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Introduction

1.1 Research Status of Photofunctional Polymer Composites

1.1.1 Photofunctional Materials

Photofunctional materials refer to the optical materials that use the principle that the optical properties of the material itself (such as refractive index or induced electric polarization) change under the action of the external field (such as electricity, light, magnetic, thermal, acoustic, and force) to achieve the detection, modulation, and energy or frequency conversion of the incident light signal. With the rapid advancements in modern science and technology, photofunctional materials are driving profound changes in many high-tech fields. Their application not only broadens the channel of energy acquisition but also exerts far-reaching influence on information storage, display technology, medical diagnosis and treatment, and other fields [1–3].

At present, the world is facing problems such as energy crisis and environmental pollution, which seriously affect the sustainable development of society. Traditional materials have gradually revealed their limitations in dealing with these complex problems. First of all, the traditional materials used for energy conversion and storage are less efficient, and it is difficult to make full use of renewable energy, resulting in significant reliance on fossil fuels, exacerbating the energy crisis. Secondly, the problem of environmental pollution is becoming increasingly prominent, and the production and use of traditional materials are often accompanied by high energy consumption and a large number of pollutants, which is not in line with the eco-friendly development model. In addition, with the increasing aging of the global population, the demand for medical health has increased significantly, but traditional materials have shortcomings in biocompatibility, intelligent responsiveness, and versatility, and it is difficult to meet the requirements of precision medicine and personalized health management [4]. For example, traditional materials used for medical device implantation are less biocompatible and may trigger inflammatory responses. In the field of disease diagnosis and treatment, traditional materials have a single function, making it difficult to achieve multifunctional synergies and dynamic response effects. In addition, the development of modern information and

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intelligence requires materials with higher performance, while the shortcomings of traditional materials in terms of flexibility, lightweight, and intelligent response limit the further breakthrough of emerging technologies [5]. At the same time, with the acceleration of digitalization, traditional materials are also showing limitations in the face of high-speed data transmission, large-capacity storage, and digital medical needs. Therefore, new, efficient, and sustainable materials are urgently needed for social development.

As an important material, photofunctional materials stand out in many fields by virtue of their excellent photoelectric conversion efficiency, photosensitive response characteristics, and photocatalytic ability, and become one of the key materials to promote the sustainable development of society. In the field of green energy, solar cells based on light-functional materials are widely used, effectively reducing the dependence on fossil energy, promoting the use of renewable energy, thus easing the energy crisis. At the same time, the photocatalytic degradation technology of photofunctional materials has shown great potential in reducing air pollution and water pollution, significantly reducing the emission of industrial harmful substances, and promoting environmental protection and green development. In the field of information storage and communication technology, photofunctional materials play a central role because of their excellent optical properties and low-loss characteristics. Optical fiber communication uses photofunctional materials to transmit data, which not only greatly improves the transmission rate but also effectively avoids electromagnetic interference, and realizes high-speed, remote, and large-capacity real-time data transmission. In the area of display technology, materials used in organic light-emitting diode (OLED) have been gradually applied to mainstream display technology with their excellent self-luminous characteristics, high contrast, and low energy consumption advantages, and have achieved the popularity of ultrathin and flexible displays [6]. In addition, photofunctional materials have also made significant progress in biomedical fields such as disease diagnosis, precision treatment, and health monitoring. For example, photodynamic therapy (PDT) relies on photosensitizers to produce reactive oxygen species (ROS) upon illumination with light at specific wavelengths, thereby selectively killing cancer cells, which is a noninvasive treatment with low side effects [7]. With its high-resolution imaging capability, fluorescence imaging technology has achieved remarkable results in the accurate diagnosis of tumors and other diseases, greatly improving the efficiency and accuracy of diagnosis and treatment. With their excellent physical and chemical properties, photofunctional materials are gradually replacing traditional materials and have widespread use in areas like energy, environmental protection, information technology, and biomedicine. They are becoming an important force to cope with global challenges and promote sustainable development.

According to the composition and structural characteristics, photofunctional materials can be divided into inorganic materials and organic materials (Figure 1.1). Both have their own characteristics in molecular structure, optical properties, and application fields, and occupy an important position in modern science and technology. Inorganic photofunctional materials usually have a highly ordered crystal

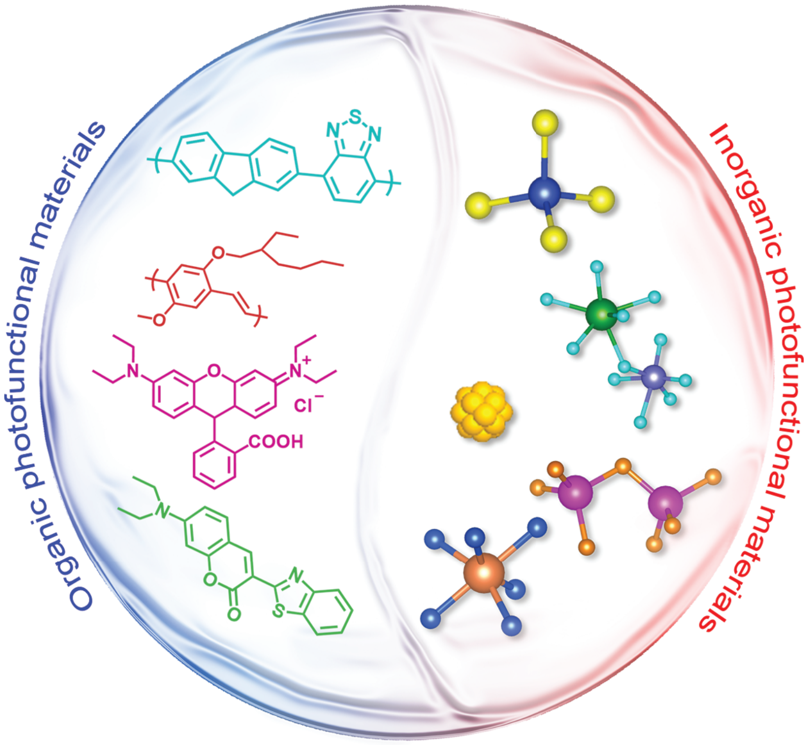

Figure 1.1 Inorganic and organic photofunctional materials.

structure, showing excellent stability, electrical conductivity, and optical properties, while organic photofunctional materials have unique advantages in some fields of application because of their good processability, flexibility, and adjustability.

Inorganic photofunctional materials are mainly composed of metals, semiconductors, or their compounds (such as oxides, nitrides, or halides). Their structure gives them excellent stability, electrical conductivity, and optical properties, making them play an important role in high-precision optoelectronic applications. For example, oxide materials (such as TiO_2 and ZnO) are widely used in the fields of photocatalysis, photodetectors, and sensors due to their excellent chemical stability and photocatalytic properties. Nitride materials, such as GaN and InN, play a key role in efficient light-emitting and high-power electronic devices, as the core material of modern LED technology. Perovskites are outstanding in the field of solar cells and photodetectors for their high photoelectric conversion efficiency and excellent machinability. In addition, gold nanoclusters (AuNCs), as a class of metallic nanomaterials with unique optical properties, have received considerable interest within the area of photofunctional materials lately. Due to their small particle size and quantum effect, AuNCs exhibit unique fluorescence characteristics and are widely used in biological imaging, sensors, and catalytic reactions.

Organic photofunctional materials are usually composed of carbon-containing molecules or polymers with conjugated π-electron systems in their molecular structures. This structure gives organic materials unique optical properties and good processing flexibility, making them show great potential in flexible electronics, wearable devices, display technology, and other emerging fields. For example, conjugated polymers (CPs) achieve efficient photoelectric conversion and luminous properties through the intramolecular π-electron delocalization effect. In addition, fluorescent dyes such as rhodamine and indole compounds are widely used in biological imaging, sensors, and laser labeling due to their excellent luminous efficiency and tunability. With the continuous development of organic materials, new organic semiconductors and fluorescent materials continue to emerge, further promoting the application of organic optoelectronic devices in the fields of intelligent display, wearable sensors, and optical communication technology.

Although inorganic and organic photofunctional materials show certain advantages in their respective application fields, there are also many shortcomings. These defects hinder their application in some fields. Inorganic materials are often brittle and difficult to adapt to flexible substrates, affecting their universality in flexible electronics, smart displays, and wearable technologies. In addition, the preparation of many inorganic materials is complex and costly, limiting the feasibility of large-scale, low-cost manufacturing. For example, although oxide and nitride materials perform well in photocatalytic and photoelectric conversion performance, the preparation process requires operating under high temperature and pressure, which makes manufacturing costly. Although the photoelectric conversion efficiency of perovskite is excellent, its stability is poor, and it is susceptible to deterioration under the influence of moisture, air, and ultraviolet light, and lacks long-term reliability. In contrast, organic materials have the advantages of flexibility and low cost, but poor stability and easy to be affected by the external environment (such as oxygen, moisture, and ultraviolet light). Organic photoelectric devices show high photoelectric conversion efficiency in the early use, but they are prone to performance degradation and short service life after long-term use. In addition, compared with inorganic materials, organic materials have lower carrier mobility, so their photoelectric conversion efficiency and luminous intensity are lower, limiting their application in high-power and high-performance optoelectronic devices.

1.1.2 Photofunctional Composites

In order to overcome the deficiency of single photofunctional materials, in recent years, researchers have developed photofunctional composites with better performance by combining inorganic materials with organic materials, giving full play to the advantages of both. These composites combine the high stability and excellent photoelectric performance of inorganic materials with the flexibility and adjustability of organic materials, showing significant advantages in many aspects [8]. Inorganic/organic composites not only have high photoelectric conversion efficiency but also improve the environmental stability of the material, and are widely used in flexible electronic devices and wearable devices. In addition, the preparation process of composites also has significant advantages. This feature greatly reduces the production cost and lays a foundation for the industrial application of composites. Therefore, the combination of inorganic and organic photofunctional materials not only makes up for their respective shortcomings but also has a wide scope for future applications [9], showing great potential in the fields of efficient optoelectronic devices, intelligent sensors, optical communication technology, and green energy.

The enhancement of performance by photofunctional polymer composites is chiefly manifested in the following ways.

Firstly, through interface optimization and electronic structure regulation, the carrier separation and migration efficiency of the composite are significantly improved. When inorganic materials with high conductivity and organic materials with excellent photoelectric properties are combined, favorable electron transport channels can be formed, which makes the transfer of charge carriers within the material more efficient. Optimizing the interface between inorganic materials and organic materials can improve the transmission path of electrons and holes, reduce interface defects and energy loss, and thus improve the photoelectric conversion efficiency.

Secondly, the combination of highly stable inorganic materials and flexible organic materials enables the composite to maintain excellent performance in extreme environments. Inorganic materials usually have high thermal and chemical stability, but lack flexibility, which is difficult to meet the application scenarios that require high flexibility, such as wearable devices. Although organic materials have good flexibility, they have poor stability and are easily degraded in high-humidity and high-temperature environments. By combining inorganic materials with organic materials, the stability advantages of inorganic materials and flexible characteristics of organic materials can be fully utilized to prepare photofunctional composites with both high mechanical flexibility and good environmental stability. This material can better adapt to complex external environments, extend service life, and maintain efficient photoelectric performance in flexible electronic devices, wearable devices, and other fields.

The multifunctional synergies of composites significantly enhance their application potential in various fields [10]. The composite of inorganic and organic photofunctional materials not only realizes complementary advantages in photoelectric conversion but also shows synergistic effects in many other functional fields. For example, by combining photocatalytic properties with photoelectric properties, composites can not only efficiently convert solar energy but also degrade environmental pollutants, thus serve as a key contributor to green energy and environmental governance.

In the field of biomedicine, composites of metal nanoclusters and organic polymers show unique versatility. For example, the excellent fluorescence properties of gold nanoclusters provide high resolution for bioimaging, while organic polymers give materials good biocompatibility and adjustability. These properties make composites show great potential in areas such as precision diagnosis, targeted therapy, and real-time imaging, which is expected to promote the development of smart medical technology.

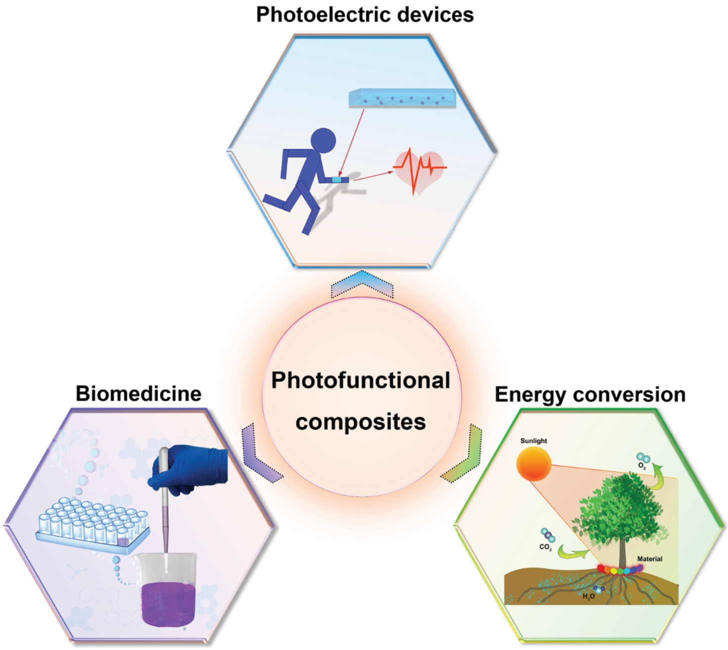

Figure 1.2 Application of photofunctional composites.

In addition, the synergistic effect of composites has also been extended to smart sensors, optical communication, and smart wearable devices, further enhancing the multifunctional integration and intelligent application performance of the material. With the steady evolution of material design and synthesis technologies, the multifunctional synergies of composites will accelerate their innovative applications in various technical fields (Figure 1.2).

1.1.2.1 Photoelectronic Devices Based on Photofunctional Polymer Pomposites

For organic photovoltaic cells, the photofunctional polymer composites can effectively increase the cell's efficiency in absorbing light and facilitate better charge transport. Photofunctional polymer materials usually have a highly conjugated structure and are able to act as donor materials and form efficient heterojunction structures with acceptor materials, thus facilitating the separation of excitons and the transport of electric charges. In addition, by introducing different side groups or adjusting the backbone structure, the energy level and electron mobility of the polymer can be adjusted, thereby improving the charge transport efficiency and the overall performance of the device [11]. However, photofunctional polymer materials still face some problems that limit their practical application, such as low photoelectric conversion efficiency, low carrier mobility, and susceptibility to photooxidation and thermal degradation under long-term light and environmental exposure conditions.

Photofunctional polymer composites usually broaden the light absorption range of the polymer matrix by introducing inorganic nanoparticles (such as perovskite [12] or quantum dots [13]) with wide spectral absorption properties, and improve the efficiency of photogenerated carrier generation. Certain metal complexes can effectively absorb specific wavelengths of light, thereby improving the light absorption efficiency of organic photovoltaic cells. At the same time, the inorganic nanoparticles form a conductive network in the polymer matrix, which helps to promote the separation and transmission of photogenerated charge, reduce the probability of charge recombination, and further improve the photoelectric conversion efficiency. In addition, photofunctional polymer composites can also be used in interface engineering to optimize the charge separation process by adjusting the energy level structure and the interface state density at the interface.

In OLEDs, photofunctional polymer materials are commonly used as the main material and charge transport layer of the light-emitting layer to provide efficient light emission. Inorganic nanoparticles (such as quantum dots) can be embedded in the light-emitting layer to widen the range of absorbed light and promote more efficient separation of photogenerated carriers [14]. However, the aging rate of photofunctional polymer materials is faster. Inorganic nanoparticles may also accumulate or migrate during long-term use, which affects the stability of the device. In addition, the interface stability between the inorganic nanoparticles and the organic light-emitting layer may reduce the charge injection and transport efficiency. From the perspective of material design, the introduction of inorganic nanoparticles into photofunctional polymer composites can broaden the emission spectrum, improve the photoluminescence quantum yield, and enhance the stability of materials [15].

1.1.2.2 Photocatalytic Application of Photofunctional Polymer Composites

In the field of photocatalytic decomposition of water, photofunctional polymer materials still have some problems. The light absorption range of these polymers is primarily confined to the visible region, resulting in poor absorption of ultraviolet and near-infrared light. To solve these problems, chemical modification of photofunctional polymer materials alone is not sufficient. By introducing inorganic nanoparticles, the light absorption range can be further broadened, and heterostructures can be constructed, using the interfacial electric field to promote the separation of photogenerated charge carriers, while enhancing the environmental stability of the material. For example, noble metal nanoparticles with local surface plasmon resonance (LSPR) effects can enhance the material's light absorption capacity in the ultraviolet to visible light range, thereby improving the efficiency of photocatalytic reactions [16]. For the inorganic nanoparticles themselves, they are prone to agglomeration or chemical corrosion in a long-term light and water environment, and there is also the problem of low efficiency of photogenic carrier separation. To this end, it is combined with a photofunctional polymer material, which will better help the inorganic nanoparticles disperse and effectively improve their stability under light [17].

1.1.2.3 Biomedical Application of Photofunctional Polymer Composites

In the field of biomedicine, photofunctional polymer composites are mainly used in diagnosis and imaging, drug delivery and therapy, tissue engineering, and regenerative medicine. Materials used in the biomedical field must first have good biocompatibility, that is, they do not cause inflammation or immune rejection after contact with biological tissues. In addition, it is best to design materials with self-adaptability and certain mechanical strength, so as to ensure their normal function in complex biological environments.

In terms of diagnosis and imaging, sensitive and highly specific biodetection and imaging require the combination of nanomaterials with excellent photoresponsive characteristics and biocompatible polymers to prepare biosafe photofunctional polymer composites [18]. Photofunctional polymer composites have been widely used in fluorescence imaging and photoacoustic imaging in biological imaging. For example, rare-earth–doped upconversion nanoparticles (UCNPs) can emit visible light under near-infrared excitation after being combined with polymers, which has the advantages of nonbiological tissue autofluorescence and no photobleaching [19]. In addition, metal nanoparticles such as gold nanoparticles can be used in photoacoustic imaging after being combined with polymers because of their good photothermal conversion ability and biocompatibility [20]. These materials can provide high-contrast and high-resolution imaging results in cell and small animal models and are suitable for a variety of biomedical research and clinical diagnosis.

In terms of biological detection, the ideal material has high sensitivity and specificity, while also enabling rapid detection. Photofunctional polymer composites are considered to be ideal materials because they combine the advantages of easy processing, flexibility, and biocompatibility of organic polymers with the advantages of inorganic materials, including high stability and special photoelectric properties, and are often used in the preparation and development of high-sensitivity biosensors. Compared with a single photofunctional polymer material, the composite prepared by introducing inorganic nanoparticles (for example, quantum dots and metal oxide nanoparticles) can significantly enhance the optical properties of the composite and improve the light absorption and luminescence efficiency [21, 22]. More importantly, by embedding specific inorganic nanoparticles in the polymer matrix, the prepared composite material can achieve specific recognition of biomolecules and improve the specificity of detection [23, 24].

In the field of therapy and drug delivery, high-load drug carriers and controllable and accurate drug release are important factors in designing materials [25]. The photofunctional polymer composite can achieve precise drug release and efficient therapeutic effect while adjusting the external light source. Compared with a single photofunctional polymer material, inorganic nanoparticles often have a high specific surface area and porous structure, which can significantly improve the drug loading capacity of the composite material and achieve intelligent drug release under the regulation of external light sources. A major use of photofunctional polymer composites is in the advancement of intelligent drug delivery systems. Through precise regulation of external light sources, controllable and accurate release of drugs can be achieved under light stimulation [26, 27]. In addition, 3D printing technology, combined with photopolymeric materials, can manufacture drug carriers and delivery devices with complex structures, such as microneedle patches and intracellular stents, which are able to precisely control the timing and location of drug release, enabling personalized treatment [28].

In terms of photothermal therapy (PTT), photofunctional polymer composites can convert light energy into heat energy for thermal ablation of tumors. In general, nanomaterials between 5 and 100 nm will have a longer residence time in tumor tissues, thus achieving better photothermal therapeutic effects [29]. Therefore, compared with inorganic nanoparticles alone, some photofunctional polymers themselves can regulate the size and structure of inorganic nanoparticles. This kind of photothermal treatment has the advantages of being noninvasive and highly selective, and can effectively reduce the damage to normal tissue. It is worth noting that by combining the photosensitizer with the polymer, ROS can be generated under specific wavelength light irradiation, so as to use PDT to kill tumor cells, which can improve the therapeutic effect and also have high selectivity [30].

Photofunctional polymer composites have a unique application in bone tissue regeneration. In particular, photofunctional polymer composites are often versatile and can integrate the photothermal effect, antibacterial property, and targeted therapy, so as to better promote the repair and growth of bone tissue [31]. For example, photoresponsive nanomaterials can promote the repair of infected bone defects through photothermal and photodynamic antibacterial action [32]. In addition, the mild photothermal stimulation generated by these materials under light can upregulate the expression of osteogenic genes and proteins, thus effectively enhancing the osteogenic effect [33]. This photoregulatory mechanism provides a new strategy for bone defect repair.

In soft tissue repair, photofunctional polymer composites are often used to prepare photoresponsive hydrogels and scaffolds. These materials are able to undergo structural changes when stimulated by specific light sources, thus promoting cell attachment and growth [34]. For example, hydrogels based on photoresponsive polymers can achieve dynamic regulation of the cellular microenvironment through photoregulation, providing ideal biocompatibility and mechanical properties for soft tissue regeneration [35]. Hydrogels that combine photofunctional polymers with inorganic nanoparticles (such as gold nanoparticles) can also be used for skin wound repair, speeding up the healing process and reducing the risk of infection [36].

1.1.3 Structure and Morphology of Photofunctional Polymer Composites

Photofunctional polymer composites have been widely used in energy, environment, biomedicine, and other fields because of their excellent performance in photoelectric properties, mechanical properties, and multifunctional synergies. Depending on their morphology and structure, these materials are divided into four principal categories: nanostructures, fibers, films, and hydrogels. Each class of materials presents unique performance advantages and application potential.

The size of photofunctional polymer nanocomposites is usually at the nanoscale and shows unique optical properties by virtue of a large specific surface area and quantum size effect. This kind of material is composed of a polymer matrix and inorganic nanoparticles (such as metal oxides, quantum dots, and precious metal nanoparticles), which combines the optical properties of inorganic materials with the flexibility and processability of polymers. For example, in solar cells, nanostructured composites can significantly improve the photoelectric conversion efficiency, while optimizing the light absorption and carrier transport performance of the material by regulating the size and distribution of the nanoparticles.

Photofunctional polymer fiber composite takes one-dimensional fibers as the main body, and realizes functionalization by embedding or coating photofunctional materials (such as inorganic nanoparticles or fluorescent dyes) in polymer fibers. Its high specific surface area, high strength, and good flexibility make it suitable for a variety of complex environments. In smart textiles, fiber composites can achieve the transmission and conversion of optical signals and realize multiparameter detection by integrating multiple functions.

Photofunctional polymer composite film is prepared by layer assembly or blending, and has uniform thickness and excellent optical properties. This kind of material not only has high transparency and good flexibility but also shows excellent light absorption and photoelectric conversion ability. In flexible displays and photoelectric sensors, thin-film composites enable high-resolution optical displays and sensitive environmental responses. Its performance and application range can be further enhanced by optimizing the interface design and material composition.

Photofunctional polymer hydrogel composites are three-dimensional networks, containing a large number of solvent molecules, by embedding photofunctional materials (such as fluorescent dyes, quantum dots, or metal nanoparticles) into the hydrogel network, giving it excellent optical properties and versatility. By adjusting

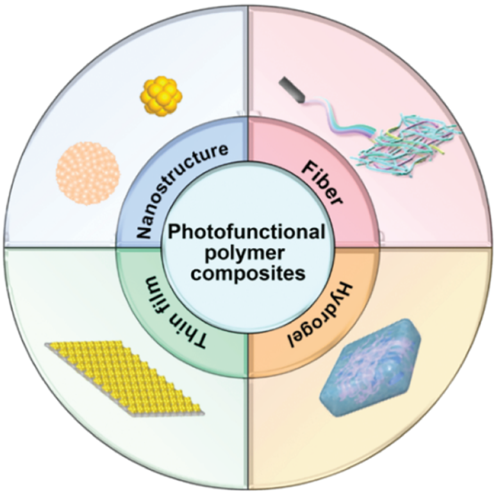

Figure 1.3 Four categories of photofunctional polymer composites.

the hydrogel network structure and the distribution of functional materials, the integration and optimization of multiple functions are realized.

The four categories of photofunctional polymer composites, namely nanostructure, fiber, film, and hydrogel, have their own characteristics (Figure 1.3). By optimizing the preparation process and interface design, the photoelectric properties and environmental adaptability of the materials can be further improved. In the future, with the continuous progress of materials science and nanotechnology, photofunctional polymer composites will achieve innovative applications in more fields, providing important support for solving the global energy crisis, environmental pollution, and medical and health problems.

1.2 Classification of Photofunctional Polymer Composites

1.2.1 Nanocomposites

Nanotechnology is instrumental in advancing the development of various key fields such as environmental energy, information science, and especially life science [37]. When the size of a substance approaches the nanoscale, its physical and chemical properties often undergo sudden changes, exhibiting unique properties that are distinct from both individual atoms/molecules and macroscopic materials, including size effects, surface effects, and quantum confinement [38]. These emerging characteristics enable nanoparticles to exhibit unprecedented functions at the microscopic scale, greatly broadening the horizons of scientific research. At present, researchers are dedicated to regulating atomic and molecular structures at the nanoscale to achieve precise control of material properties, thereby promoting the development of nanosensing, biomedicine, and other fields [39].

Compared with traditional materials, nanomaterials possess characteristics such as high catalysis, high photosensitivity, and high mechanical strength owing to their large surface area, interfacial dominant effect, and active surface state. At the nanoscale, surface tension, electrostatic force, and van der Waals interaction become dominant, correspondingly altering the photoelectrical and thermal response behaviors of the material. These characteristics not only endow nanomaterials with extensive application potential but also make them a research frontier in interdisciplinary fields such as materials science, chemistry, and physics.

Against this background, photofunctional polymer composites, as an important branch of nano-functional materials, have received increasing attention in recent years. Photofunctional polymers can be compounded with inorganic nanomaterials, bioactive molecules, etc., to prepare photofunctional composite systems. In addition, photofunctional nanocomponents such as fluorescent clusters, photosensitive nanoparticles, and photothermal conversion materials can be combined with polymer matrices to achieve multiple functional behaviors such as photoluminescence, photothermal response, light-controlled release, and photocatalysis, demonstrating broad application prospects in fields such as flexible electronics, biological imaging, and intelligent response systems.

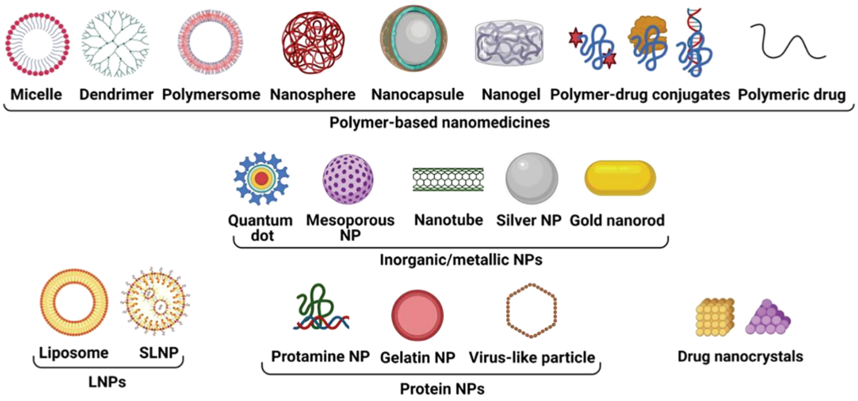

Figure 1.4 Graphical summary of common types of nanomedicines. *Source:* Younis et al. [40] / with permission of Elsevier.

