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Review article

Inorganic nanoparticle-cored dendrimers for biomedical applications: A review

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ABSTRACT

Hybrid nanostructures exhibit a synergistic combination of features derived from their individual components, showcasing novel characteristics resulting from their distinctive structure and chemical/physical properties. Surface modifiers play a pivotal role in shaping INPs' primary attributes, influencing their physicochemical properties, stability, and functional applications. Among these modifiers, dendrimers have gained attention as highly effective multifunctional agents for INPs, owing to their unique structural qualities, dendritic effects, and physicochemical properties. Dendrimers can be seamlessly integrated with diverse inorganic nanostructures, including metal NPs, carbon nanostructures, silica NPs, and QDs. Two viable approaches to achieving this integration involve either growing or grafting dendrimers, resulting in inorganic nanostructure-cored dendrimers. The initial step involves functionalizing the nanostructures'

Abbreviations: TNP, 2,4,6-trinitrophenol; MTT, 3-[4,5-dimethylthiazol-2-yl]-2, 5-diphenyl tetrazolium bromide; 5-ALA, 5-Aminolevulinic Acid; APTES, 3-Aminopropyltriethoxysilane; AAO, Anodic Aluminum Oxide; RGD, Arginine-Glycine-Aspartic Peptide; Aza, Azathioprine; CDs, Carbon Dots; CNTs, Carbon Nanotubes; mPEG-COOH, carboxylated PEG monomethyl ether; CTAB, Cetyltrimethylammonium bromide; TEOS, Tetraethylorthosilicate; $HAuCl_4$, Chloroauric Acid; CT, Computed Tomography; DCNT, Dendrimer-grafted CNTs; G, Dendrimer generation; DMNPs, Dendrimer modified magnetic nanoparticles; DGO, Dendrimer-grafted graphene oxide; DMSNPs, Dendrimer-grafted mesoporous silica NPs; DMNTs, Dendrimer-grafted MWCNTs; GDSNPs, Dendrimer-stabilized gold nanoparticles; DENV, Dengue Virus; DTA, Diatrizoic Acid; DOX, Doxorubicin; ECL, Electrochemiluminescence; Eri, Erianin; FAR, Folic Acid Receptors; FI, Fluorescein isothiocyanate; FRET, Fluorescence resonance energy transfer; FA, Folic Acid; GCE, Glassy carbon electrode; GA, Glucuronic Acid; GNPs, Gold nanoparticles; GQDs, Graphene quantum dots; GNS, Graphene nanosheets; IC_{50}, Half-maximal inhibitory concentration; HA, Hyaluronic Acid; INPs, Inorganic NPs; LOD, Limit of Detection; MNPs, Magnetic NPs; MSNPs, Mesoporous silica NPs; miRNA, MicroRNA; MRI, Magnetic resonance imaging; MWCNTs, Multi-wall CNTs; NDs, Nanodiamonds; NPs, Nanoparticles; PAMAM, polyamidoamine; PBS, Phosphate buffered saline; P-MIPs, photoresponsive molecularly imprinted polymers; PMAA, Poly(Methacrylic Acid); PEG, Polyethylene glycol; PVP, polyvinyl pyrrolidone; PPI, propylene imine; PSA, Prostate Specific Antigen antibody; QDs, Quantum Dots; rGO, Reduced graphene oxide; SiO_2, Silica; AgNPs, Silver NPs; SWCNTs, Single-wall CNTs; SPIONs, Superparamagnetic iron oxide NPs; SPR, Surface Plasmon Resonance; TEG, triethyleneglycol; TNBC, Triple-negative breast cancer; β-CD, β-cyclodextrin.

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surface, followed by the generation of dendrimers through stepwise growth or attachment of pre-synthesized dendrimer branches. This hybridization imparts superior qualities to the resulting structure, including biocompatibility, solubility, high cargo loading capacity, and substantial functionalization potential. Combining the unique properties of dendrimers with those of the inorganic nanostructure cores creates a multifunctional system suitable for diverse applications such as theranostics, bio-sensing, component isolation, chemotherapy, and cargo-carrying applications. This review summarizes the recent developments, with a specific focus on the last five years, within the realm of dendrimers. It delves into their role as modifiers of INPs and explores the potential applications of INP-cored dendrimers in the biomedical applications.

1. Introduction

The field of nanotechnology, which spans a wide variety of scientific domains, such as chemistry, medicine, engineering, electronics, optics, and biomaterials science, has had a profound impact on scientific exploration, particularly in the advancement of healthcare [1–3]. Recently, there has been a dramatic increase in the conception and utilization of nanotechnology within these domains, indicating a significant leap forward in the application of nanotechnology [4–6]. The nanotechnology industry has emerged as a formidable ally in the healthcare industry, with its applications in biomedicine expanding to encompass early disease detection and sophisticated imaging methodologies, especially in the context of cancers such as breast, lung, colon, prostate, ovarian, and cervix [7–12]. It is often the case that individuals who are suffering from these conditions are confronted by the difficult challenge of hidden or visible secondary colonies. A substantial reduction in the incidence of these diseases can be expected with the advent of diagnostic nanotechnology. It is very likely that this paradigm shift will play a major role in reshaping the landscape of medical science, increasing the precision and efficacy of diagnostic tools, which, in turn, will revolutionize the outcomes of healthcare [13–15].

In recent years, nanomaterials have attracted significant interest due to the exceptional physical and chemical properties they possess, spanning optical, electrical, and magnetic properties. As a result of their versatility, these nanomaterials have found a wide range of uses across a variety of scientific disciplines, engineering fields, and technological sectors, including electronic and electrical engineering, biomedicine, cosmetics, catalysis, diagnostics, medicine, food production, textiles, and the automotive industry [16–20]. While there is a wide array of nanomaterial types available, NPs have emerged as one of the primary choices in biomedical research, especially in the areas of diagnosis, drug delivery, and treatment [21]. NPs have unique properties that allow for the targeted delivery of drugs, imaging, and other therapies to specific areas of the body [22–26]. Additionally, they are highly versatile and can be customized for a variety of medical applications [27–29].

Within the extensive array of NPs, both organic NPs and inorganic NPs stand out prominently [30]. Particularly, INPs have been widely used in a wide range of biomedical applications, and they have played a significant role in MRI systems, drug delivery systems, gene transfer, biosensing, proteins and enzymes immobilization, cancer treatment modalities, and cell separation techniques, among other biomedical applications [31–35]. It is imperative to develop tunable and multifunctional INPs, incorporating diverse surface modifications in order to enhance their physicochemical characteristics in a variety of applications [36–38]. To fully unlock the potential of these INPs as a tool for advancing biomedical research and applications, it is crucial to improve their biocompatibility, stability, and solubility under physiological conditions [39–41]. It is clear that efforts toward advancing the efficacy and versatility of INPs in biomedical applications hold enormous promise for the future [42–44]. As an example, GNPs have been utilized as carriers for drug delivery due to their ability to effectively bind drugs via the Au–S bond, resulting in enhanced therapeutic effectiveness of the drugs [45]. Furthermore, Au complexes demonstrate heightened selectivity and potency against cancer cells, attributed to their reduced DNA-binding activity and heightened affinity towards protein targets via sulfhydryl and thiol groups [46] However, there are some obstacles that must be overcome before these remarkable discoveries are translated from laboratory settings to practical applications. These obstacles include stability under real-world conditions, substantial differences between batches, and the need for multifunctionality [47]. In an effort to overcome these challenges, researchers are exploring the possibility of using capping agents to coat the surface of NPs in order to overcome these hurdles. As a result of this approach, stability issues could be mitigated and consistent performance ensured, emphasizing the need for continued research into bridging the gap between experimental success and practical implementation in nanotechnology [48,49].

The challenges associated with the stability and consistency of NPs can effectively be mitigated or eliminated through the strategic application of a capping agent at the surface of the NPs. Capping agents, including organic ligands, surfactants, and polymers, are integral functional molecules that reside at the surface of NPs and play an important role in their function. They play a vital role in shaping the physicochemical properties and overall performance of NPs. Aside from providing steric and/or electrostatic stability to the NPs through strong adsorption at their surface and forming a protective mono-/multilayer coating on their surfaces, these agents also have many additional functional roles and advantages. Capping agents act as activators of the NPs surface for subsequent conjugation, protecting NPs from environmental factors such as moisture and unwanted chemical reactions, prolonging NPs shelf life, enabling the production of NPs of various sizes, geometries, and morphologies, and facilitating easy dispersion in various solvents. The capping agents play a pivotal role in achieving the desired physicochemical characteristics and functionality in NPs [50,51].

Various types of INPs have been coated with natural or synthetic polymers, including dendrimers/dendrons, PEG, PVP, poly-L-lysine, and chitosan [52]. In particular, dendrimers have been prominently featured in NPs research and as modifiers for NPs, providing a multitude of therapeutic possibilities for cancer research [21]. Dendrimers belong to the class of synthetic macromolecules

with an exceptionally high density of functional groups on their surface and a well-defined three-dimensional polymeric architecture. The unique characteristics of dendrimers, including their precise shape, size, molecular weight, and versatility in designing various types, have resulted in their expanded use across a wide range of applications [53]. Dendrimers typically consist of three distinct domains: the core, dendrons, and terminal functional groups. There are areas formed between the dendrons, known as dendrimeric crevices, that are capable of encapsulating guest molecules through hydrophobic or electrostatic interactions. Although dendrimers are primarily characterized by their peripheral functional groups, their overall characteristics are also influenced by the type of functionality of the core, dendrimer generation, the layer of branching units, and dendrimeric crevices [54].

Dendrimers, with their distinctive characteristics such as multifunctionality, a high density of peripheral groups and their ability to be tailored for diverse design requirements, are proving to be a superior capping agent in the formulation of multifunctional NPs. As a result of the well-defined surface groups on dendrimers, these molecules can be conjugated to an array of biomolecules, such as antibodies, aptamers, nucleic acids, targeting ligands, imaging probes, drugs, and biosensors [54]. Dendrimers can be used in a wide variety of biomedical applications because of their versatility as surface-functionalizing or coating agents [55]. Dendrimers are characterized by their internal architecture, which is marked by voids or cavities between branches. Spaces like these provide an ideal environment for the transportation of drugs, dyes, and other NPs. A notable characteristic of dendrimers is their high reactivity, and a phenomenon known as the dendritic effect describes the enhanced activity of substances encapsulated within dendritic cavities as opposed to their unentrapped counterparts [56]. As a result of dendrimers' unique properties, various dendrimer-encapsulated and dendrimer-coated INPs have been developed through various chemical processes. The advantageous properties of INP-cored dendrimers for biomedical applications can be attributed to several key factors: Firstly, their well-defined and controllable size, shape, and surface functionality allow for precise tuning of drug-loading capacities and release kinetics, ensuring optimal therapeutic outcomes [57–59]. Secondly, the inherent stability and biocompatibility of the inorganic core impart enhanced structural integrity and resistance to degradation, facilitating prolonged circulation in the bloodstream and improved bioavailability of encapsulated drugs [60, 61]. Moreover, the versatile surface chemistry of inorganic cored dendrimers enables facile conjugation of targeting ligands and therapeutic agents, enabling selective recognition and uptake by cancer cells while minimizing off-target effects on healthy tissues [21, 62]. Additionally, the ability of these dendrimers to encapsulate a wide range of therapeutic payloads, including small molecules, nucleic acids, and imaging agents, further enhances their utility in multifunctional cancer theranostics [63–65]. A remarkable advancement has been achieved in leveraging the synergistic potential of dendrimers with INPs, leading to the development of sophisticated materials with integrated functionalities [66]. These encompass capabilities ranging from tumor thermal imaging and targeted CT imaging to photothermal therapy and gene therapy, all deliverable through a singular intravenous injection. This breakthrough not only represents a significant stride in multifaceted medical interventions but also underscores the efficiency and versatility of this approach in addressing complex biomedical challenges [67,68]. In addition, intricate architecture of dendrimers, in conjunction with the versatile properties of NPs, has sparked considerable interest in their utilization across various biomedical applications, including drug delivery, nucleic acid delivery, bioimaging, diagnostics, and the advancement of biochemical sensors [69].

