Silk fibroin-based biodegradable piezoelectric composite nanogenerators using lead-free ferroelectric nanoparticles

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Abstract
Silk fibroin-based biodegradable composite-type nanogenerators are demonstrated with controllable lifetime for powering to the implantable devices. The 2D thin film- and 1D wire-type composites consist of the well-dispersed lead-free ferroelectric (BaTiO\textsubscript{3}, ZnSnO\textsubscript{3}, Bi\textsubscript{0.5}(Na\textsubscript{0.82}K\textsubscript{0.18})\textsubscript{0.5}TiO\textsubscript{3}, and K\textsubscript{0.5}Na\textsubscript{0.5}Nb\textsubscript{0.995}Mn\textsubscript{0.005}O\textsubscript{3}) nanoparticles. Ag nanowires are used to enhance the dispersion of the nanoparticles and polyvinylpyrrolidone prevents Ag nanowires from connecting with each other. A maximum output voltages and current densities of 2.2 V and 0.12 mA/cm\textsuperscript{2} in the thin film, and 1.8 V and 0.1 mA/cm\textsuperscript{2} in the wire are obtained under the motion of a foot step for when 30 wt\% KNN:Mn nanoparticles are well-dispersed in the solution because of the largest piezoelectric coupling figure of merit. The properties of water-soluble composite films are also controlled with the glycerol content up to two days.

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Introduction
Harvesting energy from mechanical energy in our living environment and human body has attracted much attention due to an
extended life time, no recharging procedures, and scalability. Since ZnO nanowire arrays have been used to fabricate such piezoelectric nanogenerators [1-6], there have been many attempts to fabricate piezoelectric energy harvesting devices by employing various nanostructured materials such as ZnO [7], BaTiO3 [8], KNNbO3 [9], xKNaNbO3-(1-x)LiNbO3 (KNNN) [10], ZnSnO3 [11], and NaNO3 [12] and 0.5Ba(2Zr0.6Ti0.4)O3-0.5(Ba0.5Ca0.5)TiO3 (BZT-BCT) [13]. Recently, the polymer-mold-supporting nanogenerators composed of nanowires and nanoparticles have been successfully demonstrated as one of promising platforms for the large-scale and super-flexible nanogenerators. These composite-type nanogenerators are very attractive for large-scale energy harvesting application because of easy fabrication, cost-effectiveness, and mechanical robustness.

The emerging technologies for such mechanical energy harvesting have been proven to be effective and promising approaches for building self-powered systems. In particular, it is highly desired for implanted biomedical devices to be self-powered without using a battery. Various mechanical energies such as heart beat and muscle stretching exist in human body enough to power the implanted devices to build nanosystems. Actually, in vivo biomechanical-energy harvesting from mechanical energies such as the muscle movement and heart beat in a live rat was already demonstrated [14]. Implantable energy harvester by periodic breathing and a self-powered artificial pacemaker using living heart in human body was also developed [15,16].

Recently, many researchers have taken key advances toward practical uses of biocompatible electronic devices that could be implanted into the body, in which the electronic devices are operated steadily without pain for a specific period of time, and then dissolve harmlessly when no longer needed without requiring an extra surgery to remove them from the body. Thus, it is essential to explore innovative technologies for developing the time-controllable biodegradable nanogenerator to power such implanted electronic devices. Until now, polydimethylsiloxane (PDMS) elastomer has been widely used as the supporting polymer in composite-type nanogenerators due to its high shear strength, low Young's modulus, and flexibility. However, it is difficult to be utilized as an efficient approach for the implantable electronic devices because of the insoluble property in water. Furthermore, it is so sticky that the device may not produce stable output performance. Here, we replace the PDMS to the silk fibroin, producing silk fibroin-based composite-type nanogenerators with biocompatible ferroelectric nanoparticles. Silk fibroin is a natural polymer with biocompatible, transparent and biodegradable properties (soluble in water), which has been used as platforms for transistors and various classes of photonic devices. Furthermore, it shows excellent mechanical properties (tensile strength ~ 100 MPa), expecting good durability and the application under various external stress [17]. Additionally, the unique time-controllable property of silk fibroin composite was demonstrated and is so desirable for operation of biocompatible nanogenerator in human skin and body.

