Contact Electrification



Controlling Surface Charge Generated by Contact Electrification: Strategies and Applications

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Contact electrification is the phenomenon in which charge is generated on the surfaces of materials after they come into contact. The surface charge generated has traditionally been known to cause a vast range of undesirable consequences in our lives and in industry; on the other hand, it can also give rise to many types of useful applications. In addition, there has been a lot of interest in recent years for fabricating devices and materials based on regulating a desired amount of surface charge. It is thus important to understand the general strategies for increasing, decreasing, or controlling the surface charge generated by contact electrification. Herein, the fundamental mechanisms for influencing the amount of charge generated, the methods used for implementing these mechanisms, and some of the recent interesting applications that require regulating the amount of surface charge generated by contact electrification.

1. Introduction

Contact electrification (or triboelectrification) is a natural phenomenon in which surface charge is generated by simply bringing two solid surfaces into contact and then separating them.^[1,2] Almost all types of materials charge easily by contact electrification, including metals, semiconductors, inorganic materials, and polymers; hence, the phenomenon is ubiquitous. As a result, the surface charge and the electric field produced by the charge affect our lives and the industry in a vast range of ways (Figure 1).^[2,3] Many of the effects are undesirable. In our daily lives, for example, we often experience the electrostatic adhesion of microscopic particles charged by contact electrification onto surfaces (e.g., lenses or computer screens), or the slight electric shock when one touches a door knob in dry weather. In industry, contact electrification can reduce the effectiveness of manufacturing processes in many different types of industries (e.g., petrochemical, chemical,

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pharmaceutical, semiconductor, and packaging). For example, in the pharmaceutical industry, charged drug particles can aggregate or separate, thus resulting in nonuniform dosage of the products.^[3] Particles adhering onto surfaces can cause fouling or prevent efficient transfer of heat. In addition, when the surface accumulates excessive amount of charge by contact electrification, electrostatic discharge (e.g., sparks) can be produced. Electrostatic discharge can damage electronic components and cause explosion of flammable materials.^[4] On the other hand, surface charge generated by contact electrification has many useful applications; examples include electrophotography, electrostatic separation of particles, electrostatic spray

coating, and electrostatic self-assembly.^[5,6] Besides contact electrification of two solid surfaces, the process of contact and separation of a solid and a liquid can also charge both the phases significantly;^[7–9] this phenomenon is also important for a wide range of applications and undesirable consequences. Therefore, there is a need to understand the fundamental strategies and methods to vary the amount of surface charge generated by contact electrification. It is important to decrease the amount of charge generated for the undesirable consequences of contact electrification, and to increase the amount of charge for useful applications. In addition, it is also important to be able to control the amount of surface charge—either to increase or to decrease—for different types of applications.

However, it can be challenging to devise ways to control surface charge because the nature of contact electrification is not well understood. For contacts involving metals, previous studies have established a linear relationship between the contact potential difference of the two contacting metallic surfaces and the amount of charge generated by contact electrification experimentally.^[10] Because the contact potential difference is proportional to the difference in the work functions of the two contacting metallic surfaces, the species that transferred from one surface to another during contact is likely to be an electron. For contacts involving only insulating materials, however, the fundamental mechanism is still a subject of debate even though the phenomenon has been known and studied since antiquity. Different mechanisms have been proposed, including electron, ion, or material transfer.^[1,3,4,11-13] In general, because of the complexity of the phenomenon, most of our understanding of the phenomenon remains empirical.





This review summarizes the main fundamental mechanisms and general methods used for modifying the materials for controlling charge (Figure 1). We divide this review into the following sections: 1) strategies for controlling surface charge, 2) strategies for increasing surface charge, and 3) strategies for decreasing surface charge. Subsequently, we will discuss several recent interesting devices based on contact electrification developed for a diverse range of applications. The development of these devices has recently generated a tremendous amount of interest in materials science, especially the general class of devices built from the triboelectric nanogenerators (TENGs).

2. Strategies for Controlling Surface Charge

A wide range of methods is available for varying the amount of surface charge of materials generated by contact electrification. Uncontrollable environmental factors, such as temperature and humidity, have been widely reported to affect the charge of materials.^[14] The method of contact can also influence the amount of charge generated; examples include the amount of pressure applied and the specific type of contact used (e.g., rubbing or contacting). When particles are involved, it has been reported that the shapes and sizes of the particles can influence the amount of charge generated.^[15]

The most basic consideration for controlling surface charge is the selection of the material with the required charging properties. One common approach is to refer to the triboelectric series:^[1] a list of materials ordered according to their tendency to charge either positively or negatively. Alternatively, the materials can be selected based on their chemical structures by referring to the many correlations established in numerous past studies.^[16,17] Many systematic investigations have been performed for correlating the amount of charge generated by contact electrification and the different types of molecular structures, such as the type and the amount of a certain functional group, and the Hammett substituent constant.

After selecting the material, a very common method for controlling the amount of charge generated is by blending or doping it with other types of materials (e.g., inorganic materials or polymers). For example, charge control agents (e.g., amine and quaternary ammonium salts) are commonly used for controlling charge of a material to a precise amount (e.g., for toner particles in electrophotography; Figure 1).^[3] The material can also be modified chemically for controlling its charging behavior. In many cases, this modification was performed by modifying the material with another type of functional group via different types of reactions, such as aminolysis and acylation.^[17] A recent example involves functionalizing nitro or methyl groups in bulk cellulose nanofibrils.^[18] Another method for controlling charge is by copolymerizing an appropriate proportion of a monomer that has the tendency to charge positively with another monomer that has the tendency to charge negatively against a reference material (Figure 2a).^[19] We have demonstrated this fundamental strategy by copolymerizing poly(ethylene glycol) diacrylate (PEGDA; average molecular weight 575) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HDFDM) (Figure 2b). These



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highly interdisciplinary, and involves the physical-chemical investigation of the separation of charge at the interface of solid, liquid, and air. His research interests also include the design and fabrication of smart chemical systems by using advanced types of materials, such as stimuli-responsive polymers.







