Constructing highly tribopositive elastic yarn through interfacial design and assembly for efficient energy harvesting and human-interactive sensing

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\textbf{ABSTRACT}

Fibers/yarns with superior triboelectrification and robust stretchability are considered indispensable building blocks for booming fiber-shaped wearable electronics. Here, a new class of highly tribopositive elastic yarn is developed through an interfacial design and assembly using polyethylene oxide/waterborne polyurethane/alliin composite as stretchable tribomaterial and polyethyleneimine/multiwalled carbon nanotubes/phytic acid polyionic nanomaterial as electrode. The contact triboelectrification and mechanical stretch behaviors of yarn are separately modulated by multiple functional groups coordination and hydrogen bond crosslinking/electrostatic interactions, realizing efficient charge transfer/accumulation capability and stretchable robustness. The optimized yarn TENG with single-electrode mode can deliver a high voltage of 137 V and power density of 2.25 mW/m\textsuperscript{2} by varying content of alliin and controlling the thickness of tribocomposite, which is superior to fiber-shaped TENGs reported thus far. Importantly, the device exhibits good electrical output stability and durability in multiple dynamic deformations or long-term service. The yarn can be easily integrated into the stretchable fabric for motion energy harvesting and can also be used as pressure/strain sensor to realize whole-body physiological signals detection and human-interactive sensing in virtual reality space. This work provides feasible proposal for the design of stretchable high-performance fiber TENGs and greatly promotes the advancement in wearable energy/sensing/interactive systems.

1. Introduction

In the era of booming development of Internet of Things (IoT) and Artificial Intelligence (AI) technologies, energy-autonomous flexible electronics that can escape from the short lifetime, demand for frequent replacement, and even potentially explosion hazard of traditional batteries are particularly in demand [1–8]. Triboelectric nanogenerator (TENG), as an emerging technology, can capture ubiquitous and irregular mechanical stimuli, particularly low-frequency (< 5 Hz) human movements, and further convert them into sustainable electricity for realizing the self-sufficient characteristic of flexible electronics [1, 9–11]. In comparison to other technologies based on physical mechanisms of thermoelectricity and piezoelectricity, etc., triboelectricity is advantageous in terms of material selection freedom, high conversion efficiency, multiple work modes, and thus has been widely used for wearable energy/sensing systems [12–16]. However, available TENG devices with planar or strip structures are difficult to adapt to irregular human movements in multiple directions and are complex to implement in practical wearable scenarios, which limits the development of wearable TENGs. Prospectively, one-dimensional fiber-shaped TENGs are highly preferable and desirable due to good shape-adaptability, air-permeability and weavability, which can be woven into breathable E-textiles or efficiently integrated with other smart garment systems [17–20].

To be more practical and efficient, fiber TENGs should be easily extensible, able to withstand mechanical deformations, and possess high triboelectrification for providing reliable and desirable output performance in long-term usage. In this regard, many attempts have been implemented to fabricate stretchable triboelectric fibers/yarns employing deformable configuration designs [19,21,22] or stretchable
electrodes/tribomaterials \cite{20,23,24}. For example, He et al. \cite{25} and Dong et al. \cite{26} developed coaxial extensible triboelectric yarns with helical structures using commercial metal wires and metal-coated yarns, respectively. They are intrinsically rigid even if they are designed with more easily deformable configurations, the wearability remains unsatisfactory. In contrast, stretchable triboelectric yarns made from conductive nanomaterials (AgNWs \cite{23}, MXene \cite{27,28}, Graphene \cite{29}, etc.) are more flexible and shape-adaptive. Unfortunately, owing to the mismatch of Young’s modulus and lack of interfacial interactions, the conductive layer tends to detach from yarn substrate and separate from tribolayer, which finally leads to device performance degradation or even device failure. Subsequently, researchers developed various triboelectric yarns based on liquid metal \cite{20,30–32} or conductive gel \cite{24,33} and achieved superior mechanical properties. The non-customizability resulting from liquid leakage or hydrogel dehydration is a non-negligible issue for these devices. The excellent electrical performances are indispensable for high-performance fiber-shaped TENG devices, however, current research works often only pay attention to the realization for device’s mechanical stretchability, ignoring the enhancement of electrical outputs and functionality of fiber TENGs, which greatly limits their practical application in the wearable system. And a majority of demonstrated yarns are tribonegative, which are usually fabricated by directly choosing elastic polymers as tribomaterials, such as thermoplastic elastomers \cite{22,31,32}, silicon rubber \cite{34,35}, etc. Although yarn with positive tribopolarity is as vital as that tribonegative yarn for the development of fiber-shaped TENGs, the relevant exploration of tribopositive yarns has rarely been investigated. Additionally, many triboelectric yarns prepared using spray/slurry-coating, injection molding, and thermal drawing techniques, etc., are limited by a long preparation time, complex equipment, high cost, or poor replicability. Therefore, it is necessary to develop stretchable triboelectric yarns with superior tribopositivity and robust mechanical properties via a simple, efficient and reproducible route to drive fiber TENGs forward rapidly.

