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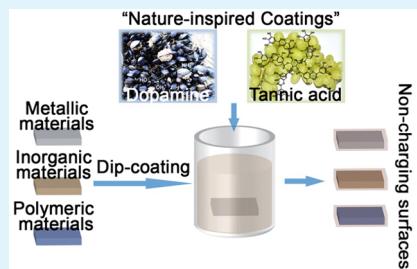
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Supporting Information

ABSTRACT: Static charge generated by contact electrification on surfaces can lead to many undesirable consequences such as a reduction in the efficiency of manufacturing processes, damage to equipment, and explosions. However, it is extremely challenging to avoid contact electrification because it is ubiquitous: almost all types of materials charge on contact. Here, we coated materials with naturally occurring polydopamine (PDA) and tannic acid (TA) for preparing noncharging surfaces. Importantly, these coatings are very versatile and can be coated on a wide range of materials, including metals, inorganic materials, semiconductors, and polymers. Once coated, the amount of charge generated was found to reduce dramatically at different humidities. The reduction in charge may be due to the radical-scavenging property of PDA and TA. This simple general approach is ideal for coating the vast variety of materials that need to resist charging by contact electrification.

KEYWORDS: noncharging surface, dopamine, tannic acid, coatings, contact electrification



1. INTRODUCTION

Contact electrification is the natural phenomenon in which static charge is generated when two solid surfaces come into contact and are then separated. While there are applications related to this phenomenon, the consequences are usually undesirable.^{1–3} In our daily lives, we frequently encounter slight annoyances associated with charge accumulated on solid surfaces by contact electrification (e.g., the adhesion of charged dust particles on surfaces or the feeling of a slight electric shock when one touches the doorknob during dry weather). In different types of industries, static charge can reduce the efficiency of many manufacturing processes (e.g., particles charged by contact electrification can adhere onto the walls of reactor vessels and hinder effective heat transfer).^{4,5} In the pharmaceutical industry, when drug powder interacts with other surfaces, the charge accumulated on the particles may lead to nonuniform blending;⁶ thus, nonuniform dosage of the products can be produced.⁷ In addition, excessive accumulation of charge by contact electrification can result in electrostatic discharges (e.g., sparks). These discharges are responsible for the damage of equipment and are known to cost the electronics industry billions of dollars per year.⁸ Most importantly, these discharges may cause explosion of flammable gases, dusts, and organic liquids (e.g., during the fueling of vehicles). Hence, considering the wide range of undesirable, costly, and dangerous consequences of contact electrification, it is important to develop strategies to prevent the generation of static charge when solid surfaces come into contact.

It is, however, an extremely challenging task to avoid these undesirable consequences because contact electrification is ubiquitous: almost all types of materials (e.g., metals,

semiconductors, inorganic materials, and polymers) charge on contact.^{9,10} Therefore, problems related to contact electrification can occur almost everywhere in our lives and in industry (e.g., petrochemical, chemical, semiconductor, and pharmaceutical). As such, general approaches for fabricating non-charging surfaces are needed for a vast range of materials and applications.

Previous studies have reported several general methods for fabricating bulk materials that resist charging. Some examples include using conductive materials (e.g., metals or conductive polymers) for dissipating the charge away from their surfaces, increasing the conductivity of the original materials (e.g., by adding antistatic agents, such as metal or carbon particles),¹¹ doping the materials with radical-scavenging molecules for destabilizing the charge,⁸ or copolymerizing a monomer that has the tendency to charge positively with another monomer that has the tendency to charge negatively.¹² In many applications, however, it is desirable to keep the bulk properties of the original materials intact; hence, changing or modifying the bulk material is not an option. Importantly, it is not practical to replace the vast quantity of existing surfaces with these bulk materials. Hence, a desirable option is to coat the surfaces of the original materials such that they are non-charging.

Different methods of coating are available for fabricating non-charging surfaces. These methods include coating a layer of conductive film for dissipating charge away,^{13,14} ionizable

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molecules (e.g., polyelectrolytes),^{15,16} and hydrophilic molecules or polymers for attracting moisture and increasing the conductivity of the surface.^{17–25} These methods, however, are typically not general enough to be compatible for the diverse types of materials that need to be noncharging. One major issue is bonding. For the coat to bind properly onto the surface of the original material, many considerations are needed: the type of coat, the type of material of the substrate, and the type of treatment (e.g., UV, plasma, or chemical treatment) needed to bind the coat onto the surface of the material. Each method, however, usually works only for a limited combination of the coating and the substrate. The use of high-energy sources (e.g., UV and plasma) to treat the surfaces may also make these methods more expensive and thus less accessible to a wider range of applications.

