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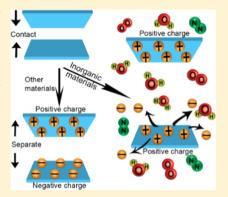
Anomalous Charging Behavior of Inorganic Materials

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Supporting Information

ABSTRACT: Surface charge on materials is important due to its wide range of consequences and applications in many industries (e.g., semiconductor). One important parameter needed for the design of devices and selection of materials is the polarity of charge of solid surfaces after the surfaces are charged by contact electrification. Currently, it is only known that one surface charges positively, whereas the other surface charges negatively after contact (i.e., in accordance to the law of conservation of charge). This manuscript describes a previously unreported anomalous charging behavior of a general class of materials: the inorganic materials. Both contacting inorganic materials charged either both positively (e.g., mica and NaCl) or both negatively (e.g., quartz and CaF₂). A close monitoring of the charge in real time showed that charge was conserved immediately after contact; however, an active interaction of the separated surfaces and the surrounding atmosphere unexpectedly changed the polarity of one surface rapidly (e.g., 1 s), thus resulting in both positively or both negatively charged surfaces. This anomalous charging



behavior fundamentally changes our understanding of the design of devices related to contact electrification of inorganic materials and the triboelectric series.

1. INTRODUCTION

Surface charge is generated when two solid surfaces come into contact and are then separated by contact electrification. After contact, one surface charges positively, whereas the other surface charges negatively (Figure 1a); this phenomenon is in accordance with the law of conservation of charge. Despite the inherently stochastic nature of contact electrification, this charging behavior has consistently been observed. For example, whenever nylon is contacted against poly(tetrafluoroethylene) (PTFE), nylon always charges positively, whereas PTFE always charges negatively. Because one contacting material always charges positively, whereas the other contacting material always charges negatively, the triboelectric series (i.e., a list of materials arranged according to their tendency to charge either positively or negatively) can be established. This series is generally reproducible by many research groups and has commonly been used by scientists for the selection of materials for applications related to contact electrification. The consistency is also observed for contacts between two identical materials. After contact, one piece of material charges positively, whereas the other piece of material charges negatively.² Despite being widely and consistently observed in the field of contact electrification, we describe in this study an anomalous charging behavior of inorganic materials: the two contacting inorganic materials can charge either both positively or both negatively after contact electrification (Figure 1b). This is the first time that this phenomenon in which both surfaces charge to the same polarity by contact electrification has been reported.

A major challenge in the field of contact electrification is that despite being an important phenomenon with a vast range of consequences (e.g., in the industry) 3 and studied for many decades, it is still poorly understood. $^{4-6}$ Importantly, at the molecular level, the charge species that transferred from one insulating surface to another insulating surface is a subject that is still under debate. Different research groups have proposed different species responsible for the transfer, including an electron, ^{7,8} an ion, ^{1,9,fo} or a small (e.g., nanoscopic) quantity of charged materials. ^{11,12} As a result, most of our knowledge related to contact electrification is empirical. Because of its stochastic nature, however, experiments are often not reproducible and different research groups have reported discrepancies (e.g., differences of the polarity of the materials).¹³ In general, the phenomenon is usually regarded as complex and unpredictable. 1,4,14

In addition to the poor understanding of contact electrification of insulating materials, most of these previous studies investigated polymers. On the other hand, surface charge on inorganic materials has a wide range of influences in our lives and in industry. For example, inorganic dust particles sticking onto surfaces can affect our lives in many undesirable ways, such as a reduction in the efficiency of solar panels, 15 failure of electrical contacts (e.g., in high-frequency tele-communications and mobile phones), 16 and stains on surfaces (e.g., glass displays and lenses). In the semiconductor industry, cleanrooms are usually needed to prevent dust particles from adhering onto silicon wafers due to attractive electrostatic

