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# Development of core–shell nanofibers in magnetoelectric sensors, fuel cells, and drug-delivery applications: a review

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Core–shell nanofibers have emerged as a versatile class of nanostructured materials due to their unique ability to integrate multiple functionalities within a single architecture. Their coaxial geometry, which combines core and shell domains, allows for precise control over composition, interfacial interactions, and surface characteristics, making them highly attractive for advanced electronic and biomedical applications. This review highlights recent advancements in the design, synthesis, and application of core–shell nanofibers, with a focus on their roles in magnetoelectric devices and drug delivery systems. For magnetoelectric devices, core–shell nanofibers provide efficient coupling between magnetic and electric order parameters, enabling the development of miniaturized, flexible, high-sensitivity sensors, energy harvesters, and transducers. Their high aspect ratio, tunable interfacial stress transfer, and enhanced magnetoelectric coupling provide new opportunities for next-generation spintronic and wearable technologies. In parallel, the unique core–shell morphology offers distinct advantages in drug delivery, such as high loading efficiency, sequential or sustained release, and protection of bioactive agents, which are crucial for wound healing, tissue engineering, and targeted therapies. Also, this review highlights recent progress in core–shell nanofiber-based electrodes for HT-PEMFCs, DEFCs, and IT-SOFCs, emphasizing their role in enhancing catalytic activity, stability, and ionic conductivity. These advancements pave the way for high-efficiency and durable fuel cell technologies for next-generation, efficient, and sustainable fuel cell systems. We further summarize the progress in electrospinning and other fabrication techniques that enables scalable production of uniform core–shell nanofibers, along with critical insights into structure–property relationships, challenges, and future perspectives. This review highlights the multifunctional potential of core–shell nanofibers as a transformative platform for next-generation devices and healthcare solutions, bridging developments in the electronic and biomedical domains.

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## 1. Introduction

### 1.1 Nanotechnology and nanofibers

The fundamental principle of nanotechnology is reducing the size of materials to nanometer dimensions, which alters their physicochemical properties due to quantum confinement, increased surface-to-volume ratios, and modified electronic and interfacial behaviors. In semiconductors, size confinement can induce quantum effects that significantly change their optoelectronic characteristics, while magnetic materials transition

to superparamagnetic behavior below a critical size. In catalytic metal nanoparticles, decreasing the particle diameter to a few nanometers can alter the crystal structure, surface topology, and electronic properties, including shifts in the Fermi level and reduction, which can potentially influence adsorption behavior and catalytic activity.<sup>1–4</sup> These nanoscale phenomena underpin the broad utility of nanostructured systems in various applications, including nanoelectromechanical system (NEMS) sensors, targeted drug delivery, tissue engineering, implant surface modification, and wound healing.<sup>5–8</sup> One-dimensional (1D) nanofibers are fiber structures characterized by diameters in the nanometer range. Recent advancements have broadened the definition of nanofibers; according to Horne *et al.*,<sup>9</sup> fibers with diameters ranging from 0 to 500 nm are nanofibers. Prabu *et al.*<sup>10</sup> extended this definition, reporting that fibers with diameters between 50 and 1000 nm are also categorized as nanofibers, while their lengths can extend to several centimeters. 1D nanofibers exhibit a high surface area-to-volume ratio,

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tunable surface functionalities, and enhanced mechanical properties as the polymer fiber diameter decreases to submicron or nanometer scales. For instance, a nanofiber is 2 cm long and 400 nm in diameter, corresponding to an aspect ratio of approximately 5000, which significantly increases the available surface area for interactions while maintaining a low total volume.<sup>11,12</sup>

The nanoscale holds particular significance for biological systems, as the characteristic dimensions of viruses, bacteria, biomolecules, carbon nanotubes (CNTs), and other nanostructures fall within this range. A comparison with these objects reveals that electrospun fibers can exhibit diameters across a relatively broad spectrum, as shown in Fig. 1(a). The principal motivation for utilizing nanofiber-based systems is that materials at the micro- and nano-scale exhibit unique physical and chemical properties not observed in their bulk forms. Likewise, tailoring materials at the nanoscale can drastically alter thermal transport, for example, reducing lattice

thermal conductivity in nanostructured thermoelectrics, thereby improving their energy conversion efficiency. Electrospinning is a versatile technique for fabricating continuous nanofibers by applying a high-voltage electric field to a polymer solution, inducing jet formation. In a standard laboratory electrospinning setup, a polymer solution or melt is fed through a spinneret nozzle with an inner diameter of approximately 10–100  $\mu\text{m}$  (Fig. 1(b)). This nozzle also acts as an electrode, across which a high electric field of 50–500  $\text{kV m}^{-1}$  is applied, while the counter electrode is positioned 10–25 cm away. The fibers are usually collected on a substrate connected to the counter electrode. Electrospun fibers exhibit superior porosity, surface area, and application versatility, rendering them highly suitable for biomedical and filtration applications. CNTs excel in strength, and hair has the largest diameter, but limited surface functionality, as illustrated in Fig. 1(c). Electrospun fibers provide a balanced combination of biocompatibility, porosity, and practical applicability. Nanofibers, in particular, can achieve



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Fig. 1 (a) Comparison of the diameters of nanofibers with biological and technological objects, (b) illustration of the electrospinning setup for preparation of nanofibers, and (c) comparison of biocompatibility, strength, porosity, surface area, diameter, and potential applications of electrospun nanofibers with CNTs and human hairs.

pronounced ME coupling by eliminating substrate clamping effects commonly encountered in thin film bilayers or nanopillars deposited on substrates.<sup>13–15</sup> Furthermore, the application of nanofibers in the medical and aerospace industries has been broadened. For example, nanofibers are being explored in the medical sector for their utility in tissue engineering scaffolds, wound dressing materials, drug delivery systems, and biosensors due to their high surface area and tunable physico-chemical properties.<sup>16,17</sup> In the aerospace and space industries, nanofiber composites contribute to the development of lightweight, high-strength structural components and radiation shielding, thereby further enhancing the performance and safety of spacecraft.<sup>18,19</sup> The food industry benefits from utilizing nanofibers in areas such as active packaging and filtration, as well as for the controlled release of nutraceuticals and preservatives.<sup>20–22</sup> Overall, the multifunctional nature of

nanofiber-based materials continues to expand their application landscape across various domains, including medical, space, food, environmental, and other advanced technological fields.

## 1.2 Core-shell nanofibers

Core-shell nanofibers are one-dimensional nanostructures characterized by an inner core material enveloped by an outer shell, typically fabricated through coaxial electrospinning or emulsion methods. This architecture enables the independent tuning of core and shell compositions, allowing for multifunctional properties and precise control over released profiles or surface functionalities. Core-shell nanofibers are widely recognized for their enhanced stability, tunable mechanical and electrical properties, and efficacy in drug delivery, catalysis, and



sensor applications. Their structure offers protective encapsulation for sensitive molecules while maintaining nanofiber flexibility and high surface area.<sup>23</sup> Furthermore, with the progression of nanofiber technology, core-shell nanofibers have emerged as an advanced architecture in which a core material is encapsulated within a surrounding shell, enabling tunable physicochemical properties and multifunctionality. This configuration simplifies fabrication compared to more complex nanofiber assemblies while offering superior performance in targeted applications. In drug delivery, core-shell nanofibers facilitate controlled release kinetics and site-specific transport of therapeutics. As catalytic supports, their high surface-to-volume ratio and dual-compartment design enhance reaction efficiency and stability. The distinct core-shell interface improves coupling efficiency and sensitivity in ME sensing. Additionally, they have been employed in the food industry for active preservation and innovative packaging, in tissue engineering as biocompatible scaffolds promoting cell adhesion and proliferation, and in water purification systems for efficient adsorption and removal of contaminants. A schematic illustrating the applications of core-shell nanofibers in drug delivery, catalysis, sensors, the food industry, tissue engineering, and water purification is presented in Fig. 2.

### 1.3 Development in core-shell nanofibers

Core-shell nanofibers offer distinct advantages over traditional and bulk composites due to their high surface-to-volume ratio, enabling enhanced functionality and efficiency. Their unique structure allows precise control over core and shell material properties, facilitating tailored applications such as ME coupling and drug delivery. Unlike bulk composites, they offer

flexibility, a lightweight design, and enhanced interfacial interactions, which are crucial for advanced devices. Scalable fabrication methods, such as coaxial electrospinning, surpass traditional composites in producing uniform, multifunctional nanostructures. These features make core-shell nanofibers ideal for next-generation biomedical, energy, and environmental technologies. However, the roots of core-shell nanofibers lie in the development of electrospinning, a technique pioneered in the 1990s for producing micro- and nanofibers using electrostatic forces.<sup>24</sup> Early studies by Reneker and Doshi (1995) laid the groundwork for electrospinning, demonstrating the ability to develop ultrafine fibers from polymer solutions.<sup>14</sup> Initial electrospinning focused on monolithic (single-component) nanofibers; however, researchers soon recognized the potential for more complex structures to enhance functionality. Core-shell nanofibers were introduced with the advent of coaxial electrospinning, which occurred around 2002–2003. Loscertales *et al.* (2002) and others demonstrated the use of a coaxial nozzle to simultaneously spin two different materials, forming a core-shell structure.<sup>25</sup> This allowed for the encapsulation of one material (the core) within another (the shell), enabling the tailoring of properties.<sup>26–28</sup> Early studies, such as those by Zhang *et al.* (2004), investigated core-shell nanofibers composed of polymers like PCL and gelatin, highlighting their potential in biomedical applications.<sup>29</sup> By the late 2000s, coaxial electrospinning was refined to improve control over fiber morphology, diameter, and composition. Innovations included emulsion electrospinning and modified coaxial/triaxial electrospinning, which enabled the use of unspinnable core materials (*e.g.*, drug solutions or lipids) by leveraging spinnable shell polymers. Alternative methods, such as self-assembly and



Fig. 2 Schematic representation of core-shell nanofiber applications, including in drug delivery, catalysis, sensors, the food industry, tissue engineering, and water purification.



phase-separation electrospinning, have emerged for producing core-shell-like structures without the need for coaxial setups.<sup>30</sup> For instance, Jiang *et al.* (2013) utilized vapor-induced phase separation to create core-shell nanofibers, thereby expanding the versatility of fabrication.<sup>31</sup> The period also saw the integration of non-polymeric materials, such as ceramics and metal oxides, into core-shell nanofibers, broadening their applications beyond biomedicine.<sup>32</sup>

Since the 2010s, core-shell nanofibers have gained traction due to their improved scalability and functionalization capabilities. Techniques like coaxial centrifugal spinning address the limitations of coaxial electrospinning, such as low production rates and high energy consumption, thereby enabling commercialization potential. Recent advancements include multiaxial electrospinning for producing multi-layered fibers and needleless electrospinning for achieving higher yields, particularly for chitosan-based nanofibers.<sup>33–35</sup> Furthermore, coaxial electrospinning remains the cornerstone for fabricating ME core-shell nanofibers due to its ability to precisely control the composition of both the core and shell. By 2015–2025, researchers had optimized parameters such as solution viscosity, flow rates, and electric field strength to achieve uniform fiber diameters (50–500 nm) and enhance interfacial strain transfer, which is crucial for ME coupling. ME-based core-shell nanofibers have evolved from niche research to a versatile platform for advanced devices, driven by innovations in coaxial, multiaxial, and needleless electrospinning, as well as novel material combinations.

Although several reviews have discussed ME composites, electrospun nanofibers, or polymer-ceramic multifunctional systems, these studies have primarily focused on bulk laminates, thin films, or general fiber fabrication techniques, without examining core-shell nanofibers as an integrated materials platform. Furthermore, recent advances from 2022 to 2025—including coaxial electrospinning optimization, self-assembled core-shell structures, and newly reported ME fiber systems such as  $\text{CoFe}_2\text{O}_4\text{-Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.89}\text{Sn}_{0.11}\text{O}_3$ ,  $\text{Ba}_2\text{Zn}_2\text{-Fe}_{12}\text{O}_{22}\text{-PZT}$ , and  $\text{NdFeO}_3\text{-PZT}$ —have not been consolidated in any existing review. To the best of our knowledge, no comprehensive article has simultaneously examined (i) the structure-property relationships of core-shell nanofibers, (ii) their strain-mediated ME coupling mechanisms, and (iii) their emerging roles in fuel cells and drug-delivery technologies. This review uniquely integrates these interdisciplinary developments, highlighting material design principles, fabrication strategies, and application-specific performance metrics. Likewise, recent progress in core-shell nanofiber-based drug carriers—including dual-drug systems, stimuli-responsive release, and coaxial fibers for tissue regeneration—remains fragmented in the literature. In addition to their roles in magnetoelectric sensing and biomedical delivery systems, core-shell nanofibers have recently emerged as promising materials for fuel cell technologies due to their tunable nanoarchitecture, enhanced surface area, and ability to integrate multifunctional components within a single fiber. By integrating recent findings from these domains and identifying key knowledge gaps, this work

offers a timely and distinctive perspective that complements and extends existing reviews.