In this study, we showed that two types of nature-inspired coatings can be used as a general approach to reduce dramatically the amount of static charge generated by contact electrification (Figure 1). The first type is a mussel-inspired

polydopamine (PDA) coating, and the second type is a plant-inspired tannic acid (TA) coating. Since their discovery, researchers have been excited about these coatings because they are reported to be extremely versatile and are capable of adhering to almost all types of materials, including metals, metal oxides, ceramics, and polymers.^{26–29} These versatile coatings may resist charging in two ways: by increasing the conductivity of the surface due to the hydrophilic groups of the PDA and TA molecules,^{30,31} and/or by their radical-scavenging property.^{8,26,32–34}

2. MATERIALS AND METHODS

Materials. Glass was purchased from Continental Lab Products (CLP). Mica ($1.5 \times 1.5 \times 0.015$ cm) was purchased from MIT corporation. Polytetrafluoroethylene (PTFE; $2.0 \times 2.0 \times 0.05$ cm), polystyrene (PS; $2.0 \times 2.0 \times 0.1$ cm), polypropylene (PP; $2.0 \times 2.0 \times 0.1$ cm), polyethylene (PE; $2.0 \times 2.5 \times 0.2$ cm), polyvinyl chloride (PVC; $2.0 \times 2.5 \times 0.2$ cm), nylon ($2.0 \times 2.5 \times 0.2$ cm), polycarbonate (PC; $2.0 \times 2.5 \times 0.2$ cm), poly(methyl methacrylate) (PMMA; $2.0 \times 2.5 \times 0.2$ cm), copper (Cu; $1.0 \times 1.0 \times 0.01$ cm), and aluminum (Al; $2.0 \times 2.0 \times 0.01$ cm) were purchased from DT Hardware Supplier. Aluminum oxide ($2.0 \times 2.0 \times 0.05$ cm) and silicon wafer (Si; $2.0 \times 2.0 \times 0.05$ cm) were purchased from Latech Scientific Supply Pte. Ltd. Acrylonitrile butadiene styrene (ABS) sheet ($2.0 \times 2.0 \times 0.1$ cm) was prepared by a 3D printer (UP! PLUS 2; Axpert Global Pte Ltd, Singapore). Tannic acid, dopamine, tris(hydroxymethyl)-aminomethane (Tris), 2,2-diphenyl-1-picrylhydrazyl (DPPH), (\pm)- α -tocopherol (Vitamin E), sodium chloride (NaCl), ethanol, acetonitrile, and dichloromethane (DCM) were purchased from Sigma-Aldrich. All chemicals were used as received. Deionized water (ultrafiltered to $18 \text{ M}\Omega\text{-cm}$ using a Milipore Milli-Q gradient system) was used in all experiments.

Preparing PDMS. Poly(dimethylsiloxane) (PDMS) was prepared by mixing a degassed elastomer base and cross-linker in a 10:1 w/w ratio (Sylgard 184, Dow Corning). The prepolymer mixture was cast onto a PS Petri dish (Thermo Fisher Scientific, Inc.), and cured at 65°C for 24 h. After curing the prepolymer, the PDMS pieces ($2.0 \times 2.0 \times 0.1$ cm or $1 \times 1 \times 0.5$ cm) were peeled off the Petri dish, washed with DCM for 24 h, and thoroughly dried before use.

Coating Surfaces with Dopamine or Tannic Acid. Dopamine (2 mg/mL) or tannic acid (2 mg/mL) in a NaCl solution (0.6 M) was dissolved in a 10 mM Tris-HCl (pH 8.5) solution. In a separate step, a solid substrate (PTFE, PS, PP, PDMS, Al, mica, or glass) was cleaned by sonication in water and acetone or ethanol. This substrate was then immersed in the buffer solution at room temperature. After 8 h, the coated surface was rinsed extensively with ultrapure water and dried under a stream of nitrogen.

