1. Introduction

Silicon is the second most abundant element on the earth and the dominant material in the established modern microelectronics industry.\(^1\)–\(^5\) It is also becoming a promising host material for future quantum processors that can be implemented using all-electrical control of silicon based devices.\(^1\)–\(^5\) Among all kinds of silicon nanostructures, the emerging silicon quantum dots (SiDdots) have received significant attention, due to their unique optoelectronic properties.\(^1\)–\(^11\) In particular, compared to many semiconductor quantum dots, the attractive merits of luminescent SiDdots include low toxicity, biodegradability, natural abundance and compatibility with the existing silicon based technologies.\(^1\)–\(^11\) While the research on SiDdots is still in its early stages, they have shown great potential in quantum computing, chemical sensing, photovoltaics, phototransistors, and bioimaging, among others.\(^1\)–\(^6,12\)–\(^38\)

Combining SiDdots and polymers into a hybrid opens the door to a new class of silicon based materials.\(^6,23\)–\(^30\) SiDdots/polymer hybrids can possess the properties of individual components, and may exhibit hybrid characteristics resulting from the synergistic interactions between SiDdots and polymers.\(^6,23\)–\(^38\) SiDdots/polymer hybrids have evinced their compelling properties in solid state lighting, solar energy harvesting and light emitting diodes (LEDs).\(^6,23\)–\(^38\) Despite that, SiDdots/polymer hybrids remain in their infancy of development.\(^6,23\)–\(^38\) The use of SiDdots has been limited to including their optical responses into SiDdots/polymer hybrids.\(^6,23\)–\(^38\) Especially, in the field of energy harvesting, the applications of SiDdots and SiDdots/polymer hybrids are currently confined to light converting photovoltaic electronics.\(^6,23\)–\(^38\) Considering their diverse photoelectric properties, the potential of environmentally benign SiDdots is far from being fully exploited in state-of-the-art SiDdots/polymer hybrids.\(^6,23\)–\(^38\)

The rapid expansion of the internet of things (IoT) requires flexible, multi-functional and self-powered optoelectronic devices owing to their wearable and portable applications.\(^39\)–\(^64\) A self-powered electronic device is capable of independent operation by harvesting kinetic mechanical energy from its working environment.\(^39\)–\(^45,56\)–\(^64\) The transduction mechanisms are based on the electromagnetic effect, electrostatic effect, and piezoelectric effect.\(^39\)–\(^42\) Thereinto, piezoelectric nanogenerators...
PNGs have been proved as a simple, cost-effective, and efficient means for generating electricity from mechanical energy in the low-frequency range.\textsuperscript{39-45,56-64} In addition, the output piezo-signals of PNGs can be used in the reliable sensing of physical or chemical motions.\textsuperscript{39-45,56-64} Nevertheless, there are still some major obstacles that can slow down and even exclude their practical implementation in the internet of things.\textsuperscript{1-5,39-45,56-64} One challenge is boosting up piezoelectric power conversion efficiency in flexible and self-powered opto-electronic devices.\textsuperscript{39-64} Moreover, how to increase their compatibility with existing silicon based infrastructure, in terms of materials design and device assembly, remains an open question.\textsuperscript{6-8,39-42} Since modern technologies depend on semiconductor silicon, the solution to this problem is very critical in accelerating the development of current and future self-powered nanosystems.\textsuperscript{6-8,39-42}

Here, we demonstrate for the first time that the inclusion of an extremely small amount of SiDs enables a significant enhancement of the piezoelectric response of the resulting SiDs/polymer hybrid. Meanwhile, the hybrid retains the photoluminescent response of the encapsulated SiDs. A flexible, luminescent, and macro-/micro-/nanoscale textured hybrid

![Fig. 1](image_url)
fabric is fabricated by electrospinning SiDs and polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) using special mixed spinning solvents (Fig. 1a). The luminous SiD hybridized fabric is further integrated into a prototype PNG device to evaluate its piezoelectric outputs (Fig. S1, 1b and S2, ESI†). Strikingly, the voltage output and current output of SiDs/PVDF-TrFE fabric comprising 0.2 wt% SiDs can reach 446 V cm$^{-3}$ and 8.1 μA cm$^{-3}$, respectively, which are almost 11 times and 19 times higher than the voltage output and current output of pristine PVDF-TrFE fabric, respectively.

Moreover, the SiDs/PVDF-TrFE based piezoelectric nanogenerator, as a power source for commercial LEDs, exhibits a highly durable and highly stable piezoelectric response in more than 10 000 uninterrupted load cycles. As a proof of concept, in the scenario of a tennis match, the developed luminescent PNG prototype device is used as a flexible and self-powered tactile sensor for real time sports monitoring and athlete physiology monitoring. It shows ultrahigh sensitivity in sensing subtle physiological signals and small external forces.

