

REVIEW ARTICLE

Recent advances in integrating 3D printing with metal-based nanomaterials for cancer theranostics

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Abstract

Cancer remains one of the leading causes of mortality worldwide, and its early diagnosis and effective treatment have long posed a major challenge in the biomedical field. Conventional cancer diagnosis and treatment strategies are plagued by inherent limitations, which greatly restrict their capacity to meet the clinical demands of personalized and precision medicine. Metal-based nanomaterials offer advantages in cancer theranostics due to their unique quantum size effect, surface effect, and interfacial effect. Their theranostic applications include multimodal imaging, tumor-biomarker detection, photothermal therapy, chemodynamic therapy, and radiosensitization. Three-dimensional (3D) printing enables the precise fabrication of complex architectures tailored to the personalized anatomical characteristics of tumor lesions, thereby effectively overcoming the drawbacks of metal-based nanomaterials, such as uneven dispersion and inadequate tumor targeting. The integration of 3D printing technology with metal-based nanomaterials leverages their complementary strengths, facilitating the construction of an innovative theranostic system characterized by customizable structure, tunable function, and integrated diagnosis and treatment. This review systematically summarizes the classification and underlying theranostic mechanisms of metal-based nanomaterials, mainstream 3D printing techniques suitable for such nanomaterials, and corresponding composite design strategies. It also outlines the latest research progress of this integrated platform in the diagnosis and treatment of prevalent malignancies. Furthermore, the current challenges and future research prospects in this field are discussed. This work aims to provide a useful overview for further fundamental research and clinical translation of 3D printing combined with metal-based nanomaterials in oncological theranostics.

Keywords: 3D printing technology; Metal-based nanomaterials; Cancer; Theranostics***Corresponding author:**Lihua Gao
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1. Introduction

Cancer continues to be one of the primary causes of global mortality. Achieving precise diagnosis and efficient therapeutic intervention has long remained a research hotspot and core challenge in the biomedical community.^{1,2} According to the latest epidemiological statistics, the global incidence and mortality rates of cancer have stayed at a persistently high level in recent years, with both new cases and deaths exceeding 10 million annually.³ Traditional cancer diagnosis predominantly relies on imaging examinations such as

computed tomography (CT), magnetic resonance imaging (MRI), and ultrasound, and these diagnostic methods have inherent drawbacks. Conventional therapeutic regimens, including chemotherapy, radiotherapy, and surgical resection, can restrain tumor progression to a certain extent. Nevertheless, they suffer from inadequate targeting capability, severe systemic adverse reactions, a high risk of residual disease and postoperative tumor recurrence, and poor capacity for postoperative tissue reconstruction, making it difficult to simultaneously achieve precise theranostics and tissue repair. Specifically, routine imaging modalities may have limited sensitivity for some early lesions and do not directly measure many molecular biomarkers. In terms of treatment, conventional strategies lack accurate tumor targeting. While suppressing tumor growth, they may inevitably damage normal tissues and trigger a series of side effects.

With the rapid advancement of nanomedicine, metal-based nanomaterials have emerged as a research hotspot in cancer diagnosis and treatment owing to their distinctive physicochemical properties and biological functions. Metal-based nanomaterials range in size from 1 to 100 nm and possess quantum size effects and surface effects, as well as interfacial effects. It should be noted that certain metal–organic framework (MOF)-derived assemblies and MXene architectures may exhibit overall dimensions exceeding 100 nm, while their functional building blocks or lamellar thickness remain within the 1–100 nm nanoscale regime.³ By regulating their composition and structure, these nanomaterials can realize multiple functions such as multimodal imaging, tumor-targeted therapy, and synergistic therapy, thus effectively compensating for the deficiencies of conventional diagnostic and therapeutic strategies.^{4,5} Compared with traditional diagnostic and therapeutic agents, metal-based nanomaterials possess unique structural superiority and functional flexibility. Their surfaces are readily available for functional modification, which allows precise accumulation in tumor tissues and reduces damage to normal tissues. Furthermore, they can integrate diverse diagnostic and therapeutic functions within a single platform, thereby overcoming the separation of diagnosis and treatment in conventional protocols and helping address the limitations of traditional cancer management.⁶ For instance, noble metal-based nanomaterials rely on localized surface plasmon resonance (LSPR) effects to realize photothermal therapy (PTT) and high-sensitivity detection;⁷ magnetic metal-based nanomaterials integrate MRI with magnetic hyperthermia therapy (MHT) into one platform;⁸ and metal-based nanomaterials with a high atomic number (high-Z) can markedly enhance the radiosensitization effect.^{9,10} All of these offer innovative

technical routes for precise oncological theranostics. Different categories of metal-based nanomaterials play vital roles in tumor detection, imaging-guided therapy, and therapeutic efficacy enhancement by virtue of their unique physicochemical characteristics. They can specifically address the shortcomings of conventional regimens, comprising insufficient sensitivity, poor targeting ability, and limited therapeutic efficiency. Accordingly, they drive the evolution of cancer diagnosis and treatment toward precision and diversification.

As an innovative manufacturing approach, three-dimensional (3D) printing enables the precise fabrication of intricate structures through layer-by-layer material deposition.¹¹ It boasts prominent merits, including personalized customization, controllable structural design, and high fabrication efficiency, and has been widely applied in the biomedical field in recent years.¹² In contrast to conventional manufacturing methods, 3D printing can accurately reconstruct the anatomical morphology of tumors and adjacent normal tissues based on patient-derived CT/MRI imaging data. It is capable of manufacturing customized theranostic scaffolds, drug delivery vehicles, and tumor models, which perfectly accommodate the clinical requirements of personalized cancer management.^{13,14}

The combination of 3D printing technology and metal-based nanomaterials combines the complementary advantages of both approaches. On the one hand, metal-based nanomaterials endow 3D-printed constructs with diagnostic and therapeutic functions. On the other hand, 3D printing serves as a stable loading and delivery platform for metal-based nanomaterials. It effectively resolves their inherent drawbacks, such as uneven dispersion, inadequate tumor targeting, and rapid metabolic clearance *in vivo*, thereby successfully constructing an integrated composite system featuring structural design, functional regulation, and synchronous diagnosis and treatment.¹⁵ Such composite systems achieve an integration of customizable architectures with multifunctional theranostic capabilities. They not only take full advantage of the personalized fabrication capability of 3D printing but also leverage the excellent theranostic performance of metal-based nanomaterials to overcome the limitations of single technologies in cancer management. This strategy further improves the precision and efficacy of tumor diagnosis and therapy and has emerged as a vital research direction in the field of precise cancer theranostics.

In recent years, the integration of 3D printing with metal-based nanomaterials has achieved groundbreaking advances in cancer diagnosis and treatment. The involved nanomaterial categories cover noble metal-based

nanomaterials, magnetic metal-based nanomaterials, high-Z metal-based nanomaterials, transition metal-based nanomaterials, and two-dimensional metal-based nanomaterials (MXene), as well as MOFs and their derivatives. A variety of mainstream 3D printing techniques have been adopted, including fused deposition modeling (FDM), stereolithography (SLA) and digital light processing (DLP), semi-solid extrusion (SSE) and direct ink writing (DIW), and selective laser sintering (SLS) and selective laser melting (SLM). Tables 1 and 2 summarize the quantitative performance of the major nanomaterial classes and printing techniques, respectively. Diversified composite design strategies have also been established, such as physical blending, *in situ* synthesis, and surface modification. Such integrated platforms have exhibited promising application prospects in the diagnosis and treatment of prevalent cancers, including bone tumors, breast cancer, reproductive system tumors, and digestive system tumors. With the continuous advancement of relevant investigations, the design and performance of these composite systems have been progressively optimized. They display unique superiority in precise tumor imaging, targeted therapy, and therapeutic effect monitoring, laying a solid foundation for the clinical translation of cancer theranostics. This review systematically summarizes the recent advances in this field. It aims to integrate existing research findings, clarify the current opportunities and challenges, and provide valuable references for subsequent fundamental investigations and clinical translation. The flowchart illustrating the application of metal-based nanomaterials combined with 3D printing technology in cancer theranostics is presented in Figure 1. This narrative review was conducted through a structured, though not systematic, literature search to ensure representative coverage of the field. PubMed, Web of Science, and Scopus were searched for articles published between January 2015 and August 2026 (with seminal earlier works included where foundational), using combinations of the following keywords: “3D printing,” “additive manufacturing,” “three-dimensional printing,” “metal-based nanomaterials,” “metallic nanoparticles,” “gold nanoparticles,” “iron oxide nanoparticles,” “MXene,” “metalorganic framework,” combined with “cancer,” “tumor,” “theranostics,” “photothermal therapy,” “chemodynamic therapy,” “magnetic hyperthermia,” and “radiosensitization.” Reference lists of retrieved articles and relevant reviews were manually screened for additional eligible studies. Studies were included if they (i) reported 3D-printed constructs (scaffolds, implants, devices, or *in vitro* models) incorporating metal-based nanomaterials and (ii) addressed cancer diagnosis, imaging, therapy, or theranostics; studies were excluded if they addressed

nonmetallic nanomaterials, nononcological applications without theranostic relevance, or conference abstracts without peer-reviewed full text.

Table 1. Quantitative comparison of metal-based nanomaterial classes used in 3D-printed cancer theranostic platforms

Material class	Typical size range	Photothermal performance (η)	Extinction/absorption characteristics	Fenton-like / CDT activity	Magnetic heating performance (SAR)	Typical loading in 3D-printed matrices	Degradation timeframe	Primary theranostic mechanisms	References
Noble metal-based nanomaterials (Au, Ag, Pt)	10–100 nm (AuNRs $\approx 10 \times 40$ nm)	$\approx 22\%–53\%$ (Au nanorods, 808 nm); Au plasmonic blackbodies permit tunable steady-state temperature	Strong LSPR extinction tunable across visible–NIR-I/NIR-II; high molar extinction coefficients ($\sim 10^8–10^9$ M ⁻¹ cm ⁻¹)	Weak intrinsic; Pt NPs exhibit peroxidase-like activity enabling TME oxidative stress regulation	N/A (non-magnetic)	$\approx 0.1–5$ wt% in PCL/PLA or hydrogel matrices	Poorly biodegradable; retained for weeks–months <i>in vivo</i> ; ultimate clearance via liver/spleen	PTT, SERS/CT multimodal imaging, radiosensitization, catalytic ROS generation	16–19
Magnetic metal-based nanomaterials (Fe ₃ O ₄ , MnO ₂ , CoFe ₂ O ₄)	10–50 nm (SPION cores $\approx 10–30$ nm)	Low intrinsic PCE; mainly used for MHT rather than PTT	No plasmonic absorption; optical signal via surface functionalization	Fe ²⁺ -mediated Fenton reaction (Fe ₃ O ₄); TME-responsive Mn ²⁺ release for T1/T2 dual MRI	$\approx 100–300$ W g ⁻¹ Fe (e.g., 168–280 W g ⁻¹ reported for coated SPIONs; field- and size-dependent)	$\approx 1–20$ wt% (FDM filaments, GelMA hydrogels, bioceramics)	Months; metabolized via ferritin/iron-recycling pathways (liver, spleen)	T2-weighted / T1–T2 dual MRI, magnetic hyperthermia (MHT), ferroptosis induction, targeted drug delivery	8,20–25

(Cont'd...)

Table 1. (Continued)

Material class	Typical size range	Photothermal performance (η)	Extinction/absorption characteristics	Fenton-like / CDT activity	Magnetic heating performance (SAR)	Typical loading in 3D-printed matrices	Degradation timeframe	Primary theranostic mechanisms	References
High-Z metal-based nanomaterials (W, Pt, Au, Bi, Ir; $Z > 50$)	20–200 nm	Bi NPs: efficient NIR photothermal conversion (photothermal agents for osteosarcoma ablation); W-based: negligible	Very high X-ray attenuation coefficients $\rightarrow$ strong CT contrast; NIR absorption for Bi-based agents	Generally weak; mainly radiosensitization via ROS amplification under X-ray irradiation	N/A (except magnetic high-Z hybrids)	Mostly coatings or dispersions; wt% loading rarely reported (typically estimated $\approx$ 0.5–10 wt%)	Poorly biodegradable; prolonged tissue retention; potential liver/kidney burden	CT contrast enhancement, radiosensitization, PTT (Bi, Au), synergistic RT/PTT/CDT	26-31
Transition metal-based nanomaterials (Cu, Mn, Fe, Zn oxides/sulfides, e.g., CuFeSe ₂ , CuS, NbC)	10–100 nm	Narrow-bandgap semiconductors with strong NIR absorption; values are system-dependent (commonly reported $\approx$ 30%–90% for CuS/CuFeSe ₂ -class agents)	Broad NIR absorption; bandgap-tunable extinction	Strong: Cu ²⁺ /Fe ²⁺ -mediated Fenton-like reactions; intrinsic CDT activity	Fe ₃ O ₄ containing hybrids inherit SAR $\approx$ 100–300 W g ⁻¹ Fe; others N/A	$\approx$ 0.5–15 wt% in bioactive glass, PLA/PEG, β -TCP matrices	Ion-release-mediated partial degradation over weeks–months; depends on matrix	PTT, CDT, TME modulation, antibacterial action, osteogenic ion release (Cu ²⁺ , Mg ²⁺ , Ca ²⁺)	32-38
Two-dimensional metal-based nanomaterials (MXene, e.g., Ti ₃ C ₂ T _x)	1–5 nm thick flakes; lateral 0.1–5 μ m	Calorimetric η up to $\approx$ 58% (808 nm); internal light-to-heat conversion efficiency approaches $\sim$ 100%, among the highest of inorganic photothermal agents	Excellent broadband NIR absorption (LSPR of 2D electron gas); high extinction in NIR-I/NIR-II	Moderate enzyme-mimicking catalytic activity; mainly PTT/PAI rather than CDT	N/A	$\approx$ 0.5–10 wt% in PLA, GelMA, or bioceramic scaffolds	Susceptible to oxidation in aqueous/air media; structural degradation over days–weeks in physiological media	PTT, photoacoustic/CT/MRI multimodal imaging, drug loading via large surface area, ICD induction	36, 39-44
MOFs and derivatives (Cu-TCPP, Cu-HHTP, ZIF-, Fe-, Bi-MOFs)	50–500 nm nanocrystals	Node/linker-dependent; porphyrin- or Cu/Fe-node MOFs show NIR-responsive photothermal behavior (system-specific)	Tunable optical properties via metal nodes and organic linkers; pore-encapsulated imaging agents	Fe/Cu-node MOFs exhibit Fenton-like CDT activity; TME-responsive degradation	N/A unless combined with magnetic nodes	1–30 wt% (estimated; <i>in situ</i> growth often not quantified)	TME-responsive (acid, GSH) degradation over hours–days; ion release kinetics tunable by framework	Multimodal imaging (CT/MRI/PAI), stimuli-responsive drug release, PTT/CDT, high-capacity loading	45-49

Notes: Values are representative ranges compiled from the references cited; PCEs and SAR values are strongly size-, morphology-, field- and instrument-dependent. The $\sim$ 100% value for MXenes refers to the internal light-to-heat conversion efficiency rather than the calorimetric photothermal conversion efficiency η . Loadings marked “estimated” were not explicitly quantified (wt%) in the cited primary studies.

Abbreviations: AuNR: Gold nanorod; CDT: Chemodynamic therapy; CT: Computed tomography; FDM: Fused deposition modeling; GelMA: Gelatin methacryloyl; GSH: Glutathione; HHTP: 2,3,6,7,10,11-Hexahydroxytriphenylene; ICD: Immunogenic cell death; LSPR: Localized surface plasmon resonance; MHT: Magnetic hyperthermia therapy; MOF: Metal–organic framework; MRI: Magnetic resonance imaging; NIR: Near-infrared; NIR-I: First near-infrared window; NIR-II: Second near-infrared window; NP: Nanoparticle; PAI: Photoacoustic imaging; PCE: Photothermal conversion efficiency; PCL: Polycaprolactone; PEG: Polyethylene glycol; PLA: Polylactic acid; PTT: Photothermal therapy; ROS: Reactive oxygen species; RT: Radiotherapy; SAR: Specific absorption rate; SERS: Surface-enhanced Raman scattering; SPION: Superparamagnetic iron oxide nanoparticle; TCPP: Tetrakis(4-carboxyphenyl)porphyrin; TME: Tumor microenvironment; ZIF: Zeolitic imidazolate framework; β -TCP: Beta-tricalcium phosphate.

