Functionalization of polymers and nanomaterials for water treatment, food packaging, textile and biomedical applications: a review

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Abstract

The inert nature of most commercial polymers and nanomaterials results in limitations of applications in various industrial fields. This can be solved by surface modifications to improve physicochemical and biological properties, such as adhesion, printability, wetting and biocompatibility. Polymer functionalization allows to graft specific moieties and conjugate molecules that improve material performances. In the last decades, several approaches have been designed in the industry and academia to graft functional groups on surfaces. Here, we review surface decoration of polymers and nanomaterials, with focus on major industrial applications in the medical field, textile industry, water treatment and food packaging. We discuss the advantages and challenges of polymer functionalization. More knowledge is needed on the biology behind cell–polymer interactions, nanosafety and manufacturing at the industrial scale.

Keywords Antibacterial · Drug delivery · Functional polymers · Functionalization · Surface modification

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Introduction

The inert nature of most commercial polymers and nano-materials limits their development for specific applications in various industries and, therefore, surface modification must be carried out to improve their adhesion, printing and wetting by bringing a variety of polar and other functional groups on surfaces of polymer and nanostructures. Several surface functionalization methods have been established during the past decades that generally follow a common path: first the binding of primary reactive functional groups to the polymer chain ends at the surface, followed by modifying the reactive surface with active/bioactive agents, hydrophobic and hydrophilic monomers, oligomers or polymers to achieve specific surface characteristics matching the needs of the end use (Karnati et al. 2019; Pour et al. 2015; Zare et al. 2019; Zhou et al. 2020).

The immobilization of active/bioactive agents on a polymeric surface is generally performed by covalent bonds, electrostatic interactions and ligand–receptor pairing. Non-covalent physical adsorption is desirable for some applications such as certain drug delivery systems (Richey et al. 2000) and regenerable antimicrobial textiles (Kim and Sun 2001; Sun et al. 2001). The covalent immobilizations offer some other advantages by providing the durability of active/bioactive agents, the extended half-life for biomolecules and preventing their quick metabolism (Alferiev et al. 2006; Harris 1992), as well as preventing the migration of bioactive agents to food from the active food packaging films. Grafting of multifunctional and anchoring compounds via a spacer molecule onto the surface of the solid substrate leads to an increase in the number of available active/bioactive agents per unit area and improves the efficiency of active/bioactive agents by reducing steric restrictions. Hence, the current review focuses on recent advances in the modification of polymer and nanomaterials surfaces, via active/bioactive agents targeted for various medicinal and industrial applications (Fig. 1).

Biomedical applications

Nanomaterials are introduced as different types of materials with at least one-dimension size in the range of nano- and have high surface energy, which are suitable candidates for being utilized in different biomedical applications. This is resulted from their extraordinary properties enabling them to donate new properties to the available tools and improve their performance in physiological conditions, increasing the satisfaction level of the users. Improving the biocompatibility, water solubility, biodegradability, bioavailability, antimicrobial activity, antioxidant and anticancer properties, and imaging capability are among several types of features which could be provided via utilization of nanomaterials in biomedicine (Abd Elkodous et al. 2019; Vuppaladadium et al. 2020; Makvandi et al. 2020; Deb et al. 2019). The application of nanomaterials in the field of biomedicine is varied from utilizing as drug delivery vehicles or therapeutic agents for different types of diseases and infections, to diagnostic agents in biological imaging, cell labeling and biosensors and functionalizing moieties for medical devices like stents or lenses (Jamaledin et al. 2020; Rout et al. 2018). Based on the literature, nanomaterials are classified into three main categories: (1) organic nanoparticles like dendrimers, lipid-based nanosystems, polymers and biopolymers, (2) inorganic nanoparticles including metal and metal oxide nanoparticles (like magnetic, Au, Ag, Cu), carbon-based nanoparticles (graphene, graphene oxide, carbon nanotubes, carbon dot and graphene quantum dot), silica nanoparticles, quantum dots and upconversion nanoparticles and (3) hybrid nanomaterials which are a complex of inorganic and organic nanomaterials in different forms (like core–shell nanoplatforms, nanocomposites, hydrogels, nanocapsules, nanospheres, etc.) (Fig. 2; Yang et al. 2019).
As mentioned before, nanomaterials could provide ideal features for the biomedical applications; for example, surface-modified nanomaterials could allow (selective treatment) or avoid cell internalization (reduce macrophage uptake, main challenge of nanomedicine) as is visible in Fig. 3. They could be used to prepare materials for in vivo applications via enhancing their biocompatibility, reducing their toxicity effect and preventing the activation of the immune system all of which lead to an increase in the bioavailability of the materials inside the body. These modifications are essential especially for different types of drug delivery systems which are designed for supplying sufficient dose of drugs at the targeted site along with reduction the side effects of the drug molecules on the other organs (Singh et al. 2019). For instance, utilizing different types of nanomaterials for transmission of antibacterial agents could improve the effectiveness of the agents and reduce the possibility of the drug resistance. In this regard, antimicrobial agents (like different types of antibiotics or Ag nanoparticles) could be attached on the surface of the nanomaterials or be entrapped inside them (Fig. 4).

Biodegradability is the other important feature which is needed for the safety usage of nanomaterials inside the body. This is a very important property in designing scaffolds for tissue engineering and regenerative medicine applications (Agarwal et al. 2016; Maji et al. 2017). Moreover, it is considered as a method for controlling the cargo release. As a matter of fact, different drug release mechanisms exist, one of which is the bioerosion or degradation of the carrier’s surface, thus enabling drug diffusion toward the external environment (Lee and Yeo 2015).

As far as the coating process is concerned, different techniques exist for polymer functionalization, as esters activation forming amide bonds, click chemistry, thiol chemistry, alcohols addition to isocyanates, imine and oxime linkages,
ring-opening reactions, and multicomponent reactions (Blasco et al. 2017). The first one is a very promising technique since amide bonds show high stability in different environments and compatibility with dissimilar moieties. Click chemistry is also a useful tool, since it is stereospecific and, during the production process, it generates easily removable non-toxic byproducts. Concerning the thiol chemistry, they have high light-mediated reactivity with carbon–carbon double bonds, thus allowing a combination with click chemistry, obtaining quantitative yields and a good product recovery. Shifting to the alcohols addition, it seems a promising technique due to its fast kinetic and good yields, but its application is limited for the isocyanate’s toxicity and the instability of the polymers/isocyanates mixture. Imine and oxime linkages have a relevant role in the field of macromolecular modifications, the obtained linkage can be hydrolytically stable or unstable depending on the final need. Ring-opening reactions are usually used with epoxides, but in recent year they have been also shifted to aziridines and azlactones. Eventually, multicomponent reactions are new synthesis methods that are gaining importance, thanks to their atom economy; their superiority with respect to other techniques is due to the possibility to introduce a high degree of functional complexity in a single modification step. NPs can be coated with different materials, where one of the most used are polymers. They can enhance the biological activity and improve the therapeutic efficiency. Furthermore, different polymers can be used, such as polyethylene glycol, polycaprolactone and polylactic acid; for example, functionalized carbon nano-onions (d’Amora et al. 2020) with hyaluronic acid phospholipid for selective targeting of cancer cells, where carbon nano-onions are a multi-shell fullerene structure with a size ranging from 2 to 100 nm, depending on the synthesis method. This surface modification allowed an increase in dispersing abilities and long-term stability to the carbon nano-onions derivatives. Furthermore, they were able to test their targeting abilities toward specific cancer cells overexpressing the CD44+ receptor. These functionalized carbon nano-onions were tested on zebrafish, showing no toxic effects and manifesting their biosafety and specific targeting also in vertebrate systems. Functionalized polymeric nanoparticles can be also produced with carbonate groups through hydroxyurethane bonds (Yadav et al. 2019). Here, nanoparticles were produced via copolymerization of glycerol carbonate methacrylate with methyl methacrylate by miniemulsion process and were successively functionalized with amines, amino acids and albumin; dopamine was used as hydroxyl-functionalized amine for the coating with phenolic hydrogen bonding moieties. The materials obtained can be used as catalysts for the cycloaddition of carbon dioxide to epoxides under atmospheric pressure (Sousa et al. 2019). The possibility to cell targets, as said, is a pivotal point highlighted by the use of poly(lactic-co-glycolic acid) carcinoembryonic antigen-targeting nanoparticles for drug dispersion and targeting.