Contact-Charging Experiment. In a typical contact-charging experiment, we first discharged the substrates coated with either polydopamine or tannic acid, and the reference material by washing their surfaces with water and drying them in air. The reference material used was either a piece of PTFE ($2.0 \times 2.0 \times 0.05$ cm) or nylon ($2.0 \times 2.0 \times 0.05$ cm). After discharging the materials, we brought the substrate into contact with the reference material. The materials were contacted 60 times. The charges of both the materials were measured using a Faraday cup connected to an electrometer (Keithley, model 6514). The surface areas of the substrates ranged from 1 to 5 cm^2 . Humidity for conducting the contact electrification experiments was either ~ 60 or $\sim 20\%$.

Measurement of Surface Resistivity. The surface resistivity of the materials (coated or uncoated) was measured using a resistivity test fixture (Keithley, 8009) connected to an electrometer (Keithley, model 6517B). We first fixed the test voltage as 1000 V. We then adjusted the current into a suitable test range (20 pA \sim 20 nA) based on the type of material. The humidity for conducting the surface resistivity measurement experiments was either ~ 60 or $\sim 20\%$.

Contact-Charging Experiments Based on PDMS Doped with Radical Scavengers. First, pieces of PDMS doped with radical

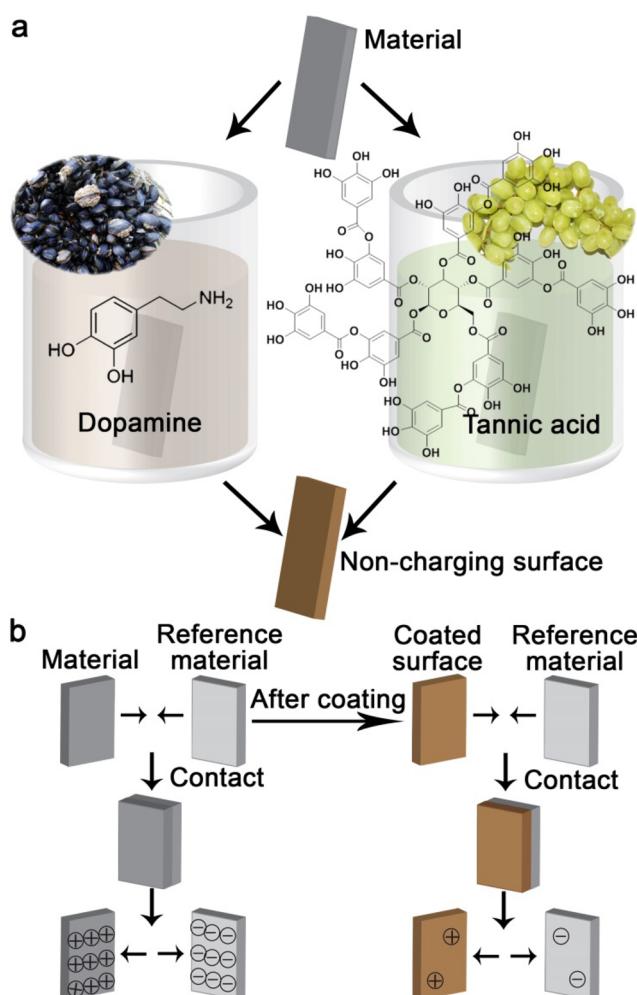


Figure 1. Nature-inspired coatings for preparing noncharging surfaces. (a) Surfaces of different materials can be coated with either polydopamine (PDA) or tannic acid (TA) by dipping the materials into solutions containing dopamine and TA respectively. (“Source of image of mussels: [CornishMussels.JPG](#), photograph by Mark A. Wilson”). (b) Static charge is generated when two materials come into contact and are then separated. Lesser charge is generated on materials coated with either PDA or TA.