Table 2. Comparison of mainstream 3D printing techniques for metal-based nanocomposite cancer theranostics

Technique	ASTM category (ISO/ASTM 52900)	Typical resolution	Representative process-speed metric	Processing temperature/energy input	Compatible matrices	Compatible metal-based nanomaterials	Typical mechanical performance	Key advantages	Key limitations	References
FDM	Material extrusion	Layer height 50–300 µm; min. feature ≈ 0.4–0.8 mm (nozzle-limited)	≈ 20–150 mm/h (nozzle traverse speed)	Nozzle 180 °C–260 °C (PLA ≈ 190 °C–230 °C, PCL ≈ 80 °C–120 °C); bed 50 °C–60 °C; low energy input	Thermoplastic filaments: PLA, PCL, PLGA; composite filaments	Magnetic (Fe ₃ O ₄ , CoFe ₂ O ₄), transition-metal oxides/carbides, MXene, noble-metal hybrids (thermally stable NPs)	Moderate; anisotropic (layer-bonding dependent); suitable for load-bearing porous scaffolds	Lowest cost; simple operation; broad material compatibility; rapid prototyping; scalable	Relatively low accuracy and surface finish; weak interlayer bonding; high temperatures may inactivate heat-sensitive NPs	23,50–56
SLA & DLP	Vat photopolymerization	25–100 µm (SLA laser spot); DLP ≈ 10–50 µm in-plane	DLP ≈ 10–100 mm/h (whole-layer curing); SLA slower, point-scanning	UV/visible light (λ ≈ 365–405 nm); ambient temperature processing; photon energy input only	Photocurable resins (PEGDA, acrylates) and ceramic-filled resins	Noble metals (Ag ⁺ in-resin photoreduction), high-Z and transition-metal NPs, MOFs (light-sensitive ones require care)	Good detail fidelity; resin parts intrinsically brittle, limited toughness; post-curing required	Ultra-high resolution and surface finish; fast DLP throughput; excellent for bionic models and microfluidics	High equipment/resin cost; brittleness; residual monomer toxicity concerns; limited to photocurable matrices; light may degrade photosensitive NPs	57–61
SSE & DIW	Material extrusion	≈ 100–500 µm (nozzle diameter); 100–600 µm	≈ 5–50 mm/s extrusion speed	Room temperature to ≈ 37 °C (no thermal curing); pneumatic/mechanical extrusion pressure (≈ 0.1–1 MPa)	Shear-thinning bioinks: gelatin, sodium alginate, Pluronic F127, GelMA, pastes/slurries	Broadest compatibility: noble-metal, magnetic, transition-metal, MXene, MOF, and metal–phenolic NPs	Matrix-dependent (hydrogel: low modulus but cell-compatible; ceramic pastes: moderate)	Mild conditions preserve NP activity; high filler loading; multi-material and cell co-printing; low cost	Limited accuracy; moderate interlayer adhesion; dimensional shrinkage; requires ink rheology optimization	62–66
SLS & SLM	Powder bed fusion	Layer 20–150 µm; min. feature ≈ 0.1–0.5 mm	SLS ≈ 10–30 mm/h build rate; SLM scan speed up to ≈ 700–1,000 mm/s	High-energy laser: SLS polymer powder bed ≈ 120 °C–180 °C (partial sintering); SLM full melting of metal powders (>1,000 °C, inert atmosphere)	Polymer powders (PA, PLA, PCL) for SLS; metal powders (Ti6Al4V, stainless steel, W) for SLM	Thermally robust NPs: W (radiation shielding), Ti-alloy matrices for drug/NP surface anchoring; high-temperature-tolerant ceramics	Superior mechanical properties; SLM parts near-full density (up to ≈ 99.5%), fatigue-resistant metal implants	Support-free forming; complex geometries; high material utilization; SLM: metallurgical bonding for permanent implants	Very high equipment and maintenance cost; high energy consumption; rough as-built surface; limited to heat-stable materials/NPs	30,67–69

Notes: Quantitative ranges are representative values reported for biomedical-grade systems in the cited references; actual performance depends on equipment, material grade, and process parameters.

Abbreviations: ASTM: American Society for Testing and Materials; DIW: direct ink writing; DLP: digital light processing; FDM: Fused deposition modeling; GelMA: gelatin methacryloyl; ISO: International Organization for Standardization; MOF: metal–organic framework; NP: nanoparticle; PA: polyamide; PCL: polycaprolactone; PEGDA: polyethylene glycol diacrylate; PLA: Polylactic acid; PLGA: Poly(lactic-co-glycolic acid); SLA: stereolithography; SLM: selective laser melting; SLS: selective laser sintering; SSE: semi-solid extrusion; Ti6Al4V: Titanium alloy; UV: Ultraviolet.

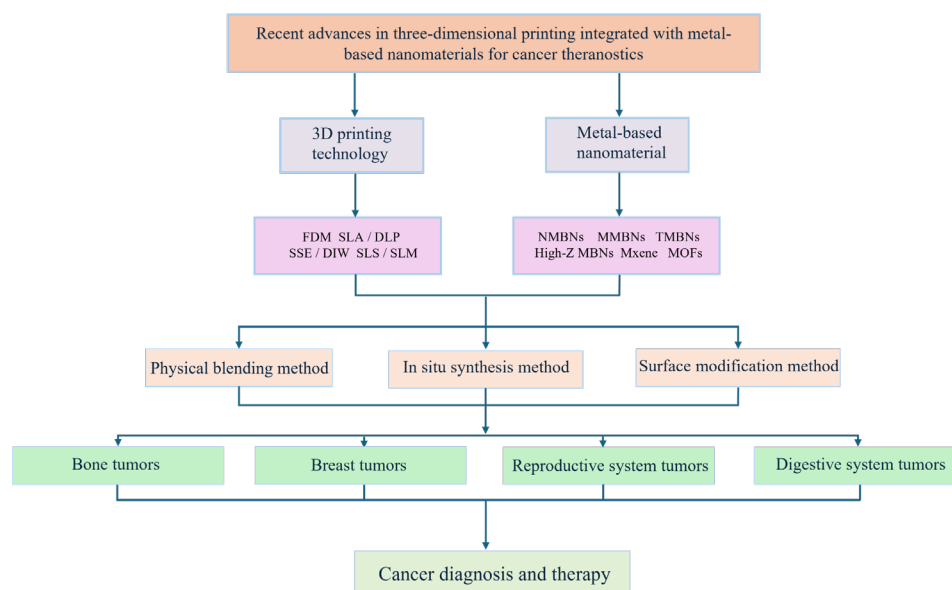


Figure 1. Schematic illustration of the combination of metal-based nanomaterials and 3D printing technology for cancer theranostics.

Abbreviations: DIW: Direct ink writing; DLP: Digital light processing; FDM: Fused deposition modeling; MMBNs: Magnetic metal-based nanomaterials; MOFs: Metal–organic frameworks; NMBNs: Noble metal-based nanomaterials; SLA: Stereolithography; SLM: Selective laser melting; SLS: Selective laser sintering; SSE: Semi-solid extrusion; TMBNs: Transition metal-based nanomaterials.

2. Main types and theranostic mechanisms of metal-based nanomaterials

Metal-based nanomaterials have become essential functional components in 3D printing-coupled integrated cancer detection and treatment systems because of their unique quantum-size, surface, and interface effects, which enable both therapeutic and diagnostic functions.^{70,71} Based on differences in constituent elements, structural features, and biomedical properties, they can be classified into six categories: noble metal-based nanomaterials, magnetic metal-based nanomaterials, high-Z metal-based nanomaterials, transition metal-based nanomaterials, MXenes, and MOFs and their derivatives. Each category has characteristic physicochemical properties that underpin distinct diagnostic and therapeutic mechanisms. [Figure 2](#) shows the pertinent uses of metal-based nanomaterials in cancer imaging and treatment.⁴

2.1. Noble metal-based nanomaterials

Noble metal-based nanomaterials, such as gold, silver, and platinum, have emerged as research hotspots in the field of precise cancer diagnosis and treatment owing to their distinctive physicochemical properties and favorable biocompatibility. Gold nanoparticles (AuNPs) possess LSPR characteristics, which can efficiently convert near-infrared (NIR) light into heat and thus support tumor PTT.¹⁶ Silver nanoparticles exert antitumor effects

via multiple pathways; they can realize photothermal conversion and reactive oxygen species (ROS) generation, directly induce tumor cell apoptosis, inhibit tumor angiogenesis, and block tumor proliferation and metastasis.⁷² Platinum nanoparticles exhibit peroxidase-like activity, which can regulate the oxidative stress state of the tumor microenvironment (TME) and boost the efficacy of chemodynamic therapy (CDT).⁷³ Such nanomaterials hold great application potential in diagnostic fields. They can serve as multimodal imaging probes for surface-enhanced Raman scattering (SERS), CT, and other imaging modalities, providing technical support for high-sensitivity early tumor detection and real-time dynamic monitoring.¹⁷ Given the drawbacks of traditional noble metal nanoformulations, including uneven delivery, single structure, and insufficient targeting efficiency, integration with 3D printing may help address some of these delivery and structural limitations. For instance, SLS enables the uniform dispersion of noble metal nanoparticles (e.g., gold and platinum) and their functionalized composites into biodegradable polymer powders such as polylactic acid (PLA) and polycaprolactone (PCL) so as to fabricate 3D porous scaffolds layer by layer.⁷⁴ SLS endows scaffolds with customizable macroscopic structures and precisely regulated pore structures, while noble metals endow the scaffolds with microscopic functions, including photothermal conversion, responsive drug release, and

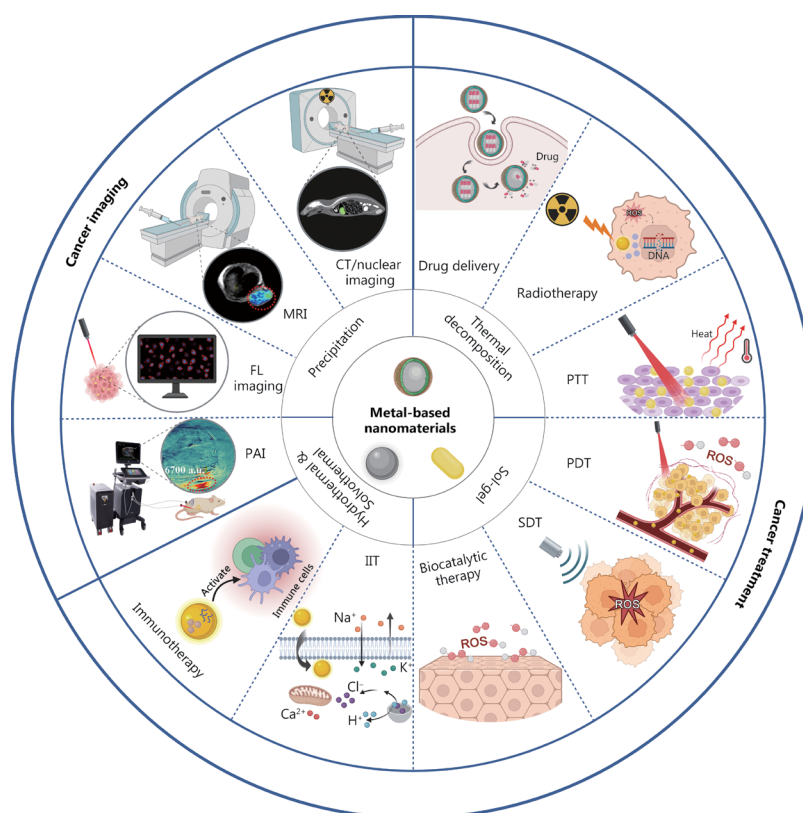


Figure 2. Applications of metalbased nanomaterials in cancer imaging and therapy. Figure reprinted from Ref.⁴

Abbreviations: CT: Computed tomography; DNA: Deoxyribonucleic acid; FL: Fluorescence; IIT: Ion interference therapy; MRI: Magnetic resonance imaging; PAI: Photoacoustic imaging; PDT: Photodynamic therapy; PTT: Photothermal therapy; ROS: Reactive oxygen species; SDT: Sonodynamic therapy.

catalytic ROS production. The synergistic effect of both strategies achieves combined local tumor treatment and bone-defect repair. In addition, DIW fabricates intricate 3D architectures by layer-by-layer deposition of noble metal nanoparticle-incorporated bioinks via precise extrusion.⁶² Its mild processing conditions avoid thermal damage to functional materials such as gold and silver, thereby preserving the surface activity and uniform dispersion of nanoparticles. Meanwhile, flexible regulation of extrusion pressure and nozzle printing paths facilitates gradient drug loading and compartmentalized embedding of cells and materials, which satisfies the personalized filling requirements of irregular wounds after tumor resection.

2.2. Magnetic metal-based nanomaterials

Benefiting from distinctive magnetic responsiveness, satisfactory biocompatibility, and tunable surface functionalization potential, magnetic metal-based nanomaterials serve as promising functional carriers for integrated cancer diagnosis and therapy. Their diagnostic and therapeutic mechanisms are mainly centered on two

core directions: diagnostic imaging and targeted therapy. In terms of diagnosis, these nanomaterials can serve as contrast agents for MRI. High-resolution visualization of tumor tissues can be attained by tuning their magnetic characteristics. Specifically, Fe_3O_4 nanoparticles are extensively utilized as T2-weighted contrast agents, whereas MnO_x -based nanomaterials are able to liberate Mn^{2+} upon TME stimulation to accomplish dual-modal T1/T2 imaging, hence elevating the sensitivity and precision of tumor diagnosis.^{20,21} From the therapeutic perspective, their predominant advantage lies in MHT. Under an alternating external magnetic field, magnetic nanoparticles convert electromagnetic energy into thermal energy via hysteresis loss to accomplish precise thermal ablation of tumor cells. Meanwhile, they can synergistically trigger tumor ferroptosis and regulate the TME to strengthen the response to immunotherapy.²² Furthermore, surface modification of magnetic metal-based nanomaterials enables targeted loading and stimuli-responsive release of chemotherapeutic drugs, which further elevates chemotherapeutic efficacy and reduces

systemic toxicity and side effects. Introducing 3D printing technologies provides essential technical assistance for the clinical translation of magnetic metal-based nanomaterials. A variety of high-precision 3D printing strategies are effectively utilized to address their inherent limitations, which include poor structural controllability, low delivery efficiency, and a tendency to aggregate. For example, FDM²³ uniformly disperses magnetic metal-based nanoparticles, including Fe_3O_4 and MnO_x , into thermoplastic filaments represented by PLA. This process also involves the fabrication of porous diagnostic and therapeutic scaffolds through layer-by-layer melt formation. Not only do these scaffolds incorporate magnetic hyperthermia, T2-weighted MRI imaging, and bone repair functions, but they also offer superior structural customizability and are cost-effective.

2.3. High-Z metal-based nanomaterials

High-Z metal-based nanomaterials are typically represented by tungsten, platinum, gold, iridium, and other elements with atomic numbers higher than 50. By virtue of their superior X-ray absorption capacity, distinctive electronic transition properties, and favorable biocompatibility, they have evolved into pivotal functional materials for precise cancer diagnosis and treatment.²⁶ Their theranostic mechanisms mainly revolve around radiosensitization, multimodal imaging, and synergistic therapeutic strategies. In diagnostic applications, high-Z metal-based elements possess high X-ray attenuation coefficients, which qualify them as ideal contrast agents for CT and remarkably boost the imaging contrast between tumor lesions and normal tissues.²⁷ In therapeutic practice, a major therapeutic advantage is their radiosensitizing capability. Such materials can amplify X-ray energy deposition and promote ROS generation, in turn aggravating radiation-induced damage to tumor DNA, and meanwhile cooperate with PTT and CDT to achieve combined treatment effects.²⁸ Moreover, rational surface functionalization confers targeted immobilization and stimuli-responsive release of chemotherapeutic agents and immune modulators, which further optimize the synergistic theranostic efficacy.²⁹ Within the whole spectrum of 3D printing techniques, SLM stands out as a predominant approach to construct high-Z tungsten-based radiation shielding devices by virtue of its high forming precision and outstanding densification performance. Adopting high-purity tungsten powder as raw material, this technology realizes layer-by-layer sintering and melting via high-energy laser beams, allowing for the accurate fabrication of tungsten-based components with homogeneous microstructure and low porosity. Tungsten constructs fabricated via SLM exhibit prominent γ -ray attenuation behaviors, laying a solid experimental foundation for the customized fabrication

of collimators used in nuclear medicine imaging and shielding components for radiotherapy.³⁰

2.4. Transition metal-based nanomaterials

Transition metal-based nanomaterials are mainly composed of copper, manganese, iron, zinc, and their corresponding oxides as well as sulfides. Because of their tunable electronic configurations, composition-dependent degradation behavior, and catalytic activity, they have emerged as superior candidates for integrated, precise cancer diagnosis and therapy. Their theranostic strategies center on TME responsiveness, which contributes to multimodal diagnosis and combinatorial treatment. In diagnostic modalities, iron-based nanomaterials are capable of modulating oxidative stress in tumor sites through Fenton reactions and can also serve as T2-weighted MRI contrast agents to attain tumor localization and therapeutic effect monitoring.³² Manganese-based nanomaterials are able to liberate Mn^{2+} under acidic TME, integrating imaging capability with immune pathway activation functions.³³ From the therapeutic perspective, these substances can mediate PTT and CDT and synergize with radiotherapy, chemotherapy, and immunotherapy. Such combinatorial modes can heighten antitumor efficacy while mitigating systemic adverse reactions.³⁴ 3D printing technologies are highly compatible with transition metal-based nanomaterials. Among diverse printing strategies, DIW stands out as the most prevalent and optimal technique for constructing personalized cancer theranostic platforms loaded with such nanomaterials. Its merits involve mild processing conditions, favorable biocompatibility, strong loading capacity for nanoparticles, and the capability to fabricate intricate porous scaffolds.⁶²