## 2. Materials and application

### 2.1 Magnetoelectrics

In recent years, there has been increased scientific focus on multiferroic materials exhibiting magnetoelectric (ME) phenomena, which are characterized by the correlation between the applied magnetic field and the corresponding electric voltage.<sup>36–41</sup> The intrinsic coupling between electric and magnetic orders in ME materials enables wirelessly induced electric charge generation, facilitating the less-invasive incorporation of these materials into next-generation electronic devices. Recent literature<sup>42–49</sup> reports the notable progress in the fundamental understanding and development of advanced ME materials. These innovations have established ME materials as a promising candidate for applications in microelectronics and engineering, such as high-speed memory devices,<sup>50,51</sup> advanced ME antennas,<sup>52–54</sup> and ME sensors,<sup>55–57</sup> among others. Additionally, ME materials enable the detection of low-intensity magnetic fields in MEMS sensor technologies for navigation and automotive applications, operating effectively at room temperature (RT). In contrast, highly complex SQUIDS need low-temperature environments.<sup>58–60</sup> Furthermore, ME materials enable the harvesting of energy from ambient magnetic fields for Internet of Things (IoT) applications, the realization of non-volatile ME random-access memory (ME-RAM) for data storage devices, and the development of highly compact, tunable antennas for radio-frequency communication in space, demonstrating enhanced efficiency relative to conventional materials.<sup>61–63</sup>

In ME composites, coupling occurs through mechanical strain that is generated in the magnetostrictive (ferromagnetic) phase, which is transferred to the piezoelectric (ferroelectric) phase, resulting in an electrical response.<sup>64–66</sup> In the direct ME effect, an in-plane magnetic field ( $H$ ) induces strain in the magnetic component through a phenomenon known as magnetostriction. This strain is mechanically transferred to the ferroelectric component, generating dielectric polarization *via* the piezoelectric effect, as illustrated in Fig. 3(a). In contrast, the converse ME effect involves an out-of-plane electric field ( $E$ ) that creates strain in the ferroelectric component through the inverse piezoelectric effect. This strain is mechanically linked to the magnetic element, resulting in changes in magnetization ( $\Delta M$ ) or domain reorientation due to the piezomagnetic impact, as shown in Fig. 3(b).

As a result, extensive research has focused on exploring the micro- and nanoscale structures of heterogeneous materials and their configurations, which include: (i) 0–3 type structures,<sup>67–69</sup> where magnetostrictive nanoparticles are dispersed within a piezoelectric matrix as shown in Fig. 2(a); (ii) 2–2 type structures,<sup>70–74</sup> characterized by alternating layers of magnetostrictive and piezoelectric phases as shown in Fig. 4(b); (iii) 1–3 type structures,<sup>75–78</sup> consisting of piezoelectric fibers or rods embedded in a magnetostriction matrix or fiber network, as illustrated in Fig. 4(c).



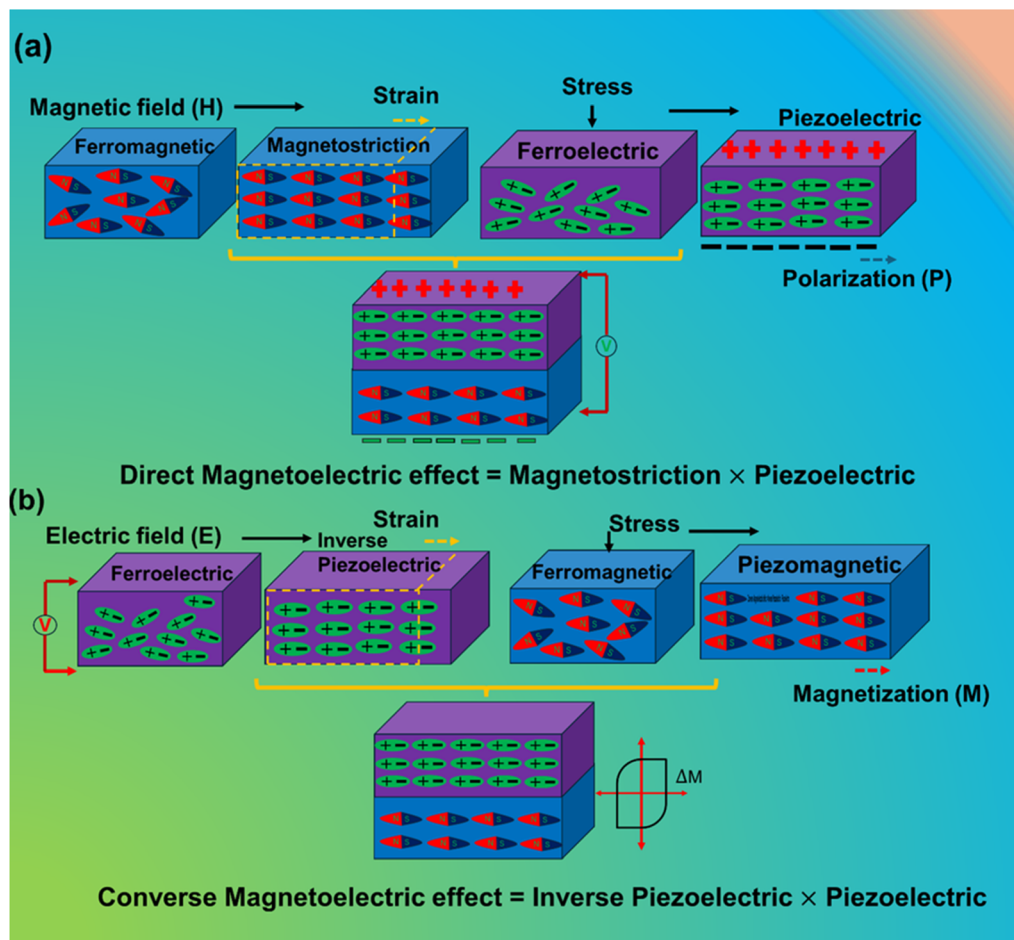


Fig. 3 Schematic illustration of the strain-mediated ME effect in a composite system: the (a) direct ME effect and (b) converse ME effect.

Efficient higher-order interfaces in composite heterostructures are critical for achieving strain transfer across phase boundaries. This maximizes ME coupling, which governs the interaction between magnetic and electric order parameters. Therefore, there is significant potential to enhance ME coupling by tailoring surface interactions in these heterostructures to optimize strain transfer, ultimately facilitating ME performance.<sup>79</sup> The phase architectures of 0-3 and 2-2 type structures

exhibit irregular spatial distributions of ferroelectric/ferromagnetic phases, which impede efficient strain transfer and consequently result in relatively weak ME coupling. In particular, 2-2 type composites, characterized by alternating layered structures of magnetostrictive and piezoelectric phases, often suffer from limited interfacial contact area and possible mechanical mismatch between layers, thereby restricting effective mechanical coupling. These factors hinder robust



Fig. 4 Composite ME materials with different types of structure, (a) 0-3, (b) 2-2, (c) 1-3 type structures.



interactions between magnetic and electric order parameters, limiting the overall ME response.

In contrast, the 1–3 type composite structure, nanofibers or core–shell nanofibers, particularly those incorporating nanofibers as the magnetostrictive phase embedded within a piezoelectric matrix, provides a more continuous and anisotropic pathway for strain-mediated coupling. Furthermore, core–shell nanofibers are sometimes described as hybrid or variant 1–3 type structures, and both constituent phases are continuous along the length of the fiber. They are co-located within the same one-dimensional structure. This configuration facilitates higher mechanical strain transfer across the interfaces, significantly enhancing the ME coupling strength compared to other composite structures. Most importantly, the nanoscale dimensions and high aspect ratio of the fibers contribute to an increased interfacial area and improved load transfer efficiency, further enhancing the ME performance.<sup>80,81</sup>

The first intrinsic ME effect was experimentally demonstrated in antiferromagnetic (chromic oxide) Cr<sub>2</sub>O<sub>3</sub> single crystals in 1961 by Folen at RT.<sup>82</sup> Over the past century, considering both material composition and dimensionality, ME materials have progressed from single-phase to particulate, laminated, and, more recently, micro- and nano-scale nanofibers and thin films. To date, more than ten distinct families of single-phase compounds have been extensively investigated as ME materials, including BiFeO<sub>3</sub>,<sup>83,84</sup> RMnO<sub>5</sub> (R = Eu, Gd, Er, Y),<sup>85,86</sup> and RMnO<sub>3</sub> (R = Gd, Tb, Dy).<sup>87,88</sup> Such studies have been driven by potential applications, including metallic memories,<sup>89</sup> universal memory,<sup>90</sup> Bennett clocking,<sup>91</sup> and resistive switching.<sup>92</sup> However, achieving strong intrinsic ME coupling at or above RT remains challenging, as most single-phase multiferroics possess relatively low Curie temperatures.<sup>93,94</sup> In general, for multiferroic crystals, the polarization (*P*) and magnetization (*M*) are coupled to the electric (*E*) and magnetic (*H*) fields through the following relations:<sup>47</sup> Landau theory describes the ME effect in a single-phase material through the expansion of the free energy expression as

$$F(E, H) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i E_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k \quad (1)$$

Here,  $\epsilon_0$  and  $\mu_0$  denote the dielectric permittivity and magnetic permeability of the medium, respectively, while  $\epsilon_{ij}$  and  $\mu_{ij}$  represent the relative dielectric permittivity and magnetic permeability of the material. The second and third terms in eqn (1) correspond to the temperature-dependent spontaneous polarization ( $P_i^S$ ) and spontaneous magnetization ( $M_i^S$ ). The fourth and fifth terms describe the influence of electric and magnetic fields on the electrical and magnetic responses, respectively. The sixth term, containing  $\alpha_{ij}$ , represents the linear ME coupling. The subsequent two terms, involving  $\beta_{ijk}$  and  $\gamma_{ijk}$ , are third-rank tensors that account for higher-order coupling effects.

Differentiation of eqn (1) concerning electric and magnetic fields, respectively, leads to polarization and magnetization, which are as follows:

$$P_i = -\frac{\partial F(E, H)}{\partial E_i} = P_i^S + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_j E_k \quad (2)$$

$$M_i = -\frac{\partial F(E, H)}{\partial H_i} = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_j + \frac{1}{2} \beta_{ijk} E_j E_k + \gamma_{ijk} E_j H_k \quad (3)$$

In practice, to eliminate the influence of material electrical conductivity, ME effects are investigated dynamically by applying an alternating magnetic or electric field to the samples. The magnitude of dynamic effects is characterized by using ME coefficients:

$$\alpha_E = \frac{\delta E}{\delta H} \text{ (V/Oe.cm) for the direct ME effect,}$$

$$\alpha_B = \frac{\delta B}{\delta H} \text{ (Oe.cm/V) for converse ME effect}$$

where  $\delta_E$  and  $\delta_B$  are the amplitudes of the ac electric field and magnetic induction in the substance, caused by a change in the magnetic  $\delta_H$  and electric  $\delta_E$  fields, respectively. However, in ME crystals, the effects are small in magnitude  $\alpha_E \sim 1\text{--}20$  mV (Oe<sup>-1</sup> cm<sup>-1</sup>) and are observed in single phase materials such as BiFeO<sub>3</sub>, Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, and SrCo<sub>2</sub>Ti<sub>2</sub>Fe<sub>8</sub>O<sub>19</sub> at low temperatures ( $T \approx 4\text{--}20$  K)<sup>95,96</sup> or under high magnetic fields ( $H \approx 10\text{--}50$  kOe) in BaFe<sub>12</sub>O<sub>19</sub> and Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> (ref. 97 and 98) which poses challenges for their practical applications.

In composite ME, the ME coupling is primarily strain-mediated, occurring at the interface between the magnetostrictive and piezoelectric phases. This coupling arises from the interaction between magnetic and electric fields *via* mechanical strain transfer across the interface. To quantitatively describe this phenomenon, a mathematical formulation based on continuum mechanics and electromagnetism, incorporating key physical quantities such as strain (*S*), displacement (*D*), electric field (*E*), magnetic field (*H*), permittivity ( $\epsilon$ ), and permeability ( $\mu$ ) is used. For general composites, the tensor notation accounts for anisotropic material properties and complex microstructures.<sup>99–101</sup> For the magnetostrictive and piezoelectric phases, the constitutive relations can be expressed as:

$$S_i = s_{ij} T_j + d_{ki} E_k + q_{ki} H_k \quad (4)$$

$$D_k = d_{ki} T_i + \epsilon_{kn} E_n + \alpha_{kn} H_n \quad (5)$$

$$B_k = q_{ki} T_i + \alpha_{kn} E_n + \mu_{kn} H_n \quad (6)$$

where  $S_i$  and  $T_j$  are strain and stress tensor components, respectively;  $E_k$ ,  $D_k$ ,  $H_k$ , and  $B_k$  are the components of the electric field, electric displacement, magnetic field, and magnetic induction, respectively;  $s_{ij}$ ,  $d_{ki}$ , and  $q_{ki}$  denote the effective elastic compliance, and piezoelectric, and piezomagnetic constants, respectively, while  $\epsilon_{kn}$ ,  $\mu_{kn}$ , and  $\alpha_{kn}$  correspond to the effective permittivity, permeability, and linear ME coupling tensor.<sup>102–104</sup> The ME coefficient can be written by solving eqn (4)–(6).



$$\alpha_{\text{ME}, ij} = \frac{\delta E_i}{\delta H_j} \approx s_{ij} \cdot d_{ki} \cdot q_{ki} \quad (7)$$

This formulation combines the sequential coupling pathway in which an applied magnetic field induces strain in the magnetostrictive phase ( $q_{ki}$ ), the strain is elastically transferred across the interface ( $s_{ij}$ ), and the piezoelectric phase converts the strain into an electric polarization ( $d_{ki}$ ). Under the assumptions of linear constitutive behavior, ideal interfacial strain transfer, and negligible intrinsic ME effects, this product–property relationship quantitatively explains the enhanced ME coefficients observed in engineered composites relative to single-phase materials, particularly at RT.

