processes

MDPI

Review

Polymer/Graphene Nanocomposites via 3D and 4D Printing—Design and Technical Potential

Ayesha Kausar [1,2,3,*], Ishaq Ahmad [1,2,3], Tingkai Zhao [1,4], O. Aldaghri [5] and M. H. Eisa [5]

[1] NPU–NCP Joint International Research Center on Advanced Nanomaterials and Defects Engineering, Northwestern Polytechnical University, Xi'an 710072, China
[2] UNESCO–UNISA Africa Chair in Nanosciences/Nanotechnology, iThemba LABS, Somerset West 7129, South Africa
[3] NPU–NCP Joint International Research Center on Advanced Nanomaterials and Defects Engineering, National Centre for Physics, Islamabad 44000, Pakistan
[4] School of Materials Science & Engineering, Northwestern Polytechnical University, Xi'an 710072, China
[5] Department of Physics, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh 13318, Saudi Arabia
* Correspondence: dr.ayeshakausar@yahoo.com

Abstract: Graphene is an important nanocarbon nanofiller for polymeric matrices. The polymer–graphene nanocomposites, obtained through facile fabrication methods, possess significant electrical–thermal–mechanical and physical properties for technical purposes. To overcome challenges of polymer–graphene nanocomposite processing and high performance, advanced fabrication strategies have been applied to design the next-generation materials–devices. This revolutionary review basically offers a fundamental sketch of graphene, polymer–graphene nanocomposite and three-dimensional (3D) and four-dimensional (4D) printing techniques. The main focus of the article is to portray the impact of 3D and 4D printing techniques in the field of polymer–graphene nanocomposites. Polymeric matrices, such as polyamide, polycaprolactone, polyethylene, poly(lactic acid), etc. with graphene, have been processed using 3D or 4D printing technologies. The 3D and 4D printing employ various cutting-edge processes and offer engineering opportunities to meet the manufacturing demands of the nanomaterials. The 3D printing methods used for graphene nanocomposites include direct ink writing, selective laser sintering, stereolithography, fused deposition modeling and other approaches. Thermally stable poly(lactic acid)–graphene oxide nanocomposites have been processed using a direct ink printing technique. The 3D-printed poly(methyl methacrylate)–graphene have been printed using stereolithography and additive manufacturing techniques. The printed poly(methyl methacrylate)–graphene nanocomposites revealed enhanced morphological, mechanical and biological properties. The polyethylene–graphene nanocomposites processed by fused diffusion modeling have superior thermal conductivity, strength, modulus and radiation- shielding features. The poly(lactic acid)–graphene nanocomposites have been processed using a number of 3D printing approaches, including fused deposition modeling, stereolithography, etc., resulting in unique honeycomb morphology, high surface temperature, surface resistivity, glass transition temperature and linear thermal coefficient. The 4D printing has been applied on acrylonitrile-butadiene-styrene, poly(lactic acid) and thermosetting matrices with graphene nanofiller. Stereolithography-based 4D-printed polymer–graphene nanomaterials have revealed complex shape-changing nanostructures having high resolution. These materials have high temperature stability and high performance for technical applications. Consequently, the 3D- or 4D-printed polymer–graphene nanocomposites revealed technical applications in high temperature relevance, photovoltaics, sensing, energy storage and other technical fields. In short, this paper has reviewed the background of 3D and 4D printing, graphene-based nanocomposite fabrication using 3D–4D printing, development in printing technologies and applications of 3D–4D printing.

Keywords: 3D printing; 4D printing; polymer; graphene; nanocomposite; photovoltaics; sensing

check for updates

Citation: Kausar, A.; Ahmad, I.; Zhao, T.; Aldaghri, O.; Eisa, M.H. Polymer/Graphene Nanocomposites via 3D and 4D Printing—Design and Technical Potential. *Processes* **2023**, *11*, 868. https://doi.org/10.3390/pr11030868

Academic Editors: Mohammad Boshir Ahmed, Md Ashraf Hossain, Mohammad Shamsuddin Ahmed and Jivan Thakare

Received: 11 February 2023
Revised: 3 March 2023
Accepted: 10 March 2023
Published: 14 March 2023

1. Introduction

Graphene has been used as an effective nanocarbon nanofiller for the polymers [1]. Graphene has been filled in numerous thermoplastics–thermosets, rubbers and conducting polymeric matrices. The nanocomposite properties have been found to enhance with small contents of graphene [2]. Various facile techniques have been used to attain the polymer–graphene nanocomposites having fine nanoparticle dispersion and superior physical properties [3]. The progressive polymer–graphene nanomaterials have been found useful in technical applications, such as energy, electronics, biomedical and engineering applications [4]. The three-dimensional (3D) and four-dimensional (4D) printing approaches have been used to design the polymer–graphene nanomaterials [5–7]. The 3D printing technique contains various processes, equipment and materials for the formation of three-dimensional objects. This approach involves the formation of 3D-printed objects using stereolithography, selective laser sintering, fused deposition modeling and other methods. The 4D printing technology is quite similar to 3D printing, however it uses advanced materials responsive towards heat, light, moisture, etc. The 3D and 4D printing techniques have been found applicable for the fabrication of graphene-based nanocomposites [8,9]. The 3D- and 4D-printed polymer–graphene revealed exclusive nanostructures and superior characteristics. The use of 3D and 4D printing for polymer–graphene nanomaterials led to several industrial developments in this field [10,11].

This review basically delivers fundamentals of graphene, polymer–graphene nanocomposites and 3D and 4D printing techniques. The main focus of this review is to portray the design, features and potential of 3D- and 4D-printed polymer–graphene nanocomposites. The review outline contains Section 1, i.e., Introduction; Section 2 on graphene and polymer–graphene nanocomposites; Section 3 for essential features of 3D and 4D printing techniques; Section 4 dedicated to 3D–4D printing polymeric–graphene nanocomposites; Section 5 explaining the working principle or mechanism of 3D–4D printing technology for polymeric–graphene nano-composites; Section 6 concerning the potential of 3D–4D printing polymeric–graphene nanocomposites; and finally, Section 5 on viewpoint and conclusions. All the sections thoroughly and comprehensively describe the outlined contents. In this leading-edge review, various notable prospects of the 3D–4D printing technology for polymeric–graphene nano-composites have been highlighted. Especially, the design versatilities, essential features and significance of 3D–4D-printed polymer–graphene nanocomposites have been stated. In this regard, indispensable aspects of various 3D–4D-printed nanocomposite systems prepared using polymers and graphene have been considered. To the best of knowledge, such a specific recent review on 3D–4D-printed polymer–graphene nanocomposites has not been seen in literature before with such well-arranged and well-interpreted recent literature and specified outline. However, on this particular review topic, some previous research reports have been observed, yet the reported literature is not in a compiled and updated form to portray the current state and potential of 3D–4D-printed polymer–graphene nanocomposite technology. Furthermore, future advances in the field of 3D–4D-printed nanocomposites are not possible for scientists–researchers before getting prior knowledge of the recent assembled literature. Therefore, this revolutionary review is designed to compile and discuss significant recent literature and advancements of these nanocomposites fabricated by 3D–4D printing techniques. In a few words, this article proposes a groundbreaking overview on the potential of polymer and graphene-based nanomaterials manufactured using printing technologies. Despite the notable properties and technical applications of the printing techniques, dedicated future research efforts are required to form high-performance 3D–4D-printed polymer–graphene nanocomposite to overcome the related challenges.

2. Graphene and Polymer–Graphene Nanocomposites

Graphene is a one-atom-thick two-dimensional nanocarbon [12]. Among carbon nanoparticles, graphene has been designated as a significant nanofiller [13]. Graphene has also been used as a source material to form other nanocarbons [14]. Graphene has a honeycomb lattice structure, consisting of sp^2 hybridized carbon atoms [15]. In graphite, graphene can be seen as stacked nanosheets, held together by van der Waals forces (Figure 1) [16,17]. Graphene has large specific surface area, high Young's modulus, strength, thermal conductivity, electron mobility and other essential characteristics [18]. Several modified forms of graphene have also been prepared, such as graphene oxide and reduced graphene oxide [19,20]. Graphene oxide is the most frequently explored oxidized form of graphene, which is usually prepared by Hummer's method [21]. Further, the reduction of graphene oxide has been performed to obtain reduced graphene oxide [22].

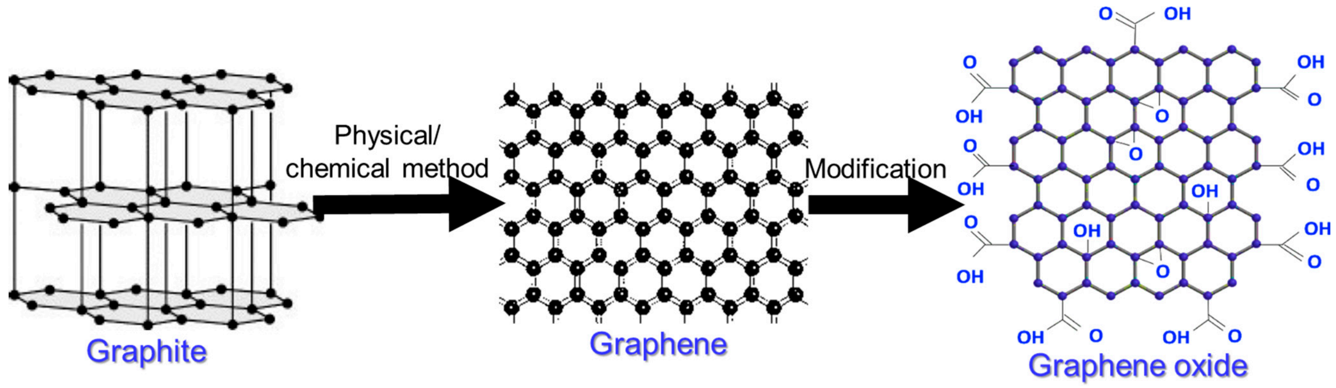


Figure 1. Graphene and modification.

Several manufacturing approaches—such as non-covalent process [23], covalent reactions [24], chemical deposition [25], electrochemical way [26], electrophoresis [27], hydrothermal technique [28], solvothermal growth [29,30] and several physical deposition techniques [31,32]—have been used to form graphene and functional graphene. The non-covalent methods develop non-covalent interactions between graphene nanosheets and other molecules. Graphene may develop π–π stacking interactions [33,34], electrostatic connections [35] and hydrophobic interactions [36]. Covalent modification of graphene may develop covalent bonding of nanosheets with different molecules through atom transfer radical polymerization [37,38], click chemistry [39] and other methods. Then the in-situ process has also been applied to develop the interactions of nanoparticles to the graphene surface [40–42]. In polymeric nanocomposites, graphene and modified graphene forms have been used as nanofillers. Owing to unique structure and properties, graphene has wide-ranging applications in technical fields, including energy devices, electronics, biomedical and nanocomposites [43,44]. Graphene dispersion has been considered important to form high-performance polymer–graphene nanocomposites [45].

Graphene has been developed as a cost-effective nanofiller for polymers having exciting physical properties [46]. Graphene has been filled in the polymers using several facile fabrication methods [47]. In this regard, graphene dispersion and matrix-nanofiller interactions have been used to enhance the compatibility of the nanocomposites [48]. The functional forms of graphene have capability of better dispersion and interface formation with the polymers. The resulting polymer–graphene nanocomposites have a number of superior characteristics, such as electrical, mechanical, thermal, non-flammability and other physical properties (Figure 2) [49].

Incidentally, several polymers and fabrication methods have been used to form the polymer–graphene nanocomposites. Zhang et al. [50] formed the polyethylene glycol and graphene-based nanocomposites through solution technique. The nanocomposites were investigated for graphene dispersion and thermal stability properties. Liu and co-workers [51] produced the polyethylene glycol–graphene-derived nanocomposites via freezing–drying method. The nanocomposites have been applied as biocompatible systems [52]. Zhang et al. [53] used the in-situ technique to manufacture the polyaniline–graphene nanocomposite. The aniline monomer was adsorbed on the graphene surface and then polymerized using initiator [54,55]. The resulting polyaniline–graphene nanocomposite was used to form the stretchable electronics [56,57]. Similarly, a number of other thermoplastic, thermosets and rubbery polymers have been reinforced with graphene to fabricate the nanocomposites [58]. Figure 3 portrays the multifunctional application areas of the high-performance polymer–graphene nanocomposites.

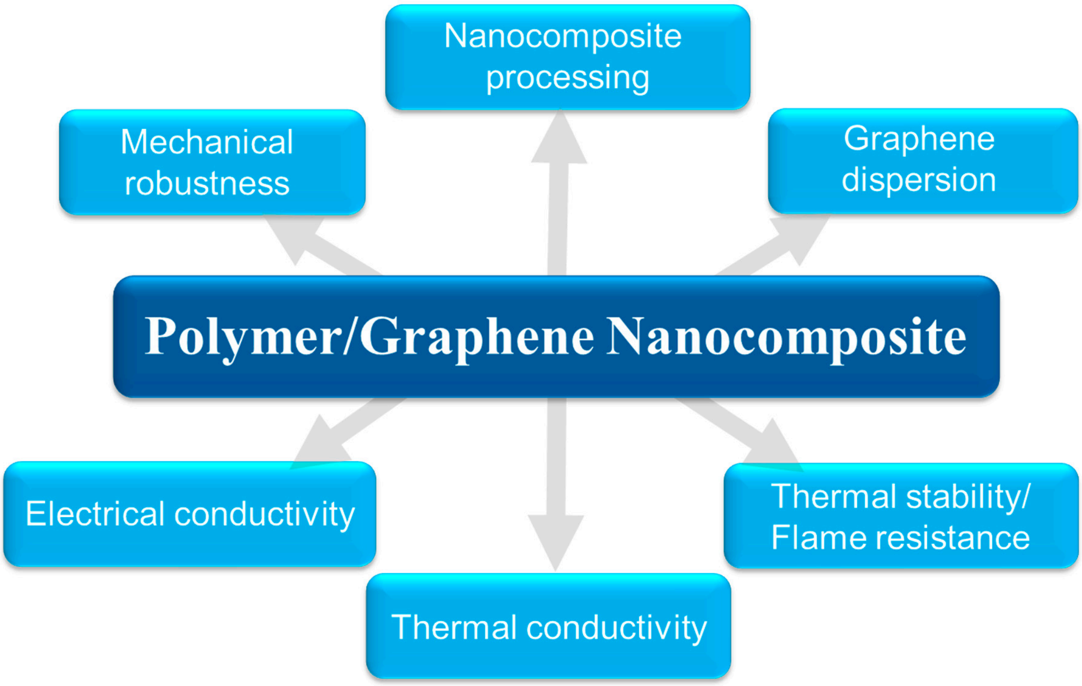


Figure 2. Properties of polymer–graphene nanocomposite.

