INVESTIGATING THE BACTERIA REPELLENCY AND DURABILITY OF THE FABRICATED SUPERHYDROPHOBIC COATINGS OH HIGH DENSITY POLY-ETHYLENE BASED FOOD CONTACT SURFACES

A Thesis

by

YASHWANTH ARCOT

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee: Mustafa Akbulut
Committee Member: Svetlana Sukhishvili
Committee Member: Melissa A. Grunlan
Department Head: Ibrahim Karaman

May 2021.

Major Subject: Materials Science & Engineering

ABSTRACT

Large epidemics of foodborne illness in the recent times have substantially increased the concerns over hygienic processing and, packaging environments in the food industries. Lack of maintenance and poor sanitation of the food contact surfaces result in air and, food-borne microbial attachment, contamination and, biofilm formation. With the increasing concerns over food safety and hygiene both for industries and consumers, it is important to keep the FCS bacteria-free, to protect the consumers from various foodborne illnesses. To resolve this problem, we plan to modify high-density polyethylene, one of the most common materials to make FCSs, used in the food industry, to manufacture of conveyor belts, storage boxes, cutting pads, and knives, using durable and superhydrophobic coating materials to prevent the formation of notches, cracks, and scratches on the surfaces that occur due to continual use, which aggravate the possibility of bacterial adhesion and cross-contamination on these HDPE based FCSs. The fabricated, highly durable, nano-diamond-based coatings on HDPE combined chemisorption of low surface energy organoflurosilane and rigid nanotexturing, achieved a static water contact angle greater than 150^{o}, and demonstrated excellent mechanical durability with water-repellency sustained after 10,000 cycles of onion peel, and spinach leaf abrasion and, fifty cycles of sand abrasion. In comparison to the bare HDPE surfaces, the coated substrates showed over 97.75% reduction in the bacterial adhesion against *Salmonella* Typhimurium LT2 and *Listeria innocua,* two of the most common foodborne bacteria, predominantly transmitted by food contamination. Also, the coated substrates successfully reduced the cross-contamination of *Salmonella* Typhimurium LT2 and *Listeria innocua* by contaminated spinach leaf significantly. With this, we prove that these durable coating mechanisms can significantly contribute to reduce the potential bacterial contamination and cross-contamination by FCS in the food processing environment. Overall we demonstrate that these coated HDPE substrates could significantly help in improving the hygiene and safety in the food processing environment.

Keywords: Food Safety and Hygiene, Nanodiamond, Food Contact Surfaces, Superhydrophobic, Food-borne Bacteria, High Density Poly-ethylene

NOMENCLATURE

WHO	World health organization
CDC	Centers for Disease Control and Prevention
FCS	Food Contact Surface
HDPE	High Density Poly-ethylene
ND	Nanodiamond
THFS	Trichloro(1H,1H,2H,2H-heptadeca-fluorodecyl) silane
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy

CONTRIBUTION AND FUNDING SOURCES

Contributors

Part 1: faculty committee recognition

This work was supervised by committee consisting of Dr. Mustafa Akbulut, Associate Professor, Artie McFerrin Department of Chemical Engineering, Texas A&M University,as the chair of my committee and, Dr. Sukhishvili, Professor, Materials Science & Engineering, Texas A&M University and, Dr. Grunlan as committee members, Professor, Biomedical Engineering Texas A&M University.

Part 2, student/collaborator contributions

All the work for the thesis was completed by the student in collaboration with Shuhao Liu, Michael Bae, William DeFlorio, graduate students from Artie McFerrin Department of Chemical Engineering.

Funding Sources

The Dissertation was funded by Food Manufacturing Technologies Program, from the USDA National Institute of Food and Agriculture

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

1. INTRODUCTION

a. Background on Food-Contamination

Food contamination is referred to as the presence of physical, chemical and, microbial contaminants on food[1,2]. Of which, microbial contamination is the most common and hazardous form, caused either my natural contamination of raw materials or, by cross contamination through carriers such as air, water, and, due to human and animal contact. Food contamination is a serious health hazard all over the world[3].

Unsafe and contaminated food account for more than 200 illnesses among consumers. Globally, about 600 million people become ill after consuming contaminated food, causing 0.42 million deaths on an annual basis[4]. The United States CDC, 2020, predicts that annually there are 250 foodborne diseases, caused due to contaminated food being consumed by people in the US[5]. Moreover, food-borne illnesses have huge economic impact on low and medium income countries, costing around $110 billion annually (World Bank Study, Washington DC, 2018). Recently, in August 2020, the CDC reported outbreak of Salmonellosis caused due to mass cross-contamination in red, yellow, white, and sweet yellow onions at one of the major onion exporting firms. This outbreak infected 1,127 consumers and 167 hospitalized cases.

Most of the foodborne diseases are caused by some common bacteria such as Salmonella [6–8], Staphylococcus aureus [9,10], Escherichia coli[10,11] and, Listeria[12]. These strains reside on the surfaces forming thick layers (ranging from few micrometers to several millimeters) called biofilms[13], and contaminate any organic materials that come in contact with them. Thought the cause for initial attachment of these bacteria is weak electrostatic interaction and Van der Waals' forces, the growth of the biofilms on the contact surfaces rapidly increases by physical attachment of the cells by complex polysaccharide[14,15]. The biofilms can survive on the contact surfaces for several days under favorable growing conditions[16].

b. *Food-contamination through Food Contact Surfaces*

A large proportion of food contamination by disease-causing bacteria, is associated with the contamination of FCSs. Improper and insufficient sanitization of the FCSs is one of the main cause for microbial growth and biofilm formation[17]. All strains of the gram negative *Salmonella*, are considered to be human pathogens. Every year, there are about 1.2 million confirmed cases of Salmonellosis, caused due to *Salmonella spp.*[18]. Balakrishnan, et.al., reported the possibility of severe contamination of the poultry birds' meat, with *Salmonella*, when unhygienic practices which include, unclean water, wooden tables, knives, and hands, used during their slaughtering[19].

Listeria monocytogenes, one of the most common strain of bacteria found in smoked fish, cooked meat, poultry produts,etc., spreads rapidly due to contaminated FCSs[20]. *Listeria monocytogenes,* can survive over a large range of temperature, from -7ºC to body temperatures. Hence, cross contamination of *Listeria* through FCSs is one of the main concern to be addressed in the food-processing industries as they can survive on fresh fruits and vegetables and frozen foods.

c. *High Density Poly-ethylene based Food Contact Surfaces*

HDPE, one of the most common materials used to construct FCSs, is extensively used in conveyor belts, storage boxes, cutting pads, and cutter blades in the food processing industry [21]. As food remains in contact with HDPE surfaces for longer times, as long as, up to 48 hours on conveyor belts or in packing boxes, there is an elevated risk of biofilm formation. Biofilms, strongly adhere to the FCSs hence, cannot always be removed by the common surface cleaning procedures[22]. HDPE substrates, with their low surface strengths and higher wear rates when compared to metal substrates, surface sanitization procedures such as aerosolized sanitizers[23], high pressure and vacuum, cold plasma[24], and UV-light and ozone surface treatments[25], become difficult around defects, cracks, and pits on FCSs and is greatly affected by the roughness of the surfaces[26]. Moreover, due to the increase in the surface area and formation of small pits or pockets on the surface where the bacteria could reside, the bacterial adhesion increases in and around these regions[27].

d. Methods to Prevent Biofilm Formation Using Anti-Bacterial Materials

Since bacterial adhesion is the first step towards its proliferation, it is important to arrest proliferation after its contact with the surface[27]. Continuous sanitization using common sanitization practices like, the use of chlorine, could contaminate the fruits and vegetables with trihalomethanes which could be a risk to consumer's health. Moreover, the bacteria develop antibiotic resistance due to the use of such chemicals for sanitization[28].

To overcome this issue, it is important to build smart contact surfaces that could attempt to prevent the first step, i.e., bacterial adhesion. This includes modification of the surfaces using antibiotic/antimicrobial agents like silver ions[29,30], anti-bacterial polymeric acids[31] and some organic oils[32]. For instance, Khan et.al., had used poly(quaternized-4-vinylpyridine-co-acrylic acid) to fabricate anti-microbial surfaces which ensured contact killing of *Escherichia coli* and *Staphylococcus aureus* by more than 90%[31] and, Dogan et.al., fabricated anti-bacterial coatings on polymeric packaging substrates using silver and zinc zeolites which displayed anti-bacterial property against *Escherichia coli* significantly[33]. Though these antibacterial coatings effective, they have loading limitations and over time, bacteria could develop resistant towards these anti-bacterial materials.

e. Applications of Superhydrophobic Surfaces

An enduring approach to develop to prevent bacterial adhesion, reducing the need for sanitization and lowering the maintenance costs of the FCSs is to develop superhydrophobic (SPH) coatings for FCSs, which display a static water contact angle greater than 150^{o}[34]. SPH surfaces are extensively being used as anti-icing[33], anti-fouling[33], drug delivery[33], textiles[35], oil-water separations[33,35] etc. Recently, the development of novel coating techniques for FCSs with proper surface texturing has been a significant area of research focus and investment by the food processing industries [36,37]. The synergistic combination of nanotexture and surface chemistry is the main principle behind the formation of SPH coatings. The control of FCS's surface chemistry involves the presence of nonpolar ligands or moieties on the surface which impart hydrophobic characteristics to surfaces with flat geometries[38–40]. The hierarchical features created on the surface of SPH coatings trap a layer of air (meta-stable air bubbles) that inhibit surface wetting and thus bacterial adhesion[41]. In the past decade, a few methods have been proposed to obtain SHP surface

coatings on to HDPE surfaces[42,43], however, durability has remained a major challenge. This has limited their efficacy of FCS applications. HDPE-based FCS, used as cutting boards and packaging boxes are continuously exposed to mechanical stresses during their use. This increases the possibility of the formation of notches, cracks, and scratches. For this reason, in addition to superhydrophobicity, the FCSs need to be mechanically durable, requiring minimum maintenance.

f. Carbon-based Materials on Superhydrophobic Surfaces

Activated carbon-based materials such as graphene[44], carbon nano-fibers[45], nanodiamonds[46] have emerged as extremely promising materials to provide surface strength, roughness and functionality to build durable superhydrophobic surfaces. Nanodiamonds (NDs), with excellent mechanical strength, high aspect ratio, and biocompatibility have been extensively used in biomedical applications such as bio-sensing, drug delivery[47–50], and anti-bacterial applications [51,52]. With recent developments in the large-scale detonation synthesis and chemical vapor deposition (CVD) methods, the price of industrial-grade nanodiamond has significantly decreased to approximately \$0.1–\$2.0 per gram[53]. The utilization of diamond microparticles in the construction of ultrahigh durability industrial tools is well established at the commercial scale. The use of NDs to prepare superhydrophobic FCSs may be one approach to satisfy the durability requirements of the food industries.