This review focuses on recent advancements in utilizing dendrimers as modifiers for INPs in biomedical applications. To the best of our knowledge, there are only a limited number of reviews available on this topic [70], so this review focuses on INPs as dendrimer cores. We present recent insights into INPs-cored dendrimers' characteristics, physiological and toxicological properties and highlight their advantages in biomedical applications. Furthermore, we discuss key challenges and future prospects in this area of research.

2. Intentions of fabricating INP-cored dendrimers

A dendrimer made up of an inorganic core is known as an inorganic core dendrimer, entails a unique process in which the inorganic nanomaterial is initially used to form the dendrimer core, following which the branches are formed and anchored. As a result of this method, direct contact between NPs and surfaces is reduced, thus minimizing the risk of cytotoxicity to healthy tissues. Esmaeili and coworkers conducted a study where MNPs were synthesized using the coprecipitation method. These MNPs were grafted to APTES and then functionalized by PAMAM through a stepwise process involving the addition of methyl acrylate and ethylenediamine, resulting in a dendron-like structure with an average diameter of 21 nm. The impact of G3–dendrimer–SPIONs on cell viability was assessed using the MTT assay. Even at a high NPs concentration of 100 μg/ml, there was no statistically significant difference in cell viability between the control (untreated) cells and those treated with NPs. This suggests that these NPs exhibit no cytotoxic effects on these cells [71]. Maiti et al. employed computational modeling to elucidate the impact of dendrimer functionalization on graphene cytotoxicity [72]. Their investigation focused on the direct interaction between a functionalized graphene sheet and a dimyristoylphosphatidylcholine bilayer, a model for cell membranes. Intriguingly, they examined a graphene-dendrimer complex with both good surface coverage and a remaining, uncoated graphene portion. This unique architecture resulted in minimal contact with the dimyristoylphosphatidylcholine bilayer. Notably, unlike pristine graphene, the functionalized complex exhibited no evidence of lipid bilayer disruption. The study suggests that the protonated dendrimer interacts favorably with surrounding water molecules, rendering the graphene-dendrimer complex less hydrophobic and consequently less stable at the lipid-water interface. This reduced hydrophobicity presumably hinders the penetration of the complex into the lipid bilayer, thereby mitigating the cytotoxic effects previously observed with unfunctionalized graphene [72].

By exploiting dendrimers' diverse properties, including their ability to carry functional groups and exhibit high electrical charges, dendrimers can be used to stabilize nanostructures and improve their water solubility. Xiao and coworkers created a novel nanoprobe of GDSNPs linked with FA and DTA to enhance tumor CT imaging [73]. They employed PAMAM dendrimers of G5 with amine termini to trap GNPs through a stepwise complexation/reduction approach, achieving higher Au loading compared to the traditional one-step method. The resulting [$(Au^0)_{120}$-G5.NH_2] NPs underwent sequential functionalization with DTA, FA via a PEG spacer, and

mPEG-COOH, followed by complete acetylation of the remaining dendrimer amine termini. The formed GDSNPs -DTA-FA displayed outstanding aqueous dispersibility in cell medium and PBS, indicating sustained water dispersibility across various aqueous media despite successive surface functionalization. The colloidal stability of GDSNPs-DTA-FA is ascribed to the expanded dendrimer periphery resulting from surface PEGylation modification [73].

Also, research indicates that dendrimers enhance biocompatibility, prolong biodistribution, and reduce toxicity by forming a protective shell that limits opsonization and corona formation [71,74]. The intrinsic properties of dendrimers, such as a substantial surface area, abundant modifiable functional groups, considerable loading capacity, distinctive drug release kinetics, and dendritic formation, inspire researchers to graft or cultivate dendrimers on other nanostructures, thereby enabling the development of multifunctional complexes [54]. Nanostructures can be interconnected by dendrimers, enabling the fabrication of intricate structures that can be used for a wide variety of applications, including biosensing and theranostics [75–77]. Moreover, dendrimers are capable of altering the optical properties of specific nanostructures, such as QDs, resulting in unique properties such as fluorescence quenching and FRET phenomena [78]. Martins and coworkers explored the formation of nanohybrids by self-assembling CDs with G4-G6 PAMAM-NH_2 dendrimers, aiming for applications in transfection and bioimaging. The nanohybrids exhibited persistent high fluorescence levels even under non-neutral pH conditions, which was attributed to the presence of dendrimers and their buffering effect on the overall structure. The cytocompatibility of these nanohybrids ranged between that of CDs (which proved non-toxic at the tested concentrations) and pristine dendrimers. Notably, the nanohybrids displayed efficient cellular internalization, surpassing the performance of CDs alone, and could be identified through fluorescence emission in different colors, depending on the excitation wavelength used [79].

INPs exhibit concentration-dependent and time-dependent cytotoxicity, thus underscoring the importance of dosage considerations and time exposure in toxicity assessments [80,81]. On a promising note, polymeric functionalization has demonstrated efficacy in enhancing NPs stability and mitigating toxicity [82]. Despite the exciting prospects offered by INP-cored dendrimers for biomedical applications, several key challenges and limitations necessitate careful consideration and resolution. Firstly, the scalability of current synthesis methods for INP-core dendrimers presents a formidable hurdle, characterized by intricate multi-step procedures and the need for specialized equipment [83,84]. To address this, the development of robust and scalable synthetic protocols is imperative to ensure cost-effectiveness and widespread availability. Secondly, achieving reproducible synthesis of INP-cored dendrimers with consistent functionality is hindered by inherent variability in current fabrication techniques [85]. Standardization of protocols and implementation of stringent quality control measures are paramount to ensure reliable therapeutic efficacy. Thirdly, the long-term stability of INP-cored dendrimers in biological environments is paramount for their successful application, necessitating strategies to mitigate factors such as aggregation, dendrimer shell degradation, and cargo leaching [86,87]. Optimization of core-shell interactions and integration of stabilizing surface modifications are indispensable for safeguarding therapeutic efficacy and ensuring safety in vivo. Overcoming these challenges demands the implementation of innovative synthetic methodologies, coupled with meticulous characterization techniques and comprehensive investigations into the biological behavior of INP-cored dendrimers. Such endeavors are indispensable for facilitating the seamless translation of these nanomaterials into clinical applications [33]. Both in vitro and in vivo studies must be intensified to surmount these hurdles and advance therapeutics employing INPs from laboratory research to clinical practice [88]. By surmounting these obstacles, the full potential of this promising class of nanomaterials can be unleashed, thereby revolutionizing the landscape of disease diagnosis and treatment.

3. Fabrication strategies for INP-cored dendrimers

Expanding upon the established field of INPs synthesis, researchers have actively explored diverse methodologies to efficiently engineer INP-cored dendrimers. These methods were inspired by strategies previously used to synthesize INPs with surfactants or polymers in the presence of colloidal synthesis of INPs [89]. This synergistic relationship capitalizes on existing expertise in achieving precise control over size, shape, and composition during INPs colloidal synthesis [90,91]. Notably, this integration introduces a novel dimension by harnessing the distinctive functionalities inherent to dendrimers. These functionalities, derived from the well-defined structure and versatile surface chemistry of dendrimers, enable meticulous control over critical properties such as surface characteristics, biocompatibility, and cargo loading/release profiles within the resultant INP-cored dendrimer architecture [92]. This convergence of established INPs synthesis methodologies with the adaptive nature of dendrimers provides a wide range of possibilities, facilitating the design and fabrication of advanced nanomaterials tailored to address an array of biomedical challenges.

Most fabrication methods for INP-cored dendrimers center around the in situ generation of INPs within a dendrimer shell. These methods utilize well-established techniques such as chemical reduction, UV irradiation, or thermal/microwave/ultrasound-assisted decomposition, all executed in the presence of dendrimers. This in situ approach confers several advantages, including controlled nucleation and growth of the INP core, facilitated by interactions with the surrounding dendrimer molecules [93–95]. In one approach to creating dendrimers with INP cores, the dendrimer, a reducing agent, and a metal salt are combined in a reaction vessel to form dendrimers with INP cores. As a result of the reduction reaction, metal ions (Me^{n+}) are converted into zero-valent metal atoms (Me^0), resulting in the precipitation of dendrimers that are cored with INPs. With this method, freshly formed NPs come into contact with dendrimer molecules within the first few minutes, thereby offering a facile and rapid synthesis procedure in which initial NPs are immediately capped with dendrimers by adsorption, electrostatic interaction, chelation, and chemisorption [96–99]. There are several factors that can affect the yield, size, and shape distribution of the NPs including dendrimer generation, metal-dendrimer molar ratios, and the activity of the reducing agents [98,99]. Kim et al. present a novel method for synthesizing dendrimer-encapsulated Pt nanoparticles with a significantly higher Pt loading compared to traditional methods [93]. Their approach utilizes a combination of chemical reduction and galvanic exchange reactions, enabling the encapsulation of over 1300 Pt atoms per dendrimer. This method

overcomes the limitations of conventional techniques restricted by the fixed number of Pt binding sites within dendrimers. The rapid and efficient synthesis (10 min) involves co-adding Cu and Pt precursor solutions to a dendrimer solution, followed by reduction with BH_4^-. This leads to selective Cu^{2+} complexation with the dendrimer and subsequent reduction to Cu nanoparticles within the dendrimer shell. These Cu nanoparticles then undergo galvanic exchange with nearby Pt^{2+} ions, leading to Pt nanoparticle formation. This cycle repeats until all Pt^{2+} ions are converted into encapsulated Pt nanoparticles. These findings are significant as they demonstrate the controllable synthesis of large and homogeneous Pt dendrimers, thereby expanding the research scope of dendrimers without constraints posed by limited atom numbers and heterogeneous oxidation states [93]. Maki et al. developed a targeted cancer therapy nanoplatform by combining GNPs, tetrahydrocurcumin (a potent therapeutic agent), and HA for precise delivery [63]. This approach involved a straightforward one-pot chemical synthesis at room temperature, employing generation 3.0 PAMAM dendrimers as both reducing and stabilizing agents for GNP fabrication. The resulting nanoparticles exhibited optimal size, charge, stability, and high drug loading efficiency of 96.45 %. Subsequent HA coating improved biocompatibility, specificity, and cellular uptake via CD44 receptor-mediated endocytosis in Caco-2 cancer cells. Moreover, the nanoplatform demonstrated pH-responsive drug release, facilitating the co-delivery of tetrahydrocurcumin and GNPs, which synergistically induced oxidative stress and mitochondrial damage in cancer cells, enhancing anti-cancer efficacy [63]. Li et al. showcased the benefits of facile one-pot synthesis by developing near-infrared-II fluorescent probes for in vivo imaging [61]. Their approach entailed synthesizing PEG-polyacylthiourea dendrimer encapsulated silver sulfide quantum dots (PEG-polyacylthiourea Ag_2S QDs) in a single step. This straightforward method enabled size adjustment of the QDs by varying reaction time and precursor concentrations. The resulting QDs exhibited robust fluorescence emission peaking at 1110 nm, ideal for near-infrared-II imaging with deep tissue penetration capabilities. Furthermore, these QDs demonstrated excellent stability and biocompatibility, rendering them suitable for in vivo applications [61].