With subtle interfacial design and assembly in this work, an elastic tribopositive yarn with high performance was successfully fabricated by orderly assembling polyethyleneimine/multiwalled carbon nanotubes/phytic acid (abbreviated as PEI/MWCNTs/PA) nanomaterials and stretchable polyethylene oxide/waterborne polyurethane/alliin (PEO/WPU/alliin, abbreviated as PWA) tribocomposite onto the yarn substrate. The electron/ion dual charge transfer induced by functional groups coordination and interfacial interaction caused by hydrogen bond crosslinking and electrostatic attraction were simultaneously introduced into triboelectric yarn, which endowed it with highly positive triboelectrification and robust mechanical stability. By adjusting controllable thickness and alliin content of PWA tribocomposite, the electrical performance was systematically optimized and output power of 2.25 mW/m was achieved. Furthermore, the output stability under

**Fig. 1.** Schematic illustration for fabrication process and potential application scenarios. (a- i) PEI amination of yarn substrate; (a-ii) A self-assembly of MWCNTs/PA layer through electrostatic attraction; (a-iii) PWA tribocomposite interface assembly via hydrogen bond crosslinking interaction and electrostatic attraction; (a-iv) Schematic diagram of tribopositive yarn/fabric TENGs for motion energy harvesting, activity monitoring, and interactive sensing. (b) Photographs of yarn in different deformable states including knotting, bending, twisting, winding, and stretching.
various deformations and repeated work cycles were also explored, confirming the durability and robustness of device. Finally, the yarn could be easily woven into an elastic energy fabric to supply power for electronics and could be inserted into a silicone rubber tube for whole body physiological monitoring and real-time human-interactive sensing, demonstrating versatile potential applications.

2. Results and discussion

2.1. Design and properties of tribopositive yarn

The stretchable tribopositive yarn consists of inner PEI/MWCNTs/PA conductive yarn and external electroactive PWA tribocomposite. Fig. 1a schematically depicts the corresponding fabrication process. Briefly, conductive yarn is prepared by alternately immersing the yarn substrate into the branched PEI cationic polyelectrolyte solution and MWCNTs/PA anionic conductive dispersion (Fig. 1a-i, ii). Through strong electrostatic attraction, PEI and MWCNTs/PA are uniformly and densely deposited on the yarn substrate (Fig. 2c, Fig. S1 and Fig. S3, Supporting Information) [36,37]. Notably, the combination of PEI polycation with abundant amino groups and PA conductive material with negatively charged phosphate groups can not only ensure the affinity of MWCNTs networks to the substrate but also compensate electrical conductivity of yarn at stretching state due to continuous ionic channels resulting from mobile ions distributed along with the PEI/MWCNTs/PA cross-linked networks. Simultaneously, PA molecules assembled on the yarn surface can also provide massive hydrogen bond cross-linking and electrostatic binding sites for subsequent assembly of tribomaterials. As everyone knows, PEO polymer is regarded as an attractive tribopositive material, yet it is a semicrystalline thermoplastic polymer with limited stretchability [38]. The eco-friendly WPU may well blend with PEO to decrease its crystallinity and increase extensibility. Moreover, the doping of polar alliin molecules is expected to give PEO/WPU composite with higher triboelectric activity [39,40]. Thus, the PWA tribocomposite with hydrogen bond crosslinking network is spontaneously assembled on the surface of conductive yarn by immersing it in the mixture of PEO, WPU, and alliin molecules (Fig. 1a, iii and Fig. S2, Supporting Information). Interestingly, the thickness of PWA tribocomposite is precisely controllable and highly uniform by adjusting assembly time, which benefits from sustainable interfacial hydrogen bonding interaction and electrostatic attraction between PEI/MWCNTs/PA conductive layer and PWA tribocomposite (Fig. S3, Supporting Information). This simple
self-assembly accompanying the successive interface design is superior to previously reported coating methods, such as spray coating, slurry casting, etc [41,42]. As shown in Fig. 1b, as-prepared tribopositive yarn can sustain multiple mechanical deformations including stretching, bending, twisting, knotting, and winding, and can be conformally applied to the non-planar human body even be woven into breathable fabrics, showing great potential in motion energy harvesting, body physiological monitoring and wearable human-machine interaction (Fig. 1a, iv).

