

# Layer-by-Layer Assembly of Light-Responsive Polymeric Multilayer Systems

João Borges,\* Luísa C. Rodrigues, Rui L. Reis, and João F. Mano\*

Layer-by-Layer (LbL) assembly is a simple and highly versatile method to modify surfaces and fabricate robust and highly-ordered nanostructured coatings over almost any type of substrate. Such versatility enables the incorporation of a plethora of building blocks, including materials exhibiting switchable properties, in a single device through a multitude of complementary inter-molecular interactions. Switchable materials may undergo reversible physicochemical changes in response to a variety of external triggers. Although most of the works in the literature have been focusing on stimuli-responsive materials that are sensitive to common triggers such as pH, ionic strength, or temperature, much less has been discussed on LbL systems which are sensitive to non-invasive and easily controlled light stimulus, despite its unique potential. This review provides a deep overview of the recent progresses achieved in the design and fabrication of light-responsive LbL polymeric multilayer systems, their potential future challenges and opportunities, and possible applications. Many examples are given on light-responsive polymeric multilayer assemblies built from metal nanoparticles, functional dyes, and metal oxides. Such stimuli-responsive functional materials, and combinations among them, may lead to novel and highly promising nanostructured smart functional systems well-suited for a wide range of research fields, including biomedicine and biotechnology.

compositions, structures, and functions for several relevant applications. This goal has been achieved by engineering several nanostructured building blocks on surfaces through many processing methods. 'Bottom-up' methods, including Langmuir–Blodgett (LB),<sup>[1–3]</sup> self-assembled monolayers (SAMs),<sup>[4–13]</sup> and Layer-by-Layer (LbL) assembly,<sup>[14–19]</sup> have been widely used to modify and effectively tailor the surface properties and simultaneously for assembling desired molecules with a high degree of control over organization and orientation. Therefore, these surface engineering strategies have been used to design and fabricate organized monolayer films (in the case of SAM methodology) and multilayer assemblies (in the case of LB and LbL assembly approaches) with precisely layered structures, compositions, properties, and functions, and thus with enhanced performance at the molecular level. Furthermore, the bulk properties of nanostructured materials and the ability to precisely tailor the surface properties and finely tune the physicochemical properties and structures of engineered func-

tional molecular assemblies have been recognized as having paramount importance for the scientific and engineering communities due to the broad range of possible applications in the biomedical, electronics, optics, catalysis, and energy research fields.<sup>[20–22]</sup>

It is well known and commonly agreed that nature provides a great source of endless inspirations for designing highly sophisticated functional materials. Hence, scientists and engineers from different areas of chemistry, physics, engineering, biology, medicine, or biotechnology have been challenged to design and engineer environmentally sensitive biomimetic surfaces that would respond to specific external stimuli (e.g. temperature, pH, ionic strength, light, mechanical stress, electric, magnetic and ultrasonic fields, electric potential, specific biological moieties) in a very controllable and predictable manner, hence adjusting to our demands. Such smart surfaces have been developed by modifying surfaces with stimuli-responsive polymeric materials that ideally exhibit reversible switchable physicochemical properties (i.e., a polymer should be switched repeatedly rather than being designed for a single event), precisely tailored structures, compositions, and functions in response to changes in the surrounding environment.

## 1. Introduction

The design and fabrication of well-defined nanostructured functional polymeric thin films and nanocomposites has been attracting substantial interest within the scientific community in the last decades owing to their promising properties,

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Moreover, such precisely tailored stimuli-sensitive polymeric systems are highly intended to mimic the behavior of dynamic smart biological systems, their properties and functions, thus enabling a better understanding of the complexity of naturally occurring processes. For example, human skin and photosynthetic organisms are two great examples of such dynamic smart biological systems and are very appealing targets for biomimetic materials science. The skin behaves as a permeable multifunctional membrane that adapts and responds to several dynamic environmental conditions, namely light, heat/cold, humidity, and mechanical stress, through self-regulation thus constituting a great example of an intelligent multiresponsive system found in nature.<sup>[23]</sup> Moreover, photosynthetic organisms, which convert solar energy into chemical energy, represent very interesting biological systems whose properties and functions could be mimicked to develop advanced, cost-effective, and highly efficient light-sensitive devices for energy-harvesting applications.<sup>[24–26]</sup>

Having this in mind, during the past decades we have witnessed a huge interest in designing advanced hierarchical stimuli-responsive functional systems that are capable to independently or simultaneously adapt and respond to one or several triggers that are inherently present in living systems, thus improving the complexity of such smart functional engineered systems. Such environmentally sensitive smart functional systems, which can be developed through many surface engineering approaches, including SAMs,<sup>[4–13,27–35]</sup> chemical grafting,<sup>[36–47]</sup> thin polymer network films,<sup>[48–59]</sup> LbL assembly,<sup>[14–19]</sup> or combinations of thereof,<sup>[60,61]</sup> have received increasing attention in the past few years because they offer great advantages in exciting widespread applications, including biomedical and biotechnological, coatings and textiles, electronics, catalysis, optics, or energy applications.<sup>[18,19,23,27–35,39,40,44–47,49,51,56–59,62–86]</sup> Thus, they aim to shed light on the development of next-generation smart functional systems that would mimic the hierarchical organization and the behavior of smart biological systems. Within such variety of techniques to functionalize and engineer surfaces, LbL assembly approach has been introduced as a powerful, highly versatile, flexible, and inexpensive strategy for modifying surfaces and preparing multilayer assemblies using an exceptional variety of materials and surfaces, as it will be described in the following section.

In this review we intend to provide a deep overview of the current achievements, developments, future challenges and opportunities in the field of light-responsive LbL polymeric multilayer systems, as well as prospect applications as novel smart functional systems in a wide range of research fields. This review begins with a brief introduction that intends to highlight the importance of stimuli-responsive materials for scientists and engineers as key elements to mimic the behavior of smart biological systems, and their broad-range of applications. In Section 2, we provide a concise description of LbL assembly approach as one of the most prominent surface engineering techniques to modify surfaces and create novel multifunctional systems or devices through the assembly of a plethora of materials, its advantages and capability to address a wide range of possible applications. Section 3 focuses on the design and fabrication of stimuli-responsive systems through



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**Luísa C. Rodrigues** (middle left) has a background in chemistry. Her PhD, received in University of Minho, Portugal, was based on the development of ionic conductive polyelectrolytes. The resource to natural materials was an applied strategy, as well as their application in photochromic device prototypes. Nowadays, she is a postdoctoral researcher at the 3B's Research Group, at the University of Minho, Portugal. Her current research interests include the incorporation of natural materials in the development of photoresponsive assemblies to be applied in bioengineered devices, promoting the progress of current medical technologies and tissue engineering.

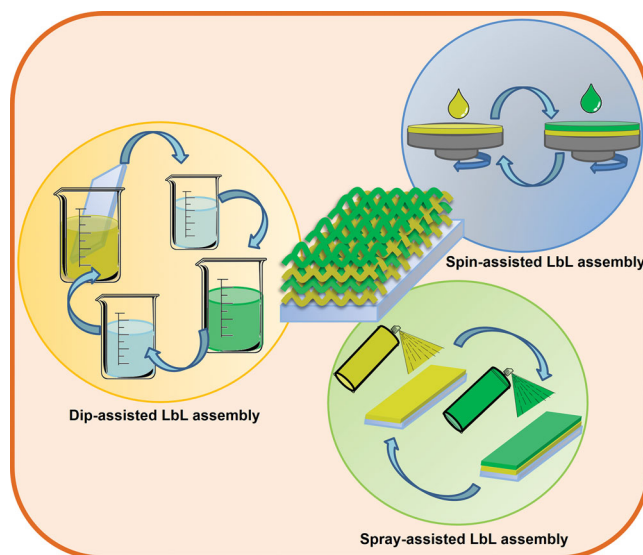
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LbL assembly of materials that display switchable properties. The responsiveness of LbL systems to several external triggers is briefly addressed with a special attention being allocated to the macromolecular systems that are sensitive to common stimuli, namely temperature, ionic strength, or pH triggers. Section 4 is devoted to the recent progresses and developments in the design and fabrication of light-responsive LbL polymeric multilayer assemblies on both two- (2D) and three-dimensional (3D) surfaces, their potential future challenges and opportunities, and possible applications. Many examples are given on light-responsive LbL polymeric multilayer assemblies built from several functional materials, namely metal nanoparticles, functional dyes, and metal oxides. The last two sections present a brief outcome of the current achievements and future perspectives on the field of light-responsive LbL polymeric multilayer systems.

## 2. Background on the LbL Assembly Technique

Layer-by-Layer (LbL) assembly is a simple, effective, reproducible, flexible and highly versatile method for modifying surfaces and fabricating robust and highly ordered nanostructured functional polymeric thin films and nanocomposites over any type of substrate. Such nanostructured functional assemblies may contain stimuli-responsive materials which turn them sensitive to a multitude of stimuli, thus rendering advanced functional systems with stimuli-responsiveness. The LbL technology, which is based on the sequential adsorption of complementary multivalent molecules on a substrate via electrostatic and non-electrostatic interactions (e.g. hydrophobic interactions, hydrogen bonding, charge-transfer interactions, host-guest interactions, biologically specific interactions, coordination chemistry interactions, covalent bonding, stereocomplexation, surface sol-gel process) or combinations of thereof, was first proposed by Iler in 1966 for the adsorption of multilayers of oppositely charged colloidal particles.<sup>[14]</sup> However, this concept was only recognized after the work of Decher and co-workers on multilayer films comprising cationic and anionic bipolar amphiphiles,<sup>[15]</sup> oppositely charged polyelectrolytes,<sup>[17,18]</sup> or combinations of thereof.<sup>[16]</sup> Although these works and the overwhelming majority of studies reported in the literature have focused on LbL assembly via electrostatic interactions, there has been also a growing interest on other intermolecular interactions due to the possibility of incorporating several charged or uncharged materials within the LbL assemblies, thus amplifying their possible applications. Since then, LbL assembly technique has attracted much attention over the past two decades.<sup>[19]</sup> LbL assembly is an easy, flexible, and versatile process which can be performed on virtually any kind of substrate of any nature, size, shape, and chemical composition (e.g. planar, porous, colloidal particles, cylindrical structures) using a wide variety of building blocks, such as polymers,<sup>[87–102]</sup> metal oxides,<sup>[103–108]</sup> carbon nanotubes,<sup>[109–114]</sup> graphene nanosheets,<sup>[115–119]</sup> dyes,<sup>[120–122]</sup> clays,<sup>[123–125]</sup> particles,<sup>[126–140]</sup> dendrimers,<sup>[141–143]</sup> as well as proteins,<sup>[144–155]</sup> enzymes,<sup>[156–159]</sup> nucleic acids,<sup>[160–166]</sup> peptides,<sup>[167–169]</sup> or viruses.<sup>[170–173]</sup> Therefore, there is absolutely no doubt that the number and variety of materials that can be assembled via LbL technique are only



**Figure 1.** Schematic illustration of the most commonly used LbL deposition methods to prepare multilayer films on 2D planar surfaces.

limited by our imagination. The LbL buildup of such plethora of materials allows a great control over the film properties, namely thickness, internal structure, chemical composition and morphology, at both nanometer and micrometer scales, and endows the multilayer films with different functionalities and capabilities to develop advanced functional systems and devices with great potential of practical application, including in the biomedical field.<sup>[174–178]</sup> Moreover, the properties of the LbL assemblies can also be tailored by playing with the number of deposited layers and/or fine-tuning the assembly conditions (e.g. solution pH, temperature, or ionic strength). The LbL buildup of the multilayer assemblies commonly occurs through a variety of deposition methods that have been already extensively reviewed, including dip-coating, spin-coating, and spraying.<sup>[177–190]</sup> **Figure 1** shows a schematic illustration of the most common LbL deposition methods for preparing multilayer films on 2D planar surfaces. Although dip-coating method is the most used to date, it has some shortcomings, namely large amount of materials and time for film preparation, thus being undesirable for industrial purposes. However, by using spraying instead of dip-coating one easily obtains homogeneously deposited films, avoids the use of large amount of materials, and significantly reduces the time needed for the deposition process, thus meeting commercial and industrial needs.<sup>[191–195]</sup> In addition, other less used but highly promising methods, such as hydrodynamic dip-coating,<sup>[196,197]</sup> perfusion,<sup>[198,199]</sup> high gravity field,<sup>[200]</sup> and inkjet printing-assisted LbL,<sup>[201–204]</sup> and LbL deposition on spherical particles<sup>[205–209]</sup> have also been reported for the multilayer buildup, thus enabling a great control over the amount, thickness, and morphology of adsorbed layers. Moreover, such methods remarkably improved the efficiency of the LbL assembly process by accelerating the adsorption process and maintenance of the multilayer films quality, and further extended the design and fabrication of multilayer assemblies from simple 2D planar platforms to more complex 3D surfaces.

Beyond the above reported key features, LbL assembly approach presents several other advantages: (i) it is



a cost-effective process, since it only requires simple laboratory equipment; (ii) allows the integration of several multicomponent materials from different sources and nature within the films; (iii) enables the incorporation of different biomolecules into the films; (iv) assures a well-defined control over the morphology, permeability, composition, thickness, structure, and mechanical properties of assembled materials; (v) provides high-stability and robustness to the films under ambient and physiological conditions, and; (vi) can be performed under mild conditions with inexpensive materials in entirely aqueous solutions, requiring no exposure to organic and/or harmful solvents or extreme assembly conditions.

