Macromolecular Nanotechnology

Microfluidic fabrication of highly stretchable and fast electro-responsive graphene oxide/polyacrylamide/alginate hydrogel fibers

Li Peng[a], Yan Liu[a,b], Jiani Huang[a], Jiahao Li[a], Jinghua Gong[a], Jinghong Ma[a,*]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, 20160, China
[b] Materials Science and Technology of Polymers, MESA+ Institute of Nanotechnology, University of Twente, P.O. Box217, 7500 AE Enschede, The Netherlands

ABSTRACT

The practical application of electro-responsive hydrogels is limited due to the slow response rate and the poor mechanical property. The electro-response rate of hydrogels can be improved by forming hydrogel fiber and adding graphene oxide (GO). Meanwhile, the incorporation of GO can also enhance the mechanical properties of hydrogels. However, the highly stretchable and fast electro-responsive hydrogel fibers are rarely reported at present. In this paper, graphene oxide/polyacrylamide/sodium alginate hydrogel fibers were prepared by microfluidic spinning and free radical polymerization. The mechanical properties, swelling properties and electro-responsive behaviors of the nanocomposite hydrogel fibers were investigated. The results show the nanocomposite hydrogel fibers could be very stretchable by adjusting GO and N,N-methylenebisacrylamide (BIS) contents. Besides, compared with hydrogel rods, the hydrogel fibers with diameter in microscale exhibit much faster swelling rate and electro-response rate. The thinner the hydrogel fiber is, the faster the electro-response rate is. This suggests that the highly stretchable and fast electro-responsive hydrogel fibers take us closer to the application of artificial muscle actuators.

1. Introduction

Electro-responsive hydrogels are usually made of polyelectrolyte and can exhibit bending in an electric field, which creates opportunities for converting the electrical energy into mechanical motion [1]. Thus, the electro-responsive hydrogels are great candidates for electro-active artificial actuators such as artificial crawler [2,3], artificial fish [4] and mechanical hand [5]. However, the practical application of traditional hydrogels is limited due to the slow electro-response rate and the poor mechanical property [6]. Moreover, the hydrogels are mostly made into bulks, rods and films, which lack flexibility in the fabrication of high-order assemblies.

Based on the above problems, researchers have done a lot of work and made great progress. Nano-materials such as graphene and carbon nanotube are usually introduced to form nanocomposite hydrogels, which improve the electro-response rate and meanwhile enhance the mechanical properties [7,8]. Tai et al. prepared graphene oxide/poly-acrylic acid (GO/PAA) nanocomposite hydrogel strip and found the bending rate was much faster than that of the PAA hydrogel strip [6]. Zhang et al. reported the incorporation of GO increased the bending angle of graphene oxide/polyacrylamide (GO/PAM) hydrogel rods in an electric filed [9].

In the last decade, hydrogel fibers have attracted considerable interest because the long, thin and flexible hydrogel fibers are useful for the fabrication of high-order assemblies such as 3D biomimetic tissue scaffold, artificial muscle systems and soft actuators [10,11]. In addition, compared with bulk hydrogels, hydrogel fibers with diameter in microscale and large aspect ratio have much faster response rate because the response rate is inversely proportional to the smallest dimension of hydrogels [12]. Recently, microfluidic spinning is emerging as powerful tools to generate hydrogel fibers at the microscale [13,14]. In the microchannel, the continuous fluid of pre-gel solution is sheathed by a second solution and then generate continuous fibers via cross-linking or solidification. There are two strategies for the formation of hydrogel fiber. Firstly, polymer solutions such as alginate [15,16], poly (lactic-*co*-glycolic acid) [17] and chitosan [18] solutions are used as pre-gel solutions, and the formation of fibers is depended on ionic crosslinking and phase separation. However, due to the poor mechanical properties, this kind of hydrogel fibers usually serves as the carriers for biomacromolecules or cells, rather than as artificial muscle materials or soft actuators. Secondly, reactants including monomer, cross-linker and initiator embedded in the pre-gel solution are also utilized to generate hydrogel fibers by alginate templating with microfluidic device [19,20]. The Ca-alginate fiber is formed in the microfluidic

spinning process and acts as the template for the subsequent free radical polymerization of monomers. In this strategy, stimuli-responsive polymer networks and nano-materials can be introduced into the hydrogel fibers, which brings them multifunctionality and better mechanical property. Unfortunately, few hydrogel fibers formed by this method have been reported at present. Yoo et al. reported the microfluidic fabrication of photochromic polydiacetylene-containing alginate hydrogel microfiber [19]. Lim et al. prepared the poly(N-isopropylacrylamide)-embedded alginate hydrogel microfiber and introduced light-responsive property by combining photothermal magnetite nanoparticles [20]. In this paper, we prepared polyacrylamide-based hydrogel microfiber by alginate templating with microfluidic device, and meanwhile improve the electro-response rate and the mechanical property of the hydrogel fiber by incorporating graphene oxide (GO).

2. Experimental section

2.1. Materials

Graphene oxide (GO) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Acrylamide (AM) was obtained from TCI Co., Ltd. Potassium peroxodisulfate (KPS, Shanghai Chemical Co., Ltd.) was purified by recrystallization in deionized water. N,N′-methylenebisacrylamide (BIS) and benzoin dimethyl ether (BDK) were purchased from Sigma-Aldrich. Sodium alginate (SA) and N,N,N′,N′-tetramethylethylenediamine (TEMED) were obtained from Aladdin Reagent Co., Ltd. Calcium chloride ($CaCl_2$) and sodium sulfate (Na_2SO_4) were purchased from Shanghai Chemical Co., Ltd. Deionized water used for all experiments was bubbled with N_2 gas for more than 1 h prior to use.