2.5. MXenes

MXenes represent an emerging category of two-dimensional layered materials fabricated via selective etching of MAX phase precursors. Benefiting from their ultrathin laminated architecture, large specific surface area, exceptional photothermal conversion efficiency, and desirable biocompatibility, they have evolved into one of the core candidates for integrated cancer theranostic research.³⁹ In diagnostic fields, MXenes can function as contrast agents for photoacoustic imaging, CT, and MRI, facilitating multimodal tumor diagnosis.⁴⁰ From a therapeutic perspective, they display the capacity to mediate PTT and CDT, as well as trigger immunogenic cell death of tumor tissues. Such effects can reinforce the outcomes of radiotherapy and chemotherapy while alleviating systemic adverse effects.⁴¹ As typical two-dimensional metal-based nanosystems, MXenes possess prominent photothermal conversion capability, enzyme-

mimicking catalytic performance, and favorable biosafety, which render them indispensable functional components for 3D-printed multifunctional tumor theranostic platforms. Given the inherent drawbacks of MXenes, including facile interlayer restacking and rapid *in vivo* clearance during delivery, rational integration with precise 3D printing strategies offers a viable route to optimize their biological performance. Among various additive manufacturing approaches, DIW has gained the most widespread application in MXene-based composites for oncological theranostics. This technique features facile operational procedures, broad material compatibility, and the capacity to construct 3D scaffolds with high porosity.⁴²

2.6. Metal–organic frameworks and their derivatives

Metal–organic frameworks are porous crystalline substances self-assembled via coordination interactions between metal ions/clusters and organic ligands. Their derivatives mainly cover MOF-derived carbon species, metal oxides, and metal nanoparticle-based composites.⁴⁵ Boasting an ultrahigh specific surface area, tunable pore architecture, favorable biocompatibility, and versatile functional designability, MOFs have emerged as distinctive candidates for precise cancer theranostics. In diagnostic research, MOFs and their derivatives can immobilize imaging agents within their porous frameworks with large surface areas to realize integrated CT, MRI, and photoacoustic multimodal imaging. Certain derivatives are also capable of elevating imaging contrast, relying on their inherent physicochemical traits.⁴⁶ In therapeutic practice, their internal channels are available for efficient drug encapsulation, which enables controlled drug release in response to TME stimuli. Meanwhile, such materials can modulate PTT and CDT to strengthen therapeutic efficacy and mitigate systemic side effects.⁴⁷ In the integrated application of 3D printing with MOFs and their derivatives, DIW is among the most commonly used techniques in integrated oncological theranostics by virtue of its mild fabrication conditions, high MOF loading efficiency, and superior biocompatibility. Utilizing the shear-thinning property of bioinks, DIW technology affords homogeneous dispersion of MOF nanocrystals and corresponding derivatives within biocompatible hydrogels or polymer matrices. Precise extrusion shaping can be accomplished at ambient temperature, which effectively averts structural collapse and functional inactivation of MOFs triggered by high temperature or intense light irradiation.

Taken together, the nanomaterials described above converge on a shared set of molecular events, which explains why their combinations often outperform single-component systems. PTT disrupts membrane and

mitochondrial integrity and triggers apoptosis, while sub-ablative temperatures increase vascular permeability and permit tumor cells to enter immunogenic death pathways.²² CDT complements this effect by converting endogenous hydrogen peroxide into hydroxyl radicals, a process that is accelerated by the acidic TME and can propagate into ferroptotic cell death.³² The lethal stress imposed by heat and ROS in turn induces immunogenic cell death, in which dying tumor cells release damage-associated molecular patterns that promote dendritic cell uptake and antigen presentation. Metal ions released from degradable nanomaterials further enhance this response by activating innate immune pathways and repolarizing macrophages from the M2 toward the M1 phenotype.⁷⁵ These modules mutually reinforce one another: heat accelerates Fenton-like reactions, while oxidative stress increases the immunogenicity of photothermally killed cells. Because heat, radicals, and ionic cues act over short distances and defined time windows, 3D printing is particularly well suited to exploit this synergy, since a printed scaffold anchors nanoparticles at the tumor interface and programs their release to match the underlying biology.

3. Key 3D printing technologies suitable for metal-based nanomaterials

Currently, 3D printing technologies have gained extensive popularity in the field of cancer diagnosis and therapy. Figure 3 illustrates their versatile applications in cancer diagnosis and treatment.⁷⁶ Nevertheless, the design and fabrication of 3D-printed platforms dedicated to tumor theranostics need to satisfy multiple core criteria simultaneously. Such systems ought to maximally preserve the intrinsic functional activity of metal-based nanomaterials and realize precise regulation of macroscopic architectures and microscopic morphologies while guaranteeing satisfactory overall biocompatibility to accommodate *in vivo* application demands.^{77,78} Beyond the above prerequisites, it is essential to take personalized characteristics into consideration, including anatomical configurations of diverse tumor sites, diverse therapeutic regimens, and postoperative tissue reconstruction requirements. At present, several mainstream 3D printing strategies with promising clinical translational potential are widely adopted for constructing metal-based nanocomposite systems, mainly including FDM, SLA/DLP, SSE/DIW, and SLS/SLM. Distinct printing approaches differ remarkably in working mechanisms, forming characteristics, and applicable raw materials, and exhibit varied compatibility with diverse metal-based nanomaterials. These discrepancies further endow them with differentiated application prospects and predominant merits in cancer theranostic practice. It deserves emphasis that the four process families discussed here were

not chosen at random. They follow the International Organization for Standardization/American Society for Testing and Materials (ISO/ASTM) 52900 taxonomy of additive manufacturing, which recognizes seven categories in all: binder jetting, directed energy deposition, material jetting, material extrusion, powder bed fusion, sheet lamination, and vat photopolymerization. The other four are mature technologies in general manufacturing, yet their fit with metal-based nanomaterials in cancer theranostics is inherently poor, so they receive no detailed treatment here. The four selected families instead span three of the seven categories, namely material extrusion (FDM and SSE/DIW), vat photopolymerization (SLA/DLP), and powder bed fusion (SLS/SLM). It is no coincidence that the overwhelming majority of reported 3D-printed metal-based nanocomposite theranostic platforms have been realized within these three. They tolerate high nanoparticle loadings, impose a controllable thermal or photonic budget, and accept biocompatible matrices, a combination the excluded processes cannot offer.

3.1. Fused deposition modeling

Fused deposition modeling, the most prevalent extrusion-based 3D printing technique, stands as an essential technical medium for fabricating nanocomposite theranostic systems. It boasts low equipment cost, straightforward operational procedures, scalable manufacturing capacity, and broad material compatibility, thus revealing promising prospects in precise cancer diagnosis and localized tumor intervention.^{50,51} Its core working mechanism is described as follows: thermoplastic polymer filaments embedded with

metal-based nanomaterials are fed into high-temperature nozzles. After thermal melting, the molten raw materials are extruded and deposited layer by layer, followed by cooling and solidification. This approach promotes the precise fabrication of tumor theranostic scaffolds and devices with tunable porosity, dimensions, and morphologies, which effectively cater to the heterogeneous characteristics of tumor tissues.⁵² Compared with certain high-precision 3D printing protocols, FDM retains superior structural tunability. Rational optimization of printing parameters allows accurate regulation of pore size, porosity, microscale morphology, and overall dimensions of scaffolds, consequently constructing hierarchical porous biomimetic architectures that closely adapt to the intricate physiological microenvironment and pathological heterogeneity of tumor tissues.⁵³ This technique also features extensive material adaptability. A variety of biocompatible thermoplastic polymers, including PLA and PCL, can serve as foundational matrices, satisfying biosafety standards and mechanical property requirements amid diverse oncological theranostic scenarios.⁵⁴ Furthermore, FDM possesses well-established and controllable processing conditions and low modification barriers, along with outstanding processing stability. It synchronously fulfills customized structural design and large-scale production demands, which to some extent broadens the research scope and clinical translation potential of medical 3D devices.⁵⁵ Owing to its favorable matrix modification potential and excellent processing compatibility, FDM is capable of efficiently integrating functional metal-based nanocomponents, hence offering solid technical

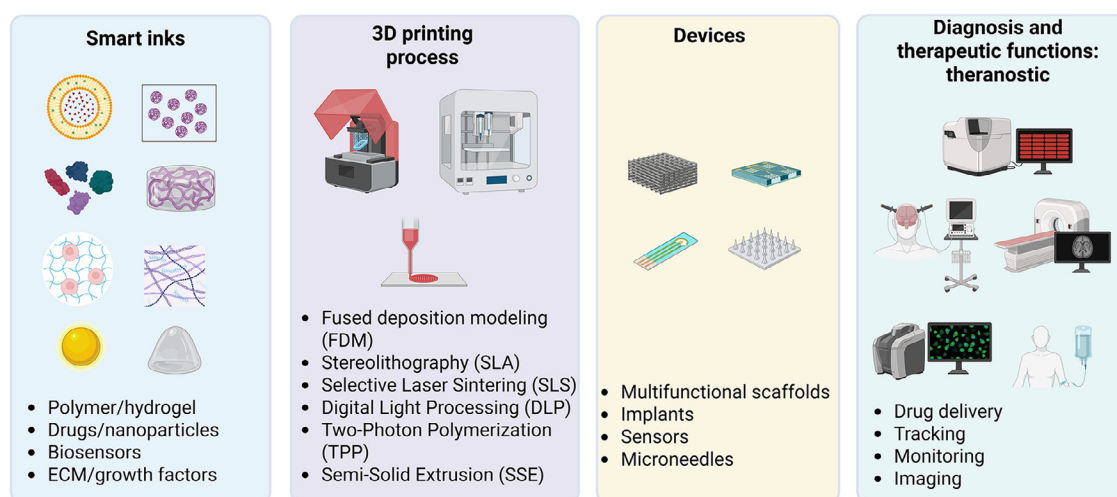


Figure 3. Applications of 3D printing technology in cancer diagnosis and treatment. Reprinted with permission from Calori *et al.*⁷⁶ Copyright © 2025 Elsevier B.V.

Abbreviation: ECM: Extracellular matrix.

backing for the construction of multifunctional integrated platforms for tumor diagnosis and treatment.⁵⁶

3.2. Stereolithography and digital light processing

As mainstream photopolymerization-based 3D printing approaches, SLA and DLP operate on the principle of layer-wise polymerization of photosensitive resins triggered by ultraviolet irradiation, and they achieve resolutions typically in the range of 25–100 μm . It should be emphasized that submicron-scale resolution (down to ~ 100 nm) is attainable only through two-photon polymerization (TPP), a distinct technique based on nonlinear two-photon absorption that is fundamentally different from the single-photon SLA/DLP processes discussed here; TPP is particularly suited for fabricating microscale scaffold architectures and microneedle arrays but is not classified within the SLA/DLP family.⁵⁷ SLA realizes precise fabrication of intricate microarchitectures through point-by-point laser scanning and solidification, while DLP achieves simultaneous curing of entire layers with the aid of digital micromirror device projection, which markedly elevates printing efficiency. Both techniques are competent in manufacturing bionic scaffolds, microfluidic chips, and tissue-engineered constructs.⁵⁸ In recent years, numerous investigations have incorporated metal-based nanoparticles into photocurable resins or surface coatings and adopted surface functionalization strategies to improve particle dispersion. Such strategies permit the fabrication of multifunctional composite scaffolds via 3D printing, which endows the resultant materials with diverse performances such as photothermal conversion, MHT,⁵⁹ CDT,⁶⁰ and multimodal imaging capability. These novel platforms exhibit promising application prospects in multiple research directions, including postoperative osteosarcoma reconstruction combined with photothermal-chemotherapy, as well as localized synergistic magnetothermal and chemodynamic therapeutic regimens.

3.3. Semi-solid extrusion and direct ink writing

Semi-solid extrusion and DIW are categorized as extrusion-based 3D printing techniques, which belong to additive manufacturing approaches relying on room- or low-temperature extrusion. Their fundamental mechanism involves extruding semi-solid inks (gels, slurries, or pastes) with shear-thinning behavior, viscoelasticity, and yield stress through microscale nozzles under pneumatic pressure or mechanical force. These inks are deposited layer by layer along predefined paths to form self-supporting 3D architectures.⁶³ Distinct from FDM, SSE and DIW eliminate high-temperature heating requirements, thereby preventing the degradation of heat-sensitive components.

Additionally, they feature low-cost equipment, superior process flexibility, and broad material compatibility.⁶⁴ Their ink systems are generally formulated by compounding polymeric matrices (e.g., gelatin, sodium alginate, and Pluronic), solvents, and functional fillers, wherein precise modulation of rheological properties is required to balance extrudability and shape fidelity.⁶⁵ These techniques are capable of fabricating porous scaffolds with high porosity and tunable interconnectivity, which are perfectly suited for biomedical applications, including bone tumor reconstruction. Meanwhile, they permit multimaterial integration and monolithic manufacturing of heterogeneous architectures, facilitating the construction of multifunctional tumor therapeutic platforms.⁶⁶ On account of their low-temperature processing, high filler-loading capacity, and controllable interfacial bonding, SSE and DIW exhibit remarkable processing compatibility with metal-based nanoparticles such as metalpolyphenol nanoparticles.⁶² This lays a solid technical foundation for the functional design and theranostic implementation of subsequent composite scaffolds.

3.4. Selective laser sintering and selective laser melting

Selective laser sintering and SLM are both powder-bed fusion 3D printing technologies. Relying on localized thermal effects induced by high-energy laser beams, they fabricate 3D architectures through layer-by-layer sintering or melting of powdered feedstocks.⁶⁷ Notably, SLS adopts solid-state or liquid-phase sintering mechanisms without complete melting of the matrix, operating at relatively lower processing temperatures. It is compatible with diverse materials encompassing polymers and composite powders and offers advantages including support-free fabrication, broad material availability, and high manufacturing efficiency. In contrast, SLM enables complete melting of metal-based powder feedstocks via high-power lasers under an inert atmosphere to achieve metallurgical bonding. The resultant components possess high densification and superior mechanical properties, which render this technique suitable for the customized fabrication of high-strength metal-based scaffolds.^{68,79} Both strategies show exceptional capability in high-precision structural replication, allowing delicate regulation of scaffold porosity, pore size distribution, and interconnectivity to satisfy dual requirements of topological configuration and mechanical performance for tumor-tissue-engineered scaffolds. By virtue of the tunable energy input of laser processing and the capacity of powder feedstocks for nanoparticle incorporation, SLS and SLM are highly compatible with metal-based nanoparticles, in turn offering feasible technical avenues for constructing

composite scaffolds integrating structural support with tumor theranostic functions.⁶⁹

4. Composite design strategies of 3D printing and metal-based nanomaterials

The core of composite design integrating 3D printing with metalbased nanomaterials lies in achieving homogeneous dispersion of nanomaterials within the matrix and efficient retention of their functional activity, alongside synergistic matching between macroscopic architectures and theranostic performance.^{48,80} Such design strategies need to conform to the inherent characteristics of 3D printing processes and satisfy pivotal criteria for oncological theranostics, encompassing targeted delivery, microenvironmental responsiveness, and longterm

efficacy. On the basis of the aforementioned paramount requirements and design principles, together with the compatibility between material systems and printing technologies, three well-established composite design strategies have been developed to date, namely physical blending, *in situ* synthesis, and surface modification. Oriented primarily toward enhancing process compatibility, sustaining the functional stability of nanomaterials, and optimizing tumor theranostic outcomes, each strategy can accommodate diverse metalbased nanomaterials and 3D printing modalities, furnishing dependable pathways for the construction of multifunctional tumor theranostic systems. Table 3 summarizes the compatibility of these strategies with the four printing techniques across the six material classes.

Table 3. Process–material compatibility matrix for 3D-printed metal-based nanocomposites

Material class	FDM	SLA / DLP	SSE / DIW	SLS / SLM	References
Noble metal (Au, Ag, Pt)	√√; AuPB/PCL scaffolds with NIR-tunable photothermal response	√√; Ag salt in PEGDA resin (DLP-printed; AgNPs generated <i>in situ</i> by thermal post-treatment); Ag in 3D-printed collagen scaffolds (UV photoreduction)	√√; AuNP-loaded Pluronic F127/alginate hydrogels (<0.5 mm forming precision)	√; Pt (IV)-loaded biopolymer scaffolds; Au/Pt-functionalized composites	18,61,74, 81,82
Magnetic (Fe ₃ O ₄ , MnOx, CoFe ₂ O ₄)	√√; Fe ₃ O ₄ /PLA composite filaments (10–20 wt%) for MHT scaffolds	NR	√√; CoFe ₂ O ₄ /GelMA bioinks (extrusion-printed, UV-crosslinked); injectable magnetic hydrogels for MHT	NR	22-24,52
High-Z (W, Bi, Gd)	NR	NR	(√); BiNP coatings on 3D-printed bioactive glass scaffolds	√; SLM-fabricated W components/collimators (shielding; NP-composite theranostics NR)	30,31
Transition metal (Cu, Mn, Fe oxides/sulfides)	√; Cu-containing PLA filaments	NR	(i) √√; FeMg-PDA NPs blended in printing inks; (ii) (√) Fe ₃ S ₄ layers grown hydrothermally on extrusion-printed akermanite scaffolds; 2D nanosheet-decorated BGC scaffolds (iii) (√); Cu-MSN-coated β-TCP scaffolds	(√); post-printing surface decoration	59,60,62, 83-85
MXenes (Nb ₂ C, Ti ₃ C ₂)	NR	NR	√√; Mxene/BG and Mxene/PLGA/βTCP composite scaffolds by lowtemperature extrusion/robocasting	NR	42,44
MOFs and derivatives	NR	(√); MOF growth on printed substrates	√√; MOF nanosheet scaffolds; <i>in situ</i> growth on printed β-TCP	NR	48,49

Notes: √√: multiple independent reports demonstrating retention of theranostic function after printing; √: demonstration in at least one study; (√): demonstration only through post-printing functionalization (e.g., surface growth or coating); and NR: not reported in the cancer theranostic context, to the best of our knowledge. All entries are limited to claims explicitly supported by the cited studies.

