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Wearable Triboelectric Generator based on a Hybrid Mix of Carbon Nanotube and Polymer Layers

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Wearable Triboelectric Generator based on a Hybrid Mix of Carbon Nanotube and Polymer Layers

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Abstract: A novel single-layer structured triboelectric generator (TEG) is proposed with a hybrid mix of carbon nanotube (CNT) and silk. Here, the mixing of two materials in liquid phase for proven effective power generation is shown. In this research, CNT provides the function of conductivity, whereas silk fibroin forms the main triboelectric generation material that is uniformly mixed with CNT, to achieve a conductive film with superior electric power generation capability. The newly proposed TEG shows very good electrical performance and great potential in simplifying TEG's structure and manufacturing process, enhancing their feasibility in future wearable applications.

1. Introduction

Wearable Electronics have promising applications in various fields ranging from self-powered sensors [1], wellness monitors [2] to shape adaptive electronics [3] as Internet of Things becoming developed. As universally known that the operations of these wearable electronics require an extra power source. However, owing to the conventional batteries lacking of the required properties such as flexibility, light weight, convenience and uniform specification, TEG as a self-sufficient power supplying source has become a most ideal and promising solution. Beside of the advantages of low cost, environmental friendliness and high availability, it could also collect low-frequency and irregular mechanical power from human motions [4], wind blowing [5] and water waves [6], showing extraordinary feasibility.

Although there have been studies that have achieved some results for wearable TEGs [7-9], it is still difficult to balance softness, safety, cost, and application requirements. For the friction materials, the synthetics materials such as PDMS, silicon rubber are mostly used, neither soft nor breathable. On the other hand, metal is usually the first choice for TEG's electrodes, which can be processed very fine and light weight but has the danger of causing metal allergy. Besides, the complicated fabrication process to turn the uncomforting friction materials and metal into wearable will increase the cost and hinder TEG's development in vast application as well.

In this paper, a skin-friendly material based simple structured TEG is proposed. Silk is chosen as the friction material, which is mixed with the non-metallic electrode material CNT at liquid phase. Then by the method of simple coating-peeling, a light-weight and soft mixed layer could be obtained for wearing and generating electricity power along with random human motions.

2. Working principle

The operating principle of triboelectric generator can be described as the coupling of contact charging and electrostatic induction. With an externally applied force, the two friction materials are brought into contact with each other. As most of the materials which deliver strong triboelectric effects are insulators, triboelectric charges will be captured on the material's surfaces. When the two friction materials get separated by external force, driven by the potential drop the generated electrons will flow in the external circuit connected between the two electrodes, which are attached to the two friction materials.

In this research, the triboelectric pair is composed of a mixing layer and an external layer. In the mixing layer silk works as the main triboelectric functional material whereas CNT works as an electrode. The external layer presents human skin or normal clothes polymers, as shown in Figure 1. Therefore, relying on a more than simple system, the proposed TEG can operate reliably through periodic contact between the mixing layer and the external part and generate electrical power.

3. Experimental results

To verify the effectiveness of the mixing-layered system as well as to allow it to provide enough power for wearables, a series of optimal parameters were verified through several sets of experiments.

3.1. Preparation of the mixing solution

There exist some precedents already for mixing silk and CNT together in previous studies [10], but the purpose to use silk was only to enhance better mechanical properties, so the amount of CNT was very tiny. In this study, the amount of CNT needs to be greatly increased for the purpose of making a conductive solution. Four mostly used solvents of sodium dodecyl benzene sulfonate (SDBS) solution, ethanol, DI water and formic acid to better disperse the CNTs were tested. As the result, DI water and formic acid are the propriate candidates for the mixing solution, without denaturing proteins like SDBS or ethanol, as shown in Figure 2. Because formic acid performed better, formic acid was set as the default solvent at this stage.

100 mg of CNTs powder was dissolved in 20 g of formic acid to obtain CNT-formic acid solution of 4 mg/ml. Silk fibroin water solution of 40mg/ml was made using the previously published method [11]. The final solution was obtained through 2 hours ultrasonic bath after mixing them together.