2. PURPOSE OF THIS STUDY

Hence, we attempt to investigate, the use of ND based bacteria-repellent coatings on HDPE surfaces to create durable, bacteria-free FCSs. NDs could be used to provide robustness, surface strength, and texture. The polymerization of 3-hydroxytyramine to poly-dopamine (PDA), can improve the apparent chemical reactivity of the NDs deposited on HDPE surfaces. The further modification of PDA coated ND surfaces using THFS, shall provide non-polar functionality on the surfaces along with nanoscale topographic features. The texture of the surfaces could be optimized in such a way that there is enough meta-stable trapped air to promote water-repellency. Chemical characterization of the coating mechanisms will be done using ATR-FTIR. The water-repellency of the surfaces will be measured using the sessile drop technique via optical tensiometry. Bacterial anti-adhesion properties of the fabricated surfaces and cross contamination by spinach leaf were demonstrated using bacterial enumeration on the substrate via FESEM. Both gram-negative *Salmonella* Typhimurium LT2 and gram-positive *Listeria innocua* bacteria shall be utilized. The mechanical durability of the coated surfaces can be tested by surface scratching using two layers of spinach leaves and, onion peels for 10,000 cycles under different forces, and sand drop for 50 cycles.

3. MATERIALS AND METHODS

a. Preparation of HDPE Surfaces

Pristine HDPE samples (2 cm × 2 cm, Small Parts, Inc., Plymouth, MI, USA) were washed with flowing Milli-Q water (with resistivity- 18.2 MΩ cm) and placed in a hot-air oven until dried. Each surface was then washed with isopropyl alcohol (Millipore Sigma, Burlington, MA, USA) and further treated with 18-Watt air plasma (PDC-32G (115 V); Harrick Plasma, Ithaca, NY, USA) for 2 minutes to clean the surface and to improve the surface fixation of ND particles on the HDPE through physisorption.

b. Deposition of ND on HDPE Samples

ND particles of 100 nm average diameter (Henan Union Precision Material Co., Ltd., China) were used to prepare a 1% w/v dispersion in ethanol (Koptec Ethanol, VWR, Philadelphia, PA, USA), using a probe-type ultra-sonic homogenizer (SJIA-2000W; Ningbo Haishu Sklon Electronic Instrument Co., Ltd., Ningbo, China) for 30 minutes. The dispersion was deposited onto the HDPE samples using the drop-casting technique to ensure that the entirety of each sample was uniformly covered by ND. The HDPE samples with physiosorbed NDs were then placed in a vacuum oven for 6 hours at 90 ^{o}C. The oven temperature was then increased to 145°C and held for 2 hours to fuse the ND particles onto the HDPE surface by infusion. The samples (ND-HDPE) were washed with ethanol 5 times to remove any unattached or loosely fused NDs and dried at room temperature, 25 ^{o}C, for 12 hours.

c. PDA Coated ND-HDPE Surfaces

To improve the number of reactive surface groups on ND-HDPE, the surfaces were treated with 18-Watt air plasma for 2 minutes. 100 μg/mL of hydroxytyramine hydrochloride (PDA; TCI chemicals, Montgomeryville, PA, USA) was added to an aqueous solution of 0.01M of tris (hydroxymethyl) hydrochloride (pH 8.0) (Acros Organics, Fair Lawn, NJ, USA). 20 mL of this solution was transferred to a 50 mL beaker and subjected to vigorous stirring at room temperature using a magnetic stirrer until the PDA dissolved[54]. The air plasma-treated ND-HDPE samples were then submerged in this PDA solution and allowed to react for 24 hours without any heating, under

mild agitation. The thus formed PDA-HDPE samples were then removed and rinsed using Milli-Q water 3 times to remove any unreacted PDA.

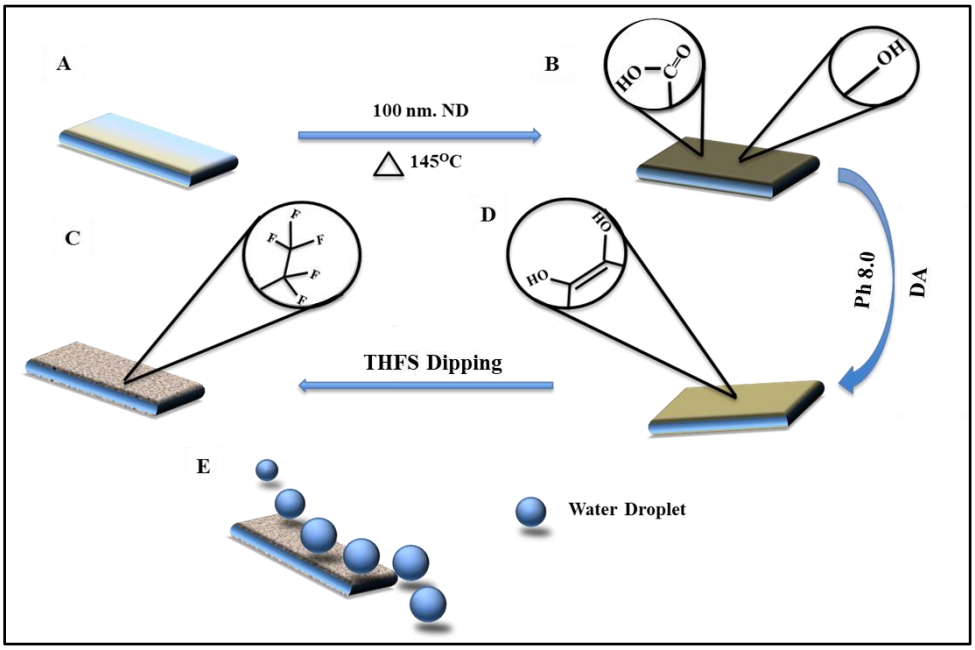

Fig. 1: Schematic showing **A**. Pristine HDPE sheets, **B.** surface functionality of ND-HDPE sheets, **C.** surface functionality of PDA formation on the PDA-HDPE surface, **D.** the hydrophobic tail after THFS dipping on SPH-HDPE sample **E.** Schematic showing the extreme water repellency of the coated substrate.

d. Fabrication of Superhydrophobic HDPE Surfaces

A freshly prepared solution of 5 mM of trichloro(1H,1H,2H,2H-heptadeca-fluorodecyl) silane (THFS), (Gelest, Morrisville, PA) in 20 mL of hexane (ACS grade; Avantor Performance Materials, LLC, Center Valley, PA, US), was used to treat the PDA-HDPE samples by dipping the samples in the solution for 12 hours at room temperature without heating or agitation. The samples were then removed and washed with hexane several times to dissolve and remove unbound THFS. For characterization convenience, the 2 cm × 2 cm SPH-HDPE samples were cut into circular pellets using a metal puncher of a diameter of ½ inch. These SPH-HDPE surfaces synthesized via the above procedure showed extreme water repellency, as shown in Fig. 2A-D and were used for further characterizations and tests.

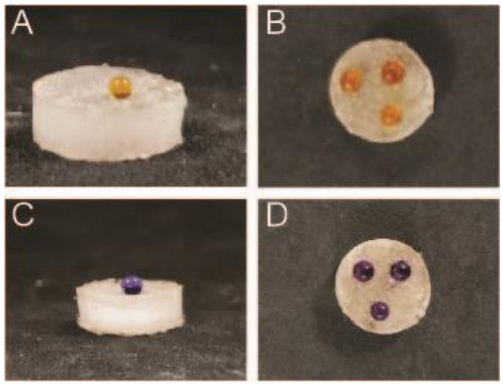

Fig. 2: High resolution digital images of SPH-HDPE substrate with colored water bead colored with **(A-B).** Nile red (TCI chemicals, Montgomeryville, PA, USA) and **(C-D)** Procion blue H-5R (Alfa Aesar, Haverhill, MA,USA)

e. Physical Characterization of the Coating

The surface wettability towards water was gauged using, static and dynamic contact angles using a tensiometer (Biolin Attension Tensiometer, Biolin Scientific, Gothenburg, Sweden). In the measurement of the static water contact angle, a droplet of volume 3 μL was dropped onto the and images were captured (Drelich, Miller, & Good, 1996; Kwok, Gietzelt, Grundke, Jacobasch, & Neumann, 1997). Analyses of these images, to determine the static water contact angles, were performed using ImageJ (National Institutes of Health (NIH), Bethesda, MD, USA) and the 'drop-analysis-LB-ADSA plugin[57]. The reported data are the mean of at least five different sample measurements taken at room temperature.

