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A Simple Method for the Fabrication of Metallic Copper Nanospheres-Decorated Cellulose Nanofiber Composite



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Herein, we report a new and simple method for the preparation of metallic copper nanospheres-decorated cellulose nanofiber composite (CuNSs/CNFs). Initially, the cellulose acetate nanofibers (CANFs) were electrospun followed by deacetylation and anionization to produce functional anionic cellulose nanofibers (*f*-CNFs). The CuCl₂ precursor was deposited on the *f*-CNFs (CuCl₂/CNFs) by a simple dipping method. Then the CuCl₂/CNFs were reduced under vacuum by using aluminum foil to produce the CuNSs/CNFs. The resultant CuNSs/CNFs composite was characterized by various microscopic and spectroscopic methods. Fourier transform infrared spectroscopy (FT-IR) confirmed the successful functionalization of anionic groups with the CNFs. The field emission scanning electron microscopy (FE-SEM) and transmission electron microscope (TEM) results confirmed the formation of CuNSs on the surface of CNFs. From the scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis, the weight percentage of Cu was found to be 23.5 wt%. The successful reduction of CuO to metallic Cu was confirmed by X-ray photoemission spectroscopy (XPS) and X-ray diffraction (XRD) analyses. Mechanism has been proposed for the formation of metallic Cu sphere on CNFs.

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1. Introduction

Metal nanoarchitectures such as nanospheres^[1], nanocubes^[2], nanorods^[3], nanoflowers^[4] and nanoflakes^[5] have recently received immense attention in nanotechnology due to their various physicochemical properties, such as large specific surface area and unique structures. Among them, copper nanospheres (CuNSs) have also gained considerable attention due to their attractive optical, catalytic, mechanical and electrical properties^[1]. The CuNSs have demonstrated an efficient role in various applications, such as energy^[6], biomedical^[7], sensors^[8] and catalysis^[9]. Particularly, due to simple process, recovery and reusability, supported-CuNSs are

often preferable materials for several industrial applications^[10]. In addition, due to strong interaction between metal nanostructures (MNSs) and supports, the supported-MNSs are highly versatile and often exhibit unique properties compared to unsupported MNSs^[11,12]. Silica, alumina, carbon materials, metal oxides and polymers are the most well-known supports for the active CuNSs. To date, several supported-MNSs including copper nanospheres (CuNSs) have been reported^[13]. In our recent investigation, we prepared various MNSs-decorated carbon nanofiber composites and found that the composites are highly efficient for catalytic organic transformations^[14,15].

Recently, the development of various electrospun nanofibers (NFs), including cellulose nanofibers (CNFs) and their composites, has significantly attracted much attention because of their unique properties, such as large surface area to volume ratio, biocompatibility, flexibility in surface functionalities, easy-handling and outstanding mechanical properties^[16–18]. Particularly, the surface modification of cellulose nanofibers with various functional groups is simple and unique^[19]. Several MNSs-immobilized CNFs compos-

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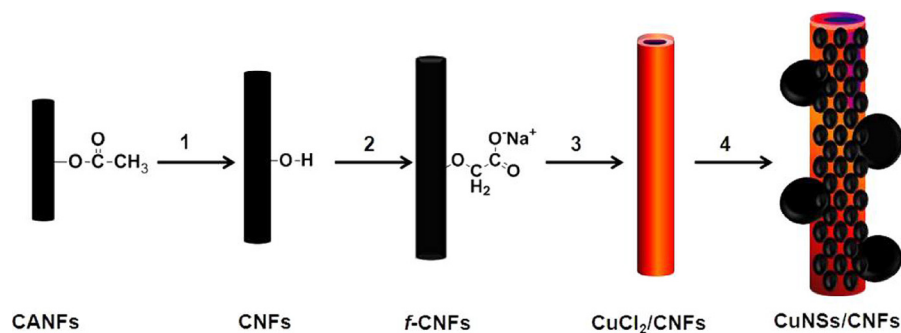


Fig. 1. Schematic illustration for the preparation of CuNSs/CNFs (1—deacetylation, 2—anionization, 3—CuCl₂ deposition and 4—reduction).

ites have been developed to date^[20–22]. The most common methods for the deposition of MNSs are metal deposition^[23], chemical reduction^[24] and in-situ deposition^[25]. Recently, Fang et al.^[24] prepared AuNPs-immobilized electrospun polyethyleneimine (PEI)/polyvinyl alcohol (PVA) nanofibers by chemical reduction method using NaBH₄ as a reducing agent. Eroglu et al.^[26] prepared PdNPs-immobilized chitosan NFs by using photosynthetic method. They found that the prepared composite is highly efficient for Mizoroki–Heck cross-coupling reaction. However, for the direct reduction of metal salts (particularly metal chlorides) to metallic nanostructures, several factors such as solvent, concentration of metal precursor, reducing agent, time and temperature need to be controlled very carefully. Herein, we report a new and very simple method for the fabrication of CuNSs/CNFs composite.

