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COMMENTARY

Fabrication strategies of porous nanohybrids based on electrospinning

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Over millions of years of evolution, nature has exhibited its remarkable prowess in designing the shape of materials, showcasing captivating structures and finely tuned functions. Among these, fibers represent a fundamental morphological form, observed in natural materials such as cotton, silk, hair, and various biological tissues. The fiber structures can present in numerous variations, with porosity being a key feature that governs their unique functions and properties.[1] Multifunctional fibrous hybrids are crucial for enhancing their application potential. Electrospinning is a facile and convenient method for fabricating fibrous hybrids to mimic natural porous materials. How to promote the integration of electrospinning with porous materials poses a big challenge for developing novel functional hybrids.

ADVANCES IN ELECTROSPINNING OF POROUS COMPOSITE MATERIALS

There are several intriguing approaches for fabricating porous composite materials using electrospinning technology, which can generally be classified into three categories. This paper focuses on two types of porous materials commonly employed in electrospinning: covalent organic frameworks (COFs) and metal-organic frameworks (MOFs).

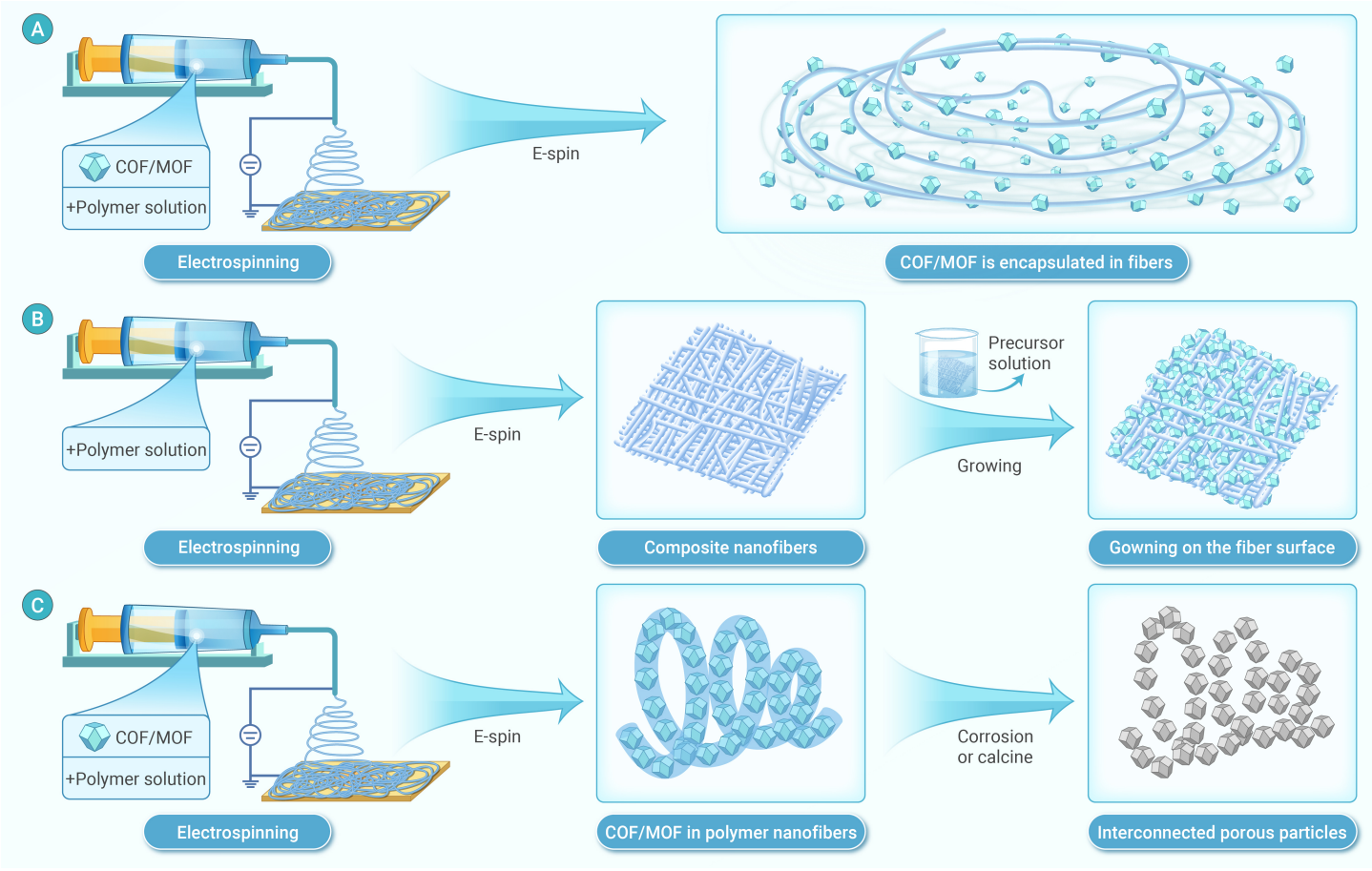

Figure 1. The electrospinning methods for generating porous fibers (A) Porous materials encapsulated in the fibers, (B) porous materials growth on the fiber, (C) defibrillated and leave porous material self-forming fibers.

ELECTROSPINNING MOLDING AFTER MIXING