Surface topography after each of the sequential steps in the coating mechanism was analyzed using FESEM (JEOL JSM-7500F, JEOL Ltd., Tokyo). Before FESEM characterization, the top surface of the substrate was coated with 7 nm thick layer of palladium and platinum (Pd/Pt) alloy using surface sputter coating instrument to ensure the electrical conductivity of the surface.

f. Bacterial Culturing

To test the susceptibility of the SPH-HDPE surfaces against bacterial adhesion, two of the most common bacteria to cause foodborne illness i.e., a gram-negative bacteria, *Salmonella* Typhimurium LT2 (ATCC 700720), and a gram-positive bacteria, *Listeria innocua* (NADC 2841), were used[58]. A procedure similar to the bacterial culturing by J.K Oh et al., was followed to obtain

the bacteria suspensions[36]. 0.6 % yeast (Becton, Dickinson, and Co., Franklin Lakes, NJ, USA) was added to a 30 g/L solution of tryptic soy broth powder (TSB; Becton, Dickinson, and Co., Franklin Lakes, NJ, USA) to prepare a TSB-yeast mixture used to culture *Listeria innocua* while *Salmonella* Typhimurium was cultured in TSB without yeast. 9 mL of TSB or TSB-yeast were added to two falcon tubes. A 10 μL loop scratch of *Salmonella* Typhimurium LT2 or *Listeria innocua*, cultured on tryptic soy agar (TSA, Becton, Dickinson, and Co., Franklin Lakes, NJ, USA) slants was added to each falcon tube respectively. These tubes were incubated aerobically for 24 hours at 37 ^{o}C (Isotemp 500 Series Economy Lab Ovens, Fisher Scientific, Waltham, MA, USA).

The second transfer of each suspension was prepared by using a loop to transfer 10 μL of each of the aerobically incubated cultures of *Salmonella* Typhimurium LT2 or *Listeria innocua* into a freshly prepared falcon tube of 9 mL TSB or TSB-yeast solution, respectively. These secondary transfers were further incubated for an additional 24 hours under conditions similar to the first transfer suspensions. The bacteria were collected by centrifuging the incubated secondary transfer suspensions (AccuSpin 400 Benchtop Centrifuge, Fisher Scientific, Waltham, MA, USA) for 15 minutes (at 15,000xg), then decanting each supernatant. Each supernatant was replaced with 9 mL of Milli-Q water and vigorously shaken. This centrifuging, decanting, and re-suspending procedure was repeated 3 to 4 times to obtain optimal bacterial concentrations of i.e., 8.8 to 9.2 $\log_{10}$ CFU/mL.

g. Bacterial Adhesion on Substrates

The pristine HDPE samples were washed with isopropyl alcohol multiple times and dried at room temperature to ensure the surfaces were bacteria-free prior to adhesion tests. The 9 mL second transfer bacteria suspensions were poured into two separate petri dishes. The pristine HDPE and SPH-HDPE (with SPH part facing towards the suspension) samples were placed into each of the bacterial suspensions. The petri dishes were closed to avoid contamination and left undisturbed at room temperature for 24 hours. Later, the samples were removed and washed gently with Milli-Q water to remove any unbound or loosely bound bacteria from the surfaces and were examined by visual characterization using FESEM. The number of attached individual-bacteria cells we counted manually in each of these FESEM micrographs to obtain the area density of the number of cells adhered i.e., number of cells attached per cm^2 of the plastic surface (denoted by $\log_{10}$#/cm^2 in Fig.4E). At least 10 FESEM images, of both HDPE and SPH-HDPE samples were

used to count the bacteria populations. This procedure was repeated for 3 times to obtain accurate results.

h. Cross-Contamination Assays

An assay was developed to evaluate potential cross-contamination of spinach leaves by route of the HDPE FCSs. Spinach leaves were selected for this assay as they have large contact areas with the FCSs and are one of the most common vegetables that belong to the ready to eat category. In this assay, 9 mL of the second transfer bacterial suspension of either *Salmonella* Typhimurium LT2 and *Listeria innocua* was transferred to a 15 mL falcon tubes, and spinach leaves (obtained from a local grocery store in College Station, Texas), all of similar size cut into pieces having same surface area, were completely submerged into the bacterial suspension. The spinach leaves had a static water contact angle of 56.9±0.62° on their adaxial side (supplementary Fig. S2A-B), before being submerged. The spinach leaves were held in these bacterial suspension for 24 hours of inoculation at room temperature. The contaminated leaves with each of the respective bacteria were transferred into new falcon tubes containing 9 mL of 0.1% aqueous peptone. The falcon tubes were subjected to vigorous shaking to detach any bacteria adhered to the spinach leaves into the peptone solution. Each bacteria-laden peptone solution was decimally diluted in series multiple times. 1.0 mL of each was added to a petri plates containing tryptic soy agar (TSA). The bacterial colony densities in each of the plates were counted after 24 hours of aerobic incubation of the petri plates at 37 ^{o}C. This experiment was repeated 3 times with each bacterial strain to determine the surface concentration of bacteria adhered to spinach leaves.

To compare the bacterial transfer from the surface of the leaf to the HDPE and the SPH-HDPE surfaces, pristine HDPE and SPH-HDPE substrates of dimensions, 2-inch × 2-inch were placed into different petri plates. The top of each sample was covered with the adaxial side of the previously contaminated spinach. The transfer of bacteria from the infected spinach onto the HDPE and SPH-HDPE surfaces was evaluated after 2 hours and 4 hours of contact time. This process repeated with both *Salmonella* Typhimurium LT2 and *Listeria innocua*. These contaminated plastic substrates were each dropped into a beaker containing 100 mL of 0.1% peptone solution and shaken vigorously to detach adhered bacteria. Finally, these bacteria-laden peptone solutions were diluted decimally and added to TSA petri plates for aerobic incubation. The bacterial population density on each of these plates was calculated after 24 hours of incubation

at 37 °C. The same procedure was repeated 3 times for each combination of HDPE sample type and bacterial strain.

i. Mechanical Durability Assays

To assess the applicability of these coatings for food industry, a surface abrasion test was performed using a nanotribometer (NTR; Anton Paar TriTec SA, Peseux, Switzerland). Two layers of spinach leaves (obtained from a local grocery store in College Station, TX), were attached to a 1/8-inch diameter nylon ball. This was used to scratch the SPH-HPDE surfaces. A normal force of 2, 5, and 10 mN was used to scratch the samples (as shown in Fig 7A). The surface abrasion was repeated for 10,000 cycles. The water-repellency of the surfaces were evaluated using static-contact angles up to 10,000 cycles after consecutive logarithmic intervals.

j. Sand-Drop Test

To test the durability of the SPH coatings, 50 g of sand (mesh 40-100) with an average particle diameter of 300µm was dropped from a height of 30cm onto SHP-HDPE samples. The samples were placed below a funnel and tilted at an angle of 45^{o}, as demonstrated by the schematic in Fig 8A. This procedure was carried out for multiple cycles and the water-repellent property of the SPH-HDPE was reevaluated by measuring the static water contact angle after 10, 20, 50 cycles.

k. Statistical Analysis

Statistical analysis was performed on log scale bacterial populations, on both *Salmonella* Typhimurium LT2 and *Listeria innocua* to detect the statistical difference in population results of the adhered bacteria, between pristine HDPE and SPH-HDPE substrates. One-way analysis of variance (ANOVA) was used to perform Tukey's post-hoc test. All statistical analysis test was done using Microsoft Excel, 2016, setting p-value for statistical difference between means as p=0.05.

4. RESULTS AND DISCUSSION

a. Chemical Characterization of the Surface Coatings

The sequential reactions were confirmed using Attenuated Total Reflectance-Fourier Transformed Infrared Spectroscopy (ATR-FTIR) using an IRPrestige-21 instrument (Shimadzu Corp., Kyoto, Japan). Spectra were obtained for ND-HDPE, PDA-HDPE, and SPH-HDPE samples, and, THFS deposited pristine HDPE samples, as shown in Fig. 3A and 3B. The functional groups in the samples were identified using IR Solution software version 1.40 (Shimadzu Corp., Kyoto, Japan). The reaction between ND-fused HDPE (represented by ND-HDPE) and PDA (represented by PDA-HDPE) was characterized using ATR-FTIR (as shown in Fig. 3A). A strong, sharp peak observed at 1460 cm^{-1}, was due to OH bending. This was observed in both the ND-HDPE and PDA-HDPE spectra[59]. A unique peak in the PDA-HDPE spectra can be observed at 1210 cm^{-1}, which was absent in the absorbance spectra of ND-HDPE. This peak was a characteristic of the presence of an aromatic amine and was due to the C-N stretching band in the aromatic amine[60,61]. An additional strong C-O stretching peak, due to the secondary alcohol present in the ND was observed in the spectra of ND-HDPE between 1200-1000 cm^{-1}. This band in the PDA-HDPE spectra, shifted by a wavelength of 60 cm^{-1} after the chemical reaction of ND with PDA. This shift in the peak was due to the conversion of a secondary alcohol, in ND-HDPE into the ether in PDA-HDPE, which confirms the reaction between ND and PDA. This reaction mechanism demonstrated here, is agreement with the reaction mechanism reported elsewhere in published literature[59]. In addition, a new peak was observed at 1050 cm^{-1} in SPH-HDPE which was absent in PDA HDPE. This peak is due to an overlap between the stretching peaks of Si-O-Si and $–CF_3$ symmetric stretching peaks which shows that there is THFS deposited onto SPH-HDPE[36,62].

