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Hybrid 2D nanofibers based on poly(ethylene oxide)/polystyrene matrix and poly(ferrocenylphosphinoboranes) as functional agents

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Abstract
Template smart inorganic polymers within an organic polymeric matrix to form hybrid nanostructured materials are a unique approach to induce novel multifunctionality. In particular, the fabrication of one-dimensional materials via electrospinning is an advanced tool, which has gained success in fulfilling the purpose to fabricate two-dimensional nanostructured materials. We have explored the formation of novel hybrid nanofibers by co-spinning of poly(ferrocenylphosphinoboranes) Fe A $\left(\left[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{PHBH}_2)\right]_n\right)$ and Fe B $\left(\left[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{PHBH}_2)\right]_n\right)$ with poly(ethylene oxide) (PEO) and polystyrene (PS). Fe A and Fe B contain main-group elements and a ferrocene moiety as pendant group and have different properties compared to their only carbon-containing counterparts. The use of PEO and polystyrene provided a matrix to spin those inorganic polymers as hybrid nanofibers which were collected in the form of a nonwoven mat. They were characterized by multinuclear NMR spectroscopy, scanning electron microscopy (SEM), and IR spectroscopy. Thermal properties of the polymers have been checked by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). $^1$H, $^{31}$P, and $^{11}$B NMR and IR spectroscopy revealed the nature and types of interactions of the components after co-spinning. The SEM micrographs identify the underlying unidirectional morphology of the generated hybrid nanofibers. Nonetheless, the DSC and TGA confirmed the significant boost toward the thermal stability of the resultant multifunctional fibers. It is believed that these unique types of multifunctional electrospun nanofibers will open new avenues toward the next generation of miniaturized devices.

KEYWORDS
dehydrocoupling, electrospinning, inorganic-organic polymer, multi-functional nanofibers, polyphosphinoborane
1  |  INTRODUCTION

Hybrid 2D structures or bio-hybrid technologies are emerging platforms in materials science for developing advanced structural and multifunctional materials, supporting several technological applications. Hybrid 2D nanostructures can be developed using various techniques and typically comprise a wide range of traditionally noncompatible constituents. They can be fabricated by either using combinations of inorganic–organic or organic–inorganic, which again have different structures ranging from simply bare nanoparticles to complex arrangement of multilayered nanofibers. There are various strategies, which are applied for producing such advanced structures and multifunctional materials. They are categorized as top-down and bottom-up approach. For instance, synthesis of nanoparticles from a homogeneous solution and further growth of nanoparticles to develop 2D structures such as nanowires or nanoflowers, can be one example of a bottom-up approach. Electrosprining for fabrication of nanofibers has emerged as a leading alternative top-down approach to develop nanostructures using bulk materials and to incorporate multifunctionality. The emergence of electrosprining could be attributed to its compatibility with various natural or synthetic polymers. Thus, electrosprining can bring together a variety of materials including proteins and other macromolecules, polymer hybrids, ceramics, and metal oxides, consequently leading to applications such as tissue engineering, wound dressing, transport and release of drugs, catalysis, filter and surface modifications among many others. For instance, there have been multiple studies showing the improvement of antibacterial characteristics of nanofibers by the inclusion of silver nanoparticles or copper nanoparticles. Similarly, various ligands could also be introduced to remove unwanted substances from a solution, using their physical adsorption properties. Moreover, the secondary structure of nanofibers can also be manipulated by tuning simple yet intertwined parameters. This has led to formation of pores on the nanofibers, parallel arrangement in two-dimensional space, formation of arrays and other hierarchical structure such as folding and stacking.

Significant efforts have been made to incorporate entities which cannot be directly used for electrosprining, such as chitosan, or inorganic polymers such as poly(ferrocenylphosphinoboranes) Fe A [[Fe(C5H5)2(C6H4CH2PHBH2)]n] and Fe B [[Fe(C5H5)2(C6H4PHBH2)]n] shown in Figure 1. In recent years, poly(phosphinoboranes) have gained attention as the P–B polymer backbone is valence-isoelectronic with a C–C backbone of most polymers used in daily life. Moreover, the P–B backbone of poly(phosphinoboranes) is polar due to the electronegativity difference and might introduce conductivity throughout the chain, which is an added advantage compared to polymers having a C–C backbone. Due to their inherent polar nature, the polymers can organize in a systematic way, which might be beneficial to construct optoelectronic devices.

