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High-Efficiency Electro spray Deposition Method for Nonconductive Substrates: Applications of Superhydrophobic Coatings

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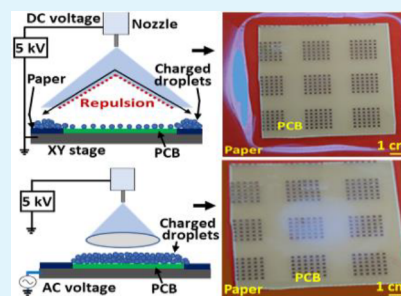
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Supporting Information

ABSTRACT: When highly insulating materials are used as substrates for electronic devices, manufacturing yields become worse, and electronic components are often damaged due to undissipated electrostatic charges on such substrates. In the case of electro spray deposition, the problem of undissipated charges is particularly vexing. If charges accumulated on the substrate are not properly compensated, a repulsive force is generated against the incoming charged droplets, which negatively affects the uniformity and deposition rate of the coating layer. In order to overcome this limitation, we demonstrated a new electro spray method, which can significantly increase the deposition efficiency even in the presence of accumulated charges on nonconductive substrates. A highly reliable superhydrophobic layer was uniformly deposited on highly insulating substrates, including printed circuit board (PCB), polyester (PET), and polyimide (PI) substrates.

KEYWORDS: electro spray deposition, charged droplet, nonconductive substrate, accumulated charges, superhydrophobic coating



INTRODUCTION

Many industrial manufacturing processes require proper coating of substrates in order to change the surface properties, such as adhesion, wettability, corrosion resistance, and wear resistance.^{1–3} Among different coating methods, spray coating is widely used, since it is a noncontact deposition method that is capable of depositing materials on demand. Conventionally, air spray methods, based on compressed air pressure, have been used to generate atomized droplets.^{3–5} However, droplets of relatively large size are produced, which could lead to slow evaporation of the solvent on substrates, resulting in the formation of voids in the deposited film.⁶ In general, it is difficult to achieve a uniform coating layer using air spray methods.

Alternatively, electro spray methods are attracting attention because of the advantages of uniform coating due to the fine atomization of droplets and rapid solvent evaporation of the droplets deposited on the substrates.^{7,8} The deposition efficiency could be improved with minimal flying mist, because charged droplets are readily attracted to substrates due to the electrical field between the nozzle and substrate holder.^{9,10} However, the substrates for electro spray deposition have been limited to surfaces with at least moderate conductivity, in order to dissipate charges of deposited droplets. Otherwise, a repulsive force is generated against the incoming charged droplets, which negatively affects the uniformity and deposition rate of the coating layer. As a result, charge dissipation behavior on substrates has become a research concern for efficient electro spray deposition.¹¹

For proper electro spray deposition, the substrate conductivity should be greater than 10^{-12} S·m⁻¹.¹² However, recent

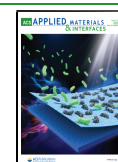
electronic devices use highly insulating substrate materials; these include the reinforced polymer used in printed circuit boards (PCB, with a conductivity of $\sim 10^{-17}$ S·m⁻¹) as well as other plastic substrates (polyethylene terephthalate, PET, $\sim 10^{-21}$ S·m⁻¹, and polyimide, PI, $\sim 10^{-15}$ S·m⁻¹).^{12–15} Until now, electro spray methods are not suitable for such nonconductive substrates. In this study, we aim to develop a new electro spray deposition method that can increase deposition efficiency regardless of the state of charge accumulation on the substrate surface.

Several attempts have been made to increase deposition efficiency on nonconductive substrates. For example, surface pretreatment techniques such as UV, plasma, and ionizing treatments have been used to modify the substrate surface. However, most pretreatments aim to change the initial state of the substrate (e.g., surface energy modification or initial discharge of the substrate).¹⁶ However, for electro spray applications, especially during the spraying process, charge accumulation on the insulating substrate increases with time due to the deposition of charged droplets. The effect of the initial treatment lasts very briefly^{10,17} and is insufficient to mitigate charge repulsion problems.

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Alternatively, researchers have attempted to deposit additional materials to change the surface properties prior to the electro spray coating process. For example, Lagaron and co-workers^{18,19} deposited a layer of electro spun wires prior to electro spray coating on a PET substrate. Then, a superhydrophobic layer could be deposited via electro spray deposition of SiO₂ solution over the electro spun wires. However, the additional presteps required to deposit extra layers might not be practical for industrial purposes.²⁰ In addition, the precoated layer might not be uniform or durable for practical applications. To the best of our knowledge, few effective techniques of electro spray deposition on insulating substrates have been reported in the literature.

In this study, we demonstrated a novel electro spray deposition method, which can be effective for a wide variety of substrates regardless of their material conductivity. For this purpose, we applied an alternating current (AC) voltage to the substrate holder, which is quite straightforward and easy to implement. After applying an AC voltage to the substrate holder, we could easily increase the deposition efficiency on highly insulating substrates in ambient conditions, without surface pretreatment or predeposition of any layers. Our method is different from other electro spray methods, since uniform coating is made possible in the presence of undissipated charges especially on the highly insulating substrates. The only disadvantage of our proposed method is the additional cost of the required high-voltage amplifier and function generator.

The use of AC voltage in the electro spray method has been discussed by Chang et al. and Muller et al.^{21,22} However, their AC electro spray method differs from our method in that they applied the AC voltage to the nozzle in order to generate bigger droplets. In our method, AC voltage was applied to substrate holder to suppress undissipated charges.

In recent years, the demand for waterproof electronic devices, such as smart phones, light emitting diode (LED) displays, solar cells, and so on, has increased.^{23,24} To meet this demand, uniform and durable superhydrophobic coatings of the devices are desired. However, few effective spray coating methods have been reported, since most electronic devices use nonconducting substrates with conductivities of far less than 10⁻¹² S·m⁻¹. The electro spray method in this study can overcome these limitations and fabricate a hydrophobic layer on insulating substrates. To understand the deposition mechanism of the electro spray method, we measured the electric current and electrostatic charges on various substrates with different conductivities and thicknesses, such as an aluminum plate (1 mm), PET film (100 μm), PI film (100 μm), paper (100 μm), glass (1 mm), and PCB (1 mm). As the spray material for the superhydrophobic coating, a fumed SiO₂ solution prepared by mixing and dissolving fumed SiO₂, epoxy resin, and curing agents in butoxyethanol was used (see **Materials and Methods**). We show that a uniform coating of SiO₂ nanostructures can be formed on the surface of various substrates using our method and that the water contact angle of the coated surface can be more than 150°, similar to the surface of a lotus leaf.²⁰ The type of coating will be useful in many industries owing to its self-cleaning, anticorrosion, anticontamination, and waterproof properties.

