Carbohydrate Polymers 110 (2014) 47–52

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Cellulose nanofibril based graft conjugated polymer films act as a chemosensor for nitroaromatic

Qingyuan Niu, Kezheng Gao, Wenhui Wu*

School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 25 January 2014
Accepted 2 March 2014
Available online 27 March 2014

Keywords:
Cellulose nanofibril
Conjugated polymer
Chemical assembly
Fluorescent sensor
Nitroaromatic

ABSTRACT

A cellulose nanofibril film is modified by chemical assembly of boronate-terminated conjugated polymer chains at its specific sites, C-6 carboxyl groups. The modified cellulose nanofibril film is used as a fluorescent sensor for nitroaromatic vapor. Thanks to the specific reactive sites, numerous loose cavities or pathways located in the film sensor's out-layer have been formed, and the fraction of easily accessible cavities of the novel fluorescent film sensor is up to 0.97, which could benefit the penetration and diffusion of analyte vapor. Therefore, the novel fluorescent film sensor exhibits high sensitivity toward nitroaromatic vapor with a fast response. The fluorescence quenching efficiency of the chemical-assembly film sensor is about 3 times larger than that of the spin-cast film sensor using the same conjugated polymer for 600 s exposure to DNT vapor. In addition, the novel fluorescent film sensor shows good reversibility.

1. Introduction

The fast and sensitive detection of explosives is of crucial significance for security checking of the explosives in airport or other public sites, land-mine detection, and so on (Che et al., 2012; Lan et al., 2009; Tao, Li, & Zhu, 2006; Wang, La, Ding, Liu, & Lei, 2012; Yang, Turnbull, & Samuel, 2010; Zhang, Lu, Gao, Ding, & Fang, 2007; Zhu et al., 2011). Currently, conjugated polymers (CPs) have been explored as optoelectronic sensor for the detection of trace nitroaromatic-based explosives, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), because the CPs backbones could display the fluorescent amplification or superquenching effects toward analytes (Thomas, Joly, & Swager, 2007). Therefore, numerous investigations have emphasized on the design and synthesis of CPs with various structures to detect nitroaromatic vapor (Basabe-Desmonts, Reinhoudt, & Crego-Calama, 2007; Feng, Li, & Yang, 2010; He, Zhang, Lue, & Fang, 2009; Long et al., 2009; Narayanan, Varnavski, Swager, & Goodson, 2008). In pioneering work developed by Swager's group, the pentiptycene-based fluorescent polymer film was an example of a highly sensitive vapor phase sensor (Yang & Swager, 1998). The incorporation of bulky and rigid three-dimensional pentiptycene moieties could prevent aggregation and self-quenching, and create the "molecular pore" in spin-cast film to benefit the penetration of the explosive vapor. Nevertheless, the sensing performance of most spin-cast sensors is heavily relied on the film thickness (Wang et al., 2012). To achieve a measurable intensity of the fluorescence signal, a sufficiently thick film is usually required, while the presence of an internal layer of a conjugated polymer film unpenetrated and unquenched by the explosive vapors would decrease the quenching efficiency. Moreover, the preparation of CPs-based spin-cast sensors with various structures needs sophisticated chemical modification or polymer backbone/side-chain functionalization.

2,2,6,6-tetramehylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibril films, CNF films, were a wise choice as ideal substrates of the chemosensors for potential application. The CNF film was prepared by selectively introducing reactive carboxyl groups on the C-6 of the cellobiose repeat unit (Fukuzumi, Saito, Wata, Kumamoto, & Isogai, 2009; Isogai, Saito, & Fukuzumi, 2011). Thus, it is easy to functionalize the CNF film, because the carboxyl groups could be reacted with amine groups in mild condition used 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) together with N-hydroxysuccinimide (NHS) as effective amidation catalyst (Follain, Marais, Montanari, & Vignon, 2010; Miao et al., 2011). The spacing of C-6 carboxyl groups on cellobiose repeat units of the cellulose chains is approximately 1.04 nm (Holt, Stoyanov, Pelan, & Paunov, 2010). In addition, the CNF film has some superior performance, such as flexibility, good portability, environmentally friendly nature, and so on (Hirota, Furihata, Saito, Kawada, & Isogai, 2010; Saito, Kimura, Nishiyama, & Isogai, 2007). Also, the raw material of CNF film, cellulose, is the most abundant organic material on

---

* Corresponding author. Tel.: +86 010 68912659; fax: +86 010 68912659.
E-mail addresses: niuqingyuan1984@126.com (Q. Niu), wuwh@bit.edu.cn (W. Wu).

http://dx.doi.org/10.1016/j.carbpol.2014.03.042

the planet in the world (Peterson, Willgert, Hansson, Malmstrom, & Carter, 2011).

To explore a simple strategy of design and fabricating ultrasensitive vapor-phase explosives, herein we report a novel fluorescent film was prepared by chemical assembly of boronate-terminated CPs at the C-6 carboxyl groups of CNF film surface. It is expected that in this strategy, due to the near 1.04 nm spacing of the C-6 carboxyl groups on cellobiose repeat unit as reactive grafting-to sites, numerous easily accessible cavities or loose pathways could be generated by grafted CP chains located in the chemical-assembly film sensor's surface, which could benefit the nitroaromatic vapor penetration into sensory out-layer of the film. As a result, with relatively simple chemical modification, the cellulose nanofibril based fluorescence film would therefore be proposed to be an excellent candidate for detecting nitroaromatic vapor.