The microscopic morphologies were characterized in Fig. 2a-b. Tribopositive yarn exhibits a seamless core-sheath structure composed of PEI/MWCNTs/PA conductive yarn (colored with silvery-white) and PWA tribocomposite (colored with purple), with uniform thickness of tribolayer and a rough wrinkled surface. Fig. 2c reveals that elastic substrate is conformally and tightly covered by PEI/MWCNTs/PA conductive layer, on which rich MWCNTs are randomly distributed without visible agglomeration, originating from the stable and uniform dispersibility of MWCNTs/PA solution. Moreover, the electrical conductivity of PEI/MWCNTs/PA yarn under different assembly cycles and tensile strains was investigated in Fig. 2d. The pristine yarn substrate becomes conductive as it is deposited with PEI/MWCNTs/PA network for the first time. With the increase in assembly times, the yarn resistance decreases gradually and tends to be stable. And when the yarn is stretched at a higher strain level, the resistance increases slightly, which is mainly related to the reduced diameter of the stretched yarn.

The phase structure of PWA tribocomposite was revealed by X-ray diffraction (XRD) measurement in Fig. 2e. Different from pure PEO film, the intensity of characteristic peaks at 2θ = 19.2° ([120] crystal plane) and 23.2° ([112] crystal plane) in the PWA tribocomposite is visibly weakened and corresponding peak shapes are widened. This illustrates that more disordered arrangements of molecular frameworks and lower crystallinity are formed in PWA tribocomposite, greatly contributing to deformation and flexibility of tribopositive yarn. Video S1 (Supporting Information) intuitively demonstrates that yarn can be easily and repeatedly stretched at different strains without any shed and fracture of surface coating. This benefits from highly entangled molecular networks resulting from hydrogen bond cross-linking in the PWA tribocomposite and stable multilayered interface interaction between substrate/conductive layer/tribocomposite [43-47]. The strain-stress curve of tribopositive yarn was further evaluated in Fig. 2f. And the yarn exhibits high mechanical strength of ≈ 31 MPa, low Young’s modulus of ≈ 0.07, and good breaking elongation of ≈ 265%. The slight fluctuations of stress-strain curve can also be observed, which may be caused by the crack or fracture of PWA tribocomposite during the tensile process. Simultaneously, the fatigue hysteresis in loading/unloading cycles was measured to explore the elastic recovery performance of tribopositive yarn. As displayed in Fig. 2g, apart from the hysteresis in the first cycle, the yarn device presents an almost coincidental hysteresis loop from the second time to the twelfth time, demonstrating robust elastic resilience and fatigue resistance. The stable and robust mechanical behavior of tribopositive yarn contributes to conformal contact to adapt to complex movements and deformations of the human body.

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In addition, according to a simple measurement in previous work [48], the ability of contact triboelectrification of tribopositive yarn is also explored, as shown in Fig. 2h and Supplementary Discussion S1. When one yarn comes into contact with a range of positive tribomaterials including PEO, PEO/WPU, copper, PET, corresponding signal waveforms are both up-down peak shapes, which are consistent with that of PWA/LTV (low-temperature vulcanized silicone rubber) tribopairs. This implies that the positive triboelectricity of PWA tribocomposite is much higher than that of positive tribomaterials commonly used in triboelectric series, which is favorable for efficient contact electrification of tribopositive yarn. Based on good mechanical robustness and superior triboelectric property, this tribopositive yarn is expected to become a promising candidate in wearable fiber TENGs.

