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Ag nanoparticle-immobilized cellulose nanofibril films for environmental conservation

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ABSTRACT

A facile method was developed to prepare biodegradable nanocomposite films. Ag nanoparticles stabilized by an NH_2-terminated fourth generation poly(amido amine) dendrimer (DENAgNPs) were covalently immobilized on 2,2,6,6-tetramethylpiperidine-1-oxyl radical-oxidized nanofibrillated cellulose (NFC) by using a condensing agent for amide bond formation between NFC and DENAgNPs. Subsequently, the films with different concentrations of DENAgNPs were prepared by filtrating DENAgNPs-NFC suspensions on filter membranes, and the dried films were characterized. As-prepared films possessed the high catalytic efficiency to decoloration of Rhodamine B in water and the excellent antibacterial performance against both Gram-positive and Gram-negative bacteria on agar plates. Thus, this novel concept of film-type nanocomposite reactor demonstrates that it is possible to prepare inexpensive catalytic and bactericidal-active films with good selectivity by easy prospective approach for realizing the environmental conservation and innovation.

1. Introduction

Numerous classes of pigments are widely used in many industries and lead to severe contamination in surface water and groundwater from the release of toxic and colored effluents [1,2]. Meanwhile, various microorganisms coexist with human body and living environments, and their rapid and uncontrolled breeding can result in some serious problems like foul smell and health disturbance [3,4]. It is, therefore, essential to develop an eco-friendly and effective materials having catalytic properties for degradation of organic compounds and antibacterial properties, and it is of great significance to minimize, in such a way, the causes of hazards in the aquatic environments and human lives. The use of nanocomposites for the protection from carcinogenic, toxic dye molecules and microbial contamination may provide solutions for the challenges faced by the health care system in this century.

Parallel to eco-friendly criteria, cellulose is the most abundant natural polymer and an almost inexhaustible raw material for the fabrication of functional materials with various high performances [5,6]. As a chemical raw material, cellulose has been used for long periods [7]. Wood is essentially a network of cellulose fiber held together by a matrix of lignin. Wood pulp is produced through a variety of processes, all of which break down and wash away the lignin. A typical cellulose wood fiber, microfibrillated cellulose (MFC), is of only tens of micrometer wide and about a millimeter long. Meanwhile, the cellulose with carboxyl functional groups has been found to be an excellent eco-friendly matrix stabilizing metal nanoparticles [8]. As a novel approach, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation introduces carboxylate and aldehyde functional groups into cellulosic materials and makes MFC to nanofibrillated cellulose (NFC) in an aqueous medium, at mild conditions of room temperature and atmospheric pressure, and at pH 10–11.

NFCs reveal unique physicochemical behaviors and possess mechanical properties that are superior to bulk cellulose [9]. NFCs have gained considerable interests as an abundant biocompatible material with potential applications in a wide variety of fields ranging from tissue scaffolds to flexible electronics. Cellulose nanomaterials have previously been studied as reinforcement materials for various polymer matrices but they have recently been integrated into different applications [10–13]. NFCs have been used as a soft matrix to accommodate inorganic fillers (like metal nanoparticles) to produce inorganic–organic composites that bring together

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the intrinsic functionalities of the fillers and the bio-interface properties of cellulose fibers [14,15].

Nanostructured catalysts can effectively eliminate the organic pollutants and present antibacterial performance [16–18]. However, secondary pollution is one of the problems limiting the widespread applications of the nanostructured catalysts [19]. In other words, a serious issue is created due to the difficulty of separating the utilized nanostructured catalysts from the treated water, especially in the case of large-scale processes [20]. In this regard, to avoid secondary pollution, we have reported the embedding of Cu nanoparticles into the cellulose nanofiber film and utilized it for 4-nitrophenol reduction [21].

Herein, Ag nanoparticles (AgNPs) protected by poly(amido amine) (PAMAM) dendrimer (DENAgNPs) were synthesized at the condition, where the ratio of metal precursor to amine terminal group of PAMAM dendrimer was optimized so as to provide the stably dispersed AgNPs [22]. Then DENAgNPs were covalently immobilized on NFC by means of the chemical reaction, which is well known to form an amide bond [23]. Finally we focused to prepare films from aqueous suspensions of DENAgNPs-NFC nanocomposites by filtration. The formation of DENAgNPs-NFC films was characterized and confirmed via conventional analytical methodologies. This film-type novel material showed both catalytic and anti-bacterial activity. The mechanisms of decoloration and anti-bacterial activity were also shown in schematically.

2. Experimental

2.1. Materials

Silver nitrate (99.99%), methanol (99.8%), N-hydroxysuccinimide (NHS), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), fourth generation (G4) PAMAM dendrimer with 64 NH_2 terminals and Rhodamine B were purchased from Aldrich Chemical Co. Other reagents and solvents were purchased from Acros Organics. All of these chemicals were used without modification. Ultrapure water was used throughout all experiments.