It is worth noting that with the development of nano-self-assembly technology and molecular engineering, the construction methods of materials have shifted from the traditional "component-oriented" approach to the "structure-oriented" one. Morphological structural units represented by nanoparticles and clusters, capsules, micelles, liposomes, and emulsion systems are becoming the core platform for constructing photofunctional composites (Figure 1.4) [40]. For example, fluorescent composite materials composed of metal nanoclusters and polymer matrices can achieve the regulation of light response at the subnanometer scale. High-resolution vesicles and micelles have significant advantages in light-controlled drug release and imaging diagnosis due to their excellent self-assembly ability and environmental responsiveness. The emulsion system, on the other hand, provides a structural template for constructing photosensitive coatings, printable devices, and so on.

Therefore, the systematic classification and analysis of photofunctional polymer composites based on structural units not only helps to understand their performance sources and action mechanisms but also provides adjustable construction strategies for material design. Exploring its construction method, optical function realization mechanism and application prospects aim to provide theoretical support and idea reference for further research and development of this type of composite material.

1.2.1.1 Composite Nanoparticles

Conjugated polymers are a type of polymer with a main chain composed of alternating saturated and unsaturated bonds giving them excellent optical and electrical properties. They are widely used in the field of optical functions due to their unique π-conjugated structure. Through methods such as co-precipitation and microemulsion, these polymers can be further synergistically assembled with other functional components (such as inorganic nanomaterials, metal ions, and biomolecules) to construct composite nanoparticles with fluorescent properties, demonstrating multifunctional application potential in imaging, sensing, and photocatalysis. As one of the important construction units of composite nanoparticles, CP nanoparticles have attracted considerable interest because of their excellent optical properties and structural tunability. In addition, precious metal composite nanoparticles, as another important type of composite system, encompass two typical structural forms: precious metal nanoparticles and nanoclusters. The size of precious metal nanoparticles is usually 2–100 nm. Due to their strong LSPR effect, they show significant advantages in aspects such as light absorption, light scattering, and photothermal conversion. Precious metal nanoclusters with a size less than 2 nm exhibit excellent fluorescence properties and high catalytic activity by virtue of the quantum confinement effect and discrete energy level structure. By constructing composite structures with other nanomaterials or polymer components (such as oxides, carbon materials, and CPs), precious metal composite nanoparticles can not only achieve high controllability in morphology and interface regulation but also show potential advantages in optical, electrical, and catalytic performance.

Conjugated polymer nanoparticles (CPNs) integrate the characteristics of CPs with the properties of nanoparticles, demonstrating many excellent properties, including: good photostability, high brightness, low toxicity, outstanding biocompatibility, size effect, and the ability to sensitize and generate ROS. Due to its unique properties, CPNs are regarded as one of the biomaterials with great application prospects and value. By regulating the main chain structure, side chain substituents, and introducing specific functional groups of CPs, their optical, electrical, and interfacial properties can be precisely adjusted, thereby meeting the application requirements of different fields. Generally speaking, the properties of CPNs are profoundly affected by the type of chromophore, the configuration of the polymer chain, the aggregation state, and the size of the particles. Meanwhile, the charge state and the type of functional groups on the particle surface also regulate their biological interface behavior. With the enhancement of intrachain or interchain interactions in polymers, it often results in enhanced aggregation and more efficient energy transfer, thereby causing redshifts in absorption and emission wavelengths [41]. In contrast, CPNs constructed by means such as coprecipitation or microemulsion methods often show a blue shift in their absorption spectra due to factors such as polymer chain contraction and disordered stacking [42]. However, CPNs constructed through self-assembly exhibit redshift phenomena due to their more loose and orderly structure. These changes in optical characteristics are mainly attributed to the regulation of the aggregation state between the side chains of the polymer by the polarity changes in the solvent environment.

On the premise of having good optical basic properties, further modification of biomolecules (such as antibodies, DNA, and proteins) onto the surface of CPNs through covalent or noncovalent interactions can construct multifunctional composite CPNs with biological functions. Figure 1.5 presents the modification methods and functional molecules of biocomposite CPNs.

At present, the biological functionalization of CPNs mainly includes three functionalization strategies. The first functionalization approach is as follows: Firstly, the monomers are modified, such as by adding alkoxy chains, targeting groups, and charges to the monomers. Then, the monomers modified with biological elements are polymerized, and the resulting polymers possess certain biological functions. Subsequently, biocomposite CPNs are prepared. In this way, a variety

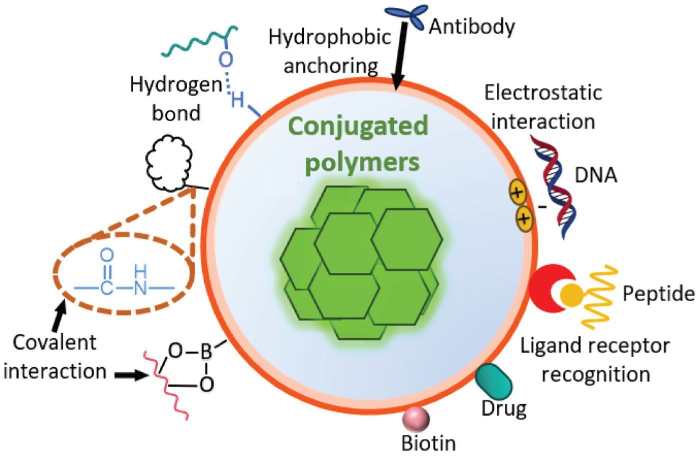

Figure 1.5 The functionalized groups of CPNs.

of CPNs that can be used for fluorescence imaging and clinical diagnosis can be prepared [43, 44].

Compared with the first functionalization method, the direct use of CPs that is easy to modify and commercialize is the most prominent feature of the second method. The specific functionalization mode is to form CPNs by encapsulating CPs with polymers containing biological functional groups through hydrophobic or electrostatic interaction, thereby achieving the biological functionalization of CPNs [45]. In addition, combining positively charged CPs with negatively charged biomolecules through electrostatic interaction is also an efficient way to obtain CPNs with the functions of biological elements. Multifunctional CPNs that can be used for cell imaging, drug delivery, and release were obtained [46, 47].

The third functional mode is an extension and deepening of the second one. Specifically, CPNs with surface carboxyl, amino, or azide modifications are first obtained through the second method. Then, through acid amine condensation catalyzed by EDC or Click coupling reaction catalyzed by Cu, molecules with specific biological functions are covalently linked to CPNs to obtain biocomposite CPNs. In this way, CPNs modified by antibodies, biotin, or affinity streptomycin can be obtained, and imaging of targeted tumor cells can be achieved [48]. CPNs have shown remarkable promise in various biological applications, including in vitro cellular and subcellular imaging, biosensing, as well as in vivo tissue imaging and disease therapy (Figure 1.6) [49].

Metal nanocomposites have shown broad application prospects in the biomedical field owing to their outstanding optical characteristics and interface regulation capabilities. By constructing multifunctional composite structures with polymers or fluorescent molecules, not only is the stability and responsiveness of the material enhanced but also precise control of optical properties is achieved, especially demonstrating unique advantages in imaging enhancement, PTT, and signal amplification. The metal-enhanced fluorescence (MEF) platform constructed based on such

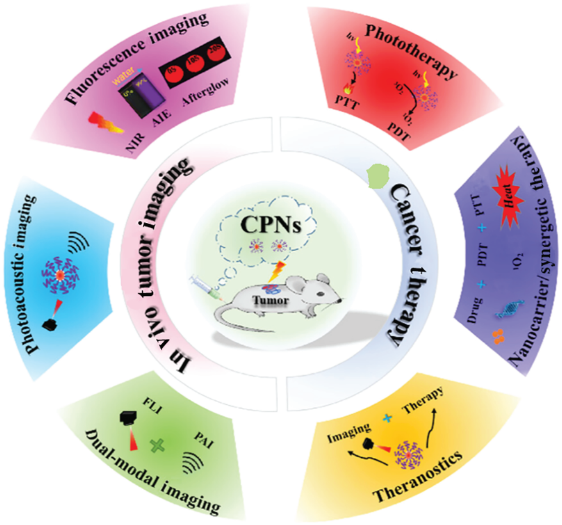

Figure 1.6 Schematic illustration of bioapplications of CPNs. *Source:* Reproduced with permission from Li et al. [49] / American Chemical Society.

a composite system has further expanded its application potential in high-sensitivity imaging and detection.

When a fluorescent substance approaches the surface of precious metal nanomaterials such as gold or silver, the phenomenon where its fluorescence emission intensity increases significantly compared to its free-state fluorescence emission intensity is called metal-enhanced fluorescence (MEF). The distance between the dyes and the nanometal, the morphology of the metal nanostructure, and the overlap degree of the emission peaks between the fluorescent substance and the metal nanomaterial are the primary factors influencing the enhanced fluorescence effect of the metal.

By exploring the electromagnetic field overlap and photoexcitation effects between gold nanomaterials and their surface dyes, it can be found that when the thickness of the silica coating between gold nanoparticles and dyes is thin, the intensity of fluorescent dyes undergoes quenching (Figure 1.7). When the thickness

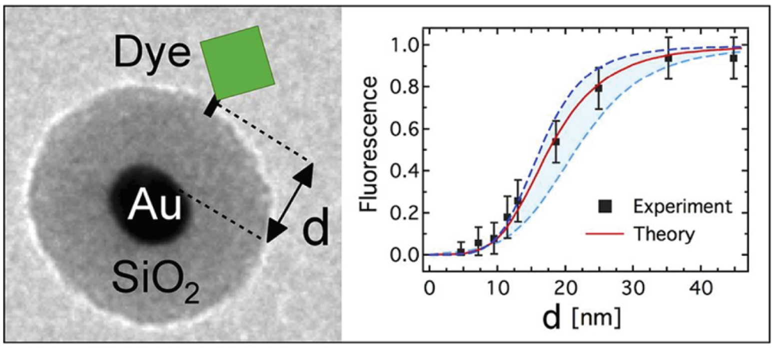

Figure 1.7 Transmission electron microscopy and fluorescence curves of Au@SiO_2-dye composite nanoparticles. *Source:* Reproduced with permission from Reineck et al. [50] / American Chemical Society.

of the silica coating gradually increases, the intensity of the fluorescent dye adsorbed on its surface gradually increases. When the thickness of the silica coating further increases, the electromagnetic field on the surface of the gold nanoparticles has a weak effect on the fluorescent dye, and its fluorescence intensity basically remains unchanged. Furthermore, there is no mutual electromagnetic field interaction between two adjacent dye molecules [50].

The MEF system in colloidal solutions has great potential in the field of biological imaging and sensing. In colloidal systems, the intermediate barrier layers of MEF can be classified into several types, such as silica, polymers, and biomolecules. These intermediate barrier layers can suppress the metal-induced fluorescence quenching and fluorescence resonance energy transfer (FRET) by regulating the distance between dyes and metal nanostructures, while optimizing the local electromagnetic field enhancement effect, thereby reducing energy loss and improving fluorescence efficiency.

Silicon dioxide is widely used in core-shell structured nanoparticles due to its multiple unique advantages, such as good light transparency, simple preparation, chemical inertness, low toxicity, thermal stability, and low cost [51]. In addition, the silica surface can be readily functionalized with various groups, endowing it with amino, thiol, and carboxyl groups, which is conducive to the subsequent modification of fluorescent molecules or biomolecules. As shown in Figure 1.8, the MEF colloid system using silicon dioxide as the intermediate barrier layer can be grouped into two types. One group is with metal nanoparticles as the core, silicon dioxide as the shell layer, and fluorescent molecules introduced in the outermost layer. Its preparation method is shown in Figure 1.8a. Another type is dye-coated silica or silica labeled with dye as the core, and metal nanoparticles [52]

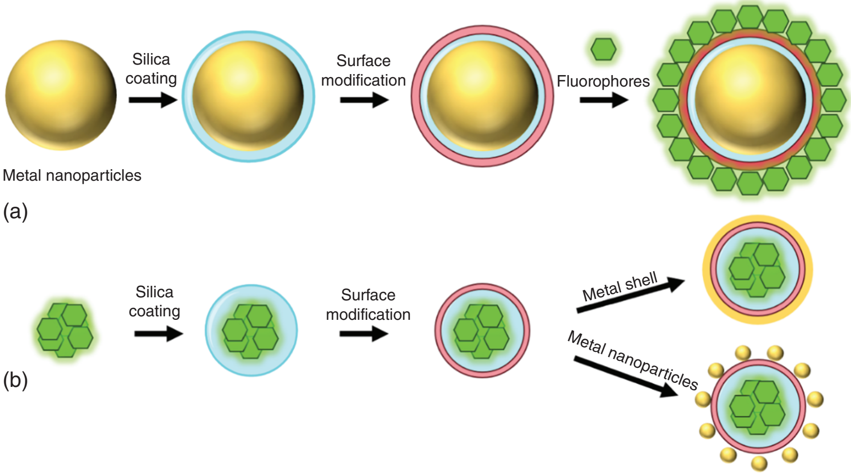

Figure 1.8 (a) With metal nanoparticles as the core, silicon dioxide as the shell layer, and fluorescent molecules located in the outermost layer; (b) with fluorescent materials as the core, silicon dioxide as the shell layer, and a metal shell or metal nanoparticles located in the outermost layer.

or continuous metal nanoshells [53] as the outermost layer. Its preparation method is shown in Figure 1.8b.

Compared with rigid materials, polymers are flexible chains in aqueous solutions, and their configuration and size can change with the variation of the surrounding environment. Therefore, when it serves as an intermediate barrier layer of MEF, the MEF effect can be regulated by changing its thickness and distance. There are several methods for introducing polymer shells on the surface of metal nanoparticles, such as in situ polymerization, the end-group functional connection method, and LbL self-assembly method. A thermally responsive poly(*N*-isopropylacrylamide) (PNIPAM) cross-linked shell was introduced on the surface of silver nanoparticles by in situ polymerization. The outermost layer introduced fluorescent molecules through electrostatic adsorption, and the distance between it and the metal surface could be controlled by changing the temperature. This not only achieved a temperature-adjustable MEF effect but also enhanced the stability of the fluorescent molecules at high temperatures [54]. Recently, the development of living radical polymerization has provided opportunities for designing and synthesizing polymers with diverse compositions and complex architectures. Polymers prepared via reversible addition–fragmentation chain transfer polymerization (RAFT) often feature end groups such as dithioesters, which can be anchored to metal surfaces through the affinity between metals and sulfur [55]. The MEF effect of this system shows reversible variation characteristics with the heating and cooling of temperature. In colloidal systems, LbL polyelectrolyte multilayer films can also be used to achieve the regulation of distance at the nanoscale [56]. Unlike on a flat surface, depositing multilayer films on a colloid requires multiple centrifugation purification steps.

Biomolecules are also often used to assemble and prepare composite nanoparticles with MEF effects, which improve their biocompatibility for application in organisms. Among them, DNA molecules or oligonucleotides are often used to regulate metal and fluorescent molecules at the nanoscale because their lengths can be precisely designed and controlled [57]. CdSe/ZnS quantum dots and gold nanoparticles were assembled using DNA molecules with thiol groups and biotin groups at both ends, respectively [58]. The surface of quantum dots is coated with streptavidin. Through biotin–streptavidin interaction and Au–S bond interaction, DNA molecules connect quantum dots and gold nanoparticles. Among them, when quantum dots are located between two gold nanoparticles, the maximum enhancement effect is achieved. This is because the electromagnetic fields of the two gold nanoparticles in this area interact with each other, generating a stronger magnetic field enhancement, namely the “hot spot” effect. DNA molecular chains remain relatively flexible in aqueous solutions [59]. This specific binding can be utilized to assemble fluorescent and metal nanomaterials. For example, assembling a layer of gold or silver nanoparticles through biotin–streptavidin interaction outside CdTe nanowires can show a significant fluorescence enhancement effect in aqueous solution [60].

Photofunctional composite nanoparticles have shown broad application potential in fields such as fluorescence imaging, PDT, and drug delivery owing to their excellent photostability, biocompatibility, and structural tunability. By introducing functional biomolecules, multiple targeting and integrated treatment can be achieved. Photofunctional composite nanoparticles are expected to achieve deeper integration in directions such as precision medicine, intelligent diagnosis and treatment, and multimodal imaging, promoting the development and transformation application of high-performance biological nanomaterials.

1.2.1.2 Emulsion

Emulsion is a relatively stable multiphase dispersion system, where one liquid is finely dispersed as small droplets in another liquid that is immiscible with it. Common emulsions always present an emulsified appearance. They are thermodynamically unstable multiphase dispersion systems. The dispersed phase, continuous phase, and emulsifier are the three main components that constitute an emulsion. Among them, the dispersed phase is the discontinuous phase that is dispersed in the emulsion in the form of droplets. The continuous phase is a continuous and integrated phase formed in the emulsion, also known as the dispersion medium.

According to the different dispersion situations, emulsions composed of oil and water can be divided into two major categories: the first is the type of emulsion where water encapsulates oil, that is, the situation where the oil phase is dispersed in water, which is expressed as oil/water or O/W. The second type is an emulsion where oil is coated with water, that is, the situation where the water phase is dispersed in the oil, which is expressed as water/oil or W/O. More complex emulsion types can also be formed, such as water containing oil and then water, that is, water/oil/water (W/O/W), or oil containing water and then oil, that is, oil/water/oil (O/W/O) (Figure 1.9).

Traditional emulsions are stabilized by surfactant molecules, which are often structured with hydrophilic head groups and hydrophobic chains. The stability of the emulsion is maintained by reducing the interfacial energy between the two phases. At the beginning of the last century, the mechanism by which solid particles stabilize emulsions was discovered and defined, respectively, by Ramsden and Pickering. The stabilization mechanisms of Pickering emulsions include the

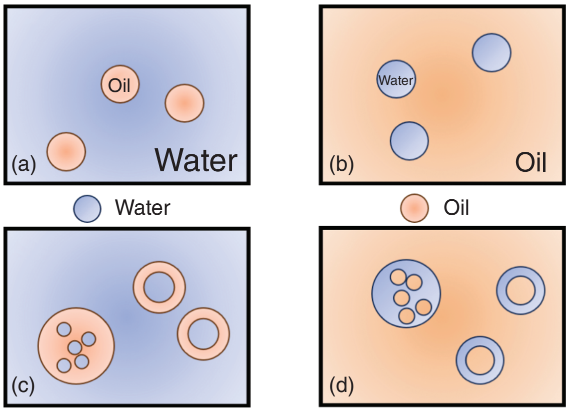

Figure 1.9 Schematic illustration of emulsion type: (a) O/W; (b) W/O; (c) W/O/W; (d) O/W/O.

interface film theory, the three-dimensional network structure theory, and the depletion interaction. Compared with surfactants, Pickering emulsions stabilized by solid particles have greater advantages, including better anticoalescence stability, minimizing the Ostwald ripening phenomenon, higher biocompatibility, and lower cytotoxicity [61]. Based on the above advantages, Pickering emulsion has broad application prospects in fields such as food, biomedicine, and cosmetics [62].

Light intensity (controlled at different wavelengths of near-infrared and ultraviolet) is another stimulating factor that has been studied for controlling Pickering emulsion systems. Although it has not attracted as much attention as more traditional stimuli (such as pH, temperature, and CO_2 concentration), it can be quite beneficial because it is usually nondestructive, precise, and easy to implement.

The use of interfacial active upconversion nano-phosphates as colloidal emulsifiers can achieve biocatalysis applications (Figure 1.10) [63]. The surface chemistry of the particles was regulated by coupling with photochromic isopropylpyran, and isopropylpyran underwent hydrophilic-lipophilic conformational changes under the action of ultraviolet light and visible light. After the introduction of near-infrared light into the system, it was observed that the upconversion nano-phosphor was excited and emitted ultraviolet photons. The emitted ultraviolet light triggered conformational changes in surface-grafted photochromic isopropylpyran. This leads to the particle surface becoming more hydrophilic, thereby stabilizing the Pickering

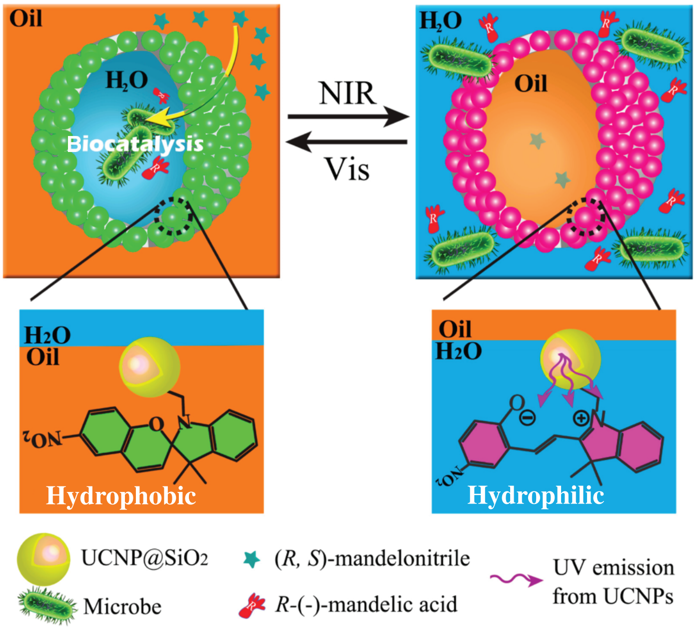

Figure 1.10 Schematic illustration of NIR/Visible light-induced phase inversion in emulsions stabilized by photochromic spiropyran-functionalized upconversion nanophosphors for optimized biocatalysis. *Source:* Chen et al. [63] / with permission of American Chemical Society.

of the o/w emulsion. Exposure to visible light will reverse the conformational changes on the particle surface, resulting in the transformation of the emulsion phase into w/o.

With the development of synthesis technology, the particles used to prepare Pickering emulsions have gradually evolved from hard particles to soft particles. Unlike rigid inorganic particles, polymer particles themselves are soft particles, and there are many types of monomers for synthesizing polymers. Through layer-by-layer (LbL) design during the synthesis process to adjust the properties of the particles and endow them with functionalization, emulsified materials with one or more specific functions or responsiveness can be developed, providing a new strategy for preparing functionalized particle emulsifiers. It has aroused extensive research by scholars.

An azobenzene monomer, (E)-6-(4-((4-(allyloxy)phenyl)diazenyl)phenoxy)hexyl methacrylate with asymmetric divinyl groups, was synthesized to create light-responsive particles [64]. When exposed to white light and ultraviolet light (365 nm), the particles undergo reversible, light-induced shape changes. Particles produced via precipitation polymerization and dispersion polymerization can respectively stabilize water-in-oil and oil-in-water Pickering emulsions, both of which exhibit reversible formation and deformation in response to light.

The application of photofunctional polymer composites in emulsion systems shows broad prospects. Relying on their response characteristics to light stimulation, reversible phase transformation, stability regulation, and multifunctional integration of emulsions can be achieved. They are particularly suitable for constructing intelligent emulsification systems, light-driven microreactors, and controllable release platforms. By compounding with inorganic photosensitive components (such as TiO_2, precious metal nanoparticles) or organic photochromic groups, these materials not only enhance the interfacial activity but also endow the emulsion system with tunability and reusability. In the future, with the in-depth development of light-response mechanisms and structural design, it is expected to achieve more breakthrough applications in fields such as bionic catalysis, environmental governance, and precise drug delivery.

1.2.1.3 Liposome

Liposomes are ultrafine vesicles composed of phospholipid bilayers, which are usually used to encapsulate drugs or other bioactive substances. Phospholipid molecules have hydrophilic heads and hydrophobic tails. During the formation of liposomes, the hydrophilic heads of phospholipids face the aqueous phases on both sides, while the hydrophobic tails form a plate-like bilayer facing each other. This structure enables liposomes to stably encapsulate water-soluble and liposoluble substances.

Liposomes can be categorized according to their structure, particle size, and the number of phospholipid bilayer membranes. Monolayer liposomes include small unilamellar vesicles (SUVs), which have particle sizes less than 100 nm, and large unilamellar vesicles (LUVs), with particle sizes ranging from 100 nm up to several micrometers. Multilamellar vesicles (MLVs) is composed of multiple layers of phospholipid bilayers, and the particle size is usually on the level of several hundred nanometers to micrometers. And multivesicular vesicle (MVV) is a large vesicle containing several discontinuous drug solution vesicles.

Based on the degree of modification, liposomes can be divided into conventional liposomes and targeted liposomes. The phospholipid bilayer of common liposomes is unmodified and prone to accumulate in the reticuloendothelial system (such as tissues and organs like the liver, spleen, lymphatic system, and lungs). The phospholipid bilayer of targeted liposomes has been modified to possess long-circulation characteristics (staying in the circulatory system for a relatively long time), active targeting characteristics (specifically binding to receptors), and sensitivity to changes in the physical and chemical environment.

Due to the environmental sensitivity of liposomes, they can be constructed as a multifunctional light-responsive nanoplatform, which not only plays an enhancing role in traditional PDT but also endows them with multiple photofunctional response characteristics through material engineering methods, providing an effective way for the integration of tumor diagnosis and treatment. The main optical functions can be seen in the following aspects.

Firstly, liposomes effectively improved the bioavailability and therapeutic performance of photosensitizers (PS). Most photosensitizers (such as PpIX, Ce6, mTHPC, and BPD) have strong hydrophobicity and are difficult to disperse directly in the aqueous phase. They tend to aggregate, leading to self-quenching and thereby affecting the generation of ROS and therapeutic effects. By encapsulating these photosensitizers into liposomes, their water solubility, stability, and cellular uptake efficiency can be significantly improved [65–68].

Secondly, liposomes have excellent light-responsive release performance, achieving precise controlled release in both space and time. By introducing lipids containing unsaturated double bonds (such as DOPC, DOTAP, and POPC), liposomes can respond to ROS, undergo oxidative disintegration of the membrane structure, and thereby release the drug-loaded components [69]. In addition, photothermal agents (such as ICG) are introduced into the thermosensitive liposome system. Under the irradiation of NIR laser (808 nm), local temperature rise occurs, triggering phase transformation of DPPC liposomes around 41 °C and achieving controlled release of the drug [70]. Such mechanisms have significantly enhanced the controllability and safety of treatment.

The liposome system supports the construction of an integrated imaging and treatment platform to achieve the function of "integrated diagnosis and treatment." The polymer liposomes constructed were co-loaded with Merocyanine 540 (MC540) and UCNPs, the latter of which can generate 540 nm visible light from 980 nm near-infrared excitation for activating MC540 (Figure 1.11). This is to achieve the dual functions of PDT and fluorescent imaging (FLI) of deep tissues [71].