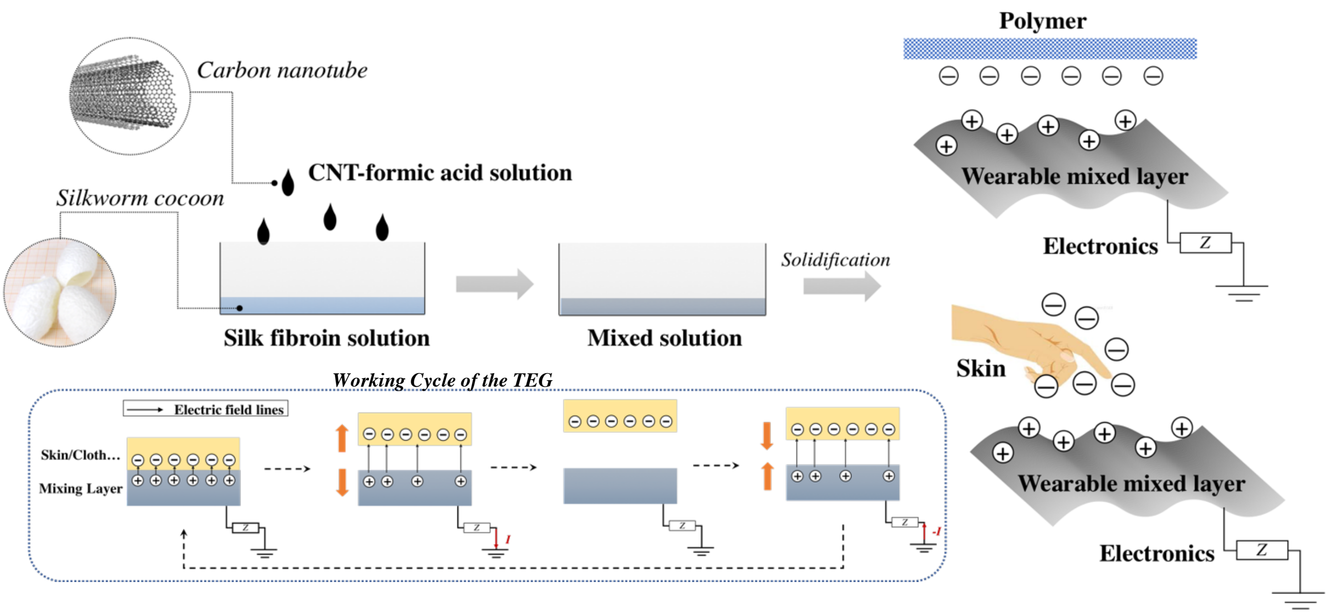


Figure 1. Schematic view of the fabrication method and working cycle of proposed wearable TEG device.

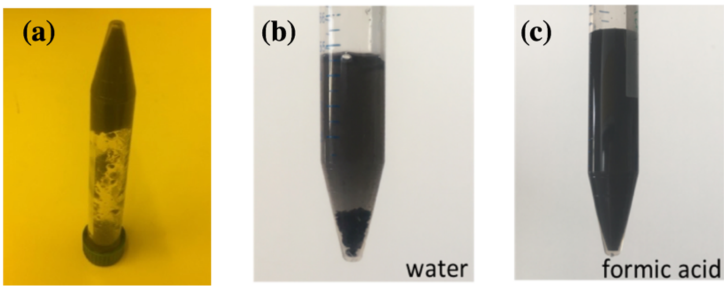


Figure 2. (a) The mixing of SDBS solution/ethanol and silk solution. SDBS and ethanol will denature the silk fibroin. (b) The mixing of DI water and silk solution. (c) The mixing of formic acid and silk solution.

3.2. Different ratios between the components in the mixing solution

CNT-formic acid solution and silk fibroin water solution were mixed in different ratios, to achieve a membrane that remains conductive after solidification, regardless of the negative impact from agglomeration. The agglomeration refers to the phenomenon that when solvent evaporates, different solutes tend to separate from each other and the same solutes tend to agglomerate with each other, resulting in separation of the surface solute after solidification, leading to uneven surface, thereby greatly reducing conductivity, stability and usability. By verifying five weight ratios $M_{CNT} : M_{Silk\ fibroin}$ of 5:1, 3:1, 1:1, 1:3, 1:5 as shown, respectively in Figure 3(a), it is concluded that ones with ratios of 5:1, 3:1 and 1:1 achieve the desired result of being conductive after solidification.