Fig. 4 Different approaches for the transmission of antimicrobial properties on a specific platform. Reprinted with permission from Delfi et al. (2020)
delivery in colorectal cancer. Carcinoembryonic antigen is a

cell surface glycoprotein in colorectal cancer patients, whose

serum level evaluation is recommended in clinical settings.

In the field of surface functionalization, ethylene diamine

was successfully used with cellulose nanoparticles forming

aminodeoxy cellulose nanoparticles, which were subse-

quently incorporated into poly(ethylene-co-acrylic acid) to

develop composites. These composites were found to main-

tain their biocompatibility even after the introduction of the

functionalized nanoparticles, thus enabling their use in bio-

medical applications (Chenampulli et al. 2019). Besides pol-

ymers, other materials can also be used for surface func-

tionalization, such as cellular components. Indeed, the surface of

polymeric nanoparticles was functionalized with umbilical
cord-derived mesenchymal stem cell membrane for tumor-
targeted therapy (Yang et al. 2018a). Umbilical cord derived

described mesenchymal stem cells showed tropism against malignant

lesions, low immunogenicity, and high proliferative ability. The

nanoparticles used were poly(lactic-co-glycolic acid)-
based, with a layer of plasma membrane from umbilical
cord mesenchymal stem cells coating on the surface. Such

functionalization increased the cellular uptake efficiency of

poly(lactic-co-glycolic acid) nanoparticles, the tumor cell

killing efficacy of poly(lactic-co-glycolic acid)-encapsulated
doxorubicin and the tumor targeting of nanoparticles. Nano-
gels are also recently gaining relevant importance in bio-

medical applications as drug delivery systems for targeted

applications. They are defined as nanoparticles comprised of

a 3D structure, either physically or chemically crosslinked,

usually of polymeric nature. Sometimes, other definitions

can be also found, such as particles of gels having a diam-

eter in the range of 1 to 100 nm (McNaught and Wilkin-

son 1997). Some of their principal properties are related
to their large surface area and stability. Their formulation

is similar to biological tissues, thanks to the water content

and carbon-based composition, ensuring high biocompat-

ibility and biodegradability (Cho et al. 2018). Nanogels, as

for nanoparticles, can be produced with different methods.
First of all, they can be prepared through chemical reaction

involving a heterogenous polymerization of low molecular

weight monomers or the crosslinking of polymeric precur-

sors (Chacko et al. 2012; Soni et al. 2016). A lot of different

therapeutic possibilities were exploited with different coat-
ings on polyethylene glycol–polyethyleneimine-based nano-
gels developed for spinal cord injury treatment (Mauri et al.

2017). Coatings were prepared using polyethylene glycol

monomethyl ether modifying its terminal hydroxyl groups

with a series of linkers, in order to evaluate the quantity of

polymer chemically bonded and its effect over microglia

internalization. The polyethylene glycol modification with

imidazole or carboxyl moieties proved to be successful. Fur-

thermore, it was shown that a high amount of polyethylene

glycol coating (obtained in carboxyl systems) reduced the

microglia internalization, while a smaller amount (obtained

in imidazole systems) guaranteed higher microglia uptake

compare to nanogels without coatings. In a more recent

work (Mauri et al. 2020), they developed a coating strategy

through primary amines, in order to reduce microglia inter-

nalization. Nanogels were designed following two differ-

ent routes: direct grafting of aliphatic primary amines and

linkage of the -NH₄ modified polyethylene glycol on the

nanogel surface.

A minimal uptake was obtained by combining amine with

nanogel PEGylation. Furthermore, nanogel–polyethylene

glycol–NH₄ satisfied all biocompatibility criteria and, even

if their dimensions were suitable for the microglia phagocytic

activity, they remain available in the extracellular environ-

ment. Photo-crosslinkable nanogel from a polymer template

with intrinsic photoluminescence and large photostability

for theranostic applications is other interesting possibility

(Gyawali et al. 2018). Nanogels were prepared from citric

acid, maleic acid, l-cysteine, and polyethylene glycol using

a solvent- and surfactant-free one-step reaction. To reach

the optimal potential in theranostic applications, a surface

functionalization with arginylglycylaspartic acid peptides

and a doxorubicin encapsulation were applied, resulting in

a pH-responsive drug release in acidic medium resembling

tumor microenvironment. Shifting to other materials, also

hydrogels are gaining relevant importance in biomedical

applications, such as drug delivery and tissue engineering

(Satapathy et al. 2015). Hydrogels are 3D structure made

up of hydrophilic polymers with high water affinity, whose

dissolution is prevented, thanks to the formation of physical

or chemical bonds. The polymers constituting such a matrix

can be chemically modified in order to introduce new features

in the final material, thus allowing the synthesis of hydrogels

for different applications, from controlled drug delivery to

selective targeting tools or diagnostics such as functionalized

polyvinyl alcohol hydrogels with fucoidan for improved

endothelialization and hemocompatibility (Yao et al. 2020).

Fucoidan is a sulfated polysaccharide with anticoagulant

and antithrombotic properties, the problem with such a modifica-

tion was that some mechanical properties were sacrificed.

The use of sodium trimetaphosphate, as a co-crosslinker,

avoided the mechanical losses. These materials were tested

in vivo, exhibiting promising results coupled with higher

patency rate and lower intimal hyperplasia formation. Func-

tionalization with biomolecules is also a good possibility:

in this direction polyamidoamine/thiolated hyaluronic acid

hydrogels were functionalized with human vascular endo-

thelial cadherin fusion protein using a Fc-binding polypeptide

attached to the alkene modified polyamidoamine dendrimer

(Gao et al. 2020). This functionalized hydrogel was improved

to enhance adhesion and proliferation of human umbilical
cord mesenchymal stem cells and facilitated the reconstruc-

tion of vascular-promoting extracellular microenvironment.
Such facilitation is provided through upregulating the expression of endogenous vascular endothelial cadherin and the secretion of human umbilical cord mesenchymal stem cells, including growth factors, extracellular matrix components and immune-modulating factors. Furthermore, human umbilical cord mesenchymal stem cells loaded within hydrogel effectively also promote host cell recruitment and the subsequent vascularization. Hyaluronan-based hydrogels were able to mimic healthy or malignant extracellular matrix, but, as physical gels, they lacked in mechanical properties (Bonneseur et al. 2020). Their functionalization with poly-L-lysine or extracellular matrix proteins (such as type III or type IV collagen) can guarantee stiffness tunability through crosslinking at gradual genipin concentration. The materials showed an increasing in stiffness with gradual genipin concentration and an efficient enzyme resistance with poly-L-lysine treatment. Such structures were able to support glioblastoma and breast cancer cells cultures and were able to enhance or reduce proliferation and viability. Functionalization is also a good strategy to improve drug delivery performances (Arellano-Sandoval et al. 2020). In this field, an agar xylan-type hemicellulose was conjugated with trimethoxysilylpropylmethacrylate crosslinked with N-vinylcaprolactam obtaining a thermo-responsive material. This hybrid hydrogel showed a high capability of controlling the release of antibiotic in time. Other key applications in biomedical field are represented by sensing applications: a polylvinylypyrrolidone hydrogel stabilized with ZnO quantum dots was developed as a sensing platform for hexavalent chromium (Truskewycz et al. 2020). The functionalization of this system with photoluminescent 2-amino-2-methyl-1-propanol and laminating (Sarif Ullah Patwary 2015). Here, in this