2.2. Preparation of nanocomposite hydrogel fibers

GO powder (0–0.06 g) was dispersed in deionized water (9.5 mL) under ultrasound, and the pH value was adjusted to 7.0 by using NaOH. Then AM (1.0 g), BIS (0.002–0.02 g) and SA (0.1 g) were added and dissolved with stirring in an ice-water bath. Finally, initiator KPS (0.01 g in 0.5 mL deionized water) and catalyst TEMED (10 μL) were added. The solution for core fluid and 200 mM $CaCl_2$ solution for sheath fluid were introduced into microfluidic device respectively (Fig. 1). Based on microfluidic spinning, the as-spun fiber was formed in the outlet pipe and coiled on a rotating aluminium cylinder. Then the as-spun fiber was uncoiled from aluminium cylinder and placed in soybean oil containing photo-initiator BDK (1%, w/v) and irradiated under UV light for 30 min, subsequently polymerized at 20 °C for 20 h to prepare graphene oxide/polyacrylamide/calcium alginate hydrogel fiber (G_mB_nPC hydrogel fiber). Finally, the hydrogel fiber was decalcified by saturated Na_2SO_4 solution to obtain graphene oxide/polyacrylamide/sodium alginate hydrogel fiber (G_mB_nPS hydrogel fiber). The number m and n represent the weight percentage of GO and BIS contents against AM, respectively. For the comparison, G_mB_nPS hydrogel rods with diameter in 6 mm were also prepared by free radical polymerization and the components were the same as the G_mB_nPS hydrogel fibers. The dried G_mB_nPS hydrogel fibers were characterized by FTIR (Nicolet 6700, Thermo Fisher). Besides, the swollen hydrogel fibers were quickly frozen in liquid nitrogen and then freeze-dried for SEM analysis (SU8010, Hitachi).

2.3. Mechanical properties

Tensile measurement was performed for the hydrogel fibers (diameter: 600 μm) and the hydrogel rods (diameter: 6 mm) using an Instron 5900 testing machine at room temperature. The distance between the two clamps is 20 mm, the crosshead speed is 20 mm/min.

2.4. Swelling properties

The hydrogel fiber (length: 3 m, diameter: 600 μm) and hydrogel rod (length: 2 cm, diameter: 6 mm) were dried to constant weight and then immersed into the deionized water to approach the equilibrium state at 20 °C. The hydrogels were removed from the excess water on the surface with filter paper and then weighted at various time intervals. The swelling ratio of hydrogel was calculated as follows:

$$\text{Swelling Ratio} = (W_s - W_d)/W_d$$

where W_s and W_d represent the weights of hydrogel in the swollen state and in dry state, respectively.

2.5. Electro-response properties

The G_mB_nPS hydrogel fiber was immersed in the 0.1 M Na_2SO_4 aqueous solution to reach swelling equilibrium and cut into 1.0 cm in length. The same solution was poured into a plastic case equipped with two parallel graphite electrodes (20 mm apart). The hydrogel fiber was placed in the centre of the electrodes (Fig. S1). A 20 V direct current (dc) voltage was applied between the electrodes. The bending angle of the hydrogel fiber was recorded.

3. Results and discussion

3.1. Preparation of nanocomposite hydrogel fibers

The coaxial laminar flow microfluidic device used to fabricate G_mB_nPS hydrogel fiber was designed and assembled as reported by our previous work (Fig. 1a) [21]. The device was composed of two glass capillaries with different sizes, where the inner cylindrical capillary was
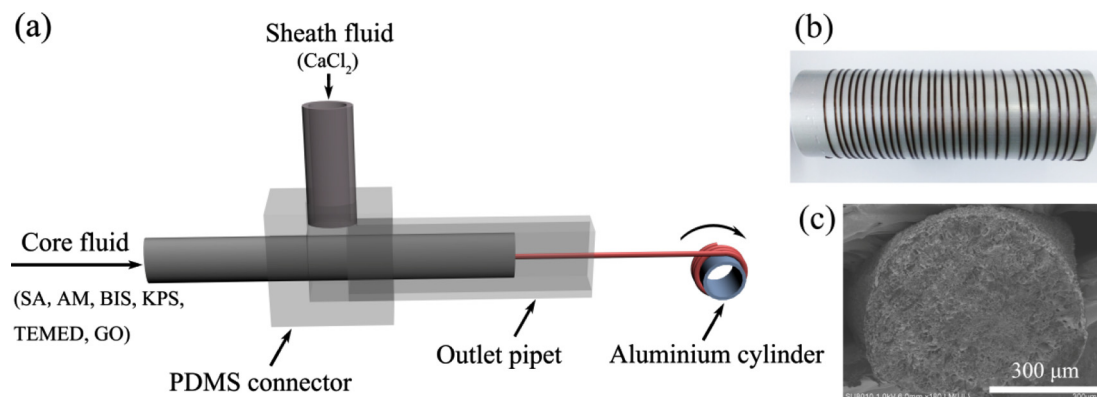

Fig. 1. (a) Schematic of the coaxial laminar flow microfluidic spinning device, (b) photograph of the continuous as-spun fiber, and (c) SEM image of the cross-section of the hydrogel fiber.