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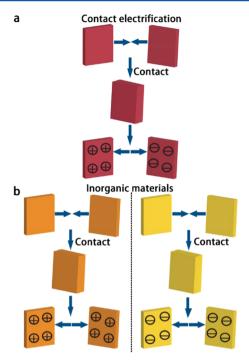


Figure 1. Anomalous contact-charging behavior of inorganic materials. (a) In the field of contact electrification, it is widely observed that when two surfaces come into contact and are then separated, one surface charges positively, whereas the other surface charges negatively. (b) Inorganic materials, however, are found to exhibit anomalous contact-charging behavior: the two contacting materials can charge either both positively or both negatively after contact.

forces.¹⁷ More severely, charged inorganic dust particles may result in dust explosions due to electrostatic discharge.¹⁸ Besides the undesirable consequences, the charging of inorganic materials by contact electrification has a wide range of useful applications, such as in electrophotography, electrostatic powder coating,¹ energy-harvesting devices,¹⁹ and electrostatic self-assembly of macroscopic crystals.^{20,21} Charging of inorganic materials also contributes to various large-scale natural phenomena, such as sand, dust storms,^{18,22,23} and lightning.²⁴ Because of these wide-ranging and profound influences, it is important to understand the charging behavior of inorganic materials.

2. METHODS

2.1. Materials. Highest grade mica sheets $(1.5 \text{ cm} \times 1.5 \text{ cm})$ × 0.16 mm) were purchased from MIT Corporation. Quartz $(1.0 \text{ cm} \times 1.0 \text{ cm} \times 0.5 \text{ mm}; \text{ double-side epi-polished}),$ aluminum oxide (Al₂O₃; 1.0 cm \times 1.0 cm \times 0.5 mm; doubleside epi-polished), magnesium aluminate (MgAl₂O₄; 1.0 cm × $1.0 \text{ cm} \times 0.5 \text{ mm}$; double-side epi-polished), silicon (Si; 1.0 cm \times 1.0 cm \times 0.5 mm; single-side epi-polished), and calcium fluoride (CaF₂; 1.0 cm × 1.0 cm × 0.5 mm; single-side epipolished) wafer were purchased from Latech Scientific Supply Pte. Ltd. Polystyrene (PS; 2.0 cm \times 2.0 cm \times 0.1 cm) was purchased from DT Hardware Supplier. Potassium bromide (KBr; 4.1 cm \times 2.3 cm \times 4.0 mm) and zinc selenide (ZnSe; 4.1 cm × 2.3 cm × 4.0 mm) were purchased from International Crystal Laboratories. Pieces of sodium chloride (NaCl; crystal window; diameter × thickness: 2.0 cm × 2 mm) were purchased from Sigma-Aldrich. Poly(vinyl chloride) (PVC; 2.5 cm \times 2.0 cm \times 3.0 mm) and poly(methyl methacrylate)

(PMMA; 2.5 cm \times 2.0 cm \times 1.5 mm) were purchased from DT Hardware Supplier. Trimethoxy(propyl)silane, (3-chloropropyl)trimethoxysilane, (3-bromopropyl)-trimethoxysilane, 2-cyanoethyltrimethoxysilane, p-bromophenyltrimethoxysilane, p-methoxyphenyltrimethoxysilane, and p-tolyltrimethoxysilane were purchased from Gelest, Inc. Poly(ethylene glycol) diacrylate (PEGDA; average molecular weight 575) was purchased from Sigma-Aldrich. Ethanol and acetone were purchased from Sigma-Aldrich. All chemicals were used as received. Deionized water (ultrafiltered to 18 M Ω ·cm using a Millipore Milli-Q gradient system) was used. A 95% ethanol solution was used as the solvent for coating the mica surfaces with self-assembly monolayers (SAMs).

