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Electrical resistivity and dielectric properties of helical microorganism cells coated with silver by electroless plating

Jun Cai*, Mingming Lan, Deyuan Zhang, Wenqiang Zhang

Bionic and Micro/Nano/Bio Manufacturing Technology Research Center, School of Mechanical Engineering and Automation, Beihang University, Beijing 100191, China

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ABSTRACT

In this paper, microorganism cells (*Spirulina platens*) were used as forming templates for the fabrication of the helical functional particles by electroless silver plating process. The morphologies and ingredients of the coated *Spirulina* cells were analyzed with scanning electron microscopy and energy dispersive spectrometer. The crystal structures were characterized by employing the X-ray diffraction. The electrical resistivity and dielectric properties of samples containing different volume faction of sliver-coated *Spirulina* cells were measured and investigated by four-probe meter and vector network analyzer. The results showed that the *Spirulina* cells were successfully coated with a uniform silver coating and their initial helical shapes were perfectly kept. The electrical resistivity and dielectric properties of the samples had a strong dependence on the volume content of sliver-coated *Spirulina* cells and the samples could achieve a low percolation value owing to high aspect ratio and preferable helical shape of *Spirulina* cells. Furthermore, the conductive mechanism was analyzed with the classic percolation theory, and the values of ϕ_c and t were obtained.

1. Introduction

The metal particle-filled polymer composites have attracted great attention and extensive studies in recent years. It has been found that these composites have great application potential for electromagnetic interference (EMI) shielding [1–5]. At present the commonly-used metal fillers are mainly high conductivity metals, such as silver, copper, and nickel. Silver has excellent electrical conductivity but the cost is high. Copper and nickel exhibit good electrical conductivity and low cost, yet they are easily been oxidized, resulting in instability properties. In order to obtain the high conductivity filler with low cost and stable performance, to fabricate core–shell particles by way of plating silver coatings onto the surface of non-metallic powders has gained great attention recently [6–10]. The physical properties of these filler particles can be systematically tuned by variation of the size and shape. However, the shapes of the existing non-metallic powders are rather single and the sizes are also non-adjustable, limiting the further improvement of their performance.

Bio-limited forming technology is to use microorganism cells with different standard shapes as templates to produce various bio-based functional particles, by way of depositing conductive or magnetic material on their surface [11]. The most prominent characteristics of bio-based functional particles are shape diversity (spherical, rodlike, filamentous, helical and so on) and hollow lightweight (soft-core in structure). So far, we have fabricated several kinds of bio-based functional particles with different shapes and functional coatings by various surface coating methods in the preceding research [12,13], which aim was to achieve promising magnetic properties.

In this paper, targeting fabricate light-weight particles with good conductive performance so as to fabricate cost effective composites for EMI shielding application, silver coating was attempted to be deposited onto the surface of helical microorganism cells with high aspect ratio by electroless plating technique. The fabrication process is introduced and the particles achieved are analyzed in detail, furthermore, the electrical resistivity and dielectric properties of composites synthesized by sliver-coated cells and resin are investigated.

2. Experimental details

2.1. Materials

The microorganism selected as forming templates were *Spirulina platens* (*Spirulina platensis*, Nordst. Geitl.), which are of natural helical shape and in blue-green color. Normally, the helical width is about 26–36 μm, the distance between two coils is about 43–57 μm, the helical number is about 4–7 (20 at most), the diameter of helical threads made up of multi-cells is about 5–8 μm, and

* Corresponding author. Tel.: +86 10 82316603/82339604; fax: +86 10 82316603.
E-mail address: jun_cai@buaa.edu.cn (J. Cai).

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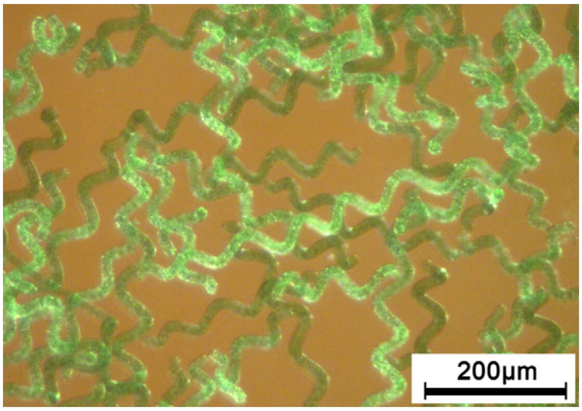

Fig. 1. Optical microscope image of *Spirulina* cells.

the thickness of unicell is about 4–5 μm, as shown in Fig. 1. An enclosed photobioreactor was used for the indoor batch culture of *Spirulina*, and culture strains were offered by the Institute of Hydrophyte, Chinese Academy of Sciences. The *Spirulina* cells were collected by a thin silk sieve with mesh number of 250 after they grown up. The collected *Spirulina* cells needed to be fixed with glutaraldehyde and osmic acid prior to use as templates, in order to keep their initial shape and enhance their mechanical strength.