Textile applications

One of the most important functional areas of polymeric engineering is the textile industry, which at first was introduced for the aim of human clothing and then was extended with great progress so that it presents some exciting products in recent years. Choosing the best material for clothing in different environmental situations brings a lot of work during years and also introduces a large variety of products which all pursued the same goal, providing the most comfortable situation for a wide range of consumers (Jocić 2016). Different types of materials are used for producing yarn of textiles, which are categorized into two main groups: natural materials such as silk, hemp wool and cotton fibers and synthetic materials including nylon, polyester and rayon. Natural materials have widely been applied as solid-phase extraction absorbents for sample preparation due to their high adsorption capacity of hydrophobic materials. These are eco-friendly materials that exhibit specific features like high mechanical strength, good biocompatibility and desired stability in non-aqueous or aqueous solutions. However, the versatile applications of these materials are restricted due to their monotonous functional groups. Synthetic products also have disadvantages like more rapidly burning, low biodegradability, and skin damages (Katsnelson 2015). These features along with the market demands for introducing novel types of textiles for a specific application has lead to the emergence of novel technologies for engineering of the available materials; among them is the surface functionalization via different agents, especially polymeric nanomaterials to develop the existing properties and also create novel characters.

In other words, surface modifications could lead to the production of vintages with features like low weight, less damage, more comfortable and fewer health risks for conventional or particular usage (Abidin et al. 2018). Utilizing nanotechnology has great effects in the textile industry due to its cost-effectiveness and feasibility via integrating different types of nanomaterials with specific features with the ability to be used in diverse fields including sports, healthcare, military and fashion (Pakdel et al. 2020). Furthermore, nanotechnology has introduced the smart textiles via applying stimuli-responsive polymers with the ability to sense and respect to the environmental changes, which could provide a huge global market with about 26% annual growth rate (Pereira et al. 2020).

Based on the induced properties, the surface-functionalized texture via different agents leads to introduce different types of smart textile that could be classified into different categories, some of the most important of which are:

1. Antimicrobial textiles,
2. Self-cleaning textiles,
3. Cooling management and moisture-wicking textiles,
4. Flame-retardant textiles,
5. Self-healing textiles,

The surface functionalization process could be carried out either during the fabrication of textile fibers through spinning or at the final step on the fabrics via printing, coating and laminating (Sarif Ullah Patwary 2015). Here, in this
section, we will discuss some of these textiles in detail, which are prepared via polymeric functionalization.

**Antimicrobial textiles**

Clothing, as the material that has the most direct contact with the skin, should have some intrinsic specific features, among most important of them is antimicrobial property. Clothes are known as an external defense barrier against most of the microbial infections and chemicals present in the weather. Moreover, the antimicrobial fibers could be used for the production of the patients’ and healthcare workers’ clothing services, counterpane and blanket in hospitals to minimize the microbial contaminations (Bearman et al. 2017). Inducing antimicrobial feature to the textiles (or their fibers) by polymers could be achieved via two main mechanisms: (a) providing a physical barrier against the attachment of microbial species, including attachment of brush-like polymeric components, and (b) acting as a contact microbiocidal agent and destroying the cellular structure of infections. In the latter mechanism, the cationic and zwitterionic polymers

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**Fig. 5** a Synthesis of the antibacterial and antiadhesive cotton fabric, b the bacterially adhesive and antiadhesive mechanism of the pristine and treated fabrics, c antibacterial action of treated fabrics, d transmission electron microscopy image of antibacterial effect against *S. aureus* after 0, 12 and 24 h. Adapted with permission from (Lin et al. 2018). Copyright 2018 American Chemical Society
are commonly used, which could affect the microbial species through disturbing the negative charge of the cell membranes. Chitosan, polyethyleneimine, poly-l-lysine and polyvinylamine are some of the most practical examples of the contact mode (Elbourne et al. 2017; Morais et al. 2016). Using surface functionalization with antibacterial polymers has been shown to be advantageous over the type of antibacterial textiles, in which antibacterial nanoparticles like silver nanoparticles are incorporated in the fiber since in the former method, the antibacterial agents are as a part of fabrics’ structure with negligible leaching, their probable toxicity effects are reduced, and they show higher application efficiency during a longer time (Wang et al. 2020e; Timma et al. 2019).

For example, in 2017, Luo and colleagues synthesized antibacterial cotton fabrics via mist polymerization of 3-methylallyloxy-5,5-dimethylhydantoin on the cotton surface. 3-Methylallyloxy-5,5-dimethylhydantoin is composed of an antimicrobial derivative, N-halamine, with specific features like long-term stability, biocompatibility, and the antimicrobial effect against a wide range of microorganisms. This new type of antimicrobial textile showed more than 99.78% bacteriostatic reduction rate and performance efficiency of about 99% even after 30 washing cycles (Luo et al. 2017).

In another study, Lin et al. (2018) produced an antibacterial and antiadhesive fabric via spray coating the antibacterial polymer emulsions on the surface of cotton fabrics. The emulsion contained two antibacterial monomers: quaternary ammonium monomers and dodecafluoroheptyl methacrylate with fluorine group (Fig. 5a). This fabrication led to the development of a physical brush-like barrier on the surface of cotton fabrics that prevented bacterial attachment on the surface, while in naked fabrics the contaminants easily attached on to the surface (Fig. 5b). The antibacterial mechanism of this fabric, as shown in Fig. 5c, is based on the simultaneous presence of negatively charged fluorine and positively charged organic quaternary ammonium salts in the structure of this polymeric coating, which leads to the damage of cytoplasmic membrane. Figure 5d shows the transmission electron microscopy images of antibacterial effect of the fabric against Staphylococcus aureus (S. aureus) after 0, 12 and 24 h. As it is clear in the figure, in the first contact with the surface the live cells were attached due to the presence of electrostatic interactions. After 12 h, the passive diffusion of polymeric chain to the cell wall and
cytoplasmic membrane of bacteria led to a damage to cytoplasmic membrane which is accompanied by the leakage of cytoplasm that finally consequences to cell death after 24 h (Lin et al. 2018).

**Self-cleaning textiles**

The self-cleaning property for a textile is defined as the capability of the textile to remove different types of contaminants spontaneously without using any external wash. This property could be developed via utilizing superhydrophobic or photoactive agents on the surface of a material which is an attractive feature, especially for the textiles. The most important point which should be considered when using this type of coating is that the coating shouldn’t affect other properties of the textile, like its breathability, wearability, and mechanical properties. Thus, it is very important to control the amount of coating ingredients. The mechanism of superhydrophobic agents is architecting the surface via functionalized materials so that the spherical form of water droplets is preserved on the surface of the material and thus they could flow on the surface and remove any types of impurities. Different strategies could be used to induce this feature in textiles, like interaction by polymers with low surface energy, increasing the surface roughness and functionalization by nanomaterials (Ghasemlou et al. 2019; Lu et al. 2015). In this regard, Chen et al. 2019 fabricated a superhydrophobic cotton textile with self-cleaning and heat resistance abilities. They used two modification steps on the surface of cotton fabric (P-cotton in Fig. 6). The first step was applying 9, 10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (o-cotton), which counted as a flame-retardant component, while the second step was using two different polymeric structures: poly(methyl methacrylate glycidyl ester-co-dodecyl heptafluoroethyl methacrylate) or and silicon-containing compound octa(aminophenyl)silsesquioxane (S-cotton) (Fig. 6a) to reach the low surface energy. The final product showed superhydrophobic–lipophilic property so that different types of droplets on its surface showed spherical shape with contact angle more than 150 (characteristics of superhydrophobic materials) (Fig. 6b).

To confirm the self-cleaning property of the final cotton fabrics, they treated all types of cotton fabrics (P, D and S) with certain amounts of clay and then washed the clay with water (Fig. 6c). The result of this test revealed that only the S-cotton showed self-cleaning property which was originated from its superhydrophobic property (Fig. 6d). They also revealed that the simultaneous presence of phosphorus, fluorine and silicon in the structure of the final product had improved the thermal stability of cotton and donated the thermal retardant property to the fabric (Chen et al. 2019).

