Self-healable sticky porous elastomer for gas-solid interacted power generation

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A previously unknown gas-solid interacted power generation is developed using triboelectric effect. We designed an adhesive, gas-tight, and self-healing supramolecular polysiloxane-dimethylglyoxime-based polyurethane (PDPU) porous elastomer based on segmented oxime-carbamate-urea. It is an intrinsically triboelectric negative material with trapped air within closed voids, exhibiting ultrahigh static surface potential and excellent compressibility. This porous PDPU generates electricity from interactions between the trapped air and the elastomeric matrix under periodical compression. The positively charged trapped air (or other gas) dominates the tribo-electricity with PDPU, inducing electron transfer from gas to the solid polymer for electricity generation. The self-healable elastomer renders gas-solid interacted triboelectric nanogenerator, GS-TENG, with high stretchability (~1200%). The inherently adhesive surface enables adherence to other substrates, allowing mechanical energy harvesting from deformations such as bending, twisting, and stretching. GS-TENG promises a freestanding wearable functional tactile skin for self-powered sensing of touch pressure, human motions, and Parkinsonian gait.

INTRODUCTION

Triboelectric nanogenerator (TENG) was proposed since 2012 for converting mechanical energy to electricity by coupling the electrification and electrostatic induction, harvesting energy from contact friction of two substances via vertical contact separation and lateral sliding (1). Because of its lightweight properties, low cost, and high performance (2, 3), TENG has been successfully applied for micro/nano-power sources, self-powered systems, blue energy harvesting, and high-voltage sources (4–6). Important progresses such as energy harvesting from human motions and water droplets/waves (7–9) have been achieved for wearable power sources, health monitoring, water energy management, charge filter, and so on (10–12). However, all the existing TENGs are confined to the interactions of solid-solid, solid-liquid, and liquid-liquid interfaces, making it essential to establish contact and full separation of two independent phases of materials (solid or liquid) with the assistance of spacer, waterproofness, or discrepant surface tensions and viscosities (13). Their typical operations are limited by their surrounding environment, relative positions to the contacting surfaces, and device lifetime. This work exploits the gas-solid interface to harness triboelectricity and tackles the challenges in controlling the gas-solid interaction to facilitate effective electron transfer between gases and soft materials, thus realizing a class of unique elastomeric material with tailorable interfacial properties for gas-solid interacted tribo-power generation.

We developed a self-healing sticky elastomer [polysiloxane-dimethylglyoxime-based polyurethane (PDPU)] that is intrinsically triboelectric negative with ultrahigh static surface potential. This soft and porous material has controllable and tightly sealed voids for trapping gas, rendering an elastomer that could be periodically compressed to interact with the trapped gas for electron transfer. This formulates a framework for power conversion from the interactions between gas and solid within a soft material without the need for physical separation of the contacting surfaces. The new series of healable PDPU elastomers contain urea-oxime-carbamate bonds in the cross-linked networks that facilitate the in situ entrainment of the surrounding gases during polymerization as the solvent evaporates, forming the discretely closed voids with trapped air or gas. Various amounts of poly(urethane-oxime) (PUO) and segmented urea-siloxane-based prepolymer (SUSP) are introduced into the polymeric backbones to control the voids and the PDPU’s mechanical properties. A porous PDPU consists of a portion with free volume and a portion occupied by the polymeric chains. The free volume portion includes defects produced by random stacking of molecules that provide the space needed for molecular and chain motion. At high temperatures (typically ~90°C), the SUSP self-organizes into the PUO through the hydrogen bonds or the condensation of -NH2/-NCO groups between PUO. These self-organized SUSP aggregates resulted in a lot of voids and interstitial spaces from the PDPU solution, in agreement with the literature (14). The resultant PDPU contains various sacrificial hydrogen bonds in the soft phase of a hard-soft multiphase system, ensuing the unique properties of the hybrid networks with dynamic supramolecular self-healing. The PDPU elastomer comprises urea-oxime-urethane units, which can undergo reversible dissociation and association, endowing it with outstanding elasticity and healability simultaneously.

Accordingly, a gas-solid interacted triboelectric nanogenerator (GS-TENG) was demonstrated without additional spacer and air gap separator. Periodic compression without physical detachment of the contacting surfaces triggers the cyclic strong-weak interactions between the PDPU and the gas in the voids, facilitating charge transfer from the gas to the polymer. Power output was generated by coupling the electrification and electrostatic induction. Furthermore, the adhesive surface of the elastomer presents reconfigurable TENG preforms that are attachable by sticking and shapeable by stacking. It shows a facile fabrication and operation than the prior arts, such as the templated polydimethylsiloxane (PDMS) sponge, porous poly(vinylidenefluoride-co-trifluoroethylene) (PVDF-TrFE), and polytetrafluoroethylene (PTFE), which require additional air gap separators (15–17). The gold nanoparticle– or carbon nanotube (CNT)–filled porous PDMSs and the printable poly(glycerol sebacate) (PGS) elastomers filled with CNTs could not self-attach to various

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substrates (18–20). This GS-TENG is compatible with various nonflat substrates, including textiles, shoes, computer mouse devices, and keyboards, owing to its ease of operation by deformation of the gas-trapped voids, harvesting energy from various mechanical motions such as compressing, folding, twisting, and stretching. Correlating the compression forces of this GS-TENG to the mechanical contact input, a self-powered electronic skin sensor was demonstrated to detect the touching force, finger bending motions, and human gait, promising intrinsically wearable sensors for self-powered smart soft robotics and healthcare monitoring.

