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# **Polymeric Janus Fibers**

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Janus fibers are a class of composite materials comprising mechanical and chemical to biological functionality. Combining different materials and functionalities in one micro- or even nanoscale fiber enables otherwise unreachable synergistic physicochemical effects with unprecedented opportunities for technical or biomedical applications. Here, recent developments of processing technologies and applications of polymeric Janus

# 1. Introduction

Combining materials of distinct properties in a single body often results in new properties not observed in the individual component materials. This applies for many different classes of materials, including polymeric fibers. In the simplest case, the desired properties can be achieved with a homogenous distribution of constituent polymers throughout the fiber crosssection, thus, fibers can be spun after combining the polymers either in a melt or solution. However, where spatial separation of the constituent polymers is relevant, the polymers are rendered fluid separately and joined directly prior to solidification. If the fibers are extruded such that the two sides run in parallel to each other, side-by-side fibers, also known as Janus fibers, are formed. In this review article, we will consistently refer to "Janus fibers", when fibers display two or more distinct continuous constituents connected at an interface along the fiber cross section. The endeavor to create two-sided fibers predates the use of the term "Janus" by at least a couple of decades.<sup>[1,2]</sup> Mainly with the aim of texturing fibers at an industrial scale, these fibers were typically processed using conventional fiber spinning methods of melt, dry, and wet spinning. Terms like "biconstituent",<sup>[1]</sup> "bicomponent",<sup>[3]</sup> "sideby-side",<sup>[4]</sup> and "conjugate"<sup>[2]</sup> were commonly used to denote such fibers. Recent literature from the past two and a half decades indicates increasing use of the term "Janus" for denoting materials with two sides, based on the two-faced Roman god Janus.<sup>[5-11]</sup> The popularity of this term can be attributed to Nobel laureate Pierre de Gennes who referred to particles with two faces of opposite properties as "Janus grains" in his 1991 Nobel Prize lecture.<sup>[5]</sup> De Gennes noted how polarapolar Janus grains would assemble into a film at a water-air interface similarly to surfactants. But unlike the impermeable

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© 2023 The Authors. ChemPlusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. fibers will be reviewed. Various examples in the fields of textiles, catalysis, sensors as well as medical applications, like drug delivery systems, tissue engineering and antimicrobial materials, are presented to illuminate the outstanding potential of such high-end functional materials for novel applications in the upcoming future.

film formed by surfactants, the film formed by the grains would have gaps that enable chemical exchange between the two sides – a completely novel feature at this time. Exploring the emergence of novel properties in materials in Janus form is one of the factors driving the surge in interest in Janus objects, including Janus fibers. Here we review the literature on processes used to produce Janus fibers and recent advances, which mainly rely on microfluidics and electrospinning to produce Janus fibers in the micro- to nanometer scale.<sup>[12]</sup> To disclose the huge potential of this material class, various potential applications ranging from catalysis to drug delivery are presented.

# 2. Janus fiber processing and applications

#### 2.1. Janus fiber spinning processes

Generally, to produce fibers, a polymer must be pliable within the fiber forming process. For instance, certain polymers decompose before reaching their melting point and, therefore, can only be processed from solution. Such polymers must then be processed into fibers using dry or wet spinning.<sup>[13]</sup> Polymers that can be melted without degrading can be processed using melt spinning.<sup>[14]</sup> Evidently, many different processes can be applied to produce Janus fibers, each having its advantages or drawbacks. Upon Janus fiber formation with different polymers, the methods for Janus fiber spinning must be adapted accordingly and will be briefly introduced in the following.

### 2.1.1. Melt spinning

In melt spinning (Figure 1), polymers are heated to their melting point. In a typical setup, solid polymer pellets are fed



**Figure 1.** Schematic drawing of the melt spinning process for Janus fiber production. The polymer is fed through a hopper, heated above its melting temperature, then extruded through the spinneret and fused to form a Janus fiber, which is collected on a winder.



into a hopper leading to a heated screw extruder. Heat is transferred through conduction by contact between the pellets and barrel of the screw extruder, melting the polymer. The melt is then conveyed through a metering pump and a filter or sand pack before finally being extruded out of a spinneret and allowed to solidify in air. A cooling tower, in which air is blown, can be included to accelerate solidification. The solidified fibers are then wound onto a collector.<sup>[14]</sup>

For producing Janus fibers, two melts are brought together right before extrusion into air, where rapid cooling occurs, and solidification takes place. There are several possibilities to achieve this. In principle, a septum in a die can be used to keep two melt streams apart right before a common opening, where the streams meet and exit (Figure 2A). An alternative is to have two streams of one polymer melt sandwiching another polymer melt and extruding this 3-layer stream through a rectangular array of holes (Figure 2B). Another approach is using a stream of melt consisting of a core and inner shell and an outer shell, where the polymer alternates from the core to the outer shell, which is extruded through a circular array of holes (Figure 2C).<sup>[15]</sup> One of the earlier works producing Janus fibers by melt spinning was reported by Saunders et al. in 1975,<sup>[1]</sup> who produced crimped fibers using nylon 6 and polyurethanes.<sup>[1]</sup> Important factors to consider, when attempting to melt spin Janus fibers, include matching melt-viscosities of the two polymers, polymer elasticity and interfacial tension effects.<sup>[1]</sup>

## 2.1.2. Solution spinning

Solution spinning techniques include dry and wet spinning as well as their subsets. The details will be discussed later in the respective sections. To obtain a spinning solution, polymers are mixed with a suitable solvent under stirring. Heating can accelerate<sup>[16]</sup> polymer dissolution and is done depending on solvent flammability and boiling point. Additives such as dyes or particles can be added, if necessary. The solutions are then filtered to remove impurities and degassed to remove air before



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**Figure 2.** Approaches to produce Janus fibers. A) A basic setup may involve a die with a single opening and a septum positioned right above the opening to separate the two streams of polymer melt until just before extrusion. The two melts then meet, exit the die as a single stream and solidify. B) A melt stream comprising three layers, with polymer B sandwiching polymer A, led through a die with holes arranged in a rectangular array. The left picture illustrates the cross section of the stream, the middle picture illustrates the side view of the stream as it approaches the openings in the die, the right picture illustrates the front view of the die. C) A melt stream comprising a core, an inner shell, and an outer shell of alternating polymer melts, led through a die with holes arranged in a circular array. Redrawn from figures in reference.<sup>[15]</sup>

spinning.<sup>[13]</sup> To produce Janus fibers by solution spinning, the same consideration of separating the solutions right until the point of extrusion and solidification also applies, as was discussed in the melt spinning section.