Abbreviations: AgNPs: Silver nanoparticles; AuNPs: Gold nanoparticles; AuPB: Gold plasmonic blackbody; BG: Bioactive glass; BGC: Bioactive glass-ceramic; BiNP: Bismuth nanoparticle; DLP: Digital light processing; FDM: Fused deposition modeling; GelMA: Gelatin methacryloyl; MHT: Magnetic hyperthermia; MOF: Metal–organic framework; MSN: Mesoporous silica nanoparticle; NIR: Near-infrared; NP: Nanoparticle; PCL: Polycaprolactone; PDA: Polydopamine; PEGDA: Polyethylene glycol diacrylate; PLA: Polylactic acid; PLGA: Poly(lactic-co-glycolic acid); SLA: Stereolithography; SLM: Selective laser melting; SLS: Selective laser sintering; SSE: Semi-solid extrusion; UV: Ultraviolet; β-TCP: Beta-tricalcium phosphate.

4.1. Physical blending

Physical blending represents the most straightforward and universal fabrication strategy for 3D-printed metalbased nanocomposites. The method involves incorporating presynthesized metalbased nanomaterials into 3Dprinting matrices (e.g., PLA and PCL) via mechanical agitation, melt blending, or ultrasonic dispersion to form homogeneous composite systems for extrusionbased or photocurable printing.⁸³ Its prominent merits involve facile manipulation and well-established procedures, eliminating the need for modifications to existing printing equipment and drastically lowering technical barriers to application. Accordingly, it stands among the most prevalent strategies for integrating 3D printing with metalbased nanomaterials in oncological theranostics at present. Numerous investigations have combined these two components through physical blending. For instance, Chen *et al.*¹⁸ incorporated gold plasmonic blackbodies (AuPBs) into PCL via physical blending and fabricated 3Dprinted scaffolds using FDM technology. Such scaffolds

manifest tunable photothermal responsiveness under NIR laser irradiation, offering an innovative tactic for bone regeneration with precisely regulated temperature via physical blending. Figure 4 illustrates the relevant schematic diagram. Moreover, Lin *et al.*⁶² incorporated metallic polydopamine (PDA) nanoparticles (FeMgNPs) into 3Dprinting inks. The resulting scaffolds exert synergistic cytotoxicity against bonemetastatic breast cancer cells through the photothermal effect of PDA and the chemodynamic effect of Fe^{3+} under NIR irradiation. Meanwhile, sustained release of Mg^{2+} facilitates neobone formation, achieving integrated therapy combining tumor ablation and bone defect reconstruction. Nevertheless, the approach has several limitations, including nanoparticle agglomeration and weak interfacial adhesion between nanoparticles and polymer matrices. These drawbacks may further compromise the longterm stability and mechanical performance of composites, which can be ameliorated by optimizing nanoparticle surface modification or introducing compatibilizers.

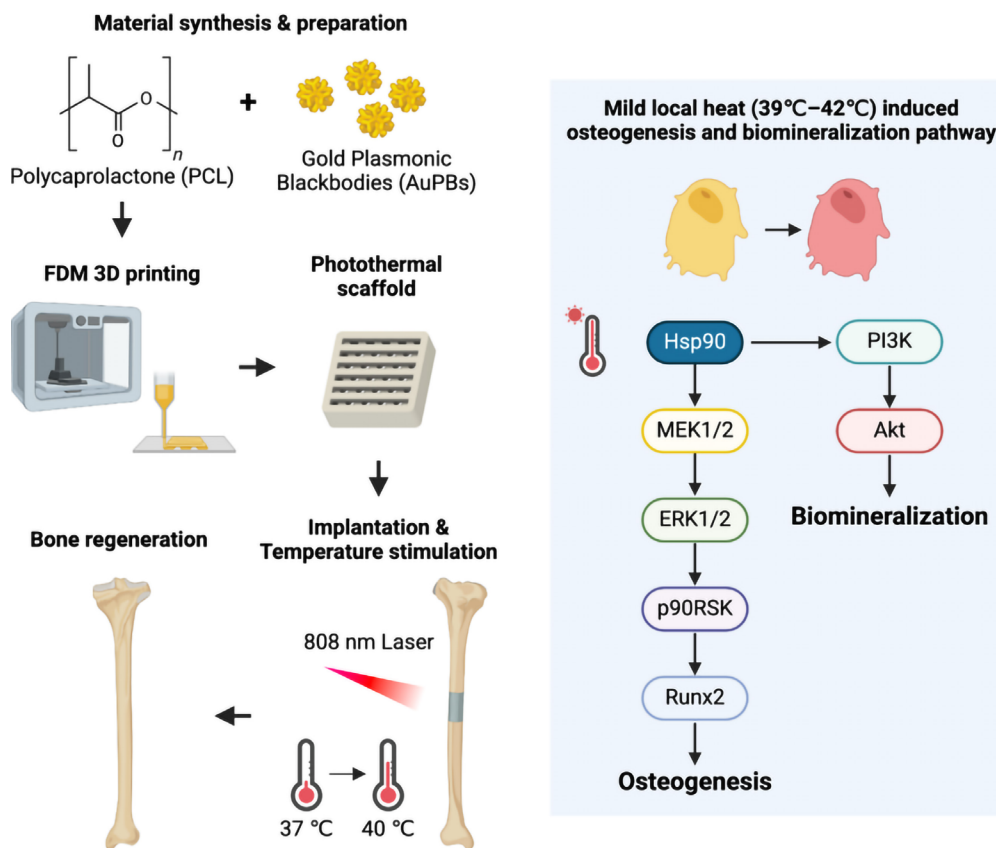


Figure 4. Schematic representation of the preparation and functional application of photothermal scaffolds for bone repair and regeneration. AuPBs were incorporated into polycaprolactone (PCL) via physical blending, and 3Dprinted scaffolds were fabricated using fused deposition modeling (FDM) technology, providing an innovative strategy for bone regeneration. Reprinted from Chen *et al.*¹⁸
Abbreviation: FDM: Fused deposition modeling.

4.2. *In situ* synthesis

In situ synthesis serves as a pivotal tactic for constructing 3D-printed metal-based nanocomposites. It denotes the *in situ* conversion of metal ions into metal-based nanoparticles of metallic phase within scaffold pores or matrices via chemical reduction, photoreduction, or biomineralization following the fabrication of 3D-printed scaffolds, thus accomplishing the integration of nanomaterials with scaffolds.⁸⁶ Unlike physical blending that pre-incorporates nanoparticles, this approach alleviates the agglomeration of pre-synthesized nanoparticles to some degree. At the same time, it enables homogeneous distribution and size control of nanoparticles inside scaffolds, further boosting the stability and functional potency of composite systems. To date, *in situ* synthesis has displayed distinctive strengths. As a case in point, Fantino *et al.*⁶¹ incorporated silver salts into polyethylene glycol diacrylate (PEGDA) photosensitive resin. After DLP-mediated 3D printing, silver nanoparticles (AgNPs) were formed *in situ* within the polymer matrix through thermal treatment, yielding composite scaffolds with outstanding thermomechanical performance and electrical conductivity. This strategy effectively bypasses printing-related challenges triggered by premixed nanoparticles, offering a critical reference for the implementation of *in situ* synthesis in functionalized 3D-printed scaffolds. Moreover, AgNPs were *in situ* fabricated inside 3D-printed collagen scaffolds via ultraviolet-assisted photoreduction in existing research.⁸¹ Controllable tuning of AgNP size and morphology was achieved by adjusting the concentration of silver nitrate precursors, which endows scaffolds with remarkable antibacterial activity and thermal stability, delivering innovative perspectives for the application of *in situ* synthesis in anti-infective bone-defect repair. Overall, the paramount merits of *in situ* synthesis reside in robust interfacial adhesion and uniform dispersion between nanoparticles and substrates, as well as flexible modulation of nanoparticle size, morphology, and loading content tailored to therapeutic demands. However, this technique embodies inherent deficiencies: it imposes rigorous constraints on reaction conditions, including pH value, temperature, and reductant categories, and requires avoidance or thorough removal of toxic residual reagents. Accordingly, further process refinement is imperative to advance its clinical translation in future work.

4.3. Surface modification

Apart from physical blending and *in situ* synthesis, surface modification functions as another core composite design strategy. Owing to its minimal disruption to printing procedures and precise functional decoration, it has been extensively adopted in the construction of tumor-therapeutic scaffolds. Surface modification refers

to immobilizing metal-based nanomaterials or their functionalized derivatives onto the surface of 3D-printed scaffolds via covalent bonding, electrostatic adsorption, or bioconjugation, thereby conferring scaffolds with functionalities such as targeted recognition, smart responsiveness, or biological activity.⁸⁴ Compared with physical blending, surface modification circumvents the interference of nanoparticles on the rheological properties of printing matrices and permits the enrichment of nanomaterials on scaffold surfaces, which amplifies their interactions with the TME. Ma *et al.*⁸⁵ fabricated beta-tricalcium phosphate (β -TCP) decorated with copper-doped mesoporous silica nanospheres (Cu-MSN-TCP) by integrating 3D printing with spin-coating technology to construct bifunctional Cu-MSN-TCP scaffolds. These scaffolds manifest favorable photothermal performance under NIR laser irradiation for efficient osteosarcoma cell elimination. Meanwhile, the released Cu^{2+} and Si^{4+} synergistically stimulate the proliferation, adhesion, and osteogenic gene expression of bone marrow mesenchymal stem cells, achieving integrated therapy of bone tumor ablation and bone defect reconstruction. This provides innovative perspectives for the application of surface modification strategies in post-operative bone tumor repair. Moreover, previous studies first fabricated 80S15C bioactive glass scaffolds via 3D printing, followed by constructing functional bismuth nanoparticle coatings on the scaffold surface through surface modification.³¹ Benefiting from the superior photothermal conversion capability of bismuth metal, the composite scaffolds can effectively eradicate osteosarcoma cells upon NIR laser irradiation while retaining favorable bioactivity to facilitate the proliferation and osteogenic differentiation of bone marrow mesenchymal stem cells. Such integrated therapy of tumor ablation and bone regeneration validates surface modification as an effective tactic to endow 3D-printed scaffolds with dual antitumor and bone-regenerative functions. The virtues of surface modification lie in controlled surface functionalization and favorable biocompatibility, alongside the flexible design of targeting ligands or responsive groups tailored to tumor types and therapeutic demands. Conversely, this approach imposes high requirements on the controllability of modification sites and long-term stability. Advanced surface characterization techniques should be integrated in future research to optimize modification efficiency and further broaden its application scenarios.

5. Latest advances in cancer diagnosis and therapy

With structural tailorability, functional tunability, and integrated diagnostic and therapeutic capabilities,

3D-printed metal-based nanoplateforms have advanced rapidly in the preclinical study and translational exploration of prevalent tumors.^{70,87} Tailored to the anatomical locations, pathological features, and theranostic demands of diverse tumors, such composite systems achieve precise adaptation and functional optimization and have been implemented in diagnostic and therapeutic research targeting bone tumors, breast tumors, reproductive system tumors, and digestive system tumors. Theranostic studies for each tumor category are centered on the functional properties of metalbased nanomaterials and the personalized merits of 3D printing, generating targeted therapeutic regimens. This delivers innovative technical support and research perspectives to break through the bottlenecks of conventional tumor theranostics and elevate overall therapeutic outcomes. Table 4 summarizes the applications of metalbased nanomaterials integrated with 3D printing technologies in various cancers.

This review specifically addresses studies in which a solid implant or device is additively manufactured as an integral construct and subsequently functionalized with metal-based nanomaterials for *in situ* tumor theranostics. Bone tumors, breast cancer, reproductive system tumors, and digestive system tumors therefore constitute the principal focus of this article. Melanoma, glioma, and hepatocellular carcinoma treated by transarterial embolization also represent promising indications for localized therapy. However, most published work on these entities still centers on free nanodrugs, locally injected hydrogels, or embolic microspheres. Fully integrated studies in which a shaped device is printed and combined with metal-based nanomaterials within a single theranostic workflow remain scarce. Accordingly, these tumor types are not assigned standalone sections here. A systematic review of this subset will become appropriate once a sufficient body of such complete, integrative studies has accumulated.

5.1. Bone tumors

In cancer theranostic applications integrating metal-based nanomaterials with 3D printing technologies, bone tumors stand as a pivotal research focus owing to their clinical hallmarks of high malignancy, frequent postoperative recurrence, and challenging bone defect reconstruction. 3D printing enables precise replication of biomimetic bone architectures, yielding scaffold carriers with superior adaptability for postoperative bone tumor repair. Meanwhile, metal-based nanomaterials, by virtue of their distinctive photothermal, magnetothermal, catalytic, and bioactive properties, endow scaffolds with multifunctional features, including tumor ablation, immune modulation, and osteogenic induction. The synergistic combination of the two approaches overcomes a key limitation in

traditional bone tumor treatment: the inherent conflict between antitumor performance and bone regeneration, permitting simultaneous precision-guided tumor theranostics and bone-defect repair. This approach delivers personalized and high-efficiency therapeutic alternatives for clinical bone tumor intervention, rendering relevant investigations a burgeoning frontier within bone tumor theranostics.

Among various functional materials suitable for 3D-printed scaffolds, MOFs have attracted widespread interest in tumor theranostics thanks to their large specific surface area, adjustable pore architectures, and plentiful metal active sites. Dang *et al.*⁴⁹ grew copper-tetrakis(4-carboxyphenyl)porphyrin (Cu-TCPP) MOF nanosheets on the surface of 3D-printed β -TCP scaffolds, fabricating Cu-TCPP-TCP composite scaffolds. On the one hand, Cu-TCPP nanosheets endow scaffolds with favorable NIR photothermal responsiveness, which can effectively kill osteosarcoma cells and ablate subcutaneous tumor tissues. On the other hand, released Cu^{2+} markedly accelerates osteogenic differentiation of human bone marrow mesenchymal stem cells and angiogenesis of human umbilical vein endothelial cells, delivering dual functions of tumor therapy and bone reconstruction and supplying intelligent scaffolds with both antitumor and pro-regenerative capacities for postoperative bone-defect repair. Beyond surface modification via direct *in situ* growth of MOF nanosheets, metal-coordination self-assembly strategies offer an efficient route toward the functionalization of 3D-printed scaffolds. Huang *et al.*⁴⁸ adopted a metal-coordination self-assembly strategy to alternately deposit Cu^{2+} and 2,3,6,7,10,11-hexahydroxytriphenylene (Cu-HHTP) on 3D-printed PCL scaffolds, constructing Cu-HHTP conductive MOF-functionalized interfaces. Such conductive MOF-engineered scaffolds not only possess efficient photothermal conversion capacity for osteosarcoma ablation but also enhance cell adhesion and expedite bone repair via hydrophilic interfaces. Furthermore, their unique catalytic activity generates ROS within the TME, promoting synergistic photothermal-catalytic therapy against osteosarcoma. This strategy opens up a new avenue for surface functionalization of 3D-printed polymeric scaffolds, whereby uniform functional coatings can be fabricated on scaffold surfaces through simple solution immersion, with promising clinical translation potential. Ternary chalcogenides, characterized by distinctive narrow band-gap properties, represent another vital candidate for photothermal agents integrated into 3D-printed scaffolds, offering innovative material insights for PTT of bone tumors. Certain studies have incorporated CuFeSe_2 nanocrystals into 3D-printed