Figure 1. A list of the general fundamental mechanisms, methods, and a few traditional applications for increasing, decreasing, or controlling surface charge generated by contact electrification. Image of nanowires: Reproduced with permission.^[44] Copyright 2009, American Chemical Society. Image of self-assembly: Reproduced with permission.^[5] Copyright 2003, Nature Publishing Group.

molecules were chosen because the polymerized PEGDA was found to have a tendency to charge positively and the polymerized HDFDM was found to have a tendency to charge negatively against many types of reference materials. Hence, different compositions of this copolymer can give rise to a wide range of charge generated (i.e., from negative to positive) when contacted against many different types of materials. Importantly, the copolymer can also be fabricated to be noncharging. For example, at around 40% PEGDA, the copolymer did not charge by contact electrification when contacted against poly(vinyl chloride) (PVC); at around 55% PEGDA, the copolymer did not charge when contacted against glass (Figure 2c).

Coating surfaces is another way to control the amount of charge generated by contact electrification. For example, coating self-assembled monolayers (SAMs) of nonionic molecules of different types of functional groups on surfaces has been demonstrated to give rise to a wide range of charging behavior.^[20–22] In one experiment, the surface of poly(ethylene terephthalate) (PET) was coated with SAMs of nonionic molecules that consisted of halogen-terminated arylsilane molecules and aminated molecules (Figure 2d). Results from contact-charging experiments showed that the SAM that consisted of the halogen-terminated arylsilane molecules tended to charge negatively, whereas SAM that consisted of aminated molecules tended to charge positively (Figure 2e).^[20,21] SAMs of ionic molecules (e.g., ammonium-terminated siloxanes) have also been used.^[12,13,22] During contact, the mobile counterions associated with the ionic molecules transfer to the other contacting surface (i.e., the "ion transfer mechanism"), leaving behind the charged ionic molecules on the surface. Hence, a surface covered with positively (or negatively) charged ionic molecules can gain a positive (or negative) charge after contact. A similar phenomenon has also been observed for layer-by-layer deposition of strong polyelectrolytes (e.g., poly(diallyldimethylammonium chloride) or poly(sodium 4-styrenesulfonate)).^[23,24] In general, many different types of coating (e.g., polymer grafting, dip coating, and many others) and methods for treating the surface (e.g., plasma or other chemical functionalization, such as oxidation or sulphonation) have been used for changing the amount and polarity of charge generated on surfaces.^[25-28]

The amount of charge generated by contact electrification can also be controlled by external stimulus.^[29–34] For example, light has been used to change the charging behavior of







Figure 2. General methods for controlling the amount of surface charge generated by contact electrification. a) Surface charge can be controlled by copolymerizing an appropriate amount of a monomer that has the tendency to charge positively [poly(ethylene glycol) diacrylate; PEGDA] when polymerized with another monomer that has the tendency to charge negatively (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate; HDFDM) when polymerized against a reference material. b) Molecular structures of the monomers. c) A range of positive and negative charge can be obtained after contacting a copolymer fabricated with different compositions against poly(vinyl chloride) (PVC) or glass. Elimination of surface charge can also be achieved as indicated by the gray arrows. a–c) Reproduced with permission.^[19] Copyright 2016, Wiley-VCH. d) Besides bulk modification, surface charge can be controlled by functionalizing the surface of a material with molecules of different functional groups. e) Results from contact electrification of poly(ethylene terephthalate) (PET) functionalized with different types of functional groups on its surface and unmodified PET. d,e) Reproduced with permission.^[20] Copyright 2017, American Chemical Society.

spiropyran-containing polymeric films.^[30,31] Upon UV irradiation, the spiropyran-containing polymer underwent a structural change from the spiropyran to the merocyanine moiety; because of this chemical change, the amount of charge and/ or the polarity of the material changed after contact electrification. Besides light, stress can be used to change the charging behavior of materials. In an interesting example, a balloon made of latex rubber charged a piece of Teflon positively when deflated (i.e., without stress), and negatively when inflated (i.e., stressed by the air pressure in the balloon).^[32] In addition, we found that the surface charge on insulating materials could be changed continuously and reversibly depending on the distance of separation between multiple charged materials.^[35] It seems that the change was due to an active exchange of charge from the materials and the surrounding atmosphere when the distance of separation was varied. In another study, an external applied electric field has been reported to change the amount and polarity of charge generated by the contact between a metal and another material.^[34]

3. Strategies for Increasing Surface Charge

One of the main methods used to increase the amount of charge generated by contact electrification is to increase the roughness of the surface. Increasing surface roughness can increase the area of contact;^[36] hence, a larger amount of charge can be generated. Many mechanical methods for roughening surfaces are possible (e.g., sand blasting).^[9,37] Micro-lithography or nano-lithography techniques (e.g., photolithography, electron beam lithography, or laser interference lithography) are commonly used for fabricating large-scale features on surfaces for increasing roughness.^[38] A commonly used technique for fabricating the general class of TENG devices is to first fabricate micrometer-scale patterns on a silicon wafer (i.e., the template) by using photolithography for protecting specific regions of the surface, followed by selective etching of the unprotected regions.^[8,39-43] After fabricating the template, the patterns are transferred onto a polymer (e.g., poly(dimethylsiloxane), PDMS) by polymerizing a layer of liquid monomer on the template (i.e.,