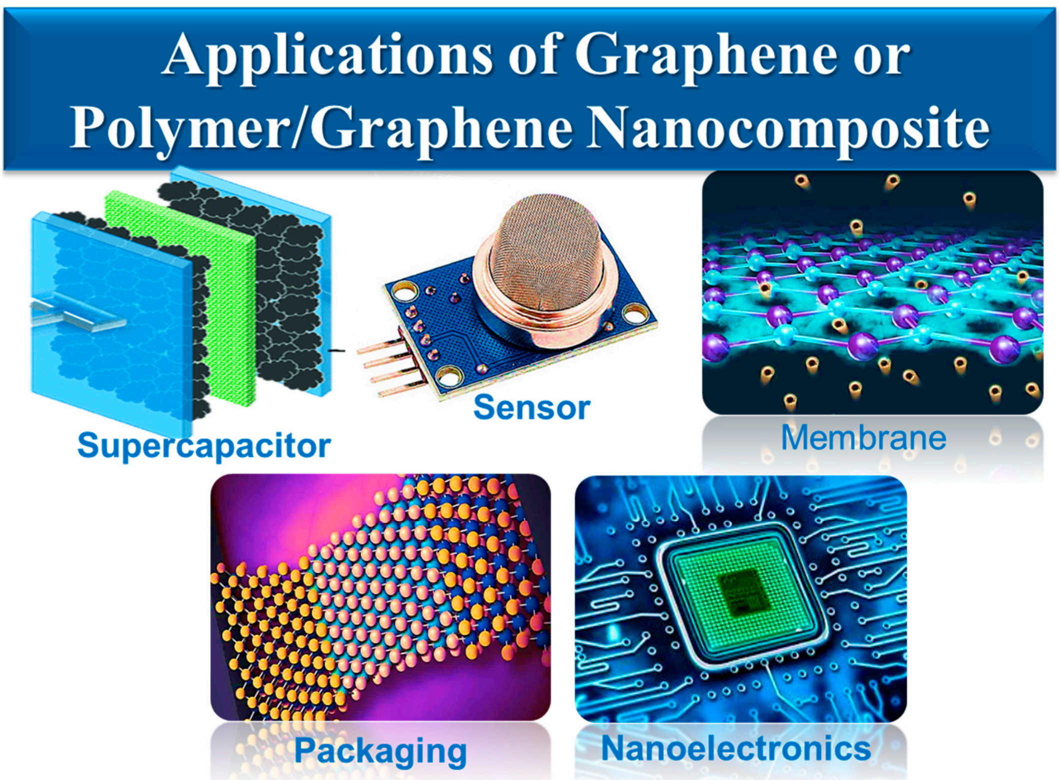


Figure 3. Applications of polymer–graphene nanocomposite.

3. Features of 3D and 4D Printing Techniques

The 3D printing is an efficient fabrication technique to develop 3D-printed objects, using appropriate processes [59]. Over past decades, 3D printing has emerged as a significant technology [60]. The controlled deposition of printable material is usually needed for facile 3D printing. An important 3D process is the layered deposition technique, which is also known as additive manufacturing [61,62]. The efficiency of 3D printing technique depends upon the choice of printable material, morphology, cost, structural complexity and selection of manufacturing process [63]. Moreover, in additive manufacturing technique, the structural geometry depends on the complexity of method [64]. In addition to additive method, the subtractive manufacturing approach has been effectively used to form the 3D-printed objects [65]. Stereolithography, selective laser sintering, fused deposition modeling, laminated object manufacturing, selective layer melting, electron beam melting, etc. have been used for the 3D printing. The printing processes have relative advantages and disadvantages to be employed for the material fabrication. Figure 4 shows the commercially available 3D printing processes having low cost and time effectiveness. Table 1 shows the advantages and challenges related to the 3D additive manufacturing process.

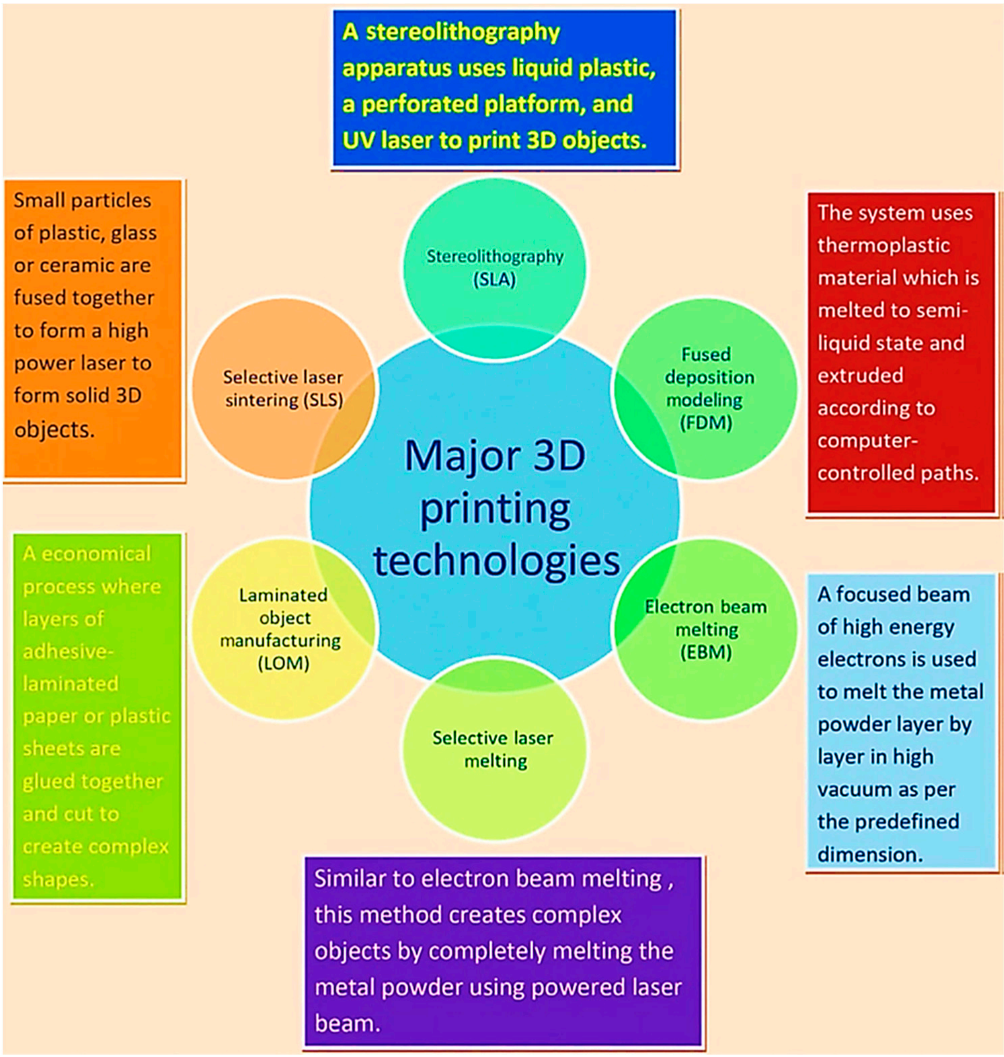


Figure 4. 3D printing technologies [59]. Reproduced with permission from Elsevier.

Table 1. Advantages and challenges of 3D additive manufacturing [64]. Reproduced with permission from Elsevier.

Advantages	Challenges
Formation of customized products from small batches, as compared to traditional mass production methods	• Production cost • Production speed must be improved
Possibility to produce 3D models directly without using any tools and molds is not required.	• Modification of additive manufacturing approach and other 3D printing approaches • Development of additive manufacturing beyond rapid prototyping • Formation of direct components and products
Can be designed in the form of digital files to easily share and facilitate the modification and customization of components and products	• To improve manufacturing efficiency • To develop and standardize new materials
Material can be saved due to the additive nature of the process. The waste materials (powder, resin) during manufacturing can be reused.	• Post processing is required • To recycle the support structure materials by minimizing the need through a good build-up orientation
Possibility to achieve novel and complex structures	• To develop multi-material and multicolor systems
Very low porosity of final products	• Stepping effect may arise from placing one layer on top of another for producing finishing layers • To validate mechanical and thermal properties
Due to the distribution, the direct interaction between local consumer or client and producer is possible.	• Issues such as intellectual property rights and nonlinear collaboration with ill-defined roles and responsibilities
Efficient printing processes, such as FDM, SLA, SLS, etc.	• Designers and engineers with deficit skills in additive manufacturing and other 3D printing approaches

Evolutions in printing technologies led to the invention of 4D printing [66]. Unlike 3D printing, 4D printing involves self-assembling of printed materials in response of external stimuli [67]. The 4D printing processes have been found innovative due to stimuli responsive programming [68]. Figure 5 proposes an outline of the 4D printing technology. Compared with 3D printing, 4D printing comprises time dimensions and monitoring. The 4D printing technique has been used for the fabrication of multipurpose next-generation sensors, actuators, self-assembling structures, robotics and other dynamic devices [69,70]. The 3D and 4D printing methods have been used in the fields of aerospace, automotive, robotics, electronics, medical implants, etc. [71,72]. Both the 3D and 4D printing procedures demand the control of manufacturing parameters, which in turn control the mechanical and geometrical properties of the printed objects [73,74]. In addition to the polymers or nanocomposites, the 3D and 4D printing techniques have also been used for metal-based materials [75]. Consequently, the advanced printing technologies have potential for future designing and manufacturing of the advanced materials [76].

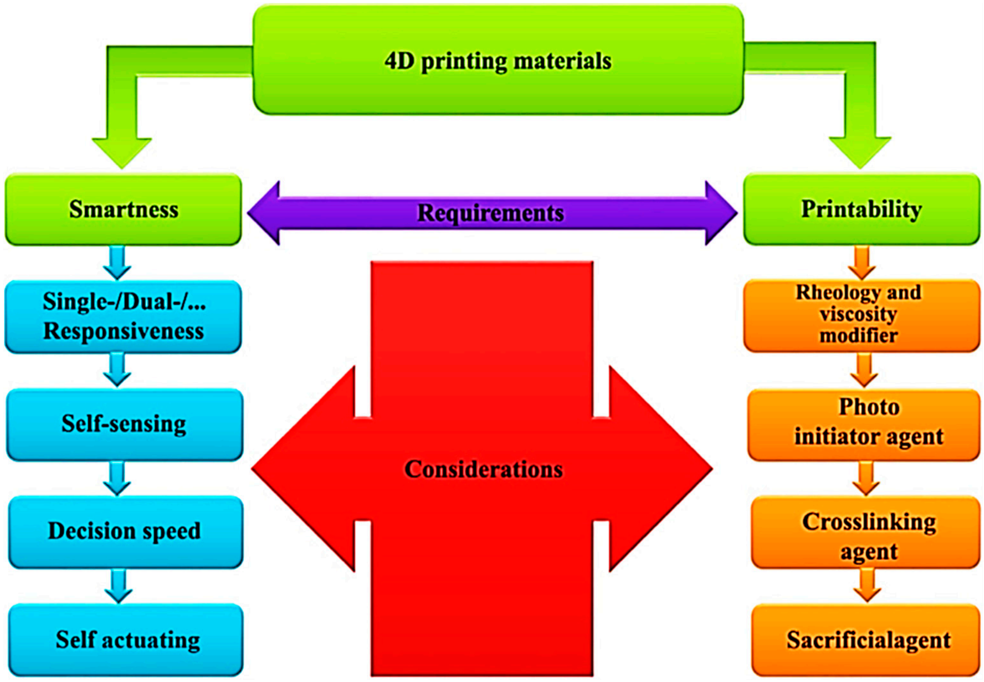


Figure 5. 4D printing methodologies [7]. Reproduced with permission from Elsevier.

4. 3D–4D Printing Polymeric–Graphene Nanocomposites

Since past decades, significant advancements have been observed in the field of 3D and 4D printing technologies [77]. The 3D and 4D printing have been applied on thermoplastic polymers, organic–inorganic nanomaterials, metals, alloys and other materials. The 3D- and 4D-printed graphene nanomaterials have been investigated for advanced characteristics, processing, technical potential and challenges [78]. The 3D printing approaches used for the graphene nanomaterials include direct ink writing [79], inkjet 3D printing [80], selective laser sintering (SLS) [81], stereolithography (SLA) [82], fused deposition modeling (FDM) [83], extrusion printing [84], binder-jet printing [85] and others. Figure 6 presents set-ups for some important printing techniques used. Direct 3D printing is based on extruding a viscous material from a pressurized syringe to create 3D shape (Figure 6a). The syringe head can move in three dimensions, whereas the platform is stationary to form layer by layer. FDM printer functions on controlled extrusion of thermoplastic filaments (Figure 6b). In FDM, filaments melt into a semi-liquid state at nozzle and extruded layer by layer on platform where it solidifies into final parts. The printed product quality is controlled by varying the printing parameters. In stereolithography, a controlled UV-laser is applied to resin reservoir for photocuring and formation of a patterned layer (Figure 6c). Characteristic polymers used in SLA include acrylic and epoxy resins. Selective laser sintering technique is similar to SLA, as both techniques are based on powder processing. However, SLS uses a laser beam for controlled path scans and printing, instead of using a liquid binder (Figure 6d). Using high-power lasers fuses powders by molecular diffusion. The product resolution is unusually determined by powder particle size, laser power, scan speed, etc.

Selection of an appropriate printing approach is important to attain the desired nanomaterial with superior properties. Consequently, the performance of printed material depends on the polymer matrix, graphene dispersion, graphene functionality, matrix-nanofiller interaction, interface formation and printing parameters (type of process, printing direction, ink viscosity, etc.). The 3D-printed polymer–graphene nanomaterials have been studied for the electrical, thermal, mechanical and other essential physical characteristics [86]. In this regard, thermoplastic polymers have been used for 3D printing. Nevertheless, some thermosets and rubbery polymers have also been processed using 3D printing. The 3D direct ink writing process involves the extrusion of polymer–graphene nanocomposite using the pressurized syringe [87].

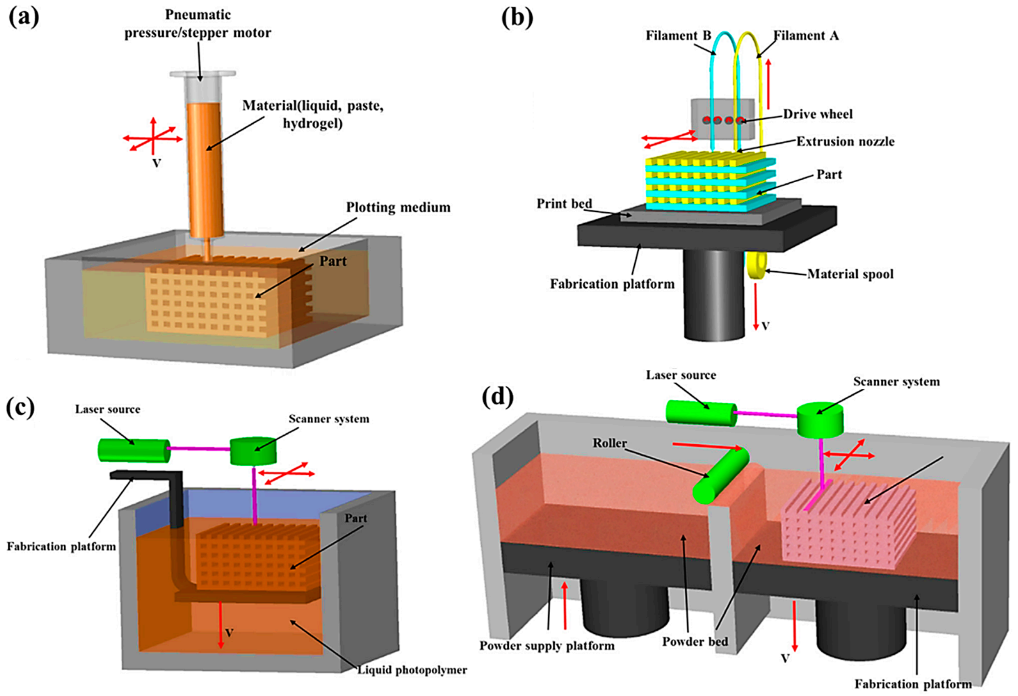


Figure 6. Schematic of (**a**) direct ink printing set-up; (**b**) FDM setup; (**c**) SLA setup; and (**d**) SLS setup [87]. FDM = fused deposition modeling; SLA = stereolithography; SLS = selective laser sintering. Reproduced with permission from Elsevier.