## 2.1.3. Dry spinning

Dry spinning (Figure 3) of polymers can be performed employing volatile organic solvents. The filtered and deaerated polymer solution is extruded through a spinneret into a drying cell, in which heated air or inert gas flows along fibers in the spinning direction to promote solvent evaporation and fiber solidification. The solidification starts on the surface of the polymer solution jet, which forms a shell around the jet, and proceeds into the core, often resulting in a characteristic dog bone cross-sectional shape.<sup>[17]</sup> Similar to melt spinning, a driving force in the early production of Janus fibers via dry spinning



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**Figure 3.** The setup for dry spinning, which is similar to melt spinning, but instead of a melt, a polymer solution is used. The solutions get in contact at the spinneret, and the solvents evaporate, thus, solidifying the fiber.

was industrial research targeting the production of textured fibers. An example of this is the Orlon 21 (acrylic) fiber produced by DuPont in the 1960s. The different hydrophobicity/hydrophilicity of the two sides resulted in different drying rates after being exposed to water. Thus, due to spatially different shrinkage, formation of helical crimps was induced.<sup>[18]</sup>

# 2.1.4. Wet spinning

Wet spinning (Figure 4) is used for polymers whose solvent is of low volatility. In wet spinning, the filtered and deaerated polymer solution is extruded through the spinneret into a coagulation bath, where the fiber solidifies due to the diffusion of the solvent from the polymer solution and the diffusion of the non-solvent into it.<sup>[13]</sup> When fabricating Janus fibers, it is important to consider the miscibility of the solvent systems to prevent jet splitting at the interface during solidification inside the coagulation bath.<sup>[19]</sup>

A 1991 patent from Monsanto describes the high throughput production of Janus fibers using a spinneret with up to 30,000 orifices.<sup>[12]</sup> Various percentages of acrylonitrile and vinyl acetate were dissolved in dimethylacetamide (DMAc), with or without the addition of p-sulfophenylmethallyl ether. These two solutions were heated to 100 °C, then extruded using the spinneret into a coagulation bath comprising an aqueous solution of 55% DMAc. After a series of post-treatments, the fibers exhibited a latent helical crimp with no visible indication



**Figure 4.** Schematic setup for wet spinning, whereby the two polymer solutions are combined at the spinneret and extruded into a coagulation bath to form the fiber.

of splitting between the two components when observed under the microscope.

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Interestingly, many early examples of Janus fiber spinning hailed from research by the textile industry, where the concern was mainly texturing, and the setup was used to demonstrate the ability to produce the fibers at a large scale. However, smaller, simpler setups are also possible for producing lower amounts of fibers at lab scale. This is especially relevant for researchers investigating the properties of novel materials and their applications. As an example, in a more recent work by Liu W. et al.<sup>[20]</sup> in 2022, wet spinning of Janus fibers yielded fibers with electrical conductivity for potential applications in smart textiles. Here, solutions of electrically insulating polyacrylonitrile (PAN) and electrically conducting polyaniline (PANI) were wet spun side-by-side. The spinneret consisted of two needles of different sizes, with the smaller one positioned eccentrically inside the larger one. The polymer solutions were then pumped using two syringe pumps, and the two polymer solution streams joined at the spinneret opening and entered the coagulation bath (a mixture of dimethylsulfoxide and water) simultaneously. The Janus fibers were subsequently collected on a spool with a winder. After post-treatment, the fibers were characterized. Scanning electron microscopy revealed a clear separation between the two sides, and resistance and conductivity measurements showed results comparable to normal heterogeneously blended PAN/PANI fibers. The advantage of the Janus configuration however lies in the lower use of PANI to achieve the same conductivity.

#### 2.1.5. Electrospinning

Electrospinning can be considered a subset of dry spinning, as fiber formation occurs due to the evaporation of solvent into the air surrounding the polymer jet. The main differences between the two processes are the dimensions of the fiberforming polymer jet and the mechanism of introducing elongational forces for fiber formation.<sup>[21]</sup> In electrospinning, the jet is much thinner compared to dry spinning, and stretching is induced via electrostatic repulsion between charges within the polymer solution. In a typical experimental setup for electrospinning Janus fibers, two polymer solutions are loaded into syringes tipped with metallic needles, which are connected to a high voltage source (Figure 5). A syringe pump extrudes the solutions, and upon exiting the needle, the solutions form a two-sided droplet, held in shape by surface tension. When electrostatic forces introduced by the high voltage source are sufficient to overcome the surface tension, a tiny stream of material is jetted from the droplet through a so-called "Taylor cone". During flight, the jet continues to elongate due to the remaining charges. The jet may additionally be elongated by attractive forces of an oppositely charged collector. During the process, the jet diameter is reduced to micrometer or even nanometer-sizes resulting in high surface to volume ratios and, thus, solvent evaporation rates that are orders of magnitude higher than those observed in dry spinning. In cases where solvent evaporation is not rapid enough to allow the deposition





**Figure 5.** Schematic electrospinning setup. The polymer solution is ejected from the spinneret using high electrostatic charges, which induce fiber formation via coulombic repulsion and, thus, stretching of the solidifying jet.

of fully dried fibers on the collector, it is possible to spin the jet into a coagulation bath, which assists in fiber solidification prior to collection. Factors that are important in electrospinning include humidity, temperature, solution viscosity, and voltage.<sup>[22]</sup> As the polymer flow rate and fiber formation in electrospinning is limited by the small sizes of Taylor cones, the typical setup of electrospinning usually involves extruding small volumes of the polymer solutions through needles and capillaries.

The simple implementation of electrospinning and the low amount of material needed to produce fibers render electrospinning a convenient method for investigating the behavior and properties of novel materials in fiber form. The needle arrangement can be variously modified to achieve different fiber configurations such as hollow,<sup>[23]</sup> core-shell,<sup>[24]</sup> core-shellshell,<sup>[25]</sup> and Janus.<sup>[26]</sup> In producing Janus fibers, various needle arrangements can be used with different degrees of success, as observed by Yu et al.<sup>[27]</sup> Two needle configurations used in their study are depicted in Figure 6. In the first arrangement (Figure 6A), two needles of the same size are joined in parallel to each other, resulting in a small contact point, colored green, where the two circles tangentially meet. In the second arrangement (Figure 6B), a smaller needle is arranged eccentrically within a larger needle, leading to a larger contact surface between the two polymer solutions as they exit the needles, thus creating a larger interface between the two polymers in the formed fiber. This difference in contact surface proved to be significant, as the frequency of successfully formed Janus fibers was higher when using the needle arrangement shown in



**Figure 6.** Rendition of the arrangement used in reference<sup>[27]</sup> A) showing two needles in parallel joined together some distance before the tip, whilst in B) an eccentric needle-in-needle configuration is shown. The areas marked in green represent the size of the contact between the two polymer solutions.

Figure 6B. The larger contact surface proved to be essential in ensuring adhesion between and preventing separation of the two sides of the polymer solution jet during flight.

## 2.1.6. Microfluidic spinning

Microfluidic spinning is a subset of wet spinning, in which the same kinetics governing fiber formation apply. However, as microfluidic spinning reflects a smaller scale compared to conventional wet spinning, fibers form more rapidly.<sup>[28]</sup> The general setup (Figure 7) of microfluidic techniques is a chip into which multiple inlets carrying either polymer solutions or coagulation buffers join within a main channel either at once or at various points along the main channel. When the polymer solution comes into contact with the coagulation buffer, it begins to solidify. Upon exiting the chip, the fiber may be partially or fully solidified. In the former case, a coagulation bath can be used to induce full fiber assembly. Microfluidic channels can be produced with complex cross-sections to generate not only round shaped fiber cross-sections, but adjustable profiles. This requires rapid solidification to avoid jet collapsing into a circular form due to surface tension.<sup>[28]</sup> The small size and smooth surface of the microfluidic channels ensures laminar flow, in which mixing between two phases only occurs by diffusion. This enables the formation of well-defined, multicomponent fibers, including Janus fibers. An early use of the side-by-side spinning using microfluidics was shown in 2004 by Jeong et al., producing Janus fibers of 4-hydroxybutyl acrylate with one side dyed and the other undyed. Jung et al. produced Janus PU fibers with one porous side by using raising bubbles during the spinning process.<sup>[6]</sup> Apart from actual fiber formation, microfluidics can be used for precisely controlling the flow and shape of fluids prior to processing using dry- and electrospinning.