In order to further make sure of the optimum ratio, a surface roughness test was carried out to confirm the severity of the agglomeration phenomenon at each ratio. The more intense the agglomeration phenomenon was, the more agglomeration appeared on the surface, leading to uneven surface and high surface roughness. The result shown in Figure3(b) indicate that CNTs and silk fibroin dispersed most completely and evenly at the ratio of 1:1 since the agglomeration didn't appear too much, which is propriate for a conductive electrode layer. When the two solutes are completely dispersed, the silk fibroin wraps the CNTs like a piece of clothing, making the carbon nanotubes thicker and more closely connected to each other. Therefore, even if the pure carbon nanotube film is easy to be peeled off, the mixing film surface tends to be much stronger and smoother.

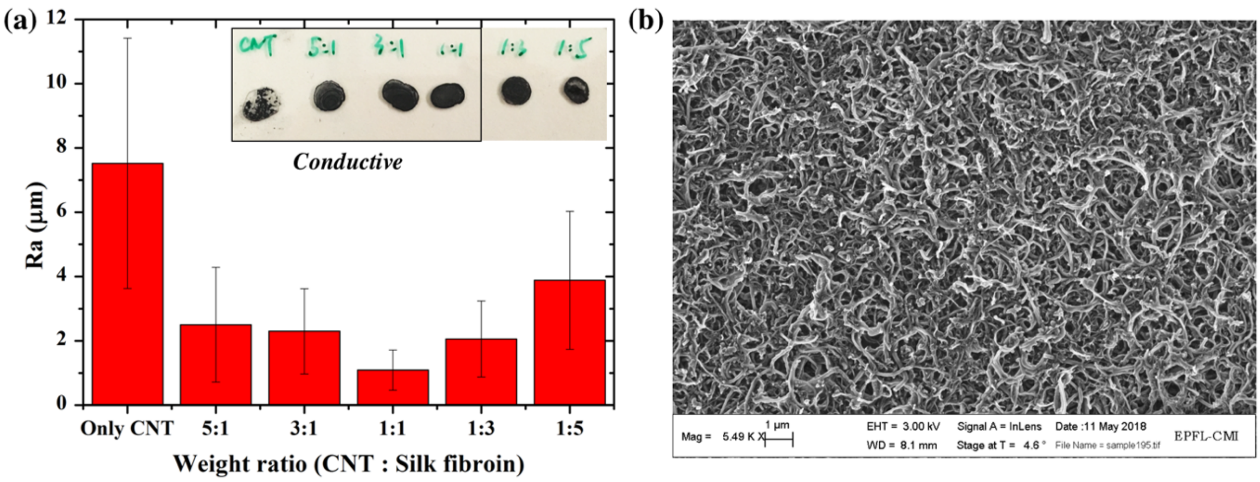
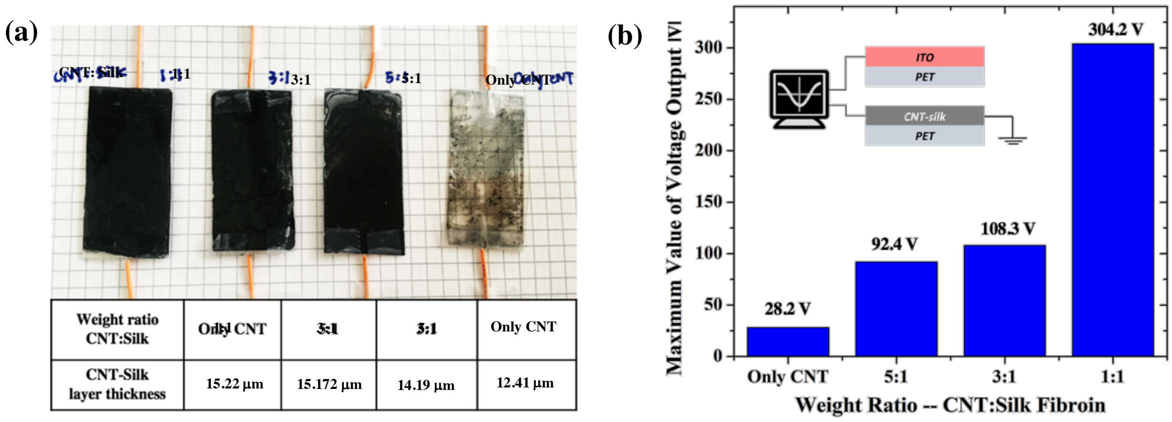