RESULTS

Synthesis and characterization of PDPU
To achieve the controllable interaction between gas and solid with effective charge transfer, we designed a sticky PDPU elastomer that can generate uniform voids to trap the gas during synthesis. This dynamic oxime-carbamate-urea–based self-healing and adhesive supramolecular elastomer is intrinsically triboelectric negative with ultrahigh surface potential; the segmental hard-soft backbones serve to tune the mechanical properties as shown in Fig. 1A. The PDPU was synthesized as shown in figs. S1 to S3: SUSP was prepared through the precipitation polymerization of bis(3-aminopropyl)–terminated poly(dimethylsiloxane) (NH₂-PDMS-NH₂, Mn = ~5000) and isophorone diisocyanate (IPDI) in H₂O-acetone mixed solvent, and as a result, the NH₂-PDMS-NH₂ oligomers were linked with IPDI units. This SUSP is known to control soft and hard segments in the PU networks as a chain-extending agent (21). PUO was synthesized by a two-step polycondensation method with IPDI as the isocyanate, polytetrahydrofuran glycol (PTMG) as the diol, and dimethylglyoxime (DMG), followed by tetraethylene glycol (TEG) as the chain extender. DMG (-N–O) was chosen as a chain extender because of its adjacent oxime groups, which facilitate the reverse chain motion (22). PTMG (-OH) was used because of its comprehensive properties and chain motion for better self-healing (23). TEG plays a role to make the polymeric backbone less crystalline and more flexible (24). IPDI is selected because of its chain mobility for better self-healing, asymmetric alicyclic structure of -NCO groups, and non-discoloring properties (25). Thus, by integrating both merits of SUSP and PUO, the resultant PDPU shows some degree of molecular
interaction between the diisocyanate (-NCO) and -NH$_2$–terminated SUSP prepolymer and dipole-dipole or intermolecular hydrogen bonding formed between the molecular linkages -NCO/-NH$_2$. $^1$H NMR (nuclear magnetic resonance), $^{13}$C NMR, and $^{29}$Si NMR analyses confirm the successful preparation of PDPUs as indicated by the presence of characteristic peaks of SUSP, IPDI, PTMG, TEG, and DMG segments in polymeric backbones (figs. S4 to S6; see the Supplementary Materials for the detailed discussion).

Three different prepolymer ratios were carried out to form the samples of PDPU-1, PDPU-2, and PDPU-3 based on the PUO:SUSP prepolymers with molar ratios (-NCO/-NH$_2$, x/y) of 2:3, 2:1.6, and 2:0.5 (fig. S2). The PDPU hydrogen bonding was verified by the characteristic Fourier transform infrared (FTIR) peaks at 3332 to 3365 cm$^{-1}$ (stretching vibration of hydrogen-bonded N–H groups), 3406 to 3500 cm$^{-1}$ (stretching vibration of non–hydrogen-bonded N–H groups), 1720 to 1725 cm$^{-1}$ (stretching vibration of hydrogen-bonded C=O urethane groups), and 1533 cm$^{-1}$ (-CONH) (fig. S7). The characteristic information of isocyanates (N=C=O) and oximes (N=O) is shown in fig. S7. Dynamic mechanical analysis (DMA) conveys that there are two different glass transition temperatures ($T_g$) for all PDPUs, low $T_g$ for the soft segment at −84.23°C to 95.32°C and high $T_g$ for the hard segment at 4.68°C to 28.09°C, suggesting the self-healing capability of the dynamic supramolecular PDPU (fig. S8). In contrast, the control sample PUO has only one $T_g$ at −2.25°C, indicating that higher cross-linking in the hard-soft segment is dominated by hydrogen bonding (26). Figure SBC shows the angular frequency ($\omega$) dependence of the storage modulus ($G'$, elastic component) and loss modulus ($G''$, viscous component) of the neat PUO, PDPU-1, PDPU-2, and PDPU-3, representing ratios of 2:3, 2:1.6, and 2:0.5 (-NCO/-NH$_2$), respectively. The values of $G'$ of all PDPUs were almost constant in the whole frequency range and were much higher than the $G''$ values. These plots show the rubbery plateau region of the cross-linked PDPUs, indicating that the intermolecular interactions were present between the NH$_2$-PDMS-NH$_2$ and urethane (-NH-COO-) groups (27).

Figure 1B shows the uniform voids distributed in a representative square PDPU (PDPU-2 with -NCO/-NH$_2$ molar ratio of 2:1.6) with side lengths of 3 cm and thickness of 3 mm (inset of Fig. 1B), which can be vertically mounted because of its stickiness. The scanning electron microscopy (SEM) image (Fig. 1C) reveals the morphology of a PDPU ribbon, which shows two cross sections with voids of average size about 0.3 mm. All the voids are closed and separately distributed in the elastomer. The smooth surface was confirmed using SEM imaging and verified by contact angle measurements comparing PDPU with voids and the dense PDPU (fig. S9, A and B). The porous PDPU elastomer presents a smooth surface with closed voids inside, which offers advantages in independent tunability of the surface property and controllable deformation of the voids with trapped gas.

