The Relationship between Static Charge and Shape

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**ABSTRACT:** The amount of charge of a material has always been regarded as a property (or state) of materials and can be measured precisely and specifically. This study describes for the first time a fundamental physical–chemical phenomenon in which the amount of charge of a material is actually a variable—it depends on the shape of the material. Materials are shown to have continuously variable and reversible ranges of charge states by changing their shapes. The phenomenon was general for different shapes, transformations, materials, atmospheric conditions, and methods of charging. The change in charge was probably due to a dynamic exchange of charge from the material to the surrounding atmosphere as the shape changed via the reversible ionization and deposition of air molecules. Similar changes in charge were observed for self-actuating materials that changed their shapes autonomously. This fundamental relationship between geometry and electrostatics via chemistry is important for the broad range of applications related to the charge of flexible materials.

**INTRODUCTION**

Charge is a fundamental property of matter. The amount of charge of a material is commonly regarded as a state of the material: it can be determined precisely and specifically. For many centuries, the amount of charge of a material has routinely been measured experimentally by different methods (e.g., by placing the material in a Faraday cup connected to an electrometer) and reported as the specific charge (or state) of the material. The notion that the amount of charge is the state of the material is mainly based on the law of charge conservation, which states that the total amount of electric charge in an isolated system is always conserved. This study, however, describes for the first time that the amount of charge of a material is surprisingly a variable—the amount of charge depends on the shape of the material. By changing its shape, we showed that the charge of a material can be changed flexibly and reversibly; thus, there is a continuous range of states of charge associated with the material. Materials can adopt a diverse range of interesting shapes and fascinating transformations of shapes in the three-dimensional space. Shapes of flexible materials can be changed by many different methods (e.g., mechanically or autonomously). We demonstrated that the amount of charge of a material changed when it was bent, twisted, coiled, or folded (Figure 1a).

Static charge is ubiquitous and has a vast range of consequences in our lives. In terms of applications, charged materials are useful for many circumstances, such as electrophotography, $^1$ electrostatic coating, $^2$ separation, and self-assembly. $^3$ In particular, there has been a lot of interest in devices that are collectively known as the triboelectric nanogenerators (TENGs) in these few recent years. $^4–^7$ These TENG devices have been used for a diverse range of applications, including the harvesting of energy from the motion of the human body or natural sources of the environment, filtration, control of electronics (i.e., “tribtronics”), and sensors. On the other hand, static charge can lead to many types of undesirable consequences, including adhesion of particles on surfaces by electrostatic forces (e.g., on computer screens), fouling, damage to equipment (e.g., electronic components by electrostatic discharge), $^8$ and explosion of flammable substances. $^9$

Importantly, the charged materials involved in many of these circumstances need to undergo a change in shape. For example, a TENG device used for generating electricity consisted of multiple layers of materials stacked in a zigzag manner. The device operated by repeatedly stretching (i.e., separating) and compressing (i.e., contacting) the multiple layers of material with the zigzag shape (Figure 1b). This motion allowed the surfaces of the different layers to come into contact easily with a high surface area of contact. $^5,^6$ Another example involves a flexible triboelectric tactile sensor (i.e.,...
For studying the relationship, our experiments involved charging insulating materials by contact electrification: the process by which static charge is generated on insulating surfaces by contacting two surfaces and separating them. Large amounts of charge can usually be generated through this simple process; hence, static charge is often present on surfaces of materials used in industry and our daily lives. Fundamentally, the mechanism (e.g., electron\textsuperscript{13,14}, ion\textsuperscript{1} or materials transfer\textsuperscript{5,16}) by which the charge is generated and the type of charged species created on the insulating surfaces after contact electrification are not well understood. At the molecular level, the charged species may originate from the chemical groups on the surface of the materials or water molecules adsorbed on the surfaces from the surrounding atmosphere.\textsuperscript{1,17,18} Alternatively, we charged the surfaces by corona discharge (i.e., the ionization of air molecules and deposition of the ions on the surface). The charging process, and the subsequent dissipation of charge, may be influenced by a number of factors, including the type of the surrounding atmosphere and the properties of the materials. For example, it is important to take into account the stability of the cation and anions on the surface as determined by the ionization energy and electron affinity of the chemical groups.\textsuperscript{19–21} Regardless of the mechanism of charging, type of charged species, and process of dissipation, we show that the phenomenon is general: the amount of charge changes whenever the shape of the material changes under different conditions, including the use of different materials (i.e., with different chemical groups on the surface), polarity of charge (i.e., positive or negative), atmospheres (e.g., different gases with high or low humidity), and method of charging (i.e., contact electrification or corona discharge). Because of its generality, the relationship between static charge and shape appears to be a fundamental principle of electrostatics.

