

# Thermo-responsive PNIPAm-based Composite Nanofibers Prepared by Electrospinning

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Flexible and wearable electronics capable of detecting the temperature, the motion and the stress in the body have been developing recently. Such devices rely heavily on the stimuli-responsive materials. Particularly, flexible materials which can give electrical response to the change of temperature are crucial for wearable healthcare electronics, and thus have received great research interests recently. Herein, a thermo-responsive copolymer was prepared by copolymerization between N-isopropylacrylamide (NIPAm) and N-methylol acrylamide (NMA). AgNO<sub>3</sub> was mixed with the P(NIPAm-co-NMA) solution to fabricate nanofibers by electrospinning, which was then converted into Ag by in-situ reduction with sodium borohydride. The electrical resistance of the composite nanofiber showed high sensitivity to the change of temperature. Furthermore, the composite nanofibers exhibited excellent stability during repeated heating-cooling cycles.

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**Keywords:** Thermo-responsive material; nanofiber; in-situ reduction; copolymerization

## 1. INTRODUCTION

Thermo-responsive materials have been receiving great research interests due to their various potential applications such as temperature sensors, drug delivery, temperature-controlled separation and so on [1-4]. Particularly, flexible thermo-responsive materials are the heart of wearable temperature sensors, which have attracted tremendous attention in the past few years. To this end, a variety of nanofibers based on thermo-responsive polymers have been prepared [5-9]. Among the various preparation methods, electrospinning has been demonstrated to be a versatile technique to prepare functional nanofibers [10-12]. For example, Guo and co-workers prepared thermo-responsive nanofibers based on poly(hydroxyethylacrylate-co-coumaryl acrylate-co-ethylmethacrylate) and loaded a hydrophilic dye into the fiber to study the temperature-dependent release behavior [7]. Webster and co-workers prepared poly(N-vinylcaprolactam) nanofibers by electrospinning, which showed a significant increase of the contact angle as the temperature increased from 20 °C to 40 °C [8].

However, it is difficult to monitor the responsive behavior of these fibers, not to mention the difficulty in high-precision detection. Flexible materials which can give electrical response to the change of temperature are highly desired for wearable electronics.

In our previous study, we prepared the copolymer P(NIPAm-co-NMA) by radical copolymerization, and cross-linked the electrospun nanofibers at a high temperature to enhance the stability of the fiber in water [13]. The surface of the nanofiber was then coated by silver nanoparticles using a chemical plating method, which exhibited a high sensitivity to temperature around the lower critical solution temperature (LCST) [13]. However, the long-term stability of those fibers still needs to be improved as the surface coating could lose during the repeated washing and heating-cooling cycles.

In the present study, AgNO<sub>3</sub> was mixed with the solution of copolymer P(NIPAm-co-NMA) to fabricate nanofibers by electrospinning, which was then converted into Ag by in-situ reduction with sodium borohydride (different reducing agents were also used for comparison). The electrical resistance of the composite nanofibers exhibited excellent thermal responsive performance. Furthermore, the composite fibers exhibited excellent cyclic thermo-responsive performance as the silver nanoparticles are mostly embedded in the polymer matrix.

## 2. EXPERIMENTAL

### 2.1 Materials

NIPAM, NMA, ammonium persulfate (APS), N,N,N',N'-tetramethylethylene-diamine (TEMED), silver nitrate (AgNO<sub>3</sub>), sodium hydroxide (NaOH), ammonium hydroxide (NH<sub>4</sub>OH), glucose, nitric acid (HNO<sub>3</sub>) and N,N-Dimethylformamide (DMF) were all purchased from Aladdin Reagent Co. Ltd (China). The monomer NIPAm was purified by recrystallization from n-hexane and NMA was purified by recrystallization from chloroform. The initiator APS was purified by recrystallization from ethanol. The other chemicals were used as received without further purification.