MATERIALS AND METHODS

Materials and Solution Preparation. Fumed silica nanoparticles (Aerosil R 972) with an average particle size of 16 nm were kindly donated by Evonik Industries, Germany. An epoxy resin (poly-

(bisphenol A-co-epichlorohydrin)), curing agent (4,4'-methylene-bis(2-chloroaniline)), and reagent (2-butoxyethanol) were purchased from Sigma-Aldrich, South Korea. First, epoxy resin solution was prepared by mixing 0.40 g of epoxy resin (in pellet form) and 0.08 g of curing agent with 9.52 g of 2-butoxyethanol using a magnetic stirrer for 8 h at 70 °C. Second, silica solution was prepared by mixing 0.40 g of fumed silica with 9.60 g of 2-butoxyethanol using a magnetic stirrer for 2 h at room temperature. Third, the epoxy resin solution (50 vol %) and silica solution (50 vol %) were mixed using a magnetic stirrer for 1 h at room temperature and then sonicating for 5 min.

In this experiment, various types of substrates were used to fabricate the superhydrophobic layer. As the coating may be applied to electronic devices, we used PCB substrates donated by Samsung Electro-Mechanics. To demonstrate spray deposition on flexible substrates, PET film (SKC Co. Ltd., South Korea) and PI film (Kapton 100HN, P. & S.S., South Korea) were used. For comparison purposes, substrates with high and moderate conductivity, such as an aluminum plate, bare glass (microscope slides, Marienfeld Superior, Germany), and paper (Jong Ie Nara, South Korea), were used.

Electro spray Deposition of Superhydrophobic Coating Layer. To supply deposition material (SiO₂ solution with epoxy resin) to a syringe needle with an inner diameter of 150 μm, an air pressure of 2.0 kPa was applied to the syringe barrel. Note that the air pressure must be low enough to prevent large droplets from dripping from the nozzle. Alternatively, a syringe pump can be used to supply ink at a constant flow rate. A high voltage (5 kV) was applied to the nozzle from the power supply (SHV30R, Conver Tech, South Korea), supplying an electrical charge to the liquid and creating an electric field, as shown in **Figures 1a,b**. To investigate the effect of AC voltage on electro spray deposition, AC voltage was applied to the substrate holder in the frequency range of (500 Hz to 4 kHz) and peak-to-peak amplitude range of (200 V to 1 kV). An arbitrary function generator (Agilent 33220A, Agilent Technologies, USA) was used to generate the

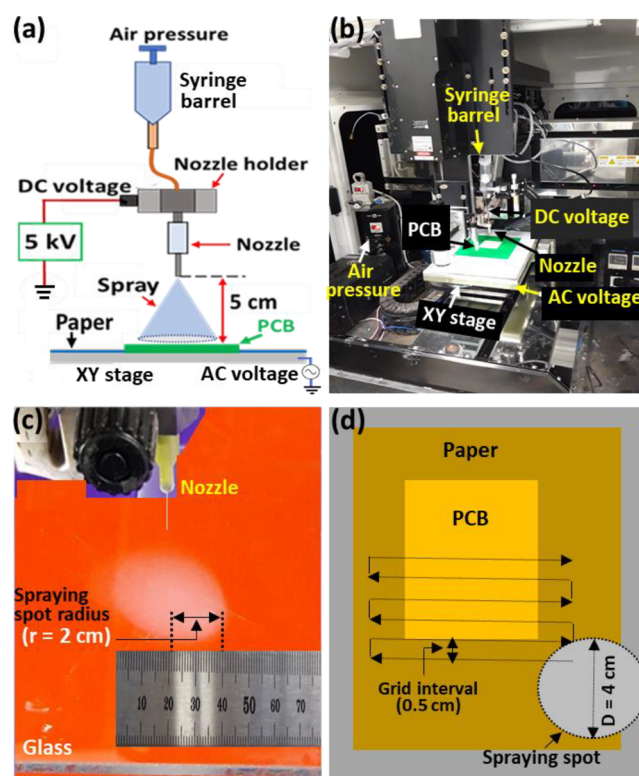


Figure 1. Schematic illustration of the electro spray process. (a) Schematic illustration of our electro spray method. (b) Photo of the experimental setup. (c) Size of an electro spray deposited spot. (d) Horizontal grid movement of the nozzle used to coat the entire substrate area (PCB).