Therefore, it seems clear that LbL assemblies fabricated with accurate control over film thickness and structure through simple deposition methodologies, such as spraying method, can be easily scaled-up and manufactured to create large area uniform coatings, thus providing the basis for addressing practical industrial and commercial requirements.<sup>[210–218]</sup> One remarkable example of LbL-based systems applicable and already scaled-up for fulfilling industrial requirements is the development of novel transparent superhydrophobic LbL functional nanocoatings, by using automatic spray-assisted LbL machines, for coating the surface of large areas, such as cars, pipelines, solar panels, or even aircrafts, and to clean fingerprints from mobile phones. Superhydrophobic LbL nanocoatings based on silica nanoparticles, which work as robust ultra water-repellent nanoprotective systems, are highly desired for corrosion protection purposes in order to prevent the deterioration of car surface through their water repellency. In addition, these low-cost superhydrophobic LbL nanocoatings, which tend to mimic the ultra-water repellent behavior of nature-inspired materials such as lotus leaf's rough superhydrophobic surface, have already demonstrated great capacity for repelling water and everyday dust, thus promoting the self-cleaning/repairing of car paintings.<sup>[216–218]</sup> By using such superhydrophobic materials one can easily keep the car surface cleaned for longer time periods. Besides the fabrication of superhydrophobic LbL functional nanocoatings, the development of transparent, antifogging, and antireflective superhydrophilic LbL nanocoatings/surfaces has also been reported.<sup>[212]</sup> Superhydrophilic LbL functional coatings are highly desired for building windows in order to maintain energy efficient and cost-effective rooms, and even for car windows and windshields that will then never need a blower to avoid the heat trapped inside the car on summer days or fogging scenarios on cold and wet winter times. With that said, during the scale-up process the major concern will be related with the design of adequate reservoirs or deposition methodologies that will allow the total and homogeneous contact of the material solutions with the substrate surface. However, as the LbL technology promotes surface modification at the nanoscale level, there will be no implication at the deposition kinetics and thermodynamics when the surface area of the substrate is increased.

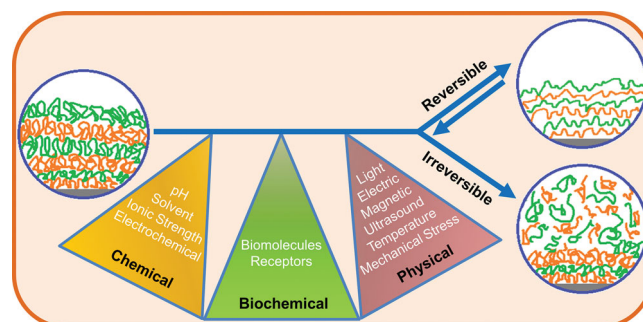
In summary, this simple, effective, versatile, and flexible way of designing advanced nanostructured functional materials constitutes a key subject of current scientific interest for researchers with different backgrounds and has shown itself to be a highly-promising tool for the scientific and engineering communities due to the practical potential applications

in a wide range of research areas, including biomedicine and biotechnology.<sup>[17–19,174–178,208–248]</sup>

### 3. Stimuli-Responsive LbL Assemblies

During the last few years, there has been an increasing interest in developing environmentally sensitive advanced nanostructured functional materials with tailored properties, structures, compositions, and functions with the main aim of designing and engineering dynamic intelligent multifunctional systems or devices that may respond to specific external stimuli. As previously reported in the introductory section, such stimuli-responsive systems, also known as smart or intelligent systems, can be developed by engineering stimuli-sensitive materials through several surface engineering approaches. Despite the different techniques to render smart functional systems, in this review we will focus on stimuli-responsive systems, specifically on light-responsive polymeric multilayer systems, developed by LbL buildup of materials that exhibit switchable properties.

Multilayer assemblies built by LbL assembly approach have shown a great potential to adapt and respond to several environmental conditions, thus leading to novel well-defined smart functional systems with controlled release properties highly suitable to meet to our demands. The responsiveness of LbL multilayer assemblies to achieve spatial, temporal and active control over the physicochemical properties and release of incorporated components can be effective by controlling specific template architectures (e.g. macroscopic planar films, spherical capsules), their internal structure, composition, or release triggers (e.g. pH, ionic strength, temperature, magnetic, electric or ultrasonic fields, light, redox potential, mechanical stress, biomolecules or ionic surfactants; **Figure 2**) as well as by regulating the assembly mechanisms within LbL films to achieve film swelling, shrinkage, degradation or even disassembly to facilitate the loading or release of desired active molecules.<sup>[123,125,230,249–317]</sup> Such response is based on the fact that synthetic macromolecules and hybrid composite materials assembled via LbL technology can change their structures and properties in response to small changes in the surrounding environment that may alter their individual chain dimensions, solubility, degradability, conformation, degree of intermolecular association, and specific secondary structure in aqueous media, and thus modify their binding affinity.<sup>[66,67,80]</sup> As illustrated in



**Figure 2.** Schematic illustration of the different chemical/biochemical/physical stimuli used to control the response of LbL multilayer assemblies displaying materials that exhibit switchable properties.

Figure 2, the independent or simultaneous application of one or several external stimuli may induce reversible or irreversible changes in the composition, structure, and properties of multilayer systems. In the case of reversible systems a well-defined control over the structure and properties of the multilayer films and capsules such as thickness, roughness, morphology, permeability, wettability, and swelling behavior can be accomplished by slight changes in the environmental conditions (e.g. pH, ionic strength, temperature, etc). Moreover, the structures and properties of the multilayer assemblies can be restored completely by returning to the initial conditions. Several examples on stimuli-responsive multilayer assemblies exhibiting reversible behavior have been reported. For example, polymeric multilayer microcapsules exhibiting great control over the loading or release of desired molecules have been constructed making use of a temperature-responsive polypeptide, such as biomimetic elastin-like recombinamer (ELR), and chitosan (CHT) biopolymer.<sup>[312,313,317]</sup> Moreover, other thermosensitive systems displaying reversible behavior, such as poly(*N*-isopropylacrylamide) (PNIPAAm)-based films, enable to control the surface wettability and loading/release properties, and have been proposed for cell sheet engineering, allowing the non-invasive detachment of cells by simply reducing the temperature.<sup>[90,95,97]</sup> Overall, both thermoresponsive polymer systems play an important role on several biomedical and biotechnological applications. Furthermore, multilayer assemblies may also disrupt when responding to specific triggers such as electric, magnetic or ultrasonic fields, light, mechanical stress, or electric potential, thus revealing an irreversible behavior. For instance, the formation and stability of multilayer assemblies was found to be dependent on the applied electric potential, which triggered the film dissolution upon achieving 1.8 V.<sup>[269]</sup> Such assemblies show enormous potential as smart drug delivery and controlled release devices.

Stimuli-responsive LbL systems can dramatically change their physicochemical properties (e.g. size, shape, conformation, thickness, solubility, swelling/shrinking behavior, hydrophilic/hydrophobic balance, or release of a bioactive molecule) by the interruption of weaker intermolecular interactions between the adsorbed layers through the application of specific external stimuli. Therefore, those assemblies are extremely important for many emerging applications in tissue engineering and regenerative medicine, protein adsorption, cell adhesion/detachment, biosensors, controlled drug delivery, bioseparation, bioreactors, actuators, diagnostics, chromatography, coatings and textiles, as well as electronics, optics, and energy.<sup>[78–85,261,284,296,306–308,310–313,317–322]</sup>

The great majority of works in the literature dealing with stimuli-responsive LbL assemblies are dedicated to macromolecular systems that are sensitive to common triggers, namely temperature, ionic strength, or pH triggers. In this regard, thermosensitive films and capsules have been widely explored and are mostly achieved by the use of synthetic thermoresponsive polymers comprising PNIPAAm derivatives, which present interesting properties for biomedical purposes.<sup>[90,95,97,125,323–325]</sup> Such polymers undergo a sharp transition in water at a lower critical solution temperature (LCST) of 32 °C, changing from a hydrophilic to a hydrophobic state upon heating.<sup>[281,326–329]</sup> This transition, which involves the disruption

of secondary forces, namely intermolecular hydrogen bonds between water molecules and the amide groups in the polymeric chains, enables not only a very precise control over cell growth, since PNIPAAm hydrophobicity allows cells to attach to it at physiological conditions, as well as a well-defined controlled release upon decreasing the temperature due to the increase of the polymer hydrophilicity.<sup>[72,330,331]</sup> Indeed, such thermoresponsive polymers allow us to finely tune the permeability and morphology of LbL films and capsules, which is vital to achieve superior performance for each application. For example, such thermosensitive polymers have great potential for cell sheet technology. However, besides PNIPAAm, other thermoresponsive polymers such as ELRs, could be used for biomedical purposes. For instance, intelligent thin coatings were fabricated in a LbL fashion by simple alternate deposition of an aqueous-soluble ELR, containing the cell attachment sequence arginine-glycine-aspartic acid (RGD), and CHT.<sup>[284,296]</sup>

Another important and widely investigated group of stimuli-responsive materials are pH-responsive polymers, in which ionizable functional groups have the ability to give or accept protons upon pH changes. In this context, Granick and co-workers<sup>[250,255]</sup> reported for the first time the fabrication of an erasable multilayer thin film by disruption of hydrogen bonding interaction between acid-base pairs through the manipulation of the surrounding environmental conditions, such as pH or ionic strength. Few years later, a similar approach was also developed by Zhang and co-workers<sup>[332,333]</sup> using a base to selectively extract the acidic component from a multilayer film. These stimuli have been used to modulate the permeability of films and capsules incorporating polyelectrolyte multilayers (PEMs) towards remote release and encapsulation of desired molecules. The preferred polyacids to be employed in LbL assemblies present a  $pK_a$  around 5 since they exhibit rapid transitional changes at relevant physiological conditions. In this concern, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) are the most commonly used polyacids to be incorporated in pH-responsive systems.<sup>[334–338]</sup> For instance, Kozlovskaya et al.<sup>[334]</sup> fabricated LbL multilayer films and capsules comprising PMAA and poly(*N*-vinylpyrrolidone) (PVPON) via hydrogen bonding. These films and capsules presented reversible swelling behavior in response to changes in solution pH and ionic strength. Upon increasing the solution pH, the carboxylic acid groups of PMAA became deprotonated, thus leading to the disruption of hydrogen bonding interactions. Moreover, PVPON is then completely removed from the multilayer system forming PMAA hydrogel films and capsules, which enable the loading of therapeutic cargo. These smart systems have demonstrated to be increasingly important when aiming for biomedical and biotechnological applications. For instance, they have already been tested in intracellular drug delivery,<sup>[339]</sup> and pH switching for the accurate control of protein adsorption or cell attachment phenomena.<sup>[340]</sup>

#### 4. Light-Responsive LbL Polymeric Multilayer Assemblies

Similar to other external stimuli, which are employed in order to induce a specific response in 2D and 3D polymeric

multilayer systems, light stimulus is specifically applied from an external source, thus offering the ability to accomplish a precise and easily adjusted spatiotemporal control over the attachment/detachment of cells or biomolecules, biosensors/diagnostics, and diffusion of encapsulated molecules for controlled drug delivery purposes. Nonetheless, 2D polymeric multilayer systems that are sensitive to light stimulus are rarely mentioned in the literature, probably due to the fact that most light-sensitive molecules respond to UV light, which is harmful to biological molecules. Such remote stimulus has the capability of being applied in a non-invasive and highly controlled fashion. Moreover, it is inherently present and widely used in natural living systems as an environmentally friendly and efficient power source, inducing much less damage to the cell membrane and proteins than conventional enzyme treatment techniques. Therefore, this stimulus is highly suitable for *in vivo* biomedical applications.<sup>[177,225,228,291,307,340–342]</sup> Moreover, light stimulus has also the capability of deeply penetrate into tissues and finely-tune its intensity, thus reinforcing its unique potential in the biomedical field. In this concern, the design and fabrication of multilayer assemblies incorporating absorbing activation centers deserves further comprehensive attention.

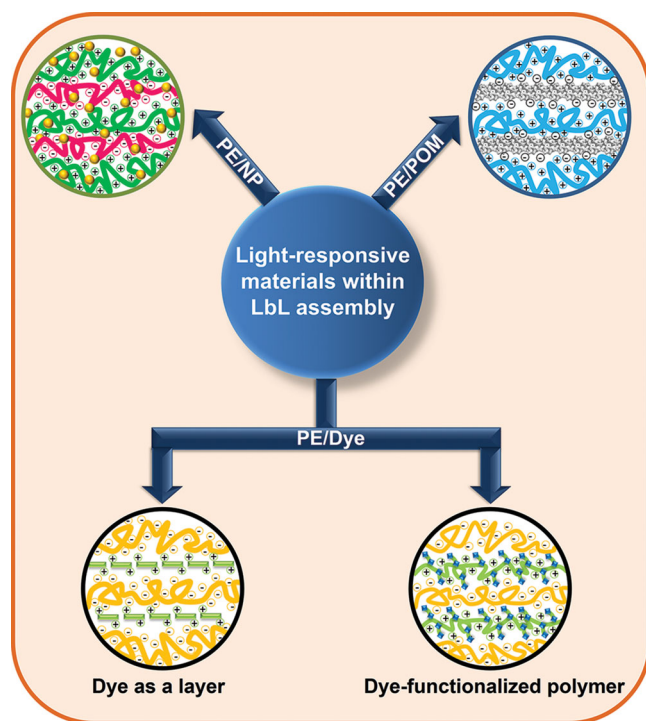
To date, the strategies adopted by few research groups willing to this goal are from different nature. Such strategies are concerned with the incorporation of several light-responsive materials, such as metal nanoparticles (NPs), functional dyes, and metal oxides in LbL multilayer systems (see Figure 3), mostly in 3D polymeric multilayer assemblies. For instance, Pasparakis, Sukhorukov, and Caruso's research groups have all included

on polyelectrolyte multilayer walls noble metal NPs or infrared (IR)-dyes that exhibit high absorption in the near-infrared (NIR) region.<sup>[228,259,291,298,341]</sup> These kind of smart delivery systems, which are highly suitable for biomedical applications due to the low absorption of NIR radiation by skin and most of the tissues, are used for photothermal drug release either alone or as components within polymer nanocomposites. Therefore, the incorporation of several light-sensitive moieties within multilayer assemblies seems to be an excellent strategy when aiming for biomedical applications because these absorbing activation centers help to shift the absorption wavelengths toward the visible spectrum region, thus surpassing the limitations imposed by UV light.

