can be introduced into the system by coupling the mechanical and chemical properties of the microcapsules and the substrates. For this purpose, the system can act in a number of functions in an autonomous way. In 2007, Verberg et al. obtained the modulation of the rolling motion of a fluid-driven, particle-filled microcapsule along a heterogeneous, adhesive substrate [90]. The determination of the release of the encapsulated nanoparticles can be utilized to repair the crack on the underlying surface. A lattice Boltzmann model for the hydrodynamics and the lattice spring model for the micromechanics of elastic solids was used. These models determine the relations between the elastic shell of the microcapsule and the surrounding fluids. Also, the Brownian dynamics model was applied for simulations of the release of nanoparticles from the microcapsule and their movement into the surrounding solution. In this way, the authors could determine the conditions where nanoparticles released from the detained capsule can repair the damage and later allow the capsules to move again along the substrate. With this work, guidelines for designing particle-filled microcapsules
were developed that have a “repair-and-go” function; this can be used to repair damage in microchannels and microfluidic devices. The following publication of Kolmakov et al. in 2010 deals with the simulation of the behavior of nanoparticle-filled microcapsules powered by an imposed shear to move over a substrate with a microcrack by using hybrid computational approaches [84]. As discussed before, the microcapsules become captured in the crack and thereby the nanoparticles can pass through the shell of the capsule and fill the damaged region. The authors focused on a simple shear flow and could obtain the conditions where the microcapsules become caught in the cracks. Moreover, the conditions could be determined where the capsules enter the cracks for a finite time and where they are activated to leave this region by the imposed flow. The flow with the dimensionless capillary number (Ca), which represents the relative importance of the viscous stress in the surrounding fluid and the elastic stress in the capsule’s shell, could be obtained. Then, the characterization of the particle after penetration of the crack surface for these two scenarios was performed. With the effect of using a pulsatile shear flow it is possible to produce an effective repair-and-go system where the microcapsules can introduce a high volume of nanoparticles into the crack and leave the fracture afterwards (Figure 17).

In further stages of the healing process the damaged surface is almost filled with nanoparticles and the microcapsule can move over the completely healed crack (Figure 18). It can be shown that the same parameters as for the motion over the unhealed surface allow the motion of the microcapsule over the crack without being captured. The results demonstrate that the amphiphilic capsule can easily move over the surface when the hydrophobic crack is filled with hydrophobic particles.

Recently Kratz et al. developed real existing flexible microcapsules filled with a solution of nanoparticles that roll across a surface that has been damaged and stop to repair any defects by releasing nanoparticles into them [91]. This behavior is visualized by fluorescence confocal microscopy (Figure 19). The authors prepared the repair-and-go system by using droplets of oil that were stabilized with a polymer surfactant and contain CdSe nanoparticles. These microcapsules can find the cracks on a surface, selectively release the nanoparticles into the crack, and move on to identify the next crack afterwards. In this
study, the microcapsules are too large to enter the cracks. With their flexible walls they have the ability to probe the crack and stay temporarily in the interior. During this procedure the microcapsules can release the nanoparticles; this is possible due to the thin microcapsule wall and the hydrophobic-hydrophobic interactions between the nanoparticles and the cracked surface.

The discussed publications demonstrated effectively how it is possible to calculate and create repair-and-go systems where the healing agents, the nanoparticles, are delivered to the cracks on the damaged substrate by the microcapsules and repair the crack upon release out of the capsule. After removal, further healing processes are also possible. These systems show a real-life selective repair property without affecting the rest of the substrate [83].

3.6 Self-repairing by damage-triggered smart containers

Self-healing materials are also important for the corrosion resistance for many transportation, marine, architectural, and military applications where long service life and acceptable performance of organic coatings (i.e., paints) are required. Furthermore, for those applications the challenge is to mitigate corrosion attack in a safe, environmentally acceptable, and cost-effective manner that does not compromise the performance of the painted component, system, or structure. In the past years, some approaches for self-healing coatings were reported with selected inorganic additives that do not have an adverse effect on workers’ health and safety or on the environment. In the following section, both primers and topcoats will be discussed [92]. The most important property is suitable solubility of the agent in the damaged environment. If the solubility is too low, not enough healing agent will be at the interface of the substrate, and this will lead to a weak healing activity. If the solubility is to high, the agent will be leached out from the coating, and afterward no protection is possible [93].