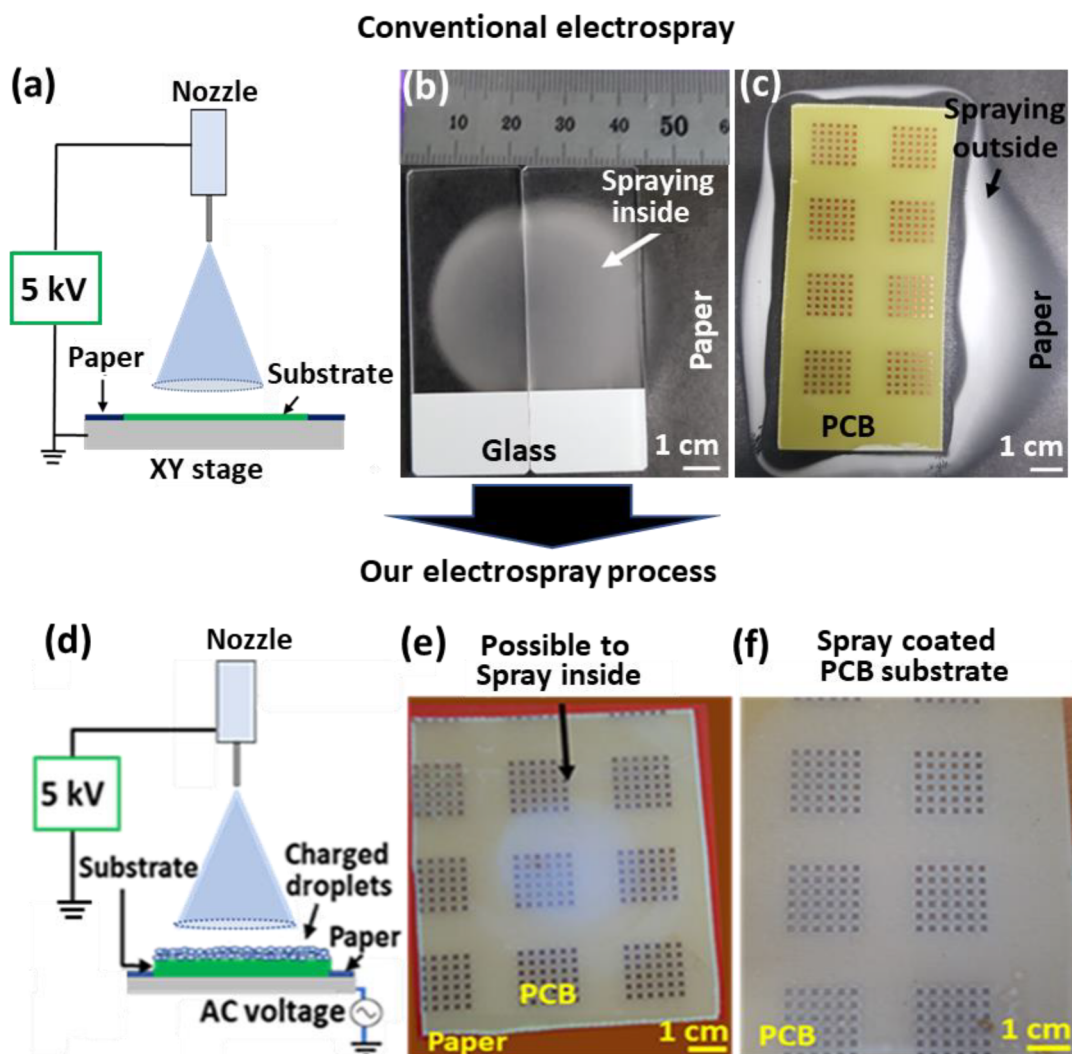


Figure 2. Schematic illustration of electro spray methods and spray deposition results. (a) Schematic illustration of the conventional electro spray method. (b) Conventional electro spray deposition at a target location on a glass substrate. (c) Improper deposition on a PCB substrate resulting from use of the conventional electro spray method. (d) Schematic illustration of the electro spray method. (e) Deposition results of our method on a target location on the PCB substrate. (f) Electro spray deposition on an entire PCB substrate using our method.

AC signal voltage. Then, the AC signal (sine wave) was amplified by a high-voltage amplifier (Model 2220, Trek, USA). For proper spray deposition, a constant 5 cm stand-off distance between the nozzle tip and collector (substrate) was maintained. To coat the entire area of the substrate, the nozzle was moved in a horizontal grid motion relative to the substrate, as shown in Figure 1d. The distance between swaths and scanning speed were set to 0.5 cm and $2 \text{ mm}\cdot\text{s}^{-1}$, respectively. The spray coating experiment was performed at room temperature ($\sim 25 \text{ }^\circ\text{C}$). After electro spray deposition, the coated layer was annealed at $120 \text{ }^\circ\text{C}$ for 1 h by placing the substrate on a hot plate (SP131320-33, Thermo Scientific, China).

Current Measurement. The deposition behavior of charged droplets can be understood by measuring the electrical current at the substrate holder.

The current measurement methods might be different according to the electro spray methods. In the case of the conventional electro spray process, the virtual ground of the operational amplifier (LF356N, JFET input operational amplifier, Texas Instruments) can be used instead of ground voltage (zero voltage) (Figure S4, Supporting Information). Then, the current signal can effectively be measured by amplifying it with a conversion factor of 10^8 times (Figure S4, Supporting Information), as described in Section S3.1.1 (Supporting Information).

However, in our method, we applied an AC voltage to the substrate holder instead of the ground voltage. Therefore, we took a different

approach to current measurement that was based on a shunt resistor, as shown in Figure S7 (Supporting Information). Here, the current-to-voltage conversion factor was as high as 20×10^6 . For the amplification, a shunt resistor of $1 \text{ M}\Omega$ was used, and the voltage difference between the two leads of the resistor was amplified 20 times. Note that the shunt resistor of $1 \text{ M}\Omega$ was used to obtain sufficient amplification. The amplified signals are subject to low-frequency drift and high-frequency noises, since one end of the shunt resistor is not connected to a voltage source. To suppress the high-frequency noise, we used a first-order low-pass filter with a cutoff frequency of 7.96 Hz. As a result, the higher-frequency components of the signal are reduced significantly, while low-frequency drift noise remains. To increase the quality of the signal, five sets of current signals were averaged. Details of the current measurement are discussed in Section S3.1.2 (Supporting Information).

Electrostatic Field Measurement. The electrostatic field caused by deposited charges on various substrates was measured with an electrostatic field-meter (FMX-004, Simco, Japan). The electrostatic field was measured during electro spray deposition, increasing spray time at 10 s intervals until the measured electrostatic field no longer increased. After that, the electro spray process was stopped to measure the rate of attenuation of the electrostatic field at 10 s intervals.

Wetting Analysis of the Coated Layer. The hydrophobicity of the coated layers was evaluated based on the water contact angle (CA).

The water CAs of prepared samples were measured by an optical contact angle meter (Phoenix 300 Touch, SEO, South Korea). Here, the shape of a distilled water drop was measured using the sessile drop method using a 5 μL water droplet on the sample surfaces at room temperature. The average water CA value was determined by measuring the CA at five fresh spots.

Surface Morphology and Thickness Analysis of the Coated Layer. The surface morphologies of the fabricated layers were inspected via high-resolution scanning electron microscopy (HRSEM) (Sigma 500, ZEISS, Germany) using an accelerating voltage of 3 kV. For comparison purposes, we investigated SEM images of both the coated and original substrates. For cross-sectional SEM imaging, specimens were prepared by cutting the substrates using a knife, and then, the surfaces of the fractures were coated with a thin layer of gold (3 nm).

The surface roughness of the gold-coated samples was evaluated by atomic force microscopy (AFM) (SPM 9700, Shimadzu, Japan), operating in dynamic mode. The surface roughness of the chosen scan area ($5 \times 5 \mu\text{m}$) was calculated in terms of the root-mean-square roughness (R_{RMS}).

