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Review

Organic/inorganic nanohybrids formed using electrospun polymer nanofibers as nanoreactors

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ABSTRACT

This review article presents recent advances on the use of electrospun nanofibers as nanoreactors to synthesize various organic/inorganic hybrid nanomaterials consisting of a polymeric matrix hosting *in situ* generated inorganic nanoparticles (NPs) for different applications. Electrospun nanofibers possess attractive properties such as controllable fiber diameters, high aspect ratio, and high surface area to volume ratio, affording their uses as a unique nanoreactor system to fabricate a range of organic/inorganic hybrid nanomaterials. In particular, the nanohybrids consisting of metal, metal oxide, metal sulfide, or metal chloride NPs can be *in situ* generated within the polymeric fiber matrix *via* different reactions such as UV and microwave irradiation, chemical reduction, heating treatment, and galvanic replacement reaction. The formed organic/inorganic hybrid nanomaterials have been used for environmental remediation, catalysis, electronic and sensing devices, energy, wound dressing, etc. Some of the key developments in this area of research will be introduced in detail.

Contents

1. Introduction . . . 32
2. Formation of electrospun polymer nanofibers . . . 33
   2.1. Basic principles of electrospun polymer nanofibers . . . 33
   2.2. Theoretical background . . . 33
3. Fabricating of organic/inorganic electrospun hybrid nanofibers . . . 34

Abbreviations: 4-ATP, 4-aminothiophenol; 4,4′-DMAB, 4,4′-dimercapto-azobenzene; 4-NTP, 4-nitrothiophenol; AAI, iron acetylacetonate; AF, acid fuchsine; AgTFA, (trifluoroacetylacetonoto) Ag(I); AO, acridine orange; CA, cellulose acetate; CMC, carboxymethyl cellulose; CNFs, carbon nanofibers; DMABA, (dimethylamino) benzaldehyde; DMF, dimethylformamide; DSSC, dye-sensitized solar cell; *E. coli*, *Escherichia coli*; EDS, energy dispersive spectroscopy; EM, electromagnetic; GA, glutaraldehyde; GCE, glassy carbon electrode; HQ, hydroquinone; Lac, laccase; LbL, layer-by-layer; MB, methyl blue; MWCNT, multiwalled carbon nanotube; NPs, nanoparticles; ODA, 4,4′-oxydianiline; OG, orange G; P4VP, poly(4-vinyl pyridine); PAA, poly(acrylic acid); PAN, poly(acrylonitrile); PANi, polyaniline; PL, photoluminescence; PE, polyelectrolyte; PEI, polyethyleneimine; PEO, poly(ethylene oxide); PET, poly(ethylene terephthalate); PI, polyimide; PLA, poly(L-lactide); PLLA, poly(L-lactic acid); Poly(MAA-co-TFA), methacrylic acid and trifluoroethyl acrylate copolymer; PMDA, pyromellitic dianhydride; PMMA, poly(methyl methacrylate); PPV, poly(p-phenylene vinylene); PPy, polypyrrole; POSS-NH_2, amino-polyhedral oligomeric silsesquioxanes; PVA, poly(vinyl alcohol); PVA-g-ct, catechol grafted PVA; PVDF, poly(vinylidene difluoride); PVP, poly(vinyl pyrrolidone); PU, polyurethane; RL, reflection loss; SEM, scanning electron microscopy; SERS, surface-enhanced Raman scattering; TBT, 1-tetra-*n*-butyl titanate; TCE, trichloroethylene; TEM, transmission electron microscopy; TEPC, tin/tin oxides encapsulated in porous carbon nanofibers; XRD, X-ray diffraction; ZVM, zero-valent metal.

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3.1. Immobilization of zero-valent metal NPs (ZVM NPs) . . . 34
3.1.1. Immobilization of Ag NPs . . . 35
3.1.2. Immobilization of Pd NPs . . . 37
3.1.3. Immobilization of Fe NPs . . . 38
3.1.4. Immobilization of Au NPs . . . 38
3.1.5. Immobilization of other monometallic NPs . . . 40
3.1.6. Immobilization of bimetallic NPs . . . 40
3.2. Immobilization of other inorganic NPs . . . 41
3.2.1. Immobilization of metal sulfide NPs . . . 41
3.2.2. Immobilization of metal oxide NPs . . . 42
3.2.3. Immobilization of metal chloride NPs . . . 43
3.2.4. Immobilization of metal carbide NPs . . . 43
4. Applications of electrospun organic/inorganic nanohybrids . . . 44
4.1. Environmental remediation . . . 44
4.2. Catalysis . . . 45
4.3. Electronic and sensing devices . . . 46
4.4. Energy . . . 47
4.5. Wound dressing . . . 48
5. Conclusion and outlooks . . . 49
Declarations of interest . . . 49
Acknowledgements . . . 49
Appendix A. Supplementary data . . . 49
References . . . 49