From eqn (7), it is evident that the characteristics of ME effects in composites can be tuned by H and E fields and by the interfacial interaction between constituent phases. Particularly attractive for practical applications are coaxial nanofiber architectures integrating ferromagnetic and ferroelectric phases, which can be fabricated relatively easily *via* electrospinning. Recent advances have yielded a range of composite materials exhibiting high ME conversion efficiency. Furthermore, as indicated by eqn (3), enhancing the ME effect in composites requires the selection of ferromagnetic components with significant piezomagnetic coefficients;  $q_{ki}$  such as metals (Ni and Co), and alloys such as FeCo,<sup>105–107</sup> FeGa,<sup>108,109</sup> Metglas,<sup>110–112</sup> Terfenol-D ( $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ ),<sup>113–115</sup> and ferrites ( $\text{NiFe}_2\text{O}_4$ <sup>116–118</sup> and  $\text{CoFe}_2\text{O}_4$  (ref. 119–121)-combined with piezoelectric materials possessing high piezoelectric constants,  $d_{ki}$ . Examples include ceramics like  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  (PZT),<sup>122–124</sup>  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$  (PMN–PT),<sup>125–127</sup>  $\text{LaNiO}_3$ ,<sup>128–130</sup>  $\text{BaTiO}_3$ ,<sup>131,132</sup> and aluminum nitride (AlN) crystals,<sup>133–135</sup> and polymers such as polyvinylidene fluoride (PVDF),<sup>136–138</sup> which are highly promising for device applications. The  $\alpha_E$  typically ranges from  $\sim 1$ – $100 \text{ mV} (\text{Oe}^{-1} \text{ cm}^{-1})$  for bulk composites, whereas for planar structures it is about  $1$ – $50 \text{ V} (\text{Oe}^{-1} \text{ cm}^{-1})$ , increasing up to  $100 \text{ V} (\text{Oe}^{-1} \text{ cm}^{-1})$  at acoustic resonance frequencies. The capability to interconvert magnetic and electric fields enables the application of the ME effect in multiferroic materials across diverse areas of science and technology. The direct ME effect serves as the foundation for devices such as sensors for detecting static and low-frequency alternating magnetic fields with sensitivities approaching  $\sim 10^{-11} \text{ T}$  at RT,<sup>139</sup> solid-state inductors and transformers tunable *via* electric fields,<sup>131</sup> and energy harvesters capable of converting alternating-current (AC) magnetic fields into direct-current (DC) voltage,<sup>140</sup> among others. The literature highlights several advanced ME composite sensors for detecting magnetic fields. Dong *et al.*<sup>141</sup> achieved the sensing of low-frequency ( $10^2 \text{ Hz}$ ) AC fields down to  $10^{-12} \text{ T}$  using a Terfenol-D/PMN–PT laminate. Zhai *et al.*<sup>142</sup> achieved pico-tesla-level ( $10$ – $12 \text{ T}$ ) detection across a broad  $10^{-2}$ – $10^3 \text{ Hz}$  range using a Terfenol-D/PZT composite. Li *et al.*<sup>143</sup> demonstrated nano-electromechanical ME sensing using FeGaB/AlN, achieving  $800 \text{ pT}$  DC detection at  $3.19 \text{ MHz}$ . Duc *et al.*<sup>144</sup> developed a  $(\text{Fe}_{80}\text{Co}_{20})_{78}\text{Si}_{12}\text{B}_{10}$ /PZT laminate sensitive to micro-tesla fields at  $5 \text{ kHz}$ , while Chu *et al.*<sup>145</sup> reported PMN–PT/FeBSi composites capable of detecting ultra-low AC fields of  $10^{-13} \text{ T}$  at  $23.3 \text{ kHz}$ .

Together, these examples highlight the remarkable dynamic range of ME sensors—from femto-tesla and pico-Tesla AC detection to nano-tesla DC measurements. The converse ME effect finds applications in electrically tunable resonators, microwave filters, and electric field-controlled data storage devices.<sup>146–149</sup> Several significant demonstrations of converse ME composites have been reported. Yinan *et al.*<sup>150</sup> developed a dual-drive DC magnetic sensor utilizing a Metglas/PZT composite, achieving a remarkably low detection limit of  $1 \text{ nT}$ . Chen *et al.*<sup>151</sup> explored the converse ME effect in a Metglas/PMN–PT composite structure, while Jia *et al.*<sup>152</sup> investigated a PMN–PT/Terfenol-D composite, reporting a notable electric-field-induced magnetization coefficient ( $\alpha_E$ ) of  $150 \text{ mG V}^{-1}$  at RT.

## 2.2 Fuel cells and drug delivery

In fuel-cell architectures, core–shell nanofibers serve multiple roles simultaneously — as catalyst supports that improve catalyst dispersion and stability, as gas-diffusion or microporous layers that regulate water management and oxygen transport, and as reinforced membrane scaffolds that maintain proton conduction under low-humidity conditions. Several recent studies demonstrate the heterogeneous ways core–shell or closely related coaxial nanofiber designs improve electrochemical performance. For example, electrospun porous carbon nanofibers bearing  $\text{TiO}_2$  hollow structures or  $\text{TiO}_2$ -derived cores coated with conductive carbon shells provide a high-surface-area, corrosion-resilient support that enhances methanol oxidation and oxygen-reduction activity while resisting particle agglomeration. Tailoring the core composition (*e.g.*, metal oxide or ceramic) and the conductivity/porosity of the carbon shell enables independent control of catalytic anchoring and mass-transport pathways, a design freedom that is difficult to achieve with particulate supports.<sup>153,154</sup> Similarly, nitrogen-doped carbon nanofiber composites with embedded  $\text{TiO}_2$  or other metal-oxide cores have been shown to act as robust anode/cathode scaffolds with improved durability and enhanced ORR/oxidation kinetics, particularly when thermal treatment and heteroatom-doping are used to tailor the electronic structure and surface chemistry. Taken together, these advances suggest that core–shell nanofiber designs offer a materials-by-architecture route to decouple catalytic, ionic, and mass-transport functions, a critical capability for next-generation, low-Pt or Pt-free electrodes.<sup>155,156</sup> For example, oxide–metal core–shell structures (such as  $\text{CoO}_x$ @Pt supported on carbon) promote strong metal–oxide interactions that suppress Pt dissolution, regulate the local electronic environment, and improve the durability of oxygen-reduction catalysts—all essential for high-performance and long-lived fuel-cell electrodes as shown in Fig. 5(a). Such engineered interfaces enable the decoupling of catalytic activity (dominated by the noble-metal shell) from structural stability (provided by the metal-oxide core), allowing for improved mass transport and enhanced long-term operational resilience.

In drug-delivery and wound-healing contexts, coaxial and core–shell electrospun fibers provide decisive advantages for controlled release, multi-drug dosing, and local



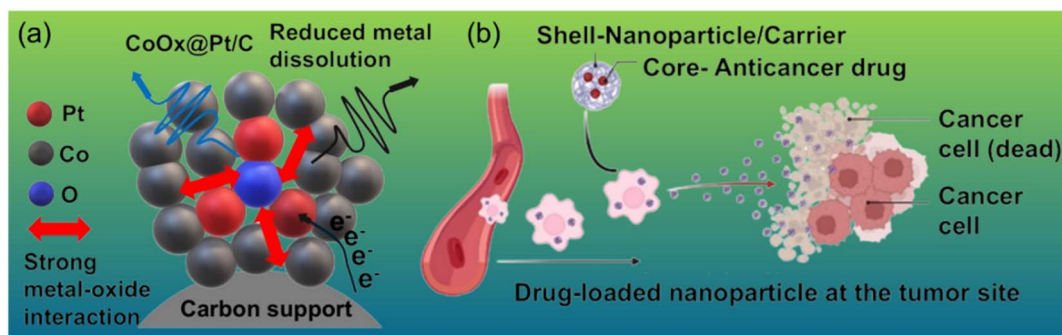


Fig. 5 Schematic illustration of the core-shell nanostructure functionality in (a) fuel-cell catalysis and (b) drug-delivery systems.

bioactivity.<sup>157–159</sup> The enclosed core enables high loading of fragile payloads (proteins, growth factors, or hydrophobic anticancer drugs) with reduced burst release, while the shell can be engineered for stimuli-responsiveness (pH, temperature, and enzymatic degradation) or surface bioactivity (adhesion and antimicrobial coatings). Recent comprehensive reviews and studies demonstrate progress in both the fundamentals and applications of core-shell fibers for therapeutics: from design rules for coaxial electrospinning and core-shell morphology control to application-specific demonstrations such as wound dressings with separate antimicrobial and healing-promoting compartments. Notably, hybrid fabrication strategies that combine self-emulsifying cores with coaxial spinning enhance the encapsulation of poorly soluble drugs (*e.g.*, paclitaxel) and accelerate dissolution without compromising sustained release properties.<sup>160</sup>

Beyond performance, recent work has also emphasized translational considerations. For fuel cells, research explores how electrospun networks can be integrated into electrode laminates and how process conditions (fiber diameter, shell porosity, and post-treatment) influence both short-term activity and long-term stability under realistic operating cycles. In drug delivery, the literature emphasizes the importance of standardized release testing, cytotoxicity, and biocompatibility assays for core-shell systems, as well as strategies for scale-up, such as needleless or multi-jet electrospinning, to enhance throughput without compromising core-shell morphology.<sup>161</sup>

Core-shell designs also provide unique advantages in biomedical and therapeutic applications, where controlled release, protection of bioactive molecules, and spatially selective drug delivery are essential. Coaxial fibers or nanoparticles with drug-loaded cores and protective or stimuli-responsive shells can transport therapeutic agents through the bloodstream, shield them from premature degradation, and release them in a controlled manner at the target site, as shown in Fig. 5(b). By tuning shell composition, porosity, and degradation kinetics, these systems can achieve sustained or on-demand release profiles, improved drug localization, and reduced systemic toxicity. Such multifunctional platforms have been explored for anticancer therapies, antimicrobial delivery, wound healing, and regenerative medicine, demonstrating the

broader utility of core-shell architectures beyond purely physical or electrochemical applications.

### 3. Core-shell nanofibers: advantages for magnetoelectric devices, fuel cells, and drug delivery

Core-shell nanofibers represent a cutting-edge class of 1D nanostructures with unique morphological and functional characteristics. The core-shell design can spatially separate different functional materials within a single fiber geometry, leading to tunable physicochemical properties and enhanced performance in various applications, including sensors, catalysis, drug delivery, energy harvesting, and wearable electronics. Core-shell nanofibers feature a core material completely encapsulated by a concentric shell, allowing for distinct functionalities in each layer. Fabricated primarily through coaxial electrospinning, this method utilizes dual nozzles to deliver core and shell solutions simultaneously, thereby enabling precise control over fiber morphology.<sup>162</sup> The core typically serves as the primary functional component, while the shell provides protection, biocompatibility, or controlled environmental interaction. Coaxial nanofibers are widely used in drug delivery, where a core containing a drug (polycaprolactone-clindamycin) is encapsulated by a biodegradable shell (silk fibroin (SF)) for sustained release.<sup>163</sup> In catalysis, coaxial nanofibers with a catalytic core (*e.g.*, metal nanoparticles) and a porous shell enhance reaction efficiency by improving the accessibility of active sites.<sup>164</sup> The active pharmaceutical ingredient is loaded in the core, while the shell controls the release kinetics in a drug delivery system. Coaxial fibers enable the precise spatial separation of functional domains, making them ideal for applications that require encapsulation, sustained release, or stimuli-responsive behaviour.