Fe A and Fe B are thermally very stable and soluble in a wide range of solvents, which helped blending them with other polymers. Co-spinning agents such as poly(ethylene oxide) (PEO) and polystyrene (PS) were used to facilitate electrosprining. These polymers provided the matrix for co-spinning of Fe A and Fe B. Additionally, the electron cloud present in polystyrene might be involved in weak interactions with the polar P–B backbone of Fe A and Fe B.

In this study, the novel combinations of a polymer matrix and ferrocene-based polymers Fe A and Fe B are presented, providing unique collective physical properties toward higher surface reactivity and conductivity of the resulting hybrid nanofibers. Moreover, the processability of smart inorganic polymers based on ferrocene has been enhanced by introducing them as functional components of generated hybrid nanofibers. This could further be optimized by adding higher quantities of the functional inorganic polymers to the electrosprining solution hence, increasing their effectiveness or influence on the collective properties of the nanofibers.

2  |  MATERIALS AND METHODS

2.1  |  Materials

PEO powder (Mw = 300 kD) and polystyrene (PS) beads (Mw = 250 kD), obtained from Sigma Aldrich, Darmstadt, Germany and Carl Roth, Karlsruhe, Germany, respectively, were used as template for co-spinning with Fe A [[Fe(C5H5)2(C6H4CH2PHBH2)]n] (Mw = 14–17 kD) and Fe B [[Fe(C5H5)2(C6H4PHBH2)]n] (Mw = 12–15 kD). Fe A and Fe B were prepared according to the literature. Tetrahydrofuran and chloroform (CHCl3) from Carl Roth, Karlsruhe, Germany were the best choices for
electrospinning due to their ability to dissolve both, the inorganic and organic polymers.

2.2 Preparation of electrospun nanofibers

Electrospinning was performed using four different solutions. Each of the solutions contained one of the poly(phosphinoboranes) and the polymer for co-spinning. Fe A/PS and Fe B/PS solutions were prepared by mixing the polymers in a ratio of 1:4 (wt/wt) in THF. Similarly, Fe A/PEO and Fe B/PEO solutions were prepared in a ratio of 5:16 in chloroform. Both poly(phosphinoboranes) dissolved rapidly in their respective solvents giving a distinctive shade of rust brown color which could also be noticed in the electrospun nanofibers. The solutions were stirred at room temperature for a couple of hours followed by ultrasonication for an hour for homogeneity. All the solutions were used within a week of preparation. The electrospinning was started by preparing four formulations with fixed concentrations of Fe A and Fe B added to respective concentrations of PEO and PS. Table 1 displays the composition and used terminology.

2.3 Electrospinning of hybrid polymer (PEO/PS) nanofibers

An electrospinning platform with options to control various parameters was used for producing nanofibers. The machine was developed by IME medical electrospinning technologies (Netherlands) and consists of a closed chamber to prevent accidental interaction with high voltage, separating the electrospinning process from outside interference, such as temperature and humidity. The setup was used in horizontal configuration with a rotating negatively charged cylinder covered with aluminum foil as collector. The prepared solutions were transferred to 3 ml syringes attached to a PTFE tube via Leur-Lock with blunt ended needles (internal diameter 0.8 mm). The syringes were placed on a programmable pump to control the flow rate while electrospinning (Figure 2). For all solutions, the flow rate was fixed at 0.3 ml/h. The collector was rotating at 2,300 rpm. Additionally, voltages applied to the spinneret and the collector were fixed at 14 and −2 kV. Electrospinning was conducted at 25°C and 28% relative humidity (Figure 2).

2.4 Preparation of polymers Fe A and Fe B

A dehydrocoupling reaction was employed to obtain the ferrocene-based poly(phosphinoboranes) from their respective monomers,[24,25] namely, the ferrocenyl phosphine-borane and ferrocenyl methylphosphine-borane adducts. Dehydrocoupling of phosphine-boranes is a well-established process and can be performed with \([\text{Rh}(\mu-\text{Cl})(\text{cod})_2]\) (cod = 1,5-cyclooctadiene) as catalyst. The polymerization process can be monitored through $^{31}$P NMR spectroscopy. The monomer contains a PH$_2$ group, the polymer a PH group. This fact can easily be detected in the proton-coupled $^{31}$P NMR spectrum. The monomer exhibits a triplet, the polymer a doublet.[24]

2.5 Scanning electron microscopy

Scanning electron microscopy (using a JSM-IT 100 InTouchScope instrument) was used to analyze the surface morphology of co-spun nanofibers at accelerating voltage of 20 kV. The fibers were removed from the aluminum foil by scratching and were fixed on the stage using carbon tape. ImageJ[27] was used for measuring diameter and statistical analysis of the generated nanofibers.