Durability and Self-Cleaning Test of the Coated Layers. To assess durability, sandpaper abrasion, tape peeling, chemical attack (HCl), and UV radiation tests were performed. Supporting Information Section S4.4 gives a detailed description of the four different durability tests.

Nescafe coffee powders were used as dust particles on substrates to demonstrate the self-cleaning capability by dropping distilled water droplets.

RESULTS AND DISCUSSION

Electrospray Deposition via Application of AC Voltage to the Substrate Holder. The liquid ink for electrospray is charged by a DC voltage at the nozzle to form a Taylor cone. When the voltage is high enough, the liquid breaks up into small charged droplets with a radius close to the Rayleigh limit.^{25,26} The atomized droplet size is closely related to the droplet charge as

$$q_{\text{R}} = 8\pi\sqrt{\gamma\epsilon_0 r^3} \quad (1)$$

Here, q_{R} is the charge of the droplets, γ is the surface tension of the liquid, ϵ_0 is the electrical permittivity of the liquid, and r is the droplet radius. In this case, the size distribution of the electrospray droplets is usually normal,^{25,27} and the droplet diameter could be less than 10 μm .

When the charged droplets are deposited on the insulating substrate, charges accumulate, which affect the spray process.^{11,28} The accumulated charges are dissipated by three main mechanisms: dissipation through ambient gas, conduction through gas–solid contact, and bulk neutralization due to the dielectric property.^{11,29} In the case of bulk neutralization, the charge decay behavior can be written as¹¹

$$q(t) \approx q_0 e^{-\frac{t}{\rho\epsilon}} \quad (2)$$

Here, q_0 is the initial charge, and ρ and ϵ are the substrate density and permittivity of the substrate, respectively. It has been reported that bulk neutralization occurs much more slowly (typically more than a few minutes) in highly nonconductive materials ($\sigma \ll 10^{-12} \text{ S}\cdot\text{m}^{-1}$).

In this study, we aimed to reduce the effect of undissipated charges by applying AC voltage to the substrate holder. The AC voltage increases the movement of electrostatic charges, aids in charge redistribution on insulating substrates, and has similar impedance reduction effects in a capacitor subject to AC voltage.^{30,31} To extend the existing concept to electrospray

application, we replaced the ground (zero) voltage of the substrate holder with an alternating current (AC) voltage, as shown in Figure 2a,d. In general, the use of AC voltage does not affect the electrical field for spray deposition, since the average AC voltage is equivalent to zero (ground) voltage. However, it can accelerate charge movement. Assuming that the substrate on the substrate holder is flat and uniform, the charges redistribution can be expressed as

$$\dot{q}(t) \approx \frac{\epsilon A}{d} \dot{V}_{\text{ac}}(t) \quad (3)$$

Here, $\dot{q}(t)$ and $\dot{V}_{\text{ac}}(t)$ are the rate of charge movement and voltage between the two surfaces of the substrate respectively, and ϵ , d , and A are the permittivity of the substrate, substrate thickness, and area of charged droplet deposition, respectively. V_{ac} is difficult to measure or predict, as it includes the effect of both AC voltage and the surface voltage caused by the deposited charges. For an AC voltage with high frequency and amplitude, the effect of AC voltage is dominant over the effect of charge accumulated on the substrate.

In this study, we investigated the AC-biased method of fabricating superhydrophobic coatings on highly insulating substrates to meet the industrial demand for waterproof electronic devices. For this purpose, we prepared a SiO_2 solution for electrospray coating of superhydrophobic layers (see Materials and Methods). The prepared solution was loaded into a nozzle with an inner diameter of 150 μm via application of pressurized air (2.0 kPa) to the syringe barrel. Then, a high DC voltage (5 kV) was applied to the nozzle connector, creating a spray of charged droplets. The DC voltage applied to the nozzle is an important parameter for generation of sprayed droplets without causing large drips (too low voltage) or unstable multijets (too high voltage), as shown in Figure S1 (Supporting Information). The sprayed charged droplets are easily attracted to the substrates due to the electrical field formed by the high DC voltage and zero voltage at the substrate holder.

For comparison, Figure 2b,c shows the typical results of conventional electrospray deposition depending on the substrate conductivity. In the case of a glass substrate ($\sigma \approx 10^{-11} \text{ S}\cdot\text{m}^{-1}$), the charged droplets are deposited in a circular shape with a radius of 2 cm when the nozzle is located 5 cm above the target location. However, in the case of a highly insulating substrate, such as PCB ($\sigma \approx 10^{-17} \text{ S}\cdot\text{m}^{-1}$), it is practically impossible to properly deposit charged particles on the target substrate, and most of the droplets are deposited outside of the substrate. Even though electrospray deposition on a glass substrate is possible, the deposited layer tends to be too thin for most practical applications. Yoon et al. reported that the thickness of a hydrophobic film on an ITO-coated glass substrate was $\sim 0.6 \mu\text{m}$, even after a long period (600 s) of electrospray deposition on the target location.³² A thickness of 1 μm or more is required for layer reliability and better functionality. The thickness of the deposited layer is limited by the insulating properties of the deposited layer, which in turn hinders charge dissipation.

Our electrospray method uses AC voltage (for example, a sine wave with 800 V magnitude and 3 kHz frequency) instead of grounded voltage on the substrate holder (the other side of the substrate coating surface). The application of AC voltage significantly improves the results of electrospraying on PCB substrates, as shown in Figure 2e,f. The entirety of the substrate can be coated using multipass spray deposition, as shown in Figure 2f. In this experiment, a horizontal grid motion of the

