Photon Excitation Effect

Contact electrification (CE) (or triboelectrification) is one of the oldest topics in science, which has been known for more than 2600 years, but its physics interpretation still remains poorly understood. In the past, CE was usually considered as an annoying effect, which can result in electrostatic discharge and even explosion/fire. Nowadays, the triboelectric nanogenerator (TENG), which is based on the effect of CE, has been invented to convert ubiquitous ambient mechanical energy into electricity. The output performance of the TENG largely depends on the amount of triboelectric charges, which are generated on insulator surfaces by CE. However, there still lacks effective methods for enhancing the triboelectric performance of materials, where the ambiguous mechanism of CE plays a key role. A core issue in CE is the identity of charge carriers and their transfer mechanism. It is generally accepted that the CE between two metals with different work functions is caused by the electron transfer. But the competition between the electron transfer theory and the ion transfer theory has been going on for decades.

Recently, the triboelectric charges generated on ceramic surfaces (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and Si\textsubscript{3}N\textsubscript{4}) has been identified as electrons by performing the triboelectric charge decay experiments under different temperatures at both macroscale and nanoscale, and the results are explained consistently by the thermionic emission theory. The thermionic emission experiments provide a strong evidence for the electron transfer process in CE involving insulator.

In this study, the CE between metal and different insulators, including polymers, were performed at nanoscale by using atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM). The decay of triboelectric charges on the insulator surface under UV irradiation was investigated. Particularly, we focus on the effects of UV light’s wavelength and intensity on the triboelectric charge decay, and the results are consistent with the photoelectron emission theory of electrons. Further, a photoelectron emission model in CE was proposed based on the Spicer’s photoemission equations.

In our experiments, the metal contact side was an Au coated silicon tip, and both the ceramic thin film (SiO\textsubscript{2}) and
the polymer thin films (poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA)) deposited on high doped silicon wafers were used as the counter insulator material samples. Figure 1 gives the experiment procedures. As shown in Figure 1a, the triboelectric charges on the insulator surface was generated by using the peakforce tapping mode, in which the tip contacts the insulator surface in a point by point “dancing” mode instead of a firm contact and rubbing on the surface as used in other studies.[27–29] The details and advantages of using the peakforce tapping mode to generate triboelectric charge have been described in our recent study.[19] In the CE between the tip and the SiO2 sample, the peakforce was set to be ~10 nN, and the peakforce in the CE between the tip and the polymer samples was set to be ~0.5 nN, since the polymers are too soft to withstand high pressure. After the CE, the triboelectric charge density on the insulator surface was measured by using the KPFM mode, as shown in Figure 1b. Further, the charging area on the insulator surface was irradiated by the UV light, and the triboelectric charge density left on the surface was measured at regular time intervals to record the charge decay. The generation of the UV light is shown in Figure 1c, a xenon lamp house was used as the light source, and the wavelength range of the xenon light was from 200 to 2500 nm. The monochromatic UV light was extracted out from the xenon light by using UV optical filters with different center wavelengths (from 240 to 380 nm). Then, the UV light was focused on the charge area by using condensing lens to increase the intensity of the UV light, and the UV light intensity was measured by using an optical power meter. In order to exclude the effect of temperature on the decay of triboelectric charges, the temperature of the insulator surface under the light irradiation was measured by using an infrared thermal imager. All of the experiments in this study were performed in a glovebox filled with nitrogen gas, hence the effect of water and oxygen on the CE and charge decay can be eliminated.