2. Results and discussion

Fig. 2a shows the digital images of the as-fabricated SiD colloidal solution under sunlight. The initial solution of SiDs was further purified by dialysis for later use. Transmission electron microscopy (TEM) was utilized to directly reveal the
size, distribution, and morphology of the dialyzed SiDs, and their dispersion in the electrospin hybrid fibers. The high resolution TEM (HRTEM) image shows that the freestanding SiDs are spherical particles, and they have good monodispersity in the used solution (Fig. 2b). The HRTEM image of individual SiDs also demonstrates high crystallinity of the as-prepared SiDs. The well resolved lattice fringes, spaced by 0.3 nm, are indicative of the (111) lattice planes of crystalline silicon.\textsuperscript{6,16–30} Moreover, TEM clearly confirmed that the SiDs were successfully incorporated within the electrospin SiDs/PVDF-TrFE micro-/nanofibers, although they readily self-organized to form nanoscale assemblies in PVDF-TrFE copolymer (Fig. 2c).

Fig. 2d–f show the photoluminescence (PL) excitation/emission spectra, CIE diagram, and fluorescence image of the as-synthesized SiDs. The SiDs show blue color fluorescent emission with the optimal excitation wavelength at 354 nm and the optimal emission wavelength at 442 nm, respectively. Also, the blue emitting SiDs exhibit an absolute PL quantum yield (QY) of 22.46%, which is adequate for some appealing applications requiring fluorescence response. Fig. 2g, h show the PL excitation and emission spectra and CIE diagram of the SiDs/PVDF-TrFE mixture. With excitation/emission peaks at 348/441 nm, the blue luminescent SiDs/PVDF-TrFE still possesses a considerable PL QY of 21.50%. Moreover, the direct fluorescence microscopy observation further demonstrates the successful inclusion of the fluorescent SiDs in the PVDF-TrFE matrix by the electrospinning process (Fig. 2I). This enables the straightforward fabrication of a blue-emissive SiDs/PVDF-TrFE hybrid micro-/nanofiber. We also noted the difference in PL excitation and emission spectra between SiDs and SiDs/PVDF-TrFE (Fig. 2d, g). Compared to those of SiDs, the PL excitation/emission peaks of SiDs/PVDF-TrFE were blue-shifted. It has been evidenced that, in addition to size effects, the surface states of SiDs play a key role in defining their photophysics.\textsuperscript{6,9,10,23–30} Hence, the blue shifts of the maximum excitation/emission peaks in PL spectra may indicate the occurrence of interactions between SiD surfaces and PVDF-TrFE molecules in the hybrid.\textsuperscript{6,23–10,62}

The macro- and micro-scale structures of one dimensional (1D) fibrous materials are of importance in determining the final electrical properties of the resulting two dimensional (2D) hybrid fabrics.\textsuperscript{65–67} Fig. 3a, b show the SEM images of the electrospun fabrics of the pristine PVDF-TrFE and the SiDs/PVDF-TrFE hybrid comprising 0.2 wt% SiDs, respectively. For the convenience of comparison, the hybrid fabrics with different SiD contents are named SiD-x. The x represents the mass ratio of SiDs to PVDF-TrFE, which is x per thousand. Combined with TEM observations (Fig. 2c), SEM revealed that the self-organization of the guest SiDs in the host matrix of PVDF-TrFE resulted in a special cowpea-like structure of individual hybrid fibers, which is quite distinct from that of individual pristine PVDF-TrFE fibers. With the increase of the SiD content, this phenomenon is more obvious (Fig. S3, ESI†). The fiber diameter distribution of electrospun fabrics was further