The first approach involves directly incorporating pre-synthesized porous materials, such as MOFs and COFs, into composite fibers by adding them to the starting slurry used for electrospinning (Figure 1A).[2] This method leverages the inherent structural stability of these porous materials, ensuring that their original pore structures remain intact even after being mixed into the slurry and subjected to the electrospinning process. However, this approach faces several challenges: (1) The proportion of the added porous polymers in the solution is greatly limited since the homogeneity of the slurry during spinning is sensitive to the proportion. Otherwise, it is very easy to clog the nozzle and thus the electrospinning process will be failed. (2) Additionally, the dispersibility of these materials in the solution is strongly influenced by the relative hydrophilicity or hydrophobicity of both the porous materials and the solvent. A key drawback of this method is that the porous materials often become encapsulated within the fiber matrix, limiting the exposure of the internal pore structures and thus hindering their effective utilization in various applications.

DIRECT GROWTH ON ELECTROSPUN FIBERS

To address the aforementioned issue, as shown in Figure 1B, another approach involves growing porous materials directly on the surface of the fiber composite, offering a potential solution. For instance, polyacrylonitrile (PAN) widely recognized as a suitable substrate for the preparation of composite fibers.[3,4] The abundant proton-acceptor groups (C≡N) on PAN fibers provide effective anchoring sites for the nucleation and growth of imine-based COFs. The presence of numerous proton donors facilitates the directed growth of COFs on the surface of PAN fibers. Precisely controlling the reaction time, the size, surface area, and pore size of the resulting COFs can be finely tuned, allowing for optimization of the overall surface area and porosity of the composite. The resulting fibers are uniformly coated with COF spheres approximately 500 nm in diameter. These materials have demonstrated exceptional efficiency in adsorbing organochlorine pesticides, achieving high performance even at low concentrations (10 ng L^{-1}) and displaying enrichment factors from 482 to 2686 times.