In this section we focus on the design and fabrication of photoresponsive multilayer assemblies by using materials that exhibit photoswitchable properties, as well as on their properties, future challenges, and potential applications.

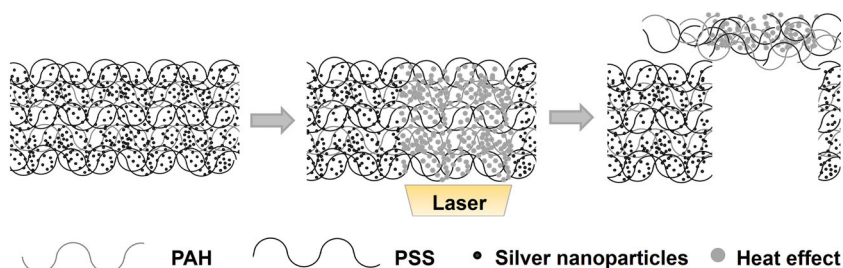
#### 4.1. Incorporation of Metal Nanoparticles within LbL Polymeric Multilayer Assemblies

The incorporation of metal NPs within LbL polymeric multilayer assemblies (i.e. polymer-based LbL films and capsules) allows the direct conversion of laser light, absorbed in the visible spectrum, into thermal energy which may result in changes in the film or capsule permeability, morphology, composition, and structure, and thus potentially leading to the rupture of the walls of such assemblies. Furthermore, the large amount of heat, produced locally within LbL assemblies, generally leads to irreversible disruption of these constructs and, subsequently, to the remote release of encapsulated therapeutics or detachment of deposited substances from surfaces.<sup>[343–346]</sup> Such metallic nanostructures display several desired characteristics, namely well-defined surface chemistry, size, shape, composition, function, and properties, which enable their appropriate surface functionalization with suitable molecules for directly improving desired applications. All these features are due to unique interactions of such metallic nanostructures embedded within the adsorbed layers with light, which turn them very useful constituents to load or release desired materials. Under light irradiation, electrons in metals are driven to collectively oscillate in phase, process commonly known as surface plasmon resonance absorption of the NPs, whose absorption cross-section is drastically more intense than for a typical dye due to their high surface-to-volume ratio. The increase in temperature acquired for the metal NPs to values above the spinodal point of water and the melting point of the metal, and the thermal stress resulting from the different thermal expansion coefficients of materials within the shell could be the reasons for the disruption of the assemblies.<sup>[347]</sup> Caruso and co-workers were the first to report the remote release of encapsulated materials from the capsule wall upon NIR irradiation of gold nanoparticles (AuNPs)-functionalized polyelectrolyte microcapsules.<sup>[347]</sup> Such strategy could be used for the controlled delivery/release of drugs encapsulated in capsules. This work was followed by the studies performed by Skirtach et al.<sup>[348]</sup> who explored in detail the fabrication of nanoengineered polyelectrolyte capsules containing gold sulfide core/gold



**Figure 3.** Schematic illustration of the different light-responsive building blocks (nanoparticle – NP, polyoxometalate – POM, dye) that can be incorporated together with polyelectrolytes (PE) in 2D and 3D LbL polymeric multilayer assemblies via electrostatic interactions.





**Figure 4.** Schematic representation of the LbL build-up of polymeric multilayer thin films incorporating polyelectrolytes and silver nanoparticles (AgNPs), and their further interaction with NIR light.

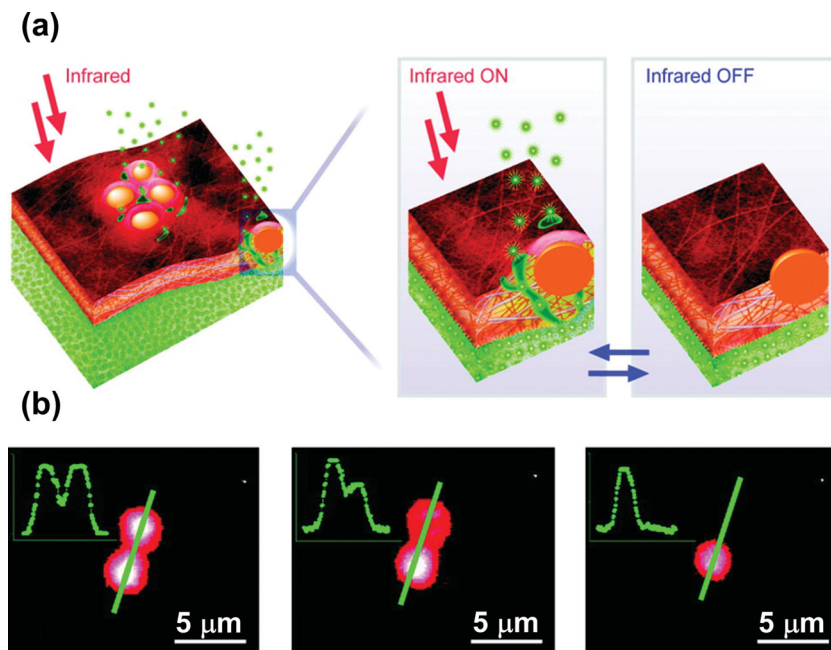
shell NPs in their walls, and their response to laser light in order to mediate the remote release of encapsulated fluorescent materials. In an attempt to fully address biomedical applications, those LbL microcapsules can be optimized by functionalizing their surface with certain specific biologically relevant molecules, such as antibodies, proteins, peptides, enzymes, nucleic acids, or growth factors, thus improving their bioactivity, binding affinity, and specificity.<sup>[349–353]</sup> **Figure 4** depicts a schematic illustration of the fabrication of LbL polymeric multilayer films incorporating silver nanoparticles (AgNPs) and polyelectrolytes, and their further interaction with NIR light that can be controlled in space.

Meanwhile, similar approaches have been followed using different colloidal templates. Several types of metals and metal nanostructures, which are useful molecules in triggering biologically inspired materials, are being included within LbL multilayer assemblies with the main aim of controlling the load or release of desired molecules.<sup>[354]</sup> The incorporation of metal NPs in LbL assemblies has been the main focus of several research groups owing to their strong light absorption as well as unique electrical, optical, catalytic, and magnetic properties when compared with those of bulk metals or metal atoms. Therefore, such properties turned LbL assemblies highly-suitable for a wide range of applications. For example, the incorporation of noble metal NPs, namely AgNPs<sup>[259,355]</sup> and AuNPs,<sup>[132,344,347,356–358]</sup> and metal oxide NPs, such as titanium dioxide (TiO<sub>2</sub>),<sup>[359–362]</sup> zinc oxide (ZnO),<sup>[363]</sup> or iron oxide (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>)<sup>[364,365]</sup> on 2D and 3D LbL multilayer assemblies has been widely investigated. Nonetheless, other materials exhibiting different sizes and shapes such as AuNP aggregates,<sup>[366–368]</sup> nanorods,<sup>[369,370]</sup> nanowires,<sup>[371]</sup> and nanobelts<sup>[372]</sup> have been also extensively studied in order to fully explore their great potential in several applications. Upon NIR irradiation, all these materials further lead to reversible changes in the permeability of polymeric multilayer systems or irreversible disruption of such multilayer films or capsule walls, thus enabling the controlled load or release of desired molecules.

Photoresponsiveness of metal NPs occurs in the NIR spectrum section, with wavelengths between 650–900 nm,<sup>[373]</sup> which reveals advantageous conditions for biomedical applications, such as controlled drug delivery, since NIR radiation is minimally absorbed by skin and most tissues. For this reason, light can penetrate into the tissues in the order of hundreds of micrometers to centimeters, thus enabling whole-body optical imaging.<sup>[373,374]</sup>

In this context, one of the first studies where remotely triggered release of encapsulated materials was revealed involved the use of very large amounts of metal NPs, resulting in the destruction of the containers.<sup>[259,347]</sup> This issue constitutes the main drawback of such processes due to the potential toxicity induced by the NPs to the surrounding environment after the disintegration of the containers,<sup>[259,375]</sup> which limits their application in the biomedical field.

Skirtach et al.<sup>[259]</sup> were the first to report the fabrication of multilayer systems containing AgNPs. In that work, poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) multilayer microshells were doped with AgNPs and their response to light irradiation studied. It was found that such capsules could be destroyed upon NIR irradiation, thus leading to the remote release of encapsulated materials. AgNPs present a higher absorption maxima at wavelengths between 380–430 nm, being this value largely influenced by the size and shape of such particles.<sup>[376]</sup> However, this range of wavelengths is not considered ideal for therapeutic treatments, as drug or gene delivery, because a wide range of biomolecules absorb light outside the so-called “biologically friendly window” (700–1200 nm). Nonetheless, upon NIR light irradiation, polymeric capsules can be also tuned in order to release desired encapsulated materials without the disruption of their walls. This goal could be achieved by using NPs with well-defined size, shape, and concentration which reduce the irradiation requirements. In this context, Skirtach et al. showed that, when using a certain particle concentration, polymeric microcontainers comprising poly(diallyldimethylammonium chloride) (PDADMAC) and PSS multilayer shells containing AgNPs or AuNPs,<sup>[377]</sup> or AuNPs aggregates<sup>[366,367]</sup> did not disrupt while releasing their encapsulated materials, being highly suitable for drug/therapeutic delivery purposes. The replacement of single NPs for aggregates within multilayer assemblies not only allows for low laser irradiation intensities but also promotes an improvement of the optical absorption at longer wavelengths in the NIR region due to the enhanced control over the localization of heat induced by such building blocks, thus enabling an enhanced release or encapsulation of desired materials. These features further enable to reversibly control the permeability of the assemblies while preserving their integrity. Moreover, such aggregates also promote an enlargement of the opened pores.<sup>[366,367]</sup> In this regard, the partial remote release observed for PDADMAC/PSS microcapsules functionalized with aggregated AuNPs further corroborated these ideas, proving that under mild laser light illumination the AuNPs produce only sufficient heat to locally release desired encapsulated contents, thus making the heat production more efficient (**Figure 5a**). Upon a second laser light exposure, the microcapsule completely released its content. Between the first and second laser light illumination, i.e., when the laser was switched off, no change in the fluorescence intensity was observed which reveals that the capsules resealed itself, thus enabling to reversibly change the permeability of polymeric microcapsules (**Figure 5b**).

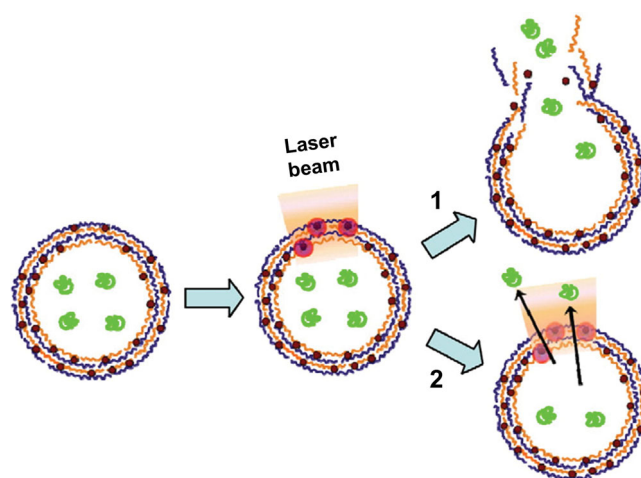


**Figure 5.** Schematic illustration of the remote release of encapsulated materials from polymeric microcapsules containing aggregates of AuNPs. a) Schematics of AuNPs functionalized polymeric nanomembranes opening channels upon laser illumination. b) Polymeric microcapsule shell acts as a reversible permeable nanomembrane. Upon laser light illumination the microcapsule (left image) partially releases encapsulated fluorescent polymeric materials and reseals (middle). After the second illumination the microcapsule completely releases its content (right). Adapted with permission.<sup>[366]</sup> Copyright 2008, American Chemical Society.

Multilayer assemblies containing AuNPs absorb light mainly in the visible region, thus changing the wavelength range of the main absorption band with the shape, size, and aggregation coefficient of such particles. This issue enables an increase in the versatility of the interaction between laser pulses and NPs, which work as sensitizers of visible and NIR radiation for microcontainers. The controlled release of encapsulated materials from AuNPs-functionalized capsules by pulsed IR irradiation and the well-defined control over the permeability of the capsules occur partially due to the laser/NPs interaction.<sup>[347,356,378–380]</sup> However, the mechano-chemical effects induced by pulsed lasers on polymeric microcapsules, such as laser ablation, cannot be neglected.<sup>[380]</sup> Figure 6 shows two possible release scenarios of encapsulated material induced by laser/NPs interaction.