To evaluate the possible effect of the voids on the intrinsic chemical structure of PDPU, small-angle x-ray scattering (SAXS) was performed on PDPU with voids and compared to that of the dense PDPU. Figure 1D confirms that the peaks and intensities of the two spectra are highly matching to each other, indicating that PDPU with voids has the same ratio of hard segments as the dense PDPU, containing interdomain spacing with an increase in hard domain length, which delivers the elasticity and healability of elastomer (28). Compared with PDPU-1 and PDPU-3, PDPU-2 with a ratio of 2:1.6 (-NCO/-NH$_2$) indicates consistent results (fig. S8D). The wide-angle x-ray scattering (WAXS) pattern shows a lattice spacing of 1.32 to 1.42 Å and 2.74 to 3.06 Å corresponding to the stacking of the urea-oxime-urethane moieties (fig. S8E). It is accordingly envisioned that the high degree of polymer chain entanglements and multiple hydrogen-bonding interactions between PUO and SUSP gave rise to the high mechanical strength of the PDPU elastomers (29).

The standard test method of ASTM D1002 was applied to evaluate the adhesion force of PDPU. As shown in fig. S9 (D and E), on two representative substrates of stainless steel and wood, PDPU-2 with a ratio of 2:1.6 (-NCO/-NH$_2$) shows higher adhesion force than PDPU-1 and PDPU-3. The maximum adhesion force of PDPU-2 on the stainless steel achieves ~0.6 MPa (Fig. 1E), which is comparable to conventional PU adhesives (30), enabling the sticky PDPU to be readily attached on various substrates such as glasses, stainless steels, and cardboards even after being placed in ambient condition for 4 months (insets of Fig. 1E). The stable adhesive property is attributed to the oximes and hydroxyl groups of the PDPU, which provide inherent bonding strength toward different surfaces. The adhesion force is comparable to the commercial PU adhesives specifically dedicated for stainless steel substrates (e.g., Teromer-6700 and Araldite 2000). The strong adhesion is a result of the microphase separation structure of PDPUs composed of soft and hard segments. The hard segments give rise to distinct hard domains that are cross-linked structures from entanglement of the polymer chains, and the soft segments (switching segment) hinder the polymer chains to reform a deformed shape (31). The adhesive property greatly contributed to the attachable and stackable devices for adaptive power sources and self-powered sensors.

The mechanical properties and healing efficiencies (the ratio of breaking elongation after healing to that before cutting) depend on the ratio of SUSP and PUO (-NH$_2$/-NCO) units (fig. S10, A and B). When the ratio of SUSP units in the PDPU was decreased, the mechanical strength of the polymer increased, but the Young’s modulus, elongation at break, and healing efficiency decreased. It indicates that high cross-linking leads to increased strength of the hard segments, thereby resulting in decreased extensibility. Among the PDPUs, PDPU-2 with a ratio of 2:1.6 (-NCO/-NH$_2$) (thereafter called as porous PDPU) shows good stretchability (1800%) and higher healing efficiency (66.7%, healing at 100°C for 4 hours) (Fig. 1F and fig. S10, A and B). In contrast, PDPU-1 could not heal, while PDPU-3 with lower cross-linking density shows lower elongation of 1000% and ~60.3% healing efficiency at the same condition. Three main factors contributed to the self-healing phenomenon in the PDPU polymer: (i) the presence of supramolecular oxime-carbamate-urea bonds, which enables PDPU chain with better mobility to enhance chain re-entanglement (32); (ii) dynamic exchange of oxime-carbamate bonds on the crack surfaces, which can undergo reversible dissociation and association reaction, enabling the self-healing and spatially controlled functionalization (33); and (iii) the low $T_g$ of the PDPU polymer, which gives a high chain mobility to the polymer chain, leading to better mechanical properties (34).

The extreme stretchability with negligible hysteresis observed in tensile loading-unloading cyclic test of the porous PDPU as shown in Fig. 1G indicates great energy dissipation due to hydrogen bond exchange. To demonstrate the elastic performance of porous PDPU, repeated cyclic tests at the strains of 100 and 500% were performed (fig. S10, C to E); 10 cycles (cycles 1 to 10) were performed without waiting time between two consecutive cyclic tests. The same PDPU film applied with 500% strain test was then allowed to relax for ...
15 min (11th cycle) and 30 min (12th cycle) at 25°C before being stretched again. Cycles 11 and 12 show good recovery in the loading-unloading curve, which is similar to the first cycle, suggesting the good elasticity of the PDPU film. It is attributed to the reversible nature of oxime-carbamate bonds, orientation of the hard segment domains, interchain or intrachain loops, stress-softening behavior, disruption of the microstructure, dissociation of hydrogen bonds, etc. (35).

Therefore, besides the excellent stretchability, PDPU is also highly compressible. Figure 1H presents that the porous PDPU could well recover to its original shape without visible hysteresis under compressive strains of 10 to 60%. The sample was subjected to a fatigue cyclic compression test by undergoing 10 loading-unloading cycles with different compressive compression strains of 50 and 60%, as shown in fig. S10 (F and G). It is observed that the PDPU can completely recover without plastic deformation after the fatigue test, indicating the excellent elasticity of the PDPU compared to reported elastomers (15, 18). The compressive stresses to PDPU at different strains were plotted with nonlinear fitting in Fig. 1I, indicating that pressures of 4.6, 14, 33.3, 79.9, 227.8, and 1115.6 kPa can produce compressive strains of 10, 20, 30, 40, 50, and 60%, respectively, indicating that controllable periodic compression can be achieved. Gas tightness of the porous PDPU was tested as shown in fig. S11 (A and B). The elastomer was attached to an opening end of a bottle with pure water. The weight loss of water was monitored at different intervals. In an open bottle case, the weight of the bottle decreases quickly to less than 10% of its original weight in 2 weeks. In comparison, the weight of the bottle sealed by a 2-mm-thick porous PDPU and even subjected to an additional compression by a 30-N weight barely decreased after 2 weeks, indicating negligible losing of water vapor. It demonstrates the excellent gas tightness of the porous PDPU, which is comparable with a 120-μm polyethylene terephthalate (PET) film. Therefore, using this sticky porous PDPU elastomer with trapped gas, it is feasible to study the controllable interaction between gas and solid by periodic compression.