DEFIBRILLATED AND LEAVE POROUS MATERIAL SELF-FORMING FIBERS

The previously mentioned method still has significant drawbacks, as it is limited to certain porous materials that could only have the ability to grow in on the fiber. To address this issue, Liu et al. showed an interesting solution to fabricate the exposed porous fibers (Figure 1C).[5] Firstly, a cobalt-based zeolitic imidazolate framework (Co-ZIF) was synthesized using established methods. During the synthesis, lanthanum (La) and manganese (Mn) were introduced to form a LaMn@Co-ZIF composite. The electrospinning method was then used to incorporate the LaMn@Co-ZIF powders into PAN fibers through a conventional mix-slurry ball-milling technique. The resulting composite fibers were subjected to heat treatment at 360°C with a heating rate of 3°C min^{-1} under flowing air and held at this temperature for 6 hours to remove the organic components. More interestingly, even after the removal of the PAN, the LaMn@Co-ZIF retained its nanofibrous network morphology (denoted as LMCF) with abundant macropores within the interwoven nanofibers. The independent LMCF particles maintain the diamond shape of the original Co-ZIF, undergoing oxidation and fusing into strings. LMCF particles are hollow structures with high porosity, e.g. a specific surface area of 197 m^2 g^{-1} and a pore volume of 0.463 cm^3 g^{-1}. Using the high porosity of LMCF and the morphology of nanofibers to increase the accessibility of reactants to the catalytic center and improve the transport of water and oxygen in the catalyst structure. The catalyst exhibited a minimal overpotential of 353 mV at a current density of 10 mA cm^{-1}, coupled with enduring stability for over 360 hours during an oxygen evolution reaction in an acidic electrolyte. Compared with the commercial Co_3O_4, LMCF is 8.6 times more conductive and about two-thirds more than IrO_x. The advantages of this solution are manifold: (1) Starting with the effective exposure of the porous material, whereby the internal components are effectively involved in the physico-chemical reaction processes; (2) After removing the PAN fibers, these porous materials still effectively maintain the tandem structure, which effectively ensures that these materials do not agglomerate; (3) This scheme may have a good scope for expansion and may apply to the preparation of a wide range of similar porous materials, thus allowing the porous material to expose pores and maintain an effective geometric arrangement in three dimensions. Due to the porous interconnected network morphology, the catalyst showed potential to replace the traditional expensive iridium catalyst for the oxygen evolution reaction. This scheme for preparing porous materials by electrospinning may apply to the preparation of more multi-purpose porous materials.

In summary, the direct electrospinning of porous polymer solutions holds promise for the fabrication of highly functionalized nanofibers. However, a major limitation of this method is the risk of nozzle clogging during fiber formation, which can adversely affect the material's porosity and functional performance. Ensuring uniform dispersibility of porous polymers within the electrospinning solution remains a significant technical challenge. Furthermore, integrating this method with advanced fabrication technologies, such as additive manufacturing, could enable the production of nanofibers with precisely tailored properties for multifunctional applications, including environmental remediation, drug delivery, and energy storage.

The *in-situ* growth of porous polymers on fibers offers the advantage of maintaining open pore structures and potentially enhancing the material's mechanical properties. However, a major limitation is the limited variety of POPs that can be effectively grown on fiber substrates, primarily restricted to polymers such as PAN and COFs. Furthermore, achieving uniform and consistent growth across the fiber surface remains a significant challenge, which may result in variability in the final material performance. Future research should focus on developing monomers and conjugation strategies to broaden the range of POPs suitable for this approach.

The fabrication of defibrillated and self-forming porous fibers presents an intriguing opportunity to create freestanding porous structures that preserve the original fiber architecture. However, a significant challenge is the risk of structural instability following fiber removal, which could compromise the material's mechanical integrity and limit its practical applicability. Future research should focus on enhancing the stability of these freestanding porous structures by incorporating cross-linking agents or employing composite materials that provide additional support during fiber removal. These advancements have the potential to accelerate the development of next-generation materials with improved functionality and broader applicability across diverse industries.

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AUTHOR CONTRIBUTIONS

Dandan Kang wrote the original manuscript. Yuheng Wen, Zeyu Wang, Qian Liao, Hailang Xu collected the data and revised the literature necessary for this work. Wenliang Song, Yaozu Liao, Il-Doo Kim and Deng-Guang Yu supervised all the tasks and revised the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

DECLARATION OF INTERESTS

Il-Doo Kim is an Editorial Board member of The Innovation Materials and was blinded from reviewing or making final decisions on the manuscript. Peer review was handled independently of this member and their research group. The other authors declare no conflicts of interest.