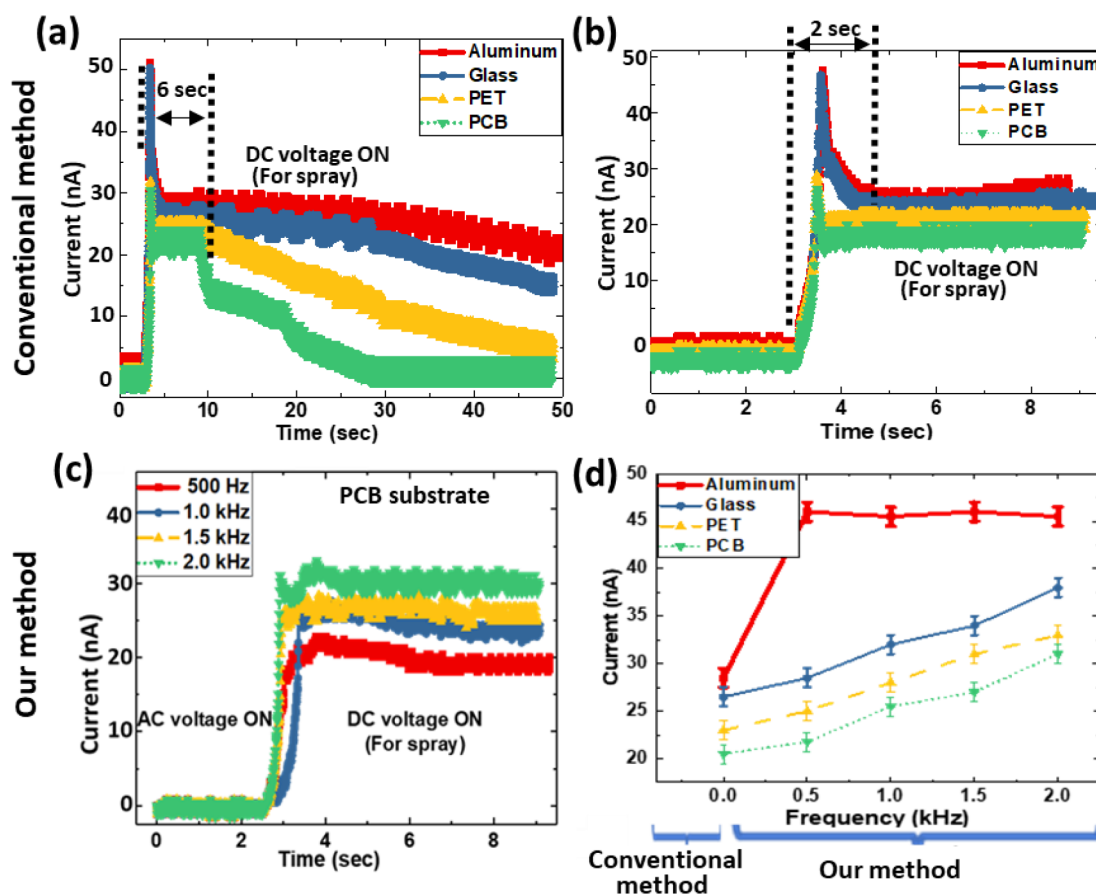


Figure 3. Current measurements. (a) Measured current during conventional electro spray deposition. (b) Magnified plot of the measured current during conventional electro spray deposition. (c) Measured current during electro spray deposition on PCB substrate using our method. (d) Comparison of average of current during electro spray deposition according to frequency of AC voltage.

nozzle with respect to the substrate was used to coat the entire substrate. The spacing between swaths and scanning speed were set to 0.5 cm and $2 \text{ mm} \cdot \text{s}^{-1}$, respectively. A comparison video of electro spray deposition with/without AC voltage can be found in [Movie S1 \(Supporting Information\)](#).

Current Behavior during Electro spray Deposition. To better understand the physics of electro spray deposition, we measured the electric current at the substrate holder.

When using the conventional electro spray method, the current measurement method is straightforward, since the ground (zero) voltage of the substrate holder can be replaced by the virtual ground of an operational amplifier to effectively amplify the current signal, as shown in [Figure S4 \(Supporting Information\)](#). However, when applying AC voltage to the substrate holder, it was necessary to use a shunt resistor to measure the voltage difference across the resistor ([Figure S7, Supporting Information](#)). Here, the measured signals were affected by low-frequency drift noise as well as high-frequency noise, because there was no direct connection of voltage source at one end of the shunt resistor.

[Figure 3a,b](#) shows the measured current during conventional electro spray deposition of SiO_2 solution onto various substrates. As shown in [Figure 3a](#), when the deposition time increases to more than 15 s, the measured current behavior changes according to the conductivity of the substrate. In the case of relatively highly conductive substrates (aluminum and glass), a higher current (or charge flow rate) was measured compared to substrates with low conductivities. Due to the charge flow

through conductive substrates, charges on the substrate surface are readily dissipated, and the current flow can last more than 60 s even in the case of deposition on the same spot. However, it should be noted that the amount of current gradually decreases over time, since the deposited layer behaves like an insulating layer, blocking charge dissipation through the substrates. For this reason, it was difficult to continuously increase the thickness of the deposited layer according to deposition time, even when using conductive substrates. In the case of electro spray deposition on highly insulating substrates, after 30–60 s, the current decreased to almost zero ([Figure 3a](#)), which indicates that after 30–60 s, there could be no further deposition of charged droplets on the substrate.

For comparison purposes, the current behavior was measured during the electro spray deposition process, as shown in [Figure 3c,d](#). Due to the presence of low-frequency drift noise in the measured signal, we investigated the current behavior in a limited time period ($<10 \text{ s}$). The current behavior was very similar to that of the conventional DC electro spray method with no apparent AC frequency component, as shown in [Figure 3c](#). [Figure 3d](#) shows the current value at zero frequency, which is the result of the conventional electro spray method. The results clearly show that the frequency of AC voltage (amplitude, 800 V) can affect the magnitude of the current, as shown in ([Figure 3c,d](#)).

Electrostatic Field Behavior during Electro spray Deposition. It has been a long-standing practice to neutralize charges of the deposited droplets for proper deposition of

incoming charged droplets from the nozzle. In the case of a conductive substrate, fast charge dissipation (high current) through the substrate is evident in the current measurement, as shown in Figure 3. However, in the case of highly insulating substrate, the charge flow (current) may not be related to the charge dissipation through the substrate. To understand the charge behavior on various substrates, the electric fields were measured using an electrostatic field meter immediately after 60 s of electro spray deposition, and the results were compared. As shown in Figure 4, when our electro spray method was used, the

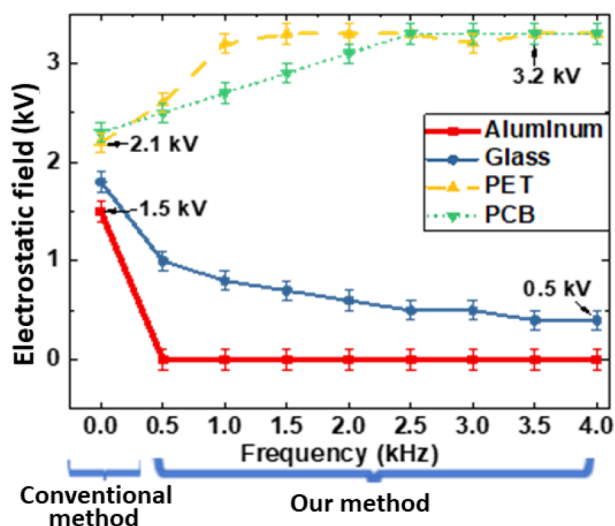


Figure 4. Electrostatic field measurement results at the center of the deposition location immediately after 60 s of electro spray deposition.