### RESULTS AND DISCUSSION

In our first demonstrations, we used thin sheets of polytetrafluoroethylene (PTFE) because they had the tendency to charge highly and were flexible for deforming into different shapes.\textsuperscript{22} We first folded a flat sheet of PTFE (1.0 \texttimes 7.0 cm and a thickness of 180 \textmu m) in half and pressed onto it gently for a few seconds. After releasing the stress, the sheet of PTFE remained bent as shown in state 1 in Figure 2a. We then discharged the sheet of PTFE by a Zerostat gun; it was verified to be discharged by measuring its charge using a Faraday cup connected to an electrometer. Subsequently, we charged one of the two sides of the bent sheet of PTFE by contact electrification. Specifically, the inner surface of the sheet of PTFE (i.e., the two surfaces that faced each other when the sheet of PTFE was bent) was contact-charged against a piece of nitrile rubber. The charged sheet of PTFE was placed into the Faraday cup and bent further (i.e., state 2 in Figure 2a) while it was in the Faraday cup. Bending the material further allowed the two charged inner surfaces that faced each other to approach closer, but they were not allowed to come into contact. The farthest distance of separation at the two ends of the sheet of PTFE that was bent to a further extent was 4.0 mm (Supporting Information, Figure S1). Surprisingly, we found that the amount of negative charge measured decreased upon bending (see plot in Figure 2a). When we returned the sheet of PTFE to its initial shape (i.e., state 1), the

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**Figure 1.** Changes in shape cause changes in the amount of charge of a material. (a) Materials with different shapes can undergo a diverse range of changes in conformation when subjected to external forces (e.g., bending or twisting). When the geometry of the material is in a compact state, the amount of charge of the material is lesser (left column) than when the material is in an extended state (right column). The charges are continuously variable and reversible. (b) Triboelectric devices reported in a previous study (by Wang and co-workers)\textsuperscript{3} that involved changes in shape and generation of charge on the surfaces of the alternating layers of the device by contact electrification for achieving the best performance. Used with permission from the ACS.
ends of the bent sheet of PTFE was smaller (see Figure S2). We further demonstrated that the reversible change in charge due to the repeated changes of shape was due to a smaller distance of separation between the charged surfaces when the sheet of PTFE was compressed; in particular, the farthest distance of separation at the ends of the sheet of PTFE was 3.0 mm when it was folded six times compared to 4.0 mm when it was folded only once (Supporting Information, Figure S1). Alternatively, the change in charge can be increased by using a larger piece of material (i.e., 1.0 × 14.0 cm and a thickness of 0.1 cm; Figure 2c). All manipulations were performed using a pair of nonconductive wooden tweezers.

Changes in the amount of charge of the individual pieces of material also occurred for other types of changes in shapes, such as twisted or spiral shapes. For this experiment, we first twisted a sheet of PTFE (1.0 × 7.0 cm and a thickness of 180 μm) with sufficient force such that it remained twisted as shown in state 1 in Figure 2d even when the force was released. This twisted freestanding sheet of PTFE was charged negatively by contacting it with nitrile rubber on only one side and placed into the Faraday cup. We then compressed the twisted sheet by pushing both ends of the sheet inward to a coiled-up shape as shown in state 2 of Figure 2d while it was in the Faraday cup. In this compressed state, the amount of negative charge decreased. It was returned to its original extended shape by pulling both ends outward (Figure 2d, state 1). By repeatedly pushing inward and pulling outward, we were able to measure the reversible change in charge. In another example, we coiled up a larger sheet of PTFE (1.0 × 14.0 cm and a thickness of 180 μm) into a spiral shape. Similarly, we first charged only one side of the sheet of PTFE and then placed it in the Faraday cup. The inner end of the sheet was raised into a three-dimensional spiral (i.e., state 1 shown in Figure 2e) and lowered into a two-dimensional spiral (i.e., state 2 shown in Figure 2e) repeatedly. A similar reversible change in charge was observed. In general, it seems from all these results that whenever the shape became more compact—so that the charged surfaces became closer to one another—the charge of the material decreased.