Moradipour *et al.*<sup>165</sup> fabricated core-shell nanofibers based on polycaprolactone/polyvinyl alcohol (PCL/PVA) and PCL/CoI) for biomedical applications such as drug delivery and wound healing. A notable application of coaxial nanofibers is in ME materials, where the core and shell are designed to couple magnetic and electric properties. ME core-shell nanofibers typically consist of a magnetic core, such as  $\text{CoFe}_2\text{O}_4$  and



$\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ , and a piezoelectric or ferroelectric shell, such as PVDF and  $\text{BaTiO}_3$ . This configuration enables the nanofibers to generate electric polarization under magnetic fields or *vice versa*, making them promising for applications in sensors, actuators, and energy harvesting devices. For example, coaxial nanofibers with a  $\text{BaTiO}_3$  core and  $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  shell have been shown to exhibit strong ME coupling, suitable for flexible electronics.<sup>166</sup> Fabricating ME nanofibers involves carefully optimizing electrospinning parameters to achieve uniform core-shell interfaces and ensure compatibility between the magnetic and electrical phases. For instance, coaxial nanofibers with a PLA- $\text{CoFe}_2\text{O}_4$  core and a PVDF-TrFE shell have demonstrated significant ME coupling, which can be utilized for energy harvesting. Therefore, continuous research and development of core-shell nanofibers are essential to fully utilize their multifunctional potential and tailor their structural and interfacial properties for advanced applications. Core-shell nanofibers are designed to optimize interfacial interactions and enable controlled transport of charge, ions, or energy across the core-shell interface.<sup>167–170</sup> They combine distinct core and shell materials to achieve multifunctionality, precise surface control, and superior performance unattainable in traditional nanofibers or bulk composites. This architecture enables efficient encapsulation and controlled release of sensitive agents, while also providing enhanced mechanical strength and structural versatility. Moreover, scalable fabrication methods, such as coaxial or emulsion electrospinning, ensure energy-efficient production for applications in drug delivery, fuel cells, energy harvesting, and environmental remediation.<sup>171–173</sup>

## 4. Fabrication methods for core-shell nanofibers

Core-shell nanofibers are fabricated using various techniques that allow precise control over their morphology, composition, and functionality. These methods enable the creation of nanofibers with tailored core and shell materials, making them suitable for applications in biomedical engineering, energy storage, catalysis, and ME systems. The primary fabrication methods include coaxial electrospinning, emulsion electrospinning, and self-assembly or coating. Each method offers unique advantages and challenges, with the choice of technique depending on the desired fiber properties, material compatibility, and application requirements.

### 4.1 Coaxial electrospinning

The coaxial electrospinning technique has emerged as a highly versatile and efficient method for fabricating core-shell nanofibers with tunable morphology and functionality. Unlike traditional single-fluid electrospinning, coaxial electrospinning employs a concentric spinneret (also known as a nozzle spinneret) composed of two coaxial needles that allow the simultaneous flow of two different polymer solutions: one designated as the core material and the other as the shell material. When subjected to a high electric field, the combined jet undergoes stretching (Taylor cone), elongation, and solidification,

ultimately forming nanofibers with a distinct core-shell structure as shown in the schematic in Fig. 6(a).<sup>174–176</sup> The successful preparation of core-shell nanofibers *via* coaxial electrospinning requires careful optimization of several process parameters, including the concentration and viscosity of the polymer solutions, the applied voltage, the distance between the spinneret and the collector, and the flow rates of both the core and shell solutions.<sup>177</sup> Each of these factors influences the morphology, diameter, and uniformity of the resulting nanofibers, as well as the stability of the Taylor cone during electrospinning.<sup>178</sup> The digital image of the Taylor cone during coaxial electrospinning and the SEM image of the PVDF-PC core-shell nanofiber are shown in Fig. 6(b) and (c).<sup>162</sup>

#### 4.1.1 Concentration and properties of polymer solution.

The concentration and viscosity of the polymer solutions play a pivotal role in determining the spinnability and morphology of the coaxial fibers. For the shell solution, sufficient chain entanglement is necessary to provide mechanical stability to the jet and to prevent jet breakup during electrospinning.<sup>179</sup> A solution that is too dilute tends to form beads or droplets, while an excessively viscous solution may hinder the electrospinning process due to difficulties in pumping and jet elongation. Similarly, the core solution must be optimized depending on whether it is a solid polymer, a liquid, or an active agent dispersed in a carrier. For instance, the core fluid may be a bioactive compound dissolved in a biocompatible polymer, as seen in drug delivery applications. In contrast, the shell fluid provides structural support and controlled release properties. Proper miscibility between core and shell solutions is not essential; however, interfacial tension and flow stability must be managed to maintain a distinct core-shell configuration. Fiber formation requires a polymer concentration above a critical value to ensure sufficient chain entanglement.<sup>180</sup> Below this threshold, beads form due to Rayleigh instability; above it, viscosity increases sharply, enabling smooth jet formation.<sup>181</sup> For example, in SF-based core-shell fibers, SF concentrations below 6% led to bead-like fibers, whereas at 8%, the viscosity reached  $\sim 2308$  cP. Similarly, increasing the PVA concentration from 3% to 9% increased the viscosity from  $\sim 92.7$  cP to  $\sim 165.1$  cP. Higher polymer concentrations generally enlarge fiber

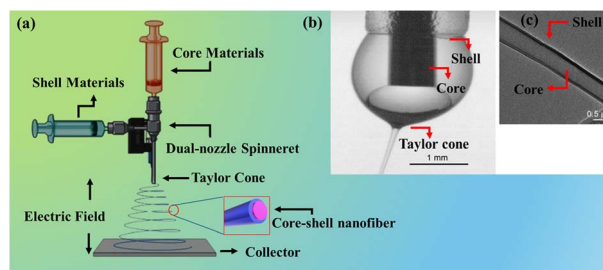


Fig. 6 (a) Schematic of the electrospinning setup for preparation of core-shell nanofibers. (b) Optical image of core-shell droplets on the nozzles of an apparatus for coaxial electrospinning. (c) SEM image of core-shell fibers of PVDF (core) and PC (shell) produced by coaxial electrospinning. (b and c) adopted from ref. 162. Copyright© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



diameters. In SF/PVA systems, increasing the SF in the shell from 6% to 8% resulted in thicker core-shell fibers. Changing PVA in the core had a lesser effect; however, at high shell/core concentrations, the core concentration also influenced the diameter.<sup>182</sup> In PVDF fibers, increasing the concentration from 25 wt% (yielding  $\sim 473$  nm) to 30 wt% increased the average diameter to  $\sim 644$  nm.<sup>183</sup> With PAN solutions, an increasing concentration also led to an increase in fiber diameter and electrical conductivity.<sup>184</sup> Higher solution conductivity enables more vigorous jet stretching, resulting in smaller fiber diameters. For instance, embedding cellulose nanocrystals (CNCs) into a PMMA shell significantly increased solution conductivity, yielding finer and more uniform PMMA-CNCs/PAN core-shell fibers.<sup>185</sup>

**4.1.2 Applied voltage.** The applied voltage is a critical parameter that governs the initiation of the Taylor cone, jet formation, and subsequent fiber elongation.<sup>186</sup> In coaxial electrospinning, the voltage must be sufficiently high to overcome the surface tension of both core and shell solutions simultaneously. Typically, the required voltage ranges from 5 to 50 kV, although the exact value depends on the conductivity and viscosity of the polymer solutions. A lower voltage may result in intermittent jet formation or bead-like structures, while excessively high voltage can cause whipping instabilities, irregular fiber diameter, or even fiber breakage. Moreover, the shell solution usually dominates the jet stability in the coaxial configuration. Therefore, the applied voltage should be tuned to balance the electrostatic force acting on the shell while ensuring the smooth encapsulation of the core fluid.<sup>187</sup> High voltage is necessary to overcome surface tension and form a stable Taylor cone. Fiber diameter typically decreases as voltage increases due to enhanced elongation, but jet instability may ensue above a critical voltage. Empirically, for PCL/PVA/Thyme core-shell fibers, increasing the voltage from 8 kV to 15 kV decreased the average diameter from  $\sim 750$  nm to  $\sim 201$  nm and promoted stable compound Taylor cone formation.<sup>188</sup> However, excessive voltage disrupts the coaxial structure, causing separate jets and loss of core-shell morphology.

**4.1.3 Distance between the spinneret and collector.** The distance between the coaxial spinneret tip and the collector strongly affects the flight time and solidification of the jet. The typical range is 10–20 cm, though it varies with solution volatility, applied voltage, and ambient conditions. Fibers may not have sufficient time to solidify if the distance is too short, resulting in ribbon-like or fused structures on the collector. Conversely, excessively long distances may reduce the electric field strength, weakening the stretching force on the jet and resulting in thicker, less uniform fibers.<sup>189</sup> The optimal distance ensures that the solvent in both core and shell solutions evaporates adequately, maintaining distinct core-shell morphology without collapsing or mixing the two phases. Additionally, the type of collector (stationary plate, rotating drum, or patterned collector) also influences fiber alignment and surface morphology.<sup>190</sup> The distance between the coaxial spinneret tip and the collector, typically 10–20 cm, significantly influences jet flight time and solidification in coaxial electrospinning, with optimal distances (e.g., 15 cm for polycaprolactone in

chloroform) ensuring complete solvent evaporation to form stable fibers, as noted by Dosunmu *et al.*<sup>191</sup> and Subbiah *et al.*<sup>192</sup> This range varies with solution volatility, applied voltage (10–20 kV for polyethylene oxide), and ambient conditions, such as 50% humidity, as reported by Huang *et al.*<sup>193</sup> Short distances (e.g., 5 cm) result in insufficient evaporation, leading to ribbon-like or fused structures (2–3  $\mu\text{m}$  wide for PLA). In contrast, long distances (25 cm) reduce electric field strength (from 0.67 kV  $\text{cm}^{-1}$  to 0.4 kV  $\text{cm}^{-1}$ ), resulting in thicker, less uniform fibers (400 nm for PVDF), as reported by Reneker and Yarin *et al.*<sup>194</sup> and Li and Xia *et al.*<sup>195</sup> The optimal distance (12–15 cm for PCL/gelatin) ensures solvent evaporation from both the core and shell, maintaining distinct core-shell morphology (100 nm core; 200 nm shell) without phase mixing.<sup>179</sup> Additionally, the collector type affects alignment; rotating drums at 1000 rpm produces highly aligned fibres (within  $10^\circ$  of the axis), whereas stationary plates yield random fibres, as shown by Teo *et al.*<sup>196</sup>

**4.1.4 Flow rates of core and shell solutions.** Flow rates are a critical parameter in coaxial electrospinning, significantly influencing jet stability and fiber morphology, requiring precise adjustment of core and shell flow rates to maintain a stable coaxial jet, as noted by Khalf and Madihally,<sup>197</sup> discussing core flow rates of 0.1–0.5  $\text{mL h}^{-1}$  and shell flow rates of 0.8–2  $\text{mL h}^{-1}$  for PLGA/Col fibers. The shell flow rate is typically higher than that of the core to ensure robust encapsulation; for instance, Mickova *et al.*<sup>198</sup> reported that a shell flow rate of 1.5  $\text{mL h}^{-1}$  with a core flow rate of 0.3  $\text{mL h}^{-1}$  for PVA-core/PCL-shell nanofibers produced uniform core-shell structures with core diameters of  $\sim 150$  nm and total fiber diameters of  $\sim 500$  nm. Excessive core flow disrupts the coaxial configuration, causing jet breakup or core exposure, as observed by Lu *et al.*,<sup>199</sup> where increasing the core flow from 0.2  $\text{mL h}^{-1}$  to 0.6  $\text{mL h}^{-1}$  (shell at 1.2  $\text{mL h}^{-1}$ ) in a PEO/PVA system led to irregular fibers with diameters up to 600 nm and partial core leakage.