Figure 3. (a) Surface roughness of samples in different weight ratios. (b) The SEM photo of 1:1 situation.

Next, the conductive mixing solutions in different ratios were respectively coated on PET substrates (2 cm × 4 cm) to fabricate triboelectric generators. The coating method was drop coating with a syringe. 0.5 ml of mixing solution was distributed onto the surface of each sample separately. The thickness of the mixing layers of different TEGs are shown as Figure 4(a). The triboelectric pair was PET and mixing layer, which worked as both of friction material and electrode. By tapping the TEGs by hand with the frequency of 3~5 Hz, the results of their power generation effect are shown as Figure 4(b).



Weight ratio CNT:Silk	1:1	3:1	5:1	Only CNT
CNT-Silk layer thickness	15.22 μm	15.172 μm	14.19 μm	12.41 μm

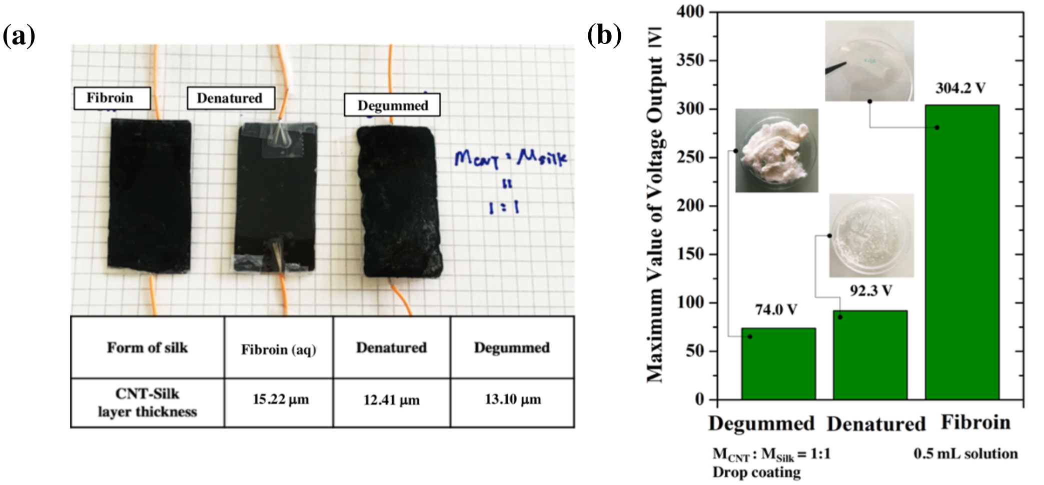
Figure 4. (a) 0.5 mL mixing solutions were drop coated on $2 \times 4\ cm^2$ *PET substrate to fabricate TEGs in different ratios. (b) The maximum output voltage achieved by the TEGs.*

In these experiments, the power generation effect was evaluated by the maximum output voltage achieved. As the result, when the ratio was 1:1, the output reached the highest value of 304.2 V. As the content of silk decreased, the output also became lower. Therefore, according to the above outcomes, the most suitable ratio is inferred to be 1:1.

3.3. Different forms of silk in the mixing solution

In many silk-related researches, three forms of silk were mostly studied: silk fibroin solution/film, degummed silk fibers before being made into solution, and denatured solids after being made into solution. In this research, mixing solutions based on different forms of silk were applied to the PET substrate at a ratio of 1:1 in the same manner and conditions as described above, as shown in Figure 5(a). From the results shown in Figure 5(b), it is obvious that different forms of silk do make difference in output power, which is firstly demonstrated so far. And silk fibroin performed much better, the inner differences in microstructures between the three forms might have influence in power generation effect, which is waiting to be further studied in the near future.