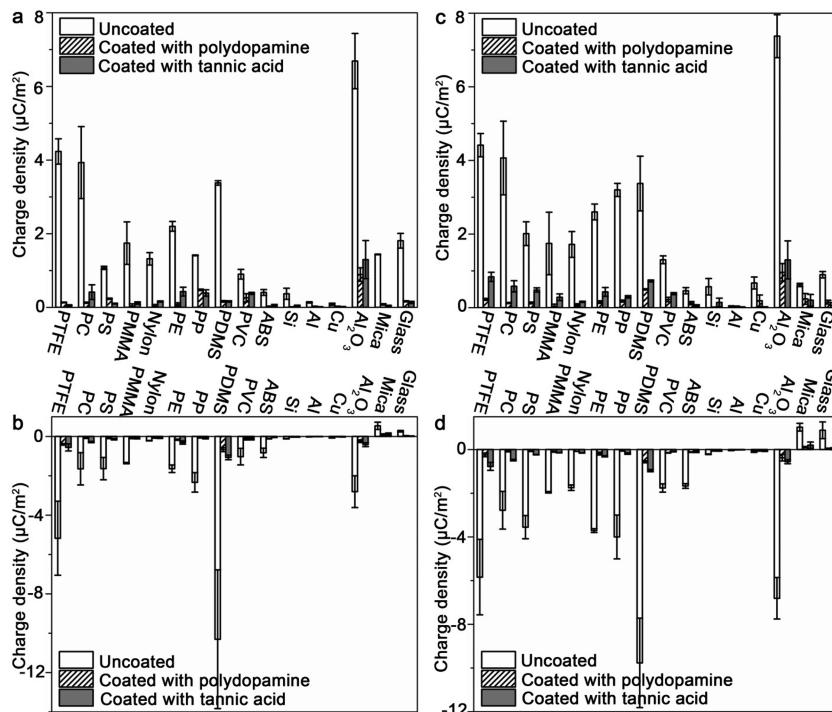


Figure 2. Amount of charge generated by contact electrification reduced for materials coated with either PDA or TA. Charge densities (i.e., charge per unit surface area of contact) of the uncoated surfaces and surfaces coated with PDA or TA after contacting them with a piece of PTFE (a) or nylon (b) as the reference material. Relative humidity (RH) was $\sim 60\%$. Charge densities of the same materials after contacting them with a piece of PTFE (c) or nylon (d) in RH $\sim 20\%$.

scavengers were prepared as previously described.⁸ The pieces of PDMS ($1 \times 1 \times 0.5$ cm) were immersed into 1 mM solutions of radical scavengers (i.e., DPPH or Vitamin E in dichloromethane) for 6 h. The PDMS pieces, swollen by the dichloromethane, were then dried in vacuum. After drying, these pieces of PDMS were contact-charged against a piece of PC ($2.0 \times 2.5 \times 0.2$ cm).

Testing the Durability of the Coating. Pieces of PTFE coated with either polydopamine or tannic acid were prepared as described in a previous section. The pieces of PTFE ($2.0 \times 2.0 \times 0.05$ cm) uncoated or coated with either polydopamine or tannic acid and the reference material (i.e., nylon; $2.0 \times 2.0 \times 0.05$ cm) was discharged by washing their surfaces with water and drying them in air. The pieces of PTFE were then contacted against the piece of nylon 1200 times.

Subsequently, we discharged the pieces of uncoated and coated PTFE and the piece of nylon again by washing with water and drying them in air. After discharge, we brought the uncoated and coated pieces of PTFE into contact with nylon 60 times. The charges of the materials were measured using a Faraday cup connected to an electrometer (Keithley, model 6514).

3. RESULTS AND DISCUSSION

In our experiments, we first coated a variety of materials using either dopamine or tannic acid.^{26,31} The procedure for coating involved simply dipping the material into an aqueous solution containing either dopamine or tannic acid for 8 h. The thickness for both types of coating was measured to be ~ 40 nm by ellipsometry; the thickness depends on the reaction time (Figure S1). To determine if the polydopamine or tannic acid was indeed coated onto the materials, we performed the following types of characterization of the surfaces. First, we analyzed the surface morphology of the uncoated surface, the surface coated with polydopamine, and the surface coated with tannic acid. After coating, we observed that the roughness of the surface increased (Figures S2 and S3); thus, it seems that the surfaces were coated. In addition, we used X-ray