2.2. Preparation of Pieces of PEGDA. The procedure for the synthesis of the piece of PEGDA polymer is as follows. First, the photoinitiator (1-hydroxycyclohexyl phenyl ketone; 0.01 g, 0.049 mmol) was placed into a vial. Subsequently, PEGDA (1 g, 1.7 mmol) was added to the vial. This mixture was mixed and was then transferred to a PDMS mold (1 cm \times 1 cm \times 0.2 cm) where it was exposed to UV light (intensity of 0.55 mW/cm² and at a wavelength of 365 nm) for 10 min.

2.3. Coating Mica Surfaces with SAMs. SAMs were coated onto the mica surfaces via a typical procedure reported previously. The mica sheets were thoroughly washed with ultrapure water and ethanol and then dried under a steady stream of ultrapure nitrogen gas. In a separate step, $110~\mu\text{L}$ of one of the silanes was dissolved in 10 mL of ethanol. The mica sheets were immersed in the silane solution for 30 min at ambient temperature. The sheets were then thoroughly rinsed with ethanol for three times and baked in an oven at 120~°C for 1 h.

2.4. Contact-Charging Experiment. A typical experiment is described as follows. The solid materials (e.g., mica, quartz, Al₂O₃, MgAl₂O₄, Si, CaF₂, KBr, ZnSe, SAM-coated mica, PVC, and PMMA) were cleaned by washing them using ultrapure water and either acetone or ethanol and drying them under a steady stream of ultrapure nitrogen gas. After cleaning, we discharged the materials by immersing them in water for 10 min and dried them naturally in air. After discharge, we measured the charge of the material using a home-made Faraday cup connected to an electrometer (Keithley, model 6514) and confirmed that the materials were indeed discharged. The materials were then brought into contact for 20 times (using a force of around \sim 3 g as measured by a weighing balance). The charges of both the materials were measured 5 s after contact. These experiments were performed in air at a humidity of $\sim 60\%$.

The procedure described above was conducted for most of the experiments reported in this study, including contacts between two pieces of the same inorganic material, two pieces of different inorganic materials, a piece of mica with a piece of SAM-coated mica, and a piece of mica with a piece of poly(ethylene glycol) diacrylate (PEGDA). For the contact between quartz with either polystyrene (PS) or poly(vinyl chloride) (PVC), the change in polarity of quartz was slower. For quartz and PS, we measured the charges of both the contacting materials around 8 s after contact. For quartz and PVC, we measured the charges around 5 min after contact.

To investigate the influence of pressure, we performed the contact-charging experiment using different pressures. We first contact-charged two pieces of mica using a low pressure (i.e., a force on the order of \sim 0.5 g as measured by a weighing balance). The charges of both pieces of mica were measured

immediately using the Faraday cup. After 3 min, we measured the charges of both the pieces of mica again. Subsequently, we repeated the experiment using a higher pressure (i.e., a force of around \sim 2 g as measured by a weighing balance). We then repeated the whole set of experiment using two pieces of

In addition, we also conducted the contact-charging experiments under a nitrogen (humidity of ~20%) and argon (humidity of $\sim 20\%$) atmosphere.

All contact-charging experiments were performed around an average of 30 times each; the error bars plotted in the graphs represent the standard deviations.

2.5. Determining the Change in Charge with Time. First, we discharged pieces of mica by immersing them in water for 10 min and drying them naturally in air. After discharge, we brought two pieces of mica into contact for 20 times. Immediately after contact (\sim 0.5 s), we measured their charges using a Faraday cup connected to an electrometer. We then repeated the experiment by contacting another two pieces of mica and measuring their charges at different times (i.e., from a range of 1-10 s after contact). The materials were handled using pairs of antistatic tweezers for the contact-charging experiment. After contact, we continued to hold on to the materials with the pairs of tweezers while waiting for the specific time to lapse before measuring their charges. Finally, we repeated the whole set of experiment described above using two pieces of quartz instead of mica.

2.6. Atomic Force Microscopy (AFM) Analysis. AFM images of the surfaces of different materials were obtained using a Dimension AFM (Bruker), operated using the tapping mode (Figures S1 and S2, Supporting Information). Oxide-sharpened SiN₃ cantilevers were used with a quoted spring constant of 0.04 N/m. Data were captured at a scan rate of 1.2 Hz.