Fig. 3  SEM of (a) pure PVDF-TrFE and (b) SiD-2 fibers. Diameter distribution histograms of (c) pure PVDF-TrFE and (d) SiD-2 fibers. (e) DSC, (f) XRD, and (g) FTIR profiles of SiDs/PVDF-TrFE hybrid fibers, with different contents of SiDs. All these fibers are fabricated by electrospinning at an applied voltage of 15 kV.
especially, it was constructed from a hybridized fiber with a delicate micro/nanoscale hierarchical structure. The host PVDF-TrFE is a semi-crystalline piezo-copolymer with five crystal forms: α, β, γ, δ and ε, and the piezoelectric output depends mainly on the content and structure of the polar β phase. Fig. 3c–g show the differential scanning calorimetry (DSC), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) data of electrospun SiDs/PVDF-TrFE fabrics with various contents of SiDs, respectively. With the increase of SiD contents, the DSC data revealed that the melting enthalpy of electrospun fabrics gradually increased, corresponding to the enhancement of the degree of crystallinity, though the melting points remained more or less the same (Fig. 3c; Table S1, ESI†). Also, in the XRD diffractograms, the intense Bragg peak at a 2θ angle of 20.2°, characteristic of the (110)/(002) lattice planes of PVDF-TrFE, definitely demonstrated the formation of polar crystalline β and γ phases in the electrospun hybrid fabrics (Fig. 3f). More obviously, each hybrid SiD-x fabric had a stronger polar phase Bragg peak than the pristine SiD-0 fabric. The relative and absolute contents of the nonpolar crystalline α form and polar crystalline β and γ forms were further identified by using IR spectra (Fig. 3g; Tables 1 and S2, ESI†). As for polar β-phase crystallites, their characteristic IR bands are located at the wavelengths of 840, 1280, and 1430 cm⁻¹, respectively. The results showed that the content of the piezoelectric β phase could be significantly increased by including a very small amount of SiDs in electrospun fabrics. Notably, the absolute content of the piezoelectric β phase of the SiD-2 fabric was more than twice that of the pristine SiD-0 fabric (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiDs (%)</th>
<th>α (%)</th>
<th>β (%)</th>
<th>γ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiD-0</td>
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<td>7.45</td>
<td>15.40</td>
<td>18.93</td>
</tr>
<tr>
<td>SiD-1</td>
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<td>10.73</td>
<td>18.69</td>
<td>18.72</td>
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<tr>
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<td>5.69</td>
<td>32.48</td>
<td>8.18</td>
</tr>
<tr>
<td>SiD-4</td>
<td>0.4</td>
<td>6.72</td>
<td>23.53</td>
<td>17.14</td>
</tr>
</tbody>
</table>

Intriguingly, for the electrospun hybrid fabrics, the formation efficiency of the polar crystalline β phase reached a maximum value with the change of the SiD content in a very small range (Tables 1 and S1, ESI†). This actually indicates the coupling and competition between SiD nucleation and electrospinning during the piezo-phase formation. Undoubtedly, the SiDs are effective in nucleating the piezoelectric β phase. When an appropriate amount of SiDs is introduced, the amount of charge in the spinning solution also increases, making the fibers more easily polarized, and then subjected to a larger electric field tensile force in the electrospinning. As a result, the formation of the crystalline β phase is greatly facilitated in such a special synergistic manner. Nevertheless, the excessive inclusion of SiDs results in an excessive increase in the amount of charge in the spinning solution. This further makes it a difficult electrospinning process. The polarization time and stretching time are shortened in the electrospinning, which eventually leads to the decrease of the content of the crystalline β form in the electrospun hybrid fibers.

The blue luminescent SiD hybridized electrospun fabrics have demonstrated their well-defined macro-/micro-/nanoscopic hierarchical textures and significantly enhanced polar crystalline phase. The hybrid fabrics were further integrated into a prototype PNG device for evaluating their piezoelectric outputs. Fig. 4a shows the composite structure and working mechanism of the flexible, luminous, and self-powered piezoelectric device prototype. Wherein, Fig. 4a-I represents one press-and-release cycle in the macroscopic state of the PNG device. Correspondingly, Fig. 4a-II represents in the microscopic state the dipole movement of the β-form piezoelectric crystals of the electrospun hybrid fibers. During electrospinning, the molecular dipoles inherent in the piezoelectric crystals are reoriented, and kept in their preferred orientation state. Initially, there is no piezo-signal generation. When the hybrid fabrics in the device are pressed, the piezoelectric crystals inside begin to deform, which makes the C–H and C–F bonds deflect accordingly. Thus, perpendicular to the chain axis, the molecular dipole movement occurs. Subsequently, piezoelectric charges are generated and accumulated on the device electrodes. The charge accumulation further produces a potential difference enabling a flow of charges from one electrode to the other electrode. This results in the generation of an instantaneous piezo-signal output on the device. Once the stress is released, the recovery of fabrics enables the relaxation of piezoelectric crystals. Consequently, the C–H and C–F bonds return to their original position, and the molecular dipoles move backwards. The piezoelectric charges on the electrodes begin to flow back, and an output piezo-signal in the opposite direction is produced on the device. In this way, the luminescent prototype device is able to perform stable and durable mechanical-to-electrical conversion in continuous working cycles by a direct piezoelectric response.

