Eliminating the Need for Biocidal Agents in Anti-Biofouling Polymers by Applying Grafted Nanosilica Instead

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ABSTRACT: A nondestructive one-step approach was applied for grafting biocide-free monodispersed silica nanoparticles (SNPs) with a diameter of 30 ± 10 nm on polystyrene, polyethylene, and polyvinyl chloride surfaces. The prepared surfaces were comprehensively characterized using spectroscopic (Fourier transform infrared attenuated total reflection, ultraviolet–visible, and X-ray photoelectron spectroscopy) and microscopic (high-resolution scanning electron microscopy and atomic force microscopy) methods. The modified polymers were found to maintain their original mechanical and physical properties, while their nanoroughness on the other hand had risen by 1.6–2.7 times because of SNP grafting. The SNP-grafted surfaces displayed anti-biofouling properties, resulting in a significant reduction in the attached Gram-positive Bacillus licheniformis or Gram-negative Pseudomonas aeruginosa bacteria compared to their nongrafted counterparts. Confocal laser scanning microscopy and scanning electron microscopy studies have confirmed that bacterial cells could not successfully adhere onto the SNP-grafted polymer films regardless of the polymer type, and their biofilm formation was therefore damaged. The presented facile and straightforward protocol allows eliminating the need for biocidal agents and resorts to grafted nanosilica instead. This strategy may serve as a feasible and safe platform for the development of sustainable anti-biofouling surfaces in biomedical devices; food, water, and air treatment systems; and industrial equipment.

INTRODUCTION

The development of safe and effective methods to prevent microbial fouling and biofilm formation is of substantial environmental, economic, and public health interest. Microorganisms attached to the surfaces of the medical devices, filters, air conditioners, and food and water treatment systems provide a persistent source of infection.1,2 Grafting biocidal agents on material surfaces is an effective method that allows reducing bacterial contamination significantly.3–5 However, biocides are associated with many disadvantages at a local and global scale.6 Their environmental contamination,7 health risks,8 and plausible aid in the development of bacterial resistance9 have all raised concerns. These reasons emphasize the demand to find methods that prevent the formation of bacterial fouling without the use of biocides. Antiadhesive materials that prevent or limit bacterial contact with surfaces may offer a sustainable solution for the prevention of biofouling without polluting the environment with antimicrobial agents and the promotion of bacterial resistance mechanisms.4,10,11 Numerous approaches that allow the reduction of microbial adhesion have been reported. These include plasma deposition of poloxazoline thin films that can provide the coated surfaces with biopassivity12 and polymer brushes that act as antiadhesive coatings in an array of applications.13 Other approaches include regulating the hydrophobicity of the surface in order to prevent bacterial adhesion14 and even UV activating it to switch its physical properties and control its topography and wettability, different variables in bacterial adhesion and growth.15 Numerous studies have taught us about the importance of surface roughness and topography, and these paramount physical traits play a role in surface interactions with various biomolecules. Surface roughness adjustments can affect the hydrodynamic performance of antifouling coatings and must therefore be accounted for in the design of novel approaches for biofouling prevention.16 The nanotopographical landscape of any given surface was also found to have crucial implications in terms of possible settlements of bacterial colonies and their response to it.17 This ongoing line of research is currently directed toward lotus-like self-cleaning surfaces18 and flow-regulating biomimetic Janus membranes,19

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up the overall surface coating (Scheme 1).

Interactions with them are based on a noncovalent hydrophobic phenomenon.30,31 The propensity of SNPs to be incorporated in various formulations for the prevention of bacterial growth has been studied to great lengths, including synergistic and multiple bioactive effects.25 as well as their utilization as a delivery platform for biocidal agents in antimicrobial and anti-biofilm research.26–28 In addition, organofunctional silanes were found to modify the surface energy and wettability that were expressed in reduced bacterial adhesion.29 The ability of bare SNPs to prevent biofouling by affecting the variable degrees of hydrophobicity or hydrophilicity is practically unexplored. We are aware of two studies who mentioned this issue in the context of biomedical effects without studying the chemical aspects of this phenomenon.30,31

In the current study, we report a one-step grafting of the in situ prepared SNPs on the surfaces of commonly used polymers such as polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC). The spectroscopic, microscopic, physical, structural, and optical properties of the modified polymer films were studied. The bare SNP-grafted surfaces have successfully repelled Gram-positive and Gram-negative bacteria without biocidal agents, offering a valuable green alternative that can help avoid the bacterial resistance effect as well as cut down on human health risks and environmental contamination.