Figure 3. General methods for increasing the amount of surface charge generated by contact electrification. a) Surface charge can be increased by patterning the surface of poly(dimethylsiloxane) (PDMS) with micrometer-sized features (e.g., lines, cubes, and pyramids). b) Electrical outputs (i.e., voltage and current) generated by a TENG device that operated based on the piece of PDMS with or without the micrometer-sized features. a,b) Reproduced with permission.^[39] Copyright 2012, American Chemical Society. c) Surface charge can be increased by patterning the surface with biomimicking features derived from materials from nature, including lotus leaf, rose petal, and cicada wing. d) Electrical performance of TENG using thin PDMS films fabricated from natural surfaces. c,d) Reproduced with permission.^[53] Copyright 2014, Wiley-VCH.

soft lithography; **Figure 3**a). Different types of micrometer-sized features on the surfaces of PDMS were obtained after peeling the polymer off the templates. Examples of the microstructures fabricated included lines, cubes, and pyramids. The 3D feature of the pyramids was fabricated by anisotropic etching of the (100) silicon wafer.^[39] These microstructured PDMS films were used in a TENG device for generating electrical outputs. Results indicated that these micrometer-sized features (especially the pyramids) enabled the TENG device to perform a few times better than the surface without any patterned features (Figure 3b). Selective etching can also be performed by first covering a polymeric film with a layer of metal nanoparticles,

which serve as the "mask." By etching the regions of the polymeric film that are not protected by the mask, an array of polymeric nanowires can be fabricated.^[44–47]

Nanoscale features on surfaces have also been fabricated by other techniques. Electrochemical anodization is commonly used for fabricating the porous anodic aluminum oxide template that is used for fabricating polymeric nanowires.^[9,37,48] Nanoscale holes on aluminum can also be fabricated by anodization.^[37] Alternatively, nanosized materials (e.g., silver nanoparticles and nanowires) can first be fabricated and then deposited on surfaces for obtaining the nanoscale roughness.^[41] Other methods of deposition can also increase the roughness of



surfaces (e.g., electrodeposition and growing of nanostructures from a seed layer). $^{\left[49,50\right] }$

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A creative method for fabricating surfaces with patterned features is through self-assembly of materials. For example, a layer of polymeric spheres (e.g., polystyrene, PS) was selfassembled onto a surface via a force-directed assembly into a hexagonal close-packed colloidal array.^[51] After assembling the spheres, the liquid PDMS monomer was covered over the spheres, polymerized and peeled off to obtain the ordered hemispherical hollow microstructures on its surface left behind by the spheres. By using this surface as a template, a piece of PDMS with embossed hemispherical microstructures was also fabricated by casting the liquid PDMS monomer over the template modified with hydrophobic molecules (for easier separation of the polymers), polymerizing the monomer, and peeling the polymer off the template. Another type of self-assembly involves the microscopic phase separation of covalently linked block copolymers (i.e., block copolymer of PS and PDMS).^[52] This block copolymer can self-assemble into spatially welldefined microdomains of different types of geometries (e.g., spheres, cylinders, and perforated lamellae). After removing PS and oxidizing PDMS, patterns such as nanodots, nanogrates, and nanomeshes on the surface can be fabricated.

Surfaces with fascinating morphology have been fabricated using materials from nature.^[53,54] For example, lotus leaf, rose petal, and cicada wing are found to have intricate nanoscale and microscale patterns on their surfaces (Figure 3c). Therefore, instead of fabricating the patterned surfaces using other techniques, these surfaces can readily serve as templates for creating small-scale patterns on surfaces. These surfaces from nature were used as templates for fabricating the microstructures and nanostructures on surfaces of PDMS. The voltages and currents generated by these surfaces with the microstructures and nanostructures via a TENG device were larger than the flat surface without the surface structures (Figure 3d). The surface fabricated from the cicada wing was found to give the best performance with a peak voltage and current of 210 V and 23 μ A, whereas the flat surface gave only 110 V and 11 μ A.

A few additional fundamental strategies for increasing the charge generated are worth noting. For example, hierarchical structures that are composed of both nanoscale and microscale features have been fabricated by using a combination of methods (e.g., sand blasting and anodization)^[9] or the templates obtained from nature (e.g., leaves).^[53] Comparisons have been performed experimentally on four types of surfaces: 1) a surface without any modification, 2) a surface with only the microscale roughness, 3) a surface with only the nanoscale roughness, and 4) a surface with the hierarchical nanoscale and microscale roughness. Results from this comparison showed that the surfaces with the hierarchical nanoscale and microscale roughness performed better than all other surfaces.^[9,37,42,53] Better contact between the surfaces can be achieved using flexible and deformable elastomers; for example, the conformal contact of PDMS with the contacting surface allows the area of contact to be increased.^[55] Fabricating surfaces with nanowires can also increase the charge generated by contact electrification. It has been reported that when a surface covered with nanowires came into contact with another surface, the nanowires bent;^[45] this bending caused frictional contacts with the other surface, thus

generating more charge than simple contacts. When both the surfaces were covered with nanowires, contacting the surfaces allowed the nanowires to interlock into each other, and increased the amount of charge generated.^[56] Another common method involves using highly chargeable materials (e.g., poly(tetrafluoro-ethylene) (PTFE) and PDMS) for increasing the amount of charge generated by contact electrification (e.g., via coating).^[9,57]