**Design and working mechanism of GS-TENG**

On the basis of a typical porous PDPU elastomer (thickness of 3 mm, void size of 0.6 mm) trapped with air, a double-electrode TENG without air gap was designed as shown in Fig. 2A. Owing to the stickiness merit of the PDPU, a unique silver nanowire (AgNW) bundle mesh (AgBM) with both advantages in transparency and...
conductivity after spraying on a polymer substrate (36) could be tightly transferred on the adhesive porous PDPU (fig. S11C). Microscope images in Fig. 2B indicate that a porous PDPU was well covered by the AgBM, serving as a highly conductive electrode with excellent transparency. An additional thin layer of dense PDPU (~0.5 mm) was further coated for protecting the AgBM; 70% optical transmittance can be maintained for the whole TENG (fig. S11D). The power generation including open-circuit voltage, transferred charge, and short-circuit current were evaluated by periodically compressing with a pressure of 22.2 kPa, as shown in fig. S12A. The sticky PDPU surfaces ensure that there is no air gap between the device–sample holder interface and the device–mechanical oscillator interface during measurement, guaranteeing that the frictional interaction would only happen between the trapped air and the PDPU. As compared in Fig. 2 (C and D) and fig. S12B, tiny outputs of 0.2 V, 2.5 nC, and 1.2 nA cm⁻² can be generated by a TENG consisting of dense PDPU with the same electrode, which could be attributed to the electron transfer induced by the contact deformation of PDPU with the testing holder (37). TENG with the porous PDPU shows much higher output voltage, transferred charge, and current density, achieving 3.8 V, 17 nC, and 35 nA cm⁻², respectively. In contrast, a porous PDMS with a similar pore size produces negligible outputs (fig. S12, C to E). We concluded that the porous PDPU is able to generate the enhanced output electricity, suggesting that the interaction of air-solid is effective for power generation. It is attributed to two reasons: one is the intrinsically highly negative triboelectric property of the PDPU, because IPDI-derived urethane (-NH-CO-O) has relatively high dynamic nature due to the steric hindrance of the cyclohexyl ring, facilitating the reconstruction of oxime-urethane units for improving the electron affinity of PDPU. Therefore, it shows much higher static surface potential (~2.36 kV) than the commonly used polymers including PDMS and PTFE (~0.23 kV) (Fig. 2E). Second, air with small particles (aerosols) commonly has positive charges. The pressure of the air in the voids could be instantaneously increased following compressive deformation of PDPU, and strong interaction will happen between the air and the elastomer to induce the electron transfer, resulting in electricity generation. Compared to the porous nonpolar polymer ferroelectrets that require a poling process at high electric field to break down the gas/air in the voids and a short decay time that affected the stability, the GS-TENG shows advantages of elimination of poling, convenience of operation, and reliable performance (38).

The working mechanism of this GS-TENG could be explained from the coupling of the triboelectric effect and electrostatic induction accompanied by the dynamic mobility of charge in the gas/air (18, 39). Compressive deformation of the PDPU exerts instantaneous increased pressure within the voids upon strong contact of the internal surfaces of elastomer (strong contact), and the enhanced friction effect leads to charge transfer from the air to the relatively negative PDPU (Fig. 2F, i), resulting in negative charges on the inner surfaces of PDPU. The positively charged air would recover to the normal pressure with redistributed potential upon the release of compression (weak contact) due to dynamic mobility of the positive charge in the voids. The nonequivalent random pores led to an instantaneous asymmetric distribution of the positive charges in air and the negative charges in elastomer, causing the electric potential difference between the two electrodes by electrostatic induction. The increasing electric potential difference upon the release state drives the free electrons to flow from the top electrode to the bottom electrode through an external circuit (Fig. 2F, ii), generating a positive current signal from the bottom electrode to the top electrode. The electric potential difference in PDPU will be fully balanced after the compression was completely released to a suspended state; no output signals will be produced (Fig. 2F, iii). Once the device was compressed again when subjected to the strong contact, the charge transfer accompanied by asymmetric distribution of the contrary charges around the voids would happen again, and the decreasing electric potential difference will be produced accordingly to drive the electron flow from the bottom electrode to the top electrode (Fig. 2F, iv), resulting in a negative current from the bottom electrode to the top electrode. This is a full cycle of the electricity generation process for the GS-TENG. An alternating electricity can be continuously generated under periodic deformation by external force.