2.7. X-ray Photoelectron Spectroscopy (XPS) Analysis. X-ray photoelectron spectra were recorded on a PHI-5000C ESCA system (PerkinElmer) with an Al K α excitation radiation source (1486.6 eV). The pressure in the analysis chamber was maintained at 10⁻⁶ Pa during measurement. All spectra were referenced to the C 1s hydrocarbon peak at 284.6 eV to compensate the effect of surface charging.

We analyzed the chemical compositions of the surfaces of the inorganic materials before and after contact electrification using X-ray photoelectron spectroscopy (XPS). In this experiment, we first cleaned and discharged two pieces of mica. We then cut a small portion of each piece of mica and analyzed its surface using XPS. Subsequently, we contacted the two pieces of mica (i.e., the large pieces that remained after cutting out the small portions) for 20 times in air at a humidity of ~60%. After contact, we again cut a small portion of each piece of mica and analyzed its surface using XPS. Hence, the analysis by XPS involved essentially the same piece of mica before and after contact electrification; in this way, we could make a fair comparison of the chemical compositions of the surface of mica before and after contact. We repeated the experiment for two pieces of quartz. We also repeated the experiment for both mica and quartz under an argon atmosphere (humidity was \sim 20%).

3. RESULTS AND DISCUSSION

Our experiments involved first cleaning and discharging the surfaces of the contacting materials (see Methods). We then brought two discharged pieces of materials into contact for 20 times. After contact, the charges of both the contacting materials were measured using a Faraday cup connected to an

electrometer (Keithley, model 6514). A typical contactcharging experiment was performed under atmospheric air at a relative humidity of ~60%, and the charges were measured 5 s after contact. As control experiments, we contacted two pieces of the same type of polymer (i.e., poly(vinyl chloride) and poly(methyl methacrylate)). Results showed that one piece charged positively, whereas the other piece charged negatively, as expected (Figure 2a).2

We then performed the contact-charging experiments for a series of inorganic materials: mica, sodium chloride (NaCl), aluminum oxide (Al₂O₃), magnesium aluminate (MgAl₂O₄), silicon, zinc selenide (ZnSe), potassium bromide (KBr), quartz,

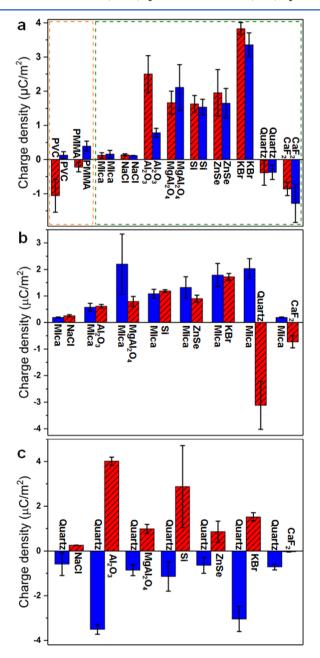


Figure 2. Inorganic materials charge to the same polarity after contact electrification. (a) Charge density (i.e., charge per unit surface area of contact) generated by contact electrification for contacts between (a) two identical polymers or inorganic materials, (b) mica and other inorganic materials, and (c) quartz and other inorganic materials. Experiments were performed in air at a humidity of ~60%.

and calcium fluoride (CaF₂). First, we contacted two pieces of the same type of inorganic material. Surprisingly, we found that when we contacted two pieces of mica against each other, both the contacting materials charged positively. After repeating the experiment for two pieces of NaCl, Al₂O₃, MgAl₂O₄, Si, ZnSe, or KBr, we found that both the contacting pieces also charged positively (Figure 2a). For quartz and CaF₂, we found that both the contacting surfaces charged negatively.