bioactive glass scaffolds, wherein high-strength porous architectures fabricated by 3D printing match the mechanical requirements of weight-bearing bone defects and achieve considerable therapeutic outcomes.³⁵ As semiconductor nanocrystals, CuFeSe₂ nanocrystals realize efficient photothermal conversion under NIR irradiation to precisely ablate osteosarcoma cells. In parallel, calcium ions released during material degradation synergistically promote osteogenic differentiation of bone marrow stromal cells and accelerate bone regeneration. When screening photothermal functional materials, transition metal carbides stand out on account of superior photothermal conversion performance and biosafety, expanding the functional dimensions and application prospects of 3D-printed scaffolds. Guo *et al.*³⁶ fabricated PLA/polyethylene glycol (PEG)/niobium carbide (NbC) composite bone scaffolds via FDM-based 3D printing, using PLA as the matrix, PEG as the plasticizer, and NbC nanoparticles as functional fillers. These scaffolds feature periodically ordered porous structures, whose steady-state temperature can be precisely regulated by tuning material compositions and irradiation parameters. From the perspective of PTT, the scaffolds exert prominent inhibitory effects on human osteosarcoma cells, with an inhibition rate up to 90%. Notably, the scaffolds exhibit excellent non-contact photothermal shape-memory recovery performance. The incorporation of PEG lowers the glass transition temperature of PLA, allowing shape-memory effects to occur within physiological temperature ranges and fostering minimally invasive implantation for irregular bone defects. Apart from the aforementioned single and simply composited functional materials, composite systems of AuNPs and reduced graphene oxide (rGO), such as AuNPs@rGO, further boost the theranostic performance of 3D-printed scaffolds through synergistic effects, emerging as a critical research direction for bidirectionally regulated bone tumor therapy. Several research groups have constructed AuNPs@rGO composite photothermal coatings and modified them on 3D-printed osteogenic scaffolds. 3D printing precisely constructs biomimetic trabecular architectures to provide a native extracellular matrix microenvironment for bone regeneration.⁸⁸ Under NIR irradiation, AuNPs amplify photothermal absorption via the “antenna effect,” attaining precise ablation of residual malignant bone tumor cells and suppression of postoperative recurrence. Incorporation of rGO boosts the electrical conductivity and bioactivity of coatings to facilitate osteoblast proliferation and differentiation. Concurrently, AuNPs modulate the bone immune microenvironment and restrain osteoclast activity, accelerating bone-defect repair and establishing a bidirectional regulatory mechanism of photothermal

antitumor activity–osteogenic regeneration. As an essential element for humans, magnesium ions play a pivotal role in regulating bone metabolism and immune responses. Complexation of magnesium ions with polyphenols endows nanomaterials with multiple bioactive functions. Inspired by clinical bone cement-augmented therapy, Hu *et al.*⁸⁹ fabricated biomimetic α/β -TCP cancellous bone scaffolds via low-temperature 3D printing, which were loaded with tea polyphenol–magnesium (TP-Mg) nanoparticles. Benefiting from the self-setting property of α -TCP, these scaffolds possess robust mechanical strength and mimic the structure and composition of natural cancellous bone. Integration of TP-Mg nanoparticles imparts prominent antibacterial capacity to scaffolds, inhibiting the growth of *Staphylococcus aureus*. In parallel, TP-Mg mediates the polarization of macrophages from the pro-inflammatory M1 phenotype to the anti-inflammatory M2 phenotype, remodeling the early-stage microenvironment of infected bone defects. Synergistic effects of Mg²⁺ and Ca²⁺ further elevate the osteoinductive potential of scaffolds, promoting late-stage regenerative healing of infected bone defects (Figure 5A). Such scaffolds hold promising application prospects for repairing infected bone defects following tumor resection. Alongside Mg–polyphenol strategies, Lee *et al.*⁹⁰ constructed 3D-printed tissue-adhesive theragenerative scaffolds by integrating tissue-specific nanospiked hydroxyapatite with Mg-containing nanospikes and adhesive DNA within a PLA matrix. The Mg-containing photothermal component enabled hyperthermia-mediated eradication of osteosarcoma and bacterial cells, whereas adhesive DNA facilitated vascularized bone healing; together, the constructs coupled controlled degradation and mechanical support with antibacterial protection, tumor ablation, angiogenesis, and osteogenesis *in vitro* and *in vivo*. Focusing on clinically prevalent implant materials, 3D-printed titanium alloy scaffolds exhibit superior mechanical performance and clinical safety yet lack antitumor functions. To address this limitation, researchers have achieved functional upgrading through drug-loading strategies. Several research teams anchored pH-responsive PEG–acetal–paclitaxel prodrug nanoparticles onto the surface of 3D-printed porous titanium alloy scaffolds via PDA modification, constructing TS@PAP composite scaffolds.⁹¹ Experimental outcomes reveal that these composite scaffolds exert remarkable cytotoxic effects against five human osteosarcoma cell lines, with cell viability declining below 5% after 72 hours. *In vivo* assays further verify that the scaffolds effectively prevent local postoperative recurrence of osteosarcoma, while the titanium alloy matrix provides reliable mechanical support for bone defects (Figure 5B). This approach offers a

prospective strategy for clinical translation of osteosarcoma postoperative bone-defect repair and recurrence prevention. A more integrated titanium-platform example couples 3D-printed porous titanium scaffolds with microwave-responsive zeolitic imidazolate framework 8 (ZIF-8) nanomaterials loaded with a chemotherapeutic drug and an immune checkpoint inhibitor in an orthotopic osteosarcoma model. Microwave hyperthermia and chemotherapy induced immunogenic tumor cell death, while checkpoint inhibition enhanced the antitumor immune response and helped suppress recurrence; during long-term implantation, Zn^{2+} released from ZIF-8 degradation could promote stem-cell osteogenic differentiation, uniting structural support, MOF-mediated thermo-chemo-immunotherapy, and bone repair in one implantable construct.⁹² In the field of MHT, cobalt ferrite (CFO) nanoparticles stand out as ideal magnetothermal agents incorporated into 3D-printed scaffolds due to their outstanding magnetic properties and magnetothermal conversion capacity, delivering innovative insights for minimally invasive osteosarcoma treatment. One research team designed high-performance magnetic hydrogels (McCFO/GelMA) composed of gelatin methacryloyl (GelMA) and highly magnetic CFO nanoparticles for osteosarcoma therapy.²⁴ Featuring shear-thinning behavior, the hydrogels are suitable as bioinks for fabricating sophisticated 3D architectures, and their porous channel structures facilitate cell migration and nutrient exchange. In one respect, CFO elevates local temperature under alternating magnetic fields to implement MHT. In another respect, CFO not only eliminates osteosarcoma cells efficiently but also stimulates osteogenic differentiation and mineralization of bone marrow mesenchymal stem cells, realizing dual functions of magnetothermal antitumor activity and bone reconstruction and providing novel perspectives for minimally invasive osteosarcoma management. Doping bioactive ceramics with multiple bioactive transition metal elements to fabricate functionalized scaffolds via 3D printing represents another vital strategy within bone tumor theranostics. Bioactive glass-ceramic scaffolds doped with transition metal elements have been synthesized by combining the sol-gel method with 3D printing.³⁷ Compared with conventional nano-photothermal agents, bioactive element-mediated functionalized scaffolds exhibit enhanced biosafety and bioactivity. Specifically, Fe-doped and Mn-doped scaffolds exert photothermal antitumor effects while significantly stimulating osteoblast differentiation, demonstrating excellent dual functionalities. They thus provide safe and effective alternatives for intelligent bone tumor treatment and postoperative bone-defect repair.

Viewed together, these studies share a design logic

rather than a single proven mechanism: 3D-printed scaffolds deliver spatially matched bone reconstruction while integrating PTT, MHT, Cu-associated catalytic ROS generation, and pH-triggered paclitaxel release to suppress osteosarcoma. NIR-responsive plasmonic/narrow bandgap or element-doped components convert light into heat for tumor killing, and CFO enables alternating magnetic field-responsive magnetothermal ablation; however, Néel/Brownian relaxation details and heat-induced protein/membrane damage are general mechanistic interpretations rather than findings reported here. Cu-based chemistry generates ROS in the TME, whereas Fe/Mn doping is reported mainly as photothermal bioactivity plus osteogenesis. Cu^{2+} released from Cu MOF/TCP systems supports osteogenic differentiation and angiogenesis; in the TP-Mg/TCP system, $\text{Mg}^{2+}/\text{Ca}^{2+}$ cues contribute to M1 to M2 macrophage repolarization, antibacterial infected defect remodeling, and enhanced osteoinduction, whereas Ca^{2+} from degrading phosphate/bioactive glass mainly promotes osteogenesis. These regenerative cues should be distinguished from direct antitumor ionic action. Whether photothermal heating accelerates Cu catalyzed ROS generation or any Fe/Fenton like contribution remains an open question requiring direct verification.

5.2. Breast tumors

Recent advances have been achieved in the precision diagnosis and treatment of breast tumors via the combination of metal-based nanomaterials and 3D printing technology. Their applications have extensively covered multiple directions, including breast cancer cell culture and *in situ* monitoring, bone metastasis therapy and regeneration, local treatment and postoperative intervention, and integrated diagnosis and therapy, as well as early screening and detection. Through precise matching between diverse nanomaterials and 3D printing techniques, limitations of conventional diagnosis and treatment have been overcome, which provides abundant research outcomes and technical support for precise and diversified intervention of breast tumors.

The integration of these approaches has demonstrated remarkable advantages in the field of breast cancer cell culture and *in situ* monitoring. One study⁹³ combined chiral gold nanorods (c-AuNRs) with 3D-printed hydrogel scaffolds. Taking advantage of the unique optical responsiveness of chiral plasmonics, background scattering interference from hydrogel matrices was effectively attenuated. Meanwhile, non-invasive monitoring of hydrogel structural remodeling was realized, and the feasibility of this strategy was validated in a 3D breast cancer cell culture system, which may offer a novel method for developing subsequent *in situ* monitoring platforms

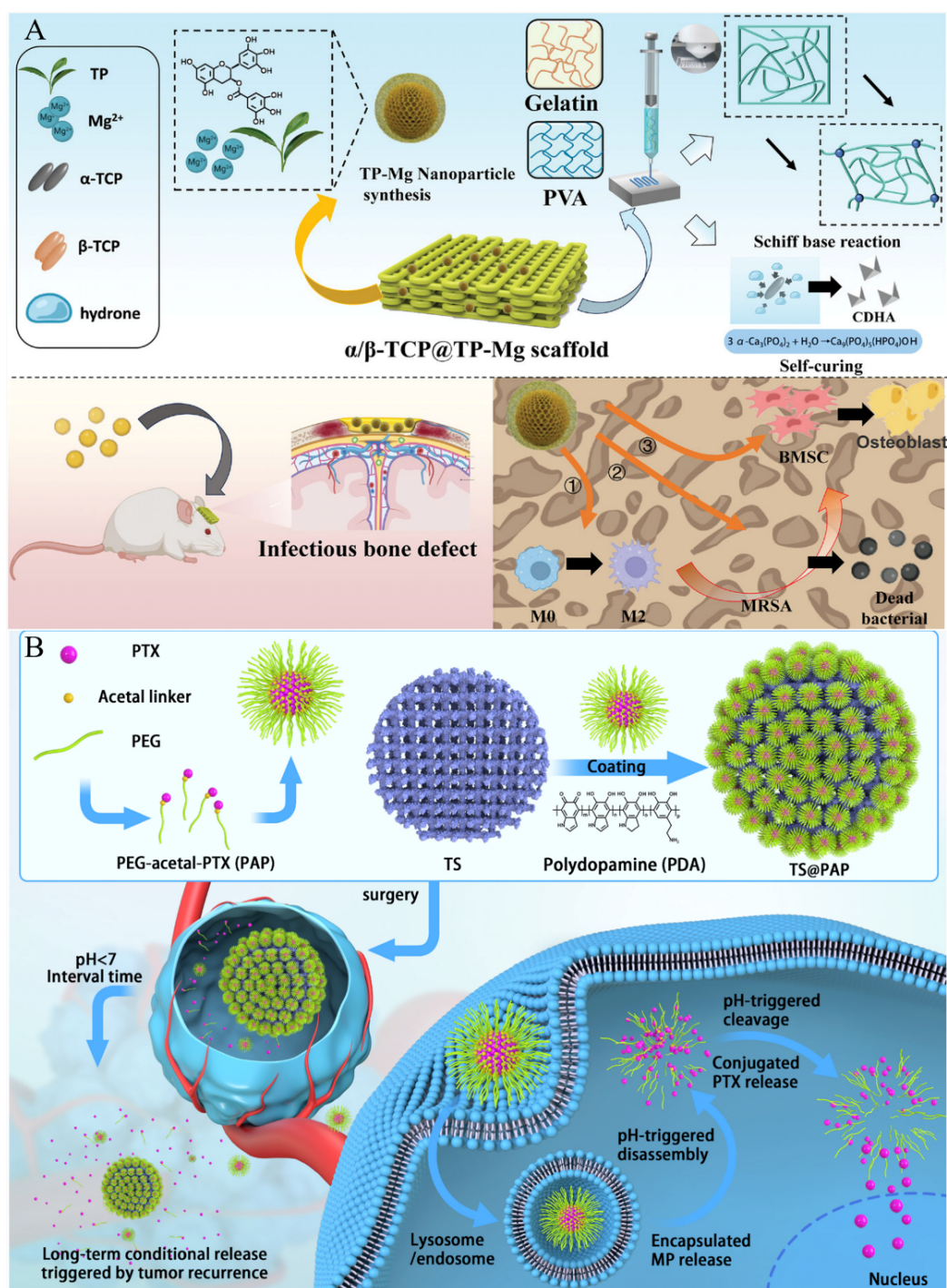


Figure 5. Schematic illustration of 3D-printed metal-based nanocomposites for bone tumor treatment. (A) α/β -TCP@TP-Mg scaffold: TP-Mg nanoparticles endow the scaffold with antibacterial activity, while *in vivo* self-curing generates bone-like apatite to promote bone-defect repair. Reprinted with permission from Hu *et al.*⁸⁹ Copyright © 2024 Wiley-VCH GmbH. (B) TS@PAP scaffold: the titanium alloy scaffold loaded with a pH-responsive PTX nanodrug enables sustained drug release in the acidic tumor microenvironment to suppress osteosarcoma recurrence, with the alloy providing mechanical support. Reprinted with permission from Fan *et al.*⁹¹ Copyright © 2023 The Authors.

Abbreviations: BMSC: Bone marrow mesenchymal stem cell; CDHA: Calcium-deficient hydroxyapatite; MRSA: Methicillin-resistant *Staphylococcus aureus*; PAP: Polyethylene glycol-acetal-paclitaxel; PDA: Polydopamine; PEG: Polyethylene glycol; PTX: Paclitaxel; PVA: Poly(vinyl alcohol); TCP: Tricalcium phosphate; TP: Tea polyphenol; TS: Titanium scaffold; α -TCP: Alpha-tricalcium phosphate; β -TCP: Beta-tricalcium phosphate.

for the extracellular microenvironment of breast cancer cells. Apart from c-AuNRs, the combination of plasmonic metal nanoparticles and 3D-printed hydrogels also opens new avenues for TME monitoring. A 3D breast cancer spheroid culture system was constructed by incorporating plasmonic metal nanoparticles into 3D-printed hydrogel scaffolds.⁹⁴ Leveraging SERS enhancement, a research platform integrating 3D cell culture, real-time sensing, and *in situ* imaging was established. This platform permits dynamic tracking of the growth and spatial distribution of breast cancer spheroids, holding promise to provide new approaches for visualized monitoring of the TME. Aiming at the clinically prevalent challenge of breast cancer bone metastasis, the synergistic application of metal-based nanomaterials and 3D printing technology achieves dual breakthroughs in therapy and regeneration. In one study, FeMg-metal PDA nanoparticles were incorporated into 3D-printed bioinks to fabricate integrated porous scaffolds.⁶² Bimetallic components exert synergistic therapeutic and regenerative functions. In particular, iron ions eliminate bone metastatic tumors via CDT synergized with PDA-mediated PTT, while sustained release of magnesium ions regulates osteoblast differentiation, thereby synchronously realizing metastatic lesion ablation and bone defect regeneration. In terms of local treatment and postoperative intervention for breast cancer, the combination of noble metal-based nanomaterials and 3D printing further improves therapeutic precision and long-term efficacy. Relevant studies fabricated bilayer degradable scaffolds via 3D bioprinting. The first layer, loaded with 5-fluorouracil (5-FU), provides sustained release, whereas the AuNP-containing second layer enhances local radiosensitization by virtue of radiosensitization properties. Synergistic dual effects effectively inhibit residual local breast tumor lesions and reduce postoperative recurrence risks, which provides novel multifunctional implantable materials for precise local postoperative intervention of breast cancer.⁹⁵ Complementing AuNP-based radiosensitization, bovine serum albumin (BSA)-coated Bi₂S₃ nanoparticles were co-printed with alginate into implantable scaffolds; when placed beneath 4T1 tumors, the scaffolds enhanced ROS generation and tumor-cell killing after a single 4 Gy X-ray exposure, reduced *in vivo* tumor growth, and showed no obvious toxicity in major organs.⁹⁶ In addition, Chang *et al.*⁹⁷ adopted a 3D-printed microfluidic device to precisely regulate reaction conditions for the controllable synthesis of BSA-coated Cu (DDC)₂ metal-organic nanoparticles. This strategy addresses insufficient effective concentrations at tumor sites caused by separate administration of disulfiram and copper ions. These nanocomposites can activate the disulfiram-copper combined therapeutic

pathway within breast cancer cells and exert anti-tumor effects via ROS-mediated cytotoxicity, which displays favorable therapeutic outcomes at both cellular and orthotopic tumor model levels. Figure 6 illustrates the fabrication process of BSA-Cu (DDC)₂ metal-organic nanoparticles. In the field of integrated diagnosis and therapy, the combination of metal-based nanomaterials and 3D-printed microswimmers promotes the synergy of targeted delivery and imaging guidance. One team constructed biodegradable microswimmers loaded with superparamagnetic iron oxide nanoparticles (SPIONs) via TPP-based 3D printing technology. The microswimmers demonstrated magnetic navigation and targeted cancer-cell labeling *in vitro* at lesion sites under precise magnetic field-driven control. Combined with matrix metalloproteinase-2-responsive degradability of the TME, they synchronously accomplish targeted drug delivery and antibody-mediated specific labeling of tumor cells, which provides a potential new paradigm for imaging-guided integrated diagnosis and therapy of breast cancer.⁹⁸ Beyond therapy and monitoring, their combination also plays a vital role in early screening and detection of breast cancer, laying a foundation for early intervention. One study established an electrochemiluminescence sensing platform based on AuNP-functionalized 3D-printed microchannels.⁹⁹ Leveraging the signal amplification effect of AuNPs and the specific recognition capacity of aptamers, ultra-sensitive quantitative detection of breast cancer cells is realized. Featuring simple operation and excellent detection performance, this platform offers new technical strategies for low-cost, rapid early screening of breast cancer.