**Mechanism of gas-solid power generation**

However, the periodical strong-weak interaction of gas-elastomer relies on the recovery of the deformed voids in shape. Therefore, changes in output performance of the GS-TENG were studied at different compressive strains ranging from 10 to 60%, revealing the threshold value of compressive strain for keeping the voids intact. As shown in fig. S13 (A to C), the output electricity increases as the compressive strain is increased from 10 to 30%. The output slightly decreases at 40% strain and then dramatically decreases at under 50 and 60% strains. It is reasonable that the higher compression can produce stronger interaction for the air and the PDPU (~40%) to generate higher power output. However, the loss of effective interaction of air-elastomer above 40% strain results in decreased outputs. To understand the void deformation that depends on the strain, the cross-section of a typical PDPU was observed with a microscope upon compression. Figure S13D shows that the deformation of voids gradually increases when increasing the compressing strain, and almost complete deformation happens under 40% strain. No damage is observed for the voids within this strain range. However, after applying with 60% compressive strain, the voids disappear obviously (fig. S13E), indicating that gas leakage happens under this large deformation. The air-PDPU interaction would be very weak when compressing more than 50% strain, reducing the electron transfer to produce lesser electricity power. Therefore, deformations smaller than 40% strain (<72 N) are important for maintaining the PDPU elastomer with intact voids, enabling higher electricity output. In addition, the GS-TENG generates higher outputs under lower compression frequency (up to 3 Hz) due to the complete deformation and recovery for adequate air-PDPU interaction (fig. S13F). Thereafter, a pressure of 22.2 kPa with a compression frequency of 2 Hz was applied on the device (strain <30%) for other performance evaluations.

To further verify that the power generation arises from the periodic interaction between gas and PDPU, a systematic study was performed to compare the electrical output, which highly depends on the properties of PDPU elastomers. Porous PDPU5s with different void sizes (0.3 to 1.5 mm) (fig. S14), porous PDPU5s of different thicknesses (2 to 5 mm), and PDPU5s trapped with various air compositions were measured to compare their capacitance changes at 1 Hz to 10 kHz upon compressions (~22.2 kPa) that are contributive on the triboelectric electricity output. As shown in fig. S15A, PDPU with bigger voids shows higher reduction in capacitance. The capacitance will increase after the compression, indicating deformation of voids. The maximum increase of capacitance was 2 pF in the sample with voids of 1.0 mm, which is much higher than that of a dense PDPU.
(0.5 nF) (fig. S15B). It is because, on the one hand, the trapped air decreases the capacitance due to its much lower dielectric constant than that of the elastomer (40) and, on the other hand, the distance between two electrodes in a porous PDPU would reduce more than that in a dense sample, increasing the capacitance rapidly at the same compression force (15). In addition, fig. S15C indicates that the capacitance change decreases from 2.6 to 0.8 pF when PDPU had the same void size of 0.6 mm but with increased thickness from 2 to 5 mm. The porous PDPU trapped with various gas compositions [such as air, nitrogen (N2), and argon (Ar)] present the identical changes (2 pF) in capacitance upon compression (fig. S15D). (For more explanations, see fig. S15.)

On the basis of the PDPU (3 mm thick) with different void sizes, electricity outputs of the devices show the same tendency with the changes in capacitance (Fig. 3, A to C). Initially, the voltage, transferred charge, and current density increased (from 2.5 V, 11 nC, and 22 nA cm−2 to 5.2 V, 27 nC, and 50 nA cm−2) when void size increased from 0.3 to 1.0 mm; thereafter, a decrease in performance was found as the void size further increased to 1.5 mm. The device with voids of 1.0 mm exhibits the maximum outputs of 5.2 V, 27 nC, and 50 nA cm−2 (Fig. 3D). It suggests that the suitable void size could bring about optimum performance, resulting from more compressible air in the system and maximum deformation of voids to enhance the air-PDPU interaction and the triboelectric output. Samples with small voids make the voids difficult to be effectively compressed by elastomer under gentle deformation, while samples with too large voids will decrease the PDPU density, leading to reduced elastomer amount between the voids to engage the effective compression of air under compression (fig. S15, E and F).

Figure 3 (E to G) shows that the triboelectric outputs of the devices gradually increase (from 3 V, 12 nC, and 25 nA cm−2 to 4.2 V, 19 nC, and 43 nA cm−2) as the thickness of PDPU was increased (void size of 0.6 mm) from 2 to 4 mm and slightly decrease to 3.5 V, 15 nC, and 31 nA cm−2 when the PDPU thickness was further increased to 5 mm (Fig. 3H). It suggests that there is an optimal thickness for this PDPU-based GS-TENG, and the thinner PDPU elastomer with lesser voids would deform lesser upon compression. By comparison, more deformation will occur when compression is applied on the thicker PDPU, which contains more voids that can enhance the gas-elastomer interaction, enabling more electron transfer to improve the output voltage. However, for PDPU that was too thick,
such as 5 mm, the increased distance between the voids’ internal surfaces and the electrode would suppress the electrostatic induction and the output electricity, suggesting that PDPU’s with suitable thickness and voids in size are important for the higher electricity output.

Furthermore, as shown in Fig. 3 (I to K), the effect of gas property on the electrical output was explored on a series of PDPU’s (3 mm thick, void size of 0.6 mm) trapped with different air compositions. Apparently, the output performances decrease as the air pressure decreases from 100 to 10% (Fig. 3L), which do not follow their consistent capacitances upon compression (fig. S15D). It indicates that the power generates from the interaction between air and PDPU, and higher air pressure could provide stronger friction with PDPU to produce higher output. To evaluate the role of the components in the air for power generation, GS-TENGs trapped with Ar and N₂ were further investigated as shown in Fig. 3 (I to K), and the outputs are lower than that of the device with 10% air. It indicates that the inert gases such as N₂, which has higher dielectric strength than Ar (41), show negligible effect on the output (similar to the device of dense PDPU). It is concluded that the gases with more active components would contribute more effective electron transfer for higher electrical output. The device trapped with 100% air in the voids exhibits the highest performance, suggesting that the interaction might occur between the oxygen or the charged particles in air with the PDPU elastomer, which has abundant active groups such as C=O, N—H, and Si—O—Si, promising good electron transfer with the air under instantaneous deformation. Therefore, this class of PDPU elastomer with alterable gas composition allows power generation with tunable outputs, enriching the potential for practical applications.

