Review Nanogenerators for Human Body Energy Harvesting

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Humans generate remarkable quantities of energy while performing daily activities, but this energy usually dissipates into the environment. Here, we address recent progress in the development of nanogenerators (NGs): devices that are able to harvest such body-produced biomechanical and thermal energies by exploiting piezoelectric, triboelectric, and thermoelectric physical effects. In designing NGs, the end-user's comfort is a primary concern. Therefore, we focus on recently developed materials giving flexibility and stretchability to NGs. In addition, we summarize common fabrics for NG design. Finally, the mid-2020s market forecasts for these promising technologies highlight the potential for the commercialization of NGs because they may help contribute to the route of innovation for developing self-powered systems.

Harvesting the Energy in the Human Body: Requirements and Uses

Micro- and nanopower **energy harvesting** (see Glossary) is a research field under rapid development [1,2]. Since 1996, when T. Starner hypothesized a wearable computer powered by the energy of the body, many researchers have been improving on the techniques for developing energy harvesters (EHs), with specific reference to on-body applications [3]. The growing interest in developing self-powered and comfortable devices arises from the goal of unlimited monitoring, where the users would not need to change the battery. Thus, humans would wear electronic systems without needing take them on and off for charging, with a remarkable advantage in specific population classes, such as older humans and infants [4,5]. Moreover, rapid advances in the development of miniaturized electronics have led to a gradual reduction in the power consumption of the end-systems, paving the way for the use of EHs as battery replacers in a variety of application fields, ranging from direct on-body applications to implantable devices.

Figure 1 lists the power consumption values of **commercial off-the-shelf (COTS)** components (i.e., datasheet values and implantable medical devices) [6]. These values are in the range of 100 nW–10 mW, which is the typical range of the power harvested from the surface of the human body [7]. Therefore, micro- and nano-energy harvesting techniques are receiving increasing interest for use in the design of flexible and stretchable self-powered systems that ensure the well-being of the wearers and will allow the development of new technologies for clinical applications [8–11]. From an energy perspective, the human body is a convenient depot: potential energy sources include biomechanical energy through the movements of the body joints, and thermal energy from the heat exchanged with the environment [12–14].

Devices able to harvest biomechanical and thermal energies from the body surface are commonly known as NGs. In 2006, Wang and Song [15] proposed the first NG prototype, and the rapid growth over this decade was significant [16], because the nano-size of NGs enables the design of systems able to maintain their original electronic and structural properties



The human body produces a huge amount of energy while performing daily activities. Harvesting this energy could represent a turning point for powering wearable devices.

Advances in physical and chemical fields enable the design of flexible and stretchable materials that adhere to the surface of the body to follow the shape of the skin.

Functional polymeric fibers allow the development of smart-clothes for harvesting the energy on the surface of the human body.

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even when they are bent, twisted, or stretched. These characteristics allow the integration of NGs into fabrics, thus achieving appropriate contact with the surface of the body.

In this review, we summarize the latest advances in the development of flexible and stretchable NGs to harvest energy directly from the body surface. We begin by introducing the three main operating principles for designing NGs and then describe the body applications of these devices. In addition, we highlight NGs based on common fabrics to describe how energy can be harvested throughout the day. Finally, we outline the market outlook of the next decade for new materials to be used to develop foldable NGs.

Working Principles of NGs

NGs for human body energy harvesting are solids with either a crystalline or amorphous structure: in a crystalline solid, the constituents of the lattice (ions, atoms, and molecules) aggregate with one another, to form an ordered and periodic pattern in space; conversely, the network configuration of the lattice structure is random for the solid matter in an amorphous state. The solid matter for developing NGs can have either lattice structure (amorphous or crystalline), and this will also depend on the nature of the elements (inorganic and/or organic) they comprise.

Until recently, the most common working principles for driving NGs were piezoelectricity and triboelectricity for transducing biomechanical energy into electricity, while the thermoelectric Seebeck effect was used to transform thermal energy.

The piezoelectric effect relies on the physical and chemical properties of the crystalline phase of the solid matter; if the lattice structure is noncentrosymmetric, the piezoelectric effect may occur under the influence of external perturbations, which produce charge separation across the structure, resulting in electrical polarization of the material.

By contrast, a triboelectric NG generates an electrical voltage through frictional contact between solid matters. Contact electrification and electrostatic induction are physical effects that lead to the generation of triboelectric charges. When two organic or inorganic materials, with different values of electronegativity, come into contact with one another, they generate triboelectric charges on their surfaces, and a voltage difference occurs from the separation of the electrical charges due to the spatial displacement of materials.

Finally, thermoelectric NGs generate electrical power when a temperature gradient occurs between two dissimilar conducting materials, generally comprising multiple couples of p- and n-type elements.

Wearable NGs

Wearable NGs placed on the human body must be comfortable and imperceptible for the wearer, almost like a garment that can conveniently harvest the energy of the body. Table 1 lists current piezo-, tribo-, and thermo-NGs for harvesting the energy on the surface of the human body. In addition, for each considered working principle, Table 1 highlights common fabrics used as substrates or active materials for developing NGs.