### 2.2 Synthesis of poly(NIPAm-co-NMA)

P(NIPAm-co-NMA) with a NIPAm: NMA molar ratio of 9:1 was synthesized following the procedure described in previous studies [13-15]. Typically, NIPAm and NMA monomers with desired ratios were added to a three necked flask with a stir bar which was then purged with nitrogen. 50 mL of deionized water was then added into the flask, followed by adding APS and TEMED. The mixture was then kept at 0 °C for 4 h and then at 25 °C for 20 h to allow the copolymerization. The resulting solution was dialyzed against deionized water for 72 h to remove unreacted monomers.

### 2.3 Preparation of nanofibers

The as prepared P(NIPAm-co-NMA) was dissolved in DMF with a concentration of 10%. Different amounts of AgNO<sub>3</sub> were added into the polymer solution and stirred at 25 °C for 12 h to

form stable solutions. The mixed solution was then electrospun into fibers using the conditions as follows: a voltage of 17 kV, a needle-to-collector distance of 20 cm and a flow rate of 1.0 mL/h. The P(NIPAm-co-NMA)/AgNO<sub>3</sub> fibers containing 20%, 30% and 40% of AgNO<sub>3</sub> are denoted as PNN/AgNO<sub>3</sub>-1, PNN/AgNO<sub>3</sub>-2 and PNN/AgNO<sub>3</sub>-3 respectively. The corresponding fibers after reduction of AgNO<sub>3</sub> into Ag are denoted as PNN/Ag-1, PNN/Ag-2 and PNN/Ag-3, respectively.

#### 2.4 Thermal treatment of the composite fibers

To stabilize the composite fibers, the fibers were heated at 130 °C for 10 h for thermal crosslinking of NMA. For in-situ reduction of AgNO<sub>3</sub>, 0.3 g of the cross-linked composite fibers were soaked in 200 ml of 0.05 M NaBH<sub>4</sub> solution and kept at room temperature for 2 h, after which the fibers were thoroughly rinsed with deionized water and dried at 60°C under vacuum for 12 h. The fibers were also reduced by glucose and vitamin C (VC) using the same procedure for comparison.

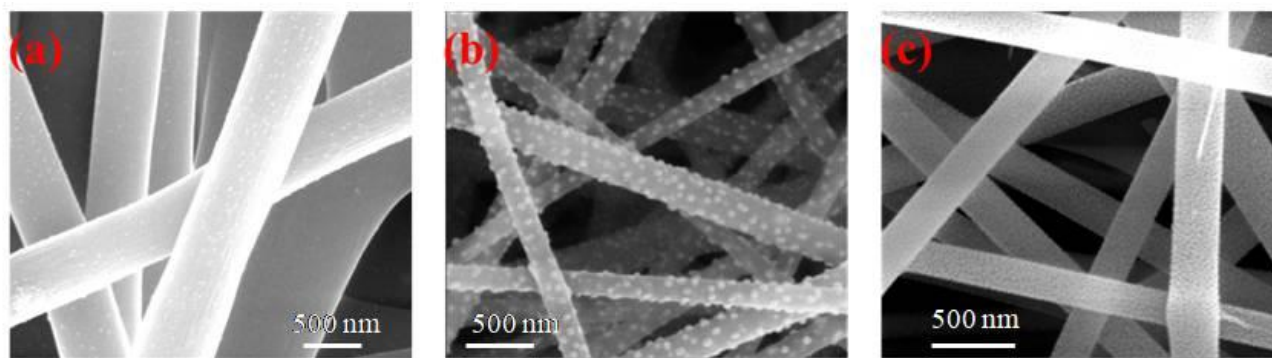
#### 2.5 Characterization

A field-emission scanning electron microscope (FESEM, JEOL JSM-7800F) was used to investigate the fiber morphology. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C min<sup>-1</sup> from 100 °C to 800 °C in air atmosphere. The response of electrical resistance to the change of temperature was assed using a procedure described in our previous study. Specifically, the electrical resistance was measured at different temperatures using a multimeter (Fluke, USA). Electrodes were attached directly to the fibrous mat saturated with water and the separation of the electrodes was set at 1 cm for all measurements. The temperature was increased using a hot stage from 30 to 62 °C with a step of 2 °C. The mats were stabilized for 10 min at each temperature before the measurement was performed.