photoelectron spectroscopy (XPS) to analyze the coated or uncoated surfaces of polystyrene (PS) (Figure S4). The appearance of the N 1s peak for the PS surface coated with polydopamine showed that the coating with polydopamine was successful (Figure S4a). For the surface coated with tannic acid, we observed an increase in the ratio of O 1s/C 1s (0.153) as compared to the ratio of O 1s/C 1s (0.118) of the uncoated PS surface; this increase is expected for a PS surface coated with tannic acid. In addition, through fitting the C 1s peaks of the high-resolution spectra, we observed the appearance of the C–O (286.6 eV), C–N (288.1 eV), and $\pi^*-\pi^*$ (291.3 eV) peaks for the surface coated with polydopamine (Figure S4c). These peaks correspond to the molecular structure of the dopamine molecule and are not present in the spectrum of the uncoated PS surface (Figure S4b). Similarly, we observed the appearance of the C–O (286.6 eV) and O–C=O (288.5 eV) peaks corresponding to the molecular structure of tannic acid (Figure S4d); these peaks are also not present in the spectrum of the uncoated PS surface. The contact angles of water on the surfaces were also measured. We found that the surfaces coated with polydopamine and tannic acid had contact angles lower than those of the uncoated surfaces (Figure S5). This result is expected because polydopamine and tannic acid contains hydrophilic functional groups (i.e., the hydroxyl and amine groups).

To show the generality of the approach, we used a variety of materials, including polymers (polytetrafluoroethylene (PTFE), polycarbonate (PC), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyamide (nylon), polyethylene (PE), polypropylene, polydimethylsiloxane (PDMS), polyvinyl chloride (PVC), and acrylonitrile butadiene styrene (ABS)), inorganic materials (aluminum oxide (Al₂O₃), mica, and glass), metals (aluminum (Al) and copper (Cu)), and a

Table 1. Surface Resistivity (Ω/sq) of the Uncoated and Coated Surfaces at Humidity of ~60%

	PDMS	PE	PS	PVC	PP
uncoated	1.1×10^{16}	3.8×10^{16}	2.8×10^{17}	2.7×10^{17}	5.3×10^{15}
coated with polydopamine	2.0×10^{14}	3.6×10^{13}	2.5×10^{13}	2.9×10^{13}	6.1×10^{13}
coated with tannic acid	9.2×10^{14}	3.8×10^{15}	5.6×10^{15}	8.3×10^{15}	1.1×10^{14}

Table 2. Surface Resistivity (Ω/sq) of the Uncoated and Coated Surfaces at Humidity of ~20%

	PDMS	PE	PS	PVC	PP
uncoated	2.4×10^{17}	3.2×10^{17}	4.2×10^{17}	8.2×10^{17}	2.9×10^{17}
coated with polydopamine	1.2×10^{15}	1.4×10^{15}	1.5×10^{15}	7.7×10^{15}	2.1×10^{16}
coated with tannic acid	8.1×10^{16}	2.3×10^{17}	1.7×10^{17}	3.7×10^{17}	1.8×10^{17}