Piezoelectric NGs

A single ZnO **nanowire** (NW) laterally bonded with silver paste onto a flexible polyimide (PI) substrate, Kapton[®], was used first as a piezo-NG to harvest the biomechanical energy on the body surface [17]. The semiconducting property of the ZnO material with metal electrodes at its ends create a Schottky barrier, at least at one end of the NW, thus preserving the piezo-potential in the ZnO-NW and driving the flow of electrons to an external load circuit. In another

Glossary

Commercial off-the-shelf component (COTS): electronic components manufactured by major

international companies for the consumer electronic market.

Energy harvesting: the process by which the wasted energy from environmental sources is recovered and stored for powering electronic systems or to prolong their operation time.

Functional materials: specialized materials that use their structural properties to perform specific tasks. Nanowire (NW): a structure, almost 1D, which is cylindrical or polyhedral with nanometric dimensions. Many different types of NW exist, including superconducting, metallic, semiconducting and insulating NWs, Smart-clothes: fabrics that detect external stimuli and react according to the surrounding environmental conditions.



Figure 1. Which Devices Can Be Powered by Energy Harvesters (Ehs)? The average power consumed by generic integrated circuit components and sensors, and by implantable devices, in the range of 100 nW–10 mW. The colors codify the power consumption ranges: green, 100 nW–1 μ W; violet, 1–10 μ W; blue, 10–100 μ W; red, 100 μ W–1 mW; yellow, 1–10 mW.

study [18], a flexion and extension movement of the index finger resulted in a 0.2% tensile strain on the structure, generating a piezoelectric potential along the wire. Although the NG structure was flexible enough to follow the movements of the finger, this prototype showed some disadvantages, such as output stability and mechanical robustness under repeated stress.

To increase the robustness of piezo-NGs, Lee *et al.* [19,20] proposed an ultrathin aluminium (Al) foil to be used as both the substrate and the electrode for the structure. The prototype enabled detection of wrinkling while fluttering the eyelashes. Another robust configuration for harvesting the biomechanical motion of arm movements relies on the development of an ultrathin ZnO film bonded onto a polyethylene terephthalate (PET) plastic substrate. The physical properties of the PET allow the mechanical rolling of the whole structure, so that it might be worn at the level of body joints [22]. The only disadvantage of this NG was the brittleness of the indium tin oxide (ITO) electrode, which limits the rolling curvature of the device to the value of 2 cm. To enhance the stretchability of this kind of piezo-NG, Pradel and colleagues [23] used silicon rubber, Ecoflex[®], for packaging ZnO ultrathin films. This ZnO-NG generates electrical output by transducing the biomechanical movements of the wrist tendons, detecting even the different movements of each finger.

For improved sensitivity and higher resolution in sensing applications, the best piezoelectric elements are polymers. In particular, P(VDF-TrFe) nanofibers may be aligned to form piezo-sheets that can harvest biomechanical motion and even detect low pressure values with a resolution of approximately 0.1 Pa [24]. Park and colleagues [25] proposed a flexible and stretchable polyvinylidene fluoride/trifluoroethylene [P(VDF-TrFe)] patch able to detect the movement of the skin due to radial and carotid pulsing, with a displacement resolution of approximately 1 μ m. Both P(VDF-TrFe)-NGs were packaged into an elastomeric matrix of polydimethylsiloxane (PDMS), which ensures both the stability and flexibility of the devices.

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NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
Piezo	Single ZnO-NW	Ag	PI film	Area:; thickness: 50 μm	Tensile strain measured: 0.05 – 0.2%	Bending radius: 2 cm	Stretching and releasing at 22 cycles/min for 120 min	Finger bending	0.25 mV	150 pA	[17,18]
	ZnO film	Al	Al foil and PMMA	Area: 13 × 5 mm ² ; thickness: 18 μm	-	Bending radius: 3 mm	Pressing and releasing at 2 Hz for 20 h	Blinking motion	0.2 V	2 nA	[19,20]
	ZnO and PVDF composite	Au	PDMS	Area: 30 × 30 mm ² ; thickness: 30 μm	-	-	-	Finger bending	0.33 V	62 nA	[21]
	ZnO film	ITO and Ag	PET	-	-	Rolling curv. radius: 2 cm	666 cycles of rolling movement (2000 s)	Rolling and muscle stretching	0.28 V	-	[22]
	ZnO film	AZO	Ecoflex	Area: 50 × 50 mm ² ; thickness: 305 μm	Compressive strain measured: -0.22%	-	-	Movement of wrist tendons	1 V	100 pA	[23]
	P(VDF-TrFe) sheet	Ag	PI	Area: 9 × 18 mm ² ; thickness: 245 μm	Ultra-high sensitivity for measuring pressure: 0.1 Pa	-	1000 cycles of bending movement at 2 Hz frequency	Skin vibration	1.5 V	40 nA	[24]
	P(VDF-TrFe) sheet	Au	PDMS	Area: 9 × 18 mm ² ; thickness: 100 μm	Precise sensor for pressures of 1 kPa and deformations below 1 µm	Bending radius: 2.5 mm	30% strain of uniaxial stretching over 1000 cycles	Radial and carotid blood vessel pulsing	0.6 V	-	[25]
	PVDF sheet	Cu	PVC and PDMS	Area: 4 × 20 mm ² ; thickness: 100 μm	Tensile strain measured: 0.5%	-	Five days of bending movement at 5 Hz frequency	Blinking motion	0.2 V	2 nA	[26]
	PVDF film	Au	PI	Area: $40 \times 70 \text{ mm}^2$; thickness: $350 \ \mu\text{m}$	Tensile strain measured: 0.001613%	-	-	Wrist bending, elbow folding, cardiac impulse, human breathing, heel strike	25 V	20 µA	[27]
	AIN film	Mo and Cr/Al	Pl and Parylene	Area: $4 \times 6 \text{ mm}^2$; thickness: $100 \ \mu \text{m}$	-	Bending radius: 5.5 mm	-	Follows deformations of skin	0.7 V	0.3 μΑ	[28]

