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Carbon nanotube-modified oxidized regenerated cellulose gauzes for hemostatic applications

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ABSTRACT

Functionalized carbon nanotubes have recently received interest because of their unique properties, especially in the biomedical field. In this research, unmodified multiwalled carbon nanotubes (MWCNTs), and functionalized carbon nanotubes with amino groups (MWCNTs-NH_2) and carboxyl groups (MWCNTs-COOH) were grafted to oxidized regenerated cellulose (ORC) gauze to fabricate novel functionalized ORC, and the performance of the functionalized gauze was investigated. The functionalized ORC was characterized by FT-IR, XPS and SEM, which showed the different kinds of CNTs grafted on its surface. The XPS results demonstrated the successful incorporation of functionalized MWCNTs in the active layer of modified ORC gauze. Meanwhile, the specific surface area of the CNTs modified functionalized ORC gauze was improved in varying degrees, whereas the porosity was slightly decreased. Furthermore, hydrophilicity experiment results presented a significant increment in water uptake of the functionalized CNTs grafted to the surface of the ORC gauze. Results of the hemostatic performance test on rabbit ear artery and liver showed that compared with the original ORC gauze, the bleeding time was significantly reduced when using the functionalized CNTs modified ORC hemostatic gauze. Moreover, the results also showed that the MWCNTs-COOH/ORC functionalized gauze had outstanding hemostatic efficiency.

1. Introduction

Oxidized cellulose (OC) and oxidized regenerated cellulose (ORC) have similar chemical structure and molecular composition; however, the primary hydroxyl cellulose groups in OC have been transformed into carboxyl groups in ORC (Kumar, 2000). ORC materials have 16–24% carboxyl content and thus are widely used as hemostatic in almost all types of surgery to stop the bleeding (Breech, 2000; Chung et al., 2004; Hernández-Cortés et al., 2010; Saito, Okita, Nge, Sugiyama, & Isogai, 2006). However, commercial ORC has shown several inherent shortcomings that limits its application. For instance, in vivo implanted ORC has relatively poor hemostatic property and biodegradability and acidic, which can harm the human body (No, Park, Lee, & Meyers, 2002).Many efforts have been made to improve the performance of hemostasis and to overcome other disadvantages (Cullen, Silcock, & Boyle, 2010).

Carbon nanotubes (CNTs), such as multiwalled CNTs(MWCNTs), have recently shown great advantages as drug carriers and in diagnoses, treatment, tissue engineering, and biomedical applications because of their excellent physical and chemical properties, such as light weight, high specific surface area, excellent electric conductivity, stable performance, and high mechanical strength (Bussy, Methven, & Kostarelos, 2013; Lu et al., 2009; Sung, Kim, Jin, Choi, & Chin, 2004; Wu et al., 2014; Yazdi et al., 2016), the poor solubility of pristine CNTs may cause aggregation and interactions within the cells, which lead to apoptosis or inflammation. However, surface functionalization of CNTs can significantly overcome these shortages by making nanotubes more hydrophilic and water soluble, more biocompatible, and less cytotoxicity (Bianco, Kostarelos, & Prato, 2011; Lacerda et al., 2011). Two different methods, namely covalent and non-covalent functionalization are used to improve the solubility or dispersion of MWCNTs in solvents (Lu et al., 2009; Zhang, Bai, & Yan, 2010). Compared with the original unmodified CNTs, the animated CNTs (CNTs-NH_2) and carboxyl CNTs (CNTs-COOH) have improved cell penetration, procoagulant effects, and biocompatibility (Burke et al., 2011; Lin et al., 2011).

In this work, the prepared functionalized ORC gauzes were

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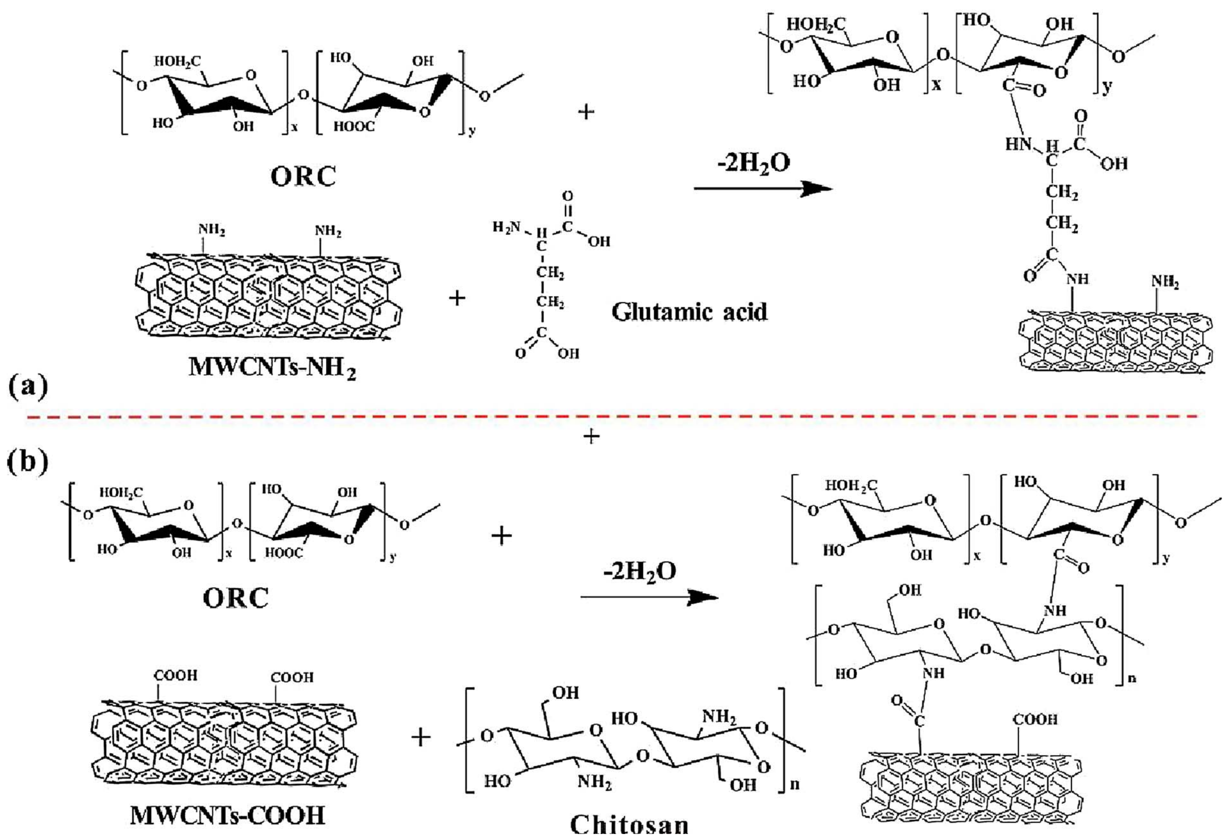