As a control experiment, the decay of triboelectric charges on SiO2, PVC and PMMA surfaces was performed in dry nitrogen atmosphere without light irradiation, and the results are shown in Figure S1 (Supporting Information). It was noticed that the SiO2 and PVC samples were both negatively charged, while the PMMA was positively charged when they contacted with the Au coated tip. And the decay of triboelectric charges on these three material surfaces was limited within 150 min. Hence, the change of the surface charge density of the samples in the following experiments was not caused by natural charge decay. Figure 2a gives the change of the triboelectric charge density on the SiO2 sample surface under direct irradiation of the xenon light source with an intensity of 1200 W m⁻² (the wavelength of the xenon light was from 200 to 2500 nm). The triboelectric charge density on the SiO2 surface decayed from ~160 μC m⁻² to less than ~10 μC m⁻² under the xenon light irradiation in 45 min. Further, the light with wavelengths less than 400 nm was filtered out from the xenon light by using the optical filter (the wavelength of the filtered xenon light was from 400 to 2500 nm). The change of the triboelectric charge density on the SiO2 surface under the irradiation of the filtered xenon light is shown in Figure 2b. It can be seen that the filtered xenon light could not remove the triboelectric charge on the SiO2 surface, and the triboelectric charge density remained almost constant under the irradiation. It implies that the photon energy for UV light (light with wavelengths from 200 to 400 nm) played a major role in the decay of triboelectric charges under the xenon light irradiation. In order to test the temperature effect on the charge decay experiments, the temperature rise of the SiO2 sample was measured. Figure 2c gives the sample position in the experiments, and the temperature distributions of the SiO2 sample under the xenon light and filtered xenon light irradiation are shown in Figure 2d,e, respectively. The results show that the maximum temperature of the sample after 10 min irradiation was less than 313 K, which is too cool to result in thermionic emission according to our recent study.[19] And also, the temperature distribution of the SiO2 samples under the irradiation of the monochromatic UV light was measured and the results are shown in Figure S2 (Supporting Information). It can be seen that the temperature of the SiO2 sample did not increase under the irradiation of the monochromatic UV light. These results suggest that the triboelectric charge decay in the experiments was induced by photoelectron emission instead of thermionic emission, and the charge carriers in the CE between SiO2 and Au-coated tip should be electrons due to that ions cannot be bombarded out of the insulator surface by UV photons. In the experiments, the light with wavelengths larger than 400 nm cannot lead to the decay of triboelectric charges. According to Einstein's equation for photovoltaics as shown in Equation (1), the shorter wavelength and the higher frequency, the higher energy of the photons will be. It was indicated that the energy of the incident photons should be higher than a certain threshold to excite the trapped electrons in the CE. This is consistent with the photoelectron emission theory, in which photons can only excite electrons when their energy is higher than the energy of the electron surface charge barrier.

\[ E = h \nu = \frac{hc}{\lambda} \]  

(1)
where $E$ denotes the energy of the photon, $h$ denotes the Planck constant, $\nu$ denotes the frequency of the light, $c$ denotes the light speed, and $\lambda$ denotes the wavelength of the light.

In order to further verify the photoelectron emission of electrons in the CE, the effects of light wavelength and intensity on the irradiation induced triboelectric charge decay were studied. Figure 3 gives the effect of the incident light wavelength on the decay of triboelectric charges on the SiO$_2$ surface. As shown in Figure 3a, it was found that the light wavelength can significantly affect the triboelectric charge decay rate. The charge decay rate was fastest when the wavelength was 240 nm. And the decay rate decreased with the increase of the wavelength. Particularly, the amount of the triboelectric charges remained constant when the wavelength rose up to 300 nm. These results can be explained by photoelectron emission theory. The energy of the photons at the wavelength of 240 nm is the highest one in the experiments (higher than the photon energy at the wavelength of 260, 280, and 300 nm). Hence, the probability of the electrons, which were trapped in the surface states of SiO$_2$. The charge decay when the light wavelength was 240 nm is shown individually in Figure 3b. It can be seen that the charge density decayed linearly at the beginning of the curve, and then the decay rate decreased when the surface charge density was close to zero. The charge decay with the light wavelength at 260 and 280 nm are shown in Figure 3c,d, respectively, and the charge decay curve was linear. Because the charge density did not decay to small enough, thus the decrease of decay rate did not appear here.