electrostatic field of the layers deposited on aluminum and glass substrates decreased from 1.5 to 0.0 kV and from 1.9 to 0.5 kV, respectively. In contrast, in the case of insulating substrates, such as PET and PCB, when applying AC voltage to the substrate holder, the electric field increased from 2.1 to 3.2 kV. The electric field results of the insulating substrates indicate that more charged droplets could be deposited without charge dissipation. Furthermore, when using AC voltage, the undissipated charges seemed to be less repulsive to the incoming charged droplets. The field meter measurements indicate that

the charge (current) flow phenomena in Figure 3d differ according to the conductivity of the substrates. For example, in the case of highly and moderately conductive substrates (aluminum and glass), the use of high-frequency AC voltage can accelerate the charge dissipation (current flow) through the substrates. However, in the case of insulating substrates, the measured current flow might be related to the induced negative charges (electrons) on the opposite side of the substrate. As a result of negative charge accumulation on the other side of the substrate, it was possible to deposit more positively charged droplets on the substrate. This increases the deposition efficiency of the electro spray method.

Hydrophobicity of the Coated Layers. The quality of the coated layer can be assessed by characterizing its hydrophobicity. The uniformly coated SiO_2 layer will show high-water-repellency properties with a significant increase in water contact angle (CA). The effectiveness of our electro spray method was clearly observed from the measured water contact angles with respect to the frequency of the AC voltage, as shown in Figures 5 and 6a. However, we found that the deposition efficiency may not sufficiently increase according to the amplitude of AC voltage, as shown in Figure 6b.

Our method is effective for all kind of substrates. Different substrates (PCB, PET, PI, glass, and paper) were compared, and the contact angles of the coated layers on all substrates were more than 150° , as shown in Figure S16 (Supporting Information). For a better understanding of the water repellency of the coated layers on PCB and PET film, refer to Movie S2 (Supporting Information).

Reliability of the Coated Layers. The hydrophobicity of the substrates comes from the microscopic structure of deposited SiO_2 .⁴ For better understanding of the microscopic structures, the surface roughness was evaluated by atomic force microscopy (AFM) and scanning electron microscopy (SEM), as discussed in Section S4.2 (Supporting Information). The surface roughness (R_{RMS}) of the coated layers on PET film using our method was about 111.83 nm, which is significantly greater than the (R_{RMS}) of 82.87 nm of the layers deposited using the conventional electro spray method. Note that the uncoated (original) PET film had a roughness of 11.03 nm.

For practical applications, the reliability of the coated layers is one of critical requirements. For the reliability, sufficient layer thickness is required, especially when exposed to various forms

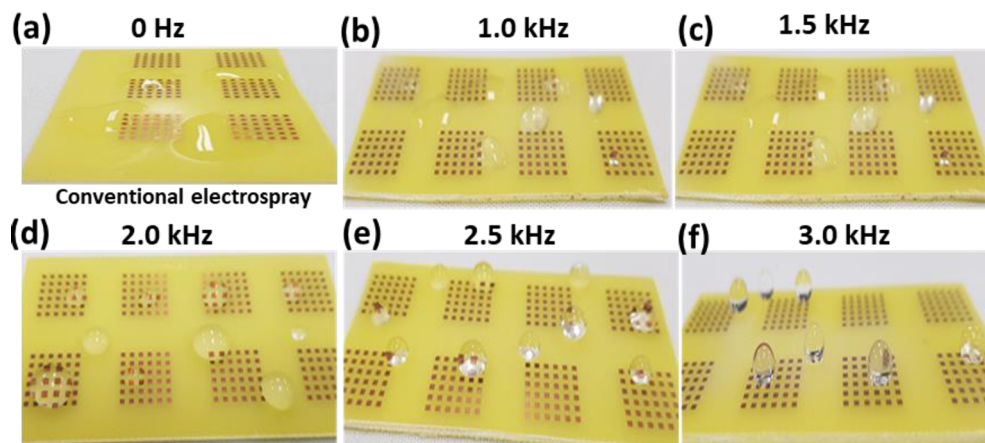


Figure 5. Water droplets on PCB substrate with different coatings. (a) Water droplets on PCB substrate after electro spray deposition by using the conventional method. (b–f) Water droplets on PCB substrate after electro spray deposition using AC voltage at different frequencies (amplitude, 800 V).

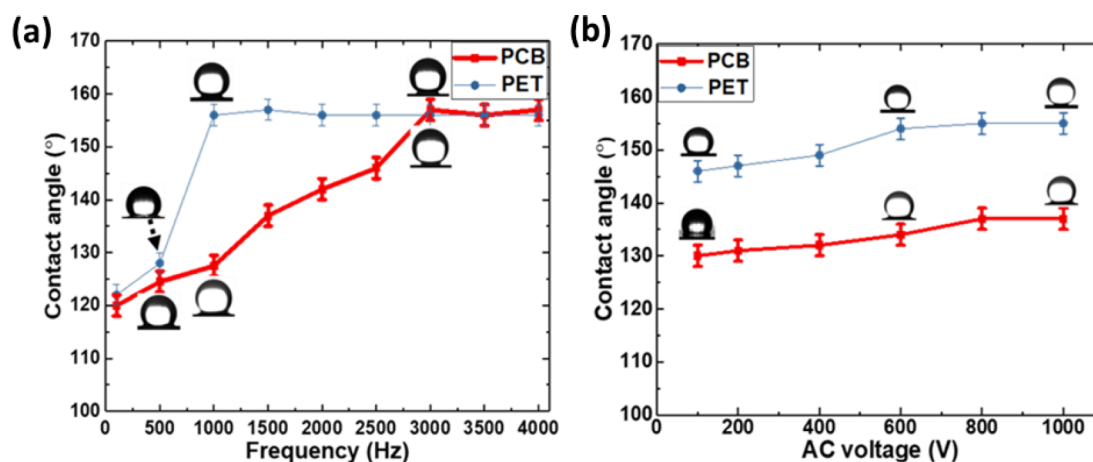


Figure 6. Hydrophobicity of the coated layers. (a) Water CA of the coated layers on PCB and PET substrates according to AC frequency (amplitude, 800 V). (b) Water CA of the coated layers on PCB and PET substrates according to the amplitude of AC voltage (frequency, 3.0 kHz).