### 3. RESULTS AND DISCUSSION

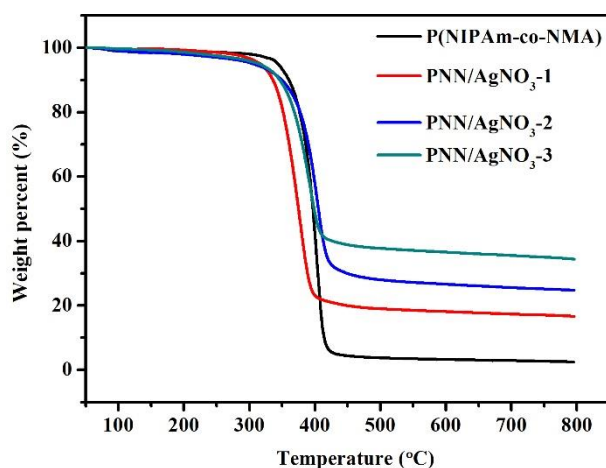
The homopolymer PNIPAm is a typical thermo-responsive polymer which has been investigated for various applications. However, its excellent solubility below the LCST hindered its application in flexible temperature sensors. To this end, other monomers (such as NMA in this work) were copolymerized with NIPAm which allows the crosslinking of the polymer chain and thus enhance its resistance to water [16-18]. To disperse the conductive filler uniformly in the matrix, AgNO<sub>3</sub> was introduced into the copolymer solution in this work. Electrospinning of the mixed solution of P(NIPAm-co-NMA) and AgNO<sub>3</sub> resulted in composite fibers with well-defined fibrous morphology (SEM images shown in Fig. 1), which is similar to the neat P(NIPAm-co-NMA) electrospun fibers. This suggests the addition of AgNO<sub>3</sub> into P(NIPAm-co-NMA) solution did not affect the spinning process of this copolymer. However, the average diameter decreased from 410 nm for the neat P(NIPAm-co-NMA) fiber (reported in our previous study [13]) to 385 nm for PNN/AgNO<sub>3</sub>-1 and

further to 357 nm and 338 nm for PNN/AgNO<sub>3</sub>-2 and PNN/AgNO<sub>3</sub>-3, respectively. It is evident that the number of particles decorated on the fiber surface increase with the increase of content of AgNO<sub>3</sub> in the composite fiber.



**Figure 1.** SEM images of P(NIPAm-co-NMA)/AgNO<sub>3</sub> fibers with different weight fractions of AgNO<sub>3</sub>: (a) 20%, (b) 30% and (c) 40%.

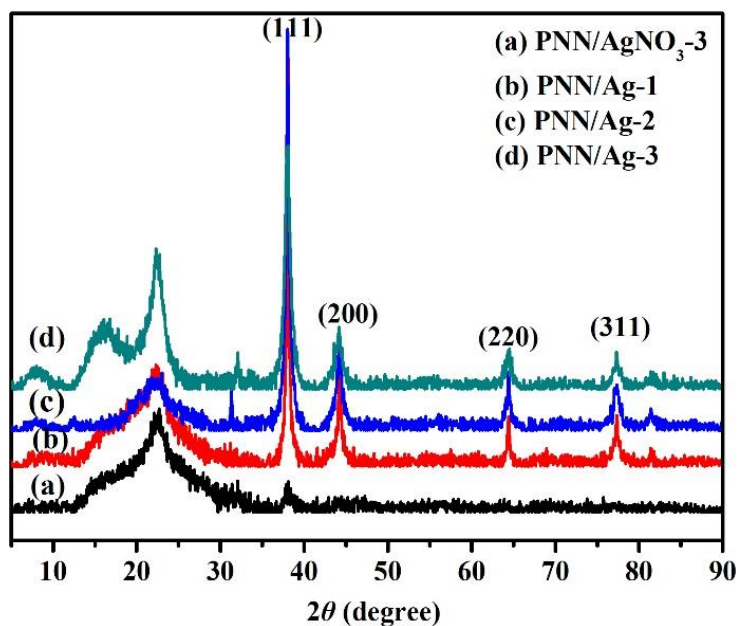
The electrospun P(NIPAm-co-NMA)/AgNO<sub>3</sub> fibers were then reduced by NaBH<sub>4</sub> to convert AgNO<sub>3</sub> into Ag and the content of Ag in the composite nanofibers was characterized using TGA. It can be seen from the curves in Fig. 2 that there is only one major mass loss at 345 °C, suggesting that there is only one type of Ag specie (which is metallic Ag) in the composite fibers. The weight fractions of Ag in the PNN/Ag-1, PNN/Ag-2 and PNN/Ag-3 fibers are 14.5%, 22.8% and 32.7%, respectively.