There is also another approach that involves the preparation of nanostructures in order to serve as the cores of dendrimers. The inorganic nanostructures can be functionalized with a variety of groups, including amines [100], silanes [101], and carboxyl groups [102], making them suitable for the conjugation of dendrimers. As a result, dendrimers can be anchored and conjugated to these functionalized nanostructures via covalent coupling, ligand exchange, electrostatic interactions, or some combination of these techniques [103]. The addition of monomers that contribute to radial growth is designated as one generation at each step of the process. This conjugation method offers several advantages over the one-pot synthesis approach, including efficient coupling, controlled uniformity, versatility in the use of any dendrimer as a capping agent, precise control over dendrimer surface density on the NP surface, as well as preservation of NP stability [103]. Tabakoglu and coworkers developed novel folate-receptor-targeted PAMAM dendrimer-functionalized mesoporous silica-coated MNPs as drug delivery agents for photodynamic therapy [104]. The synthesis involved coating the surface of MNPs with mesoporous silica, followed by functionalization with siloxane-cored PAMAM dendrons (generation 1 to 3) and targeting the surface with FA. Indocyanine green, a near-infrared dye, was loaded into the nanocarriers, and their photodynamic therapy efficiency was evaluated on MCF-7 cells. The study successfully demonstrated safe and tumor-specific drug delivery. These nanoparticles exhibited good stability under various conditions, with the highest loading capacity observed for G3. Furthermore, the presence of FA increased the loading capacity of indocyanine green and enhanced pH-sensitive drug release, essential for cancer treatment. Lochab et al. developed a novel drug nanocarrier using a surface chemistry method [105]. They chemically linked PAMAM to the surface of NDs, transforming their surface chemistry and enhancing their stability in aqueous solutions across a wide pH range. The modified NDs, known as PAMAM-tethered NDs, showed no cytotoxicity and efficiently encapsulated the poorly water-soluble drug cabazitaxel. This encapsulation reduced the size of cabazitaxel particles and enabled controlled, sustained release under acidic conditions (pH 4), resembling the tumor microenvironment. Importantly, the resulting nanocarrier exhibited significant uptake by cancer cells, resulting in a notably reduced IC_{50}, indicating enhanced therapeutic effectiveness. Comprehensive coverage of synthesis techniques and fabrication methods for some INP-cored dendrimers is available in previous publications [106–110].

4. INPs as cores of dendrimers

4.1. Metallic nanoparticles

4.1.1. Gold nanoparticles

GNPs have emerged as valuable tools in biomedicine due to their straightforward preparation, strong chemical stability, biocompatibility, well-established surface chemistry, low toxicity, and customizable size. With sizes ranging from 1 nm to 8 μm and diverse shapes like cuboctahedral and spherical, GNPs offer versatile optical properties suitable for applications such as photothermal ablation and imaging [111,112]. The integration of dendrimers with GNPs, achieved through growth or grafting on the NP surface, has been a subject of extensive investigation [113].

In a research initiative exploring the attributes of GNP-dendrimer colloidal hybrids, their drug release patterns, and cytotoxicity, PPI was grafted onto GNPs to generate a dendrimer-grafted GNP [114]. Synthesis methods involved the Turkevich method for GNPs creation and iterative Michael addition for PPI. Significant discoveries include pH-dependent release of DOX drug (with minimal release at pH = 7.4 and maximum release at pH = 5.4), a reverse association between dendrimer grafting and drug release, and a direct link between elevated dendrimer grafting and increased toxicity [114]. The study suggests that lower drug release at pH 5.4 arises from a combined effect of high osmotic pressure within the dendrimer shell and steric hindrance caused by the grafted dendrons, hindering drug diffusion from the nanocarrier [114].

Sun et al. outlined a novel heat-treatment technique for crafting dendrimer-protected GNPs with controlled sizes, achieved without the need for a reducing agent. The process involved diluting aqueous solutions of $HAuCl_4$ and PPI-G3 with different initial molar ratios,

heating the mixture to 80 °C until a purple-red color emerged. This innovative single-step synthetic approach allowed precise size manipulation and control of the GNPs' nucleation and growth kinetics by adjusting the initial molar ratios, all without employing a reducing agent [115].

For efficient cargo delivery, Golshan et al. developed nanocarriers for DOX delivery utilizing GNP-cored dendrimers (Au-G4A). This involved synthesizing a 4th generation PPI dendrimer grown on a GNP core, created by reducing $HAuCl_4$ with trisodium citrate and modifying with cysteamine to yield amine-functionalized GNPs. Au–NH_2 cores were then utilized to fabricate Au-G4A NPs by introducing acrylonitrile and reducing with lithium aluminum hydride. The investigation of bioconjugation effects on drug release behavior involved conjugating peripheral amine groups of Au-G4A with FA to produce Au-G4F. Loading both structures with DOX and subjecting them to varying pH environments (0.033 and 0.045 mg of drug/mg of dendrimers) revealed superior drug release properties attributed to enhanced cavities and drug release through the polymeric matrix [100].

Shi et al. presented a new technique to form and functionalize Au(III) ($HAuCl_4$) using G5 PAMAM dendrimers with terminal amines, resulting in GDSNPs. The method involves the spontaneous mixing of methanol solutions containing $HAuCl_4$ and G5.NH_2 dendrimers at room temperature, followed by the addition of triethylamine to create a pink solution. Subsequent washing with PBS and water yields water-soluble and stable GDSNPs for six months [116]. These GDSNPs, pre-functionalized with FA and Fluorescein isothiocyanate, exhibit potential for targeting and detecting cancer cells, with experimental assays confirming their binding to cancer cells overexpressing high-affinity FAR in vitro [117].

In a separate study, Vásquez-Villanueva et al. produced STC-GNPs and CTC-GNPs by coating GNPs with sulfonate and trimethylammonium-terminated carbosilane dendrons or carboxylate-terminated carbosilane dendrons, respectively. These coated NPs demonstrated antimicrobial and antiviral properties. The most favorable conditions for protein-GNP interaction occurred at acidic and neutral pH, with optimal results achieved using second-generation STC-GNPs and CTC-GNPs [118].

In another study, Wang et al. harnessed the combined attributes of GNPs and dendrimers to construct a bio-sensing device [119].

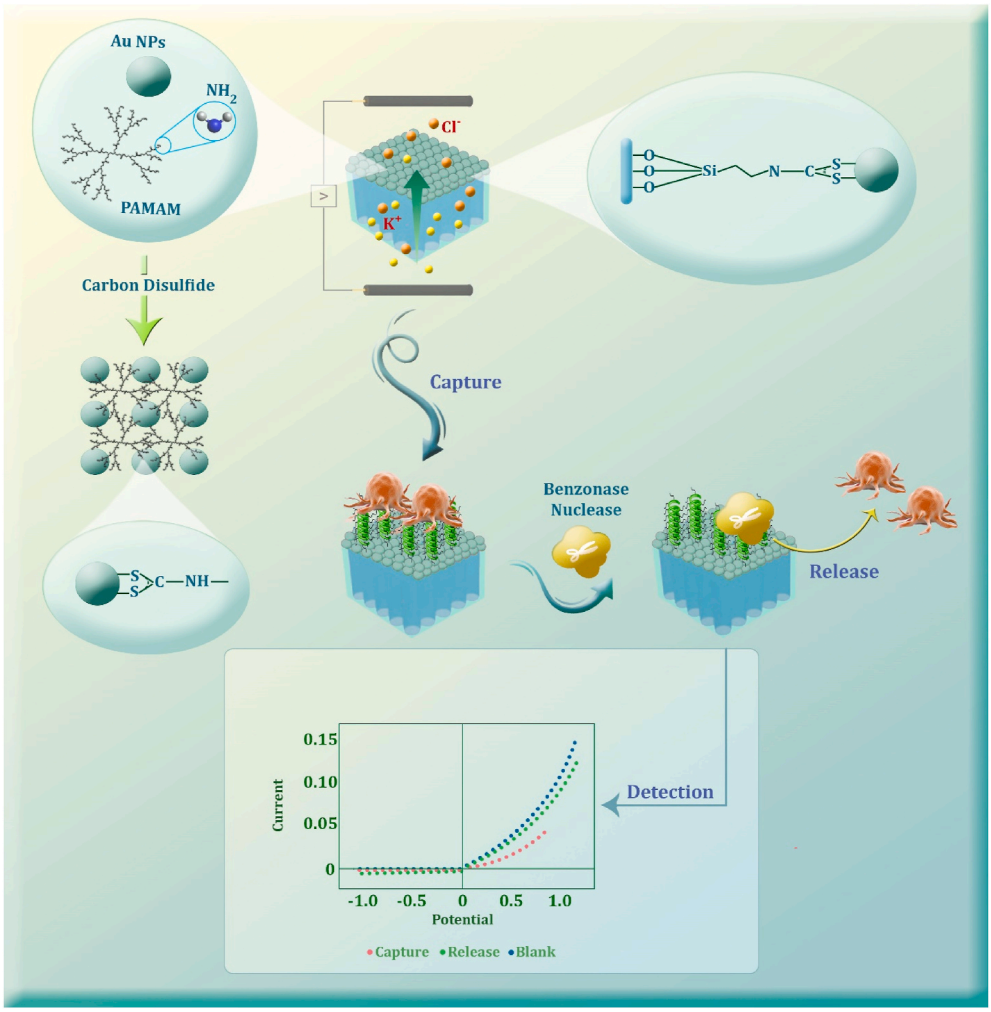

Fig. 1. Schematic illustration of the preparation of the DAN/AAO hybrid.

They engineered an ionic rectification device by crafting a dendrimer-GNP network on the surface of a nanoporous AAO membrane, specifically designed for detecting circulating tumor cells, as it is shown in Fig. 1. The fabrication process involved assembling a dendrimer-Au complex onto the nanoporous anodic aluminum oxide. This assembly of the dendrimer-NP network film was achieved by linking PAMAM dendrimer and carbon disulfide as the linker. The high surface-to-volume ratio of GNPs combined with the dense network of binding sites offered by PAMAM dendrimers creates a highly branched structure with a significantly increased surface area. This extensive surface exposes a multitude of functional groups, leading to inherent asymmetries in both the structure and surface charge density of the resulting DAN/AAO hybrid membrane. These asymmetries are believed to be the key factor behind the observed rectified ion transport behavior. Furthermore, the presence of amino groups on the DAN/AAO surface facilitates anion selectivity, allowing the hybrid membrane to selectively process negatively charged ions. Notably, the ionic rectification properties can be further tailored by manipulating the ion valence and the bulk solution's pH. This study demonstrates the successful construction of a highly sensitive platform for circulating tumor cell detection with a limit of detection as low as 80 cells mL^{-1}. This platform leverages the unique properties of the DAN/AAO hybrid, achieving sensitivity through a combination of chemical, electrical, and optical readouts. This versatile platform holds great promise for in situ studies of cell adhesion and behavior [119].

4.1.2. Silver nanoparticles

Modifying the surface of AgNPs with dendrimers has proven effective in improving their colloidal stability [120,121]. However, the use of high-generation dendrimers for AgNP stabilization is often economically unviable for commercial purposes. To address this challenge, Lataifeh et al. proposed a cost-effective method [121]. They introduced low-generation L-glutamic acid peptide dendrimers, which self-assemble on the surface of AgNPs, providing both stabilization and a consistent spherical shape to the NPs [121]. In a similar context, Vijayalakshmi et al. developed $Ag@TiO_2$ and Co@AgCl NPs stabilized with a zeroth generation triazolylchalcone dendrimer. The positioning of Ag and Ag^+ ions on the surface of Co@AgCl, rather than the core as observed in $Ag@TiO_2$, resulted in enhanced antibacterial activity for Co@AgCl due to the inherent antibacterial properties of these ions [122].