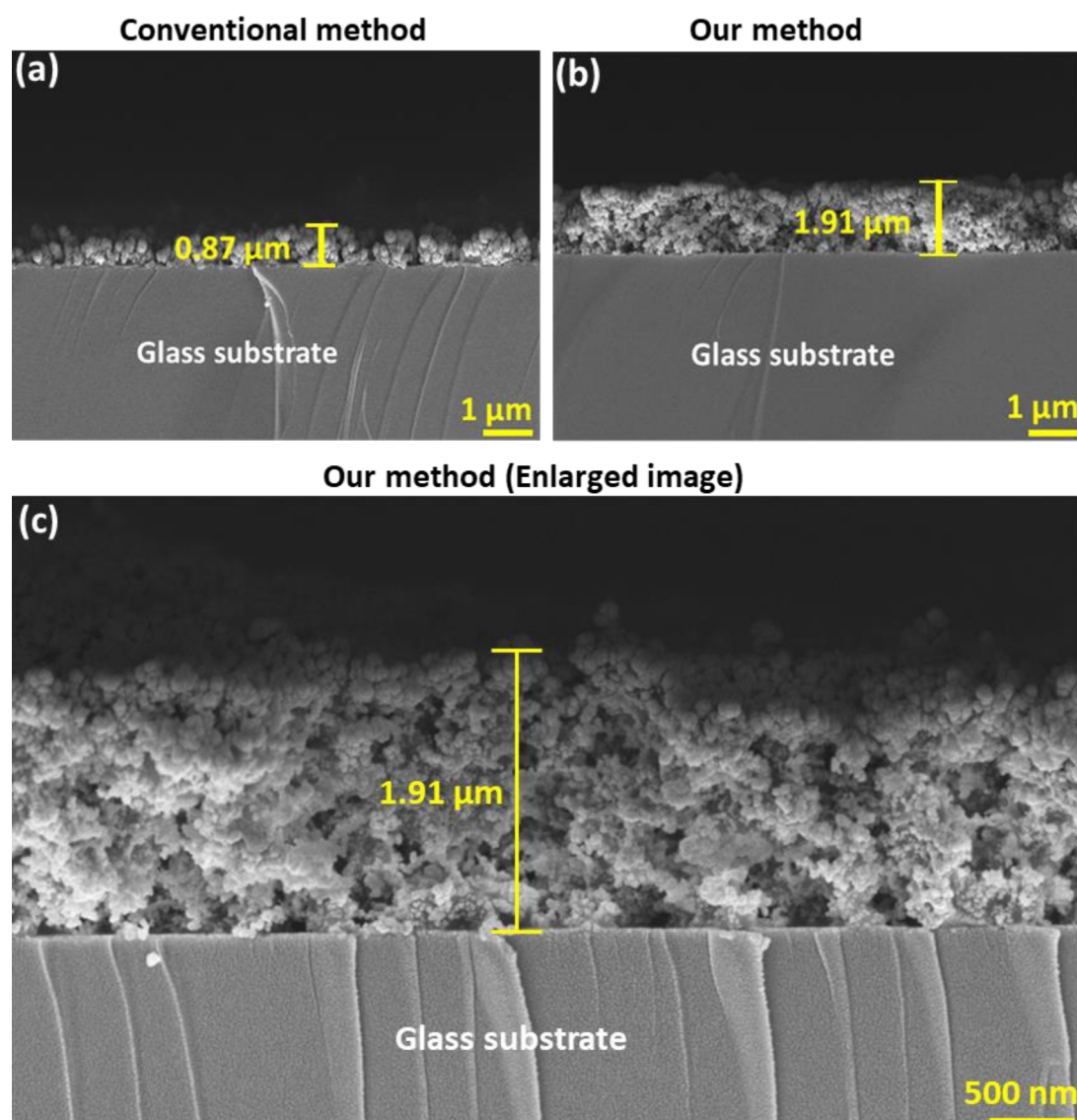


Figure 7. Cross-sectional SEM images of coated layers. (a) Cross-sectional image of coated glass substrate after 60 s of conventional electro spray deposition at the target location. (b) Cross-sectional image of a glass substrate after full area coating using AC voltage (amplitude of 800 V and frequency of 3 kHz). (c) Enlarged cross-sectional image of the coating layer on a glass substrate using AC voltage (amplitude of 800 V and frequency of 3 kHz).