Table 1. Current NGs for Harvesting Energy from the Surface of the Human Body^a

Table 1. (contil	nued)										
NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
	BaTiO ₃ and P (VDF- HFP) composite	Al	PDMS and Pl	Area: 2 \times 2 mm ² ; thickness: 350 μ m	Applied pressure: 0.23 MPa	-	5400 cycles of bending movement	Finger tapping	75 V	15 μΑ	[29]
	PZT film	Cr/Au and Ti/Au	PET	Area: 20 × 50 mm ² ; thickness: 225 μm	Tensile strain measured: 0.3%	Bending radius: 21 mm	115 000 cycles of bending movement	Wrist movement	120 V	2 μΑ	[30–32]
	PMN-PT particles	Ag-NWs	Ecoflex	-	Tensile strain measured: 200%	-	15 000 stretching cycles	Knee bending	0.7 V	50 nA	[33]
Piezo fabric	PVDF-NaNbO ₃ nonwoven fabric	PU yarns and Ag- coated PA yarns	PDMS	Area: $25 \times 25 \text{ mm}^2$; thickness: $2000 \ \mu \text{m}$	Compressive pressure: 0.2 MPa	-	1 000 000 cycles of compression test at 1 Hz	Heel strike	3.4 V	4.4 μΑ	[34]
	Single ZnO and PVDF fiber	Au	PS and PDMS	Fiber length: 20 mm; thickness: 6.2 mm	Tensile strain measured: 0.1%	-	-	Elbow folding	0.1 V	-	[35]
	PVDF filaments as spacer yarns	Ag-coated PA66 yarns	PU	Area: $53 \times 150 \text{ mm}^2$; thickness: 3.5 mm	Compressive pressure: 0.10 MPa	-	150 cycles of compression	Fabric to wear	14 V	30 µA	[36]
	BaTiO ₃ /PVC fibers	Cu	PET	-	-	-	Maximum tensile strength: 54 MPa	Elbow folding, fabric to wear	1.9 V	24 nA	[37]
Tribo	PTFE and Al (rhombic grid structure)	Al and Cu	PET	Area: $50 \times 50 \text{ mm}^2$; thickness: 0.6 mm	-	-	100 000 cycles of external contact force	Natural walking with pack load of 2 kg	400 V	230 µA	[38]
	PTFE and Al (zigzag structure)	Al	PI	Area: 38 × 38 mm ² ; thickness: 0.95 mm	Contact force: 500 N	-	100 000 cycles of external contact force	Hand palm tapping	215 V	656 µ.A	[39]
	PTFE and Al (zigzag structure)	Al	PET	Area: $30 \times 270 \text{ mm}^2$; thickness: –	Deformation amplitudes during contact force: 2.5 cm	-	-	Foot plantar pressure	840 V	55 μΑ	[40]
	FEP and Al	Al and Cu	PI	Area: $52 \times 57 \text{ mm}^2$;	-	-	180 000 cycles of external contact force	Heel strike	700 V	-	[41]