Subsequently, we contacted a piece of mica with a series of other types of inorganic materials (Figure 2b). Results showed that both the contacting materials charged positively when mica was contacted against NaCl, Al₂O₃, MgAl₂O₄, Si, ZnSe, and KBr. When mica was contacted against quartz and CaF₂, however, quartz and CaF₂ charged negatively, whereas mica charged positively. We repeated the experiment with quartz. Results showed that quartz charged negatively, whereas NaCl, Al₂O₃, MgAl₂O₄, Si, ZnSe, and KBr charged positively (Figure 2c). When quartz was contacted against CaF₂, both materials charged negatively. In general, these results indicated that mica, NaCl, Al₂O₃, MgAl₂O₄, Si, ZnSe, and KBr have a strong tendency to charge positively, whereas quartz and CaF₂ have a strong tendency to charge negatively, regardless of the material that they were in contact with.

This contact-charging behavior is unexpected: if we consider only the two contacting materials, one material should charge positively, whereas the other material should charge negatively according to the law of conservation of charge. To understand the phenomenon better, we contacted two pieces of mica and monitored their charges continuously with time. Importantly, when we measured the charges of both the pieces of mica immediately (~0.5 s) after contact, we found that one piece charged positively, whereas the other piece charged negatively (Figure 3a). Hence, charge seems to be conserved immediately after contact electrification.

After charging the materials by contact, both the pieces discharged gradually. It is widely known that any charged material left undisturbed in air discharges naturally with time; thus, the discharge was expected. Wery quickly (i.e., $\sim 1-2$ s), however, the piece of mica that was originally charged negatively did not simply discharge—it increased its charge in the positive direction (Figure 3a). We repeated the experiment for two pieces of quartz and observed a similar phenomenon: one piece of quartz charged positively, whereas the other piece charged negatively immediately after contact (Figure 3b). In a very short amount of time (i.e., ~ 1 s), the piece of quartz that was originally charged positively became negatively charged. The amounts of change in charge were significant. For the piece of mica that had an initial negative charge of $-0.46 \mu C/m^2$, it gained a positive charge of up to 0.23 μ C/m² in about 6 s. For the piece of quartz that had an initial positive charge of 0.62 $\mu C/m^2$, it gained a negative charge of up to $-0.37 \mu C/m^2$ in about 3 s. Hence, the piece of mica and the piece of quartz were able to charge up to around 50% and 60% of their initial charges, respectively, in the opposite polarity. These amounts of charge are relatively high considering that charged materials usually discharge gradually with time. After the change in polarity, we observed that the materials simply discharged gradually with time until they were completely discharged.

By analyzing the surfaces using AFM, we found that the surfaces of the inorganic materials were smooth. In general, the root-mean-square roughness was around 1 nm or less for most of the materials (Section 1, Supporting Information). To investigate the influence of surface roughness on charge, we

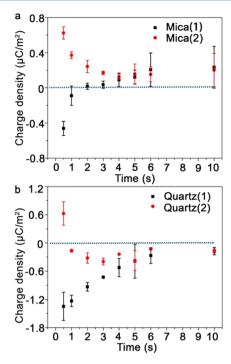


Figure 3. Anomalous change in polarity of the inorganic materials after contact electrification. (a) The initially negatively charged piece of mica became positively charged with time (data shown in black). (b) The initially positively charged piece of quartz became negatively charged with time (data shown in red). Experiments were performed in air at a humidity of \sim 60%.

increased the surface roughness of the pieces of mica and quartz by rubbing their surfaces with an abrasive material (Section 2, Supporting Information). After contacting the two rough pieces of mica (roughness ~400 nm), we found that they were still both charged positively. Similarly, the two rough pieces of quartz (roughness ~100 nm) both charged negatively after contact.

