Multifunctional cold spray hybrid coatings on flexible polymers for improved surface properties

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Research Highlights

- Cold spray deposition technique is applied for multifunctional metallization on flexible polymer substrates.
- As-cold sprayed Tin (Sn) deposit is effectively utilized as a metallic interlayer for the subsequent Copper (Cu) over-coating.
- Fabricated hybrid (Sn + Cu) coatings significantly improved surface properties in terms of electrical conductivity, hydrophobicity, and antifouling.
- The antifouling activity of the hybrid coatings is confirmed by the *in vitro* antibacterial tests.

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Abstract

Metallization of polymers, owing to the integration of unique features of dissimilar materials (i.e., polymer + metal), is becoming the central focus in polymer electronics. However, the multifunctional hybrid metallization of polymers in a high-throughput and robust manner remains challenging. In this study, we employ the emerging cold spray (CS) deposition technique to fabricate multifunctional hybrid metal coatings on flexible polymeric substrates. In this regard, Tin (Sn) particles are directly deposited on the polymer (PET) surface as an interlayer followed by the Cu over-coating to achieve hybrid (Sn+Cu) coatings on the polymer surface. The influence of important CS parameters (i.e., spray speed, spray distance, number of the spray pass) on electrical conductivity and film thickness of the resultant coatings are investigated. Moreover, characterizations on microstructure, adhesion strength, water contact behavior, and antifouling performance are conducted to analyze the resulting surface properties. Fabricated hybrid coatings show improved electrical conductivity (5.96×10^5 S.m^{-1}), adhesion strength, and surface hydrophobicity (contact angle ≈ 122°). Moreover, the antifouling activity of the hybrid coating is confirmed by the *in vitro* antibacterial tests in a manner that > 99% of the bacteria were inhibited. This work provides a successful strategy for multifunctional rapid metallization of polymer substrates with improved surface properties.

Keywords: Cold spray, additive manufacturing, polymer metallization, coating, antifouling, flexible electronics.

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1. Introduction

Polymer-based materials have been used for numerous applications owing to their advantageous properties including, lightweight, high specific strength, formability, and corrosion resistance [1,2]. In particular, flexible polymers such as poly(ethylene terephthalate) (PET), polyethylene naphthalate (PEN), polyimide (PI), poly(ether–ether–ketone) (PEEK), and polydimethylsiloxane (PDMS) has become vital for next-generation soft and stretchable printed electronics [3]. However, some major limitations of these polymers including their dielectric nature, poor erosion and wear resistance, low working temperatures (in the case of PET and PEN) [1–3], and vulnerability to UV rays damage [4] prevent their direct use in many electronics applications. Herein, functional metallization on these important materials is an effective solution to utilize them for further applications by improving their physical and mechanical properties [5].

Conventional metallization techniques to fabricate metallic coatings on polymers mainly involve vapor deposition [1,6,7], electroplating [4,6], electroless plating [1,4,8], screen printing [9], sputter coating [10,11], aerosol jet printing (AJP) [12,13], laser-induced metallization [14], and thermal spray [6,15] techniques. Besides their advantages, these methods are often limited by their low deposition rate (e.g., vapor deposition), high processing and equipment cost (e.g., laser-induced metallization,), high process temperature (e.g., thermal spray), and sample size (in case of sputter coating, electroplating, electroless plating) [1,6,7,15]. Although conventional thermal spray methods can achieve thick metal deposits in a high-throughput manner, they often lead to the degradation of the polymer structure due to their elevated process temperatures, resulting in undesired porosity, oxidation, and surface distortion of polymer substrates [7,15,16].

Recently, the cold spray (CS) deposition technique has emerged as a promising thermal spray technique for functional polymer metallization at low operational temperatures against conventional thermal spray methods [16–22]. CS process, owing to solid-state deposition of particles without melting, has intrinsic advantages including minimum or no oxidation of the functional coating and no degradation of the target surface [1,23–26]. In the CS deposition process, micron-scale (5-50 μm) metal particles are accelerated to supersonic speed using a converging-diverging nozzle. Once the particles reach a critical velocity upon impact on a target surface, the particles are plastically bonded onto the substrate surface under the high kinetic energy impact, leading to a dense and high adhesion strength metal coating [23,24,27,28]. Owing to the above-

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mentioned advantages, CS is an appropriate method for the metallization of temperature-sensitive and soft nature materials such as polymers and polymer matrix composites [1,22,25,29]. Through cold spraying, polymers can be metalized using micron-scale feedstock particles such as copper (Cu), zinc (Zn), aluminum (Al), tin (Sn), iron (Fe), and silver (Ag) for improved surface performances in terms of electrical conductivity, antifouling, mechanical, and thermal properties [1,15,30–38].

Recently, obtaining multifunctional coatings via cold spraying has gained significant attention by incorporating various mechanical and physical properties into the target surface. Some of the examples of multifunctional CS coatings include: (i) wear + increased fatigue strength; (ii), electrical conductivity + mechanical resistance; (iii) creep + corrosion resistance [24]; (iv) biocompatibility + antibacterial functionality [39]. In particular, antifouling CS Cu deposits on the metal substrates (e.g., stainless steel, aluminum substrate) were utilized against the recent global COVID-19 pandemic and promising results were reported [40–43]. To our best knowledge, however, most of the studies in the literature mainly focused on achieving antifouling coatings on metal substrates rather than polymers. Considering polymers and polymeric composites have been increasingly applied as structural materials with numerous advantages over metal substrates [2,6,44], it is of high interest to apply cold spray-based metallization on polymer targets to achieve functional antibacterial coatings. Besides, it is vital to produce multifunctional (antibacterial +conductive) hybrid coatings on flexible polymer surfaces to underline the potential of these functional coatings in various applications (e.g., flexible electronics, smart thin films, etc.) as it provides antifouling protection.

In the current situation, however, it remains challenging to achieve multifunctional coatings on flexible polymer substrates by cold spraying. The main reasons are: (i) difficulty in CS deposition of harder metal particles (e.g., Cu) on intrinsically soft polymer surfaces (e.g. PET) at low-process temperatures [45]; (ii) the erosion of the polymer surface during the over-coating of functional materials on the as-cold sprayed metal layer due to material incompatibility [1,45,46]; (iii) degradation of the polymers due to high-speed impact of metal particles under non-optimal process conditions [1]. To address these challenges for developing multifunctional metallization on polymers requires hybridizing the various feedstock materials at optimal CS operational settings.

