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# Dicarboxylic cellulose decorated with silver nanoparticles as sustainable antibacterial nanocomposite material

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ABSTRACT

Innovative antimicrobial materials are urgently needed to overcome the occurrence antibiotic-resistant bacteria infections. The current research article shows the preparation and characterization of a benign dicarboxylic cellulose/silver nanocomposite with an effective antimicrobial properties. A uniform silver nanoparticles decorated 2, 3 dicarboxylic cellulose having approximately 15 nm size were reported. Dicarboxylic cellulose/silver nanocomposite displayed excellent antibacterial activity against gram positive and gram negative bacteria. According to these results, it is anticipated that cellulose/silver nanocomposites can find interesting applications such as clinical wound healing, biofilms and the coating of biomedical materials.

## 1. Introduction

The frequent use of antibiotics produces a new generation of antibiotic-resistant microorganisms which poses a critical threat to global public health (Shao et al., 2015). Developing new materials with biocompatibility and strong antimicrobial capability are needed especially for food packaging and wound dressing. Inorganics and metal nanoparticles such as zinc oxides (Ul-Islam et al., 2014), titanium oxides (Besinis et al., 2014) and silver nanoparticles (Pinto et al., 2009) have recently emerged as effective and safe antimicrobial reagents. Silver nanoparticles have attracted great attention as effective biocides against wide range of microorganisms and can reduce many bacterial infections with long duration (Shao et al., 2015). Due to its low cytotoxicity, silver has been applied in dental, implants and wound healing materials (Sambhy et al., 2006). However, the aggregation process accompanied with silver nanoparticles formation can minimize their surface area and reduces their antimicrobial efficiency (Liu et al., 2015). Many attempts have been carried out to overcome the restrictions of silver nanoparticles by supporting with polymers (Cheng et al., 2013), graphene oxide (Shao et al., 2015), protein and peptide(Poblete et al., 2016). Most of these materials have drawbacks such as high cost, low biocompatibility and low targeting capacity toward bacteria. A facile strategy to prepare biocompatible and biodegradable silver nanocomposite is required.

Recently, several attempts have been carried out for preparing silver nanoparticles based nanocomposites as efficient and cost effective antibacterial surfaces. For example, Wei Shao et al. prepared silver nanoparticles decorated graphene oxide as antibacterial nanocomposite. The authors used glucose and starch to reduce and stabilize silver ions on the surface of graphene oxide nanosheets. The results showed that a uniform and compactly deposited silver nanoparticles with approximately 22 nm were formed. Moreover, graphene oxide silver nanocomposite displayed low cytotoxicity and effective antibacterial activity (Shao et al., 2015). A stable colloidal solutions composed of aminocellulose stabilized silver nanoparticles were prepared. Aminocellulose was reported as a reducing and capping reagent and the prepared nanoparticles were deposited on the cellulose acetate surfaces for preparing permeable and antibacterial membranes (Cheng et al., 2013). The development of new methodologies for the synthesis of novel biocomposites on the basis of using renewable and sustainable materials such as polysaccharides is a unique opportunity to increase the sustainability of materials chemistry. Functionalized polysaccharides have been studied as growth modifiers for inorganic mineralization such as calcium phosphates (Salama, 2015; Salama and El-Sakhawy, 2014). These studies presented new observations and concepts which advance a better understanding and design of distinct and homogenous polysaccharides/inorganic hybrid materials as a candidate for bone tissue engineering.

Cellulose, an inexhaustible raw material with fascinating structure and properties, (Klemm et al., 2005; Salama, 2016) can be used as environmentally friendly and biocompatible product. However, low functionality and low solubility of cellulose hampers its applications in the area of biomaterials (Salama et al., 2014). Several trials have been carried out to increase the functionality as well as the applicability of cellulose. Among others, oxidized cellulose has spurred significant interest as it contains large number of functionalized groups. These

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functional groups permit the cellulose to act as support for other functionalized organic moieties (Monier et al., 2016), amino acids (Kumari and Chauhan, 2014) and organic macromolecules. Moreover, these functional groups such as hydroxyl and carboxyl groups support the hybridization of cellulose with other inorganic or metal oxides. Recently, much attention has been paid to cellulose-based materials decorated with metal or metal oxide nanoparticles due to their potential applications in optical, electronic and catalytic fields. Among these, preparing of antibacterial cellulose-based nanocomposite might have a promising strategy for future applications of cellulose fibers where antibacterial properties are crucial.

The current study aims to use a facile, sustainable and cost-effective strategy for preparing cellulose/silver nanocomposite. Dicarboxylic cellulose was prepared and investigated as a supporting polymer and stabilizer during the reduction of silver ions to silver nanoparticles. In addition, antibacterial properties of dicarboxylic cellulose/silver nanocomposite was investigated. The prepared nanocomposite exhibited excellent antibacterial activity which suggests this nanocomposite as a promising material for wound dressing applications.

## 2. Experimental section

### 2.1. Materials

Microcrystalline cellulose (extra pure, average particle size 90 μm Acros). Silver nitrate was purchased from Alpha chemika and sodium borohydride was purchased from Fisher Scientific UK. All reagents were of analytical grade and used as received without further purifying.