4. Strategies for Decreasing Surface Charge

A very common way to decrease the amount of charge generated is by blending or doping a material with antistatic agents. A wide variety of antistatic agents is available; examples include carbon black, carbon nanomaterials, graphene, metal powder, and other conductive materials (e.g., conductive polymers such as polyaniline).^[25,58,59] By increasing the conductivity of the material, the charge generated on the surface can be dissipated faster to ground. Alternatively, the material can be blended with hydrophilic polymers for attracting water moisture from the surrounding onto the surface.^[59] An increase in the amount of water increases surface conductivity; hence, it is easier for the charge to be dissipated. Relatively recently, a fundamentally different strategy has been reported: the doping of materials with radical scavengers such as 2,2-diphenyl-1-picrylhydrazyl (DPPH), or vitamin E (Figure 4a).^[4] First, the authors analyzed the spatial distribution of charges and radicals by Kelvin force microscopy (KFM) and magnetic force microscopy (MFM) and found that the images obtained seemed to correlate spatially with each other (Figure 4b). This result suggested that radicals have the tendency to colocalize with and stabilize the charges. Therefore, when the radicals are scavenged by the radical scavengers present in the material, the charges destabilize and the surface discharges. Accordingly, the rate of dissipation of charge was found experimentally to be much faster for a piece of PDMS doped with DPPH than a piece of PDMS that was not doped with DPPH (Figure 4c). Besides bulk modification, coating of conductive materials, hydrophilic polymers, and radical scavengers (e.g., polydopamine and tannic acid) has also been demonstrated to decrease charge generated by contact electrification.^[25,55,60]

A short summary of the fundamental mechanisms, methods, and a few recent examples discussed is listed in **Table 1**.

5. Recent Applications of Contact Electrification

In recent years, many interesting devices based on contact electrification have been fabricated for a diverse range of applications. These applications can similarly be divided into three general classes: those that require the surface charge generated by contact electrification to be increased, decreased, or controlled. A large proportion of the reported devices and materials seek to increase the amount of charge generated (**Figure 5**). One important application is the harvesting of energy from human motions, including the motion of the limbs (e.g., hand, wrist, elbow, shoulder, and foot) and other types of bodily movements (e.g., breathing and blinking of the eye).^[55,61] One device is based on the contact–separation of TENG for harvesting the energy of walking—that is, the periodic stepping of the device







Figure 4. Decreasing the accumulation of surface charge by doping a material with radical scavengers. a) Scheme illustrating a piece of PDMS doped with radical scavengers (e.g., 2,2-diphenyl-1-picrylhydrazyl; DPPH). b) The distributions of charges and radicals on the surface of PDMS were analyzed by Kelvin force microscopy (KFM) and magnetic force microscopy (MFM) respectively. c) The rate of dissipation of charge was found to increase dramatically when the piece of PDMS was doped with the radical scavenger, DPPH, compared with the piece of PDMS that was not doped with DPPH. a–c) Reproduced with permission.^[4] Copyright 2013, the American Association for the Advancement of Science.

(Figure 5a).^[55] It consisted primarily of two materials: 1) a layer of gold coated on a poly(methyl methacrylate) (PMMA) substrate (i.e., the material at the bottom of the scheme shown in Figure 5a) and 2) a layer of PDMS coated onto another layer of gold and a PMMA substrate (i.e., the material on top). The layers of gold on both the top and bottom materials were connected electrically to an external circuit for the output of power. By stepping onto the top material, the layer of PDMS (i.e., a highly chargeable material) of the top material came into contact with the layer of gold of the bottom material; thus, charge was generated by contact electrification. Upon releasing, the materials were separated due to the restoring force of four supporting springs placed between the materials. As a result of the constant stepping motion, the two charged surfaces underwent repeated cycles of contact and separation. The constant change in the distance of separation between the two charged surfaces caused a corresponding change in the electric field around the surfaces, thus inducing different amounts of charge in the layers of gold on the top and bottom materials. Due to the different amounts of charge induced, electrons flowed via the layers of gold to the external circuit; hence, electrical power was harvested. A larger amount of power was reported to be generated by increasing the surface roughness of the bottom material via depositing gold nanoparticles on the layer of gold. It has been demonstrated that the device could deliver a short-circuit current of up to 2 mA, supply a power density of up to 313 W m^{-2} , and light up 600 commercial light-emitting diode (LED) bulbs instantaneously by stepping onto the device (i.e., via a force of around 500 N; Figure 5a). A smaller force (10 N) could generate an open-circuit voltage of 200 V and a short-circuit current of 170 µA. In general, the combination of contact electrification and electrostatic induction due to the periodic contact and separation of two materials

as described above is the working principle of many recent devices fabricated based on the TENG.