The syringe head moves three dimensionally to deposit the layer-by-layer material. The material viscosity and deposition speed define the product quality and properties of the printed nanocomposite. Moreover, the FDM has been found effective for printing the polymeric nanocomposite [88]. The thermoplastic polymers including poly(lactic acid), polycarbonate, acrylonitrile butadiene styrene, etc. have been processed through FDM. In this method, usually the melt extrusion of thermoplastic material and resulting filament can deposit layer by layer of material. The material is then solidified to obtain the end product. The product quality of FDM- based 3D-printed material relies on the printing parameters. SLA is another widely used 3D printing process. The SLA has been applied for the photopolymers and UV laser curing materials [89]. Using an SLA-based 3D-printing approach, the acrylic polymers and epoxy resins have been printed. Generally, the high-resolution objects have been developed via 3D printing, however it is an expensive method. For powder processing, the SLS technique has been used [90]. Typically, the powder material is sintered by heating with laser. The thermoplastic polymers, such as polyamide and polycaprolactone, have been processed using the SLS technique. The product quality and resolution of SLS-based 3D- printed objects depend on the particle size, laser power, scan speed and other parameters.

All these 3D techniques have relative advantages and disadvantages, which need to be considered before the selection of a printing process [91,92]. Qian and co-researchers [93] used the 3D direct ink printing technique for the poly(lactic acid)–graphene oxide nanocomposite. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) revealed enhanced melting temperature and thermal degradation temperature of the poly(lactic acid)–graphene oxide nanocomposite, relative to the neat poly(lactic acid). The enhancements in melting temperature of the 3D-printed poly(lactic acid)–graphene oxide nanocomposite was attributed to nanofiller dispersion and plasticity performance. Moreover, hydrogen bonding between the poly(lactic acid)–graphene oxide enhanced the matrix-nanofiller compatibility and led to high thermal stability of the nanocomposites (compared with the pristine polymer). Consequently, mechanical testing revealed high tensile strength of 3D-printed material, with 1.6 wt.% graphene oxide. The tensile strength was found 67.4% higher than the neat printed polymer. The growth in the strength of nanocomposites was due to homogeneous nanoparticle distribution in polymer using a printing technique leading to fine reinforcement effects. Thus, the 3D direct ink printing has been studied as an effective method to form high-performance nanocomposites.

Markandan and co-workers [94] fabricated the 3D-printed poly(methyl methacrylate)–graphene nanocomposite via SLA process. The 0.02–0.05 wt.% nanofiller contents enhanced the storage modulus and quasistatic failure strength of the poly(methyl methacrylate)–graphene nanocomposite. The enhancement in strength properties were credited to the facile SLA-based 3D printing approach used, causing better graphene dispersion and matrix-nanofiller interactions. Zou et al. [95] fabricated the digital light processing based 3D-printed poly(methyl methacrylate)–graphene nanocomposite. Inclusion of 1.0 wt.% graphene enhanced the microwave absorption performance of printed materials. At thickness of 2.1 mm, the maximum reflection loss of −54.4 dB was observed. Graphene addition and printing technique was accountable for enhanced radiation absorption features. Mangal et al. [96] fabricated 3D-printed poly(methyl methacrylate)–graphene nanocomposite with superior tribological properties. Inclusion of 0.1 wt.% nanofiller enhanced the surface hardness as $p < 0.001$ due to matrix-nanofiller compatibility. Salgado et al. [97] printed the poly(methyl methacrylate)–graphene nanomaterials using a liquid crystal display 3D printer. Inclusion of 0.01–0.5 wt.% graphene in bar-shaped specimens inhibited the microbial growth. Aati et al. [98] used additive manufacturing technology to print 3D poly(methyl methacrylate)–graphene nanomaterials. The 3D- printed nanocomposite with 0.25 wt.% graphene had enhanced antimicrobial features for dental applications. The 3D printing technology offered feasibility of developing high performance biocompatible and antimicrobial nanocomposites with improved properties.

Jing et al. [99] designed FDM-based 3D printing low density polyethylene–graphene nanocomposites. The FDM-based 3D-printed materials own high flexibility for structural designs. Moreover, superior mechanical properties were observed due to interfacial bonding strength between matrix and nanofiller. In addition, graphene dispersion and alignment by printing technique offered high electromagnetic interference shielding of 318 dB. The nanocomposites were suggested for the development of portable electronics and smart devices. Mohan et al. [100] designed 3D-printed low-density polyethylene–graphene nanoplatelets nanocomposites. Due to homogeneous nanofiller dispersion, the reinforcement effect was observed in the form of increase in tensile strength by 13.2% and flexural strength by 31.9%, relative to the non-printed compression molded nanocomposites. Younes et al. [101] produced polyethylene Fe_3O_4@graphene using layer-based 3D printing. Inclusion of Fe_3O_4@graphene and use of layer-based printing caused alignment of nanocomposite with magnetic field. The 0.4–1.6 wt.% nanofiller revealed 90% alignment in the matrix. The Young's modulus of the nanocomposites was considerably enhanced with nanofiller addition due to structure–mechanical property relationship and reinforcement effect [102–104]. Jing et al. [105] designed the polyethylene–graphene nanoplatelet nanocomposite using FDM-based 3D printing. Along the printing direction, through-plane thermal conductivity of the polyethylene–graphene nanoplatelet was enhanced up to 3.43 W m^{-1} K^{-1}. However, lower thermal conductivity of the FDM-based 3D-printed pristine polyethylene was observed ~0.40 Wm^{-1} K^{-1}. The enhancement in thermal conductivity was attributed to the development of complex morphology using FDM method supporting the thermal transportation in the nanomaterials. Camargo et al. [106] applied FDM-based 3D printing for the poly(lactic acid) and poly(lactic acid)–graphene nanocomposite. The 3D-printed materials were developed having complex geometries. The 3D processed poly(lactic acid)–graphene nanocomposite revealed high tensile strength and flexural strength, relative to neat printed polymer. Enhancement in the strength was suggested to the maximum reinforcement effect due to the large surface area of contact between the matrix and the nanofiller. The maximum reinforcement effect was obviously due to the FDM method applied. Ivanov et al. [107] developed poly(lactic acid) and poly(lactic acid)–graphene nanocomposite via FDM-based 3D printing. Fine nanofiller dispersion led to enhanced thermal conductivity of the nanocomposite, as compared to the pristine polymer. Bustillos et al. [108] also fabricated the poly(lactic acid) and poly(lactic acid)–graphene nanocomposite via FDM-based 3D printing technique. Figure 7 shows the morphology of 3D-printed scaffolds having interconnected porous structures. Well-defined pore size and pore size distribution were observed. A gradient pore size was used to study the differentiation and proliferation, as per the pore size distribution. Three-dimensional-printed scaffold structures revealed porosity of 13.663.2% and full connectivity throughout the structure. As compared to neat poly(lactic acid), inclusion of graphene nanofiller produced rough and irregular surface due to porous nature of the PLA-graphene. Table 2 displays the glass transition temperature (T_g) of 3D-printed and -non-printed poly(lactic acid) and poly(lactic acid)–graphene nanocomposite. After 3D printing, an increase in T_g of the filaments was observed due to the better interactions between the polymer and graphene to form a stable structure. Moreover, crystallization was increased due to the nucleating effect of the dispersed graphene nanoparticles. Figure 8 shows the load-displacement curves obtained from nanoindentation of 3D-printed neat polymer and nanocomposite. According to analysis, 3D-printed nanocomposite exhibited increase in elastic modulus and resistance to displacement by 11% and 25%, respectively, as compared to neat polymer. Due to effectiveness of FDM technique, the nanoparticle dispersion and bonding between polymer and reinforcement were enhanced leading to improved mechanical properties.

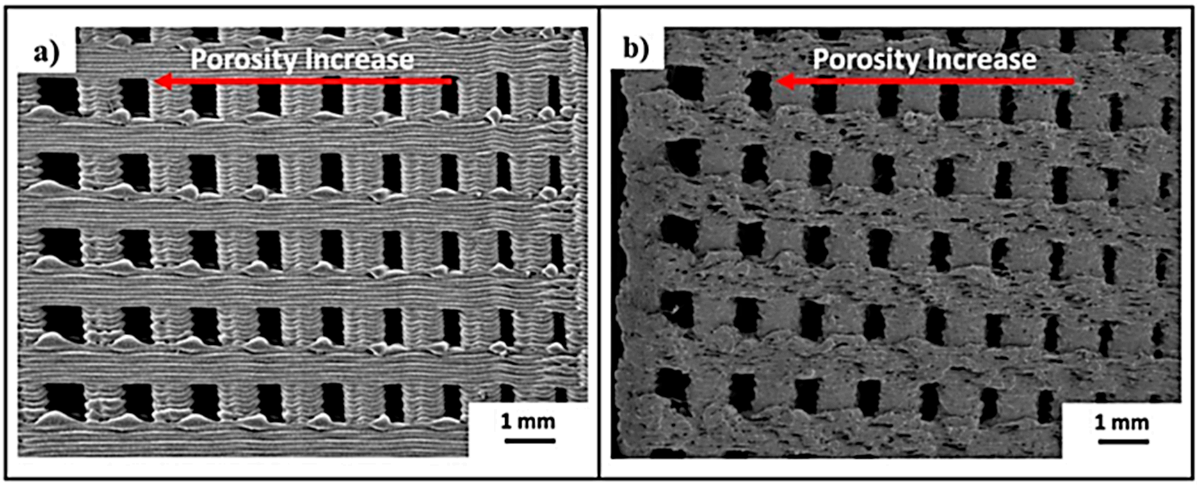


Figure 7. Graded porous structure in 3D-printed (**a**) PLA and (**b**) PLA-graphene scaffold structures [108]. PLA = poly(lactic acid); PLA-graphene = poly(lactic acid)–graphene. Reproduced with permission from Wiley.

Table 2. Glass transition (T_g), crystallization (T_c) and melting temperatures (T_m) of PLA and PLA-graphene filaments and 3D-printed samples [108]. PLA = poly(lactic acid); PLA-graphene = poly(lactic acid)–graphene. Reproduced with permission from Wiley.

Sample	T_g (C)	T_m (C)
PLA filament	59.3	168.7
PLA-graphene filament	45.9	164.1
3D-printed PLA	60.7	168.5
3D-printed PLA-graphene	51.2	165.5

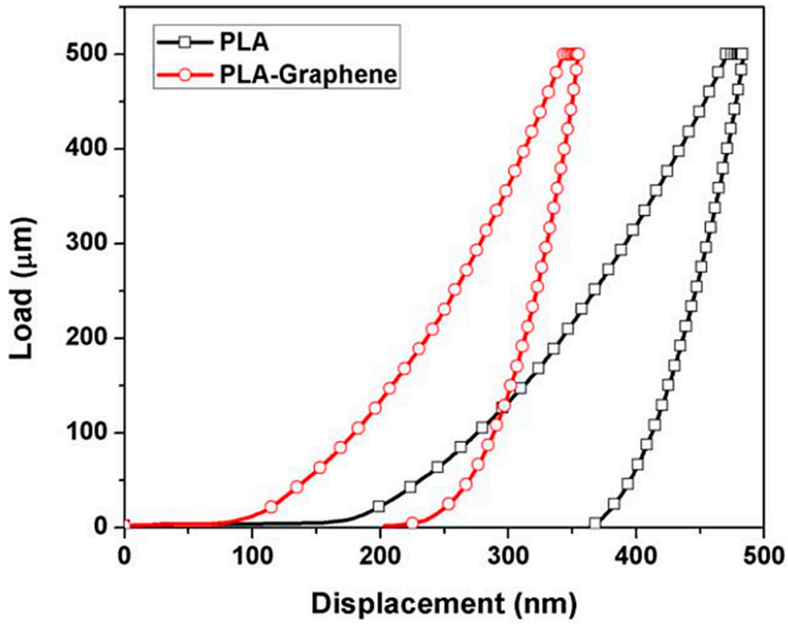
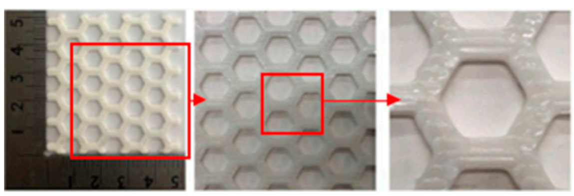
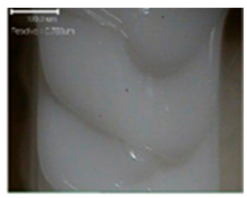
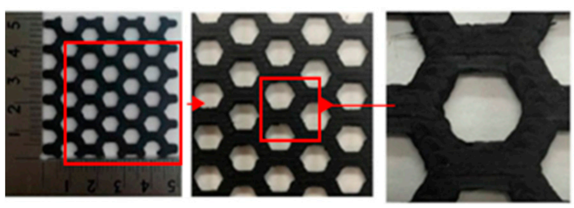
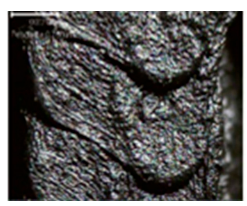


Figure 8. Representative load-displacement curves obtained from nanoindentation of 3D-printed poly(lactic acid) (PLA) and poly(lactic acid)–graphene (PLA-Graphene) [108]. Reproduced with permission from Wiley.

Kim et al. [109] applied conveyor-fused deposition-modeling-based 3D printing for the poly(lactic acid)–graphene nanocomposites. Moreover, high surface temperature and surface resistivity of 143.0 °C (for 25 V) and 118.0 Ω/sq, respectively, were observed for 3D-printed honeycomb nanocomposite. The morphology of conveyor FDM-based 3D-printed samples was studied using transmission electron microscopy (Table 3). The 3D-printed samples revealed honeycomb morphology. Gloss and shine the poly(lactic acid)–graphene nanocomposite micrographs appeared lesser than the pristine poly(lactic acid) sample. The results suggested that the brittleness of the polymer was decreased with the inclusion of the graphene nanofiller. According to TGA analysis, the nanocomposite filament had degradation temperature of 400 °C and char yield of 15%, indicating reasonably high thermal stability. The results revealed that the conveyor FDM-based 3D-printed nanocomposites were stable at high temperatures (Figure 9).

Table 3. Morphology of 3D-printed honeycomb samples by transmission electron microscopy [109]. PLA–GR = poly(lactic acid)–graphene. Reproduced with permission from Springer.

Sample	Digital Images	×6.5 Magnification
PLA		
PLA/GR		

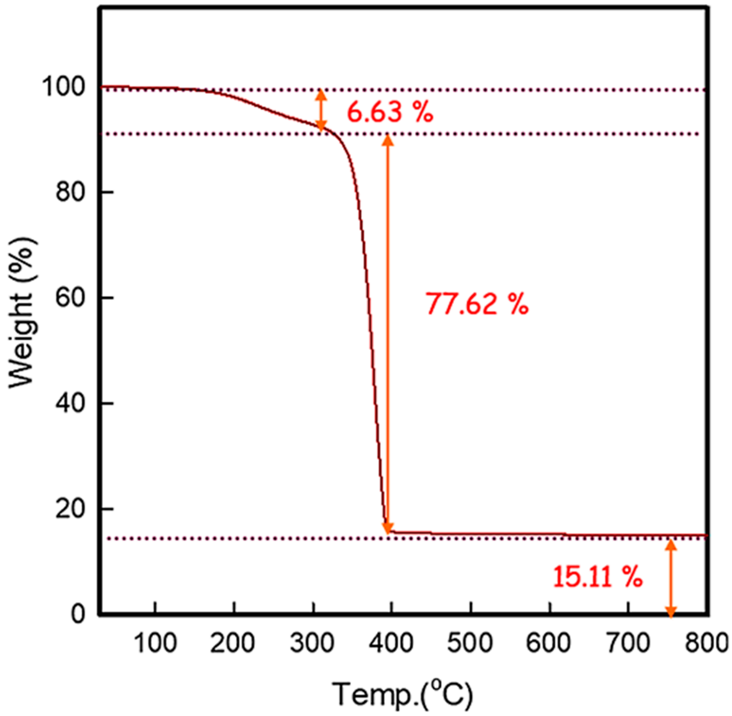


Figure 9. Thermogravimetric analysis curves of poly(lactic acid)–graphene filament for 3D printing [109]. Reproduced with permission from Springer.