The final results of the above groups of experiments are shown in the Figure 6. The black curve shows the results of different ratios whereas the blue curve shows the results of different forms of silk. Both of the curves indicate that fibroin solution in the ratio of 1:1 performed best, whose highest output power reached 311.14 μW, 38. 89 μW/cm^2, fully capable of driving a wearable sensor that requires only 1 mW power, after being made into a garment with a larger surface area.



Form of silk	Fibroin (aq)	Denatured	Degummed
CNT-Silk layer thickness	15.22 μm	12.41 μm	13.10 μm

Figure 5. (a) 0.5 mL mixing solutions were drop coated on $2 \times 4\ cm^2$ *PET substrate to fabricate TEGs with different silk forms. (b) The maximum output voltage achieved by the TEGs.*

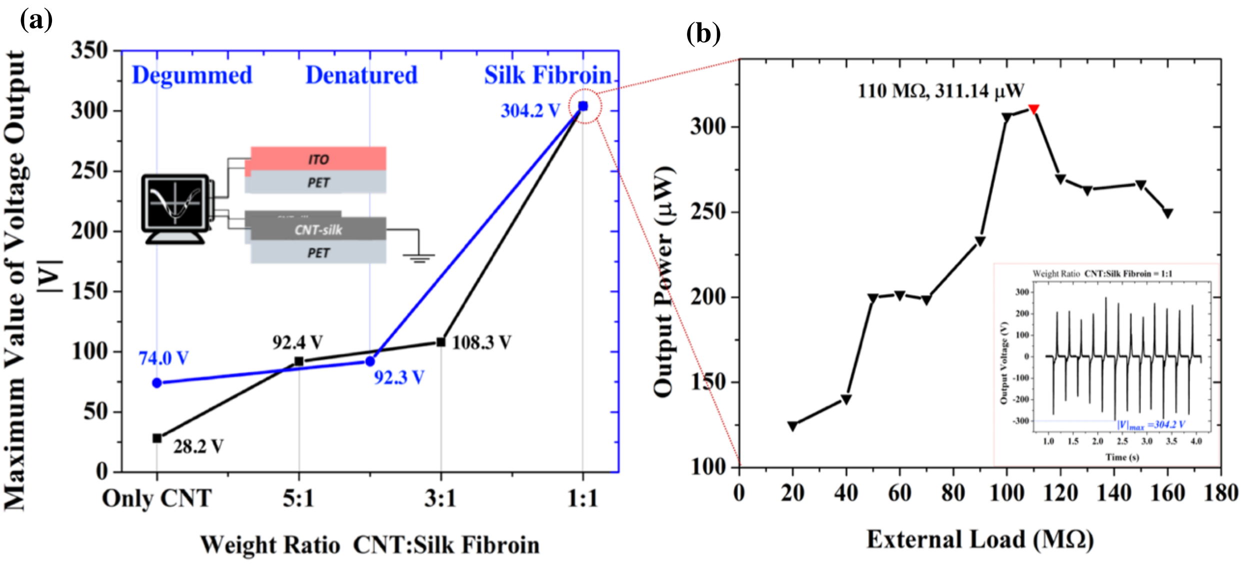


Figure 6. (a) The results of power generation effect of the two tested groups. Fibroin solution in the ratio of 1:1 performed best, whose highest output power reached 311.14μW, shown as (b).

4. Conclusion

A novel simple structured triboelectric generator with a hybrid mix of carbon nanotube and silk is firstly proposed. The mixture of silk fibroin and CNTs in weight ratio of 1:1 is demonstrated to be the optimal candidate for the TEG's performances, which achieved the highest output power of 311.14 μW, 38.89 μW/cm^2 under random hand patting. This demonstration is an important beginning of further developments, laying reliable foundation for not only membrane structure, but also the subsequent fabrication of more stretchable textile formation.

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