These reports describe a useful arc rather than a finished platform. c-AuNRs and plasmonic SERS hydrogels can report matrix remodeling and spheroid growth in 3D culture. FeMg PDA scaffolds, bilayer 5-FU AuNP implants, BSA-coated Cu (DDC)₂ nanoparticles, SPION microswimmers, and AuNP aptamer microchannels then extend the same logic from monitoring to bone metastasis, local recurrence control, image-guided delivery, and early detection. The advance is real, but most claims still stop at engineered feasibility. Optical platforms need stable calibration against matrix scattering, durable signals over time, and evidence that readouts predict tissue-level outcomes. For metastatic and postoperative bone repair, CDT and PTT injury, magnesium-driven osteogenesis, radiosensitization, and sustained 5-FU release must fit one dose, exposure, and resorption window, while also respecting load bearing, infection, recurrence, and injury to normal tissue. Microfluidic BSA Cu(DDC)₂ production may raise tumor site exposure, yet copper handling, ROS toxicity, pharmacokinetics, sterility, batch consistency, and

scale-up remain open. SPION swimmers face a harder barrier beyond proof of concept. Deep tissue magnetic control, immune recognition, clearance, and quantitative imaging must be shown together, not as separate demonstrations. Likewise, electrochemiluminescent detection will matter only if it resists patient matrix effects,

phenotypic heterogeneity, and aptamer variability and then survives comparison with established assays in diverse cohorts. The next step should be narrower and harder: fewer functions, clearer benchmarks, and head-to-head evidence under clinical manufacturing and regulatory constraints.

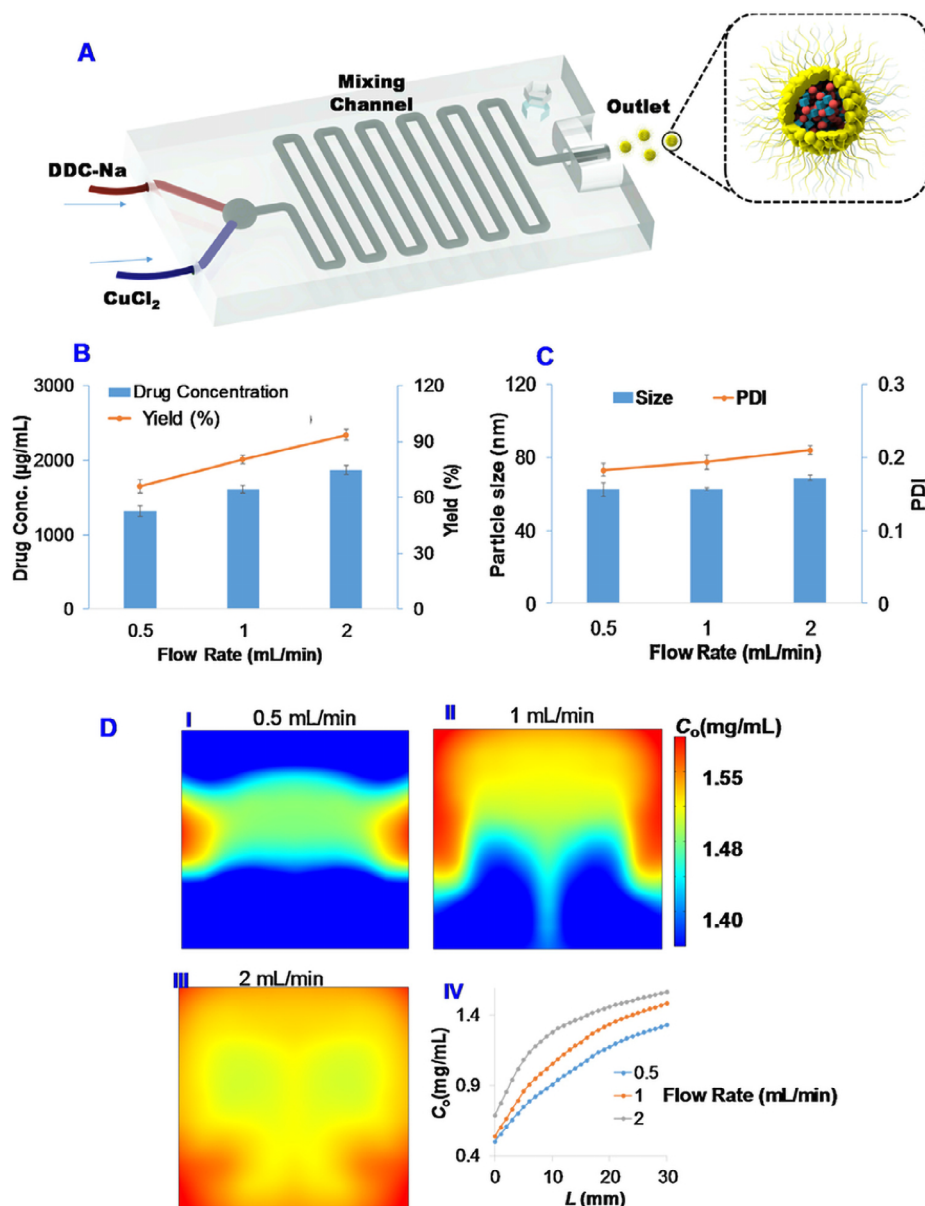


Figure 6. Fabrication of BSA Cu (DDC)₂ metal-organic nanoparticles (MONs) via microfluidic technology. (A) Synthetic route for the fabrication of bovine serum albumin (BSA) Cu (DDC)₂ MONs. (B) Variations in drug concentration and production yield under different flow rate conditions. (C) Changes in particle size and polydispersity index (PDI) of the prepared samples at diverse flow rates. (D) Numerical simulation analysis revealing the influence of flow velocity on the formation process of MONs. The contour plots display the spatial distribution of initial Cu (DDC)₂ concentration (C₀) at the outlet cross-section under different flow conditions: (I) 0.5 mL/min, (II) 1 mL/min, and (III) 2 mL/min. (IV) Simulated distribution of initial Cu (DDC)₂ concentration (C₀) along the migration distance from the initial mixing region. Reprinted with permission from Chang *et al.*⁹⁷ Copyright © 2020 Elsevier Ltd.

5.3. Reproductive system tumors

Minimally invasive diagnosis and treatment of reproductive system tumors represent a hotspot in current medical research. The combination of customized and high-precision features of 3D printing technology with unique physicochemical and biological functions of metal-based nanomaterials provides critical support for the innovation of therapeutic regimens in this field. Their synergistic effects can effectively address drawbacks of conventional diagnosis and treatment, including poor targeting ability, low delivery efficiency, and insufficient device adaptability. Leveraging properties of diverse metal-based nanomaterials, diversified therapeutic strategies with high targeting specificity and safety can be established for reproductive system tumors.

Gold nanoparticles, with superior biocompatibility, high-Z characteristics, and radiosensitization potential, serve as vital metal-based nanomaterials for the diagnosis and treatment of reproductive system tumors, particularly cervical cancer. Integration with the customized merits of 3D printing allows the construction of precise and efficient theranostic regimens. One study integrated ultrasmall AuNPs into 3D-printed Pluronic F127-alginate hydrogels for transvaginal local delivery toward targeted intervention of cervical cancer.⁸² The 3D-printed hydrogels achieved geometric accuracy of <0.5 mm, which effectively resolves challenges regarding molding controllability and lesion localization during *in vivo* administration of nanoparticles, offering a novel carrier strategy for precise local therapy of cervical cancer. On this basis, Kiseleva *et al.*¹⁰⁰ further optimized the combinatorial strategy of AuNPs and 3D printing technology and designed customized cup-shaped 3D-printed radioactive brachytherapy implants covered with gold-nanoparticle-loaded hydrogel pads, forming a composite system comprising a 3D-printed radioactive brachytherapy implant and an AuNP-containing hydrogel cushion. Radiosensitization acts as the core theranostic mechanism of this system. 3D printing technology allows accurate adjustment of dimensions and configurations of implants and hydrogel pads according to tumor size and morphology. As high-efficiency radiosensitizers, AuNPs induce ROS generation via low-energy photon and electron production during brachytherapy, therewith damaging tumor-cell DNA. In HeLa-xenografted mouse models, AuNPs penetrated approximately 100 μm into tumor tissues after subcutaneous surgical implantation of the composite system, and increased ROS accumulation was detected after irradiation. This strategy is expected to reduce the total brachytherapy dose required, thus mitigating damage to surrounding healthy tissues, and provides a novel composite scheme with clinical translation

prospects for radiosensitization-mediated precise local radiotherapy of cervical cancer (Figure 7). Additionally, Synomag®-D magnetic iron oxide nanoparticles have been combined with 3D printing technology in relevant studies.¹⁰¹ Resin-based materials are adopted to fabricate housings for laparoscopic and transrectal handheld induction heaters embedded with micro-coils. Alternating magnetic fields trigger heat generation in magnetic nanoparticles, elevating tumor temperature to an effective hyperthermia range. This magnetic fluid hyperthermia system efficiently kills tumor cell lines of ovarian and prostate cancers with more limited effects on the tested normal cells *in vitro*, delivering a handheld device scheme with clinical translation potential for precise magnetic hyperthermia of ovarian and prostate cancers. Beyond magnetic hyperthermia strategies, gadolinium-based nanoparticles manifest promising application potential in precise radiotherapy of cervical cancer attributable to their integrated diagnosis and therapy properties. One study combined AGuIX® gadolinium-based nanoparticles with 3D cell models to explore their integrated theranostic applications in locally advanced cervical cancer within the framework of clinical trials.¹⁰² Following intravenous injection, such nanoparticles passively target tumors via the enhanced permeability and retention (EPR) effect, and quantitative visualization of tumor accumulation is achieved through T1-weighted MRI. Furthermore, intratumoral nanoparticle concentrations measured clinically were reproduced in 3D cell models *in vitro*. Colony formation assays verified that AGuIX® exerts prominent radiosensitizing effects in external beam radiotherapy and brachytherapy, which favors improved local tumor control efficacy, and offers reliable evidence for clinical translation of MRI-guided precise radiotherapy mediated by metal-based nanoparticles.

Across these reports, the clearest advance is not a new nanomaterial class but tighter spatial control of radiation or heat delivery. For cervical cancer, 3D printing shapes hydrogels and brachytherapy implants with submillimeter or patient-matched geometry; AGuIX enables MRI-based tumor accumulation assessment; and AuNPs or AGuIX act as radiosensitizers. The AuNP evidence rests on molding precision, about 100 μm tumor penetration, and radiation-induced ROS in HeLa xenografts, while dose sparing for surrounding tissue remains an expectation. Retention, mucosal tolerance, imaging confirmation, and standardized dosimetry still require definition. The Synomag system shows cell-level magnetic hyperthermia against ovarian and prostate tumor lines with minor normal cell impact, but it does not yet establish thermal dosing, intratumoral distribution, organ safety, or device reproducibility. AGuIX carries the strongest translational signal because clinically

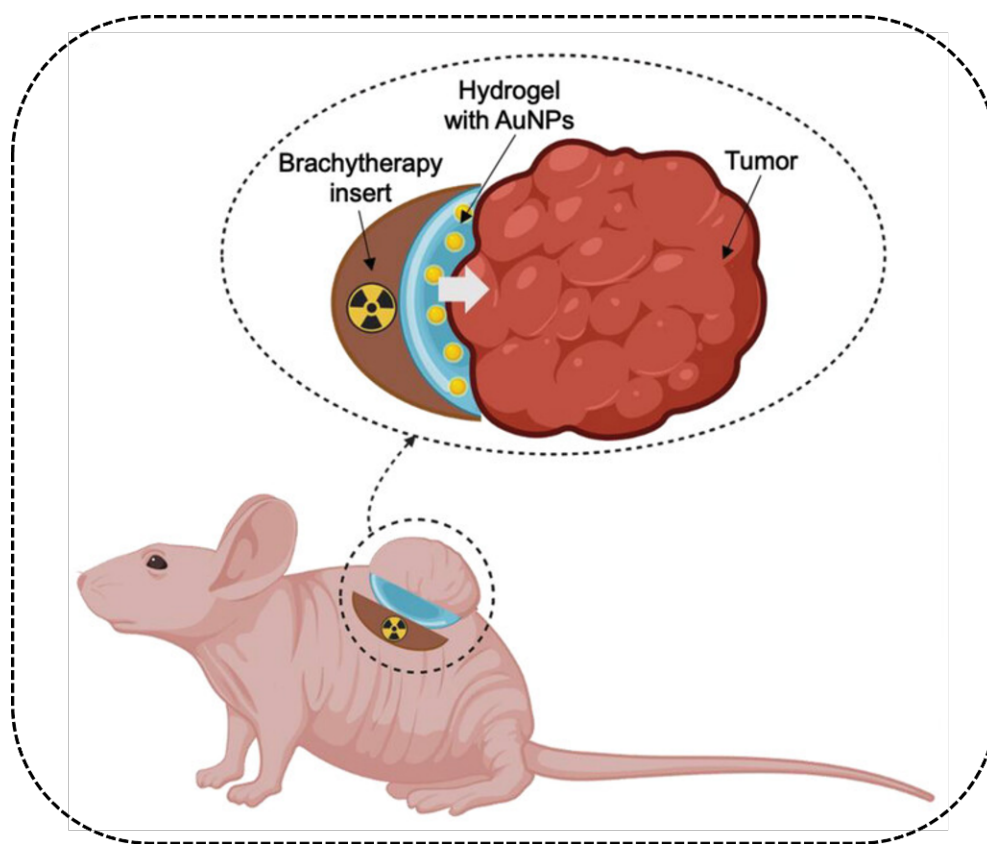


Figure 7. Schematic of cupola-shaped 3D-printed radioactive brachytherapy inserts coated with gold nanoparticle (AuNP)-laden hydrogel for preclinical brachytherapy studies. Reprinted with permission from Kiseleva *et al.*¹⁰⁰ Copyright © 2023 The Authors.

measured intratumoral concentrations were reproduced in 3D models and clonogenic assays supported sensitization during external beam radiotherapy and brachytherapy. Even so, EPR targeting, MRI quantification, and clonogenic endpoints must be linked to local control, survival, normal tissue toxicity, and long-term safety before MRI-guided radiotherapy can be considered practice-changing.

5.4. Digestive system tumors

Digestive system tumors have a high incidence and are often clinically silent in their early stages, posing challenges in early detection, limitations in existing interventions, and a lack of suitable *in vitro* models for efficacy evaluation. Metal-based nanomaterials possess multifunctional properties, incorporating PTT, SERS sensing, and electrochemical catalysis. When integrated with the precise structural construction merits of 3D printing and 3D bioprinting, they can offer innovative technical strategies for precision diagnosis and treatment of digestive system tumors. Representative tumor types include esophageal cancer and liver cancer, and relevant applications cover multiple dimensions such as interventional therapy,

biomarker detection, precancerous lesion screening, and the fabrication of biomimetic *in vitro* models.