**Experimental**

**Preparation of silk fibroin solution**

The silk fibroin solution here was prepared from Bombyx mori cocoons and was described previously [18-20]. Roughly, the cocoons were boiled for 20 min in a solution of 0.02 M sodium carbonate (Na2CO3) to remove the sericin protein. The extracted fibroin was rinsed with distilled water (DI) and then dried in ambient air for 12 h. After drying, the fibroin was dissolved in a 9.3 M lithium bromide (LiBr) solution at 60°C for 4 h, yielding a 20 wt% aqueous solution. Subsequently, the solution was dialyzed against DI water using a dialysis cassette (Slide-a-Lyzer, Pierce, MWCO 3.5 K) at room temperature for 48 h until the solution reached a concentration of 8 wt%. The obtained solution was purified using a centrifuge and a 0.8 mm syringe filter.

**Preparations of BaTiO3, ZnSnO3, BNKT, KNN:Mn, nanoparticles**

BaTiO3 (99.9%) nanoparticles were supplied by US Research Nanomaterials, Inc. The synthesis of the other nanoparticles is shown in Figure 51. ZnSnO3 nanoparticles were prepared by an aqueous solution method. 10 mmol ZnSO4·7H2O was added to 100 ml DI water and was stirred until the nanoparticles were dissolved completely. The Na2SnO3·3H2O was then poured into the solution, resulting in a 1:1 M ratio of zinc and tin precursors. The solution was violently stirred at 80 °C during 5 h. After that the products are rinsed with distilled water five times and dried in the oven at 90 °C for 1 h [11].

B0.5(Na0.68K0.32)0.5TiO3 (BNKT) and K0.3Na0.5Nb0.995Mn0.005O3 (KNN:Mn) nanoparticles were synthesized by heat treatment of chemical solutions which were prepared by sol-gel method. Bismuth nitrate pentahydrate, sodium nitrate, potassium nitrate, and titanium butoxide were used as precursors for BNKT sol [21]. Potassium nitrate, sodium nitrate, niobium pentaethoxide, and manganese acetate were used as precursors for KNN:Mn sol [22]. Acetylacetone was used as complexing agent to stabilize of alkoxide precursors. The chemical solutions were dried at 120 °C for 24 h, followed by heating at 400 °C for about 5 h to expel trace amounts of water and carbon. Then the products were calcined at 650-800 °C.

**Fabrication of silk fibroin based composite nanogenerator**

0.0125 g polyvinylpyrrolidone (PVP) was initially mixed in 0.5 g Ag nanowires (Nanotech and Beyond co., Ltd.), poured into the silk solution. The nanoparticles (BNKT, KNN:Mn, BaTiO3, ZnSnO3) are then added to the solution, producing the 30 wt% silk composite solution. The well-mixed solution was spin-coated onto the ITO/PET flexible substrate, and cured at room temperature for one day. Glycerol was used to control the biodegradable properties of the silk fibroin film. The other ITO/PET film was attached onto the composite layer, acting as the top electrodes. The Cu wires were attached to both electrodes by means of Ag paste for the measurement of the output voltage and current density.

**Microstructural analysis**

The morphologies of the synthesized ferroelectric composite were characterized by a Nano 230 field emission scanning electron microscope (FEI, USA). The crystalline
properties of the films were characterized by a high resolution X-ray diffractometer (Bruker, Germany).

**Measurement system**

I-V characteristics with the applied force were obtained under an air ambient using a Keithley 2636 A source measurement unit. To measure the current densities and voltages generated by piezoelectric silk fibroin composites, a Keithley 6485 picammeter and Keithley 2182 A voltammeter were used.

**Results and discussion**

The schematic diagrams of the fabrication process are shown in Figure 1a and detail information described in Experimental section and Figure S2. Figure 1b shows the cross-sectional scanning electron microscopy (SEM) image of the KNN:Mn nanoparticles and the crystallographic structure of the material in the inset, exhibiting a well-defined cubic morphology with an average size of about 400-500 nm. The pristine silk film and silk composite film are seen to have a uniform thickness of about 15-20 μm, as shown in Figures 1c and d. In Figure 1e, a High magnification SEM image of composite film is shown. It was clearly seen that the nanoparticles are seen to be well-dispersed in the silk matrix. BaTiO3, ZnSnO3, BNKT, and KNN:Mn nanoparticles are indexed to the tetragonal, orthorhombic, rhombohedral-tetragonal morphotropic phase boundary (MPB), orthorhombic structures. This nanoparticles are incorporated into the silk matrix as shown in Figure S3.