The 4D printing techniques have been investigated for nanocomposite processing [110]. Figure 10 shows various processes and aspects of the 4D printing technique. Frequently used 4D printing processes include direct ink writing, FDM, SLA and micro-stereolithography. The 4D-printed complex nanostructures have been studied for different external stimuli. As discussed above, 4D printing is an extended form of 3D printing with time constraint and stimuli response features. The 4D-printed nanocomposites have been used to design the smart shape memory objects. Using smart nanomaterials, such as graphene nanocomposites and shape programming, usually results in unique shape change mechanisms for developing the 4D-printed objects. Wei et al. [111] applied the FDM-based 4D printing to form the acrylonitrile–butadiene–styrene, poly(lactic acid) and graphene-derived nanocomposites. The 5.6 wt.% graphene contents were successfully reinforced in 4D-printed materials for computer-based models. The resulting nanocomposite had a linear thermal coefficient of 75 ppm$^{\circ}$C^{-1}. Thus, the use of appropriate printing process enhanced the capability of material to appropriately expand under the effect of temperature elevation. Zarek and co-workers [112] applied the SLA-based 4D printing technique to fabricate the printed polymer–graphene nanomaterial. The 4D-printed nanocomposite revealed unique and complex shape-changing structures, indicating the success of the SLA method (Figure 11). The shape memory behavior has shown the applicability of the 3D process for various printed models. The digital models were generated by commercial computer-aided design (CAD) software (Autodesk Inventor, Mill Valley, CA, USA) modified with the printer software. The printed structures have rigid wax-like surface, at room temperature. Above Tm, the structures are flexible and elastomeric. The Tm of polycaprolactone was 55 °C. Under deformation, the structures were fixed by cooling below Tm. Reheating the structures recovered the original printed shape. The shape memory program was triggered by using a heat gun and rising temperature up to 70 °C. The thermoset shape memory vascular stents were printed. The design had submillimeter thicknesses and a large number of voids. Moreover, a scaled Eiffel Tower and bird were printed. Thus, high resolution and complex models were obtained with this approach.

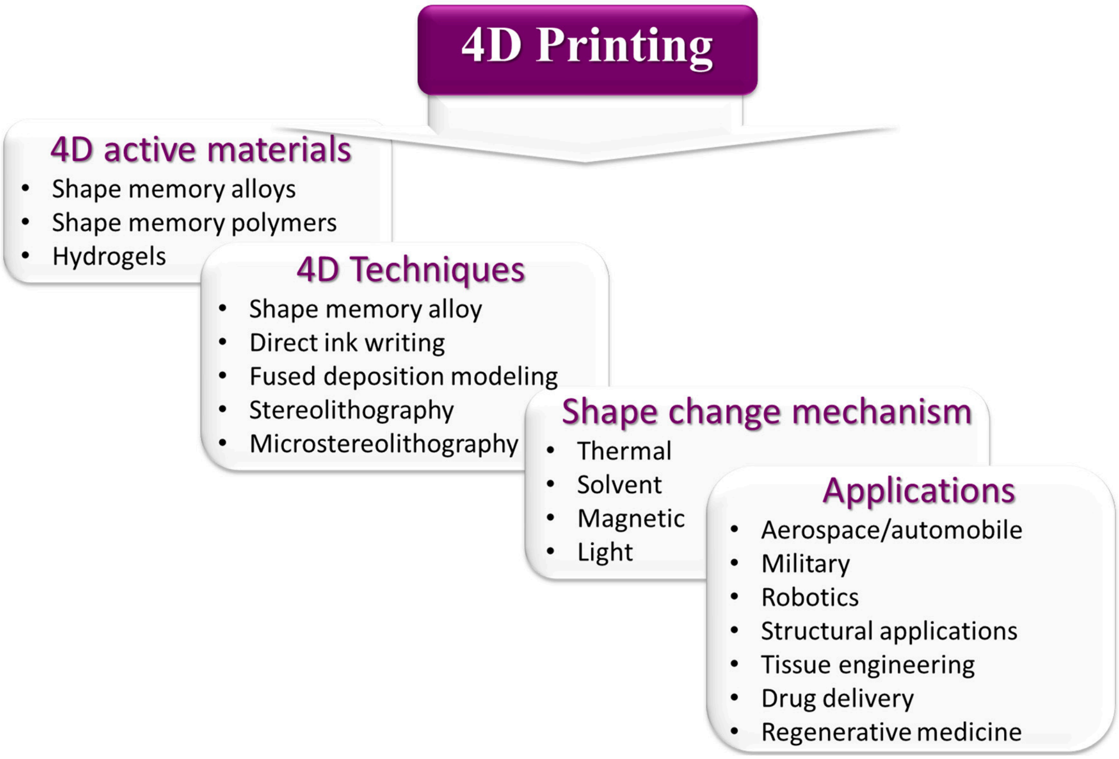


Figure 10. Aspects of 4D printing techniques.

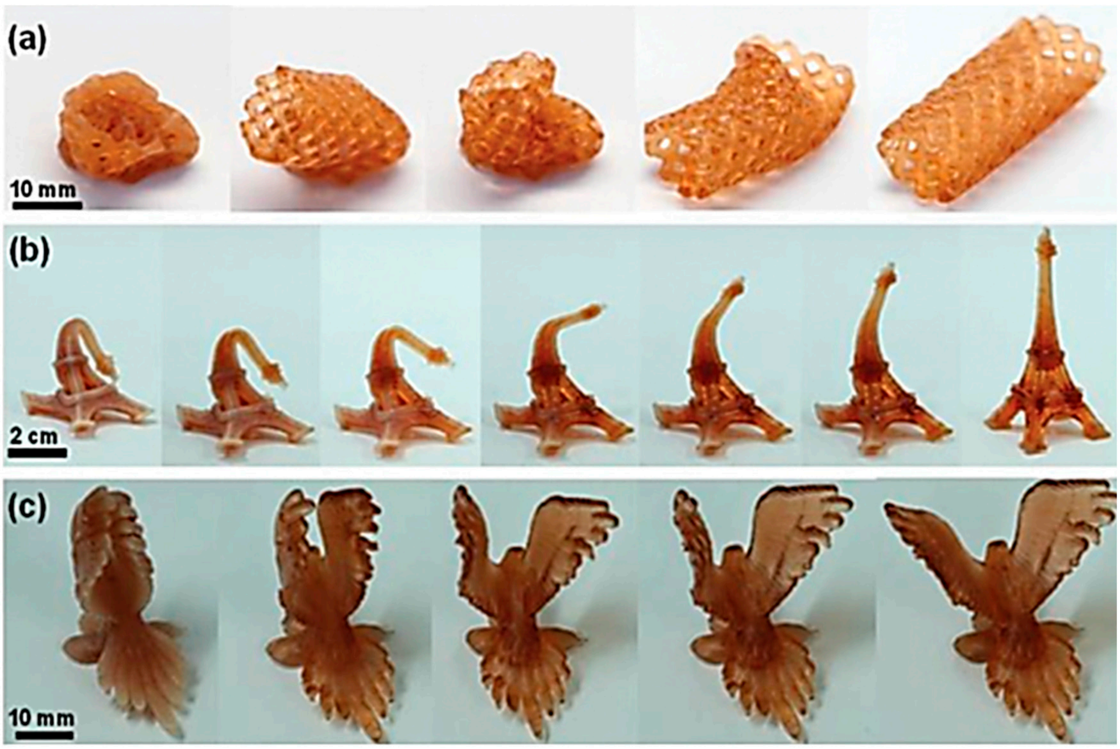


Figure 11. 4D shape-changing structures printed using stereolithography with a molten macromethacrylate can impart shape memory to nearly any object: (**a**) A model cardiovascular stent with a length of 3 cm, strut thicknesses of 600 µm and open cells of 2.5 mm × 2.5 mm, reverting to its original shape at 70 °C. Printing such a model stent takes 1 h with the Asiga printer; (**b**) an Eiffel Tower model, 6 cm tall, reverting to its original shape at 70 °C; and (**c**) a bird with a 3-cm wing span reverting to its original shape at 70 °C [112]. Reproduced with permission from Wiley.

Pyrolytic carbon microelectrodes have been considered as a promising alternative to conventional metallic counterparts for technical applications [113]. The laser printing technology has been used to convert graphene oxide or pyrolytic carbon into graphene-like materials. The highly oriented pyrolytic graphite and graphene-based nanomaterials have been applied as screen printing electrodes and other carbon electrode materials [114]. Chyan et al. [115] used a multiple pulsed laser technique to convert a wide range of substrates into laser-induced graphene (LIG). The CO_2 laser beam was applied to initiate the formation of graphene on the biodegradable substrates, such as cloth, paper, potato skins, coconut shells and cork. Using LIG on these substrates renders the derived nanomaterial useful for flexible micro-supercapacitors on renewable materials. Moreover, high-temperature engineering polymers, such as Kevlar, Kapton, polysulfones, poly(ether imide), etc., have been converted into LIG. In addition, crosslinked polystyrene has been used as substrates for LIG formation. Ludvigsen et al. [116] fabricated pyrolytic carbon microelectrodes by selective pyrolysis of SU-8 photoresist using irradiation with continuous wave semiconductor-diode laser. The SU-8 precursor was effectively converted into pyrolytic carbon upon laser irradiation. The highly porous structures were suggested for electrode application in electrochemical energy storage and biosensing.

5. Working Principle or Mechanism of 3D–4D Printing Technology for Polymeric–Graphene Nanocomposites

The 3D printing permits the formation of tailored structures from polymers and nanomaterials without using any molds or machining structures, as used in conventional manufacturing processes. Since, the conservative fabrication methods have several processing restrictions for large-scale production; 3D printing enables rapid manufacturing based on the CAD to form customized objects for desired application [117]. 3D printing has been commonly associated with additive manufacturing, layered manufacturing, rapid prototyping and solid fabrication. 3D printing processes produce 3D objects with high shape complexity. Additive manufacturing is mostly preferred by engineers. Figure 12 shows the basic principle of 3D printing. The basic principle involves the development of a product idea and then the transformation of digital data using CAD [118]. The CAD is used to create a virtual object, which is then digitally sliced. The preprocessed CAD model is scanned for virtual layered data, which is transferred to the 3D printer. Afterwards, the 3D printing of final product is performed after postprocessing. The CAM is performed layer by layer with characteristic layer thickness of 15–500 µm. For thick layers, postprocessing is used to eliminate support structures and to enhance the surface properties for desired applications. Thus, 3D printing has been widely used for the manufacturing of complex 3D objects through the fusion of layered materials [119]. The rise in 3D printing has enhanced the rapid prototyping due to cost effectiveness and fast conversion rates of CAD [120]. Due to characteristics, flexibility and the facile nature of 3D printing, this technique has been widely used in sensors, supercapacitors, tissue engineering, textiles, metamaterials and robotics [121–123].

The concept of 4D printing is considered an extension of 3D printing with the inclusion of time dimension. The materials capable of changing shapes are fabricated by multi-material 3D printing approaches, whereas 4D printing is not widely applied for such materials. The 4D printing has more specific thorough ways for mentioning the functionality or shape change induced after printing [124]. 4D printing is 3D printing of self-transforming materials when exposed to stimulus like heat, light, pressure or energy [125]. The smart materials responding to external stimulus obtained by 4D printing have been used in sensors and actuators [126]. Moreover, various research efforts have been performed to combine 3D printing with smart materials to manufacture 4D objects, responsive to external stimuli post printing. The stimuli responsive 3D fabricated structures are labeled with fourth dimension of time to yield 4D-printed structures [127]. The shape changes in 4D-printed structures have been attained through external stimuli to produce shrinkage, folding or expansion. The 4D-printed shape memory polymers have been applied as smart materials for auto-responsive 4D-printed objects. Various principles, such as object composition related to smart materials, inhomogeneity and different properties, govern for the 4D printing of structures [128]. 4D printing has been characterized according to parameters, including temperature, pressure, light, solvents, pH, humidity, etc., to induce transformation [129]. The principles of 4D printing define the properties of smart materials including mechanical properties, glass transition, rate of recovery, etc. [130].

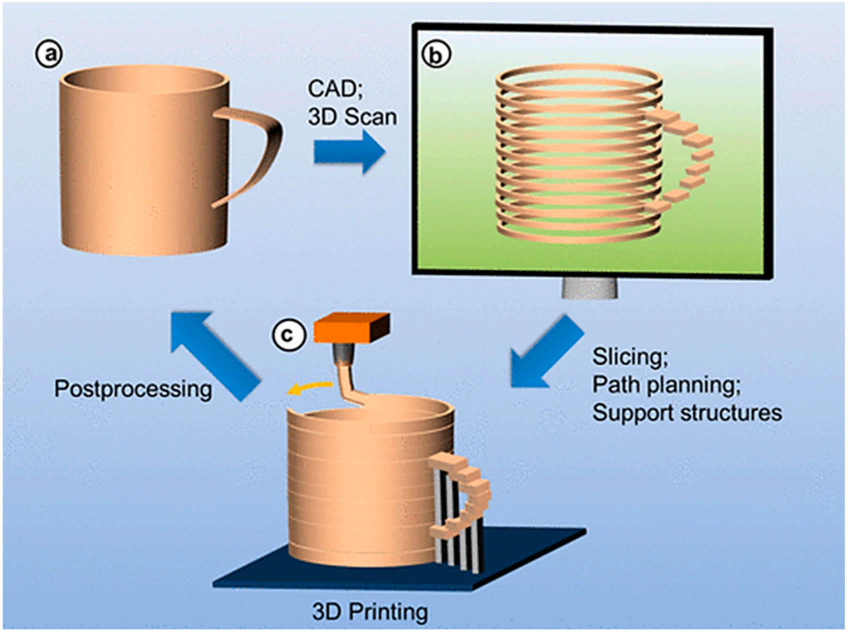


Figure 12. Basic principle of 3D printing (**a**) product idea development and the transformation of digital data via CAD; (**b**) preprocessing of CAD model into virtual layered data and later its transfer to 3D printer; and (**c**) 3D printing of final product after postprocessing [119]. Reproduced with permission from ACS.