2.2. Electrical performance optimization of tribopositive yarn TENG

The operating mechanism of tribopositive yarn TENG is based on the coupling effects of contact electrification and electrostatic induction [12,49,50]. Unlike traditional TENGs, surface charge accumulation in PWA tribocomposite of tribopositive yarn not only originates from electron transfer but also ion transfer during the contact tribo-electrification process. This characteristic of double charge transfer benefits from the cooperation between effective electron-donating groups and rich protonated amino groups distributed on the surface of PWA tribocomposite. Due to the doping of alliin molecules with high polarity, water molecules from the surrounding environment tend to be adsorbed on the yarn surface for a nano water membrane, which can provide a transfer channel for mobile ions, such as hydroxide [51-53]. As illustrated in Fig. 3a-d, when tribopositive yarn is in contact with other negative tribomaterial, electrons are transferred from PWA tribocomposite to negative tribomaterial, accompanied by the transfer of mobile ions. In this case, a large number of positive charges induced by the sum of dual transfer of electron and ion will be gathered on the PWA tribocomposite. As they move away from each other, an electrical potential difference will be established, allowing free electrons to flow from the ground to electrode until an electrostatic equilibrium is reached (Fig. 3a-ii, iii). As the negative tribomaterial approaches tribopositive yarn again, electrons flow back to the ground, resulting in reversed electrical signals (Fig. 3a-iv). Thus, repeated contact-separation movements can continuously bring alternating electricity output from the yarn TENG.

The effect of alliin content of PWA tribocomposite on electrical performance was investigated for optimizing yarn TENG. Herein, tribopositive yarn with the length of 4 cm and LTV composite fabric are prepared and separately attached to acrylic sheets interfaced with a linear motor for electrical output measurements. As shown in Fig. 3b-c and Fig. S4 (Supporting Information), stretchable tribopositive yarn with PEO/WPU tribolayer can provide a considerable output voltage of 51 V, current of 0.97 µA, and charge of 6.9 nC in single-electrode operation mode. When alliin content of 0.05 g/mL is introduced to PEO/WPU tribolayer, output voltage, current, and charge of tribopositive yarn increase by 15 V, 0.21 µA, 2.0 nC, respectively. And the electrical output further exhibits remarkable improvement as alliin content increases to 0.30 g/mL. Fig. 3d intuitively displayed output peaks of yarn TENGs versus alliin content. The alliin content of 0.30 g/mL is observed as the critical point for performance enhancement, at which output voltage and current reach maximum values of 110 V and 1.8 µA, which are 2.2 times and 1.9 times higher than that of PEO/WPU yarn device, respectively. This is closely related to the outstanding charge transfer and accumulation mechanism in the PWA tribocomposite. On the one hand, compared with PEO/WPU yarn, the PWA yarn surface is endowed with rich polar sulfide (-S=O) and amino (-NH2) functional groups due to the introduction of alliin molecules, which can work cooperatively with ester oxygen groups to lower a work function and higher affinity for electron donation than PEO/WPU tribolayer (Fig. 3e and Fig. S5 in Supporting Information) [54,55]. FTIR spectra further confirmed surface functional groups on the tribopositive yarn. As shown in Fig. 3f, in addition to absorption bands centered at 3317 cm⁻¹ (O-H and N-H) and 1100 cm⁻¹ (C-O-C), extra characteristic bands (1015 cm⁻¹) appeared in PWA tribocomposites, showing the presence of S=O polar groups [56-59]. And with alliin content increasing from 0.05 to 0.60 g/mL, the peak intensity of S=O is also gradually strengthened. It is also found that the peak at 3217 cm⁻¹ is slightly red-shifted as alliin content increases, indicating the hydrogen bond cross-linking interactions among WPU, alliin, and PEO polymer chains [43,56,57]. The multiple functional groups cooperation among sulfide, amino, and ester oxygen groups distributed on the yarn surface can significantly raise the number of transfer electrons during
contact electrification and thus lead to the larger accumulation of surface tribocharges. On the other hand, the higher alliin content of PWA tribocomposite can induce rapid and effective transfer of more mobile ions during contact triboelectrification, which also greatly contributes to the increase of surface charge density of tribopositive yarn (Fig. 3e). However, excessive alliin content (> 0.30 g/mL) may cause a thick water membrane on the yarn surface due to massive water molecule absorption, at which triboelectrification is dominated by water molecules instead of PWA tribocomposite with its triboelectric pair [52,60]. In this respect, surface charge leakage increases largely and the synergistic effect of charge transfer may be destroyed, ultimately leading to a decline in the electrical performance of yarn TENG.