An innovative approach was explored by Liu et al., who utilized Ferrocenyl Janus mixed-dendron stars for AgNP stabilization [123]. Janus particles are a distinct class of nanomaterials known for their unique "Janus-faced" structure, featuring two distinct regions with their own specific physical and chemical properties. This inherent asymmetry enables Janus particles to exhibit dual properties simultaneously, which can be strategically distributed across their mass or surface. Recently, Janus dendrimers have emerged as a novel class addressing limitations of conventional dendrimers, boasting a unique architecture with different functionalities on separate parts of their surface. Typically, this is achieved by combining a hydrophilic dendron, often containing functional groups like PEG, amino, hydroxyl, or carboxyl, with a hydrophobic counterpart utilizing aliphatic chains, poly(benzyl ether) groups [124]. The hydrophobic segment of the Janus structure, in the study conducted by Liu et al., consisted of three ferrocenyl units, while the hydrophilic part featured three TEG termini. Beyond their role in stabilization, these dendrons facilitated the synthesis of AgNPs. The ferrocenyl-containing macromolecule stabilized AgNPs, and the TEG-terminated dendrimers aided in the reduction of Ag(I) to AgNPs. The combination of ferrocenyl-terminated dendrons and TEG-terminated dendrons created conducive conditions for the reduction of Ag(I), leading to the formation of AgNPs [123].

4.1.3. Titanium nanoparticles

The biomedical applications of titanium are extensively explored due to its high biocompatibility, resistance to body fluids, and impressive corrosion resistance [125,126]. Titanium nanostructures, in particular, have shown promise for diverse biomedical uses. Some studies have investigated the incorporation or growth of dendrimers onto both titanium materials and nanostructures. In a study led by Nakanishi et al., dendrimer-protected TiO_2 NPs were synthesized to enhance the photo-degradation of organic molecules in aqueous NPs suspensions [127]. Dendrimers served as stabilizers, enhancing the stability of TiO_2 NPs in water. The synthesis process involved the hydrolysis of $TiCl_4$ in PAMAM dendrimer solutions under cooling conditions. Photodegradation assessments, particularly with 2,4-dichlorophenoxyacetic acid, revealed increased activity in dendrimer-protected TiO_2 NP suspensions compared to bare TiO_2 NPs [127]. Li et al. conducted another study focusing on amino-terminated dendrimers on TiO_2 films. Through simple iterative Michael addition and aminolysis reactions, dendrimer generations were grown. The study thoroughly examined the structure and properties of surface-immobilized amino-terminated dendrimers and assessed their functionalities using platelet adhesion and endothelial cell proliferation tests. The dendrimers exhibited outstanding performance in reducing platelet adhesion and activation, highlighting the advantages of their systematic construction. Endothelial cell culturing results indicated some degree of cytotoxicity in amino-terminated dendrimers, but successful generational growth on TiO_2 films was confirmed [128].

4.2. Magnetic nanoparticles

MNPs play a crucial role in various applications, including tissue engineering, theranostics, cancer treatment, targeted cargo delivery, Lab-on-Chip technology, and bio-imaging [129,130]. MNPs can be categorized into pure metals, metal oxides, and magnetic nanocomposites. The advantages of MNPs lie in their appropriate functionalization, colloidal stability, and low toxicity [131]. To enhance their properties further, numerous studies focus on grafting or growing dendrimers onto MNPs cores. This strategic approach aims to attain more desirable characteristics and functionalities for the effective utilization of magnetic NPs in diverse biomedical and technological applications [132,133].

DMNPs emerge as valuable candidates for cargo delivery applications. The unique combination of MNP cores and dendritic structures enhances the potential for targeted and efficient cargo transport. This innovative platform offers advantages such as improved cargo loading capacity, controlled release kinetics, and the ability to navigate through biological barriers [134]. Parsian

et al. have synthesized 4.5 and 7.5 generation dendrimers with MNPs cores as a carrier for Gemcitabine to improve the biological half-life of the drug and its delivered load effectively in the body. Gemcitabine is effectively bound to the surface of half-generations of PAMAM generation DMNPs. There are several advantages to using this carrier, such as its low toxicity, magnetic field conductivity, stability, high accessibility to tumor cells, and high uptake by the cells. It has been reported that Gemcitabine has a limited affinity for G4 and G5 dendrimers; on the other hand, the highest drug loading was obtained for DMNPs with G5.5. Moreover, Gemcitabine incorporated in the G5.5 DMNPs was more stable than free Gemcitabine. The results of this study show that drug-free NPs had no significant cytotoxicity on SKBR-3 and MCF-7 cells, while NPs loaded with Gemcitabine were 6.0 times more toxic in SKBR-3 and 3.0 times more toxic in MCF-7 cells. 94 % of the loaded drug on this carrier was retained for 6 weeks at pH 7.2 [135].

In another study, Karimi et al. have synthesized a drug carrier for DOX based on the third-generation triazine dendrimer modified with GQDs and grown onto the magnetic core (Fe_3O_4@C@TD-G3). Firstly, the magnetic core was capped with maltose to form a carbon shell, and then the magnetic-carbon complex was modified with 3-aminopropyltrimethoxysilane. Afterward, 3G dendrimer branches were formed on this core. GQDs were conjugated with amino-functionalized dendrimers via a cross-linking reaction between carboxyl groups of GQDs and amine groups of the dendrimers. The combination of Fe_3O_4@C@TD-G3 did not change the crystal structure of pure Fe_3O_4 with a cubic spinel structure. It is stated that incorporation of dendrimer functional groups on the surface would decrease Fe_3O_4 magnetization intensity. Also, Fe_3O_4@C@TDGQDs had DOX loading efficiency of 63.09 %, and DOX release was time and pH-dependent. Also, drug entrapment efficiency of Fe_3O_4@C@TDGQDs microspheres was calculated to be 63.09 %. Five structural properties explain the structure's high drug loading capacity. 1) DOX can be attached to the carrier through π-π interaction between the aromatic ring of Fe_3O_4@C@TDGQDs' carbon shell and the conjugated rings of DOX molecules, electrostatic interaction between acidic, phenolic, hydroxyl, and alkaline amino groups of DOX and carboxyl and OH groups of the Fe_3O_4@C@TDGQDs, and hydrogen bonding between the surface OH/COOH groups of the Fe_3O_4@C@TDGQDs and the NH_2/OH groups of DOX; 2) Three-dimensional structure of dendrimer with abundant branches and cavities; 3) Entrapment of DOX within the dendritic network and addition of the GQDs cavity to the drug; 4) Retention of the drug within dendrimer branches and cavities due to hydrogen bonding and hydrophobic effects between triazine dendrimer and DOX; 5) A large drug storage provided by large central hollow cavity and pores in the Fe_3O_4@C@TDGQDs microspheres. These properties would make Fe_3O_4@C@TDGQDs a highly effective drug carrier. MTT results show no toxicity of Fe_3O_4@C@TDGQDs microspheres to A549 cell lines. Fe_3O_4@C@TDGQDs microspheres can be used as a

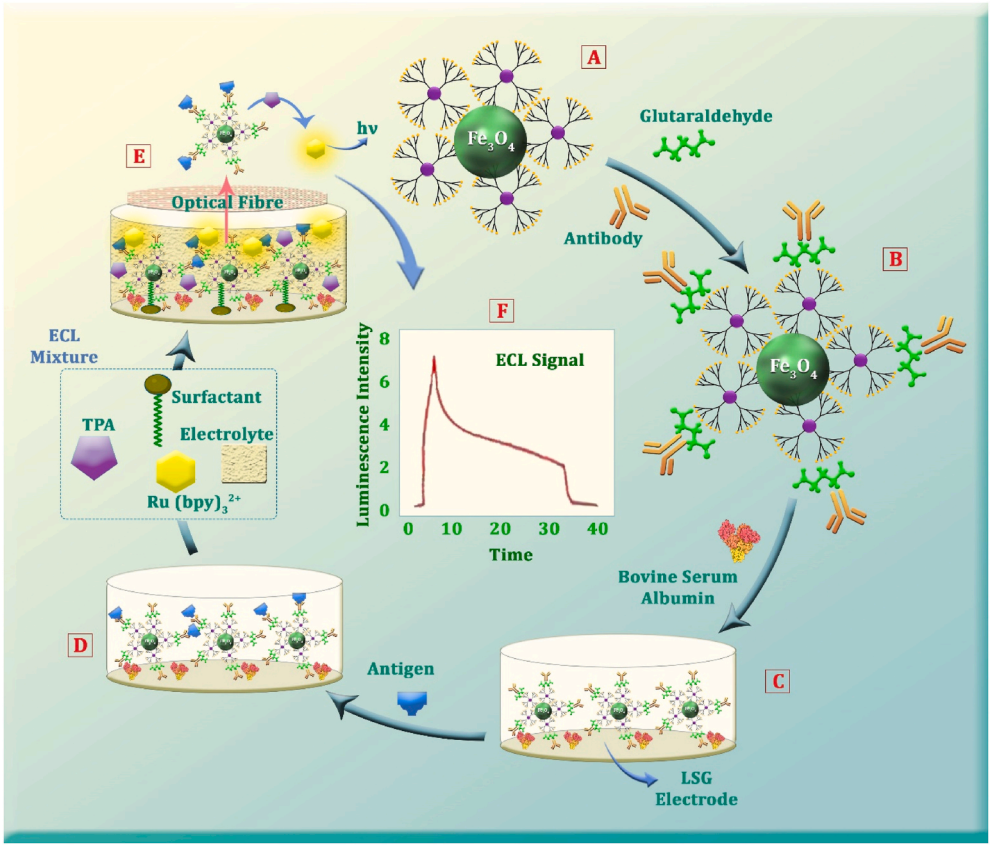

Fig. 2. The synthesis process of liver cancer antigens ECL immunosensor and its function. (A) D5 PAMAM dendrimer stabilized Fe_3O_4 NPs, (B) Conjugation of antibodies to the NPs via glutaraldehyde, (C) Placement of step (B) nanoparticles onto LSG electrode, (D) Addition of antigens to the immunosensor, (E) and (F) ECL signal measurements performed by addition of ECL mixture.

nanocarrier for safe, biocompatible, and effective drugs for medical applications [102].

Several studies have explored the application of DMNPs in bio-sensing, relying on enzymatic processes or ECL phenomenon [136–138]. Chikhaliwala et al. synthesized dendrimers with different generations grafted on magnetic NPs using $Ru(bpy)_3^{2+}$ complexes for ECL-based detection, as it is shown in Fig. 2. The structure, influenced by the amount of amine, carbonyl, hydroxyl groups, and nanostructure size, proved effective for ECL biosensing of alpha-fetoprotein and glypican-3. The detection limits were 6 pg/mL and 0.03 pg/mL for alpha-fetoprotein and glypican-3, respectively. PAMAM@Fe_3O_4 presented an efficient clinical diagnostic method, showcasing enhanced ECL with low concentration. The magnetic property of the Fe_3O_4 core provides external magnetic control, contributing to the sensitivity and specificity of biosensing [75].

Enzyme immobilization using DMNPs presents a promising avenue for applications in detection and biosensing. In a study by Shende et al. [139], biosensors based on PAMAM-MNPs were developed for the detection of glucose in saliva. The PAMAM dendrimers were systematically grown on the surface of MNPs through a repeated Michael addition process. Glucose oxidase was immobilized onto the PAMAM-MNPs using glutaraldehyde as a cross-linking agent and encapsulation by PAMAM-MNPs. A notable observation was a significant decrease in the oxidation activity of the bio-conjugated PAMAM-MNPs dendrimers between two runs, potentially attributed to the alteration in the MNP's structure during the processes. The PAMAM-MNPs biosensor exhibited a steady-state response within 4–6 days, and no disruptions were reported in the presence of artificial saliva. Particularly noteworthy was the biosensor's higher fluorescence intensity at elevated glucose concentrations in a sample. The advantages of this PAMAM-MNPs biosensor encompass cost-effectiveness, reproducibility, and noninvasive glucose detection in saliva, underscoring its potential for practical and efficient biosensing applications.