1. Introduction

For the establishment of biochemical networks, creating distinguishable structures is a ubiquitous method for biological systems to support a cascade of complex biochemical reactions [1]. In these networks, biochemical reactions usually occur in a strictly confined space which strongly influences the movement and interactions among the reactant molecules [2]. Nature shows a variety of places referring to the use of well-organized structures to maximize the precision and efficiency of biochemical reactions such as nucleus, mitochondria, Golgi apparatus, lysosomes, and the pores of channel proteins [3]. There, the local concentrations and arrangements of reactant molecules and ions are quite organized, and this has profound consequences on the chemical processes that may take place inside.

Inspired by biological counterparts, designing and constructing confined reaction environment, namely reactor, is of growing interest to chemical, biological, and materials science [4–6]. A significant portion of recent scientific research has focused on nanoreactors, and different types of nanoreactors have been proposed, such as nanocapsules based on micellar [7–9] and vesicular [10–13] assemblies that are built from low-molecular-weight molecules, macromolecular blocks, or biomacromolecular entities (*e.g.*, viruses) [14–19]. Many of these nanoreactors are being developed for use in the preparation of different types of nanoparticles (NPs) [20–22], to improve the efficiency of chemical processing, as standalone or implantable smart drug delivery vehicles [23], as nanomedicine [24], as biosensors [25], and as replacement tissues [26].

Among all these nanoreactors, there is a growing interest in nanofibers due to their attractive properties, for instance, controlled fiber diameter, high aspect ratio, high surface-volume ratio [27]. Although nanofibers can be prepared *via* various methods including self-assembly [28,29], phase separation [30], interfacial polymerization [31,32], rapidly initiated polymerization [33,34], template- or pattern-assisted growth [35], vapor-liquid-solid growth [36], and hydrothermal synthesis [37,38], electrospinning seems to be the simplest and most versatile technique capable of generating continuous nanofibers [39]. In addition, it is also one of the available inexpensive mass-production technologies. One typical example regarding the use of electrospun nanofibers as nanoreactors is to prepare Fe NPs within electrospun poly(acrylic acid) (PAA)/poly(vinyl alcohol) (PVA) nanofibers. The PAA/PVA nanofibers were first crosslinked *via* treatment at an elevated temperature, then complexed with Fe(II) ions *via* binding with PAA carboxyl groups, followed by reduction of the Fe(II) *via* sodium borohydride ($NaBH_4$) to generate Fe NPs within the nanofibrous reactor [40].

In general, organic/inorganic electrospun hybrid nanofibers can be obtained by *ex situ* or *in situ* approaches, in which inorganic NPs are respectively either mechanically dispersed into organic solution (*e.g.*, polymer) [41–43], or directly generated inside a polymer matrix by chemical [44,45], thermal [46,47], or optical decomposition of particle precursors [48,49]. The main drawback of *ex situ* method comes from the difficulty to achieve a homogenous dispersion of NPs in the organic matrix owing to the poor miscibility, high surface energy, and strong interparticle interactions [50–52]. In contrast, the *in situ* approach allows a better dispersion of NPs, as mediated by the polymer and polymer-based microenvironment, which limits the particle aggregation, confines the particle nucleation sites, and controls the resulting particle size by properly engineering the polymer functional groups [53], matrix assembly [54], and crosslinking [55].

Various types of inorganic NPs can be hosted in polymeric matrix to form organic/inorganic electrospun hybrid nanofibers for a wide range of applications. Although some investigations in these research fields have been reported [47,56–58], few reviews, by far, that provide comprehensive state of art advances regarding the formation of organic/inorganic electrospun hybrid nanofibers using nanofibrous reactor systems for different applications are available in the literature [59]. Here, the aim of this review is to give a general literature survey covering various developments of organic/inorganic electrospun hybrid nanofibers comprising of *in situ* synthesized NPs incorporated into polymeric nanofibrous matrix. Followed by a short introduction of the formation of electrospun nanofibers (including basic principles of electrospun polymer nanofibers and theoretical background), there are two major sections describing recent advances in the immobilization of different kinds of NPs into electrospun nanofibers and their corresponding applications (Table 1). Finally, some challenges and future outlooks in this area of research are briefly addressed.