In conclusion, liposomes not only solved the problems of water solubility and targeting of photosensitizers but also achieved light-controlled release, imaging guidance, oxygen environment regulation, and synergistic integration with other therapeutic methods through fine regulation of structure and function, fully demonstrating their multidimensional value in the field of photofunction. In the future,

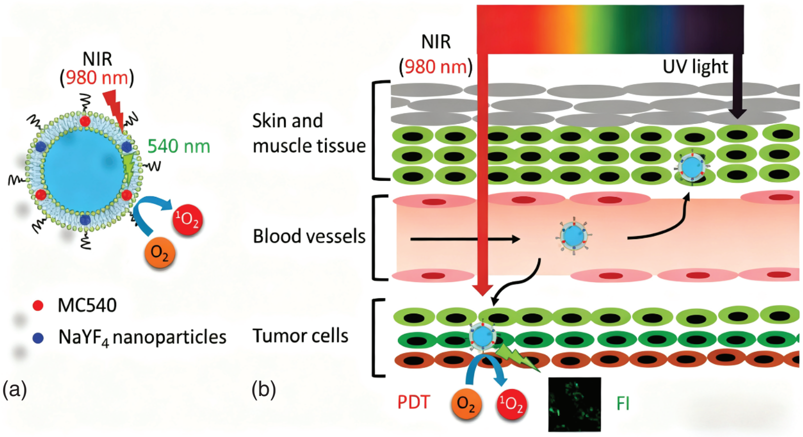

Figure 1.11 (a) NaYF4 UCN converted near-infrared irradiation to visible light at 540 nm, activating liposomal MC540 for (b) photodynamic therapy and fluorescence imaging. *Source:* Cheng et al. [71] / John Wiley & Sons / CC BY 4.0.

with the continuous optimization of liposome materials and the development of multicomponent collaborative systems, its application in personalized PDT, deep tissue treatment, and integrated diagnosis and treatment is expected to be further expanded, providing more precise, efficient, and safe solutions for clinical tumor treatment.

1.2.1.4 Micelle

Polymer micelles are dynamically stable colloids that result from the self-assembly of amphiphilic polymers in selective solvents [72]. The micellar process of polymer micelles is a thermodynamically kinetic equilibrium process. When the polymer concentration in the aqueous solution is low, the polymer exists in a free form. When the polymer concentration is higher than its critical micelle concentration (CMC), the free polymer spontaneously aggregates to form polymer micelles. Hydrophobic units cluster together to create a micelle core that minimizes exposure to the surrounding water, while hydrophilic blocks surround the core, forming a hydrophilic shell on the exterior of the micelle [73].

Polymer micelles can be classified in various ways based on their properties and structures. According to their self-assembly behaviors, they are categorized as spherical, worm-shaped, or rod-shaped micelles [74]. Based on the types of polymers used, classifications include block polymer micelles, polyelectrolyte copolymer micelles, dendritic polymer micelles, and graft copolymer micelles, among others [75]. When considering the structural characteristics of the polymers, polymer micelles can be divided into cross-linked, non–cross-linked, and noncovalently linked micelles [76]. Classification by topological structure yields linear and star-shaped polymer micelles [77]. In terms of polymer composition, they can be grouped into single-component micelles, single-molecule micelles, and mixed micelles [78]. Finally, based on functional characteristics, polymer micelles

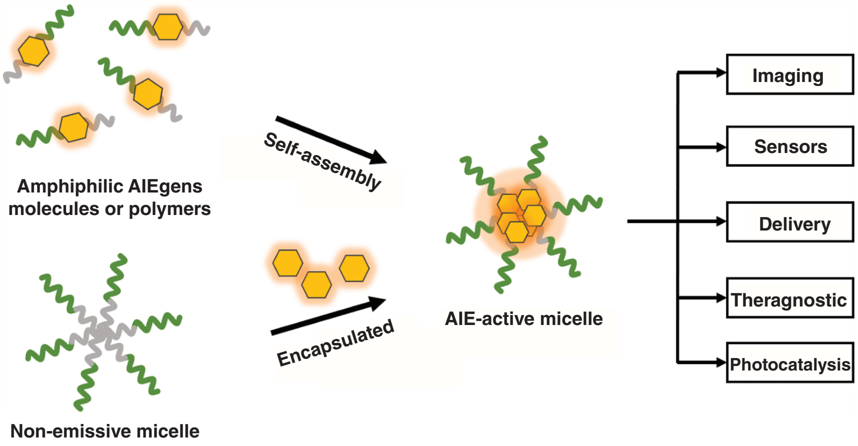

Figure 1.12 Schematic illustration of the preparation and bioapplications of AIE-active micelles.

are categorized as stimulus responsive, non–stimulus responsive, and targeted micelles, among others [79].

The optical performance of functional micelles based on aggregation-induced emission (AIE) molecules is different from the problem that traditional fluorescent materials are prone to aggregation-caused quenching (ACQ) in the aggregated state. After AIE molecules self-assemble and enter the micelle core, they instead show stronger fluorescence emission due to intramolecular rotational restriction (RIR mechanism). This enables the micelle system to have significant advantages in terms of optical functions. This type of AIE micelles not only solves the problem of low luminescence efficiency of traditional luminescent materials in biological and aqueous systems but also endows the micelles with new sensing, imaging, response, and therapeutic functions [80] (Figure 1.12).

Micelles not only possess optical properties but also have a responsive nature to external stimuli such as pH, temperature, CO_2, and light, making them an ideal platform for building "visual self-assembly systems." A CO_2-responsive block copolymer micelle, after the introduction of CO_2, transforms into vesicles, accompanied by obvious fluorescence enhancement and color change, which can reflect the transformation process of the self-assembled structure [80]. Similarly, the acid-sensitive micelles constructed by imine bonds undergo dissociation and reassembly under pH changes, and the corresponding fluorescence emission also changes accordingly [81]. Such systems can be used to monitor the drug release process, self-assembly behavior, and structural dynamic evolution in real time, and have application potential in the fields of smart materials and nanoreactors.

By selecting photofunctional molecules that have the potential for PDT or PTT, and co-loading the luminescent units with chemotherapy drugs in micelles, treatment and monitoring can be carried out simultaneously. For example, tetraphenylethylene (TPE)-modified polymers can stably load drugs after forming micelles and release drugs in response to environmental stimuli (such as pH or ROS), and fluorescence is used to visualize the release process [82]. In a specific design, dye molecules can also generate ROS under light, which are used for the photodynamic killing of tumor cells. Therefore, multifunctional micelles can achieve the “diagnosis and treatment integration” function, integrating imaging, drug loading, and treatment into one and have great prospects in the precise treatment of cancer.

The multiple roles of micelles in optical functions, ranging from enhancing basic optical properties to integrating stimulus response, imaging, biological detection, and treatment, demonstrate the multidimensional value of micelle materials. Thanks to the flexibility of molecular design and self-assembly regulation, micelles not only overcome the disadvantages of traditional luminescent materials in aqueous systems but also show broad application prospects in biological imaging, drug delivery, environmental sensing, smart materials, and light-controlled therapy. In the future, with the further development of precise structure control, multimodal signal output, and intelligent response mechanisms, micelles are expected to become an important platform for constructing high-performance photofunctional nanomaterials, providing new solutions for nanobiotechnology and intelligent diagnosis and treatment.

1.2.1.5 Capsule

A capsule is an empty micro-nano structure composed of polymers, lipids, or proteins, with a distinct shell and internal cavity. Capsules have good controllability, biocompatibility, and functional expansion ability. Its typical structure originates from the template-assisted LbL technology. Through successive deposition of polymer molecules with specific interactions (such as electrostatic interactions, hydrogen bonds, and covalent bonds) on the surface of the template, the core is finally removed to obtain hollow capsules with a stable geometric structure (Figure 1.13). This type of capsule can be precisely regulated in terms of size, shell thickness,

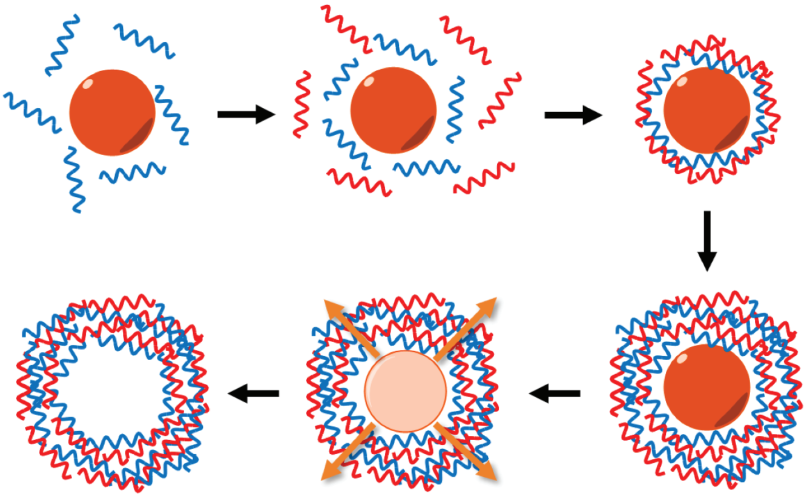

Figure 1.13 Schematic illustration of the preparation of capsules.

permeability, flexibility, and surface functional groups, and has broad application potential in nanomedicine, bionic materials, and intelligent release systems [83].

Capsules have significant physical and chemical responsiveness. Through material design, they can be endowed with the ability to respond to multiple external influences such as pH value, redox state, enzyme concentration, temperature, and light. Among them, light responsiveness is a direction that has attracted much attention in its functional expansion. By introducing photosensitive linking groups (such as azobenzenes, photosensitive amide bonds) into the vesicular shell or doping photoactive materials (such as gold nanoparticles, photosensitive dyes, semiconductor quantum dots), the capsules can undergo structural changes or chemical bond breaks under the action of light at specific wavelengths, thereby inducing changes in the permeability of the vesicular membrane, opening pores or overall deconstruction, and achieving the light-controlled release function [84].

Capsules can serve as important components of the controlled release system. Through the fine design of the shell molecular structure, a response system sensitive to visible light, near-infrared light, or ultraviolet light can be constructed, which releases encapsulated drugs, proteins, or signal molecules under local light stimulation. This light-response release process features noncontact, spatiotemporal controllability and high selectivity, and is particularly suitable for biological therapy scenarios that require precise positioning and reversible regulation [85].

In addition to drug delivery, the shell of the capsule can imitate the multilayer membrane structure of the natural thylakoid membrane, providing a structural template for artificial photosynthesis systems and photocatalytic platforms. By integrating photosensitive electron transfer molecules, organic dyes, or semiconductor materials into the capsule structure, the process of energy capture, transfer, and utilization after local photoexcitation can be achieved. Multichamber structure capsules can achieve photoactivated cascade reactions. Each chamber encapsulates different reactants or catalysts, which are successively released or activated under light stimulation, simulating the mechanism of multistep energy conversion and material synthesis in natural photosynthesis [86].

In multienzyme reactors or enzymatic catalytic platforms, light-responsive capsules can be used to activate specific reaction pathways. For example, the controllable initiation of multienzyme cascade reactions can be achieved by encapsulating a group of enzymes in capsules and only opening the capsules under specific light conditions to release the enzymes. This design can avoid mutual interference among enzymes and improve reaction efficiency and spatial resolution [87].

The diversified structure of the capsules further broadens their light-response ability. For example, spherical and ellipsoidal capsules exhibit different photoinduced release kinetics due to the difference in surface area; multilayer membrane structures can delay or control the release rate in segments. The combination of hydrophilic and hydrophobic film layers can achieve targeted protection and activation of different types of photosensitive molecules. This structure-function integration characteristic makes the capsule an ideal light-controlled delivery platform and optical functional bionic module [83].

With the development of nanomaterial science, photochemistry, and bioengineering, the application of capsules in optical functions still has broad prospects. How to achieve higher response efficiency, lower phototoxicity, stronger targeting ability, and more complex optical program control is an important direction for future research. Through molecular-level design, interdisciplinary material integration, and the introduction of advanced assembly technologies, capsules are expected to play a core role in multiple fields such as precision medicine, bionic light energy systems, optical detection, and environmental response materials.

1.2.2 Fibers

In the past few decades, remarkable advancements have been made in photofunctional polymer fibers. From the initial poly(methyl methacrylate) (PMMA)-based optical fibers to the current development of various biodegradable polymer optical fibers, these advancements have provided more possibilities for the application of optical fibers in the biomedical field. Especially, the degradable polymer optical fibers based on poly(lactic acid) (PLA), poly(ethylene glycol) (PEG), and poly(lactic-co-glycolic acid) (PLGA) can not only reduce the need for surgical intervention but also provide precise optical transmission and biological signal monitoring.

The advancement of medicine, especially the development of neuroscience, is urgently in need of multifunctional photofunctional fibers that possess higher biocompatibility, greater photoconductivity, and lower invasiveness. This is because the functions of cells or organs are coordinated and influenced by multiple signals, including electrical signals, chemical signals, and neurotransmitters, while traditional single-function probes are difficult to achieve synchronous monitoring and regulation. Photofunctional fibers enable the integration of waveguides, electrodes, and microfluidic channels, facilitating the simultaneous investigation of electrical, chemical, and mechanical signals with minimal disruption. More specifically, they can deliver drugs, nutrients, and viral vectors to deep tissues through hollow channels [88].

Two key parameters of optical fiber materials are their transparency in the spectral region required for waveguide operation and their processability in the selected manufacturing method. From an optical perspective, the materials used to manufacture optical waveguides need to have high light transmittance and an appropriate refractive index. The refractive index must be higher than that of the surrounding medium to support total internal reflection, thereby enabling the propagation of optical power within the waveguide. Meanwhile, the material should have a low absorbance and scattering to ensure low attenuation of optical power when propagating in the waveguide. In addition, the materials used to manufacture optical fibers should also have sufficient mechanical properties to meet the usage requirements [89].

1.2.2.1 Natural Material-based Fibers

Composition and Structure Natural polymer fibers are ideal candidates for biocompatible and biodegradable photofunctional fibers because they have distinctive optical and mechanical characteristics, nontoxicity, and inherent biodegradability, which are influenced by the diversity of their components. Biocompatible polymer fibers have been successfully obtained by using materials such as proteins, agar, different silks, and cellulose. Among them, the optical fibers based on bacteria and cells demonstrate superior biocompatibility and biodegradability, owing to their tissue-like characteristics. In addition, some natural fibers are applied in the biomedical field due to their excellent photofunctions, including good light conductivity and high transmittance. However, natural photofunctional polymer fibers inevitably need to evaluate the following issues [90]. For preparation, the molecular weight is difficult to control, resulting in poor stability among different batches. Furthermore, at temperatures below the melting point, this type of fiber is prone to decomposition or thermal modification, making thermoforming processes such as melt extrusion difficult. For biocompatibility, especially protein-based fibers, it may trigger an immune response. If not handled properly during collection, storage, or manufacturing, there is a risk of spreading infectious diseases.

At present, a variety of photofunctional polymer fibers based on natural materials have been developed for use in the biomedical field. Silk is a natural protein fiber material made from the silk spun by silkworms, with its main components being fibroin and sericin. Its fiber structure is unique. The external sericin protein wraps around the internal sericin protein, which is composed of β-folds, endowing the silk with high strength and luster [91]. As a biomaterial, silk, with its excellent biocompatibility and biodegradability, has become a commonly utilized fiber in clinical applications, including wound healing, suturing, tissue engineering, and textiles. In addition, by adjusting the proportion of various elements, the mechanical properties of the fiber based on the silk can be modified to suit particular requirements, and bioactive molecules can be linked to the fiber to make it more functional (Figure 1.14) [92].

Similarly, spider silk is also a kind of natural polymer fiber, which has higher tensile strength and toughness than silk, and has unique thermal, optical, and biocompatibility. Spider silk exhibits excellent light transmittance, making it potentially applicable in fields such as optical sensors. Its multilevel structure, including cross-linked structure, helical nanofiber structure, and core-shell structure, endows it with strength and toughness that surpass those of artificial fibers. The multilevel structure of spider silk, including the primary and secondary structures of the spider silk protein, the helical nanofiber structure, and the core-shell structure, endows it with strength and toughness that surpass those of artificial fibers (Figure 1.15) [93].

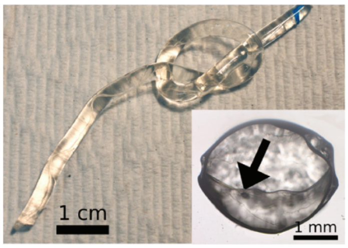

Figure 1.14 Silk waveguide with a knotted configuration and microstructured cross-section. *Source:* Applegate et al. [92] / Optica Publishing Group.

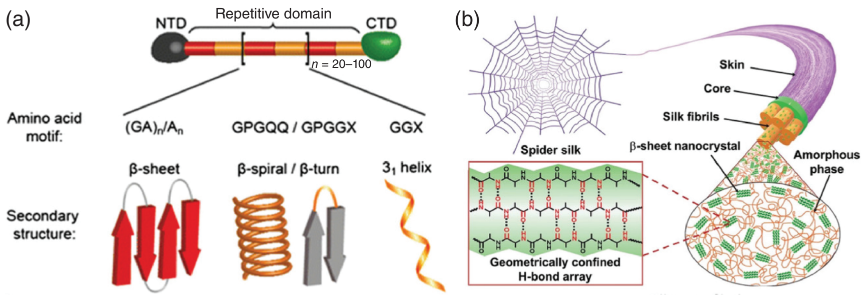

Figure 1.15 Spider silk multiscale organization: (a) molecular and secondary structural motifs, (b) hierarchical fibrous assembly. *Source:* Li et al. [93] / John Wiley & Sons / CC BY 4.0.

Meanwhile, the excellent biocompatibility of spider silk endows it with significant potential in the biomedical field, such as the treatment of cardiovascular diseases and the development of biomedical materials. Its self-repairing ability, cell affinity, and antibacterial performance further enhance its application prospects in these fields.

Cellulose, a natural material abundantly found in plants, shares many properties with silk and has been utilized in the fabrication of photofunctional fibers. Several previous studies have demonstrated that cellulose can be applied in chemical and electrochemical sensing, drug delivery, and so on. Photofunctional fibers made from cellulose exhibit high ion permeability and outstanding light transmittance across a broad spectral range. Notably, increasing the cellulose content in these materials enhances their modulus and tensile strength, allowing for the mechanical properties of the fibers to be tuned as needed. Similar to other natural fibers, cellulose-based fibers are both biocompatible and biodegradable. Furthermore, cellulose-based fibers with microstructures can serve many functions, offering significant potential for biomedical applications (Figure 1.16) [94].

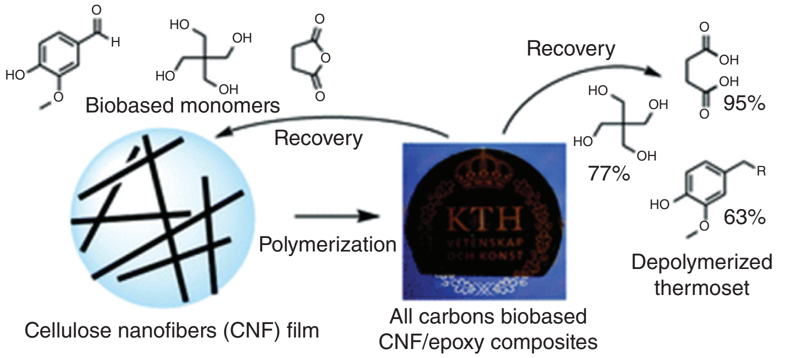

Figure 1.16 Nanofibrous network-based design for recyclable CNF/epoxy composites. *Source:* Subbotina et al. [94] / The Royal Society of Chemistry / CC BY 2.0.

Bioapplications The role of photofunctional polymer fibers in drug delivery is mainly reflected in their ability to achieve precise targeted drug release and enhance therapeutic effects [95]. Agarose hydrogel (derived from algal polysaccharides) coated with drugs combined with PTT can efficiently destroy tumor cells, with an effect similar to transcatheter arterial chemoembolization (TACE). As shown in Figure 1.17a, optical fibers not only deliver photons to deep tumor tissues but also carry photothermo-sensitizers and chemotherapeutic drugs for precision-targeted therapy. Figure 1.17b demonstrates that under laser irradiation, fiber probes doped with rare-earth ions generate localized high temperatures, activating a surface film to release the antitumor drug doxorubicin (Dox). Figure 1.17c illustrates a fiber-integrated sensor system incorporating Mach-Zehnder interferometer (MZI) and fiber Bragg grating (FBG), enabling real-time monitoring of drug release and lesion temperature. This delivery approach offers superior penetration depth and drug retention compared to conventional laser therapies, significantly enhancing

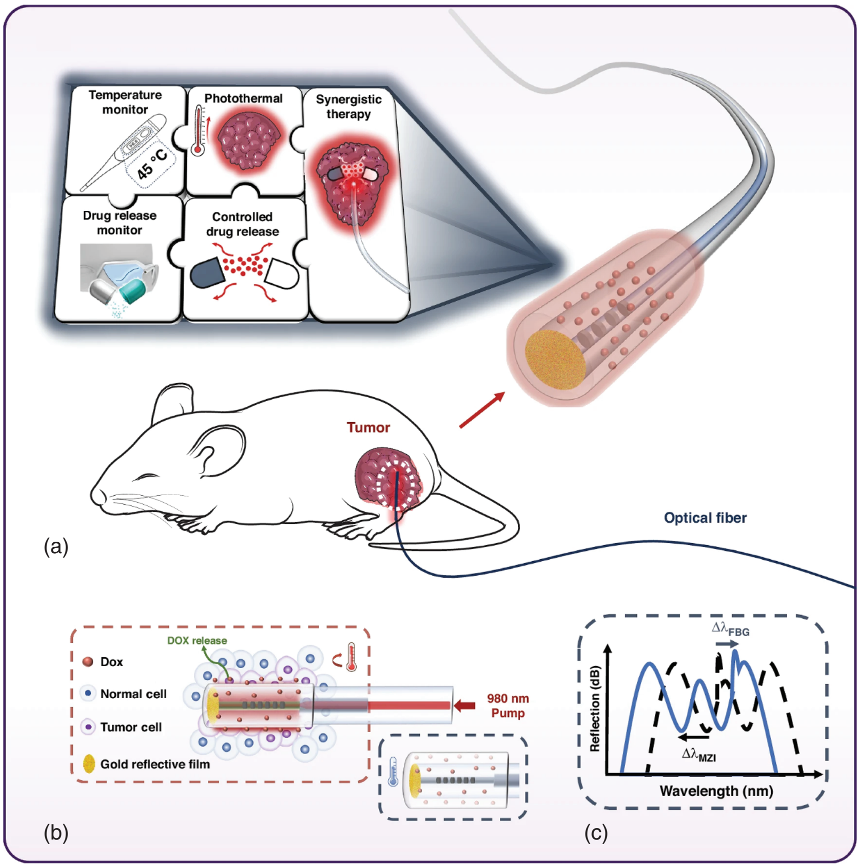

Figure 1.17 NIR-photothermal triggered fiber-optic theranostic probes with synergistic mechanism and closed-loop monitoring. *Source:* Zhang et al. [96] / Springer Nature / CC BY 4.0.

therapeutic efficacy for deep-seated tumors. These advantages enable photofunctional polymer fibers to go beyond simple therapeutic probes, providing efficient and compatible drug screening and evaluation strategies for the innovation of therapeutic drugs, and even reevaluating drugs that have been excluded due to systemic toxicity [96].

The application of natural materials in optogenetics is mainly reflected in the preparation of biocompatible fibers. Light-based stimulation is frequently contrasted with electrical stimulation for its ability to activate or suppress neuronal activity within specific brain regions. Supramolecular fibers generated via the interfacial polyelectrolyte complexation (IPC) of DNA and histones have been employed for the encapsulation and in situ differentiation of neural stem cells (NSCs) derived from mouse brain tissue (Figure 1.18) [97]. The encapsulated NSCs exhibit high viability, underscoring the good biocompatibility of these fibers as three-dimensional scaffolds. To further improve NSC encapsulation efficiency and restrict cell migration from the fibers, cell adhesion peptides (K6-PEG-RGD) are incorporated through electrostatic interactions, thereby enhancing spatial cellular organization. Immunocytochemical staining confirms the successful in situ differentiation of NSCs into oligodendrocytes within the fibers. Owing to their robust capacity for NSC encapsulation and in situ differentiation, these chromatin-inspired supramolecular fibers hold significant promise for applications in nervous system tissue engineering.

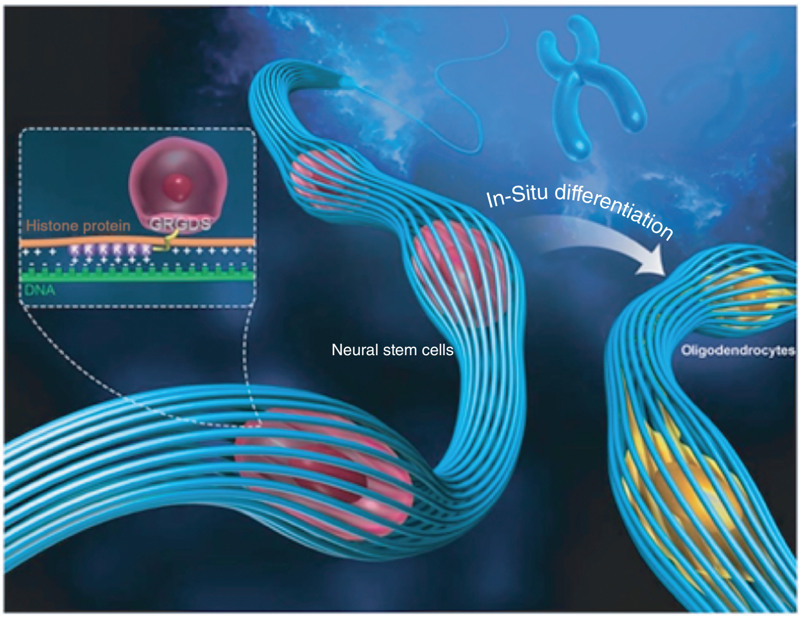

Figure 1.18 Schematic illustration of the supramolecular fibers for encapsulating NSCs and promoting their in situ differentiation. *Source:* Reproduced with permission from Zhao et al. [97] / John Wiley & Sons.

1.2.2.2 Synthetic Polymer Fibers

Synthetic polymer fibers are made from renewable resources and have better material designability because they are artificial products with adjustable physical, mechanical, and chemical properties. They can be made into degradable materials, which means they can be reabsorbed by the human body, and their degradation curves and optical properties can be adjusted and optimized to fulfill the requirements of various optical devices.

Generally speaking, chemical insertion and physical doping are two main methods for preparing photofunctional polymer fibers. In chemical methods, photoresponsive groups are inserted into polymer chains through various chemical means, including the copolymerization of photoresponsive monomers with other monomers and the postmodification of fibers. The former adopts diverse polymerization methods, including free radical, atomic transfer free radical polymerization, and reversible addition-break chain transfer. The photoresponsive part can be inserted into the polymer skeleton as the main chain or side group, and the photoresponsive dye can be inserted into the polymer chain. The latter requires functionalized photoresponsive dyes. Physical methods offer a simple and feasible preparation procedure. Photoreactive dyes are placed within or on the surface of nanofibers through physical interactions.

Poly(glycolic acid) (PGA), PEG, PLA, PLGA, poly(L-lactic acid) (PLLA), poly(dimethylsiloxane) (PDMS), and poly(vinyl alcohol) (PVA) are often used as the base materials of photofunctional polymer fibers due to their excellent biocompatibility and easy functionalization. These polymers have been widely studied and applied due to their controllable degradability, minimal propagation loss, and excellent mechanical properties. They can be degraded and absorbed in the body, leaving almost no toxic residue in a biophysical environment. Therefore, they are highly suitable for implantable medical devices, eliminating the need for additional surgery to extract the implant. These polymers exhibit excellent optical and mechanical properties in photofunctional fibers, making them have broad biomedical applications, especially in phototherapy, optogenetics, and biosensing.

Composition and Structure The application of PEG-based photofunctional polymer fibers in the biomedical field is increasing day by day, mainly owing to their specific physical and chemical properties. PEG photofunctional polymer fibers have become ideal materials in the biomedical field due to their high capacity for storing water, similarity to the extracellular matrix, and low toxicity. These fibers not only possess excellent light conductivity efficiency and optical transparency but also have mechanical flexibility and are easy to integrate, which makes them show great potential in biosensing and photoinduced therapy [98]. Glucose-responsive PEG hydrogel fiber optics can be used as a sensor to quantify the concentration of analytes, as shown in Figure 1.19.