In another investigation, Doaga et al. engineered cholesterol biosensors using MNPs as a core, serving as a substrate for the growth of PAMAM dendrimers through iterative reactions involving methyl acrylate and ethylenediamine [101]. The biosensor design necessitated the incorporation of cholesterol oxidase and cholesterol esterase for functionality. MNPs were strategically functionalized with APTES and PAMAM to enhance their performance and binding affinity to these enzymes. Functionalization with APTES resulted in a cholesterol-free response rate of 101.9 $\mu AmM^{-1}cm^{-2}$, exhibiting a dynamic range of 0.1–1 mM and a LOD of 80 μM at an operating temperature of 37 °C. Meanwhile, MNPs-PAMAM modified biosensors showed a response rate increase of 73.88 $\mu AmM^{-1}cm^{-2}$, extended linear range of 0.1–1.5 mM, and a LOD of 90 μM. Remarkably, free cholesterol biosensors retained 98 % of their activity after 25 days, while total cholesterol biosensors maintained 85 % of their activity over the same storage duration. These findings highlight cholesterol biosensors' increased performance and stability, emphasizing their application potential in biomedical and analytical applications.

MNP-dendrimers offer a versatile approach for immobilizing enzymes exclusively for enzymatic applications. In a study by Li et al. [140], melamine-glutaraldehyde dendrimer-like polymers were synthesized with aminated magnetic NP nuclei to enhance the activity and stability of lipase. The dendrimer-like polymers on the structure's surface served as effective protein binding sites for the immobilization of the enzyme. This unique structure played a pivotal role in preserving the conformation of lipase, resulting in improved thermal stability and enhanced organic solvent tolerance compared to lipase powder. Notably, even after eight cycles of use, the enzyme retained its catalytic activity. These MNP-dendrimers NPs not only elevate the stability and performance of the enzyme but also facilitate increased contact between the substrate and the enzyme's active site. The catalyst boasts advantages such as high stability, exceptional performance, accuracy, selectivity, high resolution, efficiency, and reusability. This demonstrates the potential of MNP-dendrimers as efficient and reliable tools in enzymatic processes, promising advancements in various enzymatic applications with enhanced attributes and sustained catalytic efficacy.

DMNPs find utility in isolation applications, as demonstrated by Yu et al., who engineered magnetic composite nanospheres incorporating PAMAM dendrimer PAMAM-grafted PMAA brushes [141]. Specifically designed for the identification of low abundance phosphopeptides, this nanocomposite exhibits remarkable features, including high detection sensitivity (1 fmol μL^{-1}), outstanding selectivity (1:500 M ratios of β-casein/BSA), and exceptional recyclability. The abundance of amine groups in the PAMAM-PMAA brushes, coupled with the superparamagnetism of the Fe_3O_4 core, contributes to its high-performance attributes. The nanocomposite's elevated content of functional groups imparts enhanced affinity to target molecules, enabling selective enrichment of mono, multi, or global phosphopeptides. This adaptability is achieved by adjusting bond strength through modulation of buffer polarity and acidity, positioning the nanocomposite as a promising candidate for comprehensive phosphoproteome research. The structure's advantages encompass superior magnetic properties, efficient performance, high selectivity, remarkable detection sensitivity, and easy separation, allowing for reusability for up to 5 cycles. In a comparable vein, Jiang et al. [142] conducted the synthesis of dendrimers featuring MNP nuclei adorned with TiO_2 (MS MALDI-TOF) for the isolation and enrichment of phosphopeptides. The unique interaction mechanisms at play involved PAMAM and phosphopeptides binding through electrostatic attraction, while the TiO_2 and the target phosphopeptides were held together through Lewis acid-base interactions. This strategic combination harnessed the synergistic effects of these interactions to facilitate efficient and selective isolation of phosphopeptides. This innovative approach not only underscores the versatility of dendrimers with MNP cores but also highlights their potential in advancing methodologies for phosphopeptide isolation and enrichment in mass spectrometry applications.

DMNPs exhibit versatility in modification for the isolation of small molecules, as demonstrated by Alaei et al. [143]. In their study, magnetized NPs were synthesized and coated with P-MIPs, further modified with PAMAM dendrimers to create dendrimer-modified MNPs coated with P-MIPs (DMNPs @ PMIPs) for the isolation of Aza. The active amine groups of the PAMAM dendrimer enable precise control over drug delivery behavior and drug loading ratio. This adsorbent showcases a high capacity for interaction with Aza, allowing the drug to attach to the binding site and be released into the solution under intermittent light irradiation, induced by trans–cis isomerization of the binding site. The recycling rate of Aza reaches an impressive 95 %. DMNPs@PMIPs offer notable advantages, including high adsorption capacity, stability for selective extraction, controlled photoresponsive separation from human

biological fluids or pharmaceutical samples for quantitative analysis, retrievability, and high accuracy. These features underscore the potential of modified DMNPs for efficient and controlled isolation of small molecules with applications in drug delivery and analytical chemistry.

Some investigations have employed DMNPs as MRI contrast agents, either exploiting the inherent properties of the MNP core or integrating conjugated contrast agents. Esmaeili et al. conducted a study on SPION-PAMAM for enhancing MRI contrast and enabling hyperthermia therapy. G3-PAMAM-SPION, among various dendrimer generations, demonstrated minimal toxicity at a high NPs concentration of 100 μg/ml. Key benefits of this structure include low toxicity, biocompatibility, high stability, and resistance to cellular excretion. The extended half-life in blood circulation is ascribed to the dendrimer, reducing protein absorption. Furthermore, dendrimer branches diminish the intermolecular attraction between SPIONs, augmenting water solubility. The numerous terminal amines on the dendrimer's surface allow for versatile functionalization, supporting medical applications such as drug delivery, bio-labeling, and diagnosis [71].

Almasi et al. synthesized MNPs as dendrimer cores, onto which 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA)-acetyl-PAMAM dendrimers were grown. This process yielded IO@G4PM-DOTAX-NPS, radiolabeled with Gallium-68 for PET-MR imaging. Incorporating the DOTA chelator on the NP's surface increased the hydrodynamic size and polydispersity index of IO@G4PM(DOTAx) NPs, prompting researchers to acetylate free amine groups and reduce the hydrodynamic size for IO@G4PM (DOTA3)(Ac). IO@G4PM-DOTAX-NPS exhibited prolonged blood circulation with 3.4 % ID/g uptake, and PET-CT imaging revealed distinct uptake at the tumor site. Although surface modification with PAMAM is expected to boost NP uptake in the tumor, potential liver sequestration may limit NP uptake in tumor tissue following intravenous administration [77].

Nosrati et al. developed magnetic core dendrimers as drug carriers to enhance both chemotherapy and magnetic resonance performance. The study illustrated the efficacy of curcumin loaded onto the 5th generation DMNP in treating MCF-7 cells, demonstrating controlled and gradual curcumin release for effective human breast cancer treatment. PAMAM-MNP presents several advantages, including controlled drug release, slow-release capabilities, easy preparation and scalability, efficient loading of small molecules, and inherent magnetic properties. The dendrimer's magnetic characteristics also make it suitable for applications in MRI and cancer diagnosis [60].

In a recent investigation, Nori et al. developed $Fe_{3-\delta}O_4$@Au magnetic NPs by employing a thiol-ended dendrimer. These NPs were

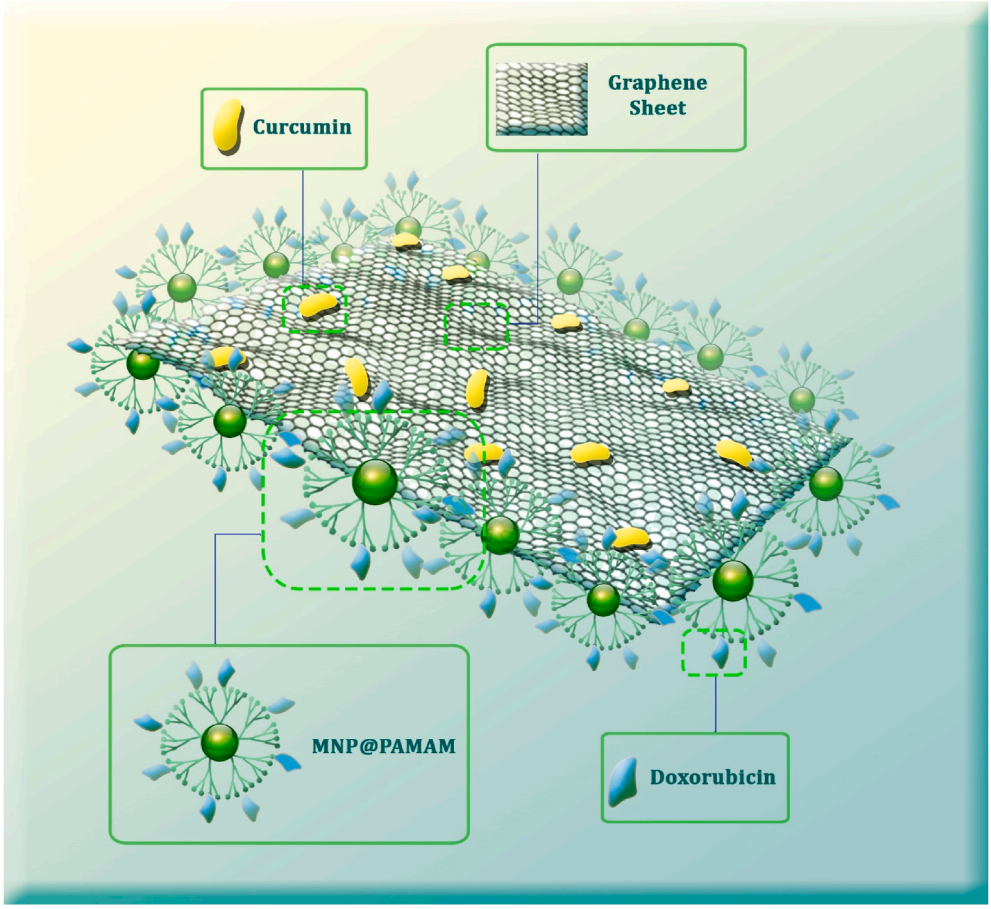

Fig. 3. Schematic illustration of Graphene and MNP-cored PAMAM dendrimer hybrid, loaded with Doxorubicin and Curcumin.

employed as carriers for the anti-cancer drug 6-mercaptopurine and assessed on breast cancer cells under RF hyperthermia. Additionally, their suitability as contrast agents for MRI imaging was explored. The results suggested that the designed magneto-dendrimer stands out as a promising option for theranostic applications in cancer therapy [62].

4.3. Carbon nanostructures

4.3.1. Graphene

Graphene, a carbon-based nanomaterial arranged in a two-dimensional structure, consists of a single layer of carbon atoms [144]. It possesses unique qualities, such as a high surface-to-volume ratio, remarkable chemical versatility, superior mechanical strength, thermal stability, electrical conductivity, and the ability to bond with various macromolecules. Due to its diverse potential applications, recent focus has shifted towards modifying graphene and its derivatives with dendrimers [145,146].