## 4.2 Emulsion electrospinning

Emulsion electrospinning is a versatile technique used to fabricate ultrafine core-shell nanofibers by electrospinning an emulsion, typically composed of two immiscible phases, such as oil-in-water (O/W) or water-in-oil (W/O).<sup>200,201</sup> In this process, the internal dispersed phase (e.g., drugs, proteins, or functional materials) is encapsulated within the continuous polymer solution phase. Under the influence of a high-voltage electric field, the emulsion is stretched into a fine jet. As the solvent evaporates during jet flight, the fibers are deposited onto a collector, with the dispersed droplets entrapped inside the polymer matrix, forming a core-shell structure as shown in Fig. 7(a).<sup>202,203</sup> This method enables the encapsulation and protection of sensitive biomolecules while allowing for controlled release, making it particularly useful in drug delivery, tissue engineering, and the development of advanced functional materials.<sup>204</sup> The preparation of core-shell nanofibers by emulsion electrospinning depends on multiple factors, including the nature of the emulsion (type, stability, and droplet size), polymer concentration, surfactant selection, applied voltage, solution conductivity, tip-collector distance,



and flow rate.<sup>205</sup> Each parameter plays a crucial role in ensuring successful fiber formation and achieving a well-defined core-shell morphology. Confocal laser scanning microscopy (CLSM) images of core-sheath structured nanofibers prepared from a W/O emulsion of PEO-FITC as the core and PEG-PLA as the shell nanofibers are shown in Fig. 7(b).<sup>201</sup>

**4.2.1 Emulsion characteristics and stability.** The success of emulsion electrospinning relies heavily on the stability of the emulsion. Typically, a hydrophilic polymer is dissolved in the aqueous phase, while a hydrophobic polymer is dissolved in the organic solvent phase. Surfactants such as PVA, PEG, or Pluronic F-127 are often added to reduce interfacial tension and stabilize droplet size. Stable emulsions with small, uniformly distributed droplets favour the formation of continuous core channels within nanofibers. If the emulsion is unstable, phase separation may occur before spinning, leading to heterogeneous fibers without a clear core-shell structure.<sup>206</sup> The type of emulsion (O/W vs. W/O) dictates the location of the core; for example, encapsulating hydrophilic drugs requires a W/O emulsion, whereas hydrophobic compounds are better suited for O/W systems. Double emulsions are particularly useful for encapsulating sensitive biomolecules such as proteins or growth factors, as the multiple interfaces protect them from organic solvents.<sup>207</sup>

**4.2.2 Polymer concentration and viscosity.** Polymer concentration determines the spinnability of the emulsion. At low concentrations, insufficient chain entanglement results in bead formation or droplet spray, rather than the formation of fibers. At excessively high concentrations, viscosity increases, making it difficult to eject a stable jet. An optimal concentration ensures smooth jet elongation, continuous fiber formation, and proper encapsulation of the dispersed phase. In emulsion electrospinning, shell-forming and core-forming polymers must be optimized.<sup>201</sup> For instance, PCL dissolved in chloroform/DMF mixtures is widely used as a shell polymer due to its hydrophobicity and mechanical strength. In contrast, hydrophilic polymers such as gelatin or PEO are often placed in the dispersed aqueous phase. Proper viscosity matching between

the phases helps avoid droplet coalescence and irregular fiber morphologies.<sup>208</sup>

**4.2.3 Surfactant and solvent selection, and evaporation rate.** Surfactants are indispensable for stabilizing emulsions. The choice of surfactant depends on the emulsion type; hydrophilic surfactants stabilize O/W emulsions, whereas hydrophobic surfactants stabilize W/O emulsions. Surfactant concentration must be carefully tuned: too little surfactant leads to phase separation, while excessive surfactant can migrate to the fiber surface during spinning, affecting fiber smoothness and surface chemistry.<sup>209</sup> Moreover, residual surfactants may influence the biocompatibility of fibers in biomedical applications. Solvent volatility critically affects emulsion stability and fiber morphology. A fast-evaporating solvent (chloroform) promotes rapid solidification of the shell polymer, which traps the dispersed phase inside, thus favouring core-shell structures. If the solvent evaporates too slowly, phase separation can occur during flight, resulting in uneven fiber formation. Often, solvent mixtures are used to balance volatility and polymer solubility.<sup>210,211</sup>

### 4.3 Self-assembly methods

Core-shell nanofibers formed by self-assembly represent an elegant bottom-up fabrication route that leverages material properties, such as phase separation, block copolymer architecture, and intermolecular interactions, thereby avoiding the need for complex spinneret setups. This section reviews key self-assembly strategies, parameters influencing morphology, and practical implementations.

**4.3.1 Phase separation via spontaneous self-assembly in single-nozzle electrospinning.** Another versatile route is the spontaneous phase separation during electrospinning from blended solutions. Liu *et al.*<sup>212</sup> produced organic core-shell nanofibers *via* single-nozzle electrospinning of a PQT-12 and PEO blend. PQT-12 migrated to the fiber surface (forming the shell) during solvent evaporation while PEO formed the core. The shell thickness and overall fiber morphology could be tuned simply by adjusting the PQT-12/PEO mass ratio, as shown



Fig. 7 (a) Schematic of preparation of core-shell nanofibers by the emulsion technique and (b) CLSM images of core-sheath structured nanofibers prepared from the W/O emulsion of PEO-FITC as the core, and PEG-PLA as shell nanofibers. (b) adopted from ref. 201. Copyright© 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.





Fig. 8 (a) Chemical structure of PQT-12 and PEO and the formation of a core-shell structure by self-assembly induced phase separation, adopted from ref. 212, (b) schematic illustration for the preparation of multifunctional core-shell nanofibers functionalized with two different types of nanoparticles loaded in the core and in the shell from a self-assembled block copolymer template via a selective solvent approach, adopted from ref. 213, Copyright© The Royal Society of Chemistry 2015, and (c) low temperature, multimaterial fiber drawing method used for the iterative size reduction of a macroscopic layered rod down to core-shell nanowires, adopted from ref. 214, Copyright© Springer Nature 2014.

in Fig. 8(a). Optimized parameters include the composition ratio (semiconductor *vs.* matrix polymer), solvent evaporation rate, polymer miscibility, and dynamics within the jet for homogeneous core-shell nanofibers.

**4.3.2 Block copolymer-directed self-assembly.** One compelling method utilizes block copolymer self-assembly. Sanwaria *et al.*<sup>213</sup> demonstrated a strategy to prepare core-shell polymer-inorganic hybrid nanofibers using a PS-*b*-P4VP diblock copolymer. Silver nanoparticles (with PS ligands) selectively reside in PS domains, forming the core, while the P4VP matrix remains as the shell. Subsequent selective solvent swelling isolates cylindrical PS core fibers, which can be functionalized with additional nanoparticles (Au and CdS) on the P4VP shell as shown in Fig. 8(b). Key parameters include block copolymer composition (block lengths and volume fraction), nanoparticle functionalization and affinity to specific blocks, and solvent selectivity—swelling P4VP without dissolving PS to form ultra-fine core-shell nanofibers.

**4.3.3 Thermal self-organization from preforms.** Although not electrospinning, a notable self-assembly approach has emerged from the thermal drawing of layered preforms. Thermally drawing a composite rod composed of core and shell materials (an As<sub>2</sub>Se<sub>3</sub> core wrapped with a PVDF sheath) produced kilometre-long core-shell nanowires as shown in

Fig. 8(c).<sup>214</sup> Post-thermal treatment induces transformations to structures such as nano-springs, peapods, and core-shell nanospheres, governed by parameters including diameter, temperature, and heat duration. Control factors include the preform layer structure and compatibility, drawing ratios (scale reduction), and treatment temperature and duration.

## 5. Core-shell nanofibers for magnetoelectric sensors

ME materials, which couple magnetic and electric order parameters through strain mediation, are at the forefront of research in sensors, energy harvesters, and spintronic devices. In conventional bulk composites or thin films, substrate clamping, poor interfacial bonding, and dimensional constraints often limit the ME coefficient. The core-shell nanofiber geometry provides an exceptionally high surface area, reduced mechanical clamping, and excellent stress transfer across core-shell interfaces, favouring stronger ME interactions than bulk or thin-film counterparts. In these fibers, the magnetostrictive phase (commonly spinel ferrites, hexaferrites, or orthoferrites) forms the core, while the piezoelectric phase (such as PZT, BaTiO<sub>3</sub>, or lead-free perovskites) forms the shell, or *vice versa*. The concentric architecture ensures that strain



generated in one phase under a magnetic or electric field is efficiently transferred to the other, enabling direct and converse ME effects.<sup>215</sup>

The first experimental demonstration of ME interactions in electrospun core-shell nanofibers was reported by Xie *et al.* (2011), who fabricated  $\text{CoFe}_2\text{O}_4$ -PZT fibers using coaxial electrospinning followed by annealing at 600 °C, as shown in the schematic in Fig. 9(a). The resulting fibers had diameters of ~200–400 nm, with a uniform concentric architecture confirmed by the TEM micrograph in Fig. 9(b). Piezo-response force microscopy under applied magnetic fields revealed strain-mediated ME coupling at the single-fiber level, establishing electrospinning as a viable route to 1D ME nanostructures, as shown in Fig. 9(c).<sup>216</sup> Building on this, Sreenivasulu *et al.* (2018) synthesized  $\text{NiFe}_2\text{O}_4$ - $\text{BaTiO}_3$  core-shell fibers *via* coaxial spinning of sol-gel precursors in PVP, followed by calcination at 700 °C. The nanofibers, with diameters in the 150–300 nm range, exhibited a ME voltage coefficient of  $\sim 0.4 \text{ mV cm}^{-1} \text{ Oe}^{-1}$  at low frequency and demonstrated magnetodielectric effects in mat assemblies.<sup>217</sup>

A significant theoretical advance was made by Petrov *et al.* (2018), who developed a continuum model for ME coupling in coaxial nanofibers. The theory predicted direct ME coefficients of tens to hundreds of  $\text{mV cm}^{-1} \text{ Oe}^{-1}$  and converse ME shifts at ferromagnetic resonance, depending on the core-shell diameter ratio, elastic constants, and magnetostrictive/piezoelectric coefficients of the chosen phases.<sup>218</sup> Experimentally, Liu *et al.* (2020) validated converse ME coupling in  $\text{NiFe}_2\text{O}_4$ -PZT fibers (diameters 200–500 nm) using NSMM as shown in Fig. 9(d), observing an electric-field-induced resonance shift with a CME

coefficient of  $-24 \text{ Oe cm V}^{-1}$ .<sup>219</sup> Shahzad *et al.* [2024] fabricated a core-shell nanofiber of  $\text{CoFe}_2\text{O}_4$ - $\text{BaTiO}_3$  nanofibers for magnetic-field-triggered release of doxorubicin, achieving 95% drug release in 30 minutes under a 4 mT field, and demonstrating  $\sim 90\%$  cytotoxicity against SK-MEL-28 melanoma cells while remaining biocompatible in homolysis assays.<sup>220</sup> After that, Ge *et al.* (2024) reported hexaferrite-BTO core-shell fibers (average diameter  $\sim 300 \text{ nm}$ ) as shown in Fig. 9(e), confirmed by MFM analysis, and prepared by coaxial spinning and high-temperature annealing, which exhibited robust ME voltage responses by measuring the polarization under an external magnetic field as shown in Fig. 9(f), in aligned mats suitable for device-level integration.<sup>221</sup>

Beyond spinel and hexaferrite systems, Yadav *et al.* (2022) demonstrated ME properties in electrospun  $\text{NdFeO}_3$ -PZT fibers, with diameters  $\sim 128 \text{ nm}$ , as confirmed by TEM analysis (Fig. 10(a)), showing ME coupling by recording polarization under an external magnetic field as shown in Fig. 10(b and c) at RT.<sup>222</sup> Furthermore, Yadav *et al.* (2022) developed a hexaferrite-PZT ME-enabled core-shell nanofiber as shown in a TEM micrograph (Fig. 9(d)). They demonstrated direct ME coupling as depicted in Fig. 10(e and f).<sup>223</sup> A notable step toward environmentally benign systems came from Hadouch *et al.* (2023), who synthesized lead-free CFO-BCTSn fibers (core and shell  $\sim 100$ – $250 \text{ nm}$ ) by coaxial electrospinning as shown in the schematic in Fig. 10(g) followed by the core-shell configuration (Fig. 10(h)), achieving a high ME voltage coefficient of  $\sim 346 \text{ mV cm}^{-1} \text{ Oe}^{-1}$  as depicted in Fig. 10(i).<sup>224</sup> Later, Yadav *et al.* (2024) demonstrated sensor-grade  $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ -PZT core-shell nanofiber ME responses ( $650$ – $730 \text{ V/T}$  at  $\sim 8.3 \text{ kHz}$ ) suitable for



Fig. 9 (a) Digital photo of an actual coaxial spinneret in the electrospinning setup, (b) TEM micrograph of CFO-PZT core-shell nanofibers, (c) the switching characteristics of piezo response in a CFO-PZT core-shell nanofiber before and after the application of an external magnetic field by using the variable field module (VFM), (a–c) adopted from ref. 216, Copyright©-The Royal Society of Chemistry 2011, (d) NSMM image of NFO-PZT core-shell nanofibers, adopted from ref. 219, (e) MFM for a fiber of NFO shell-PZT core nanofibers, adopted from ref. 221, and (f) fractional change in the remnant polarization ( $P_r$ ) as a function of magnetic field ( $H$ ), adopted from ref. 221.





Fig. 10 (a) TEM images of the core-shell  $\text{NdFeO}_3\text{-PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  nanofibers, (b)  $P$ - $E$  loops of the core-shell NF-PZT nanofibers under various magnetic fields, (c) variations in maximum polarization and electric coercivity with respect to the applied magnetic field, (a-c) adopted from ref. 222, Copyright© Elsevier-(2022), (d) TEM micrograph, (e) variations in the  $P$ - $E$  loop, (f) variations in  $\text{MP}_{\text{max}}\%$  and  $\text{MP}\%$  with respect to magnetic field, (d-f) adopted from ref. 223, Copyright© Elsevier-(2022), (g) coaxial electrospinning of core-shell nanofibers: setup schematics, (h) annealed CFO-BCTSn core-shell nanofibers, and (i) dependence of the magnetoelectric coefficient of CFO-BCTSn NFs on the DC magnetic field at RT; (g-i) adopted from ref. 224, Copyright© 2023 American Chemical Society.