Nowadays, promising approaches involving the fabrication of customized multicompartments, which allow the combination of several properties from distinct compartments and, thus, functions, for controlled delivery and release of encapsulated materials have also been addressed.<sup>[378,379]</sup> Such multicompartimentalized functional systems, which can be fabricated by coating spherical sacrificial templates (e.g. calcium carbonate, polystyrene, silicon oxide) with polyelectrolyte multilayer assemblies and embedding light-sensitive carriers, such as NPs, in the inner core, followed by dissolution of the particle template, allow the controlled loading and release of desired materials. Moreover, these systems can be further used as bio-reactors, enabling the mixing of several active agents confined in separated compartments by light irradiation, and hence the

decreasing their permeability. In spite of these findings, the authors did not make any observation regarding the system reversibility.

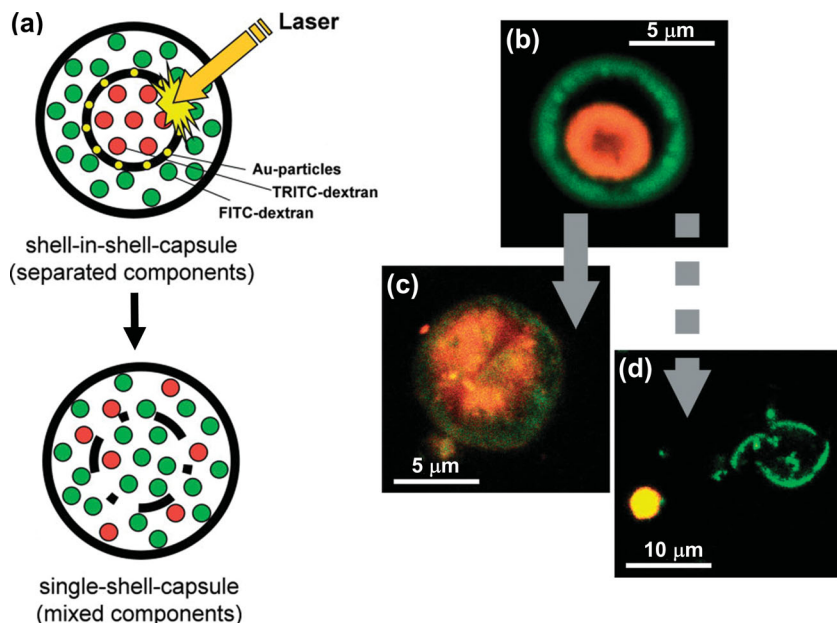


**Figure 6.** Schematic of the two possible release scenarios of encapsulated material by the laser/NP interaction. 1) Upon illumination, the NPs produce a large amount of heat that breaks the capsule wall. 2) During illumination, the NPs produce a small quantity of heat sufficient to exceed the glass transition of the polymer complex of the capsule, decreasing the shell's permeability until illumination is stopped. The increased permeability allows for encapsulated material to be released from the capsules without the shell being damaged. Adapted with permission.<sup>[380]</sup> Copyright 2010, Elsevier.

start of several reactions. Figure 7 shows a schematic illustration of such multicompartimental capsules incorporating two distinct compartments and the intermixing between the contents of both containers stimulated by laser light irradiation (Figure 7a). Moreover, confocal laser scanning microscopy (CLSM) images of such systems before (Figure 7b) and after (Figure 7c,d) laser illumination are also shown.

Recently, Sukhorukov and co-workers<sup>[381]</sup> reported the LbL assembly of polymeric microcapsules using polyelectrolyte/nanoparticle composite microcontainers incorporating PDADMAC and PSS microshells doped with citrate-stabilized AuNPs and studied the mechanical stability of such polymeric containers. It was found that doping polyelectrolyte microshells with AuNPs of increasing concentrations greatly increased their size (see Figure 8a), stiffness and strength (Figure 8b), thus providing promising interest for practical biomedical applications, namely intracellular delivery. Therefore, the increase in particle concentration not only leads to a decrease in the thermal shrinkage behavior of microcapsules but also limits the lower size that they may be shrunk to. Overall, the shells of the microcapsules shrunk upon light irradiation, thus



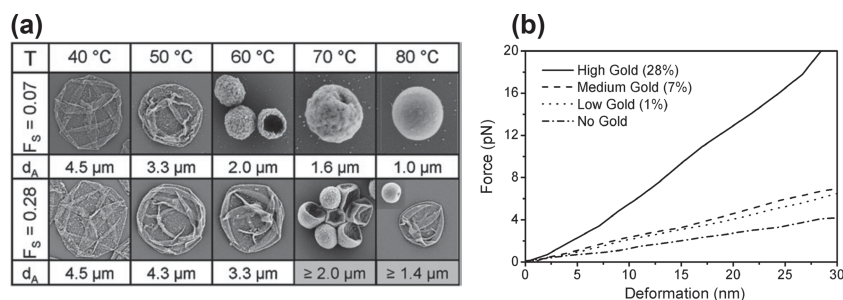


**Figure 7.** Multicompartmental LbL polymeric systems. a) Schematic illustration of a multicompartment capsule containing two compartments, and intermixing of the contents of both compartments triggered by laser light illumination, which caused the disruption of the inner shell. CLSM images taken (b) before and (c) after laser illumination of the inner shell doped with AuNPs. In some cases, the laser irradiation can further lead to the (d) rupture of the outer shell of the capsules accompanied by the release of the inner capsule. Adapted with permission.<sup>[378]</sup> Copyright 2007, Wiley-VCH.

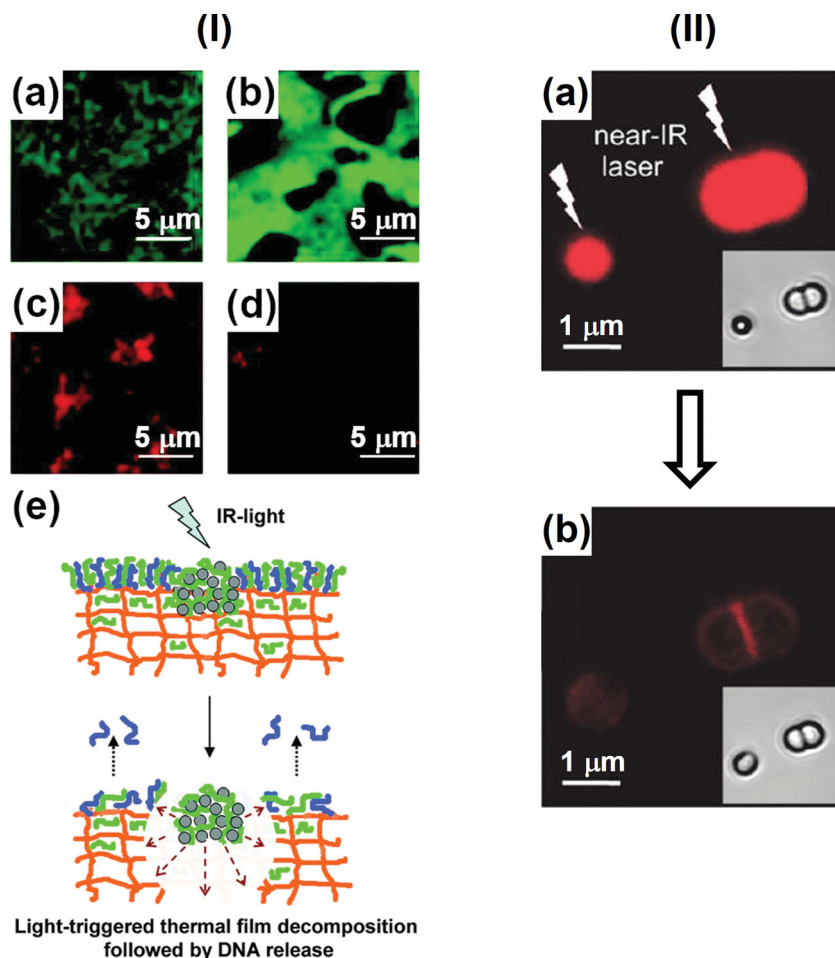
Regarding the use of AuNPs to optically induce changes in the capsule wall, Volkov et al.<sup>[382]</sup> studied the theoretical energy transfer of colloidal gold in water when irradiated with laser pulses. They demonstrated that the irradiation of AuNPs in water at high energy density can exceed the water critical temperature ( $T_c = 647$  K), thus leading to the explosive formation of vapor bubbles. Moreover, such AuNPs irradiation may induce more extensive photothermal and mechanical damage at sub-micron scale, thus providing potential interesting opportunities for biomedical applications, namely tissue engineering and wound healing. A very interesting review on NP-modified

polymeric capsules was published by Parak and co-workers, mainly focusing on the biological applications of such shells.<sup>[383]</sup> However, besides the fabrication of 3D multilayer structures, the construction of 2D planar films incorporating NPs and their light triggered release of bioactive molecules have also been the focus of few studies. In this context, Möhwald and co-workers reported the functionalization of 2D flat platforms comprising poly(L-lysine)/hyaluronic acid (PLL/HA) or PAH/PSS multilayers with absorbing heating centers, such as NPs or polymeric microcapsules modified with NPs, as well as their further use to remotely heat specific film sites, through laser light, in order to trigger the release of desired film components.<sup>[384–386]</sup> For instance, the fabrication of biocompatible PLL/HA composite multilayer films doped with AuNPs, their further activation by light stimulation, and the remote release of their contents have recently been addressed,<sup>[384]</sup> as shown in **Figure 9**.

As can be seen from this figure, PLL/HA multilayer films embedding AuNPs and DNA (Figure 9I) or AuNPs-modified polyelectrolyte multilayer capsules (Figure 9II) on their surface can lead to the release of their contents upon irradiation with laser light. Such release, which is triggered by changes in the permeability of such assemblies, is irreversible for LbL films modified with AuNPs, whereas it is reversible in the case of films modified with AuNPs-functionalized microcapsules, as the capsules retain their spherical shape after laser irradiation, thus enabling the remote release of their content. In opposition to the above mentioned studies, which reported the fabrication of multilayer assemblies based on synthetic polymers, this work focused on biopolymeric systems which open new avenues for the design and development of novel functional devices highly suitable for a variety of biomedical applications, including drug/gene/therapeutic delivery devices, coatings for implantable medical devices, supports for protein and cell adhesion, and biosensors. Moreover, Möhwald and co-workers also performed mechanical tests with highly swollen HA/PLL multilayer films and showed that the incorporation of light-sensitive AuNPs in the film surface enhanced the mechanical properties and increased the film surface properties, namely stiffness and roughness, thus greatly improving the cell adhesion.<sup>[387]</sup> They demonstrated that a single step deposition of negatively charged AuNPs on the film surface led to enormous changes in the film properties due to the complexation of the NPs with the large reservoir of PLL in the film. Generally, the increase of AuNP surface concentration led to an improvement of cell adhesion behavior (see **Figure 10**). Nonetheless



**Figure 8.** a) SEM images of thermally shrunk capsules with a AuNP surface coverage of 7 and 28% ( $F_s = 0.07$  and  $0.28$ ), top and bottom row, respectively. Each column shows an image of each type of capsule shrunk under the same conditions with their average diameter ( $d_A$ ). The two  $d_A$  values that are shaded had a broad size distribution with a significant number of fused or damaged capsules. b) The force-deformation curves of exemplified individual capsules with different gold content and different sizes. A small stiffness increase is found in shells with surface filling ratio of 0.01 or 0.07, whereas a large increase is found in shells with the highest load of gold nanoparticles. Adapted with permission.<sup>[381]</sup> Copyright 2009, Royal Society of Chemistry.