Fable 1. (cont	inued)										
NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
				thickness: 24 mm							
	Cu and CPP	Al and Cu	ΡΑ	Circular contact area: 1800 mm ² ; thickness: 100 µm	-	-	10 000 cycles of external contact force	Body movements during sleep	55 V	0.8 μΑ	[42]
	Cu and Pl	Cu	PDMS	Area: $75 \times 50 \text{ mm}^2$; thickness: –	Tensile strain measured: 22%	Curved surface up to 36 cm ⁻¹	3600 stretching cycles	Elbow and knee bending, bicep muscle tension, neck tilting, swallowing motion	600 V	45 μΑ	[43]
	Au and epoxy (zigzag structure)	Cu	PI	Area: $15 \times 30 \text{ mm}^2$; thickness: 1.64 mm	-	-	-	Finger tapping	160 V	8 μΑ	[44]
	Al and PDMS (double arch- shape structure)	ITO	PET	Area: 20 \times 40 mm ² ; thickness: -	-	-	-	Slam biceps with forearm	120 V	88 µA	[45]
	PET and PDMS (with sponge divider)	ITO and Cu	-	Area: 90 \times 270 mm ² ; thickness: 3.5 mm	-	-	-	Foot plantar pressure	220 V	40 μΑ	[46]
	PES and PDMS (arch-shape structure)	Ag-NWs	-	-	Tensile strain measured: 60%	-	10 000 stretching cycles	Breathing, coughing, swallowing, drinking, eating	35 V	4 μΑ	[47]
	Human skin and PDMS	ITO	PET	Area: $10 \times 10 \text{ mm}^2$; thickness: 1 mm	Detection limit of pressure: ~0.4 kPa	-	-	Hand palm tapping	60 V	3.5 μΑ	[48]
	Human skin and PDMS	Cu	-	Circle diameter: 15.5 mm; thickness: 1 mm	-	-	5000 cycles of external contact force	Monitoring motions of elbow, knee, heel, finger joints	40 V	2 μΑ	[49]
	Human skin and PDMS	ΙΤΟ	PET	Area: 12.5 \times 25 mm ² ; thickness: –	-	-	-	Finger tapping	200 V	12 µA	[50]
	Human skin and PDMS	Ti/Cu	Ecoflex	Area: 18 \times 22 mm ² ; thickness: –	-	-	-	Finger tapping	21.9 V	0.55 μΑ	[51]

Table 1. (continued) N

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NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
	Human skin and PDMS	Au	PI	-	Range of movement of middle joint of finger: 60–180°	-	-	Monitoring finger angle displacements	70 V	-	[52,53]
	Human skin and PDMS	Ag-NWs	PET	Area: 50 × 50 mm ² ; thickness: –	-	-	30 000 cycles of external contact force	Detecting velocity of touch	5 V	-	[54]
	Human skin and PDMS	Ag-NWs	-	Area: 20 \times 30 mm ² ; thickness: –	-	-	-	Finger tapping, elbow and wrist bending	56 V	3.1 μΑ	[55]
	Human skin and Ecoflex	Ag-NWs	-	Area: $40 \times 70 \text{ mm}^2$; thickness: 1.5 mm	Tensile strain measured: 300%	Bending radius: 20 mm	3600 cycles of external contact force	Foot plantar pressure and arm swinging	250 V	-	[56,57]
	Al and Rubber	Al	PTFE	Area: $30 \times 88 \text{ mm}^2$; thickness: $250 \ \mu \text{m}$	Stretching displacement of 100 mm	-	5000 cycles of stretching and releasing movement	Breathing, knee motion	65 V	-	[58]
Tribo fabric	Latex fabric and PDMS	Graphene	PET	Area: $30 \times 30 \text{ mm}^2$; thickness: 2.4 μ m	Contact pressure of 30-40 kPa	-	2 weeks of external contact force cycles	Fabric to wear	30.9 V	3.9 μΑ	[59]
	Nylon fabric (PA 6) and PTFE	ΠΟ	PET	Major axis: 25 mm; Minor axis: 20 mm; thickness: 100 μm	High sensitivity for measuring pressure in range: 2.5–1200 Pa	-	40 000 cycles of external contact force	Monitoring of arterial pulse at carotid, wrist, and chest	5 V	0.3 μΑ	[60]
	Latex fabric and FEP	ITO	PP	Area: $65 \times 100 \text{ mm}^2$; thickness: $90 \ \mu \text{m}$	Tensile strain measured: 5.4%; contact force: 140 N	Bending radius: 0.84 mm	-	Hand palm tapping	340 V	78 μΑ	[61]
	Denim fabric and Pl	Al	PET and sponge	Area: 50 × 50 mm ² ; thickness: 90 μm	-	-	2000 cycles of external contact force	Walking, running and sitting activities	10 V	0.75 μΑ	[62]
	AI and PDMS	Al and Cu	Fabric	Area: $20 \times 70 \text{ mm}^2$; thickness: $800 \ \mu \text{m}$	-	-	-	Fabric to wear for walking activity	17 V	0.28 μΑ	[63]

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Table 1. (continued)

NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
	AI and PDMS	Au	Au- coated fabric	Area: 70 \times 70 mm ² ; thickness: –	Bending length: 3 cm	-	-	Arm bending	139 V	39 μΑ	[64]
	Ag and ZnO/PDMS	Ag	Ag- coated fabric	-	Compressive force: 10 kgf	-	12 000 cycles of external contact force	Fabric to wear	120 V	65 μΑ	[65]
	PET and FAS/PDMS	Al foil and Ag-NWs	PA 6	Area: $30 \times 30 \text{ mm}^2$; thickness: –	-	-	12 000 cycles of external contact force	Fabric to wear	575 V	12.1 μA	[66]
	CNT and PTFE	CNTs	Cotton threads	Fiber length: 90 mm and 8 helix turns	Tensile strain measured: 2.15%, with max. tensile stress: 210 MPa	-	90 000 cycles of strain	Finger bending	9.1 V	0.1 μΑ	[67]
	Ni and Parylene	Ni	PES	Area: 100 \times 100 mm ² ; thickness: –	Bending movement: 180°	-	1000 cycles of bending movement	Fabric to wear	50 V	4 μΑ	[68,69]
	Cu coils and Silicone rubber fiber	Cu and CNT	-	Fiber diameter: 3.5 mm; fiber length: 100 mm	Tensile strain measured: 100%	-	10 800 stretching cycles	Hand motion, fabric to wear	142 V	-	[70]
	AI/PDMS and PU/PI	Carbon thread	Fabric	Area: 15 × 60 mm ² ; thickness: –	-	-	4000 cycles of sliding motion	Fabric to wear under armpit for walking activity	15 V	0.15 μΑ	[71]
	Nylon fabric (PA 6) and FEP	Ag	Fabric	Area: 100 × 100 mm ² ; thickness: 300 μm	-	-	24 000 cycles of bending movement	Fabric to wear	12.6 V	3.7 μΑ	[72]
	Nylon fabric (PA 6) and PES	Ag	Fabric	Area: $50 \times 110 \text{ mm}^2$; thickness: –	-	-	-	Bending of arm and leg joints, shaking of clothes	90 V	1 μΑ	[73]
Thermo	n: Bi ₂ Te ₃ ; p: Sb ₂ Te ₃	Ag	PDMS	Thermocouples: 2778; area: 50 × 50 mm ² ; thickness: 4 mm	Temperature gradient: 5 °C	-	-	-	250 mV	2 μΑ	[74–76]
	n: Bi ₂ Te ₃ ; p: Sb ₂ Te ₃ and PEDOT:PSS	Ag film	PI	Thermocouples: 15; area: 30 × 50 mm ² ; thickness: –	Temperature gradient: 5 °C	Bending radius: 30 mm	1000 cycles of bending movement	Worn on wrist	12.1 mV	-	[77]
	p-n: Bi ₂ Te ₃	Cu	PDMS	Thermocouples: 50; Area: -; thickness: -	Environmental temp.: 18.3 °C	-	-	Worn on wrist, on upper arm and on T- shirt, walking activity	7 mV	30 µA	[78]

Table 1. (continued)

NG type material NG active material Electrodes Substrate NG dimension Mechanical load/ tensile strain NG flexibility Durability test Human body application Voltage Current Refa Thermo fabric p: Sb ₂ Te ₃ Ag foil Silk fabric and PVA Thermocouples: area: 40 × 80 mm ² tokkness: 2.5 mm Environmental temp:: 20 °C - 100 cycles of bending and twisting movement Arm-attached, waking activity 6.02 mV - . <	× .	· · · · · · · · · · · · · · · · · · ·										
Thermo fabric p: Sb2Te3 p: Sb2Te3Ag foilSilk fabric and PVA and PVA and PVA area: 40×80 mm² thickness: 2.5 mmEnvironmental temp: 20 °C co sec-100 cycles of bending and twisting movementArm-attached, walking activity6.02 mV[79]p: Blo_SSb1.5 Te3. n: Bl2Se0.3 Te2.7AgAgPIThermocouples: 12; area: 6 $\times 25$ mm²Environmental temp: 5 °CArm-attached, walking and twisting movementFlaced on T-shirt, resting activity11.5 mV12.7 \muA[80]n: (0.98Bi, (0.02Sb)2 (0.05Sb12) (0.05Bi, 0.75Sb)2CoFlaced on T-shirt, resting activity11.5 mV12.7 \muA[80]attached, uning activityCo <t< td=""><td>NG type</td><td>NG active material</td><td>Electrodes</td><td>Substrate</td><td>NG dimension</td><td>Mechanical load/ tensile strain</td><td>NG flexibility</td><td>Durability test</td><td>Human body application</td><td>Voltage</td><td>Current</td><td>Refs</td></t<>	NG type	NG active material	Electrodes	Substrate	NG dimension	Mechanical load/ tensile strain	NG flexibility	Durability test	Human body application	Voltage	Current	Refs
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} p: B_{0.5}Sb_{1.5} \\ Te_{3} n: Bi_{2}Se_{0.3} \\ Te_{2.7} \end{array} & Ag & Ag & PI & Thermocouples: \\ \begin{array}{c} 12; area: \\ 6 \times 25 mm^{2} \\ thickness: \\ 4.7 mm \end{array} & femp: 5 \ ^{\circ}C & femp: 5 \ ^{\circ}C & femp: femp: femp: 5 \ ^{\circ}C & femp: $	Thermo fabric	n: Bi ₂ Te ₃ p: Sb ₂ Te ₃	Ag foil	Silk fabric and PVA	Thermocouples: 12; area: $40 \times 80 \text{ mm}^2$ thickness: 2.5 mm	Environmental temp.: 20 °C	-	100 cycles of bending and twisting movement	Arm-attached, walking activity	6.02 mV	-	[79]
n:(0.98Bi, 0.02Sb)2 (0.9Te,0.1Se)3; p: (0.25Bi,0.75Sb)2and the second sec		p: Bi _{0.5} Sb _{1.5} Te ₃ n: Bi ₂ Se _{0.3} Te _{2.7}	Ag	PI	Thermocouples: 12; area: $6 \times 25 \text{ mm}^2$ thickness: 4.7 mm	Environmental temp.: 5 °C	-	-	Placed on T-shirt, resting activity	11.5 mV	12.7 μA	[80]
attached, 2.6 mV – [81] running activity		n:(0.98Bi, 0.02Sb) ₂ (0.9Te,0.1Se) ₃ ; p: (0.25Bi,0.75Sb) ₂			(0.95Te,0.05Se) ₃	Ag wire	PES fiber cloth	Thermocouples: 12; area: 50 × 65 mm ² ; thickness: –	Temperature gradient: 2.9 °C	-	-	Arm-
	attached, running activity	2.6 mV	-	[81]								