We investigated the generality of the phenomenon by contacting the surface of an inorganic material with a surface that was composed of organic molecules. First, we coated the surface of mica with silane molecules. ^{30,31} We investigated seven types of silane molecules with different functional groups: trimethoxy(propyl)silane, (3-chloropropyl)trimethoxysilane, (3-bromopropyl)trimethoxysilane, 2-cyanoethyltrimethoxysilane, p-bromophenyltrimethoxysilane, p-methoxyphenyltrimethoxysilane, and p-tolyltrimethoxysilane (Figures 4a and S1, Supporting Information). After contact electrification, results showed that both the contacting materials charged positively for all of the types of coatings (Figure 4a). After analyzing the coated surfaces by AFM, we found that they were still relatively smooth (Section 1, Supporting Information).

As a second demonstration, we contacted a piece of inorganic material with a piece of polymer. In one experiment, we contacted mica against poly(ethylene glycol) diacrylate (PEGDA). We chose PEGDA because it has a high tendency to charge positively. Both the contacting materials charged positively after contact (Figure 4b). We then contacted quartz with either polystyrene (PS) or poly(vinyl chloride) (PVC). Similarly, these polymers were chosen because they have a high tendency to charge negatively. Both the pairs of materials charged negatively after contact.

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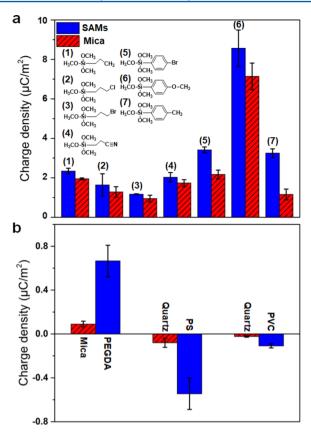


Figure 4. Anomalous charging behavior occurred for contacts between an inorganic material and a surface composed of organic molecules. (a) Contacting mica with another piece of mica coated with self-assembled monolayers (SAMs) of silanes. The type of molecules coated on the mica is shown in the inset. (b) Contacting mica against poly(ethylene glycol) diacrylate (PEGDA) and contacting quartz against polystyrene (PS) or poly(vinyl chloride) (PVC). Experiments were performed in air at a humidity of \sim 60%.

To clarify the role of contact electrification, we monitored the charges of pieces of mica and quartz that were only cleaned and discharged; that is, they were not contact-charged against any material. Results showed that they remained discharged with time (e.g., after 3 min) as expected (Figure 5). We then contacted two pieces of mica or two pieces of quartz against each other using different pressures and measured their charges immediately (\sim 0.5 s) and 3 min after contact. We found that with a higher pressure, both the contacting materials had higher initial charges. Interestingly, the change in charge was correspondingly large: the piece of mica with a larger initial negative charge due to the higher pressure acquired a correspondingly larger amount of positive charge naturally after 3 min. Hence, these results showed that contact electrification was necessary to charge the materials before they could change their polarity in air naturally. Besides contact electrification, the change in polarity was also observed when the inorganic materials were charged by depositing either positive or negative ions onto their surfaces (i.e., using a Zerostat gun).

Since the materials were left undisturbed in air after contact, the natural change in polarity with time was probably due to a constant interaction between the charged materials and air. Hence, we investigated the involvement of the surrounding atmosphere by contacting two pieces of mica under a nitrogen atmosphere (humidity $\sim 20\%$). The result obtained was

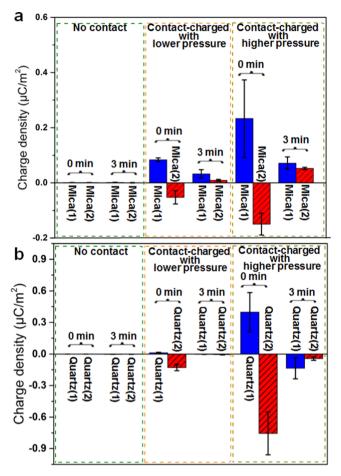


Figure 5. Change in polarity of the inorganic materials is a natural consequence of contact electrification. Experiments were performed for (a) two pieces of mica or (b) two pieces of quartz. They were either not contacted against each other (dotted box on the left), contact-charged with a low pressure (dotted box in the middle), or contact-charged with a relatively higher pressure (dotted box on the right).

different: one piece of mica charged positively, whereas the other piece of mica charged negatively in a typical contact-charging experiment (i.e., for charges measured 5 s after contact; Figure 6a). On the other hand, when we performed the experiment using two pieces of quartz under the nitrogen atmosphere, both pieces still charged negatively.