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The present study is devoted to developing CS-based hybrid coatings on flexible polymers for improved surface properties in terms of electrical conductivity, hydrophobicity, and antifouling performance. First, Tin (Sn) particles are deposited on the flexible polymer (PET) surface to achieve electrically conductive coating. The as-deposited Sn layer is then utilized as an interlayer for the Cu over-coating that provides antifouling functionality on the as-deposited Sn layer. The resulting multifunctional hybrid coatings (Sn + Cu) are thoroughly characterized in terms of electrical conductivity, film thickness, adhesion strength, microstructure, surface wettability, and antifouling performance. The novel contribution of the present work is the systematic investigation of the CS technique to develop multifunctional hybrid metallization on polymer substrates with improved surface properties.

2. Material and Methods

2.1. Materials

As a thermoplastic polymer, Poly(ethylene terephthalate) (PET) sheet (McMaster-Carr, USA, thickness=0.25 mm) was used as the flexible substrate material due to its inherent advantages including low-cost, low surface-roughness, and optical transparency [3,47,48]. Micron-scale quasi-spherical shaped Tin (Sn) (10-45 µm) [49] and irregular-shaped Copper (Cu) (5-45 µm) [8,50] feedstock particles were procured from the Centerline, U.S., and used as received. The morphology of Cu and Sn powders are shown in **Figure 1a** and **Figure 1b**, respectively. Sn was selected as the interlayer coating material due to its soft nature, corrosion resistance, and successful deposition on various polymer substrates [51–53]. Cu powder was used for over-coating material to improve the surface properties in terms of hydrophobicity and antibacterial functionality owing to the superior antifouling characteristics of Cu [20,54,55].

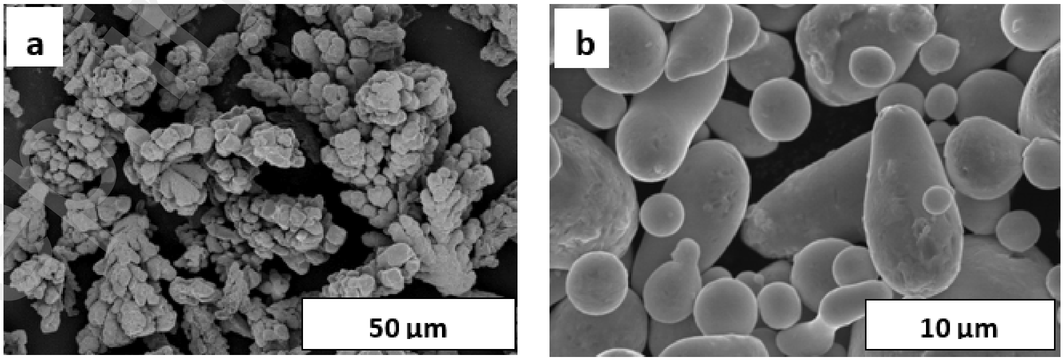

Figure 1. SEM images of the feedstock powders used in the cold spray experiments: **(a)** Cu powders and **(b)** Sn powders.

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2.2. Methodology- (Cold spray particle deposition)

Previous studies reported that continuous electrical conductivity cannot be achieved on thermoplastic polymers (e.g., ABS, Nylon6, PET) through solely cold spraying of Cu particles [8,28]. The reason behind this is the substrate erosion due to the high-velocity impact of intrinsically hard particles such as Cu onto soft-nature polymers, resulting in high porosity and surface erosion [8,56]. Substrate erosion further leads to localized plastic deformation on the surface [57]. The localized plastic deformation envelopes the impinged Cu particles, resulting in a non-uniform and discontinuous Cu layer on the polymer surface, which further prevents continuous electrical conductivity [1,8,52,58]. Alternatively, the difficulties of depositing hard metals (e.g., Cu) can be overcome by first spraying an interlayer of a soft nature with low-melting point metals such as Sn [19,37,59].

Most recently, the authors' group showed that Sn particles can be directly (one-step) deposited on the PET surface at room temperature to achieve robust electrical conductivity [49]. Herein, utilizing the interlayer strategy as shown in Figure 2, CS Cu over-coating can be achieved on the as-deposited Sn layer. As such, hybrid (Sn+Cu) multifunctional metal coatings can be developed on the polymer surfaces for improved surface properties in terms of electrical conductivity, hydrophobicity, and antifouling functionality.

In this regard, Sn and Cu particles are sequentially cold sprayed on the target polymer surface to achieve multifunctional hybrid coatings (see Figure 2). A low-pressure cold spray machine (Rus Sonic K205/407R) was used for particle deposition experiments. The details of the CS experimental setup can be found in our previous work [49]. First, Sn particles are sprayed with an axisymmetric nozzle configuration to metalize the surface in an electrically conductive manner. The as-metallized Sn layer is then utilized as an interlayer to ensure metallurgical bonding of the upcoming Cu particles on the pre-metallized layer. Next, Cu over-coating is performed using a rectangular-shaped nozzle with a larger exit aperture (i.e., 3 mm×10.35 mm) to process a wider area without any alignment problem with the pre-deposited Sn layer. It is noteworthy that, for the fabricated hybrid coatings, Sn coating provides electrical conductivity while the over-sprayed Cu layer improves the hydrophobicity and antibacterial properties of the pre-metallized surface, enabling multi-functional surface properties.

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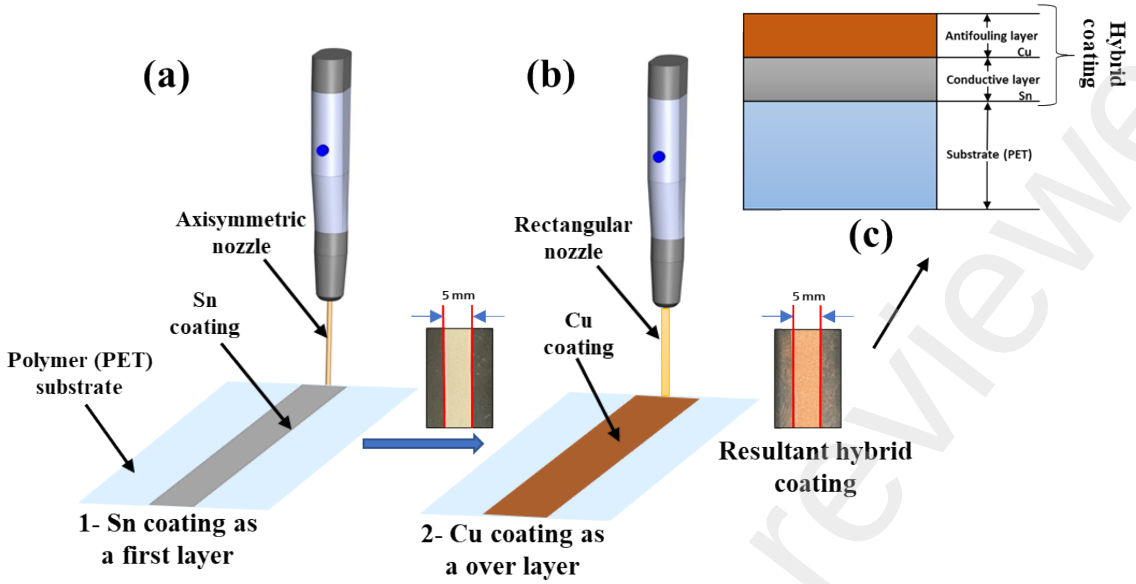

Figure 2. Fabrication process of the hybrid coating: Cold spray deposition of **(a)** Sn particles as the first layer (interlayer), **(b)** Cu particles as the over-coating; **(c)** Cross-sectional schematic view of the resultant hybrid coating.