**Figure 9.** LbL polymeric multilayer assemblies incorporating I) AuNPs or II) AuNPs-functionalized microcapsules and further release of encapsulated materials. I) CLSM images of (PLL/HA)<sub>24</sub>/PLL film with embedded AuNPs a) before and b) after NIR irradiation, and of the same film with embedded AuNPs and DNA c) before and d) after laser light illumination. PLL in the multilayer films is labeled with fluorescein isothiocyanate (FITC), and DNA with ethidium bromide (EtBr). e) Schematic illustration of the proposed mechanism of DNA release induced by the distortion of the DNA-doping PLL interaction as a result of partial thermal film decomposition around NPs aggregates. II) CLSM images of AuNP-functionalized microcapsules (PDADMAC/PSS)<sub>4</sub>/AuNPs embedded in the (PLL/HA)<sub>24</sub>/PLL film a) before and b) after exposure to NIR light. The inset figures show transmission electron microscopy images of the microcapsules before and after light illumination. Adapted with permission.<sup>[384]</sup> Copyright 2009, American Chemical Society.

such improvement was only evident until reaching an AuNP surface concentration ( $\gamma$ ) of 3%, i.e., at this concentration the film would have accumulated an amount of AuNPs that would correspond to three closed packed AuNP monolayers. Larger amounts of AuNPs led only to partial cell spreading, similar to the one observed at low AuNPs concentrations (1.5%), as shown in Figure 10. These (HA/PLL) AuNPs composite coatings could find promising applications in the biomedical field, such as in drug delivery and cell culture applications for the remote release of desired agents. Other authors also demonstrated the key role triggered by AuNPs on enhancing the mechanical properties of polyelectrolyte multilayer assemblies.<sup>[358,381,388]</sup>

Besides the incorporation of AuNPs on multilayer structures, Skirtach et al.<sup>[369]</sup> have also tested, under mild conditions, the

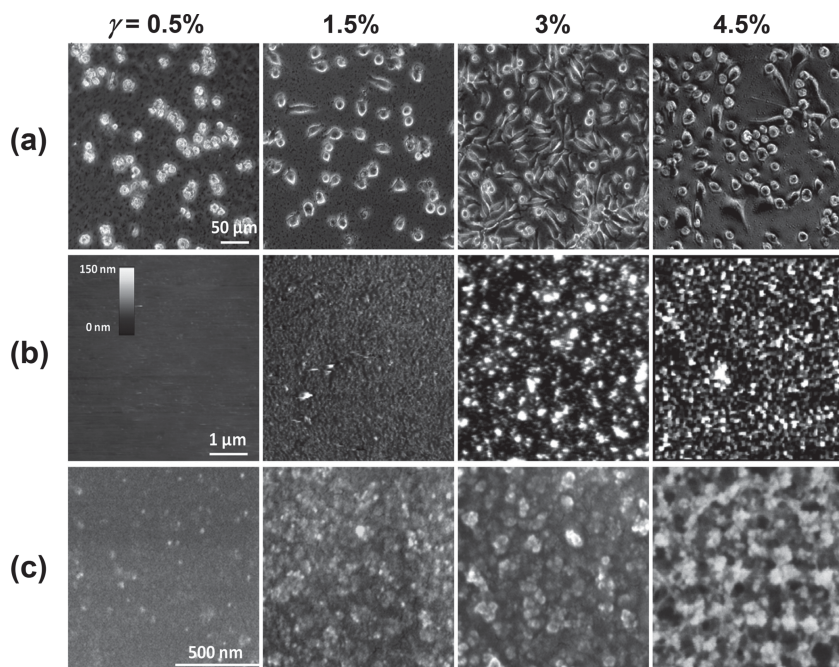
inclusion of gold nanorods with even higher absorption in the NIR region of the electromagnetic spectrum. Such nanorods, which present small size and strong absorption, were deposited on PEM capsules and subsequently used, upon laser illumination, as selective light-sensitive vehicles for opening “small” pores in the capsule walls for the remote release of encapsulated contents.

However, despite the well-known and previously stressed advantages of using NIR light irradiation for biological applications, UV light irradiation has also been used by several researchers to study the properties of LbL assembled films and polymeric capsules, and to control the release of encapsulated or loaded components.<sup>[359,389]</sup> For example, the use of UV light irradiation has been shown on several studies involving TiO<sub>2</sub> nanoparticles and related nanocomposites, that present catalytic activity and oxidative potential. This strategy offers an option to damage capsules, or detach cells, by chemically using UV irradiation,<sup>[360,361]</sup> thus leading to the release of encapsulated molecules. This induced detachment or disruption is most probably due to the transition of the wettability from hydrophilic to hydrophobic state on the basis surface. The developed mechanism is similar to the one that occurs with AuNPs, and involves the production of reactive oxygen species that could influence the stability of chemisorbed bonds, where encapsulated species can be released on demand by irradiation.<sup>[390]</sup> ZnO NPs present the same working mechanism, based on the reversible changes in wettability. However, despite the application of UV light radiation in several research fields, it is commonly accepted that this wavelength range will have limited practical applications in vivo due to the strong absorption of light by biomolecules such as proteins or DNA, and subsequently by the tissues.

In summary, the application of LbL assembly approach to regulate surface behav-

iors under external triggers, namely light-stimulus, is an excellent solution which has been employed by several research groups over the last few years. The incorporation of materials that may absorb electromagnetic radiation and reduce the irradiation requirements, such as AuNPs and TiO<sub>2</sub> NPs, within LbL assemblies assures that such systems are highly sensitive to such kind of irradiation, being extremely suitable for the development of novel smart devices, including next-generation biomedical devices. Furthermore, such versatile NPs can also be incorporated within LbL multilayers to add new functionalities to the multilayer systems, thus constituting promising building blocks presenting key physicochemical properties for several potential applications in several fields ranging from optics, electronics, photonics, catalysis, and energy conversion





**Figure 10.** Overview of the cell adhesion behavior and HA/PLL film surface morphology for different AuNP surface coverage  $\gamma$ . a) Optical microscopy (phase contrast) of the cells on the films after incubation for five days; the cell adhesion is most pronounced for  $\gamma = 3\%$ . b) AFM topography (height) images show the increase in surface roughness upon NP treatment. c) Scanning electron micrographs indicate increase of the AuNP cluster size on the film surface increases as more AuNPs are added to the films. Adapted with permission.<sup>[387]</sup> Copyright 2012, American Chemical Society.

to tissue/cell engineering, wound healing, drug/therapeutic delivery, targeting, diagnostics, or biomaterials and biosensors in biomedicine.

#### 4.2. Incorporation of Functional Dyes within LbL Polymeric Multilayer Assemblies

Dyes are colored compounds that absorb or emit light in the visible spectrum region. They present promising properties such as high versatility, optical stability and small size being highly suitable for several emerging applications, including light-based technological applications. Those that become colored or change color exclusively when under light irradiation, i.e., change their electronic and molecular structure, are known as photochromic dyes. Photochromic compounds can be regarded as photochromic switches as they can exist in two forms of different spectral properties, being thus considered active molecules. When combined with polyelectrolytes, such dyes can form hybrid materials that offer a precise approach to optically control the properties of multilayer thin films.

The use of fluorescent dyes as building blocks within LbL assembled films is difficult due to the neutralizing effect of the electrostatic charge. So, the incorporation of fluorescent labels in such assemblies could be done by adopting one of the following strategies: (a) include monomer units into the polymeric shell after capsule formation<sup>[259,381]</sup> or (b) covalent bound monomers onto a polymer constituent of the multilayer.<sup>[391,392]</sup>

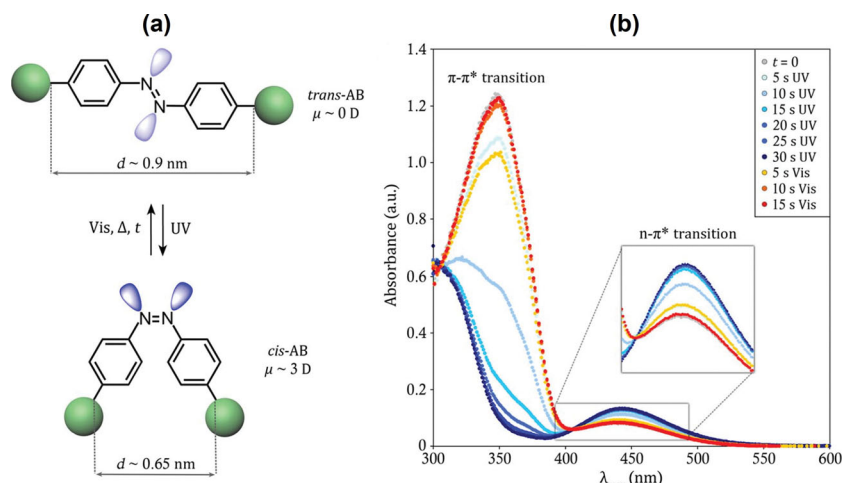
Fluorescent dyes are usually applied to enable the visualization of certain bio-inspired active materials embedded in polymeric multilayer films or polymeric microcapsules. Nonetheless, they can be replaced by inorganic fluorophores, such as quantum dots or NPs, which present enhanced photo-physical properties.<sup>[259,375,393–395]</sup>

In this regard, Skirtach et al.<sup>[259]</sup> have reported the incorporation of fluorescent IR dye (IR-806 Dye) in the outmost layer of PAH/PSS multilayer film to induce the absorption of light. In opposition to that observed in PAH/PSS shells of the non-coated microcapsules, the capsules coated with IR-806 dye disrupted when irradiated with NIR light, even at moderated intensities, thus enabling the release of encapsulated materials. However, the use of simple fluorescent dyes entails the costs of photobleaching the dye, which is irreversible and constitutes a source of active degradable by-products, such as radicals, which limit the range of possible applications as drug delivery systems.

Besides irreversible processes, reversible systems containing organic molecules have also been studied. Porphyrin and phthalocyanine dyes are planar aromatic macrocycles, being members of the larger group of porphyrinoid conjugated cyclic systems

of methine groups that present photoactivity. Moreover, such dyes contain 4 and 8 aza ( $-N=$ ) groups within the ring system, respectively.<sup>[396,397]</sup> They are highly stable and versatile building blocks, displaying great physicochemical properties, and are well-suited to be incorporated within multilayer films and microshells of LbL capsules owing to their broad catalytic, spectroscopic and self-assembly properties.<sup>[398–402]</sup> Therefore, such chromophores and multilayer systems fabricated from them are highly promising for optics, electronics, as well as biomedical applications.<sup>[403,404]</sup> Azobenzene chromophore is also a very interesting group of switchable molecules that respond to both near-UV and visible light radiation.<sup>[405,406]</sup> Such photoactive molecules are one of the most studied examples of materials exhibiting photoresponsive properties which can be integrated within 2D and 3D polymeric multilayer systems making use of the LbL assembly technique.<sup>[407–421]</sup> Such structurally simple and readily accessed molecules, which display two phenyl rings linked by an azo ( $-N=N-$ ) bond, experiment under UV light stimulation a uniquely simple, fast, efficient, clean, and reversible photochemical isomerization from the most energetically stable *trans* to the least stable *cis* geometric isomeric state, being accompanied by fast and significant changes in the physical properties such as polarity, viscosity, geometric shape, electronic structure, and absorbance (see Figure 11).<sup>[380,396,409,422–424]</sup> Such *trans*-to-*cis* isomerization states, which are highly dependent on the irradiation intensity, quantum yields and rate constants for the two processes, free volume, and on the functional groups attached to the chromophores, have been used to





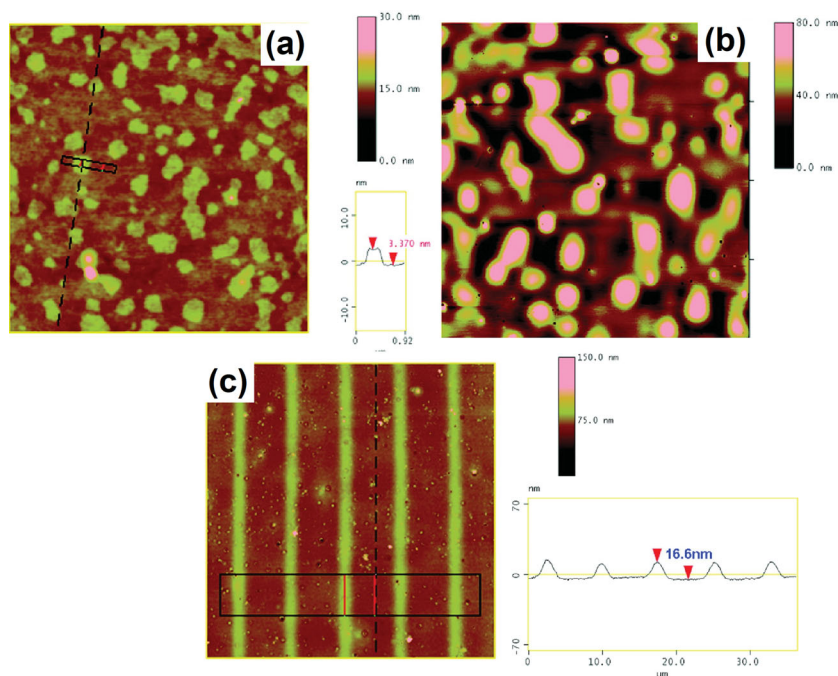
**Figure 11.** a) Geometrical and electronic changes accompanying the azobenzene isomerization process. b) Fast and reversible changes in spectral properties of an azobenzene (here, 4-(11-mercaptopundecano-xyazobenzene)) exposed to UV and visible light (intensity  $\approx 1.0 \text{ mW/cm}^2$  each). The band centered at  $\lambda_{\text{max}} \approx 365 \text{ nm}$  originates from the  $\pi\text{-}\pi^*$  transition in *trans*-azobenzene. The band centered at  $\lambda_{\text{max}} \approx 445 \text{ nm}$  originates from the  $n\text{-}\pi^*$  transition in *cis*-azobenzene. It is important to highlight that the UV-irradiated sample is not a pure *cis* isomer but a photo-stationary state comprising the *cis* form (usually up to  $\sim 90\%$ ) and the *trans* form due to the constant thermal relaxation of the former to the latter. Reproduced with permission.<sup>[424]</sup> Copyright 2010, IUPAC.

trigger several photoresponsive changes on several matrices.<sup>[425]</sup> However, the metastable *cis* isomeric form is not stable and the molecule tend to isomerize back to the *trans* state once the UV light source is removed either thermally or by optical activation, due to the increase in the free volume provided by the expansion of the films.<sup>[426,427]</sup> Overall, both *trans*-to-*cis* and *cis*-to-*trans* reactions proceed with high quantum yields and are completely reversible. The incorporation of azobenzene moieties into substrates modified with polymeric multilayer structures may lead to novel smart functional materials presenting different properties, namely polarity, molecular geometry, viscosity, solubility, degradability, and therefore adaptable self-assembling behavior, well-suited for a broad range of scientific studies covering several areas of research.<sup>[380,425–428]</sup> In addition the permeability of such LbL assemblies can be tuned by controlling the amount of azodye embedded in the polymer backbone.<sup>[429]</sup>

Tanchak et al.<sup>[430]</sup> were the first to report the photomechanical response of a light-responsive system with thermoreversible volume changes. It was found that multilayer thin films composed by azobenzene-functionalized PAA change their conformation when submitted to light irradiation, being of great value for several applications. Controlling the permeability or wettability of surfaces using dyes that have the potential to change their conformation between two isomers with different polarity and chemical properties may

be a promising strategy to obtain photo-responsive systems with high potential, for example, for the controlled release of encapsulated substances without any thermal phenomena. Wang and co-workers<sup>[415]</sup> reported the buildup of electrostatically assembled LbL films comprising highly conductive polymers, such as polyaniline (PANI), and colorful azobenzene-containing polyelectrolyte, and revealed the photoresponsive and electrochromic properties of such multilayer assemblies.