^aAbbreviations: Ag, silver; Al, aluminium; AIN, aluminium nitride; Au, gold; AZO, aluminium-doped zinc oxide; BaTiO3, barium titanate; Bi2Te3, bismuth telluride; BiSbTe, bismuth antimony telluride; BiSeTe, bismuth selenium telluride; CNT, carbon nanotube; CPP, cast polypropylene; Cr, chromium; Cu, copper; FAS, fluoroalkylsilanes; FEP, fluorinated ethylene propylene; ITO, indium tin oxide; Mo, molybdenum; NaNbO3, niobium sodium oxide; Ni, nickel; P(VDF-HFP), poly(vinylidene fluoride-co-hexafluoropropylene); P(VDF-TrFe), poly(vinylidene fluoride-co-trifluoroethylene); PA, polyamide; PA6 and PA66, nylon; PDMS, polydimethylsiloxane; PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); PES, polyester; PET, polyethylene terephthalate; PI, polyimide (e.g. Kapton³⁶); PMMA, poly(methyl methacrylate); PMN-PT, lead magnesium niobate-lead titanate; PS, polystyrene; PTE, polyethylene; PU, polyurethane; PVA, poly(vinyl acetate); PVC, polyvinyl chloride; PVDF, polyvinylidene fluoride; PZT, lead zirconate titanate; Sb2Te3, antimony telluride; Ti, titanium; ZnO-NW, zinc oxide nanowire.

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All of the NGs described above generate measurable quantities of power output in the nW range. To increase these power values, researchers have designed many NGs made from materials with better piezoelectric properties than those of ZnO and P(VDF-TrFe).

Among the possible piezomaterial alternatives, inorganic PZT and BaTiO₃ materials have been introduced: a flexible composite thin film comprising P(VDF-HFP) and hemispherical BaTiO₃ nanoparticles (NPs) has been shown to generate a voltage output up to 75 V and a current output of approximately 15 µA under finger pressure [29]. The hemispherical surface of each NP enhanced the piezo-power generation as a result of improvements in the surface contact between the active area and the electrode. The entire device, designed on a PI film, even guaranteed robustness under 2 h-long repeated bending cycles. In another application, a flexible piezoelectric PZT thin film developed on a PET substrate, with interdigitated metal electrodes, harvested energy from the biomechanical movements of the wrist, with a bending radius value of approximately 1.6 cm [30–32]; the motion of the wrist produced up to 120 V of voltage output and 2 µA of current output. Finally, Jeong et al. [33] proposed the most flexible element for the field of biomechanical energy harvesting: a piezo-elastic composite made of particles of PMN-PT and multi-walled carbon nanotubes (MWCNTs) packaged in Ecoflex[®] silicon rubber, which allowed a stretchability of up to 200% of its initial size, generating small quantities of electrical power under the folding movements of the human joints. To maintain the robustness of the device, long Ag-NWs were used as stretchable electrodes, which ensured high conductivity and electrical output stability.

Triboelectric NGs

At the early stage of the development of tribo-NGs, researchers focused on the design of tribo-NGs comprising a metal plate, positively charged, and a polymeric plate, negatively charged.

Yang and colleagues [38] proposed a tribo-NG backpack for biomechanical energy harvesting that is able to harvest the energy generated by walking with a 2.0 kg load: multiple polytetrafluoroethylene (PTFE) and Al plates, placed on a flexible PET substrate, operate as tribo-layers and form an integrated rhombic structure. During the contact and release process of the tribolayers, the NG generates power output of the order of approximately 1 mW. Tribo-NGs comprising zigzag structures of multiple PTFE and Al plates were embedded in a shoe insole to generate energy while walking [39,40]. A patch-NG made of a thin Cu cantilever spring sandwiched into a folded CPP film detects the body movements during sleep, without needing an external power source [42]. For these NGs, the power output strongly depends on good adhesion between the two active layers. Modifying the tribo-layers by adding surface porosity or by implementing micro-cubic or micro-pyramid array structures [44,45] increased the power output, possibly to values in the hundreds of volts and hundreds of microamperes.