Poly(lactic acid) (PLA) is a synthetic polyester formed by the polymerization reaction of lactic acid monomers and is one of the most widely used degradable polymers at present. Because PLA is derived from renewable resources like corn and sugarcane and has good biocompatibility and degradability, it is widely used in the fields

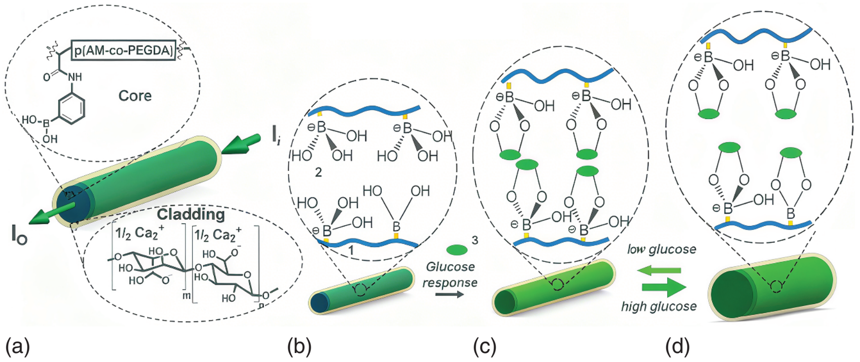

Figure 1.19 Glucose-responsive PEG hydrogel fibers for optical biosensing. *Source:* Yetisen et al. [98] / John Wiley & Sons / CC BY 4.0.

of medicine and environmental protection. The application of PLA in the biomedical field mainly benefits from its excellent mechanical properties, optical transparency, and controllable degradation characteristics. In the biological environment, PLA can gradually decompose into small lactic acid molecules through hydrolysis. These small molecules can be metabolized by the human body into carbon dioxide and water, with almost no toxic side effects [99].

Therefore, PLA has been approved for the manufacture of implantable medical devices, such as surgical sutures, fracture fixation plates, and drug sustained-release systems. In addition, PLA fibers have been developed into photofunctional polymer fibers for optical sensing and biological signal monitoring due to their low light propagation loss and high mechanical strength. PLA-based optical fibers can be used for light transmission in deep tissues to achieve photochemotherapy for tissue repair. The high transparency and moderate refractive index of PLA make it an ideal material for manufacturing waveguides. Research shows that PLA optical fibers can effectively transmit optical signals and achieve optical imaging and treatment in biological tissues. Its thermoplasticity also enables PLA to be easily processed through techniques such as melt extrusion and 3D printing, thereby meeting the demands of customized optical devices (Figure 1.20). In addition, by regulating the molecular weight and the proportion of copolymer monomers of PLA, its degradation rate and mechanical properties can be further optimized to adapt to specific biological application scenarios [100].

Elastomer photofunctional fibers such as poly(octamethylene carbonate-cooxymethylene carbonate) (POC-POMC) and PDMS have shown broad biomedical application potential due to their good mechanical flexibility and optical properties. POC-POMC photofunctional fiber is a kind of degradable elastomer material. Its transmittance of visible light (400–700 nm) is approximately 90%, and the elastic modulus is 0.1–1 MPa. It is suitable for flexible implant devices and shows excellent performance, especially in PDT. It can deliver photosensitizers and precisely act on the target tissues. Meanwhile, the degradation products are nontoxic and meet the safety requirements for in vivo implantation. PDMS photofunctional

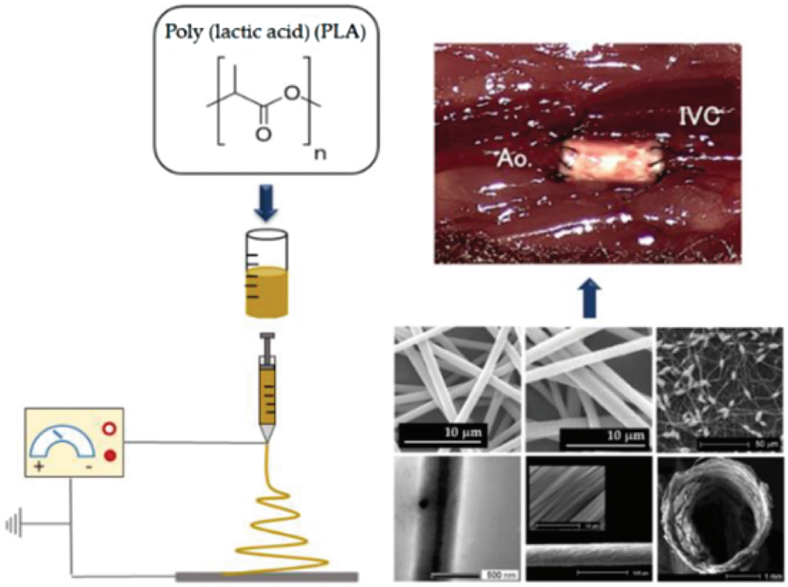

Figure 1.20 Bioapplications of hierarchically structured electrospun PLA materials. *Source:* Maleki et al. [100] / MDPI / CC BY 4.0.

fibers have garnered significant interest in the areas of optical imaging and biosensing due to their light transmittance of over 95% in the 400–800 nm band and low refractive index of approximately 1.4. Studies have shown that microstructured optical fibers based on PDMS have low optical loss (with an attenuation coefficient of approximately 0.2 dB/cm), can achieve efficient optical transmission in biological tissues, and are suitable for real-time monitoring and tissue repair. In conclusion, elastomer photofunctional fibers combine excellent optical performance and mechanical properties, providing efficient solutions for fields such as tissue engineering, phototherapy, and biosensing (Figure 1.21). Through further material modification and structural optimization, they are expected to expand their applications in complex medical scenarios [101].

Bioapplications Photofunctional polymer fibers based on synthetic materials have significant advantages in phototherapy [102]. Optical imaging offers high sensitivity, resolution, and speed, making it highly promising for investigating disease mechanisms, acquiring physiological information, and diagnosing various conditions. The role of photofunctional polymer fibers in biological imaging is mainly reflected in their optical properties of low-loss light conduction and biocompatibility, especially playing a crucial role in deep tissue biological imaging, which makes high-resolution imaging of deep structures in organisms possible. These fibers can penetrate the surface tissue and transfer light to the deep tissue, thereby imaging and analyzing the deep tissue (Figure 1.22) [103].

The citrate-based polymer fiber with photofunctions has been reported to be capable of in vivo imaging and deep tissue light propagation (Figure 1.23). As this kind of

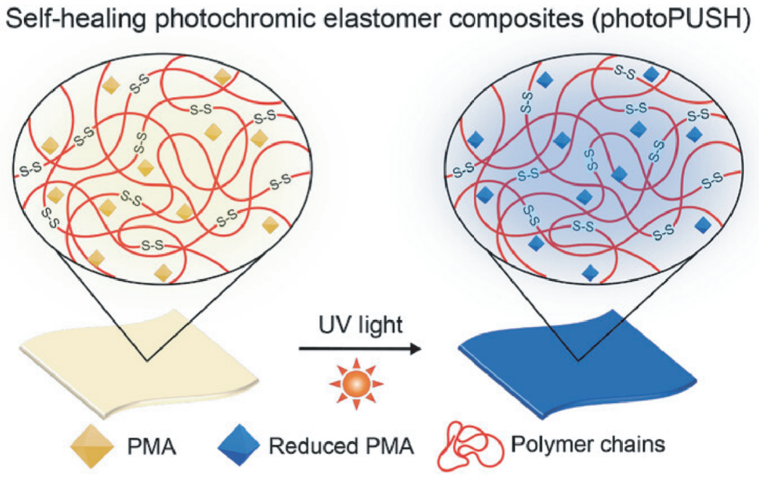

Figure 1.21 Photochromic performance of light-sensitive elastomer fiber. *Source:* Yimyai et al. [101] / with permission of John Wiley & Sons.

fiber is biodegradable and nontoxic, it can remain in the patient's body and naturally degrade after treatment without the need for surgical removal. This not only reduces the patient's pain and medical expenses but also improves the therapy effect. The degradation products of polymers at different concentrations were tested on 3T3 fibroblasts, and it was found that their cytotoxicity was low and there was a significant change compared with the FDA-approved PLGA. Subcutaneous implantation studies in rats revealed no significant difference in the in vivo foreign body response between POC or POMC and PLLA coating of optical fiber, which are widely used in biomedical implants [103].

In the future, research on photofunctional polymer fibers for biological applications will concentrate on substantially improving and optimizing various properties to overcome existing technological and market challenges. Firstly, for photothermal applications, flexible structures, and special load requirements, materials need to achieve breakthroughs in mechanical properties and thermal stability. Additionally, the potential of dye-doped fibers in sensing, wavelength conversion, and transmission applications is worth further exploration. The development of such fibers may become an important direction to fill the market gap in standard optical fiber applications. The development of specific polymer types remains highly uncertain and requires further research. For example, the batch stability of natural polymers, the controllability of the degradation process, and the potential immune response still need further study; meanwhile, the combination of natural and artificial fibers may become a new research trend.

From a long-term development perspective, the research on biocompatible optical fibers will advance in two directions in parallel: one is to develop optical fibers suitable for short-term implantation and that are fully degradable; the second is to design optical fibers that meet the long-term monitoring requirements and have sufficient stability. These advancements will rely on innovations in new materials and

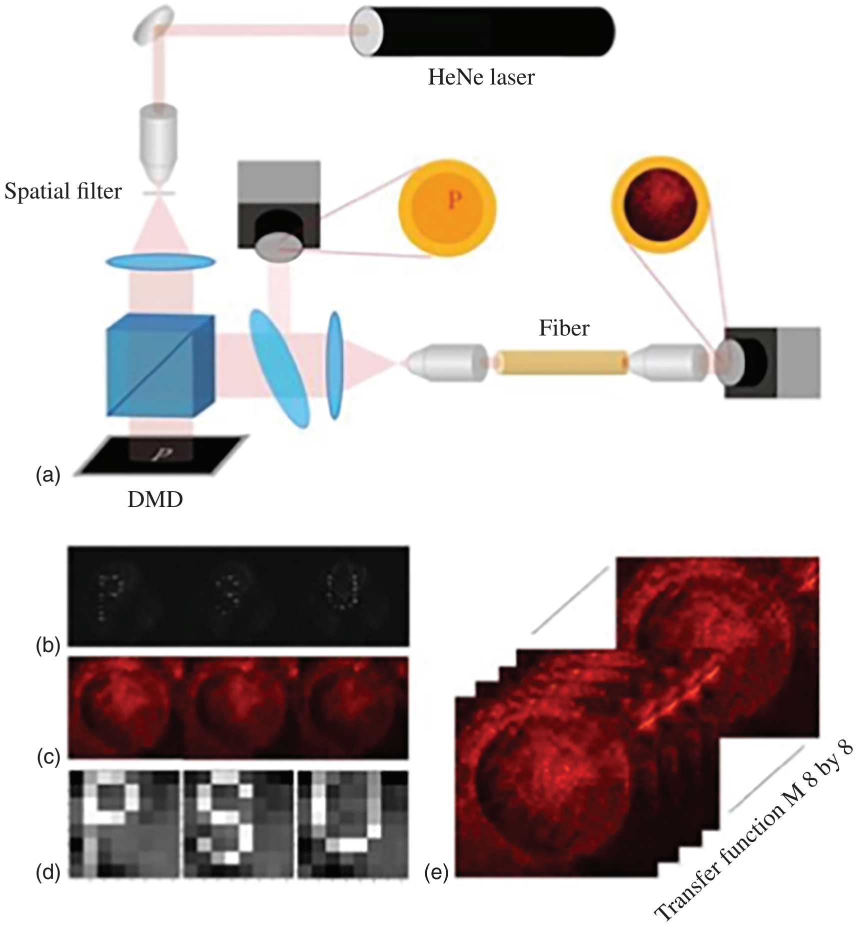

Figure 1.22 Bioimaging and image reconstruction utilizing degradable optical fibers. *Source:* Reproduced with permission from Shan et al. [103] / Elsevier.

manufacturing methods to meet the dual demands of the biomedical field for optical transmission performance and low immune response. Overall, the future of artificial polymer fibers will witness more breakthroughs in fields such as biosensing, optogenetics, and precision medicine through the deep integration of materials science, biomedical engineering, and advanced processing technologies.

1.2.3 Films

Photofunctional polymer films are a type of polymer material with special optical properties. These films achieve their functions by absorbing, emitting, reflecting, or scattering light. Due to their structural diversity and functional tunability, they are widely used in optical devices, biosensing, intelligent displays, solar cells, and biomedical fields. The focus of the research on photofunctional polymer films is to achieve an efficient light response and multifunctionalization of materials

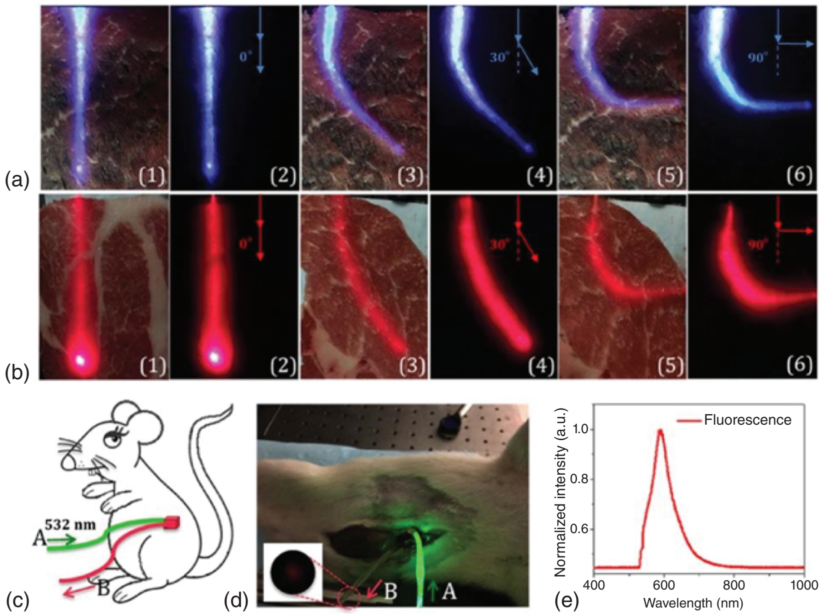

Figure 1.23 Flexible citrate fiber systems for deep tissue phototherapy. *Source:* Reproduced with permission from Shan et al. [103] / Elsevier.

by designing chemical structures and optimizing processing techniques. The performance of photofunctional polymer films is affected by multiple factors, including the chemical structure of the polymer, the thickness and uniformity of the film, and the interfacial interaction between the polymer and the substrate. The optical functional performance of films can be improved through methods such as molecular design, optimization of thin film preparation processes, and posttreatment techniques. For instance, by introducing polymers with specific functional groups, the light absorption efficiency and light stability of the film can be enhanced. By changing the thickness and uniformity of the film, the light scattering and light reflection characteristics of the film can be optimized. The adhesion and mechanical stability of the film can be improved by strengthening the interfacial interaction between the polymer and the substrate.

These films can be classified according to their functions and application fields, mainly including fluorescent films, photochromic films, photoelectric conversion films, and near-infrared (NIR) absorption films. These films have shown great application potential in fields such as biosensors, bioimaging, and drug delivery systems. In the following section, we will provide detailed information about the functional mechanisms, performance characteristics, and preparation methods of photofunctional polymer films and their potential in biological applications.

1.2.3.1 Fluorescent Film

Fluorescent films are materials that can absorb light and emit light of specific wavelengths, usually achieved by doping fluorescent dyes, quantum dots, or

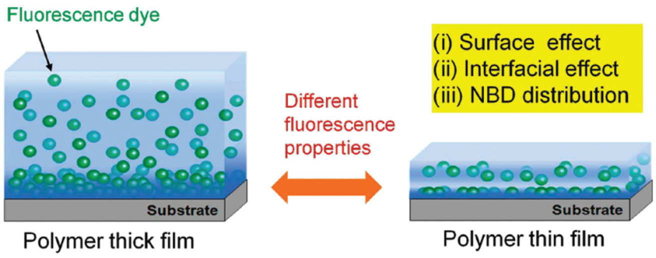

Figure 1.24 Thickness-dependent fluorescence anomalies in fluorescent films controlled by NBD interfacial aggregation. *Source:* Shundo et al. [104] / with permission of American Chemical Society.

luminescent polymers in a polymer matrix [104]. As shown in Figure 1.24, doping the fluorescent dye (6-(*N*-(7-nitrophenyl-2-oxa-1,3-diazol-4-yl)amino)hexanoic acid, NBD) into polymer films of polystyrene (PS) and hydrogenated PS produces unusual fluorescent behavior: the fluorescence lifetime and the maximum emission wavelength increase as the film thickness decreases. This is due to the fact that in thick films, NBD molecules form aggregates at the interface, but this behavior is not observed in thin films.

The mechanism of fluorescent films is mainly based on the emission properties of fluorescent segments, which enable the films to absorb light energy and reemit light of specific wavelengths. Fluorescent films usually contain photoactive components like organic dyes or inorganic quantum dots. When these photofunctional components are illuminated, they absorb light, causing electrons in the ground state to transition to an excited state. As these electrons relax back to the ground state, they release energy in the form of emission [105]. According to the various spin states in the radiation relaxation process, photoluminescence includes two emission types: fluorescence and phosphorescence. The term “fluorescence” refers to light emission that occurs between energy states with the same spin multiplicity, typically lasting no more than about 10 ns. In contrast, “phosphorescence” describes light emission between states with different spin multiplicities, and this process can persist from microseconds to several seconds [106]. The absorption and emission processes of photoluminescence can both be simplified in the Jablonski energy diagram shown in Figure 1.25.

Thin-film fluorescence sensing is an important form of fluorescence sensing. It has the advantages of high sensitivity, good designability, relatively simple instrument structure, low energy consumption, no involvement of radioactive sources, and easy portability, and has attracted special attention. The fluorescent sensing mechanism of the film mainly includes specific binding or reaction between the sensing unit and the detected molecules, as well as the disturbance of the microenvironment of the sensing unit by the detected molecules [107]. The structure of the active layer where the sensing unit is located greatly affects the sensing performance of the thin film, especially the sensing response dynamics. In addition, the fluorescence intensity and optical brightness of fluorescent films largely depend on preparation conditions, such as annealing temperature [108].

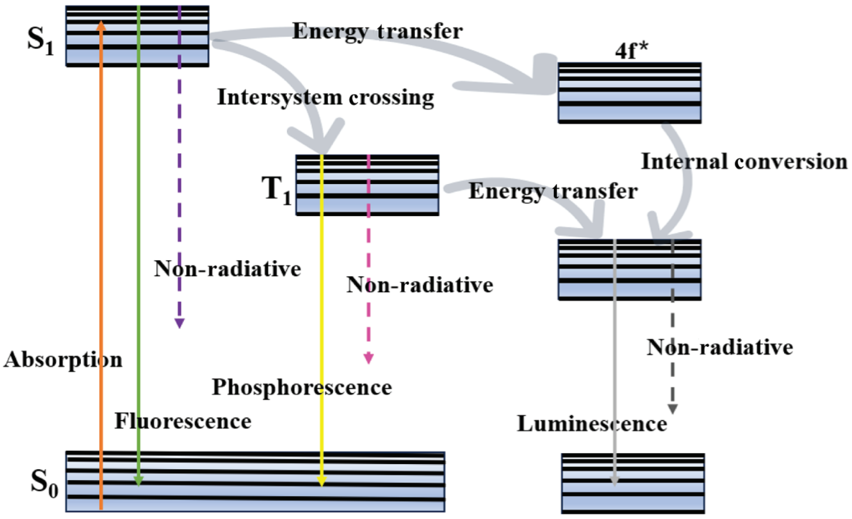

Figure 1.25 Jablonski diagram.

This type of film features high photoluminescence efficiency, spectral tunability, and excellent stability, and is widely applied in biological imaging, sensing, and display technologies. Fluorescent films are often used for real-time tracking of biomolecular dynamics, such as detecting specific proteins, DNA, or small-molecule metabolites. For example, thin films based on the FRET mechanism can be used for highly sensitive biosensing.

1.2.3.2 Photochromic Films

Photochromic functional films refer to thin film materials that can undergo specific chemical reactions under the irradiation of light of a certain wavelength, causing significant changes in their absorption spectra. However, under the irradiation of light of another wavelength or the effect of heat, they can restore their original functions (Figure 1.26) [109]. Due to its excellent optical sensitivity, it has broad application potential in fields such as sensors, erasable rewritable optical discs, camouflage, and anticounterfeiting.

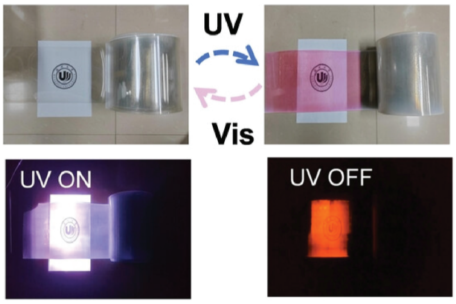

Figure 1.26 Photochromism in photofunctional polymer films. *Source:* Chen et al. [109] / John Wiley & Sons.

Photochromic functional film materials can be grouped into two major categories relying on their main components: inorganic photochromic functional films and organic photochromic functional films. Inorganic photochromic functional films, such as nano-WO_3 films [110], can be prepared by methods like electrodeposition, chemical vapor deposition, and sputtering. At present, the main components of the organic photochromic functional membrane materials under study are generally spiropyran and spirooxazine compounds, azo compounds, chloroacetic anhydride compounds, and diarylethylene compounds [111]. Compared with inorganic photochromic functional films, organic photochromic functional films can adjust their sensitive wavelengths by designing the molecular structure of photochromic compounds and are easy to be mechanically processed into films.

The color-changing mechanism of photochromic materials involves two processes: photoexcitation and structural change. When photochromic materials are exposed to light, the energy of photons is absorbed, causing excited-state transitions in the molecules within the material. This process is achieved through the excitation and transition of electrons within the molecule. When in the excited state, the molecule's electronic structure and energy levels are altered, leading to changes in both the absorption and reflection spectra of the material, thereby resulting in a color change. During the photoexcitation process, the molecular structure of photochromic materials changes, which is the basis of photochromism. The mechanism of photochromic films is mainly based on the photoinduced isomerization of molecules [112]. When these materials are exposed to light, their molecular structures change, thereby altering the light absorption properties of the materials. This structural change is reversible. When the light source is removed, the material will return to its original state. This phenomenon can be represented by the following chemical equation:

$$\mathrm{A\ (Closed\text{-}ring)} + h\nu \rightleftarrows \mathrm{B\ (Open\text{-}ring)}$$

$$\text{Or } \mathrm{A\ (trans)} + h\nu \rightleftarrows \mathrm{B\ (cis)}$$

Among them, A is the photochromic material, $h\nu$ is the photon energy. A and B can be reversibly converted under light irradiation.

Organic photochromic film materials have been widely studied and applied in some fields, but there are also some problems [113].

1) The synthesis of organic photochromic compounds is difficult, especially for some photochromic heterocyclic compounds, which leads to high costs of thin film materials and limits their application. The current research direction is to find simpler preparation methods to reduce costs.
2) The key problems in the organic light-induced chromic light storage system have not been completely solved and have not yet met the requirements for industrialization. The current research direction is to search for organic photochromic systems with reversible and detectable bistability at room temperature.
3) For most organic photochromic materials, including photochromic films prepared by various methods, the so-called reversible photochromic behavior is not unconditional and infinitely reversible. This is because during the long-term

photochromic cycle, these dye molecules will undergo side reactions such as oxidation and degradation, causing the loss of photochromic components, which in turn leads to the reduction or even loss of the photochromic performance of the material.

The fatigue resistance of photochromic materials is still not high enough. The current research directions include modifying the molecular structure of photochromism, seeking new photochromic varieties with better fatigue resistance, and enhancing their fatigue resistance through measures such as isolation and protection.

This type of film demonstrates significant value in fields such as optical switches, rewritable storage, and smart windows. This type of film features a fast light response speed, high repeatability, and excellent fatigue performance. By embedding photochromic molecules into a polymer matrix, sensors that respond to specific biomolecules can be fabricated for detecting pollutants or biomarkers in the environment. Photochromic films can also be applied for preparing intelligent systems of drug delivery, which control the release rate and time of drugs through light exposure. This system can be artificially controlled to achieve controllable and rapid release of therapeutic drugs at the lesion site (such as tumors), overcoming many shortcomings of traditional drug delivery systems (slow drug release, poor selectivity, low drug utilization rate, etc.), thereby significantly reducing damage to normal cells. For instance, films designed through azobenzene derivatives can achieve light-controlled release of drugs, effectively enhancing the targeting and safety of treatment [114].

1.2.3.3 Photoelectric Conversion Thin Film

Photoelectric conversion films are materials that harness the photovoltaic effect to directly transform solar energy into electrical energy. Their working principle mainly involves processes such as light absorption, electron excitation, and charge separation. In photoelectric conversion devices, when light illuminates the surface of a photoelectric conversion device, the semiconductor material within the device absorbs the energy of the incoming photons. In semiconductors, this photon energy can excite electrons, causing them to move from the valence band to the conduction band and thereby generate electron-hole pairs [115]. This process is the initial stage of photoelectric conversion and also the key step in converting light energy into electrical energy. Secondly, the excited electron-hole pairs will move in the semiconductor, forming electron and hole flows. Through appropriate structural design and material selection, electrons and holes can be collected on different electrodes, respectively, thereby forming voltage differences and currents. This is how light energy is converted to electrical energy.

Such films are usually prepared using π-conjugated polymers (such as polythiophene, polystyrene derivatives) or organic–inorganic composites (Figure 1.27) [116]. It features high photoelectric conversion efficiency, a wide spectral absorption range, and stable electrical performance.

Photoelectric conversion films can be used in biosensors and bioenergy collectors. By converting light energy into electrical energy, they achieve the detection of

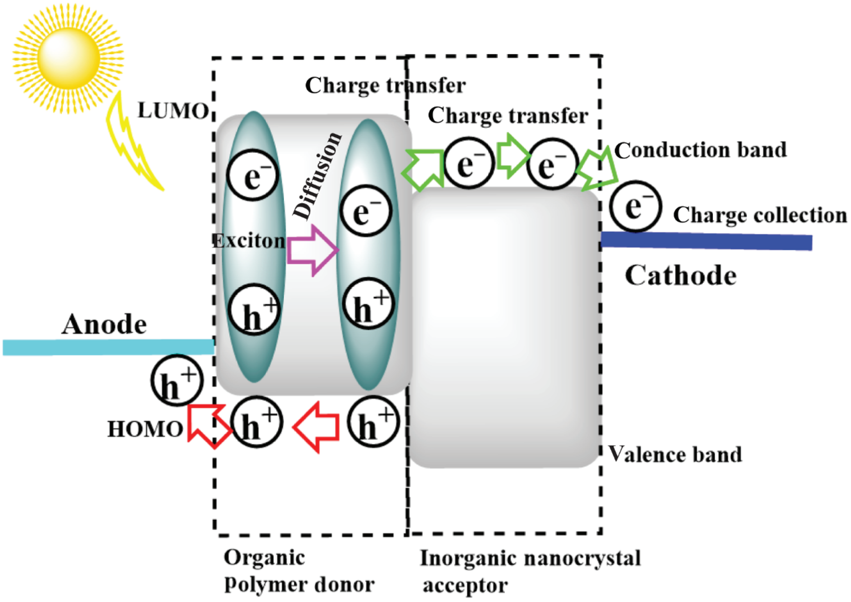

Figure 1.27 Schematic illustration of the working mechanism of organic-inorganic hybrid solar cells.

biological signals and the collection of energy. Flexible photonic devices can achieve implantable biosensing, imaging, and therapy by using biocompatible or biodegradable materials. These films bring more innovation and progress to medical health. In addition, photoconductive films have a broad spectrum of potential applications in the biomedical field. In the field of medical devices and equipment, they are one of the materials for the sensitive layer of biomedical sensors, and can also be used as a medical coating and electrode for electrophysiological monitoring equipment. In the field of diagnosis and imaging, they can be used in the key parts of photoacoustic imaging probes and also in optical coherence tomography components. In tissue engineering and regenerative medicine, they can serve as a cell culture platform and are also intelligent tissue engineering scaffold materials. Photoconductive thin films provide strong support for biomedical diagnosis, treatment, monitoring, and research.