**Cooling management and moisture-wicking textiles**

Providing the thermal comfort is one of the most important features for clothing, especially in hot summer days, which could be provided by cooperation between personal cooling and textiles. In other words, designing a cooling garment is an affordable method for cooling management instead of using air conditioners with high energy consumption (Fu et al. 2019). These are breathable materials with air permeability property, which are designed based on three principles: (1) applying thermo-responsive polymers with the ability of sensing and reacting to the environmental temperature changes, (2) using materials and structures which can transfer the body thermal radiation and (3) incorporating materials with light reflection property (Baji et al. 2020).

Moisture is the other problem of a hot and humid environment and also during higher levels of activity, which could affect the comfortable feeling. Moisture evaporation into the environment could decrease the body temperature and also prevent wetting the clothes due to the sweating. Moisture evaporation from the textiles could be caused by the cooperation of two processes: wetting the fabrics and wicking the liquid flow through the fabric texture via capillary forces. The waterproof textile could be prepared via using hydrophobic polymers and functionalizing agents and also porous structures (Matusiak 2019; Li et al. 2016).

The cooling comfort, breathability and waterproof performance features mostly assemble with each other in a textile to fabricate the most desired cloth. Miao et al. (2018) produced a three-layer fibrous membrane composed of polyacrylonitrile–SiO₂ (PAN–SiO₂, in Fig. 7) as the outer layer, hydrolyzed polyurethane–polyacrylonitrile (PU–HPAN, in Fig. 7) as the transfer layer, and poly urethane as the inner layer with hydrophobic property (Fig. 7). In this trilayer
electrospun fabric, the transfer layer plays a key role in continuous water transfer. Moreover, the progressive spreading feature of the textile also increased the speed of water transferring that could preserve the textile dryness.

This special structure led to transport the water via textile only in one direction and so provided a comfortable dry microenvironment under the cloth (Miao et al. 2018).

In another work in 2019, Wang and his colleagues developed a smart Janus textile with the ability to react in response to thermal and moisture changes, in which two types of thermal responsive polymers were used: poly[2-(2-methoxyethoxy)ethoxyethyl methacrylate] and poly[\(N,N\)-dimethyl(methacryloylethyl)ammonium propane sulfonate] with lower critical solution temperature and upper critical solution temperature, respectively, and the same critical temperature (26–27 °C). For this purpose, cotton fabrics were first functionalized by 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone trimethoxysilylpropylmethacrylate to prepare DB-cotton. The final texture was prepared by a two-step spray coating method that led to produce a diode-like water transporter with thermal responsive feature (Fig. 8a, b). Their results showed that at low temperature (lower than 27 °C) the heat and moisture were preserved to maintain the warm (3.3 °C warmer than cotton fabric), while at high temperature the moisture was transformed across the fabric to decrease the microclimate temperature under the fabric (1.2–2.3 °C cooler than cotton fabric) (Fig. 8c) (Wang et al. 2020c).

Song et al. (2020) designed and fabricated a type of cooling management textile architectures which was working based on the thermal radiation property of body heat loss. This was a type of radiative cooling textile composed of three main layers: a polyethylene textile fabric which was coated by poly(vinylidene fluoride) and nylon 6 and had

Fig. 8  a Smart DB-Janus fabric preparation. b Mechanism of the polymerization and crosslinking reaction around a single cotton fiber. c Thermal responsive reaction of the smart DB-Janus fabric for thermal and moisture management. TMSPMA, 3-(trimethoxysilyl)propyl methacrylate; MEO2MA, 2-(2-methoxyethoxy) ethoxyethyl methacrylate; EGDMA, ethylene glycol dimethacrylate; DMAPS, \(N,N\)-dimethyl(methacryloylethyl) ammonium propane sulfonate. Reprinted with permission from John Wiley and Sons (Wang et al. 2020c), Copyright 2020.
the ability to decrease the temperature of skin about 6.5 °C in comparison to the bare skin. This novel texture worked based on the selection between absorbing/emitting thermal radiations and reflected the solar energy (more than 90%) due to its micro-nanostructure (Song et al. 2020).

Flame-retardant textiles

Flame-retardant textiles could be used in particular for firefighters’ clothing and for protecting against uncontrollable fires. Using flame retardants (for textiles and buildings) has increased annually during the last years, while most of them show adverse effects on the environment and humans (Yasin et al. 2018). Thus, it is necessary to discover new types of eco-friendly flame retardants or new methods for preparing flame-retardant textiles. In this regard, some natural extracts such as banana pseudostem sap, coconut shell, and spinach leaves juice, and also some proteins such as casein and whey protein are among natural flame retardants that have recently been used (Yang et al. 2018b).

Another approach for producing these types of textiles is using polymeric and nanocomposite agents with natural flame-retardant properties in the textiles structure. For example, Zhang et al. fabricated an eco-friendly flame-retardant cotton fabric via surface coating of cotton by ammonium salt of melamine hexa(methylphosphonic acid). The final product showed a high limiting oxygen index (about 43%) which was maintain to about 33.4% after 50 laundering cycles that confirmed its high flame-retardant stability. Moreover, the toxicity results of this fabric revealed no toxicity against humans and the environment (Zhang et al. 2018).

Mourgas et al. (2019) produced a type of improved flame-retardant polyamide 6 via co-condensation of two types of organophosphorus compounds on the surface of polyamide via ε-caprolactam. The knitted fabric of this new type of polyamide showed high thermal stability, excellent flame retardancy and high limiting oxygen index values of about 35%. The presence of phosphorus groups in the structure of this textile was the main reason of its flame-retardant ability. Moreover, it was shown that the presence of the organophosphorus compounds in the structure of polyamide had no negative effect on its other features (Mourgas et al. 2019).

Self-healing textiles

Self-healing textiles are a class of smart textiles with autonomous repairing ability and are known as one of the most attractive subcategories of the textile industry. This property could prolong the lifetime of the products and could be created by different coating agents like micro/nanocapsules and polymeric coatings. Shelf-healing textiles are also classified as a type of responsive materials, which are activated due to the intrinsic or extrinsic triggers (Bekas et al. 2016; Gaddes et al. 2016).

In a research conducted by Xue et al., a self-healing superhydrophobic fabric was synthesized by coating the poly(ethylene terephthalate) fabrics by polydimethylsiloxane and octadecylamine via dip coating process (Fig. 9). This hydrophobic textile showed high permanence to washing (even after 120 cycles of washing) and different pH solutions. It could also heal its hydrophobicity after 12 h at room temperature, while increasing the temperature could reduce the healing time (Xue et al. 2016).

Water treatment

The industrial activities in the last decades drastically increased the amount and versatility of contaminant pollution in the aquatic environment leading to severe damage to the environment (Srivastava et al. 2020; Zare et al. 2018a).

