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Optical fluorescent spider silk electrospun nanofibers with embedded cerium oxide nanoparticles

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Abstract. The work demonstrates an electrospun nanocomposite of recombinant spider silk protein (rSSp) nanofibers with embedded cerium oxide (ceria) nanoparticles. RSSP (MaSp1) has been produced, extracted from goat milk, and fabricated into nanofibers using an electrospinning process. The resulting electrospun nanofibers have a mean diameter of ~50 nm. Furthermore, ceria nanoparticles of mean diameter <10 nm were added in the spinning dope to be embedded within the generated nanofibers. These nanoparticles show certain optical activity due to optical trivalent cerium ions, associated with formed oxygen vacancies. The formed nanocomposite shows promising mechanical properties such as the Young's modulus, elasticity (or elongation at break), and toughness. In addition, the electrospun mat becomes fluorescent with 520-nm emission upon exposure to UV light, due to excitation of the optically active ceria nanoparticles. Also, the formed nanocomposite shows a decay of its electric resistance over time upon exposure to cyclic loads at different humidity conditions. The synthesized nanocomposite can be utilized in different biomedical, textile, and sensing applications. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JNP.12.026016](https://doi.org/10.1117/1.JNP.12.026016)]

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1 Introduction

Spider silks (SS) are considered the strongest, most elastic, and toughest biomanufactured fibers. Web-weaving spiders have used impressive silks where the proteins in the silks can be described as nondiverged at the protein sequence level.^{1,2} In the last three decades, several research papers have studied the physical, mechanical, and chemical properties of SSs, as promising biomaterials for a variety of applications including neural system regrowth and other applications such as textile.^{3–6} However, the study of their optical and electrical properties is still lacking for the most part. The mechanical and frictional forces align the protein molecules to form the fibers ranging from 20 to under 1 μm in diameter. Mechanical properties of natural SSs are promising due to its ability to absorb the energy of the prey without damaging of the web, in addition to avoiding any rebound of the insect away from the web.⁷ Different parameters affect the properties of the protein silk fiber such as temperature, hydration state, protein concentration, and extension rate. Major ambulate silk (MaSp) is a two protein-composition in every orb-weaving SS.^{8–10} MaSp proteins are composed of GGX, GPGXX, and poly-alanine repeats, where X could

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be glutamine (Q), tyrosine (Y), or leucine (L). Recent research also revealed a hierarchical structure of the silk fibers that led to a better understanding of their promising mechanical performance.^{11,12} However, very little research has been done on the formation of nanofibers recombinant spider silk protein (rSSPs) via electrospinning process with both electrical and optical characterizations.^{13,14}

Our work suggests electrospinning of rSSP (MaSp1) nanofibers with active cerium oxide nanoparticle (ceria NPs) to create an electrospun mat with specific optical characteristics can be possibly used for biomedical applications. Ceria NPs have a strong capability to act as free radical scavenger and to capture dissolved oxygen in liquid media.^{15,16} These characteristics allow ceria NPs to find their possible applications in cancer treatment, energy applications (solar cells), or detection tools (e.g., oxygen and peroxide sensors).^{17–19} Cerium ions could exist in either an active trivalent state (Ce^{3+}) with associated charged oxygen vacancies or nonactive (Ce^{4+}) with no formed O-vacancies, with a major possibility of having mixed ionization states as a nonstoichiometric compound CeO_{2-x} . The trivalent cerium ions show fluorescence characteristics when are exposed to UV light.²⁰

Ceria nanoparticles are prepared using a simple chemical precipitation technique.²¹ Then, the embedded ceria nanoparticles are added *in situ* with SS solution and electrospun into nanofibers. In this work, the embedded ceria nanoparticles are shown to add new optical feature for the spider silk nanofibers (SS NFs), fluorescence, in addition to data on both the mechanical and electrical characterization of the formed nanocomposite.

2 Experimental Work

2.1 Materials

The recombinant spider silk dragline protein (MaSp1) was purified (90+% pure) from the milk of genetically modified goats based on the purification method mentioned in Ref. 22 and 23. The purified MaSp1 protein was found to consists of two major amino acid sequence: (1) GGA-GGX [X = tyrosine (Y), glutamine (Q), and lysine (L)], which are acting as soft flexible segments and (2) alanine blocks (AAAAAAAAAA), each block consists of 8 to 10 alanine monomeric unit forming B-sheets, which are acting as strength element in the drag line SS. The whole sequence is GGAGQGGYGGQAGQGGYGGGLGSQGAGRGGLGGQAGAAAAAAAAA and repeated for 16 times to form a giant polyamide chain with the average molecular weight of 60 to 65 kDa.