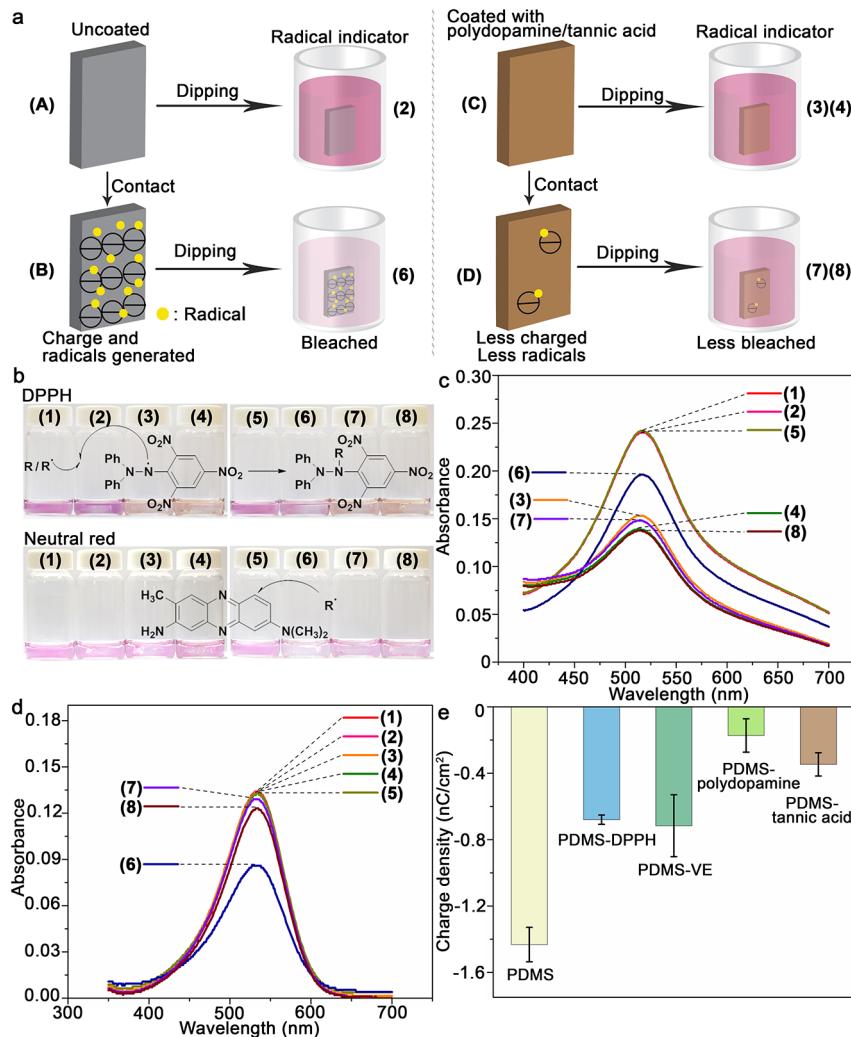


Figure 3. Radical-scavenging property of PDA and TA reduces charge generated by contact electrification. (a) Scheme illustrating the different types of experiments performed for determining that the surface coated with either PDA or TA generates lesser radicals after contact electrification; hence, it bleaches the radical indicator lesser. (b) Bleaching of diphenylpicrylhydrazyl (DPPH; 2.5 mL, 20 μM , in degassed acetonitrile; top row) and neutral red solution (NR; 2.5 mL, 5.0 μM , pH 5.0, acetate buffer; bottom row) under the following conditions. (1): pure DPPH/NR solution at 0 min; (2): uncharged PDMS in DPPH/NR solution at 40 min; (3): uncharged PDMS coated with PDA in DPPH/NR solution at 40 min; (4): uncharged PDMS coated with TA in DPPH/NR solution at 40 min; (5): pure DPPH/NR solution at 40 min; (6): contact-charged PDMS ($-2.0 \text{ nC}/\text{cm}^2$) in DPPH/NR solution at 40 min; (7): contact-charged PDMS coated with PDA ($-0.20 \text{ nC}/\text{cm}^2$) in DPPH/NR solution at 40 min; (8): contact-charged PDMS coated with TA ($-0.40 \text{ nC}/\text{cm}^2$) in DPPH/NR solution at 40 min. R represents radical scavenger, and R^* represents radical. UV-vis spectra of (c) DPPH and (d) NR solution. The curves (1)–(8) correspond to those described in part a. (e) Comparing the charge developed by contacting pure PDMS, PDMS doped with DPPH or vitamin E (1 mM), and PDMS coated with PDA or TA with PC.

semiconductor (silicon (Si)). After coating the materials with either PDA or TA, we contacted them with a piece of PTFE or nylon as the reference material. According to the triboelectric

series, PTFE has a high tendency to charge negatively, while nylon has a high tendency to charge positively. Hence, we chose these two reference materials to test the ability of the