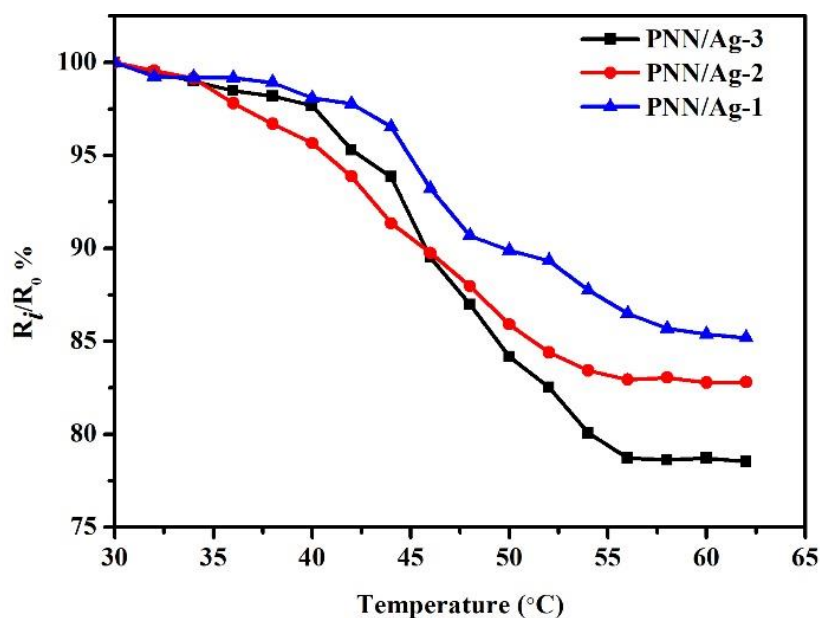
**Figure 2.** TGA curves of the neat P(NIPAM-co-NMA) and P(NIPAM-co-NMA)/Ag composite fibers.

The crystallite structure was further characterized using XRD and the diffraction patterns for the composite fibers are shown in Fig. 3. The reflections at 38.06°, 44.26°, 64.46° and 77.36° correspond to the cubic phase of (111), (200), (220) and (311) planes, respectively. This suggests the complete reduction of AgNO<sub>3</sub> into Ag. In-situ reduction of AgNO<sub>3</sub> in the PNIPAm matrix has also

been reported in previous reports [19-21]. For example, Lin et al. also demonstrated that  $\text{NaBH}_4$  is an excellent agent for in-situ reduction of  $\text{AgNO}_3$  in the PNIPAm matrix, but they did not investigate the response of the electrical resistance to the change of temperature [20].



**Figure 3.** XRD patterns of the PNN/ $\text{AgNO}_3$ -1 and P(NIPAM-co-NMA)/Ag composite fibers.



**Figure 4.** The dependence of electrical resistance on the temperature for the P(NIPAM-co-NMA)/Ag composite fibers with different contents of Ag.

