A Novel Soft Metal-Polymer Composite for Multidirectional Pressure Energy Harvesting

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Although the triboelectric effect has been known since 1913, little progress has been achieved toward generating electric energy using this effect. Recently, work was undertaken by the nanoscience research group in Georgia Tech to use this for energy harvesting and sensing purposes. During the last year, they used this effect as a competitive method for electric generation at micropower scales. Amazing results were published by the same group, who developed efficient triboelectric power sources by implementing micropatterns on flexible surfaces; a transparent pressure sensor; nanoscale patterns for powering portable devices; nanoparticles enhanced generators; and hybrid energy harvesters. All the mentioned works share the same benefit, i.e., micro/nanoscale patterns on the employed surfaces. Moreover, the above systems are based on two semiparallel electrodes with an intermediate material between them. In the resulting structures, at least two components move relative to each other for generating charges. Therefore, a matrix of layers containing a free space between them is necessary in the fabrication process. Providing a constant space between the layers is one of the challenges that has been dealt with by using several approaches, such as including a spacer; arc shape surfaces; springs; etc. Although these approaches can increase the efficiency of the system, they bring restrictions for implementing and aligning those systems in the integrated structures, especially where a soft body is requested, such as in the emerging field of soft robotics.

Here, we address the above limitations by introducing a very simple and cost effective approach to build a composite consisting of a rubber matrix embedding in a disordered fashion, conducting materials, and air gaps. In the proposed technology all parts can be developed together on a single surface or in a 3D structure. The fabrication process does not require bonding steps for assembling the system and creating air gaps, thus the overall fabrication complexity is dramatically reduced. Air bubbles remain trapped inside the sponge by means of solving sacrificing particles. The triboelectric phenomenon is promoted by periodic contact between miniature pieces of copper microwires encapsulated in a polydimethylsiloxane (PDMS) sponge. The strong advantages of this work are its simplicity and the cost effectiveness of the process, which makes it suitable for mass manufacturing and fabrication with easy-access facilities. Moreover, because the prototypes are made out of a mixture, the building process can be integrated with other fabrication methods in a broad range of scales. The possibility of trapping conductive wires in rubber opens the way to a new generation of energy harvesting devices, targeting all application fields where a flexible and soft material is used and/or needed. Moreover the fabrication process is not constrained to planar technology but fully 3D shapes can be built. The wired-sponge polymer could be tailored for consumer goods used in everyday life, for which energy harvesting mechanisms have not been considered to date, such as some parts of wheels, mattresses, toys and playgrounds, dance floors, etc. It is noteworthy that this approach could be addressed in advanced robotic systems where the body of the robot is built with soft materials via a bioinspired design paradigm.

On the other hand there are some aspects that must be considered, including that the amount of the charges generated on the wires and the polymer depends on the relative position in the triboelectric series, that the wires and polymer configuration and surface roughness are important, and that humidity affects charge generation. The encapsulation method that we use prevents the influence of environmental conditions on the generated charges. Furthermore, because microwires are used, we benefit from the small size of the structures, which increases the effective surfaces on which charges can be generated, and thus strengthen the triboelectric effect.

In Figure 1a, the method chosen for fabricating our prototype is depicted. It is also explained in detail in the Experimental Section. Figure 1b shows the fabricated prototype. A common twisted copper wire made of a matrix of thinner wires was chosen as the conductive material. The wires play a two-fold role: 1) they become charged on contact with the polymer and 2) they conduct the generated charges to the load. To increase the surface area, thin wires are desired so we divided them into their original constituent parts, down to 65 µm in diameter. We used sugar as a sacrificing material in order to create a gap between the wires and the polymer matrix, which is necessary for making and releasing a contact between two triboelectric materials. Such sacrificial material is also used for building a sponge shape structure from the polymeric matrix, in order to obtain a more elastic and compressible material. Figure 1c shows a scanning electron microscopy (SEM) image of a cross section of the wired-sponge generator, where the gaps...
between the wire and the polymer (in the shape of both sugar particles and the removed syrup layer) are visible. Since PDMS is placed nearly at the end of the triboelectric series\textsuperscript{[11]} and is flexible enough to make a sponge-shape polymer, it was selected as the main body of our composite. In order to prevent the negative influence of humidity on the generated charges and at the same time allow the manipulation of the electric generator, we encapsulated the composite sponge in a soft silicon rubber frame. The highly flexible and stretchable rubber was chosen to make it compatible with the multidirectional function of the generator, where the two opposite sides can be pressed towards each other.