**RESULTS AND DISCUSSION**

**Si NP Grafting and Modified Polymer Characterizations.** PE, PS, and PVC are relatively inert polymers and usually require substantial oxidizing agents or physical treatment for their activation.32 Tetraethyl orthosilicate (TEOS) was previously reported to serve as a SiO$_2$ precursor for the formation of Si NPs on parylene C polymers.33 In this work, we have used TEOS as a precursor for a one-step process to graft SNPs on PE, PS, and PVC surfaces using the sol–gel technique. Surfaces were precleaned in absolute EtOH prior to SNP grafting. The process, which had originated by Binyamini et al.34 was modified and performed according to Binyamini et al.33 As the TEOS molecules are drawn to the polymeric surfaces, their interactions with them are based on a noncovalent hydrophobic affinity. Following a base-catalyzed cleavage process, a two-dimensional poly (Si–OH) layer is ultimately formed, making up the overall surface coating (Scheme 1).

High-resolution scanning electron microscopy (HR-SEM) micrographs of the SNP-grafted PE, PS, and PVC polymer surfaces have confirmed SNP deposition. The deposited SNP demonstrated highly homogeneous distribution on PVC. PE and PS were found to be overlaid with the dense occasionally cracked SNP cover. The SNP-grafted films demonstrated a remarkable stability when treated by multiple rigorous sonication (overall 30 min). It can be seen on the HR-SEM micrographs that after this sonication treatment, no significant changes in the morphology of the grafted polymer surfaces were observed (Figure 1).

The average diameter for all the SNPs was found to be ~30 nm with a narrow size distribution of ±10 nm. This similar NP size on top of the different polymers has allowed us to assume that they were created through a similar mechanism, involving hydrophobic interactions with the tripodal ethoxy groups of TEOS.26 As the deposited SNPs were inspected using atomic force microscopy (AFM), they were found to have increased the overall roughness of the surfaces (Figure 2).

The $R_q$ values have shown to rise from 8.84 to 14.00 nm (for original and SNP-grafted PE surfaces, respectively) and from 3.56 to 8.76 nm (for original and SNP-grafted PVC surfaces, respectively). However, the most pronounced increase was measured for the PS surfaces, where the $R_q$ values have risen from 3.96 to 11.00 nm (for original and SNP-grafted PS surfaces, respectively). The high-resolution Si $2p$ spectra for the modified polymers performed by X-ray photoelectron spectroscopy (XPS) demonstrated the presence of a Si–O peak at the 102.5–103 eV area. The relatively broad peak pattern in the PE–SNPs films may be attributed to the charging phenomenon (Figure 3a).35

The ATR–FTIR subtractive spectra of the original and SNP-grafted PE and PVC surfaces revealed the characteristic peak of SNPs (Si–O–Si siloxane bond) at 1100 cm$^{-1}$. Also, the peaks at 2920 and 2850 cm$^{-1}$ assigned to alkane bands have decreased as the surface-grafted SNPs concealed those groups. An interesting phenomenon was observed while exploring the spectra for the SNP-grafted PS surfaces. Their C–C bond peaks (1300 cm$^{-1}$) were diminished, while the aromatic peaks for C=C–C (1500 cm$^{-1}$) did not decrease, allowing us to assume that SNPs prefer to be deposited on aliphatic rather than on aromatic areas because TEOS better forms hydrophobic interactions with aliphatic groups.

TGA showed that SNP-grafted PE and PS films have similar degradation patterns compared to their original forms with smaller weight losses across the temperature gradient (97.6 vs 97.07 and 99.52 vs 99.17% for PE and PS, and their SNP-grafted analogues, correspondingly). It was therefore found that PE films contain 0.615% SNPs on their surface, while PS contained...
increased from 465 to 480 °C. These results are in correlation with the previously reported evidence that NPs catalyze PVC dehydrochlorination and enhance chain stability in the second stage.37 However, the mechanism for this process is unclear.