Figure 2a shows high resolution X-ray diffractometer (XRD) profiles of pure silk fibroin film and composite films with 30 wt% BaTiO3, ZnSnO3, BNKT, and KNN:Mn nanoparticles. The pure silk fibroin film shows an XRD pattern of typical amorphous material, with the absence of crystallinity peaks, characterizing a silk I secondary structure which mainly consists of α-helix and random coil. For the composite films, it is clearly seen that the nanoparticles are fully crystallized, and no impure phases are observed in the samples. The crystal structures of the BaTiO3, ZnSnO3, BNKT, and KNN:Mn nanoparticles are indexed to the tetragonal, rhombohedral, rhombohedral-tetragonal morphotropic phase boundary (MPB), orthorhombic structures. The electrical properties of the films along the vertical direction were examined, showing that the films provide excellent insulating properties although the composites show a little increase in the conductivity, as shown in the inset of Figure 2b. The optical transmittance of the films are measured and plotted in Figure 2c. The 15 μm-thick silk fibroin film on ITO/PET substrate show a transmittance of about 85% in the range of 400 to 800 nm. As the 30 wt% KNN:Mn nanoparticles are added to the silk fibroin solution, the transmittance decreases up to 72%, in which the decrease in the transmittance is irrespective of the nanoparticles. The composite films are still seen to be quite transparent, as shown in Figure 2c. The composite with 50 wt% nanoparticles still shows a transmittance of approximately 65% (Figure S4a).

To measure the piezoelectric power-generating performance of the device, a direct impact approach was used. A foot of human was used to apply vertical compressive force on the devices. Figures 3a and b show a photography of the actual experimental setup for scavenging energy from the foot motion, and the output voltage and current density generated from the composite film type nanogenerator with 30 wt% KNN:Mn nanoparticles, respectively. It was clearly seen that an output voltage of 2.2 V and a current density of 0.12 μA/cm² were obtained by the normal pushing force. This power-generation performance was quite stable. Further increases in the concentration to 50 wt% decreases the output power, due to the weakness of insulation resulting to the electric breakdown (see Figure S4b in supplementary materials). Polarity-switching tests also confirm that the output voltage and current density originated from the piezoelectric phenomenon (Figure S4c). Figure S5 also shows the change of calculated piezopotentials of the composite nanogenerator with the magnitude of applied force. It can be clearly seen that the change of the piezopotentials increased linearly as the external force increased from 100 to 500 μN for the composite film type nanogenerator.

As mentioned above, we believe that the nanoparticles with same size distribution (400-500 nm) are well-dispersed in the silk fibroin matrix. However, it may not be easy to investigate how the nanoparticles are dispersed in the matrix. Furthermore, the silk fibroin solution is so low viscous that the nanoparticles

![Figure 1](image1.png) **Figure 1** (a) Schematic diagrams of the fabrication process for the silk fibroin-based composite-type nanogenerators with ferroelectric nanoparticles. (b) A SEM image of Mn doped KNN nanoparticles with an average size of about 400-500 nm. The inset shows the crystallographic structure, an orthorhombic structure. This nanoparticles are incorporated into the silk matrix as shown in (c). Low magnification (d) and high magnification (e) SEM images of the resultant composite films.
naturally and easily sink into the surface of the substrate, as shown in the left inset of Figure 3c. As expected, the composite nanogenerator with poor dispersion generates the low output voltage of less than 1 V in Figure 3c. To enhance the dispersion, Ag nanowires and PVP were used as dispersing agents and the optimization process was used to promote the dispersed distribution. It is well-known that the Ag nanowires are widely used in dispersing the nanoparticles in the composites, and developing the transparent and conducting electrodes [23-25].

Thus, the PVP was added to the solution to reduce the conductivity of the films (see the inset of Figure 3d), thereby, increase the output performance of the nanogenerator. Actually, when the nanoparticles are mixed into the silk fibroin solution with Ag nanowires (1 wt%) and PVP (12 wt%) together, a maximum output voltage and current density of 2.2 V and 0.12 μA/cm² were obtained, two times higher than that for only KNN:Mn nanoparticles in Figures 3c and d. It is thought that the PVP plays role in dispersing nanoparticles in the silk fibroin matrix and wrapping a surface of Ag nanowires in order to prevent Ag nanowires from connecting with each other [26]. The cross-sectional image in the right inset of the Figure 3c confirms that the nanoparticles are well-dispersed in the silk fibroin matrix. In the Figure S6, the calculated piezopotential difference between of aggregated and well-dispersed nanoparticles in the silk fibroin matrix is in good agreement with experimental results.