Electric energy generation is achieved via the coupling between the triboelectric and electrostatic effects. When the composite is compressed, the conductive wires come in contact with the polymer through friction, and all components become electrically charged. Most conductive materials are placed at the top of the triboelectric series,\textsuperscript{[11]} compared to the PDMS that, instead, is at the bottom; therefore, they will be charged as positive and negative, respectively. The sponge triboelectric composite is operated by applying a periodic compressive force on one of its surfaces. Within each cycle, when the composite is released from the compressive force, it recovers its original shape because of the stored elastic energy.

Figure 2a shows a schematic of the energy harvesting mechanism. At the beginning, there is no charge on the polymer surfaces and electrodes. In the first half of the work cycle, shown in Figure 2a-I, while the material is compressed, positive charges are generated on the wires, referred to as the active electrode, and negative charges are observed on the polymer. This mechanism is the result of the triboelectric charge transfer at the interface of these materials inside the composite while they make contact with each other. The produced negative triboelectric charges can be preserved on the PDMS surface for a long time because of the nature of the insulator.\textsuperscript{[12]} However, the triboelectric positive charges on the conductive wires can flow through the connected load. We place another conductive wire as a reference electrode in the composite. In contrast to the active electrode, it is completely attached to the polymer without any gap. Because it is completely covered by the same polymer and embedded in the composite, no triboelectric charge is generated on the reference electrode during one work cycle. Therefore, in this first stage, the active electrode is positively charged (unlike the reference electrode). However, no electrical current flows from the active to the reference electrode through the load connected to the two electrodes. The reason is that the active electrode and the polymer having opposite charges are in contact, and thus the system is in the equivalent mode. On the other hand, in the second half of the work cycle, once the polymer with the negatively charged surface starts to be separated from the wire, the positive charges induced on the active wire decrease. In addition, since the reference electrode has no triboelectric charge and is electrically connected to the active electrode, the electrons flow from the reference electrode to the active electrode through the load connected to the two electrodes. The reason is that the active electrode and the polymer having opposite charges are in contact, and thus the system is in the equivalent mode. On the other hand, in the second half of the work cycle, once the polymer with the negatively charged surface starts to be separated from the wire, the positive charges induced on the active wire decrease. In addition, since the reference electrode has no triboelectric charge and is electrically connected to the active electrode, the electrons flow from the reference electrode to the active electrode through the load connected to the two electrodes. The reason is that the active electrode and the polymer having opposite charges are in contact, and thus the system is in the equivalent mode. 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producing a negative current signal. Once the two materials completely attach to each other, the charged surfaces make full contact again, and there will be no change of the induced charges on the wires, thus no output current can be observed (Figure 2 a-IV).

After a few cycles, the wires/polymer interface saturates from the triboelectric point of view. As the charge transfer is stopped, the generation of charge between the active electrodes will continue due to the electrostatic effect. In other words, because the contact surface at the wires/polymer interface has been previously charged, contact and subsequent release lead to a charge flow between the electrodes. When the surfaces are in contact, the opposite charges on the two kinds of materials will almost reach equilibrium of charge distribution and, subsequently, the charges induced on the electrodes will flow back through the load. However, by releasing the contact, driving the charges between the electrodes compensates for the charge distribution in the composite, as explained above.

One of the advantages of this design is that by periodically making and breaking contact between the opposite wire and polymer surfaces, the polymer around the wire will be charged negatively. Therefore, at least one side of each wire has a cyclic connection with the polymer and this leads to charges generated by both the triboelectric and electrostatic effects.

To explore the analytical issues, we suppose that the produced negative triboelectric charges accumulate on the inner side of the tubular polymer. The generated electrostatic field between those charges and the positive ones on the conductive wire serve the stored energy. When the composite is compressed, depending on the energy conversion efficiency, a proportion of the applied energy is converted to the mentioned electrical energy. The application and release of such force in a periodic fashion allows, in each cycle, the capture and release of energy, respectively.

The difference between the amount of stored energy (in the electric field between wire and polymer) in the two modes of compressed and relaxed position serves the consumed power in the load and connected wires. We consider a small piece of wire inside an array of bubbles encapsulated by PDMS, as shown in Figure 2 a. For the sake of simplicity, we suppose it is a long conductive cylinder placed inside a tubular shape polymer. However, when the composite is compressed, due to the softness of the polymer, it will be re-shaped around the wire to obtain an almost similar cylindrical configuration. Therefore, the same coaxial wire/tube model can be used to estimate the energy stored between those materials. The entire energy of the electrostatic field in the air gap can be calculated by:

$$U = \frac{Q^2 \ln R_2 / R_1}{4 \pi \varepsilon_0 \varepsilon_r}$$

(1)

where $R_1$ and $R_2$ are the wire's radius and the distance from the wire axis to the inner side of the polymer bubble, respectively; $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of vacuum and air; and $Q$ is the generated triboelectric charge on the wire and the polymer.