From the weight loss (82.94 vs 80.22% for PVC- and SNP-treated PVC, respectively), it was calculated that the SNP-grafted PVC contained approximately 3.02% SNPs (Figure 3e–g). SNP-grafted films were also tested for their mechanical properties by measuring Young’s modulus (YM) and elongation at break (EB) (Table 1). It can be seen that grafting SNPs had no significant effects on the mechanical properties of the modified films. These observations are notable for the sustainability and applicability of the suggested method because they show that the presented modification is undisruptive for the bulk polymer features. Interestingly, water contact angles (WCAs) for the original and SNP-grafted polymers were also found to be similar, suggesting that the anti-biofouling activity described later on is not a result of dramatic changes in the hydrophobicity.

Anti-Biofouling Activity. The SNP-grafted polymers were exposed to human pathogen Pseudomonas aeruginosa38 and food spoilage Bacillus licheniformis39 bacteria for 30 min, and bacterial cell attachment was quantified using the colony-forming unit (CFU) method (Figure 4).

The tested bacteria possess a notable biofilm formation ability and therefore are very problematic for biomedical and water- or food-contacting surfaces. The presence of SNPs has notably reduced the surface accumulation of B. licheniformis. The accumulation of P. aeruginosa was also reduced, however in a less notable manner.

The confocal laser scanning microscopy (CLSM) images have confirmed that bacterial cells could not successfully form a biofilm onto the SNP-grafted polymer films. Figure 5a shows that the SNP-grafted polymer surfaces demonstrate a notable anti-biofouling capability, following their exposure to bacteria for 24 h. These images show live bacterial cells stained green and dead cells with a red stain, hence visually describing that the SNP-treated surfaces did not notably harm the bacterial viability. These results also convey the fact that using SNPs as a grafting material on the polymer surfaces can help endow these surfaces with anti-biofouling properties without having to resort to biocidal agents.

Next, we examined the inhibitory capacity of the developed surfaces during the long-term biofilm formation by B. licheniformis and by P. aeruginosa. All the SNP-grafted surfaces demonstrated a strong inhibition of biofilm formation throughout the 6 days of incubation as observed by the CLSM (Figure 5b). A fascinating finding was that the inhibition of mature (6 day) biofilm formation was more marked than that of young (24 h) biofilm. This phenomenon might be explained by the possible damage caused by the SNP-grafted surfaces to the biofilm maturation process (a critical step during biofilm formation), with a consequent inability of the bacteria to aggregate and form a confluent and mature biofilm, even if some initial adhesion (as seen following 24 h of incubation) occurred. Interestingly, SEM investigations have also shown that SNPs successfully fortify the surface inaptitude for bacterial attachment, regardless of the polymer type. It can be seen that SNP-grafted surfaces prevent biofilm formation when compared to the original silica-free surfaces (Figure 6).

The attachment of bacteria onto biocidal-free surfaces can be prevented by various physicochemical influences that include surface energy, charge, and topography.40,41 Numerous studies demonstrated a correlation between surface topography and biofilm formation, and it is known that surface topology plays an essential role in the bacterial attachment process.42 However, the predictions whether a surface would promote or suppress bacterial attachment are difficult. Gaikwad et al., who have polished tooth surfaces with nanoparticulate silica, witnessed that these surfaces were markedly easier to wash for bacterial residues because of poorer adhesion.43 Cousins et al. have experimented with spherical Si NPs as a way to control the growth of Candida albicans and concluded that the inhibited development was caused by surface topography.31 Although it is possible that differences in protein absorption could explain (at least partially) the differences in bacterial adhesion, in our experiment, we did not find the significant difference between the protein attachment onto original and SNP-grafted surfaces following exposure to the bacterial growth medium (data not shown).

Figure 1. HR-SEM images of SNP-grafted PE (a,b), PS (c,d), and PVC (e,f) films before (a,c,e) and after (b,d,f) rigorous sonication.
In this study, the obtained results allow to suggest that the examined SNP-grafted polymers are nontoxic to the bacteria, and their anti-biofouling action can thus be attributed to their influence on the surface topography. The presented findings point to the potential feasibility of using SNP grafting as a facile biocide-free approach for resisting microbial attachment on various material surfaces. Although SNP grafting does not affect the polymer properties on a macroscopic level (WCA and mechanical properties), it does introduce nanoscale changes as was demonstrated by AFM analyses. These changes in the
CONCLUSIONS

A series of widely used commercial polymers were in situ grafted with SNPs from a TEOS precursor, and the new coating layer endowed them with anti-biofouling properties. It was found that surface landscape may contribute to avoiding cellular attachment to the polymer surface.