The change in charge was general and not restricted to a specific type of material, polarity of charge, atmospheric condition, method of manipulation, or method of charging. As a demonstration, we performed the same experiment using different materials: silicone rubber, natural rubber, polypropylene (PP), polydimethylsiloxane (PDMS), and polystyrene (PVC). The pieces of materials were initially flat and charged only on one side by contact electrification with a piece of nitrile rubber. For each type of material, we charged it either positively or negatively. After placing one of the pieces of material in a Faraday cup, we repeatedly bent and relaxed it (i.e., allowing the material to return to its flat shape; Figure 3a). The manipulation was performed using pairs of tweezers made of either wood (Figure 3) or the highly insulating polytetrafluoroethylene (PTFE) (Figure S4). Results showed that the amount of charge changed repeatedly with time when the shape changed for all the different types of materials and polarity (i.e., either positive or negative) of the materials investigated (Figure 3b). In addition, we compared
the changes in charge of a piece of silicone rubber that was repeatedly bent and relaxed in different atmospheres: nitrogen (with a humidity of $\sim 2\%$), helium (with a humidity of $\sim 2\%$), and air (with a humidity of $\sim 50\%$). The changes in charge seemed similar for all three types of atmospheres (Figure 3c). Besides contact electrification, we charged a piece of silicone rubber by corona discharge (i.e., via a Zerostat gun). Corona discharge allowed the surrounding air molecules to be ionized and deposited on the surface. By repeatedly bending and relaxing the silicone rubber, similar changes in charge are observed for both positively and negatively charged silicone rubber (Figure 3d).

By the law of charge conservation, when the amount of charge of the material changed, the charge corresponding to the amount changed must have moved somewhere else. One way charge might have transferred was through the solid surfaces. We typically used a pair of tweezers to manipulate the charged pieces of materials; hence, one possibility was that charge might have moved through the pair of tweezers and out of the Faraday cup (i.e., the charge needed to move out of the Faraday cup in order for the measurement of the amount of charge to change). However, this transfer seems unlikely: we used a pair of tweezers that was either nonconductive (i.e., wooden; Figure 3) or highly insulating (i.e., PCTFE; Figure S4). For both cases, we observed the reversible change in charge. In addition, we observed similar reversible changes in charge of a sheet of silicone rubber by bending and relaxing it to its original flat state repeatedly using pairs of tweezers made of other types of highly insulating materials, such as polystyrene, ceramic, and polyoxymethylene (Supporting Information, Figure S5).22

If the charge was not transferred through the pairs of tweezers, the only other possibility was that it transferred from the material into the surrounding air and then out of the Faraday cup. To investigate if air was involved, we used a Faraday cup that was partially covered on top by a piece of aluminum. A small hole ($1.2 \times 3.0$ cm) was made in the center of the top cover so that we could manipulate the shape of the material using a pair of tweezers from outside of the Faraday cup. A flat sheet of natural rubber was inserted into the Faraday cup, and was repeatedly bent and relaxed (Figure 4). We then repeated the experiment without the partially covered top as a control experiment. Results showed that the amplitude of the difference in charge caused by the changes in shape decreased significantly when the Faraday cup was covered. This result suggested that air was involved: when charge exchanged between the material and the surrounding air, the charged air molecules were prevented from escaping the Faraday cup by the top cover. Therefore, the amount of change in charge was significantly lower when the shape changed.

To understand the reason for the involvement of air, we calculated the electric field around the materials of different...
shapes (i.e., by Comsol Multiphysics). In these calculations, we specified a typical charge density (i.e., $-1.0 \text{nC/cm}^2$) on the surface of the material. The electric field was calculated for a series of shapes: from a flat geometry to geometries with an increasing amount of bending as shown in Figure 5a. The results showed that the electric field increased around the material when the amount of bending increased. The increase in electric field with the increase in the amount of bending can be observed more clearly by plotting the electric field strength with respect to the length of the surface (Figure 5b). It is known in previous studies that an increase in the electric field can lead to an increase in the amount of ionization of the air molecules, thus allowing an increased amount of charge to be dissipated from the material into the air.$^{23−26}$ This calculation indicated that the amount of charge should decrease monotonically with increasing amount of bending of the material. We verified this expected relationship by measuring the amount of charge remaining on different materials (i.e., silicone rubber, natural rubber, and PDMS) with different amounts of bending; results showed that the amount of charge decreased monotonically with an increase in the amount of bending for the different materials investigated (Figure 5c–e).

In general, we believe that the mechanism for the continuously variable and reversible change in charge when the shape of the materials was changed is related to the phenomenon reported in our previous study (i.e., when the

Figure 4. Preventing the charged air molecules from escaping the Faraday cup by covering its top opening. The reversible change in charge was reduced when the cup was covered (“Closed Cup”) compared to when the cup was open (“Open Cup”).