Further, the reaction between PDA-HDPE and THFS was confirmed by comparing the ATR-FTIR spectra of SPH-HDPE and THFS, deposited pristine HDPE. As shown in Fig. 3B, Si-Cl_x stretching peak, observed at 578 cm^{-1}, in THFS, shifted to 558 cm^{-1} in SPH-HDPE. This 20 cm^{-1} shift could be due to the extension of the outer Si-Cl_x bonds, caused due to the chemical reaction between hydroxyl groups of PDA or carboxyl groups on ND and, Si-Cl_x groups of THFS[37,63]

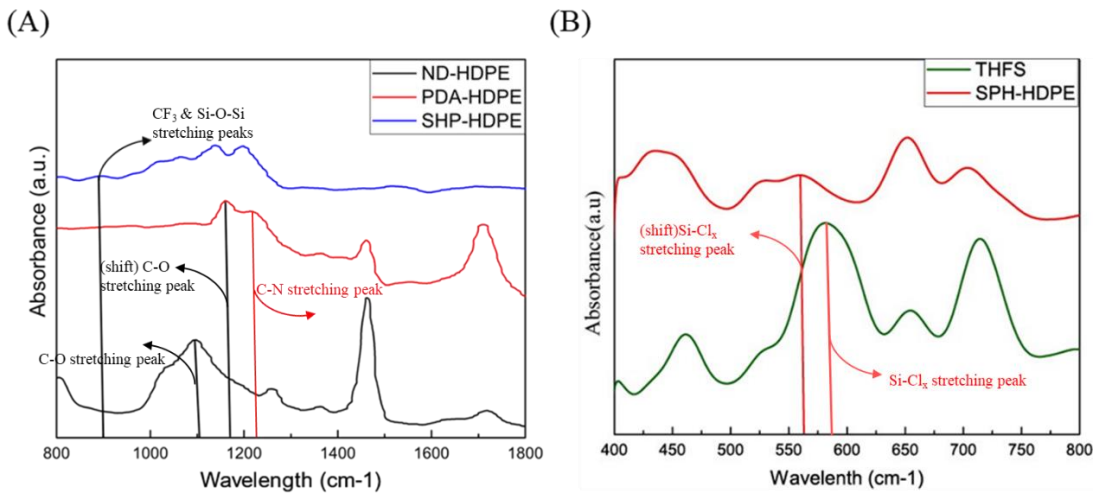

Fig. 3: Comparison of ATR-FTIR spectroscopic data of **A.** ND-HDPE, PDA-HDPE, and SPH-HDPE, between wavelengths 800-1800 cm^{-1}, **B.** SPH-HDPE and THFS between wavelengths 400-800 cm^{-1}

b. Micro-Nano Texturing and Non-Wetting Properties of Superhydrophobic HDPE Samples

The above-described procedure substantially improved the water repellency of the HDPE surfaces which were studied using static water contact angle measurement performed by the sessile-drop method. The static-contact angle of the pristine HDPE samples was found to be 88.8±0.1^o (as shown in Fig. 4I), close to the static-contact angle reported by in literature[64]. The static-contact angle decreased significantly upon ND infusion and, upon reacting with PDA due to increase in polar surface groups and roughness. The above coating mechanism on pristine HDPE, increased the static contact angle of SPH-HDPE to 151.1±0.3^o (as shown in Fig. 4L). This increase in the static contact angle could be attributed to hydrophobic surface groups (THFS) and enhanced roughness caused by the micro and nanoclusters of the attached THFS, with the cluster diameters varying from 2-5 µm on the surface. It is important to note that the topographies of the pristine-HDPE and other intermediates remained considerably smooth while the surface roughness increased significantly after reaction with THFS (Fig. 4E-4G). The topography of the SPH-HDPE surface (as shown in Fig. 4H) help to stabilize the air trapped between two adjacent clusters and thus impart extreme water repellency to the surfaces[65]. In addition to the static contact angle, the dynamic advancing and receding contact angles were measured to be 155.0±1.0° and 151.0±1.9°

with a hysteresis of 4° (<5°). This demonstrates that the surfaces of SPH-HDPE substrates are self-cleaning[66].

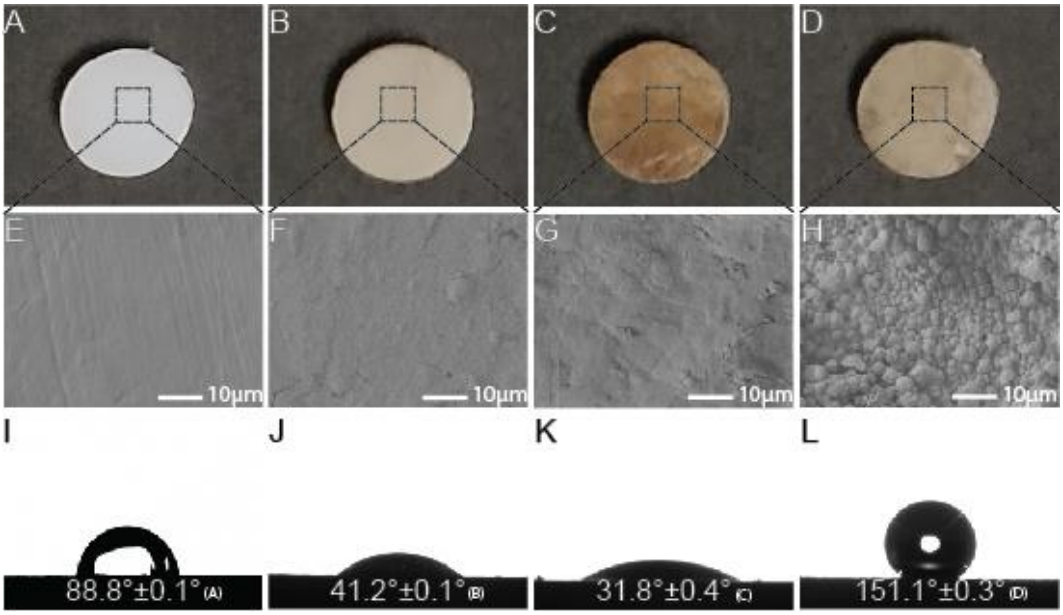

Fig. 4: Digital images of circular palettes of ½ inch diameter of **A.** pristine HDPE, **B.** ND-HDPE, **C.** PDA-HDPE, **D.** SPH-HDPE, their corresponding surface FESEM images **(E-H)**, and static water contact angles measured by sessile drop method **(I-L),** respectively. The letter A, B, C, D, beside the static contact angle values denotes the significant statistical difference between the static contact angles measured on each of the respective substrates (p-value<0.05).

c. Comparison of Bacterial Adhesion Between HDPE and SPH-HDPE Samples Using Scanning Electron Microscopy.

To evaluate the bacterial anti-adhesion property of the SPH-HDPE surfaces, the adhesion onto these surfaces was compared to that of pristine HDPE samples. Comparative data was obtained by counting the number of surface-attached bacteria in the FESEM images of SPH-HDPE and pristine HDPE samples, exposed to the cultured *Salmonella* Typhimurium LT2 and *Listeria innocua* for 24 hours, as shown in Fig.5. The FESEM images shown in Fig. 5C and 5D clearly show a substantial decrease in the bacterial attachment of both *Salmonella* Typhimurium LT2 and *Listeria innocua*, on to SPH-HDPE, after 24 hours of contact in comparison to the FESEM images of pristine HDPE, i.e. 5A and 5B respectively.

After 24 hours of exposure to *Salmonella* Typhimurium LT2 bacteria, the mean population of the on the bare HDPE surface was 6.70±0.05 $\log_{10}$ #/cm^2, whereas the population of same organism on the SPH-HDPE surface was 4.52±0.38 $\log_{10}$ #/cm^2, recording a 99.34% decrease in

the bacterial attachment on the SPH-HDPE when compared to the bare HDPE. Similarly, for *Listeria innocua* bacteria, pristine HDPE recorded a mean bacterial population of 6.63±0.15 $\log_{10}$ #/cm^2, while the mean population on SPH-HDPE was 4.98±0.41 $\log_{10}$ #/cm^2, accounting for a 97.75% reduction in the bacterial count on the SPH-HDPE surfaces, to the pristine HDPE surfaces.

These results indicate the bare HDPE surface irregularities which greatly promote bio-adhesion and formation of bacterial biofilms[27], can be overcome by coating the utilization of nanotexturing, as evidenced by the more than 97.75% reduction in the adhesion of both gram-positive (*Listeria innocua*) and gram-negative (*Salmonella* Typhimurium LT2) bacteria, with significant statistical difference between the adhesion patterns of the two bacteria onto the two surfaces, i.e. HDPE and SPH-HDPE, used in this experiment. This reduction in the attachment of both gram-positive and gram-negative bacteria could be ascribed to Cassie-Baxter wetting model of superhydrophobic surfaces, i.e., formation of hierarchical structures with stabilized air pockets at the liquid water and substrate interface[67]. These hierarchical structures formed due to THFS coating, with ridges less than 2 µm in size, firmly hold the trapped-air preventing them to be replaced by bacteria. Moreover, the reduction in the secondary interactions such as, van der Waals, structural, electrostatic and steric interactions, could be attributed to the increase in steric repulsions between the negatively charged THFS surface groups and negatively charged bacteria[68,69]. Hence by using SPH-HDPE FCS during food processing, could significantly decrease microbial attachment through carriers such as, air, water and, human and animal contact.

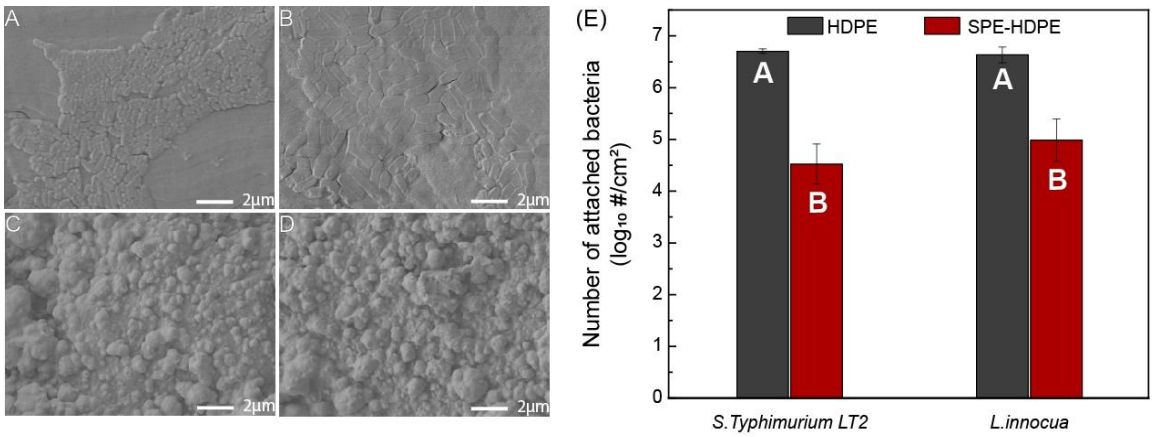

Fig. 5: Digital images of high-resolution FESEM images of *Salmonella* Typhimurium LT2 bacteria attached to **A.** HDPE **C.** SPH-HDPE, digital images of FESEM micrographs of *Listeria innocua* attached on **B.** HDPE, **D.** SPH-HDPE, **E**. graphical comparison of bacterial adhesion of gram-negative *Salmonella* Typhimurium LT2 and gram-positive *Listeria innocua* between HDPE and SPH-HDPE after exposure to bacterial suspensions for 24 hrs. There is statistically significant difference with p-value<0.05 between the mean bacterial concentrations on the two surfaces (denoted by letters A and B).