The nanofiller reinforcement in polymer matrices has been generally used for the development of nanocomposite properties and processing feasibility [131]. The nanoparticle reinforcements have been used in the 3D printing of extrusion and powder bed-based printing techniques. The characteristics of included nanoparticles have been considered important to enhance the mechanical properties of the nanocomposites [132]. The addition of nanofillers in polymers for SLS or FDM techniques permits fabrication of cylindrical and cubical-shaped structures with enhanced properties, relative to the structures fabricated with pristine polymers [133]. Consequently, nanoparticle-reinforced polymer nanocomposites offer 3D and 4D printing of various structures for real-world applications [134]. Inclusion of nanofiller showed better heat transfer rates and mechanical properties of nanocomposites using stereolithography, compared with the pristine polymers [135]. The 3D–4D nanocomposites produced using FDM technique revealed adjustable dielectric permittivity, strength and other physical properties, relative to neat polymer [136]. Thus, the flexibility of FDM printing enables facile tuning of 3D patterns [137]. The 3D–4D-printed polymer nanocomposites are still an open research topic for more promising properties and results in the near future.

6. Potential of 3D–4D Printing Polymeric–Graphene Nanocomposites

The 3D and 4D printing techniques have advantages of low cost and controlled fabrication parameters for developing high-performance materials [138]. These printing technologies have been applied in the fields of aerospace–automotive, robotics, electronics, biomedical and other industries [139]. The 3D and 4D printing techniques have been applied to develop graphene-based nanocomposites for high temperature applications [140].

High temperature 3D–4D-printed polymer–graphene nanomaterials were designed having superior thermal conductivity properties [141,142]. The 3D–4D-printed graphene heaters have been developed by applying the Joule heating effect [143]. Joule heating is the generation of heat by passage of electric current through materials. The Joule effect is desirable in electronics, laptops, smartphones, microprocessors, etc. [144]. The Joule heating effect in the graphene nanocomposites produces fewer micro-voids and has preferred graphene orientation [145]. The heaters were functional at the high temperature of 3000 K. The 3D- or 4D-printed graphene heaters have a high heating rate of ~20,000 Ks^{-1}. Chowdhury et al. [146] performed 4D printing of graphene-filled tert-Butyl Acrylate with diethylene glycol diacrylate. The shape recovery was carried out through heating above 70 °C, keeping the external strains constant. High temperature and natural convection to the atmosphere was observed for shape memory process. The nanocomposites were applicable to soft robotics as it was found responsive towards temperature-based stimuli [147].

Another important application of the 3D- and 4D-printed polymer–graphene has been observed in photovoltaics [148,149]. In this regard, graphene-based inks have been developed for printing the objects [150]. The 3D- or 4D-printed graphene architectures revealed significantly high energy conversion efficiency of ~87.5% for solar cell [151]. Li et al. [152] designed printed graphene-modified carbon counter electrodes for dye-sensitized solar cell (DSSC). The electrode was printed on FTO glass. The DSSC has power conversion efficiency of 6.53% and fill factor of 0.66. Thus, inexpensive, stable and efficient DSSC was obtained. Solar cells based on ink jet-printed polymer–graphene nanocomposites have been reported [153]. For better solar cell efficiency, morphology and microstructure of polymer–graphene need to be controlled. Moreover, nanomaterial film of uniform width and thickness has been preferred [154]. FDM or inkjet printing technique has been found useful for high efficiency DSSC. In this regard, regular FDM-based 3D printers have been found cost-effective and efficient. The 3D-printed poly(3-hexylthiophene):1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 revealed power conversion efficiency of 4–5%. Finn et al. [155] tested the 3D-printed solar cell material for mechanical fatigue using bending and torsion loadings. The results revealed that using printing techniques has considerably enhanced the lifetime and efficiency of 3D solar cells.

Besides, the 3D and 4D-printed nanomaterials have been reported for the energy storage application [156]. Consequently, the 3D- and 4D-printed graphene-based nanomaterials own high specific surface area, electrical conductivity, charge transportation and chemical stability properties for supercapacitors and other energy storage–production devices [157,158]. Integration of aligned graphene in 3D- and 4D-printed objects usually generates continuous electron transfer pathways, leading to high electrical conductivity [159]. The 3D- and 4D-printed poly(lactic acid)–graphene nanomaterials have been developed for supercapacitors [160,161]. Le et al. [162] produced inkjet-printed graphene electrodes for flexible micro-supercapacitors. The printed electrodes revealed high specific energy and specific power of 6.74 Wh/kg and 2.19 kW/kg, respectively. The electrochemical performance of the printed graphene electrodes was also found superior to the traditional synthesized polymer–graphene electrodes. Tang et al. [163] developed hybrid ink based on Fe_2O_3/graphene. The micro-supercapacitor electrodes were fabricated using direct ink writing with Fe_2O_3/graphene. The micro-supercapacitor electrodes had maximum areal capacitance of 412.3 mF cm^{-2}, high energy density of 65.4 µWh cm^{-2} and capacitance retention of 89%. Zhou et al. [164] performed 4D printing of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/graphene oxide electrodes for supercapacitors. Due to the application of printing method, the supercapacitor revealed gravimetric capacitance of 21.7 F g^{-1} and capacitance retention of ~85.8%. Zhu et al. [165] used graphene oxide-based composite ink for 3D printing. The obtained supercapacitor electrode had power densities if >4 $kW \cdot kg^{-1}$ and capacitive retention of 90%. Thus, 3D- and 4D-printed graphene-based materials have significantly expanded the design and performance space for manufacturing high-performance energy storage devices.

Lithium batteries have appeared as a promising energy storage technology due to their high energy density and capacity. Alteration of electrode design using printing techniques has been found effective for increasing the energy density and capacity of batteries [166,167]. Fu et al. [168] formed 3D-printed lithium-ion battery electrodes using graphene oxide-based composite inks. The printed electrode had mass loading of 18 mg cm^{-2}. Qiao et al. [169] fabricated 3D-printed graphene oxide-based Li-ion battery electrode. The printed electrode had high areal capacity of 14.6 mA h cm^{-2}. Moreover, the printed electrode revealed high cycling stability of 100 cycles and good rate capability of 1000 mA g^{-1}. Consequently, the 3D- or 4D-printed battery electrodes have overcome the challenges of high-rate performance and long cycling stability.

Afterwards, the 3D- and 4D-printed graphene-based nanomaterials have been used in sensors [170]. Especially, the 3D- or 4D-printed graphene nanocomposites have been applied for the strain sensors [171], flexible wearable electronic sensors [172,173] and electrochemical sensors [174]. Kumar et al. [175] fabricated 3D-printed poly(vinylidene fluoride)–graphene nanocomposites as piezoelectric and magnetic sensors. For the printed sensors, dielectric property of D_{33} = 47.6pC/N and magnetization of 0.0853×10^{-5} emu/gf have been observed. Maurya et al. [176] reported direct mask-less 3D-printed graphene-based strain gauges. The strain sensors were capable of analyzing tire-road interactions under load, variable driving speeds and tire pressure. Mahmud et al. [177] used 4D printing technique to form graphene based wearable and implantable sensing devices. The successful growth of 4D materials fulfills the requirements of cost-effective implantable sensing devices. Hence, using 3D and 4D printing technologies offers high design flexibility, tailored functions adaptability to the environment, and programmable 3D or 4D smart devices.

Thus, the high-performance 3D- or 4D-printed graphene nanocomposites revealed essential applications in high temperature materials, solar cell, supercapacitors, batteries sensors and wearable electronics [178–181].

7. Viewpoint and Conclusions

Graphene is an important nanocarbon nanomaterial. The remarkable features of graphene have been incorporated in the 3D- and 4D-printed graphene-based nanomaterials. The 3D and 4D printing techniques involve processes such as direct ink writing, inkjet 3D printing, FDM, SLA, etc. However, these processes have relative advantages and limitations when used for various materials. Therefore, choice of an appropriate printing process and parameter optimization has been found indispensable. The 3D- and 4D-printed objects integrated with the polymer–graphene nanocomposites own design and fabrication versatilities and distinct morphological properties. Consequently, the 3D- and 4D-printed graphene-based nanomaterials have been applied for the multifunctional microscale devices. The 3D- and 4D-printed graphene nanocomposites have been explored for the high temperature materials, energy and sensing applications, so far. Future efforts are obviously needed for large-scale industrial applications of the 3D- and 4D-printed graphene nanocomposites for technical fields.

Succinctly, this overview highlights the high-performance 3D- and 4D-printed polymer–graphene nanocomposites. The 3D and 4D printing techniques for nanocomposite have advantageous properties and potential, compared with the traditional printing techniques. Applications of 3D- and 4D-printed polymer–graphene nanocomposites have been observed in energy devices, electronics and high temperature materials. In the future, advancements in 3D and 4D printing technologies may lead to high-tech devices and systems. In this review, we presented outlines related to 3D and 4D printing graphene-based nanocomposites considering various printing procedures. The relationships between fabrication process, structural characteristics and applications of graphene-based nanocomposites have been summarized intensely. The 3D or 4D printing methods for manufacturing depend on the intrinsic properties of graphene-based materials. In these nanocomposites, graphene-based solution and melt have been used as convenient starting materials. However, in solution-based material complex post-treatment methods have been needed to evaporate the solvent. FDM has been widely used to process various thermoplastic and thermosetting matrices with graphene. Among all 3D printing processes, SLA seems to be a more promising method due to high resolution and interaction between graphene and laser. SLS and FDM have been widely used for graphene powder for nanocomposite prototyping and printed objects. These nanomaterials revealed enhanced thermal, mechanical and other physical properties. Similarly, 4D printing approaches have been applied to develop complex multifunctional 3D shapes with high resolution. In all of these 3D and 4D methods, basic relationship between materials characteristics and processing parameters have been found important. In the near future, new 3D and 4D printing concepts, versatile printing materials, processing approaches and manifold applications need to be researched.

Author Contributions: Conceptualization, A.K.; data curation, A.K.; writing of original draft preparation, A.K.; Review and editing, A.K.; I.A.; T.Z.; O.A.; M.H.E. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend their appreciation to the Deanship of Scientific Research at Imam Mohammad Ibn Saud Islamic University for funding this work through Research Group no. RG-21-09-49.

Data Availability Statement: Not applicable.

Acknowledgments: The authors extend their appreciation to the Deanship of Scientific Research at Imam Mohammad Ibn Saud Islamic University for funding this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kausar, A. Shape memory polymer/graphene nanocomposites: State-of-the-art. *E-Polymers* **2022**, *22*, 165–181. [CrossRef]
2. Gopal, J.; Muthu, M.; Sivanesan, I. A Comprehensive Compilation of Graphene/Fullerene Polymer Nanocomposites for Electrochemical Energy Storage. *Polymers* **2023**, *15*, 701. [CrossRef] [PubMed]
3. De Angelis, F.; Vadini, M.; Buonvivere, M.; Valerio, A.; Di Cosola, M.; Piattelli, A.; Biferi, V.; D'Arcangelo, C. In Vitro Mechanical Properties of a Novel Graphene-Reinforced PMMA-Based Dental Restorative Material. *Polymers* **2023**, *15*, 622. [CrossRef]
4. Kausar, A. *Graphene to Polymer/Graphene Nanocomposites: Emerging Research and Opportunities*; Elsevier: Amsterdam, The Netherlands, 2021.
5. Morales, M.A.; Maranon, A.; Hernandez, C.; Michaud, V.; Porras, A. Colombian Sustainability Perspective on Fused Deposition Modeling Technology: Opportunity to Develop Recycled and Biobased 3D Printing Filaments. *Polymers* **2023**, *15*, 528. [CrossRef]
6. Silvestre, R.; Garcia-Breijo, E.; Ferri, J.; Montava, I.; Bou-Belda, E. The Influence of the Structure of Cotton Fabrics on the Adhesion of Conductive Polymer Printed with 3D Printing Technology. *Polymers* **2023**, *15*, 668. [CrossRef] [PubMed]
7. Xu, D.; Shi, J.; Qiu, R.; Lei, W.; Yu, W. Comparative Investigations on Properties of Three Kinds of FDM 3D-Printed Natural Plant Powder/Poly(lactic acid) Biocomposites. *Polymers* **2023**, *15*, 557. [CrossRef] [PubMed]
8. Chen, Z.; Li, Z.; Li, J.; Liu, C.; Lao, C.; Fu, Y.; Liu, C.; Li, Y.; Wang, P.; He, Y. 3D printing of ceramics: A review. *J. Eur. Ceram. Soc.* **2019**, *39*, 661–687. [CrossRef]
9. Zhou, W.; Qiao, Z.; Zare, E.N.; Huang, J.; Zheng, X.; Sun, X.; Shao, M.; Wang, H.; Wang, X.; Chen, D.; et al. 4D-Printed Dynamic Materials in Biomedical Applications: Chemistry, Challenges, and Their Future Perspectives in the Clinical Sector. *J. Med. Chem.* **2020**, *63*, 8003–8024. [CrossRef]
10. Wang, Y.; Zhou, W.; Cao, K.; Hu, X.; Gao, L.; Lu, Y. Architectured graphene and its composites: Manufacturing and structural applications. *Compos. Part Appl. Sci. Manuf.* **2021**, *140*, 106177. [CrossRef]
11. Hartings, M.R.; Ahmed, Z. Chemistry from 3D printed objects. *Nat. Rev. Chem.* **2019**, *3*, 305–314. [CrossRef]
12. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J.W.; Potts, J.R.; Ruoff, R.S. Graphene and graphene oxide: Synthesis, properties, and applications. *Adv. Mater.* **2010**, *22*, 3906–3924. [CrossRef] [PubMed]
13. Razaq, A.; Bibi, F.; Zheng, X.; Papadakis, R.; Jafri, S.H.M.; Li, H. Review on Graphene-, Graphene Oxide-, Reduced Graphene Oxide-Based Flexible Composites: From Fabrication to Applications. *Materials* **2022**, *15*, 1012. [CrossRef]
14. Li, F.; Long, L.; Weng, Y. A Review on the Contemporary Development of Composite Materials Comprising Graphene/Graphene Derivatives. *Adv. Mater. Sci. Eng.* **2020**, *2020*, 7915641. [CrossRef]
15. Xu, M.; Liang, T.; Shi, M.; Chen, H. Graphene-Like Two-Dimensional Materials. *Chem. Rev.* **2013**, *113*, 3766–3798. [CrossRef] [PubMed]
16. Geim, A.K.; Grigorieva, I.V. Van der Waals heterostructures. *Nature* **2013**, *499*, 419–425. [CrossRef] [PubMed]
17. Sun, Z.; Martinez, A.; Wang, F. Optical modulators with 2D layered materials. *Nat. Photon* **2016**, *10*, 227–238. [CrossRef]
18. Potts, J.R.; Dreyer, D.R.; Bielawski, C.W.; Ruoff, R.S. Graphene-based polymer nanocomposites. *Polymer* **2011**, *52*, 5–25. [CrossRef]