Wang et al.<sup>[431]</sup> reported the fabrication of patterned photoresponsive multilayer thin films incorporating PAA and azobenzene-containing surfactant (AzoTEA) via LbL assembly, and their disassembly by photo-irradiation. As shown in Figure 12, when the surface of the  $(\text{PAA}/\text{AzoTEA})_8$  film (Figure 12a) was covered with a PAA layer larger aggregates (Figure 12b) were formed as the result of the electrostatic complex established between PAA and AzoTEA. In the first instance AzoTEA aggregates were disassembled in a very controlled manner by exposure to UV light irradiation, and subsequently led to the destruction of the whole multilayer film. These films were found to be stable in acetic acid solution (AcOH) at pH 4, unless submitted to UV light irradiation. Nevertheless, by using a mask, it is possible to selectively erase only desired regions of



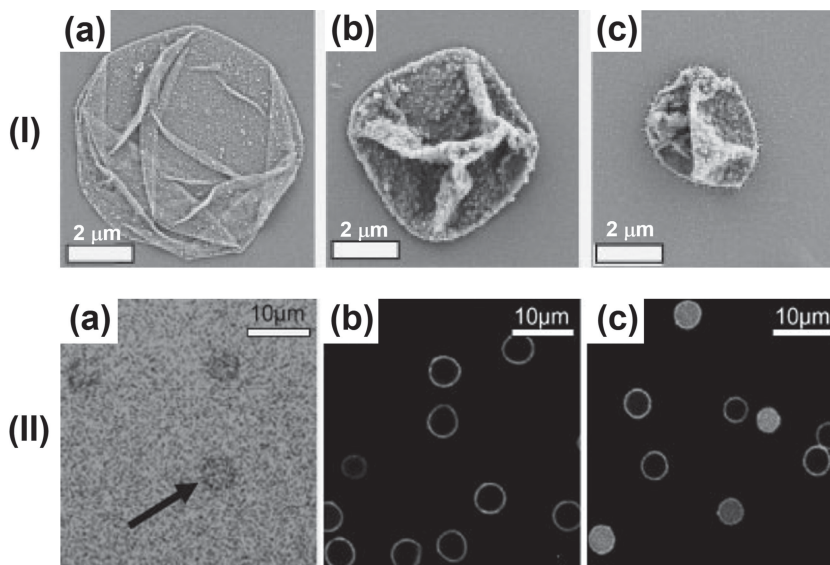
**Figure 12.** Fabrication of patterned photoresponsive multilayer thin films consisting of PAA and AzoTEA. AFM image of the surface of a)  $(\text{PAA}/\text{AzoTEA})_8$  and b)  $(\text{PAA}/\text{AzoTEA})_8/\text{PAA}$ . c) AFM image showing the selectively erased multilayer film after its irradiation with UV light for 600 s under the cover of a photomask. Adapted with permission.<sup>[431]</sup> Copyright 2010, American Chemical Society.

the multilayer film through selective photo-irradiation (Figure 12c), thus allowing the light to irradiate the surface in a precisely patterned fashion.<sup>[431]</sup> This fact, together with the accurate control of the multilayer thickness assures a new framework for the easy fabrication of precisely patterned surfaces for protein or cell adhesion as well as controlled drug delivery. Furthermore, the use of light to promote the disassembly of photoresponsive azo-polyelectrolyte multilayer systems is highly attractive because the reactions are generally clean, simple, and fast and the process does not produce additional chemicals.

In addition to the fabrication of photo-responsive multilayer systems based on synthetic polymers and azopolymers, the construction of light-sensitive systems based on natural-origin polymers and azopolymers has been attracting considerable attention within the scientific community. In this sense, Tercjak and co-workers<sup>[432]</sup> reported the fabrication of photoresponsive multilayer films comprising alternating layers of CHT biopolymer and a water-soluble azopolymer consisting of a poly(vinyl amine) backbone with an azo dye as a side chain, and evaluated the influence of pH and bilayer number on the structure and properties of the films. They found that the decrease of the pH of the CHT solution and the increase of the number of layers induced an increase in the surface and mechanical properties of the films, such as thickness, roughness, and elastic modulus, and achieved a higher level of photo-orientation due to a larger concentration of photoactive azobenzene moieties in the films and cooperative effects among them. These optically active multilayer systems could find promising applications in a wide range of fields, including in optics, electronics, as well as in biotechnological and biomedical fields, owing to the high degree of biocompatibility and biodegradability ensured by the CHT biopolymer.

Besides the construction of 2D photoresponsive multilayer assemblies containing azopolymers, the fabrication of 3D structures, such as hollow capsules, has also been receiving increasing attention. For instance, Sukhorukov and co-workers<sup>[413]</sup> reported the fabrication of light-sensitive hollow polymeric microcapsules by alternate deposition of an azobenzene polymer and PAH on a polystyrene (PS) latex sacrificial template, followed by its dissolution with tetrahydrofuran. The microcapsules evidenced a photo-induced shrinkage behavior when submitted to light illumination (see Figure 13I) and allowed the efficient encapsulation of a fluorescently labeled dextran when a mixture of dye and hollow shells was exposed to intense light irradiation (Figure 13II).

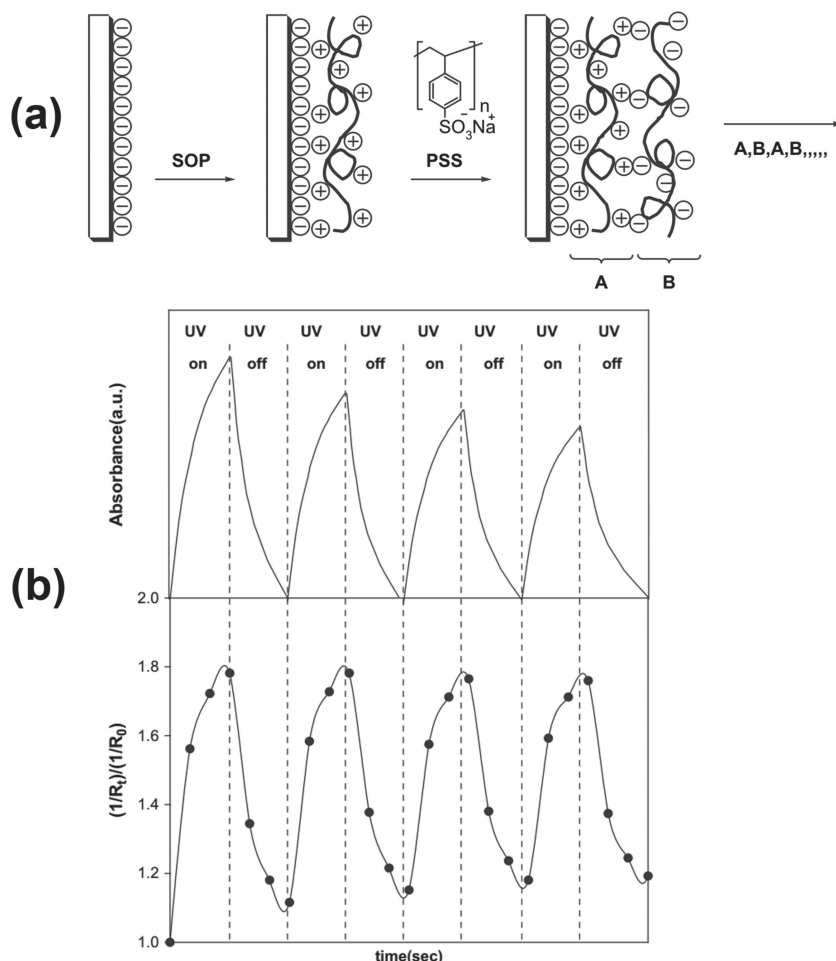
Other highly studied chromophore molecules, which belong to the class of organic photochromic switches and thus present photochromic properties, are spirooxazines (SPO) and spiropyrans (SP). Owing to their photochromic properties, these compounds have the capability of being used in biotechnology and biomedical applications, as well as optical memory



**Figure 13.** Light-responsive polymeric hollow microcapsules. I) Scanning electron microscopy (SEM) images of the capsules a) before irradiation, b) after 60 min, and c) after 8 h of light irradiation. II) Confocal laser scanning microscopy (CLSM) images illustrating the effect of light irradiation on microshells in the presence of a fluorescently labeled dextran. The capsules are permeable to the fluorescent polymer a) prior to irradiation but cannot retain the dye if b) washed unless it is c) irradiated first. Encapsulation is observed after only a few minutes of light irradiation. Adapted with permission.<sup>[413]</sup> Copyright 2007, Wiley-VCH.

devices and optical switches.<sup>[433–435]</sup> SPO molecule structurally consists of two  $\pi$  systems linked by a tetrahedral spiro-carbon. Multilayer films consisting of SPO and PSS have been fabricated making use of electrostatic-based LbL assembly, as schematically shown in Figure 14a.<sup>[436]</sup> Under UV light irradiation, the  $C_{\text{spiro}}-O$  bond of the colorless SPO is cleaved, thus leading to the hydrophilic zwitterionic merocyanine (MC) counterpart which is intensively colored.<sup>[436–438]</sup> MC compound is an isomeric opened form of SPO and SP molecules that is colored due to its extended conjugation and *quasi*-planar conformation. Reversible photoinduced ionic conductivity response, synchronized with reversible heterolytic cleavage of the  $C_{\text{spiro}}-O$  bond under UV light irradiation, was found for the multilayer films comprising PSS and SPO, and raised upon increasing UV light irradiation (see Figure 14b). Nevertheless, to the best of our knowledge, this system has never been applied to controlled release or detachment devices.

Similarly to this system, SP chromophore has been used to functionalize polymers endowing the multilayer films with light-responsive adaptive behavior.<sup>[439]</sup> Likewise to that observed behavior for SPO molecule, the irradiation of hydrophobic SP moieties with light leads to the highly polar hydrophilic zwitterionic MC counterpart that presents a larger dipole moment.<sup>[406]</sup> Pennakalathil and Hong<sup>[440]</sup> have studied the inclusion of poly(acrylate-spiropyran) (PSP)<sup>[435,438,440,441]</sup> as a sacrificial layer in a LbL system, which is triggered by irradiation with visible light. The multilayer films, constructed with 100 layers of PDADMAC and PSS bilayers, were deposited over a light-responsive sacrificial layer composed of five PDADMAC/poly(acrylate-merocyanine) (PMC) bilayers on a silicon substrate.<sup>[440]</sup> Even after the deposition of the desired PDADMAC/PSS multilayer films the sacrificial layers



**Figure 14.** a) Schematic representation of the LbL deposition process consisting of SPO and PSS multilayers. b) Absorbance change at 610 nm and photoinduced ionic conductivity response, following periodic UV irradiation, for SPO/PSS multilayers on ITO substrate at room temperature. Adapted with permission.<sup>[436]</sup> Copyright 2007, Elsevier.

were rapidly disassembled in deionized water after irradiation with visible light. This behavior was probably due to the disappearance of the attractive electrostatic interaction between the neighboring bilayer pairs, as well as to the increase of the hydrophobicity of the light responding layer due to the photoisomerization of zwitterionic PMC to neutral PSP, as confirmed by AFM measurements. Upon UV-light irradiation the neutral SP ring opens, by the heterocyclic cleavage of the bond between the oxygen of the pyran ring and the spiro-carbon, resulting in the intensely colored MC form. This process is reversible through electrocyclization upon UV-Visible light irradiation.<sup>[440]</sup> This simple yet efficient way of preparing free-standing multilayer films avoids the use of harsh release conditions, thus broadening the number and variety of materials that can be incorporated in the free-standing films and extending the potential applications in biomedical field.