Figure 5. Electric field strength around the surface of the charged material increases when the material becomes more compact. (a) Numerical calculation of the electric field surrounding a piece of charged material with different amounts of bending. (b) Plots of the electric field strength against the length of one side of the charged material, $x$, for the five different shapes shown in part a. The colors of the plots, in the order of the increasing amount of bending, are pink (flat), dark yellow green, light green, blue, and red (i.e., as indicated in the panel on the right). Experimental results for the measured amount of charge of the material versus the distance of separation between the ends of the material, $d$, for (c) silicon rubber (SR), (d) natural rubber (NR), and (e) polydimethylsiloxane (PDMS).
distance of separation between multiple charged surfaces was varied). For the purpose of discussing the mechanism, we consider a negatively charged sheet of material with an initially extended geometry as illustrated on the extreme left of Figure 6. The shape of the material is then changed by bending it. Because the charged surfaces are now closer to each other, the electric field strength around the material increases (second illustration from the left as shown in Figure 6). This increase in electric field leads to the ionization of the surrounding air molecules, thus generating positive and negative ions in the air. The positive ions are attracted to the negatively charged surface and deposit on it (third illustration from the left as shown in Figure 6). On the other hand, the negative ions are repelled from the surface and move out of the Faraday cup. When the ions leave the Faraday cup, the amount of charge measured decreases. When the shape of the material is

Figure 6. Scheme illustrating the proposed mechanism of the continuously variable and reversible change in charge of a negatively charged sheet of material when its shape is changed from an initially extended state to a bent state repeatedly.

Figure 7. Autonomous changes in charge of self-actuating materials. (a) A thin piece of polyethylene (PE) was folded into a quarter. (b) A sheet of PTFE was folded multiple times. (c) A long strip of PTFE was twisted into a two-dimensional spiral. A pressure was initially applied to keep them in their compact states 1 in the Faraday cup. When the pressure was released, the materials transformed into states 2 spontaneously and caused a rapid change in charge. The gradual release of pressure caused intermediate changes (states i) in charge for (d) the sheet of PTFE folded multiple times and (e) the strip of PTFE twisted into a spiral.
returned to its original extended state, the positive ions may desorb from the surface; hence, the surface gains back its initial amount of charge (illustration on the extreme right as shown in Figure 6). We showed that ions deposited onto a surface (e.g., by spraying ions from a Zerostat gun) from the atmosphere were able to desorb rapidly from the surface (e.g., within 1 s; see the Methods section and Figure S6 for more details on this experiment).20 Previous studies have found that, for surfaces with a net charge, charges of both polarities have the natural tendency to dissipate into the surrounding atmosphere.19 This natural tendency to dissipate may be due to the instability of the ions on the surface.19 This proposed mechanism is general for any type of transformation of shape: as long as the material is made more compact (thus allowing the charged surfaces to be closer to each other), the charge of the material will decrease according to the mechanism and vice versa.

One factor that might need to be considered is that the mechanical manipulation of the materials might lead to changes in the chemical composition of the surface.27–29 We analyzed the chemical compositions of PDMS and natural rubber in both the flat and bent states using the X-ray photoelectron spectroscopy (XPS). No difference in chemical composition was detected for the flat and bent states of both materials (Supporting Information, Figure S7).

Materials that change their shapes autonomously have attracted a lot of attention from researchers in recent years for the development of a number of technologically important fields (e.g., stimuli-responsive materials, shape-memory polymers, and 4D printing). We demonstrated that, besides changing the shapes of the materials via mechanical manipulations, the amount of charge can also be changed when charged self-actuating materials change their shapes autonomously. As a demonstration, we first charged a sheet of polyethylene (4.5 cm × 5.5 cm × 100 μm) on one side. It was then folded in half two times (i.e., folding the sheet into a quarter; state 2 in Figure 7a) with the charged surface facing inside. The folded sheet of polyethylene was then inserted inside the Faraday cup. A slight pressure was applied via a pair of tweezers to keep it in its folded state inside the Faraday cup. Upon releasing the material from the pair of tweezers, it quickly unfolded partially by itself once inside the Faraday cup to the state 1 shown in Figure 7a. A rapid increase in charge was observed during the process of unfolding.