2.6 NMR and IR spectroscopy

Multinuclear NMR spectroscopy was employed to check the purity of the electrospun polymers. NMR spectra were recorded in CDCl$_3$ with a Bruker AVANCE DRX 400 spectrometer. The chemical shifts of $^1$H, $^{11}$B, and $^{31}$P NMR spectra are reported in parts per million (ppm) at

| TABLE 1 | Polymer composition of hybrid nanofibers and their concentrations |
|---------------------------------|------------------|
| Polymer concentrations (wt/vol%) | Fe A  | Fe B  | Polystyrene | Poly(ethylene oxide) |
| Fe A/PEO                      | 2.5   | –     | –           | 8                  |
| Fe B/PEO                      | –     | 2.5   | –           | 8                  |
| Fe A/PS                       | 2.5   | –     | 10          | –                  |
| Fe B/PS                       | –     | 2.5   | 10          | –                  |
400.1, 128.4, and 161.9 MHz, respectively. Tetramethylsilane (TMS) was used as an internal standard for $^1$H NMR spectroscopy and for referencing the $^{11}$B and $^{31}$P NMR spectra to the unified scale.[28] The hybrid nanofibers were also compared with pristine polymers (PEO or PS).

FTIR spectra were recorded with a PerkinElmer Spectrum 2000 spectrometer. IR spectra of the electrospun polymers exhibited the distinctive vibrations of both pristine polymers (PEO or PS) and poly(ferrocenylphosphinoboranes) (Fe A and Fe B) without significant changes (see Figures S7 and S8 in ESI).

2.7 | Thermal analysis

Differential scanning calorimetry (DSC) (PerkinElmer, Waltham, MA) was performed under nitrogen atmosphere to analyze the change in thermal properties in the hybrid nanofibers as compared to the reference sample. 3.5 mg of each type of nanofiber was sealed in an aluminum pan for measurements. The samples were subjected to multiple heating and cooling cycles at a rate of 10°C/min from −70 to 350°C, depending on the type of polymer used for co-spinning. Thermogravimetric analysis (TGA) (Perkin Elmer) was performed to check the thermal stability and degradation of the co-spun polymers. 7.5 mg of nanofibers was placed in a ceramic cuvette under nitrogen atmosphere (flow rate 20 ml/min). The samples were heated at 10°C/min from 30 to 700°C.

3 | RESULTS AND DISCUSSION

Nanofibers were prepared from optimized concentrations of co-spinning polymers, which was obtained by analyzing various weight ratio and eliminating the concentration, which gave no fibers (checked with SEM). Moreover, the selected solvents had to dissolve Fe A, Fe B, PEO and PS, and form stable solutions for the electrospinning process. The polymers, PEO and PS, have very high molecular weights and long chains, which is ideal for electrospinning.[29] Moreover, they interact with the Fe A, Fe B polymers via hydrogen bonds and dispersion forces, therefore stabilizing the solution.

The spinning solution was loaded into the syringe and voltage was applied. Once the polymer was charged enough to overcome the surface tension, a fine jet emerged from the spinneret and deposited at the other end on the aluminum foil. The presence of Fe A or Fe B in their respective resulting nanofibers could easily be identified due to the distinctive color of the fibers as shown in Figure 3. Additionally, the presence of Fe A or Fe B in the nanofibers was also proven by NMR and IR spectroscopy (see Figures S7 and S8 in ESI).

Scanning electron microscopy showed that the morphology of the fibers is uniform with a dense network without any beads resulting in a smooth surface without any pores (Figure 4). The fibers were deposited on the collector layer by layer as nonwoven mesh.

The diameter of the nanofibers was calculated after analyzing four segmented micrographs for each sample using ImageJ. The analysis revealed that the nanofibers obtained by co-spinning Fe A/PS fibers had a mean...
The diameter of 623 nm with a standard deviation of ca. 491 nm and Fe B/PS fibers 478 nm with a standard deviation of ca. 325 nm. Similar sized fibers were also obtained when Fe A and Fe B were co-spun with PEO (mean diameter 525 nm with standard deviation ca. 252 nm, and 491 nm with standard deviation ca. 271 nm, respectively) (Figure 5).

