



Developing chitosan-based composite nanofibers for supporting metal catalysts



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ABSTRACT

Using electrospinning technique to prepare chitosan (CS) nanofibers from an inexpensive solvent such as acetic acid has been a challenge, due to the lack of sufficient entanglements in these semi-rigid polyelectrolytes. Incorporating polymers such as poly(methacrylic acid) (PMAA) into the solution lowers the entanglement concentration of the polymers, and make all three morphology regimes (polymer droplets, beaded nanofibers and nanofibers with uniform thickness) accessible to electrospinning method. Uniform composite nanofibers are found at concentrations well above the entanglement concentration. The thickness and morphology of nanofibers can be regulated by addition of small amount of organic solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The composite nanofibers are subsequently crosslinked at an elevated temperature to improve their thermal and solvent stability. The mechanical properties of the crosslinked CS/PMAA fibers can be modulated by varying the amount and molecular weight of PMAA incorporated in the blend. The composite fiber materials provide a useful platform to support a variety of catalysts. As a demonstration, palladium catalyst has been immobilized on the crosslinked CS/PMAA nanofibers to carry out Mizoroki–Heck cross-coupling reactions of aromatic halides and acrylates. We found remarkable catalytic efficiency and stability in these materials. We also demonstrate that, by the “post-modification” of the nanofibers with ligands that chelate metal catalysts, a variety of metal catalysts can be incorporated into the fiber platform, with further improved stability and activity.

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1. Introduction

Chitosan, a derivative of chitin, is a versatile, low-cost biopolymer that has found applications in food, cosmetics, drug delivery and tissue engineering [1,2]. Recently, there has been increasing interest in the use of chitosan nanofibers (e.g., by electrospinning) as solid supports for immobilization of catalysts or enzymes, to take advantage of the metal-chelating and complexation properties of chitosan and the large accessible surface area of nanofibers [3–6]. In order to make continuous nanofibers, trifluoroacetic acid (TFA) was often used as the dispersion solvent for chitosan in the electrospinning process, but TFA is both expensive and toxic [7–9]. To prepare chitosan nanofibers in inexpensive and more environmentally friendly solvents, new methods have been

explored, e.g., by the addition of a second polymer as the co-spinning agent with chitosan [10–12]. However, a general approach to obtain composite chitosan nanofibers with controlled morphology, based on mechanistic understanding of the process, is still much desired.

Blending chitosan with another polymer for electrospinning may have a few advantages in making well-defined nanofibers as supporting materials for catalysts. First, a carefully selected polymer that is compatible with chitosan in the solution may improve the process to make nanofibers with controlled morphology. Chitosan is a cationic polymer and soluble in aqueous acidic solution, in which the $-NH_2$ groups are protonated. However, the viscosity of the polyelectrolyte solution increases very rapidly with the concentration of chitosan, making it difficult to reach the minimum concentration required for the formation of continuous nanofibers by electrospinning. The blending of a polymer that improves chain interactions during the fast solvent evaporation of electrospinning process may facilitate the formation of continuous nanofibers with uniform sizes. Second, after the formation of nanofibers,

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crosslinking may be induced through the functional groups of the second polymer to enhance solvent and thermal stability of the composite nanofibers, while the chelating sites of chitosan can be kept intact for the subsequent immobilization of catalysts. This characteristic is desirable for developing materials to support catalytic reactions that may take place under harsh environmental conditions. Third, the composition and the molecular weight of the second polymer in the blend can be varied, to provide further controls over the physical properties of the nanofibers.

Herein, we reported the use of a mixture of chitosan (CS) and poly(methacrylic acid) (PMAA) in acetic acid solution to prepare blended CS/PMAA nanofibers by electrospinning (see Scheme 1). PMAA interacts with chitosan in the solution and improves chain entanglements. The concentration, viscosity and composition of the polymer solution were found to play a central role in the formation of continuous, uniform nanofibers. After the formation of composite nanofibers, PMAA in the blend was readily crosslinked by simple thermal treatment to obtain solvent-resistant materials for supporting heterogeneous catalysts. As a demonstration, palladium catalyst has been immobilized on the surface of the crosslinked CS/PMAA nanofibers to carry out Mizoroki–Heck cross-coupling reactions of aromatic halides and acrylates, and remarkable catalytic efficiency and stability were found in these materials. The mechanical properties of composite nanofiber mat can be modulated by using different molecular weights of PMAA in the blend and by varying the crosslinking temperature. The “post-modification” of the nanofibers with chelating groups, facilitates the attachment of a variety of metal catalysts on the fibers and further improves their stability. The general applicability of the approach has been demonstrated in the preparation of nanofibers from a mixture of poly(acrylic acid) (PAA) and chitosan. The result shows great promise in the use of a variety of synthetic polymers or biomacromolecules to blend with chitosan for the formation of composite nanofibers with controlled morphology and physical properties by simple electrospinning process.