2. Materials and Methods

2.1. Materials

Cellulose acetate (CA, 39.8% acetyl content having average $M_w = 30$ kDa), *N,N*-dimethylformamide (DMF) and acetone were purchased from Sigma Aldrich. Copper chloride (CuCl₂), sodium hydroxide (NaOH), and sodium chloroacetate (ClCH₂COONa) were obtained from Wako Pure Chemicals, Japan. Aluminum foil was purchased from Sumikei Alumi Haku Co. Ltd., Japan. All the other chemicals were purchased either from Sigma-Aldrich or Wako Pure Chemicals and used as received.

2.2. Preparation of cellulose acetate nanofibers (CANFs)

The CANFs were prepared according to our previously reported procedure^[27]. In a typical experiment, 18 wt% of CA solution was prepared by addition of 3.6 g of CA in 20 mL of acetone/DMF mixture (3:2 ratio). A high-voltage power supply (Har-100*12, Matsusada Co., Tokyo), capable of generating voltages up to 100 kV, was used as a source of the electric field to produce the electrospun CANFs. The above obtained 18 wt% CA solution was poured in a 5 mL plastic syringe attached to a capillary tip of about 0.6 mm in inner diameter. The Cu wire connected to an anode was inserted into the CA polymer solution, and a cathode was attached to a grounded rotating metallic collector. The tip to collector distance (TCD) was 12 cm and the applied voltage was 10 kV. All the processes were carried out at 25 °C.

2.3. Deacetylation of CANFs

In a typical deacetylation test, 100 mg of the above prepared CANFs were dipped into a 100 mL of 0.05 mol/L NaOH solution for 48 h at 25 °C. After that, the CANF samples were thoroughly washed with distilled water to remove excess NaOH and dried in an oven

at 60 °C for 4 h. The deacetylated samples (CNFs) were further used for the anionization process.

2.4. Preparation of functional anionic cellulose nanofibers (f-CNFs)

Initially, the CNFs were dipped in 1.5 mol/L NaOH aqueous solution for 30 s to produce soda cellulose (Na-CNFs) and subsequently washed with 0.05 mol/L NaOH solution and dried in air. Then the Na-CNFs were dipped into a 1.0 mol/L ClCH₂COONa solution for 6 h. Finally, the resultant *f*-CNFs were washed thoroughly with distilled water and dried in air. All these steps were carried out at 25 °C.

2.5. Preparation of CuNSs/CNFs

At first, the CuCl₂ salt was deposited on the *f*-CNFs by a simple dipping method. In a typical process, 50 mg of the *f*-CNFs were dipped into an aqueous solution of CuCl₂ (50 mL of 0.1 mol/L CuCl₂) at 25 °C for 24 h. Then the resultant fibers (CuCl₂/CNFs) were gently rinsed with distilled water to remove the excess CuCl₂. Subsequently, the CuCl₂/CNF was well covered with aluminum foil and kept under vacuum for 24 h. Fig. 1 shows the schematic illustration of the preparation of CuNSs/CNFs composite.

2.6. Characterization

Field emission scanning electron microscopy (FE-SEM, S-5000, Hitachi Co., Japan) and transmission electron microscopy (TEM, JEOL model 2010 FasTEM) were used to characterize the morphology of the nanofibers. Prior to the FE-SEM analysis, the nanofibers were sputtered with Pd–Pt. To quantify the weight percentage of Cu and Cl in CuCl₂/CNFs, scanning electron microscope (SEM) images and corresponding energy dispersive spectra (EDS) were recorded using Hitachi 3000H SEM. The same field of view was then scanned using an EDS spectrometer to acquire a set of X-ray maps for Cu and Cl using 1 ms point acquisition for approximately one million counts. The chemical functionalization of CNFs was analyzed by Fourier transform infrared spectroscopy (FT-IR, IR Prestige-21, Shimadzu, Japan). The X-ray photoelectron spectrometer (XPS, Kratos Axis-Ultra DLD, Kratos Analytical Ltd, Japan) measurements were performed to confirm the chemical state of CuNSs.

3. Results and Discussion

The FE-SEM images in Fig. 2(a–c) show the surface morphology of the CANFs, CNFs and *f*-CNFs. It can be seen that the morphology of the CANFs was smooth and continuous with fiber diameters ranging from 300 nm to 600 nm and lengths up to several millimeters. The average fiber diameter of the CANFs was calculated to be 325 ± 0.5 nm (Fig. 2(d)). Similarly, after deacetylation process, the

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