Figure 3. (a) High-resolution Si 2p XPS peaks of SNP-grafted PE, PS, and PVC. (b–d) Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of original PS, PE, and PVC and subtracted spectra of SNP-grafted PS, PE and PVC, respectively. (e–g) Thermogravimetric analysis (TGA) graphs of original and SNP-grafted PE, PS and PVC, respectively (sample weights were normalized to 10 mg).
the SNPs were more predominantly dispersed in aliphatic rather than aromatic regions of the surfaces, which helped support the importance of hydrophobic interactions between the coated polymers and the cell surfaces. The grafted polymers notably decreased bacterial adhesion with no notable killing activity, and this ability can allow the prevention of biofouling without promoting bacterial resistance. This study has therefore shown that material surfaces can be treated with a simple and available protocol for disrupting biofilm formation without the use of biocidal agents. These findings may serve as a feasible platform for the formation of sustainable anti-biofouling materials and their applications in various fields that face bacterial fouling associated problems and do not wish to use biocidal agents.

## EXPERIMENTAL SECTION

### Materials
Low-weight additive-free PE was kindly donated by Ginegar Plastic Products Ltd (Israel). The following analytical-grade chemicals were purchased from Sigma-Aldrich and used as received: PS powder, PVC powder, TEOS (99.999% purity), and 28 v/v% aqueous NH₄OH (99.99% purity). Ethanol abs. of AR grade was purchased from Gadot (Israel) and used without further purification. LB broth and LB agar were purchased from Difco (MD, USA) and used without further treatment.

### Methods

#### Grafting SNPs onto a Polymer Film Surface.
Polymer films (4 × 2 cm) (PE, PVC, or PS), precleared in an ultrasonic bath (Elmasonic S 30 ultrasonic bath, 37 kHz at full-power irradiation, 15 min in EtOH), were placed in a reaction vessel containing 30 mL of EtOH. TEOS [1.89 mL (8.4 mmol)] was inserted, and the reaction vessel was shaken for 15 min in order to prevent the formation of SNPs by the TEOS precursor. Aqueous NH₄OH (1.6 mL, 28 w/w % in H₂O) was then added to induce SNP growth on the polymeric surfaces. The reaction was performed at room temperature for 24 h under constant agitation (orbital shaker). The resulting modified film was sonicated with EtOH for 1 min to remove physically adsorbed SNPs. Next, the obtained films were left to air-dry before characterization and further processing.

#### Stability Test.
The grafted SNP polymer films (PE, PVC, or PS) were sonicated three times with EtOH for 10 min using an Elmasonic S 30 ultrasonic bath, 37 kHz at full power irradiation (overall 30 min of sonication), and then were left to air-dry. ATR–FTIR spectra (data not shown) and HR-SEM images of these polymer films were taken to examine the stability of the SNPs on the polymer surfaces.

#### Characterizations.
HR-SEM analysis was performed using a field emission scanning electron microscope model Mira-Tescan. Each sample was fixed onto a stub with a carbon adhesive tape and Pd/Au-sputtered (40 mA, 30 s) before its analysis.

WCA of the modified and original polymers were obtained using the goniometer Kruss, model FM40 easy drop (Germany), with a drop size of 10 μL of deionized water.

XPS measurements were carried out with a Kratos AXIS ULTRA system, using a monochromatic Al Kα X-ray source (hν = 1486.6 eV) at 75 W and detection pass energies ranging between 40 and 80 eV. A low-energy electron flood gun was applied for the charge neutralization. Curve-fitting analysis was based on linear or Shirley background subtraction and application of Gaussian–Lorentzian line shapes.

#### ATR–FTIR spectroscopy was performed using a Thermo Scientific Nicolet iS5 FTIR spectrometer. Films were subjected to 32 scans at a 4 cm⁻¹ resolution before and after SNP grafting. The obtained bare polymer film spectra were subtracted from the SNP spectra where they were grafted using the Thermo Scientific OMNIC software.

TGA of the polymer films was measured with a PerkinElmer Pyris 1 TGA instrument under N₂ (50 mL/min) at a heating rate of 10 °C/min before and after SNP grafting. Weight loss curves were recorded from room temperature to 800 °C for a single specimen from each polymer treatment.