1.2.3.4 Near-infrared (NIR) Absorption Films

The mechanism of near-infrared (NIR) absorption films is based on the material's absorption characteristics of near-infrared light. This type of film can absorb light in the near-infrared region (700–2500 nm) and convert it into other forms of energy, such as thermal energy. Near-infrared absorption films have extensive applications in fields such as solar energy utilization, thermal management, night vision equipment, and military stealth technology. Common NIR absorption film materials include organic materials and inorganic materials. Organic materials, such as some organic dyes and polymers, have good absorption performance and

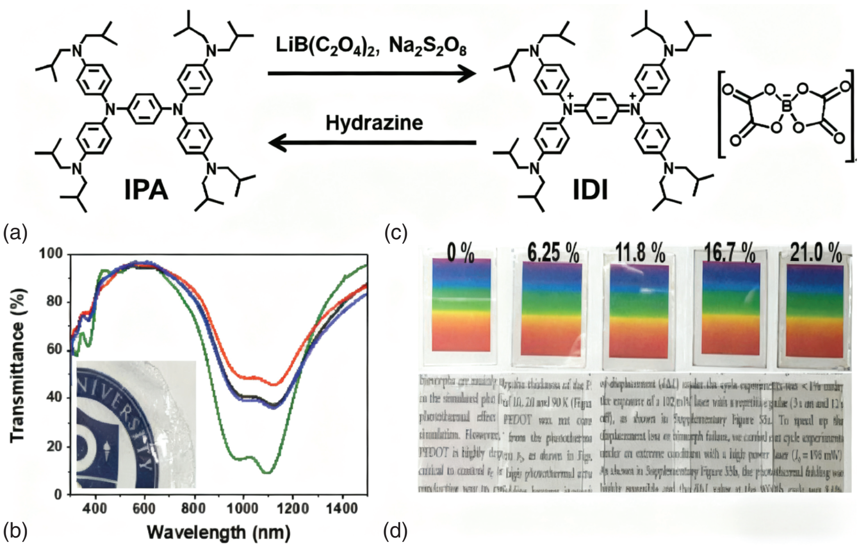

Figure 1.28 Optical properties of NIR-absorbing polymer film. *Source:* Reproduced with permission from Han et al. [117] / John Wiley & Sons.

processability. For instance, certain organic small molecule dyes can precisely absorb near-infrared light within a specific wavelength range (Figure 1.28) [117]. Inorganic materials: Semiconductor materials such as silicon, germanium can also be used as materials for NIR absorption films [118]. These materials can optimize their absorption performance by adjusting their chemical composition and crystal structure.

The mechanism of near-infrared absorption films can be explained in detail from the following aspects:

1) *Intramolecular charge transfer (ICT):* Some organic molecules have a strong absorption capacity in the near-infrared region, which is the result of ICT. This charge transfer can occur between different parts of a molecule, such as the donor–acceptor system, where electrons are transferred from the donor part to the acceptor part, leading to changes in the molecular polarizability and thereby enhancing the absorption of near-infrared light.
2) *Extension of the π-conjugated system:* By extending the π-conjugated system of a molecule, the absorption of near-infrared light by the molecule can be increased. In a π-conjugated system, electrons can move freely within the molecule. When the molecule absorbs near-infrared light, these electrons can be excited to higher energy levels, thereby achieving the absorption of light.
3) *Surface plasmon resonance (SPR) of metal nanostructures:* In metal nanostructures, SPR is a collective oscillating electron movement. When the resonant frequency of SPR of the metal matches the frequency of the incident light, enhanced light absorption occurs. This phenomenon can be used to design near-infrared absorption films. By adjusting the size, shape, and arrangement of the nanostructure, its absorption characteristics for near-infrared light can be controlled.

4) *Doping of organic materials:* Doping organic materials with specific chemical substances can modify their optical properties, increase their absorption of near-infrared light, and thereby effectively suppress infrared radiation.
5) *Thickness and structure of the film:* The thickness and microstructure of the film also affect its absorption of near-infrared light. By optimizing the thickness of the film structure, high-transparency infrared stealth films can be achieved, thereby effectively suppressing high-temperature infrared radiation.

NIR absorption films have numerous applications in the biomedical field: In PTT, NIR absorption films can convert the absorbed near-infrared light into thermal energy, which is used to kill tumor cells. For instance, polymer films doped with gold nanorods can be used in PTT, achieving efficient local heating and ablation of tumors through NIR laser irradiation [119]. NIR absorption films can also be used in drug-controlled-release systems, triggering drug release through NIR light exposure [120].

In conclusion, as a new type of polymer material, photofunctional polymer films have become a research hot spot in the intersection of materials science and biomedicine due to their unique optical properties and adjustability. From the highly sensitive biosensing of fluorescent films to the intelligent drug release of photochromic films, and then to the clean energy conversion of photoelectric conversion films and the precise PTT of near-infrared absorption films, these materials have achieved a leap from basic research to practical application through molecular design and process optimization. Their core advantage lies in achieving multifunctional integration through the precise regulation of chemical structures: Fluorescent films achieve real-time monitoring of biomolecules by mechanisms such as FRET. Photochromic films realize photocontrolled drug release through molecular isomerization. Photoelectric conversion films expand the spectral absorption range by means of π-conjugated systems. Near-infrared absorption films enhance the photothermal conversion efficiency by SPR. These characteristics not only break through the performance bottlenecks of traditional materials but also provide innovative solutions for biomedical engineering. However, the technological transformation of photofunctional polymer films still faces challenges. Problems such as the insufficient fatigue resistance of organic photochromic materials, the biocompatibility optimization of near-infrared absorption films, and the improvement of the stability of photoelectric conversion devices need to be solved urgently.

1.2.4 Hydrogel

Hydrogel, as a material with controllability, flexibility, and biocompatibility, is gradually becoming an important component of photofunctional composites [121, 122]. Traditional hydrogel is usually composed of natural polymers, for example, gelatin, chitosan, and sodium alginate. Hydrogel can be obtained from natural or synthetic polymers, such as polysaccharides and polyvinyl alcohol. These materials can form a three-dimensional network structure after absorbing water and have good swelling, elasticity, and mechanical properties [123, 124].

Hydrogels, with their unique physicochemical properties, are opening up new directions for the research of photofunctional composites. These materials are composed of a three-dimensional network structure, endowing them with a special swelling regulation ability [125]. Simply put, they can change their volume flexibly like a sponge according to the variations in the humidity, temperature, or pH of the surrounding environment. Meanwhile, hydrogels also have excellent flexibility. Even if they are repeatedly stretched and bent, they will not easily lose their original performance. This feature enables them to imitate the mechanical properties of biological tissues. In addition, hydrogels have excellent biocompatibility and have played a significant role in the biomedical field. Whether used as carriers for drug delivery or scaffolds for tissue engineering, they have shown broad application prospects [126]. From the perspective of practical application, gelatin-based hydrogels can provide a favorable growth environment for cells and promote cell adhesion and proliferation [127]. Chitosan hydrogels have both antibacterial and wound healing acceleration functions. Synthetic polymer hydrogels can achieve specific properties through precise molecular design, meeting various scientific research and application requirements.

Photofunctional hydrogels have become an emerging research trend in materials science, chemical engineering, and biomedicine over the past few years due to their unique optical properties and good processability [128]. Photofunctional hydrogels can achieve efficient processing and conversion of optical signals, and have the advantages of fast response speed, high sensitivity, and strong tunability. Furthermore, the three-dimensional network structure of hydrogels gives them unique advantages in fields such as optical sensing and optoelectronic devices [129].

Among them, the research on photofunctional hydrogel began with the exploration of light-responsive polymers, especially in applications such as light-induced deformation, swelling changes, and photocatalytic reactions. Early research focused on the molecular design of light-responsive polymers, such as the photoisomerization of azobenzene polymers, to achieve color switching and shape alteration of materials under light exposure [130]. Hydrogels have gradually demonstrated their unique intelligent responsiveness. They can respond to specific combinations of light intensities and wavelengths, and even achieve coordinated stimulus responses in multiple physical fields (light, electricity, magnetism, and force), ushering in the era of material intelligence [131].

The size effect opens up a new dimension for the performance regulation of photofunctional hydrogels. Nanoscale photofunctional hydrogels, by leveraging the quantum size effect, have a photoluminescence efficiency several times higher than that of traditional materials. Their surface plasmonic resonance peaks can be fully covered from ultraviolet to near-infrared through size adjustment, providing the possibility for optical imaging of deep tissues in organisms. However, the extremely high surface energy brought by the nanoscale size makes them prone to agglomeration during the preparation process and they have poor long-term stability. Photofunctional hydrogels with their moderate size have good processability and mechanical stability while ensuring certain optical properties and are suitable for the preparation of flexible optoelectronic device arrays [132]. The bulk photofunctional hydrogels achieve the improvement of the uniformity and stability of optical performance through the design of a three-dimensional network structure at the macroscopic scale. Multiple photofunctional units can be integrated inside to construct a complex optical signal system, meeting the strict requirements for high performance and high reliability of materials in high-end optical sensing and biomedical imaging equipment [133, 134].

1.2.4.1 Structure and Composition

Hydrogels are a kind of three-dimensional cross-linked polymer network system with macroscopic dimensions. Polymer chain segments form its internal network structure through either chemical cross-linking (such as covalent bonds) or physical cross-linking (including electrostatic interactions, hydrogen bonds, hydrophobic interactions, and more). This structure enables it to absorb water, expand, and form a stable structure similar to a colloid, while remaining insoluble. It can undergo significant and reversible volume changes between the dry and water-saturated states, providing a basis for the dynamic response of the material in different application scenarios. This process is not a simple physical adsorption but involves a complex thermodynamic equilibrium. The degree of swelling can be precisely regulated by parameters such as cross-linking density, the hydrophilicity of the polymer chain, and the osmotic pressure of the external environment [135, 136].

Hydrogel bulk materials can be grouped into natural and synthetic polymer hydrogels according to their composition [137]. Natural polymers include gelatin, chitosan, and alginate; synthetic polymers include polyvinyl alcohol and polymethacrylate.

From the perspective of material composition, natural and synthetic polymer hydrogels exhibit completely different performance characteristics. Gelatin is a protein extracted from animal tissues, featuring excellent biocompatibility and biodegradability. Its abundant functional groups, such as amino and carboxyl groups, can participate in cross-linking reactions. It can also undergo sol-gel transformation at body temperature. This characteristic enables temperature-triggered drug release in drug-controlled-release systems. Chitosan is the deacetylation product of chitin. As a natural cationic polysaccharide, it carries a positive charge in an acidic environment due to the protonation of its amino groups. It can not only interact electrostatically with negatively charged biomolecules but also exhibit broad-spectrum antibacterial activity. It is often used in wound dressings and tissue engineering scaffolds. Alginate is a polysaccharide extracted from brown algae that can form hydrogels in the presence of metal ions (such as Ca^{2+}) and is widely used in the field of biomaterials [138].

Synthetic polymer hydrogels include polyvinyl alcohol and polymethacrylate. The physical cross-linked network formed by PVA through the freeze-thaw cycle has high strength, high elasticity, and good chemical stability, and is often used to prepare gel sensors [139]. Polymethacrylate hydrogels, due to the modifiers of their side chains, can achieve light-controlled performance adjustment by grafting light-responsive groups [140].

1.2.4.2 Physical Properties

These hydrogels can exhibit adjustable physical properties, such as mechanical strength and swelling properties, under different environmental conditions. In terms of mechanical strength, the mechanical strength of the hydrogel can be significantly regulated by changing the cross-linking density, the molecular weight of the polymer chain, and the regularity of the network structure. For example, increasing the dosage of chemical cross-linking agents or enhancing the degree of physical cross-linking can make the hydrogel network tighter, thereby improving its mechanical properties, such as tensile and compressive resistance [141]. For swelling, the behavior of the hydrogel is influenced by the free volume of the network structure and the interaction between the polymer chains and the solvent molecules. In the solvent, increased free volume in the hydrogel network and strengthened affinity between the polymer chains and solvent molecules raised the swelling degree [142].

Hydrogel can respond to external environments like pH, temperature, and light. Take the temperature response as an example. Some hydrogels contain polymer segments that are sensitive to temperature, such as PNIPAM. When the environmental temperature changes, the conformation of the polymer chain will change, thereby causing the swelling or contraction of the hydrogel. In terms of pH response, the acidic or basic functional groups (such as carboxyl groups and amino groups) contained in the hydrogel material will undergo protonation or deprotonation reactions as the pH value of the solution changes [143]. This reaction will alter the charge distribution and intermolecular forces within the hydrogel, thereby causing changes in the hydrogel's volume. In addition, some hydrogels also have responsiveness to specific ions. When specific ions are present in the solution, the hydrogel will specifically bind to the ions, resulting in changes in the physical properties of the hydrogel [144].

In the field of photofunctional composites, hydrogel bulk materials can achieve light-responsiveness by embedding light-responsive molecules, such as photochromic molecules and photosensitive polymers. Photochromic molecules can undergo reversible structural changes after absorbing light of specific wavelengths, thereby altering the optical properties of the hydrogel, such as color and absorption spectra. Photosensitive polymers can undergo reactions such as cross-linking, de-cross-linking, or the movement of molecular chains under the irradiation of light, thereby altering the physical properties of the hydrogel, like mechanical strength and swelling degree. This light-responsiveness enables hydrogel bulk materials to impart them with remarkable flexibility and functional capabilities for biomedical uses [145–148].

1.2.4.3 Fluorescent Hydrogel

Fluorescent hydrogel is an advanced material that combines a three-dimensional network structure with fluorescent properties. It demonstrates unique optical response capabilities by embedding fluorophores into the hydrogel network. This material not only inherits the flexibility and environmental adaptability of traditional hydrogels but also possesses the functions of real-time monitoring and

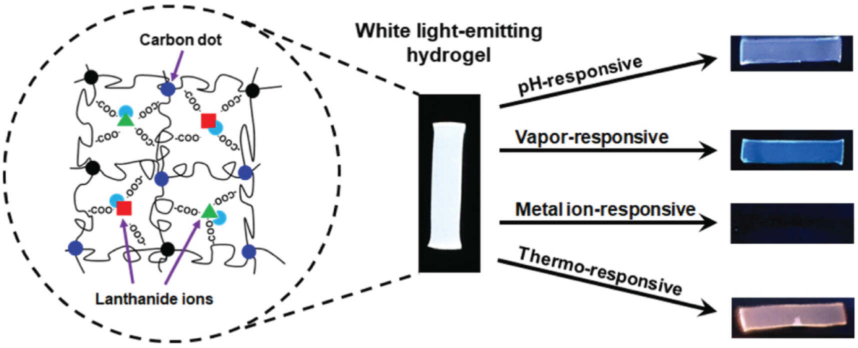

Figure 1.29 Multistimuli-responsive white-light hydrogel. *Source:* Reproduced with permission from Zhu et al. [149] / American Chemical Society.

signal feedback due to its fluorescent properties. The fluorescence behavior of fluorescent hydrogel can be regulated by external stimuli (Figure 1.29), enabling it to exhibit high adaptability and functionality in a variety of complex environments. The emergence of this material has brought new opportunities and challenges to fields like materials innovation, biomedicine, and information technology [149].

The emergence of fluorescent hydrogels stems from the demand for the expansion of the functions of traditional hydrogels. In the field of biomedicine, fluorescent hydrogels can be applied in cell labeling, drug delivery, and tissue engineering, helping researchers gain a deeper understanding of the physiological and pathological processes within organisms. In environmental monitoring, fluorescent hydrogels can detect pollutants in water bodies, providing technical support for environmental protection. In the field of information storage and encryption, the fluorescence signals of fluorescent hydrogels can be used to encode and decode information, achieving anticounterfeiting and information security. In addition, fluorescent hydrogels can also be used as smart materials to manufacture shape memory materials and self-healing materials, demonstrating great application potential [150, 151].

1.2.4.4 Photochromic Hydrogel

Photochromic hydrogel is a kind of smart material that can undergo reversible color changes under ultraviolet or visible light irradiation. This material combines the softness of hydrogel and the unique optical properties of photochromic molecules, making it show broad application prospects in a variety of fields. The color change mechanism of photochromic hydrogels is usually based on the conversion of photochromic molecules between different oxidation states or configurations, with Figure 1.30 illustrating the phase transition mechanism triggered by photothermal stimuli. For instance, inorganic materials such as tungstate and molybdate, as well as organic materials like spiropyrane and diarylethylene, undergo a transformation from colorless to colored under light exposure. This property makes them ideal optically responsive materials [152]. Significant advancements have been made in the investigation of photochromic hydrogels in recent years, especially in terms of mechanical properties, transparency, and response speed.

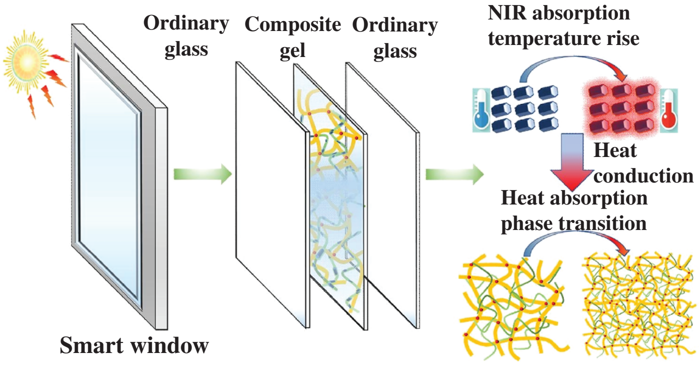

Figure 1.30 Phase transition mechanism of composite hydrogels triggered by photothermal stimuli. *Source:* Zhang et al. [152] / with permission of Elsevier.

The application scope of photochromic hydrogels is extensive, covering multiple fields from basic research to practical applications. In the field of smart windows, photochromic hydrogels can automatically adjust the light transmittance according to the light intensity, thereby achieving energy conservation and comfort [153]. In the biomedical field, photochromic hydrogels can be used for biological imaging and drug release, achieving precise drug delivery and cell labeling through light exposure [154]. In anticounterfeiting technology, photochromic hydrogels can be used to produce highly secure anticounterfeiting labels that display or hide information through light exposure. In addition, photochromic hydrogels can also be used in flexible electronic devices, such as wearable sensors and wireless communication devices, to achieve optical camouflage and information transmission [155]. These applications demonstrate the significance and potential of photochromic hydrogels in modern technology.

1.2.4.5 Photothermal Hydrogel

In today's society, the contradiction between energy demand and environmental protection is becoming increasingly prominent, and at the same time, the biomedical field is also facing many challenges. The emergence of photothermal hydrogel is timely. It can utilize renewable energy sources such as solar energy to achieve efficient photothermal conversion, providing a green and sustainable approach to solving energy problems [156]. In addition, in the field of biomedicine, photothermal hydrogels can be used for precise cancer treatment, antibacterial, wound healing, etc. Their noninvasive nature and high efficiency make them a highly promising therapeutic approach. For example, photothermal hydrogel can achieve local temperature rise through irradiation with near-infrared light, thereby killing cancer cells or bacteria while avoiding damage to the surrounding normal tissues [157]. In addition, photothermal hydrogels can also be used in the development of smart materials, such as photothermal-driven soft robots and smart sensors, providing a new material basis for the development of artificial intelligence and flexible electronics [158].

The realization of photothermal hydrogel primarily depends on the synergistic interaction between photothermal conversion units and hydrogel matrices. Photothermal conversion agents such as metal nanoparticles, semiconductor materials, and carbon-based materials can absorb light energy and convert it into thermal energy. These photothermal conversion agents are uniformly dispersed in the hydrogel matrix, such as polyvinyl alcohol and sodium alginate to form composite materials with photothermal conversion functions. When the photothermal hydrogel is exposed to light, the photothermal conversion agent absorbs light energy and generates heat. The heat is conducted through the hydrogel matrix, achieving a local temperature rise. For example, Figure 1.31 shows ultra-flexible

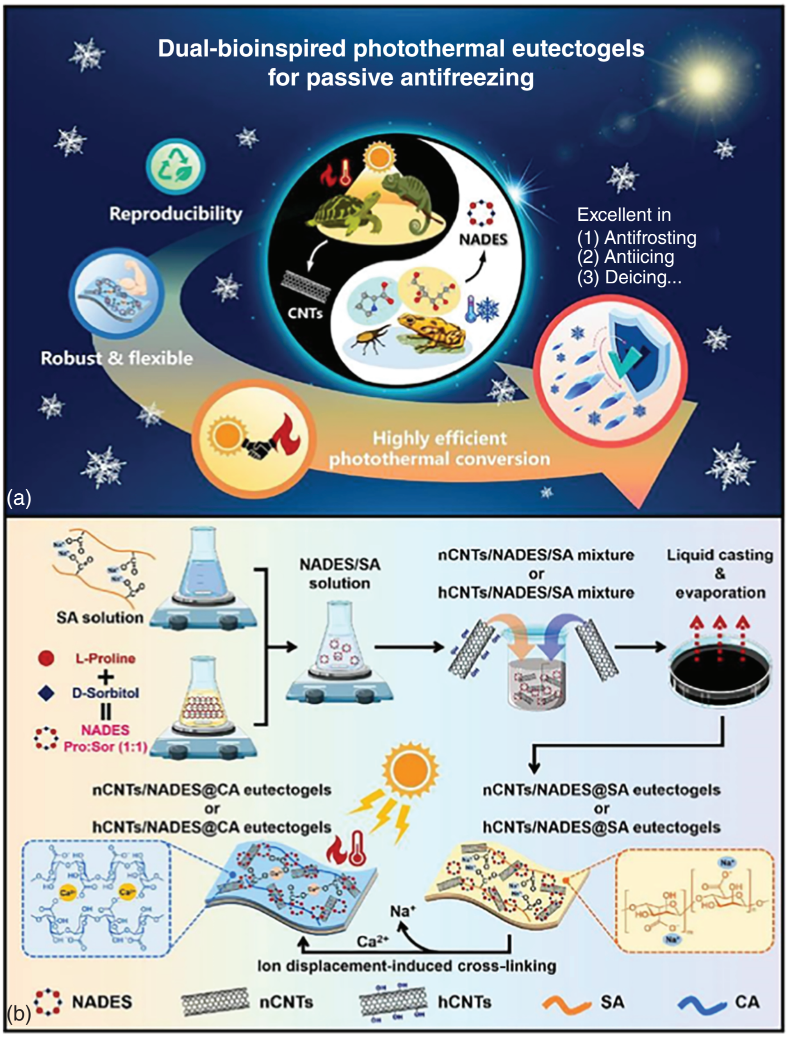

Figure 1.31 Ultra-flexible photothermal eutectogels with passive antifreezing. *Source:* Tian et al. [159] / Elsevier / CC BY 4.0.

photothermal eutectogels with passive antifreezing properties. These materials are being optimized through improved preparation processes to enhance performance and stability. Meanwhile, more in vivo experiments and clinical studies are also being carried out to verify the safety and efficacy of the photothermal hydrogel [159].

1.2.4.6 Photoelectric Conversion Hydrogel

Photoelectric conversion hydrogel is a special material capable of converting light energy into electrical energy. It is usually composed of a matrix with photosensitive properties and components capable of generating charge separation and transport. The core advantage of this material lies in its ability to directly convert light energy into electrical energy, enabling a self-power supply without the need for an external power source. It has broad application prospects in fields such as energy conversion, sensor technology, and intelligent devices, providing new possibilities for achieving efficient and sustainable energy utilization and intelligent systems.

With the development of technology, people's demand for energy is constantly increasing, and at the same time, the pursuit of environmentally friendly energy is becoming increasingly urgent. The acquisition and use of traditional energy sources are often accompanied by problems such as environmental pollution and resource depletion. In the field of energy, it can be used to manufacture solar cells, efficiently converting solar energy into electricity to provide clean energy for households and industries [160]. In the field of sensors, photoelectric conversion hydrogel can be used as the core material of self-powered sensors to detect physical quantities such as light intensity, temperature, and pressure [161]. By doping photoacid in the hydrogel diode and taking advantage of the property of photoacid releasing protons under light, the transmission of photogenerated carriers and the generation of electrical energy are achieved. This is driven by the intrinsic electric field within the hydrogel PN junction (Figure 1.32). For instance, it can be used in smart agriculture to monitor light conditions and help optimize the growth environment of crops. It can also be used in intelligent buildings to achieve automatic dimming and energy-saving control.

The realization principle of photoelectric conversion hydrogel is mainly based on the generation, separation, and transport of photogenerated carriers. When light

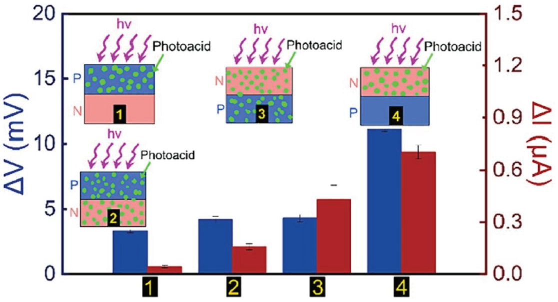

Figure 1.32 Hydrogel photoelectric response by photoacid doping. *Source:* Wu et al. [161] / with permission of Elsevier.

illuminates the hydrogel material, the photosensitive matrix absorbs photon energy, causing electrons to be excited from the valence band to the conduction band and forming electron-hole pairs. These photogenerated carriers are then separated and move in opposite directions under the influence of an internal electric field or concentration gradient within the material. By introducing appropriate electrode materials into the hydrogel, these migrating carriers can be collected, thereby generating current and voltage between the electrodes and achieving the conversion of light energy to electrical energy. For example, in ionic thermoelectric hydrogels, the absorption and conversion of light energy are achieved by combining photothermal materials and ionic thermoelectric effects. Photothermal materials convert light energy into thermal energy, generating a temperature gradient, which in turn drives the migration of ions in the hydrogel and generates a thermal voltage [162]. The photosensitive hydrogel utilizes the synergistic interaction between photothermal and thermoelectric effects. Through the photothermal layer, light energy is converted into heat, and then the thermoelectric layer converts heat into electrical energy, achieving the “photothermal—electrical” cascade conversion [163].

Furthermore, in the field of medical and healthcare, photoelectric conversion hydrogels can be used to develop wearable health monitoring devices, such as self-powered heart rate monitoring wristbands and blood glucose monitoring patches, providing convenience for people’s health management [164].

1.2.4.7 Light-controlled Release Hydrogel

Light-controlled release hydrogel is an intelligent material that can achieve the on-demand release of drugs or other substances through light stimulation. The core advantage of this material lies in its precise control ability, which enables the release of drugs within a specific time and space, thereby enhancing therapeutic effects and reducing side effects. The emergence of light-controlled release hydrogels has brought brand-new solutions to fields such as drug delivery, biomedical engineering, and environmental science.