Fig. 3. Work principle and electrical output optimization of yarn TENG. (a) Work mechanism of device in single-electrode mode. (b) Output voltage, (c) current of device at different alliin contents. (d) The electrical outputs of device versus alliin contents. (e) Comparison diagram of tribocharge accumulation mechanism between PEO/WPU and PWA tribopositive yarn TENGs. (f) FTIR spectra of alliin and PWA tribocomposites with different alliin contents. (g) Digital photo of tribopositive yarns with various diameters/PWA thickness. (h-i) Electrical outputs of yarn TENG versus diameters.
Furthermore, the effect of the thickness of PWA tribocomposite on output signals of tribopositive yarn was also investigated. A series of yarns with different diameters/tribocomposite thicknesses (Fig. 3g) were prepared by controlling assemble time and corresponding outputs were measured in Fig. 3h-i and Fig. S6 (Supporting Information). As the diameter increases from 1.51 mm (~5 µm thickness of PWA tribocomposite) to 1.71 mm (~105 µm thickness of PWA tribocomposite), the output voltage and current leap up to 137 V and 2.1 µA, respectively, which is attributed to the accumulation of more tribocharges in thicker PWA tribocomposite. A further increase in diameter/thickness leads to

![Image](image_url)
performance degeneration, resulting from an insufficient electrostatic induction in the excessive tribolayer [61]. Through the above systematic discussion, tribopositive yarn with 0.30 g/mL alliin content and 105 μm thickness of PWA tribocomposite achieves the highest electrical performance, which can be selected for subsequent study.

2.3. Output characteristics of tribopositive Yarn TENG as power source

Given the practicability of tribopositive yarn TENG, the electrical outputs versus a series of external load resistances were investigated. As shown in Fig. 4a, the output voltage exhibits a growth trend as load resistance increases. An instantaneous power density of 2.25 mW/m² shown in Fig. 4a, the output voltage exhibits a growth trend as load resistance increases. An instantaneous power density of 2.25 mW/m² calculated by the formula of $P = \frac{U^2}{R}$ (U, R, and L is the output voltage, resistance, and effective length) is obtained at a load resistance of 40 MΩ, which is superior to the vast majority of fiber-shaped TENGs reported thus far. The detailed comparison is listed in Table S1 (Supporting Information). The electrical outputs under impact frequencies were also measured in Fig. 4b. The output values of yarn TENG at fast contact frequency are higher than those at slow contact frequency, which is ascribed to faster induction rate and charge transfer. Furthermore, the power generation capacity of yarn TENG at different tensile states and repeated tensile/bend deformations was examined in Fig. 4c. Fig. S7 and Fig. S8 (Supporting Information). The output signals slightly decrease as tensile strain increase from 0% to 133%, which is mainly related to the reduced effective contact area between yarn and outside tribomaterial. However, after being repeatedly stretched (40% of strain) and bent for 500 cycles, the yarn TENG does not exhibit noticeable fluctuation in electrical outputs. Besides, the output current of yarn TENG was checked under 10800 repeated operations or after long-term storage, respectively. It is observed that the output signals of device are nearly comparable to the initial value (Fig. 4d), which further demonstrates its good output reliability and durability in long-term service.