The thermal-responsive behavior of the fibrous sheet was analysed by measuring the resistance at different temperatures, as shown in Fig. 4. It can be seen the electrical resistance

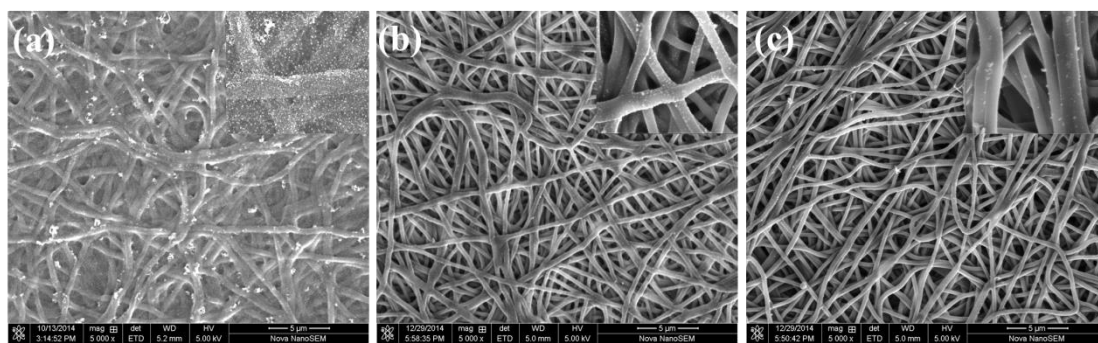
decreases with the increase of temperature for all these samples. Specifically, the resistance for PNN/Ag-1 was dropped by 15% as the temperature increases from 40 to 55 °C. It was found the decrease of resistance increases with the loading of Ag in the composite fibers. For PNN/Ag-2 and PNN/Ag-3, the resistance was decreased by 18% and 22% in the same temperature range, respectively. The decrease of resistance is due to the shrink of the PNIPAm molecule upon heating, which is particularly pronounced above the LCST and thus the responsive behavior becomes more remarkable above the LCST [22-24]. Furthermore, the PNN/Ag-3 composite fiber showed excellent cyclic performance. After repeated heating-cooling in the 30-60°C for 1000 cycles for this material, the thermal responsive performance remained almost unchanged compared to its initial performance, suggesting that the changes of volume of the nanofibers and separation between the conductive particles are reversible during the heating-cooling cycles. Both the sensitivity and stability of the change of electrical resistance are crucial for a high-performance thermal sensor. The electrical response to the change of temperature might be useful for other electrochemical applications, such as smart separators for lithium-ion batteries and supercapacitors [25, 26].

Other reducing agents such as glucose and VC were also used for in-situ reduction of AgNO<sub>3</sub> in the composite fibers (SEM images for these fibers are shown in Fig. S1 in the supporting information), as inspired by previous studies [27-30]. The TGA curves for the fibers reduced by these agents reveal that significant mass loss starts at ca. 180 °C (Fig. S2), which corresponds to the reduction of AgO into Ag. This suggests these two agents might not be able to fully convert AgNO<sub>3</sub> into Ag although no other crystalline Ag-containing compounds were detected using XRD (Fig. S3). The weight fractions of Ag in the PNN/Ag-3 reduced by glucose and VC were 24.5% and 31.6%, respectively (Fig. 4), which are both lower than that reduced by NaBH<sub>4</sub>. Furthermore, the sensitivity of resistance of these fibers to the change of temperature is lower than that reduced by NaBH<sub>4</sub>, namely the resistances were decreased by 15% and 17% as the temperature increased from 40 to 55 °C (Fig. S4), respectively, whereas the NaBH<sub>4</sub>-reduced fibers exhibited a decrease of 22% in the same temperature range as discussed above. It is thus crucial to use a strong reducing agent to convert AgNO<sub>3</sub> into highly crystalline Ag in the polymer matrix to achieve excellent thermal responsive performance.

