10th Anniversary Article



Triboelectric Nanogenerator (TENG)—Sparking an Energy and Sensor Revolution

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The study presents the fundamental scientific understanding of electron transfer in contact electrification in solid–solid and liquid–solid cases and a newly revised model for the formation of electric double layer. The potential revolutionary impacts of triboelectric nanogenerators as energy sources and sensors are presented in the fields of health care, environmental science, wearable electronics, internet of things, human–machine interfacing, robotics, and artificial intelligence.

1. Triboelectric Nanogenerators

Triboelectric nanogenerator (TENG) was first invented by Wang and co-workers for converting randomly distributed, irregular, and wasted low-frequency energy into electric power.^[1] TENG uses the coupling effect of contact electrification (CE) and electrostatic induction, and it has the advantages of low cost, easy fabrication, diverse choice of materials, and broad range of applications.^[2] TENG is a field that uses Maxwell's displacement current as the driving force for effectively converting mechanical energy into electric power/signal, regardless of whether nanomaterials are used or not. According to a literature survey, as of the end of 2019, there are more than 42 countries and regions, 400 units, and over 4000 scientists engaged in TENG research (Figure 1), and the number of articles that have been published worldwide increases exponentially. This essay is intended to summarize the answers to the following questions about the fundamentals of TENG: 1) what are the mechanisms for triboelectrification (TE); 2) what is the theoretical approach for quantifying the output of TENG; 3) what is the figure of merits for measuring the performance of TENG; and 4) what TENG can be used for.

2. TE versus CE-What Is the Difference?

Traditionally, we usually refer that the scientific term for TE is called CE, which is about a physical contact between two

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different materials that would be electrically charged after being separated. But TE and CE have significant differences. CE occurs just by physical contact of the two materials without rubbing one against the other, but TE is usually inseparably involving friction by rubbing two materials one on the other. Therefore, TE is a "convolution" of two processes between tribology and CE, so that they are inseparable in conventional understanding. We

have recently pointed out that CE is a physical effect in science, while TE is an engineering practice that may involve friction and debris.^[3] As for the case of solid–solid, CE is defined as a quantum mechanical electron transfer process that occurs for any materials, in any states (solid, liquid, gas), in any application environment, and in a wide range of temperature up to ~400 °C. Such an effect is universal and is fundamentally unique in nature.

3. Mechanisms of CE

Although TE has been known for 2600 years, there is a debate regarding whether CE is due to electron transfer, ion transfer, or even materials species transfer. This is possibly due to the limitation of measurement techniques and the complication of CE by friction process. CE occurs for all phases, including solid, liquid, and gas, and it is the most fundamental phenomenon at an interface. CE occurs between solid–solid, solid–liquid, liquid–liquid, gas–liquid, gas–gas, and gas–solid (**Figure 2**), and is playing a fundamental role in physics, chemistry, and biology.

4. Solid–Solid Cases

Recently, we found that CE between two solids is dominated, if not exclusively, by electron transfer.^[4] CE between metal and dielectric can be well described using the Fermi level model for metal and the surface states model for a dielectric. CE between dielectric and dielectric can be understood using the surface states model. It was found experimentally that CE occurs only when the two materials reach a distance shorter than bonding length, for example, in the repulsive force region in the interaction potential of two atoms (**Figure 3b1**). As for a general case, an overlapped electron cloud model was first proposed for explaining the electron transition, in which a strong overlap of the electron cloud between two atoms under stress results in a lowered potential barrier between the two, subsequently allowing electron transition from one atom to the other to





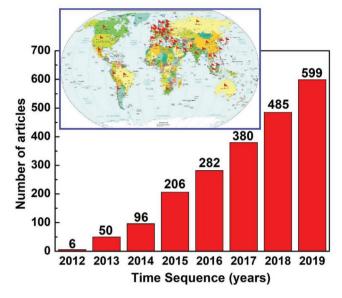


Figure 1. A literature survey from SCI database about the articles published each year in the field of TENG by December 31, 2019 and the authors' geographical distribution.

occur.^[5] A mechanical stressing is required to make the atoms close enough to maximize the overlapping of electron cloud. This model is considered a generic model for understanding CE between any two materials, and it can be extended to cases of CE for liquid–solid and liquid–liquid, and gas–solid and gas–liquid. For simplicity of description and referring, the electron transition model presented in Figure 3a2,b2 is called the Wang transition for CE. In addition, photon emission is expected in this process, which remains to be verified experimentally.