Formic acid (88%) was purchased from Alfa Aesar (Ward Hill, Massachusetts) and 1,1,1,3,3,3-hexa-fluoro 2-isopropanol (HFIP) was purchased from Oakwood chemicals (Estill, South Carolina). Triton X-100 from Sigma-Aldrich (St. Louis, Missouri) has been used as surfactant. Cerium (III) chloride heptahydrate was purchased from Sigma-Aldrich (St. Louis, Missouri) and used as precursor for ceria NPs. Ammonium hydroxide and ethanol were used during synthesis of ceria Nps.

2.2 Synthesis of Ceria NPs

Ceria nanoparticles are first synthesized using a chemical precipitation technique similar to Chen et al. but with some modifications.²⁴ Synthesis of cerium oxide nanoparticles as follows. Cerium (III) chloride heptahydrate (0.5 g, Sigma-Aldrich) is inserted into a beaker with adding 40 mL of distilled water, and the solution is stirred using a magnetic stirrer at rate of 500 rpm for 24 h. The solution is heated to 50°C in a hot water bath for 2 h with the addition of 1.6 mL of commercial ammonium hydroxide. Then, it is stirred for 22 h at room temperature. The long period of stirring fractures any remaining nanorods into nanoparticles. The solution is then centrifuged, washed with deionized water and ethyl alcohol.

2.3 Electrospinning Dope Preparation

The SS solution was initially prepared by dissolving MaSp1 protein in a mixture of formic acid of 88% and HFIP at a ratio of 1:1. 0.1 mL of Triton X-100 was added as a surfactant. The mixture

Fig. 1 Simple schematic diagram of the electrospinning setup.

was sonicated using an ultrasonication probe (Fischer, 1 W) for 3 min prior to the addition of ceria nanoparticles. The diluted ceria nanoparticles dispersion (0.02 g/L) was added to the SS solution and stirred for few minutes using vortex mixer to form the final spinning solution.

2.4 Electrospinning Process

The electrospinning unit purchased from IME Technologies (Geldrop, The Netherlands), consists of a high voltage power supply and a syringe pump, which is used to regulate the pumping rate of the polymer solution, a 5-mL plastic syringe with 30-gauge metallic needle, and a rotating metallic collector of radius 10 cm covered with nonsticky aluminum foil was used as a target. A schematic illustration of the electrospinning setup is shown in Fig. 1. The voltage power supply is connected to the needle while the collector is grounded with a separation distance of 15 cm. The voltage difference between the needle and target is 26 kV, with a flow rate of the polymer solution at 1 mL/h for 1 h running time per sample. The speed of rolling collector is set to 1500 rpm.

3 Characterization

3.1 Scanning Electron Microscopy

The electrospun fibers were characterized by field emission scanning electron microscopy (FEI Quanta 200, Hillsboro, Oregon) to characterize their morphology and fiber diameter. The electrospun mats were mounted on an aluminum stub and coated with a gold layer about 10-nm thick. The mean fiber diameter was calculated as an average of 200 measurements using Image J software.

3.2 Transition Electron Microscopy

The mean synthesized nanoparticle size was observed by transmission electron microscopy (TEM, JEOL, Tokyo, Japan), with accelerating potential of 80 kV.

3.3 Mechanical Properties Measurements

The mechanical properties of the yarns were tested using an MTS tensile tester (Synergy 100, MTS, Eden Prairie, Minnesota) with custom 10-g load cell (Transducer Technique). The electrospun mats were cut longitudinally into strips of size 1×12 cm. Each strip was twisted using a fringe twister (Lacis cord maker and fringe twister, Berkeley, California) for 10 s into yarns of

average diameters 300 to 700 μm . The twisted yarns were then fixed on C-shaped plastic holders with a fixed gap between holder's tips of 19.1 mm and secured in the tensile testing instrument. The tensile test was run at a strain rate of 5 mm/min and the average of 10 individual measurements was calculated.

3.4 Optical Activity Measurement

Spider silk protein nanofibers (rSSP NFs) with and without embedded ceria NPs were optically characterized by measuring absorbance and fluorescence intensity curves. Optical absorbance from 350 to 550 nm was measured using ultraviolet–visible (UV–vis) spectrophotometer (PG T92+, Beijing, China). From absorbance curves, the corresponding band gap of the formed nanocomposite can be determined, as discussed below. The fluorescence setup is composed of a violet light-emitting diode (LED) from Thorlab (Newton, New Jersey) with a 430-nm excitation wavelength, a monochromator (Newport Cornerstone 130, Irvine, California), which was set to obtain fluorescence intensity at wavelengths from 500 to 700 nm, an Oriel photomultiplier tube (PMT) (Newport PMT77340, Newport, Irvine, California) as a fluorescence intensity detector, and a power meter (Newport 1918-R, Newport, Irvine, California) to display PMT detection readings. Fluorescence intensity was measured by positioning the NFs solid sample holder between the UV–LED and the input port of the monochromator, so the input optical signal to the monochromator is perpendicular to the initial LED excitation signal for minimum scattering effect.²² In other words, the fluorescent signal is to be inclined by 90 deg compared to the incident light for minimum scattering effect. The output port of the monochromator was directly connected with PMT, which was directly connected to 1918-R power meter.