Multinuclear NMR studies confirmed that the respective polymers are present in their resulting nanofibers. $^1$H NMR spectroscopy showed the distinctive broad signals of the ferrocenyl protons in Fe A and Fe B around 4 ppm and indicated that the poly(phosphinoboranes) are present in very small amount compared to the co-spinning organic polymers (see Figures S1–S6, ESI). The broad signals of P–H and B–H protons were not detected due to the inherent broadness of the peaks of the polymers. $^{31}$P$[^1$H$]$ NMR spectra of the electrospun polymers showed broad signals at around ~60 ppm, which is a characteristic peak of Fe A and Fe B. The change in their chemical shifts in the $^1$H and $^{31}$P$[^1$H$]$ NMR spectra is, however, insignificant. The $^{11}$B$[^1$H$]$ NMR spectra of the electrospun polymers exhibited a very broad peak around 0 ppm along with distinctive peaks for Fe A or Fe B at around ~40 ppm for tetracoordinated boron bonded to phosphorus (see Figures S5 and S6, ESI). Interaction of the B–H protons with the organic polymer could be the reason for these changes.

In the IR spectra, $\nu_{P-H}$ and $\nu_{B-H}$ of the respective poly(phosphinoboranes) were observed at ca. 2,400 cm$^{-1}$ (see Figures S7 and S8, ESI).

Thermal characteristics of co-spun nanofibers were studied by TGA (Figure 6). The initiation for major weight loss occurred at lower temperature for Fe B (219°C) as compared to 246°C for polymer Fe A and can be attributed to degradation. However, both polymers retain 60–67% of their initial weight even at 700°C.

There was a marked difference in the initial temperature for degradation compared to the reference fibers.
Degradation of the reference fiber containing only PEO occurred at ca. 420°C, whereas degradation of Fe A/PEO and Fe B/PEO was observed at 426 and 432°C, respectively (Figure 6).

More significant differences can be found when comparing the thermal degradation for Fe A/PS and Fe B/PS with the corresponding reference sample. The difference between peaks in the thermogram for nanofibers samples blended with PS is more distinguishable as compared to that observed from PEO blended nanofibers. The degradation of the reference sample starts at 418°C. As shown in Figure 7, the same peak for hybrid fibers containing Fe A or Fe B has shifted to higher temperatures, 449 and 444°C, respectively.

Differential scanning calorimetry (DSC) was performed on the nanofibers (Figure 8a,b). Hybrid nanofibers were compared with either PEO nanofibers or PS nanofibers as reference. While analyzing Fe A/PEO and Fe B/PEO in comparison to pristine nanofibers, a typical DSC curve was obtained with one significant event. As the hybrid nanofibers and pristine nanofibers were heated from −50 to 200°C, a dominant peak was observed. The peak in positive y axis represents an endothermic process and can also be interpreted as the melting point of the respective sample.
The peak shifts toward the positive x axis for hybrid nanofibers Fe A/PEO (63°C) and Fe B/PEO (65°C) as compared to 62°C for pristine PEO nanofibers. Additionally, by calculating the area under the curve the heat required to enable the phase transition observed through DSC is 15.2 mW/mg for pristine PEO nanofibers, whereas it is 16.4 and 15.3 mW/mg for PEO Fe A and PEO Fe B nanofibers, respectively. Hence, in conjugation with similar results obtained by TGA, it can be concluded that blending of polymers Fe A or Fe B with PEO for co-spinning not only provides added functionality but also thermal stability of the corresponding hybrid nanofibers. In contrast, for Fe A/PS or Fe B/PS no significant change was observed. A typical DSC curve was observed in each sample containing PS and functionalized nanofibers, with Tg of polystyrene in case of functionalized nanofibers moving a few degrees higher to around 86°C as compared to 79°C for pristine PS polymer. Both samples functionalized with polymer Fe A and Fe B exhibit a similar curve at higher temperature. When pristine Fe A and Fe B were subjected a to similar program, they showed a typical DSC curve reflecting their glass transition temperature.