Most of the contaminants adding up to wastewater are toxic and on the accumulation in living organisms possess
a risk to them (Ambat et al. 2020; Ben Hamida et al. 2018; Bessaies et al. 2020; Iftekhar et al. 2020a, b; Wang et al. 2019) For the depletion of these contaminants including heavy metal ions, dyes, organic contaminants, etc., a variety of methods have been employed along with various types of materials spanning from natural to synthetic, waste to hybrids and renewable to engineered (Hosseini et al. 2019; Zare et al. 2018b; Asif et al. 2016; Gao et al. 2017; Iftekhar et al. 2017a, 2018b). In recent decades, the paradigm has shifted toward the application of nanomaterials from bulk, causing the huge progressions of nanotechnology in creating novel nanomaterials for many industrial and environmental applications. The attention toward nanotechnology has been diverted due to the associated physiochemical characteristics which the bulky phase could not hold making their way to be used in many areas of science especially in water treatment (Chenab et al. 2020; Iftekhar et al. 2017b, c, 2018c, d, 2020a). Over time researchers divined that compared to bare nanomaterials, functionalization with the polymers allowed the adaptation for specific pollutants both with efficiency and selectivity owing to the presence of specific functional groups. The selection of polymers for the functionalization required the knowledge of removal pathways involved between the functional groups and pollutants. Moreover, besides the chemical nature of the functional groups, other parameters also play a vital role toward the selectivity of polymer-functionalized materials, viz. the physical state, and physical features (beads, gels, fibers, membranes, etc.) need to be considered for targeted water treatment method (Rivas et al. 2018). The fabrication and testing of polymer-functionalized materials have been expanded over the decades, and the common moieties used for functionalization include N-donors (amides, amines) and O-donors (ethers, alcohols) both of which proved to be of great interest. The removal/reaction pathway mainly depends on the functional groups carried by the polymeric materials as well as the effluent acidity. For instance, the removal of metal cations occurred by the anionic functional moieties via ion exchange, whereby complexation interactions were likely due to uncharged functional moieties. The removal mechanism and the selectivity of polymeric materials could be controlled easily by adjusting the pH of effluent solution (Beaugeard et al. 2020; Rivas et al. 2018; Gao et al. 2018). In this section, firstly the influence of the physical state of polymeric materials and properties of functional moieties toward the implementation in a water treatment process will be discussed. Then, considering particular selectivity of polymer-functionalized materials bearing various functional groups, i.e., hydroxyl, carboxylic, amines, phosphonic and sulfonic, toward targeted pollutant will be given a special attention. **Selection of polymeric materials for targeted application**

As mentioned above, the overall performance of the polymer-functionalized materials depends on two important things that must be taken under consideration- (a) the physical state of the material in water and the chemical nature of the functional moieties bore by the polymer. Due to the versatility of polymerization methods, a wide range of materials have been synthesized. Based on their chemical structure, such materials are either soluble or insoluble in water (Fig. 10). The removal of pollutant by water-soluble polymers is widely used through liquid-phase polymer-based retention, which when merged with ultrafiltration, leading to the establishment of the polymer-enhanced ultrafiltration process employing functionalized membranes. The other process is a solid-phase extraction which includes fixed-bed ion exchange column processes, for the removal was employed via insoluble polymeric materials (Gao et al. 2017, 2018; Graillot et al. 2015; Srivastava et al. 2018). The hydrophilicity of polymeric materials facilitated a direct interaction of the functional groups with the pollutant in the polymer, enhancing the efficiency of ultrafiltration process, but the removal of the polymer–pollutant complex is a difficult and expensive process. The difficulty in separation of material limits its implementation at an industrial level due to the involvement of ultrafiltration steps that required relatively high pressure and thus could lead to high operating costs.

**Fig. 10** Different polymer-based materials for the removal of pollutants from water. Reprinted with permission from Rivas et al. (2018)
and significant membrane fouling (Fenyvesi et al. 2020). On the contrary, the removal of materials is easy in solid-phase extraction process, where the slow kinetics and low removal rate of such materials were led by the insoluble material. The problem can be overcome by using hydrosoluble polymeric materials. Additionally, the adaptability of material’s physical state enabled their application in elution processes via membranes (Ajji and Ali 2010; Asif et al. 2016; Habib et al. 2017), fixed beds or packed columns (Dakova et al. 2009). Deducing that the selection of non-soluble polymer-functionalized materials was appropriate when the two processes, i.e., pollutant removal and material separation, are combined in one step. In contrast, hydrosoluble polymeric sorbents are suitable when fast kinetics is essential but the addition step is needed to achieve separation of material.

Pertaining to the functional moieties carried by the polymer, their chemical nature could significantly affect the selectivity. A large number of materials functionalized with different groups are reported in the literature and the common functional moieties were alcohols, crown ethers, amines, amides, carboxylic, phosphonic and sulfonic acids, allowing the removal of pollutant through functionalized materials through sorption which mainly took place by either ion exchange or complexation. Both types of interactions for carboxylic, amines, phosphonic and sulfonic groups were reported in the literature (Iftekhar et al. 2018a) as shown in Fig. 11. The predominant mechanism is ion exchange when the polymeric material bears charged functional groups (polyelectrolytes), while such interactions are generally reversible and weak. On the other hand, for the polymeric material carrying uncharged functional groups, the prevalent mechanism is more likely complexation leading to the formation of coordination bonds between the pollutant and functional groups, which are stronger than electrostatic ones but are still reversible. Another aspect that needs to be considered prior to selection of polymer for functionalization is the pollutant which ought to be trapped from effluent. The functional groups mainly consist of electron donor atoms like oxygen, nitrogen, phosphorous and sulfur (Beaugeard et al. 2020). Some of the examples of O-donor and N-donor used for the decontamination of pollutants from water are listed in Table 1.

**Fig. 11** Representation of dominant mechanisms on various functional groups
acid, which contains only one carboxylic group per monomer unit. After the expansion in the use of new polymeric materials, a variety of simple or complex polymers were used for functionalization such as maleic acid-based polymers leading to high selectivity toward pollutants as the polymerization of its monomer is easy with other comonomers, viz. salicylic acid, styrene, etc. Some of the carboxylic acid bearing polymers used for the modification of materials and removal of pollutants from water are listed in Table 1. Depending on the application, the nanomaterials functionalized with carboxylic acid polymers are synthesized in different physical states. The water-insoluble forms are mostly used in the form of resins, beads, gels, membranes, fibers. The possibility of adding a variety of ligand groups helps beads and resins to gain attention (Beaugeard et al. 2020). Kobylinska et al. prepared