3.5 Electrical Properties

The electrical properties of the designed nanocomposite have been determined through a simple setup as shown in Fig. 2. The nanocomposite was twisted into yarns of diameters 500 to 700 μm with a length of ~ 4 cm. Each end of the yarn is attached to a metal clamp connected to a commercial multimeter. The controlled environment is then set to approximated relative humidity (RH) level and the SS's resistance is recorded as a function of time and humidity. The resistance value was generally recorded for ~ 30 min per experiment. A RH level of 99% is reached to offer a fully humid environment for the prepared nanocomposite.

4 Results

4.1 Spider Silk Nanofiber and Cerium Oxide Morphology

SEM image of the electrospun nanofibers in Fig. 3 shows that the fiber diameters are ranged around 50 ± 20 nm. With the assumption that the air gaps between the individual fibers are neglected, the approximate number of fibers contributed in yarn formation ranged from

Fig. 2 Schematic diagram of resistance measurement setup.

Fig. 3 (a) SEM image of the electrospun SS NPs and (b) the fiber diameter distribution (the fiber diameters in the range of 50 ± 20 nm).

6000 to 14,000 aligned nanofibers. Upon addition of cerium oxide nanoparticles, no significant changes have been observed in the fiber diameters.

A TEM image of freshly prepared ceria nanoparticles is shown in Fig. 4(a), with mean diameter of 6 nm. Another TEM image of aggregated ceria nanoparticles inside the nanofibers surface is shown in Fig. 4(b). It is not recommended to add any surfactant to reduce the nanoparticles aggregation, because it can reduce the formed O-vacancies inside ceria crystalline structure that can affect the optical properties of ceria nanoparticles and the entire nanocomposite negatively.²⁵

4.2 Optical Properties

The absorbance curves of the SS NPs with embedded ceria NPs are shown in Fig. 5(a). The absorbance increases within shifting to lower wavelength, which is correlated to the embedded ceria NPs. The optical allowed direct bandgap can be calculated directly from the obtained absorbance curves using²⁶

$$\alpha E = A(E - E_g)^{1/2}, \quad (1)$$

Fig. 4 (a) TEM image for the prepared cerium oxide nanoparticles and (b) aggregated nanoparticles inside the electrospun nanofibers.

Fig. 5 (a) Absorbance dispersion and (b) bandgap calculations of SS NPs with/without embedded ceria nanoparticles.

where α is the absorbance coefficient, A is the material constant that depends on the effective masses of electrons and holes in the ceria NPs, E is the absorbed photon energy, and E_g is the allowed direct bandgap.

Figure 5(b) shows the relation between $(\alpha E)^2$ versus E , and the intersection of the extrapolation of the linear part of the $(\alpha E)^2$ curve with the E -axis is equal to the allowed direct bandgap E_g . The bandgap is found to be < 3.2 eV, which confirms that cerium ions have a dominant concentration of trivalent states associated with oxygen vacancies, which can be responsible for the fluorescence properties of ceria nanoparticles and the whole nanocomposite when embedding such nanoparticles inside SS NPs.²¹

Fluorescence intensity measurements are shown in Fig. 6 of ceria NPs which were embedded *in situ* in SS NPs. The fluorescence emission appears at a wavelength close to 500 nm under 430-nm excitation, which is one of the embedded ceria NPs' optical characteristics, with corresponding electron transitions of 5d–4f molecular levels inside the cerium trivalent ionization states, with no fluorescence emission from the pure SS NPs.²⁷ Comparing to crosslinked PVA nanofibers as cited in Ref. 28, it is observed that the obtained bandgap of ceria becomes lower in case of SS compared to crosslinked PVA host. Also, the fluorescence intensity amplitude is higher in case of SS host compared to crosslinked PVA. That can be explained as the crosslinking process may affect the activity of trivalent cerium ions and the corresponding O-vacancies. That makes the SS host better in keeping the activity of trivalent cerium ions with better optical characteristics.

Fig. 6 Fluorescence intensity of SS NFs with *in situ* embedded with ceria NPs.