Figure 4 gives the effect of the incident light intensity on the decay of triboelectric charges on the SiO$_2$ surface when the light wavelength is 280 nm. It was noticed that the charge decay curve was also linear at the beginning, and the decay rate decreased when the charge density decayed to less than a certain value, as shown in Figure 4a–c. And the charge decay rate was found to be increased with the increasing of light intensity. The slope of the decay curve changed from 16.2 to 2.1 $\mu$C m$^{-2}$·min$^{-1}$ when the light intensity varied from 100 to 10 W m$^{-2}$. These results were also consistent with the photoelectron emission. In the experiments, the wavelength of the light remained unchanged. It means that the energy of the incident photons kept constant and the probability of the electrons being excited also remained unchanged in the experiments. When the light intensity increased, the number of the incident photons and excited electrons per unit time increased correspondingly, and the charge decay rate became faster.

Here, the UV light irradiation induced triboelectric charge decay on the polymer surfaces was also investigated. Figure 5 gives the effects of light wavelength and light intensity on
the charge decay on the PVC and the PMMA surfaces. We noted that the triboelectric charge density on the polymer surface was much less than that on the SiO$_2$. It may be caused by that the surface state density of the SiO$_2$ is larger than the polymers, since that the number of the dangling bond of SiO$_2$ is larger than that of polymers. Similar with

Figure 3. The effect of the incident light wavelength on the decay of triboelectric charges on the SiO$_2$ surface when the light intensity was 25 W m$^{-2}$. a) The contrast of the charge decay under different light wavelengths. b–d) The decay of triboelectric charges when the light wavelength is: b) 240 nm, c) 260 nm, and d) 280 nm.

Figure 4. The effect of the incident light intensity on the decay of triboelectric charges on the SiO$_2$ surface when the light wavelength is 280 nm. a–d) The decay of triboelectric charges when the light intensity is: a) 100 W m$^{-2}$, b) 70 W m$^{-2}$, c) 40 W m$^{-2}$, and d) 10 W m$^{-2}$.
the charge decay on the SiO₂ surface, the charge decay rate on the PVC surface also decreased with the increasing of the light wavelength, as shown in Figure 5a. The difference was that the triboelectric charge on the PVC surface could be removed by light with wavelength shorter than 360 nm instead of 300 nm. It means that the energy of photons required to remove the charge on the PVC surface is less than that on the SiO₂ surface. According to Equation (1), it can be calculated that the energy of the incident photons should be higher than 3.44 eV to excite the electrons trapped on the surface states of PVC. Particularly, the charge decay on the PVC surface was also linear at the beginning, and the decay rate decreased when the charge density decayed to less than a certain value. It indicates that the photoelectron emission mechanism on the PVC surface is the same as that on the SiO₂ surface. As shown in Figure 5b, the charge decay rate on the PVC surface also increased with the rise of the light intensity. These results suggest that the decay of triboelectric charges the PVC surface was also induced by the photoelectron emission, and the charge carriers in the CE between the PVC and the Au coated tip are electrons.

Figure 5c,d gives the effects of light wavelength and intensity on the decay of triboelectric charges on the PMMA surface, respectively. Different with the SiO₂ and the PVC, the PMMA was positively charged when it contacted with the Au coated tip. The positive charge on the PMMA surface decayed under the irradiation of the UV light with wavelength less than 360 nm. And also, the charge decay rate decreased with the increase of the light wavelength or the decrease of the light intensity. Considering the PMMA donated electrons when it contacted with the tip, the positive charge carriers on the PMMA surface should be holes. The decay of positive triboelectric charges can be explained by that the electrons were transferred from nitrogen molecules to the PMMA surface under the excitation of the UV light, when the nitrogen molecules collided with the PMMA surface.

Based on the results, a photoelectron emission model was proposed for explaining the decay of surface electrostatic charges. Figure 6a shows the situation according to the Spicer’s photoemission theory for the dielectric, where \( E_g \) is the bandgap energy and \( E_a \) is the value of the electron affinity of the dielectric. According to the Spicer’s photoemission theory, the electron in the valence band can only be excited when the energy of the incident photon higher than the charge barrier \( (E_g + E_a) \). And the quantum efficiency (QE), which denotes the ratio of the number of excited electrons to the number of the incident photons, can be expressed by the following equation \(^{26}\)

\[
\text{QE} = \frac{\left[ \frac{h \nu - \left( E_a + E_g \right)}{h \nu - \left( E_a + E_g \right)} \right]^{3/2} G(h \nu)}{h \nu - \left( E_a + E_g \right)}^{3/2} + \gamma
\]

where \( G(h \nu) \) is a constant that depends on the energy of incident photons and the properties of materials, and \( \gamma \) is a constant, which depends on the properties of materials and it is usually determined by fitting to the experimental data.