We further demonstrated that the change in charge due to the self-actuating material is general for other types of autonomous changes in shape. Examples included a sheet of PTFE that was folded multiple times (state 2 in Figure 7b) or twisted into a two-dimensional spiral (state 2 in Figure 7c). The materials were similarly placed in the Faraday cup and kept in the compact state by applying a slight pressure on them. When the pressure was released, the folded sheet of PTFE stretched out (state 1 in Figure 7b), whereas the two-dimensional spiral became a three-dimensional spiral (state 1 in Figure 7c) spontaneously. In both cases, sudden increases in charge were also observed (Figure 7b,c). For a clearer observation of the changes in charge, we released the pressure gradually in intermediate stages (i.e., states i shown in Figure 7d,e) instead of removing the pressure completely at once. For the sheet of PTFE that was folded multiple times, any sequential release in pressure at the intermediate stages caused a clear change in charge that corresponded exactly to the time of release (Figure 7d). Similar results were observed for the gradual release of pressure of the sheet of PTFE twisted into a spiral (Figure 7e). These results showed that the changes in charge were due to the changes in shape of the self-actuating material; importantly, the amount of change was controllable by the extent of the self-actuation.

This relationship between charge and shape of the material can potentially be used in different types of applications. We demonstrated simple and direct applications of the relationship: curvature sensor and force sensor. To illustrate the versatility of the method, we used a variety of different types of materials, dimensions of the materials, and shapes. Specifically, we used a thick folded piece of PTFE (thickness: 2 mm), a thin folded piece of PTFE (thickness: 0.2 mm), a thin folded piece of PVC (thickness: 0.27 mm), and a PTFE spiral. For each of these materials, it was charged on one side by contact electrification and placed in a Faraday cup connected to an electrometer. For the folded pieces of material, we bent them to a series of specific angles by pressing them vertically downward via a wooden tip while measuring their charges (Figure 8a). The relationship between the amount of charge of the material and the angle of bending is thus the calibration curve of the curvature sensor (Figure 8b); by measuring the charge of the material, we will be able to determine the curvature (i.e., via the angle of bending) of the material. For the force sensor, we repeated the experiment except that the material was placed on a weighing balance. The downward forces applied by the wooden tip onto the material for the series of specific angles were thus measured by the balance (Figure 8c). Based on the relationships between the charge and forces applied by the wooden tip, we bent them to a series of specific angles by pressing them vertically downward via a wooden tip while measuring their charges. For each of these materials, we bent them to a series of specific angles by pressing them vertically downward via a wooden tip while measuring their charges.
angle of bending and the force and angle of bending, we obtained the calibration curve of the force sensor (Figure 8d): by measuring the charge of the material, we will be able to determine the force applied onto the material. Due to the diverse types of materials and shapes used, we were able to measure a wide range of force that spanned 3 orders of magnitude.

CONCLUSION

Geometric transformations of shapes of materials in the three-dimensional space have fascinated scientists from a diverse range of backgrounds (e.g., chemists, materials scientists, physicists, mathematicians, and engineers) for centuries. On the other hand, electrostatics is a separate scientific field that has also been studied for a long time. Scientists have always regarded that the amount of charge of a material (or an object) is a property (or state) of the material; the charge of the material can be measured precisely and specifically. This study bridges these two old scientific fields: we showed that there is a fundamental relationship between geometry and electrostatics of materials. Specifically, we found the physical—chemical phenomenon wherein the amount of charge is actually variable—the amount of charge depends on the shape of the material. Our results showed that when a charged material becomes more compact (e.g., from an extended to a bent geometry), the amount of charge decreases, and vice versa. The change is continuous and reversible; hence, there is a continuous range of charge states of a material depending on its shape. This fundamental principle of electrostatics is general and not limited to a specific type of material, polarity of charge, shape, types of transformation of shapes, types of atmosphere surrounding the material, method of charging (e.g., contact electrification or corona discharge by an electrostatic gun), or method of changing the shape. We demonstrated that charge changed when the materials were manipulated mechanically or were allowed to change their shapes autonomously (i.e., by self-actuating materials). We propose that the changes in charge are a result of a dynamic exchange of charge from the surface of the material with the surrounding atmosphere: the reversible ionization of the surrounding air molecules and the deposition of ions from the air to the surfaces resulted in the changes in charge.