3.6.1 Functional active coatings

A good way to prepare well working self-healing systems is the production of nanocontainers with the ability to release encapsulated active materials in a controlled way. In this manner, a new family of self-healing multifunctional coatings could be achieved that exhibit both passive functionality and rapid feedback activity in response to damages. A known trigger leads to a release of the active material and increases the coating’s durability after healing. Furthermore, reversible and irreversible changes of the shell permeability can be induced by various stimuli. This depends on the nature of the sensitive components that are introduced into the container shell. Different triggers can be observed like tunable permeability or total rupture of the container shell [93].

Two concepts are possible for the “passive host-active guest” structure: Fabrication of an active composite layered system in which the passive coating matrix is alternated with layers bearing an active coating component or incorporation of the nanoscale containers loaded with the active components into classical coatings. The disadvantage of the first concept is the shortcoming of the stability and self-healing activity, whereas the second
concept leads to uniform distributions in the coating, and only the active material in the local environment where the damage occurs reacts and heals. Also an interesting property of the nanocontainers is the controlled release and upload that depends on the interactions of the bulk material and the material of the shell. Therefore, the shell should be sensitive to external triggers, like local pH changes, temperature changes, electromagnetic irradiation, mechanical pressure, humidity, electric potential, ionic strength, and dielectric permeability of the solvent.

3.6.2 Nanocontainers based on ion-exchange effects

Hydrophobic materials are known for their good corrosion inhibition, but in the context discussed here the disadvantage is the limited stability; they allow water to damage the underlying surface due to their molecular structure. Therefore, layered double hydroxides (LDHs) have been established where the surfactant is introduced into an inorganic host matrix. LDHs are represented by the general formula \( [\text{M}^{2+}\text{M}^{3+}x\text{(OH)}_2]^{x-}\text{A}^{-}\text{m}\cdot n\text{H}_2\text{O} \), where \( \text{M}^{2+} \) is a divalent, \( \text{M}^{3+} \) a trivalent, and \( \text{A}^{-} \) an interlamellar anion. Such components can be used as a protective layer at the surface or as nanocontainers introduced in organic coatings filled with active species or as a trap of the corrosive agents [93–95].

3.6.3 Nanocontainers with polymer shells

A smart way to introduce hydrophobic molecules in the core, while the outer shell enables water solubility, is the use of self-organizing block copolymers or lipid nanocontainers. Choucair et al. obtained such systems by using polystyrene-\( b \)-poly(acrylic acid) block copolymers in dioxane/water and dioxane/tetrahydrofuran/water mixtures [97]. The authors also could control the vesicle size by use of different additives (such as NaCl, HCl, or NaOH), solvent compositions, and hydrophilic block length. Up to now several block copolymers could be established for nanocontainers, like poly(ethylene oxide), poly(N-isopropylacrylamide), polypyrrolidines, and biodegradable polymers such as poly(\( \varepsilon \)-caprolactone), poly(\( \delta \),L-lactide, or poly(\( \delta \),L-lactic acid-co-glycolic acid). Popular triggers for these systems are temperature or pH changes [98]. Their application is limited due to their instability against aggregation and collapse. Therefore, they could be stabilized by cross-linking of the core or the shell before or after the self-assembly process [93, 95, 99–102].

3.7 Lubricant layer in a self-healing disk drive

One self-healing system that is seen and used every day is the lubricant layer on magnetic disks. Due to the fact that the storage capacity of hard disk drives is increasing in rapid fashion and also that the capacity of an average disk drive has doubled every 18 months, the components of these drives have to be evolved quickly and new technologies have to be developed. To manage these storage densities, the distance between the read/write head and the disk surface decreases. This leads to the point that the head lies only a few billionths of a meter above the disk. In this system, a contact between the head and the disk is unavoidable. A typical disk drive consists of a substrate material, typically, glass or aluminum, and a number of adhesion-promotion layers forming a metallic support structure, a magnetic layer for data storage, and a thin layer of hard, amorphous carbon. The carbon layer is very thin and protects the soft magnetic layer from damage when the head collides onto the surface of the disk. The carbon layer is also coated with an extremely thin perfluoropolyether lubricant film to minimize erosion of the carbon layer during the impact of the head. Furthermore, whenasperities are encountered, the lubricant layer must respond to heal the place where the head hits the asperity to ensure satisfactory operation. Therefore, the right film thickness and the self-healing ability of these lubricants are responsible for the long-term reliability of hard disk drives [103, 104].