Several investigations have been dedicated to creating graphene-cored dendrimers or hybrids of graphene with dendrimers, particularly for drug delivery, notably the anticancer drug DOX. Despite its effectiveness in cancer treatment, DOX often produces side effects due to its non-specific impact on tumor cells. Addressing this concern, Pourjavadi and colleagues explored the simultaneous delivery of drugs to cancer cells using a graphene-dendrimer hybrid. In this research, the edges of graphene sheets were functionalized with PAMAM dendrimers modified with magnetic NPs, as it is shown in Fig. 3. The resulting hybrid exhibited amphiphilic properties, combining the hydrophilic characteristics of dendrimer branches with the hydrophobic attributes of graphene sheets. The carrier was loaded with hydrophilic DOX through covalent interactions and hydrophobic curcumin through π-π stacking. This hybrid displayed a pH-dependent release of both drugs. The inclusion of two distinct drugs into the carrier resulted in increased cellular uptake, internalization, and a more potent chemotherapeutic effect compared to carriers loaded with a single drug [147].

In an independent study, Pooresmaeil and her team introduced an innovative carrier for DOX by combining GQDs and dendrimers. The process commenced with the modification of GQDs through citric acid pyrolysis, leading to amine-functionalized GQDs through salinization. Subsequently, the GQDs' surface served as the platform for the growth of a PAMAM dendrimer, resulting in GQDs-PAMAM. To augment nanocarrier properties, the GQDs-PAMAM was further enriched with β-CD, a torus-shaped carbohydrate, forming the glycodendrimer (GQDs-PAMAM-β-CD). The ultimate structure was loaded with DOX. The pH-sensitive behavior of DOX-GQDs-PAMAM-β-CD in drug release ensured secure and targeted drug delivery to cancer cells. It demonstrated effective cell entrance capability and displayed high efficacy in eliminating target cells, positioning it as a promising solution for cancer treatment [148].

Graphene-cored dendrimers have been tailored for gene delivery applications in a study led by Liu et al. This innovative design utilized graphene-cored dendrimers as gene delivery vectors for the plasmid DNA encoding the enhanced green fluorescent protein, pEGFP-N1. The system involved incorporating a PAMAN dendrimer with oleic-acid-functionalized graphene. Initial steps included chemically adsorbing oleic acid onto graphene and covalently anchoring functionalized graphene and PAMAN dendrimer through the amidation process. Oleic acid was chosen for its unique interaction with both graphene and PAMAN, along with its high affinity for cellular membranes. The resulting vector demonstrated dose-dependent in vitro cytotoxicity and proved biocompatible with HeLa cells. This graphene-oleate-PAMAM structure exhibited notable efficacy in GFP transfection, showcasing its potential as a biocompatible gene carrier [149]. In another innovative development, a graphene-dendrimer nanostar was engineered for the targeted delivery of a plasmid encoding metalloproteinase 9 into macrophages. The design involved creating a graphene-PAMAN-G5 structure through the cross-linking of GNS with 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide/N-Hydroxysuccinimide and utilizing generation 5 PAMAM dendrimer for gene therapy targeting. This strategic approach aimed at selectively targeting inflammatory macrophages that overexpress metalloproteinase 9 in cirrhotic livers, ultimately reducing hepatic fibrosis. Given the adverse effects associated with conventional anti-fibrotic and anti-inflammatory drugs, pMMP9-DGNS gene therapy emerges as an enticing option for enhancing hepatic function and promoting regression of the fibrosis process without causing additional harm. This approach introduces a fresh perspective to the treatment of inflammatory and fibrotic diseases [150].

Graphene-cored dendrimers emerge as a promising solution for detection and bio-sensing, exemplified in a study by Fen and coworkers [151] addressing the crucial need for early detection of DENV. With DENV posing a significant global health threat without an available vaccine, the challenge lies in devising sensitive detection methods, especially during the early febrile phase. While SPR sensors have been applied for DENV detection, their effectiveness has been deemed inadequate. In response, the research team introduced an innovative SPR sensor based on an amine-functionalized rGO-PAMAM composite. Monoclonal antibodies were immobilized on a self-assembled DSU substrate to facilitate DENV detection and quantification. The deliberate choice of rGO over graphene was driven by its advantages, including enhanced stability in organic solvents, prolonged storage without agglomeration, and superior electrical properties. The outcome was the successful detection of DENV at an exceptionally low concentration of 0.08 pM within a rapid 8-min timeframe. This achievement was realized through the utilization of an Au/DSU/amine-functionalized rGO–PAMAM/IgM thin film-based SPR optical sensor, underscoring its potential as a highly efficient and sensitive tool for DENV detection.

Jayakumara et al. [76] conducted a study introducing a nano-biosensor characterized by exceptional selectivity and sensitivity, tailored for the rapid voltammetric analysis of ultra-trace DNA hybridization. The biosensor was created by synthesizing a first-generation PAMAM dendrimer with an rGO core, employing a layer-by-layer assembly, and covalently functionalizing it with a self-assembled nanolayer of mercaptopropinoic acid onto the surface of GNPs. This meticulously engineered biosensor demonstrated rapid and highly sensitive capabilities in detecting DNA hybridization. Its potential applications extend to being a cutting-edge biodevice in genetic studies and a diagnostic method for genetic disorders, underlining its significance in advancing genetic research and facilitating accurate diagnoses.

DGO was employed as a probe to immobilize trypsin, utilizing glutaraldehyde as a coupling agent. The process involved covalently

binding trypsin to the DGO nanosheets, establishing a new amide bond with the assistance of 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide and N-Hydroxysuccinimide. Amino-terminated dendrimer was strategically assembled on the GO surface, and the amino group of DGO reacted with glutaraldehyde, which acted as a cross-linker. Finally, the amino group of trypsin bonded with the aldehyde group of the glutaraldehyde-modified dGO. This trypsin-linked DGO demonstrated efficiency in rapidly digesting proteins on plates, possessing notable features like high dispersibility, exceptional biocompatibility, a substantial enzyme loading capacity, and efficient proteolysis [152].

4.3.2. Carbon nanotubes

CNTs stand out among carbon allotropes as an intermediary structure between flat graphene and fullerene cages. Discovered in 1991 by Iijima [153], they come in SWCNTs or MWCNTs forms based on the arrangement of rolling graphene layers. CNTs exhibit distinctive features like excellent electrical and thermal conductivity, high tensile strength, elasticity, and photoluminescence, positioning them as promising nanomaterials for biomedical applications [154]. Over the past decade, CNTs have gained traction in the medical and pharmaceutical sectors due to their extensive surface area, enabling absorption and attachment to various agents such as genes, drugs, biosensors, and antibodies [155,156]. Furthermore, enhancing CNTs with dendrimers improves their biocompatibility, solubility, and chemical agent binding [157].

Research findings indicate a link between increased α2,3-sialylated glycan concentrations in the blood and specific tumors, suggesting their potential as early cancer diagnostic targets. Niu and team devised a CNT-based biosensor for α2,3-sialylated glycans, utilizing Maackia amurensis lectin for recognition. Enhancements to the biosensor included the modification of a glassy electrode by integrating PAMAM dendrimers with amino groups on the surface to carboxyl-functionalized multiwalled carbon nanotubes, improving water dispersion. Crosslinking PAMAM dendrimers to Maackia amurensis lectin with PDITC reduced toxicity, accelerated reactions, and enhanced structural stability. The addition of chitosan, valued for its film-forming ability and adhesion, contributed to improved biosensor sensitivity and electron transfer rates, facilitating the effective detection of α2,3-sialylated glycans in samples [158].

Dysregulation of miRNA is implicated in numerous genetic disorders, with increased miRNA expression identified in various cancers, positioning it as a potential biomarker for cancer diagnosis and treatment. Fengye Li and coworkers crafted an ultrasensitive electrochemical biosensor for miRNA detection. They functionalized a GCE with MWCNT-PAMAM dendrimer and immobilized a synthetic oligonucleotide capture probe containing 5′-carboxyl group terminated DNA. Utilizing the phenothiazine dye Methylene Blue as an indicator, the results showcased improved immobilization of the captured DNA, heightened sensitivity of Methylene Blue, reduced detection limit, and increased specificity, culminating in enhanced performance of the miRNA biosensor [159].

CNT-based dendrimers play a crucial role in targeted drug delivery, exemplified by Wen et al.'s development of a pH-responsive nano-system for cancer therapy involving dendrimers and CNT. They employed amine-terminated 5.0 generation PAMAM dendrimers modified with FI and FA. Covalent bonding of the nanomaterial (G5. NH_2-FI-FA) onto acid-treated MWCNTs followed, with acetylation of the remaining amine terminals to neutralize the surface's positive charge. Loading DOX onto the final structure (MWCNT/G5. NHAc–FI–FA) as the anti-cancer drug occurred through π - π stacking interactions with MWCNTs. This drug delivery system effectively targeted cancer cells overexpressing high-affinity FAR, demonstrating therapeutic efficacy with increased release in acidic pH conditions, leading to the inhibition of tumor cell growth [160].

CNTs play a role in cancer photodynamic therapy, as evidenced by Huang et al. They functionalized MWCNTs with 5.0 generation dendrimers and incorporated 5-ALA as the photosensitizer. The successful entrance of 5-ALA into tumor cells was indicated by the fluorescence of protoporphyrin IX in the cytoplasm. The final structure (5-ALA-DMNTs) demonstrated excellent biocompatibility, improved cell uptake, and targeted cell accumulation, evidenced by increased protoporphyrin IX fluorescence intensity and a significant enhancement in tumor cell eradication [161].

Qin and collaborators developed a dendrimer-based gene delivery system for transferring the GFP gene into cultured HeLa cells. The COOH-functional groups on the MWCNT surface were covalently functionalized with PAMAN dendrimers, enhancing stability and water dispersion. The electrostatic interaction between the negative charge of the DNA plasmid and the positive charge of the MWCNT-PAMAM hybrid facilitated pEGFP-N1 immobilization on the hybrid's surface. Compared to MWCNT-COOH alone, the MWCNT-PAMAM hybrid demonstrated superior immobilization, resulting in increased gene transfer performance and reduced cellular toxicity, making it a potentially efficient non-viral gene delivery system [157].

In a study conducted by Kavyani et al., the exploration of carbon nanotube-dendrimer (CNT-dendrimer) complexes in molecular delivery systems involved examining various pH levels and temperatures. Two types of dendrimers, PAMAM and Poly[PPI], were studied, with end branches modified by different chemical groups (COOH, COO^-, NH_2, NH_3^+, and OH). The presence of polar or charged chemical groups at the dendrimer's terminal branches allowed for the manipulation of cavity size. Adjusting pH at different temperatures enabled the development of CNT-dendrimer delivery systems with tailored cavities capable of encapsulating molecules of different sizes. The findings underscored the stability of the dendrimers' molecular structure and their potential for customization in drug delivery applications [162].

In a study by Saleh Mohammadnia et al., the focus was on designing a novel electrochemical sensor for Imatinib mesylate, a medication used in treating gastrointestinal stromal tumors and chronic myelogenous leukemia. Researchers successfully synthesized a hybrid nanocomposite named N,S-doped CDs/carbon nanotube-PAMAM dendrimer (N,S-CDs/DCNT) as a significant modifier. The N, S-CDs/DCNT/GCE exhibited a higher oxidation peak current for imatinib mesylate compared to GCE and DCNT/GCE. The concentration of imatinib mesylate showed a linear relationship with the oxidation peak current in the range of 0.01–100 μM, with a detection limit of 3 nM. Successful quantification of imatinib mesylate in blood-serum samples demonstrated excellent reproducibility and stability of the N,S-CDs/DCNT/GCE throughout the study [163].