Another interesting class of devices consists of wearable materials for harvesting the energy of the motion of a person via the contact electrification of the materials (or the contact between the wearable material against the skin of the person).^[49,62] In one example, Ag-coated textile (i.e., a flexible and foldable material) was covered with an array of ZnO nanorods by growing the nanostructures on the surface from a seed layer for increasing the area of contact (Figure 5b).^[49] The nanorods were then coated with an additional layer of highly chargeable PDMS. When a person moved, the contact between the PDMS-coated material and another Ag-coated textile caused both the surfaces to charge. The repeated contact and separation due to the motion of a person thus allowed electricity to be generated based on the mechanism of TENG. With the increase in contact area by the nanorods, an enhanced output performance of 120 V and 65 µA were obtained, while only 30 V and 20 µA were observed without the nanorods. Based on this wearable material, a self-powered "smart" suit was fabricated. The motion of a person wearing this suit was demonstrated to be able to power a liquid crystal display (LCD), a few LEDs, and a remote control system for keyless entry of a vehicle via a power controller (Figure 5b).

Besides harvesting energy from external bodily motions, implantable TENGs have also been developed for in vivo biomechanical harvesting of energy.^[43,63,64] In vivo harvesting of energy can be a sustainable source of power for numerous implantable medical devices and can potentially affect the lives of millions of patients. One typical implantable triboelectric nanogenerator (iTENG) that consisted of a multilayered structure is shown in Figure 5c.^[64] Charge was generated when the layer of aluminum came into contact with the layer of PTFE



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Table 1. Main strategies and recent examples for varying surface charge.

Strategy	Method	Examples ^{a)}	Mechanism	Effect ^{b)}	Ref.
Chemical modification of surfaces	Self-assembled monolayer	 Nonionic molecules with different functional groups (e.g., halides and amines) 	- Chemical modification	\$	[20]
		 Ionic molecules covalently bound onto surface with mobile counterions 	– Ion transfer	\$	[12]
	Layer-by-layer	Strong polyelectrolytes	– Ion transfer	\$	[23]
	Polymer grafting	• PtBA-g-PVDF	- Chemical modification	\$	[28]
	Other coating methods	• Conductive layer (e.g., carbon nanotubes)	 Increase in conductivity 	\downarrow	[25]
		• Hydrophilic films (e.g., dip-coating)	 Increase in conductivity 	\downarrow	[89]
		• Dip-coating of polydopamine and tannic acid	 Radical scavenging 	\downarrow	[60]
		• Films of different materials (e.g., PDMS)	- Chemical modification	\$	[8]
	Surface treatment	 Oxidation and sulphonation O₂ plasma-treated PDMS 	- Chemical modification	\$	[26]
Chemical modification of bulk	Blending/doping	 Polymers and metal oxides (e.g., Nylon, AlOx) 	- Chemical modification	\$	[90]
		 Antistatic agents (e.g., hydrophilic polymers and conductive additives, such as carbon nanomaterials or polyaniline) 	 Increase in conductivity 	\downarrow	[25]
		• Ionic charge control agents (e.g., quaternary ammonium salts)	– Ion transfer	\$	[3]
		• Radical scavengers (e.g., DPPH)	 Radical scavenging 	\downarrow	[4]
	Bulk functionalization	• Cellulose nanofibrils modified with nitro groups or methyl groups	- Chemical modification	\$	[18]
	Copolymerization	• Different proportions of monomers	- Chemical modification	\$	[19]
Modification of surface morphology	Lithography and selec- tive etching	• Wet etching after photolithography (e.g., for line, cube, pyramid microstructures)	– Increase in area of contact		[39]
		• Dry etching over a "mask" of nanoparticles (e.g., for nanowires)			[46]
	Electrochemical anodization	• Porous anodic alumina (e.g., for nanowires)			[9]
		• Nanoholes (e.g., on an aluminum surface)			
	Deposition	• Coating surface with nanomaterials			[42]
		• Electrodeposition of nanostructures		\uparrow	[41]
		• Growth of nanostructures			[91]
	Self-assembly of structures	Polymeric particle assembly			[49]
		• Block copolymer phase separation (e.g., PS- <i>b</i> -PDMS assembly)			[21]
	Biomimicking surfaces	• Leaves (e.g., lotus), rose petals, cicada wings as templates			[52]
	Physical roughening	• Abrasion, sand blasting			[37]
Stimuli-responsive methods	Light	Photochromic polymers (e.g., spiropyran-containing polymers)	– Molecular structure conversion		[31]
		Photoabsorber (e.g., P3HT:PCBM)		·	
	Stress	• Stretching latex rubber	 Photoelectric effect 	\uparrow	[29]
	Electric field	A metal and an insulating material	-	\$	[32]
	Distance of separation	 Charge changes when distance of separation of charged insulating materials is varied 	 Biasing electron transfer 	\$	[34]
			 Exchange of charge with atmosphere 	\$	[35]

a)PtBA-g-PVDF: poly(ter-butyl acrylate)-grafted poly(vinylidene difluoride); PDMS: poly(dimethylsiloxane); AlOx: aluminium oxide; DPPH: 2,2-diphenyl-1-picrylhydrazyl; PSb-PDMS: polystyrene-block-poly(dimethylsiloxane); P3HT:PCBM: poly(3-hexylthio-phene):[6,6]-phenyl-C61-butyric acid methyl ester. ^{b)} : increasing charge; ↓: decreasing charge; ↓: controlling charge.

modified with nanostructures via inductively coupled plasma (ICP) etching. The arc-shaped Ti bone provided the restoring force for keeping the two layers separated. The performance of this in vivo energy-harvesting device was investigated by implanting it between the heart and the pericardium of an adult

swine. The repeated contact and separation of the materials due to the beating motion of the heart allowed electricity to be generated by the mechanism of TENG. This iTENG exhibited good in vivo performance: 14 V and 5 μ A, which are 3.5 and 25 times better than devices demonstrated in earlier studies.