## 2.2. Applications of Janus fibers

Most of the spinning methods find their applications in the textile industry when mechanical characteristics of fibers and production rates are of the highest importance (Table 1



**Figure 7.** Schematic microfluidic spinning setup. A microfluidic chip containing separate channels for each of the polymer solutions and an additional one for a coagulant (antisolvent) converge into one, where the jet is focused, and a fiber is formed via coagulation.

Table 1. Exi	amples c	of Janus fiber settings approaching variou	: applications, segment	ed based on the applicatior	ť.			
Author	Year	Material	Solvent	Process	Diameter	Standard deviation	Application	Modification/ Postprocessing
Application	ıs in the	textile industry						
Saunder et al. <sup>[1]</sup>	1975	Polyurethanes nylon 6	none	Melt spinning	not stated	not stated	Textured fibers for tex- tiles	none
Hwan Oh et al. <sup>[96]</sup>	2006	PPT   PET	none	Melt spinning	13.5 µm	0.7 um (n=34)	New elastic polymers in textiles	Heat drawing to increase crystallinity and maximizing crimp.
Srivastava et al <sup>[8]</sup>	2008	polyvinylpyrrolidone PVP + polypyrrole	Ethanol/DMF (1:1 v/v)	Microfluidics + Electrospinning	250 nm	250 nm	Conductive/nonconduct- ive fibers	none
Carter et al. <sup>[12]</sup>	1991	Acrylonitrile   vinyl acetate   acryloni- trile/vinyl acetate/sodium p-sulfophe- nylmethallyl ether	Dimethylacetamide	Wet spinning	not stated	not stated	Textured fibers for tex- tiles	6x stretching in boiling water, washed, dried, crimped and annealed in steam
Geleji et al. <sup>[3]</sup>	1973	Polypropylene   Degraded polypropy- lene	none	Melt spinning	not stated	not stated	Mechanical investigati-on of the fibers	none
Liu W. et al. <sup>[20]</sup>	2022	Polyacrylonitrile   polyaniline	DMSO/water (97:3 v/v)	Wet spinning	Only linear density available	Only linear density available	Smart electronics	Washed 3x in water, oven at 60° to remove DMSO (coagulation buffer)
Zheng et al. <sup>[97]</sup>	2021	Sodium alginate   sodium alignate + graphene oxide	H <sub>2</sub> O	Wet spinning	148 µm	none $(n=1)$	Reversible, light-driven actuation, smart elec- tronics	Coagulation bath = calcium chloride
Application	is for cat	talysis						
Ji et al. <sup>[36]</sup>	2020	ZnO NP + PAN   $Mn_3O_4/CeO_2$ NP + PAN	DMF	Electrospinning with parallel spinneret	340 nm	50 nm	Photocatalysis	none
Liu Z. et al. <sup>[37]</sup>	2006	PVP + Ti (OBu) <sub>4</sub>  PVP Sn [(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH- (C <sub>2</sub> H <sub>3</sub> )CO <sub>3</sub> )] <sub>2</sub>	Ethanol/Acetic acid (4:1 v/v)	Electrospinning with parallel spinneret	100 nm after calci- nation	not stated	Photocatalytic dye degra- dation	Calcination treatment
Liu Y. et al. <sup>[38]</sup>	2018	$PVP + ZnAc_2 PVP + NiAc_2$	DMF	Electrospinning with parallel spinneret	619 nm, 302 nm after calci-	64 nm	Photocatalytic dye degra- dation	Calcination treatment
Cao et al. <sup>[39]</sup>	2020	$PAN   PVP + Co(NO_3)_2$	DMF	Electrospinning with parallel spinneret	500 nm, after calci- nation	100 nm, after calcin- ation	Oxygen reduction reac- tions	Peroxidization and calcination treatment
Liu H. et al. <sup>[40]</sup>	2019	PVP + Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O   PVP + Zn- (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	DMF	Electrospinning with co- axial spinneret	350 nm after calci-	50 nm	Photocatalytic dye degra- dation	ZnO deposition, calcination treatment
Chen et al. <sup>[41]</sup>	2022	Outer: Ni(Ac) <sub>2</sub> + Fe(AcAc) <sub>3</sub> + PAN + PMMA Inner: PAN	DMAC	Coaxial electrospinning	900 nm, 500 nm after calci- nation	not stated	Oxygen electrocatalyst for Zn-air battery	Modification with Co nanofiber precursor, calcination treatment
Application	ns as sen	sors						
Lv et al. <sup>[42]</sup>	2016	$PVP + CeO_2   PVP + (C_2H_5O)_4Si$	DMF	Electrospinning with parallel spinneret	500 nm, 150 nm after calci- nation	not stated	Trace peptide isolation	Calcination treatment, modification with chloro(dimethyl)octylsilane (C8)
Li F et al. <sup>[43]</sup>	2020	$PVP + SnCl_4'SH_2O \big   PVP + Ti(SO_4)_2'9H_2O$	DMF	Electrospinning with parallel spinneret	341 nm, 206 nm	17 nm	Ethanol sensing	Calcination treatment