Since that the photocurrent density is proportional to the number of excited electrons and that the number of the
incident photons is proportional to the incident light intensity, the photocurrent density $i$ can be expressed as follows

$$i = \frac{[h\nu - (E_g + E_s)]^{1/2} G(h\nu) kI}{[h\nu - (E_g + E_s)]^{1/2} + \gamma}$$

(3)

where $I$ is the incident light intensity and $k$ is the ratio constant.

Different from the Spicer’s photoemission theory, the electron is trapped in the surface states instead of valence band in CE. As shown in Figure 6b, we assume that the Fermi level of the metal is higher than the effective Fermi level of the dielectric. The electrons will transfer from the metal to the dielectric in CE, and they will be trapped in the surface states of the dielectric, as shown in Figure 6c. The trapped electrons will fill the surface states at low energy level first, and as shown in Figure 6d, the highest occupied surface state depends on the density of transferred electrons and the density of the surface states, as demonstrated in the following

$$E_s = \frac{\sigma}{eN}$$

(4)

where $\sigma$ denotes the triboelectric charge density, $E_s$ denotes the highest occupied surface states, $e$ is the electron charge, and $N$ denotes the average surface states density.

Hence, the height of the energy barrier ($W$) for the trapped electrons in CE can be expressed as follows

$$W = E_g + E_s - E_a = E_g + E_a - \frac{\sigma}{eN}$$

(5)

Further, the photoemission equation in CE can be established as follows

$$i = \frac{d\sigma}{dt} = \left[ h\nu - \left( E_g + E_s - \frac{\sigma}{eN} \right) \right]^{1/2} G(h\nu) kI$$

$$\left[ h\nu - \left( E_g + E_s - \frac{\sigma}{eN} \right) \right]^{1/2} + \gamma$$

(6)

Here, $E_i$ is used to replace $h\nu - (E_g + E_s)$ and $M(h\nu, I)$ is used to replace $G(h\nu)kI$, then

$$\frac{d\sigma}{dt} = \frac{\left( E_i + \frac{\sigma}{eN} \right)^{3/2} M(h\nu, I)}{\left( E_i + \frac{\sigma}{eN} \right)^{3/2} + \gamma}$$

(7)

In Equation (7), if $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \gg \gamma$, then

$$\frac{d\sigma}{dt} = M(h\nu, I)$$

(8)

Equation (8) indicates that the charge density decay linearly, if $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \gg \gamma$.

If $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \ll \gamma$, then $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} + \gamma = \gamma$, and then

$$\frac{d\sigma}{dt} = \frac{\left( E_i + \frac{\sigma}{eN} \right)^{3/2} M(h\nu, I)}{\gamma}$$

(9)

According to Equation (9), the charge decay rate decreases with the decrease of the charge density. And the decay curve of the triboelectric charge density when $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \ll \gamma$ can be expressed as follows

$$\sigma = \frac{4\gamma \left( eN \right)}{(M(h\nu, I)t + C\gamma)} = eN E_i$$

(10)

Based on the photoelectron emission model above, the UV light irradiation induced triboelectric charge decay in the experiments can be explained very well. In the beginning of the charge decay, the triboelectric charge density was large enough, and $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \gg \gamma$, hence the charge decayed linearly. With the decay of triboelectric charge density, the value of $\left( E_i + \frac{\sigma}{eN} \right)^{3/2}$ decreased. When the triboelectric charge density decayed to less than a certain value, there would be $\left( E_i + \frac{\sigma}{eN} \right)^{3/2} \ll \gamma$. In this case, the decay rate decreased with the fall of triboelectric charges.