d. Quantification of Bacterial Contamination Through Cross Contamination Assay

The transfer of bacteria (both *Salmonella* Typhimurium LT2 and *Listeria innocua)* onto both pristine HDPE and SPH-HDPE substrates from contaminated spinach leaves, one of the most common vegetable eaten raw by the consumers all over the world, was quantified. This was a further demonstration of the bacterial anti-adhesion property of the SPH-HDPE, as shown in Fig.6. It was observed that the average concentration of the bacteria detached from the spinach leaves, after 24 hours of inoculation, into 9 mL of 0.1% aqueous peptone solution, was 7.79±0.07 and, 7.82±0.07 $\log_{10}$ CFU/mL for *Salmonella* Typhimurium LT2 or *Listeria innocua,* respectively. After 2 hours of exposure to *Salmonella* Typhimurium contaminated leaves, 6.30 ±0.20 $\log_{10}$ CFU/mL bacteria were transferred to the pristine HDPE surfaces. Contrastingly, after 2 hours of exposure to *Salmonella* contaminated leaves, only 4.40 ±0.62 $\log_{10}$ CFU/mL was transferred to the SPE-HDPE surfaces. Similarly, after 4 hours of exposure to the *Salmonella* contaminated leaves, 6.39±0.045 and 4.4±0.50 $\log_{10}$ CFU/mL were transferred to the pristine and superhydrophobic surfaces, respectively. These demonstrate a 98.7% and 98.9% reduction in the transfer of *Salmonella* Typhimurium after 2 hours and 4 hours, respectively (as shown in Tab.1).

Similar trends were observed when the pristine and superhydrophobic HDPE samples were exposed to *Listeria innocua* contaminated spinach leaves. After 2 hours of exposure to contaminated leaves, there were transfers of 6.70±0.24 and 4.10±0.27 $\log_{10}$ CFU/mL bacteria onto

pristine and superhydrophobic modified HDPE, respectively. After 4 hours of exposure, 6.40±0.23 and 4.85±0.35 $\log_{10}$ CFU/mL, respectively, were transferred onto the pristine and superhydrophobic HDPE surfaces. The concentration of bacteria on SPH-HDPE showed a 99.8% decrease in transfer after 2 hours of exposure. Similarly, there was 97.5% reduction in the number of bacteria transferred after 4 hours of exposure to *Listeria* contaminated spinach leaves.

These assays demonstrate the efficacy of the superhydrophobic coating in reducing bacterial transfer between surfaces and the mitigating the potential for cross contamination of food products. The transfer of the bacteria from contaminated spinach leaves to HDPE is significantly retarded after the application the superhydrophobic coating. In the case of *Salmonella* Typhimurium there is a 98.7% reduction in bacterial transfer while, in the case of *Listeria innocua* the reduction in bacterial transfer is 97.5%, with statistically significant difference for adhesion of both the bacteria on spinach leaf, HDPE and SPH-HDPE, while no statistical difference was observed when the exposure time was altered. This reduction in bacterial transfer signifies that the contamination in one batch of processed food, does not affect the following batches which vastly benefits the consumers and the food processing industries.

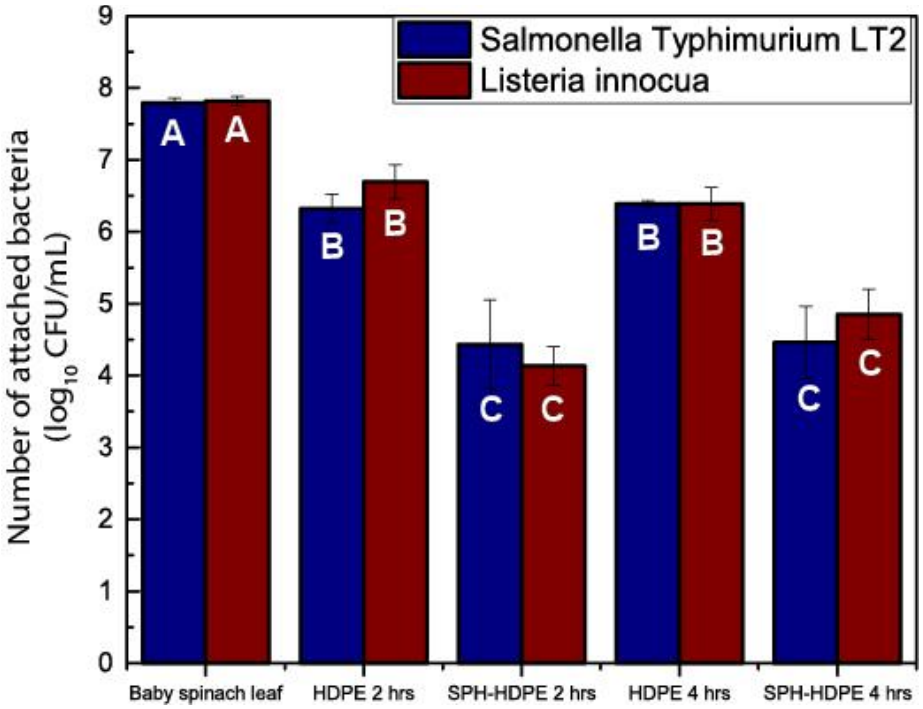

Fig. 6: Comparison showing the decrease in the concentration of attached bacteria in SPH-HDPE, in comparison to pristine HDPE for both gram-negative *Salmonella* Typhimurium LT2 and gram-positive *Listeria innocua* after 2 hours and 4 hours of exposure. Statistically significant difference was observed between the means of the bacterial populations on bare spinach leaf, HDPE and SPH-HDPE substrates (denoted by letters A, B and C respectively) with p-value<0.05.

Bacteria used for Cross Contamination	Log-scale reduction on Bacterial attachment (log_{10}CFU/mL)		Percentage reduction in Bacterial attachment (%)	
	2 hours	4 hours	2 hours	4 hours
Salmonella Typhimurium LT2	1.9±0.82	2.6±0.51	98.7	98.9
Listeria innocua	1.9±0.54	1.6±0.58	99.8	97.5

Tab. 1: Table depicting the log-scale and percentage reduction in the bacterial attachment of *Salmonella* Typhimurium LT2 and *Listeria innocua,* caused due to cross-contamination by spinach on SPH-HDPE in comparison to pristine HDPE after 2 hours and 4 hours of contact time.

e. Mechanical Durability Assay.

The durability and reusability of the coated superhydrophobic surfaces are important factors for their industrial applications[70]. To evaluate the durability of the SPH-HDPE against surface abrasion, two layers of cut spinach leaves, were attached to a nylon ball with a diameter of 1/8" using super-glue. This was utilized with a nanotribometer to abrade the SPH-HDPE, with abrasion normal forces of 2, 5, and 10mN, and the static contact angles of the abraded surfaces were recorded at every logarithmic interval, up to 10,000 cycles. The SPH-HDPE surfaces showed excellent durability with a decrease in the static contact angles of 2.7^o, 3.9^o, and 5.7^o at forces of 2, 5, and 10 mN respectively, after 10,000 cycles of abrasion (shown in Fig 7B). Further, to study the durability of the surfaces against abrasion caused by some of the heavy and firm vegetables that belong to the ready-to eat category, the first two layers of an onion were attached to the same nylon ball, of diameter 1/8" using super-glue, and higher normal forces of 10, 20, and 40 mN were applied onto SPH-HDPE substrates. The substrates showed a 2.85^o, 2.7^o, and 5.3^o, decrease in the static-contact angles after 10,000 cycles of abrasion with 10, 20, and 40 mN of applied force respectively (shown in Fig 7C). These results indicated that the SPH-HDPE surfaces retained the water-repellency properties even after 10,000 cycles of abrasion. Thus, the SPH-HDPE substrates may be appropriate for use in the manufacture of industrial-scale conveyor belts utilized in the vegetable and fruit processing industries.