AC/DC field detection.<sup>225</sup> Most recently, Saha *et al.* (2025) summarized these developments, emphasizing that optimization of electrospinning parameters (solution concentration, applied voltage 10–25 kV, flow rates 0.2–1 mL h<sup>-1</sup>, and post-annealing at 500–700 °C) is crucial to achieve uniform diameters, strong interfaces, and enhanced ME coefficients for sensor and harvester applications.<sup>215</sup> Despite these critical milestones, it is clear that research on ME core-shell nanofibers remains very limited compared to bulk composites, thin films, or 2D heterostructures. Fewer than a dozen detailed experimental studies have been reported, and only a handful of material systems—primarily CFO-PZT, NFO-BTO, hexaferrite-BTO, and rare-earth orthoferrites—have been explored. This narrow materials base and the lack of systematic studies on factors such as the core-shell ratio, fiber alignment, interfacial strain engineering, and device integration leave significant scope for further research. Exploring lead-free ferroelectrics, integrating flexible polymers with oxide cores, and developing aligned fiber arrays for magnetic sensing or spintronic devices could yield breakthroughs in ME performance. Thus, ME core-shell nanofibers represent a highly promising but underexplored frontier with ample opportunities for innovation. The

compilation of ME core-shell nanofiber structures, including the diameter, ME coefficients/sensitivities, and application-specific features, is summarized in Table 1.

## 6. Core-shell nanofibers for fuel cell applications

Recent progress in fuel-cell engineering has highlighted the effectiveness of core-shell nanofibers in addressing long-standing challenges related to catalyst stability, mass-transport limitations, and fuel crossover. Compared with traditional carbon blacks or granular ceramic catalysts, 1D nanofibers and core-shell nanofibers enable a continuous conductive framework with high porosity, improved catalyst anchoring, and enhanced electron/ion mobility. Iskandarani *et al.*<sup>226</sup> demonstrated that  $\text{P}(\text{VDF-TrFE})/\text{Pt}/\text{C}/\text{S-SiO}_2$  nanofiber cathodes maintain high performance and exceptional durability under low-humidity PEMFC operation due to their interconnected fiber network and enhanced Pt-ionomer interfacial contact. Complementary mechanistic insights from Kabir *et al.*<sup>227</sup> and Khandavalli *et al.*<sup>228</sup> demonstrate that optimized polymer-



Table 1 Compilation of ME core-shell nanofiber structures, including the diameter, ME coefficients/sensitivities, and application-specific characteristics

Core-Shell system	Fiber diameter	Core diameter	Shell thickness	ME coefficient/response	Notes	Ref. no.
CoFe <sub>2</sub> O <sub>4</sub> /PZT	200–400 nm	120–260 nm	40–140 nm	Demonstrated strain-mediated ME coupling <i>via</i> PFM $\alpha_{ME} = 0.4 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ ; magnetodielectric response	First experimental demonstration of electrospun ME core-shell fibers	216
NiFe <sub>2</sub> O <sub>4</sub> /BaTiO <sub>3</sub>	150–300 nm	90–200 nm	40–100 nm	CME coefficient = $-24 \text{ Oe} \cdot \text{cm V}^{-1}$ (electric-field-induced FMR shift)	Prepared <i>via</i> coaxial sol-gel electrospinning	217
NiFe <sub>2</sub> O <sub>4</sub> /PZT	200–500 nm	150–350 nm	50–150 nm	Strong ME voltage response under a magnetic field	Validated the converse ME effect <i>via</i> NSMM	219
Hexaferrite/BaTiO <sub>3</sub>	300 nm	200–240 nm	40–80 nm	Direct ME coupling shown <i>via</i> a <i>P-E</i> loop shift	Aligned mats exhibit device-scale ME coupling	221
NdFeO <sub>3</sub> /PZT	128 nm	80–100 nm	20–40 nm	ME sensitivity 650–730 V T <sup>-1</sup> at $\sim 8.3 \text{ kHz}$	Ultra-thin orthoferrite-PZT fibers	222
CoFe <sub>2</sub> O <sub>4</sub> /BaTiO <sub>3</sub>	180–320 nm	120–220 nm	40–100 nm		Lead-free system; strong ME voltage peak	224
Hexaferrite (Ba <sub>2</sub> Zn <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub> )/PZT	300 nm	200–260 nm	40–80 nm		Sensor-grade ME fibers; strong AC/DC ME response	225

particle interactions and controlled ionomer distribution within nanofibers significantly enhance Pt accessibility, oxygen-reduction kinetics, and catalyst utilization, underscoring the critical role of the ink microstructure and spinnability in producing high-quality nanofiber catalyst layers. Beyond electrodes, Liu *et al.*<sup>229</sup> reported that electrospun nanofiber-reinforced polymer electrolyte membranes offer superior mechanical stability, proton-transport pathways, and humidification tolerance, indicating that nanofiber engineering can also enhance membrane function. In parallel, Kallina *et al.*<sup>230</sup> demonstrated that humidity-robust nanofiber cathode layers can be realized through the use of tailored ionomer content and multilayer designs, thereby mitigating mass-transport resistance during PEMFC operation. This section provides a brief review and discussion of prominent research studies on fuel cells employing 1D nanofibers and core-shell nanofiber structures, highlighting their design strategies, functional advantages, and performance enhancements in energy conversion applications. Li *et al.*<sup>231</sup> developed core-shell TiO<sub>2</sub>/C nanofibers as catalyst supports for fuel cells, where uniformly dispersed Pt nanoparticles ( $\sim 2 \text{ nm}$ ) enhanced methanol oxidation activity and stability. SEM and TEM micrographs of TiO<sub>2</sub>/C are shown in Fig. 11(a and b), respectively. The system exhibited 7 times higher current density and a 2.5 times boost under UV light, highlighting a synergistic photo-electrocatalytic effect that is beneficial for fuel cell efficiency. Singh and Dempsey *et al.*<sup>232</sup> synthesized Pt-decorated functionalized carbon nanofibers (fCNFs) for fuel cell applications, achieving uniform Pt dispersion inside and outside the fibers as shown in Fig. 11(c). This design improved Pt utilization, CO tolerance, and long-term durability, outperforming commercial Pt/C catalysts and offering a cost-effective route for high-performance fuel cells, as shown in Fig. 11(d).

Karuppappan *et al.*<sup>233</sup> presented a highly durable Pt-C core-shell catalyst supported on carbon nanofibers (CNFs) for a proton exchange membrane fuel cell, as shown in the TEM image in Fig. 11(e). The core-shell structure refers to individual Pt nanoparticles, each consisting of a Pt core encapsulated by a thin ( $\sim 1 \text{ nm}$ ) nitrogen-doped carbon shell, which are uniformly dispersed on the CNF surface, serving as a stable and conductive support. Using a simple Pt-aniline complex coating followed by heat treatment, the researchers obtained 3–4 nm Pt nanoparticles with excellent uniformity and strong protection against aggregation or dissolution. The optimized catalyst (heat-treated at 900 °C) exhibited superior oxygen reduction reaction (ORR) activity and exceptional durability, maintaining nearly constant performance for 30 000 accelerated stress test cycles with negligible voltage loss at 0.8 A cm<sup>-2</sup>, as displayed in Fig. 11(f). Its performance exceeded the U.S. DOE 2020 stability targets, demonstrating strong potential for ultra-low Pt loading and long-lasting PEM fuel cells. Senthilkumar *et al.*<sup>234</sup> reported the direct growth of hierarchical Co<sub>3</sub>O<sub>4</sub>@NiO and Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> core-shell nanostructures on carbon fibers for bifunctional catalysis in direct urea fuel cells (DUFCs). SEM and TEM micrographs of Co<sub>3</sub>O<sub>4</sub>@NiO nanofibers are shown in Fig. 12(a) and (b), respectively. The engineered architecture enhances both urea oxidation and oxygen reduction kinetics while





**Fig. 11** (a) SEM image of  $\text{TiO}_2$  nanofibers and (b) TEM images of  $\text{TiO}_2/\text{C}$ . Upper inset: low-magnification TEM image of several fibers; lower inset: distribution of carbon thickness over different regions and fibers, (a and b) adopted from ref. 231, Copyright© Royal Society of Chemistry-(2012), (c) TEM image of Pt/fCNF-1 core-shell nanofibers, and (d) cyclic voltametric responses for methanol electro-oxidation by Pt/fCNF-1 (response after 60 min) and Pt/fCNF-2 (response after 63 min) modified electrodes (labelled) under acidic conditions (1 M methanol + 0.5 M  $\text{H}_2\text{SO}_4$ ) at a scan rate of 0.01 V vs. Ag/AgCl. (c and d) adopted from ref. 232, Copyright© Royal Society of Chemistry-(2013). (e) TEM images of Pt@CS/CNF600 core-shell nanofibers. (f) Polarization curves of (a) Pt/C, before and after 30 k AST cycles. Solid and open symbols represent the cell voltage and power density, respectively. (e and f) adopted from ref. 233, Copyright© Royal Society of Chemistry-(2019).

reducing charge-transfer resistance. The DUFC achieved a high-power density of  $33.8 \text{ mW cm}^{-2}$  using urea and  $23.2 \text{ mW cm}^{-2}$  with human urine, maintaining stable performance over 120 hours, as depicted in Fig. 12(c). The robust 3D structure offers superior durability, efficient electron/ion pathways, and potential for wastewater-to-energy conversion. Lee *et al.*<sup>235</sup> developed a novel  $\text{SiO}_2/\text{C}$  core-shell nanofiber *via* coaxial electrospinning for use as a microporous layer (MPL) in PEM fuel cells. SEM and TEM micrographs of  $\text{SiO}_2/\text{C}$  core-shell nanofibers are shown in Fig. 12(d) and (e), respectively. The hydrophilic silica core regulates water retention, while the hydrophobic conductive carbon shell ensures efficient electron transport and prevents flooding. The composite exhibits a higher surface area, strength, and conductivity than pure carbon fibers. When used in PEMFCs, it enhanced power density by 66–302% under varied humidity and temperature conditions, offering an effective strategy for improved water management and stable fuel cell operation, as displayed in Fig. 12(f). In solid oxide fuel cells (SOFCs), Choi *et al.*<sup>236</sup> developed  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3/\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (LSCM@SDC) core-shell nanofiber anodes *via* a simple electrospinning route, achieving outstanding coking resistance and ultra-low polarization resistance ( $\sim 0.11 \Omega \text{ cm}^2$  at  $800 \text{ }^\circ\text{C}$ ) under methane fuel, owing to the SDC shell that improved oxygen-ion transport and prevented carbon buildup.

Similarly, Yang *et al.*<sup>237</sup> fabricated  $\text{YCo}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  core-shell cathodes for intermediate-temperature SOFCs (IT-SOFCs), where the GDC shell facilitated oxygen-ion diffusion and charge transfer, yielding a low area-specific resistance of  $0.66 \Omega \text{ cm}^2$  and a peak power density of  $426.5 \text{ mW}$

$\text{cm}^{-2}$  at  $550 \text{ }^\circ\text{C}$ . Extending the concept to direct methanol fuel cells (DMFCs), Lee *et al.*<sup>238</sup> synthesized Pt-C core-shell catalysts supported on carbon nanofibers (Pt@CS/CNF), in which a graphitized carbon shell selectively blocked methanol while allowing  $\text{O}_2$  access to Pt sites. The optimised Pt@CS/CNF900 catalyst demonstrated superior methanol tolerance, oxygen reduction reaction (ORR) activity, and stability over 30 000 cycles, outperforming commercial Pt/C catalysts. Collectively, these studies highlight the versatility of core-shell nanofiber designs as a unifying strategy for developing high-efficiency, durable, and fuel-flexible fuel cell electrodes. Delikaya *et al.*<sup>239</sup> developed a porous electrospun carbon nanofiber network that acts as an integrated electrode and gas diffusion layer (GDE@GDL) for high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs). This design enhanced oxygen transport, reduced mass-transport resistance, and achieved a 21% higher Pt-normalised power density compared to conventional GDL-based cells. Symillidis *et al.*<sup>240</sup> fabricated conductive PANI-based core-shell polymer nanofibers supporting Pd and Pd-M (Ag, Bi, Cu) catalysts for direct ethanol fuel cells (DEFCs). The PANI shell improved conductivity, CO tolerance, and catalyst stability, while Pd-Ag and Pd-Bi combinations showed the highest ethanol oxidation activity with lower activation energies than monometallic Pd. Sanna *et al.*<sup>241</sup> studied  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ -core/Cu-doped  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ -shell nanofiber cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Electrochemical impedance spectroscopy revealed polarisation resistances as low as  $1.7 \Omega \text{ cm}^2$  at  $650 \text{ }^\circ\text{C}$ , significantly lower than those of conventional composite





Fig. 12 (a) SEM and (b) TEM images of  $\text{Co}_3\text{O}_4@ \text{NiO}$  nanofibers. (c) Polarization of the DUFs with  $50 \times 10^{-3}$  M urea at RT. (a–c) adopted from ref. 234, Copyright© John Wiley and Sons- (2018). (d) SEM and (e) TEM images of  $\text{SiO}_2@ \text{C}$  core-shell nanofibers. (f) Polarization curves (I–V curves) and power density curves (I–P curves) of FC-V, FC-C, and FC- $\text{SiO}_2@ \text{C}$  under different operating cells at 50 °C. (d–f) adopted from ref. 235, Copyright© Springer- (2018).

cathodes, with a stable nanofiber morphology after testing. Collectively, these results confirm that core-shell nanofiber engineering enhances mass transport, electrocatalytic activity, and long-term durability across multiple fuel cell technologies, from HT-PEMFCs to DEFCs and SOFCs. An overview of reported core-shell nanofiber systems for fuel cell applications, highlighting structural parameters (fiber diameter, core diameter, and shell thickness), device type, and key electrochemical performance metrics, is provided in Table 2.