The CS experiments are performed using the experimental settings listed in Table 1. We adopted the CS operational settings from our previous work [49], in which the process-structure-property relationships of the CS Sn coating on PET surface are uncovered. It is important to note that the present work mainly focuses on investigating and characterizing the cold spray Cu deposition (over-coating) on as-deposited Sn layers to fabricate multifunctional hybrid coatings (Sn+Cu) on a flexible polymer substrate (PET). A detailed study on CS deposition of Sn particles on PET surfaces can be found in the authors' previous work [49].

Table 1. Cold spray process settings used in the experiments.

Parameters	**Sn Coating**	**Cu coating**
Driving gas	Air	Air
Driving gas pressure (MPa)	0.7	0.7
Driving gas temperature (℃)	25	80
Powder feed rate (g/s)	0.2	0.1
Nozzle transverse speed (mm/s)	75	50, 100, 200
Spray distance (stand-off distance) (mm)	10	10, 30, 50
Number of spray pass	1	1, 3, 5

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2.3. Characterization Methods

The electrical resistance of the coatings was measured by the two-point probe method using a digital multimeter (Agilent/HP 34401A) while the sheet resistance properties as analyzed by a four-point probe system (Jandel, RM3-AR). A digital micrometer (REXBETI) with a resolution of 1 μm was used to measure the coating film thickness. The surface morphology, cross-section, and elemental analysis of the resultant coatings were conducted by scanning electron microscopy equipped with an X-ray (EDX) detector (Hitachi S-4800 Field Emission SEM). To evaluate the adhesion properties of the hybrid coating, cross-cut adhesion tests were conducted based on the ASTM D3359 standard [60]. The surface wettability was studied by calculating the water contact angle based on the sessile drop method [61]. Lastly, the antifouling characteristics of the resultant hybrid coatings were evaluated according to the ISO 221961 standard ('Plastics – Measurement of antibacterial activity on plastic surfaces') [62]. All the characterization studies were conducted at room temperature.

3. Results and Discussion

This section, first, characterizes the CS process for achieving hybrid (Sn+Cu) coatings. Second, the microstructure and elemental composition of the resulting coatings are investigated. Next, the electrical conductivity and adhesion strength of the fabricated hybrid coating are evaluated. Lastly, the fabricated hybrid coatings are evaluated for hydrophobicity and antifouling properties.

3.1. Characterization of Cold Spray Process

To investigate the effect of important CS Cu coating parameters (i.e., nozzle speed, spray distance, number of spray passes), a full factorial experimental design was constructed. Three variables at three levels were used to design the experimental studies. The factors are: (i) nozzle speed (50, 100, 200 m/s); (ii) spray distance (10, 30, 50 mm); and (iii) number of the spray pass (1, 3, 5 passes), while the outputs are electrical resistance (Ω) and film thickness (μm). The layout of the experimental design is presented in Table S1 (Supporting Information).

Figures 3a-c show the effect of spray distance and nozzle speed on the electrical resistance of the resultant coatings. An increase in the spray distance (SD) generally results in a decrease in

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electrical conductivity (i.e., higher resistance). It is attributed to falling gas velocity at higher SD, which generally decreases the particle deposition efficiency (DE) [63,64]. The lowest electrical resistance was obtained at SD=10 mm for all the spray conditions. As a notable result, the electrical resistance decreased at larger spray passes (N≥3). A reason for this could be the shock-peening effect due to the Cu over-coating onto the as-deposited Sn layer, which could facilitate the further consolidation of the Sn particles, resulting in a better electrical performance [1,65]. As for nozzle speed (NS), the resistance generally tends to increase at higher NS. It is likely attributed to less-particles impinging onto the pre-metalized (Sn) layer. In detail, fewer Cu particles are shot onto the target surface at higher NS, which alleviates the shock-peening phenomenon, resulting in relatively poor material consolidation.

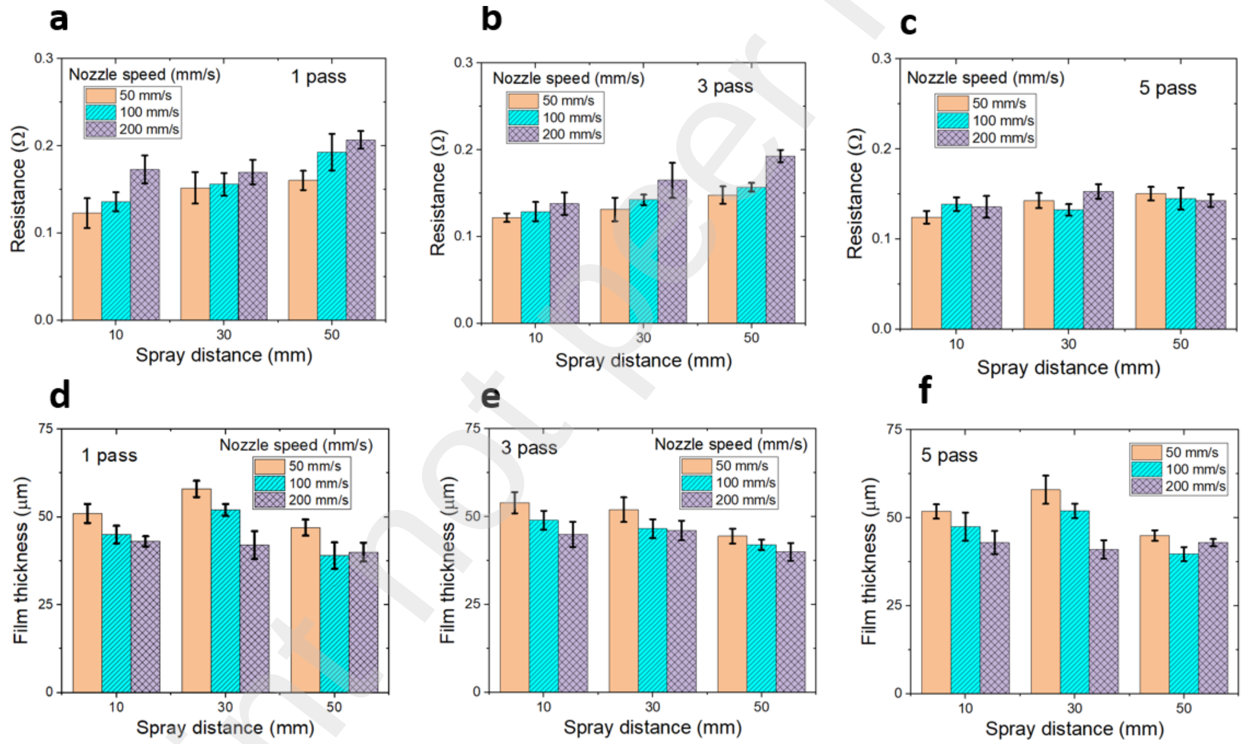

Figure 3. Effect of nozzle transverse speed, spray distance, and the number of passes on electrical resistance and coating film thickness.