The output power of the composite nanogenerator is also dependent on the piezoelectric coupling figure of merit, which is defined as $k^2 Q$. Here, $k$ is a measure of the conversion efficiency between electrical and mechanical energy in piezoelectric materials and $Q$ indicates the quality factor of the device. The maximum power generated is obtained in the generator with a high $k$ and $Q$-factor when the generator works at its resonant frequency. It may be generally acceptable that Mn doping can significantly enhance the mechanical quality factor without deteriorating other piezoelectric properties, expecting the large $Q$-factor in composites embedded with KNN:Mn nanoparticles (the $Q$-factor of the composites embedded with various nanoparticles will be separate paper) [27-29]. The electromechanical coupling factor ($k$) can be expressed by;

$$k^2 = \frac{Y \times d^2_{ij}/\varepsilon^T}{C^2}$$

where $Y$, $d_{ij}$, and $\varepsilon^T$ are Young’s modulus, piezoelectric coefficient, and dielectric constant, respectively [30,31]. Nanoindentation measurements were conducted to evaluate the resistance to deformation by external force, and show that there is no significant change in the elastic modulus (0.2-0.3 GPa) in composites. We also believe that the Ag nanowires do not affect the dielectric properties of the silk fibroin materials because of the low volume fraction (as low as 7%) [26]. Thus, it is essential in increasing the piezoelectric constant ($d_{ij}$) for the larger output power of the nanogenerator. In Figure S7, among the nanoparticles (BaTiO₃, ZnSnO₃, BNKT, and KNN:Mn), the KNN:Mn has the largest piezoelectric coefficient ($d_{ij}$) of ~270 pC/N and relatively small dielectric constant of about 730 [32]. Thus, the coupling factor of the material is expected to be the highest, leading to the largest output power, consistent with experimental results.

The composite films formed from the silk fibroin and the nanoparticles are soluble in water because of the random coil structures, which make the composites generator useless within 10 min. This may be quite meaningful when the powering devices need to disappear with the implanted electronic devices when no longer needed. But, it is essential to develop the nanogenerators that can disappear in a controlled and programmable way. For example, the medical implants, that are needed for a few weeks and then disappear, may need the nanogenerators powering to the implanted devices during the
same periods, without requiring an extra surgery to remove them from the body. Glycerol has been used to control the biodegradable properties of the silk film. That is, it is able to accelerate silk gelation, making the silk film insoluble in water due to high content of β-sheet. When the glycerol content in the blend films increases to 5 wt%, the composite films are completely dissolved after dipping in the water for 30 min. Further increases in glycerol to 20 wt% and more concentrations significantly reduced the solubility up to 48 h, as shown in the inset of the Figure 4a, and there is no significant change in the output voltage of the composite nanogenerators, as shown in Figure 4c. The result indicates that 20 wt% glycerol was a critical concentration in inducing the structural transition from random coil to β-sheet which is water-insoluble [33]. This results show that it is possible to disappear the composite films in a controlled way for transient electronics.

A nanogenerator was also made as a form of a one-dimensional (1D) wire, and the output power was measured in a same fashion. It was done by dip-coating silk fibroin-based composite-type solution onto an aluminum wire and composite layer is cured at 50°C. Then semi-cured composite wire was taped with Al foils as electrode. In Figures 5a and b, the wire consists of Al wire (diameter 1 mm) at the inner, silk fibroin composite (~20 μm), and Al sheet (~20 μm) at the outer. The nanogenerator shows the output voltage of ~1.8 V and the output current density of ~0.1 μA/cm² in Figure 5c, showing a similar output performance of thin film type nanogenerator, as shown in Figure 3. This will provide the feasibility of this 1D wire as a promising path toward the development of a robust textile nanogenerator for the future smart clothing industry.

Conclusions

In summary, we demonstrated silk fibroin-based biodegradable composite-type nanogenerators with controllable lifetime for powering to the implantable devices. The composites are fabricated as 2D thin films and 1D wires by using a silk fibroin solution and lead-free ferroelectric (BaTiO₃, ZnSnO₃, BNKT, and KNN:Mn) nanoparticles. The piezoelectric output voltage and current density reached 2.2 V and 0.12 μA/cm² in the silk fibroin composite thin film, and 1.8 V and ~0.1 μA/cm² in the wire under the motion of a foot step when 30 wt% KNN:Mn nanoparticles are dispersed. Here, Ag nanowires and PVP are used to enhance the dispersion of the nanoparticles and it is also thought that the PVP prevents Ag nanowires from connecting with each other, reducing the conductivity of the composite film. A series of composite nanogenerators with different nanoparticles were fabricated and showed that the composite generator with KNN:Mn generated the largest output power because of the largest piezoelectric coupling figure of merit. Additionally, the lifetime of the device can be also
controlled in water with glycerol concentration up to 48 h. Thus, the devices have great potential for powering to the implantable electronic device and the future smart clothing industry.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.01.004.

References

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