The application scope of light-controlled release hydrogels is extensive, covering multiple fields such as biomedicine, environmental science, and materials science. In the field of biomedicine, light-controlled release hydrogels can be applied in targeted drug delivery, cancer treatment, tissue engineering, and wound healing. In traditional drug delivery systems, achieving precise control over drug release is often challenging, which results in the accumulation of drugs at nontarget sites and increases the risk of side effects. Furthermore, for some diseases that require long-term or regular drug administration, traditional methods are difficult to meet the demands. The light-controlled release hydrogel achieves the precise spatiotemporal release of drugs through light exposure (Figure 1.33), solving these problems. For instance, in cancer treatment, light-controlled release hydrogels can precisely deliver drugs to the tumor site and release them on demand under light, thereby minimizing damage to normal tissues. By controlling drug release through light exposure, precise treatment can be achieved, reducing drug waste and side effects. In environmental science, light-controlled release hydrogels can

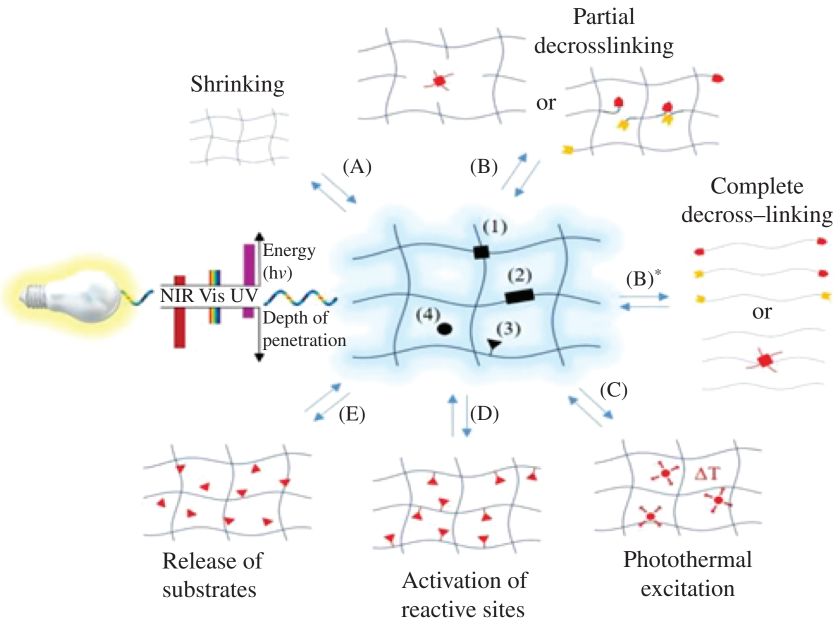

Figure 1.33 Light-activated release in hydrogels. *Source:* Li et al. [146] / with permission of John Wiley & Sons.

be used for the controllable release and degradation of pollutants, enhancing the efficiency of environmental remediation. In addition, light-controlled release hydrogels can also be used in the design of smart materials, such as light-controlled sensors and optical drivers, providing new ideas for the development of smart devices [145, 146].

Hydrogels have emerged as a prominent research focus in the biomedical field due to their excellent physicochemical properties and tunability in photofunctional composites. Hydrogel bulk materials have shown great potential in drug delivery, gene therapy, tissue engineering, PTT, and other aspects. With the continuous in-depth research on photofunctional materials, the biological applications of hydrogels will be further expanded, providing more advanced and efficient solutions for future intelligent medical care and precise treatment. There are numerous types of photofunctional bulk hydrogels, covering multiple fields such as photoresponse, photocatalysis, optical sensing, and photocontrolled drug release. These hydrogels have demonstrated great application potential in fields such as biomedicine, environmental protection, sensors, and smart materials through different photoresponsive mechanisms, combined with advanced optical materials like metal nanoparticles, quantum dots, and photoactive molecules. With the deepening of research, photofunctional bulk hydrogels will continue to play an important role in more precise light regulation and intelligent response materials. In intelligent manufacturing, it helps flexible manufacturing processes such as light printing and light molding [165].

1.3 Prospects for Bioapplications of Photofunctional Polymer Composites

Light, as an external source of stimulation, has many unique advantages. Its non-invasive nature allows it to penetrate biological tissues and reach the target area without disrupting the integrity of the surrounding tissues, providing a completely new approach to the diagnosis and treatment of diseases. At the same time, light also has high spatial resolution and precise time controllability, which makes it possible to achieve precise control of the behavior of light-responsive materials by adjusting the wavelength, intensity, and time of light irradiation [166]. Based on the light-responsive properties, photofunctional polymer composites, as an emerging research hot spot at the intersection of materials science and biomedicine, have received a great deal of attention recently. The ability of such materials to exhibit tunable physical, chemical, or biological responses to external light stimuli has brought new therapeutic and diagnostic tools to the biomedical field. By cleverly combining optical properties with other key functions such as drug release, tissue repair, and cell induction, photofunctional polymer composites have shown great potential for applications in a variety of cutting-edge fields such as precision medicine, smart drug delivery, noninvasive bio-imaging, and cancer therapy [167–169].

With the continuous progress of nanotechnology and the fine design of molecular structures, the microstructural design of photofunctional polymer composites has become increasingly delicate, providing a solid material foundation for their precise response to light stimulation [170]. The nanoscale material structure can significantly enhance the interaction between light and matter and improve the efficiency of light energy conversion [168]. The rapid development in the field of photoelectrochemistry further expands the application scope of photofunctional polymer composites, providing new ideas for their applications in biosensing [171]. In-depth research in biomaterials science has ensured the good compatibility, stability, and degradability of photofunctional polymer composites in living organisms, enabling them to safely and effectively serve biological applications.

The multifunctional integration of photofunctional polymer composites is also a core advantage in their biological applications. These materials are capable of combining various therapeutic means, such as photosensitive drug release, PDT, and PTT, to achieve synergistic therapeutic effects. The application in cancer treatment is especially remarkable. Cancer treatment has long faced challenges such as limited efficacy and significant side effects. Photofunctional polymer composites can integrate multiple therapeutic modes, among which PTT uses the material's absorption of light to convert light energy into heat energy, generating high temperatures locally to destroy tumor cells; PDT induces apoptosis of tumor cells by generating ROS through light excitation; and light-controlled release of chemotherapeutic drugs further enhances the killing effect on tumor cells. These three therapeutic modes synergize with each other, overcoming the limitations of a single therapeutic means and providing a brand new strategy for cancer treatment [172, 173].

Photofunctional polymer composites, with their unique light-responsive properties, intelligent responsiveness, and integrated multifunctionality, show a broad application prospect in the biological field. With the continuous development and improvement of related technologies, photofunctional polymer composites are expected to move from basic research to clinical applications, bringing revolutionary breakthroughs in precision medicine, disease diagnosis and treatment, and opening up a new chapter in the field of biomedicine.

In addition to the above applications in the biomedical field, by integrating photofunctional polymer composites with biological components (such as enzymes, cells, or tissues), efficient light energy conversion and intelligent environmental repair can be realized. In the field of light response, such systems not only mimic and enhance natural photosynthesis but also develop novel light-driven drug delivery systems and environmental sensing technologies, demonstrating the potential for interdisciplinary innovation. Although challenges remain in terms of stability and safety, their breakthroughs in the fields of energy, healthcare, and environmental protection provide a brand new technological path for sustainable development.

1.3.1 Biological Detection and Imaging

Biological detection and imaging technologies play a crucial role in modern medicine, drug development, and biological research. They help us to access the states and changes of molecules, cells, tissues, or organs in living organisms through different physical, chemical, and biological principles. These technologies usually combine physical principles such as optics, magnetism, and acoustics to realize real-time, noninvasive observations of structures and functions within organisms. With the continuous development of technology, these imaging techniques will play an increasingly important role in disease diagnosis, therapeutic monitoring, and drug development. For example, fluorescence imaging is based on the phenomenon that molecules emit light in the direction of long wavelengths after absorbing light energy. By exciting fluorescent molecules (e.g. dyes, quantum dots) in a sample and emitting fluorescence when they return to their ground state, the fluorescent signal is used to detect the presence and location of the target molecule. Different fluorescent dyes can emit different wavelengths of light, thus enabling multiple labeling and imaging [174]. By virtue of their special optical properties and fine design, photofunctional polymer composites can enhance the signal strength and contrast during biological detection and imaging through various mechanisms such as light response, surface enhancement effect, and quantum effect, thus significantly improving the sensitivity, resolution, and accuracy of the detection.

1.3.1.1 Fluorescence Imaging

Fluorescence bioimaging technology has found many applications in biomedical research due to its high sensitivity, noninvasiveness, and real-time imaging capability. However, traditional fluorescence imaging techniques have some limitations, such as monochromatic fluorescence being easily interfered with by biological background fluorescence, resulting in insufficient imaging accuracy.

In addition, fluorescent probes have poor intracellular stability, especially under ultraviolet irradiation, which is prone to photobleaching, limiting their application in long-term imaging.

Conjugated polymers, characterized by a rigid conjugated backbone and delocalized electronic structure, have side chains that can be modified and easily combined. These properties make them excellent fluorescent probes with outstanding light stability, strong fluorescence signals, and good biocompatibility [175].

Recently, two-photon fluorescence imaging (TPFI) has garnered a lot of attention from researchers as a noninvasive method for examining intricate biological issues. Deeper penetration, reduced autofluorescence, less scattering, and less phototoxicity are some of the major benefits of TPFI over traditional single-photon excitation methods because it is typically driven by a near-infrared excitation (700–1000 nm). The amphiphilic triblock copolymer F127 was used as a matrix to wrap the two-photon absorption (TPA) material PFBT to form micelles, and a protective shell layer of silicon dioxide was further grown on its surface (Figure 1.34a). The obtained PFBT-F127-SiO_2 NPs exhibited good dispersion, colloidal stability, good biocompatibility, a broad TPA cross-section, and a high quantum yield. The large TPA cross-section permits high imaging resolution to be achieved with less excitation power, further minimizing the photodamage of excitation light on fluorescent materials and biological targets. As shown in Figure 1.34b, high-resolution visualization of the deep cerebral vascular system can be achieved by intravenous administration in live mice, suggesting that PFBT-F127-SiO_2 NPs are useful TPA probes for vasculature imaging in vivo [176].

Furthermore, by co-encapsulating far-red/near-infrared (FR/NIR)-emitting conjugated polymer PFVBT, poly(lactic-*co*-glycolic-acid)-poly(ethylene glycol)-folate (PLGA-PEG-FOL), and PLGA, the resulting CP nanoparticles can serve as in vivo targeted fluorescent and magnetic resonance imaging dual-mode probes. As shown in Figure 1.35, the CPNs are smooth spherical structures with an average diameter of 180 nm. in vivo experiments, active endocytosis mediated by folate receptors and passive targeting brought on by the increased permeability and retention impact

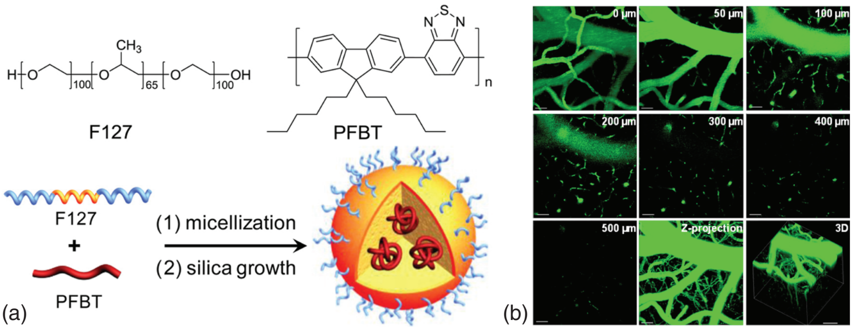

Figure 1.34 (a) Schematic diagram of the preparation of PFBT-F127-SiO_2 NPs; (b) fluorescence imaging of mice cerebrovascular system at different depths. *Source:* Reproduced with permission from Geng et al. [176] / American Chemical Society.

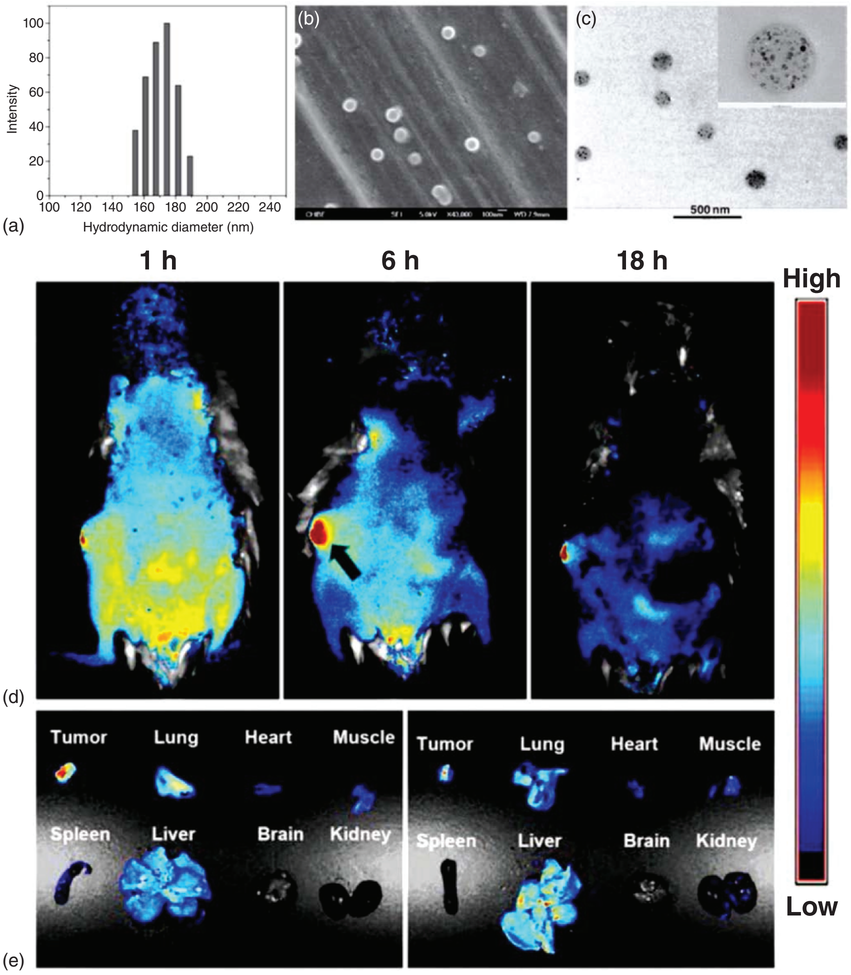

Figure 1.35 (a) Particle size distribution of CPNs; (b) and (c) SEM images of CPNs before and after modification; (d) and (e) in vivo imaging of CPNs in mice. *Source:* Reproduced with permission from Li et al. [177] / John Wiley & Sons.

were observed. The accumulation of CPNs within live tumor tissues can be observed in fluorescence imaging, enabling precise tumor monitoring [177].

1.3.1.2 Fluorescence Detection

Pathogen infections, which include those caused by bacteria, viruses, and fungi, pose a serious risk to public health worldwide. Rapid and accurate detection of pathogens is essential for early diagnosis and effective treatment of diseases, and even for ensuring public health safety and the effective prevention and control of infectious diseases. Traditional methods, such as bacterial culture and microscopic examination, have limitations in timeliness and sensitivity, making them inadequate for the immediate diagnostic and precise testing needs of clinical and public health settings. While PCR technology is highly sensitive, it is expensive and complex to use. Additionally, traditional methods can only detect the presence of pathogens individually, lacking the ability to quickly differentiate and process pathogens, which limits their efficiency and effectiveness in practical applications. In terms of visualization in pathogen detection, although fluorescence imaging technology has been widely adopted, it still faces challenges. For instance, the lack of specificity in fluorescent probes and poor stability of the fluorescence signal limit their effectiveness in pathogen detection. Therefore, by innovatively combining functional units with carrier materials, such as quantum dots, organic dyes, rare earth luminescent materials, and fluorescent polymers, which have excellent optical response properties (such as improved quantum yield, controllable emission wavelength, and good light stability), with carrier materials like nanoparticles, metal-organic frameworks, molecularly imprinted polymers, and biocompatible matrices, a novel light-functional polymer composite material fluorescence probe has been developed. This probe integrates signal amplification, target recognition, and specific response, offering a highly attractive solution for the development of next-generation microbial pathogen detection platforms that are highly sensitive, specific, rapid, convenient, and suitable for complex environments. This solution has significant practical implications.

By utilizing the differential fluorescence recovery of fluorescent quenching complexes after binding to bacteria, rapid detection and differentiation of various pathogenic bacteria can be achieved. For example, positively charged gold nanoparticles and negatively charged poly(*para*-phenyleneethynylene) (PPE) (Figure 1.36a) form electrostatic complexes in aqueous solutions, where the fluorescence of PPE can be effectively quenched by gold nanoparticles by a mechanism of energy or electron transfer. When a bacterial suspension is added to the formed fluorescent quenching complex, negatively charged bacteria can competitively bind to gold nanoparticles through electrostatic attraction and hydrophobic interactions, releasing the PPE fluorophore. Different types of bacteria have varying interactions with gold nanoparticles, leading to different abilities to displace PPE, which in turn induces varying degrees of fluorescence recovery (Figure 1.36). By adding 12 types of bacteria to the electrostatic complex system to detect characteristic fluorescence changes, and using linear discriminant analysis (LDA), the original fluorescence response signals can be converted into different standard scores. As shown in Figure 1.36c, different bacteria, including three types of *Escherichia coli*, are completely distinguished and fall into different specific regions on the discrimination map, demonstrating that minor differences in bacteria can cause significant variations in fluorescence response. Further, 64 unknown samples were selected, with 61 samples being correctly identified, achieving an accuracy of over 95%. This fluorescence-based strategy significantly reduces analysis time and allows for the simultaneous detection of multiple samples, providing a means for the differentiation and rapid diagnosis of pathogens [178].

DNA detection is of great significance in biomedical research and is widely used in genetic mutation analysis, diagnosis, and treatment of genetic diseases. Traditional methods of DNA detection, such as gel electrophoresis and PCR, have high

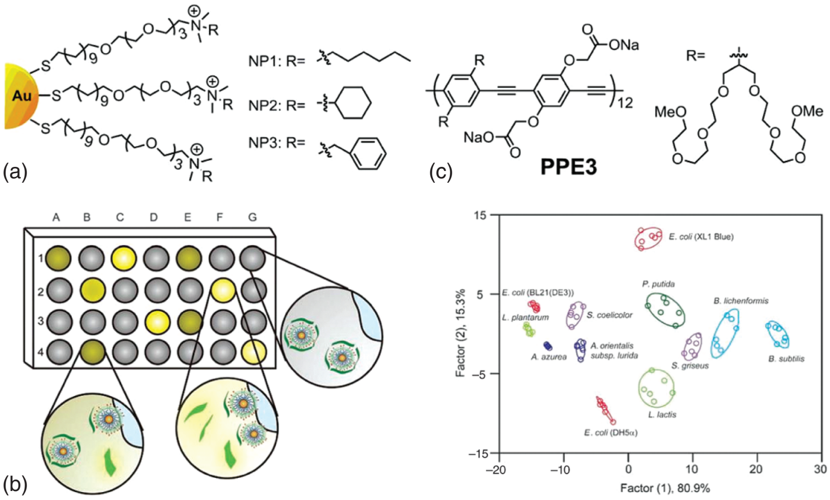

Figure 1.36 (a) Structure of gold nanoparticles and PPE3; (b) schematic diagram of fluorescence response signal of samples in microplate; (c) plot of canonical scores for the patterns of fluorescence response identified using LDA method. *Source:* Phillips et al. [178] / with permission of John Wiley & Sons.

sensitivity and specificity, but they also have the disadvantages of complex operation and long-time consumption.

In addition, fluorescence technology for biodetection has attracted much attention because of its high sensitivity and efficiency, but in practical applications, the probe's stability and biocompatibility still need to be further improved. Thus, a key area of current study is the creation of a quick, accurate, and easy DNA detection technique.

Due to the surface-enhanced Raman scattering effect, fluorescent dyes can undergo reversible adsorption or desorption on the surfaces of colloidal Au or Ag. Additionally, Au and Ag nanoparticles have a strong electron-donating ability, which allows them to undergo a PET process with dyes, quenching their fluorescence. By utilizing this principle, fluorescently labeled DNA can be covalently connected to the surface of colloidal Au nanoparticles, creating a highly sensitive DNA detection system (Figure 1.37). In this system, the fluorescent dyes are adsorbed onto the surface of colloidal Au, spontaneously forming a special ring structure, and their fluorescence is quenched by colloidal gold. After DNA hybridization, colloidal Au actively desorbs and releases fluorescein, restoring the fluorescence. This system enables highly sensitive and selective DNA detection [179].

Protein detection is of great significance in biomedical research, widely used in disease diagnosis, drug development, and cell biology studies. Conventional techniques for detecting proteins, include Western Blot and the enzyme-linked immunosorbent assay (ELISA), while highly specific, suffer from complex operations, long processing times, and limited sensitivity. Fluorescence detection technology, with its high sensitivity, rapid response, and noninvasive nature, has become a crucial method for protein detection. However, existing fluorescence probes still need improvement in terms of light stability, biocompatibility, and

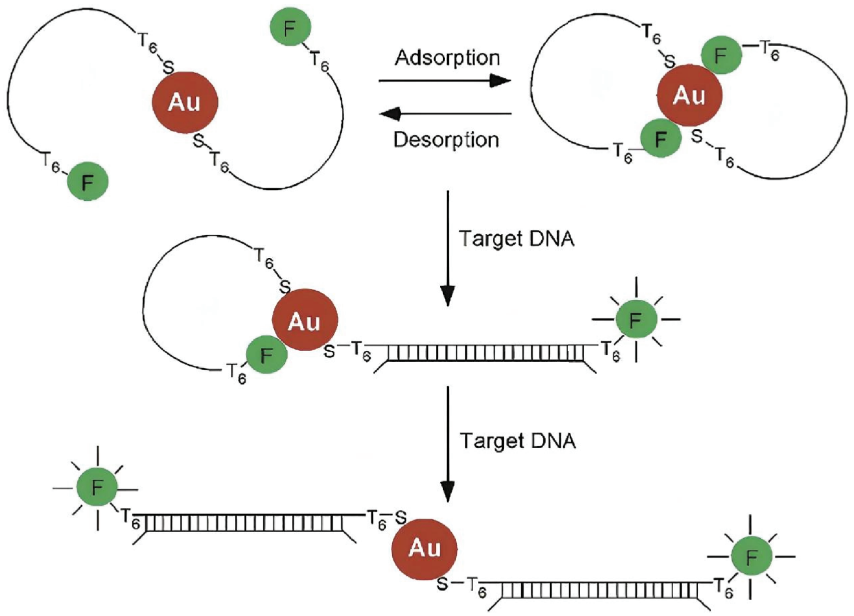

Figure 1.37 Schematic diagram of DNA detection using special "molecular beacon" induced by nano Au particles. *Source:* Maxwell et al. [179] / with permission of American Chemical Society.

detection limits. Therefore, developing organic molecular-based fluorescence platforms, which utilize their unique photophysical properties and controllable fluorescence signals, is essential for enhancing the efficiency and accuracy of protein detection.

The conformational changes of polymers can be utilized to detect proteins. By adding α-thrombin or nonspecific proteins (such as BSA) to single-stranded DNA, two composite systems are formed. Thrombin can induce ssDNA to form G-quadruplex structures, whereas nonspecific proteins do not have this ability. When cationic polyaniline derivatives are added to the solution, polyaniline forms complexes with G-quadruplex DNA through electrostatic interactions, enveloping the DNA and turning the solution orange. When polyaniline forms complexes with ssDNA, its conformation changes, enhancing coplanarity, and the solution turns purple (Figure 1.38). The color change in the solution induced by the conformational changes of CPs can be used to detect chymotrypsin directly, without the need for any substrate labeling [180].

In summary, the organic molecule-based fluorescence platform offers a new, efficient, sensitive, and stable method for protein detection. By optimizing the structure and detection mechanisms of fluorescent molecules, the efficiency and accuracy of protein detection can be significantly enhanced. In the future, with the advancement of nanotechnology and biotechnology, this fluorescence platform is expected to play a more significant role in the field of protein detection.

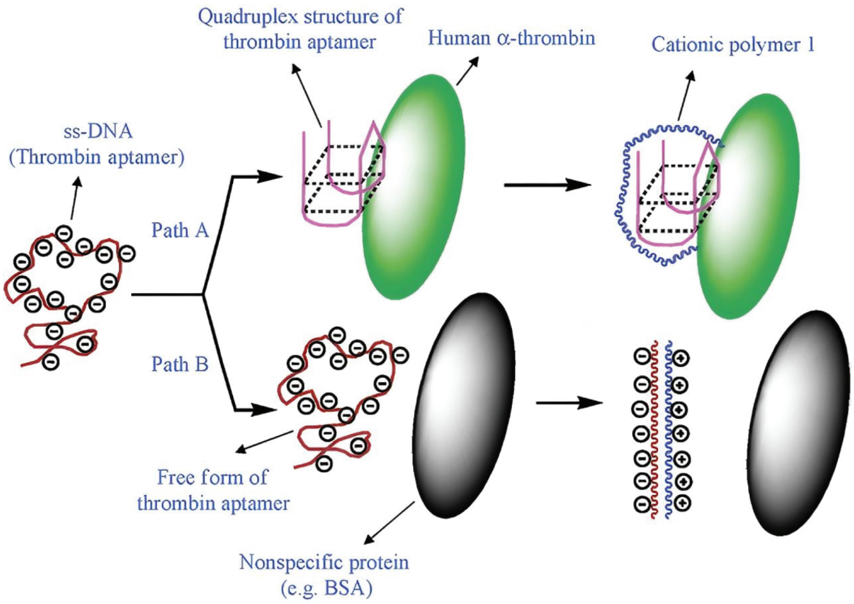

Figure 1.38 Schematic diagram of the specific detection principle of human α-thrombin using a cationic polymer and ss-DNA. *Source:* Ho et al. [180] / with permission of American Chemical Society.

In the future, as light-controlled fluorescence technology and nanomaterial science continue to advance, this new type of fluorescent probe is expected to play a more significant role in biomedical research and clinical diagnosis. Light-responsive materials have broad prospects in biological detection and imaging, particularly in precision medicine, real-time imaging, and early disease diagnosis. However, challenges such as biocompatibility, optical penetration, multifunctional integration, and standardization remain. As technology continues to evolve, especially with the integration of material science, nanotechnology, and biomedicine, light-responsive materials are poised to play an even more crucial role, potentially revolutionizing the healthcare industry.