Figures 3d-f show the effect of spray distance (SD) and nozzle speed (NS) on the resulting coating film thickness. The results indicate that there is not such a distinct trend between the film thickness and the spray distance. Although the SD longer than a threshold generally negatively affects the deposition efficacy of CS metallization on bare polymers [63,66], we observed that this trend is not followed by the over-CS coating (Cu) on the as-metallized (Sn) polymer surface. The

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reason is likely attributed to metal-to-metal particle interaction that has an intrinsically different bonding mechanism (i.e., metallurgical bonding) than that of CS metallization on polymers (i.e., mechanical interlocking) [1,6]. The authors also experienced the same phenomenon, in which the Sn film thickness on the bare PET polymer decreases in a quasi-linear trend with the increasing SD [49]. In the present study, however, the SD=30 mm led to a larger film thickness than the SD=10 where the N=1 and N=5 pass without following the general trend of CS polymer metallization. On the one hand, the spray distance of SD=50 mm led to the minimum film thickness for all the spraying conditions in Figures 3d-f, obeying the abovementioned trend. It is attributed to falling gas velocity at the higher SD [63,64,67,68], which decreases the particle impact velocity, thereby resulting in a thinner film as compared to the shorter SD (< 50 mm).

As for the NS, the lower NS resulted in relatively thicker metallization on the polymer surface. It can be attributed to the better focusing of the sprayed particles onto a certain area on the substrate at lower NS [67]. Conversely, when the NS is increased, the particles experience a shorter interaction time with the substrate, resulting in a thinner metal film on the target substrate per unit of time [69]. Overall, the minimum film thickness of 39 µm occurred at NS=200, SD=50, and N=3 while the maximum thickness of 58 µm was obtained at NS=50, SD=30, and N=1.

For the number of spray passes (N), the results indicate that the larger spray passes do not ensure thicker Cu metallization on the polymer surface. No significant increase in film thickness at larger spray passes (N>1) was observed for Cu over-coating on the as-metalized polymer surface. It is likely attributed to the potential erosion and/or non-uniformities on the polymer surface under the high-speed bombardment of the Cu particles onto the pre-metallized polymer surface [52,58,65]. As such, layer-by-layer additive manufacturing on the flexible polymer (PET) surface remained very challenging by cold spraying. Taken together, according to the design of experiments, we selected the CS settings for the further characterizations as SD=10 mm, NS=200 mm/s, and N=1 pass by considering the resulting coating's low-electrical resistance with less standard deviation, moderate coating thickness, and high-speed processing.

3.2. Microstructure Characterization

SEM characterizations in **Figures 4a-d** were carried out to evaluate the microstructure of the resultant coatings at optimal CS conditions. As seen in **Figure 4a,** no continuous and dense Cu coating was achieved on the bare PET surface. Instead of deposition, Cu particles severely eroded

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the polymer surface during cold spraying, resulting in high porosity (see **Figure 4a**). The authors also experienced the same phenomenon when cold spraying Cu on other thermoplastics such as ABS and Nylon 6 [8,28]. The reason lies in the severe localized erosions on the polymer surface due to the high-speed impingement of intrinsically hard Cu particles onto the soft thermoplastic polymers, which results in no continuous electrically conductive coating [6].

On the other hand, as shown in **Figure 4b**, a compact and dense hybrid metal (Sn+Cu) coating was achieved on the PET surface by utilizing as-metalized (Sn) film to be an interlayer for the subsequent Cu over-coating. Note that the as-deposited Sn layer increased the rigidity of the polymer, enabling the metallurgical bonding of Cu particles onto the metalized (Sn) substrate surface. As such, a micro-rough surface was obtained by metallurgically bonding the Cu particles onto the pre-deposited Sn layer (**Figure 4b**). Considering the fact that surface roughness has a positive influence on the interactions between substrate and foulant molecules [70,71], the resulting hybrid coating could be promising for antifouling applications.