Figure 5. Applications of increasing surface charge generated by contact electrification. a–d) Energy harvesting and sensing based on human interaction. a) Contact–separation TENG for harvesting of energy from human motion. Reproduced with permission.^[55] Copyright 2013, American Chemical Society. b) Fabric-based TENG as a wearable device for energy harvesting. Reproduced with permission.^[64] Copyright 2016, American Chemical Society. c) Implantable TENG for in vivo biomechanical energy harvesting. Reproduced with permission.^[64] Copyright 2016, American Chemical Society. c) Implantable TENG for in vivo biomechanical energy harvesting. Reproduced with permission.^[64] Copyright 2016, American Chemical Society. d) Wearable sensor for ultrasensitive pulse monitoring. Reproduced with permission.^[69] Copyright 2017, Wiley-VCH. e–h) Energy harvesting and sensing based on environmental interaction. e) Harvesting energy from rain by solid–liquid contact electrification. Reproduced with permission.^[71] Copyright 2015, the Royal Society of Chemistry. f) Flexible TENG for harvesting energy from air/wind. Reproduced with permission.^[73] Copyright 2014, Nature Publishing Group. h) Paper-based rollable TENG for sensing and harvesting of energy of sound. Reproduced with permission.^[73] Copyright 2015, American Chemical Society. i) Other applications of increasing surface charge. i) A force-triggered field-effect transistor based on contact electrification. ^[81] Copyright 2015, American Chemical Society. j) A self-powered gas filter. Reproduced with permission.^[81] Copyright 2015, American Chemical Society. j) A self-powered gas filter. Reproduced with permission.^[81] Copyright 2015, American Chemical Society. j) A self-powered gas filter. Reproduced with permission.^[81] Copyright 2015, American Chemical Society. j) A self-powered gas filter. Reproduced with permission.^[81] Copyright 2015, American Chemical Society. j) A self-powered gas filter. Reproduced with permission.^[81] Copyright 2015, Amer

Increasing surface charge generated by contact electrification is also useful for sensing of human activity such as bodily motion,^[65,66] bending or touching (via sensing of pressure),^[67] and physiological signals by wearable or implantable devices.^[68,69] One specific application involves an ultrasensitive pulse sensor based on a flexible TENG (Figure 5d).^[69] The surfaces of two pieces of Kapton films were first modified with nanostructures by ICP etching. For one of the Kapton films, a thin layer of Cu was deposited on its nanostructured surface; for the other piece of Kapton film, a thin layer of Cu was deposited on the back side instead. These two pieces of films were then assembled with a thin spacer sandwiched in between the films. When the device was attached onto the skin of a person, the pulse pushed against the flexible material and caused the two nanostructured surfaces to come into contact. An electrical signal was thus produced based on the mechanism of TENG. This device was demonstrated to be able to monitor human pulse reliably in real-time when placed on arteries of various locations in a body, including the carotid, brachial, radial, finger, and ankle (Figure 5d). The nanostructures were reported to be the key component for achieving ultrahigh sensitivity and allowing detail analysis of the waveform of the pulses for the diagnosis of cardiovascular system disease. Another application is a sliding TENG developed for self-powered recognition of a barcode for identification.^[65] The sliding card was fabricated with arrays of electrodes with specific uniform spacing that represented the reference information on one side of the card and nonuniform spacing that represented the coded information on the other side of the card. When the card slid against a reader that consisted of another set of electrodes covered by a layer of nanostructured polymer, contact electrification between the materials produced a series of electrical signals via the electrodes on both sides of the card. By comparing the coded signal with the reference signal, the coded information could be determined.

Fabricating devices for energy harvesting from and sensing of the environment (e.g., water,^[7,70,71] air/wind,^[72,73] acoustic/ sound,^[74,75] and acceleration and rotation^[76,77]) is another major area of research. For harvesting energy from rain or streams of water, we previously demonstrated that water could be charged by simply flowing it across a solid surface. When water was flowed continuously down a PTFE (i.e., a highly chargeable material) tube of 2 mm in diameter and 30 cm long at a flowrate of 100 mL min⁻¹, a power of up to 170 µW was generated (Figure 5e).^[7] The energy of wave can be harvested by a flexible and scalable TENG that consisted of an array of electrodes covered with a layer of nanostructured PTFE (Figure 5f).^[71] The nanostructures were fabricated by spin-coating a layer of PTFE nanoparticles onto the surface. When an incoming wave swept across the surface, charge was generated by the contact electrification between water and the nanostructured PTFE surface. Operationally, the negatively charged PTFE was able to induce charge on the electrodes. When the positively charged water covered the PTFE surface, a different amount of charge was induced on the electrodes. Therefore, the repeated changes in the amount of charge induced on the electrodes due to constant incoming waves produced electricity. This device was reported to be able to generate a power of up to 1.1 mW and light up an array of LEDs. Wind energy can be harvested by a

flutter-driven TENG that consisted of a thin flexible flag (i.e., an Au-coated textile) and a rigid substrate (i.e., Au-coated textile with a layer of PTFE on its surface; Figure 5g).^[73] The textile was fabricated with interlaced microstructures of filaments for increasing its surface roughness. Under the flow of wind, the flexible flag fluttered along with the wind and produced rapid cycles of contact and separation between the layer of PTFE and the Au-coated textile; electricity was then generated based on the mechanism of TENG. The performance of the device was tested in a wind tunnel that mimicked the natural flow of wind. The power generated increased with the velocity of the flow of the wind. At a wind speed of 15 m s^{-1} , the device generated an average power of 0.86 mW despite its relatively small dimensions (i.e., 7.5 cm × 5 cm).

