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Short communication

Simultaneous microwave-assisted synthesis, characterization, thermal stability, and antimicrobial activity of cellulose/AgCl nanocomposites

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ABSTRACT

By means of a simultaneous microwave-assisted method and a simple chemical reaction, cellulose/AgCl nanocomposites have been successfully synthesized using cellulose solution and $AgNO_3$ in *N*,*N*-dimethylacetamide (DMAc) solvent. The cellulose solution was firstly prepared by the dissolution of the microcrystalline cellulose and lithium chloride (LiCl) in DMAc. DMAc acts as both a solvent and a microwave absorber. LiCl was used as the reactant to fabricate AgCl crystals. The effects of the heating time and heating temperature on the products were studied. This method is based on the simultaneous formation of AgCl nanoparticles and precipitation of the cellulose, leading to a homogeneous distribution of AgCl nanoparticles in the cellulose matrix. The experimental results confirmed the formation of cellulose/AgCl nanocomposites with high-purity, good thermal stability and antimicrobial activity. This rapid, green and environmentally friendly microwave-assisted method opens a new window to the high value-added applications of biomass.

1. Introduction

Recently, cellulose-based nanocomposites have been receiving great attention in diverse areas [1–5]. Nanocomposites have the synergetic effect from biopolymers and inorganic materials, and provide the possibility for the enhancement of multifunctional properties. Nanocomposites of Au and bacteria cellulose nanofibers with adjustable shell thickness were prepared via a one-step bio-templated method in aqueous suspension using poly(ethyleneimine) as a reducing and linking agent [6]. Magnetic bacterial cellulose/Ag nanocomposite with high antimicrobial activity was synthesized using polydopamine as a reducing agent and stabilizer [7].

As a photosensitive material, silver chloride (AgCl) was extensively used in photometry, plating, electrochemical and biomedical fields [8–10]. Until now, many efforts have been placed on the synthesis of the AgCl-based nanocomposites [11–16]. However, there have been only few reports on the synthesis of cellulose/AgCl nanocomposites [17,18]. For example, Wang et al. [17] reported in situ synthesis of AgCl nanoparticles into bacterial cellulose membranes by

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alternately dipping of bacterial cellulose membranes in the solutions of silver nitrate and sodium chloride under ambient conditions. The AgCl with antimicrobial activity embedded in a silica matrix on cotton fabric was prepared with commercial AgCl and a reactive organic-inorganic binder [18].

Herein, we report a microwave-assisted method for the synthesis of cellulose/AgCl nanocomposites using cellulose solution and $AgNO_3$ in *N*,*N*-dimethylacetamide (DMAc) solvent. The cellulose solution was firstly prepared by the dissolution of cellulose and LiCl in DMAc. It is well known that DMAc/LiCl solution is a good system to dissolve cellulose [19]. It is worth pointing out that the main problem associated with making effective nanocomposites from inorganic materials is related to their homogeneous dispersion within the cellulose matrix. Our method is based on the one-step simultaneous formation of AgCl nanoparticles and the cellulose, leading to a homogeneous distribution of AgCl nanoparticles in the cellulose matrix. The microwave-assisted method is favorable for the crystallinity of AgCl nanoparticles and the precipitate of cellulose. DMAc acts as both a solvent and a microwave absorber, while LiCl was used as the reactant to fabricate AgCl nanoparticles.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose was obtained from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. The molecular weight of the microcrystalline cellulose was calculated from their degree of polymerization (*DP*) by multiplying by 162. The *DP* of the microcrystalline cellulose is 215–240; therefore the molecular weight of the microcrystalline cellulose is 34,843–38,894. Silver nitrate, *N*,*N*-dimethylacetamide (DMAc), and lithium chloride (LiCl) were purchased from Beijing Chemical Works. All chemicals used in the experiments were analytical grade reagents, and were used without further purification.