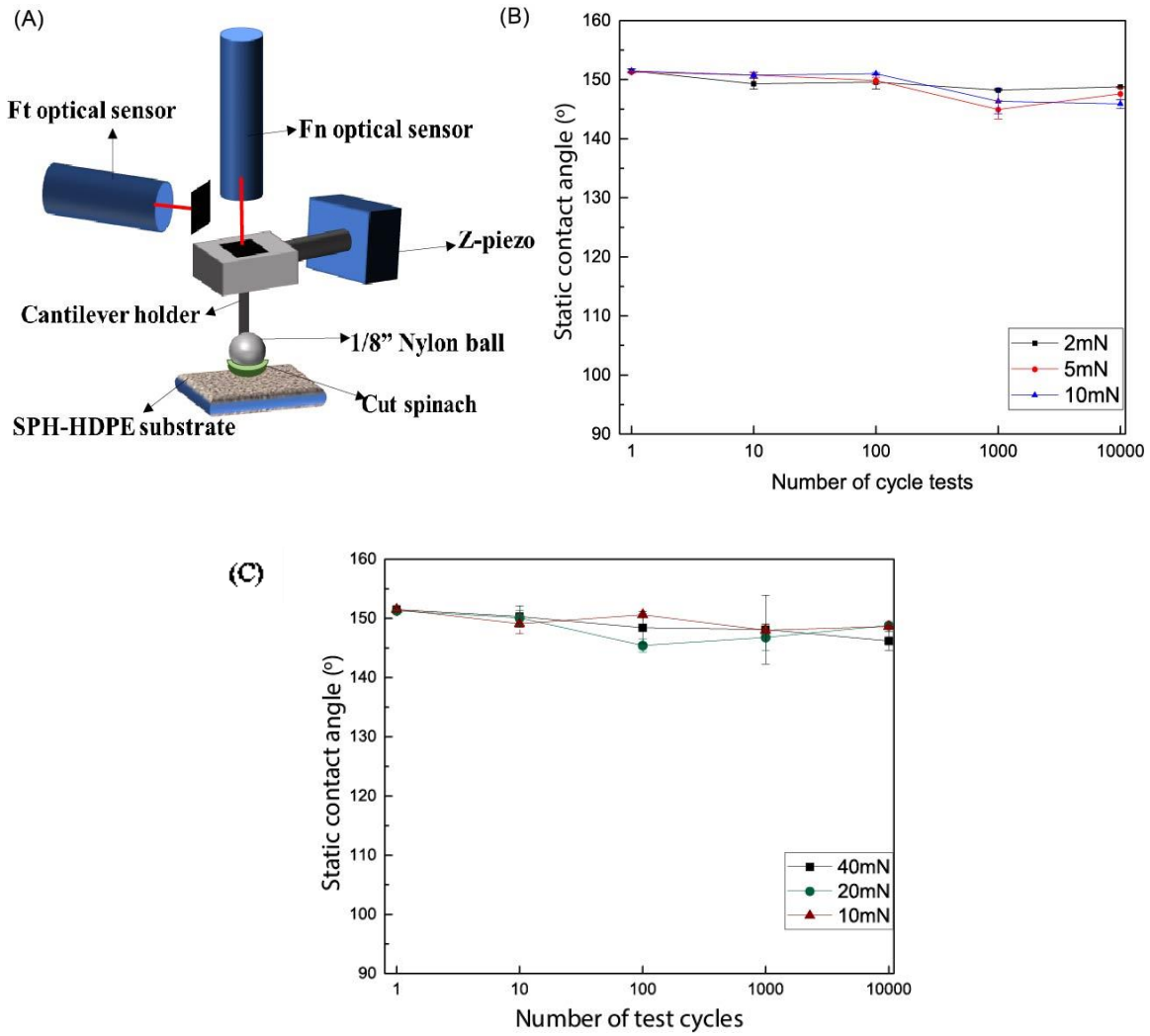

Fig. 7: **A.** Schematic showing surface scratching test being performed on SHP-HDPE surface. **B.** Graphical comparison of static-contact angle of SPH-HDPE samples up to 10,000 cycles of spinach abrasion with surface abrasion forces of 2mN, 5mN and 10mN. **C.** Graphical representation of surface abrasion performed using onion peel up to 10,000 cycles with forces of 10, 20, 40mN.

f. Mechanical Durability of Superhydrophobic Coatings by Sand-Drop Test.

To further investigate the mechanical durability of the coatings for good industrial applications, abrasion test was performed on the SPH-HDPE substrates. One often overlooked factor is the presence of sand and grit found on farm-fresh food materials such as fruits and vegetables. It is sometimes difficult to remove sand and dirt particles that adhere to fruits and vegetables by sanitization and tap water washing[71]. This sand can cause wear of SPH coatings on conveyor belts, cutting boards, and other FCSs. Hence, it is important for the bacteria resistant coatings on the FCSs to be durable against sand abrasion to maximize their effective life span in retarding the adhesion of both gram-positive and gram-negative bacteria. To evaluate the change

in the static water contact angle with sand abrasion, the sand drop test was performed on SPH-HDPE substrates[72]. The above procedure was repeated with multiple SPH-HDPE samples and data comparing the static water contact angle number of abrasion cycles performed are plotted in Fig.8B. It was observed that after 50 test cycles of dropping sand, the average reduction in the static water contact angle of the SPH-HDPE samples was 7°. This reduction in the static water contact angle after sand abrasion could be due to the wearing of the top layer of the coating and the consequent destruction of the optimal surface texturing of micro/nano hierarchical features that trap metastable air, as shown in Fig. 9[73]. Despite a 7° decrease in the static water contact angles, the SPH-HDPE surfaces after 50 cycles of sand abrasion were still highly water-repellant.

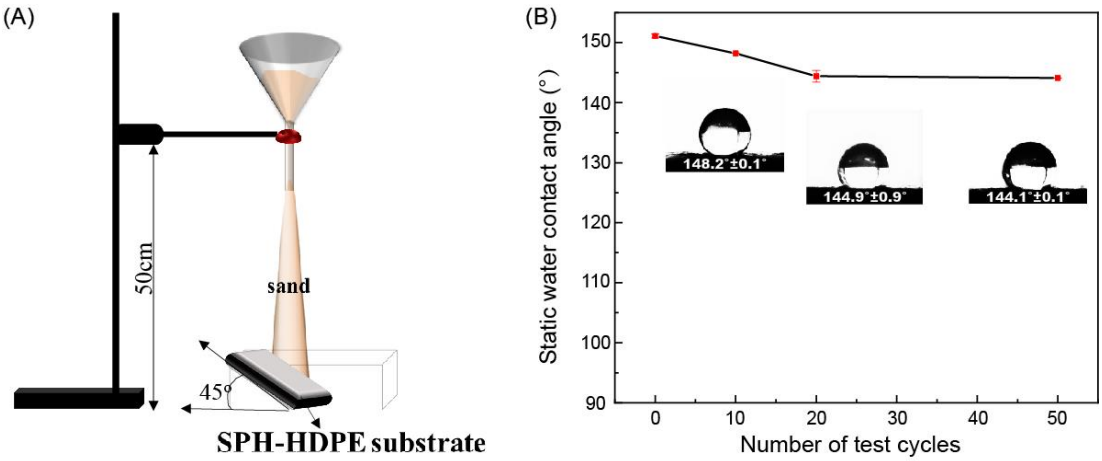

Fig. 8: **A.** Pictorial representation of sand drop tests performed to estimate the durability of the SHP-HDPE surface. **B.** Graphical comparison of the static contact angle of SPH-HDPE samples up to 50 cycles of the sand drop test.

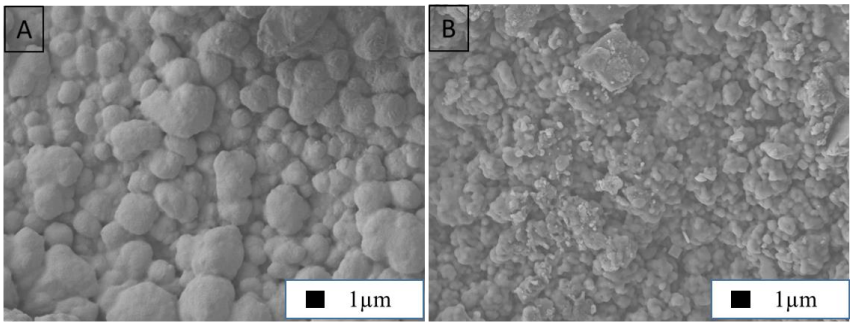

Fig. 9: High resolution FESEM micrographs of SPH-HDPE**, A.** before sand-drop test and **B.** after 50 cycles of sand-drop test.

The above results encourage the use of these novel surface coating procedures in the manufacture of hygienic FCSs. These coatings have the potential to bring down maintenance costs

in food production environments by decreasing the need for constant cleaning and reducing water consumption. Due to the constant inflation of raw material costs, decreasing the maintenance costs could play a vital role in decreasing the costs of the consumer-based products and profit maximization in the food processing industries. Improving hygiene in the food processing environment decreases the occurrence of foodborne illness and thus decreases health care expenditures.

5. CONCLUSION

Herein, we have successfully demonstrated the synthesis of durable bacteria repellent superhydrophobic coatings by thermal infusion of nanodiamonds onto pristine high density polyethylene substrates, followed by chemical functionalization of nanodiamonds by poly-dopamine and imparting superhydrophobic property by reaction with trichloro(1H,1H,2H,2H-heptadeca-fluorodecyl) silane. The static water contact angle of the thus formed superhydrophobic plastic surfaces was observed to be 151.1±0.3^{o}, with a low contact angle hysteresis. The synergistic combination of nanodiamonds, poly-dopamine, and inert non-polar ligands impart both surface strength and bacteria repellency with a decrease in the adhesion of gram-negative *Salmonella* Typhimurium LT2 by 99.34% and gram-positive *Listeria innocua* by 97.75%. Additionally, these superhydrophobic coatings decreased the transfer of bacteria from contaminated spinach leaves to plastic surfaces by *Salmonella* Typhimurium by 98.7% after 2 hours and 98.9% after 4 hours of contact time, mitigating the risk of cross-contamination. Similarly, *Listeria innocua* transfer from contaminated spinach leaves was reduced by 99.8% after 2 hours and 97.5% after 4 hours of exposure. The superhydrophobic coatings showed excellent mechanical durability, withstanding up to 10,000 cycles of surface abrasion with the highest change in static water contact angle being 6.5^{o} and 5.3^{o}, observed after abrasion of the coated surfaces with spinach leaves and onion peels respectively. Furthermore, the coatings withstood up to 50 cycles of sand abrasion with a 7^{o} change in the static water contact angle. Overall, with preparation via versatile and scalable synthesis techniques, and properties such as self-cleaning ability, superhydrophobicity, and bacteria-repellency, these coatings stand to make large safety and economic impacts when utilized in food contact surface applications within the food industries.

REFERENCES

(1) Newell, D. G.; Koopmans, M.; Verhoef, L.; Duizer, E.; Aidara-Kane, A.; Sprong, H.; Opsteegh, M.; Langelaar, M.; Threfall, J.; Scheutz, F.; der Giessen, J. van; Kruse, H. Food-Borne Diseases - The Challenges of 20years Ago Still Persist While New Ones Continue to Emerge. *Int. J. Food Microbiol.* **2010**, *139* (SUPPL. 1), S3–S15.