Fig. 4b shows the open-circuit voltage and short-circuit current outputs of the electrospun SiD-x fabrics, under a reciprocating impact of 1.5 Hz frequency and 22.5 N force. As the SiD content increased, the piezoelectric outputs of electrospun fabrics increased first, reached the maximum, and then decreased. It is noteworthy that the change of piezoelectric outputs is very consistent with the change of the polar crystalline β phase content in the fabrics (Tables 1 and S2, ESI†). The inclusion of SiDs promoted the growth of β-form crystals, which further brought about the significant enhancement of the
piezoelectric outputs of the luminescent silicon hybridized fabrics, especially compared with the pristine SiD-0 fabric. Remarkably, the voltage output and current output of SiD-2 fabric reached 446 V cm⁻³ and 8.1 mA cm⁻³, respectively, which were about 11 times and 19 times higher than the voltage output and current output of SiD-0 fabric, respectively.

The piezoelectric outputs of electrospun SiD-x fabrics were further evaluated by changing the frequency and amplitude of impact force. Fig. 4c shows the electrical outputs of SiD-2 fabric, stimulated with different forces at a fixed frequency of 1.5 Hz. As expected, with the force amplitude increased from 9.0, 13.5, and 18.0 to 22.5 N, both the voltage and current outputs of the hybrid fabric increased gradually. Especially, the short-circuit current output of the fabric was more sensitive to the change in the force amplitude. Fig. S4, ESI† shows the piezo-signals generated by the SiD-2 fabric when the force amplitude is maintained at 13.5 N, and the impact frequency is changed from 1.0 and 2.0 to 3.0 Hz. Unexpectedly, the piezo-response amplitude of the luminescent fabric remained almost unchanged with the variation of impact frequency. The piezoelectric response of the SiDs/PVDF-TrFE hybrid is quite distinct from that of state-of-the-art piezopolymers. For current elastic piezopolymers, such as poly(vinylidene fluoride) (PVDF) and cellular polypropylene, the piezoelectric output usually varies drastically with the stimulation frequency, due to the change of the dynamic modulus and strain rate with the
frequency.\textsuperscript{60-63,68-70} The frequency-independent piezoelectric output means that the luminescent silicon hybridized fabric can maintain a highly stable piezo-response in a real environment with a variety of dynamic motion modes. This might help to further extend the sensing applications of flexible and self-powered optoelectronic devices.

Long-term durable operation is essential for a self-powered optoelectronic device in practical energy harvesting or practical sensing applications. The durability of the PNG device based on luminescent SiD-2 fabric was evaluated with short-circuit current as the main parameter. Under a 22.5 N force with a frequency of 2.0 Hz, the SiD-2 fabric was subjected to more than 10 000 continuous cyclic impacts. As shown in Fig. 4d, the luminous piezofabric based PNG demonstrated excellent reliability and durability in collecting dynamic mechanical energy. It could serve as a reliable power source to power the operation of commercial LEDs (Fig. 4e). Until the end of the test, no attenuation of the direct piezoelectric signals was observed in the PNG device. More interestingly, the initial increase in the piezoelectric outputs indicates that the luminescent silicon hybridized fabric also possesses some advantages of a PVDF-Nafion based electret in terms of energy harvesting, as its ability to harvest kinetic energy can be self-improved in long-term uninterrupted load cycles.\textsuperscript{69} This should be ascribed to the unique macro-/micro-/nano-spcific hierarchical textures of the electrospun SiDs/PVDF-TrFE fabrics. Notably, the improved piezoelectric output means improved sensitivity when the luminous PNG device acts as a self-powered piezo-sensor.

As a proof of concept, in the scenario of a tennis match, an ultra-thin SiD-2 fabric based PNG prototype was employed as a flexible and self-powered tactile sensor for real time sports monitoring and athlete physiology monitoring (Fig. 5). It satisfied the requirements of ultra-high mechanical sensitivity, flexibility, and reliability in sensing a broad range of strains and pressures. Fig. 5a shows the recognition of tennis balls out of bounds.
bounds. The piezo-sensor was buried near the edge of the tennis court, and the rubber layers were attached to the upper and lower sides as protective layers. Once it was hit by a tennis ball, it generated a piezo-signal to identify the tennis ball out of bounds. Fig. 5b shows the recording of the human heart rate. A bimodal signal represents a heartbeat. The flexible piezo-sensor was able to be attached to an athlete’s chest to sense subtle pressure changes in cardiac pulsation. It generated reproducible piezo-signals that correspond to the heartbeats of the athlete. It is worth noting that when realizing cardiac rhythm monitoring, the athlete needs to hold his breath for a few seconds to avoid the effect of changes in the chest cavity caused by breathing. In addition, two heartbeat signals in the opposite directions were obtained using the forward- and reverse-