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Table 1. COI	ntinued							
Author	Year	Material	Solvent	Process	Diameter	Standard deviation	Application	Modification/ Postprocessing
Bauer et al. <sup>[44]</sup>	2018	PVP + BaAc + Ti isopropoxide   PVP + Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O + acetylacetone	Ethanol	Electrospinning with parallel spinneret	after calci- nation 19.34 μm after calci- nation	un 9	Magnetic field sensor	Calcination treatment, assembly of sen- sor
Applicatior	ns for m	agnetic and fluorescent fibers						
Starr et al. <sup>[9]</sup> Zhou et al. <sup>[10]</sup>	2013 2015	barium acetate + titanium isopropox- ide + PVP ferric nitrate + cobalt nitrate PVP + Fe <sub>3</sub> O <sub>4</sub> NPs  PVP + [Dy(BA) <sub>3</sub> phen + Eu(BA) <sub>3</sub> phen]	Ethanol DMF	Electrospinning with parallel spinneret Electrospinning with parallel spinneret	1 µm 1 µm	not stated not stated	Production of multifier- roic materials Magnetic and colour tun- able fibers for magnetic-	Drying and calcination none
Zhang et al. <sup>[98]</sup>	2015	Calcium alginate + CdTe Calcium algi- nate/CdTe and Calcium alginate/ CdS Calcium alginate/Cu <sub>vin</sub> Cd <sub>ine</sub> S	H <sub>2</sub> O	Microfluidics	70 µm	not stated	controllable fluorescent patterns	Calcination treatment
Wang et al. <sup>[46]</sup>	2015	Fe <sub>3</sub> O <sub>4</sub> NPs + PVP   Eu(BA) <sub>3</sub> phen + Tb- (BA) <sub>3</sub> phen) + PVP	DMF	Electrospinning with parallel spinneret	300 nm	not stated	Magnetic-fluorescent fi- bers	none
Wang et al. <sup>[49]</sup>	2018	CoFe <sub>2</sub> O <sub>4</sub> NPs <sub>+</sub> PAN   1,8-NAD + PVP	DMF	Electrospinning with parallel spinneret	325 nm	75 nm	Magnetic-fluorescent membranes	none
Tian et al. <sup>[52]</sup>	2019	PMMA + Tb(TTA) <sub>3</sub> -(TPPO) <sub>2</sub>   PMMA + Fe <sub>3</sub> O <sub>4</sub> NPs	DMF/CHCl <sub>3</sub> (1:9 w/ w)	Electrospinning with parallel spinneret, differ- ent charges on needles	11.72 µm	mŋ 90.0	Fluorescent magnetic probes	none
Xi et al. <sup>[53]</sup>	2018	core: PVP + OA modified Fe <sub>3</sub> O <sub>4</sub> NPs, shell: PVP + Eu(BA) <sub>3</sub> phen + Tb- (BA) <sub>3</sub> phen, ; side: PVP + CSA doped PAN	DMF/CHCl <sub>3</sub> (1:3.75 w/w)	Electrospinning with co- axial and parallel spin- neret	600 nm	not stated	Anisotropically conduc- tive membranes	none
Qin et al. <sup>[54]</sup> Application	2019 Is for an	PAN+ anthracene + rhodamine-B  PVP + coumarin-6 tibacterial fibers	DMF	Electrospinning with parallel spinneret.	400 nm	100 nm	Nanofibers for white light emission	none
Wang et	6606	PCI + lavender oill CA (cellulose		Electrospinning with	1 459 nm	0 506 iim	Antihacterial fihers	eucu
wang et al. <sup>[57]</sup> Zhao et al. <sup>[60]</sup>	2012	PCL+Tavender oli  CA (cellulose acetate) + Ag NPs PSMA-HDA-Boc  PSMA	DCM DCM	erectrospinning with parallel spinneret Electrospinning with parallel spinneret	1.424 mu mu 84.4	not stated	Antibacterial ribers Motion capture and de- tection of bacteria	none PSMA functionalization with TPEC and mannose, PSMA-HAD-Boc functionaliza- tion with catalase using PEI linkers
Yang et al. <sup>[61]</sup>	2020	PVP+CIP EC (ethyl cellulose)+Ag NP	Ethanol/acetic acid (9:1 v/v), ethanol/ acetone (1:1 v/v)	Electrospinning with parallel spinneret	0.84 µm	0.24 µm	Antibacterial wound dressing	none
Drug relea:	sing fib∈	rs						
Yu et al <sup>[11]</sup>	2016	PVP K60 + Keteprofen   EC + PVP K10 + Keteprofen	Ethanol	Electrospinning with parallel spinneret	1 µm	0.2 µm	Biphasic drug release	none
Zheng et al. <sup>[67]</sup> Lai et al. <sup>[62]</sup>	2021 2021	Tamoxifen + PVP K60   Tamoxifen + EC Na-Alginate + CMC blends + either of the added drugs	Ethanol/DCM (1:1 v/ v) H <sub>2</sub> O	Electrospinning with parallel spinneret Wet spinning with paral- lel spinneret into CaCl <sub>2</sub>	579 nm 816 nm 15 mm or 3.5 mm	77 nm 113 nm not stated	Testing influence of fiber shape on release Controlled release of co- delivered drugs	none
Wang et al. <sup>[68]</sup>	2018	PVP K90 + helicid   PVP K10 + SDS	DMAc/ ethanol (2:8 v/v) 75% ethanol	bath Electrospinning with parallel spinneret	630 nm	110 nm	Drug delivery of water- insoluble drugs	none

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Table 1. col	ntinued							
Author	Year	Material	Solvent	Process	Diameter	Standard deviation	Application	Modification/ Postprocessing
Yao et al <sup>[69]</sup>	2019	PCL + acriflavine   PVP + rhodamine-b	Acetic acid   ethanol	Dual nozzle EHD direct- ietting	20 µm	1 µm	Direct writing of Janus fibers	none
Geng et al. <sup>[70]</sup>	2017	Dexamethasone + 1,8-naphthalene an- hydride + PVP   dexamethasone + pery- lene mono-anhydride + PAN	DMF	Electrospinning with parallel spinneret	325 nm	75 nm	Biphasic drug release	none
Ji et al. <sup>[72]</sup>	2021	PVP + RCSP   PVP + AgNO <sub>3</sub>	CHCl <sub>3</sub> /DMF (4:1 w/ w)	Electrospinning with a uniaxial syringe	923 nm	288 nm	Wound healing	2 day drying
Fibers for t	issue en	gineering						
Jung et al <sup>[6]</sup>	2009	Photocurable polyurethane (NOA63), SDS solution	H <sub>2</sub> O	Microfluidics	69 µm	3 µm	Investigating cell adhe- sion and proliferation	Aqueous SDS sheath, UV light photo-
eng et al. <sup>[80]</sup>	2016	PLA   Fibroin	HFIP	Electrospinning with parallel spinneret	150 nm	not stated	Combining natural poly- mers with synthetic ones	none
Lang et al. <sup>[63]</sup>	2022	Recombinant spider silk, negatively charged variant   positively charged variant (corteine tao)	HFIP	Electrospinning with parallel spinneret	0.68 µm	0.16 µm	Selective AuNP function- alized Janus fiber	Post-treatment for increasing protein crystallinity, functionalization with AuNP
Zhang et al. <sup>[82]</sup>	2009	Polyethylene terephthalate (HSPET) -   polytrimethylene terephthalate (PTT)	DCM/Trifluoroacetic acid (2:3 v/v)	Electrospinning with parallel spinneret	800 nm	not stated	Helical fibers	none
Other uses	for Janu	is fibers						
Wang et al. <sup>[83]</sup>	2022	Sodium polyacrylate (PANa) pH 12.38   PANa pH 13.34 + SWCNT	Different pH aque- ous solutions	Wet spinning	0.55 mm, 0.37 mm	not stated	Electrically conductive helical fibers	Fiber stretching
Su et al. <sup>[84]</sup>	2020	PCL   PCL + PEO (polyethylene oxide)	CHCI <sub>3</sub>  DCM/DMF (3:2 v/v)	Electrospinning with parallel spinneret into antisolvent	ca.10 µm up to 40 µm	not esti- mated	Multihelical scaffolds for cell culture	none
Jiang et al. <sup>[85]</sup>	2014	PEO   PEO-b-P(BMA-co-CMA)	DMF	Electrospinning with parallel spinneret	1547 nm, 976 nm	366 nm, 155 nm	Spinning unspinnable polvmers	Removal of PEO sacrificial fiber side by dissolution in water
Knapczyk- Korczak et al <sup>[64]</sup>	2021	Cellulose acetate   Polystyrene	DMF	Electrospinning with parallel spinneret	1.75 µm	0.27 µm	Mist humidity harvesting	none
Lee et al. <sup>[86]</sup>	2011	PLGA   PLGA + Poly(vinyl cinnamate)	CHCl <sub>3</sub> /DMF (95:5 v/ v)	Electrospinning with parallel spinneret	20 µm	not stated	Fiber specific crosslinking	Photocrosslinking
Cai et al. <sup>[87]</sup>	2018	PVDF   PI	DMF/acetone (1:1 w/w) DMF	Electrospinning with parallel spinneret	541 nm	40 nm	Fiber membranes with enhanced thermal and mechanical stability	Thermal crosslinking
Cai et al. <sup>[88]</sup>	2020	PVDF-HFP   PI	DMF/acetone (1:1 w/w) DMF	Electrospinning with parallel spinneret	ca. 550 nm	not stated	Lithium-ion battery sepa- rator with improved per- formance	Thermal crosslinking
Yu et al. $^{[27]}$	2017	PVP K60 shellac	Ethanol	Electrospinning	710 nm	50 nm	Testing different spinner- et seturs	none
Chen et al. <sup>[5]</sup>	2015	polyvinylpyrrolidone K60 + Rhodamine b   Eudragit® L100 + ANS-NH4	Ethanol/ Dimeth- ylacetamide (8:2 v/ v)	Electrospinning	1.42 µm	0.19 µm	Investigat-ing impact of angle between needles on fibers	none
Razzaq et al. <sup>[99]</sup>	2022	Tri(propylene glycol) diacrylate   Nor- land Optical Adhesive (NOA)89	Ethanol	Microfluidics	127 µm	10 µm (n=2)	Simultaneous removal of oppositely charged dyes	PEG300 sheath, UV light photopolymeri- zation (365 nm), washed in water, air- dried overnight