4 Self-healing of nanomaterials

The following definition of a nanomaterial was given by the European Union in 2011 [105].

“[…] A natural, incidental or manufactured material containing particles, in an unbound state or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm.

In specific cases and when warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%.

By derogation from [the above], fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.”

Within this review the self-healing ability of nanomaterials that fulfill the above-mentioned properties will be
considered. Therefore, gold nanoparticles with self-healing effects after laser irradiation [106], special self-healing catalysts for artificial photosynthesis [107], and self-organizing components for solar energy conversion [108] will be discussed in more detail.

4.1 Self-healing of gold nanoparticles after laser irradiation

The largest problem that can occur during the work with metal nanoparticles is the loss of their interesting nonlinear optical properties mostly at high intensities because of the damage to their structure. Amendola et al. have pointed out that gold particles (AuNPs) exhibit good nonlinear absorption properties after laser irradiation at 532 nm in the presence of zinc phthalocyanine [14, 106, 109]. This is due their special self-healing mechanism. The gold nanoparticles were not destroyed due to photo-induced damage, which is usually observable during laser irradiation with intense laser light. This self-healing effect was investigated via transmission electron microscopy (TEM) images (Figure 20) and more in detail with size histograms. The normal size of those AuNPs before laser irradiation is around 30 nm. After laser irradiation without zinc phthalocyanines the particles become significantly smaller, whereas in the presence of zinc phthalocyanines the percentage of nanoparticles with a diameter above 30 nm is larger. This shows that not only a repair process takes place during irradiation, but also a growth process occurs.

The growth process indicates the agglomeration of small AuNPs, which were prepared via photofragmentation in the presence of zinc phthalocyanines to larger particles. In Figure 21, the supposed self-healing mechanism is depicted. The first step is the absorption of photons by the AuNP; thereby they are heated above their explosion limit and fragment into small particles with positive charges.

![TEM images of AuNP before (A) and after laser irradiation in the presence (B) and absence (C) of zinc phthalocyanines (reprinted with permission from [109]). Copyright 2009, American Chemical Society.](image)
Afterward, some of these positive charges are reduced by zinc phthalocyanine and the particles are neutralized. The loss of charge on the nanoparticles weakens the stability of their colloidal structure, leading to an agglomeration. The produced agglomerates photomelt afterward due to the high laser intensity and create larger spherical AuNPs as compared to the situation prior to the laser irradiation. Besides, they also have better optical properties. Furthermore, the molecular structure of the zinc phthalocyanines could be important for a suitable interaction with the nanoparticles, and the redox properties are certainly crucial for the reduction of the AuNPs. It is possible that also other molecules can induce such effects similar to those presented before, and therefore, the mechanism can be also of relevance in other cases for the interaction of laser pulses with plasmonic nanoparticles in the presence of organic chromophores. This example nicely demonstrates the possibility of the utilization of rearrangement/reorganization processes involving the local environment that leads to a self-healing process.

