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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

Photofunctional Polymer Composites for Bioapplications, First Edition. Xiaoyu Wang and Lidong Li.

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

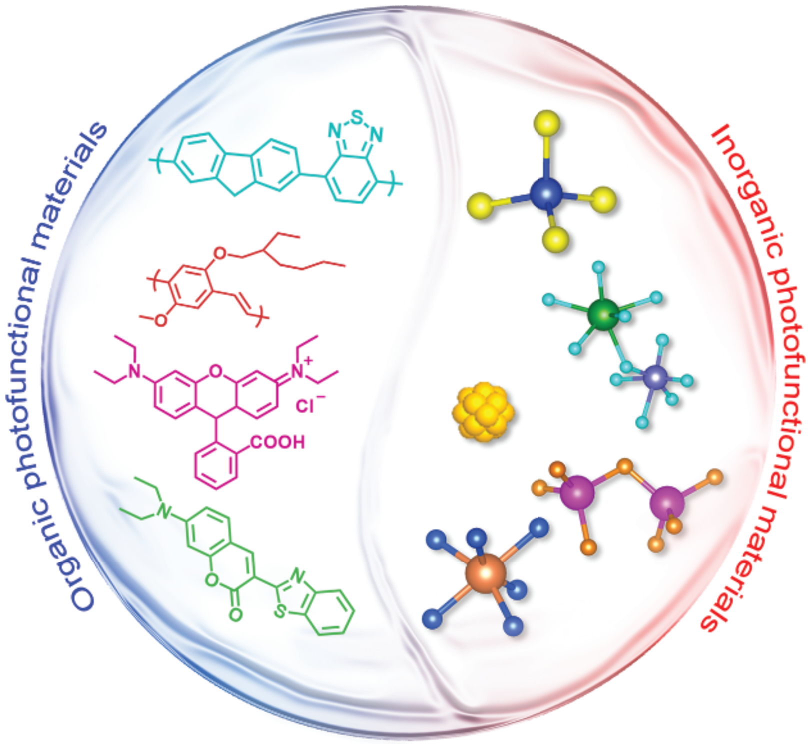

Figure 1.1 Inorganic and organic photofunctional materials.

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.

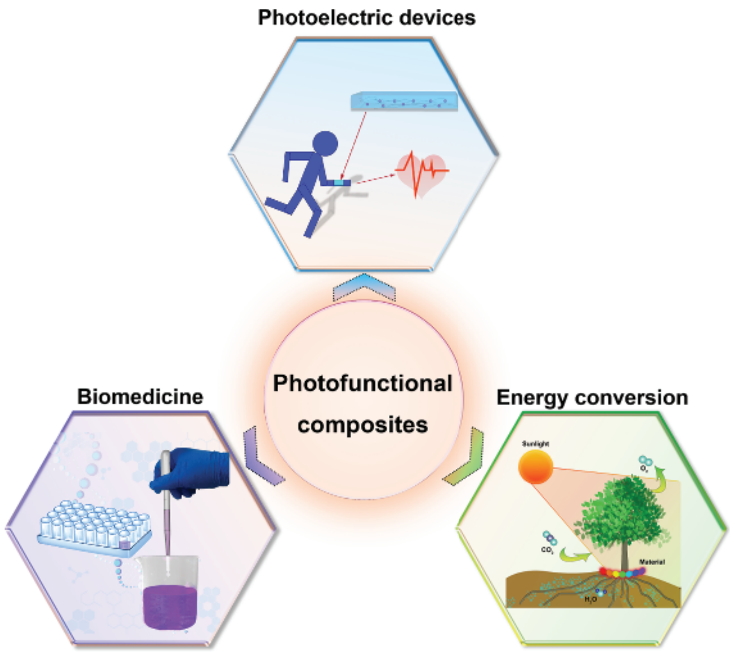

Figure 1.2 Application of photofunctional composites.

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

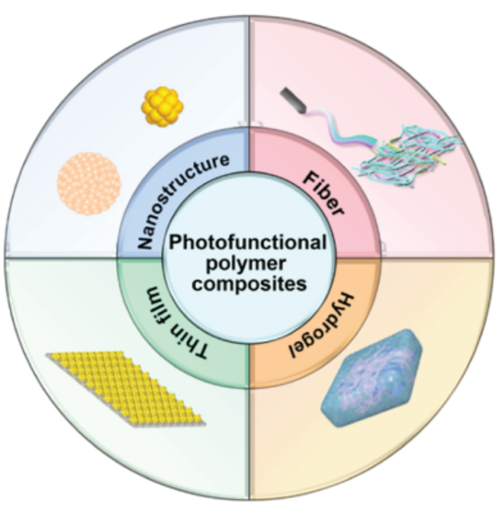

Figure 1.3 Four categories of photofunctional polymer composites.

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.

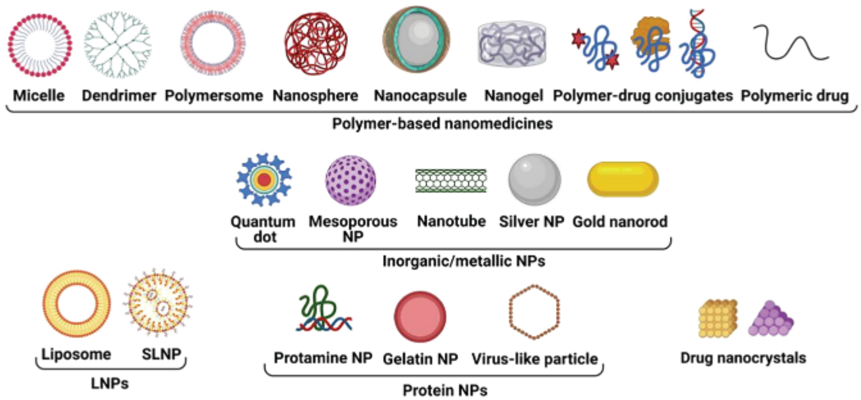

Figure 1.4 Graphical summary of common types of nanomedicines. *Source:* Younis et al. [40] / with permission of Elsevier.

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