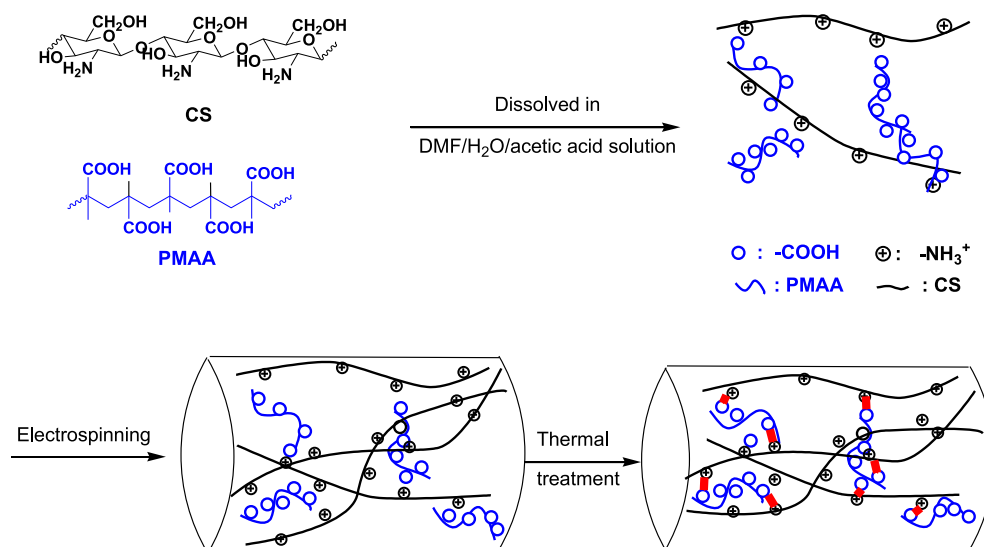
2. Results and discussion

2.1. Nanofibers obtained from electrospinning of a mixture of CS and PMAA in solution

Electrospinning is a simple technique to make continuous

nanofibers from a variety of polymers dispersed in solution [13,14]. Under the same processing conditions (e.g., applied voltage, tip to target distance and the feed rate of the solution to the capillary tip), fiber morphology largely depends on the solution properties of the polymers such as solvent, viscosity, concentration and conductivity [15,16]. For many polymer/solvent systems, three morphology regimes can be observed as: polymer droplets, beaded nanofibers and nanofibers with uniform thickness, when the solution concentration is gradually increased. Defect-free, uniform nanofibers are usually found at concentrations well above the entanglement concentration (C_e) of the polymer, at which significant entanglement of polymer chains takes place in the solution [17]. Chitosan ($M_n = 2.0 \times 10^5$ in this study) can be readily dissolved in an acidic solution such as acetic acid, in which the $-\text{NH}_2$ groups in the polymer chain are protonated ($-\text{NH}_3^+$). The specific conductance of chitosan in the acetic acid aqueous solution ($\text{CH}_3\text{COOH}:\text{H}_2\text{O} = 4:1$ in weight, 20°C) decreases sharply as the concentration of chitosan increases (Fig. S1), suggesting it is a relatively weak polyelectrolyte at the conditions. The dynamic light scattering of the chitosan solution shows a characteristic reduced intensity from salt-free polyelectrolyte solution, and a convoluted correlation function from two time scales (Fig. S2). We found it difficult to obtain continuous nanofibers from the electrospinning of chitosan, due to the lack of sufficient entanglements in these semi-rigid polyelectrolytes. For example, only bead-like polymer droplets were obtained from the electrospinning of 4 wt% of chitosan in acetic acid solution (Fig. S3) [18,19]. And as the viscosity increases rapidly in this type of polyelectrolyte solution [20,21], controlling the electrospinning process became very difficult at chitosan concentration above 4 wt%. It is not feasible to obtain smooth nanofibers by simply increasing the concentration of chitosan in the acetic acid solution.

Rather, we found that the addition of a second polymer that can interact with chitosan in the solution may resolve the chain entanglement issue during electrospinning process and provide a general approach to obtain composite chitosan fibers with controlled morphology. Fig. 1 shows how the conductivity and viscosity of the solution change with the increasing amount of PMAA ($M_n = 7.95 \times 10^4$, PDI = 2.89) added into a 4 wt% chitosan solution, and how they are compared with the pure chitosan solution at the same total polymer concentration. Apparently, PMAA, a neutral polymer by itself at the pH condition, interacts with



Scheme 1. Preparation of stable chitosan/PMAA composite nanofibers from electrospinning.

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