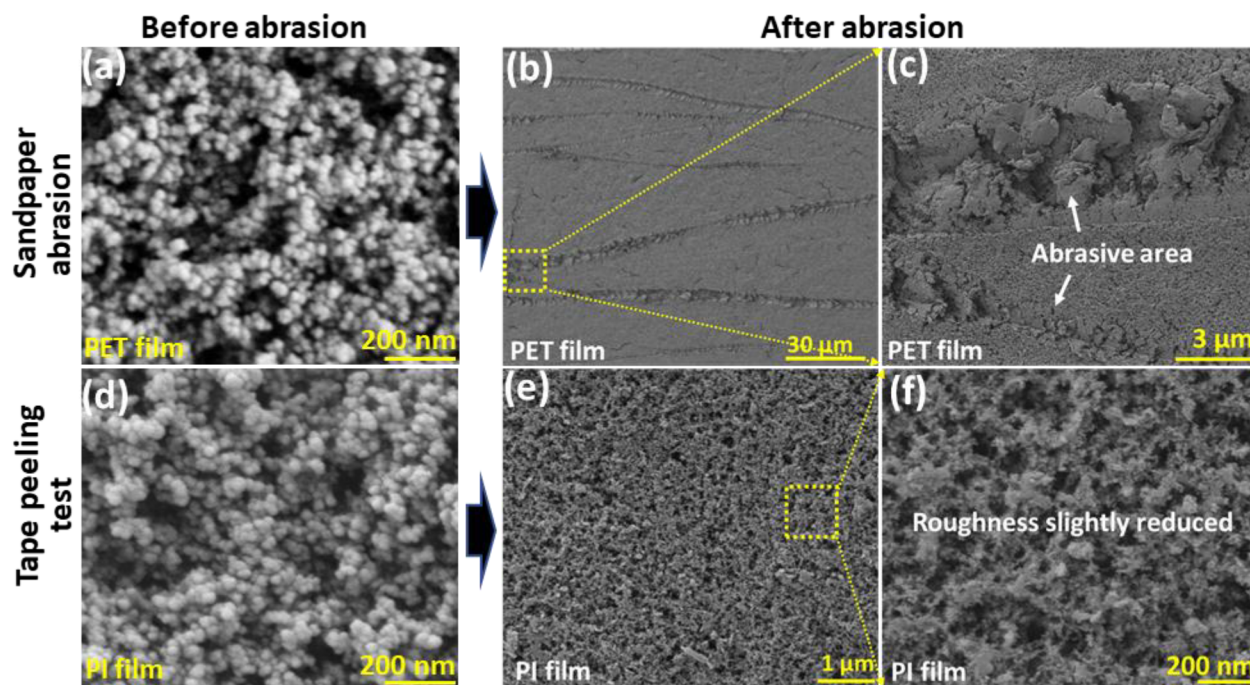


Figure 8. SEM images of the coating layers. (a) High-resolution SEM image of the coating layer on PET film before abrasion. (b) SEM image of the coating layer on PET film after five cycles of sandpaper abrasion with a 200 g weight loading. (c) Enlarged image of the coating layer after abrasion in (b). (d) High-resolution SEM image of the coating layer on PI film before the tape peeling test. (e) SEM image of the coating layer on PI film after nine repetitions of the tape peeling test. (f) Enlarged image of the coating layer after the tape peeling test in (e).

of harsh environmental conditions. To assess the thickness of the coated layer on glass substrates, we investigated cross-sectional SEM images. As shown in Figure 7a, the thickness of the coated layer was $0.87\ \mu\text{m}$ when the conventional method was used. Here, the coating was deposited at the target position for at least 60 s. The thickness may be limited by the insulating nature of the substrate; in that case, as the layer increases in thickness, the efficiency of electro spray deposition decreases. However, when applying AC voltage to the substrate holder, the coating thickness easily increased to $1.91\ \mu\text{m}$, when scanning deposition of the entire substrate was used with a swath spacing of 0.5 cm and scanning speed of 2 mm/s (Figure 7b,c). Figure 7c shows a magnified cross-sectional SEM image of the coated layer.

From the thickness comparison, it is clear that our method offers higher deposition efficiency compared to the conventional method. The deposition efficiency may gradually decrease according to the deposition time. A superhydrophobic coating with a thickness of $1\ \mu\text{m}$ is sufficient to ensure reliability in various harsh environments, and this thickness is easily achieved with the method here.

To evaluate the reliability of the coated layers, we performed sandpaper abrasion and tape peeling tests, as described in Sections S4.4.1 and S4.4.2 (Supporting Information). Even after the physical harshness, strong water repellent characteristics were observed (Movie S3, Supporting Information), and the water CA remained almost the same, as shown in Figures S21 and S22 (Supporting Information). The condition of the coatings before and after the sandpaper abrasion and tape peeling tests was investigated via high-resolution SEM images as shown in Figure 8a–f. Figure 8b,c,e,f show that the superhydrophobic property of the coatings was retained, even after the sandpaper abrasion and tape peeling tests. The coated layer also showed strong UV and chemical resistance, as discussed in Sections S4.4.3 and S4.4.4 (Supporting Information). As seen in

the magnified cross-sectional SEM image of Figure 7c, the deposited layers possessed very small pores, which was useful for hydrophobicity and mechanical reliability against scratches or mechanical friction. As a result of the scratch, the interior of the porous layer was exposed to the nanostructured surface as shown in Figure 8b,c,e,f. Due to the nanostructures, superhydrophobicity remained despite surface damages. Details of the reliability test results are discussed in Supporting Information (Section S4.4).

In addition, the coating layer showed the self-cleaning properties. The contaminated substrates were easy to wash due to the superhydrophobic layer (refer to Movie S4, Supporting Information).

CONCLUSIONS

We demonstrated a new electro spray method, which can significantly increase the deposition efficiency by applying AC voltage to the substrate holder. To explore the deposition mechanism, we measured electric current as well as the electrostatic field of the deposited layers. The measurements showed that the deposition mechanism of our electro spray method differs according to substrate conductivity. In the case of a moderately conductive substrate, such as glass, application of AC voltage to the other side of the substrate enhanced the charge dissipation through the substrate. However, in the case of insulating substrates (PET or PCB substrate), our method allowed deposition of more charged droplets without dissipation of the accumulated charges. Despite the different deposition mechanisms, our method was effective for all kinds of substrates as it enhanced the coating performance in terms of uniformity and reliability. In this case study, we showed that highly reliable superhydrophobic layers can be effectively fabricated on various substrates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c22867>.

S1. The effects of DC voltage on electrospray atomization. S2. Comparative studies of air spray and electrospray methods. S3. Mechanism of the proposed electrospray deposition method. S3.1 Electric current measurement during the electrospray deposition process. S3.1.1 Current behavior during conventional electrospray deposition. S3.1.2 Current behavior during electrospray deposition with AC voltage. S3.2. Electrostatic field measurement. S3.3. The effect of substrate thickness on electrospray deposition. S4. Characterization of the fabricated superhydrophobic layer. S4.1. Wetting analysis. S4.2. Microscopy-based characterization of the coated layer. S4.3. Transparency of the coated layer. S4.4. Durability of the coated layer. S4.4.1. Sandpaper abrasion test. S4.4.2 Tape peeling test. S4.4.3. UV irradiation test. S4.4.4. Chemical durability test with related Supporting Figures (S1–S24); Comparison of spray methods (Table S1) (PDF)

Conventional and proposed electrospray deposition processes (Movie S1) (MP4)

Water repellency test of the coated layer (Movie S2) (MP4)

Reliability test of the coated layer (Movie S3) (MP4)

Self-cleaning test of the coated layer (Movie S4) (MP4)

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Author Contributions

M.K.R. performed all experimental work and prepared the manuscript; S.O. conceived of the idea; S.H.K. performed the experiments; T.H.P. helped to design the circuit for current

measurement; T.N.N. guided the experimental work and improved the manuscript; and K.-S.K. supervised the experimental work and prepared the manuscript.

Notes

The authors declare no competing financial interest.

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