2.2. Preparation of the cellulose/AgCl nanocomposites

All experiments were conducted under air atmosphere. A typical synthesis experiment is described as follows: 1.416 g microcrystalline cellulose and 1.510 g LiCl were added into 20 mL of *N*,*N*-dimethylacetamide (DMAc) under vigorous stirring at 90 °C for 3 h. Then, the obtained cellulose solution (5 mL) was added directly into DMAc (30 mL), then that 0.169 g $AgNO_3$ was added into the resulting solution under vigorous magnetic stirring. The solution was heated to 150 °C and kept at this temperature for a certain time by microwave heating. The microwave oven used for sample preparation was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd, which was equipped with a magnetic stirring system and a water-cooled condenser outside the microwave cavity. The microwave reactor is an open reaction system. The resulting precipitate was separated from the solution by centrifugation, washed with water and ethanol several times, and dried at 60 °C for further characterization.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded in the range of $2\theta = 10°–70°$ on an X'Pert PRO MPD diffractometer operating at 40 kV with Cu Kα ($\lambda = 1.5405$ Å) radiation. Fourier transform infrared (FTIR) spectra of the cellulose/AgCl nanocomposites were obtained by a Fourier transform infrared spectrophotometer (Nicolet 510) in a range of wavenumber from 4000 to 400 cm^{-1}, using the KBr disk method. Thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) were carried out with a STA-409PC/4/H Luxx simultaneous TG/DSC apparatus (Netzsch Co., Selb, Germany) at a scan rate of 10 °C min^{-1} from room temperature to 800 °C under air atmosphere. The morphology of cellulose/AgCl nanocomposites was examined using a Hitachi 3400 N scanning electron microscopy (SEM) operating at 15 kV. All samples were Au coated prior to observation by SEM.

2.4. Antimicrobial activity studies

The antimicrobial activities of cellulose/AgCl nanocomposites have been investigated against *Escherichia coli (E. coli)* as the model Gram-negative bacteria and *Staphylococcus aureus (S. aureus)* as the model Gram-positive bacteria by the disc diffusion method. In the inhibition zone experiment, nutrient agar was poured into disposable sterilized Petri dish and solidified. Then 100 μL of *E. coli* and 100 μL of *S. aureus* were streaked over the dish and spread uniformly. Then, circular pieces of the cellulose control and the composite samples were gently placed on Petri dishes. This was done for both bacterial strains (*E. coli* ATCC 25922 and *S. aureus* ATCC 25923). The cellulose/AgCl nanocomposites were cut into a disc shape with 1.4 cm diameter, sterilized by autoclaving at 120 °C for 20 min, and were placed on *E. coli*-cultured and *S. aureus*-cultured agar plates, which were then incubated at 37 °C for 24 h. Finally, the inhibition zone was monitored.

3. Results and discussion

Fig. 1 shows the XRD patterns of the typical samples prepared by microwave heating the DMAc solution of $AgNO_3$, LiCl, and microcrystalline cellulose at 110, 130, and 150 °C for 20 min, respectively. One can see that all of the samples have similar diffraction peaks. The three diffraction peaks at around $2\theta = 14.8°$, $22.5°$, and $34.5°$ were assigned to the typical diffraction peaks of cellulose type I. The other diffraction peaks were assigned to well-crystallized AgCl with a cubic structure (JCPDS 31–1238). No peaks from impurities such as Ag were observed. Based on the results of XRD, one can conclude that all the samples consisted of the mixed phases of cellulose and AgCl crystals, indicating the successfull synthesis of the cellulose/AgCl nanocomposites.

The cellulose/AgCl nanocomposites were further examined by FTIR analysis. Fig. 2 illustrates the FTIR spectra of the cellulose/AgCl nanocomposites prepared by microwave heating at 110, 130, and 150 °C for 20 min, respectively. All the samples exhibited the characteristic absorptions of cellulose (Fig. 2). The band at ~3449 cm^{-1} is indicative of stretching vibration in OH group. The band at ~2905 cm^{-1} belongs to the