19. Wang, Y.; Li, Z.; Wang, J.; Li, J.; Lin, Y. Graphene and graphene oxide: Biofunctionalization and applications in biotechnology. *Trends Biotechnol.* **2011**, *29*, 205–212. [CrossRef]
20. Casero, E.; Parra-Alfambra, A.; Domínguez, M.D.P.; Pariente, F.; Lorenzo, E.; Alonso, F.P. Differentiation between graphene oxide and reduced graphene by electrochemical impedance spectroscopy (EIS). *Electrochem. Commun.* **2012**, *20*, 63–66. [CrossRef]
21. Chen, J.; Chi, F.; Huang, L.; Zhang, M.; Yao, B.; Li, Y.; Li, C.; Shi, G. Synthesis of graphene oxide sheets with controlled sizes from sieved graphite flakes. *Carbon* **2016**, *110*, 34–40. [CrossRef]
22. Dua, V.; Surwade, S.P.; Ammu, S.; Agnihotra, S.R.; Jain, S.; Roberts, K.E.; Park, S.; Ruoff, R.S.; Manohar, S.K. All-Organic Vapor Sensor Using Inkjet-Printed Reduced Graphene Oxide. *Angew. Chem. Int. Ed.* **2010**, *49*, 2154–2157. [CrossRef] [PubMed]
23. Wang, Y.; Yang, C.; Mai, Y.-W.; Zhang, Y. Effect of non-covalent functionalisation on thermal and mechanical properties of graphene-polymer nanocomposites. *Carbon* **2016**, *102*, 311–318. [CrossRef]
24. Criado, A.; Melchionna, M.; Marchesan, S.; Prato, M. The covalent functionalization of graphene on substrates. *Angew. Chem. Int. Ed.* **2015**, *54*, 10734–10750. [CrossRef] [PubMed]
25. Fechine, G.J.M.; Martin-Fernandez, I.; Yiapanis, G.; Bentini, R.; Kulkarni, E.S.; Bof de Oliveira, R.V.; Hu, X.; Yarovsky, I.; Castro Neto, A.H.; Oezyilmaz, B. Direct dry transfer of chemical vapor deposition graphene to polymeric substrates. *Carbon* **2015**, *83*, 224–231. [CrossRef]
26. Raccichini, R.; Varzi, A.; Passerini, S.; Scrosati, B. The role of graphene for electrochemical energy storage. *Nat. Mater.* **2015**, *14*, 271–279. [CrossRef]
27. Cui, C.; Huang, J.; Huang, J.; Chen, G. Size separation of mechanically exfoliated graphene sheets by electrophoresis. *Electrochim. Acta* **2017**, *258*, 793–799. [CrossRef]
28. Sun, L.; Wang, L.; Tian, C.; Tan, T.; Xie, Y.; Shi, K.; Li, M.; Fu, H. Nitrogen-doped graphene with high nitrogen level via a one-step hydrothermal reaction of graphene oxide with urea for superior capacitive energy storage. *RSC Adv.* **2012**, *2*, 4498–4506. [CrossRef]
29. Ji, L.; Xin, H.L.; Kuykendall, T.R.; Wu, S.-L.; Zheng, H.; Rao, M.; Cairns, E.J.; Battaglia, V.; Zhang, Y. SnS2 nanoparticle loaded graphene nanocomposites for superior energy storage. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6981–6986. [CrossRef]
30. Kausar, A. Strategies in Polymeric Nanoparticles and Hybrid Polymer Nanoparticles. *NanoWorld J.* **2019**, *5*, 1–5. [CrossRef]
31. Garlow, J.A.; Barrett, L.K.; Wu, L.; Kisslinger, K.; Zhu, Y.; Pulecio, J.F. Large-Area Growth of Turbostratic Graphene on Ni(111) via Physical Vapor Deposition. *Sci. Rep.* **2016**, *6*, 19804. [CrossRef]
32. Pirkle, A.; Chan, J.; Venugopal, A.; Hinojos, D.; Magnuson, C.W.; McDonnell, S.; Colombo, L.; Vogel, E.M.; Ruoff, R.S.; Wallace, R.M. The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO_2. *Appl. Phys. Lett.* **2011**, *99*, 122108. [CrossRef]
33. Burattini, S.; Greenland, B.W.; Merino, D.H.; Weng, W.; Seppala, J.; Colquhoun, H.M.; Hayes, W.; Mackay, M.E.; Hamley, I.W.; Rowan, S.J. A healable supramolecular polymer blend based on aromatic $\pi-\pi$ stacking and hydrogen-bonding interactions. *J. Am. Chem. Soc.* **2010**, *132*, 12051–12058. [CrossRef] [PubMed]
34. Björk, J.; Hanke, F.; Palma, C.-A.; Samori, P.; Cecchini, M.; Persson, M. Adsorption of aromatic and anti-aromatic systems on graphene through $\pi-\pi$ stacking. *J. Phys. Chem. Lett.* **2010**, *1*, 3407–3412. [CrossRef]
35. Li, H.; Rothberg, L. Colorimetric detection of DNA sequences based on electrostatic interactions with unmodified gold nanoparticles. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 14036–14039. [CrossRef] [PubMed]
36. Zhang, Y.; Zhang, J.; Huang, X.; Zhou, X.; Wu, H.; Guo, S. Assembly of Graphene Oxide-Enzyme Conjugates through Hydrophobic Interaction. *Small* **2012**, *8*, 154–159. [CrossRef] [PubMed]
37. Wang, H.X.; Zhou, K.G.; Xie, Y.L.; Zeng, J.; Chai, N.N.; Li, J.; Zhang, H.L. Photoactive graphene sheets prepared by "click" chemistry. *Chem. Commun.* **2011**, *47*, 5747–5749. [CrossRef]
38. Eigler, S.; Hirsch, A. Chemistry with Graphene and Graphene Oxide—Challenges for Synthetic Chemists. *Angew. Chem. Int. Ed.* **2014**, *53*, 7720–7738. [CrossRef]
39. Fang, L.; Xue, L.; Yang, P.; Li, X.; Wang, Z. A Facile Route to 4-Polyfluoroarylquinolin-2(1*H*)-ones and 4-Polyfluoroarylcoumarins via C–H Bond Activation. *Chem. Lett.* **2017**, *46*, 1223–1226. [CrossRef]
40. Shi, M.; Shen, J.; Ma, H.; Li, Z.; Lu, X.; Li, N.; Ye, M. Preparation of graphene–TiO_2 composite by hydrothermal method from peroxotitanium acid and its photocatalytic properties. *Colloids Surfaces A Physicochem. Eng. Asp.* **2012**, *405*, 30–37. [CrossRef]
41. Khan, M.; Tahir, M.N.; Adil, S.F.; Khan, H.U.; Siddiqui, M.R.H.; Al-Warthan, A.A.; Tremel, W. Graphene based metal and metal oxide nanocomposites: Synthesis, properties and their applications. *J. Mater. Chem. A* **2015**, *3*, 18753–18808. [CrossRef]
42. Zhu, J.; Zhu, T.; Zhou, X.; Zhang, Y.; Lou, X.W.; Chen, X.; Zhang, H.; Hng, H.H.; Yan, Q. Facile synthesis of metal oxide/reduced graphene oxide hybrids with high lithium storage capacity and stable cyclability. *Nanoscale* **2011**, *3*, 1084–1089. [CrossRef]
43. Mohan, V.B.; Lau, K.-T.; Hui, D.; Bhattacharyya, D. Graphene-based materials and their composites: A review on production, applications and product limitations. *Compos. Part B Eng.* **2018**, *142*, 200–220. [CrossRef]
44. Prolongo, S.; Jiménez-Suárez, A.; Moriche, R.; Ureña, A. Graphene nanoplatelets thickness and lateral size influence on the morphology and behavior of epoxy composites. *Eur. Polym. J.* **2014**, *53*, 292–301. [CrossRef]
45. Nasir, A.; Kausar, A.; Younus, A. Polymer/Graphite Nanocomposites: Physical Features, Fabrication and Current Relevance. *Polym. Technol. Eng.* **2015**, *54*, 750–770. [CrossRef]

46. Szeluga, U.; Kumanek, B.; Trzebicka, B. Synergy in hybrid polymer/nanocarbon composites. A review. *Compos. Part A Appl. Sci. Manuf.* **2015**, *73*, 204–231. [CrossRef]
47. Rokaya, D.; Skallevold, H.E.; Srimaneepong, V.; Marya, A.; Shah, P.K.; Khurshid, Z.; Zafar, M.S.; Sapkota, J. Shape Memory Polymeric Materials for Biomedical Applications: An Update. *J. Compos. Sci.* **2023**, *7*, 24. [CrossRef]
48. Johnson, D.W.; Dobson, B.P.; Coleman, K.S. A manufacturing perspective on graphene dispersions. *Curr. Opin. Colloid Interface Sci.* **2015**, *20*, 367–382. [CrossRef]
49. Ghasemi, I.; Gomari, S. Polymeric Nanocomposites Including Graphene Nanoplatelets. In *Handbook of Graphene*; Celasco, E., Chaika, A.N., Stauber, T., Zhang, M., Ozkan, C., Ozkan, C., Ozkan, U., Palys, B., Harun, S.W., Eds.; Wiley, Scrivener Publishing LLC: Beverly, MA, USA, 2019; pp. 481–515.
50. Zhang, S.; Xiong, P.; Yang, X.; Wang, X. Novel PEG functionalized graphene nanosheets: Enhancement of dispersibility and thermal stability. *Nanoscale* **2011**, *3*, 2169–2174. [CrossRef]
51. Liu, C.; Ye, S.; Feng, J. Promoting the dispersion of graphene and crystallization of poly (lactic acid) with a freezing-dried graphene/PEG masterbatch. *Compos. Sci. Technol.* **2017**, *144*, 215–222. [CrossRef]
52. Zhang, L.; Wang, Z.; Lu, Z.; Shen, H.; Huang, J.; Zhao, Q.; Liu, M.; He, N.; Zhang, Z. PEGylated reduced graphene oxide as a superior ssRNA delivery system. *J. Mater. Chem. B* **2013**, *1*, 749–7555. [CrossRef]
53. Zhang, K.; Zhang, L.L.; Zhao, X.S.; Wu, J. Graphene/Polyaniline Nanofiber Composites as Supercapacitor Electrodes. *Chem. Mater.* **2010**, *22*, 1392–1401. [CrossRef]
54. Singh, K.; Ohlan, A.; Saini, P.; Dhawan, S. Poly (3, 4-ethylenedioxythiophene) γ-Fe2O3 polymer composite–super paramagnetic behavior and variable range hopping 1D conduction mechanism–synthesis and characterization. *Polym. Adv. Technol.* **2008**, *19*, 229–236. [CrossRef]
55. Saeb, M.R.; Zarrintaj, P. Polyaniline/graphene-based nanocomposites. In *Fundamentals and Emerging Applications of Polyaniline*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 165–175.
56. Sawangphruk, M.; Suksomboon, M.; Kongsupornsak, K.; Khuntilo, J.; Srimuk, P.; Sanguansak, Y.; Klunbud, P.; Suktha, P.; Chiochan, P. High-performance supercapacitors based on silver nanoparticle–polyaniline–graphene nanocomposites coated on flexible carbon fiber paper. *J. Mater. Chem. A* **2013**, *1*, 9630–9636. [CrossRef]
57. Xie, Y.; Liu, Y.; Zhao, Y.; Tsang, Y.H.; Lau, S.P.; Huang, H.; Chai, Y. Stretchable all-solid-state supercapacitor with wavy shaped polyaniline/graphene electrode. *J. Mater. Chem. A* **2014**, *2*, 9142–9149. [CrossRef]
58. Bo, P.; Yunbin, X.; Jiabao, G.; Zijun, C.; Yanhuang, T.; Gang, Z.; Huanxiang, X.U. Research progress in preparation and properties of polymer/graphene composites. *China Plast.* **2022**, *36*, 190.
59. Deshmukh, K.; Houkan, M.T.; AlMaadeed, M.A.; Sadasivuni, K.K. Introduction to 3D and 4D printing technology. In *State of the Art and Recent Trends. 3D and 4D Printing of Polymer Nanocomposite Materials*; Sadasivuni, K.K., Deshmukh, K., Almaadeed, M.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 1–24.
60. Gokhare, V.G.; Raut, D.; Shinde, D. A review paper on 3D-printing aspects and various processes used in the 3D-printing. *Int. J. Eng. Res. Technol.* **2017**, *6*, 953–958.
61. Ngo, T.D.; Kashani, A.; Imbalzano, G.; Nguyen, K.T.Q.; Hui, D. Additive Manufacturing (3D Printing): A Review of Materials, Methods, Applications and Challenges. *Compos. Part B Eng.* **2018**, *143*, 172–196. [CrossRef]
62. Xu, W.; Jambhulkar, S.; Zhu, Y.; Ravichandran, D.; Kakarla, M.; Vernon, B.; Lott, D.G.; Cornella, J.L.; Shefi, O.; Miquelard-Garnier, G.; et al. 3D printing for polymer/particle-based processing: A review. *Compos. Part B Eng.* **2021**, *223*, 109102. [CrossRef]
63. Chahal, V.; Taylor, R.M. A review of geometric sensitivities in laser metal 3D printing. *Virtual Phys. Prototyp.* **2020**, *15*, 227–241. [CrossRef]
64. Ford, S.; Minshall, T. Invited review article: Where and how 3D printing is used in teaching and education. *Addit. Manuf.* **2019**, *25*, 131–150. [CrossRef]
65. Lesage, P.; Dembinski, L.; Lachat, R.; Roth, S. Mechanical characterization of 3D printed samples under vibration: Effect of printing orientation and comparison with subtractive manufacturing. *Results Eng.* **2022**, *13*, 100372. [CrossRef]
66. Joharji, L.; Mishra, R.B.; Alam, F.; Tytov, S.; Al-Modaf, F.; El-Atab, N. 4D printing: A detailed review of materials, techniques, and applications. *Microelectron. Eng.* **2022**, *265*, 111874. [CrossRef]
67. Costa, L.A.; Carvalho, B.R.; Alves, J.L.; Marques, A.T.; da Silva, A.F.B.; Esfandiari, P.; da Silva, J.F.M.; Silva, A.R.; Parente, M. 4D structures for the short-time building of emergency shelters. *Proc. Inst. Mech. Eng. Part L J. Mater. Des. Appl.* **2022**, *236*, 1869–1894. [CrossRef]
68. Shen, B.; Erol, O.; Fang, L.; Kang, S.H. Programming the time into 3D printing: Current advances and future directions in 4D printing. *Multifunct. Mater.* **2020**, *3*, 012001. [CrossRef]
69. Rayate, A.; Jain, P.K. A review on 4D printing material composites and their applications. *Mater. Today Proc.* **2018**, *5*, 20474–20484. [CrossRef]
70. Li, X.; Shang, J.; Wang, Z. Intelligent materials: A review of applications in 4D printing. *Assem. Autom.* **2017**, *37*, 170–185. [CrossRef]
71. Agarwal, R.; Malhotra, S.; Gupta, V.; Jain, V. The application of Three-dimensional printing on foot fractures and deformities: A mini-review. *Ann. 3D Print. Med.* **2022**, *5*, 100046. [CrossRef]

