

Stimuli-Responsive Polymer Nanofiber with Inorganic Nanoparticle

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Introduction

In recent years, functionalized inorganic nanoparticles and stimuli-responsive polymers have gained much more attractions not only in academic research but also in industrial application. This study aims to develop a new type of inorganic/stimuli-responsive polymer hybrid composites. The hybrid composites were composed by Poly(N-isopropylacrylamide-co-N-methylol acrylamide), Poly(NIPAAm-co-NMA) random copolymer and ZnO inorganic nanoparticles. PolyNIPAAm copolymers perform the stimuli-responsive properties and ZnO is with functional properties, such as UV-shielding, pH-buffering, anti-bacteria.

PolyNIPAAm¹ is a well-known thermal responsive polymer which contains a hydrophilic amide and a hydrophobic isopropyl group. It demonstrates lower critical solution temperature (LCST) at 32 °C in water because of hydrogen bonding interactions between the amide group and water. PolyNIPAAm is in a swollen state in water at temperature lower than LCST but shrinks in water while the temperature higher than LCST. N-methylol acrylamide (NMA)² is a post-crosslinking agent for introducing crosslinking reaction at high temperature. The crosslinking in the polymer is by interaction between original methylol groups and the amide groups produced in the displacement process. Crosslinked poly(NIPAAm-co-NMA) can keep the morphology while the polymer dipping in water. ZnO^{3,4} inorganic nano-particles were synthesized by zinc acetate precursor via in-situ process surrounding with the copolymer solution.

The electrospinning^{5,6} is an approach of assembling inorganic/ stimuli-responsive polymer hybrid composites into nanofibers. The nanofibers include the thermal responsive properties from polyNIPAAm copolymer and are also with the characteristics of ZnO nano particles.

The purpose of this study is to demonstrate a new approach of preparing thermal sensitive nanofibers with Inorganic Nanoparticles and the fiber morphology remains unchanged while dipping in water. The poly(NIPAAm-co-NMA) /ZnO nanofiber textile is suitable for future applications in biomedical devices or as biosensors.

Experimental

Materials

N-isopropylacrylamide (NIPAAm; Aldrich), N-Methylol acrylamide (NMA 48wt%; Sigma-Aldrich), ammonium persulfate (APS; Acros), sodium metabisulfite (SMBS; Showa), Zinc acetate (Acros), methanol (Aldrich), were used as received without further purification. Distilled and deionized water were used throughout this work.

Preparation of Poly(NIPAAm-co-NMA)/ZnO

The amount of NIPAAm, NMA, and deionized water was 0.045 mole, 0.005 mole, and 40ml, respectively.

APS of 6×10^{-4} mol dissolved in 2 ml deionized water and SMBS of 6×10^{-4} mol dissolved in 2 ml deionized water separately. First, NIPAAm, NMA, and deionized water were mixed in an ice bath. Second, APS was added under stirring. After well mixing, the SMBS solution was added to the overall solution slowly. SMBS and APS acted as a pair of redox initiator. Polymerization was carried out at 0-5 °C for 4 hours and at room temperature (23 °C) for 20 hours. The resulting solution was dialyzed and lyophilized by using a freeze-dryer attached to a vacuum pump until the sample weight remained unchanged.

The lyophilized poly(NIPAAm-co-NMA), 2g, were dissolved in methanol (20ml) and zinc acetate 0.4g was then added to the poly(NIPAAm-co-NMA) methanol solution with magnetic stirring. NaOH 0.16 g dissolved in 2 ml deionized water was added into the zinc acetate and copolymer solution and the temperature was kept in 50°C for 6hrs.

Electrospinning

The polymer solution used in electrospinning was prepared by dissolving Poly(NIPAAm-co-NMA)/ZnO in methanol and water mixing solution. (Methanol : Water = 95: 5). The polymer concentration was adjusted to 20 wt%. The electrospinning experiments were carried out using a standard single-nozzle process. Electrospinning was performed by applying 15 kV between the needle of syringes and a conductive collector. The working distance between the tip of needle and the collector was 10 cm. All electrospinning was performed under ambient conditions at 23°C and 45% RH.

Post-crosslinking for Poly(NIPAAm-co-NMA)/ZnO composite

The post-crosslinking steps were carried out in a furnace. The nanofiber mats were placed on a ceramic tile and kept at 110°C, 24 hours, which were for finding the optimal post-crosslinking condition.

Results and Discussion

Fig. 1(a) shows a Poly(NIPAAm-co-NMA) SEM image of the electrospun nanofibers synthesized in this study. The fiber surface was smooth and the size was uniform ~500nm. We applied the post-curing process for copolymer crosslinking. After 110 °C, 24 hours curing, the fibers were dipped in water for 48 hours and its morphology was checked by SEM, shown as Fig. 1(b), we found the fibers can still keep the fiber shape and prevent from dissolving into water. From this result, the polymer chains were crosslinked by NMA. The NMA incorporated in the polymer chain has a labile hydrogen atom which can proceed chain transfer to polymer by abstraction of the hydrogen atom of another NMA on the polymer chain. This process results in branching of the polymer chain. Scheme 1. is the illustration of the

NMA crosslinking reaction.