Considering an open-circuit condition, the released energy in each half cycle can be obtained by calculating the differential energy in the two ultimate positions, i.e., compressed and relaxed modes. Therefore, making a contact between the polymer and the wire brings the outer radius (i.e., $R_2$) very close to the $R_1$. If we suppose this to be $R_1 + \delta$, where $\delta$ illustrates a...
small quantity, $\Delta U$ defines the energy difference within a unit length of the wire as:

$$\Delta U = \frac{Q^2 \ln R_2/R_1 + \delta}{4 \pi e_\epsilon \epsilon_0}$$  \hspace{1cm} (2)

This clearly shows that the higher the distance between wire and polymer, the higher the generated energy. Furthermore, the generated energy is relative to the amount of the triboelectric charge ($Q$). It rises during the first few cycles to reach its own constant quantity due to the saturation of the charge transfer between the materials. Provided that some portion of the accumulated charges are discharged, for example due to the leakage during pressing, the materials will be charged again by repeating the cycling. This energy can be exploited as a current through the load connected to the electrodes.

To prove the concept, we built and tested a wired-sponge generator composed of a highly compressible PDMS sponge/copper wire composite (3 cm$^3$ in volume), which was encapsulated in silicone rubber (4 cm$^3$ of total volume). Outstandingly, the wired-sponge generator can be compressed from all sides down to 5 mm of thickness. The generator was placed between two parallel plastic plates and, while detecting the output voltage, it was periodically pressed by means of two different systems. In one case a sliding motion was produced (INSTRON R464 testing machine, Instron Corporation, Canton, Massachusetts, USA) with a higher pressure and less velocity compared to the second method (PS01-23x80F, Linear Motor, LINMOT, USA). Thus, we used both methods to cover a reasonable range of applied strains when different pressures are applied in the range of ≈0.54 Hz, where the external resistance between the two parallel plates is 10 M$\Omega$. Moreover, the influence of the frequency on the generated power was measured by increasing it at the constant strain of 45%. As explained above, in order to evaluate the function of the generator at higher frequencies, the tests were accomplished by means of the second setup. The results shown in Figure 3a demonstrate that the power increased up to 1.22 $\mu$W where the frequency experiences the rise up to 9.4 Hz. This behavior can be described by the fact that the average power is directly related to the frequency as well as the differential energy explained in the Equation (2). In other words, when a distinct amount of pressure is applied to the wired-sponge composite slowly (or the straining frequency is decreased) the charge separation/attachment rate is reduced and thus the average generated power is decreased.

Furthermore, the influence of the external load on the output voltage and the generated power was evaluated by connecting a series of different resistors to the wired-sponge generator (Figure 3c). The electrical capacitance of the composite under different applied strains was also measured, by means of a LCR meter (Agilent, E4980A), with a reference signal of 1 V peak-to-peak at 1 kHz (Figure 3d). Results show that the compression of the material to the 80% of the initial size causes a 45% increase of the composite capacitance, thus illustrating the decrease in the distance between the two different electrodes. In fact, the reference electrode was placed roughly in the centre of the composite while the active electrodes were distributed...
As a result, a compression from each direction brings the active electrodes much closer to the reference electrode, where, depending on the reduction of their relative positions for each part of the active electrode, the capacitance between them will be enhanced.

Due to the use of PDMS as the essential material for developing the composite in which a large amount of strain can be considered in the introduced generator, the device can be classified as an electroactive polymer energy harvester. Within this broad class of devices, the performance of the wired-sponge generator is comparable with dielectric EAPs because its function is based on the electrostatic effect rather than polar and ionic polymers. The generated power reported by those kinds of energy harvesters is in the range of µW to mW.\(^{14,15}\) Unlike the wired-sponge, which produces electrical energy directly from the mechanical pressure, they require bias voltage. It is noteworthy that the fabrication process of the proposed composite is very simple and cost effective, and there is still room to improve its performance to compete with the current polymeric energy converters.

As the video in the Supporting Information shows, this wired-sponge generator is able to lighten up a liquid-crystal display (LCD; JX5094PHT, Clover Display, Hong Kong) while being compressed periodically by human fingers (see Supporting Information for more discussion).