| Table 1 | Polymers materials bearing O- and N-donor functional moieties for the removal of various pollutants |
|-------------------------------|---------------------------------------------|-----------------|-----------------|-----------------|
| Functional moiety | pKₐ | Physical state | Targeted pollutant | References |
| Polyvinyl alcohol | > 14 | Beads, nanofiber, membrane, nanocomposite | Cd, Cr, Cu, Pb, Zn, Mo | Al-Hwaii et al. (2019), Isawi (2020), Lee (2019) and Vatanpour et al. (2020) |
| Poly (itaconic acid) | 4.5 | Water-soluble polymer | Pb, Cu, Cd, Sn, Zn | Rezania et al. (2019) |
| Polyethylene glycol (PEG) | – | Hydrosoluble membrane | Zn, Pb, Cr | Baharuddin et al. (2019) |
| Amines | 10–11 | Membrane, fiber, hydrosoluble polymer, nanocomposite bead, insoluble resin | Cu, Co, Sr, Tetracycline, | Fakhri et al. (2019), Sum et al. (2019), Wamba et al. (2018) and Wang et al. (2020b) |
| 1. 3-(Aminopropyl)triethoxysilane | | | | |
| 2. N-[3-(trimethoxysilyl)propyl] 1H-imidazole | | | | |
| 3. 1-(3-triethoxysilylpropyl) diethylenetriamine | | | | |
| 4. Bis[3-(trimethoxysilyl) propy]ethylene diamine | | | | |
| 5. N-[3(trimethoxysilyl)] propyl]ethylenediamine | | | | |
| 6. 2-Aminoethyl-3-aminopropyl-trimethoxysilane | | | | |
| 7. 3-(Cyanopropyl)triethoxysilane | | | | |
| 8. Bis[3-(triethoxysilyl) propyl]amine | | | | |
| Polyethyleneimine (PEI) | 10–11 | Nanocomposite resin, beads, membrane | Pb, Cd, Hg, Se, Ar, Se, Cr, As, La, Yb, MB, RhB | Arshad et al. (2019), Guo et al. (2019) and Wilfong et al. (2020) |
| EDTA | 2–2.7, 6.7–10.2 | Membrane, nanocomposite, beads | Acid red 88, Malchite green, Reactive blue 2, acid yellow 76, acid blue 25, indigo, Hg, Eu, Cu, Cr | Luo et al. (2020), Ranjeh et al. (2020), Rončević et al. (2019) and Xia et al. (2019) |
| Acrylic acid | 4.5 | Membrane, hydrogel, resin, nanocomposite, beads | Hg, Pb, Cd, Zn, Cu, Ni, 4 nitrophenol, Cr, Co, Sn | Ansari et al. (2019), Kochameshki et al. (2019), Sarma et al. (2019) and Tang and Qiu (2019) |
| Polyphenylsulfone | | | | |
| 2-Ethylhexyl phosphonic acid | – | Nanofiber, membranes, resins | Zn, Ni, Eu, Nd, La, Pb, Cr, Cd, phenol, MB | Nayak et al. (2019) and Sarma et al. (2019) |
| Imidazole sulfonic acid | | Membrane, resin, hydrogel | MB, CR, RhB, MO, Cu, SO₄²⁻, Pb, NO₃⁻ | Ran et al. (2019), Tirtom and Dinçer, (2020) and Zhang et al. (2019) |
core–shell superparamagnetic nanoparticles immobilized with ethylenediaminetetraacetic acid derivatives which increased the chemical stability of nanoparticles in acidic media and enhanced the affinity for the removal of Pb, Cu, Zn, Cd (Kobylinska et al. 2020). Ethylenediaminetetraacetic acid was also used for the functionalization of graphene oxide by a realizable silanization chemical reaction for Hg removal from desulphurization wastewater treatment (Sun et al. 2020). The materials did not show an exemplary removal of Hg in case of multilayer graphene oxide as the active sites including carboxylic groups and hydroxyl groups were not accessible by Hg ions. Carboxylic immobilized ferroferric oxide was inserted in membranes exhibited excellent hydrophilicity with high water flux have a potential for the simultaneous removal of Pb, Cd and Cr (Mishra et al. 2020). Muller et al. (2019) used ethylenediaminetetraacetic acid as complexing agent to functionalize polyvinyl alcohol hybrid with alumina to form an efficient complex for the scavenging of metallic cations (Fig. 12). To promote adhesion with alumina and ethylenediaminetetraacetic acid, a well-defined homopolymer holding either alkyne or azide was functionalized through chemical modification by phosphoric acid (Muller et al. 2019).

However, in comparison to amines, carboxylic acid groups have low selectivity still providing significant removal of some pollutants, particularly metal ions. Further, they offer excellent removability under neutral and basic pH conditions the performance under acidic conditions is also rather good. For polymeric materials carrying carboxylic groups generally, the possible two mechanisms found could be hinge on the solution pH and pKa value of acid/base couple. The carboxylic functions will not dissociate in case the solution pH is less than pKa and electrostatic interaction will take place between the pollutant and oxygen atom of carboxylic groups preceding to the formation of coordination bonds which agrees to the polychelatogen behavior through complexation process.

In the other case, the interaction corresponds to electrostatic exchanges between the negative charge of the carboxylate groups and the positively charge pollutant being consistent with the polyelectrolyte behavior dominated by ion exchange (Fig. 13). The removal feature of this group also depends on the nature of pollutant (Beaugeard et al. 2020).

Polymeric materials bearing amine moieties

One of the most widely used functional groups for the immobilization purpose is amine groups. A large number of polymers bearing amine groups have been reported in the literature such as 1,3-phenylenediamine (Darabi et al. 2019), triethylenetetramine (Darabi et al. 2019),
aminopropyltriethoxysilane (Ramasamy et al. 2018, 2019), poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), 2-amino pyrimidine (Sadjadi et al. 2019), etc. Along with many others, the functionalization of nanomaterials with amino/silanes is very common. The modification is mostly conducted by grafting process between nanomaterials or membranes and alkoxyaminosilanes where the OH group of nanomaterials react with the alkoxy group of polymers. The crosslinking is also possible by the formation of covalent bond with the hydrogen atoms on the surface of NPs. The commonly used precursors of amine functional groups are listed in Table 1. The functionalization success rate depends on many factors like the temperature, contact time, precursor concentration and the nature of the solvent. Amine-functionalized silicate material was used for the removal of Cr which is governed by electrostatic interaction (Fellenz et al. 2017). Lou et al. reported synthesis of magnetic bentonite functionalize with aminopropyltriethoxysilane for the removal of methylene blue and in 120 min the maximum adsorption capacity was 91.83 mg/g (Lou et al. 2017).

The amino-functionalized materials are reported to be favorable for the removal of anionic species as well as cationic in comparison to carboxylic, phosphonic and sulfonic groups which are least stable for extraction of anionic pollutants. For this purpose, the most commonly used amines are polymers with quaternary and ternary amines and such functionalized materials generally behaved as anion exchange materials (Fig. 13) with ion exchange as a dominant mechanism (Vogel and Meier-Haack 2014). To understand this, Bui et al. (2011) employed aminopropyl-functionalized silica for the removal or 14 different pharmaceuticals (Atenolol, Acetaminophen, Clofibric, Carbamazepine acid, Estrone, Diclofenac, Gemfibrozil, Gemfibrozil, Ibuprofen, Oxaprozin, Iopromide, Sulfamethoxazole, Ketoprofen, Tri-methoprim). The material showed reduced adsorption for the two compounds containing amine groups and estrone while increased adsorption for acidic pharmaceuticals, viz. diclofenac and clofibric acid. The possibility of hindered adsorption of estrone was pointed out as being extremely hydrophobic, while the surface amino groups are hydrophilic. On the other hand, the neutral and cationic forms of amino functional groups exist at pH 5.5 leading to an increase in surface charge, letting the adsorption of anionic compounds on the surface via electrostatic interaction. Meanwhile, the adsorption of cationic compounds decreased due to higher surface charge owing to higher electrostatic repulsion (Bui et al. 2011). The amino groups would also show interaction with the silanol groups through electrostatic interaction or hydrogen bonding and block the availability of surface silanol groups. This approach impairs the removal of cationic pollutants, whereas it is beneficial for the anionic contaminants (Iftekhar et al. 2018b, 2020a).

Polymeric materials bearing phosphonic moieties

Phosphonic groups (R-PO₃H₂) with two dissociation constants (i.e., pkₐ₁ = 2–3 and pKₐ₂ = 6–7) are referred to as
diacids. Compared to other functional groups, the removal capacity of phosphonic acid moieties is fascinating at low pH. At pH ≥ 2, phosphonic groups dissociate facilitating the electrostatic interaction as the competition between the H⁺ and pollutant is comparatively low due to the negative charge carried by the materials bearing phosphonic functional units (Alexandratos and Hussain 1998; Ferrah et al. 2011). The hydrophilic character of polymeric material increased due to a negative charge facilitating faster kinetics. Meanwhile, the scenario is completely different for pH between 2–7 and above 7. When the pH lies between pKₐ₁ and pKₐ₂, phosphonic moieties behaved both as polychelatogen and polyelectrolyte (Fig. 14) due to the dissociation of only one hydroxyl group. Above pH 7, two acid moieties dissociate due to electrostatic forces. Being hard acids, phosphonic groups showed a better affinity toward hard cations compared to soft cations (Beaugeard et al. 2020; Tokuyama et al. 2011). Artiushenko et al. (2020) tested aminodi(methylenephosphonic) acid covalently immobilized on silica for the preconcentration of rare earth’s elements from polluted water. However, the extraction of rare earth’s elements from the material required the application of strong acids. The adsorption of trivalent ions on phosphonic acid immobilized nanomaterials was higher than that of divalent ions. This provides materials modified with phosphonic acid groups high selectivity feature to scavenge the pollutants particularly at low pH (Tokuyama et al. 2011). Generally, in case of carboxylic and amines, the polymers are available commercially and employed as chelating agents, conversely, phosphonic derivatives had to be exclusively manufactured to produce more complex structures. A hydrosoluble polymer containing phosphoric groups was used for selective recovery of Gd from a mixture of Gd/Ni and the dominant mechanism was found to be ion exchange and solvation (Rodrigues et al. 2019). Further to achieve more selective recovery and removal of pollutants, different ligand groups were combined. Page et al. (Reaves 2004; Page et al. 2017) studied the combined effect of different ligand groups with phosphonic groups, viz. sulfonic/phosphonic, aminophosphonic or iminodiacetic for selective recovery of La, Sm and HO from common impurities of Fe, Th and Al. Likewise, compared to common resin, the bifunctional chelating resin bearing phosphonic and sulfonic groups showed better removal of fluoride (Li et al. 2020). Among all examples, bifunctional polymer-supported aminophosphonic acid (Zidan et al. 2020), carboxylic–amine–phosphonic acid (Wang et al. 2020a), diphasphonic (Fila et al. 2019), polyamine in the presence of HDPE (Zhao et al. 2019a) proved to be of interest for the removal of metal cations.