4.3.3. Fullerene

In 1985, Kroto, Curl, and Smalley [164] discovered fullerene, a unique hollow spherical carbon allotrope. Renowned for its distinctive physical and chemical properties, fullerene has become extensively utilized in diverse fields such as materials science, electronics, nanotechnology, and biomedicine. Notably, the combination of fullerene with dendrimers results in supramolecular nanocomposites, merging the characteristics of both entities, particularly the C60 fullerene with its distinctive ball-shaped structure [165–167]. The low water solubility of fullerene necessitates its conjugation with dendrimers, a critical aspect for biomedical applications [168,169].

Glycosidases are focal points in pharmacotherapy. Nierengarten et al. synthesized a robust glycosidase inhibitor, a large construct based on a fullero-dendrimer. Comprising iminosugar-terminated dendrons and a clickable]]]]fullerene hexa-adduct scaffold, the 108-valent nanoconstruct exhibited nanomolar range inhibition of the enzyme, showcasing enhanced binding compared to its 36-valent counterparts [170].

An ultra-fast growth technique facilitates the synthesis of a dendrimer based on fullerene. A derivative of tridecafullerene, initially a first-generation dendrimer featuring 132 peripheral ethyl ester groups, is created in a single dendritic growth step. In a stepwise process, twelve macromonomeric units of the fullerene hexa-adduct building block with azide functionality are produced through six synthetic steps. Subsequently, these units are attached to a central fullerene core using copper-catalyzed azide-alkyne cycloaddition conditions. This synthesis approach results in a monodisperse compound with significant fragmentation, showcasing the potential for rapid synthesis of large macromolecules by minimizing synthesis steps [171].

Kay et al. presented the synthesis of a fullerene-cored dendrimer spanning first, second, and third generations, surrounded by eight azobenzene groups functioning as potential photoswitches. The synthesis of the dendrimer follows Fre'chet's convergent method, where azobenzene derivatives [Gn]-Br react with the monomer 3,5-dihydroxybenzyl alcohol in each step, leading to a new generation of dendrons with each repetition. Subsequently, the corresponding dendritic azides [Gn]-N3 react with C60 in chlorobenzene in the final step, resulting in the formation of dendritic fullerenes. The photoresponsive characteristics of these dendrimers are verified through various experimental approaches [172].

Giannopoulos explored the potential of utilizing water-soluble C60 as a drug delivery agent for the treatment of Coronavirus Disease 2019 (COVID-19). Molnupiravir, a compound known for its efficacy in saving lives during hospitalization, was chosen for transport. The proposed formulation involves connecting a carboxyfullerene, specifically dendro fullerene, with two Molnupiravir molecules using nitrogen single bonds as linkers. The study extensively investigated the energetics of the molecular system and its interactions with water and n-octanol using classical molecular dynamics. Solvation-free energies of the drug delivery system were calculated and compared with those of the water-soluble dendro fullerene to evaluate its solubility capabilities [173].

4.4. Silica

SiO_2 is primarily found in a crystalline state, with occasional occurrences in amorphous form, constituting a major component of sand. Its versatile applications encompass electronics (semiconductor), the food and drug industries, construction, and structural materials [174,175]. MSNPs represent a promising inorganic nanomaterial with unique physicochemical properties, such as a substantial surface area, considerable pore volume, high loading capacity, tunable pore size, and stability against thermal and chemical influences [176]. These attributes position MSNPs as attractive elements in the Nanobiomedicine field, finding use in drug delivery, sensing, and biomolecule immobilization. Despite their advantages, MSNPs face limitations like toxicity and solubility, which can be overcome by integrating dendritic structures to form DMSNPs [74,177–179].

A pH-responsive nanocarrier for drug delivery was created using MSNPs. These MSNPs were prepared using CTAB and TEOS as the silica source. A pH-responsive PAMAM dendrimer, functionalized with APTES, was grown on the surface of the MSNPs. The resulting MSNPs-PAMAM-G3 was conjugated with GA, a glucose derivative acting as the targeting agent. Deferasirox, an anti-tumor drug, was loaded onto the MSNPs-PAMAM-GA. When introduced to the retinoblastoma cell line Y79, the nanocarrier demonstrated high drug-loading capacity and increased uptake by tumor cells, leading to enhanced cytotoxicity of the drug. This highlights the potential application of the nanocarrier in cancer treatment [180].

Fei et al. designed a nanocarrier for co-delivering an anticancer drug and gene to targeted tumor cells in a responsive manner. The nanocarrier involved large pore DMSNPs and β-CD-modified PAMAM G3 dendrimers (β-CD-PAMAN). The orifice rim of the DMSNPs was occupied by ROS-responsive nitrophenyl-benzyl-carbonate (NBC) groups, and disulfide-bonded azido ligands were introduced onto the inner pore channels through a heterogeneous modification method. PAMAM-CD dendrimers were then immobilized on the pores through a click reaction. Anticancer model drugs, including SN-38 and Bcl-2 siRNA, were loaded onto the structure through a self-assembly process. In the final step, the DMSNPs/dendrimer was enveloped by 4T1 cancer cell membrane (CCM), enhancing the nanocomposite's resistance against degeneration upon entering the body. The resulting anticancer drug co-delivery system displayed effective cell entrance and cargo release, proposing a novel approach for combined anti-tumor therapy [181].

With the increasing incidence of thrombotic diseases, new iterations of thrombolytic drugs have been introduced. Nattokinase (NK), an effective fibrinolytic drug known for its affordability, simple production, and minimal side effects, faces a critical drawback: rapid loss of biological activity after administration. In a recent study, Huang et al. explored a silica-dendrimer-based delivery system for NK. The synthesis process involved preparing carboxylated magnetic mesoporous silica NPs (M-MSNPs-COOH) as the dendrimer core. Conjugating this core with polyglutamic acid peptide dendrimer (M-MSNPs-G3) and grafting RGD onto M-MSNPs-G3 resulted in the final nanostructure, M-MSNPs-G3-RGD. Drug loading occurred through electrostatic interaction between NK and M-MSNPs-G3-RGD, enhancing stabilization and drug performance. The NP demonstrated an effective thrombolytic effect with low toxicity, suggesting a potential approach for the swift and straightforward diagnosis and treatment of thrombotic diseases [179].

González et al. proposed an inventive solution for antibiotic delivery and penetration through the bacterial cell wall in infectious diseases. The designed nanosystem, named "nanoantibiotics," comprises MSNPs covalently adorned with a third-generation polypropyleneimine dendrimer on the external surface (MSN-G3). Functionalizing MSNPs with the G3 dendrimer enhances drug permeability into the gram-negative bacterial cell wall, attributed to the positive surface charge and flexible dendrimer structure. Levofloxacin acts as the primary antibiotic drug, loaded into the inner pores of MSNPs. The sustained release of the antibiotic after internalization ensures a stable and effective drug dosage within targeted bacteria. The nanoantibiotic exhibits remarkable antibacterial activity, suggesting a potential novel approach for managing infectious diseases [182].

Omidi and colleagues developed a nanocomposite by combining mesoporous silica and PAMAM generation 5 using 3-glycidoxypropyltrimethoxysilane and assessed its antibacterial properties. Surface analysis revealed a substantial surface area of 1321 m^2/g and an average pore diameter of 2 nm. The composite demonstrated effective antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* at a concentration of 256 μg/mL, maintaining cell viability above 70 % after 72 h [183].

In the realm of psoriasis treatment, Yu et al. addressed challenges by utilizing Eri, a potent drug known for inhibiting cell proliferation and inducing apoptosis. To overcome Eri's limited water solubility and poor skin penetration, the researchers developed a novel carrier system, Eri-DMSNPs@FSP, based on dendritic mesoporous silica NPs responsive to UV radiation. This carrier significantly improved Eri's bioavailability and enabled sustained release. The UV-responsive erianin-loaded dendritic mesoporous silica NPs exhibited superior efficacy in inhibiting HaCat cells compared to other formulations, demonstrating their potential for targeted drug release in response to UV radiation, offering promise for psoriasis treatment [184].

In a different context, MSNPs-PAMAM dendrimer hybrid NPs were employed as a nano-drug delivery system for neuroblastoma treatment. This system provided enhanced control over drug loading and release. Hydrolysis of tetraethyl orthosilicate TEOS by hydrochloric acid resulted in the hybrid, combining hydrolyzed silica and PAMAN dendrimer. Encapsulation of black carrot anthocyanins, selectively active against neuroblastoma cells, was achieved in these hybrid NPs. Investigation of drug release kinetics and the anti-tumor effect demonstrated the direct inhibitory effect of anthocyanins. Importantly, the Silica-PAMAN hybrid showed no significant toxic effects, underscoring its potential as a targeted and controlled drug delivery system for neuroblastoma treatment [185].

Lin et al. engineered a responsive co-delivery system for cancer treatment, combining gene therapy and chemotherapy. They employed MSNPs modified with second-generation PAMAM dendrimer (G2), chitosan-grafted onto MSNPs via a disulfide linker (MSNPs–SS–COOH). The NP's inner surface housed DOX and p53 plasmid, utilizing the carrier's positive charge for effective cell entry. The developed structure exhibited outstanding biocompatibility, efficient gene transfection, and rapid intracellular drug release, leading to cancer cell apoptosis through the combined effects of gene therapy and chemotherapy [74].

Clinical molecular imaging is pivotal in cancer diagnostics and treatment planning. A multimodal imaging system was designed using hyper-branched PAMAM (G3) grafted onto synthetic amorphous silica NPs for imaging HER2-expressing cancer cells. The PAMAM-based functionalized silica NPs incorporated near-infrared fluorescence (indocyanine green), with Technetium-99 m and Anti-HER2 antibodies attached for labeling PAMAM-based functionalized silica NPs. This dual imaging probe effectively imaged HER2-overexpressing cells, demonstrating potential applications in biomedical research [186].

Chen et al. achieved targeted co-delivery of chemotherapeutic drugs using fluorescent MSNPs. Synthesized through a sol-gel process, these MSNPs featured thiol groups on both internal and external surfaces (MSNPs-S-S-NH_2). Subsequent reactions with fluorescein isothiocyanate (MSNPs -S-S-FITC) and attachment of 2nd generation PAMAM dendrimer (PAMAM-G2) facilitated hydrophobic and hydrophilic drug loading. HA conjugation onto dendrimers resulted in MSNPs-dendrimer-HA, a nanocomposite effectively targeting tumors, releasing loaded drugs, displaying a potent therapeutic effect, and making it a promising candidate for targeted cancer therapy [187].

4.5. Quantum dots

The surface modification of QDs brings about several advantages, enhancing their dispersity, water solubility, and lowering toxicity while increasing the surface area [188]. Dendrimers, when employed for quantum dot modification, not only improve these properties but also facilitate better penetration into cell membranes and cytoplasm. PAMAM dendrimers, specifically, exhibit the capability to create nanoscale holes in cell membranes, enhancing cellular uptake. Furthermore, dendrimer-based surface modification contributes to the improved clearance of QDs from the body, enhancing their biocompatibility. Another advantage lies in the incorporation of more functional groups [189,190].

Han et al. presented a fluorescent film designed for the swift and visual detection of TNP utilizing polyethyleneimine-capped QDs. The fabrication process involved a ligand exchange. The sensor relies on the fluorescence quenching phenomenon, triggered by the interaction between amino groups of PEIs, nitro groups, and phenol hydroxyl groups of TNP. Importantly, the quenching mechanism differs from FRET. Noteworthy is the specificity of the quenching efficacy towards hydroxyl groups rather than nitro groups [191].

Campos et al. harnessed the quenching phenomenon for detection, creating Silicon QDs coated with a hydroxyl-functionalized fifth-generation PAMAM dendrimer (PAMAM-OH). This single-step process involved hydrothermal treatment of APTES in an aqueous solution. The researchers attributed the heightened fluorescent signal to the abundant hydroxyl groups on the NP's surface. Similar to the prior study, the fluorescence intensity of their NP responds to variations in pH [192].