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Applications in the textile industry). Contrarily, for unraveling and presenting the potential of Janus fibers beyond improving purely mechanical characteristics, the predominating method remains electrospinning. I displays remarkable benefits for catalysts, sensors and even implements for wound healing and tissue culturing, (Table 1). This is due to the easy implementation of additional substances into the spinning dope and the variability of solvents, solvent combinations and polymers which can be employed. Conducting electrostatic forces in combination with easily tunable lower polymer viscosities of solutions, when compared to melts, much smaller fibers can be produced as opposed to other spinning approaches. This is especially pertinent when considering that in many applications the interface of the constituent polymers or the spatial vicinity of the two materials is the genesis of the unique characteristics of the Janus fiber. Hence in such cases increasing fiber diameters lead to greater distances between the two different materials and, for example, yield a lower catalytic efficiency, thus compounding the need for the smallest feasible fiber diameters.

## 2.2.1. Janus fibers for catalysis

Inorganic photocatalysts are often employed for e.g., organic dye degradation,<sup>[29]</sup> where they assist in removing pollutants from the environment, or to enhance electro-catalytic activity in energy storage and conversion systems.<sup>[30]</sup>

Typically inorganic catalysts are applied as particles,<sup>[31]</sup> as these have a high reactive surface area to volume ratio and are suitable to be applied in suspensions.<sup>[32]</sup> Despite this, spherical morphologies display inherent disadvantages, resulting in various restrictions.<sup>[33]</sup> A common problem is that some particles tend to agglomerate, which decreases their catalytic activity.<sup>[34]</sup> Furthermore, subsequent removal and recovery after the reaction can be insufficient. Immobilizing such catalysts on fibers can be an attractive alternative to particles to inhibit agglomeration and simplify removal and recovery of the catalytic material. Importantly, one prerequisite to achieve efficient fiber-based catalysts is the fiber dimensions and spatial arrangement of the catalytic components. Ideally, fibers should be small in diameter to achieve high surface to volume ratios and at the same time enable well organized arrangement of the required components.[35]

Janus fibers have attracted particular attention in this field (Table 1 **Applications for catalysis**), as the spatially defined immobilization of two different materials provides an advantage over the randomly distributed equivalents.<sup>[36]</sup> For example, a common issue with photocatalysts such as TiO<sub>2</sub> is, that the photogenerated charge carriers can recombine. Liu Z. et al.<sup>[37]</sup> approached this problem by electrospinning a Janus fiber, with the two fiber sides generated from a precursor polymer solution containing either TiO<sub>2</sub> or SnO<sub>2</sub>. The generated protofiber was then calcined, to produce the finished nanofiber. The combination of TiO<sub>2</sub> with the SnO<sub>2</sub> semiconductor formed a heterojunction at the material interfaces, resulting in divided accumulation of electrons on SnO<sub>2</sub> and holes on TiO<sub>2</sub>. The authors could show that this strategy resulted in significantly improved reaction rates as compared to pure TiO<sub>2</sub>. Similarly, Liu Y. et al.<sup>[38]</sup> used Janus nanofibers made of ZnO and NiO, exploiting the synergistic effect for improved photocatalytic organic dye degradation. They applied Poly(vinyl pyrrolidone) (PVP) solutions as a electrospinning dope loaded with ZnAc<sub>2</sub> on the one, and NiAc<sub>2</sub> on the other side of the biphasic Janus fiber. As-spun fibers were subsequently calcined at 500 °C to obtain ZnO/NiO Janus fibers. Here, the improved efficiency was not solely a result of improved charge transfers, but partially attributed to each of the interfaces producing their distinct reactive oxygen species.

Most of these strategies apply polymers as sacrificial materials to access easy fiber spinning procedures. The organic polymer components in these cases are loaded with inorganic catalysts and then spun into fibers, which are subsequently reduced to carbon scaffolds<sup>[39]</sup> or removed by calcination. Interestingly, this can be exploited to enable the production of Janus fibers from non-Janus fiber precursors, as conducted by Liu H. et al.<sup>[40]</sup> They electrospun polyvinylpyrrolidone (PVP) polymer nanofibers with inclusions of  $Fe(NO_3)_3$  and  $Zn(NO_3)_2$ , onto which ZnO<sub>2</sub> was later deposited, forming a shell. The bilayer nanofiber was then calcined, converting the core into ZnFe<sub>2</sub>O<sub>4</sub>, accompanied by a volume reduction and formation of cylindrical cavities. The resulting hollow fibers were described as hollow Janus fibers since the outer layer was composed of ZnO<sub>2</sub> and the layer facing inside consisted of ZnFe<sub>2</sub>O<sub>4</sub> (Figure 8A). Such approaches were demonstrated to be particularly beneficial for photocatalysis, since the light absorbing photocatalytic component at the outer shell is well exposed to illumination, whilst the inner layer can assist the charge transfer and catalyse reactions inside the fiber channel. This layer-by-



**Figure 8.** Examples of different Janus fibers under lower and higher magnification, emphasizing their dissimilar composition. A) SEM images of a hollow Janus fiber used to catalyse organic dye degradation reactions. Reproduced from Ref. [40] Copyright (2019), with permission from the American Chemical Society. B) SEM images of a Janus fiber made of two recombinant spider silk variants, with selectively bound gold nanoparticles on one half. Reproduced from Ref. [63] Copyright (2022), with permission from Wiley-VCH GmbH. C) SEM images of a PS/CA Janus fiber used for improved harvesting of water from air humidity. Reproduced from Ref. [64] Copyright (2021), with permission from the American Chemical Society. layer approach in hollow Janus fibers can further be extended to multiple layers, enabling even more complex material combinations for improving catalysis.<sup>[41]</sup>