The polymeric physical state of tribo-layers allows for greater flexibility than metal-based layers, although at the expense of a lower power output. The stretchability of NGs even depends on the nature of the electrodes: ITO electrodes are the most widely used for transparent conducting film in tribo-NGs, which mainly operate under compressive stress, but their brittle nature cannot withstand high tensile strain. Therefore, conducting polymers and metal or carbon nanostructures are alternatives to ITO electrodes for developing stretchable devices [82]. In particular, Yang and coworkers [43] developed an imperceptible and stretchable tribo-NG for harvesting the biomechanical energy of human joint movements. The tribo-NG comprised a wavy Kapton film sandwiched between two Cu serpentine electrodes on a PDMS substrate, supporting a tensile strain of up to 22%, making the NG structure suitable to be attached to the skin. Again, to increase the stretchability of tribo-NGs, Hwang and colleagues [47] proposed a device comprising two polymeric tribo-layers and long Ag-NW electrodes. This enabled the NG to withstand tensile strains of approximately 40% while the wearer was breathing, coughing and swallowing, among other human physiological activities.

As a basic structure of all the tribo-NGs listed above, two electrodes are mandatory for proper device operation, but in some cases they may limit the application fields and increase development costs. A single-electrode mode can overcome these limitations and expands the applicability of tribo-NGs in the research field of biomechanical energy harvesting and human-machine interfacing. According to the tribo-series [83], human skin is a triboelectric layer, which presents electrostatic charges on its surface once it is in contact with dielectric or ferroelectric materials [84]. PDMS polymer film is widely used as friction layer for developing tribo-NGs, which involve the skin layer in the generation of tribo-charges. In the scientific literature, these NGs work as self-powered tactile sensors for tracking the location, velocity, and force of human touch [48,54,55]. In addition, tribo-NGs based on the friction contact between the epidermis and PDMS polymer can monitor human motion by measuring the angle displacements of the main body joints [49,52,53]. However, the PDMS polymer may be not suitable for following all movements of the limbs, due to its elongation limit. Thus, Lai and coworkers [57] developed a tribo-layer made of Ecoflex® silicon rubber in which Ag-NWs were dispersed internally to form a stretchable electrode. This tribo-NG sustained tensile strains of over 300%, making the device conformable for electronic-skin applications.

Thermoelectric NGs

Bi₂Te₃ and Sb₂Te₃ are conventional n- and p- type elements for developing the multiple thermocouples constituting the thermo-NGs, as a result of their high thermoelectric efficiency at room temperature. However, the brittle nature of these inorganic compounds does not allow for NG flexibility, making it necessary to use polymeric materials for supporting and packaging the thermoelectric elements to impart the desirable flexibility to the NG structure.

A flexible thermo-NG adheres to the body surface better than a rigid one, optimizing the thermal conductance between the skin and the generator, thereby increasing the temperature difference between the hot and cold sides of the NG. For example, Hyland and colleagues [78] wrapped a rigid thermo-NG in a PDMS polymer, increasing the device area, but conferring a minimum of flexibility for the entire structure. In this way, the NG was easily placed on the chest and the researchers tested the performance of the device under different walking speeds. To enhance the flexibility of the device, Jo and colleagues [85] designed a PDMS polymer substrate with several holes that were filled by columns of thermoelectric elements. The entire structure comprised eight p-n junctions in 250 mm², with a thickness of >4 mm, although this does not allow for large bending movements.

To enhance thermo-NG flexibility, We and coworkers [77] proposed a hybrid composite thermo-NG formed by infiltrating an organic conducting polymer, the PEDOT:PSS, into the pores of an inorganic thermoelectric film. The minimum value of the NG bending radius was approximately 3 cm and, thus, it could be worn on the wrist. In addition, this NG supports over 1000 cycles of bending movements without showing significant degradation in output performance. Another example of a flexible thermo-NG is the wavy-shape module presented by Francioso and colleagues [74,76]. The researchers assembled the p- and n-thermolegs on a wavy substrate made of two PDMS layers covered with a thin layer of Kapton. The former PDMS layer was Ag filled to enhance the contact between the skin and the hot thermojunctions, while the latter insulates the cold junctions from the hot ones. This wavy-shape NG counts up to 2778 p-n thermocouples and generates 250 mV when the temperature gradient is approximately 5 K. This voltage output is high for the field of energy harvesting by body heat, although the authors performed only simulation tests.