In terms of sensing the environment, a 3D symmetric TENG ball has been developed for monitoring multiaxis acceleration and rotation.^[76] The TENG ball was a hollow sphere that contained encapsulated steel balls. The inner surface of the hollow TENG ball was coated with PTFE-covered Al electrodes; the electrodes were divided into four quadrants by gaps that electrically separated the quadrants. When accelerated or rotated, contact electrification between the steel balls and the inner layer of PTFE generated charge. This charge on the steel balls induced charge on the respective electrodes according to the direction of acceleration or rotation, thus providing different signals for sensing acceleration and rotation. This TENG ball can be used for the monitoring of environmental disturbances and human activities. Another example involves a paper-based TENG for harvesting of energy and recognition of sound (Figure 5h).^[75] The device consisted of two flexible pieces of contacting materials: a thin PTFE-coated Cu film and a thin Cu-coated layer of paper with an array of holes. Nanowires were fabricated on the surface of PTFE by ICP etching for increasing the effective contact area. The holes allowed incoming sound wave to propagate through the materials and caused vibration between the two layers. The repeated cycles of contact and separation of the surfaces of PTFE and Cu generated electricity based on the mechanism of TENG. This device delivered a power density of up to 121 mW m⁻² under 117 dB. Due to the flexibility of the device, it could be rolled into a cylinder shape and used as a microphone with good sound-recording capability (e.g., speech or music) from all 360° directions.

Contact electrification can also be used for controlling the source-gate electrostatic potential of a contact electrificationbased field-effect transistor (CE-FET) (i.e., "tribotronics").[78,79] The CE-FET was composed of a metal-oxide-semiconductor field-effect transistor (MOSFET) and a multilayered structure that consisted of silicon and an insulator (i.e., the silicon-oninsulator; SOI) at the bottom of the MOSFET, as illustrated in Figure 5i.^[79] A layer of Al that was deposited at the bottom of the SOI served as the gate electrode. The other contacting material consisted of a layer of Kapton coated on a layer of Al, which was connected electrically to the source electrode. When this movable layer of Kapton/Al was brought into contact with the Al coated at the bottom of the SOI, charge was generated by contact electrification. Hence, the gate potential of the CE-FET could be controlled by varying the distance of separation between the two charged surfaces, d; the source-drain current, $I_{\rm D}$, could then be controlled accordingly. Compared to



piezotronic devices, the CE-FET has significantly larger range of control and choice of materials.^[79]

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In terms of the environment, the removal of the particulate matter (PM) from the exhaust fumes of automobile is highly desirable in urban areas. Devices for the filtration of gas based on contact electrification have been developed.^[80,81] One selfpowered device consisted of multiple PTFE pellets (2 mm in diameter) in a gas channel sandwiched between a top and a bottom electrode (Figure 5j);^[81] vibration of the engine of the automobile allowed the pellets to move and charge against the electrodes. Hence, a large electric field on the order of MV m⁻¹ between the negatively charged PTFE pellets and the positively charged electrodes was generated. This electric field allowed the PM to be deposited onto the pellets, thus separating the particles from the gas stream. The authors reported removal efficiencies of 95.5% and 97.2% for PM2.5 and PM10 respectively, when actual exhaust fumes from an automobile was passed through the gas channel. In terms of water treatment, low-cost and energy-efficient methods for disinfection of water are urgently required, especially in developing regions. Systems based on contact electrification have been developed for breaking down the membranes of microorganisms by electroporation.^[82,83] In one demonstration, a system consisted of metallic meshes coated with copper oxide nanowires (CuONWs) was immersed into the water that needed to be treated. In a separate step, a TENG device was operated outside of water by contacting two materials (i.e., an Al foil and a plastic film) for the generation of charge.^[83] The output of the TENG device was connected electrically to the CuONWs-coated electrodes; the strong electric field produced by the nanowires caused the electroporation to occur. Complete disinfection of bacteria and viruses was reported for both raw tap water and lake water.

In many circumstances, the surface charge generated by contact electrification needs to be eliminated. For example, it is important to prevent the damage of electronic components due to electrostatic discharge produced by contact electrification.^[4] It has been demonstrated that polymers doped with small amounts of radical-scavenging molecules (e.g., DPPH) can be used to protect the electronic components (Figure 6a) by the mechanism as described, as described in Section 4. The

demonstration involved four independent circuits; each of the circuits consisted of a junction field-effect transistor connected to a LED. The four transistors were treated differently: intact (labeled "1" in Figure 6a), metal shield removed but the gate was covered with a layer of PS doped with DPPH ("2"), metal shield removed but the gate was covered with pure PS ("3"), metal shield removed and no polymer covered the gate ("4"). The transistors were exposed to repeated cycles of positive and negative electrostatic discharge via an electrostatic gun. An undamaged transistor should go through the repeated cycles of "on" and "off" states as indicated by the LED; however, if the transistor was damaged, the LED should always be "on." Results showed that the electrostatic discharge damaged all the transistors except for the one that was covered with PS doped with DPPH ("2"). Hence, the radical-scavenging molecules prevented the accumulation of static charge that could damage the electronic components. In addition, antistatic surfaces for preventing the adhesion of microscopic particles are desirable in many circumstances.^[19] Using the method of copolymerizing an appropriate proportion of a monomer that tended to charge positively when polymerized and a monomer that tended to charge negatively when polymerized (as discussed in Section 2), it has been demonstrated that the surface of the copolymer (i.e., at 38% PEGDA) prevented the adhesion of microscopic dextrose powder (Figure 6b).