## 7. Core-shell nanofibers for drug delivery applications

Controlled drug delivery has long been a challenge in biomedicine, where achieving precise dosage, sustained release, and protection of fragile biomolecules is crucial. Electrospun core-shell nanofibers offer a unique solution by providing a high surface-to-volume ratio, tunable porosity, and the ability to encapsulate drugs within the fiber core while protecting them with a polymer shell. This architecture not only prolongs release kinetics but also prevents premature degradation of sensitive molecules such as proteins, peptides, and nucleic acids. Therefore, core-shell nanofibers prepared by coaxial or emulsion electrospinning have emerged as promising carriers for drug delivery, tissue engineering, and wound healing.

### 7.1 Establishing encapsulation and release control

The concept of drug-loaded core-shell fibers was first rigorously demonstrated by Jiang *et al.* (2006), who fabricated BSA-dextran as the core and PCL (with PEG modification) as the shell *via* coaxial electrospinning, as shown in Fig. 13(a). The resulting

fibers had diameters of approximately 200–500 nm, as shown in Fig. 13(b). They demonstrated tunable release rates by modifying the inner feed rates and PEG concentration in the shell, allowing BSA to be released gradually over periods ranging from one week to more than one month, with markedly reduced burst release compared to blend spinning.<sup>242</sup> Maleki *et al.* (2013) fabricated a PLGA/PLA shell and a TCH core using the coaxial electrospinning method, with a nanofiber diameter of ~200–800 nm, as confirmed by TEM analysis (Fig. 13(c)). This analysis demonstrates that the shell thickness can be precisely controlled to regulate the release duration.<sup>243</sup>

### 7.2 Biopolymers and protein stability

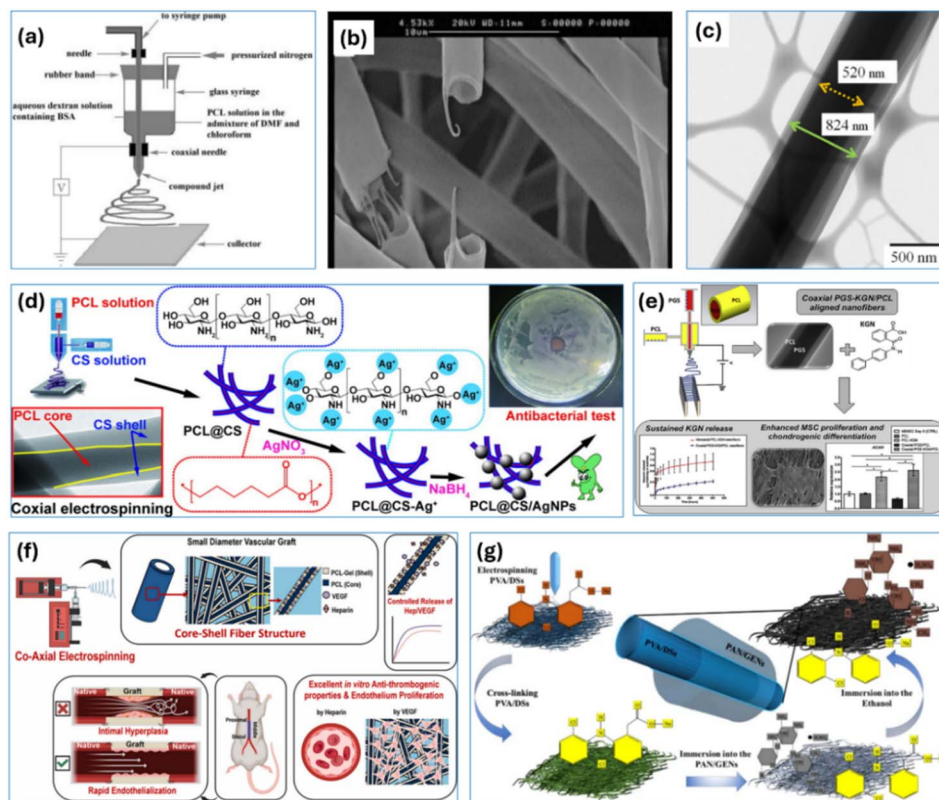
After 2016, the literature broadened: Kalwar *et al.* [2016] used chitosan-PCL and Ovideo *et al.* [2021] used core-shell nanofiber systems, which were explicitly fabricated by coaxial electrospinning, confirming that PCL core/chitosan shell geometries are practicable for biomedical cargo, as illustrated in Fig. 13(d) (ref. 244) and wound-care uses,<sup>245</sup> respectively. Emulsion and aqueous coaxial methods improved compatibility with biologics, allowing for the loading of growth factors, enzymes, and peptides with reduced burst release from 2017 to 2024. Recent reviews<sup>246–248</sup> highlight advances in electrospun systems, such as triaxial structures, responsive shells, nanoparticle-hybrid cores, and solvent strategies that preserve protein activity. Yet, protein loaded core-shell fibers still represent a small fraction of studies, leaving a broad scope for quantitative bioactivity metrics, systematic stabilization research, and translation-oriented efforts in sterilization, scale-up, and regulatory pathways.



**Table 2** Overview of reported core-shell nanofiber systems for fuel-cell applications, highlighting structural parameters (fiber diameter, core diameter, and shell thickness), device type, and key electrochemical performance metrics

Core-shell system	Fiber diameter	Core diameter	Shell thickness	Fuel-cell type	Key performance highlights	Ref. no.
TiO <sub>2</sub> core – carbon shell (TiO <sub>2</sub> @C)	200–400 nm	~150–300 nm	~20–80 nm	DMFC/methanol oxidation	7× higher oxidation current; strong photo-electrocatalytic enhancement	231
Functionalized CNF core – Pt shell nanoparticles (Pt/f-CNF)	250–400 nm	CNF core with uniformly anchored Pt	Thin f-C shell around CNF	DMFC	High CO tolerance; enhanced durability vs. Pt/C	232
Pt core – N-doped carbon shell on a CNF support (Pt@C/CNF600)	Pt particles 3–4 nm; shell ~1 nm	3–4 nm Pt	1 nm N-doped carbon	PEMFC (cathode)	Excellent stability (30 000 AST); surpasses DOE targets; improved ORR	233
Co <sub>3</sub> O <sub>4</sub> core – NiO shell (Co <sub>3</sub> O <sub>4</sub> @NiO)	100–250 nm	80–150 nm	20–60 nm	Direct urea fuel cell (DUFC)	Power density: 33.8 mW cm <sup>-2</sup> (urea), 23.2 mW cm <sup>-2</sup> (urine); 120 h stability	234
Co <sub>3</sub> O <sub>4</sub> core – MnO <sub>2</sub> shell (Co <sub>3</sub> O <sub>4</sub> @MnO <sub>2</sub> )	120–260 nm	90–160 nm	~30–100 nm	DUFC	Enhanced bifunctional activity (OER/ORR); strong chemical stability	234
SiO <sub>2</sub> core – carbon shell (SiO <sub>2</sub> @C)	300–600 nm	200–350 nm	80–150 nm	PEMFC (microporous layer, MPL)	Strong hydrophilicity; improved water management; better conductivity	235
Ce <sub>0.9</sub> Gd <sub>0.1</sub> O <sub>1.95</sub> core – Cu-doped LSM shell (CGO@LSM)	150–300 nm (from SOFC cathode NF synthesis)	100–200 nm	30–80 nm	SOFC (cathode)	Very low polarization resistance (1.7 Ωcm <sup>2</sup> @ 650 °C)	241
PANI core – Pd/Pd–Ag/Pd–Bi catalyst shell polymer nanofibers	200–450 nm (PANI NF)	Conductive PANI	Pd, Pd–Ag, Pd–Bi nanoparticle shells	DEFC	Highest ethanol oxidation with Pd–Ag & Pd–Bi; high CO tolerance	240
Porous carbon network (GDE@GDL) with core-shell-like graded layers	Micro–nano hybrid	—	—	HT-PEMFC	21% higher Pt-normalized power density; improved O <sub>2</sub> diffusion	239





**Fig. 13** (a) Configuration of the coaxial electrospinning setup used for preparing core-shell structured fibers composed of PCL as the shell and dextran containing BSA as the core. (b) The morphology changes in the core-shell structured fibers during BSA release after 21 days. (a and b) adopted from ref. 242, Copyright© 2006 Wiley Periodicals, Inc., (c) TEM images of dual nanofibers (scale bar was 500 nm), core solution: [PLGA, 0.5 wt%, chloroform (8): DMF (2)] (67%) + [TCH 5.94 wt%, methanol] (33%), 0.3 mL h<sup>-1</sup>, shell solution: [PLGA, 2 wt%, chloroform (8): DMF (2)], 3 mL h<sup>-1</sup>, 10 kV, 15 cm, adopted from ref. 243, Copyright© Society of Plastics Engineers-2013, (d) coaxial electrospinning of polycaprolactone-chitosan for antibacterial activity, adopted from ref. 244, Copyright© 2016 Elsevier B.V. All rights reserved, and (e) Kartogenin-loaded coaxial PGS/PCL aligned nanofibers for cartilage tissue engineering, adopted from ref. 250, Copyright© 2019 Elsevier B.V. All rights reserved. (f) Small-diameter vascular graft composed of core-shell structured micro-nanofibers for neointimal hyperplasia, adopted from ref. 251, Copyright© 2024 Elsevier Ltd All rights reserved. (g) Illustration skims of core-shell nanofibers for dual simultaneous drug delivery, adopted from ref. 252.

### 7.3 Tissue engineering and wound healing

Hou *et al.* (2017) fabricated biodegradable, bioactive core-shell fibrous mats *via* coaxial electrospinning using a PCL shell and PGS core system with surface-immobilized heparin, yielding scaffolds with favorable chemical, mechanical, and biological characteristics for broad tissue-engineering applications.<sup>249</sup> Silva *et al.* [2020] reported the development of aligned core-shell nanofibers composed of a PGS (core) and a PCL (shell), engineered to mimic the anisotropic architecture of articular cartilage while enhancing mechanical strength as illustrated in Fig. 13(e).<sup>250</sup> Kartogenin, a small chondrogenic molecule, was encapsulated within the PGS core, allowing for sustained release over a period of up to 21 days. This controlled delivery promoted proliferation and chondrogenic differentiation of human mesenchymal stem/stromal cells without the need for exogenous growth factors such as TGF- $\beta$ 3, highlighting the potential of KGN-loaded coaxial nanofibers as promising scaffolds for cartilage tissue engineering. Al Fahad *et al.* (2024) developed a small-diameter vascular graft using coaxial electrospun micro-nanofibers with a PCL/gelatin shell loaded with heparin and VEGF and a PCL core—demonstrating

sustained release ( $\sim$ 79% heparin;  $\sim$ 86% VEGF over 25 days), as shown in Fig. 13(f) with excellent mechanical performance, full endothelialization, smooth muscle regeneration, and 100% patency in rat aorta implants.<sup>251</sup> Kharaghani *et al.* (2019) designed core-shell PVA/PAN nanofibers *via* coaxial electrospinning for dual-drug delivery as depicted in Fig. 13(g), enabling the simultaneous release of water- and organic-solvent-soluble drugs for tailored therapeutic applications.<sup>252</sup> Li *et al.* (2021) reported a core-shell GelMA-PDLLA nanofiber-hydrogel composite scaffold with enhanced porosity, water retention, and angiogenic activity, which accelerates chronic diabetic wound healing *in vivo*, as shown in Fig. 14(a).<sup>253</sup> Guo *et al.* (2022) developed a core-shell coaxial fiber membrane loaded with CTG in the core and CIP in the shell, achieving controlled release, antibacterial performance, and improved fibroblast proliferation, as well as enhanced scald wound repair in rats,<sup>254</sup> as illustrated in Fig. 14(b).

Abadi *et al.* (2025) engineered core-shell PCL-CS/PVA nanofibers *via* coaxial electrospinning to co-deliver PIO-NEs and GEM over 14 days as shown in the schematic in Fig. 14(c), achieving sustained and controlled release ( $\sim$ 80% of PIO;





Fig. 14 (a) Nanofiber/hydrogel core-shell scaffolds with a three-dimensional multilayer patterned structure for accelerating diabetic wound healing, adapted from ref. 231. (b) Dual drug-loaded nanofiber membranes based on coaxial electrostatic spinning technology adopted from ref. 254, Copyright© 2022 Elsevier B. V. All rights reserved. (c) The schematic of nanofiber preparation for localized melanoma therapy delivering Pioglitazone nano-emulsions and a gemcitabine dual-loaded system, adopted from ref. 255, Copyright © 2025, Springer Nature. (d) Core-shell chitosan-polycaprolactone nanofibers for controlled curcumin release, adopted from ref. 256, Copyright© 2025 Elsevier B. V. All rights are reserved.