Fig. 6  Demonstration of a SiD-2 fabric based self-powered piezo-device to be integrated into a capacitor/sensor/transmitter system to monitor vital health signs. As a core component, the SiD-2 device acts as a nanogenerator to charge commercial capacitors for energy storage, while it acts as a piezo sensor to monitor the human respiratory rate. (a) Charging curves of different capacitors by the SiD-2 device. (b) Equivalent circuit of a self-charging power system based on the SiD-2 device. (c) Photograph of the used SiD-2 fabric. (d) Schematic illustration of the wireless data transmission process from the SiD-2 device to a cell phone. (e) Respiratory signals received under normal and fast breathing conditions, respectively. The inset shows the amplified signal of one respiratory cycle. SiD-2 fabric size: 20 mm × 20 mm × 0.080 mm.
connected circuits, respectively, which proved that the heart rate monitoring was indeed realized by the piezoelectric effect. Fig. 5c shows the sensing of human joint motions. The ultrathin soft piezo-sensor demonstrated highly conformable attachment to human skins. It was attached to an elbow of the athlete to show its sensitivity in sensing large-scale human body movements. The piezo-sensor produced repeatable piezo-signals with the repeated bending and stretching motions of the elbow. When the elbow is bent, the piezo-sensor receives a large extension force and produces a strong piezo-signal. In turn, when the elbow is stretched, the piezo-sensor is subjected to a smaller squeezing force, resulting in a corresponding weak piezo-signal.

The electrospun SiD-2 fabric attained a very high voltage output density of 446 V cm⁻³ (Fig. 4b). It also showed the ability for long-term durable operation (Fig. 4d). By controlling the electrospinning conditions, the SiD-2 fabric can be fabricated with a very small thickness for human integrated applications.77–78 As shown in Fig. 6, the ultra-thin SiD-2 fabric, with an area of 20 mm × 20 mm and a thickness of 80 µm, was utilized to assemble an ultra-flexible piezo-device, which was further integrated into a capacitor/sensor/transmitter system to monitor human vital signs. The SiD-2 device acted as a sustainable power source to charge commercial capacitors for energy storage (Fig. 6a–c). Meanwhile, it acted as a self-powered piezo-sensor to monitor the human respiratory rate (Fig. 6c–e). The detected respiratory signals fully complied with the realistic respiration cycles in both the depth and rate of inhalation/exhalation, and the different respiration patterns were clearly distinguished between normal breathing and fast breathing.79–81 Using a computer as the transmitter and a mobile phone as the receiver, the computer transmitted the monitored breathing signals to the mobile phone in real time via Bluetooth.

3. Conclusions

In summary, we have demonstrated the incredible potential of earth abundant silicon based quantum dots for flexible and self-powered optoelectronics. The inclusion of an extremely small amount of blue luminescent SiDs enabled the straightforward electrospinning of ultrathin, flexible, and silicon hybridized PVDF-TrFE fabrics with well defined macro-, micro-, and nanoscopic hierarchical textures and with a significantly enhanced piezoelectric response. The piezo hybrid fabrics showed the highest ever, to our knowledge, direct piezoelectric output without sacrificing the photoluminescent response of encapsulated SiDs. The voltage output and current output of SiDs/PVDF-TrFE fabric comprising 0.2 wt% SiDs reached 446 V cm⁻³ and 8.1 µA cm⁻², respectively, which were almost 11 times and 19 times higher than the voltage output and current output of pristine PVDF-TrFE fabric, respectively. Moreover, the luminous hybrid fabric based prototype piezoelectric nanogenerator could serve as a reliable power source to power the operation of commercial LEDs, and exhibited a highly durable and highly stable piezoelectric response in more than 10 000 uninterrupted load cycles. As a proof of concept, in the scenario of a tennis match, the developed luminescent fabric based prototype device was further employed as a self-powered tactile sensor for real time sports monitoring and athlete physiology monitoring. It showed ultrahigh mechanical sensitivity, flexibility, and reliability in sensing a broad range of strains and pressures. We believe that the present study provides a new perspective to improve the compatibility of emerging autonomous optoelectronic devices with existing silicon-based infrastructure to accelerate the development of current and future self-powered autonomous micro/nanosystems.

4. Experimental section

The detailed experimental process is presented in the ESI.†

Author contributions


Conflicts of interest

There are no conflicts to declare.

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