1.3.2 Photodynamic Therapy (PDT)

1.3.2.1 Principle of Photodynamic Therapy

Photodynamic therapy (PDT) is a method that utilizes the interaction of photosensitizers and specific wavelengths of light to kill diseased cells or bacteria through the production of ROS (especially singlet oxygen). This treatment primarily relies on the reaction of photosensitizers with oxygen molecules under excitation light, generating destructive singlet oxygen, thus achieving therapeutic effects. The mechanism of photosensitizers can be divided into two types (Figure 1.39): Type I mechanism is also known as the free radical mechanism. ROS like superoxide anions ($O^{2-\cdot}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals ($\cdot OH$) are produced by the direct electron exchange between photosensitizers and oxygen molecules

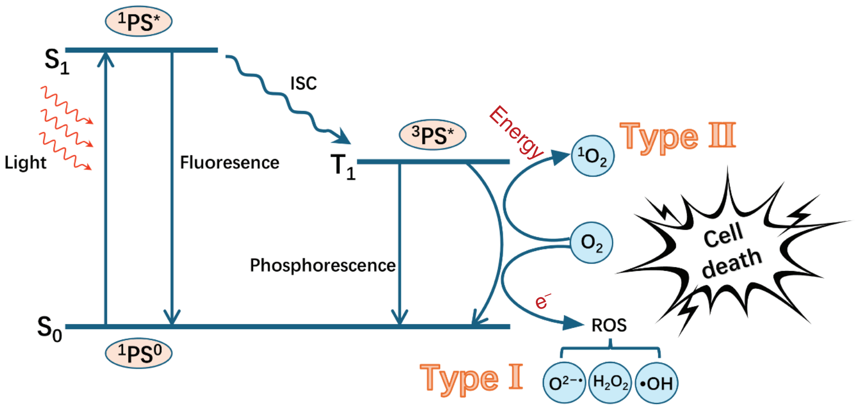

Figure 1.39 The ROS production mechanism of photosensitizers.

once they reach an excited state. These ROS are highly reactive and are capable of damaging proteins, nucleic acids, and cell membranes, resulting in cell death and damage. The Type II mechanism, also known as the singlet oxygen mechanism, is more common in PDT. Photosensitizers absorb photon energy, move from the ground state (S_0) to the excited state (S_1), and then intersystem cross (ISC) to the triplet excited state (T_1). These photosensitizers then interact with ground-state oxygen (O_2) in the triplet state, transferring energy to create singlet oxygen ($^1O_2$). $^1O_2$ is one extremely reactive ROS that can directly oxidize biomolecules, leading to the destruction of cell structure and function, ultimately causing cell apoptosis or necrosis.

1.3.2.2 Application of Photofunctional Polymer Composites in Photodynamic Therapy

Photodynamic therapy (PDT) has introduced new approaches to tumor diagnosis and treatment. Many fluorescent dyes are used not only for fluorescence imaging but also as photosensitizers, which produce ROS under light exposure, leading to cell damage. To address the issues of poor water solubility, easy aggregation, rapid metabolism by the body, and limited functionality in traditional photosensitizers, strategies such as modifying targeting molecules and encapsulating with polymer matrices can be employed to construct composite systems that better meet the clinical needs of PDT. For example, CS-2I was named by rhodamine-based photosensitizer with NIR emission, water-solubility, and an aggregate-induced emission (AIE) effect. By improving intersystem crossing, the heavy atom effect encourages the production of singlet oxygen. For bacterial imaging studies, co-culturing CS-2I with different bacteria demonstrated its unique staining capacity for gram-positive bacteria, making it useful for rapidly identifying and characterizing gram-positive bacteria in mixed bacterial cultures, with the possibility of long-term imaging with fluorescence tracking. When exposed to a 660 nm laser for 10 min, low concentrations of CS-2I can significantly kill drug-resistant bacteria, showing great potential as an alternative to antibiotic treatment. Furthermore, photosensitizer

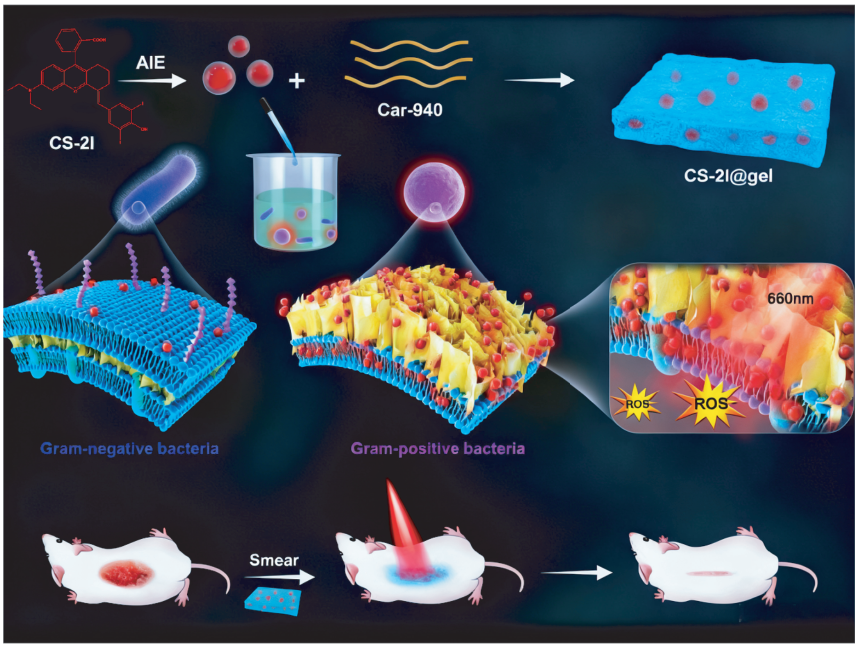

Figure 1.40 AIE photosensitizer hydrogel for selective elimination of gram-positive bacteria and promotion of wound healing. *Source:* Zeng et al. [181] / with permission of John Wiley & Sons.

CS-2I was mixed with carbomer 940 to create a hydrogel (CS-2I@gel) with PDT effect for antibacterial. The CS-2I@gel exhibits excellent adhesion, biocompatibility, and injectability. When applied to a mouse model of wound infection, it effectively inhibits bacterial proliferation through PDT, promoting wound healing (Figure 1.40). The composite hydrogel system is based on the PDT effect, and multiple biological functions work together to help antibacterial and wound treatment [181].

Porphyrin is a classic macromolecular heterocyclic compound with 26 π electrons on its ring, forming a highly conjugated system. As a natural photosensitive molecule, porphyrin exhibits excellent light capture capabilities and long excited state lifetimes. However, its practical applications are hindered by poor tumor selectivity and the tendency to self-aggregate, leading to quenching. To address these issues, a simple liquid-phase exfoliation method can be used to prepare COF nanodots. These COF nanodots form a highly ordered, periodically porous crystal material through strong covalent bonds, with porphyrin monomers precisely fixed within the framework. This arrangement effectively prevents self-aggregation and enhances PDT efficiency. Furthermore, by modifying the amphiphilic nanocarrier DSPE-PEG with hydrophobic interactions, the resulting CONDs-PEG exhibits excellent biocompatibility, physiological stability, the ability to produce ROS, and efficient tumor accumulation and renal metabolism in in vivo experiments [182].

To reduce the phototoxic effects of traditional photosensitizers on normal tissues, tumor-specific activatable dye molecules or composite systems can be designed according to the changes in the physiological microenvironment of tumor tissues (e.g. abnormal pH and GSH levels, overexpression of certain bioenzymes and nucleic acids) for use in bioimaging and PDT. For example, a case of pH-activatable photosensitive dye can be constructed by encapsulating diethylaminobenzene- and phenyl-substituted aza-BODIPYs in peptidomimetic micelles (cRGD-NEt_2Br_2BDP, NP). This photosensitive dye has an inhibited ROS production capacity under normal physiological conditions (pH = 7.4); targeting $\alpha v\beta_3$ overexpressing cancer cells through its cRGD nanomicellar shell, it was selectively activated in the weakly acidic environment of the tumors (pH < 7.0), restoring near-infrared fluorescence emission, while efficiently generating unilinear oxygen species in the presence of light ($\Phi_\Delta = 56\%$). In U87MG tumor-bearing mouse imaging experiments, the photosensitive dye showed bright NIR fluorescent signals in the tumor region, demonstrating the ability to achieve tumor-specific detection. In in vivo experiments, intravenous injection of photosensitizer micelles followed by light illumination resulted in a gradual reduction of tumor volume in mice, whereas the tumor volume of control mice remained unchanged, demonstrating the good PDT effect of the photosensitizing dye [183].

In atherosclerotic plaques, macrophages constitute about 20% of the lesion cells. According to the excessive ROS produced by activated macrophages at the lesion site (inducible nitric oxide synthase stimulates the production of peroxynitrite), ROS-activatable photosensitizer composite materials can be designed to target and kill these activated macrophages, facilitating PDT for atherosclerosis. By covalently attaching the photosensitizer Ce6 to hyaluronic acid (HA), amphiphilic HA-Ce6 conjugates can self-assemble into MacTNP nanoparticles in water. Due to the aggregation of Ce6 within the nanoparticles, conjugated stacking results in a self-quenching effect, which quenches the fluorescence of MacTNP and inhibits the generation of singlet oxygen. After MacTNP is taken up by activated macrophages, higher-than-normal levels of peroxynitrite degrade the backbone of HA, releasing Ce6, and strong NIR fluorescence can be observed inside the cell with a high label-to-target background ratio, which can be used for targeted imaging of macrophages (Figure 1.41). Additionally, under light exposure, MacTNP significantly reduces the survival rate of activated macrophages while showing no phototoxicity in other cells, indicating that the photosensitizer's photodynamic activity has been restored. This makes it highly valuable for selective NIR fluorescence imaging and PDT of atherosclerotic lesions in vivo [184].

Photodynamic therapy, as one possible therapeutic approach, has shown significant potential in treating tumors and infectious diseases. However, it still faces challenges such as the selectivity of photosensitizers, limitations in treatment depth, and unevenness in treatment. To overcome these challenges and achieve broader clinical application, further technological innovation and clinical research are needed. The development of photodynamic sterilization technology includes the creation of new photosensitizers and nanomaterials to enhance the efficiency and depth of photodynamic sterilization, as well as the clinical translation of this

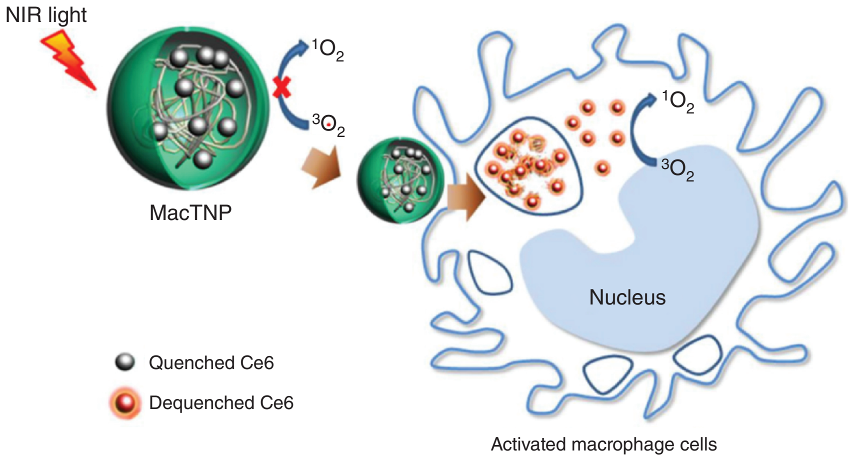

Figure 1.41 Schematic diagram of the process of activation of macrophages to activate the photosensitizer response. *Source:* Kim et al. [184] / Ivyspring International Publisher / CC BY 4.0.

technology. For example, integrating artificial intelligence and big data technologies can enable intelligent and personalized applications of photodynamic sterilization, providing more precise solutions for disease treatment.

1.3.3 Light-controlled Release

1.3.3.1 Principle of Light-controlled Release

The release mechanism triggered by light stimulation is a significant direction in the application of light-responsive materials, particularly in biomedical fields like drug delivery, gene therapy, and tissue engineering. By stimulating with external light, these materials can precisely control the release rate and timing of the substances, leading to more precise and controllable therapeutic outcomes. Common light-responsive release mechanisms include thermal response, photopolymerization, and photo-switching. The thermal response mechanism relies on the temperature changes in the material caused by light exposure. Light energy is converted into heat through photothermal conversion, which activates the material's temperature sensitivity. When the material is exposed to light, its temperature rises to a critical point, causing changes in the polymer chain conformation and triggering the drug release. This mechanism is commonly used in temperature-sensitive materials, such as thermoresponsive hydrogels or nanoparticles, which can produce localized heating effects under light, allowing drugs to be released from the carrier [185].

The photopolymerization release mechanism involves the depolymerization or cleavage of polymers triggered by light, leading to the release of drugs. For example, when a photosensitive group undergoes a depolymerization reaction under ultraviolet or visible light, it releases the drug or therapeutic molecule. This mechanism is commonly used in drug delivery systems made from photopolymerizable or photosensitive cross-linkable polymers. When an external light source illuminates the material, the polymer structure breaks down, allowing the drug to be released from the carrier [186].

The light switch release mechanism relies on the conformational changes or charge state alterations in materials triggered by light stimulation. These changes alter the material's hydrophilicity, solubility, or charge distribution, thereby controlling drug release. Such materials typically contain photosensitive switch groups, such as spiropyran [187]. This mechanism is widely applied in materials with reversible light regulation capabilities, such as certain nanoparticles or hydrogels containing photosensitive groups. These materials can undergo structural changes under different lighting conditions, thereby regulating the drug release rate.

1.3.3.2 Application of Photofunctional Polymer Composites in Light-controlled Release

Using photoisomeric molecules as the "switch" for drug loading and delivery systems, their structural and hydrophobic properties can be altered by light exposure, enabling noninvasive, precise, and on-demand drug administration. When exposed to ultraviolet light, spiropyran undergoes an opening reaction, transforming from a hydrophobic structure to a more hydrophilic flower-like structure. A mesoporous silica is loaded with the model drug curcumin (CUR). The closed-loop state of spiropyran that is anchored on the shell's surface can serve as a drug release switch. Given that high-energy UV light can damage tissues and has limited tissue penetration, directly using UV light to trigger the opening mechanism in clinical settings is impractical. Therefore, the drug-loaded silica shell incorporates UCNPs doped with lanthanides, which convert near-infrared incident light into UV light, inducing the opening of spiropyran and the release of the drug, effectively addressing this issue (Figure 1.42). Additionally, the UV light from UCNP can activate CUR to produce ROS, demonstrating significantly enhanced antitumor efficacy in in vivo experiments [188].

The light-controlled release system has significant potential in personalized treatment. By precisely controlling the timing and dosage of drug release, it can target specific lesion areas, reducing side effects in healthy tissues and thus enhancing treatment outcomes. This precise control gives the light-controlled release system a significant advantage in treating complex diseases such as cancer and inflammation, enabling the customization of treatment plans based on individual patient conditions.

Hydrogel scaffold, characterized by its abundant water content, adaptable mechanical characteristics, and availability of nutrients, closely matches the characteristics of natural extracellular matrices. They are frequently employed in tissue engineering and regenerative medicine as 3D cell carriers. By controlling the degradation of hydrogels, therapeutic cells can be delivered to injured or diseased tissues, promoting tissue repair and regeneration. In hydrogel degradation, the two most prevalent processes are hydrolysis and enzymatic degradation, but these methods cannot adjust or stop the degradation rate or control it spatially. In contrast, photodegradation allows for external control over the degradation

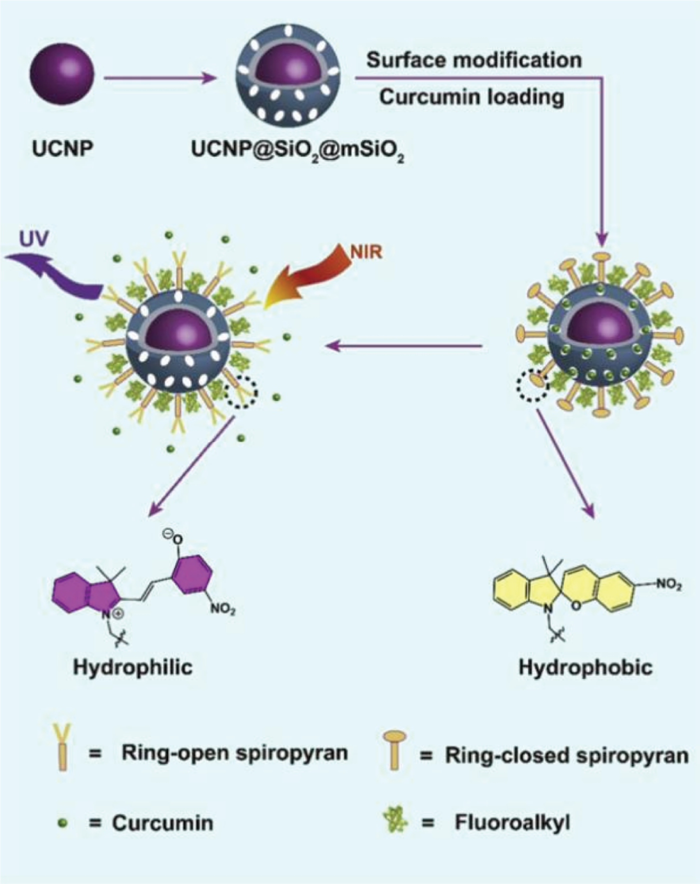

Figure 1.42 Schematic diagram of the infrared light-responsive drug release system based on spiropyran. *Source:* Liu et al. [188] / with permission of Elsevier.

process in terms of space and time, enabling controlled cell release. By introducing different photodegradable *o*-nitrobenzyl (*o*-NB) groups into the framework of PEG macromolecular monomers and initiating their copolymerization, photodegradable hydrogels can be formed, while encapsulating human mesenchymal stem cells (hMSC). After encapsulation, the cell viability is approximately 90%, indicating that this hydrogel has low cytotoxicity. Under 365 nm light irradiation, different *o*-NB linkers exhibit varying apparent degradation rate constants, allowing for different rates of hMSC release within various gels [189].

In addition to applications in tissue engineering, early cancer detection and diagnosis depend on the dynamic collection and release of cancer cells. Polymer molecular brushes refer to a type of special-structured polymer material formed by fixing one end of the macromolecular chains on the substrate surface (or polymer chains) through chemical or physical interactions. Due to the steric hindrance repulsion between high-density molecular chains, the polymer chains present a highly extended conformation, forming a structure similar to a “brush.” As a powerful surface functionalization technique, it can be used to prepare artificial stimulus-responsive surfaces to mimic the dynamic functions of living systems. Poly(SP-*co*-NiPAAm) polymer brushes are grafted onto silicon nanowire arrays, which contain two response units: photoresponsive SP and thermoresponsive NiPAAm. Under visible light and above the phase transition temperature of PNiPAAm, the SP unit forms a hydrophobic closed loop configuration, while the PNiPAAm unit also assumes a hydrophobic spherical conformation. The hydrophobic surface can effectively adsorb biotin-BSA through hydrophobic interactions, and further bind to cancer cell capture agents biotin-anti-EpCAM by biotin–streptavidin interaction. It is capable of effectively and precisely identifying cancer cells (MCF-7) that express EpCAM. Under the illumination of 365 nm ultraviolet light and below the LCST temperature, the SP unit opens its loop, and PNiPAAm transforms into a coil conformation, thereby making the smart surface hydrophilic and leading to the desorption of biotin-BSA and biotin-anti-EpCAM, thus achieving the controllable release of cancer cells and demonstrating a dual response (Figure 1.43) [190].

1.3.4 Photothermal Therapy (PTT)

1.3.4.1 Principle of Photothermal Therapy

Photothermal therapy (PTT) is a novel cancer treatment that turns light energy into heat, thereby precisely targeting and destroying tumor cells. Compared to traditional treatments, PTT offers noninvasive, precise, and synergistic advantages. However, PTT still faces several challenges, such as low conversion efficiency, poor biocompatibility, and limited targeting ability [191]. These issues limit the clinical application of PTT, making the development of new PTT materials a key research focus. The core principle involves using specific light sources to irradiate photosensitive materials with photothermal properties, which absorb light and convert it into heat, leading to a localized temperature increase. This temperature rise can damage, coagulate, or kill tumor cells, achieving therapeutic effects. PTT relies on photosensitive materials, such as metal nanoparticles, carbon-based materials, and photosensitive molecules, which can efficiently absorb specific wavelengths of light (typically near-infrared light) and convert it into heat. Common PTT materials include gold nanoparticles (AuNPs), graphene, and carbon nanotubes [192]. Compared to traditional treatments like chemotherapy and radiotherapy, PTT offers noninvasive, controllable, and fewer side effects. By designing and optimizing photosensitive materials, PTT can effectively target and destroy tumor cells while minimizing damage to normal tissues. PTT is primarily used in cancer treatment, particularly for the local treatment of deep-seated tumors. In addition, it is effective in treating skin conditions, infectious diseases, and even as an adjuvant therapy in some wound healing processes.

1.3.4.2 Application of Photofunctional Polymer Composites in Photothermal Therapy

Compared to the more established PDT, PTT is hindered by the performance limitations of traditional photothermal agents, leading to slower clinical progress.

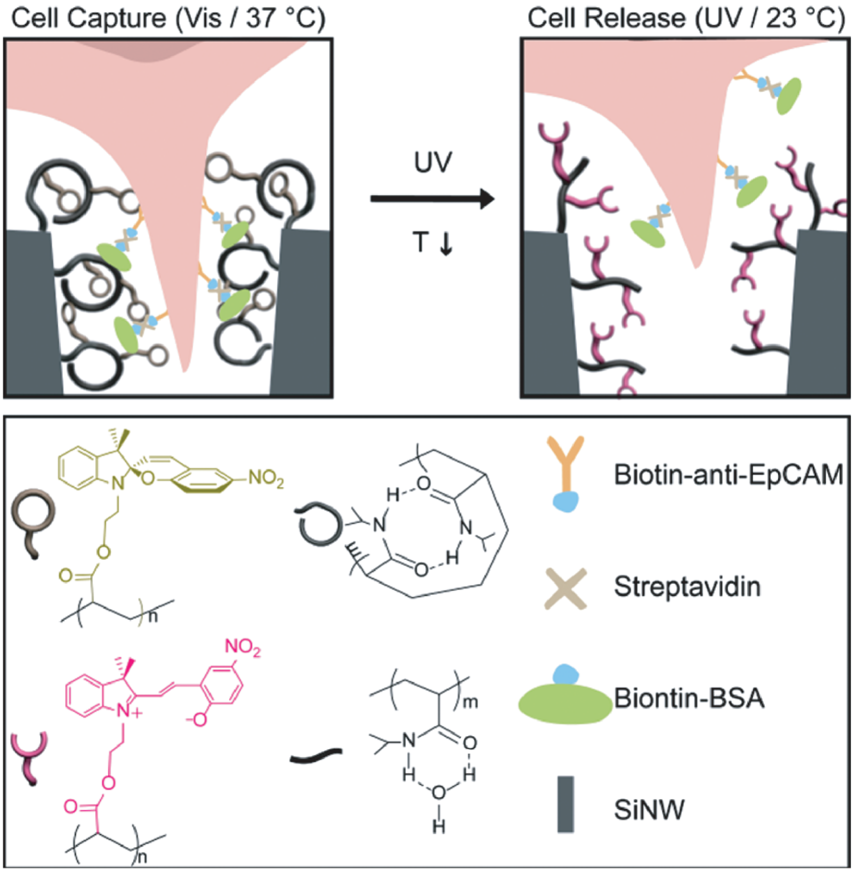

Figure 1.43 Schematic diagram of the principle of dual-responsive intelligent surface capturing and releasing cancer cells. *Source:* Hao et al. [190] / with permission of John Wiley & Sons.

For example, gold nanorods are known for their poor light stability, large size, and high cost; other inorganic photothermal materials, such as carbon nanomaterials, are nonbiodegradable and likely to stay in the body for a prolonged period of time, which raises questions regarding possible long-term toxicity. In contrast, organic polymers and small molecules offer excellent biocompatibility, designability, and ease of incorporation, making them highly promising for practical applications. Moreover, the excited photothermal agents under intense light may harm healthy tissues and skin. Therefore, it is crucial to prevent the decay of excitation energy through radiation transition pathways, enhance the photothermal conversion efficiency of photothermal agents, reduce the required intensity of excitation light, and ensure the safety of phototherapy in vivo.

For example, the -CF_3 group of tfm-BDP can rotate freely without any energy barrier, which promotes ultra-efficient nonradiative decay, enhancing the conversion of light energy into heat. DSPE-PEG is employed as the matrix for encapsulation

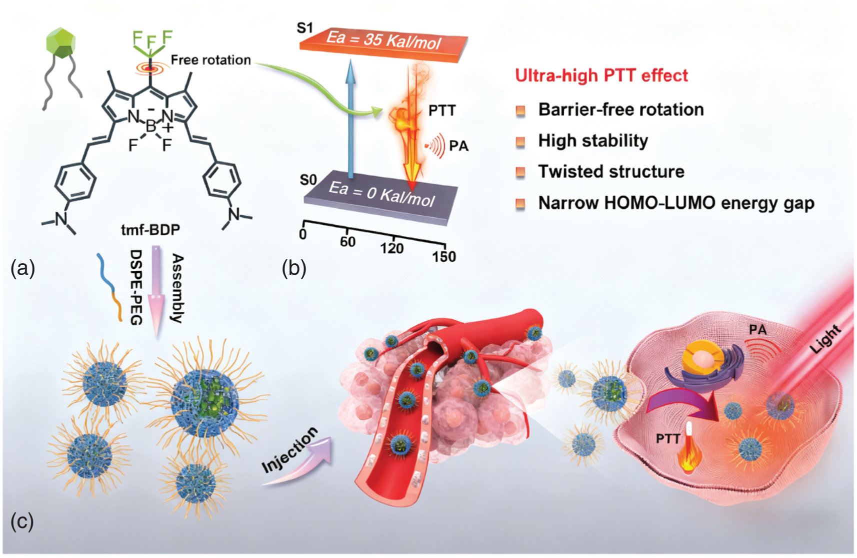

Figure 1.44 Schematic diagram of self-assembly and PTT of tmf-BDP nanoparticles. *Source:* Xi et al. [193] / with permission of John Wiley & Sons.

of tfm-BDP. The molecular twist in tfm-BDP impedes parallel π–π stacking (H aggregation), while still allowing the $-CF_3$ group to rotate freely. Because of their increased permeability and retention impact, PEG-coated nanoparticles can accumulate at tumor sites while maintaining greater stability in the circulation (Figure 1.44) [193].

In addition to chemical modification strategies, the aggregation of dye molecules can induce fluorescence quenching and inhibit photodynamic processes, thereby enhancing the material's photothermal conversion efficiency. For example, by introducing PEG as a hydrophilic segment into squaraine, an amphiphilic dye, PSQ, was synthesized. Due to its inherent planar structure, PSQ can form H-aggregates in aqueous solutions through π–π stacking and self-assemble into uniform nanospheres, PSQ-NSs, relying on hydrophilic–hydrophobic interactions with the PEG chain. The formation of these H aggregates inhibits fluorescence emission and intersystem crossing, resulting in PSQ-NSs exhibiting strong near-infrared (NIR) absorption, highly quenched fluorescence, good water solubility, physiological stability, and biocompatibility, while achieving an ultra-high photothermal conversion efficiency of 81.2%. Additionally, NIR light irradiation can generate strong photoacoustic (PA) signals from PSQ-NSs, which can be used as a PA contrast agent to guide the timing and location of irradiation for precise PTT. in vivo experiments showed that intravenous injection of PSQ-NSs followed by laser irradiation can ablate tumors in mice (Figure 1.45) [194].