This result is important for any general circumstance or application that involves the change in shape of a charged material. Importantly, both these old scientific fields (i.e., shape and electrostatics) have actively been used in applications of current exciting fields of research. For example, research that involves the change in shapes of materials includes stimuli-responsive materials, soft robotics, and 4D printing of active materials, whereas research that involves electrostatics includes the general class of TENG devices designed creatively for a diverse range of applications reported in these recent few years. Therefore, the combination of changes in shape and electrostatics also has many interesting applications (e.g., flexible TENG devices). It is important to take this phenomenon into consideration for applications (e.g., in the engineering designs of the charged flexible materials) in which the amount of charge at different states of the material needs to be properly determined. As illustrations of the usefulness of this phenomenon, we demonstrated simple and direct applications of this phenomenon as curvature and force sensors. In addition, it should be interesting for students of elementary science to learn about the variable and reversible charge states of materials depending on shape when studying about the fundamentals of electrostatics. It would be interesting to see further developments from researchers of different backgrounds for fully establishing the relationship theoretically and in practical circumstances.

METHODS

Materials. Silicone rubber was purchased from Nilaco Japan. Natural rubber, polyethylene, and all types of tweezers used were purchased from As One. Ceramic materials (i.e., zirconia and alumina) were purchased from Nichias corporation. Polytetrafluoroethylene (PTFE) was purchased from Suzuki scientific instruments Inc.

Sheets of PTFE of dimensions 1.0 × 7.0 × 0.018 cm, 1.0 × 14.0 × 0.018 cm, and 1.0 × 14.0 × 0.1 cm were used in the experiments to make the different shapes of PTFE as described in the main text. For the larger structure with multiple folds, we used a slightly thicker (0.1 cm) and larger (1.0 × 14.0 cm) PTFE sheet, made cuts (∼0.04 cm deep) in the sheet on both sides alternately, and then folded it accordingly. The thinner sheet of PTFE was not able to withstand the large structure and crumpled during the change in shape.

Polydimethylsiloxane (PDMS) was prepared using a standard protocol as follows. First, we mixed a 10:1 ratio of Sylgard and hardener (Dow Corning) at room temperature and removed air bubbles using a centrifuge. We then poured the mixture into a Petri dish to a height of 1.0 mm. This mixture was kept at room temperature overnight, followed by heating at 70 °C for 1 h.

The sheet of polyvinyl chloride (PVC) was fabricated by dissolving 2.5 g of PVC powder (average MW 85 000, Sigma-Aldrich) in 50 mL of tetrahydrofuran (THF) at room temperature. The mixture was stirred with a magnetic stirrer until all the PVC powder fully dissolved. After that, the PVC solution was poured into a glass Petri dish that was 100 mm in diameter and 15 mm deep. The solvent was evaporated in an oven operated at 80 °C overnight for obtaining the sheet of PVC that was 0.27 mm thick.

The Faraday cup (model: ADCMT, 8031) consisted of an inner cup and an outer cup. The inner cup had a diameter of 4.5 cm, height of 8.75 cm, and wall thickness of 2.5 mm. The outer cup had a diameter of 9.0 cm, height of 17.0 cm, and wall thickness of 3 mm. The Faraday cup was attached to an electrometer (model: ADCMT 8252 digital electrometer) by a TRIAX-BNC cable.

All the numerical calculations of the electric fields were performed using the finite element method provided by Comsol Multiphysics (Comsol Inc.) software.

Contact-Charging Experiments. Before the experiments, the materials were first discharged using an electrostatic (Zerostat) gun. The materials were verified to be discharged before use. For charging the materials by contact electrification, the surfaces of the two materials were brought into contact 2–6 times with a force of contact of ∼0.2 N. PTFE was charged negatively by contacting it against nitrile rubber. Polyethylene was charged negatively by contacting it against natural rubber. Silicone rubber was charged positively by contacting it against PTFE and was charged negatively by contacting it against natural rubber. Natural rubber was charged positively by contacting it against PDMS and was charged negatively by contacting it against mica. PDMS was charged positively by contacting it against PTFE and was charged negatively by contacting it against natural rubber.
Polypropylene was charged positively by contacting it against PTFE and was charged negatively by contacting it against mica. PVC was charge positively by contacting it against PTFE and was charged negatively by contacting it against nitrile rubber. For the experiments that involved materials that were folded (i.e., either once or multiple times), a flat slab of the material was first folded and pressed gently for a few seconds for obtaining the crease(s) of the folded structure. For charging one side of the material, it was first flattened and placed onto the surface of a piece of stainless steel as the bottom substrate. The top surface of the material was then charged by contact electrification with the respective contacting material while the bottom surface of the material rested firmly on the stainless steel. We tested that when a piece of material was in contact with the stainless steel only, the amount of charge generated was negligible (e.g., for a piece of PTFE, the amount of charge generated by the stainless steel was only $\sim 0.01$ nC). For experiments that involved materials that were twisted or curled into a spiral shape, the materials were coiled around a cylindrical tube that was covered with nitrile rubber. This process thus twisted the material into its desired shape and charged only one side of the material at the same time. In some experiments, one side of the material was charged by releasing ions of either positive or negative charge from an electrostatic (Zerostat) gun while the material rested on the surface of stainless steel. The charge of the materials was measured by placing the material into the Faraday cup connected to the electrometer. The shape of the material was changed by using pairs of tweezers while the material was inside the Faraday cup. Most of the experiments were conducted in ambient air conditions with a relative humidity of around 40–50%. Experiments were also performed in a glovebox that was purged with either nitrogen or helium gas with a humidity of $\sim 2$–3%.