### 2.2. Preparation of dicarboxylic cellulose

Oxidation of cellulose was performed by oxidizing the vicinal hydroxyl groups at the positions $C_2$ and $C_3$ with $NaIO_4$. 1 g of cellulose suspended in 100 mL deionized water was stirred with 0.9 gm of $NaIO_4$ and the flask was covered by several aluminum foils. The mixture was stirred by a magnetic stirrer at 55 °C controlled by water bath. After 5 h, the residual $NaIO_4$ was decomposed by the addition of excess ethylene glycol, and the aluminum foil was removed. Oxidized cellulose was subsequently washed and further reacted with sodium chlorite in 1 M acetic acid solution for 24 h at room temperature. The oxidized product was centrifuged and washed with deionized water until the conductivity of the filtrate was < 10 μS/cm. The aldehyde content of the periodate oxidized cellulose was determined using an oxime reaction and the carboxyl content after the chlorite oxidation was analyzed by conductometric titration as reported in literature (Liimatainen et al., 2012).

### 2.3. Preparation of silver decorated dicarboxylic acid cellulose nanocomposite

Silver nanoparticles decorated dicarboxylic cellulose nanocomposite was prepared by stirring homogeneous suspension of dicarboxylic cellulose (2 mg/mL) with 19.8 mL of deionized water. After treating by ultrasonication for 5 min, the desired amount of $AgNO_3$ were added into 10 mL of diluted dicarboxylic cellulose suspensions and heated to 80 °C to achieve a concentration of 2 mM. Sodium borohydride solution is then added dropwise into the silver nitrate solution and allowed to react at room temperature for 15 min to give a yellow colloidal solution. The color of the reaction mixture turns from dark brown to gray and finally dark green. The synthesized dicarboxylic cellulose/silver nanocomposite was centrifuged at 10000 rpm for 10 min, washed three times using deionized water and freeze-dried.

### 2.4. Antibacterial test

The antibacterial activities of the dicarboxylic cellulose/silver nanocomposite was evaluated using agar disk diffusion method (Ul-Islam et al., 2014). The examined materials were placed on the seeded agar plate. After 48 h of incubation at 37 °C, the diameters of the inhibition zones were measured.

### 2.5. Characterization

Fourier transform infrared spectroscopy (FT-IR) was done on a FTIR (Mattson 5000 FTIR spectrometer) using KBr discs in the range of 4000–500 $cm^{-1}$. The UV–visible absorption spectra were recorded JASCO V-650 spectrophotometer in the range of 200–700 nm. Scanning electron microscopy was done on Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K. Transmission electron microscope (TEM) images were taken with a JEOL JEM-2100 electron microscopy at 100k × magnification, with an acceleration voltage of 120 kV. The surface charge of dicarboxylic cellulose was measured through ζ-potential analysis of the samples on a Malvern Zetasizer.

## 3. Results and discussion

### 3.1. Periodate and chlorite oxidation of cellulose

Neat cellulose was subjected to periodate oxidation to generate (−CHO) functional groups which further oxidized to generate dicarboxylic cellulose. The aldehyde and carboxyl contents of the cellulose after sequential periodate-chlorite oxidation were calculated. The aldehyde content is 1.59 *m*mol/g and the carboxyl content is nearly the same. This result indicated that all the aldehyde groups were converted to carboxyl groups after oxidation. Moreover, the distribution of the negative charges throughout the surface of the dicarboxylic cellulose was confirmed with ζ-potential as showed in Fig. 1F. The decoration of silver nanoparticles on the surface of dicarboxylic cellulose was performed through the reduction of the silver ions ($Ag^+$). Dicarboxylic cellulose was treated with silver nitrate solution to enhance the binding of positively charged $Ag^+$ ions on the surface of negatively charged dicarboxylic cellulose (−30.4 mV, ζ-potential value). The initial incubation of $Ag^+$ ions with dicarboxylic cellulose caused rapid binding of positively charged $Ag^+$ with the negative charges on the dicarboxylic cellulose. This binding between silver ions and carboxyl groups of dicarboxylic cellulose plays a crucial role for avoiding microparticles. The surface bound $Ag^+$ ions were reduced to silver nanoparticles via reduction with sodium borohydride to form dicarboxylic cellulose/silver nanocomposite through the oxidized cellulose fibers.

### 3.2. TEM analysis

Transmission electron microscopy (TEM) was used to analyze the morphological aspects of dicarboxylic cellulose/silver nanocomposite. Fig. 1A reveals silver nanoparticles formation through an almost-transparent dicarboxylic cellulose nanofibers. The silver nanoparticles represented by dark spots are shown in Fig. 1A and B. TEM image showed that silver nanopartcles (black dots) are spherical and uniformly dispersed on dicarboxylic cellulose fibers. The inset image in Fig. 1C is the dicarboxylic cellulose/silver nanocomposite with lower magnification. The size distribution of deposited silver nanoparticles is relatively narrow and with a mean diameter of about 15 nm (Fig. 1E). These results suggest that dicarboxylic cellulose fibers play an important role in the process of nucleation and stabilization the formed silver nanoparticles and helped efficiently in preventing their agglomeration. The crystallinity of silver nanoparticles was further evaluated by high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). HRTEM image (Fig. 1C) shows that silver nanoparticles were embedded on the surface of dicarboxylic cellulose fibers and displayed multitwinned structure. In addition, the measured fringe lattice of silver nanoparticles is 0.236 nm which attributes to the (111) plane. The