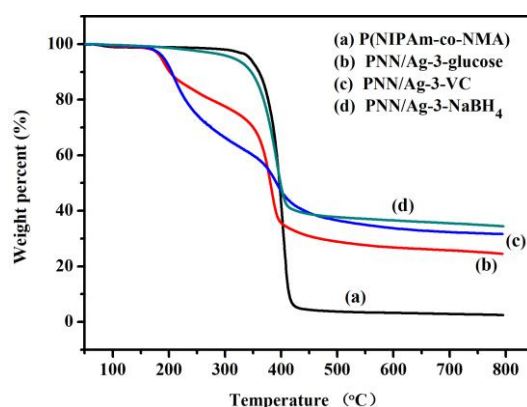
#### 4. CONCLUSIONS

P(NIPAm-co-NMA)/Ag composite nanofibers were prepared by first electrospinning of the mixed solution of P(NIPAm-co-NMA) and AgNO<sub>3</sub>, followed by in-situ reduction of AgNO<sub>3</sub> by NaBH<sub>4</sub>. The composite nanofibers exhibited high sensitivity to the change of temperature and the thermo-responsive behavior was repeatable during long-term heating-cooling cycles due to the encapsulation of Ag nanoparticles in the polymer matrix. This work might pave the way for practical application of thermo-responsive nanofibers in wearable temperature sensors.

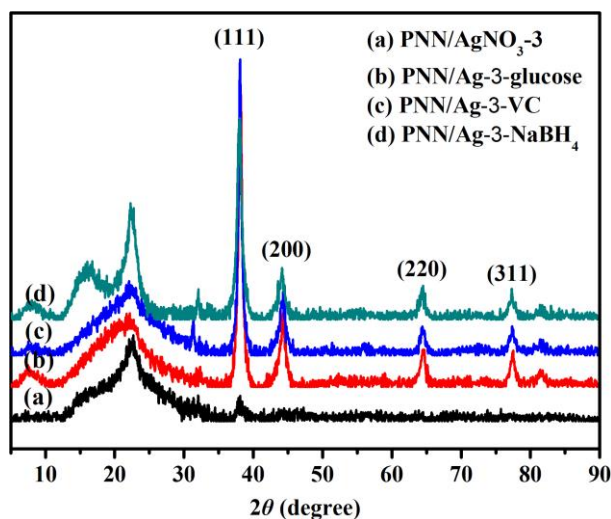
SUPPORTING INFORMATION



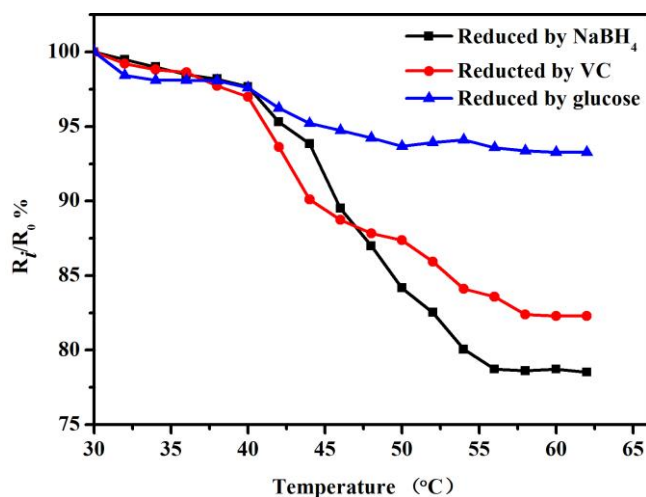
**Figure S1.** SEM images of P(NIPAm-co-NMA)/Ag composite fibers reduced with different agents: (a) NaBH<sub>4</sub>, (b) glucose and (c) vitamin C.



**Figure S2.** TGA curves for the neat P(NIPAm-co-NMA) fiber and P(NIPAm-co-NMA)/Ag composite fibers reduced with different agents.



**Figure S3.** XRD patterns for the P(NIPAm-co-NMA)/Ag composite fibers reduced with different agents.



**Figure S4.** The dependence of electrical resistance on the temperature for the PNN/Ag-3 composite fibers reduced with different agents.

#### ACKNOWLEDGEMENTS

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