The photoelectron emission experiments provide a strong evidence for the electron transfer in CE between metals and
insulators, including polymers. In addition, the discoveries in this paper may have more implications. For example, Wang’s group predicted that the photon can be emitted in CE due to the electron transfer.\cite{10, 31} And the emitted photon can be in UV, visible light, microwave, and even THz waves. The photon emission in CE was not directly observed in this study, but the results could give the same clues about it. The electron can be excited into vacuum under the UV light irradiation, which means that the photon emitted when the electron transits from vacuum to the surface states should be in UV energy range. In CE, the gap between the effective Fermi levels of two dielectric in the contact is usually smaller than the gap between the vacuum level and the effective Fermi level of the dielectric. Hence, the emitted photon can be in the light with wavelength larger than UV, and it implies that the wavelength of the emitted photon as predicted by Wang.\cite{30} More importantly, the threshold wavelengths for removing the trapped electrons on SiO\textsubscript{2}, PVC, and PMMA surfaces were different. It means that the energy distribution of the trapped electrons in CE is material dependent. Correspondingly, the wavelength of emitted photon induced by the electron transfer in CE may also depend on the material. Hence, the spectroscopy based on the photon emission in CE, which was mentioned in previous study,\cite{30} can not only be used to study electronic transition during CE, but also can be a new material characterization method.

In conclusion, the decay of CE-induced electrostatic charges on the dielectric surface under UV light irradiation is studied. It is found that the light wavelength and intensity can affect the charge decay rate significantly, and there exists a threshold photon energy for releasing the triboelectric charges on the surface, which is 4.1 eV for SiO\textsubscript{2} and 3.4 eV for PVC. The energy of the photons should be higher than the threshold energy to be able to effectively excite the surface electrostatic charges. The results suggest that the photoelectron emission of the electrons trapped in the surface states of the dielectric materials is responsible for the decay of the electrostatic charges. Further, a photoelectron emission model is proposed to describe light-induced charge decay. The findings in this paper provide a strong evidence about the electron transfer in the CE between metals and dielectrics, including polymers.

**Experimental Section**

Sample Preparation and Characterization: The SiO\textsubscript{2} layer of 100 nm in thickness was deposited on high doped silicon wafer by thermal oxidation. The PVC and PMMA films were prepared on the high doped silicon substrate by spin coating. The mass fraction of PVA and PMMA solutions in the corresponding spin process were both 2%. The rotational speed used here was 2000 r min\textsuperscript{-1}. The thickness of the PVA, PMMA films was 500 nm. And the XPS spectra of the samples before and after 10 min irradiation of the UV light with the wavelength at 240 nm are shown in Figures S3–S5 (Supporting Information). It was found that the structure of the SiO\textsubscript{2} and the PVC remained unchanged after the irradiation of UV light. For the PMMA, the XPS spectra show that the C–O and the C=O would break under the irradiation of the UV light.

UV Light Generation: The xenon lamp house used here was NEWPORT-6700S and xenon lamp was XBO-150W (NEWPORT, USA). The cutoff wavelength of the UV optical filters was from 200 to 2500 nm, and the bandwidth of the UV optical filters was 10 nm. The optical power meter used to measure the intensity of the UV light was PM100D (THORLABS, USA).

Temperature Measurement: The infrared thermal imager used here was FOTRIC-222s (FOTRIC, USA).

AFM Equipment: All the experiments were performed on a commercial AFM/KPFM equipment Icon (Bruker, USA). The Au-coated silicon tip used here is NSC 18 (MikroMash, USA; coating: Au; tip radius: 25 nm; spring constant: 2.8 N m\textsuperscript{-1}). In the peakforce tapping scanning, the scan size was set to 5 µm and the scan rate was 4 Hz. And the peakforce was \approx 10 nN when the tip was scanning the SiO\textsubscript{2} sample and the peakforce was \approx 0.5 nN when the tip was scanning the PVA or PMMA samples. The triboelectric charges were detected in the KPFM mode, while the tapping amplitude was set to 350 mV, the lift height was 50 nm and the scan size was 10 µm.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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