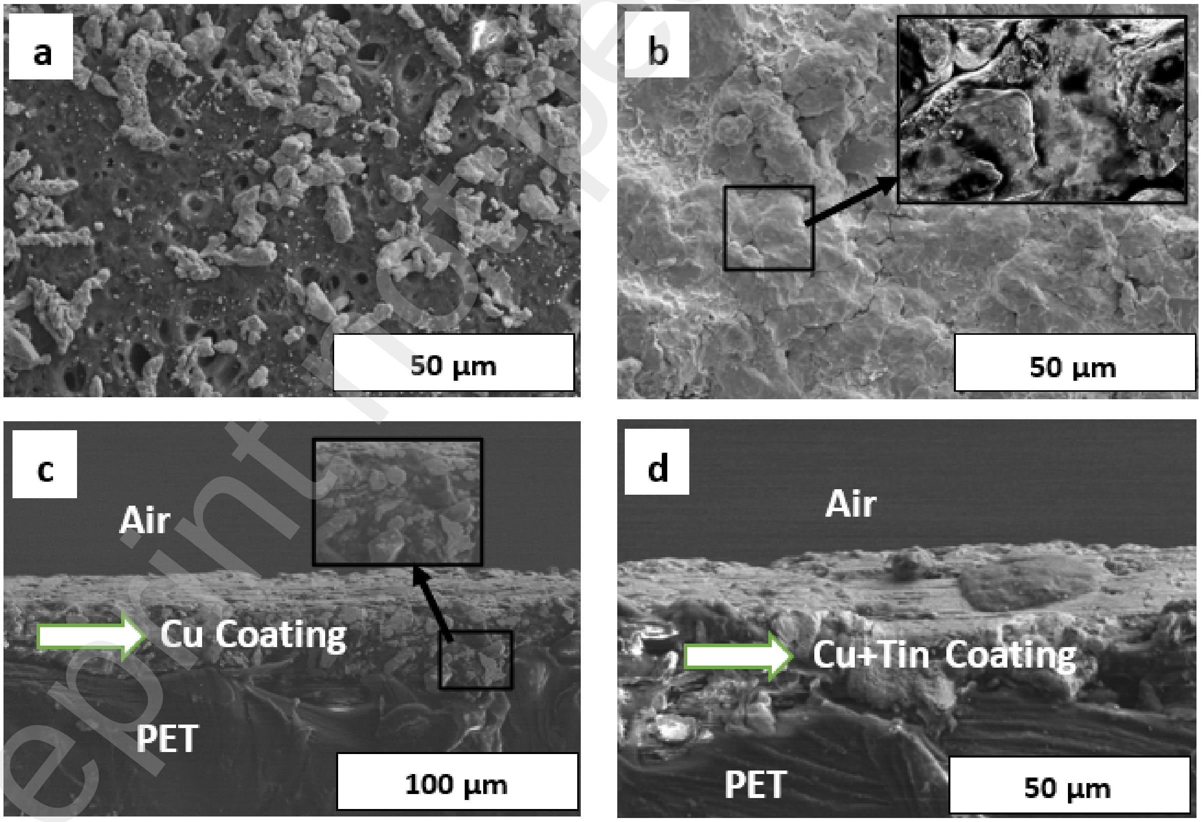

Figure 4. Surface SEM images of **(a)** Cu coating and **(b)** Hybrid (Sn+Cu) coating; Cross-sectional SEM images of the **(c)** Cu coating, and **(d)** hybrid coating.

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We further investigated the microstructure by analyzing the cross-section of the CS deposits. **Figure 4c** and **Figure 4d** show the cross-section view of solely Cu coating and hybrid (Sn+Cu) coating on a PET surface, respectively. It can be clearly seen in **Figure 4c** that although Cu particles impinged onto/into the bare PET substrate, a consolidated dense coating was not achieved. It is attributed to the discontinuous particle impingement onto/into the target surface, which could not constitute a dense metal deposition. As seen in **Figure 4a**, instead of continuous deposition with self-bonding Cu particles severely eroded the polymer surface, which resulted in high porosity. On the other hand, Cu particles are successfully bonded on the pre-deposited Sn layer which produced a self-bonded and dense hybrid coating structure on the PET surface (see **Figure 4d**). Given these results, the Sn layer effectively served as an interlayer to facilitate the Cu deposition on a soft polymer (PET) surface, which is not applicable on a bare PET surface by solely cold spraying Cu particles.

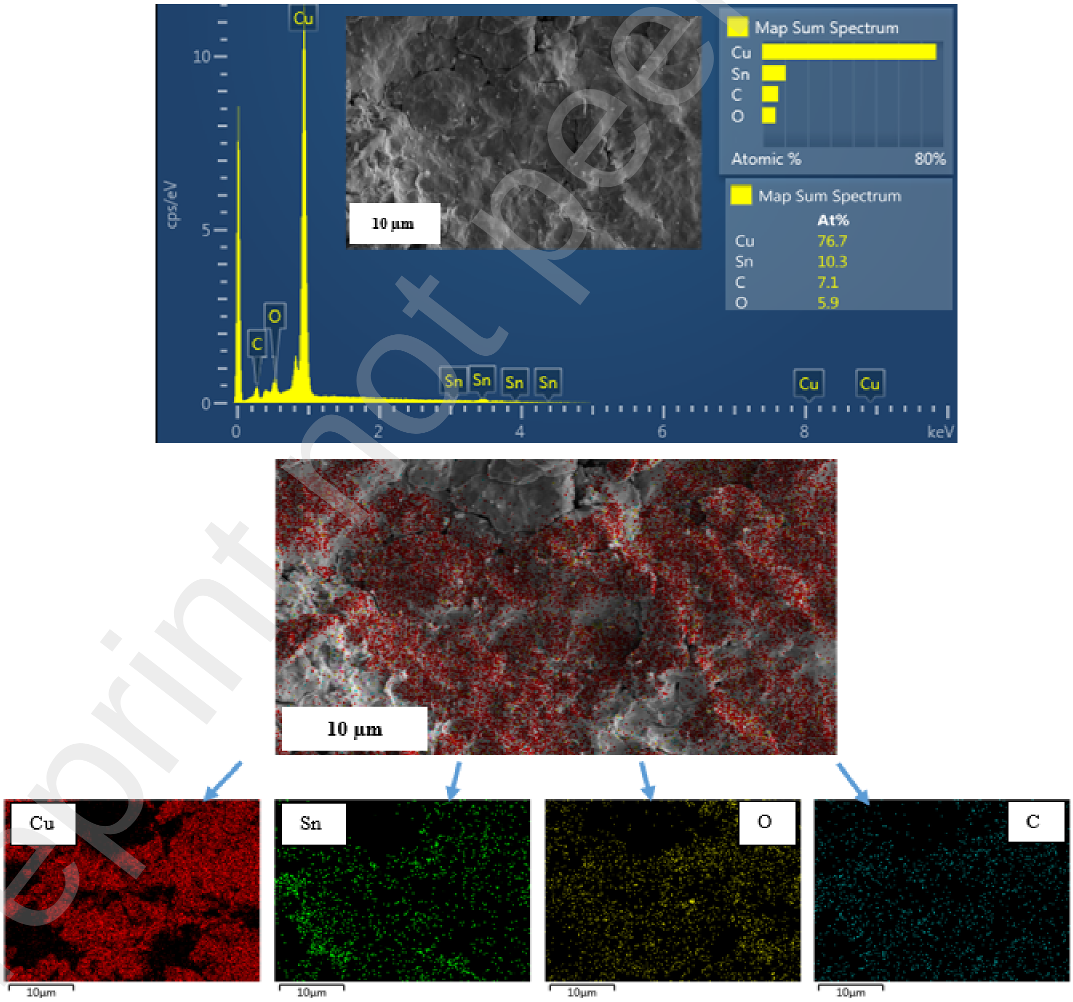

Figure 5. EDX analysis of the hybrid (Sn+Cu) coating.

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EDX results of the hybrid coating on the PET sample are also given in **Figure 5** in terms of atomic percentage (At %) (top panel) and elemental distribution map (bottom panel). According to the EDX analysis results, the main elements on the coated PET surface are copper, tin, carbon, and oxygen, having the atomic ratio (at%) of 76.7% Cu, 10.3% Sn, 7.1% C, and 5.9% O, respectively. As such, EDX results suggest that the PET surface was successfully coated with Cu and Sn particles. It can also be seen that the fabricated hybrid coating has some amount of oxide content. The reason for this could be the formation of the oxide layer on the resultant coating over the storage time. Overall, the results reveal that employing Sn deposit as an interlayer could help to achieve Cu over-coating, which could further improve the surface properties in terms of hydrophobicity and antifouling. Thus, the following subsections accordingly discuss the electrical performance, hydrophobicity, and antifouling properties to better understand and test the multifunctionality of the resultant hybrid coating.