Notably, the most significant differences between air (humidity \sim 60%) and nitrogen (humidity of \sim 20%) are the oxygen-containing gaseous molecules: oxygen and water vapor. We repeated the experiment in an argon atmosphere (humidity \sim 20%). Similar to nitrogen, one piece of mica charged positively, whereas the another piece of mica charged negatively (Figure 6b). For quartz, however, there was a probability of \sim 50% that one piece charged positively and another piece charged negatively.

The chemical compositions of the surfaces of mica and quartz were analyzed using X-ray photoelectron spectroscopy (XPS) before and after contact in air (humidity ~60%; see Methods). Two pieces of mica were contacted against each other and two pieces of quartz were contacted against each other. Results showed that N 1s peaks appeared on the surfaces of both the pieces of mica and quartz after contact (Table 1). The appearance of these peaks indicated that the surfaces interacted with the surrounding atmospheric air (i.e., nitrogen

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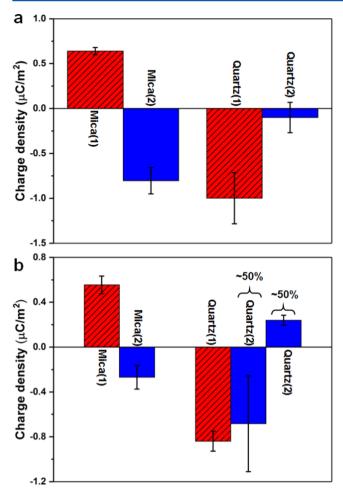


Figure 6. Contact-charging mica and quartz in different atmospheres. Charge densities of mica and quartz after contact electrification in (a) nitrogen (humidity \sim 20%) and (b) argon (humidity \sim 20%). When two pieces of quartz were contact-charged in argon, one piece of quartz has a 50% probability of charging either negatively or positively, whereas the other contacting piece of quartz always charges negatively.

Table 1. Chemical Composition of the Surfaces of Mica and Quartz Before and After Contact Electrification in Air (humidity of \sim 60%) as Analyzed by XPS

	samples ^a	O (%)	C (%)	K (%)	Al (%)	Si (%)	N (%)			
Before Contact										
	mica (1)	55.1	13.9	3.7	13.0	14.3	0			
	mica (2)	55.8	13.7	3.5	12.5	14.5	0			
	quartz (1)	50.8	22.8			26.4	0			
	quartz (2)	57.4	14.1			28.5	0			
After Contact										
	mica (1)	52.4	17.3	3.5	12.5	13.5	0.8			
	mica (2)	54.7	17.0	3.4	10.8	13.5	0.8			
	quartz (1)	54.3	17.8			27.3	0.6			
	quartz (2)	58.5	11.9			29.2	0.5			

^aThe symbol (1) or (2) represents the same piece of material before and after contact.

in air). With regards to the oxygen-containing gaseous molecules, results showed that when a piece of material was charged positively after contact (e.g., due to the contact of two pieces of mica), the percentage of O 1s decreased compared to that before contact (Table 1). When a piece of material was charged negatively after contact (e.g., due to the contact of two

pieces of quartz), the percentage of O 1s increased. The same trend is observed when the materials were contact-charged under an argon atmosphere (Table 2).