Owing to high power density, output reliability and robust deformability, tribopositive yarn is further woven into stretchable fabric TENG as wearable power source for efficiently activating electronics. Fig. 4e and Fig. S9 (Supporting Information) describe the woven structure of fabric TENG prepared by simply weaving tribopositive yarn (warp) and commercial elastic yarn (weft). Due to intrinsic alternating signal pulses, electrical outputs of fabric TENG need to be modulated through a rectifier bridge and stored in commercial capacitors for use (Fig. S10 in Supporting Information). The charging capacity of fabric TENG (~5 × 7 cm²) across different capacitors and under various charging frequencies was firstly investigated in Fig. 4f-g. Capacitors with capacitances of 1, 2.2, 10, 47, and 100 μF can be rapidly charged to 12, 11, 7.3, 4.6, 3 V in 100 s respectively. The lower capacitance of capacitor obtains the faster charging efficiency at the same potential. Moreover, fabric TENG presents different charging rates for a capacitor of 4.7 μF at multiple charging frequencies. High operating frequency is beneficial to accelerate the charging speed. When continuous charging and discharging a capacitor with a capacitance of 10 μF, as demonstrated in Fig. 4h, the fabric TENG exhibits a sustainable and reliable working state. A piece of woven fabric sewn on the bottom of sock can easily light up LED arrays with the “NUS” logo to full brightness in single-electrode mode and also successfully drive a digital alarm clock under continuous foot stepping (Fig. 4i, Fig. S11, Video S2 and Video S3 in Supporting Information). These demonstrations confirm the capability of fabric TENG to capture enough motion energy for driving microelectronics without any external power supply.

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2.4. Tribopositive yarn TENG as wearable self-powered sensor

Using flexible sensors to extract physiological signal characteristics of joints, key parts, and even the whole body is of great significance for health management and disease prevention. To better facilitate body sensing, the proposed tribopositive yarn is embedded in a slender silicon rubber tube to form a coaxial pressure/strain sensor, as displayed in Fig. 5a and Fig. S12 (Supporting Information). With the applied vertical pressure increasing from 0.35 kPa to 26.25 kPa, the voltage signal increases from 2 V to 7 V (Fig. 5b). And the sensitivity displays two sensory intervals, i.e., high sensitivity of 1.1 V/kPa at below 5.25 kPa pressure and relatively low sensitivity of 0.08 V/kPa at beyond 5.25 kPa pressure, which is determined by the effective contact area between two tribomaterials in the contact-compression process. Moreover, the sensor can respond to repeated tensile stimuli or different tensile strains. As shown in Fig. 5c, as the yarn sensor is repeatedly stretched and quickly released, the real-time voltage shows a periodically synchronous increment/ decrement. And when the yarn sensor is stretched from 25% to 125% strain, the electrical output almost linearly increases from 0.97 V to 3.90 V (Fig. S13, Supporting Information), exhibiting good real-time responsiveness.

Based on the above advantages, this yarn sensor can be well adapted to complex forms of body physiological signal detection in a user-interactive manner. As presented in Fig. 5d and Fig. S14 (i-ii) (Supporting Information), voltage signals caused by chewing, swallowing, coughing, nodding and turning head can be collected by fitting yarn sensor on the volunteer’s neck. Noted that signal difference in amplitude between a slight nod and severe nod can also be distinguished clearly. This capture for subtle physiological signals may be used to guide the rehabilitation of patients with movement disorders such as paralysis or systemic atrophy. Furthermore, the yarn sensor is capable of perceiving vocal cord vibration caused by saying words or short sentences, such as, “Hello,” “Hi,” “nana,” and “Oh, my god”. Each word/sentence is recorded six times in Fig. 5e. It is observed that the corresponding voltage curve exhibits a specific waveform and signal characteristic in each curve is highly similar, indicating good accuracy and reproducibility for speech recognition. This capability is expected to help individuals prevent and diagnose throat diseases, such as damaged vocal cords. In addition to making a sensitive response to stimuli at the skin level, the yarn TENG sensor can also track joint movements throughout the whole body. As displayed in Fig. 5f, the sensor is attached to the waist of volunteer for sitting or standing posture detection. Once the volunteer’s spine arches backward, the sensor will immediately generate an upward voltage signal, otherwise, it will deliver a downward signal, which can remind individuals to keep the correct physical shape. Additionally, the yarn sensor can independently achieve the detection of metacarpophalangeal joint vibration (Fig. S14 (iii)), proximal interphalangeal joint bending (Fig. 5g), elbow bending (Fig. 5h), ankle rotation (Fig. 5i) and knee bending movements (Fig. 5j), which, in turn, allows real-time manipulation of object movements in real/virtual space for realizing human-interactive sensing. Fig. 5k also displays the amplitude difference of voltage signal caused by different foot activities including walking and running, which can be used to predict movement style. These demonstrations illustrate that the yarn TENG sensor enables complex physiological characteristics and movement behaviors to be transformed into quantified and readable voltage signals, thereby guiding individual lifestyle to be healthy and intelligent.