3.3. Characterization of the electrical conductivity and adhesion strength

In this section, CS-based fabricated hybrid coating on the PET polymer substrate was characterized for electrical conductivity and adhesion strength. For this purpose, a red color light-emitting diode (LED) light was assembled on the circuit using a silicone adhesive. **Figure 6a** illustrates the CS hybrid coating on the flexible polymer substrate under various deformations. As seen in **Figure 6a**, the circuit remained highly conductive even under severe bending and twisting deformation, which indicates high adhesion and stability of the resultant coatings. Also, as seen in **Figure 6b,** we observed the relative resistance (R/R_o) change of the electrodes for 30 days of storage. The resistance did not increase more than 20% over a one-month storage period, indicating the long-time stability of the resultant hybrid coating.

The electrical resistivity of the resultant hybrid coating was calculated using **Eq.1** where 4.532 is the correction factor, R_s is the average sheet (Ω/sq), and t is the thickness (µm) of the metal film [72]. The average sheet resistance (R_s) of the resulting coating was measured as 0.0074 Ω/sq using a 4-point probe system at a constant current of 100 mA. Hence, the resistivity of the fabricated hybrid coating on the flexible PET surface was calculated as 1.677×10^{-6} Ωm, where the CS conditions are SD=10 mm, NS=200 mm/s, and N=1 pass. The resistivity results indicate a high-electrical performance to utilize the multifunctional hybrid coating on the PET polymer for flexible electronics applications.

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$$P = 4.532 \times R_s \times t \tag{1}$$

Lastly, we characterized the adhesion strength of the hybrid coating according to the ASTM D3359 cross-cut tape test method [60], and the results were evaluated based on the ASTM tape test scale. According to the cross-cut tape test, the hybrid coating achieved a score of 5B level, having less than 5% removed area on the coating (see **Figure 6c**), indicating a strong interfacial adhesion strength.

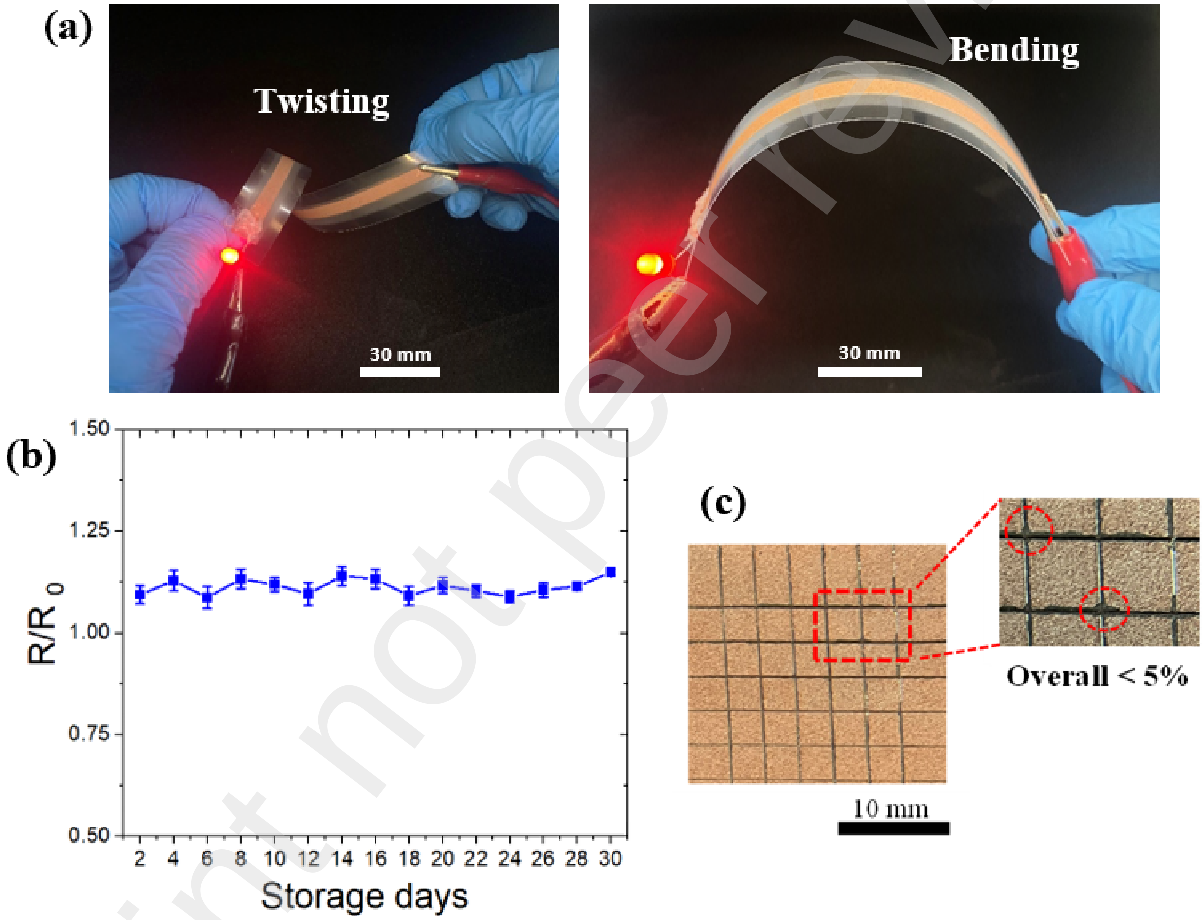

Figure 6. (a) Testing the electrical stability of the fabricated hybrid coating under different mechanical conditions of twisting (left panel) and bending (right panel), **(b)** The relative resistance (R/R_0) change of the hybrid coating with storage days; (Electrode length=20 mm and width=5 mm), and **(c)** Cross-cut adhesion test results.