2. Experimental

2.1. Materials

4-Bromobenzyl bromide, EDC, NHS, 2-(N-Morpholino) ethanesulfonic acid (MES), 9,10-diphenylanthracene, 4-bromoaniline and 2,2,6,6-tetramehylpiperidine-1-oxyl (TEMPO) were obtained from Aladdin-Reagent Co., Ltd. 3,6-Dibromocarbazole, tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$) and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) were purchased from SynSwitch. Other reagents and solvents obtained from commercial suppliers were used without further purification.

2.2. Instrumentation

Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Bruker TENSOR 27. Polymer powder was pressed into discs with KBr and then FTIR spectrum was measured. The FTIR spectra of film samples were measured directly. Gel permeation chromatography (GPC) was carried out on a Waters GPC515-2410 System with THF as an eluant. ^1H NMR spectrum of the solution containing 15 mg polymer powder and 5 mL $CDCL_3$ was recorded with a Bruker Avance III 600 NMR spectrometer (600 MHz). Water contact angles of the films were measured using a JC2000C1 contact-angle instrument at ambient temperature with a drop size of 0.5 μL. Contact angles were taken 1 min after droplet deposition on the surface, and averaged over three drops in various locations. UV–vis absorption and photoluminescence (PL) spectra of samples were recorded using a Shimadzu UV-1700 Ultraviolet Spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer, respectively.

2.3. Synthesis of boronate-terminated conjugated polymer chains (PFC)

The mixture containing 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (502 mg, 1 mmol), 3,6-dibromocarbazole (325 mg, 1 mmol), THF (15 mL) and K_2CO_3 aqueous solution (2 M, 10 mL) were stirred and degassed with N_2 for 30 min. Then $Pd(PPh_3)_4$ (24 mg, 2.0 mol%) was added under N_2. After refluxing (about 69 °C) for 48 h, the end groups were capped by heating the mixture under reflux with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (200 mg, 0.4 mmol) for another 6 h. The mixture was cooled and poured into methanol. The precipitates were collected by filtration, and washed with abundant methanol and water, respectively, for several times. After removal of organic solvents and water, the solid was extracted with acetone for 48 h using Soxhlet apparatus. Finally, the PFC ($\bar{M}_n$: 6760, PDI: 1.49) was obtained after being dried at 40 °C under vacuum for 3 days.

2.4. Preparation of Br-containing reactive sites in CNF film surface (Br@CNF film)

The CNF films (20 mm × 20 mm, 64 mg) were immersed into MES buffer (20 mL, pH = 5.0). EDC (226 mg) and NHS (38 mg) were added and the mixture was slowly stirred for 30 min at 4 °C. Then 4-bromoaniline (177 mg) dissolved in DMF (5 mL) was added, and the mixture was stirred at room temperature. After 24 h, the Br-modified CNF films were taken out and washed twice with sequence of DMF, water and methanol. At last, the samples were used soxhlet extraction with THF for 24 h and dried in a vacuum oven.

2.5. Synthesis of PFC@CNF films

After the PFCs (800 mg) were dissolved in THF (30 mL), K_2CO_3 aqueous solution (2 M, 20 mL), the Br@CNF films (20 mm × 20 mm, 300 mg) were added. After degassing with N_2 for 30 min, $Pd(PPh_3)_4$ (24 mg) was added quickly. The reaction was then refluxed at 69 °C for 12 h. After cooling to room temperature, the PFC@CNF films were taken out and rinsed two times with sequence of THF, DCM, methanol, and water. To exclude simple entangling/physisorption of the PFC chains within the nanofiber cellulose network, the samples were used soxhlet extraction with THF for 24 h and dried in vacuo.

2.6. Preparation of PFC-modified filter paper (PFC@CELL paper)

Filter paper (20 mm × 20 mm, 0.510 g) and DMF (25 mL) were added in a 100-mL flask. The mixture was stirred and degassed with N_2 for 30 min. Then NaH (1.14 g) was added to this mixture. After 30 min, the solution of 4-bromobenzyl bromide (2.12 g) and DMF (5 mL) was added, and stirred for another 24 h. After reaction, the mixture was put into water (500 mL), Then the Br-modified filter papers were rinsed twice each with solvent following sequence of DMF, water and methanol. The Br-modified filter paper was used soxhlet extraction with methanol and dried in vacuo.

The mixture containing PFC (800 mg), THF (30 mL), K_2CO_3 aqueous solution (2 M, 20 mL), and the Br-modified filter papers (20 mm × 20 mm, 400 mg) was stirred and degassed with N_2 for 30 min. Then $Pd(PPh_3)_4$ (24 mg) was added quickly. The reaction was then performed at 69 °C for 12 h. After cooling to room temperature, the samples were rinsed two times each with THF, DCM, methanol, water and THF. The samples were then Soxhlet extracted using THF and dried under vacuum at 30 °C.

2.7. Synthesis of PFC(SC) films

The PFC solution (0.45 mg in 1 mL THF) was spin-casted onto a quartz substrate (microscope slide, length: 24 mm, width: 24 mm and thickness: 1 mm) at a spin rate of 1000 rpm. Then, the PFC(SC) films were dried at 30 °C under vacuum for 1 day.

3. Results and discussion

3.1. Synthesis and characterization

To graft conjugated polymer chains covalently onto the CNF film surface, we followed the reaction route illustrated in Scheme 1. First, 4-bromoaniline was reacted with the C-6 carboxyl groups of the CNF film surfaces through pre-activation by EDC/NHS to form Br-containing reactive sites (Br@CNF film). Next, the additional diboronate-terminated monomers were added to prepare boronate-terminated conjugated polymer. Finally, the PFCs were bonded onto the Br@CNF film surfaces via “grafting to” technique,