(2) Petruzzelli, A.; Blasi, G.; Masini, L.; Calza, L.; Duranti, A.; Santarelli, S.; Fisichella, S.; Pezzotti, G.; Aquilanti, L.; Osimani, A.; Tonucci, F. Occurrence of Listeria Monocytogenes in Salami Manufactured in the Marche Region (Central Italy). *J. Vet. Med. Sci.* **2010**, *72* (4), 499–502.

(3) Fung, F.; Wang, H. S.; Menon, S. Food Safety in the 21st Century. *Biomed. J.* **2018**, *41* (2), 88–95.

(4) World Health Organization. Food Safety (WHO) https://www.who.int/news-room/fact-sheets/detail/food-safety. (accessed Jan 12, 2021).

(5) Centers for Disease Control and Prevention (CDC) https://www.cdc.gov/foodsafety/foodborne-germs.html (accessed Jan 12, 2021).

(6) Angelo, K. M.; Nisler, A. L.; Hall, A. J.; Brown, L. G.; Gould, L. H. Epidemiology of Restaurant-Associated Foodborne Disease Outbreaks, United States, 1998-2013. *Epidemiol. Infect.* **2017**, *145* (3), 523–534.

(7) Finstad, S.; O'Bryan, C. A.; Marcy, J. A.; Crandall, P. G.; Ricke, S. C. Salmonella and Broiler Processing in the United States: Relationship to Foodborne Salmonellosis. *Food Res. Int.* **2012**, *45* (2), 789–794.

(8) Chittick, P.; Sulka, A.; Tauxe, R. V.; Fry, A. M. A Summary of National Reports of Foodborne Outbreaks of Salmonella Heidelberg Infections in the United States: Clues for Disease Prevention. *J. Food Prot.* **2006**, *69* (5), 1150–1153.

(9) Marquez, L.; Koy, T. H.; Baker, C. R.; Graf, J.; Whaley, E. M.; Campbell, J. R. Foodborne Illness Outbreak Due to Staphylococcus Aureus among Hospital Staff

Following Hurricane Harvey. *Infect. Control Hosp. Epidemiol.* **2019**, *40* (1), 115–117.

(10) Zhang, H.; Ye, Y.; Yang, B.; Gu, Q.; Zhu, Y.; Que, F.; Liu, Y.; Yu, Y.; Yu, D.; Zhang, X. Characterization of an Unusual Foodborne Illness Including an Outbreak and Sporadic Illness Caused by Three Bacterial Pathogens Via a Takeaway Service. *Foodborne Pathog. Dis.* **2019**, *16* (9), 616–621.

(11) Hedberg, C. W.; Savarino, S. J.; Besser, J. M.; Paulus, C. J.; Thelen, V. M.; Myers, L. J.; Cameron, D. N.; Barrett, T. J.; Kaper, J. B.; Osterholm, M. T. An Outbreak of Foodborne Illness Caused by Escherichia Coli O39:NM, an Agent Not Fitting into the Existing Scheme for Classifying Diarrheogenic E. Coli . *J. Infect. Dis.* **1997**, *176* (6), 1625–1628.

(12) Schlech, W. F. Special Section: Food Safety. *Clin. Infect. Dis.* **2000**, *31* (1), 770–775.

(13) Brooks, J. D.; Flint, S. H. Biofilms in the Food Industry: Problems and Potential Solutions. *Int. J. Food Sci. Technol.* **2008**, *43* (12), 2163–2176.

(14) Galié, S.; García-Gutiérrez, C.; Miguélez, E. M.; Villar, C. J.; Lombó, F. Biofilms in the Food Industry: Health Aspects and Control Methods. *Front. Microbiol.* **2018**, *9* (MAY), 1–18.

(15) Palmer, J.; Flint, S.; Brooks, J. Bacterial Cell Attachment, the Beginning of a Biofilm. *J. Ind. Microbiol. Biotechnol.* **2007**, *34* (9), 577–588.

(16) Osimani, A.; Garofalo, C.; Clementi, F.; Tavoletti, S.; Aquilanti, L. Bioluminescence ATP Monitoring for the Routine Assessment of Food Contact Surface Cleanliness in a University Canteen. *Int. J. Environ. Res. Public Health* **2014**, *11* (10), 10824–10837.

(17) Scott, E.; Bloomfield, S. F. The Survival and Transfer of Microbial Contamination via Cloths, Hands and Utensils. *J. Appl. Bacteriol.* **1990**, *68* (3), 271–278.

(18) Scallan, E.; Hoekstra, R. M.; Angulo, F. J.; Tauxe, R. V.; Widdowson, M. A.; Roy, S. L.; Jones, J. L.; Griffin, P. M. Foodborne Illness Acquired in the United States-Major Pathogens. *Emerg. Infect. Dis.* **2011**, *17* (1), 7–15.

(19) Balakrishnan, S.; Sangeetha, A.; Dhanalakshmi, M. Prevalence of Salmonella in Chicken Meat and Its Slaughtering Place from Local Markets in Orathanadu , Thanjavur District , Tamil Nadu. **2018**, *6* (2), 2468–2471.

(20) Muhterem-uyar, M.; Dalmasso, M.; Sorin, A.; Manios, S. G.; Hernandez, M.; Kapetanakou, A. E.; Melero, B.; Minarovi, J.; Stessl, B.; Skandamis, P. N.; Jordan, K.; Rodríguez-l, D.; Wagner, M. Environmental Sampling for Listeria Monocytogenes Control in Food Processing Facilities Reveals Three Contamination Scenarios. **2015**, *51*, 94–107.

(21) Chaturongkasumrit, Y.; Takahashi, H.; Keeratipibul, S.; Kuda, T.; Kimura, B. The Effect of Polyesterurethane Belt Surface Roughness on Listeria Monocytogenes Biofilm Formation and Its Cleaning Efficiency. *Food Control* **2011**, *22* (12), 1893–1899.

(22) Joseph, B.; Otta, S. K.; Karunasagar, I.; Karunasagar, I. Biofilm Formation by Salmonella Spp. On Food Contact Surfaces and Their Sensitivity to Sanitizers. *Int. J. Food Microbiol.* **2001**, *64* (3), 367–372.

(23) Oh, S. W.; Gray, P. M.; Dougherty, R. H.; Kang, D. H. Aerosolization as Novel Sanitizer Delivery System to Reduce Food-Borne Pathogens. *Lett. Appl. Microbiol.* **2005**, *41* (1), 56–60.

(24) Zhang, M.; Oh, J. K.; Cisneros-Zevallos, L.; Akbulut, M. Bactericidal Effects of Nonthermal Low-Pressure Oxygen Plasma on S. Typhimurium LT2 Attached to Fresh Produce Surfaces. *J. Food Eng.* **2013**, *119* (3), 425–432.

(25) Ozen, B. F.; Floros, J. D. Effects of Emerging Food Processing Techniques on the Packaging Materials. *Trends Food Sci. Technol.* **2001**, *12* (2), 60–67.

(26) McKellop, H.; Clarke, I.; Markolf, K.; Amstutz, H. Friction and Wear Properties of Polymer, Metal, and Ceramic Prosthetic Joint Materials Evaluated on a Multichannel Screening Device. *J. Biomed. Mater. Res.* **1982**, *16* (2), 177.

(27) Zhang, X.; Wang, L.; Levänen, E. Superhydrophobic Surfaces for the Reduction of Bacterial Adhesion. *RSC Adv.* **2013**, *3* (30), 12003–12020.

(28) Davidson, P. M.; Harrison, M. A. Resistance and Adaptation to Food Antimicrobials, Sanitizers, and Other Process Controls. *Food Technol.* **2002**, *56* (11), 69–78.

(29) Cowan, M. M.; Abshire, K. Z.; Houk, S. L.; Evans, S. M. Antimicrobial Efficacy of a Silver-Zeolite Matrix Coating on Stainless Steel. *J. Ind. Microbiol. Biotechnol.* **2003**, *30* (2), 102–106.

(30) Erdohan, Z. Ö.; Çam, B.; Turhan, K. N. Characterization of Antimicrobial Polylactic Acid Based Films. *J. Food Eng.* **2013**, *119* (2), 308–315.

(31) Khan, M.; Wu, Z.; Mao, S.; Shah, S. N. A.; Lin, J. M. Controlled Grafted Poly(Quaternized-4-Vinylpyridine-: Co -Acrylic Acid) Brushes Attract Bacteria for Effective Antimicrobial Surfaces. *J. Mater. Chem. B* **2018**, *6* (22), 3782–3791.

(32) Yuan, G.; Chen, X.; Li, D. Chitosan Films and Coatings Containing Essential Oils: The Antioxidant and Antimicrobial Activity, and Application in Food Systems. *Food Res. Int.* **2016**, *89*, 117–128.

(33) For, C. O.; Ackaging, F. O. O. D. A /z z c a c f -p S. **2009**.

(34) Li, X. M.; Reinhoudt, D.; Crego-Calama, M. What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces. *Chem. Soc. Rev.* **2007**, *36* (8), 1350–1368.

(35) Shome, A.; Maji, K.; Rather, A. M.; Yashwanth, A.; Patel, D. K.; Manna, U. A Scalable Chemical Approach for the Synthesis of a Highly Tolerant and Efficient Oil Absorbent. *Chem. - An Asian J.* **2019**, 1–10.

(36) Oh, J. K.; Liu, S.; Jones, M.; Yegin, Y.; Hao, L.; Tolen, T. N.; Nagabandi, N.; Scholar, E. A.; Castillo, A.; Taylor, T. M.; Cisneros-Zevallos, L.; Akbulut, M. Modification of Aluminum Surfaces with Superhydrophobic Nanotextures for Enhanced Food Safety and Hygiene. *Food Control* **2019**, *96* (July 2018), 463–469.