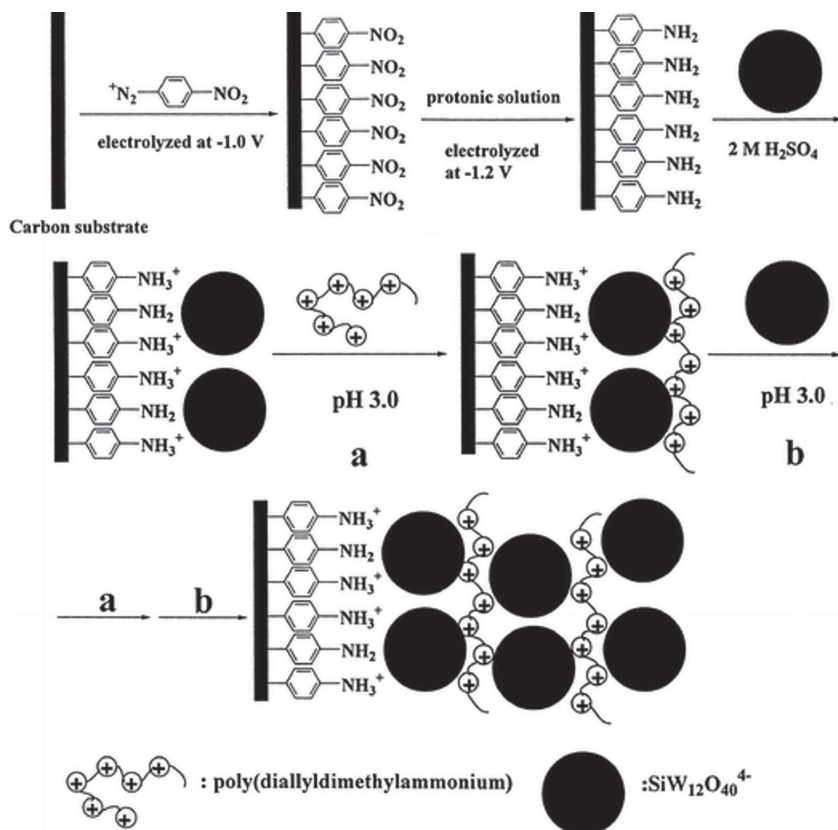
Last but not least, the fabrication of hybrid LbL assemblies containing dendritic macromolecules and the factors influencing their construction have been explored within the last two decades.<sup>[442–448]</sup> This class of materials is constituted by highly branched macromolecules that have unique core-shell

structures consisting of an initiator core, interior layers of repeating branch-cell units attached to the initiator core, and exterior terminal functional groups attached to the outermost interior generation.<sup>[447]</sup> Dendrimers, with regular and highly branched 3D structure, are very promising materials for biomedical applications providing high local densities of active functional groups and though several functionalities that simultaneously solve problems of biocompatibility, toxicity, in vivo stability and specificity.<sup>[449,450]</sup> Moreover, the chemical and physical properties of these materials can be tuned by the introduction of appropriate terminal functional groups as well as internal components,<sup>[405,451]</sup> which make them auspicious candidates for biomedical and biotechnological applications, including biosensing, drug/gene delivery, tissue/cell engineering, catalysis, photonics, electronics, and molecular targets.<sup>[448,452–457]</sup>

The construction of electrostatically assembled LbL films incorporating dendrimers and different types of polymeric materials such as azobenzene molecule,<sup>[458]</sup> PAA,<sup>[459]</sup> sulfonated PANI,<sup>[460]</sup> PSS,<sup>[461]</sup> and poly(glycerol)<sup>[462]</sup> is possible since dendrimers often contain charged surface groups such as amine or carboxyl residues in their constitution.<sup>[448]</sup> Moreover, dendrons with negatively charged carboxylate terminal groups would exhibit electrostatic affinity toward the positively charged layered double hydroxides (LDH) nanosheet surface.<sup>[463]</sup> The combination and modification of dendrons with other functional species, such as anthracene, fullerene, porphyrin, or azobenzene moieties,<sup>[458]</sup> to produce poly(amidoamine) dendrimers have been investigated by several research groups as photoresponsive materials to be applied in several devices.<sup>[464–466]</sup> Nevertheless, the fabrication of such materials is still challenging, thus deserving further comprehensive attention.

As reported above, dendrimer-based LbL assemblies have been widely applied in promising applications such as biosensing and drug delivery. However, when aiming for biosensing purposes, one needs to improve the response induced by such dendrimers, by modifying them for instance with electron transfer mediators or NPs. Moreover, small therapeutic drugs can be covalently attached to the dendrimer surface in order to increase the water solubility of hydrophobic drugs or included in the dendrimer interior through host-guest complexation. Therefore, LbL assemblies incorporating dendrimers can be promising platforms for the development of advanced drug delivery systems. In spite of the already disclosed applications of such assemblies, there is still plenty of room for novel scientific investigations that will fully address dendrimer properties, toxicity and potential behavior in human body.





**Figure 15.** Schematic illustration of the preparation of ultrathin silicotungstic heteropolyanion  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ /poly(diallyldimethylammonium chloride) (PDADMAC) multilayer films. Reproduced with permission.<sup>[467]</sup> Copyright 2000, Royal Society of Chemistry.

#### 4.3. Incorporation of Metal Oxides within LbL Polymeric Multilayer Assemblies

Another strategy commonly used for the preparation of photo-responsive multilayer systems consists in the incorporation of metal oxides within LbL multilayer assemblies. The LbL buildup of composite films incorporating polyoxometalate (POM) clusters has been widely studied along the years in order to evaluate their optical, electrochemical, catalytic, photochromic, electrochromic, and photoluminescent properties.<sup>[467–485]</sup> POMs are highly versatile, thermally stable, and water-soluble building blocks, being thus of great relevance for promising applications in several fields, including biomedical, photoluminescent, photochromic, electrochromic, electronic, optical, magnetic, and catalysis research fields.<sup>[486–494]</sup> **Figure 15** shows a schematic representation of the LbL assembly process consisting of POM and PDADMAC multilayers.

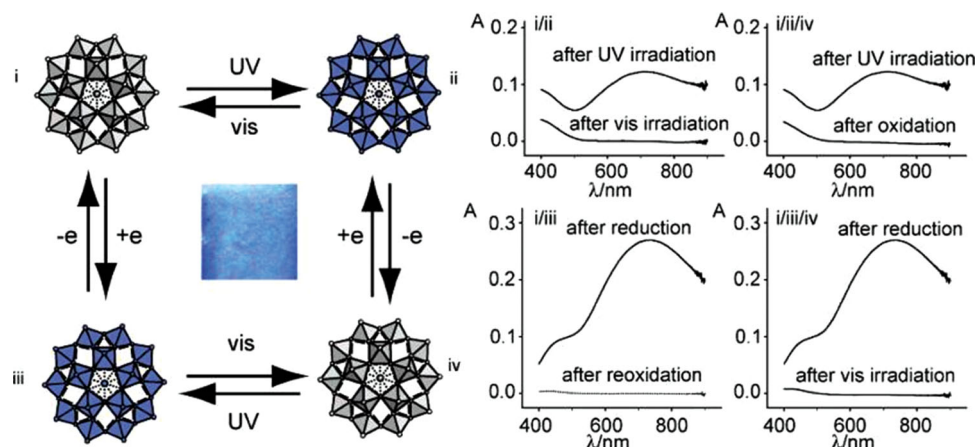
When seeking for photochromic hybrid materials, POMs are associated with organic amines,  $\pi$ -conjugated molecules, or polymers. In such kind of systems the mechanism that usually allows the photoreducible site in the POM is based on the light-induced transfer of a proton from a hydrogen-bonded atom in the organic molecule to a bridging oxygen atom. This issue has been reported as a reversible option of photoresponsive films where the bleaching process is observed when the hybrid material is put in the dark, being the process accelerated by heat and

the presence of oxygen. Such mechanism was recently proposed by Dessapt et al.<sup>[495]</sup> who reported the combination of kinetic studies and theoretical calculations to reveal that the photochromic behavior of organoammonium polyoxomolybdates was based on the homolytic dissociation of  $\text{N}^+-\text{H}$  bonds involved in the  $\text{N}^+-\text{H}\cdots\text{O}$  hydrogen bond associated with the reducible  $\text{Mo}(\text{VI})$  site.<sup>[495]</sup> Moreover, it was postulated that such kind of observation could be extended to other types of POMs.

Several reports have appeared over the last decade on inorganic-organic hybrid light-responsive LbL multilayer assemblies incorporating POMs and organic molecules. For instance, multilayer thin films incorporating dye-POM composite systems such as  $[\text{BW}_{12}\text{O}_{40}]^{5-}$  or  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  with heterocyclic planar and rigid phenothiazine or phenoxazine composite films, and iron-substituted crown-type POM  $[\text{P}_8\text{W}_{48}\text{O}_{184}\text{Fe}_{16}(\text{OH})_{28}(\text{H}_2\text{O})_4]^{20-}$  with methylene blue dye have been prepared by electrostatic LbL assembly approach.<sup>[496,497]</sup> Furthermore, multilayer assemblies comprising Preyssler- or Keggin-type POMs ( $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  and  $[\text{SiMo}_{11}\text{VO}_{40}]^{5-}$ , respectively) and poly(ethyleneimine) (PEI),<sup>[277]</sup> poly(4-vinylpyridine) (P4VP)<sup>[498,499]</sup> or PAH,<sup>[500]</sup> europium phosphomolybdate  $[\text{EuP}_2\text{Mo}_{22}\text{O}_{78}]^{11-}$  or Keggin-type POM and natural-based polymers, such as CHT,<sup>[501,502]</sup> lanthanide POM ( $[\text{EuP}_4\text{W}_{34}\text{O}_{122}]^{17-}$ ,  $[\text{EuSi}_2\text{W}_{22}\text{O}_{78}]^{13-}$ ) or europium derivative of the Preyssler-type POM  $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$  and PAH,<sup>[503,504]</sup> and Keggin-type POM  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and 1,12-diaminododecane<sup>[505]</sup> have also been fabricated by the same technology.

In this concern, Kurth and co-workers<sup>[499]</sup> showed that multilayer films based on Keggin-type POM  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  and P4VP reversibly changed their color from transparent to blue by either photo- or electroinduced stimulation or by combination of both modes (see **Figure 16**), thus showing excellent photochromic and electrochromic properties.

Nagaoka et al.<sup>[277]</sup> designed and fabricated photochromic multilayer films comprising Preyssler-type POM  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  and PEI multilayers using LbL assembly technology. It was shown that the outermost PEI layer could be detached by UV light irradiation in aqueous solution, thus exposing the underlying POM layer (see **Figure 17I**). Such polymer release was assigned to the photoreduction of the tungsten atom ( $\text{W}^{6+} \rightarrow \text{W}^{5+}$ ). Further dipping of the substrate into the PEI solution enabled the deposition of a new PEI layer, thus allowing a reversible and high degree of control over the surface properties. Although this work acts as a proof-of-concept which demonstrates the feasibility of such light-responsive systems to disassemble desired layers, to the best of our knowledge, such concept has never been effectively tested and applied to any smart delivery device. The authors also reported the photopatterning of the detached



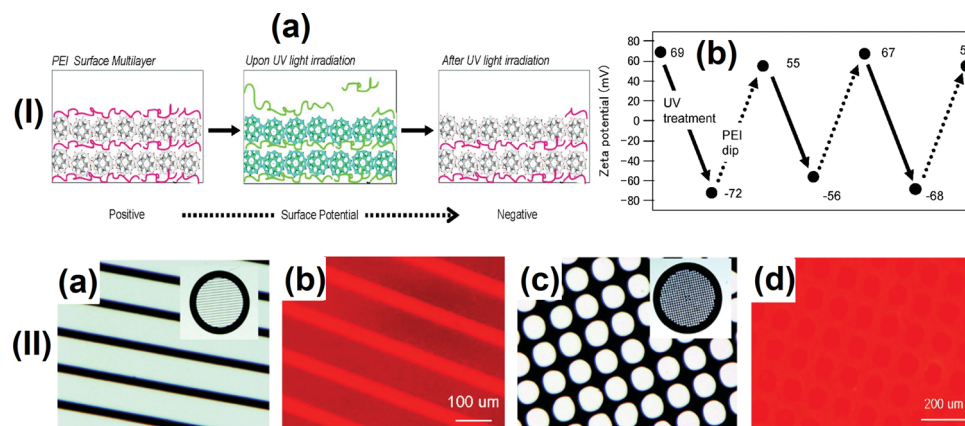
**Figure 16.** Schematic illustration of the photochromic and electrochromic behaviors of the  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  Preyssler-type POM/P4VP multilayer film. The multilayer film can be colored by either irradiation with UV light ( $i \rightarrow ii$ ) or by reduction ( $i \rightarrow iii$ ) or by both modes in succession. Bleaching is effected by irradiation with visible light ( $ii \rightarrow i$ ) or oxidation ( $iii \rightarrow i$ ). In addition, photoinduced coloration ( $i \rightarrow ii$ ) can be followed by oxidation ( $ii \rightarrow iv$ ), or electrochemically induced coloration ( $i \rightarrow iii$ ) can be followed by bleaching with visible light ( $iii \rightarrow iv$ ). Also shown are the corresponding spectra (right). The center of the figure shows a representative photograph of a colored window. Reproduced with permission.<sup>[499]</sup> Copyright 2006, American Chemical Society.