## 2.2.2. Janus fibers as sensors

The spatially defined bifunctional nature of Janus fibers also provides high potential in analytical applications (Table 1 Applications as sensors). As described in the previous chapter, fibers can be produced consisting of a polymer matrix and inorganic inclusions, which are then calcined to yield inorganic fibers. If the chosen materials have complementary adsorptive traits, they can for example be employed in the first stages of many analytical procedures involving the isolation of the analyte. This was well illustrated by Lv et al.<sup>[42]</sup> who developed a Janus fiber to improve the isolation efficiency of low-abundance peptides and phosphopeptides. Their Janus fiber consisted of one half CeO<sub>2</sub>, which has an affinity for phosphate groups, whilst the other half was made of SiO<sub>2</sub>. Subsequently, SiO<sub>2</sub> was further functionalized with silane containing a hydrophobic C8 moiety. The resulting fiber was on one side highly affine for phosphate groups, whilst promoting hydrophobic interaction dominated adsorption on the other. In addition to providing a higher affinity for peptides exhibiting both phosphate modifications and a high hydrophobicity, the bifunctionality also enabled separate elution of substrates on either side of the spectrum, providing a simple way to purify peptides for mass spectrometric analysis.

In direct analytic applications, Janus fibers can be used for the immediate detection of substances, as shown by Li F. et al.<sup>[43]</sup> who produced TiO<sub>2</sub>/SnO<sub>2</sub> Janus fibers. These exhibited good ethanol gas sensing properties and were improved by a heterojunction of the two materials. It assisted with charge transfer and, thereby, an increased degradation of ethanol, which could be measured due to the emitted electrons. This is a good example of how the employment of Janus fibers can enable the production of smaller and more sensitive components for use in analytical devices, due to the higher sensitivity of the fibers requiring less of them to be used, decreasing spatial requirements.

#### 2.2.3. Magnetic and fluorescent fibers

Magnetic Janus fibers have an especially profound role in analytical applications (Table 1 **Applications for magnetic and fluorescent fibers**). One extraordinary approach was published by Bauer et al.<sup>[44]</sup> who used side by side spun fibers to improve magnetosensing devices. The advantage of their fibers as compared to conventional one-phase strategies is that the magnetostrictive cobalt ferrite and piezoelectric barium titanate components share an interface. Thus, when a magnetic force is applied to the magnetostrictive side of the fiber, it undergoes a shape change, transferring a force to the piezoelectric side. This further results in measurable electrical polarization thereof. By arranging these nanowires between electrodes, they managed

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to fabricate a very small and sensitive magnetic field sensor, which with further refinement displays high potential as an application in microelectronic components.

Magnetoresponsive materials, especially in combination with fluorescence, display applications ranging from magnetic resonance imaging, to cell labelling and tracking.<sup>[45]</sup> The fluorescence activity of such materials is commonly attained by adding fluorescent lanthanide  $\mathsf{complexes}^{^{[46,47]}}$  or fluorescent organic molecules<sup>[48,49]</sup> to magnetic materials. Additional magnetic functions can be introduced e.g., by incorporating  $Fe_3O_4$ nanoparticles into a polymer matrix.<sup>[50]</sup> Crucially, it was shown that simply blending of the two functional components can result in quenching of the fluorescent agent by the undesired absorption of exciting light or absorption of the emitted fluorescence by nanoparticles, reducing fluorescence yields.<sup>[51]</sup> Tian et al.<sup>[52]</sup> circumvented this issue by producing polymeric Janus fibers with one side composed of Fe<sub>3</sub>O<sub>4</sub> nanoparticles embedded in a poly(methyl methacrylate) (PMMA) matrix, whilst the other side consisted of the same polymer containing fluorescent Tb(TTA)<sub>3</sub>(TPPO)<sub>2</sub>. The polymer matrix was retained, since its role was to immobilize the inorganic substances, whilst substrate accessibility was also not required, as the fibers had no catalytic role. The side-by-side arrangement of the fluorophore and magnetic component showed a remarkable increase in fluorescence yields compared to randomly mixed samples, whilst also retaining the magnetic ability. Interestingly the fluorescence varied not only dependent on the concentration of nanoparticles, but also on the spatial arrangement of the fibers, as for example aligned fibers showed a higher fluorescence yield than unaligned ones.

Alternatively, a core-shell fiber can also be produced with  ${\rm Fe}_3{\rm O}_4$  nanoparticle-loaded polymers in the core, whilst the shell is made of a fluorophore containing polymer. At the same time, such a fiber can be electrospun in a side-by-side arrangement with another polymeric fiber, thus rendering Janus fibers with three different spatially defined properties. In fact, by combining magnetic/fluorescent core-shell fibers with electrically conductive fibers in a side-by-side arrangement, Xi et al.[53] demonstrated their potential for producing anisotropically conductive materials, such as their nanofiber array membrane, which exhibited desirable defined conductive and insulating properties, similar to anisotropically conductive films. By aligning the nanofibers parallel to each other using their magnetic characteristics, the unidirectional arrangement enabled conductivity along the fibers, whilst impeding current when applied perpendicularly, due to the insulative qualities of the fluorescent fiber. This work demonstrated the great potential of designing multifunctional Janus fibers with tailored properties rendering them highly attractive in the field of advanced microelectronics. Moreover, the ability to separate fluorescent molecules with overlapping absorption and fluorescence spectra also represents an advantage of Janus fibers, as the distance dependent Forster resonance energy transfer (FRET) can be avoided by placing the donor and acceptor fluorophore into separate halves of the fiber, thus also enabling potential uses of such fluorescent fibers in display technology.<sup>[54]</sup>



# 2.2.4. Antibacterial uses of Janus fibers

Other important fields for multifunctional materials are the medical sector<sup>[55]</sup> and food industry.<sup>[56]</sup> In both of these industries, detection and destruction of pathogens plays a significant role, and Janus fibers have been shown to be promising candidates to realize new material concepts addressing this issue (Table 1 Applications for antibacterial fibers).[57-59] Zhao et al.<sup>[60]</sup> demonstrated the advantages of using such bifunctional and spatially segregated fibers to specifically detect E. coli. They produced Janus fiber fragments made of two modified variants of polystyrene-co-maleic anhydride (PSMA). On one side the polymer was subsequently modified with a mannose conjugated fluorophore, whilst peroxide degrading enzyme catalase was immobilized on the other side. In this study, catalase was used to degrade hydrogen peroxide, whereby the produced oxygen propelled the fiber fragments forward in solution, while the mannose moieties on the other side were used to specifically bind E. coli. Upon binding of the bacteria to the fiber surface, the conjugation of the mannose with the fluorophore triggered an aggregation induced emission effect of the fluorophore. The resulting change in fluorescence emission enabled the quantification of the number of contaminating bacteria.

Furthermore, to prevent bacterial infestation, wound dressings can be made of Janus fiber nonwoven meshes designed to actively combat bacteria. A common problem is that antibiotic drugs are released too quickly or that the regulated interplay of two drugs is desired to attain a more holistic effect. In this regard, Janus fibers also offer a few interesting applicational possibilities. As shown by Yang et al.,<sup>[61]</sup> side-by-side fibers can be produced, which have a short- and long-term antimicrobial effect. This was achieved by making one side of the antibiotic ciprofloxacin doped PVP, whilst the other side was made of ethyl cellulose in which Ag nanoparticles were embedded. The ciprofloxacin-loaded polymer showed a quick release of the antibiotic, which would be desired for initial wound disinfection, whilst the ethyl cellulose Ag particle laden side ensured a sustained antibacterial activity. Interestingly, the combined fibers outperformed each of the single components demonstrating not only that multi-functional materials can be realized in a Janus setup, but also synergistic effects can be induced.