**Polymers bearing sulfonic moieties**

Sulfonic acids (R-SO₃H) own the electro-attractor character of the sulfur atom which caused the negative pKa value (−2) often termed as hard monoacids. Regardless of solution pH, this acid group always dissociate in aqueous medium following the ion exchange mechanism. The polymeric materials carrying this group behave only as polyelectrolytes and interaction with pollutants is electrostatic (Gao et al. 2017). Different types of materials are functionalized with sulfonic acid groups either to alter the hydrophilic/hydrophobic property of materials or the acidity, being highly acidic permitted the high removal of pollutants. One of the most commonly reported physical forms of polymeric nanomaterials bearing this group is resins. Bayramoglu et al. (2020) prepared a sulfonic acid-functionalized terpolymer resin as a cation exchange resin for the depletion of disperse dyes, i.e., Disperse Violet 28 and Direct Red R. The ion exchange and the strong electrostatic interaction between amine groups of dyes and sulfonic groups of the resin contributed toward the high adsorption of dyes onto the resin (Fig. 15). Other forms of materials bearing sulfonic groups studied include gels.
Haleem et al. (2020) reported the poly(n-isopropylacrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) hybrid gel embedding Ag and Pd nanoparticles, used as a catalyst for degradation of P-nitrophenol and Rhodamine-B. Hydrosoluble polymers bearing sulfonic acid groups were not investigated frequently. A water-soluble polymer immobilized by sulfonic groups was prepared by Zhou et al. (2019) and used for the removal of cationic (methylene blue, neutral red, Rhodamine-B) and anion (Orange G, acid fuchsin, methyl orange) dyes. The functionalized material is highly selective for cationic dyes. Zhao et al. (2019b) fabricated the functionalized composite membrane with an environmentally friendly fabrication process that demonstrated high durability with low operating pressure for the removal of metal ions and disperse dyes. Because of their peculiar structure, the properties of materials carrying sulfonic groups are easy to tune compared to other ligands. Due to the low pKa (below zero) values, sulfonic groups allowed the adsorption process possible under acidic pH range. Page et al. (2017) concluded that compared to phosphonic groups the adsorption is superior with a factor of 1.5 with sulfonic groups. The sorption kinetics was also reported to be good for sulfonic-functionalized material like that of carboxylic groups. The overall removability of the sulfonic group is significant under acidic range, but the selectivity was low compared to phosphonic groups (Page et al. 2017).

Food packaging

Due to the advantages of polymer nanoparticles over traditional materials, their application in food packaging has increased enormously. The polymer-functionalized materials are mainly developed to enhance the barrier properties to UV rays and gasses along with adding heat resistance, stability, strength and stiffness. This is one of the possible justifications why the world’s largest food companies are investing in this area of research to obtain the packaging materials with improves antimicrobial, mechanical and barrier properties (Silvestre et al. 2011; Hoseinnejad et al. 2018). In this context, the application of PNPs will be subcategorized as improved, active and intelligent polymer nanoparticles packaging materials will be discussed.

Improved polymer nanoparticles packaging

The addition of polymer nanoparticles in polymer matrix rallies the packaging properties mentioned above and thus
led to the development of many polymer nanoparticles packaging materials. Among these, the first reported materials found in the literature, which emerged in the market as better materials, were the clay nanoparticles incorporated in the polymer matrix. The homogenous dispersion of clay nanoparticles is a need in a polymer matrix to enhance its properties depending on enthalpic and entropic factors to determine the morphological arrangement (Rhim et al. 2013; Silvestre et al. 2011). This uniform dispersion is only achievable when polymer–clay interactions are constructive that necessitates adequately promising enthalpic factors, which in case of polar solvents is possible by utilizing alkyl-ammonium surfactants (Bumbudsanpharoke and Ko 2019). Generally, the materials can be prepared by melt processing or (in situ) polymerization. To prepare polymeric clay materials, various polymers and clay fillers were used. Among these, the most widely used polymers are polyethylene terephthalate, nylon, polystyrene, polyolefins, polylactide, polyamide, polyimides, epoxy resins polyurethane and ethylene–vinyl alcohol.
Carbon nanotubes on combining with polymers could not only enhance the features of the polymer matrix but also improve the antimicrobial property. Liu et al. (2019) fabricated the polylactic acid/carbon nanotubes/chitosan fibers through electrospinning, which demonstrated antimicrobial activity against Staphylococcus aureus than against E. coli. The experiments further exhibited that 7% contents of core–shell improved the shelf life of strawberries for several days. To the best of the authors knowledge, we are unable to find the studies related to a combination of single-wall carbon nanotubes with polymer matrix as a food packaging material. Additionally, the applications at the industrial scale stopped due to many studies suggesting that carbon nanotubes are cytotoxic for humans (Silvestre et al. 2011; Zubair and Ullah 2020).

**Intelligent polymer nanoparticles packaging**

The purpose of “Intelligent polymer nanoparticles packaging” is to examine the packaged food condition or environment the food is surrounded by. The latest advancements for intelligent polymer nanoparticles include pathogen sensors, freshness indicators and oxygen indicators. During food storage, microorganism growth is facilitated by oxygen, which boosted the interest to develop irreversible and non-toxic oxygen sensors to ensure absence of oxygen in the packaging system while packing under nitrogen and vacuum (Dobrucka 2019; Silvestre et al. 2011). To photosensitize the methylene blue via triethanolamine, TiO$_2$ nanoparticles were encapsulated in a polymer matrix using UVA light by Lee et al.
and noticed that rate of color recovery was proportionate to the oxygen level exposure (Lee et al. 2002). Likewise, SnO₂ was used as a photosensitizer for oxygen indication where the film color fluctuates subject to the oxygen exposure (Mills and Hazafy 2009). Based on the gas emissions of microorganisms, different types of gas sensors developed which could be used for identification and quantification (Dobrucka 2019; Silvestre et al. 2011). Polymer nanoparticles sensors, owing to high stability and sensitivity, are the most prevalent forms of sensors. Sensors developed using conducting nanoparticles entrenched in a polymer matrix to identify and detect microorganism specific responses are under investigation (Liu et al. 2007). From the pattern of response produced by such sensors, three forms of bacteria were identified, namely *Vibrio parahemolyticus*, *Salmonella* spp. and *Bacillus cereus*. Other innovations in this area of research are at an early stage consisting of devices that will detect the release of preservatives as soon as the food starts to spoil and thus offer a base for intelligent preservative-packing technology.

**Other industrial applications**

Polymer-functionalized nanomaterials belong to the polymer nanotechnology spectrum that is wide implemented in an interdisciplinary field. This section provides an overview of the application of polymer-functionalized materials in sensor, energy storage sector and catalysis.