Table 3 Summary of core-shell nanofiber systems used in drug-delivery applications, including fiber diameters, core and shell dimensions, therapeutic payloads, and corresponding release behaviours

Core-shell system	Fiber diameter	Core diameter	Shell thickness	Drug/payload	Release behavior	Ref.
PCL core – SF shell	200–450 nm	120–250 nm	50–150 nm	Clindamycin	Sustained release for wound healing	163
PCL/PVA or PCL/Col core-shell	200–600 nm	120–350 nm	80–150 nm	Biomedical drugs	Controlled/sustained	165
BSA-dextran core – PCL-PEG shell	200–500 nm	120–300 nm	50–200 nm	BSA protein	Release adjustable (1 week – 1 month)	242
TCH core – PLGA/PLA shell	200–600 nm	150–350 nm	50–200 nm	Tetracycline	Sustained antibiotic release	243
CTG core – CIP shell	300–700 nm	200–450 nm	80–200 nm	Ceftazidime + ciprofloxacin	Controlled dual-drug release; improved wound healing	254
PCL-CS/PVA core-shell	250–550 nm	150–300 nm	50–150 nm	PIO + GEM	Sustained (14 days)	255
Chitosan-PCL core-shell	250–600 nm	150–350 nm	50–200 nm	Curcumin	Antimicrobial; wound healing	256

~77% of GEM), which significantly inhibited proliferation and induced apoptosis in A375 melanoma cells *via* P53 and PPAR $\gamma$  pathways.<sup>255</sup> Furthermore, Mosallanezhad *et al.* (2025) developed core-shell chitosan-PCL nanofibers loaded with curcumin for controlled wound therapy. These fibers demonstrated a favorable morphology, enhanced structural and release properties, and strong antimicrobial performance, indicating their promise for infection-resistant wound dressings, as shown in Fig. 14(d).<sup>256</sup> Together, these studies emphasize the versatility of core-shell architectures in controlled drug delivery, tissue regeneration, and wound management. A summary of core-shell nanofiber systems used in drug-delivery applications, including fiber diameters, core and shell dimensions, therapeutic payloads, and corresponding release behaviours, is

provided in Table 3. Furthermore, Table 4 summarizes details of parameters involved in the preparation of core-shell nanofiber fabrication techniques.

## 8. Challenges, limitations, and future directions of core-shell nanofibers

Despite significant progress, the development and deployment of core-shell nanofibers in magnetoelectric sensors, fuel-cell systems, and drug-delivery platforms still encounter several critical challenges that prevent their transition from laboratory research to practical use. One major issue is scalability. Although coaxial and emulsion electrospinning are excellent for producing uniform fibers on a laboratory scale, they suffer from





**Table 4** Comparison of core-shell nanofiber fabrication techniques and their parameters

Parameters	Self-assembly methods			
	Coaxial electrospinning	Emulsion electrospinning	Single-nozzle phase-separation	Block copolymer self-assembly
Material loading	Core/shell 8–20 wt% each (independent solutions; need viscosity matching)	Total polymer 8–20 wt% (continuous phase); dispersed phase fraction 5–30% depending on core	8–20 wt% (polymer solution for ES)	0.5–5 wt% (micelles); up to 10–20 wt% (gels)
Blend/block design	Independent choice of core (magnetostrictive, drug, and NPs) and shell (piezo/structural polymer)	Core encapsulated <i>via</i> immiscible emulsion droplets; surfactant stabilizes phase boundaries	30–70% minor phase viscosity for shell/core $\geq 1-2$	Volume fraction of the minority block = 0.2–0.35 $\chi N \geq 10-15$
Operating field/force	Dual nozzle high-voltage (HV) 10–25 kV; tip-collector 10–20 cm; flow rate balance 0.2–1.0 mL h <sup>-1</sup>	Single-nozzle HV (10–25 kV); 10–20 cm; flow rate 0.2–1.0 mL h <sup>-1</sup> (continuous phase dominates)	HV: 10–30 kV; tip-collector 10–20 cm; 0.2–1.0 mL h <sup>-1</sup>	Ambient assembly; selective swelling; RT–80 °C
Evaporation/consolidation	Solvent evaporation for both streams; annealing removes the porosity and improves crystallinity	Solvent evaporation fixes the shell first; dispersed droplets lock in; annealing may remove the surfactant	Fast-evaporating solvent favours shell localization; anneal at 60–500 °C (inorganics)	Solvent selectivity + drying drives segregation; optional NP incorporation
Output geometry	Continuous fibers, typically 150–800 nm in diameter, with transparent concentric shells	Continuous mats; diameter: 100–700 nm; core domain size follows droplet size	Random mats; diameter: 100–800 nm typical nanofibers	Extracted nanofibers (discrete); morphology depends on $\chi N$
Best for	Precise core-shell alignment, tunable diameter ratio, and multifunctional innovative fibers for sensors	Encapsulation of bioactive proteins, or drugs, in scalable mats with phase-separation-driven shells for medical	Thin reactive shells, sensing, and simple tooling for biomedical	Functional shells/cores; multi-NP hybrids and biomedical
				Thermal self-organization
				Bulk preforms (100% solids)
				Pre-stacked core/shell glass or polymer with viscosity-matched layers
				Thermal draw above softening/glass- <i>T</i> ; ~180–230 °C (PVDF shell); higher for silica cores
				No solvent; thermal relaxation after draw sets nano-geometry
				Kilometre-long arrays, 50 nm to 1 μm diameter
				Ultrahigh uniformity, photonics, and scalable optical/electrical arrays for industry

low throughput and high sensitivity to process variations, making it difficult to produce large-area, industrial-scale fibers with consistent core-shell structures. Ensuring reproducibility—especially uniform core diameters, shell thicknesses, and concentricity—requires precise control over solution viscosity, voltage, flow rates, humidity, and solvent evaporation. These factors become more difficult to regulate during scale-up, often leading to structural inconsistencies and batch-to-batch differences. Furthermore, many high-performance materials involve costly precursors or require multiple steps of annealing and calcination, which increase fabrication costs, especially for metal oxides, perovskites, and noble-metal catalysts used in fuel cells.

Another key concern is toxicity and environmental safety, particularly for lead-based piezoelectric systems, such as PZT and PMN-PT. While these materials offer strong magnetoelectric coupling, their inherent lead content limits their use in biomedical devices, wearable technology, and environmentally regulated commercial products. Restrictions from standards such as RoHS and REACH greatly limit their real-world application, highlighting the need for lead-free options like BCTSn, BaTiO<sub>3</sub>, KNN, and zinc- or barium-based hexaferrites. However, matching the magnetoelectric performance of lead-based systems while maintaining processability and long-term stability remains an ongoing research challenge.

Device integration and long-term stability are also critical issues. Arranging core-shell nanofibers into ordered arrays and incorporating them into multilayer device architectures require advanced assembly methods that are not yet standardized. In magnetoelectric sensors, defects at the core-shell interface, inadequate strain transfer, or microcracking from repeated magnetic and electric cycling can reduce coupling efficiency. In fuel cells, durability issues such as catalyst detachment, carbon corrosion, ionomer redistribution, or shell degradation in humid, acidic, or high-temperature environments can compromise performance. Drug-delivery fibers must also sustain structural integrity during storage and implantation, prevent uncontrolled burst release, and ensure the biocompatibility of both organic and inorganic elements. These challenges emphasize the importance of robust interfacial engineering, better encapsulation techniques, and stronger mechanical reinforcement of core-shell structures.

Looking ahead, several opportunities can help advance core-shell nanofiber technologies. New fabrication methods—like real-time controlled coaxial electrospinning, 3D-assisted fiber patterning, and hybrid printing-electrospinning platforms—offer promising paths for scalable and precise structural control. Innovations in interface engineering, defect reduction, and domain alignment can further improve coupling efficiency and stability. For biomedical use, creating stimuli-responsive shells that react to pH, temperature, or magnetic/electric fields will be essential for enabling personalized or on-demand therapies. For fuel cells, enhancing ionomer distribution, controlling shell porosity, and stabilizing catalyst-support interactions are crucial for high performance under low-humidity conditions. Using computational tools such as AI-based material design and multiphysics simulations can speed up

optimization and predict long-term behavior *in vivo* or under operational stresses. Ultimately, collaboration across disciplines—materials science, chemical engineering, electronics, and biomedicine—is vital to transforming core-shell nanofibers from laboratory prototypes into reliable, scalable, and commercially viable solution technologies.

## 9. Conclusion

Core-shell nanofibers represent a transformative class of one-dimensional architectures, whose tunable interfaces, high aspect ratios, and multifunctional compositions enable superior performance in magnetoelectric sensing, fuel cell catalysis, and drug delivery applications. Despite significant progress, several critical research gaps must be addressed before these systems can advance toward technologically relevant devices and scalable commercialization. First, optimizing interfacial coupling remains a major challenge across all areas. In magnetoelectric systems, inadequate strain transfer, interfacial defects, and uncontrolled core-shell ratios greatly limit ME coefficients and device sensitivity. Similarly, fuel-cell nanofibers need improved catalyst-support interactions and controlled ionomer distribution to achieve durable and efficient electrochemical performance. For drug-delivery fibers, ensuring long-term shell stability and preventing burst release are key obstacles. Second, there is an urgent need for reliable, lead-free alternatives to traditional high-performance piezoelectric materials, such as PZT and PMN-PT. Although promising candidates—such as BCTSn, BaTiO<sub>3</sub>, KNN, and Zn- or Ba-based hexaferrites—have been developed, their electromechanical response and long-term reliability still fall short of lead-based systems. Bridging this gap is crucial for enabling sustainable, biocompatible magnetoelectric devices, particularly in biomedical and wearable applications that require strict regulatory standards. Third, flexible and integrated device architectures are a promising yet underdeveloped area. For magnetoelectric sensing, integrating aligned or woven coaxial nanofibers into soft substrates could support wearable or implantable devices. In fuel cells, multilayer nanofiber electrodes and microporous layers need to be engineered for mechanical durability under varying humidity and temperature conditions. For biomedical uses, seamless integration with hydrogels, scaffolds, and tissue-mimicking platforms will be vital for clinical translation. Lastly, commercialization challenges persist throughout the field. Coaxial electrospinning faces issues with low throughput and batch variability. Maintaining uniform core-shell morphology at an industrial scale is difficult due to sensitivities to viscosity, flow rate, voltage, and humidity. Material costs—especially for noble metals, rare-earth ferrites, and high-purity polymers—further limit scalability. Moreover, the lack of standardized testing protocols for ME performance, drug release kinetics, mechanical stability, and long-term degradation complicates cross-study comparisons. Overall, while core-shell nanofibers offer exceptional multifunctionality and potential, realizing their broader use depends on overcoming these challenges through interdisciplinary advances in interface engineering, scalable



manufacturing, predictive modeling, and device integration. With ongoing innovation, core-shell nanofibers are positioned to drive the next generation of sensing, energy, and biomedical technologies.

NSMM Near field scanning microwave microscope  
MFM Magnetic force microscope

## Author contributions

Sandeep Kumar Yadav: visualization, resources, methodology, investigation, formal analysis, conceptualization, writing – original draft. Vishwa Prakash Jha: theoretical analysis, conceptualization, writing – review & editing. Durga Prasad Pabba and Arun Thirumurugan: supervision, resources, project administration, methodology.

## Conflicts of interest

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

## Abbreviations

ME	Magnetoelectric
1D	One-dimensional
CNTs	Carbon nanotubes
nT	Nano-tesla
PZT	$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$
PMN-PT	$(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$
AlN	Aluminum nitride
Terfenol-D	$\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$
PCL	Polycaprolactone
PVA	Polyvinyl alcohol
PCL	Polycaprolactone
Col	Collagen
PVDF	Polyvinylidene fluoride
DOX	Doxorubicin
N-CMCS	N-carboxymethyl chitosan
SF	Silk fibroin
cP	Centipoise
CNCs	Cellulose nanocrystals
PMMA	poly(methyl methacrylate)
PAN	Polyacrylonitrile
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic acid)
PEG	Polyethylene glycol
PEO	polyethylene oxide
nm	Nanometer
$\mu\text{m}$	Micrometer
FITC	Fluorescein isothiocyanate
PGS	Poly(glycerol sebacate)
GelMA	Gelatin methacryloyl
PDLLA	Poly(D, L-lactic acid)
CTG	Centella total glucoside
CIP	Ciprofloxacin
PIO-Nes	Pioglitazone nanoemulsions
GEM	Gemcitabine
PQT-12	Poly(3,3''-didodecyl quarter thiophene)

## Data availability

No data were used for the research described in the article.

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