Since the detailed preparation of NFC used in the present study is described elsewhere [21], a brief description is given here. MFC was prepared by removal of wax and lignin from the sliced wood (softwood) by means of chemical treatment. MFC suspended in an aqueous solution of TEMPO and sodium bromide was oxidized by slowly pouring sodium hypochlorite (13 vol%) under constant stirring at room temperature and pH 10 throughout the reaction. Thus-obtained NFC was rinsed thoroughly with water, centrifuged and stored in the wet state.

2.2. Fabrication of DENAgNPs-NFC composite films

The synthesis procedure at optimum ratio (0.01:1) of Ag^+:NH_2 group (in dendrimer) for preparation of small size of stable metal nanoparticles was followed the previous report [22]. The formation of nanoparticles was confirmed by the observation of a surface plasmon resonance band at 443 nm in an ultraviolet (UV)–visible absorption spectrum, while this band was absent for an $AgNO_3$ solution (Fig. S1 in Appendix A). All AgNPs were almost spherical, and its average size was 6.2 nm, as apparent from transmission electron microscopic (TEM) results in Fig. S2 in Appendix A.

The covalent crosslinking between NFC and DENAgNPs was done based on the well-known amidation reaction [23–25]. NFC in water (1 wt%) was reacted with equimolar coupling reagents, EDC and NHS to form a stable NHS-carboxylated NFC. After that, an aqueous DENAgNPs solution was added to accomplish the formation of DENAgNPs-NFC. The existence of DENAgNPs in DENAgNPs-NFC was confirmed by a plasmon band in comparison with spectra of NFC and DENAgNPs, as shown in Fig. S3 in Appendix A. The schematic representation of the formation of DENAgNPs-NFC nanocomposites is illustrated in Fig. 1.

The DENAgNPs-NFC films were prepared by the filtration of aqueous DENAgNPs-NFC suspensions on the cellulose acetate filter membrane with 47 mm diameter and 0.2 μm pore size. Then the DENAgNPs-NFC films were separated from the filter membrane. By way of comparison, films with different amount of DENAgNPs were prepared by varying an addition of an aqueous DENAgNPs solution in the reaction solution like 0 mL, 1 mL, 2 mL or 3 mL, and they were named as Film A, Film B, Film C and Film D, respectively. If the addition was increased more than 3 mL, the aggregation or precipitation of DENAgNPs in the NFC suspension was observed.

2.3. Characterization

UV–visible absorption spectra were recorded on a Jasco V-670 spectrophotometer. TEM observation was carried out on a Hitachi H-7000 instrument equipped with a CCD camera, operating at a voltage of 100 kV. Specimens were prepared by spreading a small drop (2 μL) of diluted suspensions onto standard carbon-coated copper grids and drying. Fourier transform-infrared (FT-IR) absorption spectra were recorded on a Nicolet 6700 spectrometer. X-ray photoelectron spectroscopic (XPS) measurement was carried out on a VG Scientific Model ESCA Lab 250 spectrometer. Thermogravimetric analysis (TGA) was performed using a TA instrument Q500 under nitrogen flow at a heating rate of 10 °C/min.

2.4. Catalytic and antibacterial reactions

Rhodamine B was used as a model organic dye to evaluate the catalytic activity of DENAgNPs-NFC films. The film was immersed into an aqueous Rhodamine B solution (10 mg/L, 100 mL), and an aqueous $NaBH_4$ solution (0.1 M, 1 mL) was added to initiate the decoloration reaction. During keeping in darkness, the pink color of Rhodamine B gradually vanished with catalytic reduction of dye. The efficiency of the catalysis was monitored by UV–visible absorption spectrometry.

Antibacterial activities were investigated for *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) as models for Gram-negative and Gram-positive bacteria, respectively. The activity was evaluated by the size of the inhibited clear zone on the disc diffusion method. The microorganisms were cultivated in tubes containing 5 mL of sterile nutrients: Luria–Bertani (LB) for *E. coli* and tryptic soy broth (TSB) for *S. aureus* were incubated for 24 h at 37 °C. The bacteria cells were diluted to a final concentration of OD_{600} = 0.05 and placed onto LB and TSB agar plates. Sample membranes were cut into disk shape of 0.5 cm diameter and UV-sterilized for 20 min. Then, the disks were placed onto the agar plates with the bacteria culture, and the plates were incubated for 24 h at 37 °C. Clear zones of inhibition formed around the disks were measured and compared with control samples.

3. Results and discussion

3.1. Characterization of DENAgNPs-NFC films

Due to the TEMPO oxidation treatment, primary hydroxyl groups at the C6 position of cellulose molecules are oxidized to sodium carboxylate groups (COONa). Sodium ions, counter ions of oxidized cellulose, can be exchanged with metal ions to provide cellulose–metal complex in the aqueous metal salt solution [21]. However, the active sites are limited and fewer amounts of metal particles are only loaded on the NFC networks. Hence, the present study focused to combine AgNPs-encapsulated PAMAM dendrimer