Table 2. Chemical Composition of the Surfaces of Mica and Quartz Before and After Contact Electrification in Argon (humidity of \sim 20%) as Analyzed by XPS

samples ^a	O (%)	C (%)	K (%)	Al (%)	Si (%)	N (%)					
Before Contact											
mica (1)	56.5	13.5	4.7	12.4	12.9	0					
mica (2)	56.7	14.0	5.4	11.8	12.2	0					
quartz (1)	54.0	17.5			28.5	0					
quartz (2)	53.5	18.1			28.5	0					
After Contact											
mica (1) (+)	<i>b</i> 54	.0 1	7.6 4.0	6 10.5	13.2	0.1					
mica (2) (-)	58	3.3	1.0 7.3	5 11.5	11.5	0.1					
quartz (1) (-	,	.2 18	8.2		27.5	0.2					
quartz (2) (+	$-)^{b}$ 52	7 19	9.7		27.4	0.2					

"The symbol (1) or (2) represents the same piece of material before and after contact. "The symbol (+) represents the piece that was measured to be positively charged after contact. "The symbol (-) represents the piece that was measured to be negatively charged after contact.

There may be different ways by which the charged surface can interact with the surrounding atmosphere. For example, the surfaces may consist of a variety of ions and radicals, which may react with the surrounding gaseous molecules. Another possibility is that the electric field produced locally by the charged surface may be able to ionize gaseous molecules. 32,33 Previous studies have reported that the charged surface may consist of regions (or a mosaic) of positive and negative charges of similar amounts at the nanoscopic scale after contact electrification.¹¹ Alternatively, the surface may adsorb water vapor from the atmosphere naturally and change their charges according to a previous study.³⁴ In addition, the dynamic process of contact and separation during contact electrification may cause changes of the charge at the interface of solid and water adsorbed from the atmosphere according to the results reported in a previous study.³⁵

4. CONCLUSIONS

This previously unreported anomalous charging behavior of the general class of inorganic materials is surprising because it has been widely observed that contact electrification causes one surface to charge positively and the other surface to charge negatively (i.e., in accordance to the law of conservation of charge). We found that the origin of this anomalous behavior is due to an unexpected natural change in polarity of one of the contacting materials with time after an active interaction with the surrounding atmosphere. Charged materials are only known to discharge in air without any change in polarity. As examples, we charged pieces of polymers by contact electrification and found that they discharged with time without any change in polarity as expected (Section 3, Supporting Information). The fundamental mechanism by which the polarity changes is not fully understood. Results from our experiments indicated that the atmospheric air, in particular, the oxygen-containing molecules (e.g., oxygen and/or water vapor) may be involved in the change in polarity. Further work will be needed to investigate why charged inorganic materials can change their polarity when left undisturbed in air but not other classes of materials (e.g., polymers). In particular, we determined that there is no change in polarity for an "inorganic polymer" (i.e., a polymer that does not contain any carbon atoms in their polymeric backbones; poly(dimethylsiloxane), PDMS; Section 3, Supporting Information).³⁶ Another interesting observation is that some inorganic materials have the tendency to charge positively, whereas others have a tendency to charge negatively (e.g., NaCl charged positively, whereas CaF2 charged negatively; and silicon charged positively, whereas quartz and SiO₂ charged negatively). Further work may include studying and comparing the chemical compositions and/or the crystalline structures among the inorganic materials and with other classes of materials.

It is important to understand this anomalous charging behavior due to the far-reaching influences of surface charge generated by contact electrification. In fact, a large number of interesting devices have recently been reported by material scientists and engineers based on this triboelectric charging effect (e.g., the class of triboelectric nanogenerators); hence, it is important to understand the behaviors of materials after contact. In addition, this anomalous charging behavior changes the way we understand the triboelectric series. Currently, the series is strictly limited to the case in which one material charges positively, whereas the other material charges negatively. Our results showed that inorganic materials need to be considered separately in the triboelectric series.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b02478.

AFM images of the surfaces of the inorganic materials, effect of surface roughness, charging behaviors of polymers (PDF)

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Notes

The authors declare no competing financial interest.

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