Self-healability, stretchability, and built-up capability

Owing to the self-healing capability and excellent elasticity of the PDPU, the GS-TENG promises to recover its function even after damage or under extreme deformations. Here, we studied the power generation of device upon stretching and after self-healing from damages. Figure 4A shows a PDPU completely cut off using knife. Although with abundant voids, the PDPU was able to heal well after heating at 100°C for 4 hours. The device shows comparable output voltage to the device before damage (Fig. 4B). Five thousand cycles of test were carried out on a device. Figure S16 (A to C) shows that the uniform voids were maintained in the device, with the intact AgBM tightly attached on the PDPU. It proves to retain stable sheet resistance even after 5000 compression cycles. Besides, to realize the...
electricity generation upon stretching, a conductive electrode that consisted of liquid metal particles [eutectic gallium indium particles (EGaInPs)] and silver flakes was embedded in the PDPU. The stretchable electrode could avoid detachment from the PDPU during stretching and deformation. Figure 4C shows the cross section of a stretchable GS-TENG, which could sustain its high conductivity at a strain of 1200% (fig. S16, D and E). When keeping the same impacting area of 1 cm$^2$ on the devices, gradually decreased output voltage from 0.5 to 0.05 V with increased strain is observed in Fig. 4D. It is attributed to the increasingly deformed voids upon increased strain, weakening the gas-PDPU interaction and producing lesser output electricity. Even so, this GS-TENG can recover its original output capability after being released from stretching. The device was demonstrated to maintain the comparable output voltage after 50 cyclic tests at 1200% strain (fig. S16F), exhibiting application potential under extreme conditions. Owing to the stickiness of PDPU, it is interesting to realize the attachable and scalable power sources. An example was shown in Fig. 4E, where four devices (3 cm by 3 cm) with AgBM electrodes can be tightly combined into one bigger device like a jigsaw, meeting various power and spatial requirements. As a power source, an optimized built-up GS-TENG by four devices can generate a high voltage of 16 V (movie S1). It can drive a 10-μF capacitor to 2 V in 270 s (Fig. 4F), and tens of commercial light-emitting diodes (LEDs) in series can be instantaneously lit up (Fig. 4G).

GS-TENG self-powered electronic skin
This sticky GS-TENG with high deformability can be attached or mounted on various substrates such as computer mouse devices, textiles, and shoes, showing energy-harvesting ability from the various human motions for multimode wearable power source (Fig. 5A). In
addition, the working mechanism of the GS-TENG is by virtue of the deformation of the voids with gas. Therefore, the device could be capable of generating electricity under various deformations. As demonstrated in Fig. 5 (B to D), bending, twisting, and stretching can be applied on the device, generating around 0.5 V under the repetitive deformations. The interesting distinct signals in various waveform and duration allow different deformations to be detected by the self-powered GS-TENG. Figure 5E shows that the output voltages of a device (1 cm²) increase as the compression force increases from 4.4 to 31.1 kPa. A linear correlation of the pressure as a function of the output voltage was established (Fig. 5F), showing a comparable sensitivity (0.017 V kPa⁻¹) with that of the previously reported elastomer–TENG pressure sensor (42). It promises an important application of self-powered tactile sensor for soft robotics, for example, an assumptionistic smart glove for the gripper (Fig. 5G), rendering the accurate manipulation for objects. Using the working mechanism of the GS-TENG in terms of stretching, the device can serve as electronic skin for human motion sensing. An example was verified in Fig. 5H and movie S2, where the output voltage signals of a device self-attached on a human finger increased from 0.2 to 0.5 V as the bending radius of the finger is increased, promising the self-powered sensor for human motion monitoring. More interestingly, the GS-TENG can be attached on the heel to recognize the abnormal gait. Figure 5I shows the voltage outputs of a device triggered by the normal gait and the shuffling gait (dragging the feet with shorter strides, typically found in Parkinsonian patients; movie S3) (43). Apparently, there are two signals in one cycle under the shuffling gait rather than a single peak in the case of the normal gait. These distinct waveforms render the GS-TENG capable of recognizing and rehabilitating the shuffling gait, and it is of great importance for self-powered sensing for toddler gait care and Parkinsonian patients that normally suffer from the shuffling gait.

DISCUSSION
In conclusion, by designing a sticky porous PDPU elastomer with excellent gas tightness and intrinsically high affinity for electrons, we demonstrate the first GS-TENG for power generation from mechanically repetitive strong-weak interactions between gas and PDPU. The gases with more active components such as air with charged particles would dominate the interaction with PDPU, realizing electron transfer induction and continuous power generation. This sticky GS-TENG shows good self-healability and outstanding elasticity, and it can be spliced as devices with different dimensions for various applications capable of harvesting mechanical energy from multiple deformations including bending, twisting, and stretching, promising for wearable power sources regardless of flat or curving substrates such as computer mouse devices, textiles, and shoes. As an attachable electronic power skin with high sensitivity in output voltage and signal waveform, this GS-TENG could sense the different mechanical deformations, and detecting the touching forces, human motions, and Parkinsonian gaits at different tensile strains was demonstrated, delivering a simplified self-powered sensor for soft robotics tactile sensing and human healthcare.