4.3 Mechanical Properties

Regarding the mechanical properties, Fig. 7 shows the mechanical properties of SS NPs with and without adding ceria nanoparticles at normal RH (16%). As shown in Fig. 7, all the mechanical properties such as elastic modulus, tensile strength, maximum strain, strength at break, and energy of break are reduced when ceria NPs are added. Table 1 summarizes the comparison between SS only and SS with added ceria NPs. However, this difference can be considered a tradeoff compared to both optical and electrical benefits from adding ceria NPs. Figure 8 shows stress-strain analysis of SS NPs nanofibers with embedded ceria NPs at normal RH (RH = 16%) and fully humid surrounding medium (RH ~ 99%). The number of samples was about five and the average curve is shown in Fig. 7. The standard deviation is also shown in the table. As seen from Table 2, the elastic modulus is reduced ~50%. Also, the tensile strength and strength at break (at the elastic limit) are reduced as well. The maximum strain is

Fig. 7 Stress-strain mean curve for SS nanofibers and SS nanofibers embedded with ceria NPs.

Table 1 Mean values of mechanical properties comparison between SS NFs and SS NFs embedded with ceria NPs.

	SS NFs	SS NFs with ceria NPs
Elastic modulus (MPa)	1.89 ± 0.31	1.14 ± 0.17
Tensile strength (MPa)	3.57 ± 0.50	1.96 ± 0.44
Maximum strain (%)	16.09 ± 4.2	10.06 ± 2.51
Strength at break (MPa)	11.13 ± 1.88	3.05 ± 0.56
Energy to break (kJ/m ²)	24.67 ± 7.97	4.84 ± 1.49

Fig. 8 Stress-strain mean curve for nanocomposite of SS NFs embedded with ceria NPs at different RH values.

Table 2 Mean values of mechanical properties comparison between SS nanofibers embedded with ceria NPs at different RH values.

	Normal RH (RH = 16%)	RH = 99%
Elastic modulus (MPa)	1.14 ± 0.17	0.58 ± 1.01
Tensile strength (MPa)	1.96 ± 0.44	0.69 ± 0.49
Maximum strain (%)	10.06 ± 2.51	19.66 ± 8.32
Strength at break (MPa)	3.05 ± 0.56	1.82 ± 0.67
Energy to break (kJ/m ²)	4.84 ± 1.49	5.45 ± 2.72

Fig. 9 Cyclic resistance of the nanocomposite; SS with ceria NPs, at RH levels of 99% and 16% “normal condition of the lab” (section A: resistance decay over time at RH = 99%, section B: rapid increase of resistance at normal lab environment at RH = 16%, and section C: cyclic return of resistance decay over another full humid environment at RH = 99%).

approximately doubled, and the energy of break (area under the curve) is increased a small amount. For each measurement, five samples are used, then, the mean values and standard deviations are calculated.

4.4 Electrical Properties

For the electric resistance measurement in the case of RH ~ 99%, as shown in Fig. 9 in section A, the resistance values are observed as exponential-like decay for the SS NPs with increasing the exposure time to the humid environment. This may be due to the shrinkage of the SS proteins. In more detail, as the RH reduced down to 16%, the resistance elevates by the trend shown in Fig. 9. When the RH returned back to the 99%, the resistance drops again. The shrinkage of the SS yarns could be due to distortion of the fibroin chains by water, which were aligned along the nanofibers axis. The required time for a significant drop of the measured resistance was found to be relatively high, up to 20 min at the saturation level. However, in normal RH levels, the resistance starts to increase substantially with relatively short rise time. The resistance alteration at different RH values was shown to be cyclic during the variation of RH due to a cyclic shrinkage nature of silk spider proteins with approximately no change in the macroscopic state of the yarn itself. The diameter of the yarn is reduced up to 50% of its original diameter during the first 1 to 2 min at RH 99%, and then the diameter stays constant. The length of the yarn is found to be approximately constant. That can give an explanation of the cyclic effect of SS/ceria nanofibers is due to mainly the cyclic shrinkage/extension of the SS proteins rather than a change in the outer dimensions of the yarns.

5 Conclusions

The work demonstrates the acquiring electrospun SS NPs for fluorescence through embedding ceria nanoparticles. Ceria nanoparticles with a largely Ce^{3+} ionization state have been added

in situ to MaSp1 SS protein solution and then electrospun into nanofibers. The average electrospun fiber diameter is around 50 nm with embedded ceria nanoparticles of mean size around 6 nm. The nanocomposite shows fluorescence characteristic with visible emission under UV excitation and with direct optical bandgap around 3.2 eV. The manufactured nanocomposite shows a maximum strain up to 20%. The electric resistance of the nanocomposite is found to decay with time in humid environment. The increase and decrease in nanocomposite electrical resistance show a kind of cyclic behavior when the humidity is changed. So, our contribution is to fabricate multifunctional nanocomposite with having different characteristics including biocompatibility, optical fluorescent, and quite electrical conductive in humid environment. This work can be helpful in applying the electrospun SS NPs in biomedical applications due to its small diameters, biocompatibility, and the ability to implement different materials to impart different functionalities. Also, the synthesized nanocomposite using ceria NPs could be very useful in cancer treatment due to its properties of being free radical scavenger and capturing dissolved oxygen in liquid media.

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