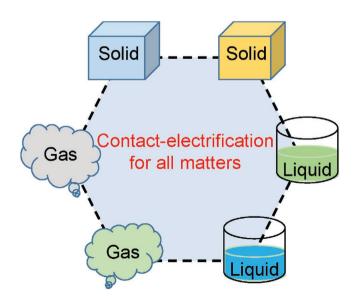


Figure 2. Schematic illustrating that CE is a universal phenomenon that occurs between phases of solid-solid, solid-liquid, liquid-liquid, gas-liquid, gas-gas, and gas-solid, for all of the known matters.



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tronics and piezo-phototronics for the third-generation semiconductors.

5. Liquid-Solid Cases

CE between liquid-solid is the formation of the electric double layer (EDL). The classical model for EDL is an adsorption of a layer of ions on the solid surface, which tends to attract the ions of opposite sign of charges, while repelling the ions of the same sign of charge in the solution, forming a distribution of electric potential near the liquid-solid interface. Recently, it was proposed by Wang that the formation of EDL has two steps.^[4] The first step is an electron exchange process between liquid and solid surfaces as proposed for CE, which makes the atoms on the solid surface to be ions. The second step is the interaction of the ions with the ions in the liquid, resulting in a gradient distribution of cations and anions near the interface. The traditional model ignores the first step, just considering the second step. In practice, electron exchange and ion adsorption occur simultaneously and coexist in the liquid-solid interaction, which has been recently verified experimentally.^[6,7] Such a revision about the model for EDL could subsequent affect some related understanding about the interface chemistry, electrochemistry, and even cellular-level interactions. Therefore, for simple referring and easy mentioning, the two-step model is called the Wang model for EDL.

Our study is to use a Kevin probe to measure the charges delivered on a solid surface by dropping a droplet of solution after vaporizing the water. Figure 4a-f shows the time decay curve of the CE charges left on solid surfaces after contacting with a droplet of deionized (DI) water.^[7] It is found that all of the charge decay curves follow the electron thermionic emission model, hence the removable charges are electrons and the "sticky" charges are ions. The solid surfaces can gain or lose electrons, while the ions adsorbed on the surfaces can be cations and anions, indicating both physical adsorption and chemical adsorption are possible. The electron transfer and the ion transfer are marked in Figure 4a-f. It can be seen that the ratio of electron transfers to ion transfers (E/I) highly depends on the type of solid. For the CE between the AlN and the DI water, more than 88% of the total transferred charges are electrons. But in the CE between the Si₃N₄ and the DI water, electron transfer is only 31% of the total charge



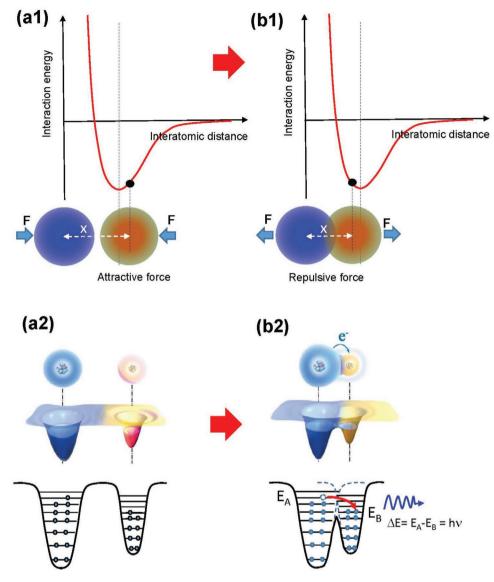


Figure 3. The overlapped electron-cloud model proposed for explaining CE and charge transfer between two atoms for a general case. a1,b1) Interatomic interaction potential between two atoms when the force between the two is attractive and repulsive, respectively, by applying an external compressive force. Experiments found that electron transfer occurs only when the two atoms are in the repulsive interaction, for example, in the case when the two atoms have strong electron-cloud overlap. a2,b2) Schematic of the electron cloud and potential energy well model of two atoms belonging to two materials A and B when they are separated and in close contact, respectively. Electron transition from A atom to B atom is possible due to the lowered potential barrier by the external force, resulting in the occurrence of CE. This is simply referred to as Wang transition for CE.

transfer. The polarity of the transferred electrons and transferred ions does not have to be necessarily to be the same in liquid–solid CE. As shown in Figure 4a, the MgO gains electrons and adsorbs positive ions at the same time in the CE between MgO and DI water, indicating possible chemical adsorption of the ions. For the CE between AlN and DI water, the AlN loses electrons and obtains negative ions (Figure 4f). These results suggest that the electron transfer and ion transfer in liquid–solid CE are independent of each other depending on the intrinsic characteristic of the solid surface.