The in-situ synthesised ZnO size is ~50 nm, as shown in Fig. 2(a), and the ZnO nanoparticles stably suspended in polymer solution at least for 2 days. The Poly(NIPAAm-co-NMA)/ZnO nanofibers were made by electrospinning. The SEM of composites fibers showed that there were some ZnO rich nodes in the fibers, Fig. 2(b). TEM image, Fig. 2(c) further confirmed that the ZnO was distributed in the fibers and surrounded with copolymer.

X-ray diffraction pattern of the Poly(NIPAAm-co-NMA)/ZnO composite powder was illustrated in Fig. 3. All diffraction peaks in the XRD diagram showed that the crystals have the typical wurtzite structure of ZnO (JCPDS, 80-0075) and there were no peaks of Zn(OH)₂ or Zinc Acetate. The XRD result confirmed that zinc acetate precursors have been converted into ZnO completely.

LCST was determined by DSC. Due to introducing NMA into the polymer chain, the LCST of the copolymer was raised from 32 °C to 42.07 °C. The copolymer with NMA became more hydrophilic and the LCST increased. Comparing the LCST of the Poly(NIPAAm-co-NMA) and poly(NIPAAm-co-NMA)/ZnO composite, their LCST temperature were 42.07 °C and 38.45 °C, respectively. The LCST of the composite was lower than copolymer only. It may be caused by the interaction between polymer chains and ZnO nanoparticles. The composite copolymer became more hydrophobic. The ZnO was trapped in the fibers and the composite fibers still perform the thermal sensitive properties.

Conclusion

The properties of Poly(NIPAAm-co-NMA)/ZnO nanocomposite fibers were investigated. The fiber membranes can keep the morphology while dipping in water and with thermal sensitive ability. The present fibers could be useful for a wide application of sensor, optical, and antibacterial membranes.

References

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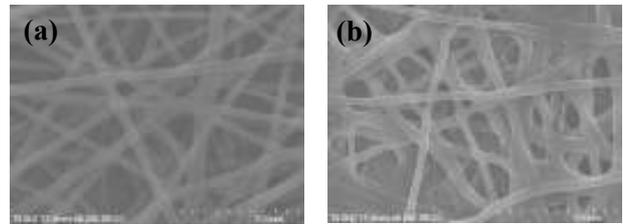
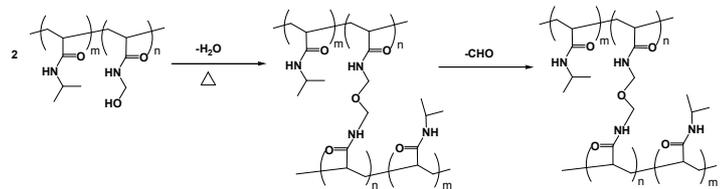


Fig. 1 The SEM pictures of (a) Poly(NIPAAm-co-NMA) electrospun nanofibers. (b) Crosslinked /Water dipping Poly(NIPAAm-co-NMA) electrospun nanofibers.



Scheme 1. Schematic illustration of the NMA crosslinking reaction

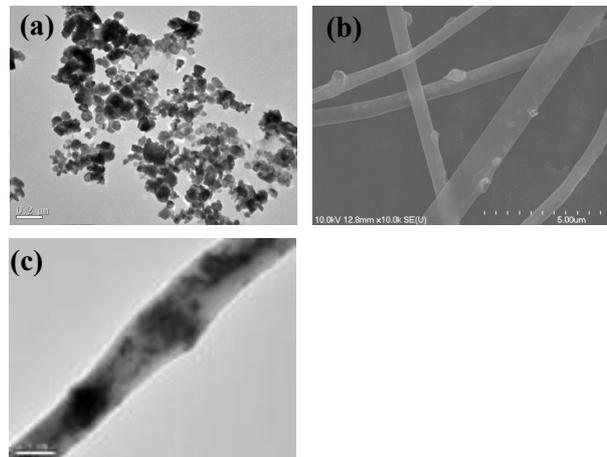


Fig. 2 (a)The TEM pictures of ZnO in-situ synthesized ; (b) SEM picture of Poly(NIPAAm-co-NMA)/ZnO Composite fibers (c) TEM of composite electrospun fiber.

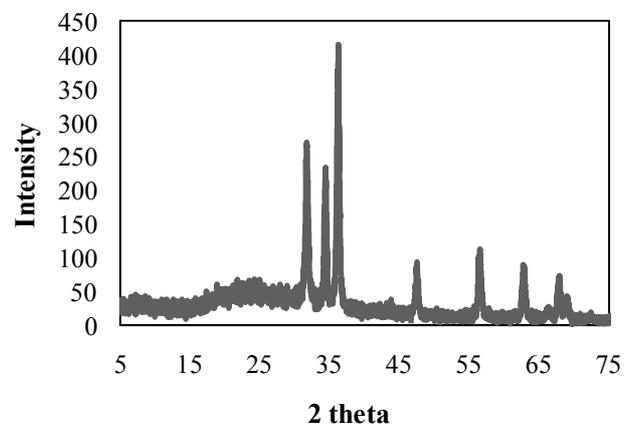


Fig. 3 XRD diagram of Poly(NIPAAm-co-NMA)/ZnO Composite.