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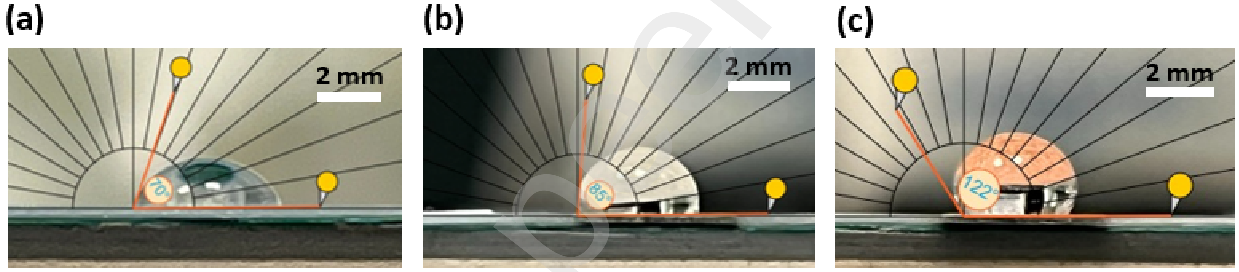
3.4. Water Contact Behavior

Water contact angle (WCA) data of the bare PET, solely Sn coating, and hybrid coating (Sn+Cu) on the PET samples is investigated to characterize the surface wetting properties. As seen **in Figures 7a-c**, the contact angle of bare PET, Sn-coated, and hybrid-coated PET surfaces were recorded as 70°, 85°, and 122°, respectively. As compared to solely Sn-coated polymer, the Sn+Cu-coated polymer surface turns out to be hydrophobic (contact angle > 90°), which is attributed to the hydrophobic nature of Cu deposits [73–75]. The hydrophobicity of the resultant hybrid coating can be explained as a result of reduced surface energy due to the dendritic-shape morphology of the Cu particles (see Figure 1a) [73] and the micro-roughness of the resultant coatings [75]. The results are comparable with the literature, in which CS Cu deposits on metals, glasses, and ceramics improved surface hydrophobicity [42,76,77].



Contact angle (deg.)	PET	Sn coated PET	Sn+Cu coated PET
	70°±15	85°±10	122°±10

Figure 7. Water contact behavior of the **(a)** bare, **(b)** Sn coated, **(c)** hybrid (Sn+Cu) coated PET samples (Cu weight ratio is 70 wt% for the hybrid coating).

Up to here, in the over-coating CS experiments, we used a Cu content (i.e., weight ratio) of 70 wt%. Here, we also studied the effect of Cu content on the surface wetting characteristics of the hybrid coating. It is clear in **Figure 8** that the Cu weight ratio affects the surface hydrophobicity. To elaborate, an increase in the Cu content from 15 to 70 wt% led to larger water contact angles. The water contact angle increased from 85° for the as-Sn coated PET (control substrate) to 130° for the hybrid coating with 70 wt% Cu. The results suggest that the hybrid coating significantly improved the hydrophobicity of the bare PET surface, thereby having the potential for such applications where surface hydrophobicity is desired such as antifouling and self-cleaning surface applications.

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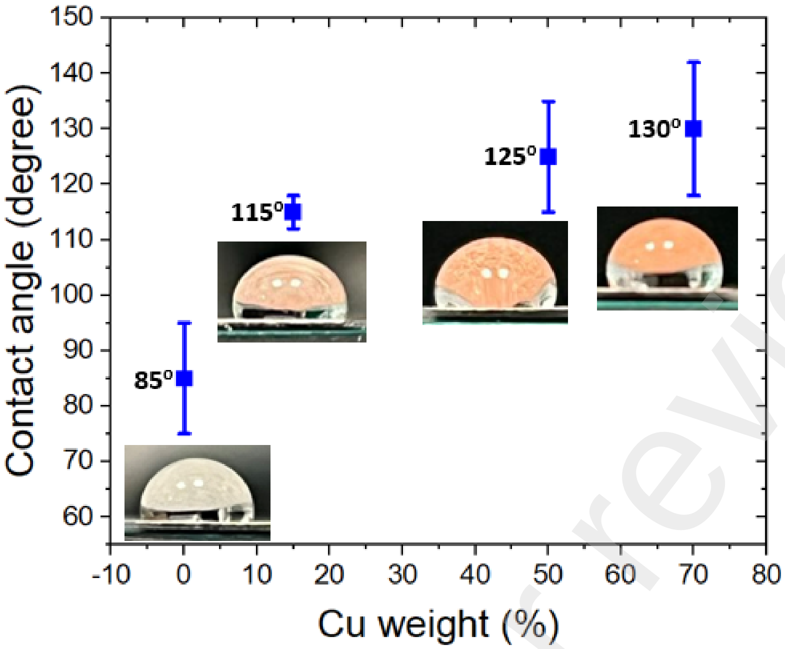

Figure 8. Contact angle variation of the hybrid coatings with different Cu weight ratios.

3.5. Antifouling Properties

The antifouling functionality – a protection when the surface is in contact with different foulants such as proteins, bacteria, and marine organisms - is an important and desired surface property in such applications where the foulant-repelling coating is of great necessity [39]. Herein, the antifouling performance of the developed hybrid coatings was assessed by examining the inhibition of bacterial growth on their surfaces. The antibacterial activity of the coatings was tested using Escherichia coli (*E. Coli*) and Staphylococcus aureus (*S. aureus*) bacteria, which are widely used in the antifouling test for various surfaces [78–80]. Testing was modified from the standard methods of the International Organization for Standardization [ISO 221961; 'Plastics – Measurement of antibacterial activity on plastic surfaces']. Six specimens (50 cm × 50 cm) with Sn-coated PET surface were considered as the untreated and bacterial viability control groups. In addition, three samples of the same dimensions for hybrid coatings (Sn+Cu) serving as the treatment group were prepared. Detailed information regarding the antibacterial test procedure is presented in the Supporting Information of this work. The treated and untreated samples were then placed in the incubator at 35°C for 24 hours to evaluate the test results.