6. Liquid-Liquid Cases

CE between liquid–liquid is rather difficult to probe. Recently, using single-electrode-based TENG as a probe and by measuring the current generated by the TENG, once it is inserted slowly across oil–water interface, charges were detected at the interface.^[8] Although the nature of the charges remains to be investigated, this work shows that TENG can act as a probe. By reducing the size of the TENG into tip shape and possibly in scanning mode, a new probe for studying the charging behavior at liquid–liquid and also liquid–solid interfaces can be developed.



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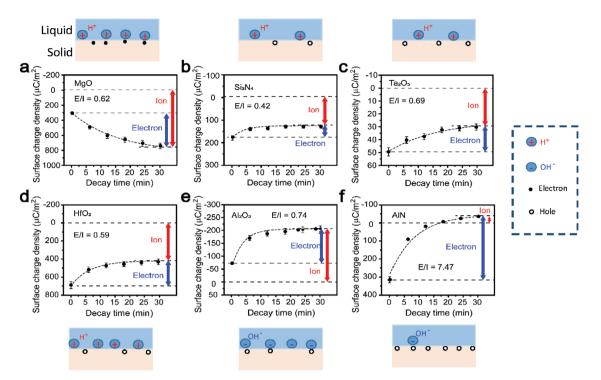


Figure 4. Kevin probe measurement of the surface charge density decay on inorganic nonmetallic solid materials after contacting with one droplet of DI water at room temperature on a) MgO, b) Si_3N_4 , c) Ta_2O_5 , d) HfO₂, e) Al₂O₃, and f) AlN surfaces, and the amount of the electron transfer (E) and the ion transfer (I) in the CE between the DI water and different insulators. The charge density was measured at 433 K after drying the water. The corresponding schematics on the top and bottom of the figures are the distribution of electrons/holes and ions on solid surface via chemical or physical adsorption (from ref. [7]).

7. The First Principle Theory of TENG

The driving force for the TENG is the Maxwell's displacement current, which is caused by a time variation of electric field plus a media polarization term. However, for power generation, the polarization should include a term that is contributed by the strain field such as piezoelectric effect and CE effect. In the case of TENGs, triboelectric charges are produced on surfaces simply due to CE between two different materials. To account for the contribution made by the contact electrification-induced electrostatic charges in the Maxwell's equations, an additional term $P_{\rm s}$ was added in displacement vector D by Wang in 2017,^[9] that is

$$\boldsymbol{D} = \boldsymbol{\varepsilon}_0 \boldsymbol{E} + \boldsymbol{P} + \boldsymbol{P}_{\rm s} \tag{1}$$

Here, the first-term polarization vector P is due to the existence of an external electric field, and the added term P_s is mainly due to the existence of the surface charges that are independent of the presence of electric field. Substituting Equation (1) into Maxwell's equations, and define

$$D' = \varepsilon_0 E + P \tag{2}$$

The reformulated Maxwell's equations are^[3]

$$\nabla \cdot \boldsymbol{D}' = \boldsymbol{\rho}' \tag{3}$$

 $\nabla \cdot \boldsymbol{B} = 0 \tag{4}$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{5}$$

$$\nabla \times \boldsymbol{H} = \boldsymbol{J}' + \frac{\partial \boldsymbol{D}'}{\partial t} \tag{6}$$

where the volume charge density and the density of current density can be redefined as

$$\rho' = \rho - \nabla \cdot \boldsymbol{P}_{\rm s} \tag{7}$$

$$J' = J + \frac{\partial P_s}{\partial t} \tag{8}$$

which satisfies the general rule of conservation of charges: $\nabla \cdot J' + \frac{\partial \rho'}{\partial t} = 0$. Starting from Equations (3–6), a full solution regarding the output current, potential, and power for TENG has been derived. In Equation (8), the term that contributes to the output current of TENG is related to the driving force of $\frac{\partial P_s}{\partial t}$, which is simply named as the Wang term in the displacement current.

