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Metal-based bacterial cellulose of sandwich nanomaterials for anti-oxidation electromagnetic interference shielding

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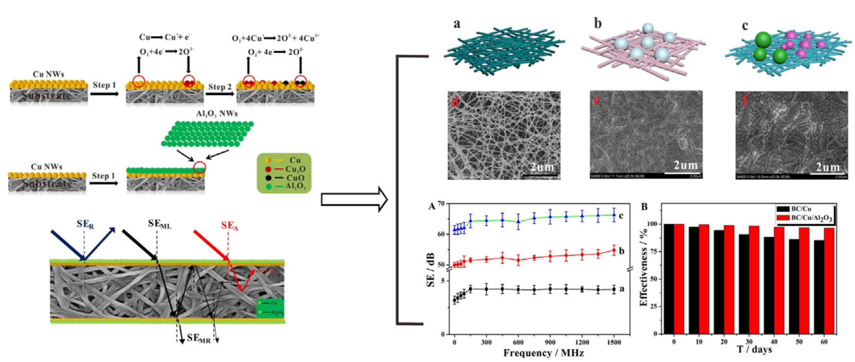
HIGHLIGHTS

- Bacterial cellulose was successively functionalized by magnetron sputtering and RF reactive sputtering for the first time.
- As-prepared BC/Cu/Al_2O_3 sandwich structure shows excellent electromagnetic interference (EMI) shielding effectiveness (SE).
- The anti-oxidation of sandwich nanomaterials was exposed to hamper oxidation of Cu nanostructure layers.
- This work demonstrates that BC is a promising substrate material in EMI field.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, bacterial cellulose was successively functionalized by magnetron sputtering and RF reactive sputtering with copper (Cu) and Al_2O_3 to endow it with unique anti-oxidation electromagnetic shielding properties while concomitantly improving hydrophobic, mechanical, and thermal properties. The surface topographies and chemical properties of BC/Cu/Al_2O_3 nanocomposites were examined by different analysis instruments to conclusively testify that metal-based nanoparticles were evenly deposited on the surfaces. This sandwich structure of the nanocomposites enhanced their thermal stability, hydrophobicity, mechanical properties, and electromagnetic interference (EMI) shielding effectiveness (SE). EMI effects of these nanocomposites were also investigated by the four-point probe, uniaxial testing machine and a vector network analyzer (VNA). The results indicated that the sandwich nanoscale materials showed good mechanical properties (41.3 Mpa) and excellent EMI shielding (65.3 dB).

1. Introduction

Nowadays, telecommunication devices have been widely used in various areas, e.g. industrial/commercial instruments, military equipments and scientific devices. These devices make our lives much easier while they also bring our society unbearable threat because the

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electronic devices generate electromagnetic pollution [1]. Consequently, to shield electromagnetic radiation pollution, a great deal of attention has been paid to the development of a novel materials for electromagnetic interference (EMI) shielding [2,3]. Recently, graphene-based materials with light weight and excellent conductivity have been developed [4]. Several graphene-based/polymers composites have been reported, e.g. rGO/PEI (the EMI SE of this material reaches to 20 dB) [5], rGO/Epoxy (21 dB) [6] and rGO/PS (48 dB) [7]. Similarly, graphene with magnetic filler in polymers were also investigated to improve EMI SE (shielding effectiveness), such as Fe_3O_4/rGO/PVC (13 dB) [8], SnO_2/rGO (40 dB) [9] and Fe_3O_4/rGO/PANI (51 dB) [10]. Nevertheless, graphene-based materials with high expense and relatively large thickness restrict its commercial application and large-scale production [11]. Meanwhile, because of metal-based shielding materials endow with its high permeability and low surface resistance, they have been extensively explored in practical application.

Recently, as a promising alternative material, copper (Cu) has also been used because it possesses lower cost than Ag and similar conductivity to Ag. Cu nanoparticles, in fact, have been studied since it facilitates high-speed fabrication and possesses lower cost than tin-doped indium oxide (ITO) [12,13]. However, because Cu nanoparticles are easily to be oxidized in an ambient atmosphere, the instability of Cu nanoparticles hampers its potential application. Therefore, to address this issue, increasing attention has been paid to study fillers or additives, such as conductive polymers, oxide nanostructures and metal films [14,15]. Bacterial cellulose (BC) as synthesized by a microbial fermentation displays fascinating features including ease of chemical modification, high ultrafine porosity (Fig. S1), biocompatibility, cost, high retention and liquid-holding capacities, high mechanical strength and moldability during formation in comparison with electrospinning and natural cellulose [16,17]. Meanwhile, BC has an ultrafine three-dimensional structure with 30–70 nm diameter and microfibrils. BC by virtue of its physical and chemical versatility can be endowed it with many practical applications, such as electrochemical device, supercapacitance, composite reinforcement, biomedical area and substrate materials [18–20]. Especially, BC as advanced eco-friendly substrates has recently been extensively studied [21–23].