4 | CONCLUSIONS

This work has shown the possibility of fabricating nanofibers containing functional inorganic polymers, that is, poly(ferrocenylphosphinoboranes), while using organic polymers such as PEO and PS as matrix. Four types of nanofibers were electrospun, each containing at least 2% (w/v) of inorganic polymer. The average diameter of these elongated continuous uniform nanofibers was between 475 and 625 nm for all samples. NMR spectroscopy confirmed the interaction between the inorganic and organic polymers. It was observed that the addition of ferrocene-based polymers increased the thermal stability of the hybrid nanofibers. Thus, it can be concluded that co-spinning of inorganic polymers (functional agent) with organic polymers (matrix) results in improved collective properties of the generated nanofibers with the possibility of higher conductivity conveyed by the inorganic polymer.[35,36] This concept can help develop nanofiber mats with high surface reactivity or positively charged surface for varieties of interaction with macromolecules; furthermore, the presence of metal atoms (iron in ferrocene) in the nanofibers can be used for redox chemistry and/or conductivity.

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REFERENCES

[1] Y. Cui, B. Li, H. He, W. Zhou, B. Chen, G. Qian, Acc. Chem. Res. 2016, 49, 483.
[2] L. Mao, W. Ke, L. Pedesseau, Y. Wu, C. Katan, J. Even, M. R. Wasielewski, C. C. Stoumpos, M. G. Kanatzidis, J. Am. Chem. Soc. 2018, 140, 3775.
[3] T. Ribeiro, C. Baleziaio, J. P. S. Farinha, Materials 2014, 7, 3881.
[4] C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sanchez, Adv. Mater. 2011, 23, 599.
[5] F. Liebig, R. Henning, R. M. Sarhan, C. Prietzel, M. Bargheer, J. Koetz, Nanotechnology 2018, 29, 185603.
[6] Z. Niu, F. Cui, E. Kuttner, C. Xie, H. Chen, Y. Sun, A. Dehestani, K. Schierle-Arndt, P. Yang, Nano Lett. 2018, 18, 5329.
[7] G. Massaglia, Quaglio, M. in Semiconductors—Growth and Characterization (Eds: R. Inguanta, C. Sunseri), InTech, Rijeka 2018, p. 159.
[8] H. R. Pant, M. P. Baigai, K. T. Nam, Y. A. Seo, D. R. Pandeya, S. T. Hong, H. Y. Kim, J. Hazard. Mater. 2011, 185, 124.
[9] H. S. Lim, J. H. Baek, K. Park, H. S. Shin, J. Kim, J. H. Cho, Adv. Mater. 2010, 22, 2138.
[10] A. Shankar, A. F. M. Seyam, S. M. Hudson, J. Text. Apparel. Tech. Manag. 2013, 8, 1.
[11] D. Li, Y. Xia, Adv. Mater. 2004, 16, 1151.
[12] A. Repanas, S. Andriopoulou, B. Glasmacher, J. Drug Deliv. Sci. Technol. 2016, 31, 137.
[13] H. Schreuder-Gibson, P. Gibson, K. Senecal, M. Sennett, J. Walker, W. Yeomans, D. Ziegler, P. P. Tsai, J. Adv. Mater. 2002, 34, 44.
[14] B. Maze, H. Vahedi Tafreshi, Q. Wang, B. Pourdeyhimi, J. Aerosol Sci. 2007, 38, 350.
[15] E. Formo, E. Lee, D. Campbell, Y. Xia, Nano Lett. 2008, 8, 668.
[16] C. Hellmann, A. Greiner, J. H. Wendorff, Polym. Adv. Technol. 2011, 22, 407.
[17] D. Liu, S. Liu, X. Jing, X. Li, W. Li, Y. Huang, Biomaterials 2012, 33, 4362.
[18] S. Singh, M. Ashfaq, R. K. Singh, H. C. Joshi, A. Srivastava, A. Sharma, N. N. Verma, Biotechnol. 2013, 30, 656.
[19] Y. Sang, Q. Gu, T. Sun, F. Li, C. Liang, J. Hazard. Mater. 2008, 153, 860.
[20] D. Kai, G. Jin, M. P. Prabhakaran, S. Ramakrishna, Biotechnol. J. 2013, 8, 59.
[21] Z. Ma, M. Kotaki, R. Inai, S. Ramakrishna, Tissue Eng. 2005, 11, 101.

SUPPORTING INFORMATION

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