AFM topographic imaging was performed using an Innova Atomic Force Microscope with a NanoDrive Controller (Bruker, California) operating in a tapping mode, in air, at room temperature. Surface images with a scan rate of 1.0 Hz were acquired at a fixed resolution of 512 × 512 data points. Bruker 0.01–0.025 Ω cm antimony (n)-doped silicon tips (model: RTESPA-CP) were used. The roughness parameter such as the root mean square (Rₚ) was calculated for scanned areas of 10 × 10 μm using the NanoScope Analysis software.

| Surface | WCA [deg] | EB [%] | YM [MPa] |
|---------|-----------|-------|----------|
| PE      | 86.6 ± 1.3| 1227.7 ± 121.6 | 163.9 ± 34.1 |
| PE–SNPs | 91.8 ± 2.3| 1034.7 ± 69.8 | 176.0 ± 14.8 |
| PS      | 76.9 ± 4.2| 3.2 ± 0.8 | 710.6 ± 41.3 |
| PS–SNPs | 82.1 ± 1.1| 3.9 ± 0.4 | 701.9 ± 61.8 |
| PVC     | 75.7 ± 3.7| 37.6 ± 5.4 | 825.5 ± 32.5 |
| PVC–SNPs| 66.1 ± 4.6| 36.9 ± 6.6 | 761.3 ± 60.3 |

Figure 4. Effect of SNP-grafted surfaces on *P. aeruginosa* and *B. licheniformis* accumulation. The CFU counts of the bacteria accumulated on the SNP-grafted surface were normalized following the bacterial counts on the uncoated surfaces. The data present an average of two independent biological experiments, each one performed in triplicates.
AFM images and roughness calculations were obtained for different sample places, and the most typical areas are presented.

The mechanical properties of the polymer films [YM and percent of EB (PE)] were determined using an Instron 3345 instrument with an Instron force transducer load cell (Norwood, MA, USA). Tests were performed at a speed of 3 mm/s. PE was calculated by dividing the extension at the moment of rupture by the initial gauge length of the samples and multiplying by 100 and is expressed in percentage. YM was determined by the ratio of the stress along an axis over the strain along that axis in the range of stress and is expressed in megapascal. All measurements were performed in triplicate for each film type.

**Bacteriology. Anti-Biofouling Activity Assay.** The generated films were sterilized with ethanol (70 v/v % in deionized water) and placed into a sterile 12-well PS plate. Around 10 μL of Gram-positive *B. licheniformis* (*B. licheniformis*) s12744 wild-type strain suspension grown in the lysogeny broth (LB; 10 g tryptone, 5 g yeast extract, 5 g NaCl per liter) or 10 μL of Gram-negative *P. aeruginosa* PA14 (*P. aeruginosa*) wild-type strain suspension grown in LB to a stationary phase was spotted onto the coated substrates and incubated for ~30 min at 37 °C to allow initial bacterial adhesion onto the surfaces. Next, 3 mL of fresh tryptic soy broth with a 0.5% yeast (TSB; 17 g of pancreatic digest of casein, 3 g of papain digest of soybean, 2.5 g of dextrose, 12443
5 g of sodium chloride, and 2.5 g of dipotassium phosphate per liter) medium was added to the plates with B. licheniformis or 3 mL of fresh LB to the plates with P. aeruginosa and incubated overnight at 37 °C. Following a washing procedure for the substrates with distilled water, the adhered bacterial cells were swabbed and plated on the LB agar plates for CFU quantitation. The swab and the surface were inserted into 1 mL of sterile water (into a 15 mL plastic tube) and vortexed for 30 s. After overnight incubation at 37 °C, the CFUs of viable bacteria were quantified similarly as described recently.

SEM Bacteria Imaging. The polymer films that had been incubated with B. licheniformis for 1 day were also incubated with glutaraldehyde and paraformaldehyde (Karnovsky fixative) for 2 h. Following these incubations, the samples were washed twice with a phosphate buffer saline without Ca²⁺ and Mg²⁺. The samples were then sequentially washed with the H₂O/ EtOH solution (with an elevation concentration of EtOH from 20 to 100%) to dehydrate them. They were then dried by a critical point drier, followed by a platinum/gold sputtering. The films were examined using a benchtop SEM JEOL JCM-6000PLUS NeoScope at an accelerating voltage of 15 kV.

Figure 6. SEM images of the original (right) and SNP-grafted (left) films incubated with B. licheniformis for one day at 37 °C.

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