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The Elongation Performance of *Spirulina*-templated Silver Micro Springs Embedded in the Polydimethylsiloxane

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Abstract

Helical conductive particles have attracted much attention in preparing stretchable conductive materials because of their structural flexibility and uniform strain distribution under deformation. In this paper, *Spirulina*-templated silver micro springs were fabricated using electroless deposition of silver onto *Spirulina* surface. To investigate their potential application as conductive fillers for stretchable materials, they were mixed into polydimethylsiloxane (PDMS) uniformly, and then the mixture was spin coated on a polyfluortetraethylene (PTFE) plate to form a thin film, during which, micro springs tended to align its major axis along the radial direction of the plate. The tensile tests of micro springs were carried out using the film along the alignment direction of micro springs on the custom-made setup. Under the optimal condition of coating thickness of 0.67 μm, helical pitch of 29 μm and annealing temperature of 300 ˚C, the average elongation of micro springs can reach up to ~106.9%, which indicates that the as-prepared *Spirulina*-templated silver micro springs are promising flexible conductive fillers for fabricating stretchable conductive materials.

Keywords: micro springs, elongation, electroless deposition of silver, *Spirulina*, stretchable conductive fillers

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1 Introduction

Unconventional foldable and stretchable electronics show great potential for fabricating the functional devices, such as flexible circuitry[1,2], sensors[1–4] and wearable electronics[4,5], *etc*. To date, the main strategy to prepare stretchable electronics is the inclusion of highly conductive metallic nanostructures such as silver nanoparticles (AgNPs)[1,4,5], silver nanowires (AgNWs)[3,4] and copper nanowires (CuNWs)[2] into elastic polymer matrices. However, the poor elasticity of these normal conductive fillers limited the further development of stretchable electronics. Therefore, researchers turn to conductive fillers with stretchable architectures, such as wrinkled microstructures[6], helical coil forms[7,8], which can accommodate larger strain without degrading the electrical resistance.

Among these researches, the helical conductive particles attracted more attention since they can accommodate large tension and compression with uniform strain distribution. Different strategies have been developed for the helical particle fabrication, the main routes include yet not limited to the following: self-growing methods[9–13], bio-templated methods[14–20], 3D direct writing[21–24] and rolled-up nanotechnology[25–28], *etc*. Among them, the 3D direct writing and rolled-up nanotechnology afford precise control of shapes and dimensions within small margin of error, yet the low-production is an obstacle, limiting them to the precise situation applications; the self-growing method is noteworthy for mass-production and good elasticity, yet the yield uniformity remains low[13] and the composition materials are limited to carbon based or oxidation based, resulting in the relative low electrical conductivity[2]. Compared with that, the bio-templated method using the exquisite shapes presented by nature is promising as it is facile, convenient and high productivity[29]. Especially, the *Spirulina* platens are naturally of intact helical microstructures and exhibit prolific reproductive capacity, moreover, their structural parameters such as diameter, helical pitch, and/or length can be easily adjusted by changing the cultivation conditions[30,31], so it is an ideal template to fabricate conductive micro springs by coating different nanomaterials.

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So far, different techniques have been developed to explore the potential applications of bio-templated micro springs, such as serving in conductive materials[17], THz electromagnetic responses[20], targeted delivery[14], *etc*. Yet, there is little research on the mechanical property of such bio-templated micro springs, to our knowledge, only Zhang *et al*.[19] investigated nanomechanical properties of the copper micro spiral based on *Spirulina*. In order to further explore such bio-templated micro springs' potential applications in the flexible conductive materials and improve the performance of stretchable electronics, it is necessary to study their elastic or elongation performance in polymers.

Herein, we used *Spirulina* as templates to fabricate silver-coated micro springs by electroless deposition technology, and investigated the effects of coating thickness, helical pitch and annealing temperature on the elongation of such micro springs in the Polydimethylsiloxane (PDMS). Firstly, we adjusted the structure shape of *Spirulina* template so as to fabricate silver micro springs with better flexibility. *Spirulina* templates with different helical pitches were achieved by changing the concentration of nutrient solution. Secondly, to ensure the excellent silver coating in the experiments, we optimized eletroless deposition process. The silver coating thickness was controlled by changing the electroless deposition processing time to gain high-quality coating. After that, we re-prepared micro springs using different *Spirulina* templates with superior coating quality. Moreover, we adopted annealing treatment as a post processing to further improve the quality of silver coating. To reveal the elongation of as-prepared micro springs in polymers, they were mixed into the PDMS uniformly, and then the mixture was spin-coated on a polyfluortetraethylene (PTFE) plate to align the micro springs in the formed thin film. Finally, the tensile tests were carried out using the solidified film on custom-made setup.

2 Materials and method

2.1 *Spirulina* strains preparation

The *Spirulina* platens (*Spirulina* platensis, Nordst. Geitl.) were selected as forming templates for their natural helical shape. Normally, their helical width is about 26 μm – 36 μm, the helical pitch is about 43 μm – 80 μm, the helical number is about 4 – 7 (20 at most), and the diameter of helical thread is about 5 μm – 8 μm. All these parameters can be adjusted in a certain range by changing culture conditions of *Spirulina*. The cultured original strains were offered by the Institute of Hydrophyte, Chinese Academy of Sciences.

The original *Spirulina* (strain-1 with helical pitch of 73 μm) was indoor batch cultured in an enclosed photobioreactor in conventional nutrition solution, then they were harvested by Stainless Cell Cribble (200 mesh) after 20 days, by when the yield of *Spirulina* is high enough. In order to get *Spirulina* strains with narrowed helical pitch, we cultured original *Spirulina* in 50%, 35% and 20% diluted nutrition solution simultaneously, *Spirulina* strains were picked and observed under the optical microscope (Olympus, BX51) equipped with a digital camera (Canon, 600D) every five days. When the *Spirulina* strains obtained uniform morphology with different narrowed helical pitches, we measured their helical pitches by randomly picking 10 samples of *Spirulina* in the field of microscope and harvested them for the following electroless deposition.

2.2 *Spirulina*-templated silver micro springs preparation

The harvested *Spirulina* strains were prefixed, activated and electroless deposited silver onto their surface. The detailed process can be found in our previous literatures[16,17]. During the eletroless deposition process, the 1 g wet activated *Spirulina* cells were mixed with 100 mL reducing agent solution, and 100 mL silver-ammonia salt solution was added by a dropping funnel with a speed of approximate 2 seconds per drop. When nearly half of the silver-ammonia salt solution was dropped (about 20 min), we collected sample-1 from the reaction solution. Subsequently, we collected other samples every 10 min until all the silver-ammonia salt solution had been dropped in the reducing agent solution in 45 min. By controlling the electroless deposition processing time, the micro springs with different coating thickness were prepared. The as-prepared micro springs were swashed by deionized water and absolute ethanol respectively, and followed with absolute ethanol assisted drying treatment in a vacuum drying oven.

The overall morphology of the micro springs was observed by optical microscopy (Olympus, BX51), and cross section views of the micro springs were characterized by Scanning Electron Microscopy (SEM, JSM-6010LA, JEOL, Ltd.). The coating thickness was