PEI layer, with highly-site selective adsorption of small fluorescent particles, by the inclusion of photomasks in the substrate just before the image-wise UV irradiation (Figure 17II). The obtained films displayed a well-defined form which resembled the used photomasks. Indeed, the photochromism exhibited by the POM layer is the main reason for the disappearance of the electrostatic interaction at the interface between PEI and  $(\text{NaP}_5\text{W}_{30}\text{O}_{110})^{14-}$ , being the hydrogen bonding interaction between the nitrogen of PEI and transferred hydrogen generated instead of the electrostatic bonding.<sup>[277,488]</sup>

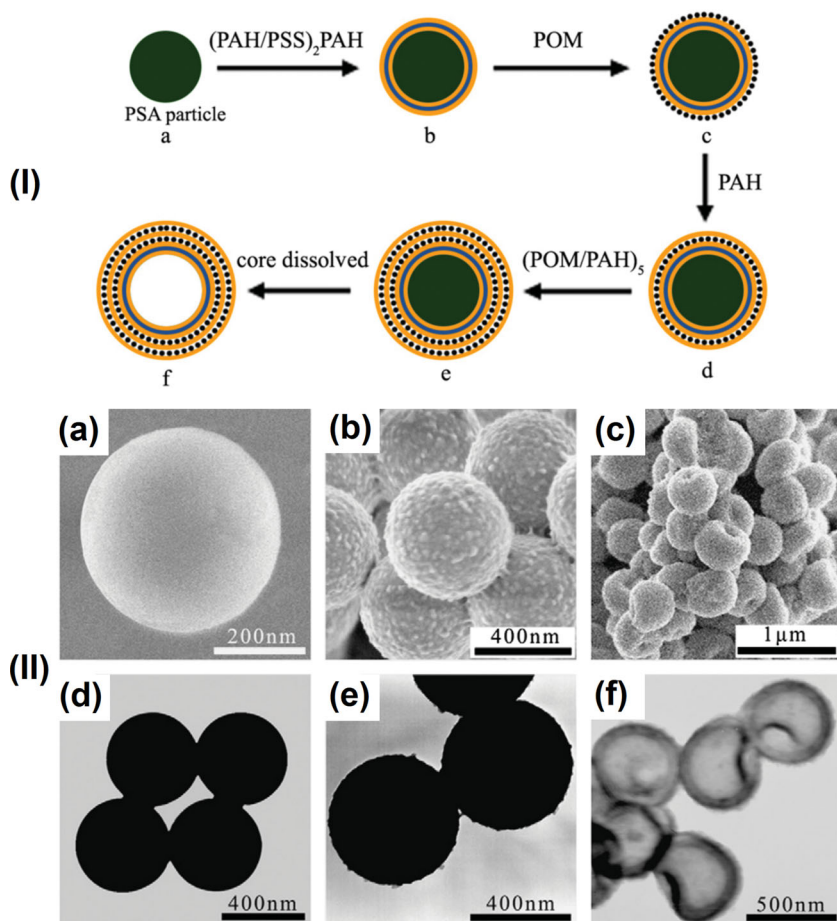
Beyond 2D planar surfaces, hybrid LbL multilayer assemblies incorporating POMs and polymers have also been constructed on the shell of 3D spherical capsules,<sup>[506–512]</sup> obtained after the removal of the particle core by suitable solvents. For instance, Xu and co-workers<sup>[506]</sup> and Cui et al.<sup>[510]</sup> constructed hybrid multilayer films comprising different types of POMs and PAH on the surface of manganese carbonate ( $\text{MnCO}_3$ ), PS, or

poly(styrene-acrylic acid) (PSA) core particles (see Figure 18). After the formation of the multilayer shells, the sacrificial particle core was dissolved with appropriated solvents, and hollow capsules were then obtained (Figure 18I). Such capsules showed an apple-like shape (see Figure 18II) probably due to the fact that the shell was not consistent enough to maintain the initial spherical structure of the PSA latex particles and would collapse at the thin place. Nonetheless, the hollow capsules remained intact over the fabrication process, as confirmed by the absence of holes of rupture on it. These capsules incorporating POM-based materials could be potentially used as highly versatile reactors, which would enable to mix several compounds.

Although several promising potential applications have already been assigned to this technology, i.e., to inorganic-organic hybrid POM-based multilayer assemblies, to the best of our knowledge none has been effectively tested. Meanwhile, as the LbL assembly technique is well established<sup>[277,496–512]</sup> and



**Figure 17.** Fabrication of photochromic multilayer films comprising Preyssler-type POM  $\text{NaP}_5\text{W}_{30}$  and PEI multilayers. I) Schematic illustration of the a) photodetachment of the outer layer of  $(\text{NaP}_5\text{W}_{30}\text{O}_{110})^{14-}$ /PEI multilayer films, and b) zeta potential switching for the multilayer films by alternate irradiation with UV light for 15 min in aqueous solution and further dipping in a PEI solution for 20 min. II) Optical microscope images of the a,c) copper TEM grid photomasks and b,d) fluorescence microscope images of fluorescent particles assembled on a photopatterned  $(\text{PEI}/\text{NaP}_5\text{W}_{30})_3/\text{PEI}$  surface. The inset images in a) and c) show overall images of the photomasks (both of 3 mm diameter). Adapted with permission.<sup>[277]</sup> Copyright 2008, American Chemical Society.



**Figure 18.** Construction of organic-inorganic hybrid multilayer assemblies incorporating POMs and polyelectrolytes on the shells of 3D spherical structures. I) Schematic illustration of the LbL assembly of PAH, PSS and POM [Mo<sub>72</sub>Fe<sub>30</sub>] on PSA latex particles and further hollow microcapsules. The first stage (a–b) involves stepwise deposition of polyelectrolyte on PSA colloidal particles. (b–e) Alternative assembly of PAH and POM [Mo<sub>72</sub>Fe<sub>30</sub>] on spherical PSA particles. (e–f) Dissolution of PSA cores and formation of hollow microcapsules. II) SEM (a–c) and TEM (d–f) images of PSA latex particles (a, d), [(PAH/PSS)<sub>2</sub>(PAH/[Mo<sub>72</sub>Fe<sub>30</sub>])<sub>6</sub>PAH] capsules assembled on PSA particles (b, e), and hollow [(PAH/PSS)<sub>2</sub>(PAH/[Mo<sub>72</sub>Fe<sub>30</sub>])<sub>6</sub>PAH] capsules (c, f). Adapted with permission.<sup>[510]</sup> Copyright 2009, Elsevier.

the photoremoval of the electrostatic interactions between the interfacial layers will generate instability, and subsequently film disassembling, promising devices are envisaged which will cover several practical applications. Therefore, in our point of view the fabrication of hybrid multilayer assemblies incorporating POMs may be successfully applied to create advanced and smart biomedical devices, including drug delivery or cell detachment systems, and tissue engineering devices or prototypes. However, the in vivo application of such systems is for now only a desired issue that would face further insights and challenges, thus deserving an in-depth research.

## 5. Concluding Remarks

LbL assembly of multilayer films is a highly promising strategy to create dynamic smart systems both from simple 2D planar platforms and complex 3D substrates. The main advantages

of this technique are its low-cost, flexibility, and versatility which allows the incorporation of a plethora of materials (e.g. biomacromolecules, inorganic compounds, organic molecules, colloids) in the multilayer system. Moreover, such powerful technology enables the modification of any kind of surface as well as the fabrication of robust and highly ordered nanostructured polymeric thin films and nanocomposites with tailored architectures, structures, compositions, thicknesses, properties, and functions well-suited for several applications in emerging areas such as biomedicine, biosensing, drug delivery, tissue engineering and regenerative medicine, electronics, optics, textiles, and so forth.

Smart systems incorporating polymers with optically addressable properties are being widely investigated within the last few years due to their extremely mild conditions responsiveness and potential applications in the biomedical and biotechnological fields, especially in tissue engineering, and as drug delivery vehicles or cell detachment supports. Moreover, inspired by nature, such light-responsive systems can be also combined with other external triggers in order to design and develop novel promising dynamic smart multifunctional materials exhibiting complex multiresponsive behavior, improved sensitivities, capabilities and functions, and desirable properties to adjust to our demands. Although much has been achieved to date on stimuli-responsive LbL assemblies, there are still remaining scientific and technical challenges and opportunities that need to be addressed and new avenues to be explored in several research fields. In this context, the work of many research groups such as Möhwald, Sukhorukov, Caruso, or Sukhishvili's research groups on photoresponsive mul-

tilayer assemblies is well-known and of great interest for the scientific community, mainly due to their great contribution to fully understand the environmental conditions behind the disruption of polymeric thin films and polymer-based microcapsules, constructed via LbL assembly approach, to further release or encapsulate active desired molecules in a very controlled fashion.

To date, most of the studied films were designed, developed, and investigated for near-UV irradiation. Depending on the strategies employed and on the UV irradiation intensity, different responses can be achieved. For instance, the incorporation of NPs in LbL multilayer films and polymeric capsules is undoubtedly one of the most efficient ways to trigger an optical response and to damage structures, such as microcapsules, and subsequently release encapsulated materials through UV light irradiation. However, UV and visible light are not the best choice for applications in devices with medical purposes because human body is opaque to this radiation section. Oppositely, NIR



radiation has proven to be a very promising tool for triggered drug delivery,<sup>[356]</sup> photothermal cancer treatment,<sup>[359]</sup> and in vivo imaging<sup>[360]</sup> overcoming many of the drawbacks coming from UV and visible light irradiation. As stated above, one of the main shortcomings of UV-Visible light irradiation is its minimal absorption by skin and tissues, which would only enable the penetration into the body up to 10 cm. In this context, the use of NIR light is particularly attractive for biomedical applications since most of the tissues do not absorb or at least show weak absorption of NIR radiation, and such radiation does not induce significant heating in the application area.

A well-known strategy to obtain light-responsiveness to NIR radiation section consists in including Ag and/or AuNPs in the LbL multilayer assemblies. Such particles not only improve the optical, mechanical, electrical, magnetic, and catalytic properties of LbL assemblies, but also allow an enhanced control over the release of encapsulated materials. These metal NPs absorb photons and convert them into heat using low energy irradiation sources, thus potentially affecting all the materials in the surrounding environment. The size and shape of the particles can significantly decrease the demand of irradiation needed, as well-proved by the use of nanorods and aggregates. The nanorods also allow the attainment of a reversible system due to the small size of the pores produced that get sealed when irradiation is stopped. However, due to the incorporation of particles within the LbL assemblies, the remote release of (bio)-degradable materials, resulting from the disruption of the capsules, still encloses toxicity concerns. Therefore, the evaluation of the materials in terms of toxicity, biodegradability, and biocompatibility is a crucial step when looking for biotechnological or biomedical applications.

In this review we have provided an overview about the fabrication of photoresponsive LbL multilayer assemblies using different building blocks (e.g. polymers, metal NPs, functional dyes, metal oxides) with well-defined architectures, compositions, properties, and functions as well as their potential applications. Moreover, future challenges and opportunities concerning the combination of such materials and light stimulus to create precisely assembled 2D and 3D dynamic smart functional systems or devices with controlled accessibility and tailored architectures, structures, properties, and functions for several “new cutting-edge applications” are also addressed.

## 6. Future Perspectives

The overwhelming majority of studies reported in the literature are focused on the fabrication of LbL multilayer assemblies with light-induced responsiveness without taking many considerations about the polymer features, stability, and toxicity induced by its by-products which are key issues to address several practical applications. Moreover, most of the works on light-sensitive systems are based on synthetic polymers. Therefore, in order to obtain a real system, that could resemble the natural living systems and be applied in biomedical devices, natural-based materials should be used and explored. The use of natural-inspired polymeric systems offers great advantages for several applications, namely biomedical applications, owing to the high levels of similarity with biomolecules.<sup>[513]</sup> Furthermore, natural-based

materials also overcome some undesired issues, such as toxicity and instability, often perceived with synthetic polymers. In addition, when aiming for the application of smart photoresponsive devices in the biomedical field, the adjustment to NIR radiation in replacement to UV and visible light is highly required, due to the low absorption of NIR radiation by skin and most of the tissues. Having this in mind, new chromophore groups are needed with larger two-photon absorption cross sections, as well as new procedures that would allow a reduction of the resource to high power density-lasers, actually associated to efficient drug release. The speed, diversity, modularity, and reversibility of generated stimuli-responsive LbL assemblies is also a key point in order to design and engineer desirable and novel functional smart materials exhibiting complex responsive behavior highly suitable to be applied in various research fields including in chemistry, physics, biology, materials science, medicine, engineering, or biotechnology. Moreover, a better understanding of the structure-property relationship and wavelength correlation in such switchable materials is vital in order to shed light on the mechanisms and processes of molecules formation as well as improve and rational design “next generation” smart multifunctional systems with specific response features and tailored properties and functions increasingly attractive for practical applications in a wide range of areas, such as biotechnology and biomedicine. Besides the materials used, topography plays also a very important role on how light interacts with surfaces. One great example of the use of natural-based textured materials and their response to light irradiation found in nature is the case of butterfly's wings. The cuticle on the scales of the butterflies, which is composed of semitransparent natural polymer chitin separated by thin air layered nanostructures (known as laminae), selectively reflect certain wavelengths of light depending on the exact structure and interspatial distances of light-interacting layers. By learning from these natural systems and trying to mimic their behaviors, novel coatings, patterned surfaces, or smart photonic materials, that would change color on demand, could be designed and fabricated, which would be very useful for several emerging applications, such as in biomedicine, biotechnology, textiles, energy, or optics.

Furthermore the evaluation of the in vivo performance of the biomedical or biotechnological devices developed through the use of switchable materials is also a crucial issue that has not been studied in detail and, thus, deserves further comprehensive attention in the near future. This is a very limitative step that will allow us to transpose the knowledge gathered from the research laboratories to practical clinical applications, thus having a great impact on our daily lives. In this concern, while remarkable progress has been achieved to date through the introduction of stimuli-responsive materials, exciting opportunities and challenges still remain open in the field of smart materials in order to obtain real devices with proper specificity and uniqueness, and proven applicability in the biotechnology and biomedical fields.

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