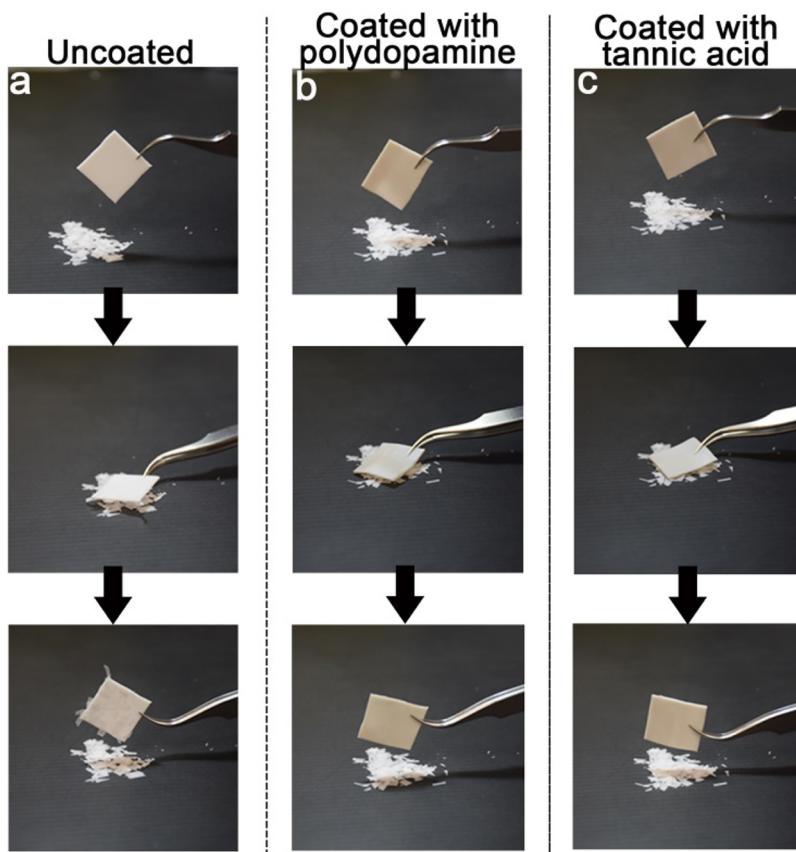


Figure 4. PTFE coated with PDA or TA resists charging and adhesion to pieces of paper after contacting with a piece of nylon 1200 times. A piece of (a) uncoated PTFE, (b) PTFE coated with polydopamine, or (c) PTFE coated with tannic acid was brought close to the pieces of paper.

coated surfaces to resist charging in both the positive and negative directions. After contacting the materials 60 times, we measured the charges of both the contacting materials using a Faraday cup connected to an electrometer. Results showed that the charges generated by contact electrification on the materials coated with either PDA or TA were dramatically lower than those of the uncoated materials for all the materials investigated in both high (~60%) and low humidity (~20%) (Figure 2). Materials coated with PDA seemed to charge slightly less than materials coated with TA. The charge of the reference material (i.e., PTFE and nylon) used for contacting the materials also reduced (Figure S6).

Both PDA and TA contain hydrophilic groups (e.g., hydroxyl and amine groups), which may make the surfaces more hygroscopic. With more water molecules, the surfaces are generally believed to be more conductive and more effective in dissipating static charge away. To determine whether the increase in surface conductivity is the mechanism for greatly reducing the amount of charge generated, we measured the surface resistivity of the materials when the humidity was either at 20 or 60% (Tables 1 and 2). After coating, we found that the surface resistivity decreased very significantly at humidity of 60%: 10^{13} to $10^{14} \Omega/\text{sq}$ for surfaces coated with PDA and 10^{14} to $10^{15} \Omega/\text{sq}$ for surfaces coated with TA. However, the resistivity of these coated surfaces is still in the insulative range ($>10^{12} \Omega/\text{sq}$), and materials dissipate charge poorly in this range. For charge to dissipate by conduction, the surface conductivity needs to be either in the conductive range (i.e., $<10^5 \Omega/\text{sq}$) or the dissipative range (i.e., 10^5 to $10^{12} \Omega/\text{sq}$).^{10,35} In addition, when the humidity was at 20%, the surface

resistivity was much higher: 10^{15} to $10^{16} \Omega/\text{sq}$ for surfaces coated with PDA and 10^{16} to $10^{17} \Omega/\text{sq}$ for surfaces coated with TA. On the other hand, these surfaces were still able to resist charging well at 20% humidity (Figures 2c and d). Therefore, surface conduction may not be the primary mechanism for reducing the charge generated.

Alternatively, the radical-scavenging property of PDA and TA may enable the surfaces to resist charging by contact electrification. A recent study reported an interesting mechanism that radical scavengers (e.g., diphenylpicrylhydrazyl (DPPH) and vitamin E (VE)) were capable of reducing the amount of charge generated.⁸ Fundamentally, the authors observed that both charge and radicals were generated simultaneously during contact electrification. They proposed that since radicals can stabilize charge, the removal of the radicals by radical scavengers can cause the charge to dissipate easily. Accordingly, we showed that the radical-scavenging property of PDA and TA can remove radicals generated by contact electrification (Figure 3a). We immersed various types of materials into a DPPH solution: (A) an uncharged piece of PDMS, (B) a piece of PDMS charged by contact electrification, (C) an uncharged piece of PDMS coated with either PDA or TA, and (D) a charged piece of PDMS coated with either PDA or TA (Figures 3b and c). Because DPPH is a radical scavenger, any bleaching of the solution indicates that radicals are present and have reacted with DPPH. Our results showed that (B) bleached the DPPH solution, while (A) did not; hence, radicals were indeed generated by contact electrification. (C) also bleached the solution; this indicates that PDA and TA are radical scavengers since DPPH is, by itself, a radical. (D)

bleached the solution further. Comparatively, however, the difference in the amount bleached between (D) and (C) was much less than that between (B) and (A). Hence, we conclude that much lesser radicals were generated by contact electrification when the PDMS was coated with either PDA or TA.