MATERIALS AND METHODS
Materials
Bis(3-aminopropyl)–terminated poly(dimethylsiloxane) (H₂N-PDMS-NH₂, Mn = 2500 to 4000, Gelest DMS-A21) was purchased from Gelest Inc. PTMG (average Mn = ~1000; Sigma-Aldrich, USA) and TEG (99%; Sigma-Aldrich, USA) were dried in a vacuum at 100°C for 12 hours before use and directly used after drying. IPDI (a mixture of isomers, 98%; Alfa Aesar, USA) and N,N′-dimethylacetamide (DMAc; anhydrous, 99.8%; Alfa Aesar, USA) were used without further purification. The catalyst dibutyltin dilaurate (DBTDL; 95%; Sigma-Aldrich, USA), acetone (AR; ≥99.5%; Sigma-Aldrich, USA), and DMG (≥99%; Sigma-Aldrich, USA) were used as received. The remaining chemicals and solvents were purchased from Sigma-Aldrich, USA. All chemicals were used as received without further purification unless otherwise noted. Deuterated solvents for NMR analysis were purchased from Cambridge Isotope Laboratories Inc.

Synthesis of the SUSP
SUSP was obtained in a one-step precipitation polymerization (prepolymer method) as follows: Polymerization reaction was performed at ambient temperature in the absence of stabilizers or surfactants. In a glass bottle of 500-ml capacity, amine-terminated H₂N-PDMS-NH₂ and IPDI were individually dissolved in acetone, typically in a molar ratio of the functional groups -NH₂/NCO = 2/1.6. The H₂N-PDMS-NH₂-acetone mixture was slowly dropped into the IPDI-acetone solution under strong agitation (400 rpm), followed by the addition of Milli-Q water (acetone/water = 70/30). Thereafter, the polymerization was allowed to continue for 180 min at ambient temperature. At the end of the polymerization, the SUSP particles were isolated by 15-min centrifugation at 3000 rpm, which were rinsed twice with acetonitrile and dried up at 70°C for 8 hours under vacuum. SUSP formation was depicted in fig. S1.

Synthesis of the SUSP cross-linked PDPU polymer
PDPU cross-linked networks were readily synthesized by step-growth polymerization in three steps according to fig. S2. Before synthesis, SUSP was first mechanically stirred with DMAc (5 ml) at 100°C for 90 min. In the first step, NCO-terminated prepolymer (IPDI-PTMG) was synthesized by the reaction of IPDI and PTMG-1000 with a 2:1 molar ratio at 85°C for 3 hours under nitrogen atmosphere. Two drops of DBTDL catalyst were added, and the resultant prepolymer mixture was kept stirring at 75°C for 3 hours. The weight fraction of NCO [weight % (wt %) NCO] in the prepolymer was verified according to ASTM D2572. A determined amount of TEG in 10 ml of DMAc was added to the IPDI-PTMG solution. Second, the IPDI-PTMG precursor and the chain extender DMG were reacted at 60°C for 5 hours to obtain a cross-linked carbamate-oxime bond (PUO)–based prepolymer. Last, the reactor was heated to 70°C, and the determined amount of cross-linked SUSP solution was added to the PUO prepolymer to form the cross-linked PDPU network. The PDPU was diluted by DMAc for further characterization.

Fabrication of the porous PDPU
The porous PDPU was fabricated by liquid–liquid phase inversion process or forced-drying process techniques. Briefly, the technique involves having the polymers transformed from the liquid state into the solid-state film using solid free-form fabrication. The amine-terminated SUSP and NCO-terminated PUO were individually dissolved in DMAc at a concentration of 10 (w/v) for 3 hours at 75°C and mixed at a ratio of 3:7. The pre-suspension was placed in a PTFE dish (30 mm length by 30 mm width by 5 mm thickness) and waited for 15 min at room temperature and then brought to the

polymerization temperature at 75±room 80°C for 3 to 5 hours, followed by curing at 100° to 130°C for 10 to 21 hours at different gases and air pressure condition. During the polymerization, the gas composition was tuned in a mini glove box to obtain the uniform size and distribution of voids. The controlled uniform size and distribution of the pores are related to the solidification process and interaction between the SUSP and PUO, which is tended to self-organize the -NH₂/-NCO group through hydrogen bonds and the condensation as shown in fig. S2. The same procedure was followed for all samples. For comparison, a dense PDPU film was obtained by casting PDPU elastomers in a PTFE dish without any solvent at a 2:1.6 ratio.

**PDPU for mechanical measurement**

PDPU was dried at ambient temperature for a long time, because certain amounts of the isocyanate groups will not react with hydroxyl groups, capable of producing the dense PDPU without voids for comparison. Besides the samples for GS-TENG fabrication, the other PDPU was prepared with dimensions of 40 mm length by 10 mm width by 4 mm thickness and used for the mechanical properties testing. To check whether residual solvent has any influence on the formation of porous films, a control experiment was designed as follows: A 30 wt % DMAc solution of PDPU was used to cast the polymer films under the same conditions as those described above. To remove residual DMAc, the film was predried in a vacuum oven at 50°C for 3 hours and then the mold was gradually heated from 40° to 100°C over 24 hours. The corresponding porous PDPU films were obtained by drying the resulting emulsions at above specified temperature in a glass mold.