**Negligible Charge of the Pairs of Tweezers Used.** For handling the materials, we typically used a pair of tweezers that was made of either wood or polychlorotrifluoroethylene (PCTFE) and had a length of 14.0 cm. The pair of tweezers was discharged by a Zerostat gun and verified to be discharged by measuring its charge in a Faraday cup before using it for manipulating the materials in our experiments. We demonstrated that the pairs of tweezers used did not affect our measurements of charge. For this demonstration, we first discharged a pair of tweezers (i.e., the routine procedure that we performed before using it for all our experiments) made of either wood or PCTFE and measured its charge. We then used the pair of tweezers for handling a piece of charge silicone rubber and changed its shape between the bent and extended states repeatedly 20 times. After the experiment, we measured the charge of the pair of tweezers again. Results showed that the charges of the pair of tweezers that we used (i.e., for both wood and PCTFE) were negligible (on the order of $\sim 0.001$ nC) both before and after handling the materials (Figure S8).

On the other hand, the changes in charge due to the changes in shape of the materials observed in our experiments were usually much higher at an order of magnitude of $\sim 0.1$ nC or more. Therefore, the changes in charge cannot be due to the pair of tweezers used for manipulation.

**Charge Measurement Not Dependent on Location of Material in Faraday Cup.** In our experiments, the measurement of charge changed when the shape of the material changed; however, it did not change when the location or orientation of the material was simply changed within the Faraday cup without a change in shape. As a demonstration, a piece of silicone rubber ($1.7 \times 1.2$ cm, and a thickness of 1.0 mm) was inserted into the Faraday cup vertically and at different depths. Depth was defined as the distance between the top of the Faraday cup and the center of the vertically inserted piece of silicone rubber. Results showed that the measurements of the charge at different depths (from 2.5 cm beneath the top of the inner cup to deeper depths) were very similar (Figure S3a)—changes in charge on the order of $0.1$ nC and more (i.e., the magnitude of the change in charge measured when shape was changed) were not observed when the charged material was placed at different depths in the Faraday cup. All the measurements of the changes in charge due to the changes in shape in this study were performed when the materials were inserted far beyond the depth of 2.5 cm beneath the top of the inner cup of the Faraday cup (i.e., typically $\sim 5$ cm or lower).

For an even clearer demonstration, another experiment was performed in which the amounts of the changes in charge due to the changes in location (and orientation) of the charged material within the Faraday cup were compared with the amounts of the changes in charge due to the changes in shape. A piece of PTFE was first charged and then placed in five different positions within the Faraday cup (Figure S3b); the exact location and orientation of the piece of PTFE at all the positions are listed in Table S1. At each position, the shape of the PTFE was changed between states 1 and 2 as shown in Figure 2a. The results showed that the charges of the PTFE at different positions did not change significantly; however, the changes in shape changed the amount of charge measured. Any slight changes in location or orientation during manipulation of the materials (i.e., when their shapes were changed) were far less than the large differences in location or orientation investigated in this experiment. Therefore, the changes in charge observed in this study were due to the changes in shapes of the materials and not due to the slight changes of location or orientation of the charged materials within the Faraday cup.

**Ions Deposited from the Atmosphere Desorb Rapidly from the Surface.** When ions from the atmosphere were deposited onto a surface, they could desorb rapidly from the surface. As a demonstration, a piece of material (i.e., either the thin piece of PTFE with a thickness of 0.018 cm or the thick piece of PTFE with a thickness of 0.1 cm used in this work) was first placed on top of the inner Faraday cup. The top of the outer Faraday cup was then covered completely by a piece of aluminum foil except for a small hole of dimensions $1.2 \times 3$ cm. Ions (either positive or negative ions) were then sprayed onto the piece of material through the hole (i.e., for focusing the flow of ions onto the surface of the material) by a Zerostat gun. These ions were generated via electrostatic discharge by the Zerostat gun: the high potential at the sharp tip of the gun ionized the surrounding air molecules. Subsequently, the ions in air deposited onto the surface of the material. Because the material was on top of the inner Faraday cup, we were able to record the real-time measurement of charge via the electrometer connected to the Faraday cup.