In this work, the three dimensional structure of BC provided a platform for nanoparticles electroplating to interfere with EMI SE. The EMI mechanisms involved within BC/Cu/Al_2O_3 nanocomposites were investigated by RF reactive sputtering method. This study therefore focused on comparing their stability with Al_2O_3 grown on Cu layers. Especially, the protecting mechanism of Al_2O_3 on Cu films was investigated. These results showed Al_2O_3 film could be a good oxidation barrier layer for Cu nanosheets. This mechanism may provide a new method to fabricate stable metal-based nanomaterials. A synthetical investigation into sandwich nanomaterials and their underlying application for EMI shielding was analyzed.

2. Materials and methods

2.1. Materials

The BC was obtained from in-house lab (Jiangnan University, China); Aluminum, Copper (purity: 99.99%) targets were purchased from Hefei Department of Crystal Material Technology Co., Ltd. (Hefei, China). In addition, peptone, glucose, mannitol and NaOH of analytical grade were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China).

2.2. Synthesis of BC

BC pellicles were produced using the static incubation method reported [24]. The synthesized cellulose was promptly treated with 0.1 M NaOH for 8 h at 80 °C to clear culture liquid and the cells, following by repeatedly rinsing to neutral with distilled water [16]. Then, the pretreated BC membrane was freeze-dried before coating. The thickness of membrane was measured by screw-thread micrometer.

2.3. Sputter coating process

A magnetron sputter (JZCK-420B, Juzhi Co., Ltd., China) was employed to deposit Cu nanoparticles on the surface of nano-sized BC aerogel. A high purity Cu target (purity: 99.99%; diameter: 50 mm) was mounted on the cathode, and the pure BC aerogel was placed on the anode facing the target by direct current (DC) magnetron sputtering. The flow of Argon (Ar, purity: 99.99%) gas was set to 24 sccm. During sputtering, a sputtering power (30, 50 and 70 W) was set at 0.8 Pa. The deposition thickness of Cu layers on the surface of BC was controlled by altering different coating time. A high purity Aluminum target (purity: 99.99%; diameter: 50 mm) was sputtered on BC/Cu film forming protective layer by RF reactive sputtering method (Fig. 1). Gas flow rates of Ar and oxygen (O_2, purity: 99.99%) were set as 24 sccm and 3 sccm, respectively. A sputtering power (40 W) was set at 0.8 Pa. Coating time was 30 min. Initially, the target was placed below the substrate at a distance of 80 mm and the target Cu and Al particles were sputtered on BC film facing the target with rotating speed of 90 rpm to achieve uniform deposition. Besides, the chamber was evacuated to a pressure of 6.5×10^{-4} Pa before introduction of bombardment gas. Water-cooling was applied to control the temperature of the substrate to protect substrate from deformation [25,26]. Substrate temperature was about room temperature before sputtering.

2.4. Characterization

The surface morphologies and chemical characteristics of pure BC membrane, BC/Cu and BC/Cu/Al_2O_3 nanocomposites were studied by Field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Company, Japan), Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus, Thermo Electron Corporation, Waltham, MA, USA), X-ray diffraction (XRD, Bruker AXS D8, Germany) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Scientific Escalab, USA). Thermogravimetric analysis (TGA, 1100SF; Mettler Toledo International Trading Co., Ltd. Shanghai, China) was used to analyze thermal stability of nanocomposites. Contact angle measurement (DCAT-21, Data Physics Corporation, Germany) was employed to examine the surface

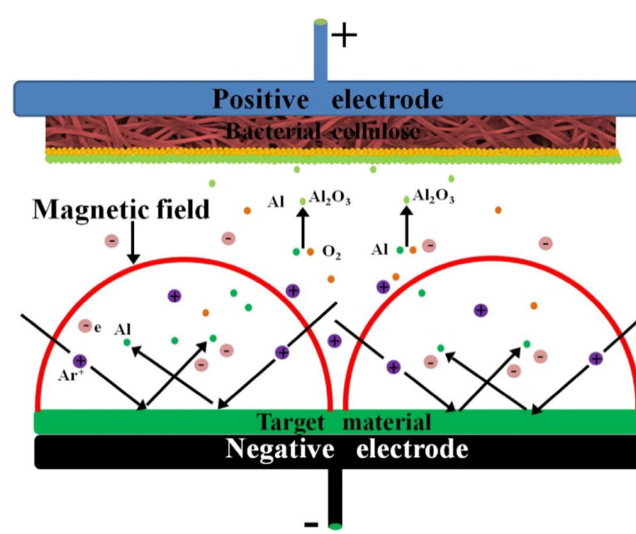

Fig. 1. The process of formation of BC/Cu/Al_2O_3 nanocomposites by RF reactive sputtering method.