## 2.2.5. Drug delivery

Not only the targeted release of antibiotics is pertinent to Janus fibers, but in more broad terms also the release of drugs (Table 1 **Drug releasing fibers**). In some of these cases, the modulation of the release of a drug is desired to improve effectiveness or long-term sustainability.<sup>[65]</sup> This can be achieved with Janus fibers by for instance using two polymers with different solubilities in water. Wang et al.<sup>[66]</sup> fabricated Janus fibers made of the water soluble PVP and insoluble zein, which were loaded with the same drug. The fast dissolution of the PVP enabled a quick initial release, followed by a slow and steady release from the zein fiber. The modulated release of

one or several different drugs could also be adjusted using a soluble and insoluble fiber side, with further additives or polymer combinations to increase/decrease the release rates for each side,<sup>[11]</sup> or by modulating the shape of each fiber side,<sup>[67]</sup> thus enabling further tuning to increase the timing and effectiveness of some drug combinations. Lai et al.<sup>[62]</sup> produced alginate Janus fibers incorporating different amounts of carboxymethyl cellulose additive in each fiber half to regulate the release rate of the model drugs malachite green and minocycline hydrochloride, which were loaded in the corresponding fiber subsections (Figure 8B). Generally, Janus fibers display a high potential as drug delivery vehicles. They enable encapsulation and release of hydrophilic and hydrophobic<sup>[68]</sup> drugs based on the combination of the polymers and, due to their morphology, can be directly processed into bandages or fiber meshes, which are easy to handle.<sup>[69,70]</sup>

#### 2.2.6. Tissue engineering

The combination of antibacterial properties with tissue regenerative abilities is also desirable in the field of regenerative medicine (Table 1 Fibers for tissue engineering), since the contemporary effect of wound disinfection and tissue regeneration can be combined to result in a faster and improved recovery.<sup>[71]</sup> Ji et al.<sup>[72]</sup> used an adapted electrospinning process termed uniaxial electrospinning, making use of the phase separation between the PVP and PCL fiber components for producing Janus fibers with an evenly circular diameter. Before electrospinning, the PVP was mixed with an AgNO<sub>3</sub> to produce antibacterial Ag nanoparticles in the fiber, whilst the mixture for the other fiber component consisted of 1:1 PVP and PCL imbued with Rana chensinensis skin peptides, to accelerate wound healing and re-epithelization.[73] The Janus nanofiber membranes, which were produced thereof, were used in vivo on mice to heal inflicted skin wounds, whereby it was shown, that the combination of Ag nanoparticles and skin peptides yielded the fastest wound healing with even hair follicles starting to regrow.

Multifunctional properties are also desired in the field of tissue engineering. Resembling the fibrillar characteristics of natural extracellular matrices, fibers are of particular interest as they can be used as scaffolds to guide cell adhesion and motility.<sup>[74]</sup> It is well understood, that cells are highly sensitive to various environmental factors such as (bio-)chemical composition, hydrophilicity, presence of growth factors, mechanical properties etc. Consequently, the characteristics of scaffold materials have a profound impact on cell motility and differentiation. The ability of Janus fibers to combine different distinctly modified or loaded polymers provides various avenues to modulate their characteristics. Beside varying the stiffness<sup>[75]</sup> and degradability of the fibers,<sup>[76]</sup> the topography can also be varied.<sup>[77]</sup> Jung et al.<sup>[6]</sup> for instance produced a Janus fiber of polyurethane. Although having the same polymer on both sides, the Janus characteristic referred to the fact, that on one side the polyurethane was imbued with bubbles implemented during the microfluidic spinning process. This resulted



in a porous structure on one side, whilst the other was nonporous. The nonporous segment functioned to improve the mechanical stability of the fibers, and the porous surface improved cell adhesion. Cells first adhered to the porous surface and spread there, before also gradually spreading onto the nonporous surface, eventually forming cell sheets. With the immense combinations of polymers and their modifications, the possibilities of using Janus fibers in exploring cellular behavior are practically endless.

Especially in the context of regenerative medicine and tissue engineering new biocompatible materials are always sought after. In many instances not only biocompatibility is desirable, but also biodegradability, so that the scaffolds made thereof may eventually be replaced by native tissue or more generally degraded by the body.<sup>[78]</sup> In such applications, polymers such as polylactic acid (PLA) or polycaprolactone (PCL) are often employed,<sup>[79]</sup> but these sometimes lack the adjustability in mechanical or chemical aspects. By combination of these materials in a side-by-side arrangement, the desired traits can be more concretely adapted. Additionally, the more conventional biopolymers can also be combined with other natural polymers such as silk fibroin as shown by Peng et al.<sup>[80]</sup> who electrospun a Janus fiber of PLA and fibroin, which showed a significant change in the mechanical traits.

Recombinant spider silk has also been used for producing Janus fibers offering a huge variety of highly accurate genetical and chemical modifications, whilst also providing good biocompatibility. This was exemplarily shown by Lang et al.<sup>(63)</sup> who electrospun a Janus fiber of a genetically modified cysteine tagged spider silk protein variant and an untagged recombinant spider silk protein. The respective Janus fibers were further processed by modification of the sulfhydryl moieties of the cysteines with gold nanoparticles via thiol-maleimide mediated coupling. This resulted in a fiber which was half functionalized with gold nanoparticles, whilst the other half was unfunctionalized and devoid of a metal shell (Figure 8**C**).

#### 2.2.7. Other applications

There are many other applications of Janus fibers, which do not fall in any of the aforementioned categories (Table 1 **Other uses for Janus fibers**). One which is notable is in the field of water harvesting. Knapczyk-Korczak et al.<sup>[64]</sup> produced Janus fibers combining hydrophobic polystyrene (PS) with hydrophilic cellulose acetate (CA) in a side by side arrangement. The composite fibers showed a more than cumulative effect in adsorbing the humidity of fog rendering them a highly efficient system for water harvesting. Furthermore, the authors described a size-dependent mechanical effect as the flattened morphology of PS-CA fibers displayed significantly improved tensile strength when compared to pure CA or PS fibers.

Similarly, the swelling of the polymers upon exposure to water can also be used to exert contraction or extension of Janus fibers. The interactions of Janus fibers with aqueous environments are of great interest, as these entail uses on the body or within it. The most basic application would be smart textiles, which may adapt to intense moisture and sweating. Zakharov et al.<sup>[81]</sup> described how a swelling-dependent actuating Janus fiber could be used to manipulate arranged weaves of regular fibers, giving the whole fabric a functionality by incorporating only a few Janus fibers. In general, the introduction of two mechanically different materials can be used to determine the fiber shape through curling and introduce shapes ranging from bent fibers to shapes as complex as helices<sup>[82,83]</sup> or alternating multihelical assemblies,<sup>[84]</sup> with a vast amount of potential applications ranging from inductive microelectromechanical components, sensors, actuators etc.<sup>[83]</sup> to uses in cell culture for 3D biomaterials and Janus cellular patterning.<sup>[84]</sup>

Janus fibers can also be used as a precursor to single material fibers, by using one half of the fiber as a sacrificial polymer, which is later removed. This approach is relevant when dealing with a polymer which might otherwise not be spinnable, thus enabling the production of polymer fibers of materials which would otherwise inherently form particles if electrospun.<sup>[85]</sup> This broadens the morphologies of such polymers to fibrous scaffolds like mats and meshes, granting easier applications in fields like catalysis or biomedical engineering.