Liu *et al.*¹⁰³ immobilized AuNPs on the surface of braided nitinol esophageal stents to fabricate a NIR light-triggered synergistic photothermal-chemotherapy platform (Figure 8). In this system, AuNPs serve as high-efficiency photothermal converters that generate localized hyperthermia under laser irradiation while activating temperature-responsive coatings to regulate the release of anti-tumor drugs. Possessing anti-migration functions, such stents enable precise and controllable local hyperthermia and drug delivery at tumor-stenotic sites, offering an emerging interventional strategy with mechanical support and active therapeutic functions for malignant esophageal stricture. Beyond interventional therapy for solid digestive tumors, metal-based nanomaterials and 3D printing technology can also be integrated into portable sensing devices, extending applications toward rapid detection of tumor-associated biomarkers. One study designed a liposome-encapsulated $\text{Cu}_{2-x}\text{Ag}_x\text{S}$ nanoparticle-mediated photothermal immunoassay system, which was integrated with an

assemblable 3D-printed detection device for routine monitoring of cardiac troponin I.¹⁰⁴ These nanoparticles possess outstanding photothermal conversion efficiency; upon NIR excitation, they produce temperature signal variations recorded by portable thermal imagers and assessed via smartphones. The modular 3D-printed device enables assembly of the detection components and visualization of the thermal signal, with potential for extension to digestive tumor biomarkers, such as alpha-fetoprotein and carcinoembryonic antigen, establishing a novel paradigm of portable photothermal sensing for point-of-care rapid diagnosis. Leveraging the structural modulation advantages of 3D-printed micro-nanostructures and the SERS sensing properties of noble metal-based nanomaterials, non-invasive early screening for digestive precancerous lesions can also be achieved. Nian *et al.*¹⁰⁵ developed denatured collagen-targeted peptide-modified silver nanoparticle probes (Ag@DCTP), which were combined with PEGDA-based ink-printed collagen-capture chips to accomplish SERS-specific detection of denatured type I and type IV collagen in blood. The probes specifically recognize denatured collagen, with silver nanoparticles amplifying Raman signals efficiently via strong surface plasmon resonance effects. 3D printing allows precise construction of 3D microstructures of chips, facilitating efficient capture and enrichment of collagen biomarkers in serum. This detection platform provides a non-invasive and highly sensitive diagnostic strategy for evaluating liver fibrosis progression and early screening of malignant transformation from liver fibrosis to hepatocellular carcinoma. Apart from early diagnosis and lesion screening, 3D bioprinting combined with metal-based nanomaterials can construct biomimetic *in vitro* tumor models for liver cancer-related drug screening and toxicity assessment. Wang *et al.*¹⁰⁶ fabricated a micro-nanochannel-structured 3D-bioprinted hepatic microtissue platform functionalized with iron oxide-based magnetic nanomaterials to build an integrated biosensing system. Relying on 3D-printed biomimetic microenvironments to maintain the physiological activity of hepatic tissues and the superior physicochemical sensing performance of magnetic nanomaterials, precise toxin detection is accomplished, which provides an innovative biomimetic research platform for hepatic lesion modeling and *in vitro* screening of candidate anti-tumor drugs. To further improve hepatic tissue biomimicry and *in situ* sensing performance, the integrated application of composite functional metal-based nanomaterials and 3D-bioprinted organ-on-a-chip has gradually become a research hotspot. A study constructed a 3D-bioprinted liver-on-a-chip embedded with graphene quantum dot-coated AuNPs plasmonic sensors.¹⁰⁷ This chip possesses

favorable performance in secreting liver function-related proteins and expressing drug-metabolizing transporter genes, providing a high-quality organ-on-a-chip platform for liver injury monitoring, drug metabolism evaluation, and early diagnosis of liver cancer.

What links these studies is control at interfaces: heat at a stenotic lumen, signal at the point of care, and tissue-like readout *in vitro*. The esophageal stent is the most intervention-ready concept, because mechanical support is joined to photothermal conversion and drug release governed by temperature. It still needs proof in malignant stricture models that hyperthermia, drug exposure, and resistance to migration can be tuned without mucosal injury or uncontrolled restenosis. The portable photothermal immunoassay is elegant, but the reported target is cardiac troponin I, so extension to alpha-fetoprotein or carcinoembryonic antigen remains a claim to be tested rather than an established digestive cancer assay. The collagen-targeted SERS chip is more specific to hepatocarcinogenesis, yet denatured type I and type IV collagen in blood must be separated from confounding fibrosis, inflammation, and other collagen sources before malignant transformation can be inferred. The printed hepatic microtissues and plasmonic liver-on-chip are useful for toxin detection and metabolism-related readouts. Their weakness is functional depth. Protein secretion and transporter expression are encouraging, but vascularization, zonation, immune input, chronic stability, and correlation with patient drug response are still missing.

Collectively, the studies surveyed above reveal a coherent structure–function–application logic in which the intrinsic physicochemical property of each nanomaterial class dictates its diagnostic and therapeutic roles in 3D-printed platforms. Noble metals, relying on strong LSPR and high molar extinction coefficients, dominate PTT and biosensing, exemplified by AuPB-loaded PCL scaffolds with tunable temperature output under NIR irradiation¹⁸ and AuNP-functionalized microchannels for ultrasensitive detection of breast cancer cells.⁹⁹ Magnetic nanomaterials such as Fe₃O₄ and CoFe₂O₄ couple magnetic responsiveness with MRI contrast generation, uniting T2-weighted imaging with magnetic hyperthermia and ferroptosis induction in printed composite scaffolds.^{23,24} High-Z elements exploit superior X-ray attenuation for CT imaging and radiosensitization through amplified ROS production, as realized in bismuth-coated bioactive glass scaffolds for osteosarcoma³¹ and gold-enhanced brachytherapy implants for cervical cancer.¹⁰⁰ Transition metal sulfides and oxides, endowed with narrow bandgaps and Fenton-like activity, integrate PTT with CDT and bioactive ion release to achieve combined tumor ablation

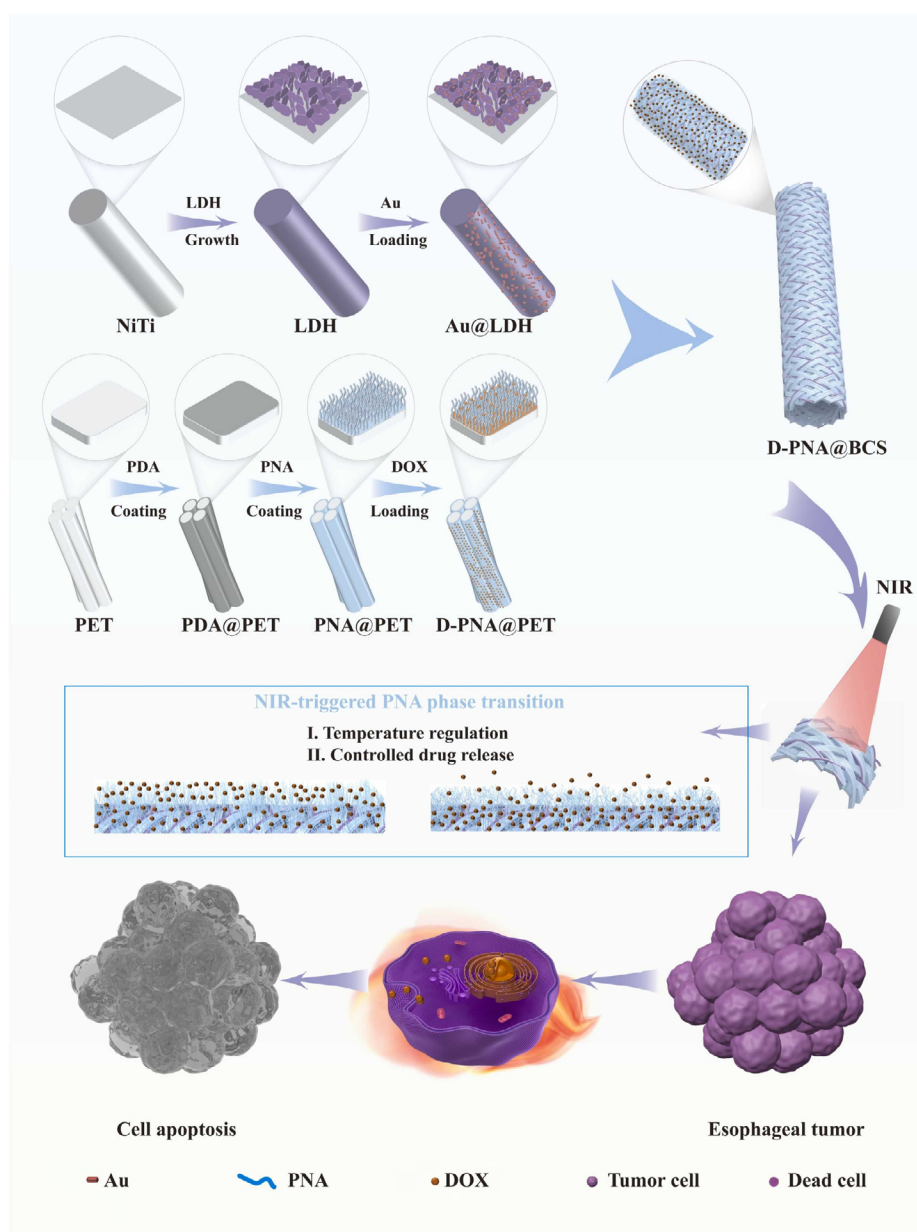


Figure 8. Schematic illustration of the fabrication of D-PNA@BCS stent and its application in synergistic photothermo-chemotherapy. Reprinted with permission from Liu *et al.*¹⁰³ Copyright © 2025 Elsevier B.V.

Abbreviations: Au: Gold; BCS: Braided composite stent; DOX: Doxorubicin; LDH: Layered double hydroxide; NiTi: Nickel–titanium alloy (Nitinol); NIR: Near-infrared; PDA: Polydopamine; PET: Polyethylene terephthalate; PNA: Poly(N-isopropylacrylamide-co-acrylamide).

and bone regeneration.^{35,49} MXenes and MOFs extend this logic further, the former offering exceptionally high photothermal conversion efficiency for photoacoustic imaging and photothermal ablation,^{39–42} and the latter providing tunable porosity and TME-responsive degradation for multimodal imaging and stimuli-responsive drug release.^{45–49} Across all classes, diagnostic capability and therapeutic efficacy are not independent

attributes but direct manifestations of the same underlying physicochemistry. Recognizing this unified logic, in which plasmonics enables PTT and biosensing, magnetism couples magnetic hyperthermia with MRI, high atomic number underpins radiosensitization and CT contrast, and redox activity drives CDT, is essential for the rational selection of nanomaterial classes in the design of next-generation 3D-printed theranostic constructs.

Table 4. Applications of metal-based nanomaterials combined with 3D printing technology in different cancers

Tumor type	3D-printed metal-based nanocomposites	Core mechanism	References
Bone tumor	Cu-TCPP-TCP composite scaffold	Cu-TCPP nanosheets endow the scaffold with favorable near-infrared photothermal performance, which can effectively kill osteosarcoma cells and ablate subcutaneous tumor tissues. The released Cu ²⁺ markedly promotes osteogenic differentiation of human bone marrow mesenchymal stem cells and angiogenesis of human umbilical vein endothelial cells, achieving dual functions of tumor therapy and bone regeneration.	49
Bone tumor	Cu-HHTP cMOF	It possesses efficient photothermal conversion capability for osteosarcoma ablation. Meanwhile, the hydrophilic interface improves cell adhesion and facilitates the bone repair process.	48
Bone tumor	CuFeSe ₂ nanocrystals	Efficient photothermal conversion can be realized under near-infrared irradiation to precisely ablate osteosarcoma cells. Simultaneously, calcium, silicon, phosphorus, iron, copper, and selenium ions released from material degradation synergistically promote osteogenic differentiation of bone marrow stromal cells and accelerate bone regeneration.	35
Bone tumor	PLA/PEG/NbC composite bone scaffold	In terms of photothermal therapy, the scaffold exhibits a significant inhibitory effect on HOS osteosarcoma cells. In addition, it displays excellent non-contact photothermal shape memory recovery performance.	36
Bone tumor	AuNPs@rGO composite photothermal coating	Under near-infrared irradiation, AuNPs enhance photothermal absorption via the “antenna effect,” enabling precise ablation of residual malignant bone tumor cells and inhibiting postoperative recurrence. The introduction of rGO improves the electrical conductivity and biological activity of the coating and promotes proliferation and differentiation of osteoblasts.	88
Bone tumor	α/β -TCP biomimetic cancellous bone scaffold	The α/β -TCP biomimetic cancellous bone scaffold possesses high mechanical strength and mimics the structure and composition of natural cancellous bone. The incorporation of tea polyphenol–magnesium nanoparticles endows the scaffold with prominent antibacterial properties and optimizes the early microenvironment of infected bone defects.	89
Bone tumor	nHA/nMg-aDNA/PLA 3D-printed theragenerative scaffold	Mg-containing nanospikes in a 3D-printed nHA/aDNA/PLA scaffold provide photothermal hyperthermia against osteosarcoma and bacteria, whereas aDNA promotes vascularized bone healing, enabling time-regulated tumor ablation, antibacterial protection, angiogenesis, and osteogenesis.	90
Bone tumor	TS@PAP composite scaffold	The scaffold presents a significant killing effect on five human osteosarcoma cell lines and effectively prevents local postoperative recurrence of osteosarcoma. Meanwhile, the titanium alloy matrix provides reliable mechanical support for bone defects.	91
Bone tumor	ZIF-8/Ti microwave-responsive composite scaffold	Microwave-responsive ZIF-8 loaded with a chemotherapeutic drug and an immune checkpoint inhibitor is integrated onto 3D-printed Ti scaffolds. Microwave hyperthermia plus chemotherapy induces immunogenic tumor death, checkpoint inhibition enhances antitumor immunity and suppresses recurrence, and ZIF-8-derived Zn ²⁺ promotes osteogenesis while porous Ti provides mechanical support.	92
Bone tumor	MeCFO/GelMA	Cobalt ferrite enables magnetic hyperthermia under an alternating magnetic field. It can not only efficiently kill osteosarcoma cells but also stimulate osteogenic differentiation and mineralization of bone marrow mesenchymal stem cells, realizing dual functions of magnetothermal antitumor therapy and bone reconstruction.	24
Breast cancer	(c-AuNR)-embedded 3D-printed hydrogel nanocomposite	The unique optical response of chiral plasmons effectively weakens background scattering interference from the hydrogel matrix; meanwhile, non-invasive monitoring of hydrogel structural remodeling is achieved.	93

(Cont'd...)

Table 4. (Continued)

Tumor type	3D-printed metal-based nanocomposites	Core mechanism	References
Breast cancer	FeMg-SC	Bimetallic components synergistically exert dual functions of treatment and repair. Iron ions cooperate with polydopamine-mediated photothermal therapy through chemodynamic therapy to eliminate bone metastatic tumors, while sustained slow release of magnesium ions regulates osteoblast differentiation, simultaneously eliminating metastatic lesions and repairing bone defect tissues.	62
Breast cancer	3D-printed biodegradable multifunctional implant	The first layer loads chemotherapeutic drug 5-FU for long-term sustained release, and the second layer incorporates gold nanoparticles to enhance local radiation killing efficacy via radiosensitization. The dual synergistic effect effectively inhibits residual local breast tumor lesions and reduces the risk of postoperative recurrence.	95
Breast cancer	Bi ₂ S ₃ @BSA/alginate implantable radiosensitizer scaffold	BSA-coated Bi ₂ S ₃ high-Z nanoparticles are co-printed with alginate into implantable scaffolds. Under X-ray irradiation, the scaffolds amplify ROS generation and 4T1 tumor-cell killing; implantation beneath 4T1 tumors suppresses tumor growth after a single 4 Gy dose without obvious major-organ toxicity.	96
Breast cancer	BSA Cu(DDC) ₂ MON	It activates the disulfiram-copper combined therapeutic pathway in breast cancer cells and exerts antitumor effects through ROS-mediated cytotoxicity.	97
Breast cancer	3D-printed biodegradable microswimmer	The hydrogel skeleton loads superparamagnetic iron oxide nanoparticles, enabling targeted locomotion of the microswimmer under an external rotating magnetic field. Overexpression of MMP-2 in the tumor microenvironment triggers enzymatic degradation of the hydrogel, thereby accomplishing targeted delivery, controlled drug release, and integrated non-invasive magnetic resonance imaging diagnosis and treatment.	98
Breast cancer	Au-BPE@3D-printed microchannel biosensor	Relying on the signal amplification effect of AuNPs and specific recognition capability of aptamers, ultrasensitive quantitative detection of breast cancer cells is realized.	99
Cervical cancer	Therapeutic nanoparticle-loaded Pluronic F127/alginate 3D-printable hydrogel delivery system	Pluronic F127/alginate composite hydrogel exhibits temperature-responsive sol-gel transition behavior and excellent 3D-printable rheological properties, which can stably encapsulate therapeutic nanoparticles. After 3D printing and implantation into cervical lesions, slow hydrogel erosion and porous network diffusion achieve long-term and controlled nanoparticle release, elevate local tumor enrichment concentration, reduce systemic side effects, and realize efficient local treatment of cervical cancer.	82
Cervical cancer	3D-printed radioactive brachytherapy implant	The core therapeutic mechanism relies on radiosensitization. 3D printing enables precise customization of implant and hydrogel pad size and configuration according to tumor size and morphology. As high-efficiency radiotherapy sensitizers, AuNPs induce ROS generation by producing low-energy photons and electrons during brachytherapy, thereby destroying the DNA structure of tumor cells.	100
Malignant esophageal stricture (Esophageal cancer)	Gold nanoshell-modified 3D-printed multifunctional esophageal stent	As high-efficiency photothermal conversion agents, Au nanoshells generate localized hyperthermia under laser irradiation and simultaneously activate temperature-responsive coatings to control antitumor drug release.	103
Digestive system tumors	Cu _{2-x} Ag _x S@liposome nanocomposite 3D-printed detection device	Cu _{2-x} Ag _x S nanoparticles possess outstanding photothermal conversion efficiency. Upon near-infrared excitation, distinct temperature signal variations are generated, recorded by a portable thermal imager, and further evaluated via a smartphone.	104

(Cont'd...)