Fabric NGs

NGs based on fabrics represent a significant innovation for harvesting energy directly from the body surface, because humans generally wear clothes throughout the day. In particular, fabrics

made of polymeric materials are common in the textile market because of their low-cost, largescale manufacturing. Therefore, adding an active polymer into common fabrics could represent a new trend in developing smart-clothes for harvesting energy. Among all the working principles for designing NGs, the triboelectric principle is the most used because it relies on the contact-release process of any materials with different electronegativity values; as opposed to piezoelectric and thermoelectric ones, which depend on the physical and chemical properties of the chosen active elements for harvesting the energy. For example, NGs based on piezoelectric fabrics should be flexible and almost stretchable, and only the PVDF polymer ensures both these features. Zeng and colleagues [34] proposed a wearable NG made of PVDF-NaNbO₃ nonwoven fabric as the active material, and conductive yarns as electrodes. This NG works under compressive stress and shows great stability over 1 000 000 compression-release cycles, which is higher than a NG made of only NaNbO₃-NWs elements [86]. PVDF monofilaments can be also '3D spacers' between two knitted layers made of nylon yarns, thus resulting in an all-fiber NG [36]. The technologies for knitting 3D-spacer fabrics are well used in the textile industry; therefore, this example of piezo-NG can open the way for clothes to be easily designed for harvesting energy.

Regarding the design of textile-based NGs, which exploit the triboelectric effect, nylon fabric represents a good choice as a contact layer for the generation of energy when it rubs against polymeric materials, such as PDMS [56], PTFE [60], fluorinated ethylene propylene [61,72], and polyester (PES) [73], among others. Again, denim fabric in the contact-release process with PI represents a tribo-NG well suited for harvesting biomechanical energy [62]. However, these fabric NGs do not rely on knitting techniques, but rather are single or multiple patches assembled on fabrics. Thus, Liu and coworkers [87] proposed a tribo-NG textile without a multilayered structure, where PET fibers interlace at the top surface of the fabric and penetrate across its thickness on the bottom side, so the final structure looks like a 3D-penetrated fabric. Again, Zhao and colleagues [88] fabricated a textile tribo-NG by weaving Cu-coated PET (Cu-PET) warp yarns and PI-coated Cu-PET weft yarns. This NG shows washability capability, resulting in its suitability for common daily use. However, to have greater stretchability, a conductive polymer should replace the Cu metallic material.

Developing thermo-NGs based on fabric structures is difficult since the brittle nature of the inorganic thermoelectric elements does not allow for their integration into textiles. However, Lu and colleagues [79] deposited thermoelectric p-n columns on both sides of a silk fabric. In this way, the NG supports multiple bending and twisting movements, thus opening the possibility to integrate thermo-NGs into clothes. Again, by using a sewing process, Kim and coworkers [80] utilized conductive fabric threads for electrically connecting in series the thermo-columns into a PI substrate. Then, the entire structure was sewn into a T-shirt for harvesting thermal energy while walking. In addition, Siddique and colleagues [81] proposed a similar structure using PES fabric as the substrate, Ag threads as the conductive element, and p- and n-type Bi₂Te₃ as the thermoelectric elements. The textile and flexible thermo-NG can easily wrap the forearm for harvesting thermal energy even in harsh environments. Finally, by coating commercial fabrics with PEDOT:PSS polymer, it would be possible to develop flexible and foldable thermo-NGs. Although such a polymer properly works in a temperature range of approximately 300–390 K, which may be compatible with human activities, the voltage output is too low for considering this NG as being able to harvest human thermal energy [89].

Concluding Remarks and Future Perspectives

The current promising progress in the field of nanotechnology enables the development of new devices (NGs) for harvesting mechanical and thermal energy directly from the surface of the body. NGs will bring many exciting opportunities for continuously powering wearable systems, since the scientific research on wearables opens new prospects for the non-invasive

Outstanding Questions

Are NGs really wearable and comfortable for end-users?

If a human wears NGs all day long, what is the amount of harvested power? Are NGs efficient enough for supplying energy to small and lowpower wearable devices?

Are NGs sufficiently reliable for long-term use?

Is the commercial market for NGs realistically promising for companies?



Figure 2. Market Forecast for the Mid-2020s. The graph shows the money that is predicted to be spent during the mid-2020s for developing useful materials for the design of wearable NGs. Data from IDTechEX (www.idtechex.com).

monitoring of human health in the medical and fitness fields [90-92]. Therefore, the overall impact of NGs may expand with progress on new foldable and stretchable materials, which make devices comfortable for the end-users (see Outstanding Questions). IDTechEx, a business analysis company, has provided the market forecast for the mid-2020s on recently developed materials for NGs (Figure 2). Thus, companies around the world are likely to invest many billions of dollars with particular regard to the field of functional materials.

In addition, the improvements in the design of extensible electrodes and malleable electronic components could transform rigid devices into pliable ones, thus achieving smart systems for a range of applications, such as biomedical devices, components for soft robotics, and humanmachine interfacing, among others.

In summary, with the maturation of the technologies proposed in this review, in the near future we could have electronic devices powered by NGs that harvest energy directly from the surface of the body.

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