Materials Letters 210 (2018) 337–340

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Temperature-responsive cellulose sponge with switchable pore size: Application as a water flow manipulator

Yirui Du [a], Huan Cheng [a], Yingzhan Li [a], Bijia Wang [a], Zhiping Mao [a], Hong Xu [a], Linping Zhang [a], Yi Zhong [a], Xiaolin Yan [b], Xiaofeng Sui [a,*]

[a] Key Lab of Science and Technology of Eco-textile, Ministry of Education, Donghua University, Shanghai 201620, People's Republic of China
[b] Inner Mongolia Agricultural University, Hohhot, People's Republic of China

ARTICLE INFO

Article history:
Received 13 July 2017
Received in revised form 27 August 2017
Accepted 4 September 2017
Available online 6 September 2017

Keywords:
CNF sponge
PNIPAM
ATRP
Temperature-responsive
Flow manipulation

ABSTRACT

In this study, cellulose nanofiber (CNF) sponges were successfully prepared and modified with temperature-responsive poly-(N-isopropylacrylamide) (PNIPAM) *via* surface-initiated atom transfer radical polymerization (SI-ATRP). The structure and properties of the obtained CNF-g-PNIPAM sponges were characterized with FTIR, SEM, TGA and compression tests. Water permeation experiments were carried out to investigate the temperature-sensitivity of the sponge, excellent water flow manipulation could be achieved. The CNF-g-PNIPAM sponge holds great potential in applications such as temperature-trigged microfluidic devices, water/oil separation and filtration.

1. Introduction

Porous materials are widely used and have been developed for various applications, such as separation, filtration, and load-bearing [1–3]. Cellulose-based sponge materials have been extensively explored for coupling the favorable features of having low density and high specific surface area, with the favorable properties of cellulose, including biodegradability, non-toxicity, low cost, and easy modification [4,5].

Cellulose sponges could be converted into "smart" materials upon modification with a stimuli-responsive polymer [6]. Poly(N-isopropylacrylamide) (PNIPAM) is a wildly applied temperature-responsive polymer, it undergoes a reversible and rapid coil-to-globule transition in aqueous solution at the lower critical solution temperature (LCST) of 32 °C [7,8]. Lu et al. [9] prepared a hybrid porous material by blending PNIPAM with carboxyl-modified cellulose nanofibers. Deng et al. [10] crosslinked PNIPAM inside porous cellulose nanofibers microspheres to achieve temperature-trigged drug release. The reusability and evenness of polymer layer have not been explored in these works.

The manipulation of fluids has drawn increasing attention due to its widespread application in filtration, water/oil separation, microfluidic devices [11]. Compared to physical methods, flow manipulator utilized chemical methods have many advantages, such as easy operation, low energy demanding, and requiring no additional instruments [11].

Herein, we report the preparation of a stable and reusable, temperature-responsive porous material based on PNIPAM modified CNF sponge (PNIPAM-g-CNF). Surface-initiated atom transfer radical polymerization (SI-ATRP) was utilized to ensure the formation of stable and uniform polymer layers. With switchable pore size the as prepared CNF sponge is a promising temperature-triggered water flow manipulator (see scheme 1).

2. Experimental section

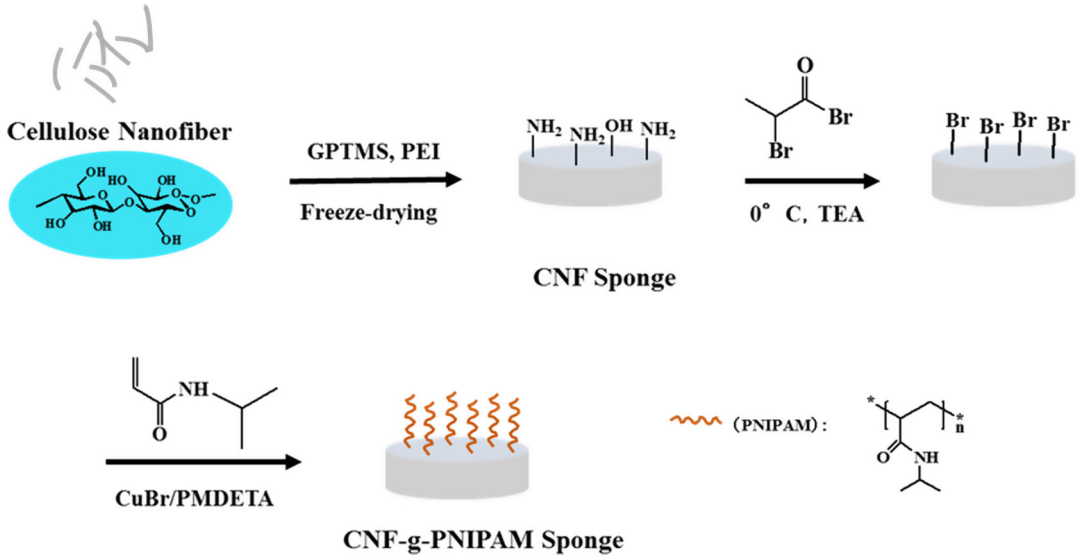
2.1. Preparation of CNF-g-PNIPAM sponge

N-isopropylacrylamide (NIPAM, Aladdin) and Copper (I) bromide (CuBr) were purified before use, while other chemicals were purchased from Aladdin and used as received.