2.2. Electroless silver plating

The fixed *Spirulina* cells are non-conductive, so activation pretreatment was needed before electroless plating process. This was carried out as following, first they are stirred in an acidic stannous chloride bath containing 20 g/l of $SnCl_2 \cdot 2H_2O$ and 40 ml/l of concentrated HCl acid for 15 min at room temperature (sensitization step), secondly they are rinsed thoroughly with deionized water, thirdly they are transferred to the silver–ammonia bath containing $AgNO_3$ (2 g/l) and $NH_3 \cdot H_2O$ (2 ml/l) and stirred in bath for 15 min at room temperature (activation step).

After pretreatment, the activated *Spirulina* cells were put into the reducing agent solution, then the silver–ammonia salt solution was added gradually, during which mechanical stirring was applied to avoid aggregation of the cells. The plating bath compositions and operation conditions were given in Table 1. The ratio of silver–ammonia salt solution to the reducing agent solution was 1:1. The electroless silver plating process was carried out at room temperature. The silver-coated cells were dehydrated in an alcohol series and dried in vacuum drying chamber at 120 °C for 4 h.

2.3. Morphology characterization

The morphology of the *Spirulina* cells was examined by a XSY-1 optical microscope with SONY DSC-H50 photographic camera and a scanning electron microscope (SEM, Cambridge CamScan CS3400). The composition analysis was made using energy dispersive spectrometer (EDS, Oxford INCA). The crystal structures were characterized by employing the X-ray diffraction (XRD, Rigaku D/max-3) with Cu Kα radiation at a voltage of 40 kV, a current of 40 mA, step size 0.02°, scanning rate 8°/min and wavelength 1.5418 Å.

Table 1
The bath composition and operation conditions.

Silver–ammonia salt solution		Reducing agent solution	
$AgNO_3$	3.5 g	HCHO (38%)	1.1 ml
$NH_3 \cdot H_2O$	20 ml	C_2H_5OH	95 ml
H_2O	80 ml	H_2O	3.9 ml
Time	15 min	Load	200 ml/g

2.4. Electrical resistivity

The silver-coated *Spirulina* cells were mixed with resin, and this mixture was vigorously stirred by hand for several minutes to make them more homogeneous. Then the curing agent was added at the mass ratio of 2% and stirred for another 10 min. The composites were placed in the air for curing at least 48 h, and then machined to sizes suitable for various measurements. The concentrations of silver-coated *Spirulina* cells in the composites varied from 0 to 50 vol.%. The resistivity measurements of composites were carried out by a SZT-2A four-probe meter.

2.5. Dielectric properties

The silver-coated *Spirulina* cells were put into melted paraffin wax; vigorous stirring was used to make the mixture more uniform. Then the mixture was injected into the mould to produce toroidal samples for dielectric measurement after cooling. The toroidal sample, $7^{+0.03}_{-0.02}$ mm in outer diameter and $3^{+0.05}_{0}$ mm in inner diameter, approximately 2 mm in thickness, was placed in a coaxial measurement fixture. The concentrations of silver-coated *Spirulina* cells in the samples ranged from 10 to 40 vol.%. A vector network analyzer (AV3627, CETC) was used to measure the dielectric properties of the samples over a frequency range of 2–18 GHz.

3. Results and discussion

3.1. Morphological properties of silver-coated cells

Fig. 2 shows the SEM images of *Spirulina* cells after electroless plating of silver. It can be observed that there are fewer agglomerates, which indicates the *Spirulina* cells dispersed uniformly in the solution during the electroless plating. Furthermore, the *Spirulina* cells after plating kept their initial helical shape, and the surface coatings are homogeneous, continuous and compact. The EDS results (Fig. 3) reveal that the principal components of *Spirulina* cells are carbon and oxygen, and the composition of the plated cells is mainly silver (up to 93.01 wt.%), which indicate that the *Spirulina* cells have been successfully deposited with silver coating with a certainty thickness. Fig. 4 shows cross-section SEM image of *Spirulina* cells after electroless plating of silver. It can be seen that the silver-coated helical particle is hollow, and the outer silver coating thickness is about between 0.6 μm and 0.8 μm. In addition, the density of silver-coated *Spirulina* cells is approximately 1.65–1.7 g/cm^3 according to the test result, so they are lightweight particles.

3.2. Phase structure of silver-coated cells

Fig. 5 shows the XRD pattern of the silver-coated *Spirulina* cells. It is seen from Fig. 5 that, the diffraction peaks that appeared at 2θ = 38.1°, 44.4°, 64.2°, 77.4° and 81.5° correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of silver, respectively, which exhibit face-centered cubic (fcc) structure.

3.3. Optical microscope images of samples containing silver-coated cells

Fig. 6 shows optical microscope images of samples containing different volume faction of silver-coated *Spirulina* cells. It is seen from all images that the silver-coated *Spirulina* cells mixed in resin