Photothermal therapy (PTT) has made significant advancements in cancer treatment in recent years, particularly in the use of nanomaterials for targeted therapy. With the development of nanotechnology, a variety of photothermal

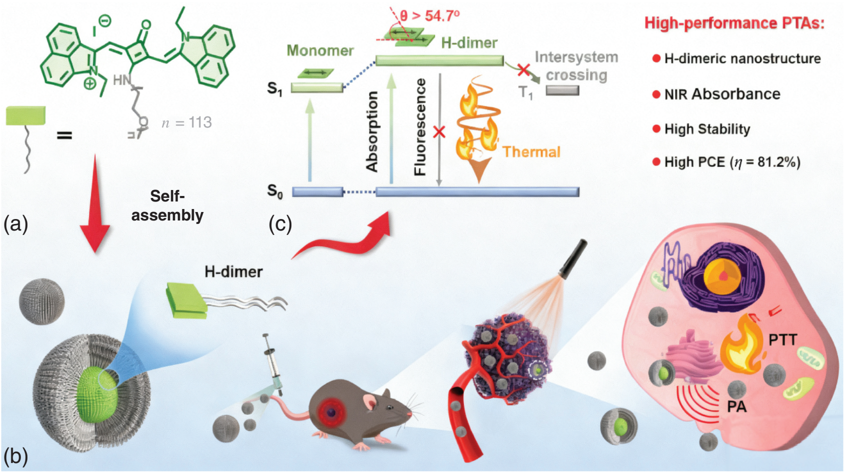

Figure 1.45 Schematic diagram of self-assembly and PTT of H dimer nanospheres formed by PSQ. *Source:* Wang et al. [194] / with permission of John Wiley & Sons.

materials, including gold nanoparticles, carbon-based nanomaterials, and sulfides, have been widely applied in PTT. However, several challenges remain. Firstly, the limited depth of light penetration restricts the effectiveness of treating deep-seated tumors. Secondly, precise temperature control is challenging, as both excessively high or low temperatures can affect treatment outcomes or harm healthy tissues. Additionally, the targeting ability of photosensitive materials is insufficient, potentially affecting normal tissues outside the treatment area and increasing side effects. The biocompatibility and long-term stability of these materials are also concerns, as some may trigger immune responses or toxicity issues. Lastly, the uniformity and reproducibility of treatments impact their effectiveness. Therefore, improving the precision and controllability of treatments remains a critical challenge for PTT.

1.3.5 Photocatalytic Effect

Photocatalysis is essentially a process where, under light exposure, a photocatalyst absorbs photon energy to accelerate specific chemical reactions, with the catalyst itself remaining unchanged before and after the reaction. The photocatalyst absorbs photon energy, causing electrons in the valence band (VB) to move to the conduction band (CB). This process also results in positively charged holes in the valence band, which form photogenerated electron-hole pairs. Photogenerated electrons and holes on the catalyst's surface can engage in reduction and oxidation processes, respectively. The core objective of photocatalysis is to mimic natural photosynthesis by using the most abundant and cleanest solar energy on Earth to drive valuable chemical reactions. By designing photofunctional polymer composites, it is possible to enhance energy conversion efficiency and reduce dependence on fossil fuels, providing a sustainable solution to address energy crises and environmental pollution.

The following are several key applications of photofunctional polymer composites in photocatalysis.

1.3.5.1 Photocatalytic CO_2 Reduction

The reduction and conversion of CO_2 is one of the effective methods to address climate change and reduce greenhouse gas emissions. Photofunctional polymer composites can convert CO_2 into fuel using solar energy. Under light conditions, the photocatalyst absorbs light energy, which excites electrons from the valence band to the conduction band, generating electron-hole pairs. The conduction band electrons are captured by CO_2 receptors on the catalyst surface and reduced to useful hydrocarbon fuels. Meanwhile, the valence band holes typically drive the oxidation of water to produce oxygen [195]. This process, known as photocatalytic CO_2 reduction, offers a new approach for biofuel production. By incorporating narrow-bandgap materials, plasma materials, upconversion materials, and dye-sensitized materials into photofunctional polymer composites, the spectral response range of the photocatalyst can be broadened. Combining light-absorbing materials with electron transport materials enhances the separation efficiency of photogenerated charges and accelerates the CO_2 reduction reaction rate. Protecting the sensitive components from corrosion through coating, core-shell structures, or by combining with stable carriers improves the stability of the photocatalyst, ensuring that the photocatalytic material maintains high catalytic performance over extended periods [196].

In the field of photocatalytic CO_2 reduction, CPs have emerged as a promising platform due to their tunable bandgap and ease of modification. Among these, conjugated microporous polymers excel in CO_2 adsorption and tunable photoelectric properties, making them an efficient organic semiconductor catalyst. To address issues such as spontaneous electron-hole recombination and low electron transfer efficiency within the catalyst, constructing conjugated microporous polymers with donor (D) and acceptor (A) components can significantly enhance charge separation and photocatalytic activity. For instance, ImI-CMP, a conjugated microporous polymer material with an imidate cation in its backbone, doped with Co(II) as a co-catalyst, exhibits a strong built-in electric field due to the presence of the imidate cation. This built-in electric field drives the separation of photogenerated charges and the directed transport of electrons. Additionally, the π-conjugated structure of the polymer provides intramolecular transport channels for electron transfer, enabling rapid charge transfer within the molecule during the photocatalytic process. Moreover, the strong electrostatic interaction between the imidate ring cation and carbon dioxide molecules facilitates the enrichment and activation of carbon dioxide. Using $[Ru(bpy)_3]Cl_2$ as a visible light photosensitizer and triethanolamine (TEOA) as the electron donor (Figure 1.46), ImI-CMP can effectively reduce CO_2 to CO under visible light irradiation [197].

The morphology of the three-dimensional porous CP network is highly advantageous for the efficient loading of photocatalysts. By supporting polyaniline (PANI) on a three-dimensional poly(*N*, *N*-dimethylacrylamide) (PDMA) framework, a novel flexible photoelectrode has been developed. The molecular channels of this electrode network provide a rich array of surface functional groups, which can

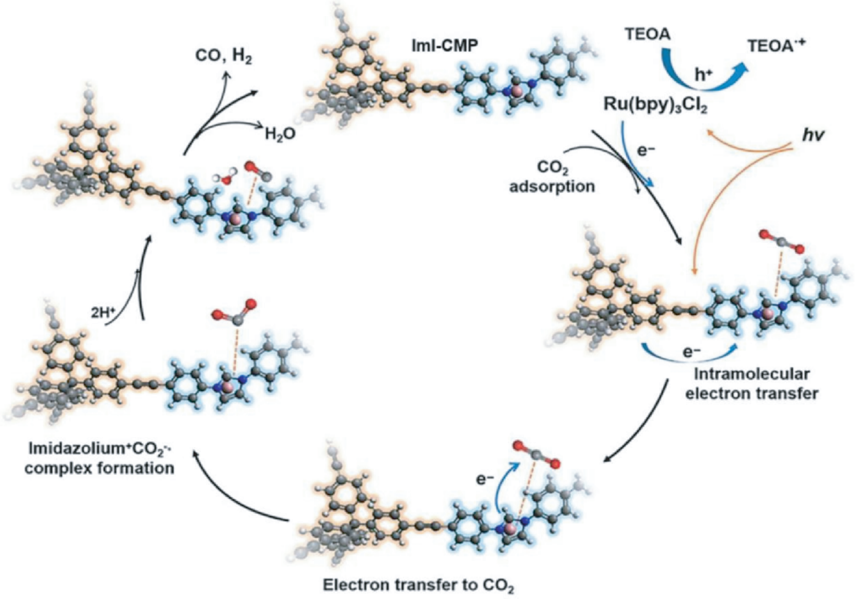

Figure 1.46 Mechanism of photocatalytic reduction of CO_2 by ImI-CMP. *Source:* Reproduced from Zhao et al. [197] / with permission of Elsevier.

assist in regulating the structure of photocatalytic self-assembly. This overcomes the structural and loading limitations of traditional inorganic photoelectrodes when loading functional molecules or materials, allowing for a stable and large-scale loading of Co(II) catalysts. Through strong chemical bonds throughout the network, a stable and high-density interface contact between the electrode substrate and the photocatalyst is achieved, enhancing the efficiency of photoelectron transfer. Under sunlight, this photoelectrode can reduce CO_2 to methanol with a conversion efficiency of 70%. When the area is expanded from 1 to 100 cm^2, the photoelectrode can continuously generate a stable photocurrent, demonstrating the excellent application prospects of this flexible photoelectrode material in large-scale solar energy conversion devices [198].

Photocatalytic CO_2 reduction technology offers new solutions to the challenges of global warming and the energy crisis. Through advancements in materials and technology, this technology promises to achieve efficient, stable, and sustainable CO_2 conversion. Future research will focus on developing new materials, gaining deeper insights into reaction mechanisms, and innovating technologies. It is expected that this technology will be broadly applied in energy, environmental protection, and chemical industries, providing crucial support for sustainable development.

1.3.5.2 Photocatalytic Production of H_2

Similar to the photocatalytic reduction of carbon dioxide, photocatalytic hydrogen production also requires a photocatalyst to absorb light energy and excite electrons in the conduction band, reducing H^+ to H_2. Hydrogen, a high-calorific value gas, is an environmentally friendly energy source that produces no greenhouse gases during combustion. Converting solar energy into chemical energy for hydrogen production through a photocatalytic system is a viable solution to environmental and energy challenges.

Enhancing the conjugation degree of photocatalyst molecules improves the photocatalytic hydrogen evolution process. Therefore, constructing a two-dimensional conjugated framework into a three-dimensional porous material significantly boosts photocatalytic activity. A novel two-dimensional fully π-conjugated donor–acceptor covalent organic framework (SP^2c-COF) has been developed using 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) and **poly(1,5-diaminonaphthalene)** (PDAN). Due to complete conjugation, the SP^2c-COF photocatalyst exhibits a narrow bandgap, enhancing its light absorption in the visible region. The introduction of electron-deficient units (−CN) endows the material with a D-A structure, which further strengthens conjugation through electronic effects, aiding in the separation of photogenerated excitons and the inhibition of charge recombination. To further optimize photocatalytic activity, 3-ethylrotenone (ERDN) groups, as electron-deficient units, were grafted onto the edges of the framework. The enhanced electronic effect more effectively splits excitons, thereby improving photocatalytic hydrogen evolution performance (2120 μmol/g/h). The ordered two-dimensional lattice features a rich one-dimensional channel network with high porosity, providing ample space for numerous reaction sites, promoting mass transport, and minimizing the electron transfer distance to the reaction center. These advantages are incorporated into the framework, enabling the material to effectively produce hydrogen gas even with low-energy photon input (Figure 1.47) [199].

The photocatalytic system based on organic conjugated molecules, due to the short excited state lifetime of these molecules, requires the involvement of a sacrificial agent to complete the catalytic process. In contrast, natural photosynthesis utilizes thylakoid membranes to spatially separate photogenerated charges, ensuring high light energy conversion efficiency. Inspired by this, the partitioning and transfer capabilities of liposomes can be utilized to overcome the rapid recombination of photogenerated charges, helping to construct a photocatalytic system that does not require a sacrificial agent, thus achieving the complete decomposition of water under light. In the half-reaction for hydrogen evolution reaction (HER), the catalytic center is [(TCPP)Pt], where TCPP = meso-tetra(4-carboxyphenyl)porphine, which has a monolayer thickness and is functionalized with hydrophobic pentafluoropropionic acid groups to insert into the hydrophobic region of the lipid bilayer. In the half-reaction for water oxidation reaction (WOR), Ir-bpy serves as the reaction center and is incorporated into the MOF based on $[Ru(bpy)_3]^{2+}$. HER- and WOR-MOF nanosheets are assembled in the hydrophobic and hydrophilic regions of liposomes composed of lecithin and cholesterol, respectively, using redox shuttle Fe^{3+} and tetrachlorobenzoquinone to link the two half-reactions in series. For the half-reaction of hydrogen evolution, the tetrachlorobenzoquinone system provides electrons and is oxidized itself. At the lipid/water interface, tetrachlorobenzoquinone oxidizes Fe^{2+} to Fe^{3+}. Fe^{3+} then oxidizes the photoactivated $[Ru(bpy)_3]^{2+}$ to form $[Ru(bpy)_3]^{3+}$, which continues the half-reaction of oxygen

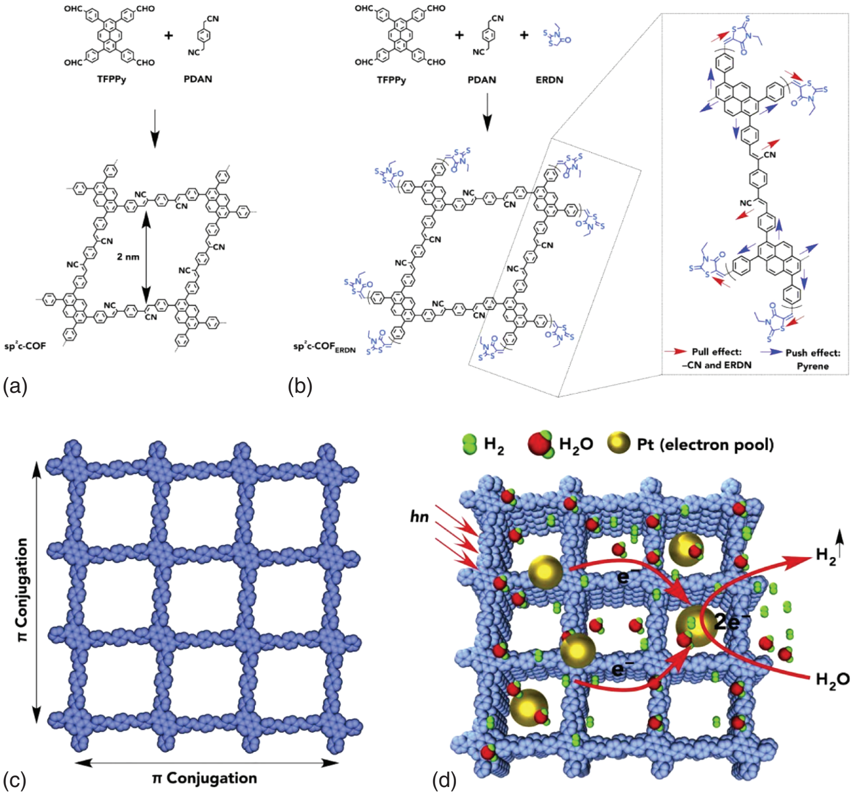

Figure 1.47 Schematic diagram of (a) sp^{2}c-COF structure without electron deficiency ERDN end group; (b) sp^{2}c-COF structure with electron deficiency ERDN end group; (c) π conjugation along x and y directions in the two-dimensional crystal layer of sp^{2}c-COF; (d) sp^{2}c-COF photocatalytic hydrogen evolution. *Source:* Jin et al. [199] / with permission of Elsevier.

evolution, completing the entire process. The full decomposition of photocatalytic water was achieved by ultrafast electron transport based on a lipid system and effective charge separation of the lipid bilayer, with an apparent quantum yield of (1.5±1)% [200].

1.3.5.3 Light-driven Biotransformation

The use of traditional fossil fuels has led to severe environmental pollution and greenhouse gas emissions, with limited reserves. Photobiological conversion technology harnesses solar energy to drive the biosynthesis process, converting greenhouse gases like carbon dioxide into valuable biofuels. This not only meets energy needs but also reduces environmental pollution, aligning with the principles of sustainable development [201]. The efficiency of light energy conversion in natural photosynthesis is relatively low. By constructing photobiological conversion systems, the capture and utilization of light energy can be optimized, enhancing overall light energy conversion efficiency and thus producing biofuels more efficiently. Microorganisms have limited metabolic pathways, making it challenging to directly and efficiently convert carbon dioxide into complex biofuels. Photobiological conversion systems, by incorporating photosensitive materials and optimizing microbial metabolic pathways, can achieve more efficient biosynthesis, expanding the range and yield of biofuels produced by microorganisms [202].

Light-driven biotransformation is a process where microorganisms or algae convert organic matter into biofuels using light energy. In this process, photofunctional polymer composites typically enhance light utilization efficiency, promote photosynthesis, and improve conversion efficiency. Improving the efficiency of photosynthesis with photofunctional polymer composites is a critical aspect of biofuel production. For example, algae such as spirulina and purple bacteria can use sunlight to perform photosynthesis, converting carbon dioxide into organic compounds, ultimately producing biofuels like biodiesel and acetic acid [203].

Perylene diimide derivatives (PDI) and poly(fluorene-co-phenylene) (PFP) were used as photosensitizers to coat the surface of the nonphotosynthetic bacterium *Moorella thermoacetica*, forming a P/N heterojunction (PFP/PDI) layer (Figure 1.48). This led to the creation of a hybrid photosynthetic system, integrating organic semiconductors with bacteria, that efficiently transforms CO_2 into acetic acid. The PFP/PDI heterojunction enhances the separation efficiency of photogenerated holes and electrons. The cationic side chains of PDI and PFP can penetrate the bacterial cell membrane, ensuring efficient electron transfer. *M. thermoacetica* can harvest photoexcited electrons from the PFP/PDI heterojunction, driving the Wood-Ljungdahl pathway to synthesize acetic acid from CO_2 under light, achieving an efficiency of 1.6%, comparable to previously reported inorganic–bacterial hybrid systems [204].

Organic optoelectronic composites, such as organic semiconductors combined with microorganisms or algae, can be used as a photosynthetic promoter. These materials can effectively capture light energy and transfer the energy to organisms through the charge separation process, promoting their photosynthesis and thus improving the production efficiency of biofuels.

In addition, the $WO_3/MoO_3/g\text{-}C_3N_4$ heterojunction, used as an electrode material for a photo-assisted biological cathode, was combined with the electrosynthesis bacterium *Serratia marcescens* Q1 to construct a photo-assisted microbial electrosynthesis system, achieving the efficient synthesis of acetic acid from inorganic carbon sources. The system demonstrated enhanced photocurrent and acetic acid production under light exposure, revealing the effective separation and transport of photogenerated charge carriers within the heterojunction. This discovery provides a new strategy for photo-driven microbial electrosynthesis [205].

As an emerging biotechnology, the photobiological conversion system has broad application prospects in biofuel production, carbon dioxide fixation, and the synthesis of high-value chemicals. By continuously optimizing the combination of photosensitive materials, microorganisms, and electron transfer media, and enhancing the overall performance and economic efficiency of the system, photobiological conversion technology is expected to offer more effective solutions for dealing with upcoming environmental and energy issues.

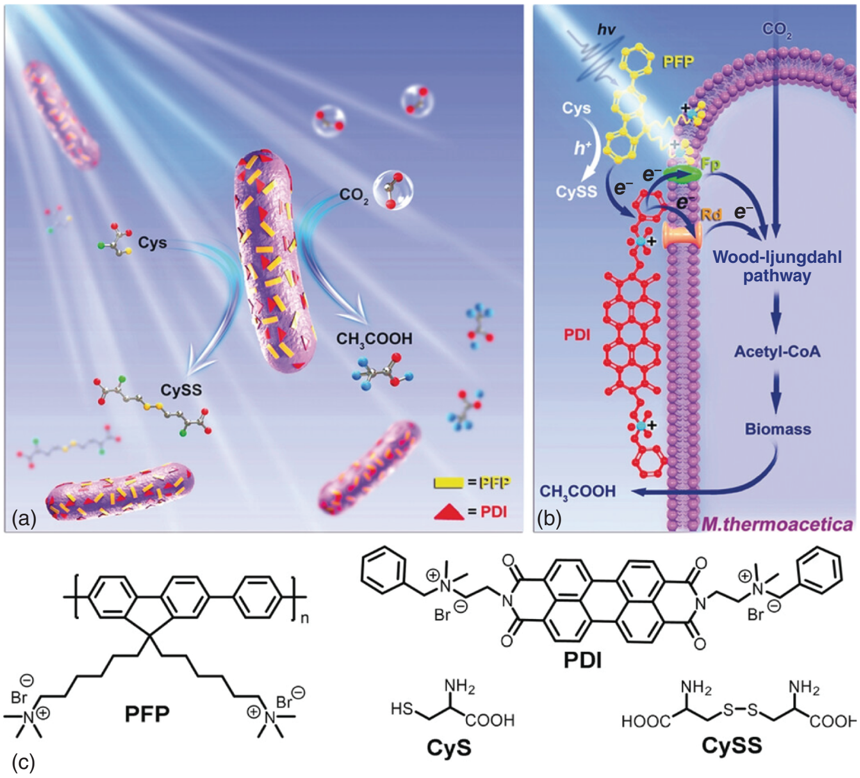

Figure 1.48 Schematic diagram of an organic semiconductor–nonphotosynthetic bacterial hybrid system producing acetic acid driven by solar energy. *Source:* Gai et al. [204] / with permission of John Wiley & Sons.

1.3.5.4 Photocatalytic Therapy

Photodynamic therapyhas the advantages of being spatiotemporally controllable and not limited by drug resistance, but its application scenarios have a high demand for oxygen. On the other hand, the eradication of pathogenic microorganisms by PTT requires a long period of high temperature, which inevitably has certain side effects on normal tissues. Therefore, it is very important and promising to develop a treatment modality that combines the advantages of both. The essence of life activities relies on various oxidation-reduction reactions and metabolic processes involving substance exchange. Thus, effective intervention in pathological processes can be achieved through photocatalytic modulation of electron transfer and ROS metabolism in organisms.

Conjugated polymers, due to their excellent photoelectric conversion efficiency, ease of functionalization, and good biocompatibility, are among the key contenders for in vivo catalysts for photo-mediated redox reactions. Unlike inorganic catalysts, which often require complex systems of multiple materials, CPs can achieve in vivo photocatalytic reactions more easily through simple doping or functionalization, showing potential for applications in the biomedical field. Three different CP-based

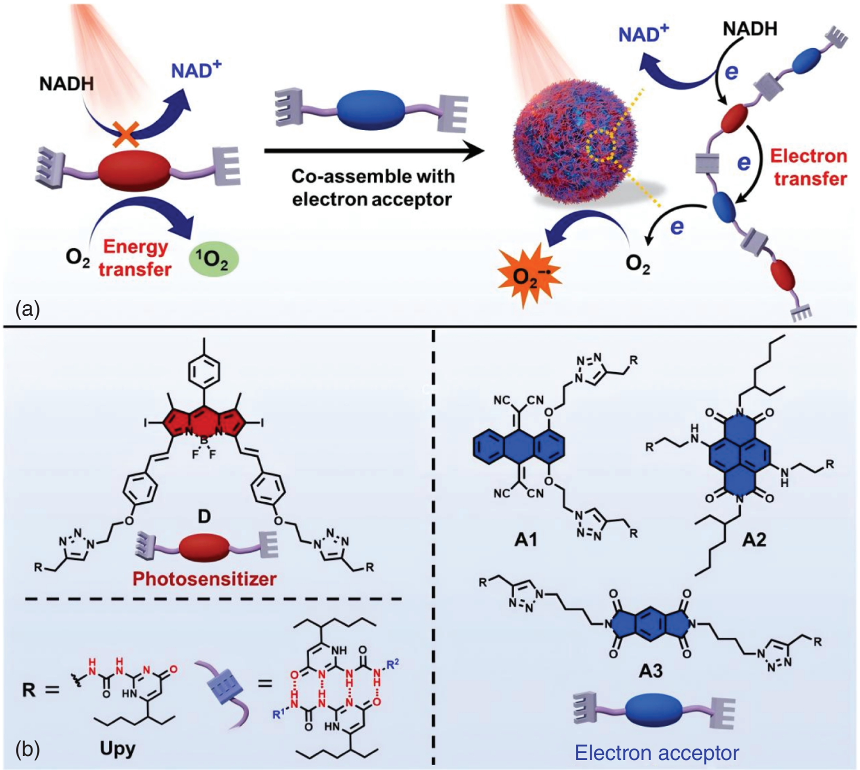

Figure 1.49 Schematic diagram of the structure and assembly of supramolecular composite photosensitizers and the photoinduced oxidation of NADH and the production of $O_2^{-\cdot}$. *Source:* Teng et al. [206] / ISpringer Nature / CC BY 4.0.

electron acceptors were designed and assembled with conventional BODIPY-based type II photosensitizers via quadruple hydrogen bonding to prepare supramolecular composite photosensitizers (Figure 1.49). Under light conditions, the shortened molecular distance and matched redox potentials between the photosensitizer molecules and electron acceptors facilitate transfer of the photoinduced electron of the photosensitizer to the acceptor, which further transfers electrons to oxygen to generate superoxide radicals. Additionally, this process generates strong oxidizing cationic radicals of the photosensitizer, which can effectively oxidize NADH in living cells, disrupting the coenzyme balance and breaking the mitochondrial electron transport chain, thereby achieving cell killing without relying on oxygen. This system exhibits the highest NADH oxidation turnover frequency, which surpasses that of conventional transition metal catalysts by one to three orders of magnitude. in vivo experiments using mouse models have shown significant tumor ablation effects. This method of utilizing photocatalytic reactions can inhibit the growth of pathogenic microorganisms by different principles from PDT and PTT, achieving disease treatment without being influenced by the tissue microenvironment [206].

Carbon monoxide (CO) is a crucial endogenous signaling molecule that significantly influences physiological processes such as immune regulation, inflammation, and oxidative stress. CO regulates the immune system by modulating the secretion of pro-inflammatory cytokines, thereby reducing the damage to normal cells caused by excessive pro-inflammatory cytokines secreted by macrophages in inflamed areas. Additionally, CO can selectively kill tumors by regulating mitochondrial function and triggering oxidative stress. However, gas therapy based on CO poses a risk of CO poisoning. Therefore, using intracellular endogenous CO_2 to catalyze the in situ generation of CO is a controllable and precise solution [207].

A CP poly(hexadecylfluorene-*co*-thiophene) derivative (PFT) with photocatalytic CO production activity was synthesized and encapsulated in liposomes for targeted delivery to macrophages. PFT can produce CO in situ within cells, facilitating the transition of macrophages from M1 to M2 polarization. The release of pro-inflammatory cytokines including TNF-α, IL-6, and IL-1β can be decreased by M2 macrophages, thereby achieving antiinflammatory effects (Figure 1.50) [208].

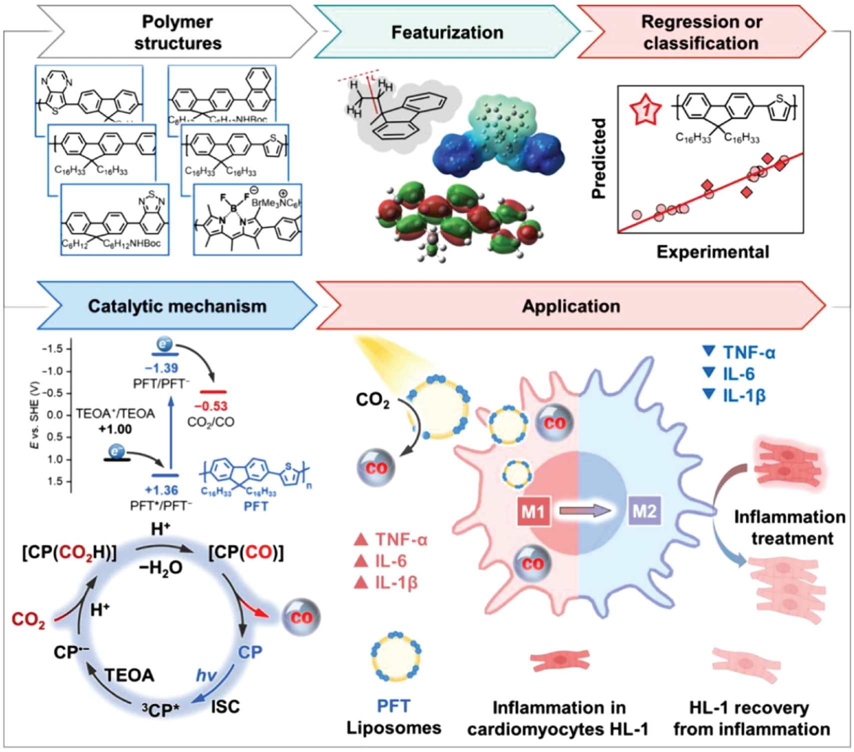

Figure 1.50 Schematic diagram of the principle of intracellular PFT photocatalytic CO production and immune regulation for inflammation treatment. *Source:* Zhu et al. [208] / with permission of American Chemical Society.

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