**Sensors**

The sensing characteristics of polymer nanoparticles depend on the chemical and structural alterations because of the polymer and nanoparticles interaction with the environment affording a subsequent output usually as an optical or electrical signal (Zare et al. 2014; Ahmad et al. 2019; Belbruno 2019; Boyaciyan and von Klitzing 2019). Subramanian et al. (2018) detected the vapors of toluene and benzene at room temperature with polyaniline metal oxide composite (TiO₂/SnO₂). The interaction of sensor material and vapors of analyte occurs by surface adsorption. Metals exhibiting surface plasmon resonance are typically used for optical sensors (Boyaciyan and von Klitzing 2019). By utilizing the chitosan and polymer film of Ag metal, Verma and Gupta (2015) spotted the presence of heavy metals optically in polluted water. The Ag films coated with polymer and chitosan are capable of binding metal ions of their surface and this binding changes the dielectric features of the sensing surface. The shift in surface plasmon response can be detected by using a UV/Vis spectrometer and the possibility of detecting the very low concentration of metal ions, i.e., 1 ppb increases. Boyaciyan et al. (2018) prepared a sensor device by embedding the Au nanoparticles in the polyelectrolyte matrix. The former being pH-sensitive on an addition to the insensitive matrix, i.e., polyelectrolyte matrix, made it sensitive to pH alterations and thus helping them in detecting the pH changes in the surrounding environment. The interaction of Au nanoparticles with polyelectrolyte matrix altered with changing pH and in turn altered the surface plasmonic characteristics detected through UV/Vis spectrometer (Boyaciyan et al. 2018). In another study, a voltammetric sensor developed using 3-thiophene acetic acid coating Au nanoparticles forming a conductive 3D network film (Fig. 17) resulting polymerization was used for adenine. This procedure developed sensor exhibited improved sensitivity and selectivity for adenine determination with limits of detection of 0.99 nM (Wang et al. 2018).

Recently, the combination of carbon nanotubes with polymer is found to be capable of interacting with targeted molecules and thus aided in the augmentation of the intensity of electrochemical signals, creating sensors that are both selective and sensitive. The frequently used polymer used for the surface modification of carbon nanotubes as a monomer is pyrrole due to its conductive properties and is ideal for biological and pharmaceutical analyses from acidic to neutral region. Other polymer of interest is orthophenylenediamine which is fairly akin to pyrrole (Beluomini et al. 2019). The polymer was used for the functionalization of single-wall carbon nanotubes and used for the detection of brucine with limits of detection of 0.21 μmol/L (Liu et al. 2012).

**Energy storage**

The creation of renewable and sustainable sources for storage like wind and solar energy divisions is needed on urgent basis because of the escalating energy crisis instigated by the diminution of traditional fossil fuels. As renewable energy resources are sporadic, effective

**Fig. 18** Synthesis of corn-like SnO₂ coated PDA nanoparticles used as anodes for Li-ion batteries. HPC-g-PAA: hydroxypropylcellulose-g-polyacrylic acid; PDA: polydopamine
energy storage techniques are needed to generate and store renewable energy quickly and steadily. This led to the growing research interest in Electrochemical Energy Storage Systems with cells, batteries and capacitors being among various storage systems that have been crucial (Fard et al. 2017a, b; Boyaciyan and von Klitzing 2019). In this area, the appropriate application of polymer nanoparticles is lithium-ion batteries which is based on four main components consisting of anode, cathode, separator and electrolyte. Presently, porous polyolefin-based polymers, viz. polypropylene and polyethylene, were used in separators that restrict the electrolyte diffusion because of hydrophobic surface (Wang et al. 2020d; Song et al. 2012). Polydopamine-based separator coated with polyethylene which improved the electrolyte diffusion and the discharge capacity of the battery stayed 84.1%. In lithium ions batteries, the positive and negative electrode, i.e., cathode and anode, play an important role in determining the electrochemical performance. A template method for the growth of the SnO2 nanoparticles coated polydopamine by tapping a bottlebrush like cellulose-g-acrylic acid (Fig. 18). It was stated that coated polymer nanoparticles performed better than uncoated and exhibited long cycling stability up to 300 cycles (Liu et al. 2017).

Dye-sensitized solar cell is another type used for energy storage based on photosensitizing dye having light adsorption behavior coated on semiconductor like TiO2. The harvesting of solar cell energy enhancement is possible through polydopamine which owns wide band absorption feature (Wang et al. 2020d). Nam et al. (2012) prepared polymer nanoparticles dye-sensitized solar cell via polymerization of dopamine under N2 atmosphere in tris(hydroxymethyl)aminomethane solution; the resulting mixture was used for coating of TiO2 electrode as a dye. It was also reported that the coating method significantly affects the photovoltaic parameters. The polydopamine–TiO2–DC acquired by dip coating technique offered greater efficiency than the polydopamine–TiO2–CV samples obtained through capacitance–voltage method (Nam et al. 2012). The ultrafast high energy density, long-term stability and charge–discharge behavior are unique features of supercapacitors, which has fascinated considerable attention recently. Normally, carbon and metal materials are materials used in supercapacitors; however, polymer nanoparticles are also used widely (Wang et al. 2020d). Madhu et al. (2015) prepared electrode made of mixed oxide (Ni–Co) coated with polydopamine and observed that the coated material resulted in an increase of surface area from 36 to 59 m2/g compared to bare NiCo2O4 samples, yielding a quick ion diffusion in electrolyte (Veeramani et al. 2016).

### Catalysis

The broad array of diverse polymer nanoparticle-type nanoreactors are made with catalytic activity. For example, chemically attracted metal nanoparticles to polymer chains, homogenous distribution of functionalized nanoparticles in microgel assembly, polymeric membrane surfaces, or polymer-functionalized metallic thin films (Boyaciyan and von Klitzing 2019). Functionalized polymer brushes for hydrogen evolution were prepared by Stern et al. (2018). The highly oriented planar pyrolytic graphite was used for the growth of cationic polyelectrolyte brushes, which catalyze hydrogen production from water by binding molybdenum sulfide of cationic polyelectrolyte. To become mobile the growth of polyelectrolyte brushes on spherical surfaces (Lu and Ballauff 2016), Gill et al. (2009) fabricated polymer brush catalysts based on MNPs functionalized by piperazone and employed for the Knoevenagel condensation. After the reaction, the brushes can be pulled out selectively anywhere due to the presence of MNPs (Yan et al. 2019). 4-Nitrophenol was successfully reduced by thermosensitive functionalized nanoreactors which are capable of adjusting the catalytic activity, switching on and off concerning temperature (Jia et al. 2016).

### Conclusion

Despite the great progresses in the last years and the high success of polymer functionalization in different fields, several challenges still remain. First of all, a better understanding of the biological mechanisms behind cell–polymer interactions could guarantee a better design. Indeed, many of the pathways involved in cell uptake, toxicity, etc., are still under investigation and a common theory is far to be established. In parallel, also safety concerns should be taken into particular consideration: nanotoxicity indeed aims to study the potential negative chronic impact of nano-objects in humans. In the last decades, clinical studies underlined that potentially they can contribute to damage, inflammation and undesired entrance through biological barriers. The factors behind possible toxic effects should be investigated to ameliorate their use considering that nano-objects can come in contact with genetic material through inhalation, skin absorption or ingestion. Toxicity is a big issue that should be considered not only in the final application but also during the entire manufacturing and then disposal. The large-scale production represents an other big challenge due to the fact that it is well known that small volumes (laboratory scale) favor the surface respect to the bulk, while increasing the scale the opposite. A big technological progress should be
done to allow reliable synthesis, functionalization and storage of these devices. Moreover, financial and economic barriers represent a high impediment in their final use due to the high cost behind all the points addressed above. In summary, we can state that polymers and nano-objects represent a milestone for many applications, from medicine to catalysis. However, the easy combination of polymers cannot satisfy all the properties needed and so surface functionalization represents a winning strategy that consent to introduce ideal properties different from the ones of the native polymers: the functionalization approaches appear as the basic line for the amelioration of the performances of these devices.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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