72. Khalid, M.Y.; Arif, Z.U.; Ahmed, W. 4D Printing: Technological and Manufacturing Renaissance. *Macromol. Mater. Eng.* **2022**, *307*, 2200003. [CrossRef]
73. Van Manen, T.; Dehabadi, V.M.; Saldívar, M.C.; Mirzaali, M.J.; Zadpoor, A.A. Theoretical stiffness limits of 4D printed self-folding metamaterials. *Commun. Mater.* **2022**, *3*, 43. [CrossRef]
74. Tejada-Ortigoza, V.; Cuan-Urquizo, E. Towards the Development of 3D-Printed Food: A Rheological and Mechanial Approach. *Foods* **2022**, *11*, 1191. [CrossRef]
75. Khorsandi, D.; Fahimipour, A.; Abasian, P.; Saber, S.S.; Seyedi, M.; Ghanavati, S.; Ahmad, A.; De Stephanis, A.A.; Taghavinezhaddilami, F.; Leonova, A.; et al. 3D and 4D printing in dentistry and maxillofacial surgery: Printing techniques, materials, and applications. *Acta Biomater.* **2021**, *122*, 26–49. [CrossRef] [PubMed]
76. Quanjin, M.; Rejab, M.; Idris, M.; Kumar, N.M.; Abdullah, M.; Reddy, G.R. Recent 3D and 4D intelligent printing technologies: A comparative review and future perspective. *Procedia Comput. Sci.* **2020**, *167*, 1210–1219. [CrossRef]
77. Wu, J.-J.; Huang, L.-M.; Zhao, Q.; Xie, T. 4D Printing: History and Recent Progress. *Chin. J. Polym. Sci.* **2018**, *36*, 563–575. [CrossRef]
78. Yang, D.; Mei, H.; Yao, L.; Yang, W.; Yao, Y.; Cheng, L.; Zhang, L.; Dassios, K.G. 3D/4D printed tunable electrical metamaterials with more sophisticated structures. *J. Mater. Chem. C* **2021**, *9*, 12010–12036. [CrossRef]
79. Wan, X.; Luo, L.; Liu, Y.; Leng, J. Direct Ink Writing Based 4D Printing of Materials and Their Applications. *Adv. Sci.* **2020**, *7*, 2001000. [CrossRef] [PubMed]
80. Guo, Y.; Patanwala, H.S.; Bognet, B.; Ma, A.W. Inkjet and inkjet-based 3D printing: Connecting fluid properties and printing performance. *Rapid Prototyp. J.* **2017**, *23*, 562–576. [CrossRef]
81. Shirazi, S.F.S.; Gharehkhani, S.; Mehrali, M.; Yarmand, H.; Metselaar, H.S.C.; Kadri, N.A.; ABU Osman, N.A. A review on powder-based additive manufacturing for tissue engineering: Selective laser sintering and inkjet 3D printing. *Sci. Technol. Adv. Mater.* **2015**, *16*, 033502. [CrossRef] [PubMed]
82. Kafle, A.; Luis, E.; Silwal, R.; Pan, H.M.; Shrestha, P.L.; Bastola, A.K. 3D/4D Printing of Polymers: Fused Deposition Modelling (FDM), Selective Laser Sintering (SLS), and Stereolithography (SLA). *Polymers* **2021**, *13*, 3101. [CrossRef] [PubMed]
83. Ponnamma, D.; Yin, Y.; Salim, N.; Parameswaranpillai, J.; Thomas, S.; Hameed, N. Recent progress and multifunctional applications of 3D printed graphene nanocomposites. *Compos. Part B Eng.* **2021**, *204*, 108493. [CrossRef]
84. Jiang, Z.; Diggle, B.; Tan, M.L.; Viktorova, J.; Bennett, C.W.; Connal, L.A. Extrusion 3D Printing of Polymeric Materials with Advanced Properties. *Adv. Sci.* **2020**, *7*, 2001379. [CrossRef]
85. Mostafaei, A.; Elliott, A.M.; Barnes, J.E.; Li, F.; Tan, W.; Cramer, C.L.; Nandwana, P.; Chmielus, M. Binder jet 3D printing—Process parameters, materials, properties, modeling, and challenges. *Prog. Mater. Sci.* **2021**, *119*, 100707. [CrossRef]
86. Singh, S.; Ramakrishna, S.; Berto, F. 3D Printing of polymer composites: A short review. *Mater. Des. Process. Commun.* **2020**, *2*, e97. [CrossRef]
87. Wang, X.; Jiang, M.; Zhou, Z.W.; Gou, J.H.; Hui, D. 3D printing of polymer matrix composites: A review and prospective. *Compos. Part B Eng.* **2017**, *110*, 442–458. [CrossRef]
88. Sood, A.K.; Ohdar, R.; Mahapatra, S. Parametric appraisal of mechanical property of fused deposition modelling processed parts. *Mater. Des.* **2010**, *31*, 287–295. [CrossRef]
89. Melchels, F.P.W.; Feijen, J.; Grijpma, D.W. A review on stereolithography and its applications in biomedical engineering. *Biomaterials* **2010**, *31*, 6121–6130. [CrossRef] [PubMed]
90. Gu, D.D.; Meiners, W.; Wissenbach, K.; Poprawe, R. Laser additive manufacturing of metallic components: Materials, processes and mechanisms. *Int. Mater. Rev.* **2012**, *57*, 133–164. [CrossRef]
91. Zhang, Z.; Corrigan, N.; Bagheri, A.; Jin, J.; Boyer, C. A versatile 3D and 4D printing system through photocontrolled RAFT polymerization. *Angew. Chem.* **2019**, *131*, 18122–18131. [CrossRef]
92. Pan, H.M. Advanced Materials in 3D/4D Printing Technology. *Polymers* **2022**, *14*, 3255. [CrossRef]
93. Qian, Y.; Li, C.; Qi, Y.; Zhong, J. 3D printing of graphene oxide composites with well controlled alignment. *Carbon* **2021**, *171*, 777–784. [CrossRef]
94. Markandan, K.; Seetoh, I.P.; Lai, C.Q. Mechanical anisotropy of graphene nanocomposites induced by graphene alignment during stereolithography 3D printing. *J. Mater. Res.* **2021**, *36*, 4262–4274. [CrossRef]
95. Zuo, Y.; Yao, Z.; Lin, H.; Zhou, J.; Lu, J.; Ding, J. Digital light processing 3D printing of graphene/carbonyl iron/polymethyl methacrylate nanocomposites for efficient microwave absorption. *Compos. Part B Eng.* **2019**, *179*, 107533. [CrossRef]
96. Mangal, U.; Min, Y.J.; Seo, J.-Y.; Kim, D.-E.; Cha, J.-Y.; Lee, K.-J.; Kwon, J.-S.; Choi, S.-H. Changes in tribological and antibacterial properties of poly(methyl methacrylate)-based 3D-printed intra-oral appliances by incorporating nanodiamonds. *J. Mech. Behav. Biomed. Mater.* **2020**, *110*, 103992. [CrossRef]
97. Salgado, H.; Gomes, A.T.P.C.; Duarte, A.S.; Ferreira, J.M.F.; Fernandes, C.; Figueiral, M.H.; Mesquita, P. Antimicrobial Activity of a 3D-Printed Polymethylmethacrylate Dental Resin Enhanced with Graphene. *Biomedicines* **2022**, *10*, 2607. [CrossRef] [PubMed]
98. Aati, S.; Chauhan, A.; Shrestha, B.; Rajan, S.M.; Aati, H.; Fawzy, A. Development of 3D printed dental resin nanocomposite with graphene nanoplatelets enhanced mechanical properties and induced drug-free antimicrobial activity. *Dent. Mater.* **2022**, *38*, 1921–1933. [CrossRef] [PubMed]

99. Jing, J.; Xiong, Y.; Shi, S.; Pei, H.; Chen, Y.; Lambin, P. Facile fabrication of lightweight porous FDM-Printed polyethylene/graphene nanocomposites with enhanced interfacial strength for electromagnetic interference shielding. *Compos. Sci. Technol.* **2021**, *207*, 108732. [CrossRef]
100. Mohan, V.B.; Bhattacharyya, D. Mechanical, electrical and thermal performance of hybrid polyethylene-graphene nanoplatelets-polypyrrole composites: A comparative analysis of 3D printed and compression molded samples. *Polym. Plast. Technol. Mater.* **2020**, *59*, 780–796. [CrossRef]
101. Younes, H.; Kuang, X.; Lou, D.; DeVries, B.; Rahman, M.M.; Hong, H. Magnetic-field-assisted DLP stereolithography for controlled production of highly aligned 3D printed polymer-Fe_3O_4@ graphene nanocomposites. *Mater. Res. Bull.* **2022**, *154*, 111938. [CrossRef]
102. Li, Z.; Young, R.J.; Wilson, N.R.; Kinloch, I.A.; Vallés, C.; Li, Z. Effect of the orientation of graphene-based nanoplatelets upon the Young's modulus of nanocomposites. *Compos. Sci. Technol.* **2016**, *123*, 125–133. [CrossRef]
103. Peng, R.D.; Zhou, H.W.; Wang, H.W.; Mishnaevsky, L., Jr. Modeling of nano-reinforced polymer composites: Microstructure effect on Young's modulus. *Comput. Mater. Sci.* **2012**, *60*, 19–31. [CrossRef]
104. Sun, R.; Li, L.; Feng, C.; Kitipornchai, S.; Yang, J. Tensile behavior of polymer nanocomposite reinforced with graphene containing defects. *Eur. Polym. J.* **2018**, *98*, 475–482. [CrossRef]
105. Jing, J.; Chen, Y.; Shi, S.; Yang, L.; Lambin, P. Facile and scalable fabrication of highly thermal conductive polyethylene/graphene nanocomposites by combining solid-state shear milling and FDM 3D-printing aligning methods. *Chem. Eng. J.* **2020**, *402*, 126218. [CrossRef]
106. Camargo, J.C.; Machado, R.; Almeida, E.C.; Silva, E.F.M.S. Mechanical properties of PLA-graphene filament for FDM 3D printing. *Int. J. Adv. Manuf. Technol.* **2019**, *103*, 2423–2443. [CrossRef]
107. Ivanov, E.; Kotsilkova, R.; Xia, H.; Chen, Y.; Donato, R.K.; Donato, K.; Godoy, A.P.; Di Maio, R.; Silvestre, C.; Cimmino, S.; et al. PLA/Graphene/MWCNT Composites with Improved Electrical and Thermal Properties Suitable for FDM 3D Printing Applications. *Appl. Sci.* **2019**, *9*, 1209. [CrossRef]
108. Bustillos, J.; Montero, D.; Nautiyal, P.; Loganathan, A.; Boesl, B.; Agarwal, A. Integration of graphene in poly(lactic) acid by 3D printing to develop creep and wear-resistant hierarchical nanocomposites. *Polym. Compos.* **2018**, *39*, 3877–3888. [CrossRef]
109. 1Kim, H.; Lee, S. Characterization of Electrical Heating of Graphene/PLA Honeycomb Structure Composite Manufactured by CFDM 3D Printer. *Fash. Text.* **2020**, *7*, 1–18.
110. Joshi, S.; Rawat, K.; Karunakaran, C.; Rajamohan, V.; Mathew, A.T.; Koziol, K.; Thakur, V.K.; Balan, A.S. 4D printing of materials for the future: Opportunities and challenges. *Appl. Mater. Today* **2020**, *18*, 100490. [CrossRef]
111. Wei, X.; Li, D.; Jiang, W.; Gu, Z.; Wang, X.; Zhang, Z.; Sun, Z. 3D Printable Graphene Composite. *Sci. Rep.* **2015**, *5*, 11181. [CrossRef]
112. Zarek, M.; Layani, M.; Cooperstein, I.; Sachyani, E.; Cohn, D.; Magdassi, S. 3D Printing: 3D Printing of Shape Memory Polymers for Flexible Electronic Devices (Adv. Mater. 22/2016). *Adv. Mater.* **2016**, *28*, 4166. [CrossRef]
113. Chang, Y.; Cao, Q.; Venton, B. 3D printing for customized carbon electrodes. *Curr. Opin. Electrochem.* **2023**, *9*, 101228. [CrossRef]
114. Zhang, W.; Zhu, S.; Luque, R.; Han, S.; Hu, L.; Xu, G. Recent development of carbon electrode materials and their bioanalytical and environmental applications. *Chem. Soc. Rev.* **2016**, *45*, 715–752. [CrossRef]
115. Chyan, Y.; Ye, R.; Li, Y.; Singh, S.P.; Arnusch, C.J.; Tour, J.M. Laser-Induced Graphene by Multiple Lasing: Toward Electronics on Cloth, Paper, and Food. *ACS Nano* **2018**, *12*, 2176–2183. [CrossRef] [PubMed]
116. Ludvigsen, E.; Pedersen, N.; Zhu, X.; Marie, R.; Mackenzie, D.; Emnéus, J.; Petersen, D.; Kristensen, A.; Keller, S. Selective Direct Laser Writing of Pyrolytic Carbon Microelectrodes in Absorber-Modified SU-8. *Micromachines* **2021**, *12*, 564. [CrossRef] [PubMed]
117. Deshmukh, K.; Muzaffar, A.; Kovářík, T.; Křenek, T.; Ahamed, M.B.; Pasha, S.K. Fundamentals and applications of 3D and 4D printing of polymers: Challenges in polymer processing and prospects of future research. In *3D and 4D Printing of Polymer Nanocomposite Materials*; Sadasivuni, K.K., Deshmukh, K., Almaadeed, M.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 527–560.
118. Zhou, X.; Ren, L.; Song, Z.; Li, G.; Zhang, J.; Li, B.; Wu, Q.; Li, W.; Ren, L.; Liu, Q. Advances in 3D/4D printing of mechanical metamaterials: From manufacturing to applications. *Compos. Part B Eng.* **2023**, *254*, 110585. [CrossRef]
119. Ligon, S.C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117*, 10212–10290. [CrossRef]
120. Li, M.; Zhou, S.; Cheng, L.; Mo, F.; Chen, L.; Yu, S.; Wei, J. 3D Printed Supercapacitor: Techniques, Materials, Designs, and Applications. *Adv. Funct. Mater.* **2023**, *33*, 2208034. [CrossRef]
121. Xiong, C.; Zhang, Y.; Ni, Y. Recent progress on development of electrolyte and aerogel electrodes applied in supercapacitors. *J. Power Sources* **2023**, *560*, 232698. [CrossRef]
122. Channegowda, M.; Kp, S.; Athreya, Y.; Kumar, S.G.; Mk, S.K. Perspective—Supercapacitor-Powered Flexible Wearable Strain Sensors. *ECS Sensors Plus* **2023**, *2*, 017002. [CrossRef]
123. Wei, Q.; Zhou, J.; An, Y.; Li, M.; Zhang, J.; Yang, S. Modification, 3D printing process and application of sodium alginate based hydrogels in soft tissue engineering: A review. *Int. J. Biol. Macromol.* **2023**, *232*, 123450. [CrossRef]
124. Wang, Z.; Xiang, L.; Lin, F.; Tang, Y.; Cui, W. 3D bioprinting of emulating homeostasis regulation for regenerative medicine applications. *J. Control. Release* **2023**, *353*, 147–165. [CrossRef]