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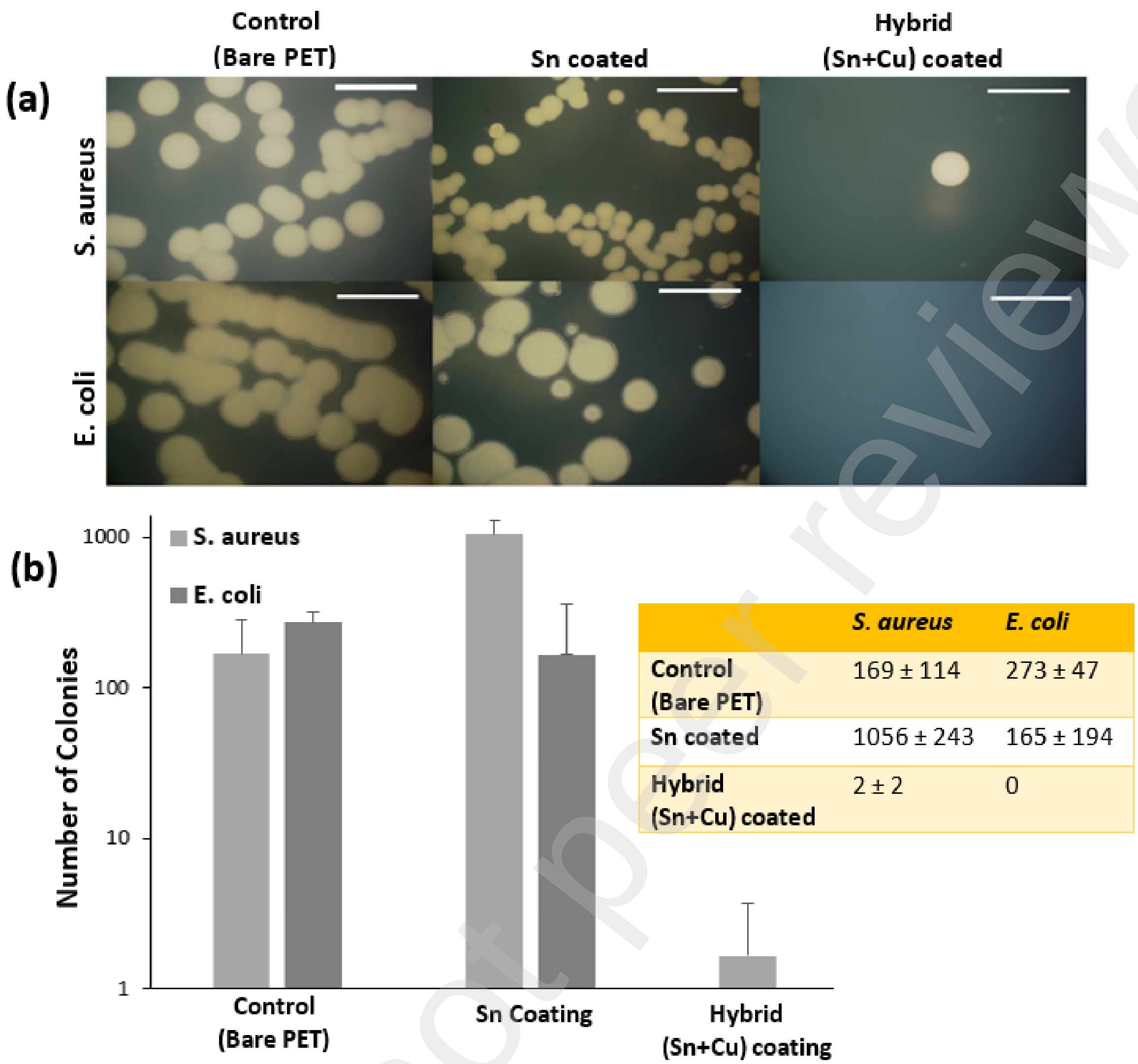

	S. aureus	*E. coli*
Control (Bare PET)	169 ± 114	273 ± 47
Sn coated	1056 ± 243	165 ± 194
Hybrid (Sn+Cu) coated	2 ± 2	0

Figure 9. Antibacterial characterization of the cold spray coated surfaces against *S.aureus* (top panel) and *E.coli* (bottom panel) **(a)** Bacteria culture of fluid from the surface of hybrid coating and controls after 24 hours of incubation (scale bar is 2 mm), **(b)** Bacterial growth on the surfaces and the average number of colonies produced with standard deviations (all experimental groups have an n=3).

The antibacterial qualities of the various coatings are demonstrated in **Figures 9a-b**. **Figure 9a** shows portions of the agar plates after bacteria culture. As seen in Figure 9a, there were thick groupings of bacteria for the control and Sn-coated surfaces demonstrating that most of the streaked bacteria were still viable. On the hybrid coating surfaces, the handful of viable colonies produced by *S. aureus* and these colonies were isolated. **Figure 9b** shows the count of the colonies produced from culturing the bacteria from the surfaces of the test specimens. Despite the bacteria growing on both the control group and on the Sn-coated surface, only a negligible amount of either

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bacteria strain survived 24 hours of exposure to the hybrid coating surface. In the case of *S. aureus,* only a handful of bacteria survived to be able to produce colonies and for *E. coli* none of the bacteria were still viable after 24 hours. The antibacterial test results indicate that ~100% of the bacteria were already extinguished by the CS-based hybrid coating on the PET surface after 24 hours of exposure. The disappearance of bacterial colonies shows that CS Cu over-deposits demonstrate superior antibacterial potential owing to the increased surface hardness during the CS process, which led to significant Cu ion diffusion to inhibit the bacteria [81]. The *in-vitro* antifouling test revealed that the Cu-over coating on the Sn layer showed a promising antifouling performance by resisting the colonization of bacteria, resulting in inhibiting ~100% of the bacteria colony.

4. Conclusions

In this study multifunctional hybrid metallization on a flexible polymer (PET) via cold spray (CS) technique was comprehensively studied to improve the surface properties in terms of electrical conductivity, hydrophobicity, and antifouling performance. In this regard, first, the Sn particles were directly cold sprayed to achieve electrically conductive coating on the polymer surface. The subsequent Cu deposition ensured the hydrophobic and antifouling over-coatings without compromising the electrical conductivity of the pre-deposited Sn layer. The following results can be drawn from the present work:

- Utilizing the metallic interlayer strategy, the Cu particles can be successfully over-deposited on the pre-metallized (i.e., as-Sn coated) polymer surface to achieve hybrid (Sn + Cu) multifunctional metal coatings (i.e., electrically conductive + hydrophobic + antibacterial).
- The resulting hybrid coatings showed excellent electrical conductivity (5.96×10^5 $S.m^{-1}$), flexibility, stability, and adhesion strength under various deformation conditions (i.e., bending, twisting).
- Cu over-coating significantly increased the surface water contact angle as compared to Sn coated surface (from 85° (Sn coated PET) to 122° (hybrid coating)), ensuring hydrophobic surface characteristics.
- An increase in the Cu weight ratio of the over-coating led to a higher water contact angle (1 30°), indicating better hydrophobic properties.

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- *In-vitro* antibacterial test results revealed that the fabricated hybrid coatings can inhibit >99% of bacteria.
- Overall, this study unrevealed the immense potential of the CS technique for producing multifunctional hybrid metallization on flexible polymers in a rapid, high-throughput, and effective manner. Therefore, this study can be potentially applied to various areas including printed electronics, smart thin films, polymer sensors, multifunctional hybrid electronics, and many more.

CRedit Authorship contribution statement

Duygu G. Ruzgar: Conceptualization, methodology, formal analysis, investigation, design, experiments, characterization, data curation, application, writing manuscript
Semih Akin: Conceptualization, methodology, experiments, investigation, characterization, data curation, writing manuscript
Seungjun Lee: Experiments, characterization
Julia Walsh: Antifouling characterization, writing manuscript
Hyowon (Hugh) Lee: Antifouling characterization, supervision, review & editing
Martin B.G. Jun: Conceptualization, methodology, resources, supervision, review & editing
All authors commented on the manuscript.

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