Fig. 1. Scheme of reactions: preparation of functionalized MWCNTs-NH_2/ORC (a), MWCNTs-COOH/ORC (b), respectively.

strengthened with CNTs. MWCNTs were used simply because of their cost advantage compared with to single-walled CNTs (SWCNTs) (Zhang et al., 2007). We mainly divided our research into four parts: (1) the ORC gauze was prepared with nitrogen dioxide/carbon tetrachloride (NO_2/CCl_4). (2) Original unmodified MWCNTs-coated ORC gauze was prepared by subsequent treatment of ORC gauze with a solution of original unmodified MWCNTs in chitosan/acetic acid solution. (3) Aminated CNTs-modified ORC gauze was prepared by subsequent treatment of ORC gauze with a solution of aminated CNTs in glutamic acid/acetic acid solution. (4) Carboxylated CNTs-grafted ORC gauze was prepared by subsequent treatment of ORC gauze with a solution of carboxyl CNTs in chitosan/acetic acid solution. Dicyclohexylcarbodiimide (DCC) can improve the efficiency of chitosan, ORC and carboxylated CNTs reactions between carboxyl and amine groups. Through surface structure observation, and analysis of chemical and physical properties, biological safety and effectiveness, the novel functionalized CNTs/ORC hemostatic materials can achieve more effective hemostasis and promote wound healing.

2. Materials and methods

2.1. Materials

Viscose filament yarn made of regenerated cellulose, which was firstly oxidized by NO_2/CCl_4, used as the starting material, was obtained from Xinxiang city, Henan province, China. The Carbon nanotubes used in this study were prepared from Beijing Dao King, Ltd., China, including multiwalled carbon nanotubes (MWCNTs), aminated CNTs (MWCNTs-NH_2) and carboxylic CNTs (MWCNTs-COOH). The CNTs were multiwalled carbon nanotubes, with the diameter of 10–20 nm, length of 10–30 mm and special surface area higher than 200 m^2/g. Chitosan with deacetylation degree (DD) > 90% and low molecular weights (Mw) (Mw: 2000), were purchased from Zhejiang Golden-Shell Biochemical Co., Ltd., China. Glutamic acid was supplied by Yi Jiang Chemical Co., Ltd, Shanghai, China. Dicyclohexylcarbodiimide (DCC) was purchased from Aladdin Industrial Corporation. All the reagents were of analytical grade and used without further purification. The male New Zealand white rabbits were supplied by the Second Affiliated Hospital of Harbin Medical University (Harbin, Heilongjiang Province, China). The protocol was approved by the Ethics Committee of the First Affiliated Hospital of Harbin Medical University. All animals were handled in accordance with the Chinese National Institutes of Health Guidelines for the Care and Use of Laboratory Animals.

2.2. Preparation of ORC gauze

Prior to oxidation, the viscose filaments were knitted on a needle knitting machine to obtain regenerated cellulose gauze. In brief, using 20 wt % NO_2 in CCl_4 as oxidant, added the regenerated cellulose gauze into the flask, while the proportion of the gauze to the solution volume was 1:42.6 (g/mL). The reaction system was kept at 19.5 °C and stirred constantly. The regenerated cellulose gauze was oxidized for 40 h. Then, the oxidized gauze was washed thrice with 50% (v/v) ethanol aqueous solution, followed by washing the gauze five times with ethanol. Finally, oxidized gauze was frozen-dried at −50 °C in vacuum for 72 h (He, Wang, Wu, Huang, & Zhang, 2011).

2.3. Preparation of carbon nanotube-coated oxidized regenerated cellulose

CNTs suspension was prepared as follows: various amounts of CNTs (MWCNTs, MWCNTs-NH_2 and MWCNTs-COOH) were placed in 50 mL