125. Kameoka, M.; Watanabe, Y.; Shiblee, N.I.; Kawakami, M.; Ogawa, J.; Khosla, A.; Furukawa, H.; Zhang, S.; Hirai, S.; Wang, Z. 4D Printing of Hydrogels Controlled by Hinge Structure and Spatially Gradient Swelling for Soft Robots. *Machines* **2023**, *11*, 103. [CrossRef]
126. Kuang, X.; Yue, L.; Qi, H.J. Introduction to 4D Printing: Concepts and Material Systems. In *Additive Manufacturing Technology: Design, Optimization, and Modeling*; Zhou, K., Ed.; Wiley-VCH: Weinheim, Germany, 2023; pp. 1–42. [CrossRef]
127. Singh, S.; Mali, H.S. 4D printing for product development: State of the art and future scope. *Innov. Process. Mater. Addit. Manuf.* **2023**, *1*, 293–306. [CrossRef]
128. Sloutski, A.; Cohn, D. Reverse thermo-responsive biodegradable shape memory-displaying polymers. *Polymer* **2023**, *267*, 125640. [CrossRef]
129. Pourmasoumi, P.; Moghaddam, A.; Mahand, S.N.; Heidari, F.; Moghaddam, Z.S.; Arjmand, M.; Kühnert, I.; Kruppke, B.; Wiesmann, H.-P.; Khonakdar, H.A. A review on the recent progress, opportunities, and challenges of 4D printing and bioprinting in regenerative medicine. *J. Biomater. Sci. Polym. Ed.* **2023**, *34*, 108–146. [CrossRef] [PubMed]
130. Kocharyan, H.; Karanjgaokar, N. Development of adaptive granular metamaterials for impact mitigation. *Extreme Mech. Lett.* **2023**, *58*, 101943. [CrossRef]
131. Fu, X.; Lin, J.; Liang, Z.; Yao, R.; Wu, W.; Fang, Z.; Zou, W.; Wu, Z.; Ning, H.; Peng, J. Graphene oxide as a promising nanofiller for polymer composite. *Surf. Interfaces* **2023**, *37*, 102747. [CrossRef]
132. Meng, Z. Effects of Chemical and Physical Features of 2D Nanofillers on the Mechanical and Viscoelastic Properties of Polymer Nanocomposites. *Bull. Am. Phys. Soc.* **2023**, *1*, 20–22.
133. Bazhanov, D.A.; Poteryaev, A.A.; Shapagin, A.V.; Shcherbina, A.A. Ethylene-Vinyl Acetate Copolymers as Potential Thermoplastic Modifiers of Photopolymer Compositions. *Polymers* **2023**, *15*, 131. [CrossRef]
134. Idowu, A.; Thomas, T.; Boesl, B.; Agarwal, A. Cryo-Assisted Extrusion Three-Dimensional Printing of Shape Memory Polymer–Graphene Composites. *J. Manuf. Sci. Eng.* **2023**, *145*, 041003.
135. Thongchom, C.; Refahati, N.; Saffari, P.R.; Saffari, P.R.; Niyaraki, M.N.; Sirimontree, S.; Keawsawasvong, S. An Experimental Study on the Effect of Nanomaterials and Fibers on the Mechanical Properties of Polymer Composites. *Buildings* **2021**, *12*, 7. [CrossRef]
136. Nikita, K.; Patel, D.; Patel, G. Additive Manufacturing of Multifunctional Polymer Nanocomposites: From 3 D to 4 D. In *Nanotechnology-Based Additive Manufacturing: Product Design, Properties and Applications*; Wiley: Hoboken, NJ, USA, 2023; Volume 1, pp. 277–313. [CrossRef]
137. Du, J.; Fu, G.; Xu, X.; Elshahawy, A.M.; Guan, C. 3D Printed Graphene-Based Metamaterials: Guesting Multi-Functionality in One Gain. *Small* **2023**, 2207833. [CrossRef]
138. Pugliese, R.; Regondi, S. Artificial Intelligence-Empowered 3D and 4D Printing Technologies toward Smarter Biomedical Materials and Approaches. *Polymers* **2022**, *14*, 2794. [CrossRef]
139. Ahmed, A.; Arya, S.; Gupta, V.; Furukawa, H.; Khosla, A. 4D printing: Fundamentals, materials, applications and challenges. *Polymer* **2021**, *228*, 123926. [CrossRef]
140. Ren, L.; Wu, W.; Ren, L.; Song, Z.; Liu, Q.; Li, B.; Wu, Q.; Zhou, X. 3D Printing of Auxetic Metamaterials with High-Temperature and Programmable Mechanical Properties. *Adv. Mater. Technol.* **2022**, *7*, 2101546. [CrossRef]
141. Farzinazar, S.; Wang, Y.; Owens, C.A.-H.; Yang, C.; Lee, H.; Lee, J. Thermal transport in 3D printed shape memory polymer metamaterials. *APL Mater.* **2022**, *10*, 081105. [CrossRef]
142. Muthe, L.P.; Pickering, K.; Gauss, C. A Review of 3D/4D Printing of Poly-Lactic Acid Composites with Bio-Derived Reinforcements. *Compos. Part C Open Access* **2022**, *8*, 100271. [CrossRef]
143. Liang, Z.; Yao, Y.; Jiang, B.; Wang, X.; Xie, H.; Jiao, M.; Liang, C.; Qiao, H.; Kline, D.; Zachariah, M.R.; et al. 3D Printed Graphene-Based 3000 K Probe. *Adv. Funct. Mater.* **2021**, *31*, 2102994. [CrossRef]
144. Chen, W.; Wang, Z.; Bets, K.V.; Luong, D.X.; Ren, M.; Stanford, M.G.; McHugh, E.A.; Algozeeb, W.A.; Guo, H.; Gao, G.; et al. Millisecond conversion of metastable 2D materials by flash Joule heating. *ACS Nano* **2021**, *15*, 1282–1290. [CrossRef]
145. Xia, T.; Zeng, D.; Li, Z.; Young, R.J.; Vallés, C.; Kinloch, I.A. Electrically conductive GNP/epoxy composites for out-of-autoclave thermoset curing through Joule heating. *Compos. Sci. Technol.* **2018**, *164*, 304–312. [CrossRef]
146. Chowdhury, J.; Anirudh, P.V.; Karunakaran, C.; Rajmohan, V.; Mathew, A.T.; Koziol, K.; Alsanie, W.F.; Kannan, C.; Balan, A.S.S.; Thakur, V.K. 4D Printing of Smart Polymer Nanocomposites: Integrating Graphene and Acrylate Based Shape Memory Polymers. *Polymers* **2021**, *13*, 3660. [CrossRef]
147. Xiao, Y.Y.; Jiang, Z.C.; Zhao, Y. Liquid Crystal Polymer-Based Soft Robots. *Adv. Intell. Syst.* **2020**, *2*, 2000148. [CrossRef]
148. Chen, G.; Seo, J.; Yang, C.; Prasad, P.N. Nanochemistry and nanomaterials for photovoltaics. *Chem. Soc. Rev.* **2013**, *42*, 8304–8338. [CrossRef]
149. Yang, W.; Xu, X.; Gao, Y.; Li, Z.; Li, C.; Wang, W.; Chen, Y.; Ning, G.; Zhang, L.; Yang, F.; et al. High-surface-area nanomesh graphene with enriched edge sites as efficient metal-free cathodes for dye-sensitized solar cells. *Nanoscale* **2016**, *8*, 13059–13066. [CrossRef] [PubMed]
150. Inshakova, E.; Inshakova, A.; Goncharov, A. Engineered Nanomaterials for Energy Sector: Market Trends, Modern Applications and Future Prospects. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *971*, 032031. [CrossRef]
151. Li, Y.; Gao, T.; Yang, Z.; Chen, C.; Kuang, Y.; Song, J.; Jia, C.; Hitz, E.M.; Yang, B.; Hu, L. Graphene oxide-based evaporator with one-dimensional water transport enabling high-efficiency solar desalination. *Nano Energy* **2017**, *41*, 201–209. [CrossRef]

152. Li, X.; Liu, L.; Liu, G.; Rong, Y.; Yang, Y.; Wang, H.; Ku, Z.; Xu, M.; Zhong, C.; Han, H. Efficient Dye-Sensitized Solar Cells with Potential-Tunable Organic Sulfide Mediators and Graphene-Modified Carbon Counter Electrodes. *Adv. Funct. Mater.* **2013**, *23*, 3344–3352. [CrossRef]
153. Jung, S.; Sou, A.; Banger, K.; Ko, D.H.; Chow, P.C.; McNeill, C.R.; Sirringhaus, H. All-inkjet-printed, all-air-processed solar cells. *Adv. Energy Mater.* **2014**, *4*, 1400432. [CrossRef]
154. Vak, D.; Hwang, K.; Faulks, A.; Jung, Y.-S.; Clark, N.; Kim, D.-Y.; Wilson, G.J.; Watkins, S.E. 3D Printer Based Slot-Die Coater as a Lab-to-Fab Translation Tool for Solution-Processed Solar Cells. *Adv. Energy Mater.* **2015**, *5*, 1401539. [CrossRef]
155. Finn, M., III; Martens, C.J.; Zaretski, A.V.; Roth, B.; Søndergaard, R.R.; Krebs, F.C.; Lipomi, D.J. Mechanical stability of roll-to-roll printed solar cells under cyclic bending and torsion. *Sol. Energy Mater. Sol. Cells* **2018**, *174*, 7–15. [CrossRef]
156. Wu, X.; Mu, F.; Lin, Z. Three-dimensional printing of graphene-based materials and the application in energy storage. *Mater. Today Adv.* **2021**, *11*, 100157. [CrossRef]
157. El-Kady, M.F.; Shao, Y.; Kaner, R.B. Graphene for batteries, supercapacitors and beyond. *Nat. Rev. Mater.* **2016**, *1*, 16033. [CrossRef]
158. Armelin, E.; Pérez-Madrigal, M.M.; Alemán, C.; Díaz, D.D. Current status and challenges of biohydrogels for applications as supercapacitors and secondary batteries. *J. Mater. Chem. A* **2016**, *4*, 8952–8968. [CrossRef]
159. Elder, B.; Neupane, R.; Tokita, E.; Ghosh, U.; Hales, S.; Kong, Y.L. Nanomaterial Patterning in 3D Printing. *Adv. Mater.* **2020**, *32*, e1907142. [CrossRef]
160. Lyu, Z.; Lim, G.J.; Koh, J.J.; Li, Y.; Ma, Y.; Ding, J.; Wang, J.; Hu, Z.; Wang, J.; Chen, W.; et al. Design and Manufacture of 3D-Printed Batteries. *Joule* **2021**, *5*, 89–114. [CrossRef]
161. Chu, T.; Park, S.; Fu, K. 3D printing-enabled advanced electrode architecture design. *Carbon Energy* **2021**, *3*, 424–439. [CrossRef]
162. Le, L.T.; Ervin, M.H.; Qiu, H.; Fuchs, B.E.; Zunino, J.; Lee, W.Y. Inkjet-printed graphene for fleible micro-supercapacitors. In Proceedings of the 2011 11th IEEE International Conference on Nanotechnology, Portland, OR, USA, 15–18 August 2011; pp. 67–71.
163. Tang, K.; Ma, H.; Tian, Y.; Liu, Z.; Jin, H.; Hou, S.; Zhou, K.; Tian, X. 3D printed hybrid-dimensional electrodes for flexible micro-supercapacitors with superior electrochemical behaviours. *Virtual Phys. Prototyp.* **2020**, *15*, 511–519. [CrossRef]
164. Zhou, Y.; Parker, C.B.; Joshi, P.; Naskar, A.K.; Glass, J.T.; Cao, C. 4D Printing of Stretchable Supercapacitors via Hybrid Composite Materials. *Adv. Mater. Technol.* **2021**, *6*, 2001055. [CrossRef]
165. Zhu, C.; Liu, T.; Qian, F.; Han, T.Y.-J.; Duoss, E.B.; Kuntz, J.D.; Spadaccini, C.M.; Worsley, M.A.; Li, Y. Supercapacitors Based on Three-Dimensional Hierarchical Graphene Aerogels with Periodic Macropores. *Nano Lett.* **2016**, *16*, 3448–3456. [CrossRef]
166. Shen, K.; Mei, H.; Li, B.; Ding, J.; Yang, S. 3D Printing Sulfur Copolymer-Graphene Architectures for Li-S Batteries. *Adv. Energy Mater.* **2018**, *8*, 1701527. [CrossRef]
167. Wu, B.; Guo, B.; Chen, Y.; Mu, Y.; Qu, H.; Lin, M.; Bai, J.; Zhao, T.; Zeng, L. High Zinc Utilization Aqueous Zinc Ion Batteries Enabled by 3D Printed Graphene Arrays. *Energy Storage Mater.* **2023**, *54*, 75–84. [CrossRef]
168. Fu, K.; Wang, Y.; Yan, C.; Yao, Y.; Chen, Y.; Dai, J.; Lacey, S.; Wang, Y.; Wan, J.; Li, T.; et al. Graphene Oxide-Based Electrode Inks for 3D-Printed Lithium-Ion Batteries. *Adv. Mater.* **2016**, *28*, 2587–2594. [CrossRef]
169. Qiao, Y.; Liu, Y.; Chen, C.; Xie, H.; Yao, Y.; He, S.; Ping, W.; Liu, B.; Hu, L. 3D-Printed Graphene Oxide Framework with Thermal Shock Synthesized Nanoparticles for Li-CO_2 Batteries. *Adv. Funct. Mater.* **2018**, *28*, 1805899. [CrossRef]
170. Wen, N.; Zhang, L.; Jiang, D.; Wu, Z.; Li, B.; Sun, C.; Guo, Z. Emerging flexible sensors based on nanomaterials: Recent status and applications. *J. Mater. Chem. A* **2020**, *8*, 25499–25527. [CrossRef]
171. Christ, J.F.; Aliheidari, N.; Ameli, A.; Pötschke, P. 3D printed highly elastic strain sensors of multiwalled carbon nanotube/thermoplastic polyurethane nanocomposites. *Mater. Des.* **2017**, *131*, 394–401. [CrossRef]
172. Zhang, J.; Liu, E.; Hao, S.; Yang, X.; Li, T.; Lou, C.; Run, M.; Song, H. 3D Printable, ultra-stretchable, Self-healable, and self-adhesive dual cross-linked nanocomposite ionogels as ultra-durable strain sensors for motion detection and wearable human-machine interface. *Chem. Eng. J.* **2022**, *431*, 133949. [CrossRef]
173. Xiang, D.; Zhang, X.; Harkin-Jones, E.; Zhu, W.; Zhou, Z.; Shen, Y.; Li, Y.; Zhao, C.; Wang, P. Synergistic effects of hybrid conductive nanofillers on the performance of 3D printed highly elastic strain sensors. *Compos. Part A Appl. Sci. Manuf.* **2020**, *129*, 105730. [CrossRef]
174. Cardoso, R.M.; Kalinke, C.; Rocha, R.G.; Dos Santos, P.L.; Rocha, D.P.; Oliveira, P.R.; Janegitz, B.C.; Bonacin, J.A.; Richter, E.M.; Munoz, R.A. Additive-manufactured (3D-printed) electrochemical sensors: A critical review. *Anal. Chim. Acta* **2020**, *1118*, 73–91. [CrossRef]
175. Kumar, V.; Singh, R.; Ahuja, I.P. 3D printed graphene-reinforced polyvinylidene fluoride composite for piezoelectric properties. In *4D Printing*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 51–66.
176. Maurya, D.; Khaleghian, S.; Sriramdas, R.; Kumar, P.; Kishore, R.A.; Kang, M.G.; Kumar, V.; Song, H.-C.; Lee, S.-Y.; Yan, Y.; et al. 3D printed graphene-based self-powered strain sensors for smart tires in autonomous vehicles. *Nat. Commun.* **2020**, *11*, 5392. [CrossRef]
177. Mahmud, M.A.P.; Tat, T.; Xiao, X.; Adhikary, P.; Chen, J. Advances in 4D-printed physiological monitoring sensors. *Exploration* **2021**, *1*, 210033. [CrossRef]
178. Sun, J.; Sun, Y.; Jia, H.; Bi, H.; Chen, L.; Que, M.; Xiong, Y.; Han, L.; Sun, L. A novel pre-deposition assisted strategy for inkjet printing graphene-based flexible pressure sensor with enhanced performance. *Carbon* **2022**, *196*, 85–91. [CrossRef]
179. Li, Q.; Wu, T.; Zhao, W.; Li, Y.; Ji, J.; Wang, G. 3D printing stretchable core-shell laser scribed graphene conductive network for self-powered wearable devices. *Compos. Part B Eng.* **2022**, *240*, 110000. [CrossRef]

180. Tan, H.W.; Choong, Y.Y.C.; Kuo, C.N.; Low, H.Y.; Chua, C.K. 3D printed electronics: Processes, materials and future trends. *Prog. Mater. Sci.* **2022**, *127*, 100945. [CrossRef]
181. Wang, F.; Xu, Z. Graphene and graphene oxide-reinforced 3D and 4D printable composites. In *3D and 4D Printing of Polymer Nanocomposite Materials*; Sadasivuni, K.K., Deshmukh, K., Almaadeed, M.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 259–296.