In Equation (6), the displacement has two terms. The first term $\frac{\partial D'}{\partial t}$ represents the displacement current due to time variation electric field and the electric field-induced medium polarization, and it can generate corresponding magnetic field. This is known as the origin of electromagnetic wave, which was first proposed by Maxwell. The second term $\frac{\partial P_i}{\partial t}$ is the displacement current due to nonelectric field but owing to external strain

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field. The first term is dominant at high frequency for wireless communication, while the second term is the low frequency or quasistatic term that is responsible for the energy generation. In general cases, the two terms are approximately decoupled and can be treated independently. However, if the external triggering frequency is rather high, so that the two terms $\frac{\partial D'}{\partial t}$ and $\frac{\partial P_i}{\partial t}$ can be effectively coupled, the interference between the two terms can be significant, but such case may occur in gigahertz range.

8. Figure of Merits of TENG

It is well known that solar cell is characterized by efficiency and thermal electricity is represented by a ZT factor. The performance of an TENG is characterized by two factors: the materials figure of merit is the surface charge density; and the structure factor.^[10] The method for measuring the surface charge density has been standardized and tabulated for over 50 polymer materials.^[11] The structure of figure of merit can be calculated numerically.^[12]

9. Technological Impacts of TENG

Ever since its first invention in 2012, a vast effort has been adopted worldwide for TENG research for demonstrating its applications in medical science, environmental science, wearable electronics, textile-based sensors and systems, internet of things, security, and many more. The applications of TENG are mainly in four categories (**Figure 5**):

1. As nanopower and micopower sources for small, wearable, distributed, and possibly flexible electronics. With the fast development of internet of things and sensor networks, all of the small electronics have to be powered. Considering their large mobility, harvesting energy from the environment is essential for the sustainable operation of these distributed electronics.^[2] Considering the high output voltage and low output current of TENG, a power management circuit is required in order to effectively use the harvested energy for charging an energy storage unit, which is called a self-charging power pack for the self-powered system.^[13] An energy conversion efficiency ranging from 50% to 85% has been demonstrated depending on the operation modes of TENGs.

- 2. As self-powered sensors with a range of applications in internet of things and sensor networks. The development of artificial intelligence and big data relies on sensor networks that provide the huge required data. But most of the sensors require external power to operate. It is essential to have sensors that response to the environmental changes without power, for example, active sensors. As for motion, vibration, and triggering sensors, TENG can be an ideal choice, which produces output signal that can be wirelessly transmitted even without amplification.
- 3. As high-voltage sources. A unique characteristic of TENG is high output voltage, which can be used in many occasions that require a high voltage, such as driving electrostatics and excitation of plasma.^[14,15]
- 4. For harvesting water wave energy toward the blue energy dream. Because TENG has an outstanding output efficiency at low frequency in comparison to electromagnetic generator, it is unique for harvesting water wave energy. By integrating many units of TENG into networks, it is possible to harvest energy from ocean water, which is referred to as the blue energy.^[16,17] Recently, TENG has reached an energy harvesting efficiency of 28% by triggering in water.^[18]

In conclusion, we presented a summary about the fundamentals related to TENG. This is a new invention, and it is anticipated to have many unique applications in fields such

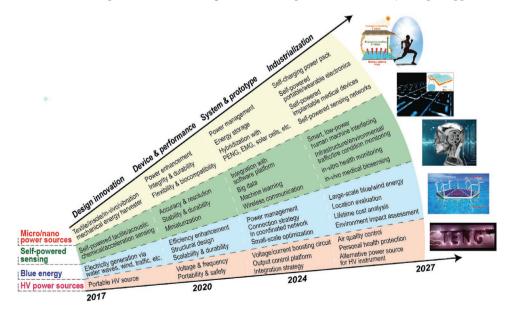


Figure 5. Four application fields of TENG and a road map defined for the development of TENG technologies. Reproduced with permission.^[14] Copyright 2019, Wiley-VCH.

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as health care, environmental science, wearable electronics, internet of things, human–machine interfacing, robotics, and artificial intelligence. We also hope that TENG will inspire a revolution in energy and sensors.^[19,20] The opportunity brought by TENG for materials is exploring a range of organic and inorganic materials and composite for enhancing the surface structures, surface triboelectric charge density, permittivity, and robustness for long-term operation. Such studies are about to start.

Conflict of Interest

The author declares no conflict of interest.

Keywords

contact-electrification, self-powered sensors, triboelectric nanogenerators

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