Cellulose nanofiber (CNF) sponge was fabricated using the multi-chemical crosslinking between cellulose nanofiber, γ-glyci doxypropyltrimethoxysi (GPTMS) and branched polyethylenimine (PEI) through freezing-drying method. Noticeably, the introduction of PEI can not only further enhance the mechanical properties of the cellulose sponges but also provide the sponges with active amino groups which act as the reactive sites for the linkage of ATRP initiator.

* Corresponding author.
E-mail address: suixf@dhu.edu.cn (X. Sui).

http://dx.doi.org/10.1016/j.matlet.2017.09.012
0167-577X/



Scheme 1. Schematic preparation for the synthesis of CNF-g-PNIPAM sponge.

Cellulose sponges (0.2 g) were immersed into a solution containing 50 mL dichloromethane (CH_2Cl_2) and Triethylamine (TEA, 1.01 g, 10 mmol). 2-Bromisobutyryl bromide (BiBB, 2.30 g, 10 mmol) in 10 mL of CH_2Cl_2 was added dropwise into the mixture at 0–5 °C. The reaction was kept at room temperature for 12 h under stirring in a nitrogen atmosphere.

N-isopropylacrylamide (NIPAM, 2.4 g, 21.2 mmol) and pentamethyldiethylenetriamine (PMDETA, 21 μL, 0.1 mmol) were added into a reaction flask containing MeOH/H_2O mixed solution (1:1 v/v, 8 mL), the mixture was deoxygenated by bubbling with nitrogen. CuBr (14.3 mg, 0.1 mmol) and $CuBr_2$ (2.2 mg, 0.01 mmol) were added into another reaction flask, purged with nitrogen flow for 30 min. Subsequently, the monomer, ligand and catalyst mixture solution was transferred into a flask containing initiator-modified CNF sponges (CNF-Br), and kept at room temperature for 24 h. The resulted CNF-g-PNIPAM sponges were finally rinsed thoroughly and dried in vacuum oven.

To estimate the graft ratio, the CNF-g-PNIPAM samples were weighed before and after the modification with PNIPAM. The graft ratio (G, wt%) was calculated according to Eq. (1) [12]:

$$G = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 (g) is the dry weight of the CNF-Br sample and W_2 (g) is the dry weight of the CNF-g-PNIPAM sample.

2.2. Characterization

FT-IR was carried out on PerkinElmer Spectrum Two in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. The morphologies of the CNF-based sponges were studied by SEM (Hitachi TM-1000 scanning electron microscope, Japan). The thermal stability of samples were examined on a thermogravimetric analyzer (NETZSCH 209F1, German). The mechanical properties of sponges (diameter 19 mm, scale distance 14 mm) were evaluated through compression test (Changchunxinke universal testing machine, China).

The cellulose sponge was fixed to a filter holder connected to a water column, the flux of deionized water was measured by recording the time used for 10 mL water to be filtered through the sponge under atmospheric pressure (recording ended when water stopped dripping). The permeation of water at 25 and 40 °C were repeated for 6 cycles. The water flux F (mL cm^{-2} s^{-1}) was calculated by Eq. (2) [13]:

$$F = \frac{V}{\pi r^2 \times T} \quad (2)$$

where V (mL) is the volume of deionized water. T (s) is the time for water to pass through the sponge and r (cm) is the diameter of the CNF-g-PNIPAM sample.

3. Results and discussion

The FT-IR spectra of CNF, CNF-Br, CNF-g-PNIPAM and PNIPAM are shown in Fig. 1a. The absorption peak centered at 1740 cm^{-1} in the CNF-Br spectrum can be attributed to the C=O from the ATRP initiator (2-bromisobutyryl bromide). The modification of PNIPAM brushes on the surface of CNF sponge was evidenced by the appearance of peaks at 1641 cm^{-1} and 1544 cm^{-1} in CNF-g-PNIPAM, corresponding to amide I and amide II stretch vibrations in PNIPAM respectively [7].

Thermal stability of the CNF, CNF-g-PNIPAM and PNIPAM were studied using TGA (Fig. 1b). Two decomposition rates are observed in CNF-g-PNIPAM from the DTG curves, one is 267 °C which is due to the thermal decomposition of CNF and another is about 400 °C close to the decomposition temperature of PNIPAM, confirming that the PNIPAM brushes were successfully grafted from CNF sponge. While the shift in DTG peaks for CNF and CNF-g-PNIPAM suggested change in the crystalline structure of the sponge upon PNIAM modification [14], which could lead to changes in porosity and specific area as well. The SEM images shown in Fig. 1(c–f) were in agreement with this argument. The results also showed that the CNF-g-PNIPAM sponge was stable at temperatures up to 100 °C, which means it could easily endure the temperature fluctuations from 25 °C to 40 °C applied in the following flow manipulation experiments.

The SEM images of pristine CNF sponges displayed a random porous structure (Fig. 1c). After the surface modification of PNIPAM *via* ATRP, the surface of cellulose sheets became rougher and fully covered with a thick PNIPAM layer (Fig. 1f), indicating successful modification of CNF sponges with PNIPAM [7,12]. The graft ratio is about 11.3% according to Eq. (1).

Mechanical properties are crucial for further applications of matrixes. As demonstrated in Fig. 2, the CNF sponge has a compres-