In order to evaluate how the size of the sugar particles affects the efficiency of the generator, dedicated samples were prepared by using wires from coaxial antenna cable as the active electrode. Three different types of coaxial cable-sponge generator were prepared by using sugar particles with various sizes as a sacrificing layer (see Experimental Section for details). Figure 3 summarizes how the size of the sugar particles, and thus the

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**Figure 3.** a) The measured stress and the average output power versus the applied strain to the wired-sponge generator, when the compressing frequency is 0.54 Hz. b) The dependency of the output power from the applied frequency while the constant strain is 45%, and the connected load is 5 ohm. c) The dependence of the output power and the root mean square voltage from various resistors connected as the external load where the generator is pressed down to 45% of strain under the frequency of 2.5 Hz. d) The measured electrical capacitance of the wired-sponge generator while various strain is applied. e) The output power of the coaxial cable-sponge generator in three cases corresponding to sponge templates obtained with different sugar particles. f) A comparison of the elasticity of the composites when different particle templates are used to fabricate the coaxial cable-sponge generator.
PDMS porosity, influences the output power in only 2 cm of wire length. The generated power increases when larger particles (average diameter of 1 mm) are used with a constant displacement. Indeed, as the size of particles increases, the gap between wires and polymers increases as well. Consequently, as Equation (2) shows, the produced power is increased supposing that the affected parameters for the triboelectric charging remain fixed, and Q can be considered the same for all cases.

To investigate the elasticity of the different composites made by various sugar particles, the stress-strain curve is shown in Figure 3f. As it confirms, in order to obtain a softer composite we need to use smaller particles. In fact, by increasing the size of particles, the mold is filled with fewer particles compared to when smaller ones are used. In other words, the more gaps between the sugar particles, the more polymer is needed to fill the same dimension of composite, and thus a harder composite is obtained. Furthermore, as expected, an elastic hysteretic behavior is a result of the rubber composite mechanical characteristics.

We have illustrated that by using the structure presented, we are able to sense the pressure applied to each side of the soft composite. Therefore, as future work, because this method is very cost effective and free of external powering process, we will investigate how to use the wired-sponge generator in a new generation of pressure sensors. Furthermore, as mentioned above, the triboelectric energy harvesters can considerably benefit from having nanopatterns on the surfaces that experience contact, and thus in future work will investigate how to increase the potentialities of the current device.

Experimental Section

Preparation of the Wired-Sponge Generator: A solution of water and sugar with a 1:3 volume ratio was prepared and heated to its boiling point. The sugar particles had an average dimension of 300 µm. 40 cm of a 0.65 mm copper wire bundle was untwisted and 65 µm wires were obtained. They were washed by submerging in acetone (10 min), isopropanol (10 min), and water. Then the wires were immersed in the solution for a few seconds, to become covered by the syrup. After that, in order to make this layer thinner, the syrup was dropped away as much as possible. Afterwards, the sugar particles with an average diameter of 300 µm were sprinkled on the sticky wires to attract the particles around the wires. This step was done in a cubic metal mold and followed by adding more sugar and applied pressure from the top side in order to form the sugar template for the PDMS sponge. During this step, a 0.65 mm wire, which was already covered by a PDMS thick layer, was also placed at the center of the block, and served as a reference electrode. Then the mold was carefully removed. The final sugar block containing the wires and the reference electrode was ready to be filled by a rubber. Therefore, a dish of PDMS in a ratio of 10:1 by weight was prepared and the sugar block was placed inside. The surface edge of the PDMS pre-polymer was a bit lower than the upper side of the sugar template in order to let the inside air bubbles to come out easier. PDMS was absorbed and filled the small gaps between sugar particles due largely to the capillary force. This process was assisted by vacuum for 5 h, and then cured in the ambient condition by leaving for 48 h, followed by a conventional oven curing at 85 °C for 10 min. After that, the sugar was dissolved in water assisted by ultrasonic wave exposing and heating up to 50 °C. Finally, it was dried in the vacuum oven at 80–100 °C for 2 h. In addition, the flexible frame was prepared by Ecoflex 0010 around the composite in a metal mold.

Preparation of the Coaxial Cable-Sponge Generator: The outer shield conductors of a typical coaxial antenna cables (composed of a net of wires with 100 µm in diameter) were used as the trapped wires inside the sponge cubes. Another copper wire with a diameter of 1 mm was covered by a PDMS layer resulting in a diameter of 4 mm, and it was placed in the middle of the mentioned shield, serving as a reference electrode. The wires were washed by immersing in acetone, isopropanol, and water, for 10 min each. Then the same procedures, explained above for making wired-sponge generators, were carried out to complete the composite in a 20 mm³ cubic mold, except for the last step, relative to the encapsulation in an Ecoflex frame, which in this case was avoided. The process was repeated using sugar particles with different dimensions (20 µm, 300 µm, and 1 mm of average diameter) in order to obtain sponges with different porosity. For each type, two samples were prepared and tested.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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