2.5. Tribopositive yarn TENG for human-interactive sensing

To expand the potential application, the above yarn sensors are further integrated into garments for realizing human-machine interaction sensing. As depicted in Fig. 6a-i, a wearable human-machine interface based on triboelectric glove with four yarn sensors is designed and sensors No. 1, 2, 3 and 4 are designed as the forward-movement sensor, backward-movement sensor, leftward-movement sensor, and rightward-movement sensor in this scenario, respectively. It is possible to achieve flight control of virtual drone in different directions by using multiple gestures to trigger corresponding yarn sensors. The control system is depicted in Fig. 6a, which consists of the
triboelectric glove, processing circuit, Arduino for data collection and a virtual display interface. As shown in Fig. 6 b-i, when the index finger bends or squeezes against the thumb side, middle finger side and little finger bends, sensors from No. 1 to No. 4 will generate corresponding voltage signals, thus commanding the drone to move forwards, leftwards, rightwards and backwards, respectively (Fig. 6 b-iii). Voltage signal patterns of sensors in responses to corresponding gestures are recorded in Fig. 6 b-ii. Moreover, simultaneous triggering of two sensors allows for more flight direction of drone, such as right-forwards and left-forwards. Video S4 (Supporting Information) intuitively demonstrates real-time control for drone by triboelectric glove. In addition, another interactive manipulation of playing golf in virtual space is also presented. As shown in Fig. 6c, sensors No. 1, 2, 3 are used as finger bending sensor, foot pressure sensor, and arm bending sensor respectively, which are integrated into commercial oversleeve and the bottom of sock. The illustrations schematically show the structure of yarn or fabric sensors in this demo. Fig. 6d-i displays output patterns, in which the positive voltage peak of sensors No. 1, 2 and 3 are defined as trigger commands for grabbing club, adjusting posture, and striking ball, respectively. Once the volunteer holds the club in real space, that is, the index finger bending triggers sensor No. 1, the virtual golfer takes the same action immediately, as shown in Fig. 6d-i, ii. Similarly, when the left foot moves slightly or elbow bends, sensors No. 2 and No. 3 will work, allowing the virtual golfer to make posture adjustment and stroke actions, respectively. In particular, if the elbow bends at different angles (30° and 90°), sensor No. 3 will generate signal peaks with notable amplitude differences for controlling the strike strength of virtual golfer, thereby realizing multiple landing modes, such as ground ball or flying...
Fig. 6. Tribopositive yarn TENG for human-interactive sensing. (a) Flow chart of the control system for manipulation in virtual space. (b) A glove stitched with four yarn sensors for flight direction control of a virtual drone: six hand gestures corresponding to the drone movements in the six directions (b-i); the signal patterns of sensors corresponding to the six hand gestures (b-ii); corresponding actions of drone including forward/backward control, leftward/rightward control, and right-forward/left-forward control (b-iii). (c) Schematic diagram of sensors distribution on the volunteer body, including finger bending sensor (sensor 1), foot pressure sensor (sensor 2) and arm bending sensor (sensor 3) and the structure of adopted tribopositive yarn and fabric sensors. (d) Signal patterns of three sensors and corresponding actions (grasping the club, adjusting posture, and striking ball) of virtual golfer.
ball. The corresponding actions of golfer in virtual space are presented in Fig. 6d–ii and an intuitive demonstration can be found in Video S5 (Supporting Information). These demonstrations illustrate the feasibility of using yarn TENG to manipulate objects in the virtual world, which is expected to facilitate the advancement of wearable TENGs in human-machine interaction and artificial intelligence. Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2022.106956.