In addition, we repeated the experiment using neutral red (Figures 3b and d). Neutral red has been used previously for detecting the presence of radicals.^{36–38} The advantage of using neutral red is that it is not a radical; thus, it does not react directly with PDA or TA. As such, (C) did not bleach the neutral red solution. Similarly, the difference in the amount of neutral red bleached between (D) and (C) was much less than that between (B) and (A). Judging by the differences in the absorbance peaks at 535 nm, the amount of radicals generated reduced by ~91% for PDMS coated with PDA (i.e., the difference between the peaks (7) and (3) in Figure 3c is ~91% smaller than the difference between (6) and (2)) and ~78% for PDMS coated with TA (i.e., the difference between the peaks (8) and (4) is ~78% smaller than the difference between (6) and (2)).

As a comparison, we prepared the materials used in the previous study for investigating the influence of radical scavengers on contact electrification: pieces of PDMS doped with either DPPH or VE.⁸ We contacted these pieces of doped PDMS and the PDMS coated with either PDA or TA against a piece of PC. Results showed that the charges of the PDMS coated with PDA and TA were less than that of the PDMS doped with DPPH and VE (Figure 3e); hence, the radical-scavenging property of PDA and TA is good compared with those reported previously. There may be several reasons for these lesser amounts of charge: the amount of molecules coated may be different from the amount doped; PDA and TA can react with more radicals per molecule than DPPH (dopamine:DPPH = 2:1 and tannic acid:DPPH = 25:1; see methods in the Supporting Information and Figures S7 and S8 for more details);^{39–41} the radical-scavenging property of PDA and TA may be regenerated by a cyclic oxidation process in air.⁴²

For practical purposes, the coatings need to retain their noncharging property after multiple contacts with other materials. To test the durability of the coatings, we first contacted pieces of PTFE uncoated or coated with PDA or TA with a piece of nylon 1200 times. After contact, we discharged the materials and then contacted them with a piece of nylon another 60 times. Our measurements showed that the uncoated piece of PTFE charged highly ($-6.7 \mu\text{C}/\text{m}^2$), while the coated pieces did not charge much ($-0.2 \mu\text{C}/\text{m}^2$ for PTFE coated with PDA and $-0.5 \mu\text{C}/\text{m}^2$ for PTFE coated with TA). When the uncoated PTFE was brought close (1 mm) to small pieces of paper, it was able to attract them onto its surface (Figure 4). However, when the pieces of PTFE were coated, they did not have any observable effect on the pieces of paper.

4. CONCLUSIONS

To summarize, we found that coating surfaces with either PDA or TA is a general approach for preparing noncharging surfaces. Fundamentally, these coatings resist charging probably because of their radical-scavenging property. There are many advantages of using these coatings for preparing noncharging surfaces. (1) Most importantly, they are highly versatile and can be applied to surfaces of virtually any type of material. This approach is far more general than existing coating methods. Because contact electrification occurs on almost all types of materials, this

general approach is ideal for avoiding the undesirable consequences of static charge. (2) In addition, the charge of the contacting surface also reduced. (3) Surface coating has the advantage that the bulk properties of the materials remain unchanged. (4) The method of coating is simple: the materials only need to be dipped in a solution containing either dopamine or tannic acid at room temperature. Hence, this technique can potentially be applied to large surface areas easily. (5) The method is green as it involves molecules that are naturally available and does not involve any external input of energy. (6) For the case of tannic acid, the coating is inexpensive and colorless. (7) In addition, these coatings are known to be multifunctional and exhibit many other desirable properties; for example, they have been demonstrated to be antibacterial, antifouling, radical scavenging, antioxidant, and others.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07711.

Characterization of the coated surface and experimental details of determining the reaction stoichiometry of DPPH with dopamine or tannic acid (PDF)

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Notes

The authors declare no competing financial interest.

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