Table 4. (Continued)

Tumor type	3D-printed metal-based nanocomposites	Core mechanism	References
Liver cancer	AgNPs-functionalized 3D-printed SERS chip	It can target and recognize denatured collagen and achieve efficient Raman signal amplification relying on the strong surface plasmon resonance effect of AgNPs. 3D printing precisely constructs the 3D microstructure of the chip, enabling efficient capture and enrichment of collagen biomarkers in serum.	105
Liver cancer	Portable micro-nanochannel bio-3D-printed liver microtissue biosensor	The micro-nanochannels simulate the physiological microenvironment of the liver and maintain the metabolic and biological functions of hepatocytes. When deoxynivalenol invades liver microtissues, it induces hepatocyte injury and changes in the electrochemical potential of the microenvironment. Magnetic nanomaterials mediate signal transduction and amplification, realizing highly sensitive detection of hepatotoxic substances and providing a novel bionic sensing strategy for liver injury screening and hepatotoxicity evaluation.	106
Liver cancer	Hepar-on-a-chip	The 3D-bioprinted liver organ chip is integrated with graphene-based gold plasmonic sensing materials. The 3D biomimetic microenvironment maintains the physiological functions of hepatocytes, while the plasmonic resonance of AuNPs and the optoelectronic conduction advantages of graphene sensitively capture toxin-induced alterations in the hepatocyte microenvironment, achieving highly sensitive detection of liver injury and precise evaluation of drug hepatotoxicity.	107

Abbreviations: 5-FU: 5-Fluorouracil; aDNA: Adhesive DNA; AgNPs: Silver nanoparticles; AuNPs: Gold nanoparticles; BPE: Bipolar electrode; BSA: Bovine serum albumin; c-AuNRs: Chiral gold nanorods; cMOF: Conductive metal-organic framework; DDC: Diethyldithiocarbamate; DNA: Deoxyribonucleic acid; GelMA: Gelatin methacryloyl; HHTP: 2,3,6,7,10,11-Hexahydroxytriphenylene; HOS: Human osteosarcoma; MeCFO: Methacrylate-functionalized cobalt ferrite; MMP-2: Matrix metalloproteinase-2; MON: Metal-organic nanoparticle; nHA: Nanohydroxyapatite; nMg: Magnesium-decorated nanospiked hydroxyapatite; NbC: Niobium carbide; PAP: Poly(ethylene glycol)-acetal-paclitaxel; PEG: Poly(ethylene glycol); PLA: Poly(lactic acid); rGO: Reduced graphene oxide; ROS: Reactive oxygen species; SERS: Surface-enhanced Raman scattering; TCP: Tricalcium phosphate; TCPP: Tetrakis(4-carboxyphenyl)porphyrin; TS: Titanium scaffold; ZIF-8: Zeolitic imidazolate framework-8.

6. Challenges, clinical translation, and future perspectives

6.1. Process-specific nanomaterial stability and characterization

Each additive manufacturing process imposes a distinct physicochemical stress on metal-based nanomaterials, and the resulting changes in crystal phase, redox valence, and surface ligands must be verified experimentally rather than assumed. FDM is the most thermally demanding of the polymer-based routes. Nanoparticles reside within molten polymer at 180 °C–250 °C for extended periods. These conditions can oxidize redox-active phases (e.g., oxidation of Fe²⁺ to Fe³⁺ in magnetite and Cu⁺ to Cu²⁺ in copper sulfides), strip labile surface ligands, and promote particle coarsening. Differential scanning calorimetry and thermogravimetric analysis of the composite filament, together with X-ray photoelectron spectroscopy of the printed part, constitute the minimum characterization set for this process.^{50,108} SLA/DLP impose a different stress.

Exposure to intense ultraviolet irradiation reduces metal ions, for example, Ag⁺ to Ag⁰ and Au³⁺ to Au⁰. This reduction is deliberately exploited to generate nanoparticles *in situ*,^{61,81} when unintended, however, it alters the oxidation state and dissolution behavior of pre-synthesized particles. Ultraviolet-visible and Fourier-transform infrared spectra recorded before and after curing provide direct evidence of such changes, while nanoparticle-induced light scattering additionally limits the cure depth.⁵⁸ In SLS/SLM, powders experience extreme thermal gradients. Crystal-phase transformation, surface oxidation, and partial melting of nanoscale additives are all documented risks, and their occurrence should be confirmed by X-ray diffraction and high-resolution transmission electron microscopy.^{67,68} SSE/DIW are chemically the mildest of these processes, but the high shear at the nozzle can align anisotropic nanoparticles or, for plate-like MXenes, induce their restacking. Rheological measurements, combined with scanning electron microscopy of filament cross-sections, are therefore recommended.⁶³⁻⁶⁵

6.2. Biocompatibility, biodegradation, and long-term biosafety

Although metal-based nanomaterials are routinely described as “biocompatible,” their toxicological profiles are in fact governed by valence state, administered dose, particle size, and dissolution kinetics. Within the acidic TME and in endo/lysosomal compartments, sustained ion release can initiate ROS-mediated oxidative stress, mitochondrial dysfunction, and inflammatory signaling.^{109,110} These are precisely the pathways exploited by CDT and PTT. Consequently, tumor selectivity arises from spatial confinement rather than from distinct molecular targets, and any off-target leakage is converted directly into systemic toxicity. Element-specific hazards compound this concern. Cu^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, and Mn^{2+} all perturb intracellular redox homeostasis, and chronic manganese overload is well documented to cause neurotoxicity. Ag^+ binds avidly to thiol groups, is cleared slowly, and may produce argyria-like cutaneous deposition. Poorly degradable high-atomic-number elements, including gold, bismuth, platinum, tungsten, and gadolinium, preferentially accumulate in the liver, spleen, and kidney.^{109–111} *In vivo*, noble metals, high-atomic-number compounds, and carbides such as NbC are essentially non-biodegradable and are eliminated only through the slow dissolution of trace ionic species. By contrast, MnO_x , iron oxides, transition-metal sulfides, and zirconium-, iron-, or manganese-based MOFs degrade into ions that feed endogenous homeostatic pathways, with Cu^{2+} cleared predominantly via the hepatobiliary route.^{46,109} Importantly, degradability does not equate to safety. The degradation rate must be matched to the therapeutic window: excessively rapid dissolution can transiently exceed local tolerance, whereas excessively slow dissolution converts the scaffold into a long-term metal depot. Moreover, degradation behavior established for free intravenously administered nanoparticles cannot be assumed to transfer to matrix-embedded composites.¹⁰⁸ Accordingly, we recommend that future studies routinely incorporate standardized *in vitro* cytotoxicity panels that include normal cell types such as fibroblasts, hepatocytes, and neurons; long-term (at least six months) implantation studies in large animals with histopathological examination of both per-implant and distal organs together with biodistribution tracking; hemocompatibility and immunotoxicity assessment; and structure-toxicity correlation reporting that specifies loading fraction, particle size, and ligand chemistry. Only in this way can biosafety be established as a design variable rather than a post hoc observation.

6.3. Nanoparticle retention, release kinetics, and systemic safety of implants

Retention behavior is dictated primarily by how nanoparticles are incorporated into the composite. In physically blended systems, nanoparticles are held in place only by van der Waals forces and polymer chain entanglement, giving rise to a pronounced initial burst followed by release governed by diffusion and matrix erosion.⁸³ Nanoparticles synthesized *in situ* become partially embedded within the matrix wall, which markedly suppresses the burst phase; release is thereafter dominated by slow ion liberation as the scaffold degrades.^{81,86} Surface-modified scaffolds concentrate nanoparticles at the scaffold–tissue interface and thereby maximize local availability, although initial surface release is comparatively rapid, and covalent coatings retain particles far more effectively than electrostatic adsorption.^{31,84} Directly comparable, quantitative leakage data, ideally expressed as cumulative mass percent released over time under identical sink conditions, remain scarce and constitute an important gap in standardization. Once particles or ions escape the matrix, they enter the interstitial fluid and, depending on their size and solubility, drain toward regional lymph nodes or gain access to the systemic circulation. Local implantation nevertheless reduces systemic exposure substantially, because the scaffold functions as a depot. The same property, however, implies prolonged low-level exposure of adjacent tissues, the long-term consequences of which remain poorly characterized.¹⁰⁸ The central translational question is whether local concentrations can be maintained within the therapeutic window, high enough to sustain CDT and PTT yet below the toxicity threshold of healthy tissue. At present, this question rests largely on *in vitro* half-maximal inhibitory concentration values and short-term rodent studies. We therefore recommend that future studies routinely report (i) cumulative release profiles for both particles and ions, (ii) local versus systemic metal concentrations, and (iii) histopathology of per-implant and distal organs.

6.4. Sterilization, batch consistency, and regulatory landscape

Sterilization, a step that remains essentially unaddressed in this literature, interacts critically with the chemistry of nanocomposites. Autoclaving (typically 121 °C) is incompatible with polyester matrices such as PLA and PCL, because moist heat accelerates polymer hydrolysis.¹¹² Gamma irradiation, for which 25 kGy serves as the reference dose under ISO 11137, generates free radicals

that can crosslink or cleave the polymer chains and may reduce metal ions or strip surface ligands. Ethylene oxide sterilization (ISO 11135) operates at low temperature and is the chemically gentlest option, but it demands rigorous validation of residual gas. Low-temperature methods, namely ethylene oxide or hydrogen peroxide plasma, should therefore be prioritized for heat-labile polymer–nanoparticle composites, whereas all-metal implants produced by SLM tolerate both autoclaving and gamma irradiation.¹¹³ In every case, post-sterilization functional verification, including photothermal heating curves, magnetic heating efficiency, and ion-release profiles, should serve as a mandatory release test. Equally important, every printed implant must be demonstrably equivalent to the validated design.¹¹⁴ A tiered quality-control strategy can be built from four complementary tests: (i) micro-CT verification of pore size, porosity, and interconnectivity; (ii) scanning electron microscopy or transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy mapping to quantify dispersion uniformity and detect agglomerates; (iii) X-ray photoelectron spectroscopy to confirm oxidation state and ligand integrity after printing and sterilization; and (iv) inductively coupled plasma mass spectrometry of digested samples to assess batch-to-batch loading consistency. Quantitative acceptance criteria, for example, a threshold on the coefficient of variation of metal content, would convert qualitative claims of “uniform dispersion” into auditable manufacturing specifications. Finally, a 3D-printed implant that releases metal-based nanomaterials constitutes, in regulatory terms, a combination product whose classification determines the entire evidence pathway. In the United States, a primary structural or mechanical mode of action may place the product under the device regulatory framework, potentially involving a 510(k) premarket notification, De Novo classification, or premarket approval, whereas a primary pharmacological mode of action, as with chemodynamic metal ions, triggers drug review, with United States Food and Drug Administration guidance on nanotechnology additionally invoked. In the European Union, Rule 19 of Regulation (EU) 2017/745 (the Medical Device Regulation) assigns nanomaterial-containing devices to class IIb or III according to the potential for internal exposure and the hazard profile of the material. In China, the National Medical Products Administration regulates additively manufactured implants as medical devices, while patient-matched devices fall under the customized-device provisions and require supplementary safety evaluation of the nanomaterial component. Across all three jurisdictions, the evidentiary pillars are remarkably consistent: ISO 10993 biocompatibility testing, sterilization

validation, shelf-life stability, and manufacturing quality control.¹¹⁵ Early engagement with regulators should therefore be treated as a design-stage decision rather than a post-development formality.¹¹⁶

6.5. Tumor microenvironment adaptability and scalable manufacturing

Even when integrity, retention, and biosafety are adequately addressed, performance ultimately depends on interaction with the TME, the least controlled variable in the field. Elevated interstitial fluid pressure and collapsed vasculature limit convective transport. Dense, cross-linked extracellular matrices restrict nanoparticle penetration to a few hundred micrometers, a range comparable to the roughly 100 μm depth reported for AuNPs released from 3D-printed brachytherapy implants.¹⁰⁰ Immunosuppressive cell populations, meanwhile, blunt the very immune activation that many platforms are designed to induce.⁷⁵ As a result, effective concentrations at residual tumor cells frequently fall below therapeutic thresholds, imposing selective pressure that favors resistant clones and metastatic spread. TME adaptation should therefore be treated as an explicit design requirement. First, TME-responsive chemistries that respond to pH, ROS, enzymes, or hypoxia can confine release to pathological conditions, building on pH-responsive prodrug strategies developed on 3D-printed titanium scaffolds.⁹¹ Second, pore architectures and degradation rates should be engineered to remodel the peritumoral stroma rather than merely fill defects.³⁶ Third, immune effectors can be recruited deliberately, for example, through Mg^{2+} - or Cu^{2+} -mediated M1 macrophage polarization.^{37,89} Fourth, efficacy should be validated in immune-competent, orthotopic, and organoid models rather than in subcutaneous xenografts.¹¹⁷ A parallel practical barrier is manufacturing itself. Personalized implants currently involve manual image segmentation, design, ink preparation, and post-processing, and each step constitutes a variability bottleneck. Meaningful progress requires design standardization, through modular, parametrically tunable scaffold libraries that echo design-control principles; design automation, through artificial intelligence-assisted image-to-scaffold pipelines and topology optimization; process intensification, through high-throughput printing arrays with in-line rheological monitoring and closed-loop feedback; and cost rationalization, for example, through improved SLM throughput and powder recycling for metallic implants.¹¹⁸ Scalability and personalization are not mutually exclusive. Point-of-care printing hubs operating under standardized, regulator-audited workflows offer a plausible translational model. It should be noted, however, that to the best of our knowledge and based on publicly available trial registries,

no 3D-printed implant or device incorporating metal-based nanomaterials for cancer theranostics has yet been registered in a clinical trial. This review has therefore drawn exclusively on preclinical evidence, a situation that in itself reflects the developmental stage of the field. The nearest translational anchors are instructive in their limitations. AGuIX gadolinium nanoparticles are being evaluated in the phase I/II NANOCOL trial for locally advanced cervical cancer,¹⁰² yet this is an intravenously administered nanodrug assessed in conjunction with 3D cell models, not a printed nanocomposite device. Conversely, 3D-printed titanium alloy implants and SLM-fabricated tungsten collimators are already in routine clinical use,^{30,68} but they carry no nanoparticle-mediated therapeutic function. In other words, the two enabling technologies have each reached the clinic independently, while their integration, the subject of this review, remains largely at the preclinical stage. This preclinical-to-clinical gap appears to reflect the compounded evidentiary burdens identified above. Nanoparticle biosafety, release and therapeutic-window data, sterilization and batch consistency, and TME-relevant efficacy models must all be satisfied simultaneously within a single combination product. We therefore regard the current scarcity of clinical translation not as a limitation of this review's coverage but as arguably one of the field's most important unmet milestones. We would also caution against the assumption that personalized printing necessarily accelerates translation: in the absence of standardized evidence packages acceptable to regulators, customization may add regulatory complexity rather than reduce it.

6.6. Future perspectives and outlook

The challenges outlined above collectively define a coherent research agenda. At the material level, degradable and low-toxicity nanomaterials should be engineered around single-atom catalysts,¹¹⁹ core-shell architectures, and precise ligand modification, and assembled into nano-units that integrate TME responsiveness, active targeting, and immune activation within a single construct. At the manufacturing level, mild printing conditions and *in situ* functionalization, such as low-temperature photocuring, shear-optimized bioinks, and coaxial or gradient printing, guided by artificial intelligence and topology optimization, can minimize nanoparticle inactivation while precisely matching porosity, mechanics, degradation, and release kinetics. At the mechanistic level, quantitative structure-function-efficacy mapping is urgently needed, including the molecular circuitry underlying ferroptosis and cuproptosis induction and antitumor immune activation,¹¹⁷ so that empirical iteration can give way to predictive design. At the translation level, standardized preclinical pipelines

based on organoids, large-animal models, and defined endpoints, aligned with the biosafety, release-reporting, and quality-control frameworks proposed above, together with intelligent high-throughput fabrication, should be established. Finally, the most promising clinical niches are those in which 3D printing offers unique and difficult-to-replicate value: multimodal integrated theranostics, synergistic immunotherapy depots, and simultaneous postoperative repair with tumor suppression, a list that may be extended further by four-dimensional printing and real-time imaging-guided therapy. With coordinated efforts spanning the full innovation chain, from materials science and additive manufacturing to nanomedicine and clinical oncology, 3D-printed metal-based nanocomposite systems are positioned to become a cornerstone platform for personalized precision cancer theranostics.

7. Conclusion

The integration of 3D-printing techniques with metal-based nanomaterials offers promising opportunities for cancer theranostics. This review has summarized representative categories of metal-based nanomaterials, compatible 3D-printing approaches, and three major composite fabrication strategies. The preclinical applications of these platforms in bone and tumors of the breast, reproductive system, and digestive system have demonstrated considerable potential for combined tumor ablation and tissue reconstruction. Nevertheless, several bottlenecks remain to be addressed, including nanomaterial stability during printing, long-term biosafety, controlled nanoparticle release, batch consistency, and regulatory barriers. Further advances in material design, manufacturing optimization, and preclinical model development will facilitate the clinical translation of such multifunctional 3D-printed theranostic platforms for precision oncology.

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Conflict of interest

The authors declare that they have no competing interests.

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