The Janus morphology can also be used to compartment reactions as shown by Lee et al.<sup>[86]</sup> They spun Janus fibers made of PLGA, whereby one side included a photoactivated crosslinker. The produced fibers could be irradiated with light and only one half of them would be crosslinked. Varying the degree of crosslinking results in implications for the polymer stability, stiffness, or drug release properties, thus being an interesting way of modulating fibers without the need of combining different polymers. Such compartmentalized reactions may also be employed for stabilizing a fiber mesh once it has been assembled, thus making them resistant for load bearing applications. Another alternative to achieve such a stabilizing effect was demonstrated by Cai et al.<sup>[87]</sup> who produced mechanically enhanced and thermally stable membranes made of Janus fibers by electrospinning polyvinylidene fluoride (PVDF) and polyimide (PI) side-by-side into fibers. The membrane produced thereof, was heat-treated resulting in annealing of the PVDF sides with one another, reinforcing the stability of the membrane, making it potentially applicable for high temperature filtration processes and, with further adjustments,<sup>[88]</sup> for applications in the field of lithium batteries.

# 3. Summary

When summarizing all the different applications of Janus fibers, it becomes obvious that this material class displays a huge and highly diverse potential (Figure 9, Table 1). Approaching Janus fibers makes sense, when two materials need to be placed in close proximity to synergistically fulfill a certain task. This is desired in applications such as catalysis or some sensing approaches, but also in the biological field, for example when a nerve cell should simultaneously be in contact with a conductive and cell adhesive material. On the other hand, Janus fibers can also be employed to separate constituents, which



would interfere with each other if randomly distributed in a single fiber, as for example different fluorophores with overlapping spectra. Naturally, in some cases the combination of two materials in a side-by-side configuration can also be used for improved mechanical characteristics, different wetting behaviors or attaining directed conductive/isolating properties.

When compared to core-shell fibers, which can also be used to achieve some of the above-mentioned applications, the decision between using these or Janus fibers is largely context dependent. Generally, if both surfaces need to be exposed to the surroundings, Janus fibers are the preferred choice. Nonetheless, the combination of core-shell fibers in a Janus fiber may also be used to allow for even more variations.<sup>[89]</sup> Furthermore, Janus fibers with more than two sides such as triaxial arrangements can be spun.<sup>[90]</sup> Hence, there is a large host of options for producing multicomponent fibers of Janus morphologies enabling precise tuning and optimization of the products.

The directionality of the fibers in membranes and films can also be of great benefit, as these can be used to make distinct hydrophobic/hydrophilic surfaces based on the fiber orientation or the selective conductivity thereof, as with for example the herein mentioned anisotropically conductive membranes. Moreover, drug loaded Janus fibers or bandages thereof can also be combined with other morphologies, such as for instance films,<sup>[91]</sup> granting them even more options for modulating drug release rates.



**Figure 9.** A) Janus fiber diameters from Table 1 separated based on the spinning method used, with their respective standard deviations (if given) directly after spinning in red, or after calcination in blue if calcined. B) Chart showing the frequency of the methods used for spinning the Janus fibers in Table 1.

# 4. Perspectives

In applications of Janus fibers, dimensions play a crucial role. In most of the cases, the active area of the Janus fiber is at the exposed interface where the two materials get into contact. Consequently, increasing fiber diameters of Janus fibers will result in loss of synergistic efficiency, and spinning two seperate fibers might be more attractive due to scalability and simplicity. Therefore, electrospinning nano- or micro-fibers has attracted most interest in producing such functional materials. Nevertheless, this technology comes along with restrictions in scalability. Besides simply placing multiple side-by-side-nozzles next to each other in one setup, there is currently no possibility of significantly increasing production rates. Furthermore, this setting might result in extensive maintenance as each nozzle needs to be controlled for clogging. Especially for industrial applications, where large scale processes need to be conducted, it might be questionable if the superior efficiency based on a high volume-to-surface ration can counterbalance the extended effort to produce such materials. In the end, taking the economical point of view into account, the potential use of Janus fibers for industrial applications will be highly dependent on the durability of such materials in the application. But there are also applications like sensors, where small dimensions are desired. Here, large interfaces of the sensing material with the medium play a crucial role regarding loading capacity, sensitivity, and response time. Furthermore, the overall size of a sensor defines the spatial resolution of the measurement. Therefore, high free functional surfaces in a small, but open porous volume will enable significant reduction of the size of sensors. One attractive application in the medical field might be (bio)sensors that can be introduced into the body using minimal invasive methods. Combined with microelectronics and biocompatible materials, such sensors might be suitable to remain in the body for a long time and be applied for example in the field of immuno-detection applications. The use of electrospun fibers has already been successfully demonstrated for detecting E. coli O157:H7 and BVDV cells,<sup>[92]</sup> cancer-derived exosomes,<sup>[93]</sup> and in various other immune-sensing applications.<sup>[94]</sup> It is obvious, that advanced opportunities applying multi-phase fibers will further drive progress in this field. Janus fibers display high potential in tissue engineering and regenerative medicine. Whenever living cells come into contact with materials aiming for regeneration of bio-functional tissue, material requirements are strictly determined by the cell's and tissue's nature, which is not negotiable. To successfully address these specific demands, multiple functions need to be combined such as release of e.g. growth factors, exposure of cell adhesion sites on the material's surface, physicochemical triggers like electrical conductivity or surface charge, mechanical properties and various more. Strikingly, taking a look to the latest literature, most of these features like drug delivery,<sup>[62]</sup> antimicrobial properties,<sup>[57–59]</sup> conductivity,<sup>[63]</sup> healing promotion,<sup>[72]</sup> and biologically attractive 3D morphologies<sup>[84]</sup> have already been realized and can be recombined in future work to develop multi-functional materials. Furthermore, electrospinning can produce Janus fibers with dimensions that

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mimic the fibrillar features of collagen fibers in the extracellular matrix, which display diameters in the range of a few hundred nanometers to micrometers.<sup>[95]</sup> Ongoing innovations in analytical tools and devices that allow for in-depth research of cell-material interactions and intense scientific efforts in cell biology and tissue engineering progressively sharpen design criteria for such medical materials.

In summary, it can be predicted, that future explorations on Janus materials will be essentially driven by the demand on high-end functional materials with highly specific requirements. Scientific progress in the fields of materials, processing and applications will further underscore the potential of this attractive concept and trigger the demand on industrial-scale processing of advanced Janus fibers. Unlimited possibilities in terms of material formulations and combinations, morphologies and arrangements, as well as modifications and functions allow the assumption, that Janus fibers are just at the beginning of their success story.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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