Kavosi et al. employed a parallel fluorescent quenching principle with a FRET process to detect the PSA antigen. Although dendrimer-modified GNPs were used instead of QDs, this study is being addressed here due to the analogous underlying mechanism. The researchers developed a combination of CdTe QDs with attached antibodies and aptamer-PAMAM-GNPs with attached antigens. In the presence of PSA, an immunocomplex forms, causing fluorescence reduction. PSA detection relied on monitoring this reduction after the fluorophore and quencher closed during the sandwiched immunocomplex formation between antibody-PSA-aptamer. The

multiple functional groups on dendrimers amplified sensitivity in PSA detection, and the expansive surface area of PAMAM dendrimers facilitated efficient immobilization of the PSA aptamer, enhancing sensitivity and dynamic range [193].

Conversely, linking the target molecule to dendrimer-modified QDs can amplify fluorescence intensity. In the work of Liu et al., CdTeSe QDs were functionalized with PAMAM dendrimers using the solvent evaporation method for the detection of Cry1Ab protein, both in vivo and in vitro. Their findings indicated that the presence of Cry1Ab protein resulted in heightened fluorescence intensity, aligning with the Langmuir binding isotherm equation. The boosted fluorescence intensity was associated with a potential hydrogen bond formation between Cry1Ab protein and COOH-terminated PAMAM-functionalized QDs, introducing a new radiative process that hampers nonradiative pathways [194]. Similarly, Xu et al. illustrated that 3.0G quaternary ammonium PAMAM dendrimer-modified QDs functioned as detectors for the pesticide *p*-fluorophenoxyacetic acid, exhibiting increased fluorescence intensity upon exposure. The fluorescence intensity enhancement was more pronounced in instances where the acidity of the pesticides was stronger [195].

It is worth noting that alterations in fluorescence emission intensity accompany the increasing generations of PAMAM dendrimers attached to QDs, yet no observable shift occurs in the emission wavelength. Moreover, the quantum yield of water-soluble QDs shows an increase parallel to the generation of ester-terminated PAMAM dendrimers [190].

Access to brain tissue for brain cancer diagnostics faces challenges due to the blood-brain barrier. QDs, owing to their ultra-small size, are potential candidates for brain diagnostics; however, their high toxicity remains an obstacle. Bai et al. addressed this concern by modifying CdTe/CdS core-shell QDs with PAMAM dendrimers. These modified QDs exhibited lower toxicity, good dispersibility, and water-solubility. The modification induced a blue shift in the absorption band with increasing dendrimer generation and a shift to a higher emission wavelength of 650 nm. Additionally, the excitonic peak of the core/shell CdTe/CdS QDs shifted to a shorter wavelength with increasing dendrimer generations, consistent with quantum size effects. This modification also extended the photoluminescence lifetime of QDs. Furthermore, the photoluminescence intensity of dendrimer-modified QDs decreased in acidic conditions due to the surface charge characteristics of dendrimer-modified QDs [196].

Dendrimers play a crucial role as stabilizers in achieving colloidally stable QDs in aqueous solutions. A comparison of size, charge, and optical properties between QDs functionalized with the 4th and 5th generations of PAMAM and amphiphilic polymer-covered QDs revealed a slight blue shift in the emission maximum for both modifications compared to hydrophobic core/multi-shell QDs in toluene. The PAMAM-coated QDs exhibited significantly higher quantum yields than the QD-PMAO–Jeffamine sample, displaying a Zeta potential exceeding 50 mV, indicating exceptional colloidal stability in aqueous dispersion. The abundant terminal amino groups of PAMAM dendrimers facilitate bioconjugation reactions [197].

Toxicity associated with drugs involves different dimensions, such as target toxicity, immune hypersensitivity, and off-target toxicity. Recent progress in drug delivery through nanotechnology has significantly contributed to mitigating toxicity, enhancing drug solubility, and optimizing targeted drug delivery. In a recent investigation, Edet et al. introduced an innovative drug delivery system for isoniazid employing heteroatom-functionalized QDs (QD-NBC and QD-NBS). Density functional theory calculations demonstrated the stability of these functionalized QDs, featuring an adequate energy gap suitable for drug delivery. The adsorption energy range of the drug on the QDs highlighted a substantial interaction between the drug and the quantum dot surface, indicating their suitability for isoniazid delivery [198].

In another study, Samanta et al. delved into the influence of attachment chemistry on the resulting FRET cascade in QDs functionalized with Y-shaped DNA tiles, forming a dendritic structure as originally proposed by previous reports [199]. Within this structure, a photonic energy cascade occurs from the quantum dot core to the periphery through multistep FRET. The dendrimers' high dye packing density effectively channels photonic energy to the redder spectrum region. This hybrid structure serves as a chemically-driven self-illuminating nanoantenna, capable of concentrating energy to an apex [200,201].

The diagnosis and treatment of TNBC present a formidable medical challenge due to the absence of specific receptors. TNBC cells are characterized by the Memo enzyme, a metal-binding enzyme linked to Cu(II) ion for oxidase activity, playing a vital role in breast cancer cell motility. To leverage this unique attribute, a gene delivery system based on carbon QDs (CQDs) was developed, capable of detecting Cu(II) ions in cells. Synthesized carbon QDs were coupled with first-, second-, and third-generation PAMAM dendrimers (CDP1, CDP2, CDP3) through a carbodiimide coupling reaction. Subsequent modification of CDP3 with the RGDS (Arg-Gly-Asp-Ser) peptide enabled the recognition of overexpressed integrin in TNBC. Assessment of the nanocarrier demonstrated that CDP3 exhibited enhanced gene complexation, superior protection against enzymatic digestion, and improved gene transfection with reduced toxicity, establishing it as a promising nanocarrier for TNBC gene therapy [202].

5. Conclusions and future prospects

Over the past two decades, dendrimer chemistry has undergone significant advancement, leading to the creation of intricately designed macromolecules with precise control over their size, structure, and surface properties. This targeted approach has paved the way for the development of multifunctional nanocarriers, holding tremendous promise in the realm of biomedicine. One particularly intriguing avenue involves harnessing INPs as cores for dendrimer growth or attachment. INPs encompass a diverse array of nanomaterials, including metal NPs, MSNPs, QDs, and CDs, each offering unique properties such as tunable optical characteristics, high surface area, and inherent biocompatibility, making them well-suited for various biomedical applications. However, INPs often lack essential functionalities necessary for optimal biological performance. This is where dendrimers step in, serving as versatile modifiers to enhance the properties of INPs. Through strategic attachment onto the INP surface, either via "grafting-from" or "grafting-to" approaches, researchers can incorporate these hybrid nanostructures with a multitude of advantageous properties. These include enhanced biocompatibility, facilitated by the dendrimer's ability to mask the surface chemistry of the INP core, thereby minimizing potential interactions with biological systems that may lead to adverse immune responses or cytotoxicity. Additionally, dendrimers

contribute to improved solubility of hydrophobic INPs by providing hydrophilic surface groups, facilitating their dispersion in physiological fluids and enhancing their biological performance. Furthermore, dendrimers play a crucial role in imparting tunable stability to these hybrid nanocarriers, acting as a protective layer for the INPs core to prevent aggregation and degradation in biological environments. Moreover, their intricate branching structure offers a high cargo loading capacity, enabling efficient encapsulation of therapeutic agents, imaging probes, or other biomolecules. The versatility of dendrimers extends to their functionalization potential, where the terminal groups on their periphery can be readily modified to incorporate targeting moieties, stimuli-responsive functionalities, or other bioactive molecules, thereby enabling the creation of highly targeted and stimuli-responsive drug delivery systems. Through careful selection of both the INP core and dendrimer type, researchers can engineer hybrid nanostructures with tailored properties precisely suited for specific biomedical applications. This integration of dendrimers with INPs represents a promising frontier in nanomedicine, offering unprecedented opportunities for the development of advanced therapeutics, diagnostics, and biomedical imaging agents with enhanced efficacy and specificity.

Recent studies indicate that INPs, particularly those based on metals, have the potential to overcome challenges associated with drug resistance in cancer therapy. Au and Ag have demonstrated positive interactions with biomolecules on and within cells. While dendrimers have been utilized as drug delivery systems, their full potential remains untapped. An intriguing application involves using dendrimers as modified polymers for INPs. This modification enhances NPs' stability and provides multiple binding sites for conjugating various ligands and therapeutic molecules like monoclonal antibodies, peptide chains, and plasmids. Additionally, dendrimers' hydrophilic nature allows the encapsulation of drug molecules and therapeutic biomolecules, leading to the development of novel drug delivery systems based on their unique physicochemical properties. Progress in dendrimer research has driven the creation of multifunctional, highly selective nanocarriers, responding to the demand for combination therapeutic approaches. Over the past ten years, dendrimer-based delivery systems have gained prominence, promising to significantly enhance the effectiveness of existing cancer treatments and extend their application to clinical settings. Dendrimers in biomedical applications have vast potential, with ongoing research anticipated to yield novel combination therapies and innovative drug and gene products. Furthermore, the use of dendrimers in conjunction with therapeutic agents such as monoclonal antibodies, peptide chains, and plasmids holds promise for overcoming current limitations in cancer treatments.

While dendrimers exhibit considerable promise as carriers for therapeutic applications, a comprehensive assessment of their safety and efficacy is imperative before progressing to in vivo trials. To overcome associated dendrimer toxicities, one viable approach involves surface modifications using biocompatible compounds, a strategy that mitigates their cationic nature. This consideration brings forth the intriguing prospect of employing dendrimers as modifiers of INPs, presenting a twofold advantage. Firstly, the surface modification of NPs holds the potential to mitigate the cationic charge of dendrimers, thereby addressing concerns related to dendrimer toxicity. This modification contributes to the overall safety profile of the nanocarrier system. Secondly, the presence of dendrimers on NP surfaces introduces a stabilizing effect on the resulting nanocomplex, fostering enhanced compatibility with therapeutic agents such as nucleic acids and drugs. This intricate interplay not only augments the therapeutic potential of these nanocomplexes in cancer treatment but also opens avenues for exploring synergistic effects between dendrimers and therapeutic payloads. However, the journey toward practical application of dendrimer-based NPs encounters challenges associated with scaling up production. Historically, various techniques have been employed, and a rationalized approach is crucial for overcoming production hurdles and ensuring the reproducibility and consistency needed for clinical translation. A deeper understanding of the exact mechanisms underlying these production challenges is pivotal for addressing concerns related to in vivo toxicity and optimizing the development of dendrimer-based nanocarrier systems for therapeutic interventions in cancer and beyond.

Overall, dendrimers and dendrimer-based INPs have emerged as transformative agents, paving the way for a wide range of potential applications in the biomedical field, with a specific focus on enhancing and advancing cancer treatment in the foreseeable future. Employing ingenious and sophisticated designs, the creation of multifunctional INPs becomes a tangible reality, showcasing versatility in addressing various aspects of cancer care, encompassing therapeutic interventions, diagnostics, and imaging techniques. The vast potential of dendrimers within the area of biomedical applications is profound, offering a broad range of possibilities. Further exploration through ongoing research is expected to unlock new horizons, potentially leading to the formulation of innovative combination therapies and the introduction of novel drug and gene products. The collaborative synergy between dendrimers and INPs holds the promise of reshaping cancer treatment landscape, providing not only advanced therapeutic approaches but also transformative breakthroughs in diagnostics and imaging technologies. As exploration in this field deepens, research is likely to uncover innovative approaches, ultimately shaping the future landscape of cancer care with effective solutions.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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