4.2 Long-lasting oxygen-evolving catalysts for artificial photosynthesis

The most important reaction that uses light energy to drive the oxidation of water at an oxygen-evolving catalytic site within photosystem II (PSII) is the photosynthesis. For a better understanding of these mechanisms, Ferreira et al. investigated in 2004 the structure of PSII of the cyanobacterium *Thermosynechococcus elongatus* [110]. The obtained data strongly suggested that the oxygen-evolving center contains a cubane-like Mn₃CaO₄ cluster linked to a fourth mangan atom by a mono-µ-oxo bridge. Furthermore, the authors pointed out the details of the surrounding coordination sphere of the metal cluster and the consequences for a possible oxygen-evolving mechanism. Synthetic photosynthesis transforms solar light into chemical energy, i.e., by splitting water into hydrogen and oxygen. The problem is that this reaction takes place in a very oxidizing environment. The standard redox potential for the O₂/H₂O electron couple is 1.23 V vs. normal hydrogen electrode (NHE). Under these conditions an oxidative damage of the catalyst is observable. As a consequence, strategies have to be developed that can preserve the catalyst activity [107]. To achieve the realization of a synthetic system that performs “water splitting” and oxygen production without the use of extreme driving potentials, Kanan et al. investigated in 2008 a catalyst that is formed upon the oxidative polarization of an inert indium tin oxide electrode in phosphate-buffered water containing Co(II) at a bias of 1.3 V (vs. NHE), also named Nocera’s Co-Pi catalyst [111]. The authors further indicated with different analytical techniques the existence of phosphate in an approximately 1:2 ratio with cobalt in this material. Furthermore, the pH dependence of the catalytic activity revealed that the hydrogen phosphate ion is the proton acceptor in the reaction. The Co-Pi catalyst revealed good activity in the water oxidation reaction. The self-healing effect lies here in the self-repair of the electrode due to dissolution processes of the Co(II) complex. The transformation of the catalyst in the redox process is connected with the ligand exchange and biased structural reorganization. The different natures of the oxidation states of the cobalt, Co(II), Co(III), and Co(IV), species that are involved in the catalytic cycle lead to the necessity to repair the cobalt-based oxygen-evolving film [112]. It is known that Co(II) is a high-spin ion, whereas Co(III) and Co(IV) are low-spin ions. Therefore, Co(II) is labile to ligand substitution, and Co(III) and Co(VI) species are rather inert in an oxygen atom ligand field [113]. This fact leads to the release of cobalt ions in solution when the metal is reduced back to Co(II) within the catalytic cycle. Only when the electrode is maintained at 1.3 V vs. NHE no further dissolution of the cobalt takes place until the bias is removed and the cobalt redeposition is performed during the oxidation of Co(II) to Co(III) upon extended reapplication of the external bias. A mostly quantitative recovery of the film after 14 h was observed. The addition of phosphate to the corroding films leads to reparation and redeposition of the cobalt on the catalytic film, which represents the self-repairing process in this system, and a high turnover number of the catalyst is possible due to this self-healing process [107].
4.3 Dynamic self-assembly of nanoscale components for solar energy conversion

Naturally occurring photosynthetic systems use complex pathways of self-repair and therefore to elongate the lifetime of these systems because of the impact of photodamage during the processing cycle. For this reason, Ham et al. investigated a complex composed of two recombinant membrane scaffold proteins, a phospholipid 1,2-dimyristoyl-sn-glycerol-3-phosphocholine and single-walled carbon nanotubes, which mimics this process [114]. These three components can self-assemble into a configuration where the lipid bilayers aggregate on the surface of the carbon nanotube, also called nanodiscs (NDs) (Figure 22). In addition, a platform for the attachment of light-converting proteins was formed. Furthermore, the authors showed that the system can disassemble later upon addition of a surfactant and rearrange upon its removal over a large number of cycles.

Additionally, the authors pointed out that the assembly is thermodynamically metastable, and the transition can only be reversible after exceeding a minimum value of surfactant concentration; as a consequence the controllability of the process is high. The photoelectrochemical activity is only present in the assembled state of the complexes. In addition, the authors demonstrated a regeneration cycle by using surfactant to switch between assembled and disassembled states. This regeneration results in an increased photoconversion efficiency of more than 300% over 168 h and a significant extension of the lifetime of the system. In conclusion, the authors demonstrate the first synthetic photoelectrochemical complex that can disassemble by using a chemical trigger and can reassemble in a specifically orientated way based on intermolecular forces and a controllable equilibrium [108].

5 Conclusion and outlook

The intense research on self-healing materials led to significant progress in this important research field. Nanoscopic processes have been introduced into different materials leading to self-healing properties. On contrary, reports on self-healing nanomaterials are still rather scarce. However, the intense research of the past decade led not only to the development of several new self-healing materials (up to the development of new commercial products), but also the basic knowledge of the underlying principles and mechanism was also tremendously deepened. This knowledge will be the basis for the development of new strategies and the design of novel self-healing materials in the future. These will be mainly micro- as well as macroscopic materials, in which the self-healing process can also be based on nanoscopic events as well as special compounds. However, the development of new self-healing nanomaterials will also grow, considering further the special properties of these materials. The importance and applications of nanomaterials will rise in the future, increasing the demand for self-healing of these materials that are due to their special properties very prone to damage. Amazingly, the self-healing of nanomaterials seems to be one step ahead compared to the healing of “normal” materials concerning the restoration of special properties besides mechanical properties. The self-healing of macroscopic materials is currently mainly based on the restoration of mechanical properties. Only very few

Figure 22 Schematic representation of the reversible self-assembly process (reprinted with permission from [114]). Copyright 2010, Macmillan Publisher Ltd: Nature Chemistry.
exceptions are published up to now. In contrast, the self-healing of nanomaterials often involves the restoration/preservation of other properties, in particular, optical properties. In this context, research on nanomaterials can be pioneering for an extension on macroscopic properties.

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