3. Conclusion

In summary, a highly stretchable stretchable yarn composed of PWA tribocomposite and conductive polyionic nanomaterial is proposed for the first time through subtle interfacial design and assembly route. The cooperation of abundant functional groups and hydrogen bond crosslink/electrostatic interactions realize good positive triboelectrification and robust mechanical extensibility at the same time. The optimum single-electrode yarn TENG using PWA tribocomposite with 105 µm thickness and 0.30 g/mL alliin content is capable of providing a high output voltage of 137 V and power density of 2.25 mW/m, which is attributed to efficient charge accumulation mechanism resulting from electron/ion dual transfer. Moreover, triboelectric yarn TENG exhibits output stability and durability even after repeated stretching/bending or multiple working cycles. The yarn can be woven into an energy fabric for collecting human motion energy and can also be embedded in a slender silicone rubber tube to form a robust pressure/sensor for detecting body physiological signals and joint actions. More importantly, the yarn sensor can be integrated into the garment, enabling real-time human-interactive control in the virtual space with the help of signal processing circuit. This work opens a new window for the design of high-performance E-yarns based on triboelectric effect to facilitate advances in personal energy/information/health management and digital wearable interactive systems.

4. Experimental section

4.1. Preparation of conductive yarn

The stretchable conductive yarn was manufactured using interfacial assembly technology. Firstly, the yarn substrate (1.50 mm diameter) was rinsed with acetone, alcohol, and deionized (DI) water to remove surface impurities. The cleaned and pre-stretched yarn was immersed into PEI solution (20% w/v, Sigma-Aldrich) for introducing amine groups to the surface. Simultaneously, the MWCNTs (length of 0.5–2 µm, > 95% wt% purity) were uniformly dispersed in PA/alcohol solution (50% w/w, Sigma-Aldrich) using ultrasonic vibration for obtaining 5 mg/mL of MWCNTs/PA dispersion. Subsequently, aminated yarn was treated with MWCNTs/PA conductive solution to obtain stretchable conductive yarn. These processes could be repeated several times until desired conductivity was obtained.

4.2. Fabrication of electroactive tribopositive yarn

PEO (7 wt%) solution was obtained by dissolving PEO powders (average Mw = 100,000) into DI water under magnetic stirring at 50 °C. Subsequently, the WPU polymer (PU-3011) was added to the PEO polymer solution in a mass ratio of 1:1 to prepare the PEO/WPU mixture. Afterward, alliin (S-Allyl-L-cysteine sulfoxide, C\textsubscript{3}H\textsubscript{12}N\textsubscript{3}O\textsubscript{5}S) solutions with different contents (0.05, 0.15, 0.30, 0.45, 0.60 g/mL) were mixed with PEO/WPU solution and subjected to a subsequent mechanical stirring at room temperature for uniform PEO/WPU/alliin mixture. At last, conductive yarns prepared above were vertically immersed in PEO/WPU/alliin mixture and further assembled to obtain the positive PWA tribocomposite. Note that the thickness of tribolayer can be precisely controlled by adjusting assembly time. When the assembly times are 5 s, 10 s, 40 s, 80 s, 120 s, the diameters of tribopositive yarn with 1.51 mm, 1.58 mm, 1.71 mm, 1.87 mm, 2.07 mm can be prepared, respectively. The diameter of yarns was measured by digital thickness gauge.

4.3. Characterisation and measurement

The field-emission scanning electron microscope (FE-SEM, Hitachi Regulus 8230) was employed to observe the surface and cross-sectional morphology. An electronic tensile machine was used for measuring the mechanical properties. The surface chemical composition was examined by Fourier transform infrared spectrometer (FTIR Spectrometer, NEXUS-670). The phase structure was revealed by X-ray diffraction spectroscopy. The electrical outputs were measured via a programmable electrometer (Keithley 6514). The output data were acquired and saved by a multichannel oscilloscope (DSOX3034A, Agilent).

CRediT authorship contribution statement

Zhijing Bai: Conceptualization, Methodology, Investigation, Visualization, Formal analysis, Writing – original draft.
Tianyi He: Methodology, Software.
Zixuan Zhang: Data curation, Software, Visualization.
Yunlong Xu: Data curation, Investigation, Writing – review & editing.
Zhi Zhang: Methodology, Writing – review & editing.
Qiong-feng Shi: Methodology.
Yaqin Yang: Methodology.
Buguang Zhou: Validation, Formal analysis.
Minglu Zhu: Methodology.
Jiansheng Guo: Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.
Chengkuo Lee: Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.106956.

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Z. Bai et al.

Nano Energy 94 (2022) 106956


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