Results showed that the measurement of charge increased immediately after the spraying of the ions (either in the positive or negative direction depending on whether positive or negative ions were sprayed; Figure S6). However, in around less than 1 s, the amount of charge reduced very significantly. Therefore, the ions sprayed and deposited on the surface
tended to desorb from the surface. To investigate the contribution of free ions in the air with respect to the measurement of the charge, we conducted the control experiment in which we sprayed the ions from the Zerostat gun directly into the Faraday cup (i.e., without the material covering the top of the Faraday cup). In this case, the measurement of charge increased; however, the measurement of charge remained high and did not decrease subsequently (probably because the ions deposited on the conductive surface of the inner cup were neutralized by the ground). This control experiment demonstrated that only a change in charge of the solid surface, but not the ions in the air (i.e., free ions in air that were not deposited on the surface), resulted in the rapid decrease of charge. This experiment showed that the fundamental mechanism proposed in this study is plausible. As discussed in Figure 6, when the negatively charged material was bent, the higher electric field around the material caused the ionization of the surrounding air molecules. The positive ions of the ionized air then deposited on the surface for reducing the electric field from the surface (i.e., by reducing the amount of net negative charge on the surface). After the charged material was extended back to its original state, the electric field around the material decreased; hence, the positive ions originally deposited from atmosphere desorbed from the surface.

Curvature Sensor and Force Sensor. For the sensors that involved the bending of half-folded sheets of material, we used either a thick piece of PTFE (2.5 cm × 7.5 cm × 2 mm), a thin piece of PTFE (2.5 cm × 7.5 cm × 0.2 mm), or a thin piece of PVC (1.5 cm × 3 cm × 0.27 mm). The long sheet of material was folded into half along the longest side. The material was contact-charged to a specific amount of charge on one side by nitrile rubber. For calibrating the curvature sensor, the folded sheet of material was placed inside the Faraday cup. Specifically, the bottom of the Faraday cup was first covered with a layer of double-sided tape, and then, one half of the folded sheet of material was adhered onto the tape. For controlling the bending of the folded sheet, a wooden tip was used to press the top flexible half of the folded sheet of material vertically downward. The wooden tip was pressed against the folded sheet of material at a series of specific heights that corresponded to specific angles of bending of the material. The angles of bending were determined by taking images of the folded material pressed by the wooden tip and measuring the angles of the material by image processing software (Photoshop, Adobe). The charges of the folded material pressed to different angles of bending were measured by the electrometer. Hence, the relationship between charge and bending of the folded sheet of material was obtained. For calibrating the force sensor, half of the folded sheet of material was adhered onto a weighing balance. A wooden tip was used to press the top flexible half of the folded sheet vertically downward at a series of specific heights for obtaining different specific angles of bending. The angles of bending were controlled to be the same as those used for the curvature sensor. The vertical forces applied by the wooden tip were measured by the weighing balance at the different angles of bending. Together with the charges measured at the different angles of bending, the relationship between the force and charge of the material was obtained.

For the sensor that involved the extension of the spiral, we used a long thin sheet of PTFE (1.5 cm × 15 cm × 0.2 mm). It was coiled onto a metal rod with a diameter of 3.5 mm for forming the spiral. The spiral was contact-charged to a specific amount of charge on one side by nitrile rubber. For calibrating the curvature sensor, the initially 2-dimensional spiral was placed inside the Faraday cup. The outermost end of the spiral was fixed to the bottom of the Faraday cup. The innermost part of the spiral was adhered to a wooden tip. The innermost part of the spiral was then extended upward to a series of specific heights. The charges corresponding to the different heights of extension were measured by the electrometer. Hence, the relationship between charge and height of extension of the spiral was obtained. For calibrating the force sensor, the outermost part of the spiral was adhered onto a weighing balance. The innermost part of the spiral was then extended upward to a series of specific heights that corresponded to those of the curvature sensor. The losses in weight of the spiral due to the lifting of the spiral by the wooden tip to different heights were measured by the weighing balance. These losses in weight were the forces applied by the wooden tip onto the spiral. Hence, the relationship between force applied and charge of the spiral was obtained.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.9b01108.

Additional data and figures including geometries of materials, changes in charge, XPS spectra, and charge measurements of tweezers (PDF)

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Notes

The authors declare no competing financial interest.

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