Controlling the amount and polarity of the surface charge is important for many applications.^[84,85] The charge generated by a TENG device can be used to control the level of muscle contraction by neural/muscle stimulation: this control can be used for training a limb for rehabilitation. A stacked TENG has been demonstrated for stimulating the sciatic nerve and common peroneal nerve of an anaesthetized live rat (Figure 7a).^[84] The stacked TENG consisted of five plates of TENG that were made of PDMS and copper assembled in a zigzag structure as illustrated in Figure 7a (scheme on the top left). When compressed, charge was generated by contacting the surfaces of PDMS and copper. Current (0.6-1.0 µA) could be generated by different forms of human motion (e.g., repeated tapping onto the device) based on the mechanism of TENG. For neural stimulation, the TENG device was connected electrically to the



Figure 6. Applications of eliminating surface charge generated by contact electrification. a) Eliminating static charge by doping materials with radical scavengers for the protection of electronic components. Reproduced with permission.^[4] Copyright 2013, American Association for the Advancement of Science. b) Antistatic surface for preventing adhesion of microscopic particles. Reproduced with permission.^[19] Copyright 2016, Wiley-VCH.

(a) Protection of electronics







Figure 7. Applications of controlling surface charge generated by contact electrification. a) Stacked TENG for direct neural stimulation. Reproduced with permission.^[84] Copyright 2017, Elsevier. b) Quantitative control of the total ionization charges in mass spectrometry by TENG. Reproduced with permission.^[86] Copyright 2017, Nature Publishing Group. c) Water–air triboelectric nanogenerator (WATENG) for chemical (CO₂) sensing. Reproduced with permission.^[87] Copyright 2017, American Chemical Society.

sciatic nerve of an anaesthetized live rat through a neural electrode. The electromyography signals generated from the gastrocnemius medialis and tibialis anterior muscles indicated the successful direct neural stimulation by the stacked TENG. The degree of muscle contraction of the rat can be varied by controlling the output generated from the stacked TENG (e.g., via changing the number of the stacked plates, size of each plate, and/or material of the plates). Controlling surface charge can also be useful for molecular mass spectroscopy (Figure 7b).^[86] Basically, a TENG device was connected electrically to a nanoelectrospray ionization emitter through a controllable resistor. When the voltage at the emitter (provided by the TENG device) was higher than a threshold, electrons leaked from the emitter into air, thus ionizing the sample. The dark-field images of the emitter showed the generation of an electrospray plume when triggered by the TENG. Since the voltage on the emitter is controllable via the resistor, the TENG-based system was able to quantitatively control the total ionization charges in the mass spectrometry. This system is reported to have unprecedented control over the total ionization charge compared to the traditional method (i.e., driven by a supply of dc current). The signature fragment ion (m/z 182.118) of cocaine, for example, can only be observed by this TENG-based system, instead of the traditional system. With respect to sensors, some devices





require the charge generated by contact electrification to be controlled.^[87,88] For example, sensing of CO₂ can be achieved by controlling the amount of charge generated via contact electrification (Figure 7c).^[87] The device consisted of a multilayered structure: a top piece of indium tin oxide (ITO) electrode (layered on a PET substrate) coated with polyethylenimine (PEI), a piece of PDMS, a piece of sponge filled with water, and a bottom piece of ITO electrode (layered on a PET substrate). When a downward pressure was applied for contacting the top piece of ITO coated with PEI and the piece of PDMS, charge was generated. The pressure in turn allowed the piece of PDMS to squeeze the water out of the sponge; the contact electrification between the water that was expelled from the sponge and the bottom surface of the PDMS increased the overall charge generated. Because PEI was capable of absorbing CO₂, the changes in the chemical composition of PEI due to the absorption of CO₂ led to changes in the amount of charge generated by the contact electrification of PEI and PDMS. The linear range of sensing has been demonstrated to be up to 30 000 ppm for relatively fast changes in the concentration of CO₂ (e.g., via human breathing).

6. Conclusion

Surface charge generated by contact electrification has a vast range of influences-both beneficial and undesirable-in our lives and in industry. Hence, it is important to increase, decrease, or control the surface charge generated for many different specific circumstances. After a long history of research, various fundamental mechanisms and methods for regulating the surface charge generated have been reported; these strategies have led to the fabrication of many types of devices for different applications. It is particularly exciting that, in recent years, through the development of advanced types of materials with highly desirable properties, treatment methods (e.g., nanofabrication for modifying surfaces), and technologies for fabrication (e.g., small-scale fabrication of devices), many more of these fundamental mechanisms, methods, materials, and devices have been developed for a diverse range of interesting applications. On the other hand, however, major challenges remain. For example, in order to harvest sufficient energy for powering many of the common electronic devices that we use in our daily lives, the surface charge generated by contact electrification still need to be further increased significantly. Meanwhile, many of the methods reported for decreasing charge cannot totally eliminate or prevent the generation of surface charge effectively (e.g., many sensitive electronic components can still be damaged). The ranges of control provided by many of the stimuli-responsive methods described are limited. Therefore, there is currently still a great need to find more effective ways to increase, decrease, or control the generation of charge by contact electrification.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

contact electrification, energy harvesting, nanogenerators, surface charge, triboelectrification

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