**Fabrication of the GS-TENG**

AgNWs (diameter of 70 nm, length of 100 to 200 μm, XFNANO, China) were sprayed on a PTFE film to assemble the AgBM with high transparency and conductivity. A sticky PDPU was attached on the PTFE to transfer the AgBM for both sides followed by peeling off, and two conductive wires were connected externally as the electrodes for testing, followed by spin-coating the thin layers of PDPU on the AgBM for protection, achieving a GS-TENG with good transparency. In addition, Ag flakes (Sigma-Aldrich, 10 μm, purity ≥99%) and liquid metal (EGaInPs) were mixed with PDPU solution in a weight ratio of 1:2:1. The resultant conductive solution was blade-coated on both sides of PDPPUs and cured as the electrodes, which were protected by the additional PDPU thin layers. Some parts of the electrode were left to connect with the conductive tapes for measurement, realizing a stretchable device with excellent deformability.

**Elastomer characterization**

¹H NMR spectrometers (NMR, 400 MHz Bruker DPX 400), ¹³C NMR (400 MHz Bruker DPX 400), ²⁹Si NMR (400 MHz, JEOL ECA400), and FTIR (FTIR-ATR, PerkinElmer, Frontier) were used to investigate the chemical structure of the synthesized PDPU. ¹H NMR and ¹³C NMR were carried out at room temperature using tetramethylsilane as the internal reference, and the deuterated solvents were used as internal lock reference. SAXS and WAXS measurements were performed using SWAXS Xenocs Nano-inXider with λ = 0.154 nm. The scattering patterns were recorded using Dectris Pilatus3 hybrid pixel detectors placed at sample-to-detector distances of 0.938 and 0.079 m from the PDPUs for the SAXS and WAXS measurements, respectively. Fit2D software was used to analyze the obtained SAXS data. Laboratory shear strength adhesion tests were carried out in accordance with ASTM D1002 standards using an MTS Criterion Model 43 (MTS Systems Corporation, Eden Prairie, MN, USA) test system with metal substrate (iron plates) and organic substrate (wood pieces) adherends at room temperature. Samples were adhered at 100°C for 20 hours with a 300-g weight used as a compression source. Samples were tested to a strain rate of 1.0 mm/min. The thickness of the PDPPUs was measured using screw gauge. Dynamic viscoelastic rheological properties were conducted by using a Physica MCR 501 rheometer (Anton Paar, USA). All measurements were performed at 25°C at 1 Hz oscillation with an 8-mm probe (PP08-150, Anton Paar, USA) maintained at a gap of 0.2 mm. Optical transparency was measured using UV-vis-NIR Lambda 950. DMA (TA Instruments, DMA Q800) was performed at a constant frequency of 1 Hz to measure the dynamic mechanical behavior of PDPPUs, which were heated and cooled from −130° to 130°C at a rate of 3°C min⁻¹ in a liquid N₂ environment. The PDPU was cut into rectangular dimensions of 20 mm by 10 mm by 2 mm for the tensile sample property test, performed on an MTS Criterion Model 43 (MTS Systems Corporation, Eden Prairie, MN, USA) testing system with a load cell of 500 kN at a speed of 100 mm min⁻¹ at room temperature. Tensile stress-strain experiments were analyzed in accordance with ASTM D638-10 standards. The compression tests were performed with an Instron 5567 testing system using load cells of 500 N and 30 kN at a strain rate of 2 mm min⁻¹. The contact angle of PDPU was measured with a video-based optical contact angle measurement system (DataPhysics OCA 15 Pro). The PDPPUs with voids were observed using a microscope (Olympus SXZ16) and an inverted microscope (Nikon ECLIPSE TS100). Field-emission SEM (JEOL 7600) was used to reveal the morphology and void size of samples.

**Electrical measurement**

Keithley 2400 source meter was used to measure the resistance of the conductor under different strains. A multifunctional stretching stage (Smart Memories, Singapore) was used to stretch the PDPU and device for various measurements. MFIA Impedance Analyzer (Zurich Instruments) was applied to test the capacitance. A mechanical shaker (Sinocera, model JZK-20) and a force gauge (Sinocera, model CL-YD-303) were used to compress the device and record the force for measurement. Surface potential of materials was measured using an electrostatic voltmeter (Trek, model 542 A). The output voltage and transferred charge of the GS-TENG were tested with an oscilloscope (Tektronix, MDO 3024, impedance = 10 megohms) and an electrometer (Keithley 6514 electrometer, input resistance = 200 teraohms). A low-noise current preamplifier (Stanford Research Systems, model SR570, impedance = 4 ohms) was used to measure the output current. All electrical measurements were carried out in ambient conditions (room temperature, 23 ± 1°C; relative humidity, 65 ± 3%). The finger bending motion detection was performed by mounting the device on latex glove to monitor the real-time output voltages at different bending angles. The gait analysis was carried out by mounting the device between socks and shoes to record the output voltage signals when walking with normal gait and shuffling gait. This study was approved by the institutional review board (IRB), Nanyang Technological University (IRB-2017-08-038). Informed consent form was obtained from all the participants.
synthesis, characterizations, and analysis of the elastomer. J.W. contributed EGaInP/Ag flake stretchable electrode. X.Z. assisted in electrical testing and analysis. P.S.L. supervised this project. J.X., G.T., and P.S.L. wrote the paper. All authors discussed the results and commented on the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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Self-healable sticky porous elastomer for gas-solid interacted power generation

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