(37) Liu, S.; Zheng, J.; Hao, L.; Yegin, Y.; Bae, M.; Ulugun, B.; Taylor, T. M.; Scholar, E. A.; Cisneros-Zevallos, L.; Oh, J. K. Dual-Functional, Superhydrophobic Coatings with

Bacterial Anticontact and Antimicrobial Characteristics. *ACS Appl. Mater. Interfaces* **2020**.

(38) Manna, U.; Carter, M. C. D.; Lynn, D. M. “shrink-to-Fit” Superhydrophobicity: Thermally-Induced Microscale Wrinkling of Thin Hydrophobic Multilayers Fabricated on Flexible Shrink-Wrap Substrates. *Adv. Mater.* **2013**, *25* (22), 3085–3089.

(39) Feng, X.; Jiang, L. Design and Creation of Superwetting/Antiwetting Surfaces. *Adv. Mater.* **2006**, *18* (23), 3063–3078.

(40) Yan, Y. Y.; Gao, N.; Barthlott, W. Mimicking Natural Superhydrophobic Surfaces and Grasping the Wetting Process: A Review on Recent Progress in Preparing Superhydrophobic Surfaces. *Adv. Colloid Interface Sci.* **2011**, *169* (2), 80–105.

(41) Attard, P. Thermodynamic Analysis of Bridging Bubbles and a Quantitative Comparison with the Measured Hydrophobic Attraction. *Langmuir* **2000**, *16* (10), 4455–4466.

(42) H. Yıldırım Erbil, A. Levent Demirel, Yonca Avcıı, O. M. Transformation of a Simple. *Science (80-.).* **2003**, *299* (February), 1377–1380.

(43) Shen, L.; Ding, H.; Cao, Q.; Jia, W.; Wang, W.; Guo, Q. Fabrication of Ketjen Black-High Density Polyethylene Superhydrophobic Conductive Surfaces. *Carbon N. Y.* **2012**, *50* (11), 4284–4290.

(44) Chen, Z.; Dong, L.; Yang, D.; Lu, H. Superhydrophobic Graphene-Based Materials : Surface Construction and Functional Applications. **2013**, 5352–5359.

(45) Meng, L.; Park, S. Superhydrophobic Carbon-Based Materials : A Review of Synthesis , Structure , and Applications. **2014**, *15* (2), 89–104.

(46) Cao, N.; Yang, B.; Barras, A.; Szunerits, S.; Boukherroub, R. Polyurethane Sponge Functionalized with Superhydrophobic Nanodiamond Particles for Efficient Oil / Water Separation. *Chem. Eng. J.* **2017**, *307*, 319–325.

(47) Chen, M.; Pierstorff, E. D.; Lam, R.; Li, S. Y.; Huang, H.; Osawa, E.; Ho, D.

Nanodiamond-Mediated Delivery of Water-Insoluble Therapeutics. *ACS Nano* **2009**, *3* (7), 2016–2022.

(48) Schrand, A. M.; Huang, H.; Carlson, C.; Schlager, J. J.; Osawa, E.; Hussain, S. M.; Dai, L. Are Diamond Nanoparticles Cytotoxic? *J. Phys. Chem. B* **2007**, *111* (1), 2–7.

(49) Mochalin, V. N.; Shenderova, O.; Ho, D.; Gogotsi, Y. The Properties and Applications of Nanodiamonds. *Nat. Nanotechnol.* **2012**, *7* (1), 11–23.

(50) Passeri; D.; Rinaldi; F.; Ingallina; C.; Carafa; M.; Rossi; M.; Terranova; M. L.; Marianecci; C. Biomedical Applications of Nanodiamonds: An Overview. *J. Nanosci. Nanotechnol.* **2015**, *15* (2), 972-988(17).

(51) Qin, S.; Wang, D.; Wang, J. X.; Pu, Y.; Chen, J. F. Polyhedral Oligomeric Silsesquioxane-Coated Nanodiamonds for Multifunctional Applications. *J. Mater. Sci.* **2018**, *53* (23), 15915–15926.

(52) Cao, W.; Peng, X.; Chen, X.; Wang, X.; Jin, F.; Li, Q.; Chen, H.; Jiang, C.; Ye, Z.; Xing, X. Facile Synthesis of Cationic Polymer Functionalized Nanodiamond with High Dispersity and Antibacterial Activity. *J. Mater. Sci.* **2017**, *52* (4), 1856–1867.

(53) Nanodiamond Price https://offer.alibaba.com/ %7BSearch options: diamond powder nanodiamond%7D (accessed Jan 22, 2021).

(54) Zeng, Y.; Liu, W.; Wang, Z.; Singamaneni, S.; Wang, R. Multifunctional Surface Modification of Nanodiamonds Based on Dopamine Polymerization. *Langmuir* **2018**, *34* (13), 4036–4042.

(55) Drelich, J.; Miller, J. D.; Good, R. J. The Effect of Drop (Bubble) Size on Advancing and Receding Contact Angles for Heterogeneous and Rough Solid Surfaces as Observed with Sessile-Drop and Captive-Bubble Techniques. *J. Colloid Interface Sci.* **1996**, *179* (1), 37–50.

(56) Kwok, D. Y.; Gietzelt, T.; Grundke, K.; Jacobasch, H. J.; Neumann, A. W. Contact Angle Measurements and Contact Angle Interpretation. 1. Contact Angle Measurements by

Axisymmetric Drop Shape Analysis and a Goniometer Sessile Drop Technique. *Langmuir* **1997**, *13* (10), 2880–2894.

(57) Stalder, A. F.; Melchior, T.; Müller, M.; Sage, D.; Blu, T.; Unser, M. Low-Bond Axisymmetric Drop Shape Analysis for Surface Tension and Contact Angle Measurements of Sessile Drops. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *364* (1–3), 72–81.

(58) Teixeira, P.; Silva, S.; Araújo, F.; Azeredo, J.; Oliveira, R. Bacterial Adhesion to Food Contacting Surfaces. *Commun. Curr. Res. Educ. Top. Trends Appl. Microbiol.* **2007**, No. July 2015, 13–20.

(59) Barras, A.; Lyskawa, J.; Szunerits, S.; Woisel, P.; Boukherroub, R. Direct Functionalization of Nanodiamond Particles Using Dopamine Derivatives. *Langmuir* **2011**, *27* (20), 12451–12457.

(60) Pham, M. C.; Oulahyane, M.; Mostefai, M.; Chehimi, M. M. Multiple Internal Reflection FT-IR Spectroscopy (MIRFTIRS) Study of the Electrochemical Synthesis and the Redox Process of Poly(1,5-Diaminonaphthalene). *Synth. Met.* **1998**, *93* (2), 89–96.

(61) Stewart, J. E. Vibrational Spectra of Primary and Secondary Aliphatic Amines. *J. Chem. Phys.* **1959**, *30* (5), 1259–1265.

(62) Zeitler, V. A.; Brown, C. A. The Infrared Spectra of Some Ti-O-Si, Ti-O-Ti and Si-O-Si Compounds. *J. Phys. Chem.* **1957**, *61* (9), 1174–1177.

(63) Wheeler, L. M.; Neale, N. R.; Chen, T.; Kortshagen, U. R. Hypervalent Surface Interactions for Colloidal Stability and Doping of Silicon Nanocrystals. *Nat. Commun.* **2013**, *4*, 1–10.

(64) Banik, I.; Kim, K. S.; Yun, Y. Il; Kim, D. H.; Ryu, C. M.; Park, C. S.; Surd, G. S.; Park, C. E. A Closer Look into the Behavior of Oxygen Plasma-Treated High-Density Polyethylene. *Polymer (Guildf).* **2003**, *44* (4), 1163–1170.

(65) Cassie, A.; Liu, T. L.; Chen, Z.; Kim, C. Soft Matter. **2015**, *1*, 1589–1596.

(66) Bhushan, B.; Jung, Y. C. Wetting, Adhesion and Friction of Superhydrophobic and Hydrophilic Leaves and Fabricated Micro/Nanopatterned Surfaces. *J. Phys. Condens. Matter* **2008**, *20* (22).

(67) Belaud, V.; Valette, S.; Stremsdoerfer, G.; Bigerelle, M.; Benayoun, S. Wettability versus Roughness: Multi-Scales Approach. *Tribol. Int.* **2015**, *82* (PB), 343–349.

(68) Yegin, Y.; Oh, J. K.; Akbulut, M.; Taylor, T. Cetylpyridinium Chloride Produces Increased Zeta-Potential on Salmonella Typhimurium Cells, a Mechanism of the Pathogen's Inactivation. *npj Sci. Food* **2019**, *3* (1), 1–7.

(69) Lehrke, G.; Hernaez, L.; Mugliaroli, S. L.; von Staszewski, M.; Jagus, R. J. Sensitization of Listeria Innocua to Inorganic and Organic Acids by Natural Antimicrobials. *LWT - Food Sci. Technol.* **2011**, *44* (4), 984–991.

(70) Wang, N.; Yuan, Y.; Wu, Y.; Hang, T.; Li, M. Wetting Transition of the Caterpillar-Like Superhydrophobic Cu/Ni-Co Hierarchical Structure by Heat Treatment. *Langmuir* **2015**, *31* (39), 10807–10812.

(71) Dakwa, V.; Eyles, A.; Gracie, A.; Tamplin, M.; Ross, T. Removal of Grit from Baby Leafy Salad Vegetables by Combinations of Sanitiser and Surfactant. **2019**, *2019*, 1–9.

(72) Xu, L.; Geng, Z.; He, J.; Zhou, G. Mechanically Robust, Thermally Stable, Broadband Antireflective, and Superhydrophobic Thin Films on Glass Substrates. *ACS Appl. Mater. Interfaces* **2014**, *6* (12), 9029–9035.

(73) Yanagishita, T.; Murakoshi, K.; Kondo, T.; Masuda, H. Preparation of Superhydrophobic Surfaces with Micro/Nano Alumina Molds. *RSC Adv.* **2018**, *8* (64), 36697–36704.